PHYSICAL REVIEW A VOLUME 55, NUMBER 3 MARCH 1997

Expansions of density functionals in terms of homogeneous functionals: Justification and nonlocal representation of the kinetic energy, exchange energy, and classical Coulomb repulsion energy for atoms

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(Received 9 August 1996)

For atoms or molecules, a general argument is given justifying expanding well behaved density functionals in series of functionals that are homogeneous to different degrees with respect to density scaling. Employing only appropriate local homogeneous functionals $\langle\rho^k\rangle$, few-term fits of atomic Hartree-Fock $T[\rho]$, $E_x[\rho]$, and $J[\rho]$ (kinetic energy, exchange energy, and classical Coulomb repulsion energy density functionals) are shown to give excellent results, as do self-consistent calculations on atoms using this $E_x[\rho]$ plus an earlier obtained representation of $E_c[\rho]$. The representations may be local (as the one for E_c) or nonlocal, where nonlocal products of two or more $\langle\rho^k\rangle$ can be included. [S1050-2947(97)10302-X]

PACS number(s): 31.15.Pw, 03.65.Db

I. INTRODUCTION

Recently we have been studying [1,2] the development of a functional expansion approach to the density-functional theory of electronic structure, in which functionals of concern are expanded in terms of their own functional derivatives. In Ref. [1], a general formulations was described showing how a typical well-behaved one of these functionals can be expanded up to a constant in terms of its functional derivatives of higher and higher orders,

$$Q[\rho]=C+\int \rho(\mathbf{r})\frac{\delta Q[\rho]}{\delta\rho(\mathbf{r})}d^3r-\frac{1}{2}\int\int \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\frac{\delta^2 Q[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}d^3r_1d^3r_2+\frac{1}{3!}\int\int\int \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\rho(\mathbf{r}_3)\times\frac{\delta^3 Q[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)}d^3r_1d^3r_2d^3r_3-\cdots, \quad (1)$$

and it was shown that the approximations available, such as local-density approximation (LDA), generalized gradient approximation weighted density approximation, were included as special cases. This scheme, however, is limited by the fact that to implement it fully one has to know functional derivatives of all orders. Later, it was discovered [2–4] that the correlation-energy density functional $E_c[\rho]$ and its kinetic component $T_c[\rho]$ can be expanded to good accuracy in terms of homogeneous functionals with respect to coordinate scaling of degrees 0, -1, $-2,\ldots,(1-n),\ldots$. In particular, a rather compact local form for $E_c[\rho]$ was obtained [2],

$$E_c[\rho]=aN+b\int \rho^{2/3}(\mathbf{r})d^3r+c\int \rho^{1/3}(\mathbf{r})d^3r, \quad (2)$$

where N is the number of electrons in the system and a, b, and c are parameters. Results for atoms and molecules are remarkably accurate. This method, however, cannot be applied to expand the $T_s[\rho]$, $E_x[\rho]$, and $J[\rho]$ density functionals, whose homogeneities in coordinate scaling are exactly known (2, 1, and 1, respectively).

In this paper, first another scheme for the functional expansion will be examined, in which a well-behaved functional is expanded in terms of *homogeneous functionals with respect to density scaling* (hereafter called density-homogeneous functionals). This scheme does not necessarily have to have functional derivatives explicitly in the expansion, and one is able to expand such energy density functionals as $T_s[\rho]$, $E_x[\rho]$, and $J[\rho]$. We will consider the special case in which $T_s[\rho]$, $E_x[\rho]$, and $J[\rho]$ take the form of power series built from strictly local density functionals. The particular analytical forms are quite restricted because of their homogeneity properties. Promising numerical results are found for atoms and ions.

Since any power of ρ is as good a variable as ρ for determining Q, an alternative to Eq. (1) is an expansion

$$Q[\rho^\alpha]=C+\int \rho^\alpha(\mathbf{r})\frac{\delta Q[\rho^\alpha]}{\delta\rho^\alpha(\mathbf{r})}d^3r-\frac{1}{2}\int\int \rho^\alpha(\mathbf{r}_1)\rho^\alpha(\mathbf{r}_2)\frac{\delta^2 Q[\rho^\alpha]}{\delta\rho^\alpha(\mathbf{r}_1)\delta\rho^\alpha(\mathbf{r}_2)}d^3r_1d^3r_2+\frac{1}{3!}\int\int\int \rho^\alpha(\mathbf{r}_1)\rho^\alpha(\mathbf{r}_2)\rho^\alpha(\mathbf{r}_3)\times\frac{\delta^3 Q[\rho^\alpha]}{\delta\rho^\alpha(\mathbf{r}_1)\delta\rho^\alpha(\mathbf{r}_2)\delta\rho^\alpha(\mathbf{r}_3)}d^3r_1d^3r_2d^3r_3-\cdots, \quad (3)$$

where α is any number. The case of most interest is $\alpha=1/3$.

II. THEOREMS GOVERNING FUNCTIONAL EXPANSION IN TERMS OF DENSITY-HOMOGENEOUS FUNCTIONALS

Theorem 1. For any well-behaved functional $Q[\rho]$, assume that the series of Eq. (1) exists and converges and assume that we may regard as accurate this expansion truncated after the nth-order contribution ($n+1$ terms). Then in principle $Q[\rho]$ can also be expanded in terms of density-homogeneous functionals of any $(n+1)$ distinct orders.

Proof. Rewrite Eq. (1) as

$$Q[\rho]=\sum_{i=0}^{n} Q_i[\rho], \tag{4}$$

where $Q_i[\rho]$ stands for the ith term on the right-hand side of Eq. (1). Now, assume that one has another expansion of $Q[\rho]$,

$$Q[\rho]=\sum_{j=0}^{n} H_j[\rho], \tag{5}$$

where $H_j[\rho]$ is a density-homogeneous functional of degree n_j, that is [2],

$$\int \rho(\mathbf{r})\frac{\delta H_j[\rho]}{\delta\rho(\mathbf{r})}d\mathbf{r}=n_jH_j[\rho]. \tag{6}$$

Employing Eq. (6), one readily obtains the relationship between the $Q_i[\rho]$ and the $H_j[\rho]$,

$$Q_i[\rho]=\sum_{j=0}^{n}\frac{n_j!}{i!(n_j-i)!}H_j[\rho] \tag{7}$$

for $i=1,2,\dots,n$. Solving Eqs. (5) and (7) simultaneously, one then obtains the $(n+1)$ quantities $H_i[\rho]$ by elementary linear algebra. If one assumes $n_j=j$, for example, the result is

$$\begin{aligned}
H_0[\rho]&=Q[\rho]-Q_1[\rho]-Q_2[\rho]-Q_3[\rho]-\cdots,\\
H_1[\rho]&=Q_1[\rho]+2Q_2[\rho]+3Q_3[\rho]+\cdots,\\
H_2[\rho]&=-Q_2[\rho]-3Q_3[\rho]-\cdots,\\
H_3[\rho]&=Q_3[\rho]+\cdots,\\
&\vdots
\end{aligned} \tag{8}$$

The theorem is thereby proved.

A few examples of this theorem are given in the Appendix. Note that in order to have a nontrivial solution from the above equations, the n_j must be distinct from each other. Otherwise, the determinant of coefficients will be zero. By Eq. (3) above, the n_j are not necessarily integers. Note also that the above theorem only guarantees the existence of the $H_j[\rho]$. Their analytical forms are rather complex. Since each $H_j[\rho]$ in the solution is a combination of all $Q_i[\rho]$, each of which, as shown in Eq. (1), is expressed as an integral involving a functional derivative of ith order, the analytical form of $H_j[\rho]$ should, in principle, depend both on functional derivatives of all n orders and on all distinct n_j's chosen. Meanwhile, it is this very complexity that stimulates one to suppose that there may be some cancellation happening among these functional derivatives such that a good approximation for a given $H_j[\rho]$ does not necessarily explicitly depend on all functional derivatives of $Q[\rho]$. We will consider special cases of this argument for three energy density functionals, $T[\rho]$, $E_x[\rho]$, and $J[\rho]$, in this paper. Another problem with this kind of expansion of Eq. (5) is convergence. What we know is only that given the $Q_i[\rho]$ from Eq. (1), one is able to obtain all the $H_j[\rho]$ by linear combinations of them. We do not know if Eq. (5) converges faster or slower than Eq. (4). Since the form of $H_j[\rho]$ depends on its homogeneity, one hopes that by a careful choice of n_j for a given case, one may be able to find the best series of Eq. (5) so that it converges faster than Eq. (4).

Suppose now that $Q[\rho]$ is a power series of some *strictly local* functionals $H_j(\rho)$ (which means that each H_j is integral of a function of the density ρ),

$$Q[\rho]=\sum_{j=1}^{n} C_j[H_j]^j, \tag{9}$$

where the C_j are constants to be determined. It is shown in the following theorem that this form will guarantee that each term in this expansion possesses a certain homogeneity property with respect to density scaling if its homogeneity in coordinate scaling is known.

Theorem 2. Given the functional

$$Q_j[\rho]=C_j[H_j]^j, \tag{10}$$

where the H_j is a homogeneous and local functional, if it is homogeneous of degree m in coordinate scaling, it takes the form

$$Q_j[\rho]=C_j\left[\int \rho^{[1+(m/3j)]}(\mathbf{r})d^3r\right]^j. \tag{11}$$

Further, if $Q_j[\rho]$ is homogeneous of degree k in density scaling, j is determined by the relation

$$j=k-\frac{m}{3} \tag{12}$$

Proof. It is known [1] that any strictly local functional $L[\rho]$ satisfies the identity

$$L[\rho]=-\frac{1}{3}\int \mathbf{r}\cdot\boldsymbol{\nabla}\rho(\mathbf{r})\frac{\delta L[\rho]}{\delta\rho(\mathbf{r})}d^3r. \tag{13}$$

Taking the functional derivative of Eq. (10) with respect to ρ, one obtains the identity

$$Q_j[\rho]=-\frac{1}{3j}\int \mathbf{r}\cdot\boldsymbol{\nabla}\rho(\mathbf{r})\frac{\delta Q_j[\rho]}{\delta\rho(\mathbf{r})}d^3r. \tag{14}$$

Meanwhile, because Q_j is homogeneous of degree m in coordinate scaling [5],

$$-\int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\frac{\delta Q_j[\rho]}{\delta\rho(\mathbf{r})}d^3r=mQ_j[\rho]. \tag{15}$$

Combining Eqs. (14) and (15), one finds

$$\int \rho(\mathbf{r})\frac{\delta Q_j[\rho]}{\delta\rho(\mathbf{r})}d^3r=\frac{m+3j}{3}Q_j[\rho], \tag{16}$$

TABLE I. Accurate and fitted values of the total kinetic energy $T[\rho]$, the exchange energy $E_x[\rho]$, and the Coulomb repulsion energy $J[\rho]$ of the first- and second-row neutral atoms using Hartree-Fock densities (a.u.). Accurate values are from Ref. [11] of the text. Fitted values are from Eqs. (20), (22), and (23) of the text.

	$T[\rho]$		$E_x[\rho]$		$J[\rho]$	
Atom	Fitted	Accurate	Fitted	Accurate	Fitted	Accurate
H	0.327	0.500	−0.244	−0.3125	0.297	0.3125
He	2.875	2.862	−1.010	−1.026	1.948	2.051
Li	7.487	7.433	−1.729	−1.781	3.948	4.062
Be	14.682	14.573	−2.623	−2.667	7.134	7.156
B	24.496	24.529	−3.680	−3.744	11.673	11.853
C	37.400	37.388	−4.947	−5.045	17.990	17.751
N	53.852	54.401	−6.435	−6.596	26.383	25.973
O	74.165	74.809	−8.113	−8.174	36.854	36.567
F	98.982	99.409	−10.031	−10.00	49.967	49.852
Ne	128.90	128.55	−12.198	−12.11	66.037	66.147
Na	162.55	161.86	−14.087	−14.02	79.481	80.034
Mg	200.66	199.61	−16.078	−15.99	95.094	95.811
Al	243.19	241.87	−18.135	−18.07	112.14	112.82
Si	290.36	288.85	−20.309	−20.28	131.52	131.91
P	342.36	340.71	−22.603	−22.64	153.29	153.19
S	399.39	397.50	−24.998	−25.00	177.15	176.81
Cl	461.40	459.46	−27.521	−27.51	203.65	202.90
Ar	528.92	526.81	−30.179	−30.19	232.95	231.61

which shows that $Q_j[\rho]$ is homogeneous of degree $(m+3j)/3$ in density scaling. Finally using the explicit form of $Q[\rho]$ in Eq. (10) and taking functional derivatives with respect to density at both sides of Eq. (16), one arrives at Eq. (11). Equation (12) also follows.

This theorem is a generalization of Theorems 1 and 2 in the Appendix of Ref. [2], where strictly local functionals were considered. The theorem shows, interestingly, that a product of strictly local functionals is no longer strictly local. It does not satisfy Eq. (13), which is the test for strict locality of a functional; instead, it satisfies Eq. (14).

III. EXPANSION OF $T[\rho]$, $E_x[\rho]$, AND $J[\rho]$ FOR ATOMS

The Hartree-Fock kinetic-energy density functional $T[\rho]$ (or its density-functional version $T_s[\rho]$), the exchange-energy density functional $E_x[\rho]$ and the classical Coulomb repulsion energies $J[\rho]$ are, respectively, coordinate homogeneous functionals of degree two, one, and one [6]. In addition, $J[\rho]$, whose analytical form is

$$J[\rho]=\frac{1}{2}\int\int\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3r_1d^3r_2, \tag{17}$$

is homogeneous of degree two with respect to density scaling. Therefore, we would like to infer that, to some level of approximation,

$$T[\rho]=\sum_{j=1}^{n}C_j\left[\int\rho^{[1+(2/3j)]}(\mathbf{r})d^3r\right]^j, \tag{18}$$

TABLE II. Accurate and fitted values of the total kinetic energy $T[\rho]$, the exchange energy $E_x[\rho]$, and the Coulomb repulsion energy $J[\rho]$ for the third-row neutral atoms using Hartree-Fock densities (a.u.). Values as in Table I.

	$T[\rho]$		$E_x[\rho]$		$J[\rho]$	
Atom	Fitted	Accurate	Fitted	Accurate	Fitted	Accurate
K	601.32	599.16	−32.655	−32.677	258.25	257.31
Ca	678.81	676.76	−35.196	−35.212	285.97	284.90
Sc	761.07	759.73	−38.007	−38.031	319.92	318.45
Ti	848.79	848.41	−40.970	−40.993	357.31	355.27
V	942.19	942.88	−44.070	−44.089	397.88	395.34
Cr	1041.3	1043.3	−47.518	−47.489	446.84	442.96
Mn	1147.0	1149.9	−50.694	−50.686	489.07	485.58
Fe	1258.6	1262.3	−54.182	−54.190	539.18	535.99
Co	1376.9	1381.4	−57.825	−57.835	593.05	590.09
Ni	1501.9	1506.9	−61.611	−61.624	650.52	648.01
Cu	1634.4	1639.0	−65.841	−65.793	719.27	716.70
Zn	1773.6	1777.8	−69.666	−69.640	777.65	775.89
Ga	1919.4	1923.3	−73.496	−73.517	836.21	835.17
Ge	2072.7	2075.4	−77.415	−77.444	898.02	897.06
As	2232.2	2234.2	−81.396	−81.432	962.51	961.62
Se	2399.1	2399.9	−85.458	−85.493	1029.4	1028.9
Br	2573.6	2572.4	−89.623	−89.635	1099.6	1099.1
Kr	2755.7	2752.1	−93.894	−93.852	1173.2	1172.3

$$E_x[\rho]=\sum_{j=1}^{n}C_j\left[\int\rho^{[1+(1/3j)]}(\mathbf{r})d^3r\right]^j, \tag{19}$$

and

$$J[\rho]=C_J\left[\int\rho^{6/5}(\mathbf{r})d^3r\right]^{5/3}, \tag{20}$$

where $T[\rho]$ and $E_x[\rho]$ are series expansions of different density-homogeneous functionals, while $J[\rho]$, because of its simple density scaling homogeneity, has only one term in its expansion. Notice that when one truncates at $j=1$ in Eqs. (18) and (19), one obtains the classical Thomas-Fermi and Dirac formulas. For $J[\rho]$, there have been several modeling attempts [7–9] in terms of local density-functional formulas. Equation (20) is much simpler and compact and, as is shown below, gives better results. It may be mentioned that using Sobolev and Hölder inequalities, Gadre, Bartolotti, and Handy [10] obtained a bound for Coulomb energies in the same form as Eq. (20),

$$J[\rho]\leqslant 1.1648\left[\int\rho^{6/5}(\mathbf{r})d^3r\right]^{5/3}. \tag{21}$$

In our formula, the fitted constant for $J[\rho]$ is $C_J=1.0829$, which is smaller than 1.1648 and thus satisfies this bound.

Coefficients appearing in Eqs. (18)–(20) were obtained by using the least-square-fit procedure and the accurate Hartree-Fock values of $T[\rho]$, $E_x[\rho]$, and $J[\rho]$ for first- to third-row neutral atoms [11]. We truncated the expansion series at $j=3$. Thus,

TABLE III. Predictions of the total kinetic energy $T[\rho]$, the exchange energy $E_x[\rho]$, and the Coulomb repulsion energy $J[\rho]$ for isoelectronic ions of Be using Hartree-Fock densities (a.u.). Values are the same as in Table I.

	$T[\rho]$		$E_x[\rho]$		$J[\rho]$	
Ion	Predicted	Accurate	Predicted	Accurate	Predicted	Accurate
Be	14.682	14.573	−2.623	−2.667	7.134	7.156
B^+	24.348	24.238	−3.442	−3.492	9.532	9.610
C^{+2}	36.490	36.409	−4.258	−4.315	11.901	12.034
N^{+3}	51.106	51.082	−5.073	−5.135	14.260	14.444
O^{+4}	68.193	68.258	−5.888	−5.956	16.612	16.848
F^{+5}	87.757	87.934	−6.702	−6.776	18.962	19.248
Ne^{+6}	109.79	110.11	−7.517	−7.596	21.310	21.646
Na^{+7}	134.29	134.79	−8.331	−8.415	23.656	24.042
Mg^{+8}	161.28	161.97	−9.146	−9.235	26.005	26.436
Al^{+9}	190.71	191.64	−9.959	−10.054	28.347	28.831
Si^{+10}	222.83	223.82	−10.772	−10.874	30.698	31.224
P^{+11}	257.02	258.50	−11.586	−11.693	33.032	33.617
S^{+12}	293.87	295.68	−12.400	−12.513	35.374	36.010
Cl^{+13}	333.20	335.36	−13.214	−13.332	37.717	38.402
Ar^{+14}	375.00	377.54	−14.027	−14.152	40.060	40.794
K^{+15}	419.26	422.21	−14.841	−14.971	42.401	43.186
Ca^{+16}	465.99	469.39	−15.654	−15.790	44.742	45.577

$$T[\rho]=C_{T1}\int \rho^{5/3}(\mathbf{r})d^3r+C_{T2}\left[\int \rho^{4/3}(\mathbf{r})d^3r\right]^2 +C_{T3}\left[\int \rho^{11/9}(\mathbf{r})d^3r\right]^3, \tag{22}$$

$$E_x[\rho]=C_{X1}\int \rho^{4/3}(\mathbf{r})d^3r+C_{X2}\left[\int \rho^{7/6}(\mathbf{r})d^3r\right]^2 +C_{X3}\left[\int \rho^{10/9}(\mathbf{r})d^3r\right]^3. \tag{23}$$

Hartree-Fock densities [12] were used through the fit and prediction processes. To find the best fits, we recognized that while E_x is relatively small, T and J are large numbers. To determine the coefficients, for E_x we minimized the sum of squares of absolute errors; for T and J, we minimized the sum of squares of the absolute percentage errors. Coefficients found were $C_{T1}=3.26\,422$, $C_{T2}=-0.02\,631$, $C_{T3}=0.00\,498$; $C_{X1}=-0.85\,238$, $C_{X2}=0.00\,4911$, and $C_{X3}=-0.00\,0074$. For C_J, the fitted value for the first 36 atoms is 1.0829. Note that the coefficients in both Eqs. (22) and (23) alternate in sign and that their magnitudes decrease rapidly as j increases in both.

Tables I and II show the fitted and accurate values of T, E_x, and J for the first 36 neutral atoms. Excellent agreement with accurate values is observed. One finds that except for hydrogen, the average relative percentage errors are less than 1% for all three quantities. Meanwhile, in order that one may see whether these formulas are applicable to positive ions, Tables III and IV tabulate the results for the Be isoelectronic series and the Ne positive-ion series, respectively. Very good agreement between predictions and accurate values is found, and one should note that these tables represent predictions involving only previously determined parameters.

As j increases, the factors multiplying the coefficients in the expansions of Eqs. (20) and (21) increase. This is compensated, however, by the coefficients themselves, which decrease faster. So the expansions converge nicely. Contributions of the successive terms in T and E_x for the atoms He and Kr are shown in Table V. The main contributions come from the first term, and the contribution for the third term is less than 10%. Another observation is that as N gets larger, the contributions from latter terms become more important.

IV. SAMPLE CALCULATIONS ON ATOMS AND MOLECULES

The ultimate test for approximate density functionals is how well they perform in variational calculations. In Table VI we give the results of self-consistent energy calculations on atoms, employing, for the exchange-correlation potential in the Kohn-Sham equation, the functional derivative of the

TABLE IV. Predictions of the total kinetic energy $T[\rho]$, the exchange energy $E_x[\rho]$, and the Coulomb repulsion energy $J[\rho]$ for Ne ions of using Hartree-Fock densities (a.u.). Values are the same as in Table I.

	$T[\rho]$		$E_x[\rho]$		$J[\rho]$	
Ion	Predicted	Accurate	Predicted	Accurate	Predicted	Accurate
Ne	128.90	128.55	−12.198	−12.110	66.037	66.147
Ne^+	127.31	127.82	−11.672	−11.617	58.817	58.939
Ne^{+2}	124.99	126.31	−10.989	−10.994	51.143	51.233
Ne^{+3}	122.01	123.90	−10.231	−10.268	43.337	43.376
Ne^{+4}	118.19	120.47	−9.362	−9.446	35.478	35.655
Ne^{+5}	114.02	115.91	−8.447	−8.552	28.060	28.329
Ne^{+6}	109.79	110.11	−7.517	−7.596	21.309	21.646
Ne^{+7}	102.90	102.63	−6.638	−6.843	15.716	16.348

TABLE V. Percentage contribution of different terms in expansion of T and E_x for atoms He and Kr. See the text.

	First term	Second term	Third term
		T Contribution	
He	101.3%	-1.3%	0.0%
Kr	106.9%	-13.7%	6.8%
		E_x Contribution	
He	101.1%	-1.1%	0.0%
Kr	108.9%	-17.8%	8.9%

exchange functional of Eq. (23) above and the correlation functional of Eq. (2) [2,3].

It has already been shown that Eq. (2) is quite accurate for molecules [3]. However, one does not necessarily expect such high accuracy for Eqs. (20) and (23) when applied to molecules.

V. COMPARISON WITH GRADIENT-CORRECTED DENSITY FUNCTIONALS

The major conclusion of this work is that the types of functional expansions we are using, employing integrals $\langle\rho^k\rangle$ in profusion, are highly promising for finite systems. The classical LDA is good but not good enough for accurate work on atoms and molecules. The traditional way to correct the LDA is to introduce gradient approximation or generalized gradient approximation, in which integrals involving gradients of the density are introduced to correct the zeroth-order, uniform electron gas approximation, which is the LDA.

The viewpoint in the present paper is different. The argument is that atoms and molecules are far from uniform. Indeed, their essential nature is exponential falloff from nuclei. The evidence that the LDA is the best starting point is not strong. Note that an atom is a spherically symmetric, not a translationally invariant, entity, and that even ‘‘first-order gradient terms’’ appear to be allowed in their description [13,14]. Furthermore, note that values of several integrals $\langle\rho^k\rangle$ clearly provide a lot of information about the density, including information about local gradients of the density. If methods using integrals $\langle\rho^k\rangle$ prove accurate, they will be much more convenient to use than methods requiring calculations of local gradients.

To strengthen this statement of optimism, consider the problem of a simple exponentially decaying density, $\rho=\exp(-r)$. How well can this density be predicted from two or three or more values of integrals $A_k=\langle\rho^k\rangle$? How well can the second-order gradient term $T_2=\langle\nabla\rho\nabla\rho/\rho\rangle$ be predicted from A_k values? Information theory tells one how to solve this problem. Maximize $-\langle\rho\ \ln\rho\rangle$ subject to constraints $A_k=\langle\rho^k\rangle$ for a few k, with a Lagrange multiplier for each k. Even two terms give remarkable accuracy, as the following table shows:

k values used	Calculated T_2/true T_2
1, 3/2	1.304
1, 4/3	1.008
1, 101/100	0.982

In this particular case, in fact, if two k values that are very close to 1 are used, the exact T_2 is obtained, and also the exact density. The exponentially decaying nature of atomic and molecular densities thus appears to be a factor that calls strongly for the use of the quantities $\langle\rho^k\rangle$ in density-functional theory of atoms and molecules. Since the old parameter r_s is proportional to $\rho^{-1/3}$, this argument is no less than an appeal for renewed emphasis on r_s expansions in atomic and molecular work.

The nonlocal functionals of Eqs. (18)–(20) are not size consistent. We do not believe, however, that this vitiates the general ideas we are proposing here.

TABLE VI. Self-consistently calculated total electronic energies for the first- and second-row neutral atoms (a.u.).

Atom	True [a]	Calculated [b]	Error	Error (%)
H	-0.500	-0.436	0.064	12.80
He	-2.904	-2.897	0.007	0.25
Li	-7.478	-7.416	0.062	0.83
Be	-14.67	-14.60	0.07	0.48
B	-24.65	-24.58	0.07	0.29
C	-37.84	-37.77	0.07	0.22
N	-54.59	-54.46	0.13	0.22
O	-75.07	-75.02	0.05	0.06
F	-99.73	-99.77	-0.04	-0.04
Ne	-128.94	-129.03	-0.09	-0.07
Na	-162.25	-162.30	-0.05	-0.03
Mg	-200.05	-200.09	-0.04	-0.02
Al	-242.35	-242.36	-0.01	-0.00
Si	-289.36	-289.33	0.03	0.01
P	-341.26	-341.17	0.09	0.03
S	-398.11	-398.03	0.08	0.02
Cl	-460.15	-460.07	0.08	0.02
Ar	-527.54	-527.43	0.11	0.02

[a] Reference [15].

[b] Method of Sec. IV.

ACKNOWLEDGMENTS

Support from the National Science Foundation is gratefully acknowledged. Suggestions from Professor Weitao Yang and discussions with Dr. Y. A. Wang were helpful.

APPENDIX: EXAMPLES OF THE BASIC THEOREMS

Example 1. Consider a simple one-variable function $f(x)$. Suppose that near the point x_0, $f(x)$ can be expanded in terms of a Taylor series

$$f(x)=f(x_0)+f'(x_0)(x-x_0)+\frac{1}{2}f''(x_0)(x-x_0)^2+\frac{1}{3!}f'''(x_0)(x-x_0)^3+\cdots, \tag{A1}$$

where f', f'', and f''' stand for its the first-, second-, and third-order derivatives, respectively, and x_0 is not necessarily equal to 0. By rearrangement (assumed valid), one obtains

$$f(x)=\left[f(x_0)-f'(x_0)x_0+\tfrac{1}{2}f''(x_0)x_0^2-\frac{1}{3!}f'''(x_0)x_0^3+\cdots\right]$$
$$+[f'(x_0)-f''(x_0)x_0+\tfrac{1}{2}f'''(x_0)x_0^2-\cdots]x$$
$$+\tfrac{1}{2}[f''(x_0)-f'''(x_0)x_0+\cdots]x^2+\cdots, \tag{A2}$$

so that

$$f(x)=C+C_1x+C_2x^2+\cdots, \tag{A3}$$

which shows that $f(x)$ can be expanded in terms homogeneous in x. Equation (A3) looks like a McLaurin expansion for $f(x)$ expanded about the point $x_0=0$, but it is generally not such an expansion. The constant C in Eq (A3) is not, in general, $f(0)$; the point $x_0=0$ may not be within the convergence domain. Equation (A1) is not a series of homogeneous functions; Eq. (A3) is.

Example 2. Now take

$$F[\rho]=\int\frac{\rho(\mathbf{r})}{1+\rho(\mathbf{r})}d\mathbf{r}. \tag{A4}$$

This is a nonhomogeneous functional, but it is not as easy as in the forgoing example to show that it can be expanded in terms of density-homogeneous functionals. We compute

$$Q_1[\rho]=\int\frac{\rho(\mathbf{r})}{1+\rho(\mathbf{r})}d\mathbf{r}-\int\frac{\rho^2(\mathbf{r})}{[1+\rho(\mathbf{r})]^2}d\mathbf{r},$$
$$Q_2[\rho]=\int\frac{\rho^2(\mathbf{r})}{[1+\rho(\mathbf{r})]^2}d\mathbf{r}-\int\frac{\rho^3(\mathbf{r})}{[1+\rho(\mathbf{r})]^3}d\mathbf{r}, \tag{A5a}$$
$$Q_3[\rho]=\int\frac{\rho^3(\mathbf{r})}{[1+\rho(\mathbf{r})]^3}d\mathbf{r}-\int\frac{\rho^4(\mathbf{r})}{[1+\rho(\mathbf{r})]^4}d\mathbf{r},$$
$$\vdots$$

Then, from Eq. (8), we obtain

$$H_0[\rho]=0,$$
$$H_1[\rho]=\int d\mathbf{r}\left[\frac{\rho(\mathbf{r})}{1+\rho(\mathbf{r})}+\frac{\rho^2(\mathbf{r})}{[1+\rho(\mathbf{r})]^2}+\frac{\rho^3(\mathbf{r})}{[1+\rho(\mathbf{r})]^3}+\frac{\rho^4(\mathbf{r})}{[1+\rho(\mathbf{r})]^4}+\cdots\right],$$
$$H_2[\rho]=-\int d\mathbf{r}\left[\frac{\rho^2(\mathbf{r})}{[1+\rho(\mathbf{r})]^2}+\frac{2\rho^3(\mathbf{r})}{[1+\rho(\mathbf{r})]^3}+\frac{3\rho^4(\mathbf{r})}{[1+\rho(\mathbf{r})]^4}+\cdots\right], \tag{A5b}$$
$$H_3[\rho]=\int d\mathbf{r}\left[\frac{\rho^3(\mathbf{r})}{[1+\rho(\mathbf{r})]^3}+\frac{3\rho^4(\mathbf{r})}{[1+\rho(\mathbf{r})]^4}+\cdots\right],$$
$$\vdots$$

It can be verified that Eq. (6) is rigorously satisfied for each H_j in Eq. (A5b).

Example 3. Suppose that $Q[\rho]$ when expanded as in Eq. (1) becomes simply

$$Q[\rho]=Q_0[\rho]+Q_1[\rho], \tag{A6}$$

with all other terms in Eq. (4) zero. Now try expressing Q in terms of two homogeneous functionals as

$$Q[\rho]=H_{n_0}[\rho]+H_{n_1}[\rho], \tag{A7}$$

that is, as the sum of functionals of degree n_0 and n_1, respectively. Then

$$Q_1[\rho]=n_0H_{n_0}[\rho]+n_1H_{n_1}[\rho], \tag{A8}$$

and

$$Q_2[\rho]=-\tfrac{1}{2}n_0(n_0-1)H_{n_0}[\rho]-\tfrac{1}{2}n_1(n_1-1)H_{n_1}[\rho]=0. \tag{A9}$$

Solving Eqs. (A7) and (A8), one gets

$$H_{n_0}[\rho]=\frac{n_1}{n_1-n_0}Q[\rho]-\frac{1}{n_1-n_0}Q_1[\rho],$$
$$H_{n_1}[\rho]=-\frac{n_0}{n_1-n_0}Q[\rho]+\frac{1}{n_1-n_0}Q_1[\rho]. \tag{A10}$$

It may be straightforwardly verified that

$$\int\rho(\mathbf{r})\frac{\delta H_{n_0}[\rho]}{\delta\rho(\mathbf{r})}d\mathbf{r}=n_0H_{n_0}[\rho] \tag{A11}$$

and

$$\int\rho(\mathbf{r})\frac{\delta H_{n_1}[\rho]}{\delta\rho(\mathbf{r})}d\mathbf{r}=n_1H_{n_1}[\rho], \tag{A12}$$

where n_0 and n_1 in principle are arbitrary numbers. Note, however, that for the exactly truncated series one also has Eq. (A9), which forces $n_0=0$ and $n_1=1$. The generalization of this result is that whenever there are k terms in the expansion of Eq. (A6), an equivalent exact representation of Q exists that is the sum of k homogeneous functionals of degrees 0, 1,...,k.

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