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Kinetic-energy functionals via Padé approximations

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A representation of the kinetic-energy functional as the product of a homogeneous-gas functional and a Padé approximation in the density gradient is developed and shown to describe accurately the kinetic energy of atomic systems.

The exact kinetic-energy functional of the electron density remains unknown, but limiting forms in the case of slowly varying densities can be derived via the gradient expansion[1-3] and local wave-vector analysis.[4-6] In the former, the expansion

$$T \equiv \int d\mathbf{r} [\tau(\rho_\uparrow) + \tau(\rho_\downarrow)] \tag{1a}$$

$$= \int d\mathbf{r} \sum_{m=0}^{\infty} [\tau_{2m}(\rho_\uparrow) + \tau_{2m}(\rho_\downarrow)] \tag{1b}$$

$$= \sum_{m=0}^{\infty} T_{2m} \tag{1c}$$

in terms of the spin-up and spin-down electron densities is used. The first four terms are[7]

$$\tau_0(n) = \tfrac{3}{10} (6\pi^2)^{2/3} n^{5/3} , \tag{2a}$$

$$\tau_2(n) = \tfrac{1}{72} \frac{|\nabla n|^2}{n} , \tag{2b}$$

$$\tau_4(n) = \tfrac{1}{540} (6\pi^2)^{-2/3} n^{1/3} \left[\left(\frac{\nabla^2 n}{n} \right)^2 - \frac{9}{8} \left(\frac{\nabla^2 n}{n} \right) \left| \frac{\nabla n}{n} \right|^2 + \frac{1}{3} \left| \frac{\nabla n}{n} \right|^4 \right] , \tag{2c}$$

$$\tau_6(n) = \tfrac{1}{45360} (6\pi^2)^{-4/3} n^{-1/3} \left[13 \left(\frac{\nabla\nabla^2 n}{n} \right)^2 + \frac{2575}{144} \left(\frac{\nabla^2 n}{n} \right)^3 + \frac{249}{16} \left| \frac{\nabla n}{n} \right|^2 \frac{\nabla^4 n}{n} + \frac{1499}{18} \left| \frac{\nabla n}{n} \right|^2 \left(\frac{\nabla^2 n}{n} \right)^2 \right.$$
$$\left. - \frac{1307}{36} \left| \frac{\nabla n}{n} \right|^2 \frac{\nabla n \cdot \nabla\nabla^2 n}{n^2} + \frac{343}{18} \left| \frac{\nabla n \cdot \nabla\nabla n}{n^2} \right|^2 + \frac{8341}{72} \frac{\nabla^2 n}{n} \left| \frac{\nabla n}{n} \right|^4 - \frac{1\,600\,495}{2592} \left| \frac{\nabla n}{n} \right|^6 \right] . \tag{2d}$$

n symbolizes either $\rho_\uparrow$ or $\rho_\downarrow$. When n varies too quickly, the integrated series in T_{2m} does not converge. For atoms, T_6 is infinite. Considerable work has been directed toward eliminating this divergence by such global modifications as truncation of the series in T_{2m}, multiplication by N-dependent coefficients,[8-10] or variation of the integrated terms.[11,12]

Recently, local modifications of the series have been proposed by Pearson and Gordon,[13] based upon an asymptotic-series approach, and by Plumer and Stott[6] (after Meyer, Wang, and Young[5]) based upon a second-order perturbation theory plus dominant-wave-vector analysis.[14] Both approaches involve changing the contri-

bution of τ_{2m} at each value of n. Since the convergence of the gradient expansion depends explicitly on local ratios such as $|\nabla n|/n$, such local modification schemes are likely to be successful at producing an accurate, though approximate, functional. The present article is a contribution to this goal.

We wish to rewrite the series in τ_{2m} as a Padé approximation of the general form

$$\tau(n) \approx \tau_0(n) P_{N,M}(\tau_2(n)/\tau_0(n)) , \tag{3}$$

where

$$P_{N,M}(x) = \sum_{i=0}^{N} a_i x^i \bigg/ \sum_{i=0}^{M} b_i x^i . \tag{4}$$

Justifications for this form and the first few coefficients are obtained from a few areas. First, consider the perturbation-theory functional in the dominant-wave-vector approximation[5,6,14]

$$\tau(n) = \tau_0(n) + \frac{\lambda}{8} \frac{|\nabla n|^2}{n} , \tag{5a}$$

$$\lambda = \frac{1 - f(y)}{3y^2 f(y)} , \tag{5b}$$

$$f(y) = \frac{1}{2}\left[1 + \frac{1 - y^2}{2y} \ln\left| \frac{1+y}{1-y} \right| \right] , \tag{5c}$$

$$y = \frac{1}{12}(3\pi^2)^{-1/3} \frac{|\nabla n|}{n^{4/3}} = \left[\frac{3\tau_2}{20\tau_0} \right]^{1/2} . \tag{5d}$$

Since the expansion in Eq. (5a) is truncated at quadratic terms in $|\nabla n|^2$, we retain terms up to y^2 in λ, yielding

$$\tau(n) = \tau_0(n) \frac{1 + 0.95\tau_2/\tau_0}{1 - 0.05\tau_2/\tau_0} , \tag{6}$$

which is exactly of the form in Eq. (4) with $N = 1 = M$, $a_0 = 1 = b_0$, $a_1 = 0.95$, and $b_1 = -0.05$. For very small τ_2/τ_0, this Padé form duplicates the gradient expansion truncated at $m = 1$, as required.

For a rough idea of the behavior for larger values of τ_2/τ_0 we consider the gradient expansion for a locally exponential density variation,

$$n = A \exp[\alpha(x + y + z)] . \tag{7}$$

This yields

$$\tau_4 = \frac{6}{10} \frac{\tau_2^2}{\tau_0} , \tag{8a}$$

$$\tau_6 = -\frac{37911}{140} \frac{\tau_2^3}{\tau_0^2} . \tag{8b}$$

The important feature is the extremely large negative coefficient in the τ_6 term, indicating that

$$P_{N,M}(x) \xrightarrow[x \to 0]{} 1 + x + c_2 x^2 + c_3 x^3 + \cdots \tag{9}$$

will not be adequately represented by any truncation at the quadratic term. The exact magnitude of the coefficients may vary [e.g., replacement of $|\nabla^i n/n|$ by $|\nabla n/n|^i$ in Eqs. (2c) and (2d) yields different values], but it is apparent that the cubic term will be negative and of considerable importance locally.

The final information used in determining the Padé form is the fact that

$$\tau(n) = \frac{1}{8} \frac{|\nabla n|^2}{n} = \tau_w \tag{10a}$$

for one-electron atoms and two-electron Hartree-Fock atoms. As emphasized by Acharya, Bartolloti, Sears, and Parr,[8] this form is central to the proper description of atomic kinetic energies, especially in the tail of the wave functions for the valence-electrons. Since this is the region

where $\tau_2/\tau_0 \gg 1$, we enforce the limit

$$P_{N,M}(x) \xrightarrow[x \to \infty]{} 9x . \tag{10b}$$

Equations (6), (9), and (10) require at the minimum $N = 4$ and $M = 3$, yielding the explicit form

$$P_{4,3}(x) = \frac{1 + 0.95x + a_2 x^2 + a_3 x^3 + 9b_3 x^4}{1 - 0.05x + b_2 x^2 + b_3 x^3} . \tag{11}$$

The power series coefficients in Eq. (9) are then

$$c_2 = a_2 + 0.05 - b_2 , \tag{12a}$$

$$c_3 = a_3 + 0.05c_2 - b_2 - b_3 . \tag{12b}$$

The values of the parameters b_2, b_3, a_2, and a_3 can be determined by fitting the kinetic-energy functional globally to known total kinetic energies. We have used Hartree-Fock electron[15] densities and kinetic energies for He, Ne, Ar, and Kr only to determine the values[16] shown in Table I. It is apparent that our expectations were correct about the power-series coefficients resulting from the Padé fit. [The Hartree-Fock values are not reproduced exactly even for these atoms in Table II because the constraints $b_3 > 0$, and nonvanishing of the denominator in Eq. (11) restrict the possible parameter values.]

We calculated the kinetic energies for a variety of other atoms (not used in the fit) in Table II, using the proper spin-density functional and not the unpolarized one used by Murphy and Wang[3(a)] and others.[17] [The results for T_0 are corrected values to Ref. 3, with the differences being especially large for N (~ 0.9) and Mn (~ 2.85) with three and five unpaired spins, respectively.] The Padé values are a considerable improvement over the gradient-expansion results whether truncated at T_2 or T_4 and are as good as the asymptotic-series truncation values for the few cases where the latter are available. The accuracy of the Padé values is especially impressive across the (first row) transition-metal series.

Finally, we show the function $P_{4,3}(x)$ in Fig. 1, along with the Weizacker, zeroth-, and second-order gradient expansions (i.e., $9x$, 1, and $1 + x$, respectively). In this display, Eq. (5) or any Padé form $P_{2,1}$ in x (e.g., $\gamma^{(1)}$ in Ref. 6) would always lie above the $1 + x$ line and approach $9x$ from above. In general, this would overestimate global kinetic energies since even the piecewise form $1 + x$ for $0 \le x \le \frac{1}{8}$ and $9x$ for $x \ge \frac{1}{8}$ yields values of 3.62707, 137.157, 530.032, and 2735.40 for He, Ne, Ar, and Kr, respectively.

TABLE I. Padé-approximation parameters.[a]

i	a_i	b_i	c_i
0	1	1	1
1	0.95000	−0.05000	1.00000
2	14.28111	9.99802	4.33309
3	−19.57962	2.96085	−32.32185
4	26.64777	. . .[b]	. . .[b]

[a] a_2, a_3, b_2, b_3 determined by least-squares fitting to Hartree-Fock values for He, Ne, Ar, Kr. Results shown in Table II.
[b] Not calculated.

TABLE II. A comparison of atomic kinetic energies (hartrees) from Hartree-Fock densities.

Atom	Exact[a]	T_0	T_2	T_0+T_2 (% error)	Padé[b] (% error)
H	0.500000	0.45896	0.055556	0.51452 (+2.90) 0.5300 (+6.00)[c] 0.5116 (+2.32)[d]	0.51562 (+3.12)
He	2.86168	2.56054	0.317969	2.87850 (+0.59) 2.9631 (+3.54)[e] 2.8740 (+0.43)[d]	2.87639 (+0.51)
Li	7.43273	6.70062	0.804425	7.50504 (+0.97)	7.44941 (+0.22)
Be	14.5730	13.1286	1.51800	14.6466 (+0.51) 14.990 (+2.86)[e] 14.730 (+1.08)[d]	14.4223 (−1.03)
B	24.5291	22.0720	2.45081	24.5228 (−0.03)	24.2089 (−1.31)
C	37.6886	34.0144	3.58440	37.5988 (−0.24)	37.2533 (−1.15)
N	54.4009	49.4771	4.90815	54.3852 (−0.03)	54.0643 (−0.62)
O	74.8094	67.8965	6.46078	74.3573 (−0.60)	74.1625 (−0.86)
F	99.4093	90.4598	8.18319	98.6429 (−0.77)	98.6959 (−0.72)
Ne	128.547	117.761	10.0683	127.829 (−0.56) 129.78 (+0.96)[e] 128.39 (−0.12)[d]	128.221 (−0.25)
Na	161.859	148.809	12.2837	161.093 (−0.47)	161.718 (−0.09)
Mg	199.614	184.017	14.7324	198.749 (−0.43) 201.49 (+0.94)[e] 199.70 (+0.05)[d]	199.578 (−0.02)
Al	241.877	223.443	17.4245	240.868 (−0.42)	242.008 (+0.05)
Si	288.854	267.315	20.3434	287.659 (−0.41)	289.139 (+0.10)
Cl	459.482	426.865	30.4560	457.321 (−0.47)	460.117 (+0.14)
Ar	526.817	490.017	34.2721	524.289 (−0.48) 530.43 (+0.69)[e] 526.34 (−0.09)[d]	527.617 (+0.15)
K	599.164	557.735	38.3603	596.096 (−0.51)	600.001 (+0.14)
Ca	676.758	630.259	42.6855	672.945 (−0.56) 680.86 (+0.54)[e]	677.300 (+0.08)
Sc	759.735	707.714	47.2218	754.936 (−0.63)	759.917 (+0.02)
Ti	848.405	790.634	51.9509	842.585 (−0.69)	848.227 (−0.02)
V	942.884	879.246	56.9338	936.180 (−0.71)	942.509 (−0.04)
Cr	1043.31	973.752	62.0959	1035.85 (−0.72)	1042.86 (−0.04)
Mn	1149.87	1074.47	67.4666	1141.94 (−0.68)	1149.70 (−0.01)
Fe	1262.44	1179.74	73.1039	1252.85 (−0.76)	1261.45 (−0.08)
Co	1381.41	1291.32	78.9550	1370.28 (−0.81)	1379.75 (−0.12)
Ni	1506.87	1409.44	84.9290	1494.37 (−0.83)	1504.75 (−0.14)
Cu	1638.95	1534.31	91.2072	1625.52 (−0.82)	1636.77 (−0.13)
Zn	1777.85	1666.23	97.6249	1763.86 (−0.79) 1780.11 (+0.13)[e]	1776.03 (−0.10)
Kr	2752.05	2591.77	141.897	2733.66 (−0.67) 2757.10 (+0.18)[e]	2751.51 (−0.02)

[a]Exact results from Ref. 15.
[b]Padé result from Eqs. (3) and (11) with the coefficients in Table I.
[c]$T_0+T_2+T_4$ results of Ref. 13.
[d]Local truncation value from Ref. 13.
[e]$T_0+T_2+T_4$ results of Ref. 2. These used a spin-unpolarized kinetic-energy functional, which is the same as the spin-polarized functional for closed-shell atoms.
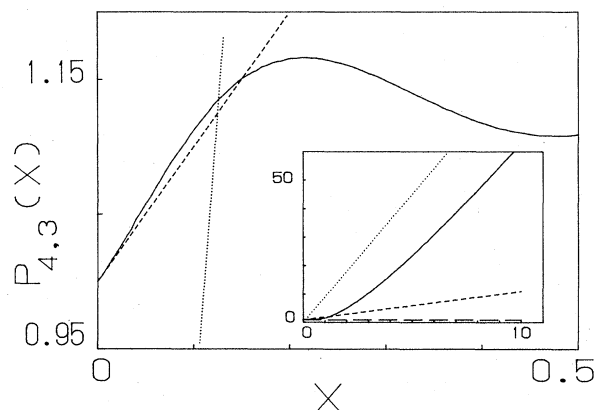
FIG. 1. Padé function in Eq. (11) (——) and various other functions $9x$ ($\cdots$), $1+x$ (---), and 1 (- -).

Our fundamental conclusion is that the kinetic-energy functional becomes larger than the second-order gradient expansion as $|\nabla n|/n^{4/3}$ increases from zero, then must become smaller than this expansion, and finally must become larger as $|\nabla n|/n^{4/3}$ increases without bound. It never becomes negative though. This behavior provides a stringent test of any general kinetic-energy functional. From a practical viewpoint, the approximate representation of $\tau(n)$ in terms of a Padé function provides an accurate kinetic-energy functional with the *proper behavior in the tail of atomic wave functions* [in contrast to the series truncation[13] which approaches[18] $\tau_0(n)$]. This is important for the treatment of chemically interesting effects.

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[18]Note that the Padé form could be varied to approach $\tau_0(n)$ by changing the limit in Eq. (10b) to be unity instead of $9x$. Then $P_{3,3}$ would be the appropriate form with $a_3 = b_3$.