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Convergent sum of gradient expansion of the kinetic-energy density functional up to the sixth order term using Padé approximant

A. Sergeev¹, F.H. Alharbi^{1,2}, R. Jovanovic¹, and S. Kais^{1,2,3}

¹ Qatar Environment & Energy Research Institute, Qatar Foundation, Doha, Qatar.

² College of Science & Engineering (QEERI), Hamad Bin Khalifah University, Doha, Qatar.

³ Department of Chemistry, Physics, and Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907, USA.

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E-mail: falharbi@qf.org.qa

Abstract. The gradient expansion of the kinetic energy density functional, when applied to atoms or finite systems, usually grossly overestimates the energy in the fourth order and generally diverges in the sixth order. We avoid the divergence of the integral by replacing the asymptotic series including the sixth order term in the integrand by a rational function. Padé approximants show moderate improvements in accuracy in comparison with partial sums of the series. The results are discussed for atoms and Hooke's law model for two-electron atoms.

1. Introduction

For all electronic systems, Hohenberg and Kohn [1] proved the existence of a “universal functional” that accounts for the total energy except those contributions due to an external potential (mainly due to the electron-nuclei Coulombic interaction). The main challenge is that the universal functional is not known and thus Kohn and Sham [2] devised an alternative approach to approximate the “universal functional”. In this approach, the kinetic term for non-interacting electrons was treated exactly but the exchange-correlation term are left unknown. Furthermore, in their initial work, Hohenberg and Kohn [1] suggested that the components of the “universal functional”; namely, the kinetic, exchange, and correlation contributions, can be expanded using gradient based expansions.

Since then, many approximations have been developed. For kinetic energy, the starting point has been mostly Thomas–Fermi functional. In the limit of infinitely extended uniform density, the kinetic energy $T_s[\rho]$ is simply Thomas–Fermi kinetic energy $T_{TF}[\rho]$ (in density functional form) [3, 4, 5]. For slowly varying densities, corrections to T_{TF} can be derived using gradient expansions. Different approaches have been used and they agree in most cases. The most frequently used procedures are Kirzhnits expansion [6, 7, 8, 9], partition-function approach [10, 7], and Grammaticos-Voros algebraic method [11, 12]. As a result, the kinetic energy density functional (KEDF) can be arranged in the following series:

$$T_s[\rho(\mathbf{r})] = T_0 + T_2 + T_4 + T_6 + \dots, \quad (1)$$



where $T_0 = T_{\text{TF}}$, which will be presented in the next section, $T_n = \int \tau_n d\mathbf{r}$, and the kinetic energy densities τ_n collect terms that have gradients of the total order n . With the exception of solid state systems [13], the sixth-order term of the gradient expansion generally diverges for a finite system.

To eliminate the divergence, many additional approximations have been suggested. Pearson and Gordon [14] suggested local truncation of the gradient expansion with additional corrections to avoid vanishing densities. Also, many alternative approximate re-summation methods [15, 16, 17, 18] including Padé approximants [19, 20, 21] were suggested. The suggested Padé approximants are mostly based on τ_2/τ_0 expansions to resemble different asymptotic behaviors [19, 20, 21]. Obviously, each approach has advantages and disadvantages and each has a range of applicability.

In this paper, we present a systematic approach that allows to avoid regions where higher order terms are relatively large and are no longer “small corrections” while taking advantage of these terms in areas where they are small and improve the accuracy. So, we use a Padé approximant to have a convergent sum of gradient expansion approximation up to the sixth-order term. In many cases, adding of the correction $T_4[\rho]$ usually makes the result less accurate, because this correction is valid only asymptotically for heavy atoms. Moreover, since $T_6[\rho]$ diverges for finite systems, the knowledge of τ_6 is assumingly -from the first glance- useless. By using the proper Padé approximant, it is possible to “sum” approximately the gradient expansion of kinetic energy so that the approximant has some asymptotic behavior, but suppresses divergent terms in a region away from asymptotics.

The proposed Padé approximant improves the accuracy when there exists a significant region of \mathbf{r} where

$$|\tau_6(r)| < |\tau_4(r)|. \quad (2)$$

In case of a finite system, $\rho(r)$ decreases exponentially for large distance, and all gradients of ρ are roughly proportional to ρ . Therefore, taking into account Equations (5) and (6), for large r $\tau_4(r) \sim \rho^{1/3}(r)$ and $\tau_6(r) \sim \rho^{-1/3}(r)$, and for sufficiently large r , the inequality (2) is not satisfied. We guess that for small r , the behavior of τ_4 and τ_6 may depend on the presence of Coulomb singularity in the potential. In case of atoms, we have unfavorable inequality $|\tau_6(r)| > |\tau_4(r)|$ both for small r and for large r , with a narrow intermediate region where the inequality (2) holds. We expect this approximation to work very well for confined harmonic potentials such the case of treating quantum dots [22, 23].

2. The method

As aforementioned, in the limit of uniform density [3, 4], the kinetic energy $T_s[\rho]$ is

$$T_{\text{TF}} = C_{\text{TF}} \int \rho^{5/3} d\mathbf{r}, \quad C_{\text{TF}} = \frac{3}{10} (3\pi^2)^{2/3} \quad (3)$$

Any effect due to slowly varying densities can be accounted for approximately as corrections to Eq. 3 using gradient expansions. So, the kinetic energy density functional can be organized in a series as in Eq. 1. Using Kirzhnits expansion approach, Kirzhnits [6], Hodges [7], and Murphy [8] have derived the second-, forth-, and sixth-order terms respectively. These terms are

$$\tau_2 = \frac{1}{72} \frac{(\nabla \rho(\vec{r}))^2}{\rho(\vec{r})}, \quad (4)$$

$$\tau_4 = \frac{(3\pi^2)^{-2/3}}{540} \rho^{1/3} \left[\left(\frac{\nabla^2 \rho}{\rho} \right)^2 - \frac{9}{8} \left(\frac{\nabla^2 \rho}{\rho} \right) \left(\frac{\nabla \rho}{\rho} \right)^2 + \frac{1}{3} \left(\frac{\nabla \rho}{\rho} \right)^4 \right]. \quad (5)$$

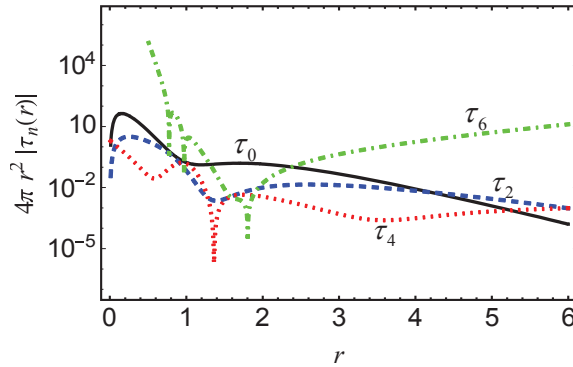


Figure 1. Gradient expansion corrections for the density of kinetic energy of beryllium atom, in logarithmic scale. The black, blue, red, and green lines are for τ_0 , τ_2 , τ_4 , and τ_6 respectively. Obviously, the correction τ_6 diverges as $r \rightarrow \infty$, while τ_4 converges, but very slowly.

and

$$\begin{aligned} \tau_6 = \frac{(3\pi^2)^{-4/3}}{45\,360} \rho^{-1/3} & \left[13 \left(\frac{\nabla\nabla^2\rho}{\rho} \right)^2 + \frac{2575}{144} \left(\frac{\nabla^2\rho}{\rho} \right)^3 + \frac{249}{16} \left(\frac{\nabla\rho}{\rho} \right)^2 \left(\frac{\nabla^4\rho}{\rho} \right) \right. \\ & + \frac{1499}{18} \left(\frac{\nabla\rho}{\rho} \right)^2 \left(\frac{\nabla^2\rho}{\rho} \right)^2 - \frac{1307}{36} \left(\frac{\nabla\rho}{\rho} \right)^2 \left(\frac{\nabla\rho \cdot \nabla\nabla^2\rho}{\rho^2} \right) + \frac{343}{18} \left(\frac{\nabla\rho \cdot \nabla\nabla^2\rho}{\rho^2} \right)^2 \\ & \left. + \frac{8341}{72} \left(\frac{\nabla^2\rho}{\rho} \right) \left(\frac{\nabla\rho}{\rho} \right)^4 - \frac{1\,600\,495}{2592} \left(\frac{\nabla\rho}{\rho} \right)^6 \right]. \quad (6) \end{aligned}$$

Generally, the sixth-order term diverges for atoms and molecules. Actually, it diverges when the density vanishes at any position. A study of the gradient expansion for atomic isoelectronic series [24] shows that that $T_0 + T_2$ is more accurate approximation than $T_0 + T_2 + T_4$ in almost all cases, except for highly ionized Ar-like ions. A similar study for all neutral atoms [25] shows that $T_0 + T_2$ is more accurate than $T_0 + T_2 + T_4$ for all atoms up to potassium. Only for heavier atoms, the situation reverses. It rises the question of whether the fourth order term T_4 and the diverging sixth-order density τ_6 could be of any use for the case of finite systems.

A typical behaviour of the gradient correction for an atomic system is illustrated here for the case of a beryllium atom. We took the electron density from the Hartree–Fock data of Clementi tables [26]. The components of kinetic energy gradient expansion up to the 6-th order term are shown on Figure 1. It is clear that in a narrow region of $1.6 < r < 1.9$, the gradient expansion seems convergent, i.e. $|\tau_6| < |\tau_4| < |\tau_2| < |\tau_0|$. However, everywhere else τ_6 is no longer a small correction to the lower order terms. For sufficiently large $r > 6$, we have an opposite inequality $|\tau_6| > |\tau_4| > |\tau_2| > |\tau_0|$, that means that all corrections become erroneous.

So, the objective is to “sum” the gradient expansion at each point r by replacing it by another function that has some asymptotic behavior, but suppresses the divergent terms in a region away from asymptotics. Let’s consider a family of densities parameterized by a dummy variable $g > 0$,

$$\rho_g(\vec{r}) = g\rho(r), \quad (7)$$

so that the original density ρ can be recovered from this family of functions by setting $g = 1$. Then, the gradient expansion for the density can be organized as in the following series

$$\tau_g(\vec{r}) = g^{5/3} \left(\tau_0(\vec{r}) + g^{-2/3}\tau_2(\vec{r}) + g^{-4/3}\tau_4(\vec{r}) + g^{-6/3}\tau_6(\vec{r}) + \dots \right). \quad (8)$$

The expression in parenthesis in Eq. 8 is obviously a power series in

$$x = g^{-2/3}. \quad (9)$$

So, asymptotically for small x we have

$$f(x) = \tau_0 + \tau_2 x + \tau_4 x^2 + \tau_6 x^3 + \dots, \quad (10)$$

where

$$f(x) = g^{-5/3} \tau_g(\vec{r}). \quad (11)$$

We would like to replace $f(x)$ by an approximation $\tilde{f}(x)$ having the same asymptotic expansion as $f(x)$ given by Eq. 10. We seek to have $\tilde{f}(1) \approx \tau_0 + \tau_2 + \tau_4 + \tau_6$ if $|\tau_6| < |\tau_4| < |\tau_2| < |\tau_0|$ and $\tilde{f}(1) \approx \tau_0 + \tau_2$ if $|\tau_6|$ is large.

The Padé approximant [2/1] to the series Eq. (10) is defined as a ratio of two polynomials of degree 2 and 1 in x ,

$$f^{[2/1]}(x) = \frac{a_0 + a_1 x + a_2 x^2}{b_0 + b_1 x} \quad (12)$$

with $b_0 \neq 0$ that has the same expansion in x up to the third order,

$$f^{[2/1]}(x) = f(x) + o(x^3). \quad (13)$$

Explicitly

$$f^{[2/1]}(x) = \tau_0 + \tau_2 x + \frac{\tau_4^2 x^2}{\tau_4 - \tau_6 x}. \quad (14)$$

Notice that if $\tau_6 \rightarrow \infty$, then $f^{[2/1]}(1) = \tau_0 + \tau_2$.

We define $\tau^{[2/1]} = f^{[2/1]}(1) = \tau_0 + \tau_2 + \frac{\tau_4^2}{\tau_4 - \tau_6}$ and $T^{[2/1]} = 4\pi \int_0^\infty r^2 \tau^{[2/1]} dr$ where the later equation is written in case of spherical symmetry. If the integrand has poles, i.e. $\tau_4 = \tau_6$ for some r , then the integral can be defined through Cauchy principal value.

In similar way, we consider here the Padé approximant $\tau^{[1/1]} = \tau_0 + \frac{\tau_2^2}{\tau_2 - \tau_4}$ along with the partial sum $\tau_0 + \tau_2 + \tau_4$. Even if the integral of this partial sum converges, the convergence is slow because of behavior $\sim \rho^{1/3}$ for large r . For the Padé approximant $\tau^{[1/1]}$, much faster convergence $\sim \rho^{7/3}$ is expected as obtained and presented in the next section.

3. Results and discussions

3.1. Hooke's law model for two-electron atoms

The Hamiltonian for the Hooke's law model for two-electron atoms is given by

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{\omega^2}{2}(r_1^2 + r_2^2) + \frac{1}{r_{12}}. \quad (15)$$

The ground state wavefunction is known analytically for some values of ω . For $\omega = 1/2$, it is [27, 28]

$$\Psi(r_1, r_2) = N_0 \left(1 + \frac{1}{2}r_{12}\right) e^{-(1/4)(r_1^2 + r_2^2)}, \quad (16)$$

where

$$N_0 = \left[4\pi^{5/2} \left(8 + 5\pi^{1/2}\right)\right]^{-1/2}. \quad (17)$$

and the density is (corrected Eq. (7) from [27])

$$\rho(r) = N_0^2 e^{-\frac{1}{2}r^2} \left\{ \left(\frac{\pi}{2}\right)^{1/2} \left[\frac{7}{4} + \frac{1}{4}r^2 + \left(r + \frac{1}{r}\right) \operatorname{erf}(2^{-1/2}r) \right] + e^{-\frac{1}{2}r^2} \right\}. \quad (18)$$

If $\omega \neq 1/2$, then we used a variational approach with the trial wavefunction in the form similar to Hylleraas variational function for helium [29, 30, 31]

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i,j,k \geq 0, i+j+k=N} C_{ijk} \left(r_1^i r_2^j e^{-\alpha_1 r_1 - \alpha_2 r_2} + r_2^i r_1^j e^{-\alpha_1 r_2 - \alpha_2 r_1} \right) r_{12}^k \quad (19)$$

with $\alpha_1 = 2\sqrt{\omega}$, $\alpha_2 = 3.2\sqrt{\omega}$ (ideally, the values of α_1 and α_2 should be chosen by minimizing the energy, but since it involves non-linear equations, we did it numerically for $N = 8$, and then tried to approximate the near optimal values by a simple analytic formula). Calculations were done for increasing set of basis functions with $N = 10, 12$, and 16 for $\omega = 1/2$, and the results agree with the results determined from the exact solution for the density, 18. For several other values of ω , calculations were done for $N = 10$. The results are shown in Table 3.1 and for the case of $\omega = 1/2$, the gradient expansion corrections and their sums up to n -th order are shown on Fig. 2 and Fig. 3 respectively. For $\omega < 1$, it appears that the Padé approximant [2/1] is the most accurate, and for $\omega \geq 1$ the partial sum $T_0 + T_2$ is the best.

Table 1. Comparison of kinetic energy obtained from density ρ by summation of gradient expansion using different methods, for Hooke's law model. (The results are presented as percent error.)

ω	T_s	Percent error ($E_T = 100 T_s - T /T_s$)				
		E_{T_0}	$E_{T_0+T_2}$	$E_{T_0+T_2+T_4}$	$E_{T[1/1]}$	$E_{T[2/1]}$
1/4	0.30036	-12.7	-1.67	15.6	0.48	-1.15
1/2	0.63525	-11.9	-0.78	16.5	1.27	-0.26
1	1.32757	-11.3	-0.19	15.4	1.81	0.33
4	5.62884	-10.7	0.45	15.1	2.4	0.98

Practically, for the system of two non-interacting particles with the same density ρ , $\psi(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_1)\phi(\vec{r}_2)$ where $\phi_1^2 = \phi_2^2 = \frac{1}{2}\rho$. In the ground state, $\phi_1 = \phi_2 = \sqrt{\rho}$. So, we obtain

$$\begin{aligned} T_s &= - \int d\mathbf{r}_1 d\mathbf{r}_2 \psi(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{2} (\nabla_1^2 + \nabla_2^2) \psi(\mathbf{r}_1, \mathbf{r}_2) \\ &= - \int d\mathbf{r} \phi(\mathbf{r}) \nabla^2 \phi(\mathbf{r}) = \int \tau_K(\rho) d\mathbf{r} \end{aligned} \quad (20)$$

where

$$\tau_K(\rho) = \frac{1}{8} \frac{(\nabla \rho)^2}{\rho} - \frac{1}{4} \nabla^2 \rho. \quad (21)$$

In radial coordinates,

$$T_s = 4\pi \int r^2 \tau_K(\rho) dr, \quad (22)$$

where

$$\tau_K(\rho) = \frac{1}{8} \frac{(\rho')^2}{\rho} - \frac{1}{4} \rho'' - \frac{1}{2} \frac{\rho'}{r}. \quad (23)$$

Because of spherical symmetry, the integration reduces to integration over radius, $\tilde{T} = 4\pi \int_0^\infty r^2 \tilde{\tau} dr$, where $\tilde{\tau}$ is an approximation to the density of kinetic energy, and \tilde{T} is corresponding approximation to the total kinetic energy.

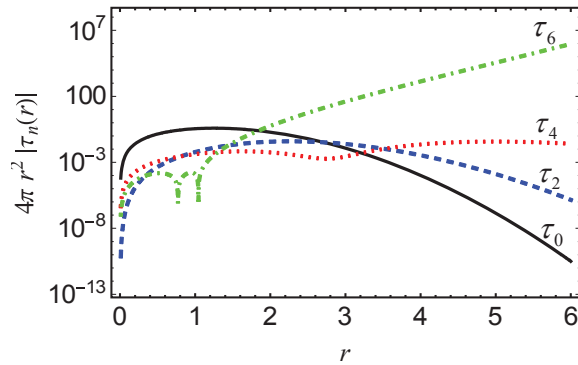


Figure 2. Gradient expansion corrections for the density of kinetic energy, in logarithmic scale. The black, blue, red, and green lines are for τ_0 , τ_2 , τ_4 , and τ_6 respectively. Obviously, the correction τ_6 diverges as $r \rightarrow \infty$, while τ_4 converges, but very slowly.

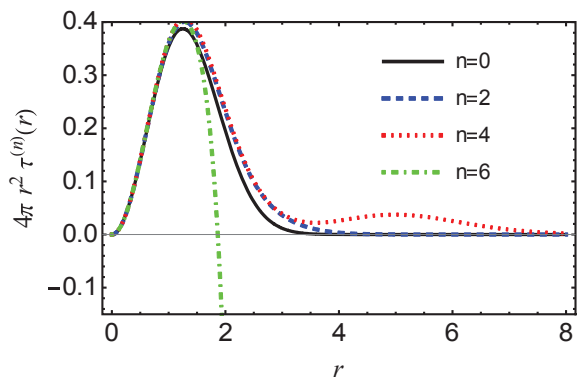


Figure 3. Sum of several first terms of gradient expansion, $\tau^{(0)} = \tau_0$ (black), $\tau^{(2)} = \tau_0 + \tau_2$ (blue), $\tau^{(4)} = \tau_0 + \tau_2 + \tau_4$ (red), and $\tau^{(6)} = \tau_0 + \tau_2 + \tau_4 + \tau_6$ (green) for Hooke's law model. Clearly, the 6-th order sum diverges when $r > 1$. It appears that the most accurate partial sum is $\tau^{(2)}$, and the curve for Padé approximant $\tau^{[2/1]}$ coincides with $\tau^{(2)}$ within accuracy of the plotting.

Table 2. Comparison of kinetic energy obtained from density ρ by summation of gradient expansion using different methods, for atoms. (The results are presented as percent error.)

Atom	T_{HF} (a.u.)	Percent error ($E_T = 100 T_s - T /T_s$)				
		E_{T_0}	$E_{T_0+T_2}$	$E_{T_0+T_2+T_4}$	$E_{T^{[1/1]}}$	$E_{T^{[2/1]}}$
He	2.8617	-10.5	0.59	3.57	2.01	0.53
Li	7.4328	-10.1	0.62	3.09	2.00	0.61
Be	14.573	-9.9	0.50	2.9	1.86	0.53
Ne	128.55	-8.4	-0.55	0.95	0.50	-0.51
Ar	526.81	-7.0	-0.49	0.69	0.32	-0.43
Kr	2752.05	-5.9	-0.69	0.18	-0.09	-0.63
Xe	7232.13	-5.2	-0.68	0.07	-0.17	-0.62

3.2. Atomic densities

For the atoms, we calculated the densities using Hartree–Fock wavefunctions from Clementi Atomic Data Tables [26]. The results of summation of the gradient expansion are given in Table

3.2. For He, we found that the gradient expansion and its summations are similar to the case of Hooke's law model for two-electron atoms, but the sixth-order term diverges even faster. As a result, the Padé approximant improves the partial sum $\tau_0 + \tau_2$ only in a narrow range of $r \sim 0.6$, where τ_6 is comparable with τ_0 . Outside of this range, $\tau^{[2/1]} \approx \tau^{(2)}$. Therefore, results of integration of these functions are very close, but still the Padé approximant gives some small improvement in comparison with the partial sum.

While for Li and Be, we found that the gradient expansion and its summation is similar to the case of helium atom, but the sixth-order term diverges much faster. As a result, the Padé approximant does not improve accuracy in comparison with the partial sum.

For heavier noble-gas atoms (Ne, Ar, Kr, and Xe), we found that the Padé approximant [2/1] is still slightly more accurate than the sum of two terms, but the Padé approximant [1/1] is even more accurate. Calculations show that in these cases $\tau_4 < \tau_2$ in the most important area of integration when $\tau(r) > 0.01$. It explains the good accuracy of the Padé approximant [1/1] which is based on fourth order expansion. However, we found that $\tau_6(r) > \tau_4(r)$ for almost all r , which is probably the reason of relatively poor performance of the Padé approximant [2/1] that is based on sixth order expansion.

4. Conclusion

Here, we take advantage of the known higher order corrections to the density of the kinetic energy, τ_4 and τ_6 , to improve the accuracy of the gradient expansion. Simple adding of the correction $T_4 = \int \tau_4(\mathbf{r}) d\mathbf{r}$ usually makes the result less accurate, because this correction is valid only asymptotically for heavy atoms. Moreover, since $T_6 = \int \tau_6(\mathbf{r}) d\mathbf{r}$ is given by a divergent integral for finite systems, the knowledge of τ_6 is assumingly useless, from the first glance. In this paper, we present a systematic approach that allows to avoid regions where higher order terms are relatively large and are no longer "small corrections" while taking advantage of these terms in areas where they are small and improve the accuracy.

We expect that this approximation can improve the accuracy in case when there exists a significant region of \vec{r} where $|\tau_6(\vec{r})| < |\tau_4(\vec{r})|$. We found that for atoms, this region is quite narrow, presumably because of the presence of Coulomb singularity. In this case the method has only small advantage over the method of plane summation. Our second example is Hooke's law model for two-electron atoms, where the Coulomb attraction $-Z/r$ is replaced by a harmonic binding $\frac{\omega^2}{2}r^2$. In the latter case, we found that the method works only in case of sufficiently weak binding, $\omega \leq 1/2$. So, we expect this approximation to work very well for confined harmonic potentials such the case of treating quantum dots.

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