PHYSICAL REVIEW LETTERS

Relevance of the Slowly Varying Electron Gas to Atoms, Molecules, and Solids

John P. Perdew, Lucian A. Constantin, and Espen Sagvolden

Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118, USA

Kieron Burke

Department of Chemistry, University of California, Irvine, California 92697, USA

We present a Thomas-Fermi-inspired density scaling under which electron densities of atomic, molecular, or condensed matter become both large and slowly varying, so that semiclassical approximations and second-order density gradient expansions are asymptotically exact for the kinetic and exchange energies. Thus, even for atoms and molecules, density-functional approximations should recover the universal second-order gradient expansions in this limit. We also explain why common generalized gradient approximations for exchange do not.

In a remarkable series of papers towards the end of his life, Schwinger [1] (sometimes with Englert [2]) put the semiclassical theory of neutral atoms on a firm footing. They carefully proved a variety of results, including a clear-cut demonstration that the local density approximation (LDA) becomes exact for exchange as Z, the nuclear charge, tends to ∞. The large-Z expansion of the energy of atoms whose rigor they established,

$$E = -0.7687Z^{7/3} + 0.5Z^2 - 0.2699Z^{5/3} + \ldots, \quad (1)$$

is extremely close to the total (Hartree-Fock) energies of neutral atoms (less than 0.5% error for Ne), an example of the "unreasonable utility of asymptotic estimates" [1]. But their derivations are specific to neutral atoms, and they eschew exploring any relation to "the density-functional formalism" [2], preferring to express all quantities in terms of the external potential. Their results are rarely used within density-functional theory (DFT).

In the quarter century since, Kohn-Sham DFT has become a widely used tool for electronic structure calculations of atoms, molecules, and solids [3]. Here, the noninteracting kinetic energy T_S is treated exactly, and only the density functional for the exchange-correlation energy, $E_{XC}[n]$, must be approximated. For E_{XC}, LDA [4] is useful for solids but insufficiently accurate for chemical bonding. The density gradient expansion can be derived from the slowly varying electron gas, but fails for real molecules and solids, whose gradients are not small. The development of modern generalized gradient approximations (GGA) [5,6], using gradients beyond leading order, improved accuracy and led to the widespread use of DFT in many fields. Anomalously, modern successful GGAs for exchange have gradient coefficients that are about double that of the gradient expansion, and even the relevance of LDA to exponentially localized densities is often questioned [7].

But Thomas-Fermi (TF) theory [8,9], with its local approximation to T_S, is the simplest, original form of DFT, and yields the leading term in Eq. (1). Since $E =$

$-T$ for atoms and correlation is $O(Z)$, Eq. (1) is an expansion for T_S. The Scott correction [10] (Z^2 term) arises from the 1s-region electrons [1], while the $Z^{5/3}$ term includes second-order gradient contributions to T_s [1].

We introduce a methodology that generalizes Schwinger's results to molecules and solids and to other components of the energy. It explains why local approximations become exact for large numbers of electrons, and when the gradient expansion is accurate for real matter. It explains the doubling of the coefficient for exchange, and why the analog [(Eq. (5)] of Eq. (1) fails for correlation.

To begin, define the scaled density

$$n_\zeta(\mathbf{r}) = \zeta^2 n(\zeta^{1/3}\mathbf{r}), \qquad 0 < \zeta < \infty \quad (2)$$

for any electron density. If $n(\mathbf{r})$ contains N electrons, $n_\zeta(\mathbf{r})$ contains ζN electrons. We only ever consider integer ζN, but study energies as smooth functions of ζ. Changing ζ is exactly equivalent to changing Z in TF theory, and approximately so in reality. This scaling is defined for all systems, not just atoms. An example of our scaling is shown in Fig. 1.

As ζ grows, the density becomes both large and slowly varying on the scale of the local Fermi wavelength
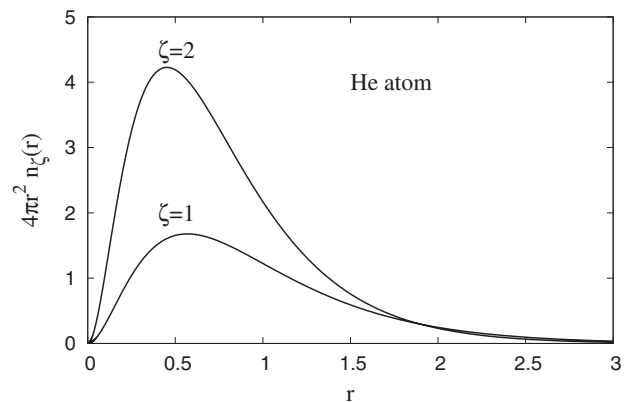

FIG. 1.   Scaled radial density of He atom.

$\lambda_F(\mathbf{r}) = 2\pi/k_F(\mathbf{r})$, where $k_F(\mathbf{r}) = [3\pi^2 n(\mathbf{r})]^{1/3}$. Under this scaling, the dimensionless gradients $s = |\nabla n|/(2k_F n)$ and $q = \nabla^2 n/(4k_F^2 n)$ (commonly used in gradient expansions) vary as

$$s_\zeta(\mathbf{r}) = s(\zeta^{1/3}\mathbf{r})/\zeta^{1/3}, \qquad q_\zeta(\mathbf{r}) = q(\zeta^{1/3}\mathbf{r})/\zeta^{2/3}. \quad (3)$$

In Fig. 2, we plot s for accurate densities [self-consistent nonrelativistic ones, from the optimized effective potential (OEP), the Kohn-Sham potential for exact exchange] of both Kr and Rn. The gradient expansions for the kinetic and exchange energies are expected [4] to become exact as the density $n(\mathbf{r})$ becomes slowly varying on the scale of λ_F, i.e., when $s \to 0$ and $|q/s| \to 0$ everywhere. The second condition is needed because $s \to 0$ for an infinitesimal amplitude but rapid variation around a uniform density.

Under ζ scaling of a mono- or polyatomic density, as $\zeta \to \infty$ and as s and $|q/s| \to 0$ (except in regions to be discussed), the gradient expansion becomes asymptotically exact so that (aside from possible oscillations [2])

$$T_S[n_\zeta] = \zeta^{7/3}T_S^{(0)}[n] + \zeta^{5/3}T_S^{(2)}[n] + \zeta T_S^{(4)}[n] + \dots,$$
$$E_X[n_\zeta] = \zeta^{5/3}E_X^{(0)}[n] + \zeta E_X^{(2)}[n] + \dots, \quad (4)$$

where $T_S^{(j)}[n]$ is the jth order contribution to the gradient expansion of T_S (i.e., $T_S^{(0)}$ is the TF kinetic energy, $T_S^{(2)}$ is 1/9 the von Weizsäcker term [12], etc.), and similarly for exchange [13]. The terms displayed in Eq. (4) are those of the gradient expansion that remain finite for exponentially localized densities, and also those for which the gradient expansion becomes asymptotically exact as $\zeta \to \infty$ for analytic densities (unless the density has nuclear cusps, when $T_S^{(4)}$ must be excluded). The gradient expansions of Eq. (4) are "statistical" approximations in the sense that their relative errors vanish as $\zeta N \to \infty$.

Evanescent regions are classically forbidden regions in which the kinetic energy density $\tau'(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r})^* \times (-\nabla^2/2)\psi_i(\mathbf{r})$ of the Kohn-Sham orbitals is negative and the gradient expansion must fail. To investigate the contributions to $T_S[n_\zeta]$ and $E_X[n_\zeta]$ from evanescent and nu-

FIG. 2. Reduced density gradient for noble gas atoms.

clear cusp regions, we note that each can be represented by an exponential density $a\exp(-br)$. For this density, the evanescent region $r > r_e(\zeta)$ is defined loosely by the conditions $s > 1$ and $|q/s| > 1$ [found from the second-order gradient expansion of $\tau'(\mathbf{r})$]. Its radius $r_e(\zeta)$ decreases like $\ln(\zeta)/\zeta^{1/3}$ as $\zeta \to \infty$. In this region, the considered terms of the gradient expansion each contribute of order $\zeta^{2/3}$ to T_S, and of order $\zeta^{1/3}$ to E_X [with the convention that $\ln(\zeta)$ is of order 1]. All of these contributions are of lower order than those shown in Eq. (4), and thus asymptotically unimportant. Similarly, the nuclear cusp regions $r < r_c(\zeta)$ can be defined loosely by the condition $|q/s| > 1$; their radii $r_c(\zeta)$ decrease like $\zeta^{-2/3}$ as $\zeta \to \infty$. In these regions, the local contributions dominate. The local terms contribute of order $\zeta^{4/3}$ to T_S and $\zeta^{2/3}$ to E_X, and are again asymptotically unimportant [once we truncate the gradient expansions of Eq. (4)] at second order). Our evanescent regions coincide with the edge surface of Ref. [14], but the cusps do not.

The total electron number scales up as ζ, but in the evanescent and cusp regions it remains of order ζ^0. The *exact* exchange energy contributions from evanescent and cusp regions we estimate as $\zeta^{1/3}$ and (at most) $\zeta^{2/3}$, respectively. All orders of ζ are unchanged if the bound 1 is replaced by a smaller positive value, or if the spherical evanescent region is replaced by a planar one.

To appreciate the significance of asymptotic exactness, ζ-scale any density (even a single exponential). Using modern linear response techniques, construct the KS potential and orbitals for each value of ζ [15]. As $\zeta \to \infty$, deduce the local and gradient expansion approximations for T_S and E_X exactly, without ever studying the properties of the uniform or slowly varying electron gas. The system is becoming increasingly semiclassical, and the orbitals well described by their WKB approximations. Semiclassical approximations require only that the potential be smooth locally, not globally.

The behavior of correlation under this scaling is, however, recalcitrant. The gradient relative to the screening length $t = |\nabla n|/(2k_s n)$, where $k_s(\mathbf{r}) = \sqrt{4k_F(\mathbf{r})/\pi}$, controls gradient corrections to correlation. But $t_\zeta(\mathbf{r}) = t(\zeta^{1/3}\mathbf{r})$ does *not* change under our scaling, so that the density does *not* become slowly varying for correlation. Nonetheless, the local approximation still becomes exact, if the PBE GGA [6] is a reliable guide (as motivated later):

$$E_C[n_\zeta] = A_C\zeta\ln\zeta + B_C\zeta + \dots \quad (5)$$

where $A_C = -0.02072$ is correctly given by LDA, while $B_C^{\mathrm{LDA}} = -0.00452$ and $B_C^{\mathrm{PBE}} = 0.039\,36$. These numbers can be found by applying these approximations to the TF density. Because t never gets small, B_C has not only LDA and GEA (gradient expansion to second order) contributions, but higher-order contributions too. This expansion is far more slowly converging than those of T_S and E_X, and much less relevant to real systems.
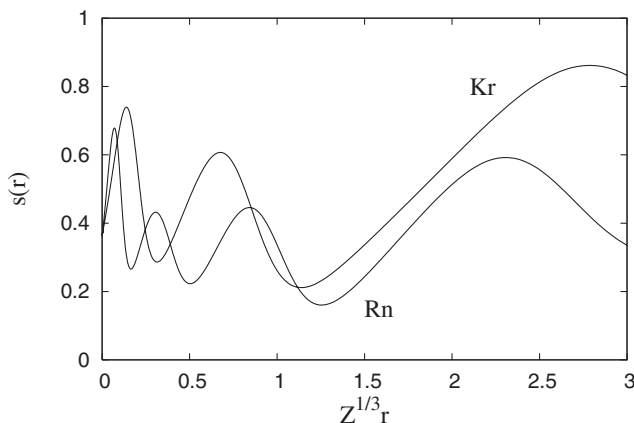
TABLE I.   Noble gas atomic XC energies compared with local and gradient expansion approximations (Hartree).

	E_X			E_C		
Atom	LDA	GEA	Exact	LDA	GEA	Exact
He	-0.884	-1.007	-1.026	-0.113	0.103	-0.042
Ne	-11.03	-11.77	-12.10	-0.746	0.559	-0.390
Ar	-27.86	-29.29	-30.17	-1.431	1.09	-0.722
Kr	-88.62	-91.65	-93.83	-3.284	2.06	$\cdots$
Xe	-170.6	-175.3	-179.1	-5.199	3.15	$\cdots$
Rn	-373.0	-380.8	-387.4	-9.026	4.78	$\cdots$

TABLE II. $\Delta C = \lim_{Z\to\infty}(E_X - E_X^{\mathrm{LDA}})/Z$ (Hartree).   The "gradient" contribution arises from the expansion to order ∇^2, while the remainder is the "cusp."

ΔC	GEA	PBE	B88	TPSS	Exact
Total	-0.098	-0.174	-0.202	-0.159	-0.196
Gradient	-0.098	-0.174	-0.217	-0.0977	-0.0977
Cusp	0.00	-0.000	$+0.015$	-0.0617	-0.0979

In Table I, we list the exact [16], LDA, and GEA results for the noble gas atoms using the known second-order gradient terms [13,17]. LDA gets relatively better and better as Z grows, and the GEA for exchange does even better, but the GEA for correlation strongly overcorrects the LDA, making correlation energies positive [17]. Thus this simple analysis explains why the gradient expansion yields good answers for T_S and E_X, but bad ones for correlation. These explanations complement those already existing based on holes and sum rules [18], but add the crucial ingredient that under this scaling the gradient expansion becomes asymptotically exact for T_S and E_X.

But Eq. (4) for either E_X or T_S is far less accurate at $\zeta = 1$ than Eq. (1) is for E at $Z = 1$. Careful inspection of the origin in Fig. 2 shows that the exact curves approach a finite s value at the origin, about 0.376, the hydrogenic value. The large-Z expansion is not the same as scaling to large ζ, except in TF theory. The gradients near the nucleus do *not* become small on the Fermi wavelength scale, no matter how large Z is. This region will contribute a term of order Z^2 to the kinetic energy and of order Z to the exchange energy at all levels, from LDA to exact. LDA applied to the TF density produces the leading term in E_X, $0.2208Z^{5/3}$. Gradient corrections are of order Z, but so too is the cusp correction, i.e., the asymptotic expansion in large Z inextricably mixes these contributions (unlike in T_S). Table I lists E_X for noble gas atoms, calculated at the self-consistent nonrelativistic OEP level. We fit $(E_x + 0.2208Z^{5/3})/Z$ as a function of $Z^{-1/3}$, finding $E_X(Z) = -0.2208Z^{5/3} + (C^{\mathrm{LDA}} + \Delta C)Z + \dots$.

Extraction of C^{LDA} from LDA energies is difficult, because of shell-structure oscillations. We estimate $0 \gtrsim C^{\mathrm{LDA}} \gtrsim -0.03$. However, for any other calculation of E_X, we find $(E_X - E_X^{\mathrm{LDA}})/Z$ is smooth, with fit results shown in Table II. The large underestimate of GEA shows that gradient corrections from the slowly varying gas account for only half the entire contribution. Assuming $C^{\mathrm{LDA}} = 0$, $E_X(Z) \sim -0.2208Z^{5/3} - 0.196Z$. This yields less than 10% error for He, and less than 2% for Ne.

Popular GGAs such as PBE and B88 [5] have second-order gradient coefficients that are about twice the correct coefficient for a slowly varying density, as they must to reproduce accurate exchange energies of atoms. But with an incorrect coefficient, they cannot predict accurate sur-face energies for metals [19]. The origin of the enhanced gradient coefficient of the GGA for exchange now has a simple explanation. In order to be asymptotically exact for large Z, and hence accurate for most finite Z, the functional accounts for both the slowly varying term and the cusp correction. No GGA can get both effects right individually. B88 is closest to being exact for ΔC, because of the fitting to noble gas atoms [5].

PBE preserves the nearly correct uniform-gas linear response of LDA for XC together [6], which produces a ΔC also close to exact, and a GGA close to that of a hole model [18]. A "buried $1s$" region has small s, looking to a GGA like a region of slowly varying density. However, a meta-GGA that employs $\tau(\mathbf{r})$ can recognize that this is a rapidly varying region, and thus get both aforementioned effects right. The TPSS meta-GGA [20] recovers the gradient expansion to fourth order, while yielding a good estimate for ΔC (Table II).

Figure 3 plots the difference in exchange energy densities relative to LDA in the different approximations. PBE simply mimics GEA, being almost a factor of 2 larger everywhere. But TPSS produces a much greater contribution from the region near the nucleus (via Fig. 1 of Ref. [20]), while reverting to the GEA value at the inner radii of the other atomic shells, where s is small.

In Fig. 4, we plot the correlation energy in three different approximations: LDA, PBE, and Moller-Plesset second-order perturbation theory (MP2) [21]. (TPSS is almost identical on this scale to PBE.) Also included are dashed lines that correspond to the high-density limit of Eq. (5) using LDA and PBE inputs for B_C. Real atoms are so far
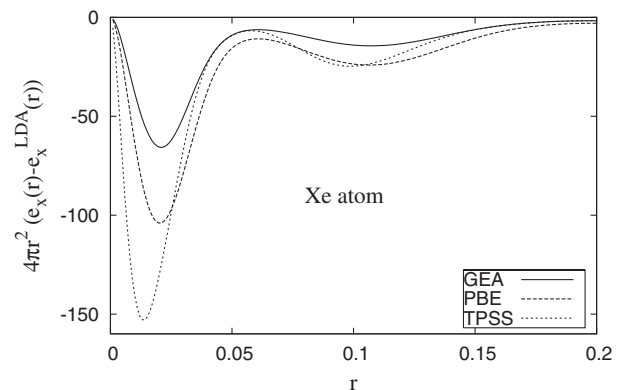

FIG. 3.   Radial exchange energy density differences for Xe for different approximations (atomic units).

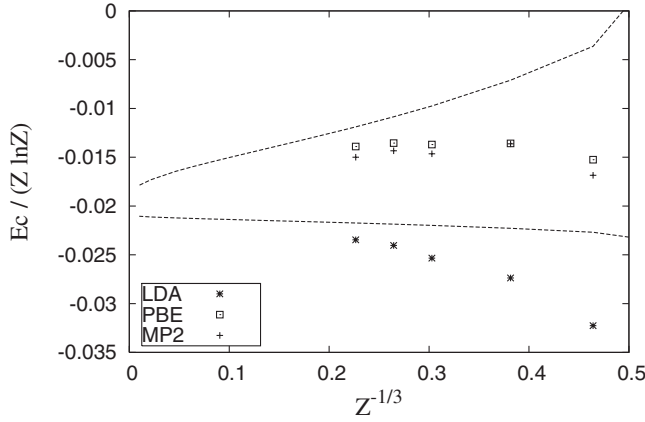P H Y S I C A L   R E V I E W   L E T T E R S

FIG. 4.   Scaled correlation energies for noble gas atoms (Hartree). The dashed lines correspond to the high-density limit of Eq. (5) for LDA (lower) and PBE (upper curve).

from the asymptotic limit for correlation that asymptotic exactness is much less relevant in this case.

Table III shows the correlation energies of closed-shell atoms as predicted by PBE, TPSS, and MP2 [21], along with essentially exact values [16] where known. The agreement among these values is generally good.

Last, we relate this scaling to others. The most standard is uniform coordinate scaling [23] [$(\gamma^3 n(\gamma\mathbf{r}))$], under which T_S/γ^2 and E_X/γ remain unchanged. More recently, number scaling, in which $n(\mathbf{r})$ becomes $\nu n(\mathbf{r})$, has been proposed [24]. In the large ν limit, all gradients in the bulk become small on both local length scales, making even the gradient expansion for correlation asymptotically exact. The present scaling can be regarded as a product of these, with $\nu = \gamma^3 = \zeta$. A slowly varying product with bounded density is $n(\nu^{-1/3}\mathbf{r})$, $\nu \rightarrow \infty$.

Our ζ scaling allows the results of Schwinger's derivations to be applied throughout DFT, yielding insight into the performance of approximate functionals. Even for uncondensed matter, such functionals should incorporate the

TABLE III.   Noble gas atomic correlation energies (Hartree). The fixed-node Diffusion Monte Carlo (DMC) values [22] are upper bounds.

Atom	LDA	PBE	TPSS	MP2	DMC	exact
He	-0.113	-0.042	-0.043	$\cdots$	-0.042	-0.042
Ne	-0.743	-0.351	-0.354	-0.388	-0.376	-0.390
Ar	-1.424	-0.707	-0.711	-0.709	-0.667	-0.722
Kr	-3.269	-1.767	-1.771	-1.890	-1.688	$\cdots$
Xe	-5.177	-2.918	-2.920	-3.089	-2.647	$\cdots$
Rn	-9.026	-5.325	-5.33	-5.745		$\cdots$

second-order gradient expansions (although GGA total exchange energies then degrade due to 1*s* regions).

[1] J. Schwinger, Phys. Rev. A **22**, 1827 (1980); **24**, 2353 (1981).
[2] B.-G. Englert and J. Schwinger, Phys. Rev. A **29**, 2339 (1984); **32**, 26 (1985); **32**, 36 (1985); **32**, 47 (1985).
[3] *A Primer in Density Functional Theory*, edited by C. Fiolhais, F. Nogueira, and M. Marques (Springer-Verlag, NY, 2003).
[4] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[5] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[6] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).
[7] *Density-Functional Theory of Atoms and Molecules*, edited by R. G. Parr and W. Yang (Oxford, New York, 1989).
[8] L. H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542 (1926).
[9] E. Fermi, Z. Phys. **48**, 73 (1928).
[10] J. M. C. Scott, Philos. Mag. **43**, 859 (1952).
[11] V. Sahni, J. Gruenebaum, and J. P. Perdew, Phys. Rev. B **26**, 4371 (1982).
[12] D. A. Kirzhnits, Sov. Phys. JETP **5**, 64 (1957).
[13] P. R. Antoniewicz and L. Kleinman, Phys. Rev. B **31**, 6779 (1985).
[14] W. Kohn and A. E. Mattsson, Phys. Rev. Lett. **81**, 3487 (1998).
[15] Q. Zhao, R. C. Morrison, and R. G. Parr, Phys. Rev. A **50**, 2138 (1994).
[16] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. Froese Fischer, Phys. Rev. A **47**, 3649 (1993).
[17] S.-K. Ma and K. A. Brueckner, Phys. Rev. **165**, 18 (1968).
[18] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16533 (1996); **57**, 14999(E) (1998).
[19] L. A. Constantin, J. P. Perdew, and J. Tao, Phys. Rev. B **73**, 205104 (2006).
[20] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
[21] J. R. Flores, K. Jankowski, and R. Slupski, Collect. Czech. Chem. Commun. **68**, 240 (2003); K. Jankowski (private communication).
[22] A. Ma, N. D. Drummond, M. D. Towler, and R. J. Needs, Phys. Rev. E **71**, 066704 (2005).
[23] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).
[24] G. K-L. Chan and N. C. Handy, Phys. Rev. A **59**, 2670 (1999).