

Semiclassical Origins of Density Functionals

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The relation between semiclassical and density-functional approximations is clarified. Semiclassical approximations both explain and improve upon density-gradient expansions for finite systems. We derive highly accurate density and kinetic energy functionals of the potential in one dimension.

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Modern density functional theory is an extremely popular method for solving electronic structure problems in many fields, due to its balance of reasonable accuracy with computational efficiency [1]. The standard approach is to solve the Kohn-Sham (KS) equations with a given density-functional approximation to the unknown exchange-correlation (XC) energy [2]. However, because no systematic approach to functional approximation exists, there is now a veritable zoo of approximations from which to choose [3–6]. Those in common use can be loosely divided into two classes: nonempirical functionals, such as the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [6], largely developed by Perdew and co-workers, that start from the uniform and slowly varying gases, and empirically fitted functionals that are typically more accurate for systems close to the fit set [3–5]. The former apply more broadly and are more commonly used in physics, especially for bulk metals. The latter are more popular in chemistry and are more accurate for specific systems and properties, such as transition-state barriers.

However, semiclassical methods are standard in physics, and, in a tour de force, Schwinger [7] used semiclassical methods to rigorously derive the asymptotic expansion of the energies of neutral atoms for large Z . Now, in the pre-KS world of pure density functional theory (DFT), i.e., Thomas-Fermi (TF) and related theories, there is a long history of derivation of density functionals via semiclassical arguments, including the gradient expansion for both the kinetic [8] and exchange [9] energies, by considering an infinite slowly varying electron gas. But its failure for finite systems led to these other approaches to XC functional construction.

To understand the essential difference between solids of moderate density variation and all finite systems, consider the cartoons of Fig. 1. Both prototypes can be treated semiclassically, i.e., via expansion in \hbar , which is equivalent to an expansion in gradients of the potential. For the valence electrons of a simple metal, the Fermi energy E_F is everywhere above the (pseudo)potential, and periodic boundary conditions apply. This makes semiclassics simple, because there are no turning points, evanescent regions, or Coulomb cores. In finite systems (and typical insulators), E_F cuts the potential surface, leading to turning

points and evanescent regions. Without a pseudopotential, there are also Coulomb cores, which require special treatment. The dominant term (in a sense specified below) in all cases is correctly given by the local density approximation, but in the latter case there are important *quantum* corrections, which produce many features missing from semilocal density approximations, such as shell structure, self-interaction, etc.

Our semiclassical analysis applies to all systems and explains the universality of local approximations (without mentioning the uniform gas). For slowly varying densities, it is equivalent to the density-gradient expansion but includes quantum corrections for other cases. These corrections explain why the gradient approximation had to be “generalized” (GGAs) and why local and semilocal approximations miss essential features of the kinetic energy. Insights based on our approach have already produced a derivation of an important empirical parameter (the β of Ref. [3]) and a revised version of PBE that is proving successful in many contexts [10]. Ultimately, the theory suggests that potential functionals [11] provide a more promising and systematic route to higher accuracy.

We begin by discussing an asymptotic limit for all matter that corresponds to a semiclassical expansion, of which Schwinger’s results are a specific example. The approach to the limit identifies the essential failure of the gradient expansion for finite systems. We illustrate this with a model in one dimension and find much more accurate results by correcting this. We close with a discussion of the implications for modern DFT development.

We (re)introduce a potential scaling [12]:

$$v_{\text{ext}}^{\zeta}(\mathbf{r}) = \zeta^{4/3} v_{\text{ext}}(\zeta^{1/3} \mathbf{r}), \quad N \rightarrow \zeta N, \quad (1)$$

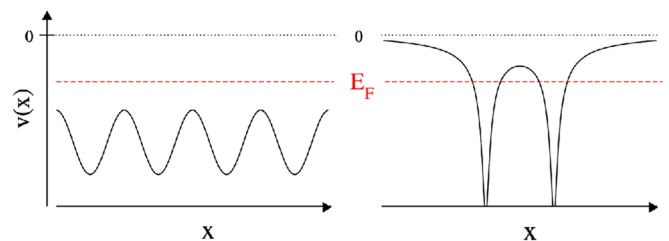


FIG. 1 (color online). Cartoons of potential and Fermi energy in a simple metal (left) and molecule (right).

where $v_{\text{ext}}(\mathbf{r})$ is the one-body potential. For molecules with nuclear positions \mathbf{R}_α and charges Z_α , under this scaling, $Z_\alpha \rightarrow \zeta Z_\alpha$ and $\mathbf{R}_\alpha \rightarrow \zeta^{-1/3} \mathbf{R}_\alpha$. In an electric field, $\mathcal{E} \rightarrow \zeta^{5/3} \mathcal{E}$. We say an approximation is large- N *asymptotically exact* to the p th degree (AE p) if it recovers exactly the first p corrections for a given quantity under the potential scaling of Eq. (1). For neutral atoms, scaling ζ is the same as scaling Z , which is well-known:

$$E(\zeta) = -0.768\,745\zeta^{7/3} + \zeta^2/2 - 0.269\,900\zeta^{5/3} + \dots \quad (2)$$

and is “unreasonably accurate” [7], with less than 10% error even for H. An approximation that reproduces these three coefficients is AE2 and is likely to be very accurate. Lieb [12] showed that Thomas-Fermi theory becomes *exact* in the limit $\zeta \rightarrow \infty$ for *all* systems. However, TF theory recovers only the first term in Eq. (2), while Schwinger derived all three but only for neutral atoms.

Because of this exactness for any system, as $\zeta \rightarrow \infty$,

$$n^\zeta(\mathbf{r}) \rightarrow \zeta^2[n^{\text{TF}}(\zeta^{1/3}\mathbf{r}) + n^{\text{QC}}(\zeta, \mathbf{r})/\zeta^{1/3} + \dots], \quad (3)$$

where n^{QC} becomes negligible compared to n^{TF} everywhere except in regions whose size is vanishing. So consider instead scaling the density rather than the potential, denoted by a subscript:

$$n_\zeta(\mathbf{r}) = \zeta^2 n(\zeta^{1/3}\mathbf{r}). \quad (4)$$

This density scaling is unusual, in that both the coordinate [13] and the particle number are scaled [14] (N to ζN). The universal functional is

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle, \quad (5)$$

where Ψ is any antisymmetric wave function with density $n(\mathbf{r})$ and \hat{T} and \hat{V}_{ee} are the kinetic and Coulomb repulsion operators, respectively. For large ζ , we find

$$F[n_\zeta] = \zeta^{7/3} F^{\text{TF}}[n] + \zeta^{5/3} F^{\text{WD}}[n] + \zeta F_2[n] + \dots \quad (6)$$

by using the arguments of Ref. [15], i.e., that the gradients of the density become small almost everywhere under this scaling. Here $F^{\text{TF}}[n] = T_S^{(0)}[n] + U[n]$, where T_S is the noninteracting KS kinetic energy, U the Hartree energy, and a superscript (j) denotes the j th order contribution to the gradient expansion of a functional. The second term is $F^{\text{WD}}[n] = T_S^{(2)} + E_X^{(0)}$, i.e., the leading gradient correction to the kinetic energy $T^W/9$, where $T^W = \int d^3r |\nabla n|^2 / (8n)$ is the von Weizsäcker term (W) [8], and the Dirac correction (D), i.e., the local approximation to exchange, while $F_2[n] = T_S^{(4)} + E_X^{(2)}$. Thus, scaling the density in this way justifies using the complete WD correction to TF theory (rather than just one or the other).

Next, we compare the expansion of Eq. (2) with that of Eq. (6). Since $T = -E$ for atoms, and $T \approx T_S$ to the order with which we are working, we see that ζ scaling the density produces Eq. (6), which is the usual gradient

expansion, but misses the ζ^2 term of Eq. (2). This quantum correction has long been recognized as missing from TF theory, but the gradient expansion misses it altogether. If TF theory is AE0, why is TFW not AE1? The answer is that, for systems like those on the left of Fig. 1, without turning points, edges, or Coulomb cores, there is no quantum correction, and the gradient expansion is the asymptotic expansion. For all others, there are quantum corrections to the energy, qualitatively changing its asymptotic expansion. Because $E_F \rightarrow \infty$ as $\zeta \rightarrow \infty$, these can be calculated with semiclassical techniques, just as Schwinger did for atoms.

To give an explicit example of these principles, we consider noninteracting spinless fermions in 1D in a potential $v(x)$ with infinite walls at $x = 0$ and L . For this case, $v^\zeta(x) = \zeta^4 v(\zeta x)$, and the analog of Eq. (6) is

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

where $T^{(0)} = \pi^2 \int dx n^3(x)/6$, $T^{(2)} = -T^W/3$, etc. [16]. Even a flat box [$v(x) = 0$] yields some insight. Then

$$T^\zeta = \frac{\pi^2}{6L^2} \left(\zeta^5 N^3 + \zeta^4 \frac{3}{2} N^2 + \zeta^3 \frac{1}{2} N \right), \quad (8)$$

and the exact ground-state density is

$$n^\zeta(x) = \frac{k_F^\zeta}{\pi} - \frac{\sin(2k_F^\zeta x)}{2L \sin(\zeta \pi x/L)}, \quad (9)$$

where $k_F^\zeta = \zeta \pi(\zeta N + 1/2)/L$. As $\zeta \rightarrow \infty$, $n \rightarrow \zeta^2 N/L$ and T is dominated by its leading term, agreeing with TF theory [12]. For $N = 1$, $T[n_\zeta] = \pi^2(5\zeta^5 - 2\zeta^3 + \dots)/(12L^2)$, missing the quantum correction. The second term in Eq. (9) contains quantum oscillations and is of $O(\zeta)$, i.e., 1 order less, everywhere but at the edges (a region of size L/ζ), where it cancels the dominant term.

How can one calculate exactly the leading correction to the dominant term in $E[v^\zeta]$ for any system? As $\zeta \rightarrow \infty$, $v^\zeta(\mathbf{r})$ dominates over kinetic energy, and the system becomes semiclassical. In d dimensions, the diagonal Green's function for noninteracting particles satisfies

$$g[v^\zeta](\hbar, \mathbf{r}, E) = \zeta^{1-4/d} g[v](\hbar/\zeta^{1/d}, \zeta^{1/d}\mathbf{r}, E/\zeta^{4/d}). \quad (10)$$

So as $\zeta \rightarrow \infty$, effectively $\hbar \rightarrow 0$. Furthermore, in 1D [17]:

$$g(x, E) = g^{\text{semi}}(x, E) \left[1 + O\left(\frac{1}{E^{3/2}} \frac{dv}{dx}\right) \right], \quad (11)$$

where g^{semi} is approximated semiclassically. We can extract, e.g., the density from the Green's function, via $n(x) = \oint_C d\mathcal{E} g(x, \mathcal{E}) / (2\pi i)$, with C any contour in the complex energy \mathcal{E} plane that encloses all of the eigenvalues E_1, \dots, E_N along the real axis. By choosing a vertical line along $\mathcal{E} = E_F + i\eta$, which is then closed by a large circle enclosing all of the occupied poles, the smallest $|\mathcal{E}|$ used is E_F , which is growing with ζ . The semiclassical approximation is *combined* with the best choice of contour to give a density error of $O(1/\zeta)$.

In any situation, this yields

$$n^{\text{TF}}(x) = k_F(x)/\pi, \quad t^{\text{TF}}(x) = k_F^3(x)/6\pi, \quad (12)$$

where $k(x) = \sqrt{2[\mathcal{E} - v(x)]}$ and the subscript F implies evaluation at E_F . Insertion of the left result into the right produces $T^{(0)}[n]$, i.e., TF theory. In the situation on the left of Fig. 1, the next corrections are precisely those of the gradient expansion [16]. But real systems have corrections at lower orders, because of Coulomb cores, turning points, and evanescent regions. We illustrate these deviations from Eq. (12), by calculating $n^{\text{semi}}(x)$ for a 1D box with potential $v(x)$, $0 \leq x \leq L$, and $E_F > v(x)$ everywhere. Note that WKB yields the exact results for $v = 0$, but only once the boundary conditions are imposed. The WKB wave function satisfying the boundary conditions on the left is $\sin\Theta(x)/\sqrt{k(x)}$, and $\Theta(x) = \int_0^x dx' k(x')$ is the semiclassical phase, yielding

$$g^{\text{semi}}(x, \mathcal{E}) = \frac{\cos\Theta(L) - \cos[2\Theta(x) - \Theta(L)]}{k(x) \sin\Theta(L)}. \quad (13)$$

The first term yields the TF result, so

$$t_S^{\text{QC}}(x) = k_F^2(x)n^{\text{QC}}(x)[1 + \beta(x)\gamma(x)]/2 - \frac{k_F(x)\beta(x)}{4T_F} \left(\frac{1}{6} + \cot\alpha(x) \frac{\cos 2\Theta_F(x)}{\sin\alpha(x)} \right), \quad (17)$$

where $\beta(x) = \pi[T_F^{(2)}/T_F + k_F^{-2}(x)]/(2T_F)$, $\gamma(x) = \pi[1/2 - \csc^2\alpha(x)]/[2k_F^2(x)T_F]$ and $T_F^{(2)} = \int_0^L dx' /k_F^3(x')$. Important features of these results include: (i) exact when $v = 0$, where $k_F = \pi(N + 1/2)/L$; (ii) highly nonlocal functionals of the potential through Θ_F , which is set globally; (iii) TF theory retains only the first terms, and E_F differs because of this; (iv) even if low-lying orbitals have turning points, these do not appear in our expression, once $E_F \geq v_{\text{max}}$; and (v) the Maslov index of n^{semi} differs by $1/2$ from that of individual eigenstates.

We plot results for $v(x) = -80\sin^2(2\pi x)$, a well with two deep valleys. The four lowest single particle energies are -46.32 , -42.50 , 10.18 , and 37.25 , so that the lower two have turning points. In Fig. 2, we show the density, both exact and approximate, for $N = 4$ particles and the corresponding $t_S(x)$ in Fig. 3. The density is not automatically normalized, but its error is less than 0.2%. Evaluating $T_S^{(0)}$ tests the accuracy of a density: The exact value is 153.0; it is 115.5 in self-consistent TF, 114.6 in non-self-consistent TFW, and 151.4 for n^{semi} . In fact, t_S^{semi} is ill-behaved right at the end points, so we model its approach to the boundaries with a simple parabola for $x < 0.0875$, with a constant chosen to match the logarithmic derivative at that point. The resulting integrated T_S is 156.2, compared to the exact result 157.2.

We emphasize that the correct semiclassical treatment has reduced the error in self-consistent TF theory by a factor of 40. Thus the semiclassical approach is far more powerful and systematic than the usual gradient expansion. How then do density functionals achieve the accuracy

$$n^{\text{QC}}(x) = -\frac{1}{4\pi} \oint_C \frac{d\mathcal{E}}{k(x)} \frac{e^{2i\Theta(x)} + e^{-2i[\Theta(x) - \Theta(L)]}}{e^{2i\Theta(L)} - 1}. \quad (14)$$

The semiclassical quantization condition is $\Theta(L)/\pi$ an integer, so $\Theta_F(L) = \pi(N + \delta)$, $0 \leq \delta \leq 1$. The most convenient choice is $\delta = 1/2$. As $N \rightarrow \infty$, $E_F \gg \eta$ for the dominant contributions to the integral, so we expand all quantities to first order in η . Substituting $u = T_F \eta$ and $y = \tau_F(x)/T_F$,

$$n^{\text{QC}}(x) = -\frac{\Im\{e^{2i\Theta_F(x)}\}}{2\pi T_F k_F(x)} \int_0^\infty du \frac{e^{-yu} + e^{-(1-y)u}}{e^{-u} + 1}, \quad (15)$$

with $\tau_F(x) = \int_0^x dx'/k_F(x')$ the classical time for a particle at E_F to travel from 0 to x , $T_F = \tau_F(L)$, and finally

$$n^{\text{semi}}(x) = \frac{k_F(x)}{\pi} - \frac{\sin 2\Theta_F(x)}{2T_F k_F(x) \sin\alpha(x)}, \quad (16)$$

where $\alpha(x) = \pi\tau_F(x)/T_F$. Similarly, by defining $t_S(x) = \oint_C d\mathcal{E}[\mathcal{E} - v(x)]g(x, \mathcal{E})/(2\pi i)$, we find

needed for chemical and materials applications? The answer already appears for the flat box. Inserting the exact density in $T^{(0)}$ yields $\frac{\pi^2}{6L^2}(\zeta^5 N^3 + \zeta^4 \frac{2}{8} N^2 + \zeta^3 \frac{3}{8} N)$, i.e., reasonably accurate quantum corrections, because most of the contribution comes from regions of not-too-rapidly varying density. In the double-well potential, $T_S^{(0)}$ on the exact density is only 4 times worse than our semiclassical approximation. Thus semilocal functionals, applied to the highly accurate densities from the KS scheme, contain typically good approximations to the quantum corrections in the energy. In fact, for the flat box, the leading gradient correction *worsens* the energy. If we alter the coefficient of T^W from $-1/3$ to $+0.424$, the corresponding ‘‘general-

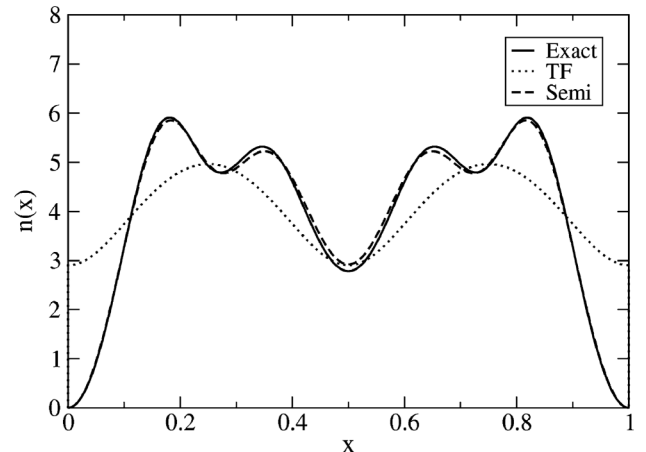


FIG. 2. Densities for $v(x) = -80\sin^2(2\pi x)$ for $N = 4$.

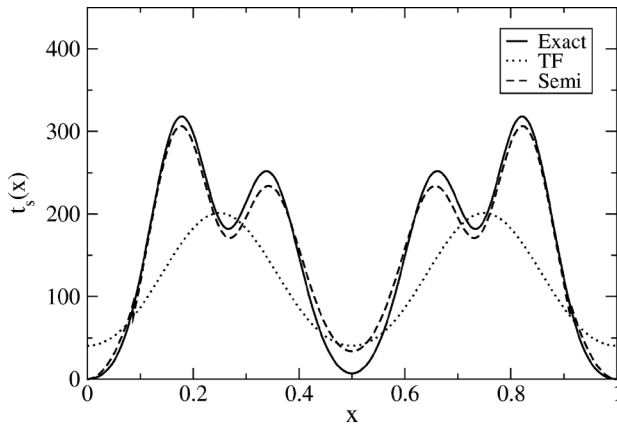


FIG. 3. Kinetic energy densities of Fig. 2.

ized" gradient expansion is AE1 and far more accurate for particles in boxes.

So what does this mean for modern electronic structure theory? Most importantly, this work unites rigorous proofs about TF theory [12], Schwinger's semiclassical results for neutral atoms [7], and modern functional development for KS calculations.

Exchange.—We have shown that the local approximation to exchange becomes exact as $\zeta \rightarrow \infty$ for all systems, consistent with the fact that all popular functionals recover this limit. Furthermore, to be AE1 for E_X of atoms, their small gradient limit must be about double that of the gradient expansion [15], and this is also true for both empirical [3] and nonempirical functionals [6]. These functionals agree for moderate gradients and differ for large gradients. For periodic systems without turning points, the gradient expansion is AE to the order of the gradients. Restoring the original gradient expansion greatly improves lattice parameters [10]. Finally, recent beyond-GGA functionals that recover the fourth-order gradient expansion yield good approximations for the enhanced gradient coefficient in atoms [15].

To apply the methods developed here directly to atoms, we need to generalize them to include turning points, evanescent regions, and Coulomb cores. Such a scheme might produce a derivation of a GGA beyond the small gradient limit.

Correlation.—As the behavior of E_C is not governed by a simple asymptotic expansion [15], we have not found a universal limit in which local correlation becomes exact. Consistent with this, most nonempirical E_C functionals are designed to be exact when the density is uniform [6], but this condition is violated by empirical functionals [4].

Now E_{XC} for a large jellium cluster is dominated by a bulk contribution (exact in the local density approximation) and a surface contribution, which can be accurately approximated by a GGA. Restoring the density-gradient expansion for E_X in PBE yields a highly accurate surface exchange energy, so the analog is to recover the surface correlation energy [18].

KS kinetic energy.—A holy grail for many years [19] has been to find an accurate kinetic energy functional $T_S[n]$ bypassing the construction of KS orbitals. Almost all approaches begin from a semilocal expression, sometimes enhanced by nonlocality based on linear response. This study shows that, if one is interested in total energies, a vital feature is to be asymptotically correct for neutral atoms. Thus, as $\zeta \rightarrow \infty$ in either potential or density scaling, the functional *must* reduce to TF. For atoms, the gradient expansion of $T_S[n]$ works rather well. The coefficient of Z^2 is -0.65 in TF theory, -0.53 if $T^{(2)}$ is included, and -0.52 if $T^{(4)}$ is added [20]. Thus each successive term in the gradient expansion brings it closer to being AE1, since the exact value is $-1/2$. Generalizing the gradient expansion to make it AE2 produces a more accurate functional for total energies of both atoms and molecules [20]. Last, our example here shows how much simpler the kinetic energy is as a functional of the potential than of the density.

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