

Corrections to Thomas-Fermi Densities at Turning Points and Beyond

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Uniform semiclassical approximations for the number and kinetic-energy densities are derived for many noninteracting fermions in one-dimensional potentials with two turning points. The resulting simple, closed-form expressions contain the leading corrections to Thomas-Fermi theory, involve neither sums nor derivatives, are spatially uniform approximations, and are exceedingly accurate.

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Semiclassical approximations are both ubiquitous in physics [1,2] and notoriously difficult to improve upon. Most of us will recall the chapter on WKB in our quantum textbook [3], yielding a simple and elegant result for the eigenvalues of a particle in a one-dimensional potential. The more sensitive will have recoiled at the surgical need to stitch together various regions (allowed, turning point, and forbidden) to find the semiclassical eigenfunction. Summing the probability densities in the allowed region yields the dominant contribution to the density, but what are the leading corrections?

A little later, we should have learned Thomas-Fermi (TF) theory [4,5]. Thomas derived what we now call the TF equation in 1926, without using Schrödinger's equation [6]. He calculated the energies of atoms, finding results accurate to within about 10%. TF theory has since been applied in almost all areas of physics [7]. For the electronic structure of everyday matter, TF theory is insufficiently accurate for most purposes, but gave rise to modern density functional theory (DFT) [8]. The heart of TF theory is a local approximation, and the success of semilocal approximations in modern DFT calculations of electronic structure can be traced to the exactness of TF in the semiclassical limit [9,10]. So, what are the leading corrections?

Despite decades of development in quantum theory, the above questions, which are intimately related, remain unanswered. Both the WKB and the TF approximations can be derived from any formulation of nonrelativistic quantum mechanics, but none yields an obvious procedure for finding the leading corrections. Mathematical difficulties arise because \hbar multiplies the highest derivative in the Schrödinger equation. Physically, the problem is at the dark heart of the relation between quantum and classical mechanics.

Here we derive a definitive solution to both these questions in a limited context: Noninteracting fermions in one dimension. Researchers from solid-state, nuclear, and chemical physics have sought this result for over 50 years [11–21]. The TF density for the lowest N occupied orbitals is

$$n^{\text{TF}}(x) = p_F(x)/(\hbar\pi), \quad p_F(x) \geq 0, \quad (1)$$

where $p_F(x)$ is the classical momentum at the Fermi energy E_F , chosen to ensure normalization, and vanishes elsewhere. This becomes

$$n^{\text{sc}}(x) = \frac{p_F(x)}{\hbar} \left[\left(\sqrt{z} \text{Ai}^2(-z) + \frac{\text{Ai}^2(-z)}{\sqrt{z}} \right) + \left(\frac{\hbar\omega_F \csc[\alpha_F(x)]}{p_F^2(x)} - \frac{1}{2z^{3/2}} \right) \text{Ai}(-z) \text{Ai}'(-z) \right]_{z=z_F(x)}, \quad (2)$$

where $p_F(x)$ is analytically continued into evanescent regions, ω_F is the classical frequency at E_F , and $z_F(x)$ and $\alpha_F(x)$ are related to the classical action from the nearest turning point; Ai and Ai' are the Airy function and its derivative (details within). Equation (2) contains the leading corrections to Eq. (1) for *every* value of x , without butchery at the turning points. The primary importance of this work is the *existence* of Eq. (2) and its derivation. A secondary point is the sheer accuracy of Eq. (2): For $N > 1$, its result is usually *indistinguishable* (to the eye) from exact, as in Fig. 1.

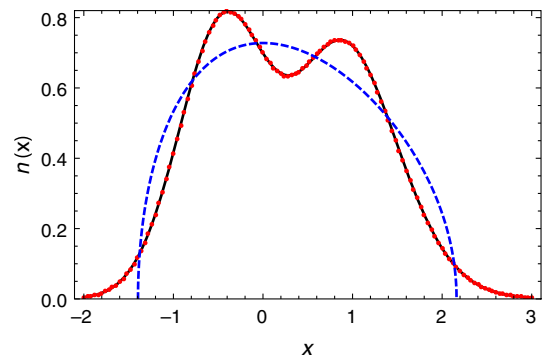


FIG. 1 (color online). Thomas-Fermi (dashed) and semiclassical (dotted) approximations to the density (solid) of 2 particles in a Morse potential, $v(x) = 15(e^{-x/2} - 2e^{-x/4})$.

Generalization of Eq. (2) could prove invaluable in any field using semiclassics or in orbital-free DFT [22].

The crucial step in the derivation is the use of the Poisson summation formula [23,24]. While long-known [24–26] for the description of semiclassical phenomena, it has been little applied to bound states. Although the bare result of its application appears quite complicated, each of the resulting terms, which include contributions from every closed classical orbit at the E_F , can be simplified and summed. We assume only that the potential $v(x)$ is slowly varying with dynamics lying on a topological circle. Accuracy improves as the number of particles grows except when E_F is near a critical point of $v(x)$.

To begin, at energy E , the left (x_-) and right (x_+) classical turning points satisfy $v(x_{\pm}) = E$. The action, measured from the left turning point, is

$$S(x, E) = \int_{x_-(E)}^x dx p(x, E), \quad (3)$$

where $p(x, E) = \sqrt{2m[E - v(x)]}$ is the classical momentum. The WKB quantization condition [2,25,27] is then

$$S[x_+(E_j), E_j] = \pi\hbar \left(j + \frac{1}{2} \right), \quad j \in \mathbb{N}. \quad (4)$$

The accuracy of WKB quantized energies generally improve as either j or m grows, \hbar shrinks, or the potential is stretched such that its rate of change becomes smaller [2,28]. But the WKB wave function is singular in the turning point region [2,27,29–31]. Langer [32] obtained a semiclassical wave function for the case where turning points are simple zeroes of the momentum:

$$\phi_j(x) = \sqrt{\frac{2m\omega_j}{p_j(x)}} z_j^{1/4}(x) \text{Ai}[-z_j(x)], \quad (5)$$

where $\omega_j = \hbar^{-1} \partial E_j / \partial \lambda|_{\lambda=j}$ is the frequency of the corresponding classical orbit, and $z_j = [3S_j(x)/2\hbar]^{2/3}$. In a classically forbidden region, $-p(x) = -i|p(x)| = e^{3i\pi/2}|p(x)|$, ensuring continuity through the turning point. The Langer solution can also be used for problems with two turning points [33]. In this work we match Langer functions from each turning point at the midphase point x_m^j , where $S_j(x_m^j) = \hbar(j + 1/2)\pi/2$. This procedure ensures continuity everywhere.

Our task is to use Langer orbitals to find the asymptotic behavior of the density of N occupied orbitals,

$$n(x) = \sum_{j=0}^{N-1} |\phi_j(x)|^2. \quad (6)$$

We use the Poisson summation formula:

$$\sum_{j=0}^{N-1} f_j = \sum_{k=-\infty}^{\infty} \int_{-1/2}^{N-1/2} d\lambda f(\lambda) e^{2\pi i k \lambda}, \quad (7)$$

where $f(\lambda)$ is essentially any continuous function with bounded first derivatives (except for a finite number of points) that matches the f_j when $\lambda \in \mathbb{N}$ [23,24,34]. Write

$$n(x) = n_0(x) + n_1(x), \quad (8)$$

where $n_0(x)$ is the contribution from $k = 0$, and $n_1(x)$ is all the rest. Then, for $m = 1$,

$$n_0(x) = 2 \int_{-1/2}^{N-1/2} d\lambda \frac{\omega_\lambda \sqrt{z_\lambda(x)}}{p_\lambda(x)} \text{Ai}^2[-z_\lambda(x)]. \quad (9)$$

The lower bound of the integral corresponds to the stable fixed point of the potential well, and the upper bound defines E_F as that obtained by solving Eq. (4) for $j = N - 1/2$, where N is the number of particles in the system. Hereinafter, a subscript F denotes evaluation at E_F , and x is treated as a parameter. For instance, to approximate the integral in Eq. (9) we employ the transformation $\lambda \rightarrow p_\lambda(x)$. Integrating by parts, using the Airy differential equation [35], changing variables, and neglecting higher-order terms from the lower bound of the integral in Eq. (9), we find

$$n_0(x) \sim \hbar^{-1} p_F(x) g_+[z_F(x)] + \int_{z_{-1/2}(x)}^{z_F(x)} dz \sqrt{z} \frac{\partial f}{\partial z} g_-(z), \quad (10)$$

where

$$g_{\pm}(z) = z^{1/2} \text{Ai}^2(-z) \pm z^{-1/2} \text{Ai}'^2(-z), \quad (11)$$

$f(z) = p(z)/\sqrt{z}$, and $\text{Ai}'(z) = d\text{Ai}(z)/dz$.

Equation (10) is useful for the extraction of the dominant terms in an asymptotic expansion for $n_0(x)$. As N grows, the coefficients $\sqrt{z} \partial f / \partial z$ become ever more slowly varying functions of the energy. Integrating by parts, ignoring the remaining higher-order contribution, and using

$$\left. \frac{\partial f}{\partial z} \right|_{E_F, x} = \frac{\omega_F}{p_F(x) \alpha_F(x)} - \frac{p_F(x)}{2\hbar z_F^{3/2}(x)}, \quad (12)$$

where $\alpha_F(x) = \sqrt{z_F(x)} \hbar^{-1} \partial z_\lambda(x) / \partial \lambda|_{\lambda=N-1/2}$ (e.g., $= \omega_F \int_{x_-(E_F)}^x dx' / p(x')$ for $x_-(E_F) < x < x_m$). We find

$$n_0(x) \sim \hbar^{-1} p_F(x) g_+[z_F(x)] + \left. \frac{\partial f}{\partial z} \right|_{E_F, x} A_0[z_F(x)], \quad (13)$$

where $A_0(z) = \text{Ai}(-z) \text{Ai}'(-z)$.

To evaluate the $k \neq 0$ components of Eq. (7), we use the integral representation of $\text{Ai}^2(-z)$ [35] and change the variable to $G_\lambda(x) = 2\pi k\lambda - z_\lambda(x)t$,

$$n_1(x) = 2 \sum_{k=-\infty}^{\infty} \lim_{T \rightarrow \infty} \int_{-T}^T dt \kappa(t) \int_{G_{-1/2}}^{G_F} \frac{dG_\lambda \omega_\lambda \sqrt{z_\lambda}}{P_\lambda \frac{\partial G_\lambda}{\partial \lambda}} e^{iG_\lambda}, \quad (14)$$

where the sum is over all $k \neq 0$, and $\kappa = i \exp(it^3/12)/(4\sqrt{i\pi^3 t})$. Integration by parts assuming negligible contributions from the lower bound yields, to leading order in \hbar (or $1/N$):

$$n_1(x) \sim 2 \frac{\omega_F \sqrt{z_F}}{P_F} \sum_{k=-\infty}^{\infty} (-1)^k \lim_{T \rightarrow \infty} \int_{-T}^T dt \frac{\kappa(t) e^{-iz_F t}}{2\pi k - y_F t}, \quad (15)$$

where $y_F = \alpha_F/\sqrt{z_F}$. The factor $(2\pi k - y_F t)^{-1}$ may be expressed as geometric series in $ty_F/(2\pi k)$, with a radius of convergence $R_F = |2\pi k/y_F|$, which becomes arbitrarily large as $|k|$ becomes greater and $|y_F|$ becomes smaller. This condition is generally fulfilled when $v(x)$ has an infinite number of bound states, or if the semiclassical limit is approached by stretching the coordinate [10,21,36]. Assuming any errors introduced by this sequence of operations vanish in the semiclassical limit the integrals required for the evaluation of $n_1(x)$ can be performed [35] and the results summed to give an asymptotic expansion for $n_1(x)$ in terms of $A_0[z] = \text{Ai}[-z]\text{Ai}'[-z]$, $A_1[z] = \text{Ai}^2[-z]$ and $A_2[z] = \text{Ai}^2[-z]$:

$$n_1(x) \sim \frac{\omega_F}{P_F} \sum_{p=0}^2 \sum_{j=0}^{\infty} (-z_F)^{-3j-p} \xi_{3j+p}(\alpha_F) A_p[z_F], \quad (16)$$

where $\{\xi_j(\alpha_F)\}$ corresponds to different power series in $\alpha_F(x)$, e.g.,

$$\xi_0(\alpha) = \sum_{k=1}^{\infty} \frac{(-1)^{k-1} 2(2^{2k-1} - 1) B_{2k}}{(2k)!} \alpha^{2k-1}, \quad (17)$$

where B_{2k} denotes the $2k$ th Bernoulli number [37]. Equation (17) may also be expressed as $-1/\alpha + \csc \alpha$. However, to extract the leading term of $n_1(x)$, only the term with highest power in $z_F(x)$ needs to be considered, yielding

$$n_1(x) \sim \frac{\omega_F}{P_F(x)} \left[\csc[\alpha_F(x)] - \frac{1}{\alpha_F(x)} \right] A_0[z_F(x)]. \quad (18)$$

The sum of Eqs. (13) and (18) yields Eq. (2). The relative orders of each term in \hbar only become explicit after accounting for the $z_F(x)$ dependence, which changes in different regions (see below). For instance, while the

rightmost term in Eq. (2) has a multiplying factor of \hbar^{-1} , it is canceled by the \hbar^{-1} in $z_F^{-3/2}(x)$. Equation (2) also illustrates the vital balance between the asymptotic expansions constructed for $n_0(x)$ and $n_1(x)$. The former [see Eq. (13)] contains the pole α_F^{-1} of the Laurent series for $\csc(\alpha_F)$ about $\alpha_F = 0$ (turning point), whereas Eq. (17) contains all remaining terms of the series.

Further, if we choose

$$t(x) = \sum_{j=0}^{N-1} p_j^2(x) |\phi_j(x)|^2 / 2, \quad (19)$$

similar steps produce

$$t^{\text{sc}}(x) = \frac{p_F^2(x)}{6} n^{\text{sc}}(x) + \frac{p_F(x) \omega_F}{3 \sin \alpha_F(x)} A_0[z_F(x)]. \quad (20)$$

Equations (2) and (20) define closed form global uniform semiclassical approximations to $n(x)$ and $t(x)$, which are asymptotically exact as $\hbar \rightarrow 0$ or $N \rightarrow \infty$.

These approximations simplify in different regions.

Classically allowed.— For $z_F(x) \gg 1$, the asymptotic form of the Airy function applies, leading to

$$n^{\text{sc}}(x) \rightarrow \frac{p_F(x)}{\hbar \pi} - \frac{\omega_F \cos[2S_F(x)/\hbar]}{2\pi p_F(x) \sin \alpha_F(x)} \quad (21)$$

(simplifying Eq. (3.36) of Ref. [15]; see also [19]). The dominant smooth term arises from the direct short-time classical orbit [18,25]. The oscillatory contributions arise from single [in $n_0(x)$] and multiple [in $n_1(x)$] reflections from each turning point [18,19,25,38].

Evanescent.— For x far outside the classically allowed region for the density $-z_F(x) \gg 1$ and

$$n^{\text{sc}}(x) \rightarrow \left[\frac{p_F(x)}{3S_F(x)} - \frac{\omega_F}{p_F(x) \sin \alpha_F(x)} \right] \frac{e^{-2|S_F(x)|/\hbar}}{4\pi}, \quad (22)$$

generalizing the approximation of Ref. [15]. Similarly,

$$t^{\text{sc}}(x) \rightarrow \left[\frac{p_F^3(x)}{3S_F(x)} - \frac{3\omega_F p_F(x)}{\sin \alpha_F(x)} \right] \frac{e^{-2|S_F(x)|/\hbar}}{24\pi}, \quad (23)$$

Turning point.— At a Fermi energy turning point x_0 , where $v'(x_0) \neq 0$, the leading term in the density is known:

$$n^{\text{sc}}(x_0) = c_0 \hbar^{-2/3} |dv/dx|^{1/3}, \quad (24)$$

where $c_0 = (2/9)^{1/3}/\Gamma^2(1/3)$ [15]. In addition,

$$t^{\text{sc}}(x_0) = -d_0 |dv/dx|, \quad (25)$$

where $d_0 = 1/[9\Gamma(2/3)\Gamma(1/3)]$.

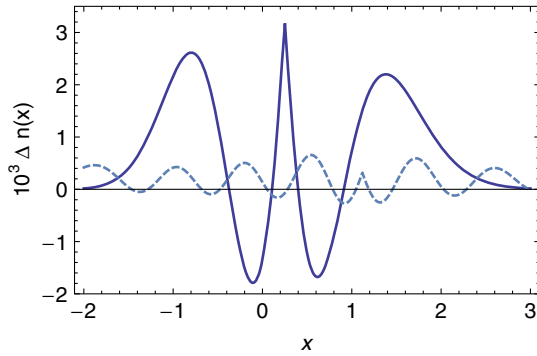


FIG. 2 (color online). Error in semiclassical density for $N = 2$ (solid), and $N = 8$ (dashed) in the Morse potential of Fig. 1.

The present development unifies all earlier partial results [15,19,36,38]. In Fig. 1, we showed how accurate the semiclassical density is in a Morse potential that supports 21 levels. In Fig. 2, we plot the density error for 2 and 8 particles. The cusp in the center is at the midphase point $x_m^{N-1/2}$, where the left- meets the right-turning point solution. To quantify, we define a measure of density difference as

$$\eta = \frac{1}{N} \int_{-\infty}^{\infty} dx |n^{\text{sc}}(x) - n(x)|, \quad (26)$$

which only vanishes when two densities are identical pointwise, and remains comparable in magnitude to the pointwise difference. In Fig. 3, we plot this error measure for the uniform approximation for the number density in Eq. (2) and for the TF density [Eq. (1)] as a function of N . As N grows, η shrinks until levels close to the unstable point of the well are included.

In Fig. 4, we plot $t(x)$. The TF result clearly misses the oscillations and everything beyond the turning points. The

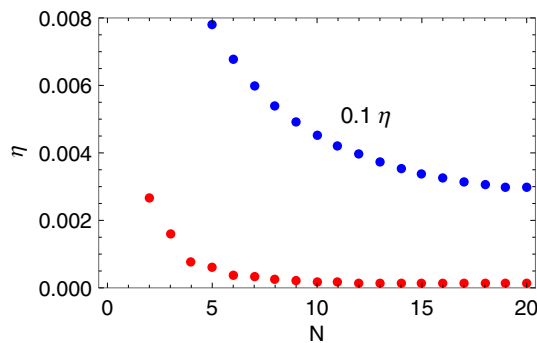


FIG. 3 (color online). Integrated measure of error [Eq. (26)] in TF density multiplied by 0.1 (top) and semiclassical uniform approximation (bottom) for the Morse potential of Fig. 1.

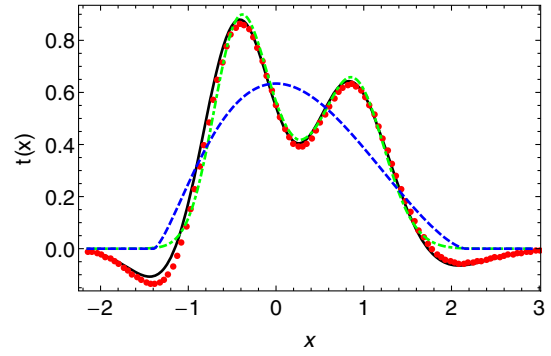


FIG. 4 (color online). Thomas-Fermi (dashed), uniform semiclassical (dotted), and exact (solid) kinetic energy density for 2 particles in the Morse potential of Fig. 1. The value of $\pi^2[n^{\text{sc}}(x)]^3/6$ is also shown (dot-dashed).

exact $t(x)$ becomes negative near the turning points and this effect is well captured by the uniform semiclassical approximation. Brack *et al.* [39] noted that $t^{\text{loc}}[n] = \pi^2 n^3/6$ evaluated on the exact density can yield an accurate approximation, but only in the classically allowed region. The improvement of the uniform approximation with increasing N is reflected in Fig. 5, in which η_T is defined analogously to Eq. (27) except with the exact T in the denominator. We find qualitatively similar results for several other systems including those with uncountable (Rosen-Morse [40] potential) and countable spectra (simple harmonic oscillator and quartic oscillator). Longer accounts of the derivation, performance, and relation to DFT are in preparation.

Equation (2) cannot be applied to three dimensions, Coulomb potentials, multicenter problems, or interacting particles, whereas TF theory can be applied to almost any fermionic problem. But Eq. (2) strongly suggests corrections to TF exist (even if they can only be evaluated numerically), are extremely accurate, and must reduce to

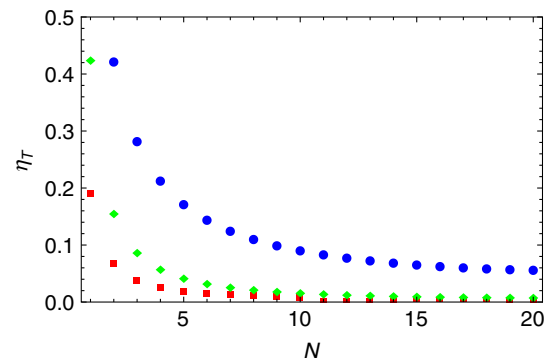


FIG. 5 (color online). Error (see text) in kinetic energy densities in the Morse potential of Fig. 1 with the semiclassical uniform approximation (squares), Thomas-Fermi theory (dots), and $t^{\text{loc}}[n^{\text{sc}}]$ (rhombs).

Eq. (2) where applicable. Without Eq. (2), we would have no reason to search for them. Now we have.

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