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Almost exact exchange at almost no computational cost in electronic structure

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Potential-functional theory is an intriguing alternative to density-functional theory for solving electronic-structure problems. We derive and solve equations using interacting potential functionals. A semiclassical approximation to exchange in one dimension with hard-wall boundary conditions is found to be almost exact (compared to standard density-functional approximations). The variational stability of this approximation is tested, and its far greater accuracy relative to the local-density approximation demonstrated. Even a fully orbital-free potential-functional calculation yields little error relative to exact exchange, for more than one orbital.

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I. INTRODUCTION

Electronic-structure problems in chemistry, physics, and materials science are often solved via the Kohn-Sham (KS) method of density-functional theory (DFT) [1,2], which balances accuracy with computational cost. For any practical calculation, the exchange-correlation (XC) energy must be approximated as a functional of the density. The basic theorems of DFT guarantee its uniqueness, but they give no hint about constructing approximations. The early local-density approximation (LDA) [2], much used in solid-state physics, was the starting point for today's more accurate methods, such as the generalized gradient [3,4] and hybrid [5] approximations. However, no systematic approach for their derivation is known, so a plethora of XC approximations have been created [6].

This lack inspires many approaches beyond traditional DFT, such as orbital-dependent functionals such as exact exchange (EXX) [7,8], use of the random-phase approximation [9], and (first-order) density-matrix functional theory [10]. While these can produce higher accuracy, their computational cost is typically much greater, and as of yet none has yielded a universal improvement over existing methods. Hybrid functionals replace some fraction of generalized gradient exchange with exact exchange, they are standard in molecular calculations, and they yield more accurate thermochemistry in most cases [6]. Furthermore, range-separated hybrids [11], where the exchange is treated in a Hartree-Fock fashion, typically yield much improved band gaps for many bulk solids [12]. However, their computational cost in plane-wave codes can be up to 1000 times higher [13], making such methods much less useful in practice.

Potential-functional theory (PFT) is an alternative approach to electronic-structure problems that is dual [14] to DFT. Recently, the formalism of pure PFT has been developed [15–17], and approximations for noninteracting fermions in simple model systems have been tested [18,19]. The leading corrections to Thomas-Fermi theory are explicit functionals of the potential [18,20,21], and inclusion of these yields approximations that are typically much more accurate than their DFT counterparts. Explicit PFT approximations have only been available for noninteracting one-dimensional (1D) models so far.

We take advantage of the KS mapping within PFT and solve the corresponding variational problem using the KS potential as a basic variable. We show that this implies a practically useful orbital-free approach, if one finds the required explicit potential-functional approximations. We illustrate this by testing a recent semiclassical expression that is a potential-functional approximation for the density matrix in one dimension [22]. Even for only one occupied orbital, the error is less than 5% compared to that of an LDA exchange calculation (LDAX), and it is negligible for two or more orbitals, as we show in Fig. 1. No explicit density-functional approximation for exchange comes close to this level of accuracy. If such a formula existed for three dimensions, the cost of (almost) EXX would be vanishingly small, relative to an LDA calculation. While our one-dimensional formula [see Eq. (9)] cannot be immediately applied to real-world calculations (even single atoms), our results show what should be possible if an extension to atomistic systems could be found.

II. POTENTIAL-FUNCTIONAL THEORY FOR INTERACTING PARTICLES

To begin, the ground-state energy of N electrons in an external potential $v(\mathbf{r})$ is given by

$$E_0 = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{\rm ee} + \hat{V} | \Psi \rangle, \tag{1}$$

where the search is over all normalized antisymmetric Ψ, and $\hat{T}$ is the kinetic energy operator, $\hat{V}_{\rm ee}$ is the electron-electron repulsion, and $\hat{V} = \sum_i v(\mathbf{r}_i)$ is the one-body operator. We use Hartree atomic units ($e^2 = \hbar = m_e = 1$) and suppress spin indices for simplicity. The universal potential functional [17] is

$$F[v] = \langle \Psi_0[v] | \hat{T} + \hat{V}_{\rm ee} | \Psi_0[v] \rangle, \tag{2}$$

where $\Psi_0[v]$ is the ground-state wave function of $v(\mathbf{r})$, so

$$E_0 = \min_{\tilde{v}} \left(F[\tilde{v}] + \int d\mathbf{r}\, n[\tilde{v}](\mathbf{r}) v(\mathbf{r}) \right), \tag{3}$$

where $n[v](\mathbf{r})$ is the ground-state density of $v(\mathbf{r})$. In the exact case, $\tilde{v}(\mathbf{r}) = v(\mathbf{r})$.

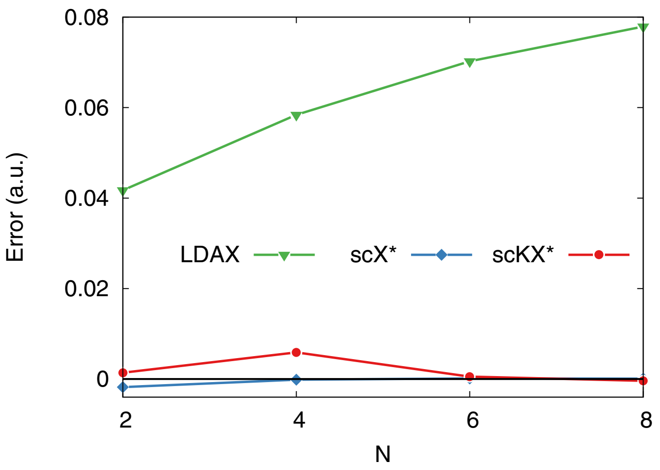

FIG. 1. (Color online) Energy error made by LDA exchange (LDAX), non-self-consistent (*) semiclassical exchange (scX), and semiclassical kinetic and exchange (scKX) for N spin-unpolarized, interacting fermions in a 1D well (see Table I).

In PFT, once $n[v](\mathbf{r})$ is given, $F[v]$ can be deduced, either by a coupling-constant integral or a virial relation [17]. When applied to noninteracting fermions, an approximation $n_{\mathrm{s}}[v_{\mathrm{s}}](\mathbf{r})$ yields an approximation $T_{\mathrm{s}}[v_{\mathrm{s}}]$, where $v_{\mathrm{s}}(\mathbf{r})$ is the potential in this noninteracting case. Now we introduce a potential approximation to the XC energy, $E_{\mathrm{XC}}[v_{\mathrm{s}}]$, and ask the following: How can these two approximations be used to find E_0 of interacting fermions?

To deduce the answer, write F as a functional of $v_{\mathrm{s}}(\mathbf{r})$ rather than $v(\mathbf{r})$ [16]:

$$\bar{F}[v_{\mathrm{s}}] = F[v[v_{\mathrm{s}}]] = T_{\mathrm{s}}[v_{\mathrm{s}}] + U[v_{\mathrm{s}}] + E_{\mathrm{XC}}[v_{\mathrm{s}}], \tag{4}$$

i.e., all are functionals of the KS potential [which is uniquely determined by $v(\mathbf{r})$], where U is the Hartree energy and E_{XC} is everything else. Given $n_{\mathrm{s}}[v_{\mathrm{s}}](\mathbf{r})$, we can determine T_{s} and U. Applying Eq. (3) yields, via the Hohenberg-Kohn theorem [14],

$$E_0 = \min_{\tilde{v}_{\mathrm{s}}} \left(\bar{F}[\tilde{v}_{\mathrm{s}}] + \int d\mathbf{r}\, n_{\mathrm{s}}[\tilde{v}_{\mathrm{s}}](\mathbf{r})\, v(\mathbf{r}) \right), \tag{5}$$

and the minimizing KS potential $v_{\mathrm{s}}(\mathbf{r})$ satisfies [16]

$$\left.\frac{\delta E_{v_0}[\tilde{v}_{\mathrm{s}}]}{\delta \tilde{v}_{\mathrm{s}}(\mathbf{r})}\right|_{v_{\mathrm{s}}} = 0 \tag{6}$$

for both the interacting and noninteracting systems. If $\chi_{\mathrm{s}}[v_{\mathrm{s}}](\mathbf{r}',\mathbf{r}) = \delta n_{\mathrm{s}}[\tilde{v}_{\mathrm{s}}](\mathbf{r}')/\delta \tilde{v}_{\mathrm{s}}(\mathbf{r})|_{v_{\mathrm{s}}}$ is the one-body density-density response function,

$$v'_{\mathrm{s}}[v_{\mathrm{s}}](\mathbf{r}) = v_0(\mathbf{r}) + \int d\mathbf{r}'\, \chi_{\mathrm{s}}^{-1}[v_{\mathrm{s}}](\mathbf{r}',\mathbf{r}) \left.\frac{\delta E_{\mathrm{HXC}}[\tilde{v}_{\mathrm{s}}]}{\delta \tilde{v}_{\mathrm{s}}(\mathbf{r}')}\right|_{v_{\mathrm{s}}}, \tag{7}$$

where $E_{\mathrm{HXC}}[\tilde{v}_{\mathrm{s}}] = U[\tilde{v}_{\mathrm{s}}] + E_{\mathrm{XC}}[\tilde{v}_{\mathrm{s}}] = U[\tilde{v}_{\mathrm{s}}] + E_{\mathrm{X}}[\tilde{v}_{\mathrm{s}}] + E_{\mathrm{C}}[\tilde{v}_{\mathrm{s}}]$, and [16]

$$v'_{\mathrm{s}}[v_{\mathrm{s}}](\mathbf{r}) = -\int d\mathbf{r}'\, \chi_{\mathrm{s}}^{-1}[v_{\mathrm{s}}] \left.\frac{\delta T_{\mathrm{s}}[\tilde{v}_{\mathrm{s}}]}{\delta \tilde{v}_{\mathrm{s}}}\right|_{v_{\mathrm{s}}}. \tag{8}$$

Equations (7) and (8) are the self-consistent equations for minimizing approximate functionals in PFT (which have some approximate v_{s} as minima). They generalize the results of Ref. [14], which only exploits the exact $T_{\mathrm{s}}[v_{\mathrm{s}}]$, beyond the special case when $v'_{\mathrm{s}} = v_{\mathrm{s}}$. The solution of Eq. (7) yields the minimizing KS potential $v_{\mathrm{s}}(\mathbf{r})$, once $n_{\mathrm{s}}[v_{\mathrm{s}}](\mathbf{r})$ and $E_{\mathrm{HXC}}[v_{\mathrm{s}}]$ are given. An approximation that satisfies Eq. (8) together with Eq. (7) is variationally consistent (see also Ref. [16]). If an approximation does not satisfy Eq. (8), it could yet be proven practically viable by a direct numerical minimization of Eq. (5). This is also numerically convenient as Eq. (7) requires computing the inverse of χ_{s}, which becomes costly as N increases. Below, we proceed with a direct minimization of Eq. (5) via the Nelder-Mead algorithm.

Our results so far apply to any approximate PFT calculations, including fully realistic systems and approximate correlation. Here we test them on a model in which explicit approximations have been derived. Contour integration techniques [15,18] yield a semiclassical potential-functional approximation (PFA) to the one-body reduced density matrix,

$$\gamma_{\mathrm{s}}^{\mathrm{sc}}(x,x') = \sum_{\lambda=\pm} \frac{-\lambda \sin\left[\theta_{\mathrm{F}}^{\lambda}(x,x')\right]\mathrm{cosec}\left[\alpha_{\mathrm{F}}^{\lambda}(x,x')/2\right]}{2T_{\mathrm{F}}\sqrt{k_{\mathrm{F}}(x)k_{\mathrm{F}}(x')}}, \tag{9}$$

of N fermions in a one-dimensional potential inside a box, whose chemical potential is above the potential everywhere. Here $\theta^{\pm}(x,x') = \theta(x) \pm \theta(x')$, $\alpha^{\pm}(x,x') = \alpha(x) \pm \alpha(x')$, $\theta(x) = \int_0^x dx' k(x')$ denotes the semiclassical phase, $k(x) = \sqrt{2[\mathcal{E} - v(x)]}$ is the wave vector, $\mathcal{E}$ is the energy, $\alpha(x) = \pi\tau(x)/T$, $\tau(x) = \int_0^x dx' k^{-1}(x')$ is the traveling time of a classical particle in the potential $v(x)$ from one boundary to the point x at a given energy, and $T = \tau(L)$ [15]. A subscript F denotes evaluation at the Fermi energy, which is found by requiring the wave functions to vanish at the edge, i.e., $\Theta_F(L) = (N + 1/2)\pi$. The derivation and implications for DFT of this expression are given elsewhere [22]. As $x \to x'$, the diagonal reduces to the known semiclassical approximation for the density [15] from which the noninteracting kinetic energy is obtained through a coupling-constant integral [17]. For a given electron-electron repulsion, $v_{\mathrm{ee}}(u)$, where $u = |x - x'|$ denotes the separation between electrons, the semiclassical exchange is

$$E_{\mathrm{X}}^{\mathrm{sc}}[v_{\mathrm{s}}] = -\frac{1}{2}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \left|\gamma_{\mathrm{s}}^{\mathrm{sc}}[v_{\mathrm{s}}](x,x')\right|^2 v_{\mathrm{ee}}(u). \tag{10}$$

III. ILLUSTRATION

We test both the accuracy and the stability of the semiclassical approximations relative to standard DFT by performing a sequence of calculations with different contributions treated via PFT: (a) nonvariational, semiclassical exchange approximation evaluated on the KS potential from LDAX; (b) variational, semiclassical exchange approximation; (c) variational, semiclassical approximation of all energy components. In all cases, we put the "electrons" in pairs in a 1D box of unit length, with a one-body potential $v(x) = -5\sin^2(\pi x)$, and repelling each other via $\exp(-\alpha u)$ with $\alpha = 4$, which ensures that the exact Hartree and exchange potentials show realistic decay within the box without reducing to a contactlike interaction (where LDA would perform artificially well [23]). This choice ensures that the condition on the Fermi energy [15] is satisfied for all N. Here the *exact* solution is a full OEP calculation using the exact orbital expression for exchange, yielding the

TABLE I. Total EXX energy and respective errors of self-consistent as well as perturbative post-LDAX (*) calculations within LDAX, scX, and scKX for N spin-unpolarized fermions interacting via $\exp(-4u)$ in an external potential $v(x) = -5\sin^2(\pi x)$ within a box of unit length.

			error × 10^3				
N	$E^{\rm EXX}$	$E_{\rm X}^{\rm EXX}$	LDAX	scX*	scKX*	scX	scKX
2	2.81	−0.52	41.72	−1.79	1.40	−3.10	−29.60
4	39.04	−1.26	58.41	−0.15	5.89	−3.86	−1.14
6	126.10	−2.10	70.24	0.14	0.53	−1.20	0.47
8	283.70	−2.98	77.91	0.08	−0.40	−0.10	−1.76

exact KS kinetic and exchange energies and KS potential on the self-consistent EXX density. Next, we define LDAX and check its performance. The (spin-polarized) LDAX energy per electron is

$$\epsilon_{\rm X}^{\rm LDA}(n(x)) = -\frac{\arctan\beta}{\pi} + \frac{\ln(1+\beta^2)}{2\pi\beta} \qquad (11)$$

with $\beta = 2\pi n(x)/\alpha$. In Table I we report exact total energies and errors of several approximate calculations as a function of the (double) occupation of orbitals. LDAX makes a substantial error for $N = 2$, which grows with N, although $E_{\rm X}$ itself grows, so the fractional error vanishes [15] as $N \to \infty$. A modern generalized gradient approximation might reduce this error by a factor of 2 or 3. In Table II, we list the total energy and its various components for four particles in the well. For each approximation, $\Delta E_{\rm X} \approx \Delta E$, implying that their densities (and hence their potentials) are highly accurate [24]. Small differences in the different energy components almost cancel by the variational principle.

A. Nonvariational, semiclassical exchange

First we find $E_{\rm X}$ in a post-LDA calculation of the exchange energy using the semiclassical approximation of Eq. (10) evaluated on the self-consistent potential from LDAX, i.e., $E_{\rm X}^{\rm sc}[v_{\rm s}^{\rm LDAX}]$. The error is plotted in Fig. 1 and tabulated in Tables I and II, denoted scX*, where the asterisk denotes nonvariational. Even for $N = 2$, the error is an order of magnitude smaller than LDAX. As N grows, the error shrinks very rapidly, even in absolute terms, because the semiclassical corrections to LDAX capture the leading corrections in powers of $1/N$ [18,19]. We even use the semiclassical kinetic energy (scKX) on the LDAX KS potential, and we see that, although the errors can be much larger, they are still far below those of LDAX. These results show that the semiclassical exchange and even kinetic energy can be extracted from a simple LDAX self-consistent calculation, yielding much smaller errors than LDAX. But such a recipe can be criticized for not being variational, i.e., not the result of any self-consistent minimization.

TABLE II. Energy components of self-consistent calculations within LDAX, semiclassical exchange (scX), and a semiclassical approximation of all energy components (scKX) for four "electrons" in the same problem as in Table I.

		error × 10^3		
	EXX	LDAX	scX	scKX
E	39.04	58.41	−3.86	−1.14
$T_{\rm s}$	49.44	1.22	0.34	1.22
$V_{\rm ext}$	−12.72	−1.38	0.07	4.56
U	3.58	0.003	0.02	−5.90
$E_{\rm X}$	−1.26	58.56	−4.29	−1.02

B. Variational, semiclassical exchange

Our second calculation uses the semiclassical PFT exchange within a regular KS-DFT calculation. We expand the KS potential in Chebyshev polynomials and use the Nelder-Mead method [25,26] to minimize the energy. A similar technique has been used for EXX [27,28]. Because the semiclassical approximation is not designed for variational minimization, this method can find very unphysical minima, but these are always accompanied by large errors in density normalization. If normalization deviates by 1% or more from N, we add a large penalty to the total energy, excluding such solutions, leading to the good results of Table I.

In Tables I and II, we list the scX results of this procedure. The error remains much smaller than that of LDAX, and rapidly reduces with increasing N, just as our previous semiclassical approximations for the density and kinetic energy [15,17–19]. However, errors are also typically much larger than those of the non-self-consistent calculation (scX*), showing that the variational properties are less robust than in LDAX. This is unsurprising, given that LDAX satisfies a crucial symmetry condition that scX does not [17,19]. To illustrate better the improvement in going from LDAX to scX, we plot the exchange energy densities in Fig. 2, and their errors. The scX density greatly improves over the LDAX density everywhere in space (except where LDAX accidentally matches the exact value). This is in stark contrast to the well-known difficulty of defining and comparing energy

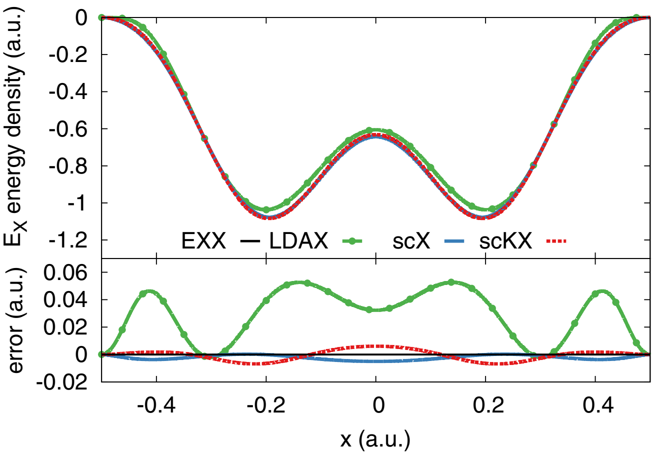

FIG. 2. (Color online) Exchange energy density of four spin-unpolarized fermions for the same problem as in Table I. The upper plot shows the EXX energy as well as the result from a self-consistent calculation via LDAX, scX, and scKX. The respective errors are plotted in the lower panel.

densities in generalized gradient approximations and other DFT approximations [29].

C. Variational, semiclassical total energy

Having saved the best for last, we finally run a pure PFT calculation, using semiclassical expressions for all energy components, not just the exchange energy, by directly minimizing Eq. (5). This scKX is a true orbital-free calculation, the PFT analog of orbital-free DFT, with results shown in Tables I and II.

First, note that because we have now approximated the kinetic energy, we would be doing extremely well to even match an LDAX calculation. However, in every case, the errors are *smaller* than LDAX. This is the basic criterion for a successful orbital-free functional: its errors are smaller than typical errors in XC approximations. However, we also note that for any $N > 2$, its errors are so small (below 2 mH) that they match those of exact exchange for most practical purposes. Of course, for $N = 1$ or 2, we can always use the exact result, since $E_x = -U/N$ is known and easy to evaluate.

Looking more closely at Table I, it is remarkable that scKX is more accurate than scX for $N = 4$ and 6. If we look at the individual energy components in Table II, we see that, e.g., the Hartree energy is far more accurate in scX than scKX, while the reverse is true for E_x. This implies that the density is quite inaccurate in scKX, but substantial cancellation of errors occurs. In Fig. 3 we plot both the KS potentials and density errors for the different calculations, showing the much greater errors in scKX. The cancellation of errors might be due to the balanced nature of the calculation, since *all* energy components have been derived from a single approximation for the density matrix [16,17]. Only extensive testing for many different circumstances can determine if this is a general phenomenon, and if so, where it fails. Thus minimizing our PFA reproduces the result of a self-consistent EXX KS calculation. As the number of electrons increases, not only does the PFA computational effort not increase significantly, but the accuracy also increases. The Fock integral required in EXX or hybrid calculations scales formally as $\Omega^2 N^2$, where Ω is the number of real-space grid points used in our 1D box. Our semiclassical expression simply scales as Ω^2. As N increases, Ω should scale linearly in order to preserve the ratio of grid points to orbital nodes. Thus the Fock integral scales as N^4 while our approximation scales much more favorably as N^2. In quantum chemistry, evaluation of the Fock energy has been the focus of much effort to improve the scaling, but at best the scaling can be reduced to roughly N^3 (e.g., when localized basis sets and various optimization techniques are used). The scKX calculation is completely orbital-free, and thus it is not necessary to solve the KS equation. Either due to direct diagonalization or the orthogonalization of orbitals depending on the method used, the KS scheme scales as N^3, while scKX scales as N^2 due to exchange (the other energy components scale as N). Thus PFT can reproduce the result of an EXX KS calculation while requiring a fraction of the computational cost. Substituting EXX with our semiclassical exchange may also be done for a hybrid functional (although treated within the OEP framework), where the fraction of EXX mixed in with a standard DFT functional may be replaced. Calculating this EXX energy is often the costliest part for hybrid calculations.

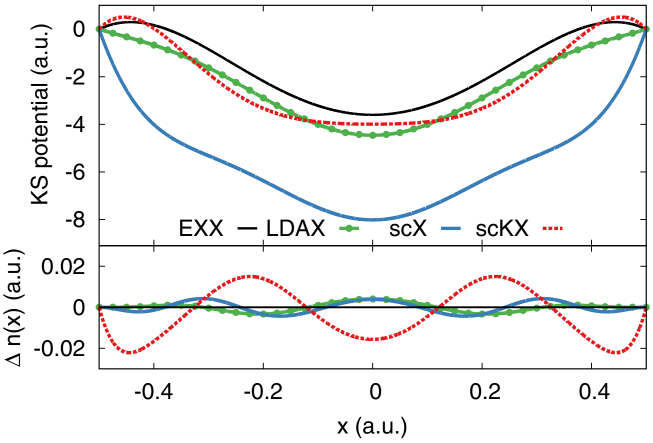

FIG. 3. (Color online) Upper plot: Converged KS potentials of EXX, LDAX, scX, and scKX runs for the same problem as in Table I with four spin-unpolarized fermions. Lower plot: Error in the respective, converged densities with respect to EXX.

IV. CONCLUSION

In conclusion, we have derived the equations for interacting PFT and solved them for a model problem. A PFT approximation to E_x in one dimension is found to be *almost* exact and does not require any orbital information. In both accuracy and efficiency, the PFT approximation performs better than standard DFT. Ongoing work to extend the method to 3D systems could speed up electronic-structure calculations by several orders of magnitude. Unfortunately, the 1D formulas tested here cannot be applied even to spherical systems such as atoms, since they do not include turning points or evanescent regions. While formulas as explicit as Eq. (9) seem unlikely in three dimensions [30], approximations starting from Eq. (9) might be devised; alternatively, numerical methods that calculate the leading quantum corrections in three dimensions might be devised.

In fact, an approximation that could be applied to atoms is given for the density and kinetic energy density in Ref. [31], which is the generalization of the density approximation used here [15]. If that method can be generalized to yield a density matrix, it could be applied to spherical situations, such as atoms, but not molecules or solids. Our work here shows the *promise* of exchange-based PFT: The leading semiclassical corrections to the local approximation, as a functional of the potential, yield absurdly accurate results. While the ability to extract a simple analytic form is clearly an artifact of one dimension, the accuracy of these calculations is not (very likely). If analogous functionals for general 3D problems could be found, they would likely be as accurate and remove all practical barriers to using exact exchange in electronic-structure calculations, especially in solids. We are currently pursuing several paths toward finding them, either numerically or with cruder approximations. The present work shows that such research is well worth pursuing.

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