Electronic structure via potential functional approximations

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In the original form of density functional theory (DFT), suggested by Thomas and Fermi (TF) and made formally exact by Hohenberg and Kohn, the energy of a many-body quantum system is minimized directly as a functional of the density. Its modern incarnation uses the Kohn-Sham (KS) scheme, which employs the orbitals of a fictitious non-interacting system, such that only a small fraction of the total energy need be approximated. With the goal to simulate ever larger molecular and solid state systems, interest is rapidly reviving in finding an *orbital*-free approach to DFT. The major bottleneck in modern calculations is the solution of the KS equations, which can be avoided with a pure density functional for the kinetic energy of non-interacting fermions, T_s. Despite decades of effort, no generally applicable approximation for T_s has been found.

We consider the *potential* as a more natural variable to use in deriving approximations to quantum systems. In exact potential functional theory (PFT) we obtain the ground-state (gs) energy from

$$E_v = \min_{\Psi} \left(\langle \Psi \mid \hat{T} + \hat{V}_\mathrm{ee} + \hat{V} \mid \Psi \rangle \right) , \tag{1}$$

where $\hat{T}$ is the kinetic energy operator, $\hat{V}_\mathrm{ee}$ the inter-electronic repulsion, $\hat{V}$ the one-body potential, and Ψ are N-particle wavefunctions. Defining

$$F[v] = \langle \Psi_v \mid \hat{T} + \hat{V}_\mathrm{ee} \mid \Psi_v \rangle, \tag{2}$$

with Ψ_v denoting the gs wavefunction of potential $v(\mathbf{r})$, the exact gs energy is given by

$$E_v = F[v] + \int d^3r \; n[v](\mathbf{r}) \, v(\mathbf{r}) , \tag{3}$$

n denoting the gs density. In practice, this requires two separate approximations, $F^\mathrm{A}[v]$ and $n^\mathrm{A}[v]$, yielding a direct approximation $E_v^\mathrm{A,dir}$.

In a recent letter[1] we go beyond those results by considering explicit potential functional approximations to interacting and non-interacting systems of electrons. We show that (i) the universal functional, $F[v]$, is determined entirely from knowledge of the density as a

functional of the *potential*, such that only *one* approximation is required, namely $n^{\mathrm{A}}[v]$, (ii) the variational principle imposes a condition relating energy and density approximations, (iii) a simple condition guarantees satisfaction of the variational principle, (iv) with an orbital-free approximation to the non-interacting density as a functional of the *potential*, T_{s} is automatically determined, i.e., there is no need for a separate approximation, and (v) satisfaction of the variational principle improves accuracy of approximations.

We *deduce* an approximation to F from any $n^{\mathrm{A}}[v](\mathbf{r})$ by introducing a coupling constant in the one-body potential, $v^{\lambda}(\mathbf{r}) = (1 - \lambda) v_0(\mathbf{r}) + \lambda v(\mathbf{r})$, where $v_0(\mathbf{r})$ is some reference potential. Via the Hellmann-Feynman theorem (and for the choice $v_0 = 0$) we obtain

$$F[v] = \int d^3r \left\{ \bar{n}[v](\mathbf{r}) - n[v](\mathbf{r}) \right\} v(\mathbf{r}), \tag{4}$$

where $\bar{n}[v](\mathbf{r}) = \int_0^1 d\lambda \, n[v^{\lambda}](\mathbf{r})$. This establishes that the universal functional is determined *solely* by the knowledge of the density as functional of the *potential*. Moreover, insertion of $n^{\mathrm{A}}(\mathbf{r})$ on the right *defines* an associated approximate $F^{\mathrm{cc}}[n^{\mathrm{A}}[v]]$, where cc denotes coupling constant.

Furthermore, consider the variational principle. In PFT, this yields[2]

$$E_v^{\mathrm{A,var}} = \min_{\tilde{v}} \left(F^{\mathrm{A}}[\tilde{v}] + \int d^3r \, n^{\mathrm{A}}[\tilde{v}](\mathbf{r}) \, v(\mathbf{r}) \right), \tag{5}$$

with a possibly different value from $E_v^{\mathrm{A,dir}}$ for a given pair of approximations $\{F^{\mathrm{A}}, n^{\mathrm{A}}\}$. We also show that this minimization over trial potentials $\tilde{v}$ can be avoided, such that $F^{\mathrm{cc}}[n^{\mathrm{A}}[v]]$ does yield $E_v^{\mathrm{A,var}}$, if, and only if,

$$\chi^{\mathrm{A}}[v](\mathbf{r}, \mathbf{r}') = \chi^{\mathrm{A}}[v](\mathbf{r}', \mathbf{r}), \tag{6}$$

where $\chi^{\mathrm{A}}[v](\mathbf{r}, \mathbf{r}') = \delta n^{\mathrm{A}}[v](\mathbf{r})/\delta v(\mathbf{r}')$. This condition is satisfied by the exact response function, but not necessarily by an approximation $n^{\mathrm{A}}[v]$; furthermore, enforcing Eq. (6) on $n^{\mathrm{A}}[v]$ improves upon the accuracy.

Of much more practical use is the application of these results to the *non-interacting* electrons in a KS potential, mimicking inter-electronic interactions via the Hartree (v_{H}) and exchange-correlation (v_{XC}) contribution:

$$v_{\mathrm{s}}(\mathbf{r}) = v(\mathbf{r}) + v_{\mathrm{H}}[n_{\mathrm{s}}^{\mathrm{A}}[v_{\mathrm{s}}]](\mathbf{r}) + v_{\mathrm{XC}}^{\mathrm{A}}[n_{\mathrm{s}}^{\mathrm{A}}[v_{\mathrm{s}}]](\mathbf{r}) . \tag{7}$$

For a given $E_{\mathrm{XC}}^{\mathrm{A}}$, which determines $v_{\mathrm{XC}}^{\mathrm{A}}$, this equation can be easily solved by standard iteration techniques, *bypassing* the need to solve the KS equations via a given $n_{\mathrm{s}}^{\mathrm{A}}[v_{\mathrm{s}}]$, where

the subscript S denotes single-particle quantities. However, once self-consistency is achieved, we need T_s to extract the total energy of the interacting electronic system. All our derivations apply equally to the non-interacting problem, so we deduce:

$$T_s[v] = \int d^3r \left\{ \bar{n}_s[v](\mathbf{r}) - n_s[v](\mathbf{r}) \right\} v(\mathbf{r}), \tag{8}$$

which is the analog of Eq. (4) for non-interacting electrons in the external potential $v(\mathbf{r})$ (which is called $v_s(\mathbf{r})$, when it is the KS potential of some interacting system). This *defines* a kinetic energy approximation determined solely by the density approximation, $T_s^{cc}[n_s^A[v]]$. This result eliminates the need for constructing approximations to the non-interacting kinetic energy, T_s.
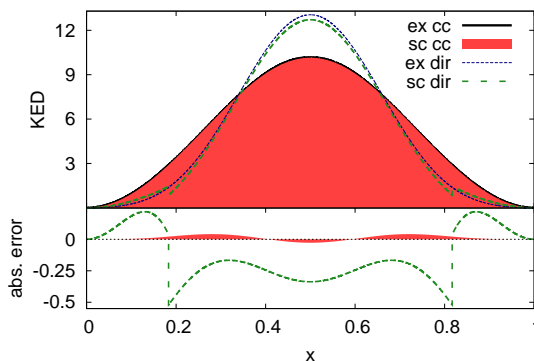

FIG. 1: Top panel: Exact (ex) KED of the coupling-constant (cc) and the direct (dir) approach (black and blue) with the corresponding semiclassical (sc) approximations (red and green) for one particle in $v(x) = -5 \sin^2(\pi x)$, $0 < x < 1$. Bottom panel: Absolute errors.

To illustrate the power of these results, we consider a simple example of non-interacting, spinless fermions in a one-dimensional box with potential $v(x)$. In Fig. 1 we plot exact and approximate kinetic energy densities (KED) demonstrating that our coupling-constant approach from Eq. (8) evaluated on $n_s^A[v]$ from Ref. [3] yields both locally and globally more accurate results, and required no separate approximation for the KED.

Potential functional approximations to the density, $n_s^A[v]$, are presently being developed via a systematic asymptotic expansion in terms of the *potential*, which has already been found in simple cases[3, 4]. The leading terms are local approximations of the TF type, and the leading corrections, which are relatively simple, nonlocal functionals of the *potential*, greatly improve over the accuracy of local approximations in a systematic and understandable way. However, a practical realization of the presented approach awaits general-purpose

approximations to $n_{\rm s}^{\rm A}[v](\mathbf{r})$ for an arbitrary three-dimensional case. We have shown here that it no longer awaits the corresponding kinetic energy approximations.

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