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Design of kinetic functionals for many-body electron systems: Combining analytical theory with Monte Carlo sampling of electronic configurations

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In a previous work [L. Delle Site, J. Phys. A: Math. Theor. **40**, 2787 (2007)], the derivation of an analytic expression for the kinetic functional of a many-body electron system has been proposed. Though analytical, the formula is still nonlocal (multidimensional) and thus not ideal for numerical applications. In this work, by treating the test case of a uniform gas of interacting spinless electrons, we propose a computational protocol which combines the previous analytic results with the Monte Carlo sampling of electronic configurations in space. This, we show, leads to an internally consistent scheme to design well founded local kinetic functionals.

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The design of electronic kinetic density functional is becoming a field of rapidly growing interest due to the central role played by this quantity in orbital-free density functional (OFDFT) methods. Such methods allow for large computational advantages compared to standard Kohn-Sham (KS)-based techniques since they are computationally much less demanding.[1–5] Moreover, as the calculations are performed only in real space, they allow for an optimal design of an interface with classical codes to the aim of connecting the electronic and the larger atomistic scales within a unified computational framework.[6,7] The criterion to measure the validity of the OFDFT approach is based on the quality of the kinetic functional employed.[8] In principle, if we had the exact kinetic functional, the variational problem based on the Hohenberg-Kohn theorem would not require the KS orbital-based approximation anymore (in the KS approach, the kinetic energy is the *exact* kinetic energy of *noninteracting* electrons, whereas the exchange and correlation part of the kinetic energy is embedded into the exchange-correlation functional which, in the practice of DFT, is only an *approximation* of the real one). In practice, we must design kinetic functionals, which are physically well founded and computationally less demanding than the KS-based approaches. The most popular currently used kinetic functional consists of the Thomas-Fermi and Weizsäcker terms, which are local, plus a linear response term which is nonlocal.[1] Recently, one of the authors of the current work has explored a different path than that above; this is based on obtaining a kinetic functional for a system of N electrons whose two central quantities are the one particle electron density $\rho(\mathbf{r})$ and the $(N-1)$-conditional probability density $f(\mathbf{r}_2,\ldots,\mathbf{r}_N|\mathbf{r}_1)$.[9,10] The first is defined as $\rho(\mathbf{r}_1)=N\int_{\Omega_{N-1}}\psi^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)d\mathbf{r}_2,\ldots,d\mathbf{r}_N$ [where Ω_{N-1} is the $3(N-1)$-dimensional spatial domain of the electrons and ψ is the $3N$-dimensional wave function of the electronic ground state normalized to 1]. f represents the probability density of finding an $N-1$ electron configuration, $(\mathbf{r}_2,\ldots,\mathbf{r}_N)$, for a given fixed value of $\mathbf{r}_1$. Here, electrons are treated as *spinless* fermions, i.e., in this context, as particles characterized by a wave function which is zero at any coalescence point (i.e., points where two electrons coincide) under the approximation that the explicit effects of the spin can be in the first instance neglected. The function f satisfies the following properties (see also Refs. 11–15 for the properties of f and its derivation):

$$\int_{\Omega_{N-1}} f(\mathbf{r}_2,\ldots,\mathbf{r}_N|\mathbf{r}_1)d\mathbf{r}_2,\ldots,d\mathbf{r}_N=1, \quad \forall\ \mathbf{r}_1, \tag{1}$$

$$f(\mathbf{r}_1,\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_{j-1},\mathbf{r}_{j+1},\ldots,\mathbf{r}_N|\mathbf{r}_j)=0$$

$$\text{for } i=j, \quad \forall\ i,j=1,N, \tag{2}$$

$$f(\mathbf{r}_1,\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_j,\ldots,\mathbf{r}_{k-1},\mathbf{r}_{k+1},\ldots,\mathbf{r}_N|\mathbf{r}_k)=0$$

$$\text{for } i=j, \quad \forall\ i,j\neq k. \tag{3}$$

In terms of ρ and f, the equation to determine the ground state of the systems writes[9,10]

$$E_0=\min_{\rho}\left(\min_{f}(\Gamma[f,\rho])+\frac{1}{8}\int\frac{|\nabla\rho(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}d\mathbf{r}_1 + \int v(\mathbf{r}_1)\rho(\mathbf{r}_1)d\mathbf{r}_1\right), \tag{4}$$

where $v(\mathbf{r}_1)$ is the external potential and

$$\Gamma[f,\rho]=\int\rho(\mathbf{r}_1)\left[\frac{1}{8}\int_{\Omega_{N-1}}\frac{|\nabla_{\mathbf{r}_1}f(\mathbf{r}_2,\ldots,\mathbf{r}_N|\mathbf{r}_1)|^2}{f(\mathbf{r}_2,\ldots,\mathbf{r}_N|\mathbf{r}_1)}d\mathbf{r}_2,\ldots,d\mathbf{r}_N + \frac{(N-1)}{2}\int_{\Omega_{N-1}}\frac{f(\mathbf{r}_2,\ldots,\mathbf{r}_N|\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_2,\ldots,d\mathbf{r}_N\right]d\mathbf{r}_1. \tag{5}$$

Equation (4) is expressed in a.u., i.e., $\hbar,m,e,4\pi\epsilon_0$ are all equal to 1. This approach, up to this point, is formally rigorous; however, to proceed further, it requires an explicit expression for f. This latter is then built on the basis of the mathematical prescription of Eqs. (1)–(3) and a physical *first principles* argument. The physical argument used in this case is rather simple, though powerful, that is, in contrast to the case of a gas of noninteracting electrons; the gas of interacting electrons is characterized by the presence of the Coulomb electrostatic term acting pairwise between electrons. The next step consists of writing f in terms of such an interaction in a way that Eqs. (1)–(3) are satisfied.[16] The proposed analytic form, consistent with the requirements above, reads[9,10]

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$$f(\mathbf{r}_2, \ldots, \mathbf{r}_N|\mathbf{r}) = e^{\bar{\bar{E}}(\mathbf{r})} \cdot \prod_{n=2,N} e^{-\gamma E_H(\mathbf{r},\mathbf{r}_n)} \times \prod_{i>j\neq 1} e^{-\gamma E_H(\mathbf{r}_i,\mathbf{r}_j)}, \tag{6}$$

with the normalization condition

$$e^{-\bar{\bar{E}}(\mathbf{r})} = \int \prod_{n=2,N} \prod_{i>j\neq 1} e^{-\gamma E_H(\mathbf{r},\mathbf{r}_n)-\gamma E_H(\mathbf{r}_i,\mathbf{r}_j)} d\mathbf{r}_2, \ldots, d\mathbf{r}_N, \tag{7}$$

where $E_H(\mathbf{r}_i,\mathbf{r}_j)=\frac{\rho(\mathbf{r}_i)\rho(\mathbf{r}_j)}{|\mathbf{r}_i-\mathbf{r}_j|}$ and γ is a free parameter to be optimized by minimizing Γ (with respect to γ) for a fixed ρ. The resulting kinetic functional consists of a local term [the Weizsäcker term, the second term on the right hand side (rhs) of Eq. (4)] and an N-dimensional nonlocal term known as the *nonlocal Fisher information* functional, which we will indicate as $I[\rho]$ (Ref. 11) [first term on the rhs of Eq. (5)]. The other term in Γ is the Coulomb electron-electron term, which we will indicate as $C[\rho]$, and is also a multidimensional integral. The aim of this work is to show, for a uniform gas how by employing a Monte Carlo sampling of the electronic configurations in space, the nonlocal kinetic term $I[\rho]$ (and in general the functional $\Gamma[f,\rho]$) can be reduced *numerically* to a local functional. Moreover, within the same approach, one can perform numerically an *optimal* choice of the f by minimizing Γ with respect to γ. The advantage with respect to previous methods is that in this case, the effects of the correlations between the electrons regarding the kinetic functional are automatically incorporated into a local functional. Moreover, within the OFDFT approach, the optimization procedure for f and the reduction of the functional from nonlocal to local can also be used as an intermediate step within a full self-consistent procedure, as suggested by Eq. (4). This means that the kinetic functional for an OFDFT algorithm can also be calculated on the fly without any adjustable empirical parameters. This, as Eq. (4) shows, is valid beyond the case of uniform gas that here we use as an illustrative example.[17]

Monte Carlo evaluation of the nonlocal part of the kinetic functional. At this point, the problem we must address to the aim of obtaining a local functional from Eq. (5) is that of reducing the $3N$-dimensional integrals to three-dimensional ones. The Metropolis Monte Carlo (MC) approach has been shown to be ideal for this kind of problems (see standard textbooks in the field, e.g., Ref. 18 or 19). In general, the choice of this kind of stochastic algorithms is a natural one for high-dimensional problems since their efficiency, relative to any other nonstochastic method, increases as the number of dimensions of the integral increases. In this case, the integration is done with respect to the variables $\mathbf{r}_2, \ldots, \mathbf{r}_N$ for a fixed value of $\mathbf{r}_1$ at a given density $\rho(\mathbf{r}_1)$. By performing the integration for a large number of fixed $\mathbf{r}_1$ values, we then obtain the expression of the functional local in $\mathbf{r}_1$. In order to evaluate Eq. (5) within the MC approach, we need to rewrite it as follows: $\Gamma[f,\rho]=\int\rho(\mathbf{r}_1)\{I[\rho(\mathbf{r}_1)]+C[\rho(\mathbf{r}_1)]\}d\mathbf{r}_1$, where the key quantities $I[\rho(\mathbf{r}_1)]$ and $C[\rho(\mathbf{r}_1)]$ at a fixed $\mathbf{r}_1$ can be conveniently written in the following form:

$$I[\rho(\mathbf{r}_1)] + C[\rho(\mathbf{r}_1)] = \left[\frac{1}{8}\int_{\Omega_{N-1}} dr^{N-1} f \left| \frac{\vec{\nabla} f}{f} \right|^2 + \frac{1}{N}\sum_{i=1,N}\sum_{j>i}\int_{\Omega_{N-1}} dr^{N-1} \frac{f}{|\mathbf{r}_i - \mathbf{r}_j|} \right]_{\rho(\mathbf{r}_1),\gamma}. \tag{8}$$

In the above equation, the two integrand functions are written as a product of f that acts here as a weighting function and another function (of all the coordinates). This is the form suitable for the *importance sampling MC* algorithm.[18] In fact, the integrals can be stochastically evaluated by using

$$I[\rho(\mathbf{r}_1)] + C[\rho(\mathbf{r}_1)] = \frac{1}{M}\sum_{m=1,M} \left[\frac{1}{8} \left| \frac{\vec{\nabla}_1 f}{f} \right|^2 + \frac{1}{N}\sum_{i=1,N}\sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right]_{\rho(\mathbf{r}_1),\gamma}, \tag{9}$$

where M is the number of randomly chosen configurations, or configurational space points, at which the function in the square brackets is sampled. The sum in Eq. (9) converges to the integral of Eq. (8) when the configurations are generated according to f. In practice, since f is not known explicitly (the normalization factor is a multidimensional integral), a Markov chain is constructed with limiting density f. For the case of a uniform gas, the Metropolis MC algorithm consists of randomly displacing the present configuration of the system of N electrons and then accepting the new configuration, in a way that the density of particles on average stays constant, with probability (i.e., with acceptance rule),

$$a(\text{old} \rightarrow \text{new}) = \min\left(1, \frac{f_{\text{new}}}{f_{\text{old}}}\right). \tag{10}$$

The robustness of the algorithm lies on the fact that the terms in the sum [Eq. (9)] can be evaluated at each configuration with a relatively low computational cost. In fact, this is trivial for the $1/|\mathbf{r}_i-\mathbf{r}_j|$ term, while some algebra reduces the term $|\vec{\nabla}_1 f/f|^2$ as a function of $\vec{\nabla}_1 E_H(\mathbf{r}_1,\mathbf{r}_n)$.

We modeled a uniform distribution of electrons by means of a system of N electrons (with $N=10$, 25, 50, 100, and 250) in a cubic box. The MC scheme works as follows: one electron is selected at random and a trial move is attempted. We adopt a trial move as a uniformly distributed displacement of a randomly selected electron. Explicitly, the acceptance rule is

$$\frac{f_{\text{new}}}{f_{\text{old}}} = e^{-\gamma[E_H(\mathbf{r}_1,\mathbf{r}_k^{\text{new}})-E_H(\mathbf{r}_1,\mathbf{r}_k^{\text{old}})]} \prod_{i\neq 1,k} e^{-\beta[E_H(\mathbf{r}_i,\mathbf{r}_k^{\text{new}})-E_H(\mathbf{r}_i,\mathbf{r}_k^{\text{old}})]}, \tag{11}$$

where k labels the attempted moved electron. If the move is accepted, the terms of the sum in Eq. (9) are evaluated for the average in the new configuration; otherwise, another instance of the quantities evaluated in the old configuration entries the average. Periodic boundary conditions and minimum image convention were imposed. In practice, each dis-

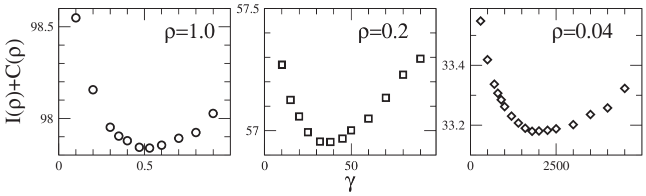

FIG. 1. The three panels show the values of γ that minimize the functional $I[\rho(\mathbf{r}_1)]+C[\rho(\mathbf{r}_1)]$ at three representative densities (for $N=100$ electrons). Energies and densities are expressed in a.u.

placed electron was in turn the center of the box and only one instance of each particle was used in evaluating the quantities in Eqs. (11) and (9). Periodic replicas of the system would be necessary for the evaluation of the slowly decaying "Coulomb" dependence of $C[\rho(\mathbf{r}_1)]$ which is not the quantity of interest in this work. In contrast, for the evaluation of $I[\rho(\mathbf{r}_1)]$, it would be physically wrong, within the approximations done, to count correlations of periodic replicas; in fact, by construction, f is characterized only by the interaction of the N particles explicitly treated. Moreover, we have numerically shown that, for the range of density chosen, both the values γ that minimize $\Gamma[f,\rho]$ and $I[\rho(\mathbf{r}_1)]$ do not depend on the size N of the system; thus, for the purposes of this paper, we did not need to worry about the finite size dependence of $C[\rho(\mathbf{r}_1)]$. Of course, if one wants to treat the whole functional (i.e., kinetic plus Coulomb term), for example, to calculate total energies, then the size effects and the effects of the periodic images have to be taken carefully into account.

For the case of uniform gas, once the sum in Eq. (9) is obtained, the integral $\Gamma[f,\rho]$ is calculated by just multiplying $I[\rho(\mathbf{r}_1)]+C[\rho(\mathbf{r}_1)]$ by the number of electrons N.

Numerical results. We performed the calculation at several densities, selected in a way to resemble those of real metals. For each density, we evaluated the sum in Eq. (9) at different values of γ, searching for the value yielding the minimum in the sum. Figure 1 shows the minimum found for Γ as a function of γ for three different densities: (a) high, resembling the realistic case of Pt ($\sim 1.0\ e/\text{bohr}^3$), (b) intermediate, resembling Ti ($\sim 0.2\ e/\text{bohr}^3$), and (c) low, resembling Na ($\sim 0.04\ e/\text{bohr}^3$). The numerical evidence of the existence of a minimum corroborates the conjecture that the problem is variational and allows one to find the optimal γ that in this way is no longer an empirical parameter. Having the optimal γ for the different densities, we can numerically express $I[\rho(\mathbf{r}_1)]$ and then fit the numerical results to a *convenient* functional form so that we can have an analytic expression. The formula we obtain is $I[\rho(\mathbf{r}_1)]=A+B\ln[\rho(\mathbf{r}_1)]$, with $A=0.860\pm0.022$ and $B=0.224\pm0.012$. Note that the functional form of the fit was suggested by observation of the plotted data: at this point, we do not attempt to give a physical meaning to it. The calculated values of $I[\rho(\mathbf{r}_1)]$ at the optimal γ are plotted in Fig. 2 together with the fit. Finally, we can propose a new *local* kinetic functional for slowly varying densities, ready for OFDFT based codes,

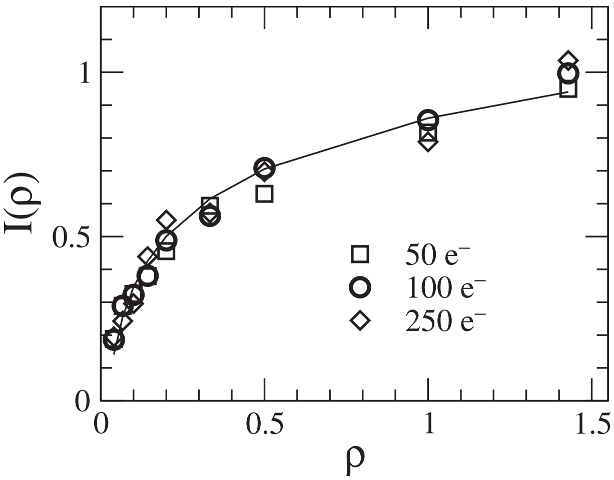

FIG. 2. Calculated values of $I[\rho(\mathbf{r}_1)]$ for $N=50$, 100, and 250 electrons. The continuous line is the fit we propose (see text).

$$K[\rho]=\frac{1}{8}\int\frac{|\nabla\rho(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}d\mathbf{r}_1+\int\rho(\mathbf{r}_1)[A+B\ln\rho(\mathbf{r}_1)]d\mathbf{r}_1. \tag{12}$$

In conclusion, we have illustrated a computational protocol which combines analytical and stochastic numerical approaches to address the problem of designing local kinetic functional for OFDFT based codes. We have applied it to the test case of uniform interacting gas of spinless electrons and given arguments from which it emerges the general character of the approach for any system in the ground state. Anyway, it must be said that despite being an ideal system, the uniform gas has been often employed to develop tools for realistic calculations (see, e.g., the very recent work of Drummond and Needs[21]), often under the approximation of spinless particles. For this reason, the specific results of this work are already relevant beyond the role of illustrative example. The approach shown here is internally (mathematically) consistent and computationally not expensive and rather flexible. It may represent a direction along which to proceed since it can be technically improved by both the mathematical and computational points of view by improving the functional form of f (as discussed in Refs. 16 and 17) and the sampling of the electronic configurations.

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[16] Of course, since among the properties required for f there is also that of mimicking the fermionic character, the *indirect* interaction of the Pauli principle is also included. In the case of spinless particles, the Pauli principle is included in a crude way, that is, by the fact that two particles cannot have the same state or position $\mathbf{r}$. In principle, one may design an f which can separate the interaction coming from the Pauli principle and thus yielding the Thomas-Fermi term in the limit of uniform noninteracting gas and that coming from the Coulomb term, which reproduces the interacting character. Here, for simplicity, we have used only the Coulomb term since this form of f does capture the essential physics of an *interacting* gas and it is numerically simple. However, in principle, it would not be difficult to include specific effects (see also Ref. 17).

[17] In particular, although the hypothesis of spinless particles is often used in many applications of DFT, it would not be difficult, though computationally more demanding, to incorporate the spin explicitly in the current approach. In this case, one may follow a *first principles* argument where although the Coulomb interaction between electrons is still the central point, however, it must be expressed taking into account the effects of the spin. This may be achieved by modifying f so that electrons with same spin tend to avoid each other (in a long range fashion), while those with opposite spin tend to "condense" but the electrostatic interaction keeps them apart (in a short range fashion) (Refs. 22–24). Following this principle, f can be written in the same way but factorizing it in a term considering couples with the same spin and another considering those with opposite spin. They may have different constants, α, β, multiplying the term in the exponential. In turn, f can be optimized minimizing Γ with respect to α and β. Finally, by imposing that the total spin is zero, one can perform the sampling of the electronic configurations considering, for each spatial configuration, also the spin configurational space.

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