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# A real-space stochastic density matrix approach for density functional electronic structure

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 The recent development of real-space grid methods has led to more efficient, accurate, and adaptable approaches for large-scale electrostatics and density functional electronic structure modeling. With the incorporation of multiscale techniques, linear-scaling real-space solvers are possible for density functional problems if localized orbitals are used to represent the Kohn-Sham energy functional. These methods still suffer from high computational and storage overheads, however, due to extensive matrix operations related to the underlying wave function grid representation. In this paper, an alternative stochastic method is outlined that aims to solve directly for the one-electron density matrix in real space. In order to illustrate aspects of the method, model calculations are performed for simple one-dimensional problems that display some features of the more general problem, such as spatial nodes in the density matrix. This orbital-free approach may prove helpful considering a future involving increasingly parallel computing architectures. Its primary advantage is the near-locality of the random walks, allowing for simultaneous updates of the density matrix in different regions of space partitioned across the processors. In addition, it allows for testing and enforcement of the particle number and idempotency constraints through stabilization of a Feynman-Kac functional integral as opposed to the extensive matrix operations in traditional approaches.

## 1 Introduction

Density functional theory (DFT) quantum simulation methods are contributing a great deal to a basic understanding of condensed phase problems such as liquid structure[1] and catalyst mechanisms.[2,3] Yet 30 years after the initial development of the Car-Parrinello method,[4] we are limited to simulations of a few hundred atoms for a few hundred picoseconds in time, even on advanced supercomputer architectures.

The Car-Parrinello[4] and related[5,6] algorithms are based on approximate solution of the Kohn-Sham equations in a chosen basis. For periodic systems a natural basis set for the occupied orbitals is the plane-wave basis.[5] In recent years it has been recognized that real-space methods hold several advantages over plane-wave approaches.[7–15] These advantages include near-locality in iterative updates, adaptivity, and the possibility of linear-scaling algorithms[16] due to the spatial decay of the density matrix coupled with multiscale solvers for the Poisson and electronic energy minimization problems.

Even with the initial optimism concerning real-space methods, they have not yet fully developed into a widely used set of mainstream tools in quantum chemistry and *ab initio* dynamical modeling. The wave-function based representation leads to large storage requirements and computational overhead directed at various matrix operations related to maintaining density matrix idempotency and dealing with non-orthogonal orbitals during energy minimization.[13] Efficient multiscale eigenvalue solvers, even though they can process

much of the global information on coarse scales, still require solution of matrix equations that scale faster than linear with system size.[11,15]

In light of these issues, in Ref. 11 we suggested a potential alternative new direction for DFT modeling based on a stochastic hybrid of DFT and Quantum Monte Carlo (QMC) approaches. The goal is to model the single-particle density matrix (1-DM) directly without resorting to an orbital-based representation. There has been significant progress in the development of orbital-free DFT methods in recent years,[17–19] with the consistent issue the representation of the kinetic energy portion of the total energy. The present approach allows, at least in principle, for an exact representation of the kinetic energy. An alternative stochastic orbital approach has been developed recently, with promising results.[20] In addition, we mention the powerful theoretical concept of the integral formulation of DFT,[21–23] which may provide another avenue for large-scale simulation; in this case, the kinetic energy part of the energy is represented with high-dimensional integrals involving oscillatory integrands. Preliminary Monte Carlo results[24] were presented for a model problem (non-interacting electrons in a harmonic well) to illustrate the theory.

The underlying motivation for the stochastic approach can be linked to two "hard walls" facing the quantum modeling field.[25,26] First, there is the wall related to the representation and storage of the wave function for large systems. Second, there is a wall related to physical constraints on the processor speed for classical computers: we are approaching the atomic limit in the scale-down of processor component size. It is apparent that we will continue to be driven towards increasing

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parallelization. Thus, it may be advantageous to further develop massively parallel special-purpose machines designed for specific scientific tasks such as quantum simulation. (Major progress in this direction has been made in the area of classical molecular dynamics simulations.[27]) In the past, such efforts have been made, but typically the commodity processors have developed so quickly that, by the time of production of the special purpose machine, it had already become obsolete.

The present paper is directed at exploring a theoretical and computational approach for a direct statistical computation of the 1-DM in DFT. We first present the theoretical background for and an outline of the method. Then preliminary results on simple models are presented to illustrate the theory. Finally, the approach is summarized and possible future directions are outlined. The purpose is to give a general outline of a potentially new approach for DFT electronic structure on parallel machines and hopefully stimulate further work in this area.

## 2  Background Theory and Methods

### 2.1  Variational Calculations and Constraints

Here we consider quantum mechanical problems in a single spatial dimension to maintain a simple notation. Consider first an action functional

$$S[\psi] = -\frac{1}{2}\int \psi^* \frac{d^2}{dx^2}\psi dx + \int \psi^* V\psi dx - E\int \psi^*\psi dx \quad (1)$$

which includes the total energy for the particle and a constraint for wave function normalization. The Lagrange multiplier for the normalization constraint is the energy eigenvalue of the ground state.

We can invent a steepest descents type algorithm[10] for minimizing the total energy with a constraint as

$$\frac{\partial \psi}{\partial \tau} = -\frac{\delta S[\psi]}{\delta \psi^*} = \frac{1}{2}\frac{\partial^2 \psi}{\partial x^2} - (V - E)\psi \quad (2)$$

This equation has the appearance of a diffusion equation with a branching (last) term. The Lagrange multiplier $E$ should be varied until the population is stabilized in a Monte Carlo model of the diffusion process.[28]

### 2.2  Diffusion Monte Carlo: Importance Sampling

It is well known that, when studying atomic systems governed by Coulomb potentials, direct Monte Carlo modeling of Eq. 2 suffers from severe noise due to the Coulomb singularity.[29] To overcome this problem, an importance sampling scheme was developed[30] (reviewed in Refs. 28 and 31). In this approach, Eq. 2 is rewritten to solve for the function $f = \psi_T\psi$, where $\psi_T$ is a trial function designed to accurately mimic the true

wavefunction $\psi$. Then the resulting diffusion equation (DMC) is

$$\frac{\partial f}{\partial \tau} = \frac{1}{2}\frac{\partial^2 f}{\partial x^2} - \frac{\partial}{\partial x}\left(f\frac{\partial \ln \psi_T}{\partial x}\right) - [E_L - E]f \quad (3)$$

where $E_L(x) = H\psi_T/\psi_T$, the local energy. The "potential" $E_L(x)$ is much smoother than the bare potential $V$, leading to reduced statistical noise in the sampling (see below).

While progress has been made,[32,33] it has proven difficult to use DMC (or other quantum Monte Carlo methods) to generate accurate forces on nuclei for molecular dynamics due to the noisy sampling and other heavy computing contraints. It is thus interesting that a paper has recently appeared that presents molecular dynamics simulations of 32 water molecules using as the underlying potential surface the energies computed with the variational Monte Carlo (VMC) method.[34] VMC results already incorporate a large fraction of the correlation energy, but the DMC approach pushes the percentage of the computed correlation energies included up to nearly 100%.[35] At any rate, these preliminary VMC results are a landmark study in the quantum simulation field, and support the notion that forces accurate enough for molecular modeling are within the realm of possibility.

### 2.3  Forward and Backward Kolmogorov Sampling

As written above, the DMC equation is called the forward Kolmogorov equation or the Fokker-Planck equation.[36] The Langevin-type equation that models the DMC differential equation above as a random walk[28] is

$$x_{\tau+d\tau} = x_\tau + bd\tau + \xi\sqrt{d\tau} \quad (4)$$

where

$$b = \frac{\partial \ln \psi_T}{\partial x} \quad (5)$$

and $\xi$ is a Gaussian random number with standard deviation 1. This drift force tends to drive the sampling into regions where the magnitude of $\psi_T$ is large. At long times the sampling generates a steady-state distribution dictated by $\psi_T$. If the sampling is modified with a branching process,[35] then the sampled distribution mimics the exact function $f = \psi_T\psi$. The core computational step is very simple, however, namely the iteratative updates of the Langevin Eq. 4. Averages along these random walks then produce the desired quantum expectation values as shown in Refs. 35 and 28.

We can rewrite Eq. 3 in the following backward form (which involves the adjoint operator):

$$\frac{\partial f}{\partial \tau} = \frac{1}{2}\frac{\partial^2 f}{\partial x^2} - \left(\frac{\partial f}{\partial x}\right)\left(\frac{\partial \ln \psi_T}{\partial x}\right) - \left[\frac{\partial^2 \ln \psi_T}{\partial x^2} + E_L - E\right]f \quad (6)$$

This form can be viewed as evolving trajectories from a final location backwards in time (or equivalently on an upside-down potential),[36] where Eq. 4 still applies but now

$$b = -\frac{\partial \ln \psi_T}{\partial x} \tag{7}$$

This form is important for the Feynman-Kac solution of partial differential equations discussed below.

### 2.4 Feynman-Kac Formulae

Consider the statistically averaged function (Feynman-Kac type path integral)

$$F(t) = \left\langle \exp\left(-\int_0^t c[x(s)]\,ds\right) \right\rangle_{\psi_T^2} \tag{8}$$

where the averaging is over all paths $x(s)$ generated by the forward sampling in Eq. 4, and $c(x) = E_L(x) - E$. The $\psi_T^2$ subscript outside the averaging brackets indicates sampling on the trial function distribution. Now take the derivative of the log of $F(t)$ with respect to $t$ and set it to zero to obtain

$$E = \frac{\left\langle E_L(X_t)\exp\left(-\int_0^t c[x(s)]\,ds\right)\right\rangle_{\psi_T^2}}{\left\langle \exp\left(-\int_0^t c[x(s)]\,ds\right)\right\rangle_{\psi_T^2}} \tag{9}$$

which is the same as

$$E = \frac{\left\langle E_L(X_t)\exp\left(-\int_0^t E_L[x(s)]\,ds\right)\right\rangle_{\psi_T^2}}{\left\langle \exp\left(-\int_0^t E_L[x(s)]\,ds\right)\right\rangle_{\psi_T^2}} \tag{10}$$

for the wave function based problem, since $E$ is a constant. This formula involves DMC sampling on the potential surface generated by the trial function, and the exponential factors alter the averaging to produce the desired (and in principle exact) ground state energy. This gives an alternative view of the usual derivation of the DMC computation of the energy.[28] Ref. 35 terms this approach "pure diffusion" Monte Carlo and points out the possible concern that one or a few trajectories can dominate the averaging. This statistical issue was not observed for the simple problems addressed numerically below, however.

With the branching process incorporated into the DMC sampling (through particle multiplication and destruction based on the local energy term),[28,35] the exact ground state energy can be estimated from

$$E = \langle E_L \rangle_f \tag{11}$$

which is an example of the statistical "law of averages".[37] The above DMC algorithm is based on the equilibrium distribution produced by the forward (Fokker-Planck) sampling. Physical quantities are then computed as statistical averages generated by the stochastic trajectories.

As shown in Refs. 36, 38, and 39, the backward sampling, while formally equivalent, produces a very different outcome. Namely, the purpose of the backward sampling is to generate the *solution of the differential equation itself* (the function $f = \psi \psi_T$):

$$f(x,t) = \left\langle \psi_T^2(X_t^x)\exp\left(-\int_0^t c[x(s)]\,ds\right)\right\rangle_{\psi_T^2} \tag{12}$$

where now $c[x(s)]$ is the potential term in Eq. 6, and $X_t^x$ is the final location (at time $t$) of a trajectory started at $x$ (all trajectories used to obtain $f(x,t)$ start from the point $x$). The function $\psi_T^2(X_t^x)$ is the initial condition for the function that then evolves to the final distribution $f(x,t) = \psi_T \psi$. This is a remarkable formula, first proved by Kac;[40] in the mathematical literature, it is typically called the Feynman-Kac formula.[39]

### 2.5 Equations for the 1-DM

Assuming real occupied orbitals, the 1-DM in DFT is given by

$$\gamma(x,y) = \sum_{i=1}^{N_{el}} \phi_i(x)\phi_i(y) \tag{13}$$

where the set of $\phi_i(x)$ are the solutions of the Kohn-Sham equations (which we aim to avoid solving directly).

In a thorough theoretical study of the 1-DM in Hartree-Fock theory, Dawson and March[41] obtained several useful results that we apply here to the non-interacting case relevant to DFT. There it was shown that the exact 1-DM minimizes the Hartree-Fock total energy, and thus a diffusion equation similar to that for the wave function above applies. The appropriate constraints are then for the total number of electrons and for the 1-DM idempotency.[23]

A Schrödinger-like equation for the 1-DM can be derived

$$H_x\gamma(x,y) = E(x,y)\gamma(x,y) \tag{14}$$

where the Hamiltonian $H_x$ involves only the $x$ coordinate, and

$$E(x,y) = \frac{\sum_{i=1}^{N_{el}} \varepsilon_i \phi_i(x)\phi_i(y)}{\sum_{i=1}^{N_{el}} \phi_i(x)\phi_i(y)} \tag{15}$$

which is clearly not a constant, even when the exact Kohn-Sham states are inserted.

Then the following DMC-type equation for the 1-DM (similar to Eq. 3) can be obtained:

$$\frac{\partial f(x,y)}{\partial \tau} = \frac{1}{2}\frac{\partial^2 f}{\partial x^2} - \frac{\partial}{\partial x}\left(f\frac{\partial \ln \gamma_T}{\partial x}\right) - [E_L(x,y) - E(x,y)]f \tag{16}$$

where $f = \gamma_T \gamma$, $E_L = H_x \gamma_T / \gamma_T$, and $E(x,y)$ is the Lagrange multiplier for the idempotency constraint on the 1-DM.[41]

For a many-electron problem, the major gain in computational efficiency by reducing the high-dimensional wave function ($3N_{el}$ dimensions) to a 6-dimensional 1-DM has been offset by the loss of the single-constant Lagrange multiplier $E$ with replacement by the (unknown) function $E(x,y)$. One goal then is to develop an algorithm for estimating the change in going from the trial energy function $E_L(x,y)$ to the exact one $E(x,y)$. With this important caveat, the Feynman-Kac formulas go directly over to the 1-DM case. A central problem is then to attempt to devise a *near-local* method that drives the $E_L(x,y)$ function towards the exact one during the stochastic process (see below).

### 2.6 Estimating $E(x,y)$: The local virial theorem

Enforcing a global energy minimization procedure to obtain the exact 1-DM under the constraints of fixed particle number and idempotency is a computationally demanding and highly nonlocal process. What is desired is a more local constraint that, when satisfied, produces the exact 1-DM.

Constraints of this form exist, namely local virial theorems derived for wave function and density functional theories.[42–44] Here we follow the work of Nagy and March,[44] and assume a 3-D form for the equations for consistency with the original works; the variables $x$ and $y$ signify the full 3D spatial vectors. Bader[42] derived a local form of the virial theorem as

$$\mathcal{V}(x) + 2G(x) = \frac{1}{4}\nabla_x^2 \gamma(x,x) \qquad (17)$$

where

$$G(x) = \frac{1}{2}\nabla_x \nabla_y \gamma(x,y)|_{x=y} \qquad (18)$$

and

$$\mathcal{V}(x) = \mathrm{Tr}\sigma = -x \cdot \nabla_x \cdot \sigma + \nabla_x \cdot (x \cdot \sigma) = \mathcal{V}_b(x) + \mathcal{V}_s(x) \quad (19)$$

The last expression shows the division of the virial into bulk and surface terms. The tensor $\sigma$ is the quantum stress tensor given in terms of the 1-DM as

$$\sigma(x) = \frac{1}{4}[(\nabla_x \cdot \nabla_x + \nabla_y \cdot \nabla_y) - (\nabla_x \cdot \nabla_y + \nabla_y \cdot \nabla_x)]\gamma(x,y)|_{x=y} \qquad (20)$$

If any trial 1-DM is inserted into the above formulas, the identity holds. If the bulk virial $\mathcal{V}_b(x)$ is replaced by the appropriate potential energy density consistent with the virial theorem (for the harmonic oscillator problem here the bulk virial term becomes $-2V(x)\gamma(x,x)$), then the identity holds only for the exact (stationary state) 1-DM.

To connect to the numerical results on simple model model problems below, this calculation was carried through analytically for the case of 4 noninteracting electrons in a harmonic

well with arbitrary trial $\alpha$ parameter (see below for the definition of the Gaussian trial functions from which the 1-DM is obtained via Eq. 13). This is the simplest two-state case that exhibits oscillations in the 1-DM.

The result for the potential density is

$$-2V(x)\gamma(x,x) = -2x^2\left[\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}e^{-\alpha x^2}\left(1+2\alpha x^2\right)\right] \qquad (21)$$

while the bulk virial is

$$\mathcal{V}_b(x) = -2x^2\left[\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}e^{-\alpha x^2}\alpha^2\left(1+2\alpha x^2\right)\right] \qquad (22)$$

These are equal only when $\alpha = 1$, the exact energy-minimizing solution.

The goal then will be to include in the stochastic process an additional near-local constraint of this form aimed at driving the trial 1-DM towards the exact value for a given DFT functional. This avenue will require extensive development and is beyond the scope of the present paper. The above discussion gives optimism that including such a constraint in the stochastic process may lead to accurate improvements beyond the assumed trial function $\gamma_T(x,y)$. A related local virial theorem in density functional theory was given by Nagy and Parr.[43]

Updating the 1-DM as discussed above in order to better satisfy the local virial theorem could lead to deviation from the idempotency stability in the 1-DM analogue of Eq. 8. The stability can be checked by the following forward sampling formula (that may also be helpful in developing iterative schemes for updating $E(x,y)$):

$$\left\langle E_L(X_t,y)\exp\left(-\int_0^t c[x(s)]\,ds\right)\right\rangle_{\psi_T^2} = \left\langle E(X_t,y)\exp\left(-\int_0^t c[x(s)]\,ds\right)\right\rangle_{\psi_T^2} \qquad (23)$$

where $c[x(s)] = E_L(X_s,y) - E(X_s,y)$. The above formula is obtained by setting the time derivative of Eq. 8 to zero.

### 2.7 Algorithm outline

Solving for the 1-DM $\gamma(x,y)$, given a trial 1-DM $\gamma_T(x,y)$, can be viewed from the following perspective. We choose a physical point in space $y$ and first sample the forward DMC equation for the 1-DM in a restricted domain of $x$ in which the 1-DM is appreciably non-zero. The sampling is effected by iterating the 1-DM analogue of Eq. 4 (that models Eq. 16) for the $x$-trajectory. The restricted range will depend on the physical system studied; for systems with a band gap, the decay of the 1-DM is exponential in space. The initial location for each trajectory should be drawn from the distribution constructed from the square of the trial 1-DM $\gamma_T(x,y)$. For the simple

one-dimensional examples studied here, this can be accomplished by starting all trajectories at the point $y$, updating Eq. 4 for roughly 1000 steps, and then initiating the data analysis from the current $x$ location. The time step $d\tau$ was chosen in the range 0.01 to 0.001 au, and trajectories were run out to a time $t$ at which either a) no significant change in the averaged functions occurs or b) a clear exponential decay (or growth) in the Feynman-Kac integral (Eq. 8) is apparent, indicating necessary updates of the function $E(x,y)$. If the walker locations are binned, the resulting distribution should accurately model the $\gamma_T^2(x,y)$ distribution.

At this point, an additional force in Eq. 4 should be added that pushes the sampling towards a modified $\gamma(x,y)$ that better satisfies the equality of the bulk local virial term and the local potential energy density as discussed above. The constraint force will arise from a least squares minimization of the deviation of the two forms of the local potential energy density. This process should be repeated until a stable $\gamma(x,y)$ is obtained. Then an updated Lagrange multiplier for the idempotency constraint can be obatined from $H_x\gamma(x,y)/\gamma(x,y) = E(x,y)$. The new $E(x,y)$ should then be tested by insertion into Eq. 8 to see if a stable Feynman-Kac integral results, or by evaluating Eq. 23. If the integral is not stable, then a stochastic process could be developed to further adjust $E(x,y)$ until stability is obtained.

The purpose of the above process is to iteratively update the idempotency Lagrange multiplier $E(x,y)$ by incorporating a local virial theorem based constraint. Ultimately, we desire updated values of the 1-DM $\gamma(x,y)$ that improve upon the trial function $\gamma_T(x,y)$. With the updated $E(x,y)$ function, better converged values of $\gamma(x,y)$ can be obtained by using the backward sampling scheme at several selected points near the central point $x = y$.

The electron density, the key component for computing forces on the nuclei, involves only the diagonal element of the 1-DM. As discussed below, in order to calculate the total energy, the Laplacian of the 1-DM must be computed along with possible terms in the potential that involve the gradient of the charge density. Both the Laplacian and the gradient require information only near the diagonal of the 1-DM where $x = y$. Thus accurate function values are required only at several points near the diagonal. The equation for the 1-DM corresponding to Eq. 12 is used to obtain those several function values. Since only a few points are required, a large number of trajectories can be run in order to obtain well converged results for those 1-DM values.

It is important to note that the dimensionality is not a large issue when implementing the stochastic methods. In 3D space Eq. 4 is again iterated with one equation for each spatial dimension. Then the walkers move in 3-space (for each $y$ location), not the $3N_{el}$ space for wave function based QMC methods.

## 3  Results and Discussion

Based on the above theoretical discussion, some preliminary results illustrating aspects of the algorithm are presented here.

We consider two one-dimensional problems to illustrate the ideas discussed above: the ground state of the one-dimensional harmonic oscillator (for the wave function calculations) and four noninteracting electrons in a harmonic well (for the density matrix calculations). This two-level 1-DM problem is simple but does display spatial nodes. The potential in atomic units is taken as $V(x) = x^2/2$, so the total energy for the first case is 0.5 au and for the second case is 4 au.

For the trial wave functions we consider Gaussian functions with a scaled width:

$$\phi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \exp\left(-\alpha x^2/2\right) \qquad (24)$$

and

$$\phi_1(x) = \sqrt{2\alpha}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} x \exp\left(-\alpha x^2/2\right) \qquad (25)$$

The trial and exact 1-DM's and resulting $E_L(x,y)$ and $E(x,y)$ can be constructed from these eigenfunctions using Eq. 13 (the exact result is for $\alpha = 1$).

We first examine the DMC wave function approach given by Eq. 3 along with the Feynman-Kac functional integral Eq. 8. Fig. 1 illustrates the stability of the Feynman-Kac integral when the proper normalization constant $E$ is included. This result shows the connection between complicated global constraints and stabilization of the Feynman-Kac integral. The same qualitative behavior is observed for the density matrix case discussed below: when a function $E(x,y)$ (that is obtained from an idempotent density matrix) is inserted, a stable diffusion process is observed. This does not guarantee an exact solution for the density matrix case, however, since there are an infinite number of idempotent density matrices – what is desired is an idempotent density matrix that minimizes the total energy.[23] The relation of the stability of the functional integral corresponding to Eq. 8 to global idempotency constraints does not appear to have been noticed before, and this deserves further analysis.

Figs. 2 and 3 show the construction of the trial and exact wavefunctions from the forward and backward sampling approaches. The first case requires averaging of the distribution modeled during forward sampling, while the second case directly utilizes Eq. 12 to obtain the solution. The backward form has an advantage in obtaining the solution at a few selected $x$ values, since the stochastic solution at each of those $x$ values results from averaging trajectories all starting from those points; that is, the solution is obtained point by point, not as an average over a distribution.

Turning to the density matrix problem, Fig. 4 shows the variation of the total energy with the parameter $\alpha$, with a min-
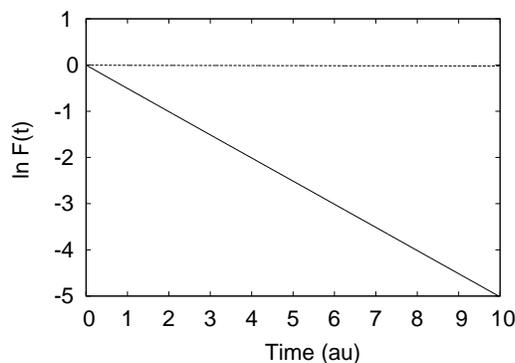
**Fig. 1** Plot of the ln of $F(t)$ in Eq. 8 with and without inclusion of the exact energy $E$. The flat line at zero exhibits the stability of the diffusion process with the proper normalization constraint in the Feynman-Kac integral, while the lower line with slope -1/2 displays the exponential decay expected in the absence of the normalization constraint. Forward sampling was employed here and the trial $\alpha = 0.8$ was used.
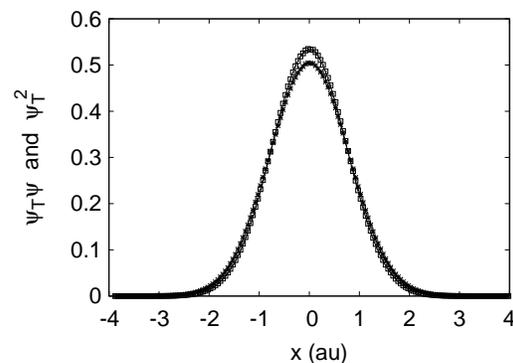
imum at the exact value. The variational character of the related Hartree-Fock method is discussed extensively by Parr and Yang.[23]

The total energy for the non-interacting case is given by

$$E = -\frac{1}{2} \int \left[ \frac{d^2 \gamma(x,y)}{dx^2} \right]_{x=y} dx + \int V(x) \gamma(x,x) dx \qquad (26)$$

As mentioned above, for each point along the $x$ integration, values of $\gamma(x,y)$ only for the $x = y$ diagonal (for the electron density) and points nearby the diagonal (for the kinetic energy and any gradient terms in the potential) are required in evaluating the energy.

Fig. 5 displays the local energies from the above formula, illustrating the global nature of the energy minimizing principle; the local energy for the exact solution can be greater or less than a trial local energy, but the integral is a minimum for the exact 1-DM. This result shows the importance of developing local constraints that, when satisfied, can produce the exact 1-DM.

Finally, Fig. 6 shows the numerical apporixmation for the trial ($\gamma_T^2$) and exact ($\gamma_T \gamma$) functions generated with forward sampling. The modeled case is for $y = 1$ which displays a node in the 1-DM at roughly $x = -0.7$. The nodal structure is a general feature of the 3-dimensional 1-DM (for a chosen $y$ value) – the value of the 1-DM at $x = y$ is always positive (the electron density), but the 1-DM tends to decay and display exponentially damped oscillations (for systems with a band gap) away from the central point.

This result in which the exact 1-DM is computed appears promising, but of course the known exact $E(x,y)$ function was inserted in the computation. In general this function is not
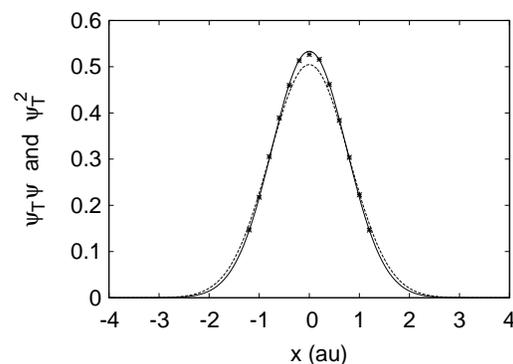


**Fig. 2** Trial function squared $f = \psi_T^2$ (lower curve at $x = 0$) and exact $f = \psi_T \psi$ for the ground state wave function of the harmonic oscillator computed as the average density over the stochastic trajectories. Forward sampling was employed here and the trial $\alpha = 0.8$ was used. Excellent agreement of computed and exact results is obtained. For normalization purposes, the numerical results were scaled to the analytic results at $x = 0$.



**Fig. 3** Computed Feynman-Kac estimate of the function $f(x,t) = \psi_T \psi$ (at long times) using Eq. 12. Backward sampling was employed and the trial $\alpha = 0.8$ was used.

known and must be estimated as part of the stochastic process as discussed above.

## 4 Conclusions

This paper, building on our previous work,[11] has discussed a possible new direction for DFT calculations that utilizes stochastic methods to solve directly for the 1-DM of DFT without the introduction of spatial orbitals used to represent the many-electron wave function.

A connection was established between the stability of Feynman-Kac (path) integrals and the imposition of the global constraints of normalization and idempotency for the 1-DM. The stability of the Feynman-Kac integral does not guarantee
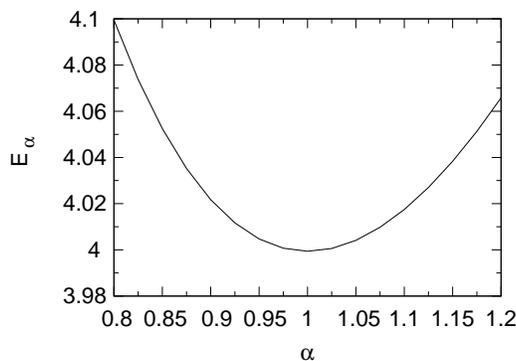
**Fig. 4** The analytic total energy for 4 noninteracting electrons in a harmonic well as a function of $\alpha$. The result illustrates the variational character of the density matrix calculation.
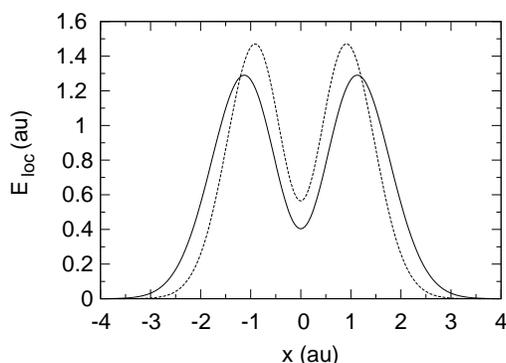


**Fig. 5** The local energy for the trial ($\alpha = 0.8$, lower curve at $x = 0$) and exact 1-DM's. The total energies for these two 1-DM's are shown in Fig. 4.



**Fig. 6** Numerical values (obtained by averaging the stochastic trajectories) for $\gamma_T(x,y)^2$ (lower curve at $x = 1$) and $f = \gamma_T\gamma$ using Eq. 16. A trial $\alpha = 0.8$ was used and the $y = 1$ location was used. There is a node in $\gamma_T$ at roughly $y = -0.7$. For normalization, the numerical results were scaled to the analytic functions at $y = 1$.

high parallelism and linear scaling algorithms.

This paper is an initial discussion aimed at stimulating further effort built on the stochastic sampling ideas. Several parts of the proposed approach require further efforts, however. Clearly developing an algorithm that can push the approximate 1-DM towards the exact one based on a local virial theorem (as part of the stochastic sampling) while still ensuring near idempotency is the primary area for further work. Next, optimal methods for self-consistency should be developed. Finally, efficient ways to generate relatively accurate trial 1-DM $\gamma_T(x,y)$ functions should be explored. Trial 1-DM generation here may not necessarily rely on wave function methods, but could utilize such theories as the optimized Thomas-Fermi and multiple scattering perturbation theories developed some time ago.[45,46]

Perhaps the present stochastic path integral approach will provide the possibility for a more practical approach for electronic structure that still is "optimally local" in the sense of the integral formulation. It is also likely that the recently developed impressive grid-based tensor-structured methods[47] and high-order numerical methods[48] can be exploited helpfully for a significant reduction in the storage and computational cost of the present method.

the exact (energy minimizaing) idempotency Lagrange multiplier $E(x,y)$, however, since there exists an infinite number of possible idempotent 1-DMs. Progress towards solution of this difficulty was suggested via usage of a local virial theorem first derived by Bader.[42] The incorporation of this additional constraint during the stochastic process will be the focus of future work.

The approach outlined here is a computational middle ground between approximate orbital-free methods[18] and the beautiful integral formulation of density functional theory.[21,23] The latter theory is the true embodiment of DFT, involving only the electron density as the fundamental variable. A reason for the difficulty in implementing this theory since it was formulated involves the high-dimensional integrals for the kinetic energy (resulting from the path integral formulation) that are highly oscillatory in nature. An important feature of all of these orbital-free approaches is that most of the numerical work is relatively local in real space, allowing for
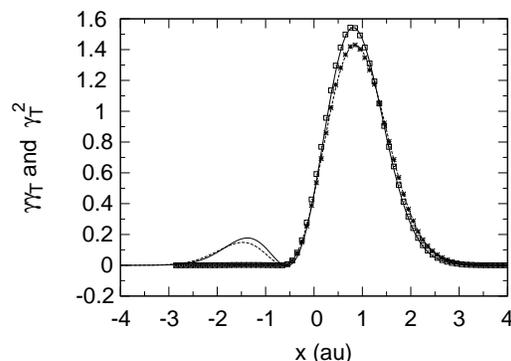
## 5   Acknowledgments

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