Hellman-Feynman operator sampling in Diffusion Monte Carlo calculations

R. Gaudoin\textsuperscript{1} and J. M. Pitarke\textsuperscript{2,3}

\textsuperscript{1}Donostia International Physics Center (DIPC), Manuel de Lardizabal Pasealekua, E-20018 Donostia, Basque Country, Spain
\textsuperscript{2}CIC nanoGUNE Consolider, Mikeltegi Pasealekua 56, E-2009 Donostia, Basque Country, Spain
\textsuperscript{3}Materia Kondentsatzearen Fisika Saila, UPV/EHU, and Unidad Física Materiales CSIC-UPV/EHU, 644 Posta kutxatila, E-48080 Bilbo, Basque Country, Spain

(Dated: February 1, 2008)

Diffusion Monte Carlo (DMC) calculations typically yield highly accurate results in solid-state and quantum-chemical calculations. However, operators that do not commute with the Hamiltonian are at best sampled correctly up to second order in the error of the underlying trial wavefunction, once simple corrections have been applied. This error is of the same order as that for the energy in variational calculations. Operators that suffer from these problems include potential energies and the density. This paper presents a new method, based on the Hellman-Feynman theorem, for the correct DMC sampling of all operators diagonal in real space. Our method is easy to implement in any standard DMC code.

Diffusion Monte Carlo (DMC) is widely used for the computation of properties of solids and molecules \cite{Gaudoin2007}. Frequently, it is used as a check on other methods \cite{Pita2009} or even as an input \cite{Monkhorst1976}. It is therefore very important that DMC be as accurate as possible. However, other than for the total energy, standard DMC calculations are not as definitive as one would hope, since operators that do not commute with the Hamiltonian cannot be sampled exactly within standard DMC. Here we present a simple yet effective addition to standard DMC that plugs that gap and is easy to implement.

DMC by construction yields the normalized expectation value $\langle \hat{O} \rangle_{DMC} = \langle \Psi_T | \hat{O} | \Psi_T^n \rangle / \langle \Psi_T | \Psi_T^n \rangle$, which is generally not the true ground-state expectation value $\langle \hat{O} \rangle = \langle \Psi_0 | \hat{O} | \Psi_0 \rangle / \langle \Psi_0 | \Psi_0 \rangle$. In fact, it is not even $\langle \hat{O} \rangle_{fn} = \langle \Psi_T^n | \hat{O} | \Psi_T^n \rangle / \langle \Psi_T^n | \Psi_T^n \rangle$, the ground-state expectation value constrained by a nodal structure of the fermionic many-body wavefunction that is given by $\Psi_T$. $\Psi_T$ is a trial wavefunction that approximates the generally unknown ground-state wavefunction $\Psi_0$ and is real. In its basic and most common form $\Psi_T^n$ is the ground state for a fixed nodal structure given by that of $\Psi_T$. In addition to this fixed-node approximation operators that do not commute with the Hamiltonian are generally subject to a further error, the leading term of which is linear in the difference between $\Psi_T$ and $\Psi_T^n$. In conjunction with Variational Monte Carlo (VMC), this error can be reduced by one order \cite{Inagaki2004} by using $\langle \hat{O} \rangle_{VMC} = 2 \langle \hat{O} \rangle_{DMC} - \langle \hat{O} \rangle_{VMC}$. Correct sampling can be achieved, e.g. by using forward walking \cite{Pita2009}, reptation Monte Carlo \cite{Pita2009}, and other methods \cite{Reza2004}. Many of these methods aim to sample $\Psi_T^n | \Psi_T^n \rangle$, rather than the usual DMC distribution $\Psi_T | \Psi_T^n \rangle$. They are therefore not straight forward additions to the DMC algorithm. Alternatively, the Virial theorem or the related Hellman-Feynman (HF) theorem \cite{Gaudoin2007} can be used to evaluate operator expectation values \cite{Gaudoin2007} which in the case of DMC, however, involves numerical derivatives of noisy data.

In this Letter, we present a method based on the application of the HF theorem to the DMC algorithm directly. Our method - Hellman-Feynman sampling (HFS) - can be tagged onto the usual sampling of operators with nearly no extra computational overhead. The aim is to maintain the basic DMC algorithm that samples $\Psi_T | \Psi_T^n \rangle$. Now, the total energy is evaluated correctly within standard DMC, and crucially operator expectation values can be cast as HF derivatives of the total energy. Keeping in mind that ultimately the DMC algorithm is nothing but a large sum that yields the total energy, we see the HF derivative can be applied without problem to the algorithm itself! One advantage over numerical derivatives is that the resulting formula can handle several operators simultaneously in a single DMC run and maintaining orbital occupancy for perturbed Hamiltonians ceases to be a problem. The DMC algorithm only involves numbers, so non-commutability of operators - the source of the difficulties - is no issue either. Writing down the DMC algorithm as a mathematical formula and applying the HF derivative to it yields an object that when sampled using standard DMC produces the exact operator expectation value. It has to by construction.

In the following, we present a schematic overview of the DMC algorithm, which however is sufficient to derive the relevant formulas. The basic idea of DMC is to split the imaginary-time propagator $\exp(-\Delta t \hat{H}) \approx \exp(-\Delta t \tilde{\hat{H}}) \exp(-\Delta t \tilde{\hat{V}})$ for sufficiently small time intervals $\Delta t$ into a kinetic and potential term and then to iterate it. This ultimately \cite{Gaudoin2007} gives rise to a real-space drift-diffusion process sampled using Monte Carlo (MC), augmented by an exponential growth term whereby $N_w$ so-called walkers are propagated in parallel. Courtesy of this growth term, at each propagation or (imaginary) time step $i$ the walker $j$ acquires a multiplicative weight: $e^{-\Delta t(E_{ij}^L - E_j^0)}$, where $E_{ij}^L = \hat{H} \Psi_T | \Psi_T$ evaluated at the real-space position of walker $j$ at time step $i$ and $E_j^0$ is an estimate for the ground-state energy also at time step $i$. The walker $j$ then samples the Hamiltonian at the new position $i+1$ and propagates to the next step $i+1$, and so forth.
i. The total weight of walker \( j \) at time step \( i \) becomes
\[
\omega_{i,j} = \sum_{k=1}^{i} e^{-\Delta t (E_{k,j}^L - E_0^i)}, \quad \text{where } E_0^i = \frac{1}{i} \sum_{l=1}^{i} E_l^0
\]
and the presence of \( E_0^i \) ensures normalization. At time step \( i \) the estimator for an operator that a DMC code yields is
\[
\overline{O}^L_i = \sum_j \omega_{i,j} O^L_{i,j},
\]
where \( O^L_{i,j} = \hat{O} \Psi_T / \Psi_T \) and the wavefunction \( \Psi_T \) is evaluated for walker \( j \) at time step \( i \). For brevity, we use this bar-average \( \overline{O}^L_i \) where applicable and note that \( \overline{O}^L_i \) has to be averaged over all \( i \) to yield the final DMC estimate \( \langle \hat{O} \rangle_{DMC} \). Since the ground-state energy is not known, an estimate chosen such that Eq. \( \[11\] \) remains normalized has to be used. This is the growth estimator \( E_0^i \) \[11\] and is updated at each step, hence the index \( i \). Note that \( E_0^i \) is independent of \( j \), i.e. it is the same for every walker and thus a property of the DMC process as a whole. For reasons of numerical stability, DMC is implemented by allowing walkers to die or multiply such that the walker’s survival probability optionally augmented by residual weights corresponds to Eq. \( \[11\] \).

Given a perturbed Hamiltonian \( H(\alpha) = \hat{H} + \alpha \hat{O} \) and the associated fixed-node ground state energy \( E_{fn}^0(\alpha) = \langle H \rangle_{DMC} \), first-order perturbation theory for \( \Psi_{fn}^0 \) yields a fixed node equivalent of the HF theorem \[12\]
\[
\langle O \rangle_{fn} = \frac{\partial E_{fn}^0(\alpha)}{\partial \alpha} \bigg|_{\alpha=0},
\]
where \( \langle O \rangle_{fn} \) converges to the correct ground-state expectation value as the nodes of \( \Psi_T \) become exact though \( \Psi_T \) itself need not. Note that while \( \langle H \rangle_{DMC} = \langle H \rangle_{fn} \) we have \( \langle \hat{O} \rangle_{DMC} \neq \langle \hat{O} \rangle_{fn} \), unless \( \langle \hat{O}, \hat{H} \rangle = 0 \), so Eq. \( \[3\] \) is not trivial. The energy \( E_{fn}^0(\alpha) \) is accessible exactly within standard DMC as the Hamiltonian \( \hat{H}(\alpha) \) commutes with itself. Analytic operator estimators can then be derived by applying the HF theorem to the formula expressing the DMC algorithm Eq. \( \[2\] \). Using Eqs. \( \[11\] \) and \( \[2\] \) the expectation value at time step \( i \) becomes
\[
E_i(\alpha) = \sum_j \sum_{k=1}^{i} \omega_{i,j}^L(\alpha) \prod_{j=1}^{i} e^{-\Delta t (E_{k,j}^L(\alpha) - E_0^i(\alpha))},
\]
Here, \( E_{i,j}^L(\alpha) = E_{i,j}^L + \alpha O_{i,j}^L \) and \( E_0^i(\alpha) = E_0^i + \Delta E_0^i(\alpha) \), so the weight of the wavefunction is
\[
\Omega_i = \sum_j \sum_{k=1}^{i} \omega_{i,j} \exp \left( -\Delta t \sum_{k=1}^{i} (E_{k,j}^L - E_0^i) \right).
\]
Evaluating \( \Delta E_0^i \) to first order gives the growth estimator of an operator:
\[
O_i^{GR} = \frac{\partial E_{fn}^0(\alpha)}{\partial \alpha} \bigg|_{\alpha=0} = \frac{\partial \Delta E_0^i(\alpha)}{\partial \alpha} \bigg|_{\alpha=0} = X_i.
\]
In other words, the DMC sampling of \( X_{i,j} \) by virtue of the HF theorem yields a growth estimator of the true expectation value of \( \hat{O} \). Interestingly, the growth estimator, if the residual weights are chosen to be zero, appears to be similar to Eq. \( \[13\] \) of Ref. \[7\]. Applying the HF theorem to the energy estimator Eq. \( \[11\] \) yields a second estimator
\[
E_i^F = \frac{\partial E_{fn}^0(\alpha)}{\partial \alpha} \bigg|_{\alpha=0} = \overline{O}^L_i - t (E_t^L X_i - E_t^L \cdot X_i).
\]
Equations \( \[8\] \) and \( \[9\] \) are of course evaluated at \( \alpha = 0 \) and are therefore accessible in a regular DMC calculation. We see that for \( O_i^F \) the standard estimator \( \overline{O}^L_i \) is augmented by a correction term \( \Delta O_i^F = -t (E_t^L X_i - E_t^L \cdot X_i) \). Several observations can be made. First, in the case of the \( \Psi_T \) being the ground state \( \Psi_{fn}^0 \) for a given nodal structure the correction term is zero (\( E_{i,j}^L \) is a constant!) and only \( \overline{O}^L_i \) contributes as it should. Furthermore, the new estimator \( O_i^F \) and the usual one \( \overline{O}^L_i \) sample an observable and are both independent of the auxiliary DMC parameter \( t \). It follows that \( E_t^L X_i - E_t^L \cdot X_i \sim 1/3 \). Thirdly, since the growth estimator Eq. \( \[8\] \) is derived from the “averaged” quantity \( E_0^i \) rather than \( E_0^i \), Eq. \( \[8\] \) is itself already averaged over \( i \) and therefore the final estimate at \( i \). This is in contrast to Eq. \( \[9\] \) which still has to be averaged over all \( i \) to yield the final DMC estimate. Using \( E_0^i \) yields an estimator \( O_i^{GR} \) which when averaged over \( i \) gives \( O_i^{GR} \). Finally, within the fixed-node approximation the correction term in Eq. \( \[9\] \) can be viewed as a direct measure of the error of the trial wavefunction with respect to a certain operator. In the remainder of the paper we will only discuss the direct estimator Eq. \( \[9\] \).
or for that matter the growth estimator Eq. (8)? Looking at the definition of the DMC algorithm one sees that it is based on splitting the Hamiltonian into a kinetic energy kernel that gives rise to the diffusion part of the algorithm and a potential energy term that has to be diagonal in real space. The diffusion part always being the same it follows that \( \Delta \hat{H} = \alpha \hat{O} \) has to be diagonal in real space too. Using for example \( O^L = T^L = \frac{\hat{V} \hat{\Psi}_T}{\hat{\Psi}_T} \) therefore actually corresponds to sampling the real space many-body operator given by the function \( T^L \), rather than the kinetic energy. The result using Eq. (9) is

\[
\int \frac{\hat{V} \hat{\Psi}_T}{\hat{\Psi}_T} \left[ \hat{\Psi}_0 \right]^2 dV \text{ which in general is not the desired expectation value } \langle \hat{T} \rangle_{fn} = \int \frac{\hat{V} \hat{\Psi}_T}{\hat{\Psi}_0} \left[ \hat{\Psi}_0 \right]^2 dV. \]

Nevertheless, \( \langle \hat{T} \rangle_{fn} \) is accessible within DMC by using \( \langle \hat{H} \rangle_{fn} = \langle \hat{H} \rangle_{fn} - \langle \hat{V} \rangle_{fn} \) since the last two quantities can be sampled using standard DMC and HFS, respectively.

In the following, we give a few examples to demonstrate the applicability of HFS. We apply the method to sample (i) the density of Helium and (ii) the Ewald energy of a homogeneous electron gas with and without interactions. All data are given in atomic units and we used the CASINO [13] package. The target for the number of walkers was between 200 and 400 and the residual weights were allowed to fluctuate between 0.5 and 2. While we did not perform extensive studies it seems the algorithm works with and without residual weights. The only modification to the code consisted of adding a variable \( X \) to each walker, updating \( X \) and applying Eq. (9). Other than that we used the code as-is in a standard setup.

Figure 1 shows the electron density (arbitrary units) of He, as obtained from standard DMC and from our HF method. When the well-converged (i.e. \( \Delta O^F \ll O^F \)) correlated wavefunction supplied with CASINO is used both calculations yield essentially the same result (solid line); when an “incorrect” trial wavefunction (which we have chosen to be the same as the “correct” one but with the radial term heavily skewed) is used, only our new method (dotted line) recovers the correct density, albeit the noise in the data is larger. Equally, the interaction energy is also recovered (DMC correct wavefunction: 0.947, incorrect wavefunction 0.791, incorrect wavefunction HFS: 0.958). We have also performed DMC calculations of the Hydrogen density, where we systematically deformed the known exact wavefunction. Suffice it to say, as for He we again see confirmation of our algorithm. An interesting point to add here regards the extent to which the wavefunction could be skewed. It turns out - rather plausibly - that if the wavefunction ceases to actually sample certain parts of phase space HFS cannot recover the true form. Nevertheless it seems capable of correcting relatively strong errors in the wavefunction (viz. the rarely sampled asymptotically decaying part of the wavefunction in Fig. 11), but the details are clearly a topic for further investigation.

As in standard DMC sampling, the worse the trial wavefunction \( \hat{\Psi}_T \), the larger the noise when using HFS. However, when looking at the raw data before averaging over \( i \) (not shown) we observed that the noise in the HFS data rises during the progression of the sampling, hence standard error estimation does not work. The source can be traced to sampling over histories \( X_i \). Limiting their depth results in a constant noise term though also reintroduces a systematic bias. Also, in a recent paper [14] Warren and Hinde observe that using the forward-walking method in DMC necessitates a rapidly growing number of walkers as the dimensionality of the quantum system is increased. These two issues then lead us to the question as to whether HFS works for larger systems. We have therefore looked at an unpolarized homogeneous electron gas at \( r_s = 1 \). We used a finite simulation cell (periodic boundary condition) with 54 electrons. The data we plot shows the Ewald interaction energy with no additional finite size corrections. We show in Fig. 2 results for a fully interacting system that we have obtained by using trial wavefunctions with either no Jastrow factor, a partially optimized Jastrow factor, or a fully optimized one. We show the mixed DMC estimate \( \langle O \rangle_{DMC} \), the corrected estimate \( \langle O \rangle_{DMC} = 2 \langle O \rangle_{DMC} - \langle O \rangle_{VMC} \) which contains a second-order error, and the results for HFS. The MC runs start at 0 with a short equilibration phase and we start sampling at time step 2000. The corrected estimate using the fully optimized Jastrow factor ought

![Figure 1: The “exact” Helium density (solid line) was derived using the well optimized wavefunction provided by the CASINO package. The difference (not shown) between standard DMC sampling and HFS is essentially zero (\( \Delta O^F \ll O^F \)). In addition, results using a trial wavefunction with wrong radial function are presented. Standard DMC yields a smooth but rather poor density. HFS, while noisier (see inset), follows the correct density even in the asymptotic region far from the nucleus where despite little information HFS corrects for the wrong behaviour.](image-url)
to give the best result. Clearly all three HFS estimates are very close but especially the non-optimized wavefunctions yield quite noisy data. Nevertheless, even in that case the results are a lot better than using the pure DMC output for the best wavefunction. However, they are all also better than the corrected $\langle \hat{O} \rangle_{\text{cDMC}}$ results of the partially/non-optimized wavefunction. Regarding the noise one also has to keep in mind the difficulty of the task: The interaction energy is dominated by the region where the electrons get close to each other but that is where the error of the non-optimized wavefunctions is largest. HFS essentially has to build a cusp from scratch.

Fig. 3 repeats the same analysis for a non-interaction Hamiltonian where the Slater determinant (no Jastrow factor) is the exact solution, whence the HFS data and the standard DMC data in that case being identical. This is of course consistent with Eq. (9) and proves that given the correct nodes, HFS yields the correct answer. Apart from that Fig. 3 is essentially a mirror image of Fig. 2. In general, we see that unless the wavefunction is well optimized the HFS estimate is considerably better, despite the noise in the data. Such situations might occur when the system is dominated by the bulk while we are interested in sampling data in the surface region. Optimization based on the total energy or variance would result in a sub-optimal wavefunction away from the bulk and hence erroneous standard sampling.

In conclusion, by applying the HF theorem directly to the DMC algorithm we have introduced a new method to sample a large class of operators exactly within standard DMC. Our method works for both small and large systems and is easy to add to standard DMC, enabling the sampling of a large class of operators (densities, interaction energies, etc.): Only one extra variable per operator ($X_{i,j}$) need be added to the walkers, involving no more than an extra summation step during sampling; simple algebra (Eqs. (8) and (9)) does the rest. Future work is needed to better understand, estimate, and deal with the noise and its slow increase with simulation time. This is currently under investigation. Similarly, the effect of residual weights needs to be looked at in more detail. A promising line of research already under way is to look at the second derivative. This might allow efficient DMC sampling of the fixed-node density-response function and related quantities, the study of which is currently not feasible due to being numerically too demanding.

R.G. would like to thank W.M.C. Foulkes, B. Wood, and N. Hine of Imperial College for helpful discussions. The authors acknowledge partial support by the University of the Basque Country, the Basque Unibertsitate eta Ikerguela, the MCyT, and the EC 6th framework Network of Excellence NANOQUANTA (Grant No. NMP4-CT-2004-500198).

[1] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Rev. Mod. Phys. 73, 33, 2001.
[2] M. Nekovee and J. M. Pitarke, Comput. Physics Commun. 137, 123 (2001).
D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980). See also R. M. Dreizler and E. K. U. Gross, Density-Functional Theory. An Approach to the Quantum Many-Body Problem, Springer, 1990.

P. A. Whitlock, D. M. Ceperley, G. V. Chester, and M. H. Kalos, Phys. Rev. B 19, 5598 (1978).

K. S. Liu, M. K. Kalos, and G. V. Chester, Phys. Rev. A 10, 303 (1974).

S. Baroni and S. Moroni, Phys. Rev. Lett. 82, 4745 (1999).

J. Casulleras and J. Boronat, Phys. Rev. B 52, 3654 (1995).

R. P. Feynmann, Phys. Rev. 56, 340 (1939).

G. Ortiz and P. Ballone, Phys. Rev. B 50, 1391 (1994).

In practice one uses importance sampling (R. C. Grimm and R. G. Storer, J. Comput. Phys. 7, 134 (1971)), which changes the kinetic diffusion kernel into drift-diffusion and replaces the potential energy by the much smoother local energy $E_L = [H\Psi_T]/\Psi_T$. The process then samples $\Psi_T\Psi_f$ rather than just $\Psi_f$.

Inverting $E_0^i = \frac{1}{2} \sum_{i=1}^i \tilde{E}_i^0$ then gives $\tilde{E}_i^0 = IE_i^0 - (i - 1)E_{i-1}^0$.

When using the HF theorem in conjunction with numerical derivatives, problems appear if the underlying Hilbert space changes with $\alpha$. This is not the case here.

R. J. Needs, M. Towler, N. Drummond, and P. Kent, CASINO version 1.7 User manual (University of Cambridge, 2004).

G. L. Warren and R. J. Hinde, Phys. Rev. E 73, 056706 (2006).