Diffusion Monte Carlo with lattice regularization

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(Dated: March 23, 2022)

We introduce an efficient lattice regularization scheme for quantum Monte Carlo calculations of realistic electronic systems. The kinetic term is discretized by a finite difference Laplacian with two mesh sizes, \( a \) and \( a' \), where \( a'/a \) is an irrational number so that the electronic coordinates are not defined on a particular lattice but on the continuous configuration space. The regularized Hamiltonian goes to the continuous limit for \( a \to 0 \) and provides several advantages. In particular, it allows the inclusion of non-local potentials in a consistent variational scheme, substantially improving the accuracy upon previous non-variational approaches.

PACS numbers: 02.70.Ss, 31.10.+z, 31.25.-v

In the last few decades, enormous progress has been made in computing the physical properties of many-electron systems with numerical methods based on first principle quantum mechanics. In particular, quantum Monte Carlo (QMC) techniques have proven very successful mainly because they allow the explicit inclusion of electronic correlation in a many-body wave function (WF). Moreover, projection QMC methods such as diffusion Monte Carlo (DMC) can improve upon a given guiding WF \( \Psi_G \) by stochastically projecting a state \( \Psi_{FN} \) much closer to the exact ground state (GS) of the Hamiltonian \( H \). \( \Psi_{FN} \) is obtained within the fixed-node approximation (FNA), which yields the lowest solution of the Schrödinger equation with the same nodes as \( \Psi_G \). If \( \Psi_G \) is appropriately optimized, the method usually provides a good upper bound \( E_{FN} \) for the GS energy \( E_{GS} \):

\[
E_{FN} = \frac{\langle \Psi_{FN} | H | \Psi_{FN} \rangle}{\langle \Psi_{FN} | \Psi_{FN} \rangle}.
\]

(1)

In general, in a QMC calculation, one accesses a mixed-average estimate of the total energy:

\[
E_{MA} = \frac{\langle \Psi_G | H | \Psi_{FN} \rangle}{\langle \Psi_G | \Psi_{FN} \rangle},
\]

(2)

which coincides with \( E_{FN} \) since \( \Psi_{FN} \) satisfies the equation \( H \Psi_{FN} = E_{FN} \Psi_{FN} \) within the nodal pockets of \( \Psi_G \).

While the QMC methods can be extended to large systems containing many electrons, the computational effort increases dramatically with the atomic number \( Z \). The most common way to overcome this difficulty is to replace the core electrons by pseudopotentials, an approximation which is usually rather good as the core is chemically inert. Since the pseudopotentials are in most cases non local, \( H \) contains a non-local potential \( V^P \), i.e. \( \langle x | V^P | x' \rangle \neq 0 \) even when \( |x - x'| \neq 0 \), where \( x \) denotes an all electron configuration with positions \( \{ r_i \} \) and spins \( \{ \sigma_i \} \). Consequently, the standard DMC approach cannot be applied and the so called “locality approximation” (LA) is employed, which approximates the non-local potential \( V^L(x) = \langle x | V^L | x' \rangle/\langle x | \Psi_G \rangle \). A major drawback of this approach is that \( E_{FN} \) (Eq. 1) is no longer available since it does not coincide with \( E_{MA} \) (Eq. 2) accessible in a DMC calculation: \( \Psi_{FN} \) is now the best solution with the same nodes as \( \Psi_G \) for the approximate Hamiltonian with potential \( V^{LA} \) and not for the Hamiltonian \( H \). Even though \( E_{MA} \) equals \( E_{GS} \) if \( \Psi_G \) is exact, it is otherwise not bounded by \( E_{GS} \) and no rigorous information about the quality of \( \Psi_{FN} \) is given by \( E_{MA} \). For instance, it is not possible to ascertain the quality of the nodes of \( \Psi_G \) since a lower \( E_{MA} \) may correspond to a worse \( \Psi_{FN} \), namely with higher \( E_{FN} \). Empirically, the method appears to work, but its drawback has limited the impact of this technique to a wider range of applications.

In this Letter, we present a lattice regularization of the many-electron Hamiltonian which removes the above difficulties when using non-local potentials within the FNA. We demonstrate the utility of our lattice regularized DMC approach in cases where the LA yields inaccurate results.

Regularization of the Hamiltonian. We consider the Hamiltonian in atomic units:

\[
H = -\frac{1}{2} \sum_i \Delta_i + V(x),
\]

(3)

and, for the moment, assume a local potential, \( V(x) = \sum_j -Z_j/|\vec{R}_i - \vec{R}_j| + \sum_{i<j} 1/|\vec{r}_i - \vec{r}_j| \), where \( \vec{R} \) and \( \vec{r} \) indicate the ionic and electron positions, respectively.

The Laplacian is approximated by a finite difference form

\[
\Delta_i \approx \Delta_i^a = \Delta_i^{a,p} + \Delta_i^{a',1-p} + O(a^2),
\]

(4)

where \( \Delta_i^{a,p} \) is an appropriate Hermitian lattice operator defined by a mesh size \( a \), a constant \( \eta \), and an arbitrary function \( p(\vec{r}_i) \):

\[
\Delta_i^{a,p} f(x_i, y_i, z_i) = \eta/a^2 [p(x_i + a/2)(f(x_i + a) - f(x_i))
+ p(x_i - a/2)(f(x_i - a) - f(x_i))] + x_i \leftrightarrow y_i \leftrightarrow z_i.
\]
For \( p = \eta = 1 \), \( \Delta^{a,p} \) coincides with the usual discretized form of the Laplacian on a lattice with mesh size \( a \). By combining two such operators in Eq. 4 with mesh sizes \( a \) and \( a' \), and \( a'/a \) an irrational number, the electron coordinates \( \{ \vec{r}_i \} \) are still defined in the continuous space because the two meshes are incommensurate and the diffusion process described by this discretized Laplacian can cover all the configuration space. Moreover, in Eq. 4 the function \( p \) can be arbitrarily spatial dependent as long as \( 0 \leq p \leq 1 \) to ensure that \( p \) and \( 1-p \) are both positive. In order to optimize the efficiency of the diffusion process, we have carefully chosen the constant \( a'/a \) and the function \( p \) as:

\[
\begin{align*}
 p(\vec{r}) &= 1/(1 + Z^2/4|\vec{r} - \vec{R}|^2), \\
 a'/a &= \sqrt{Z^2/4 + 1},
\end{align*}
\]

where \( \vec{R} \) and \( Z \) are the position and the atomic number of the nucleus closest to the electron in \( \vec{r} \). Therefore, if the electron is very close to a nucleus, the smaller mesh \( a' \) is used, while, in the valence region where \( |\vec{r} - \vec{R}| >> 1/Z \), the electron can make steps of larger amplitude \( a' \), thus reducing the QMC correlation time.

If \( \eta = 1 + O(a^2) \), the resulting finite difference Laplacian \( \Delta^{a} \) coincides with the continuous \( \Delta \) up to \( O(a^2) \). To further improve the accuracy of the approximation and work with reasonably large value of \( a \), we regularize also the potential \( V \rightarrow V^a \) so that our final regularized Hamiltonian, \( H^a = -1/2 \sum_i \Delta^a_i + V^a \), fulfills the following three conditions: i) \( H^a \rightarrow H \) for \( a \rightarrow 0 \); ii) for the chosen guiding WF \( \Psi_G \), for any \( a \) and any \( x \), the local energy \( e_L(x, \Psi_G) = \langle x|H|\Psi_G(x)\rangle/\langle x|\Psi_G(x)\rangle \) of the continuous Hamiltonian \( H \) is equal to \( e_L^a(x, \Psi_G) \) corresponding to the Hamiltonian \( H^a \); iii) the discretized kinetic energy is equal to the continuous one calculated on the state \( \Psi_G \), i.e. \( (-1/2 \sum_i \Delta^a_i) \psi_G^a = (-1/2 \sum_i \Delta_i) \psi_G^a \). While the condition (iii) determines the constant \( \eta \), the condition (ii) leads to the following solution for \( V^a \):

\[ V^a(x) = V(x) + \frac{1}{2} \left[ \sum_i (\Delta^a_i - \Delta_i) \psi_G(x) \right] \]

Notice that the condition (ii) yields another important property for \( H^a \): if \( \Psi_G \) is an eigenstate of \( H \), it is also an eigenstate of \( H^a \) for any \( a \), as can be derived by simple inspection using that \( \Delta^a \) is Hermitian. Thus, by improving \( \Psi_G \), a better \( a \rightarrow 0 \) convergence is also expected.

**Non-local pseudopotential.** The above regularization also applies when we include in the potential \( V \) a non-local potential of the form \( V^P = \sum_j v^P(\vec{r}_j) \) where

\[
 v^P(\vec{r}_i) = \sum_j \left[ v_j(|\vec{r}_i - \vec{R}_j|) + \sum_{l \leq l_{\text{max}}} v^l_j(|\vec{r}_i - \vec{R}_j|) P_l \right].
\]

The sum over \( j \) is here restricted to the pseudoatoms, \( P_l \) is the \( l \)-angular-momentum projection centered on the pseudoatom at \( \vec{R}_j \), and \( l_{\text{max}} \) the corresponding maximum angular momentum considered. The functions \( v_j \) and \( v^l_j \) are radial, and \( v^l_j \) vanishes outside a core radius \( r_c^l \).

In a QMC calculation with pseudopotentials \( \Psi_G \), the angular integration to evaluate the projection \( P_l \) is performed numerically on a regular polyhedron defined by \( N_V \) vertices and by employing a quadrature rule for the integration on a sphere. Therefore, the non-local pseudopotential \( v^P \) acts on a configuration \( x \) by means of a finite number of matrix elements equal to \( N_V N_{\text{core}} \), where \( N_{\text{core}} \) is the number of electrons within the core radius of a pseudoatom. In the following, we will assume that, in the continuous Hamiltonian \( H \), the pseudopotential is by definition discretized with a finite number \( N_V \) of vertices. Then, the regularization \( H \rightarrow H^a \) follows by simple substitution of \( V(x) \rightarrow V(x) + V^P \) in Eq. 4.

**Lattice regularized diffusion Monte Carlo (LRDMC).** Although \( H^a \) is an Hamiltonian defined on a continuous space, all techniques valid on a lattice can be straightforwardly applied here since \( H^a \) acts on a configuration exactly as a lattice Hamiltonian, namely:

\[
 \langle x|H^a|\Psi_G \rangle = \sum_{x'} H^a_{x,x'} \langle x'|\Psi_G \rangle,
\]

where, for a given \( x \), the number of matrix elements \( H^a_{x,x'} \) are finite and can be computed even in the presence of non-local pseudopotentials. In particular, we can resort to the same scheme used in the efficient lattice Green function Monte Carlo algorithm \( \Psi \). The resulting algorithm, valid for a continuous regularized Hamiltonian, is the LRDMC. The corresponding Green function matrix elements are \( G_{x,x'} = \Psi_G(x')/(\Delta x' - H^a_{x,x'})/\Psi_G(x) \), and, provided they are all non-negative, the positive distribution \( \Psi_G(x)/\Psi_G(x) \) is statistically sampled. Note that, since the spectrum of \( H^a \) is not bounded from above, we need to take the limit \( \Lambda \rightarrow \infty \), which can be handled with no loss of efficiency as described in Ref. 8. The LRDMC algorithm is very simple: given a walker with configuration \( x \) and weight \( w \), a new configuration \( x' \neq x \) is obtained with probability \( p_{x',x} = G_{x',x}/N_x \), where \( N_x = \sum_{x' \neq x} G_{x',x} \) is the normalization. The walker weight is then changed by a factor \( w \rightarrow w \exp(-\tau_x e_L(x, \Psi_G)) \) where \( \tau_x = -\log(r)/N_x \) is a diffusion time determined by a single random number \( 0 < r \leq 1 \). Then, the usual branching scheme is used to control the fluctuations of the walker weights.

Within this approach, the time-step error of the standard DMC method is not present, but is replaced by the error of the Laplacian discretization. By performing LRDMC simulations of \( H^a \) for different \( a \)'s, we can approach the GS properties of a continuous system in the limit \( a \rightarrow 0 \). The method becomes less efficient as \( a \rightarrow 0 \) since the computational time increases like \( 1/a^2 \), similarly to the DMC efficiency which is limited by \( 1/\Delta \tau \),
where $\Delta \tau$ is the imaginary time step for the diffusion process.

Since the Green function $G_{x'x}$ can be made strictly positive only for bosons, we have to introduce here the analogous of the FNA on a lattice \[ \text{I, II, III} \] by modifying few of the matrix elements of the regularized Hamiltonian $H^\alpha$. For each configuration $x$, the matrix elements $H^\alpha_{x'x}$ which yield $G_{x'x} < 0$ are set to zero and included in the so called sign-flip term, $V_{sf}(x) = \sum_{x' \neq x} \Psi_G(x') H^\alpha_{x'x} / \Psi_G(x) > 0$, which is then added to the diagonal element $H^\alpha_{x,x}$ \[ 3 \]. The resulting effective Hamiltonian $H^{\text{eff}}$ has the same local energy as $H^\alpha$, it is non frustrated, and its GS WF has the same signs as the guiding function $\Psi_G(x)$. The GS energy of $H^{\text{eff}}$ can be efficiently computed with the mixed average $E_{MA}$ and, for a local Hamiltonian $H$, we recover the standard DMC result $E_{MA} = E_{FN}$ in the limit $\alpha \to 0$ as shown in Fig. 4. Moreover, when $H$ contains non-local pseudopotentials, $E_{MA}$ for the GS of $H^{\text{eff}}$ is certainly lower than the expectation value $E_G$ of the Hamiltonian $H^\alpha$ on $\Psi_G$, and represents an upper bound of the variational energy $E_{FN}$ with the Hamiltonian $H^\alpha$ in Eq. 1 as was shown for the lattice FN approach \[ 3 \]. This important upper bound property has been so far only obtained within the lattice regularization proposed here, whereas, in the DMC approach, it is not true in general that $E_G \geq E_{MA} \geq E_{FN}$.

Computation of $E_{FN}$. Another advantage of our lattice regularization is that we can also compute directly and accurately $E_{FN}$ for the Hamiltonian $H$ by introducing a more general effective Hamiltonian characterized by the parameters $\gamma \geq 0$ and $0 \leq \alpha < 1$ \[ 11 \]:

\[
\begin{align*}
H_{x,x}^{\text{eff}} &= H_{x,x}^\alpha + (1 + \gamma)V_{sf}(x) + \alpha(1 + \gamma)V_{sf}^P(x) \quad (9) \\
H_{x',x}^{\text{eff}} &= -\gamma H_{x',x}^\alpha \quad \text{if } \Psi_G(x') H_{x',x}^\alpha / \Psi_G(x) > 0 \\
H_{x',x}^{\text{eff}} &= (1 - \alpha(1 + \gamma))H_{x',x}^\alpha \quad \text{if } \Psi_G(x') V_{sf}^P(x') / \Psi_G(x) < 0 \\
H_{x,x}^{\text{eff}} &= H_{x,x}^\alpha \quad \text{otherwise},
\end{align*}
\]

where $x' \neq x$ and $V_{sf}^P(x) = \sum_{x' \neq x} \Psi_G(x') V_{sf}^P(x'/x) / \Psi_G(x) < 0$. This Hamiltonian also satisfies $G_{x,x} > 0$ and reduces to the standard lattice FN one for $\alpha = \gamma = 0$.

The parameter $\gamma$ allows one to evaluate $E_{FN}$ in the presence of the non-local contribution of $V^P$ as

\[
E_{FN} = E_{MA}(\gamma) - (\gamma + 1) \frac{dE_{MA}(\gamma)}{d\gamma}, \quad (10)
\]

where we used that $H = H^\alpha - (\gamma + 1) \partial_\gamma H^{\text{eff}}$ and applied the Hellmann-Feynman theorem to the last term. To estimate $E_{FN}$, we compute the derivative with respect to $\gamma$ in an approximate but variational way, the best variational estimate being for $\gamma = 0$ \[ \text{I} \]:

\[
E_{FN} \leq E_{MA}(0) - |E_{MA}(\gamma) - E_{MA}(0)| / \gamma, \quad (11)
\]

where the equality sign holds in the limit of small $\gamma$. Notice that, for $\alpha = 1$ and $\gamma = 0$, the LA is recovered, i.e. all the off-diagonal matrix elements of $V^P$ are included in the diagonal ones of $H^{\text{eff}}$. Even though it is not guaranteed that $E_{MA}$ is variational for $\alpha > 0$, with the present scheme we can evaluate $E_{FN}$ and improve upon the locality approximation by optimizing $\alpha$. Indeed, the variational energy $E_{FN}$ corresponding to a given value of $\alpha$ can be estimated efficiently using correlated sampling to evaluate $E_{MA}$ for $\gamma = 0$ and $0 < \gamma \leq 1/\alpha - 1$ as in Eq. 11. Remarkably, this approach allows us to work close to the locality approximation, even with $\alpha = 0.95$ and $\gamma = 0.05$, with statistical errors for $E_{FN}$ similar to the ones for $E_{MA}$.

Results and perspectives. We have first tested the performance of the LRDMC approach on the silicon pseudodatom using three Hartree-Fock pseudopotentials which differ in the construction, functional form and core radius. For each pseudopotential, we employ three WF’s with the same determinantal component and, consequently, the same nodes, but with different Jastrow factors. We use no Jastrow factor, a two-body, and a sophisticated three-body Jastrow factor \[ 13 \].

As shown in Fig. 2, the energy estimate $E_{MA}$ computed within DMC changes significantly with the guiding WF $\Psi_G$, and differs from the variational expectation value, $E_{FN}$, which we compute with the LRDMC scheme for $\alpha = 0, 0.5$ and 0.9. For all cases, the statistical uncertainty does not allow us to discriminate between the LRDMC energies obtained for $\alpha = 0.5$ and $\alpha = 0.9$, and a shallow minimum seems to lie between these two values. The optimal $E_{FN}$ is almost free of the localization error and the weakest dependence on $\Psi_G$ is obtained for Lester’s pseudopotential \[ 14 \], which has the smallest core radius in the non-local component. Interestingly, since $E_{FN}$ for $\alpha \approx 1$ is very close to the minimum, the LA seems to yield good WF’s. However, the value of $\alpha$ should be optimized for each case since there is no general reason why $\alpha = 1$ should give the best energy. In principle, in the case of systems with lower symmetry, the value of $\alpha$ should be closer to 0 due to the non conservation of the total angular momentum. A stringent test case for our LRDMC algorithm is the scandium atom: the LA for transition metals yields
The other hand, the LRDMC FN results, obtained with a Hartree-Fock determinant with no Jastrow, a two-body and a three-body Jastrow factor. A more accurate guiding WF corresponds to a smaller difference between the 2-body and a three-body Jastrow factor. A more accurate guiding WF is employed. The LRDMC mixed-average energy (eV) for the scandium atom.

| 2-body | 3-body |
|--------|--------|
| VMC    | DMC    | LRDMC  |
| 1.099(30) | 1.396(19) | 1.407(16) |
| 1.416(43) | 1.452(34) | 1.492(41) |

TABLE I: Comparison of \( 4s^23d^n \rightarrow 4s^33d^{n+1} \) excitation energy (eV) for the scandium atom.

large errors in the DMC total energies, and performs the worst for the scandium atom [15]. As before, we keep the determinantal part of the WF fixed, and employ a 2-body [16] and a 3-body [17] Jastrow factor. The determinantal component is an antisymmetrized geminal function expanded over a \((5s5p5d)\) Gaussian-type basis in order to cure near degeneracy effects, and optimized in the presence of the 2-body Jastrow factor. We employ Dolg’s pseudopotential [15] and compute the \( 4s^23d^n \rightarrow 4s^33d^{n+1} \) excitation energy which is reported in Table I. It is apparent that the LA does not only affect the DMC total energies but also the DMC energy differences: the DMC excitation energy computed with the 2-body Jastrow factor differs from the experimental value by more than three standard deviations. On the other hand, the LRDMC FN results, obtained with \( \alpha = 0.5 \), are much less sensitive to \( \Psi_G \), and are compatible with the experiment even when a simple 2-body Jastrow factor is employed. The LRDMC mixed-average excitations are also closer to the experimental value than the LA ones, probably because the variational treatment of non-local pseudopotentials gives a better cancellation of errors. Remarkably, we found that a LRDMC simulation with off-diagonal pseudopotentials is computationally much more stable and efficient than the standard DMC approach since the negative divergences coming from the pseudopotentials close to the nodes are converted to finite hopping terms in the LRDMC scheme.

We have presented an efficient lattice regularization scheme for QMC calculations on realistic electronic systems. The main advantage of the LRDMC approach is the possibility to work with non-local potentials within a fully consistent and variational scheme which is much more accurate than the standard DMC method. Moreover, this projection method allows one to deal with several length scales through the use of multiple lattice spaces, with great reduction of autocorrelation times for heavy atoms or complex systems. We believe that this framework can have a wide spread of important applications ranging from nuclear physics [18] to the chemistry of transition metal compounds.

This work was partially supported by INFN, by MIUR (COFIN 2003), and by Stichting voor Fundamenteel Onderzoek der Materie (FOM). We acknowledge G. Bachelet and S. De Gironcoli for useful discussions.

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