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Diffusion Monte Carlo Method with Lattice Regularization

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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', chosen so that the electrons can diffuse in a configuration space which is in practice indistinguishable from the continuum, and the different length scales in the system can be efficiently taken in account. The regularized Hamiltonian goes to the continuous limit for $a \to 0$ and allows the inclusion of nonlocal potentials in a consistent variational scheme, substantially improving the accuracy upon previous nonvariational approaches.

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In the last few decades, quantum Monte Carlo (QMC) techniques [1] have proven very successful in studying many-electron systems, mainly because within this framework the electronic correlation can be explicitly included in a many-body wave function (WF). Moreover, projection QMC methods such as the diffusion Monte Carlo (DMC) scheme can improve upon a given guiding WF Ψ_G by stochastically projecting a state $\Psi_{\rm FN}$ much closer to the exact ground state (GS) of the Hamiltonian H. $\Psi_{\rm FN}$ is obtained within the fixed-node approximation (FNA), which yields the lowest solution of the Schrödinger equation with the same nodes as Ψ_G. If Ψ_G is appropriately optimized, the method usually provides a good upper bound

$$E_{\rm FN} = \langle \Psi_{\rm FN} | H | \Psi_{\rm FN} \rangle / \langle \Psi_{\rm FN} | \Psi_{\rm FN} \rangle \tag{1}$$

for the GS energy $E_{\rm GS}$. In a QMC calculation, one accesses a mixed-average estimate of the total energy

$$E_{\rm MA} = \langle \Psi_G | H | \Psi_{\rm FN} \rangle / \langle \Psi_G | \Psi_{\rm FN} \rangle, \tag{2}$$

which coincides with $E_{\rm FN}$ since $\Psi_{\rm FN}$ satisfies the equation $H\Psi_{\rm FN} = E_{\rm FN}\Psi_{\rm FN}$ within the nodal pockets of Ψ_G.

While the QMC methods can be extended to large systems, 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 a pseudopotential [2] $V^{\rm P}$, which is in most cases nonlocal, i.e., $\langle x | V^{\rm P} | x' \rangle \neq 0$ even when $|x - x'| \neq 0$, where x denotes a spatial-spin configuration of all the valence electrons. Consequently, the standard DMC approach cannot be applied and the so-called locality approximation (LA) is introduced [3–5], which approximates the nonlocal potential $V^{\rm P}$ with the local $V^{\rm LA}(x) = \langle x | V^{\rm P} | \Psi_G \rangle / \langle x | \Psi_G \rangle$.

A major disadvantage of the locality approximation is that the expectation value $E_{\rm FN}$ of the Hamiltonian H on the fixed-node solution is no longer accessible since it does not coincide with the mixed-average computed in a DMC calculation. The fixed-node state $\Psi_{\rm FN}^{\rm LA}$ is now the best solution with the same nodes as Ψ_G for the approximate Hamiltonian with potential $V^{\rm LA}$. Consequently, the estimate $E_{\rm MA}^{\rm LA} = \langle \Psi_G | H | \Psi_{\rm FN}^{\rm LA} \rangle / \langle \Psi_G | \Psi_{\rm FN}^{\rm LA} \rangle$ is no longer the same as the expectation value of the Hamiltonian H on $\Psi_{\rm FN}^{\rm LA}$. The only known property of $E_{\rm MA}^{\rm LA}$ is that it equals the exact energy $E_{\rm GS}$ if Ψ_G is exact. Otherwise, it is not bounded by $E_{\rm GS}$ and it gives no rigorous information about the quality of $\Psi_{\rm FN}^{\rm LA}$. In particular, a lower $E_{\rm MA}^{\rm LA}$ may, in fact, correspond to a worse solution $\Psi_{\rm FN}^{\rm LA}$, namely, with a higher expectation value of the Hamiltonian H.

In this Letter, we present a lattice regularization of the many-electron Hamiltonian which removes the above difficulties when using nonlocal potentials within the FNA. We demonstrate the efficiency of our lattice regularized DMC approach as well as its usefulness in cases where the locality approximation yields inaccurate results.

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

$$H = -\frac{1}{2}\sum_i \Delta_i + V(x), \tag{3}$$

where, for the moment, we assume a local potential. We first approximate the Laplacian by a finite difference form with two mesh sizes a and $a' (>a)$, where a/a' is defined as an irrational [6] number. The diffusion process based on these two meshes overcomes the lack of ergodicity present in a strict lattice evolution, and the electron coordinates $\{\vec{r}_i\}$ assume values practically indistinguishable from the continuum. Moreover, the scheme is designed to account for the different length scales in the system by using the smaller step a close to a nucleus and the larger a' in the valence region. As can be seen in Fig. 1, a double mesh significantly increases the efficiency of the diffusion process, yielding a large reduction of the step-size error compared with the use of only one lattice.

Our discretized Laplacian has the following form:

$$\Delta_i \approx \Delta_i^a = \Delta_i^{a,p} + \Delta_i^{a',1-p} + O(a^2), \tag{4}$$

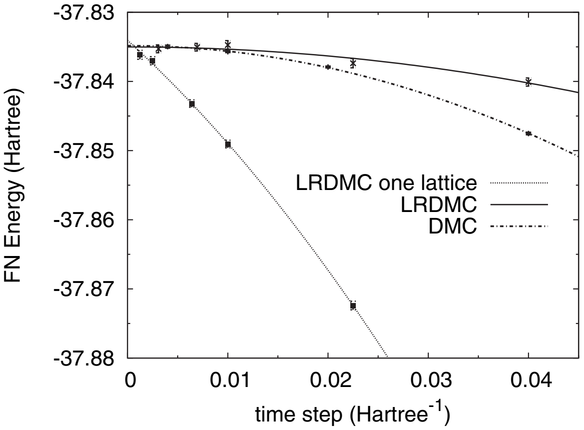

FIG. 1. FN energies for the all-electron carbon atom computed within DMC, LRDMC, and a LRDMC scheme where only one discretization lattice is employed (LRDMC one lattice). The lattice spacing a is here mapped to the time-step τ as $a = \sqrt{\tau}$.

where $\Delta^{a,p}$ is a Hermitian lattice operator defined by a mesh size a, a constant η, and an arbitrary function p:

$$\begin{aligned}\Delta_i^{a,p} f(x_i, y_i, z_i) = \eta/a^2\{&p(x_i + a/2)[f(x_i + a) - f(x_i)]\\ &+ p(x_i - a/2)[f(x_i - a) - f(x_i)]\}\\ &+ x_i \leftrightarrow y_i \leftrightarrow z_i.\end{aligned}$$

For $p = \eta = 1$, $\Delta_i^{a,p}$ coincides with the usual discretized form of the Laplacian on a lattice with mesh size a. The constant η behaves as $1 + O(a^2)$ and is introduced to reduce the error coming form the discretization of the kinetic term: it is determined by requiring that the discretized kinetic energy is equal to the continuous one calculated on the state Ψ_G, i.e., $\langle\Psi_G|\Sigma_i\Delta_i^a|\Psi_G\rangle = \langle\Psi_G|\Sigma_i\Delta_i|\Psi_G\rangle$. The function p $(0 \leq p \leq 1)$ is instead used to weight the contributions of the two meshes so that the smaller step a is used close to a nucleus and the larger a' far away from the nuclei. The optimal function p and ratio a'/a are found to be

$$p(\vec{r}) = 1/(1 + Z^2|\vec{r} - \vec{R}|^2/4), \tag{5}$$

$$a'/a = \sqrt{Z^2/4 + 1}, \tag{6}$$

where $\vec{R}$ and Z are the position and the atomic number of the nucleus closest to the electron in $\vec{r}$.

To further improve the accuracy of the approximation and work with larger values of a, we regularize also the potential $V \rightarrow V^a$ by requiring that, for the chosen guiding WF Ψ_G, the local energy $\langle x|H^a|\Psi_G\rangle/\langle x|\Psi_G\rangle$ of the Hamiltonian $H^a = -\frac{1}{2}\Sigma_i\Delta_i^a + V^a$ equals for each value of a the local energy of the continuous Hamiltonian H. This condition leads to the following solution for V^a:

$$V^a(x) = V(x) + \frac{1}{2}\left[\frac{\Sigma_i(\Delta_i^a - \Delta_i)\Psi_G}{\Psi_G}\right](x). \tag{7}$$

Note that the correct limit $H^a \rightarrow H$ for $a \rightarrow 0$ is preserved and that the regularization of V yields another important property for H^a: if Ψ_G is an eigenstate of H, it is also an eigenstate of H^a for any a, as can be easily derived using that Δ^a is Hermitian. Thus, by improving Ψ_G, a better $a \rightarrow 0$ convergence is also expected.

Nonlocal pseudopotential.—We consider atomic pseudopotentials with a nonlocal component of the form $\Sigma_{l \leq l_{\max}} v^l(|\vec{r}|)P_l$, where P_l is the l-angular-momentum projection and the radial function v^l is zero outside a given core radius. The total nonlocal potential V^{P} is obtained by summing the contributions from all the electrons and pseudoatoms.

Since the angular integration to evaluate the projection P_l can be performed by a numerical quadrature on a regular polyhedron defined by N_{V} vertices [5,7], the nonlocal V^{P} acts on a configuration x by means of a *finite* number of matrix elements equal to $N_{\mathrm{V}}N_{\mathrm{core}}$, where N_{core} is the number of electrons in the configurations x within the core radius of a pseudoatom. Therefore, we can proceed as if each atomic pseudopotential were by definition discretized with N_{V} points so that V^a becomes

$$\langle x'|V^a|x\rangle = V^a(x)\delta_{x,x'} + \langle x'|V^{\mathrm{P}}|x\rangle, \tag{8}$$

where $V^a(x)$ is the local component of Eq. (7) and the configuration x' is defined on a mesh with steps determined by the chosen numerical quadrature. In this way, we have three meshes—the two kinetic meshes with steps a and a', and one pseudopotential mesh.

Lattice regularized diffusion Monte Carlo (LRDMC) method.—Although H^a is a 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,

$$\langle x|H^a|\Psi_G\rangle = \sum_{x'} H^a_{x,x'}\langle x'|\Psi_G\rangle, \tag{9}$$

where, for a given x, the number of matrix elements $H^a_{x,x'}$ are *finite* even in the presence of nonlocal pseudopotentials. In particular, we can resort to the same scheme used in the efficient lattice Green function Monte Carlo algorithm [8–10]. The corresponding transition matrix elements are $G_{x',x} = \Psi_G(x')(\Lambda\delta_{x',x} - H^a_{x',x})/\Psi_G(x)$ and, provided they are all non-negative, the positive distribution $\Psi_G(x)\Psi_{\mathrm{GS}}(x)$ 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. [10].

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 [8–10] and modify few of the matrix elements of the Hamiltonian H^a. For each configuration x, the matrix elements $H^a_{x',x}$ which yield $G_{x',x} < 0$ are set to zero and included in the so-called sign-flip term, $\mathcal{V}_{\mathrm{sf}}(x) = \Sigma_{x' \neq x}, \ \Psi_G(x')H^a_{x',x}/\Psi_G(x) > 0$, which is then added to the diagonal element $H^a_{x,x}$ [8]. The resulting effective Hamiltonian $H^{\rm eff}$ has the same local energy as H^a and its GS WF has the same signs as the guiding WF Ψ_G.

The GS energy of $H^{\rm eff}$ can be efficiently computed with the mixed-average estimator $E^{\rm eff}_{\rm MA}$ which also equals the mixed estimator for the Hamiltonian H^a:

$$E^{\rm eff}_{\rm MA} = \frac{\langle \Psi_G | H^{\rm eff} | \Psi^{\rm eff}_{\rm FN} \rangle}{\langle \Psi_G | \Psi^{\rm eff}_{\rm FN} \rangle} = \frac{\langle \Psi_G | H^a | \Psi^{\rm eff}_{\rm FN} \rangle}{\langle \Psi_G | \Psi^{\rm eff}_{\rm FN} \rangle} \tag{10}$$

where $\Psi^{\rm eff}_{\rm FN}$ is the GS of $H^{\rm eff}$. For a local Hamiltonian H, we recover the standard DMC result $E_{\rm MA} = E_{\rm FN}$ in the limit $a \to 0$ as shown in Fig. 1.

When nonlocal pseudopotentials are included, the lattice FN theorem [8] applied to $H^{\rm eff}$ yields

$$E_G \geq E^{\rm eff}_{\rm MA} \geq \langle \Psi^{\rm eff}_{\rm FN} | H^a | \Psi^{\rm eff}_{\rm FN} \rangle / \langle \Psi^{\rm eff}_{\rm FN} | \Psi^{\rm eff}_{\rm FN} \rangle, \tag{11}$$

where E_G is the expectation value of the Hamiltonian H on Ψ_G. The above relation is valid for each a and, therefore, also in the limit $a \to 0$ when $H^a \to H$. This important upper bound property does not generally hold in the DMC approach.

Computation of $E_{\rm FN}$.—We now extend the effective Hamiltonian $H^{\rm eff}$ to include the parameters $\gamma(\geq 0)$ and α $(0 \leq \alpha < 1)$ [11]. The parameter γ allows us to compute the expectation value of the Hamiltonian H^a on the fixed-node solution in the presence of nonlocal pseudopotentials [Eq. (11)]. The parameter α sets the degree of localization used in the effective Hamiltonian: it smoothly connects the LA ($\alpha = 1$) to the standard lattice FN approach described above ($\alpha = 0$) where the pseudopotential terms yielding a non-negative $G_{x',x}$ are not approximated. The new effective Hamiltonian $H^{\alpha,\gamma}$ is

$$\begin{aligned}
H^{\alpha,\gamma}_{x,x} &= H^a_{x,x} + (1+\gamma)\mathcal{V}_{\rm sf}(x) + \alpha(1+\gamma)\mathcal{V}^{\rm P}_{\rm sf}(x),\\
H^{\alpha,\gamma}_{x',x} &= -\gamma H^a_{x',x} \quad \text{if } \Psi_G(x')H^a_{x',x}/\Psi_G(x) > 0,\\
H^{\alpha,\gamma}_{x',x} &= (1-\alpha(1+\gamma))H^a_{x',x} \quad \text{if } \Psi_G(x')V^{\rm P}_{x',x}/\Psi_G(x) < 0,\\
H^{\alpha,\gamma}_{x',x} &= H^a_{x',x} \quad \text{otherwise},
\end{aligned} \tag{12}$$

where $x' \neq x$ and a new sign-flip term is introduced, $\mathcal{V}^{\rm P}_{\rm sf}(x) = \Sigma_{x' \neq x} \Psi_G(x') V^{\rm P}_{x',x}/\Psi_G(x) < 0$. This Hamiltonian satisfies $G_{x',x} > 0$ and reduces to $H^{\rm eff}$ for $\alpha = \gamma = 0$.

To evaluate the expectation value of H^a on the GS solution $\Psi^{\alpha,\gamma}_{\rm FN}$ of $H^{\alpha,\gamma}$, we use the identity

$$E_{\rm FN}(\alpha,\gamma) = E_{\rm MA}(\alpha,\gamma) - (\gamma+1)\frac{\partial E_{\rm MA}(\alpha,\gamma)}{\partial \gamma}, \tag{13}$$

where $E_{\rm FN}(\alpha,\gamma) = \langle \Psi^{\alpha,\gamma}_{\rm FN} | H^a | \Psi^{\alpha,\gamma}_{\rm FN} \rangle / \langle \Psi^{\alpha,\gamma}_{\rm FN} | \Psi^{\alpha,\gamma}_{\rm FN} \rangle$ and $E_{\rm MA}(\alpha,\gamma) = \langle \Psi_G | H^a | \Psi^{\alpha,\gamma}_{\rm FN} \rangle / \langle \Psi_G | \Psi^{\alpha,\gamma}_{\rm FN} \rangle$. This relation is obtained by using that $H^a = H^{\alpha,\gamma} - (\gamma+1)\partial_\gamma H^{\alpha,\gamma}$ and applying the Hellmann-Feynman theorem to the last term. The best variational $E_{\rm FN}$ energy is for $\gamma = 0$ [11], which we estimate by computing the derivative with respect to γ in an approximate but variational way:

$$E_{\rm FN}(\alpha,0) \leq E_{\rm MA}(\alpha,0) - [E_{\rm MA}(\alpha,\gamma) - E_{\rm MA}(\alpha,0)]/\gamma, \tag{14}$$

where the equality sign holds in the limit of small γ.

The parameter α is used to improve upon the locality approximation and its value is optimized to yield the lowest $E_{\rm FN}(\alpha,0)$. Even though it is not guaranteed that $E_{\rm MA}(\alpha,\gamma)$ is variational for $\alpha > 0$, with the present scheme we can evaluate the variational $E_{\rm FN}(\alpha,0)$ using correlated sampling to compute $E_{\rm MA}(\alpha,\gamma)$ for $\gamma = 0$ and $0 < \gamma \leq 1/\alpha - 1$ as in Eq. (14).

Results and perspectives.—We have first tested the performance of the LRDMC approach on the silicon pseudoatom 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 [12]. As shown in Fig. 2, the energy estimate $E^{\rm LA}_{\rm MA}$ computed within DMC changes significantly with the guiding WF Ψ_G, and differs from the variational expectation value, $E_{\rm FN}(\alpha,0)$, 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 localization error is significantly reduced for optimal $E_{\rm FN}(\alpha,0)$ and the weakest dependence on Ψ_G is obtained for Lester's pseudopotential [13], which has the smallest

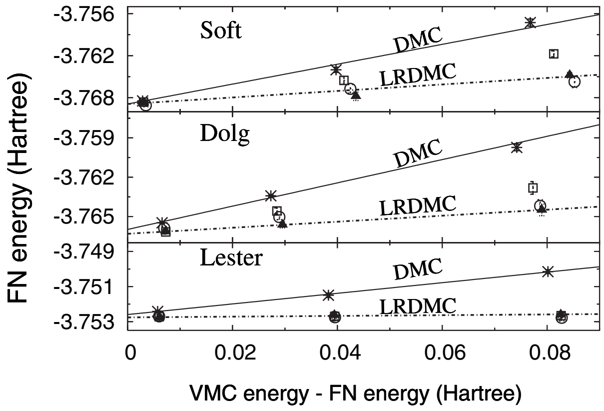

FIG. 2. FN energies of the silicon pseudoatom computed within DMC ($E^{\rm LA}_{\rm MA}$) and LRDMC [$E_{\rm FN}(\alpha,0)$] schemes. For different pseudopotentials (Soft [18], Dolg's [19] and Lester's [13]), we use as guiding WF's a Hartree-Fock determinant with no Jastrow, a two-body, and a three-body Jastrow factor. A more accurate guiding WF corresponds to a smaller difference between the variational Monte Carlo (VMC) calculations and the FN energies. The LRDMC energies are computed for $\alpha = 0.9$ (filled triangles), $\alpha = 0.5$ (open circles), and $\alpha = 0$ (open squares). The linear fits for the DMC and the LRDMC ($\alpha = 0.9$) data are shown.

TABLE I. Comparison of $4s^2 3d^n \rightarrow 4s^1 3d^{n+1}$ excitation energy (eV) for the scandium atom.

				LRDMC		
	α	VMC	DMC	$E_{\rm MA}(\alpha, 0)$	$E_{\rm FN}(\alpha, 0)$	Expt.
2-body	0.0	1.099(30)	1.381(15)	1.408(12)	1.417(31)	1.43
2-body	0.5	1.099(30)	1.381(15)	1.394(11)	1.441(25)	
3-body	0.5	1.303(29)	1.436(22)	1.448(9)	1.478(22)	

core radius in the nonlocal component. Interestingly, since $E_{\rm FN}(\alpha, 0)$ for $\alpha \simeq 1$ is very close to the minimum, the LA seems to yield in this case good WF's.

A stringent test case for our LRDMC algorithm is the scandium atom: the LA for transition metals yields large errors in the DMC total energies, and performs the worst for the scandium atom [14]. As before, we keep the determinantal part of the WF fixed, and employ a 2-body [15] and a 3-body [16] 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 [14] and compute the $4s^2 3d^n \rightarrow 4s^1 3d^{n+1}$ 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 3 standard deviations. On the other hand, the LRDMC FN results are less sensitive to Ψ_G, and are compatible with the experiment even when a simple 2-body Jastrow factor is employed. Also the LRDMC MA excitations appear to be closer to the experimental value than the DMC ones.

Since estimating $E_{\rm FN}(\alpha, 0)$ is computationally more demanding because of the need to evaluate two mixed-average energies [Eq. (14)], a practical compromise is to use $E_{\rm MA}(0, 0)$ as energy estimate: $E_{\rm MA}(\alpha, 0)$ at $\alpha = 0$ is variational and its computation is more efficient than the DMC evaluation of $E_{\rm MA}^{\rm LA}$. For pseudoatoms with large effective atomic number such as iron and scandium, we find that, due to the use of a double kinetic mesh within LRDMC, the gain in efficiency over DMC is at least a factor of 2. Moreover, we observe that a LRDMC simulation with off-diagonal pseudopotentials is computationally much more stable than DMC even when a very crude wave function or a very large lattice mesh a are employed. The reason for this greater stability is that 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 nonlocal 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 [17] to the chemistry of transition metal compounds.

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[1] W. M. C. Foulkes *et al.*, Rev. Mod. Phys. **73**, 33 (2001).

[2] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979); P. A. Christiansen, Y. S. Lee, and K. S. Pitzer, J. Chem. Phys. **71**, 4445 (1979).

[3] B. L. Hammond, P. J. Reynolds, and W. A. Lester, Jr., J. Chem. Phys. **87**, 1130 (1987).

[4] M. M. Hurley and P. A. Christiansen, J. Chem. Phys. **86**, 1069 (1987); P. A. Christiansen, *ibid.* **88**, 4867 (1988).

[5] L. Mitáš, E. L. Shirley, and D. M. Ceperley, J. Chem. Phys. **95**, 3467 (1991).

[6] In practice, during the computation, a/a' is the closest rational number which can be represented by a given machine precision. The resulting numerical grid for the electrons is practically indistinguishable from the continuum even for a single precision floating point arithmetic.

[7] S. Fahy, X. W. Wang, and S. G. Louie, Phys. Rev. B **42**, 3503 (1990).

[8] D. F. B. ten Haaf *et al.*, Phys. Rev. B **51**, 13039 (1995).

[9] M. Calandra Buonaura and S. Sorella, Phys. Rev. B **57**, 11446 (1998).

[10] S. Sorella and L. Capriotti, Phys. Rev. B **61**, 2599 (2000).

[11] S. Sorella, cond-mat/0201388.

[12] C. Filippi and C. J. Umrigar, J. Chem. Phys. **105**, 213 (1996).

[13] I. Ovcharenko, A. Aspuru-Guzik, and W. A. Lester, Jr., J. Chem. Phys. **114**, 7790 (2001).

[14] H.-J. Flad and Michael Dolg, J. Chem. Phys. **107**, 7951 (1997).

[15] The pseudopotentials of Ref. [13] diverge at the origin as $-Z_{\rm eff}/r$, so our two-body Jastrow factor has the form $\exp(\frac{ar}{1+br})$ to satisfy the cusp conditions for the nucleus ($a = -Z_{\rm eff}$) and the antiparallel electrons ($a = 1/2$).

[16] M. Casula, C. Attaccalite, and S. Sorella, J. Chem. Phys. **121**, 7110 (2004).

[17] K. E. Schmidt and S. Fantoni, Phys. Lett. B **446**, 99 (1999).

[18] We used the code of E. Shirley to generate norm-conserving Hartree-Fock pseudopotential with the construction by D. Vanderbilt, Phys. Rev. B **32**, 8412 (1985).

[19] A. Bergner *et al.*, Mol. Phys. **80**, 1431 (1993).