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Comparison of polynomial approximations to speed up planewave-based quantum Monte Carlo calculations

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ABSTRACT

The computational cost of quantum Monte Carlo (QMC) calculations of realistic periodic systems depends strongly on the method of storing and evaluating the many-particle wave function. Previous work by Williamson et al. (2001) [35] and Alfè and Gillan, (2004) [36] has demonstrated the reduction of the $O(N^3)$ cost of evaluating the Slater determinant with planewaves to $O(N^2)$ using localized basis functions. We compare four polynomial approximations as basis functions – interpolating Lagrange polynomials, interpolating piecewise-polynomial-form (pp-) splines, and basis-form (B-) splines (interpolating and smoothing). All these basis functions provide a similar speedup relative to the planewave basis. The pp-splines have eight times the memory requirement of the other methods. To test the accuracy of the basis functions, we apply them to the ground state structures of Si, Al, and MgO. The polynomial approximations differ in accuracy most strongly for MgO, and smoothing B-splines most closely reproduce the planewave value for of the variational Monte Carlo energy. Using separate approximations for the Laplacian of the orbitals increases the accuracy sufficiently to justify the increased memory requirement, making smoothing B-splines, with separate approximation for the Laplacian, the preferred choice for approximating planewave-represented orbitals in QMC calculations.

1. Introduction

Quantum Monte Carlo (QMC) methods can accurately calculate the electronic structure of real materials [1–3]. The two most commonly used QMC methods for zero temperature calculations are variational Monte Carlo (VMC), which can compute expectation values of operators for optimized trial wave functions, and fixed-node diffusion Monte Carlo (DMC), which improves upon VMC results by using the imaginary-time evolution operator to project the trial wave function onto the ground state subject to the fixed-node boundary condition [4]. QMC has been used to calculate a variety of properties such as cohesive energies, defect formation energies, and phase transition pressures [5–32]. The accuracy is limited mostly by

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the fixed-node approximation [4,22] and the computational power required to reduce statistical uncertainty (the subject of this paper).

Minimizing the time for a QMC calculation of a property (e.g., energy) to a given statistical accuracy requires minimizing the evaluation cost of the orbitals – used in the trial wave function $\Psi(\mathbf{R})$ – at each sampling point $\mathbf{R}$ of the electron coordinates. The QMC energy, E_{QMC}, is a weighted average of the *local energy*,

$$E_L(\mathbf{R}) = \frac{H\Psi(\mathbf{R})}{\Psi(\mathbf{R})}, \tag{1}$$

at N_{MC} stochastically-chosen configurations:

$$E_{\text{QMC}} = \frac{1}{N_{\text{MC}}} \sum_{i=1}^{N_{\text{MC}}} w_i E_L(\mathbf{R}_i). \tag{2}$$

The statistical uncertainty in E_{QMC} is proportional to $1/\sqrt{N_{\text{MC}}}$. Thus, repeated evaluation of the wave function $\Psi(\mathbf{R})$ and the Hamiltonian H acting on the wave function, which requires both the wave function and its first and second derivatives, reduces the statistical uncertainty in the calculated property. The root-mean-square fluctuation of the local energy in VMC

$$\sigma_{\text{VMC}} = \sqrt{\frac{1}{N_{\text{MC}}} \sum_{i=1}^{N_{\text{MC}}} (E_L(\mathbf{R}_i) - E_{\text{VMC}})^2} \tag{3}$$

indicates the quality of $\Psi(\mathbf{R})$ because the individual local energies equal the average when $\Psi(\mathbf{R})$ is an exact eigenfunction of H. QMC simulations frequently use the Slater–Jastrow form of the wave function [1], $\Psi(\mathbf{R}) = J(\mathbf{R})D(\mathbf{R})$, where $J(\mathbf{R})$ is a Jastrow factor [33] (in this work, a simple electron–electron Jastrow with no free parameters is used to impose the electron–electron cusp condition) and $D(\mathbf{R})$ is a Slater determinant [34] of single-particle orbitals.

The orbitals used in QMC wave functions typically come from density-functional or Hartree–Fock calculations and, in periodic systems, are Bloch functions of the form

$$\phi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{4}$$

where $u_{n\mathbf{k}}(\mathbf{r})$ has the periodicity of the crystal lattice, n is the band index, and $\mathbf{k}$ the crystal momentum. The periodic function, $u_{n\mathbf{k}}(\mathbf{r})$, is represented by a linear combination of basis functions. Frequently QMC calculations are performed using simulation cells larger than the primitive cell to reduce Coulomb finite-size errors. However, since $u_{n\mathbf{k}}(\mathbf{r})$ is periodic in the primitive cell, representing it by basis-function expansions in just the primitive cell is sufficient to simulate larger cells.

The computational cost per N-electron Monte Carlo move of evaluating the Slater determinant is $O(N^3)$, when spatially-extended basis functions are used to represent the orbitals, since N orbitals are evaluated for each of the N electrons, and each orbital is a sum over $O(N)$ basis functions. Spatially-localized basis functions avoid the linear scaling of the number of basis functions with system size since only those basis functions that are non-zero at a given point contribute to the wave function value at that point, resulting in $O(N^2)$ scaling.

Planewaves, despite their undesirable scaling, are a popular choice for basis functions for the density-functional and Hartree–Fock methods because of their desirable analytic properties. The advantage of a planewave representation is that planewaves form an orthogonal basis, and, in the infinite sum, a complete single-particle basis. Thus, adding more planewaves to a truncated basis (as is always used in practice) systematically improves the wave function representation towards the infinite single-particle basis limit. The energy of the highest frequency planewave included in the sum, the cut-off energy $E_{\text{cut}} = \hbar^2 {G_{\text{cut}}}^2/2m_{\text{e}}$, characterizes a given truncated planewave basis by setting the smallest length scale about which the wave function has information. Thus, a planewave-based orbital ϕ_{PW} is a sum over each planewave $\mathbf{G}$ below the cutoff multiplying a real- or complex-valued coefficient $c_{\mathbf{G}n\mathbf{k}}$ unique to that planewave, the band index n, and the crystal momentum $\mathbf{k}$:

$$u_{n\mathbf{k}}(\mathbf{r}) = \phi_{\text{PW}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}n\mathbf{k}} \exp(\imath \mathbf{G}\cdot\mathbf{r}). \tag{5}$$

Williamson et al. [35] first applied the pp-form spline interpolation method to approximate planewave-based orbitals by localized basis functions in QMC calculations. They report an $O(N)$ reduction in the time scaling. Alfè and Gillan [36] introducing the related method of B-spline approximation in QMC, report significant reduction in the calculation time while maintaining planewave-level accuracy.

This work compares the three methods previously applied to QMC (pp-splines [35], interpolating B-splines [37], and smoothing B-splines [36,38]) with a fourth method (Lagrange polynomials) originally implemented by one of us in QMC but heretofore unpublished. Section 2 introduces, compares and contrasts the four methods. Section 3.1 compares the accuracy of the polynomial methods in reproducing the QMC energies and fluctuations in the local energy relative to the corresponding values from the planewave expansion. Section 3.1 also studies whether it is advantageous to construct separate approximations for the gradient and the Laplacian of the orbitals. Section 3.2 compares the time cost in QMC calculations of