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Efficient localized basis set for quantum Monte Carlo calculations on condensed matter

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We present an efficient scheme for representing many-body wave functions in quantum Monte Carlo (QMC) calculations. The scheme is based on B splines (blip functions), which consist of localized cubic splines centered on the points of a regular grid. We show that blip functions are unbiased, systematically improvable, and conveniently obtained from any standard plane-wave density functional theory (PW-DFT) code, and therefore provide a convenient and natural interface between PW-DFT and QMC calculations. We present tests on a 16-atom system of Si in the β-tin structure, and on 2- and 8-atom systems of MgO in the NaCl structure. We show that already with such small systems the speed-up of blip functions with respect to plane waves is between one and two order of magnitudes, without compromising the accuracy.

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The quantum Monte Carlo (QMC) technique[1] is becoming one of the standard ways of studying condensed matter, because its accuracy is generally better than that of widely used techniques such as density functional theory (DFT). It has been applied to a wide range of problems, including the reconstruction of semiconductor surfaces,[2] the energetics of point defects in insulators,[3] optical excitations in nanostructures,[4] and the energetics of organic molecules.[5] At present, one of the obstacles to the more general use of QMC is its large demand on computer time. The choice of basis set has a significant effect on computer requirements. We propose and test here a basis set that has many of the properties of plane waves, currently widely used in DFT calculations, but with the advantage of being localized. We shall show that this localized basis achieves essentially the same accuracy as plane wave basis sets, but is very much faster for QMC calculations.

In QMC, the trial many-body wave function $\Psi_{\mathrm{T}}(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ consists of a Slater determinant D—or more generally a linear combination of Slater determinants—of single-electron orbitals $\psi_n(\mathbf{r}_i)$ multiplied by a parametrized Jastrow correlation factor $J(\mathbf{r}_1,\ldots,\mathbf{r}_N)$. In the variational Monte Carlo technique (VMC), J is "optimized" by varying its parameters so as to reduce the variance of the "local energy" $\Psi_{\mathrm{T}}^{-1}(\hat{H}\Psi_{\mathrm{T}})$, where $\hat{H}$ is the many-electron Hamiltonian. Since VMC by itself is not usually accurate enough, the optimized Ψ_{T} produced by VMC is used in the diffusion Monte Carlo technique (DMC), which achieves the exact ground state within the fixed nodal structure imposed by the Slater determinant D. At each QMC step it is necessary to evaluate $\Psi_{\mathrm{T}}(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ in each of the replicas (QMC "walkers"), which involves the evaluation of the single electron orbitals $\psi_n(\mathbf{r}_i)$. A crucial issue in the efficiency of the calculations is therefore the representation of $\psi_n(\mathbf{r}_i)$. One common approach is using plane waves (PW). The big advantages of PW are that their accuracy is systematically improvable (by increasing the PW cutoff) and they are unbiased. Moreover, many DFT codes are written in terms of PW, so the technology is highly developed and easily accessible. However, PW are not well suited for QMC calculations because for the evaluation of each $\psi_n(\mathbf{r}_i)$ one has to sum over all PW in the system. Since this has to be done for M orbitals and N electrons, with M proportional to N, the cost of evaluating the many-body wave function involves $O(N^3)$ operations, with a prefactor depending on PW cutoff, which can be very large for "hard" systems, like MgO. The storage required for a PW representation is proportional to N^2.

This problem with PW can be overcome by using localized basis sets. One possibility is to use Gaussians, but the drawback is that they are biased and generally difficult to improve systematically. An option which combines the best of both worlds is to use a B-splines basis (blip functions), already proposed for $O(N)$ DFT calculations.[6] Here we propose and test the use of blip functions in QMC calculations. We will show that blip functions share all the advantages of PW, i.e., are systematically improvable and unbiased. They are also closely connected with PW, and can therefore be obtained from PW-DFT codes. However, they are localized; therefore the evaluation of each orbital $\psi_n(\mathbf{r}_i)$ has a cost which is independent of the size of the system and indeed of blip-grid spacing (connected to the PW cutoff). The storage required for blip functions is not much worse than PW and has the same $O(N^2)$ scaling. The B-spline basis that we will describe appears to have something in common with the spline basis set used in recent QMC calculations by Williamson *et al.*,[7] though the technical details of their basis were not reported.

As described in detail elsewhere,[6] the blip functions consist of localized cubic splines centered on the points of a regular grid, each function being nonzero only inside a region extending two grid spacings in each direction from its center. For a cubic grid spacing a, the blip function $\Theta_s(\mathbf{r})$ centered on the grid point at position $\mathbf{R}_s=(X_s,Y_s,Z_s)$ is given by

$$\Theta_s(\mathbf{r}) = \phi((x-X_s)/a)\,\phi((y-Y_s)/a)\,\phi((z-Z_s)/a), \qquad (1)$$

where $\phi(\xi)$ is

$$\begin{aligned}\phi(\xi) &= 1-\frac{3}{2}\xi^2+\frac{3}{4}|\xi|^3, \quad 0 \leqslant |\xi| \leqslant 1\\ &= \frac{1}{4}(2-|\xi|)^3, \quad 1 \leqslant |\xi| \leqslant 2\\ &= 0, \quad |\xi| \geqslant 2. \end{aligned} \tag{2}$$

The function and its first two derivatives are continuous, discontinuities appear only in the third derivative, and all higher derivatives are zero. Each single-particle orbital is then represented as

$$\psi_n(\mathbf{r}) = \sum_s a_{ns}\Theta_s(\mathbf{r}). \tag{3}$$

For any position **r**, there are only 64 nonzero blip functions, whatever the nature and size of the system, so that the number of operations to compute $\psi_n(\mathbf{r})$ is the same for any material.

The close relationship between *B*-splines and PW has been discussed elsewhere.[6] In the PW representation, the single-particle orbitals are given by

$$\psi_n(\mathbf{r}) = \sum_{\mathbf{k}} c_{n\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{4}$$

where the wave vectors **k** go over the reciprocal lattice vectors of the superlattice, with k less than the PW cutoff k_{max}. The relationship between the PW coefficients $c_{n\mathbf{k}}$ and the blip coefficients $a_{n\mathbf{s}}$ can be understood by considering blip waves $\chi_{\mathbf{k}}(\mathbf{r})$ defined by

$$\chi_{\mathbf{k}}(\mathbf{r}) = \sum_s e^{i\mathbf{k}\cdot\mathbf{R}_s}\Theta_s(\mathbf{r}). \tag{5}$$

For small k, the $\chi_{\mathbf{k}}(\mathbf{r})$ are essentially identical to plane waves $\exp(\mathbf{k}\cdot\mathbf{r})$, apart from a **k**-dependent factor $\gamma_{\mathbf{k}}$:

$$e^{i\mathbf{k}\cdot\mathbf{r}} \simeq \gamma_{\mathbf{k}}\chi_{\mathbf{k}}(\mathbf{r}). \tag{6}$$

The factor $\gamma_{\mathbf{k}}$ is the Fourier transform of a single blip function $\Theta(\mathbf{r})$ and is given by $\gamma_{\mathbf{k}}=\gamma_{k_x}\gamma_{k_y}\gamma_{k_z}$, where $\mathbf{k}=(k_x,k_y,k_z)$ and

$$\gamma_k = \frac{3}{k^4}(3-4\cos k+\cos 2k). \tag{7}$$

At larger k, the $\chi_{\mathbf{k}}(\mathbf{r})$ differ significantly from $\exp(\mathbf{k}\cdot\mathbf{r})$, as they must, because $\chi_{\mathbf{k}}(\mathbf{r})$ is periodic in **k** space: the number of independent $\chi_{\mathbf{k}}(\mathbf{r})$ functions is equal to the number of sites on the blip grid.

There is a "natural" choice of blip grid spacing a, given by $a=\pi/k_{\mathrm{max}}$. With this choice, the region $k \approx k_{max}$, where blip waves and plane waves differ most, is the region where the plane-wave coefficients $c_{n\mathbf{k}}$ are very small. However, the precision with which blip waves reproduce plane waves in the region $k < k_{max}$ can always be improved by refining the blip grid.

The procedure to obtain the blip coefficients a_{ns} from the plane-wave coefficients of orbitals $\psi_n(\mathbf{r})$ obtained from a DFT calculation is straightforward. For the relationship between blip waves and plane waves [see Eqs. (3), (4), and (7)], it follows that

$$a_{ns} = \sum_{\mathbf{k}} c_{n\mathbf{k}}\gamma_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_s}. \tag{8}$$

The coefficients a_{ns} can therefore be evaluated using fast Fourier transform routines.

We have implemented blip functions in the appropriately modified CASINO code.[8] To test the implementation we present now three cases in which we compare the energy and the standard deviation in VMC and DMC calculations performed using PW or blip-function representations of the single-particle orbitals. Calculations with blip functions are presented for two values of the grid spacing, the *natural grid* spacing $a=\pi/k_{\mathrm{max}}$, and a two times finer grid obtained with $a=\pi/2k_{\mathrm{max}}$. Results are reported in Table I. All calculations have been performed at the Γ point.

The first case is a 16-atom cell of silicon in the β-tin structure (this system was chosen because there is already considerable QMC experience with Si, and because we are currently using QMC to investigate the relative energetics of the diamond and β-tin structures of Si). The single-particle orbitals have been obtained using the PWSCF code,[9] with Hartree-Fock pseudopotentials (*p* channel chosen to be the local part) and PW cutoff energy of 15 Ry. VMC calculations are reported for 3.2×10^6 steps of length 1 a.u. in all three cases. No Jastrow factor has been used for these VMC calculations. We found it useful to perform these tests without the Jastrow factor because it enabled us to make cross-checks of some individual components of the energy with DFT calculations. DMC calculations have been performed using 320 walkers for 10 100, 12 700, and 10 100 steps of length 0.03 a.u. for PW and blip-function calculations with the coarse and the fine grid spacing, respectively. Diffusion to the ground state is already achieved after ≈100 steps. In VMC the natural grid is not dense enough for this system, with the largest difference being in the kinetic energy (of ≈0.06 eV/atom). The standard deviation on the energy is also slightly larger. However, with the fine grid the blip-function results agree identically with the PW ones within a statistical error of only a few meV/atom. In Table I we also report the time taken to perform one VMC step on an Origin 3000 machine. Already for this small system, with such a modest PW cutoff, the speed-up with blip functions is almost a factor of 6. The timings between the two blip-function calculations should in principle be identical, the small difference between the two is probably due to the larger sparsity in memory of the blip coefficients a_{ns} for the case with a finer grid, and we found that this is machine dependent. For DMC the computational speed-up is more that a factor of 10, and the energy is already correct with the natural grid, which means that the nodal surface is essentially the same as the PW one already with the natural grid.

The second test we performed was a perfect crystal of MgO in its zero-pressure NaCl structure. The unit cell in this case contained only 2 atoms and had face-centered-cubic (fcc) geometry. Single-particle orbitals were obtained again using the PWSCF code, with Hartree-Fock pseudopotentials (*d* channel chosen as the local part for both Mg and O) and a PW cutoff of 200 Ry. No Jastrow factor has been used in these calculations. VMC calculations have been done with

TABLE I. Comparisons of the various components of the total energy (in eV/atom) and timings between VMC and DMC for a 16-atom Si system in the β-tin structure, and an MgO crystal in the NaCl structure. Standard deviation of the total energy σ (eV/atom) is also reported. The MgO crystal has been simulated using a 2-atom face-centered-cubic cell and an 8-atom simple-cubic cell. PW calculations have been performed with a cutoff energy of 15 Ry for Si and 200 Ry for MgO. Blip calculations have been performed using two different grid spacings: $a=\pi/k_{\mathrm{max}}$ and $a=\pi/2k_{\mathrm{max}}$, where k_{max} is the modulus of the largest PW vector.

		PW	Blips ($a=\pi/k_{\mathrm{max}}$)	Blips ($a=\pi/2k_{\mathrm{max}}$)
Si β-tin, 16 atoms				
VMC				
	E_{kin}	43.864(3)	43.924(3)	43.862(3)
	E_{loc}	15.057(3)	15.063(3)	15.058(3)
	E_{nl}	1.533(3)	1.525(3)	1.535(3)
	E_{tot}	−101.335(3)	−101.277(3)	−101.341(3)
	σ	4.50	4.74	4.55
	T (s/step)	1.83	0.32	0.34
DMC				
	E_{tot}	−105.713(3)	−105.711(4)	−105.715(4)
	σ	2.29	2.95	2.38
	T (s/step)	2.28	0.21	0.25
MgO-NaCl, 2 atoms, fcc cell				
VMC				
	E_{kin}	199.449(24)	199.465(15)	199.418(15)
	E_{loc}	−239.899(27)	−239.861(15)	−239.855(15)
	E_{nl}	−26.906(12)	−26.889(8)	−26.902(8)
	E_{tot}	−224.527(4)	−224.465(3)	−224.523(2)
	σ	28.7	35.8	28.3
	T (s/step)	101×10^{-3}	8.3×10^{-3}	8.9×10^{-3}
DMC				
	E_{tot}	−228.429(10)	−228.433(7)	−228.427(9)
	σ	22.1	28.9	22.3
	T (s/step)	89×10^{-3}	7.1×10^{-3}	7.5×10^{-3}
MgO-NaCl, 8 atoms, sc cell				
VMC				
	E_{kin}	178.349(49)	178.360(22)	178.369(22)
	E_{loc}	−225.191(50)	−225.128(24)	−225.177(23)
	E_{nl}	−17.955(25)	−17.974(11)	−17.976(11)
	E_{tot}	−227.677(8)	−227.648(4)	−227.669(4)
	σ	14	15	14.5
	T (s/step)	7.8	5.6×10^{-2}	7.1×10^{-2}

3.36×10^{7}, 1.6×10^{8}, and 1.6×10^{8} steps of length 0.3 a.u. for PW and the two blip functions cases. DMC calculations have been performed using 1600 walkers for 10.79×10^{4}, 23.98×10^{4}, and 11.53×10^{4} steps of length 0.005 a.u. for the three cases.[10] Diffusion to the ground state is achieved after the first few hundred steps. Similarly to the previous case, blip-function VMC energies and standard deviation agree identically with those obtained using PW for the dense blip grid, and the speed-up obtained with blip functions is more than a factor of 10. DMC energies are also in this case correct already when the coarse grid is used, but the variance is significantly improved when the fine grid is used.

Finally, the third test consists of the same MgO crystal simulated in a simple-cubic (sc) cell containing 8 atoms. Single-particle orbitals were obtained in analogy to the previous case, i.e., same pseudopotential and same PW cutoff of 200 Ry. No Jastrow factor has been used. VMC calculations have been done with 0.32×10^{6}, 1.6×10^{6}, and 1.6×10^{6} steps of length 0.3 a.u. for PW and the two blip-function cases. The important thing to notice in this case is the speed-up obtained with blip functions, which is over two order of magnitudes. We have not attempted DMC calculations as they would be impractical for the PW case.

We note that despite we have chosen to use PW cutoffs of 15 Ry and 200 Ry for Si and MgO, respectively, we found that by using a much larger cutoff energy (typically 32 Ry for Si and 500 Ry for MgO) the variance of the energy can be further significantly improved. Of course, increasing the PW cutoff leads to a direct increase in the PW computational time, but has hardly any effect in the calculations that employ blip functions. We have also found that by using a much larger PW cutoff the blip-function natural grid is already accurate enough, as expected.

We have presented here a robust and efficient scheme based on *B*-splines to represent the trial wave functions in QMC calculations. We have shown that this scheme shares all the advantages of plane waves, but offers a much better scaling behaviour with respect to the number of atoms in the system and the hardness of the pseudopotentials used in the calculations. This scheme has been implemented in the CASINO code,[8] and we have presented tests on three different cases. The largest system considered here (in terms of number of plane waves) was an MgO crystal in the NaCl structure simulated with a sc unit cell containing 8 atoms. We have shown that already for this relatively small system the speed-up obtained using blip functions is over a factor of 100. Since *B*-splines can easily be obtained from PW, they also provide a natural and convenient interface between QMC and PW-DFT codes. Moreover, this technique can be used in conjunction with “linear-scaling” techniques for QMC calculations, as reported elsewhere.[7,11] We conclude by noting that we are now attempting to calculate the formation energy of a Schottky defect in MgO using a cell containing 54 atoms. This calculation would be impossible to perform if we had to use PW (results will be reported elsewhere[12]).

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[10] With the choice of 1 a.u. and 0.3 a.u. for VMC time steps for Si and MgO, respectively, the probability of accepting the move is roughly 50% in both cases. The requirement of a shorter time step for MgO is due to the higher spacial variability of the wave functions for this system, also reflected by the need of a higher PW cutoff. For DMC, the time steps of 0.03 a.u. and 0.005 a.u. for Si and MgO, respectively, results in an undetectable time step error within the statistical error of a few meV/atom.

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