Efficient Real Space Solution of the Kohn-Sham Equations with Multiscale Techniques

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Abstract

We present a multigrid algorithm for self consistent solution of the Kohn-Sham equations in real space. The entire problem is discretized on a real space mesh with a high order finite difference representation. The resulting self consistent equations are solved on a heirarchy of grids of increasing resolution with a nonlinear Full Approximation Scheme, Full Multigrid algorithm. The self consistency is effected by updates of the Poisson equation and the exchange correlation potential at the end of each eigenfunction correction cycle. The algorithm leads to highly efficient solution of the equations, whereby the ground state electron distribution is obtained in only two or three self consistency iterations on the finest scale.

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The plane wave pseudopotential method has proven to be an excellent computational strategy for solving large scale electronic structure problems in condensed phases [1,2]. Notable strengths of the method are the ability to use fast Fourier transforms for updating the self consistency equations, lack of dependence of the basis on atom positions, and the clear control of convergence with the cutoff energy determined by the shortest wavelength mode. However, the method can encounter difficulties in treating widely varying length scales. The problems are especially severe for surfaces, clusters, or systems where the pseudopotential varies rapidly near the nucleus such as first row elements or transition metals. Also, charged systems present significant complications in a plane wave code. In recent years, considerable effort has been focused on alternative real space approaches utilizing finite elements or finite difference representations [3–10]. Advantages of these approaches include the ability to handle finite or periodic systems with equal effort and the locality of each iteration step. Locality leads to simplicity in developing domain decomposition parallel algorithms. In addition, it is relatively straightforward to implement adaptive grid refinement techniques in order to focus effort in spacial regions with large variations in the computed functions, for example near the nuclei in electronic structure computations [6,11]. Finally, representation directly in real space allows for the use of multigrid (MG) algorithms with their excellent convergence characteristics and scaling properties [12].

Several groups have employed MG algorithms for various portions of the solution process for self consistent electronic structure computations. White, et al. [3], developed a finite elements method for electronic structure which utilized an MG solver for the Poisson equation. Davstad [5] discretized the Hartree-Fock equations for diatomic molecules and solved the resulting two dimensional equations with a combination of the MG method and a Krylov subspace method for the coarsest grid equations. Gygi and Galli [6] proposed an adaptive coordinate approach which places increased resolution near the nuclei using curved grids. They solved the Poisson portion of the problem with MG techniques. Briggs, et al. [7] have developed an MG solver for the Kohn-Sham (KS) equations which utilizes MG methods for both the eigenvalue and Poisson problems. Their MG eigenvalue solver uses a double discretization approach and a linearized version of the MG method. Recently, Ancilotto, et al. [8] have presented a similar method for solution of the KS equations, and have applied the method to calculations on charged lithium clusters. They show that the MG approach is as accurate and more efficient than the corresponding Car-Parrinello method. Modine, et al. [9] developed an adaptive grid real space method which employs MG preconditioning for solution of the Poisson equation. Finally, we have developed high order MG methods for solving the KS equations including all the electrons [10]. Typical of the MG solvers to date is the requirement of 20 or more self consistency cycles to obtain convergence. In this letter, we present a high order multigrid algorithm for solving the self consistent Kohn-Sham equations which obtains convergence in an order of magnitude less numerical effort. The method utilizes the nonlinear Full Approximation Scheme (FAS), full multigrid (FMG) eigenvalue technique of Brandt, et al. [12] with the further inclusion of new methods for the self consistency portion of the problem.

The first step in development of the MG algorithm is the discretization of the problem in real space. Here we employ a high order finite difference representation. This approach has been shown to yield accurate results in pseudopotential and all electron calculations [4,10]. Consider the KS equations [13] in the Local Density Approximation (LDA):
\[ \left[ -\frac{1}{2} \nabla^2 + v_{eff}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \]  

(1)

The one-electron effective potential is:

\[ v_{eff}(\mathbf{r}) = v_{es}(\mathbf{r}) + v_{xc}(\rho(\mathbf{r})), \]

(2)

with the electrostatic portion of the potential (nuclear potential plus Hartree potential) given by:

\[ v_{es}(\mathbf{r}) = \sum_i \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \]

(3)

This potential can be obtained by real space numerical solution of the Poisson equation:

\[ \nabla^2 v_{es}(\mathbf{r}) = -4\pi \rho_{tot}(\mathbf{r}), \]

(4)

where \( \rho_{tot} \) is the total charge density on the grid due to the electrons and nuclei. The exchange-correlation potential in our spin restricted LDA computations is calculated with the VWN functional [14].

The Laplacian operator is discretized with a high order finite difference representation [15]. In the present work, a 12th order form is used. The high order expression yields a large gain in accuracy, which reduces the number of required grid points significantly. The same Laplacian is used for solution of the Poisson and KS equations, resulting in a consistent level of accuracy throughout the solver. Due to this consistent representation on all levels, the only parameter controlling the accuracy of the solution is the fine grid spacing \( h \). The other quantities are diagonal in the coordinate representation. The real space discretization scheme offers efficient calculation of electron densities and, as a result, the exchange-correlation potentials. The nuclear charge density is the discretized form of the Dirac delta function. The wavefunctions are vectors of length \( N_g \), the total number of grid points on a given level. Integration is performed by simple trapezoidal summation on the three dimensional domains. The boundary conditions on the orbitals for the finite systems examined here are set to zero, while the electrostatic potentials on the boundary are obtained via multipole expansion of the total charge density to quadrupole order.

The KS eigenvalue problem is nonlinear since one simultaneously solves for both the eigenvalues and the eigenfunctions. Therefore, we have employed the FAS eigenvalue technique of Brandt, et al. [16]. This method allows for solution of nonlinear problems with efficiencies similar to linear ones. Here we outline the FAS method of solution for the eigenvalue and Poisson problems. Both solvers are required for the self consistent problem.

The discrete equations can be represented on the current finest grid as:

\[ L^h U^h = f^h. \]

(5)

For the Poisson problem \( L^h \) is the finite difference Laplacian on the fine grid with spacing \( h \), \( U^h \) is the electrostatic potential \( v_{es}(\mathbf{r}) \), and \( f^h \) is \(-4\pi \rho_{tot}(\mathbf{r})\). Upper case for the potential denotes the exact numerical solution. Below, lower case implies the current approximation. In the eigenvalue equations \( U^h \) becomes \( U^h_i \), the eigenfunctions, where the index \( i \) indicates the orbital number. The eigenvalue operator \( L^h \) is the Hamiltonian minus \( \lambda_i \), where \( \lambda_i \) is
the eigenvalue for orbital $i$, and there is no source term $f^h$. The eigenvalue has the same value on all levels at convergence and therefore is not labeled with a grid size.

In the FAS method, the desired functions are represented on each grid level. The discrete equations on the coarse level, however, are modified by the inclusion of a defect correction term which is required to yield zero correction at convergence. Suppose we have an approximate solution on the fine grid $h$, $u^h$, which is obtained by relaxation sweeps on the grid:

$$L^h u^h = f^h.$$  

We have used Gauss-Seidel or Successive Over-Relaxation updates for these smoothing steps. The coarse grid problem with grid spacing $H = 2h$ can then be constructed as:

$$L^H u^H = I^H_f^h + \tau^H,$$  

where $I^H_f$ is the restriction operator which takes a local average of the fine grid function. Full weighting restriction is employed here, which weights the local points according to trapezoid rule integration. The defect correction is:

$$\tau^H = L^H I^H_f u^h - I^H_f L^h u^h.$$  

The coarse grid equation is iterated to obtain an improved solution at that level. In a two grid method, the fine grid function is then corrected via:

$$u^h \leftarrow u^h + I^h_H (u^H - I^H_f u^h),$$  

where $I^h_H$ is the interpolation operator. These operations can be recursively extended to yet coarser grids. By inclusion of multiple levels, errors of all wavelengths are rapidly damped in the fine grid function. The only change required on grids two or further from the finest grid is that an additional term $I^H_f \tau^h$ must be included in the defect correction to incorporate information from the previous level.

In solving the eigenvalue equations in KS theory, some additional components are required. On all grids except the coarsest, the orbital equations are updated just as outlined above. However, on the coarsest level, constraints must be imposed to maintain wavefunction separation. If one had the exact solution on a fine grid $U^h_i$ and then restricted the orbitals to the next coarser level, the functions would no longer be orthogonal. Hence, the constraints on the coarsest level can be implemented by solving a linear matrix equation:

$$\langle u^H_i, I^H_f u^h_j \rangle = \langle I^H_f u^h_i, I^H_f u^h_j \rangle.$$  

These equations, since they are implemented only on the coarsest scale, require very little computational overhead, and can be solved either via exact matrix inversion or by iterative methods. The matrix size is of order $q \times q$, where $q$ is the number of orbitals. The eigenvalue is also updated on the coarsest level by computing the Rayleigh quotient:

$$\lambda_i = \frac{\langle L^H_i u^H_i - \tau^H_i, u^H_i \rangle}{\langle u^H_i, u^H_i \rangle}.$$
Finally, the convergence can be improved by including subspace orthogonalization via Ritz projection. At the end of an MG correction cycle, a Gram-Schmidt orthogonalization is first performed on the finest level, followed by diagonalization of the Hamiltonian in the basis of the occupied orbitals:

\[ \omega^T L \omega z_i - \lambda_i z_i = 0 \]  

where \( \omega \) symbolizes the \( q \times N_g \) matrix of eigenfunctions on the grid, and the \( z_i \) are the coefficients used to improve the occupied subspace. This matrix problem is thus also of size \( q \times q \).

The FMG approach is initiated by first iterating the self consistent problem on the coarsest level used for the eigenvalue problem. The initial approximation for the eigenfunctions is a set of random numbers of magnitude one. The coarsest level is chosen so that the eigenvalues have the same ordering as on the finest level. For the systems studied here, a coarse grid of \( 8^3 \) or \( 17^3 \) is required, depending on the problem. The Poisson solver extends the levels up to a \( 3^3 \) grid where only the one central point is iterated. In most of these calculations the finest grid employed is of size \( 65^3 \), so the eigenvalue solver comprises three or four levels, while a total of six levels is utilized for the Poisson solver on the finest scale. During the initial iterations on the coarsest level, the eigenfunctions are first relaxed and orthogonalized via a Gram-Schmidt process, and then the potential is updated. Once an initial approximation is obtained on the coarse level, the solution is interpolated to the next finer level, where the MG correction cycles are initiated.

At the beginning of each MG V-cycle, the effective potential is updated once upon entry to the new finest level with the FAS method. Subsequently, the potential is updated at the end of each eigenfunction correction cycle; since the changes to the potential are relatively smooth, the potential corrections are performed with a simple V-cycle using the previous potential as input. A schematic diagram of the MG solver is presented in Figure 1. The Poisson equation is typically solved with only a few relaxation sweeps on the finest scale on either side of the V-cycle. During each eigenfunction correction cycle, the eigenfunctions are relaxed 3 times on each side of the V-cycle. The solution of the entire electrostatic portion of the problem thus requires similar computational effort as for the update of a single eigenfunction. This algorithm differs from those of Refs. \cite{7,8} by inclusion of updates of the eigenvalues and enforcement of the constraints on the coarsest level only without resorting to linearization of the equations.

We have explored two approaches for the eigenfunction correction cycles. In the first, each eigenfunction is carried through the V cycle starting with the lowest energy function, and the effective potential is updated at the conclusion of the cycle. This sequential method leads to a rapidly convergent effective potential since the low lying states are quickly stabilized. In the second approach, all eigenfunctions are corrected simultaneously, and the effective potential is updated upon conclusion of the V cycle. For small systems the first approach is preferred since the Poisson updates are quite inexpensive. However, as we discuss below, the scaling of the two approaches differs, and the second method is preferable for larger systems. Its convergence behavior is slightly less dramatic, requiring three or four self consistency updates as opposed to two for the first method. The algorithm can readily be adapted for either approach depending on the problem.

We have performed calculations on atoms, ions, and small molecules to test the conver-
gence and accuracy of the method. The numerical results presented here were obtained with the second approach discussed above. The convergence behavior is illustrated in Fig. 2 in calculations on the 4 electron Be atom and the 14 electron CO molecule. Comparison is made to recent MG and Car-Parrinello pseudopotential calculations [8] on the 8 valence electron C$_2$ molecule. The FAS-FMG approach leads to significant acceleration; we emphasize that the present calculations include the nuclear singularity in the effective potential, making it a more challenging scenario for convergence to the ground state. We computed total energies for atoms and ions to obtain atomic ionization potentials at the LDA-VWN level (Table I). The total energy obtained for the He atom is -2.8345 au vs. the exact value of -2.8348 au. The computations on the ions are performed with equal effort as for the neutral species, and the IP results are of satisfactory accuracy [16]. Finally, we present the eigenvalues of the CO molecule computed at the Xα level for comparison with previous numerical work [17] (Table I). The computation was performed on a large 129$^3$ domain since the dipole moment of CO is a sensitive function of the overall domain size. We obtained a dipole value of 0.25 D C−O$^+$ compared to the previous result of 0.24 D in fully converged numerical calculations [18], and 0.10 D in finite difference pseudopotential calculations [4]. As discussed in Ref. [3], the most severe errors in real space all electron calculations occur in the regions around the nuclei. The limitations on the accuracy of our uniform domain results is a consequence of these errors. Two improvements are suggested: inclusion of pseudopotential techniques to remove the core and/or local grid refinements in the neighborhood of the nucleus [4,11]. We have generalized a second order multigrid local mesh refinement method [19] to arbitrary order and will include these refinements in the KS solver in future work [11]. Since the refinements are truly local, they require only modest computational overhead.

To conclude, we discuss the scaling properties of the various steps in the FAS-FMG algorithm for the case where the orbitals span the whole domain. With $q$ orbitals and $N_g$ fine grid points in the domain, the scalings of the important components of the algorithm are as follows: relaxation of orbitals ($qN_g$), relaxation of potential ($N_g$), Gram-Schmidt process ($q^2N_g$), Ritz projection ($q^2N_g$ to construct the matrix and $q^3$ to solve), computation of the eigenvalues on the coarse grid ($qN^H_g$), and solution of the constraint equations on the coarse grid ($q^2N^H_g$ to construct the constraint matrix and $q^3$ to solve). The most costly portion of the algorithm for the small systems examined here is the relaxation step for the orbitals. For large systems where orbital localization is possible, each of the steps becomes linear scaling with the number of electrons. The two algorithms for implementing self consistency discussed above differ in that the first approach, while exhibiting stronger convergence to the ground state, leads to a $qN_g$ scaling which persists even with localized orbitals.

We have presented a new method for solution of the KS equations in real space which utilizes nonlinear multigrid techniques to solve the self consistent equations. The purpose has been to illustrate the rapid convergence behavior of the FAS-FMG algorithm in relation to other electronic structure methods. The efficiency is a result of the preconditioning on coarser levels and nonlinear treatment during the MG correction cycles. The combination of real space discretization with FAS-FMG multiscale techniques of solution leads to order of magnitude improvement in convergence behavior relative to other MG methods and the Car-Parrinello approach, and it should thus prove a useful numerical strategy for solving large scale electronic structure problems.

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TABLES

|                  | h   | Ref. 16 | FAS-FMG |
|------------------|-----|---------|---------|
| He→ He⁺          | 0.15| 0.969   | 0.974   |
| Li→ Li⁺          | 0.35| 0.198   | 0.193   |
| O→ O²⁺           | 0.12| 1.843   | 1.821   |

| Orbital         | Ref. 17 | FAS-FMG |
|-----------------|---------|---------|
| 1s(O)           | -18.745 | -18.832 |
| 1s(C)           | -9.912  | -9.940  |
| σ(2s)           | -1.045  | -1.060  |
| σ*(2s)          | -0.489  | -0.494  |
| π(2p)           | -0.413  | -0.407  |
| σ(2p)           | -0.304  | -0.302  |

TABLE I. Calculations on Atomic Ionization Potentials and Eigenvalues for the CO molecule.
The LDA calculations of Ref. 16 used a form for the correlation energy which interpolated between
the Wigner form for low densities and the Gell-Mann/Brueckner form at high densities. For the
CO calculation, the grid spacing was $h = 0.1335 au$ and the bond length was taken as 1.13Å. All
energies are in hartrees.
FIG. 1. The FMG scheme. The fine grid solution is initiated with the interpolated functions from the coarse grid approximation (bottom of figure). At the end of each V cycle the potential is updated (indicated by x).

FIG. 2. Convergence behavior. The top curve is the Car-Parrinello result of Ref. 8. The second curve is the MG result of Ref. 8. The next is our result for the CO molecule with the FAS-FMG solver. The bottom curve is the FAS-FMG result for the Be atom.