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J.-L. Fattebert

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# Adaptive Localization Regions for $O(N)$ Density Functional Theory calculations

**J.-L. Fattebert**

Center for Applied Scientific Computing, Lawrence Livermore National Laboratory, Livermore, CA 94551

E-mail: fattebert1@llnl.gov

**Abstract.** A linear scaling approach for general and accurate pseudopotential Density Functional Theory calculations is presented. It is based on a Finite Difference discretization. Effective  $O(N)$  scaling is achieved by confining the orbitals in spherical localization regions. To improve accuracy and flexibility while computing the smallest possible number of orbitals, we propose an algorithm to adapt localization regions during computation. Numerical results for a polyacetylene chain and a magnesium oxide ring are presented.

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## 1. Introduction

One way to think about linear scaling approaches based on localized orbitals — such as the one described in this paper — is to consider those as Linear Combination of Atomic Orbitals (LCAO)-type methods with flexible orbitals, adapted to their environment. Localized orbitals are expanded in a generic numerical basis set which can be systematically improved to achieve a prescribed accuracy.

The Plane Waves (PW) method is an example of a systematically improvable basis set commonly used in pseudopotential Density Functional Theory (DFT) simulations, in particular when one wants to avoid any bias due to the numerical basis set, when high numerical accuracy is needed or when dealing with systems such as metals with almost free electrons. The numerical solution of the Kohn-Sham equations — eigenstates — is expanded directly in terms of  $M$  elementary Plane Waves and the accuracy of the solution can be systematically improved by enlarging the basis set. In contrast, Linear Combination of Atomic Orbitals (LCAO) type method use a numerical basis set made of atomic-like orbitals specific to the physical system one tries to simulate and the solution is expressed as a linear combination of those. In the PW approach, because the numerical basis set is quite larger than in LCAO, one can limit the calculation to just the few eigenstates we are interested in —  $N$  occupied states. In that case, the major computational work is in determining these eigenstates —  $O(M \cdot N^2)$  scaling with  $M \gg N$  — and the work in the  $N$ -dimensional subspace defined by those states — such as inverting the overlap matrix or determining the occupation numbers by diagonalizing an  $N \times N$  matrix — becomes quite small in comparison ( $O(N^3)$ ). LCAO approaches in contrast can be viewed as methods dealing with a fixed and predetermined subspace, of dimension an order of magnitude

larger than  $N$ , in which one needs to determine the occupation in the form of a single particle Density matrix.

In this paper we focus on an  $O(N)$  complexity algorithm as an alternative to PW, sharing some of the goals and features with this reference approach, in particular using an unbiased and systematically improvable numerical basis set, and calculating the minimal number of electronic states needed in this basis set. Note that the PW basis set is just one example of a systematically improvable and unbiased numerical basis set. Alternative approaches such as Finite Differences or Finite Elements achieve the same goal, each with their pros and cons, and have been used successfully applied to DFT simulations [1, 2, 3, 4, 5]. In this paper we will use the Finite Difference approach as a discretization scheme. The algorithm described below could be easily combined with other real-space discretizations however. To reduce computational complexity we will introduce spherical localization regions (LR) in which the electronic states will be confined. Each state is described by values at each point of the finite difference grid inside a given localization region, *i.e.* by  $O(1)$  degrees of freedom. To keep the number of electronic states in the calculation as small as possible, we will allow the localization regions to adapt their locations and sizes according to their environment. Looking at localized orbitals linear scaling approaches as LCAO methods with a basis of flexible orbitals adapted to their environment, one realizes that one may be able to reduce the number of those orbitals by making them more flexible and still describe accurately  $N$  electronic wave functions. In this paper we explore the limit of this idea: including in the calculation a number of localized orbitals equal to the number  $N$  of electronic states we want to compute accurately.

Note that the idea of representing the electronic structure by floating orbitals was already proposed 40 years ago with the Floating Spherical Gaussian Orbital Model [6]. In this simple model, only 4 parameters per orbitals — center coordinates and radius — are optimized to minimize the total energy, while the Gaussian shape is fixed. In that perspective the model described in this paper additionally optimizes the shape of the orbitals, making use of today's much larger computer power and leading to a much greater accuracy.

Numerous ideas have been proposed in the last 15 years to achieve linear scaling in electronic structure calculations (see for instance [7]). A few of those approaches are closely related to our methodology and essentially try to achieve the same goal, that is linear scaling with PW accuracy using localized orbitals. Following the idea of Hernandez and Gillan [8], the CONQUEST code was developed using B-splines Finite Elements as the underlying numerical basis[9]. Note that this code also offer a fixed orbitals LCAO-like option. A similar approach, but using a Plane Wave-like basis set for localized orbitals was implemented in the ONETEP code[10]. Tsuchida and Tsukada [11] on the other hand used a Finite Elements discretization in conjunction with the Kim-Mauri-Galli functional. In contrast to the methodology presented below, those techniques, as well as the technique described in Ref.[12], use fixed localization regions centered on atoms. This lack of flexibility is compensated for by a larger number of localized orbitals.

In this paper we focus on the problem of defining appropriate localization regions in which to confine localized orbitals. We recently proposed an algorithm to automatically adapt the centers of localizations regions. It essentially boils down to a regular update of the localization centers using the center of charge of the confined orbital as new target. Such an approach presents several advantages over using fixed localization regions. In particular accuracy is improved by optimizing the positions of

localization regions. It also enables molecular dynamics simulations without spurious Pulay forces[13, 14]. In this paper we extend this idea and explore a new algorithm to adapt not only the position of the localization regions, but also their sizes. This is motivated by the fact that calculations going beyond the ground state of insulators often present some less localized Maximally Localized Generalized Wannier Functions (MLGWF), or a less peaked distribution of their spreads. Also in complex and multi-species systems, one can expect anomalous shapes for some MLGWF as observed for instance in amorphous silicon[15]. Another area where size adaptation could be quite useful in studying systems for which electronic structure properties vary significantly with system size and for which determining a priori the size of LR based on error measurement on smaller reference systems may not be adequate.

## 2. Computational Method

### 2.1. Linear scaling strategy

Our approach is based on the idea proposed in Ref. [12] and later extended in Ref. [13, 14]. The first step to achieve linear scaling is to express the DFT energy functional in terms of a set of general non-orthogonal orbitals  $\{\phi_i\}_{i=1}^N$  [16]:

$$\begin{aligned}
 E_{KS}[\{\phi_i\}_{i=1}^N] &= \sum_{i,j=1}^N K_{ij} \int_{\Omega} \phi_i(\mathbf{r}) (-\nabla^2) \phi_j(\mathbf{r}) d\mathbf{r} \\
 &+ \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{XC}[\rho] \\
 &+ \sum_{i,j=1}^N 2K_{ij} \int_{\Omega} \phi_i(\mathbf{r})(V_{ext}\phi_j)(\mathbf{r}) d\mathbf{r}.
 \end{aligned} \tag{1}$$

where  $\rho$  is the electronic density

$$\rho(\mathbf{r}) = 2 \sum_{i,j=1}^N K_{ij} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}). \tag{2}$$

The  $N \times N$  matrix  $K$  is a single particle density matrix which expresses the occupation of each electronic states for a set of general nonorthogonal orbitals. If only the occupied valence states are being included in the computation, it is simply  $S^{-1}$ , the inverse of the overlap matrix. The energy  $E_{XC}$  models the exchange and correlation between electrons.

Given an external potential  $V_{ext}$  — defined by the various atomic species, their respective positions and pseudopotentials — the ground state of the physical system is obtained by minimizing the energy functional (1). We discretize this energy functional on a uniform real-space mesh. We represent the orbitals, the electronic density and the potential by their values at each node of the mesh. To approximate the Laplacian operator, we use the Mehrstellen Finite Difference scheme[2].

To achieve an effective linear scaling, localization constraints on the orbitals are added to this minimization procedure. Namely we impose that each orbital strictly vanishes outside a specific spherical localization region. We also adapt the minimization algorithm to satisfy the constraints along the way. Our minimization procedure is based on the steepest descent directions preconditioned by multigrid. The

process is accelerated by a non-linear extrapolation scheme[13]. Note that we compute the matrix  $K$  in  $O(N^3)$  operations using a standard diagonalization procedure for an  $N \times N$  matrix. Because  $N$  is kept small by adapting the localization regions (see Section 2.3), operation on  $N \times N$  matrices remain relatively cheap for the range of values we are currently targeting ( $N$  up to 5000)

Restricting orbitals to confinement regions introduces some approximation since there is in general no solution to our original problem which satisfy exactly the localization constraints. This truncation error however decays rapidly with the size of the localization regions. We observed numerically an exponential convergence for both the energy and forces in various systems[13]. By choosing localization regions large enough one can even reduce truncation error to a quantity smaller than discretization. The minimum size of localization regions necessary to achieve a prescribed accuracy directly affects the crossover point, that is the minimal system size for which any gain can be achieved by an  $O(N)$  approach. Also, because the energy functional is no longer invariant under rotations inside the occupied space in the presence of localization constraints, local minimas are possible and have been observed[14].

## 2.2. Maximally Localized Generalized Wannier Functions

The concept of Maximally Localized Generalized Wannier Functions (MLGWF) is very useful in justifying and understanding  $O(N)$  approaches based on orbital localization. Given a position operator  $\hat{X}$ , one can define the center of charge associated with  $\hat{X}$  for an orbital  $\phi$  as

$$\bar{X}(\phi) = \langle \phi | \hat{X} | \phi \rangle. \quad (3)$$

The spread associated with the operator  $\hat{X}$  for the orbital  $\phi$  is defined by

$$\sigma_{\hat{X}}(\phi) = \left[ \langle \phi | \left( \hat{X} - \langle \phi | \hat{X} | \phi \rangle \right)^2 | \phi \rangle \right]^{1/2} \quad (4)$$

and quantifies the degree of localization of  $\phi$  around its center of charge  $\bar{X}(\phi)$ .

The spread functional

$$\sigma_{\hat{X}}^2(\{\phi_i\}_{i=1}^N) = \sum_{i=1}^N \sigma_{\hat{X}}^2(\phi_i) \quad (5)$$

expresses the total spread for the  $N$  orbitals  $\{\phi_i\}_{i=1}^N$ .

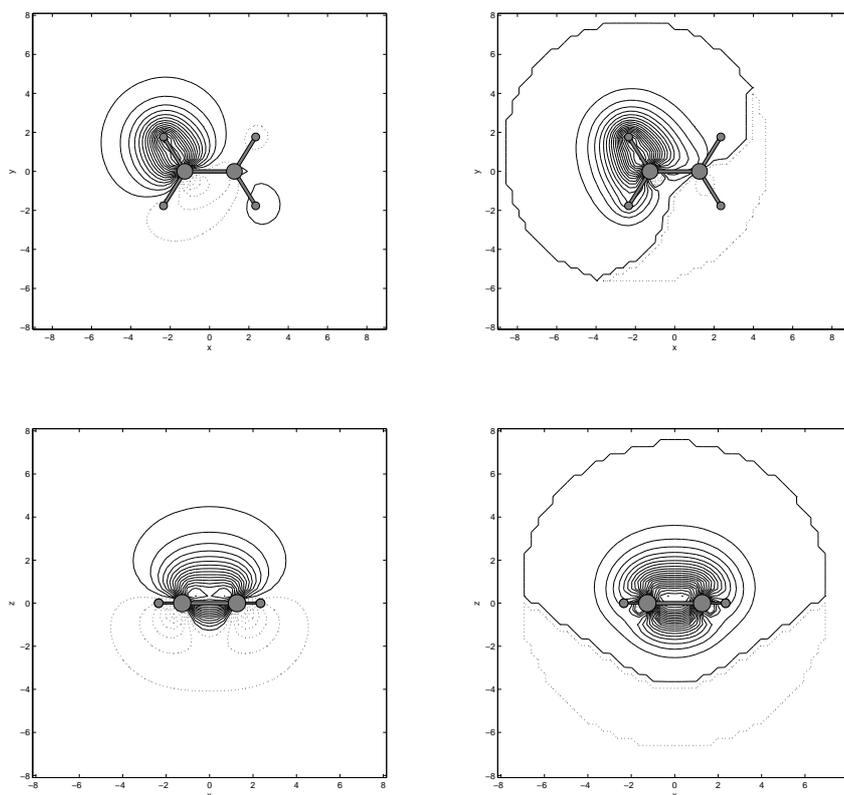
Now given a set of orthonormal functions  $\{\psi_i\}_{i=1}^N$ , we can define an orthogonal transformation

$$\phi_i = \sum_{j=1}^N a_{ij} \psi_j.$$

where  $a_{ij}$  are the matrix elements of an orthogonal matrix  $A$ . Finding a matrix  $A$  which minimizes the sum of the spread functional (5) associated with  $m$  position operators — positions operators for direction x, y, z typically —,

$$\sigma_{\{\hat{X}^{(k)}\}_{k=1}^m}^2(\{\phi_i\}_{i=1}^N) = \sum_{k=1}^m \sigma_{\hat{X}^{(k)}}^2(\{\phi_i\}_{i=1}^N) \quad (6)$$

can be formulated as a simultaneous diagonalization problem and efficiently solved using the algorithm proposed in Ref.[17]. The functions which minimize this spread functional — not unique in general — are by definition the Maximally Localized



**Figure 1.** Two types of MLGWF in  $C_2H_4$  (left) and the corresponding strictly localized orbitals obtained by  $O(N)$  scheme (right). Isovalues are orbital dependent. Dotted lines correspond to negative isovals. Isovalues for localized orbitals are chosen in such a way that the limit of the localization regions appear clearly.

Generalized Wannier Functions (MLGWF) introduced by Marzari and Vanderbilt[18]. For periodic boundary conditions, the position operator for extended systems proposed by Resta [19] should be used. To avoid introducing complex numbers, we use the equivalent six trigonometric operators proposed in Ref.[17] ( $m = 6$ ).

Being able to find a representation of the electronic subspace in terms of localized orbitals such as MLGWF justifies  $O(N)$  algorithms based on imposing localization constraints on orbitals. This is illustrated in Figure 1 where MLGWF and localized orbitals obtained by minimization under localization constraints are plotted side by side for the  $C_2H_4$  molecule. Their similarity is striking, even if MLGWF are orthogonal while localized orbitals are not.

### 2.3. Adaptive Localization Regions

To get a linear scaling algorithm through orbitals localization, one has to choose appropriately the localization regions (LR) in which the orbitals are going to be

confined. If the dimension of the subspace spanned by the set of localized orbitals is much larger than the number of occupied states  $N$ , that choice is less important since the larger number of degrees of freedom can compensate for the lack of accuracy of the underlying orbitals. The most straightforward solution is then to have orbitals localized in regions centered on atoms in numbers large enough to describe at least the valence states around each atom. Using such an approach, one may end up with trial subspaces that are much larger than  $N$ . Techniques usually used in LCAO algorithms can then be used to reduce complexity in determining the single particle density matrix  $X$  and fill up the occupied states [8]. Resulting unoccupied states usually have the role of a numerical buffer and the density of states for the highest energies is not to be considered physical[20].

Our current approach is different. As in the standard  $O(N^3)$  PW approach, we solve for and represent only the states we are interested in. To do that, we let the localization regions adapt to their environment, optimizing both their location and their size during a calculation. Based on the analogy between MLWF and localized orbitals, we use the centers of charge defined by (3) and spreads of the localized orbitals defined by (4) to iteratively update the localization regions. LR centers are moved towards centers of charge, while localization radii are rescaled to be proportional to the spread of the confined orbitals. To avoid a diverging total spread during the optimization process, the total volume of all the LR is kept fixed to a constant value  $V_0$ .

In summary, localization regions are adapted following this simple scheme:

*Until convergence, do:*

- Iteratively minimize functional (1) for fixed LR for a fixed number of iterations or until convergence to a certain tolerance is reached
- For each orbital  $\phi_i, i = 1, \dots, N$ , compute the  $m$  components of the centroids of charge,

$$Q_i^{(k)} = \langle \phi_i | \hat{X}^{(k)} | \phi_i \rangle, k = 1, \dots, m$$

and the spreads

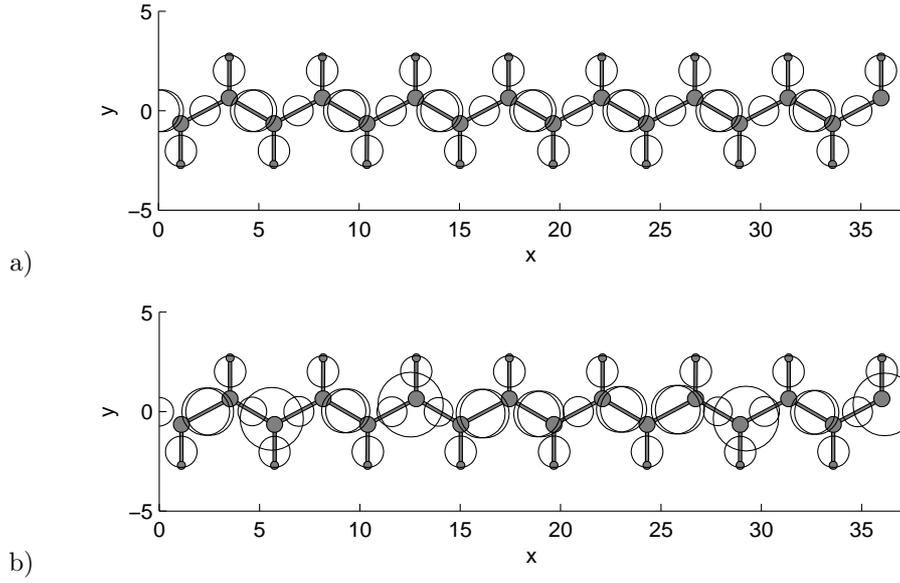
$$\sigma_i = \left[ \sum_{k=1}^m \langle \phi_i | \left( \hat{X}^{(k)} - Q_i^{(k)} \right)^2 | \phi_i \rangle \right]^{1/2}$$

- Move LR centers to  $\mathbf{Q}_i$ .
- Set LR radii to  $R_c^{(i)} = \alpha \sigma_i$  with  $\alpha$  such that  $(4\pi/3) \sum_{i=1}^N (R_c^i)^3 = V_0$ .

In a molecular dynamics simulation or geometry optimization, only one cycle of this algorithm is usually sufficient at every ionic step. But multiple iterations are required for a new configuration with no good initial guess.

### 3. Numerical results

To illustrate the algorithms described in this paper, we use a polyacetylene chain  $(C_2H_2)_8$  as a test system. This is a convenient system since it contains a small number of electrons but is large enough (periodic cell of length 37.12 Bohr along chain axis) to fully contain all the localization regions in our test and includes totally disconnected ones. It allows affordable  $O(N^3)$  reference calculations to compare with results of approximative  $O(N)$  scheme. We use the same geometry as used in other theoretical studies[21]. This system is made of 40 fully occupied valence states. We also consider

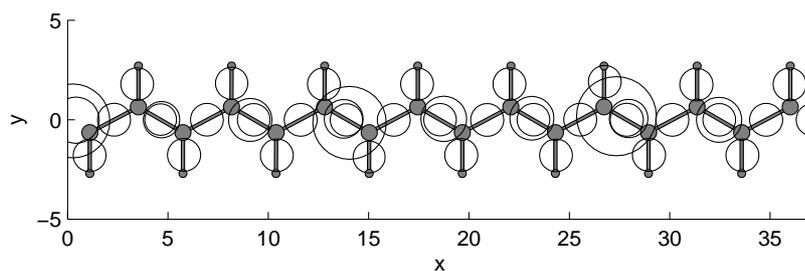


**Figure 2.** Projection in molecular plane of MLGWF for polyacetylene chain  $(C_2H_2)_8$ . Open circles have radii equal to half their MLGWF spread and are centered at Wannier centers. Circles with coincidental projections have been shifted for a better display. a) Number of MLGWF equal to number of fully occupied states (40). b) Same calculation with 3 additional empty states.

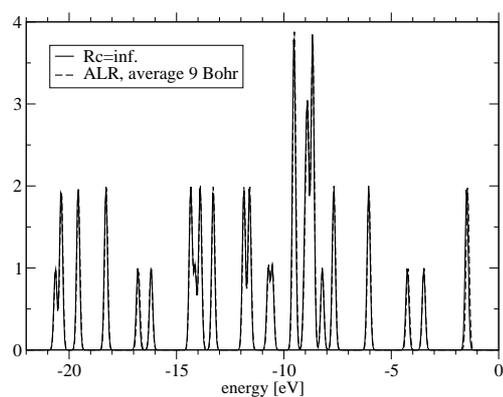
the lowest 3 empty conduction states which are fully localized on the molecule. We use the local density approximation (LDA) to model the exchange and correlation term.

We start by computing MLGWF for the subspace spanned by the 40 fully occupied states as well as for the subspace including 3 additional (unoccupied) states. Results are shown in Figure 2. The result obtained in the first case is quite natural: two MLGWF on each  $C-C$  bond, one on each  $C-C$  and  $C-H$  bond. When including 3 conduction states, the situation becomes more complicated.

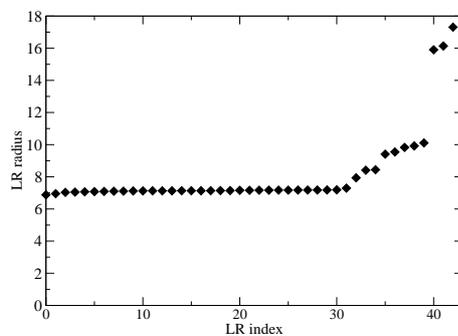
For the calculations with adaptive localization regions, we first compute the ground state of the system without any unoccupied states. LRs are centered at Wannier centers and have all a radius of 7 Bohr which is large enough to obtain an accurate Density of States. Using the electronic density from that first calculation, we compute the Kohn-Sham potential and freeze it before adding 3 additional states. Three additional LRs associated to these states are also added and centered on 3 carbon atoms as uniformly as possible. We then run our Adaptive Localization Algorithm with a total volume  $V_0$  corresponding to an average localization radius of 9 Bohr. This leads to localization radii that range from 7 to 17 Bohr, thus allowing wider spreads for some states while preserving the accuracy of the occupied states. Positions and spreads of optimized orbitals are shown in Figure 3. The resulting Density of States is plotted in Figure 4. It is almost undistinguishable from the reference  $O(N^3)$  calculation. The error on the band gap is  $0.022[eV]$ . The localization radii are shown in Figure 5. The localized orbital with the largest spread is shown in Figure 6. It is still quite localized with respect to the global system, but spread over 5 atoms unlike MLGWF for systems with no unoccupied states which typically spread



**Figure 3.** Positions and spreads of adaptive localized orbitals in polyacetylene ads.



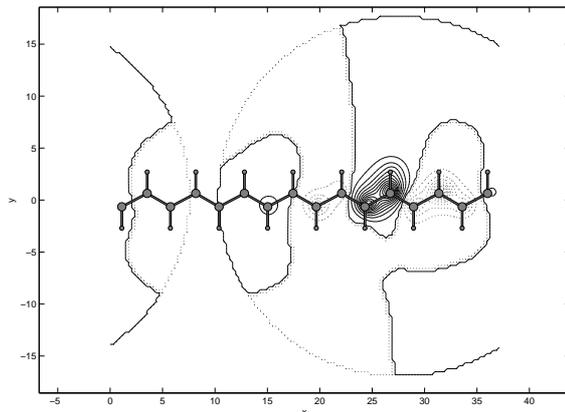
**Figure 4.** Density of States for polyacetylene chain  $(C_2H_2)_8$  with 3 unoccupied states. Comparison between  $O(N^3)$  calculation and adaptive localization regions approximation.



**Figure 5.** Polyacetylene chain  $(C_2H_2)_8$ : Radii distribution for LR (Localization Region) indices with 3 unoccupied states after adaptation. The average localization radius was 9 Bohr.

over one bond/two atoms.

As a second numerical example, we consider a magnesium oxide ring  $(MgO)_8$ . For this application, we use the PBE exchange and correlation functional. In our



**Figure 6.** Contour plot of adapted localized orbitals with widest spread for polyacetylene chain  $(C_2H_2)_8$  calculation with 3 unoccupied states and an average localization radius of 9 Bohr.

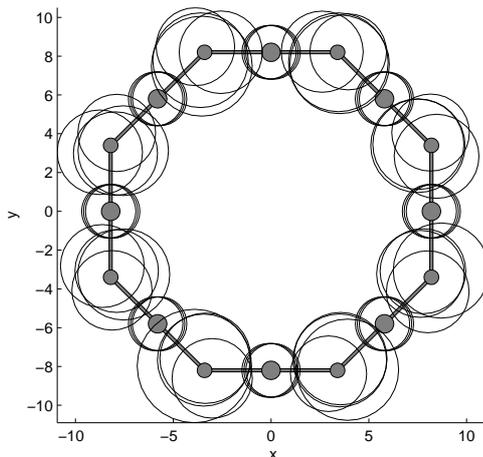
**Table 1.** Numerical results for  $(MgO)_8$  ring: accuracy and range of localization radius in atomic units (a.u.). The error is defined as the difference with the results obtained without localization constraints on the electronic wave functions.

average adaptive radius	6 [Bohr]	7 [Bohr]	8 [Bohr]
error energy [Ha/atom]	$3.4 \cdot 10^{-3}$	$9.6 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$
average error forces[a.u.]	$2.7 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	$3.5 \cdot 10^{-4}$
range localization radius [Bohr]	4.0 - 9.5	5.0 - 10.1	5.5 - 11.7

pseudopotential approximation, we treat the semicore 2p states of the Mg atoms explicitly which leads to a total of 56 doubly occupied orbitals for the 16 atoms ring. One major difference between this system and the previous example is the ionic nature of the chemical bonds between oxygen and magnesium atoms. The ratio between maximum and minimum spreads of MLGWF is about 2 when considering just the unoccupied states. The ground state computation of this system can benefit from adaptive localization regions. Localization regions obtained for this system are plotted in Figure 7. Table 1 shows the error measured on the energy and forces for calculations with 3 different localization sizes. It shows in particular an exponential decay of the error with the average radius of the localization regions.

#### 4. Concluding remarks

The Finite Difference approach provides an appropriate framework to achieve Plane waves accuracy and linear scaling using localized orbitals. Flexible adaptive localization regions enable calculation of the states of interest only, without the need to use a larger subspace including many unoccupied states with no physical significance. Adapting positions seems more important than adapting sizes for simple problems where most MLGWF have similar spreads. Localization regions adaptivity



**Figure 7.** Projection in molecular plane of positions and radii of adaptive localized orbitals (open circles) in  $(MgO)_8$  ring for an average localization radius of 8 Bohr. Radii have been rescaled by a factor 0.5 for a better display.

in size becomes however important in complex multi-species systems or when some conduction states need to be computed accurately.

While we have a good general understanding of the electronic structure representation in terms of MLGWF for the valence states in insulating systems, the situation is more complicated when we go beyond ground state calculations of perfect crystals or organic molecules. Having a better understanding of the electronic structure representation by a set of localized orbitals such as MLGWF in general may be key to design efficient linear scaling algorithms applicable to general and complex systems. Finally, error estimators functions of truncations radii would be extremely useful in an automatic LR adaptation scheme. In particular for systems for which electronic structure properties vary significantly with system size and for which determining a priori the size of LR based on error measurement on smaller reference systems may not be adequate.

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