Linear-scaling ab-initio calculations for large and complex systems

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A brief review of the SIESTA project is presented in the context of linear-scaling density-functional methods for electronic-structure calculations and molecular-dynamics simulations of systems with a large number of atoms. Applications of the method to different systems are reviewed, including carbon nanotubes, gold nanostructures, adsorbates on silicon surfaces, and nucleic acids. Also, progress in atomic-orbital bases adapted to linear-scaling methodology is presented.

I. INTRODUCTION

It is clearer every day the contribution that first-principles calculations are making to several fields in physics, chemistry, and recently geology and biology. The steady increase in computer power and the progress in methodology have allowed the study of increasingly more complex and larger systems [1]. It has been only recently that the scaling of the computation expense with the system size has become an important issue in the field. Even efficient methods, like those based on Density-Functional theory (DFT), scale like \( N^{2-3} \), being \( N \) the number of atoms in the simulation cell. This problem stimulated the first ideas for methods which scale linearly with system size [2], a field that has been the subject of important efforts ever since [3].

The key for achieving linear scaling is the explicit use of locality, meaning by it the insensitivity of the properties of a region of the system to perturbations sufficiently far away from it [1]. A local language will thus be needed for the two different problems one has to deal with in a DFT-like method: building the self-consistent Hamiltonian, and solving it. Most of the initial effort was dedicated to the latter [2] using empirical or semi-empirical Hamiltonians. The SIESTA project [4] started in 1995 to address the former. Atomic-orbital basis sets were chosen as the local language, allowing for arbitrary basis sizes, what resulted in a general-purpose, flexible linear-scaling DFT program [6]. A parallel effort has been the search for orbital bases that would meet the standards of precision of conventional first-principles calculations, but keeping as small a range as possible for maximum efficiency. Several techniques are presented here.

Other approaches pursued by other groups are also shortly reviewed in section II. All of them are based on local bases with different flavors, offering a fair variety of choice between systematicity and efficiency. Our developments of atomic bases for linear-scaling are presented in section III. SIESTA has been applied to quite varied systems during these years, ranging from metal nanosstructures to biomolecules. Some of the results obtained are briefly reviewed in section IV.

II. METHOD AND CONTEXT

SIESTA is based on DFT, using local-density [1] and generalized-gradients functionals [9], including scalar-relativistic effects, and non-linear partial-core corrections [10]. The one-particle problem is then solved using linear combination of atomic orbitals (LCAO). There are no constraints either on the radial shape of these orbitals (numerically treated), or on the size of the basis, allowing for the full quantum-chemistry know-how [14] (multiple-\( \zeta \), polarization, off-site, contracted, and diffuse orbitals). Forces on the atoms and the stress tensor are obtained from the Hellmann-Feynman theorem with Pulay corrections [6], and are used for structure relaxations or molecular dynamics simulations of different types.

Firstly, given a Hamiltonian, the one-particle Schrödinger equation is solved yielding the energy and density matrix for the ground state. This task is performed either by diagonalization (cube-scaling, appropriate for systems under a hundred atoms or for metals) or with a linear-scaling algorithm. These have been extensively reviewed elsewhere [3]. SIESTA implements two \( O(N) \) algorithms [6,11] based on localized Wannier-like wavefunctions.

Secondly, given the density matrix, a new Hamiltonian matrix is obtained. There are different ways proposed in the literature to perform this calculation in order-\( N \) operations.

(i) Quantum chemists have explored algorithms for Gaussian-type orbitals (GTO) and related technology [14]. The long-range Hartree potential posed an important problem that has been overcome with Fast Mul-
tipole Expansion techniques plus near-field corrections [10]. Within this approach, periodic boundary conditions for extended systems require additional techniques that are under current development [17].

(ii) Among physicists tradition favors more systematic basis sets, such as plane-waves and variations thereof. Working directly on a real-space grid was early proposed as a natural possibility for linear scaling [18]. Multigrid techniques allow efficient treatment of the Hartree problem, making it very attractive. However, a large prefactor was found [13] for the linear scaling, making the order-N calculations along this line not so practical for the moment. The introduction of a basis of localized functions on the points of the grid (blips) was then proposed as an operable method within the original spirit [10]. It is probably more expensive than LCAO alternatives, but with the advantage of a systematic basis. Another approach [20] works with spherical Bessel functions confined to (overlapping) spheres wisely located within the simulation cell. As for plane-waves, a kinetic energy cutoff defines the quality of the basis within one sphere. The number, positioning, and radii of the spheres are new variables to consider, but the basis is still more systematic than within LCAO.

(iii) There are mixed schemes that use atomic-orbital bases but evaluate the matrix elements using plane-wave or real-space-grid techniques. The method of Lippert et al. [21] uses GTO’s and associated techniques for the computation of the matrix elements of some terms of the Kohn-Sham Hamiltonian. It uses plane-wave representations of the density for the calculation of the remaining terms. This latter method is conceptually very similar to the one presented earlier by Ordejón et al. [3], on which SIESTA is based. The matrix elements within SIESTA are also calculated in two different ways [1]: some Hamiltonian terms in a real-space grid and other terms (involving two-center integration) by very efficient, direct LCAO integration [22]. While SIESTA uses numerical orbitals, Lippert’s method works with GTOs, which allow analytic integrations, but require more orbitals.

Except for the quantum-chemical approaches, the methods mentioned require smooth densities, and thus soft pseudopotentials. A recent augmentation proposal [23] allows a substantial improvement in grid convergence of the method of Lippert et al. [21], possibly allowing for all-electron calculations.

III. ATOMIC ORBITALS ADAPTED TO LINEAR SCALING

The main advantage of atomic orbitals is their efficiency (fewer orbitals needed per electron for similar precision) and their main disadvantage is the lack of systematics for optimal convergence, an issue that quantum chemists have been working on for many years [14]. They have also clearly shown that there is no limitation on precision intrinsic to LCAO.

Orbital range. The need for locality in linear-scaling algorithms imposes a finite range for matrix elements, which has a strong influence on the efficiency of the method. There is a clear challenge ahead for finding short-range bases that still give a high precision. The traditional way is to neglect matrix elements between far-away orbitals with values below a tolerance. This procedure implies a departure from the original Hilbert space and it is numerically unstable for short ranges. Instead, the use of orbitals that would strictly vanish beyond a certain radius was proposed [22]. This gives sparse matrices consistently within the Hilbert space spanned by the basis, numerically robust even for small ranges.

In the context of SIESTA, the use of pseudopotentials imposes basis orbitals adapted to them. Pseudatomic orbitals (PAOs) are used, i.e., the DFT solution of the atom with the pseudopotential. PAO’s confined by a spherical infinite-potential wall [23], has been the starting point for our bases. Fig. 1 shows s and p confined PAOs for oxygen. Smoother confining potentials have been proposed as a better converging alternative [24].

A single parameter that defines the confinement radii of different orbitals is the orbital energy shift [25], $\Delta E_{PAO}$, i.e., the energy increase that each orbital experiences when confined to a finite sphere. It defines all radii in a well balanced way, and allows the systematic convergence of physical quantities to the required precision. Fig. 2 shows the convergence of geometry and cohesive energy with $\Delta E_{PAO}$ for various systems. It varies depending on the system and physical quantity, but $\Delta E_{PAO} \approx 100 - 200$ meV gives typical precisions within the accuracy of current GGA functionals.

Multiple-ζ. To generate confined multiple-ζ bases, a first proposal [26] suggested the use of the excited PAOs in the confined atom. It works well for short ranges, but shows a poor convergence with $\Delta E_{PAO}$, since some of these orbitals are unbound in the free atom. In the split-valence scheme, widely used in quantum chemistry, GTOs that describe the tail of the atomic orbitals are left free as separate orbitals for the extended basis. Adding the quantum-chemistry [14] GTO’s tails to the PAO bases gives flexible bases, but the confinement control with $\Delta E_{PAO}$ is lost. The best scheme used in SIESTA calculations so far is based on the idea [27] of adding, instead of a GTO, a numerical orbital that reproduces the tail of the PAO outside a radius $R_{DZ}$, and continues smoothly towards the origin as $r^l(a - br^2)$, with $a$ and $b$ ensuring continuity and differentiability at $R_{DZ}$. This radius is chosen so that the norm of the tail beyond has a given value. Variational optimization of this split norm performed on different systems shows a very general and stable performance for values around 15% (except for the $\sim 50\%$ for hydrogen). Within exactly the same Hilbert space, the second orbital can be chosen as
the difference between the smooth one and the original PAO, which gives a basis orbital strictly confined within the matching radius \( R_{DZ} \), i.e., smaller than the original PAO. This is illustrated in Fig. 1. Multiple-\( \zeta \) is obtained by repetition of this procedure.

**Polarization orbitals.** A shell with angular momentum \( l + 1 \) (or more shells with higher \( l \)) is usually added to polarize the most extended atomic valence orbitals \( l \), giving angular freedom to the valence electrons. The (empty) \( l + 1 \) atomic orbitals are not necessarily a good choice, since they are typically too extended. The normal procedure within quantum chemistry \([4]\) is using GTOs with maximum overlap with valence orbitals. Instead, we use for SIESTA the numerical orbitals resulting from the actual polarization of the pseudoatom in the presence of a small electric field \([25]\). The pseudoatomic problem is then exactly solved (within DFT), yielding the \( l + 1 \) orbitals through comparison with first order perturbation theory. The range of the polarization orbitals is defined by the range of the orbitals they polarize. It is illustrated in Fig. 3 for the \( d \) orbitals of silicon.

The performance of the schemes presented here has been tested for various applications (see below) and a systematic study will be presented elsewhere \([3]\). It has been found in general that double-\( \zeta \), singly polarized (DZP) bases give precisions within the accuracy of GGA functionals for geometries, energetics and elastic/vibrational properties.

**Other possibilities.** Scale factors on orbitals are also used, both for orbital contraction and for diffuse orbitals. Off-site orbitals can be introduced. They serve for the evaluation of basis-set superposition errors \([28]\). Spherical Bessel functions are also included, that can be used for mixed bases between our approach and the one of Haynes and Payne \([20]\).

### IV. BRIEF REVIEW OF APPLICATIONS

**Carbon Nanostructures.** A preliminary version of SIESTA was first applied to study the shape of large hollow carbon fullerenes \([1]\) up to \( C_{540} \), the results contributing to establish that they do not tend to a spherical-shape limit but tend to facet around the twelve corners given by the pentagons. SIESTA has been also applied to carbon nanotubes. In a first study, structural, elastic and vibrational properties were characterized \([29]\). A second work was dedicated to their deposition on gold surfaces, and the STM images that they originate \([30]\), specially addressing experiments on finite-length tubes. A third study has been dedicated to the opening of single-wall nanotubes with oxygen, and the stability of the open, oxidized tubes for intercalation studies \([31]\).

**Gold Nanostructures.** Gold nanoclusters of small sizes (up to \( Au_{75} \)) were found \([22]\) to be amorphous, or nearly so, even for sizes for which very favorable geometric structures had been proposed before. In a further study the origin of this striking situation is explained in terms of local stresses \([8]\). Chains of gold atoms have been studied addressing the experiments \([32]\), which show them displaying remarkably long interatomic spacings (4 - 5 Å). A first study \([33]\) arrives at the conclusion that a linear gold chain would break at interatomic spacings much smaller than the observed ones. It is illustrated in Fig. 4 \([34]\). A possible explanation of the discrepancy is reported elsewhere \([34]\).

**Surfaces and Adsorption.** A molecular dynamics simulation was performed \([35]\) on the clean surface of liquid silicon close to the melting temperature, in which surface layering was found, i.e., density oscillations of roughly atomic amplitude, like what was recently found to happen in the surface of other liquid metals \([36]\). Unlike them, though, the origin for silicon was found to be orientational, reminiscent of directed octahedral bonding. Adsorption studies have also been performed on solid silicon surfaces, Ba on Si(100) \([39]\) and \( C_{60} \) on Si(111) \([40]\). Both works study adsorption geometries and energetics. For Ba, interactions among adsorbed atoms and diffusion features are studied. For \( C_{60} \), STM images have been simulated and compared to experiments.

**Nucleic Acids.** Feasibility tests on DNA were performed in the early stages of the project, by relaxing a dry B-form poly(dC)-poly(dG) structure with a minimal basis \([41]\). In preparation of realistic calculations, a thorough study \([28]\) of 30 nucleic acid pairs has been performed addressing the precision of the approximations and the DZP bases, and the accuracy of the GGA functional \([42]\), obtaining good results even for the hydrogen bridges. Based on that, a first study of dry A-DNA has been performed, with a full relaxation of the structure, and an analysis of the electronic characteristics \([41]\).

### V. CONCLUSIONS

The status of the SIESTA project has been briefly reviewed, putting it in context with other methods of linear-scaling DFT, and briefly describing results obtained with SIESTA for a variety of systems. The efforts dedicated to finding schemes for atomic bases adapted to linear-scaling have been also described. A promising field still very open for future research.

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FIG. 1. Confined pseudoatomic orbitals for oxygen. s in (a) and (b); p in (c) and (d). Rc is the confinement radius obtained for ΔEPAO = 250 meV. The original PAOs are represented with thinner lines. The split smooth functions are presented with thicker lines in (a) and (c), while the resulting double-ζ orbitals are plotted with thicker lines in (b) and (d).

FIG. 2. Convergence with energy shift ΔEPAO of (a) lattice parameters of bulk Si (•), Au (⋆), and MgO (●), and bond length (Δ) and angle (χ) of H2O; and (b) corresponding cohesive (bond) energies.
FIG. 3. $d$ polarization orbitals for silicon for two different confinement conditions. (a) Obtained with the electric-field polarization method, and (b) the confined $d$ PAOs.

FIG. 4. Cohesive energy (a), and stretching force (b) in a linear gold chain as a function of interatomic distance. Black dots are for the translationally invariant chain, white circles and squares are for supercells of 4 and 8 atoms, respectively, where the system is allowed to break.
\[ E = 0.25 \text{ eV} \]

\[ E = 0.01 \text{ eV} \]
