Practical quantum mechanical simulations of materials, which take into account explicitly the electronic degrees of freedom, are presently limited to about 1000 atoms. In contrast, the largest classical simulations, using empirical interatomic potentials, involve over $10^9$ atoms. Much of this $10^6$-factor difference is due to the existence of well-developed order-$N$ algorithms for the classical problem, in which the computer time and memory scale linearly with the number of atoms $N$ of the simulated system. Furthermore, such algorithms are well suited for execution in parallel computers, using rather small interprocessor communications. In contrast, nearly all quantum mechanical simulations involve a computational effort which scales as $O(N^3)$, that is, as the cube of the number of atoms simulated. Such an intrinsically more expensive dependence is due to the delocalized character of the electron wavefunctions. Since the electrons are fermions, every one of the $\sim N$ occupied wavefunctions must be kept orthogonal to every other one, thus requiring $\sim N^2$ constraints, each involving an integral over the whole system, whose size is also proportional to $N$.

Despite such intrinsic difficulties, the last decade has seen an intense advance in algorithms that allow quantum mechanical simulations with an
$O(N)$ computational effort. Such algorithms are based on avoiding the spatially extended electron eigenfunctions and using instead magnitudes, such as the one-electron density matrix, that are spatially localized, thus allowing for a spatial decomposition of the electronic problem. This strategy exploits what has been called by Walter Kohn the *nearsightedness* of the electron-gas [1]. Its implementation requires, or is greatly facilitated, by the use of a spatially localized basis set, such as a linear combination of atomic orbitals (LCAO). This paper gives a brief overview of such methods and describes in some detail one of them, the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA).

1. Order-$N$ Algorithms

Despite its relatively recent development, there are already good reviews of $O(N)$ methods for the electronic structure problem, such as those of Ordejon [2] and Goedecker [3]. Here we will only explain briefly the basic difficulties and lines of solution, emphasizing the more practical aspects. Although some methods, such as that of Car and Parrinello, use a direct minimization approach, it is pedagogically convenient to consider the solution of the electronic problem as a two-step process. First, one needs to find the Hamiltonian (and eventually the overlap) matrix in some convenient basis. Second one has to find the solution of Schrödinger’s equation in that representation, that is, the electron wavefunctions or density matrix as a linear combination of basis functions. Since the effective electron potential, and therefore the Hamiltonian, depends on the electron density, this two-step process has to be iterated to selfconsistency. Although both steps require highly nontrivial algorithms to be performed with $O(N)$ effort, from a physical point of view the second one involves more fundamental problems and solutions. We will therefore give first, in this section, an overview of the second step, and leave for the next section the technical solution of the first step (the construction of the Hamiltonian), in the context of SIESTA.

Although $O(N)$ methods have been developed for Hatree–Fock calculations as well, here we will restrict ourselves to density functional theory (DFT) because the methods are more mature and easier to understand in this context. There are numerous good introductory reviews on DFT like in Ref. [4]. A central magnitude in most $O(N)$ methods is the one-electron density operator

$$\hat{\rho} = \sum_i |\psi_i\rangle f(\epsilon_i) \langle \psi_i|.$$  

Its representation in real space is the density matrix

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_i f(\epsilon_i) \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}'),$$