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The Finite Difference Method in Electronic Structure Calculations

J. L. Fattebert

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Title: The Finite Difference Method in Electronic Structure Calculations
Name: Jean-Luc Fattebert
Affil./Addr.: Lawrence Livermore National Laboratory
Livermore, CA 94551
Phone: (925) 424-5296
E-mail: fattebert1@llnl.gov

The Finite Difference Method in Electronic Structure Calculations

Definition

The Finite Difference method is a numerical technique to calculate approximately the derivatives of a function given by its values on a discrete mesh.

Overview

Since the development of quantum mechanics, we know the equations describing the behavior of atoms and electrons at the microscopic level. The Schroedinger equation [[Schroedinger equation for chemistry](#)] is however too difficult to solve for more than a few particles because of the high dimensional space of the solution — $3N$ for N particles. So various simplified models have been developed. The first simplification usually introduced is the Born-Oppenheimer approximation [[Born-Oppenheimer approximation](#)] in which atomic nuclei are treated as classical particles surrounded by quantum electrons. But many more approximations can be introduced, all the way up to classical molecular dynamics models where interacting atoms are simply described by parameterized potentials depending only on the respective atomic positions. The choice of an

appropriate model depends on the expected accuracy and the physical phenomena of interest.

For phenomena involving tens or hundreds of atoms and for which a quantum description of the electronic structure is needed—to properly describe chemical bonds making/breaking, or hydrogen bonds for instance— a very popular model is Density Functional Theory (DFT). [Density Functional Theory] In DFT, the 3N-dimensional Schroedinger problem is reduced to an eigenvalue problem in a 3-dimensional space, the Kohn-Sham (KS) equations. The electronic structure is described by N electronic wave functions (orbitals) which are the eigenfunctions corresponding to the N lowest eigenvalues of a non-linear effective Hamiltonian H_{KS} .

Another simplification often introduced in DFT is the use of so-called pseudopotentials (see *e.g.* [12]). These are effective potentials modeling the core of an atom, that is the nuclei and the core electrons which do not participate to chemical bonds, assuming these core electrons do not depend on the chemical environment. Beside reducing the number of electronic wave functions to compute, the benefit of using pseudopotentials is to remove the singularity $1/r$ of the Coulomb potential associated to a nuclei. Indeed these potentials are built in such a way that the potential felt by valence electrons is as smooth as possible. This opens the way for various numerical methods to discretize DFT equations, in particular the Finite Difference (FD) method which is the object of this article.

The FD method (see *e.g.* [4]) started being used in the 1990's as an alternative to the traditional *Plane Waves*(PW) (or pseudo-spectral) method used in the physics and material sciences communities [3; 1]. The PW method had been a very successful approach to deal with DFT calculations of periodic solids. Besides being a good basis set to describe free electrons or almost free electrons as encountered in metallic systems and being a natural discretization for periodic systems, its mathematical

properties of spectral convergence helped reduce the size of the basis set in practical calculations. With growing computer power, researchers in the field started exploring *real-space* discretizations in order to facilitate distributed computing on large parallel computers. A simple domain decomposition leads to natural parallelism in real-space: for p processors, the domain Ω is split into a set of p spatial sub-domains of equal sizes and shapes, and each sub-domain is associated to a processor. Each processor is responsible to evaluate operations associated to the local mesh points and *ghosts* values are exchanged between neighboring sub-domains to enable FD stencil evaluations at sub-domains boundaries. [1]

In a FD approach, it is also easy and natural to impose various boundary conditions beside the typical periodic boundary conditions. It can be advantageous to use Dirichlet boundary conditions for the Coulomb potential for charged systems or polarized systems in lower dimension. The value at the boundary can be set by a multipole expansion of the finite system. This cancels out Coulomb interactions between periodic images. A real-space discretization also open the door to replacing the simple Coulomb interaction with more complicated equations which model for example the presence of an external polarizable continuum, such as continuum solvation models [6]. Local mesh refinement techniques can also be used to improve numerical accuracy [5].

Like PW, a FD approach provides an unbiased discretization and accuracy can be systematically improved by reducing mesh spacing. Many of the advantages of *real-space* algorithms can be translated in some way into PW approaches. But doing so is not always natural, appropriate, or computationally interesting. It appears that one of the greatest potential for *real-space* methods is in $O(N)$ complexity algorithms.

The discussion in this article is restricted to parallelepiped domains. This is appropriate to treat most solid state applications where the computational domain has to coincide with a cell invariant under the crystal structure symmetry. For finite systems

surrounded by vacuum, this is also a valid approach as long as the domain is large enough so that boundary conditions do not affect the results. From a computational point of view, parallelepiped domains allow for the use of structured meshes which facilitates code implementation and improves numerical efficiency, allowing in particular FD discretizations and matrix-free implementations.

Equations

For a molecular system composed of N_a atoms located at positions $\{\mathbf{R}_I\}_{I=1}^{N_a}$ in a computational domain Ω , the KS energy functional [Density Functional Theory] can be written (in atomic units)

$$\begin{aligned}
 E_{KS} [\{\psi_i\}_{i=1}^N, \{\mathbf{R}_I\}_{I=1}^{N_a}] = & \sum_{i=1}^N f_i \int_{\Omega} \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) d\mathbf{r} \\
 & + \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{\rho_e(\mathbf{r}_1) \rho_e(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{XC}[\rho_e] + \int_{\Omega} \psi_i^*(\mathbf{r}) (V_{ext} \psi_i)(\mathbf{r}) d\mathbf{r} \\
 & + E_{II}[\{\mathbf{R}_I\}_{I=1}^{N_a}].
 \end{aligned} \tag{1}$$

with the orthonormality constraints

$$\int_{\Omega} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij}. \tag{2}$$

Eq.(??) uses the electronic density ρ_e defined at each point in space by

$$\rho_e(\mathbf{r}) = \sum_{i=1}^N f_i |\psi_i(\mathbf{r})|^2 \tag{3}$$

where f_i denotes the occupation of orbital i . In Eq. (1), the first term represents the kinetic energy of the electrons, the second the electrostatic energy of interaction between electrons. E_{XC} models the exchange and correlation between electrons. This term is not known exactly and needs to be approximated. [Density Functional Theory] Exchange and correlation functional of the type Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA) are typically easy to implement and computationally efficient in a FD framework. V_{ext} represents the total potential pro-

duced by the atomic nuclei and includes any additional external potential. E_{II} is the energy of interaction between atomic cores.

The ground state of a physical system is represented by the orbitals that minimize (1) under the constraints (2). It can be found by solving the associated Euler-Lagrange equations —Kohn-Sham (KS) equations—

$$H_{KS}\psi_j = \left[-\frac{1}{2}\nabla^2 + V_H(\rho_e) + \mu_{xc}(\rho_e) + V_{ext} \right] \psi_j = \epsilon_j \psi_j, \quad (4)$$

which must be solved for the N lowest eigenvalues ϵ_j and corresponding eigenfunctions ψ_j . The Hartree potential V_H represents the Coulomb potential due to the electronic charge density ρ_e and is obtained by solving a Poisson problem. $\mu_{xc} = \delta E_{xc}[\rho_e]/\delta \rho_e$ is the exchange and correlation potential.

From the eigenfunctions $\psi_j, j = 1, \dots, N$, one could construct the single-particle density matrix

$$\hat{\rho}(\mathbf{r}, \mathbf{r}') = \sum_i f_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}') \quad (5)$$

For a FD discretization, Eq. (5) become a finite dimensional matrix of dimension M given by the number of nodes on the mesh. Even if this matrix becomes sparse for very large problems, the number of non-zero elements is prohibitively large. It is usually cheaper to compute and store the N eigenfunctions corresponding to occupations numbers $f_i > 0$ without ever building the single particle density matrix.

Finite differences discretization

Let us introduce a uniform real-space rectangular grid Ω_h of mesh spacing h —assumed to be the same in the all directions for simplicity— that covers the computation domain Ω . The wave functions, potentials and electronic densities are represented by their values at the mesh points \mathbf{r}_{ijk} . Integrals over Ω are performed using the discrete summation rule

$$\int_{\Omega} u(\mathbf{r}) d\mathbf{r} \approx h^3 \sum_{\mathbf{r}_{ijk} \in \Omega_h} u(\mathbf{r}_{ijk}).$$

For a function $u(\mathbf{r})$ given by its values on a set of nodes the traditional FD approximation $w_{i,j,k}$ to the Laplacian of u at a given node $\mathbf{r}_{i,j,k}$ is a linear combination of values of u at the neighboring nodes

$$w_{i,j,k} = \sum_{n=-p}^p c_n (u(x_i + nh, y_j, z_k) + u(x_i, y_j + nh, z_k) + u(x_i, y_j, z_k + nh)) \quad (6)$$

where the coefficients $\{c_n\}$ can be computed from the Taylor expansion of u near $\mathbf{r}_{i,j,k}$. Such an approximation has an order of accuracy $2p$, that is for a sufficiently smooth function u , $w_{i,j,k}$ will converge to the exact value of the derivative at the rate $O(h^{2p})$ as the mesh spacing $h \rightarrow 0$. High order versions of this scheme have been used in electronic structure calculations [3].

As an alternative, compact FD schemes (*Mehrstellenverfahren* [4]) have been used with success in DFT calculations [1]. For example, a 4th order FD scheme for the Laplacian is based on the relation

$$\begin{aligned} & \frac{1}{6h^2} \left\{ 24u(\mathbf{r}_0) - 2 \sum_{\substack{\mathbf{r} \in \Omega_h, \\ \|\mathbf{r}-\mathbf{r}_0\|=h}} u(\mathbf{r}) - \sum_{\substack{\mathbf{r} \in \Omega_h, \\ \|\mathbf{r}-\mathbf{r}_0\|=\sqrt{2}h}} u(\mathbf{r}) \right\} \\ &= \frac{1}{72} \left\{ 48(-\nabla^2 u)(\mathbf{r}_0) + 2 \sum_{\substack{\mathbf{r} \in \Omega_h, \\ \|\mathbf{r}-\mathbf{r}_0\|=h}} (-\nabla^2 u)(\mathbf{r}) + \sum_{\substack{\mathbf{r} \in \Omega_h, \\ \|\mathbf{r}-\mathbf{r}_0\|=\sqrt{2}h}} (-\nabla^2 u)(\mathbf{r}) \right\} \quad (7) \\ & \quad + O(h^4), \end{aligned}$$

valid for a sufficiently differentiable function $u(\mathbf{r})$. This FD scheme requires only values at grid points not further away than $\sqrt{2}h$. Beside its good numerical properties, the compactness of this scheme reduces the amount of communication in a domain-decomposition based parallel implementation. In practice, this compact scheme consistently improves the accuracy compared to a standard 4th order scheme.

Pseudopotentials on a mesh

Accurate calculations can be performed on a uniform mesh by modeling each atomic core with a pseudopotential. For instance a separable nonlocal Kleinman-Bylander (KB) potential $V_{ps}(\mathbf{r}, \mathbf{r}')$ in the form

$$(V_{ps}\psi)(\mathbf{r}) = v_l(\mathbf{r})\psi(\mathbf{r}) + \sum_{i=1}^p \int_{\Omega} v_{nl,i}(\mathbf{r}) E_i^{KB} v_{nl,i}^*(\mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}' \quad (8)$$

where E_i^{KB} are normalization coefficients. The radial function v_l contains the long range effect and is equal to $-Z/r$ far enough from the core charge Z . The functions $v_{nl,i}(\mathbf{r})$ are the product of a spherical harmonics Y_ℓ^m by a radial function which vanishes beyond some critical radius.

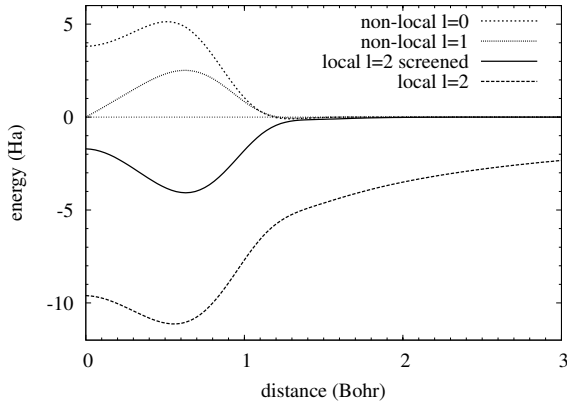


Fig. 1. Example of norm-conserving pseudopotential: Chlorine. The local potential (before and after adding compensating Gaussian charge distribution) is shown as well as the radial parts of the non-local projectors $l = 0, 1$

To reduce the local potential v_l to a short range potential v_l^s , we use the "standard trick" of adding to each atom a Gaussian charge distribution (with spherical symmetry, centered at the atomic position) which exactly cancels out the ionic charge. The sum of the charge distributions added to each atom is then subtracted from the electronic density used to compute the Hartree potential and leads to an equivalent problem. The correction added to the local atomic potential makes it short range, while the integral of the charge used to compute the Hartree potential becomes 0. Since the

functions v_l^s and $v_{nl,i}$ are non-zero only in limited regions around their respective atoms, the evaluation of the dot products between potentials and electronic wave functions on a mesh can take advantage of this property to reduce computational cost. An example of pseudopotential is represented in Fig. 1.

With periodic boundary conditions, the total energy of a system should be invariant under spatial translations. A finite mesh discretization breaks this invariance. To reduce energy variations under spatial translations, the pseudopotentials need to be filtered. Filtering can be done in Fourier space using radial Fourier transforms. [1] Filtering can also be done directly in real-space. In the so-called "double-grid" method [11], the potentials are first evaluated on a mesh finer than the one used to discretize the KS equations before being interpolated onto the KS mesh.

In order to get smoother pseudo-wave functions and increase the mesh spacing required for a given calculation, one can relax the norm-conserving constraint when building pseudo-potentials. FD implementations of the Projected Augmented Wave (PAW) method [10], and the ultrasoft pseudopotentials [9] were proposed. While these approaches reduce the requirements on the mesh spacing, their implementations are much more complex than standard norm-conserving pseudo-potentials methods and they require the use of additional finer grids to represent some core functions within each atom.

Real-space solvers

Among the various algorithms proposed for solving the KS equations [Fast methods for Large eigenvalues] algorithms developed for PW can be adapted and applied to FD discretizations. The two approaches use similar number of degrees of freedom to represent the wave functions and thus have similar ratios between the number of degrees of freedom and the

number of wave functions to compute. However some aspects are quite different between the two approaches and affect in particular their implementation.

PW discretizations make use of the fact that the Laplacian operator is diagonal in Fourier space not only to solve for the Hartree potential, but also to precondition steepest descent corrections used to optimize wave functions. For FD, the most scalable and efficient solver for a Poisson problem is the multigrid method (see *e.g.* [2]). Solving a Poisson problem on a mesh composed of $O(N)$ nodes is achieved in $O(N)$ operations with a very basic multigrid solver.

The multigrid method has also been used as a preconditioner to modify steepest descent directions and speed up convergence [1; 7]. Preconditioned steepest descent directions can be used in combination with various solvers, either in self-consistent iterations or direct energy minimization algorithms [Self-Consistent Field iterations]. The Full Approximation Scheme (FAS), a multigrid approach for solving non-linear problems, has also been used in FD electronic structure calculations to directly solve the non-linear KS equations using coarse grid approximations of the full eigenvalue problem [14].

Forces, geometry optimization and molecular dynamics

Calculating the ground state electronic structure of a molecular system is usually only the first step towards calculating other physical properties of interest. For instance to optimize the geometry of a molecular system [Molecular optimization] or to simulate thermodynamic properties by molecular dynamics [Calculation of ensemble averages] the electronic structure is just a tool to calculate the forces acting on atoms in a particular configuration.

Knowing the ground state electronic structure for a given atomic configuration $\{\mathbf{R}\}_{I=1}^{N_a}$, one can compute the force acting on the ion I by evaluating the derivative of

the total energy with respect to the atomic coordinates \mathbf{R}_I . Using the property that the set $\{\psi_i\}_{i=1}^N$ minimizes the functional E , one shows that

$$\mathbf{F}_I = -\nabla_{\mathbf{R}_I} E_{KS}(\{\psi_i\}_{i=1}^N, \{\mathbf{R}\}_{I=1}^{N_a}) = -\frac{\partial}{\partial \mathbf{R}_I} E_{KS}(\{\psi_i\}_{i=1}^N, \{\mathbf{R}\}_{I=1}^{N_a}) \quad (9)$$

(Hellmann-Feynman forces, [8]). Since the mesh is independent of the atomic positions, the wave functions do not depend explicitly on the atomic positions and the only quantities that explicitly depend on R_I are the atomic potentials. Thus in practice, the force on atom I can be computed by adding small variations to \mathbf{R}_I in the x , y , and z directions, and computing finite differences between the values of E_{KS} evaluated for shifted potentials but with the electronic structure that minimizes E_{KS} at R_I , *i.e.* *without recomputing the wave functions*.

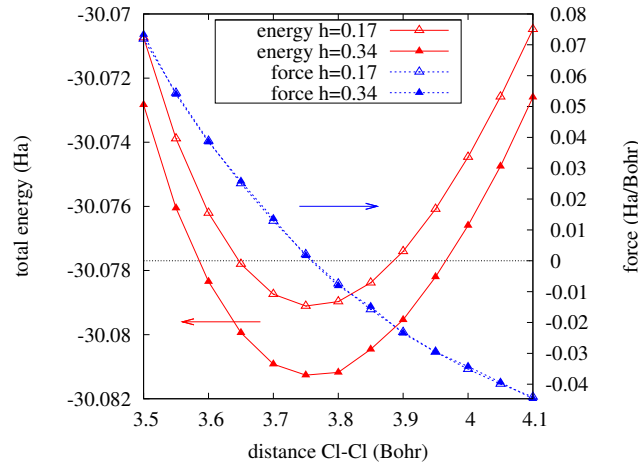


Fig. 2. Energies and forces for Cl_2 molecule as function of the distance between the two atoms for two different meshes.

The FD method is not variational: the energy does not systematically decrease when one refines the discretization mesh. Energy can converge from below (see Fig. 2). Usually the energy does not need to be converged to high precision in DFT calculations. One typically relies on systematic errors introduced by discretization which only shifts the energy up or down. As illustrated in Fig. 2 for the case of a Cl_2 molecule, other

physical quantities of interest can be converged, such as force in this case, can converge before the energy.

By repeating the process of calculating the electronic structure, deriving the forces and moving atoms according to Newton's equation for many steps, one can generate molecular dynamics trajectories. As an alternative to computing the ground state electronic structure at every step, the Car-Parrinello molecular dynamics approach can be used. It was also implemented for a FD discretization [13]

$O(N)$ complexity algorithms

Probably the main advantage of FD over PW is the ability to truncate electronic wave functions in real-space to obtain $O(N)$ complexity algorithms. [Linear scaling methods] Typical implementation of DFT solvers require $O(N^3)$ operations for N electronic orbitals, while memory requirements grow as $O(N^2)$. The $O(N^2)$ growth comes from the fact that the number of degrees of freedom per electronic wave function is proportional to the computational domain size— one degree of freedom per mesh point— since quantum wave function live in the whole domain. The $O(N^3)$ scaling of the solver is due to the fact that each function needs to be orthogonal to all the others.

The first step to reduce scaling is to rewrite Eq.(1) in terms of non-orthogonal electronic wave functions

$$E_{KS} [\{\phi_i\}_{i=1}^N, \{\mathbf{R}_I\}_{I=1}^{N_a}] = \sum_{i,j=1}^N 2 \int_{\Omega} S_{ij}^{-1} \phi_j^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \phi_i(\mathbf{r}) d\mathbf{r} \\ + \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{\rho_e(\mathbf{r}_1) \rho_e(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{XC}[\rho_e] + \sum_{i,j=1}^N \int_{\Omega} S_{ij}^{-1} \phi_j^*(\mathbf{r}) (V_{ext} \phi_i)(\mathbf{r}) d\mathbf{r} \quad (10)$$

with

$$\rho_e(\mathbf{r}) = 2 \sum_{i,j=1}^N S_{ij}^{-1} \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r}) \quad (11)$$

and $S_{ij} = \int_{\Omega} \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r}) d\mathbf{r}$. Here we assume that all the orbitals are occupied with two electrons.

This formulation does not reduce computational complexity since for instance the cost of orthonormalization is just shifted into a more complex calculation of the residuals for the eigenvalue problem. However the flexibility gained by removing orthogonality constraints on the wave functions enables the possibility of adding locality constraints: one can impose *a priori* that each orbital is non-zero only inside a sphere of limited radius and appropriately located [7]. This is quite natural to impose on a real-space mesh and lead to $O(N)$ degrees of freedom for the electronic structure. This approach is justified by the Maximally Localized Wannier functions representation of the electronic structure [Linear scaling methods]. Cutoff radii of 10 Bohr or less leads to practical accuracy for insulating system (with a finite band gap). While other ingredients are necessary to obtain a truly $O(N)$ complexity algorithm, real-space truncation of orbitals is the key to reduce computational complexity in mesh-based calculations.

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