Improved Density Mixing Methods for *Ab Initio* Calculations

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Abstract

Density mixing ...

1. Introduction

Density functional theory (DFT), and its implementation using the Kohn-Sham (KS) equations, forms a developed and widely successful foundation for performing first-principles calculations. The ability of DFT to extract accurate, quantum mechanical predictions efficiently has lead it to becoming the go-to method for calculations in materials science (ref), nuclear physics (ref), and more (ref). In its simplest form, DFT is an exact (by construction) reformulation of quantum mechanics in the *ground state*. It expresses the ground state energy variationally as a functional of a 3-dimensional electron density $\rho(\mathbf{r})$ instead of the more complex $3N$-dimensional manybody wavefunction $\Psi(\{\mathbf{r}_i\})$. In practice, one solves the KS equations,

$$\hat{H}^{KS}[\rho]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}), \tag{1}$$

producing a set of single particle orbitals ϕ_i associated with the KS system (details in Section. 2.1). The electron density is then calculated from these single particle wavefunctions as such,

$$\rho(\mathbf{r}) = \sum_{i\in occupied} |\phi_i(\mathbf{r})|^2 . lllllll \tag{2}$$

The solutions ϕ_i depend on the input $\hat{H}^{KS}$ through the electron density ρ. This is therefore a *non-linear* system of equations, where both Eq. (1) and Eq. (2) are required to be satisfied simoulteniously in order to solve KS DFT. Non-linear systems such as this can be solved using an iterative or self-consistent process. Namely, one seeks the fixed-point of the mapping KS mapping F (denoting the process in Eq. (1) and Eq. (2)),

$$F[\rho^{in}] = \rho^{out}, \tag{3}$$

which is solved by $\rho^* = \rho^{in} = \rho^{out}$ for a given external potential and electron number[1]. The idea of density mixing is then to find the fixed-point density by 'optimally' combining $\{\rho_n^{in}, \rho_n^{out}\}$ to drive ρ_{n+1}^{in} toward ρ^* – here, n denotes the iteration number. Optimising the self-consistent process by choosing the best available density mixing scheme is imperative for the success of KS DFT. Each update of the density requires diagonalisation of $\hat{H}^{KS}$ to re-solve the system and obtain an output density; this is a cumbersome task, and is ideally executed as little as possible. The aim of this project is to implement a proposed density mixing scheme (appropriate for planewaave DFT codes) by Marks and Luke [ref].

2. Background Theory

2.1. Density Functional Theory

Density functional theoroy (DFT) is an exact (by construction) reformulation of quantum mechanics for systems in their ground state. Its foundation are the Hohenberg-Kohn theorems... implemented in practice using the Kohn-Sham (KS) equations (hereafter 'KS DFT'). Now we know we need a technique for fixing the root (or fixed point) of the density in KS DFT, we can begin to study mathematically how one can achive that, what the best methods will be, and what the pitfalls are for DFT in particular.

2.2. The Iterative Process for Solving a Set of Non-linear Equations

Many problems in Physics take the form... and KS DFT, as discussed, is no different. The SCF operator

[1] $N = \int \rho(\mathbf{r}) d\mathbf{r}$.

2.3. Fixed-Point Iterations

Study, into to linear response regime, good initial guess. analysis of M

2.4. Linear Mixing

Improves on fixed point iterations, but suffers from slow convergence, or sloshing instabilities.

2.5. Pulay Mixing

Most popular method, method in CASTEP, DIIS.

2.6. Broyden's Methods

Another method in CASTEP, less popular, but important prerequisite for MSB1 and MSB2.

3. Multisecant Broyden Methods and Their Implementation in CASTEP

This follows the work of Marks and Luke (ref) who propose two multisecant Broyden methods (based on the good and bad Broyden method) to improve mixing. Theory of the method... Implementation into CASTEP...

4. Results

First compare standard techniques already in CASTEP. Give background into how they are implemented, the parameters they use, how they compare. Now compare to the Marks and Luke method.

5. Conclusions

Acknowledgements

Appendix A. Derivation of Newton's Method

Appendix B. Derivation of Broyden's Methods