An Efficient and Robust Technique for Achieving Self Consistency in Electronic Structure Calculations

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Abstract

Pulay’s Residual Metric Minimization (RMM) method is one of the standard techniques for achieving self consistency in ab initio electronic structure calculations. We describe a reformulation of Pulay’s RMM which guarantees reduction of the residual at each step. The new version avoids the use of empirical mixing parameters, and is expected to be more robust than the original version. We present practical tests of the new method implemented in a standard code based on density-functional theory (DFT), pseudopotentials, and plane-wave basis sets. The tests show improved speed in achieving self consistency for a variety of condensed-matter systems.

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1 Introduction

The requirement of self consistency between the electronic charge density and the potential plays a key role in ab initio electronic structure calculations. The iterative search for self consistency generally involves some form of charge density mixing at each step. A standard and widely used mixing method is the RMM-DIIS technique (Residual Metric Minimization – Direct Inversion of the Iterative Subspace), first introduced by Pulay for Hartree-Fock calculations\[1, 2\], but now also used in density-functional theory\[3\]. The modified Broyden technique introduced by Vanderbilt and Louie\[4\] and Srivastava\[5\] and generalised by Johnson\[6\] can be shown\[7, 8\] to reduce to the Pulay technique for a suitable choice of weights; in practice, these weights give the fastest convergence, and are often used, though can lead to instability at convergence\[6, 9\]. We describe here a new technique for charge-density mixing, and we show that
it is more robust and sometimes significantly faster than the Pulay and the modified Broyden methods.

We recall that a self-consistency cycle in an \textit{ab initio} calculation proceeds as follows: an input density $\rho(r)$ is used to generate a potential $v(r)$; from this, a Hamiltonian or Fock matrix is formed; the eigenfunctions of the latter are then used to create an output density $\rho'(r)$. The residual $R(r)$ associated with a given input density is defined as $R(r) \equiv \rho'(r) - \rho(r)$. The self-consistent density is the $\rho(r)$ for which $R(r) = 0$ everywhere. The idea of charge mixing in its simplest form is that one should attempt to move towards self consistency at each step by linearly ‘mixing’ $\rho(r)$ and $\rho'(r)$ in some proportions and using the result as input to the next cycle. The Pulay technique is a sophisticated generalization of this idea, which works by minimizing the norm $|R|$ of the residual, defined as

$$
| R | = \left[ \int dr \, R(r)^2 \right]^{1/2} .
$$

In making a robust method for seeking self consistency, we regard it as highly desirable that $|R|$ should decrease at every step. We shall show that, as self consistency is approached, our new method achieves this, though the Pulay method does not. In the following, we summarize the Pulay method before outlining our new formulation, which we call guaranteed-reduction-Pulay (GR-Pulay). We then present a number of practical test cases within DFT, which demonstrate the advantages of GR-Pulay.

\section{The GR-Pulay method}

At each iterative step, the Pulay method works with a set of $s$ densities, which at iteration number $n$ are denoted by $\rho_n(r), \rho_{n-1}(r), \ldots, \rho_{n-s+1}(r)$. (In practical calculations, $s$ is typically 5. Of course, in the early stages of the search, when $n < s$, the set of densities is taken to be $\rho_n(r), \ldots, \rho_1(r)$.) In going to the next iteration, a new density $\rho_{n+1}(r)$ is created, and the oldest previous density $\rho_{n-s+1}(r)$ is discarded. The procedure for generating $\rho_{n+1}(r)$ involves the concept of the present ‘optimal’ density $\rho_n^{\text{opt}}(r)$, which signifies the linear combination of the present densities:

$$
\rho_n^{\text{opt}}(r) = \sum_{i=0}^{s-1} \alpha_i \rho_{n-i}(r)
$$

having the smallest norm of the residual, subject to the condition $\sum_{i=0}^{s-1} \alpha_i = 1$. To determine the coefficients $\alpha_i$, it is assumed that we are close enough to self consistency for variations of the densities and their associated residuals to be linearly related. This means that the residual associated with any linear combination of the present densities, as in eqn (\ref{eqn:rho_opt}), is simply $\sum_{i=0}^{s-1} \alpha_i R_{n-i}(r)$, where $R_{n-i}(r)$ is the residual associated with input density $\rho_{n-i}(r)$. The residual...
yields a unique and simple formula for the $\alpha$ combination of present densities. But the new density $\rho$ where $\rho$ linear regime, the value of $A$ becomes unimportant.

Since the residuals $R_n(r)$ are all known, the constrained minimization of $\| R_n \|$ is equivalent to the constrained minimization of a bilinear form, and this yields a unique and simple formula for the $\alpha_i$.

The present optimal density $\rho_n^{\text{opt}}(r)$ is the ‘most self-consistent’ linear combination of present densities. But the new density $\rho_{n+1}(r)$ clearly cannot be chosen to be $\rho_n^{\text{opt}}(r)$. The reason for this is that each new iteration must introduce new variations of the density, so that $\rho_{n+1}(r)$ cannot be allowed to lie in the subspace spanned by the present densities. In the conventional implementation of the Pulay scheme, the new density is usually chosen to be a linear combination of $\rho_n^{\text{opt}}(r)$ and its output density $\rho_n^{\text{opt}}(r)$:

$$\rho_{n+1}(r) = (1 - A) \rho_n^{\text{opt}}(r) + A \rho_n^{\text{opt}}(r) .$$

The value of the mixing coefficient $A$ is empirically chosen (typically to be about 0.8), and the efficiency of the self-consistency search depends on the choice of $A$. If $A$ is not appropriately chosen, a variety of problems can occur, including slow convergence or even failure to converge. The problem is that the best choice of $A$ depends on the physical system being treated.

The new mixing scheme proposed here resembles the Pulay method in that it works with $s$ densities $\rho_n(r)$, $\rho_{n-1}(r)$, $\ldots$, $\rho_{n-s+1}(r)$ at each step, and goes from one iteration to the next by discarding the oldest density $\rho_{n-s+1}(r)$ and creating a new density $\rho_{n+1}(r)$. However, the set of $s$ densities is required to have a crucial property: the norm of the residual $R_n(r)$ associated with $\rho_n(r)$ is required to be no greater than the norm of the residual associated with any linear combination $\sum_{i=0}^{s-1} \alpha_i \rho_{n-i}(r)$, with the usual condition $\sum_{i=0}^{s-1} \alpha_i = 1$. We shall see immediately how to ensure this property.

Our procedure for generating $\rho_{n+1}(r)$ is as follows:

- delete $\rho_{n-s+1}$ and add $\rho_{n}$, so that the set of densities is $\rho_{n}'$, $\rho_{n}$, $\rho_{n-1}$, $\ldots$, $\rho_{n-s+2}$.
- put $\rho_{n}'$ through a cycle, so that we have its output $\rho_{n}''$ and hence a full set of residuals $R'_n$, $R_n$, $R_{n-1}$ $\ldots$, $R_{n-s+2}$.
- make linear combinations:

$$\hat{\rho}_n = \alpha_1 \rho'_n + \alpha_2 \rho_n + \alpha_3 \rho_{n-1} + \ldots + \alpha_s \rho_{n-s+2} ,$$

and determine the coefficients $\alpha_i$ so as to minimize the norm of the residual of $\hat{\rho}_n$, subject to the usual condition that the $\alpha_i$ sum to unity. Denote by $\rho_{n+1}$ the density $\hat{\rho}_n$ that yields the minimum residual.

\[\footnote{We note that Pulay implicitly chose $A=1$; we also note that as the scheme enters the linear regime, the value of $A$ becomes unimportant.}\]
delete $\rho_n$ and replace by $\rho_{n+1}$, so that the new set of densities is $\rho_{n+1}$, $
abla \rho_n, \ldots, \rho_{n-s+2}$.

Clearly the new set has the same property as the old: the newest density $\rho_{n+1}$ has the minimal residual norm that can be achieved by taking linear combinations of the present densities. In particular, $| R_{n+1} | < | R_n |$, so that the residual at iteration $n+1$ is less than that at iteration $n$. Moreover, it can be shown that the decrease of the residual in an $s$-level scheme is greater than the decrease in an $s'$-level scheme, provided $s > s'$. We note that in GR-Pulay, as in the original Pulay scheme, the computational effort in each iteration consists of a single self-consistent cycle. This is true, provided $R_{n+1}(r)$ is accurately enough given by the linear approximation, which is clearly the case as self-consistency is approached.

3 Applications

Although our GR-Pulay scheme is completely general, our practical interest here is in the pseudopotential, plane-wave implementation of DFT, and our tests have been done on a variety of condensed-matter systems using the CASTEP code[10]. The use of a modified Broyden technique[6] (shown by Kresse[8] and Eyert[8] to reduce to the usual Pulay technique for a suitable choice of the weights) in DFT condensed-matter work has been explored by many workers, including Johnson and Kresse, and it is one of the standard options in CASTEP; it is implemented with the weights chosen so that it is directly equivalent to the Pulay technique. The systems chosen for our tests are: bulk silicon (two atom primitive cell); bulk magnesium chloride (three atom cell); bulk aluminium (one atom stacked fcc); bulk plutonium dioxide (three atoms stacked fcc); bulk iron (one atom stacked fcc); and the platinum(001) surface (five atoms in five layers, slab geometry). These systems provide example of insulating, semiconducting and metallic behaviour, as well as extreme inhomogeneity of electron density.

We have made efforts to achieve an unbiased comparison of Broyden and GR-Pulay; all parameters in each run were the same for the two techniques, as were the initial conditions. When searching for self-consistency, CASTEP applied a criterion of energy change between successive iterations to the Broyden method, while we apply a criterion of absolute size of the norm of the residual (expressed as a fraction of the norm of the charge density) to the GR-Pulay method. We checked that in all cases our criterion was as strict as the energy difference criterion (i.e. the norm of the residual when CASTEP had converged using Broyden was no smaller than the norm of the residual when CASTEP had converged using GR-Pulay). We note that, in the context of the search for self-consistency between a charge density and a potential, it is important to apply a convergence criterion to the norm of the residual (for this is what determines whether or not self-consistency has been reached) and not an energy difference; cases where the change in energy is small from one iteration to the next, but the norm of the residual is relatively large, can be envisaged.
In Table 1 we report timings for the Pulay/Broyden technique and our GR-Pulay technique within CASTEP, run on a PC (400MHz Pentium II with 256MB of memory) under Linux. The calculations employed standard pseudopotentials (either norm-conserving\cite{11, 12} or ultrasoft\cite{13}) and plane wave cutoffs of between 100 and 300 eV (depending on the system; the efficacy of individual methods should be independent of the plane wave cutoff). The criteria for self consistency are an energy change of $5 \times 10^{-6}$ eV per atom for the Pulay/Broyden technique and $|R|/|\rho| < 10^{-4}$ for the GR-Pulay technique. The first two runs (Si and MgCl$_2$) involved relaxation of the atomic positions and the third (Al) the determination of the unit cell size (these were pursued until the RMS force on the atoms was below 0.01 eV/Å, and the RMS stress below 0.1 GPa). The next three cases (PuO$_2$, Fe and Pt(001)) were all single point energy calculations. For the first three, the number of iterations required to reach the self-consistent ground state starting from scratch (i.e. at the first iteration) is given in brackets after the time. For the last three, the total number of self-consistent iterations is given in brackets after the time. Our timings demonstrate that GR-Pulay can be over twice as fast as the Pulay/Broyden method; in all cases, this is because GR-Pulay requires fewer iterations to find the ground state than Pulay/Broyden. It is also related to the number of line searches performed during wave function minimisation between self-consistent iterations; modern plane wave DFT codes perform several line searches (until either convergence or a maximum number of iterations are reached), and differing numbers of these searches will also contribute to the different times. Monitoring the rate of decrease of the residuals in both cases showed that the GR-Pulay method typically achieved a much greater rate than Pulay/Broyden (which is not surprising, given the results).

4 Conclusions

We have shown that our proposed reformulation of the Pulay mixing scheme offers three kinds of advantage over the original scheme. First, no empirically chosen mixing parameters are needed, so that less experience is required to use the scheme successfully. Second, the residual is guaranteed to decrease at every iteration, so that instability cannot occur, at least as self-consistency is approached. Third, our practical tests show that the new scheme can sometimes be significantly faster than the original one.

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| System     | Pulay/Broyden | GR-Pulay |
|------------|---------------|----------|
| Si(R)      | 6.93 (9)      | 5.56 (7) |
| MgCl₂(R)   | 30.19 (13)    | 25.35 (13) |
| Al(CR)     | 29.50 (36)    | 12.34 (12) |
| PuO₂       | 20.91 (15)    | 16.47 (10) |
| Fe(spin)   | 63.02 (34)    | 33.05 (14) |
| Pt(001)    | 670.47 (15)   | 688.72 (14) |

Table 1: Timings (in seconds) for the Pulay/Broyden and GR-Pulay methods applied to different systems using the CASTEP code. Numbers in brackets after the time indicate iterations required to reach the self-consistent ground state starting from initial conditions for the first iteration. (R) indicates geometry optimisation, (CR) cell optimisation and no letter a single point energy.