Self-Consistency in Density Functional Theory

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Motivation

- Kohn-Sham (KS) density functional theory (DFT) has achieved astonishing success as a method for modelling materials and chemicals from first principles.
- Due to this, KS DFT software, e.g. CASTEP [1], consumes a considerable fraction of the worlds supercomputing power, meaning effective numerical implementation of KS DFT is of paramount importance.
- Increasingly *efficient* and *robust* numerical solutions of KS DFT can provide access to previously unexplored areas of science.
- For example, when searching for novel (meta-)stable phases of matter, thousands of individual KS DFT calculations are typically performed per 'structure search'. These searches can be limited by the KS DFT implementations failing to find a solution. Hence, it is possible that physically relevant regions of the potential energy surface are uncharted.
- This work studies the iterative methodology utilised in order to achieve a so-called *self-consistent solution* to KS DFT.

Theory

- KS DFT presents a *non-linear eigenvalue problem*,

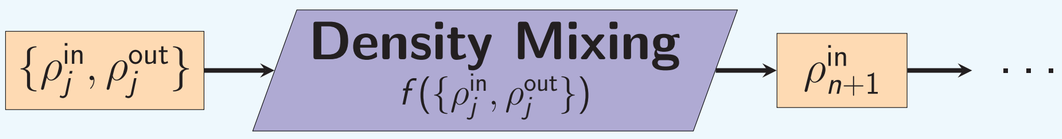
$$\hat{H}^{KS}[\rho^{\text{in}}(\mathbf{r})]\phi_i = \epsilon_i \phi_i, \tag{1}$$

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

- The single particle wavefunctions $\{\phi_i\}$ are used to define an output particle density ρ^{out}, which in general is different to the input particle density ρ^{in} used to construct the KS Hamiltonian, $\hat{H}^{KS}$.
- Finding a particle density that satisfies both Eq. (1) and Eq. (2) simultaneously defines self-consistency, $\rho^* = \rho^{\text{in}} = \rho^{\text{out}}$.
- **Density mixing** is an iterative procedure that generates an improved estimate for the ground state density for the subsequent iteration by combinding the input-output density pairs of previous iterations.
- A density mixing scheme thus defines the form of the function

$$\rho^{\text{in}}_{n+1} = f(\{\rho^{\text{in}}_j, \rho^{\text{out}}_j\}) \tag{3}$$

for $j \in [1, n]$ defining the iteration number.



- The most widely adopted and generally best performing density mixing scheme is a *preconditioned* version of Pulay's *discrete inversion in the iterative subspace* (DIIS) technique.
- This method extrapolates over a subspace spanned by the history of iterative densities to predict a subsequent density that will minimise the subsequent difference between input and output densities.
- The method is typically preconditioned with the *Kerker preconditioner*, based on the isotropic dielectric response of the homogeneous electron gas.

References

[1] S. J. Clark *et al.* First principles methods using castep. *Zeitschrift fuer Kristallographie*, 220 (5-6), 567-570 (2005).

[2] L. D. Marks and D. R. Luke. Robust mixing for ab initio quantum mechanical calculations. *Phys. Rev. B 78, 075114*, (2008).

[3] A. S. Banerjee *et al.* Periodic Pulay method for robust and efficient convergence acceleration of self-consistent field iterations. *Chem. Phys. Lett 647, 31â35*, (2016).

Alternative Methods

- A Kerker preconditioned *multisecant Broyden* technique was implemented in CASTEP, based on the work of Marks & Luke in Ref. [2] – Fig. (1).

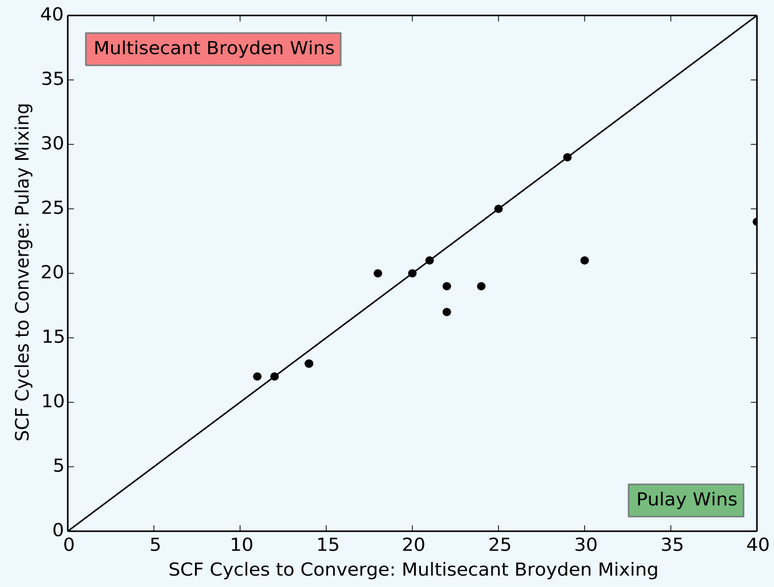


Figure 1: Comparison of SCF cycles to converge across a representative range of DFT input systems: Pulay mixing vs. multisecant Broyden mixing.

- Pulay's DIIS is most efficient when the history of densities span a reasonable volume of phase-space. Periodic Pulay mixing [3] improves the sample of densities in the iterative subspace by including *linear mixing* steps in between Pulay mixing steps, thus allowing the DIIS to be more effective – Fig. (2).

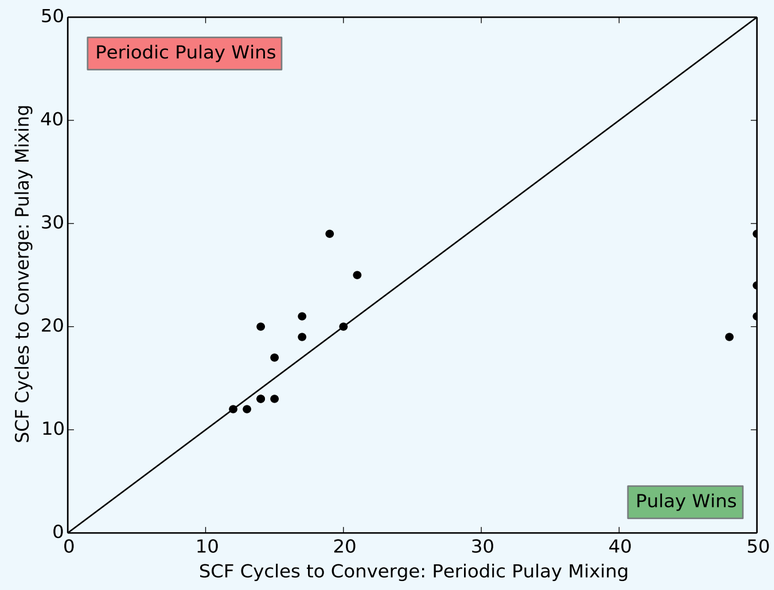


Figure 2: Comparison of SCF cycles to converge: Pulay mixing vs. Periodic Pulay mixing.

- A preconditioner was constructed that implements a local, real-space density dependence into the dielectric through the susceptibility model,

$$\chi_0(\mathbf{r}, \mathbf{r}') = \alpha\left(\rho^{\text{in}}_n(\mathbf{r})\right)^{\beta} \delta(\mathbf{r} - \mathbf{r}'). \tag{4}$$

- This model implicitly includes inhomogeneity and anisotropy of an input system directly into the preconditioner, for some appropriate choice of $\{\alpha,\beta\}$. In this work, these parameters were derived by considering an inhomogeneous extension of the Thomas-Fermi screening model, labelled 'ITF' in Fig. (3): $\alpha = 4(3/\pi)^{1/3}$, $\beta = 1/3$.

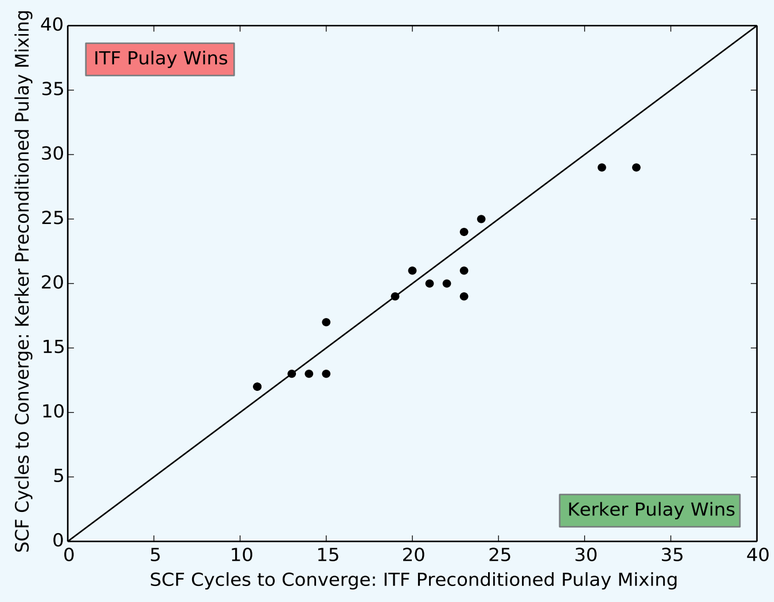


Figure 3: Comparison of SCF cycles to converge, Pulay mixing: Kerker Preconditioned vs. ITF Preconditioned.