**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 world’s 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,

\[ \hat{H}_{KS}[\rho]\psi_i = \epsilon_i \psi_i, \]  

(1)

\[ \rho^{\text{out}}(r) = \sum_{i=\text{occupied}} |\psi_i(r)|^2. \]  

(2)

- The single particle wavefunctions \( \{\psi_i\} \) are used to define an output particle density \( \rho^{\text{out}} \), which in general is different to the input particle density \( \rho^{\text{in}} \) 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 combining the input-output density pairs of previous iterations.
- A density mixing scheme thus defines the form of the function

\[ \rho^{\text{in}}_{j+1} = f(\{\rho_j^{\text{in}}, \rho_j^{\text{out}}\}) \]  

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

\[ \{\rho_j^{\text{in}}, \rho_j^{\text{out}}\} \rightarrow \text{Density Mixing} \rightarrow f(\{\rho_j^{\text{in}}, \rho_j^{\text{out}}\}) \rightarrow \rho_{j+1}^{\text{in}} \rightarrow \ldots \]

- 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.

**Alternative Methods**

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

\[ \chi(r, r') = \alpha (\rho^{\text{in}}(r))^{3/2} \delta(r - r'). \]  

(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): \( \alpha = 4(3/\pi)^{1/3}, \beta = 1/3 \).

**References**