Methods for Accelerated Convergence of the Electron Density in Density Functional Theory

Nick Woods

Supervisor: Dr. Phil Hasnip

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Intro

Kohn-Sham (KS) DFT solves the following eigenequation to obtain occupied single particle KS orbitals (ψ_i)

$$H^{KS}[\rho]\psi_i = \epsilon_i \psi_i$$

$$\rho(\mathbf{r}) = \sum_{i \in \text{occupied}} |\psi_i|^2$$

The solutions $\{\psi_i\}$ depend on the input H^{KS} through $\rho(\mathbf{r})$

Introduction

$$F : \begin{cases} \rho^{\text{in}} \rightarrow H^{KS}[\rho^{\text{in}}] \\ \downarrow \\ \text{Solve KS equation} \\ \downarrow \\ \rho^{\text{out}} \sim \sum |\psi^2| \end{cases}$$

$$F[\rho^{\text{in}}] = \rho^{\text{out}}$$

$$\rho^{\text{in}} \neq \rho^{\text{out}}$$

Achieving Convergence

Methods to achive convergence:

Density Mixing – Find optimal form of

$$\rho^{\text{in}}_{n+1} = f(\{\rho^{\text{in}}_n, \rho^{\text{out}}_n\}) \quad n \in [1, \text{iteration history length}]$$

Preconditoners – Apply a preconditioning matrix P specific to problem to assist f

Density Mixing

Simplest update one can imagine

$$\rho_{n+1}^{\text{in}} = F[\rho_n^{\text{in}}] = \rho_n^{\text{out}}$$

Fixed-point iteration

Analysis of this update highlights difficulties of the SCF process

Density Mixing

If $\rho = \rho^* + \delta\rho$ then the fixed-point iteration formula can be linearised,

$$\begin{aligned}\delta\rho^{\text{in}}_{n+1} &= \frac{\delta F}{\delta\rho}\delta\rho^{\text{in}}_n \\ &= \frac{\rho^{\text{out}}_n}{\rho^{\text{in}}_n}\delta\rho^{\text{in}}_n \\ &= M\delta\rho^{\text{in}}_n\end{aligned}$$

linear response

Density Mixing

Convergence: $\delta\rho^{\text{in}}_{n+1} \to 0$ as $n \to \infty$

$$\implies (M)^n \delta\rho^{\text{in}}_1 \to 0$$

What conditions required for M^n to tend to zero?

Diagonalising M in its orthonormal eigenbasis gives

$$((M^d)^n)_{ii} = (\lambda_i)^n |\mathbf{e}_i\rangle\langle\mathbf{e}_i|$$

$$\implies M\delta\rho^{\text{in}}_n \to 0 \text{ iff } |\lambda_i| < 1 \ \forall \ i$$

Density Mixing

In general not true!

Could imagine scaling M with a parameter α which guarantees this – *linear mixing*

The eigenvalues in this case $\sim \alpha\{|\lambda_i|\}$.

What is the problem with this?

Density Mixing

Need a more sophisticated scheme than linear mixing or fixed-point iterations

CASTEP uses (variants of) Pulay method, multisecant Broyden (quasi-Newton)

Both need to be executed using limited memory (can't store $N_{\text{gridpoints}} \times N_{\text{gridpoints}}$ matrix) and prefer convergence in a low number of SCF cycles (diagonalising H^{KS} expensive)

Density Mixing

My project: investigate possible improvements

Robust mixing for ab initio quantum mechanical calculations
L. D. Marks and D. R. Luke
Phys. Rev. B 78, 075114 2008

A multisecant Broyden technique – general idea is to treat history of iterates as sampling phase space rather than a path to te solution

Preconditioners

Can now think about specific problem (KS DFT) to investigate what makes a good preconditioner

In KS DFT, pertubations in density (like those induced in density mixing) propagate through F as such

$$\delta V_h(\mathbf{r}) = \int \frac{\delta\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}',$$

$$\delta\rho(\mathbf{r}) = \int \chi^{\mathrm{DFT}}(\mathbf{r},\mathbf{r}')\delta V_h(\mathbf{r}')\, d\mathbf{r}'.$$

Preconditioners

$$\delta \tilde{V}_h(\mathbf{G}) \sim \frac{\delta \tilde{\rho}(\mathbf{G})}{|\mathbf{G}|^2}$$

Charge sloshing – unique to KS DFT (from Hartree potential)

Continous overcorrection of V_h and ρ

Preconditioners

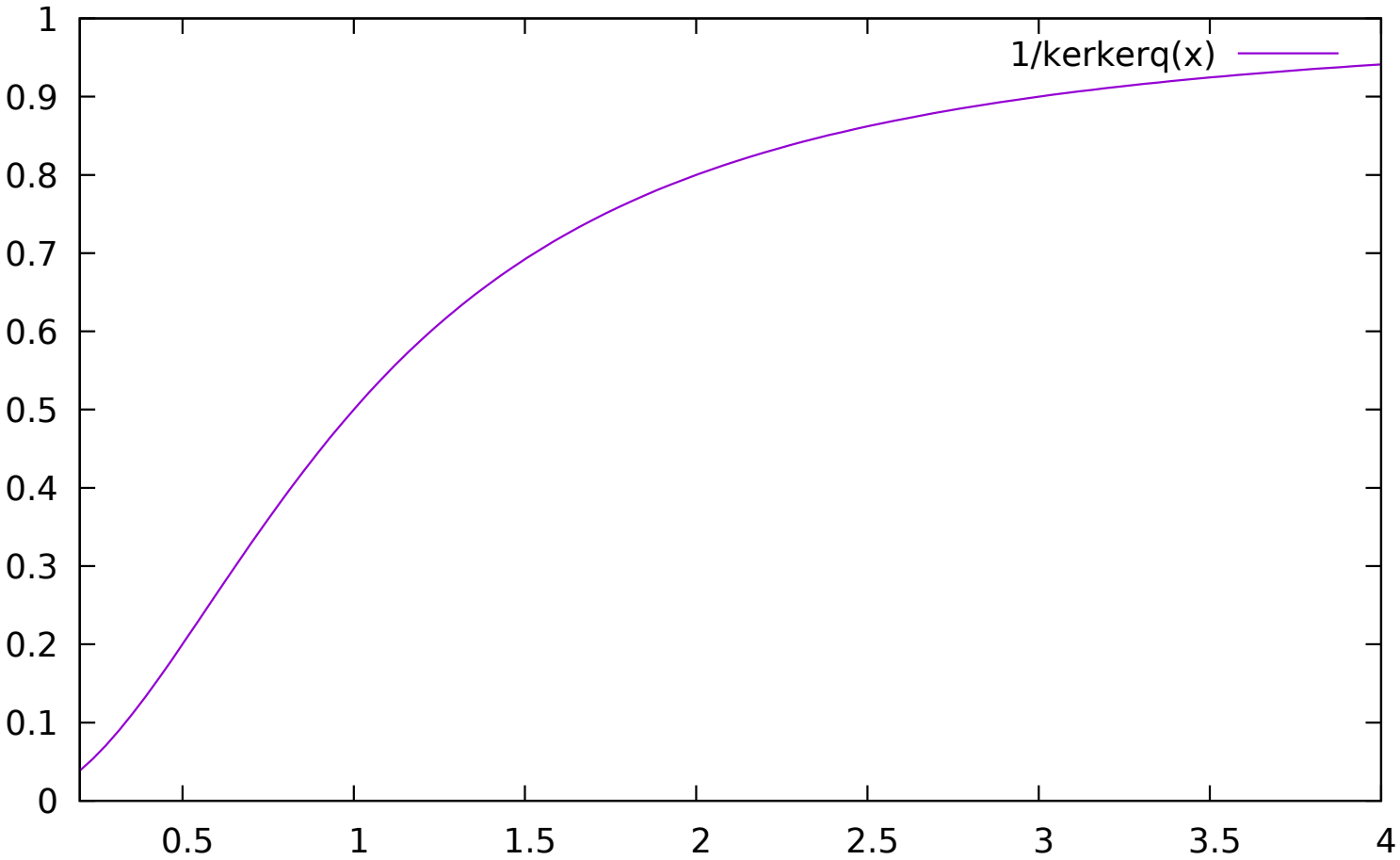
Preconditoner should weight low **G** vectors less, to avoid sloshing

It turns out that the preconditioning matrix, M from earlier, is closely related to the DFT dielectric of system, ϵ

Use dielectric model to precondition $\delta\rho$

CASTEP uses Kerker dielectric model (Jellium) – $\epsilon \sim \delta_{GG'} \frac{1}{G^2}$

Preconditioners



Preconditioners

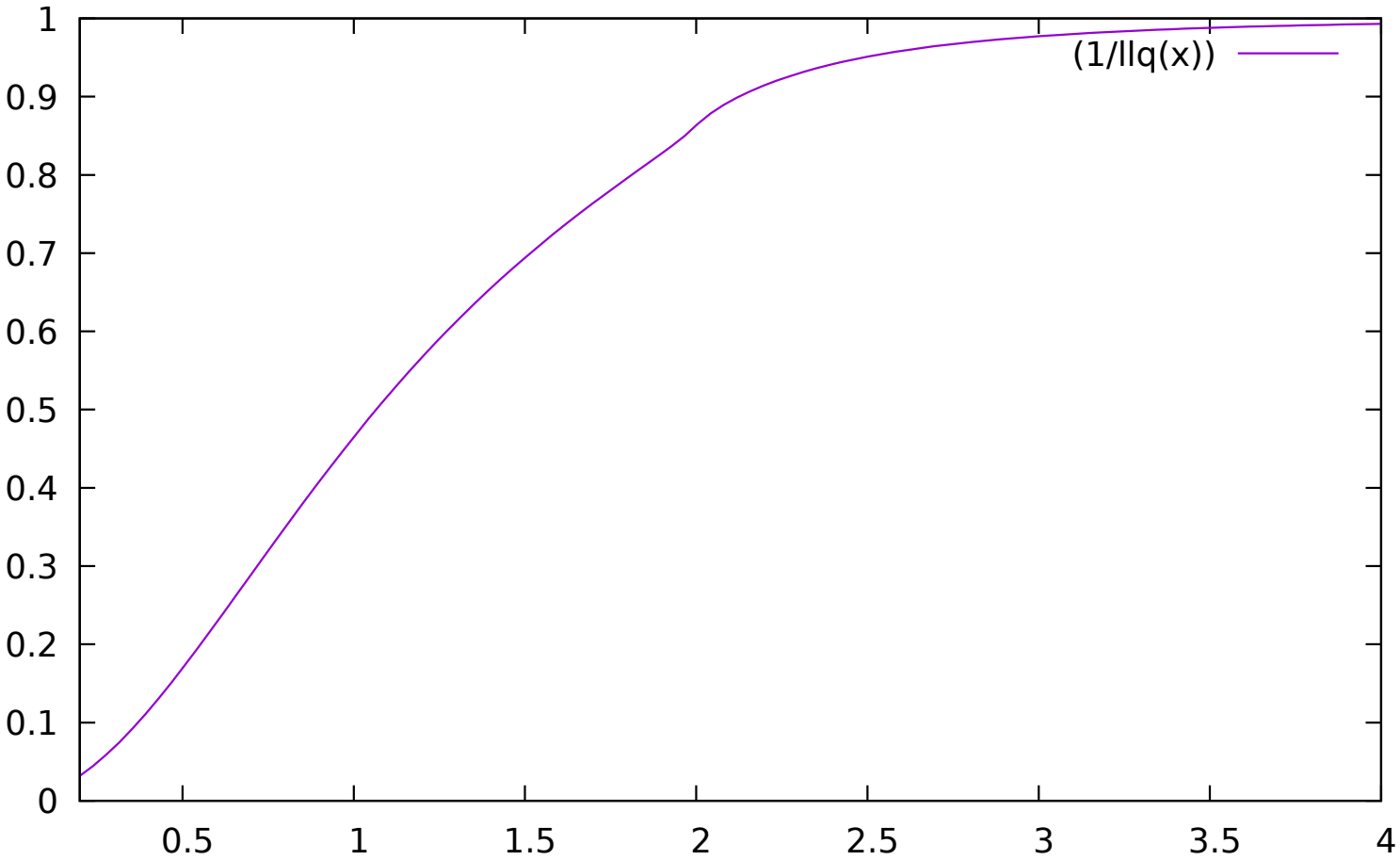
My project: investigate better preconditioners than Kerker

First, a better dielectric model

New model dielectric function and exchange-correlation potential for semiconductors and insulators Zachary H. Levine and Steven G. Louie Phys. Rev. B 25, 6310 1982

Still isotropic – include anistropy?

Preconditioners



Preconditioners

Both models include two parameters

How do they map onto each other?

What are the optimal parameters?

To come...