Methods and
Algorithms in
CASTEP

Nick Woods

Kohn-Sham
Theory In
Software

1. Initial
Guess

2. Calculation
of Occupied
Orbitals

3. Self-
Consistency
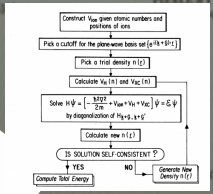
What's in the Box?

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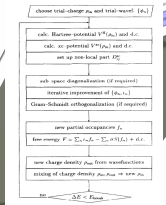
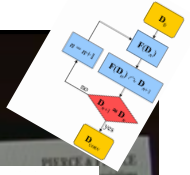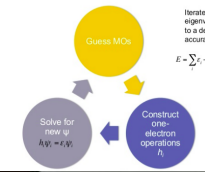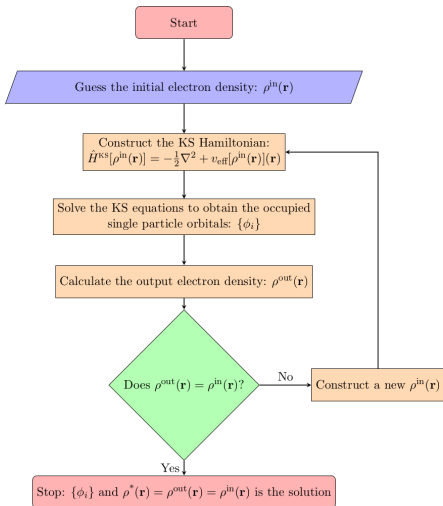Supervisors: Dr. Phil Hasnip and Prof. Mike Payne

August 24, 2018

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Start

Guess the initial electron density: $\rho^{\text{in}}(\mathbf{r})$

Construct the KS Hamiltonian:
$\hat{H}^{\text{KS}}[\rho^{\text{in}}(\mathbf{r})] = -\frac{1}{2}\nabla^2 + v_{\text{eff}}[\rho^{\text{in}}(\mathbf{r})](\mathbf{r})$

Solve the KS equations to obtain the occupied
single particle orbitals: $\{\phi_i\}$

Calculate the output electron density: $\rho^{\text{out}}(\mathbf{r})$

Does $\rho^{\text{out}}(\mathbf{r}) = \rho^{\text{in}}(\mathbf{r})$?

No → Construct a new $\rho^{\text{in}}(\mathbf{r})$

Yes

Stop: $\{\phi_i\}$ and $\rho^*(\mathbf{r}) = \rho^{\text{out}}(\mathbf{r}) = \rho^{\text{in}}(\mathbf{r})$ is the solution

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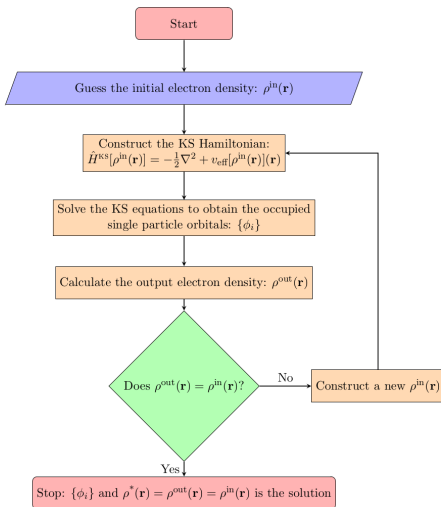
} How?

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Start

Guess the initial electron density: $\rho^{\text{in}}(\mathbf{r})$

} How?

Construct the KS Hamiltonian:
$\hat{H}^{\text{KS}}[\rho^{\text{in}}(\mathbf{r})] = -\frac{1}{2}\nabla^2 + v_{\text{eff}}[\rho^{\text{in}}(\mathbf{r})](\mathbf{r})$

} Don't do

Solve the KS equations to obtain the occupied
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} How?

} Don't do

} How?

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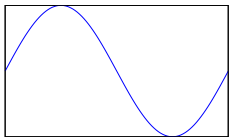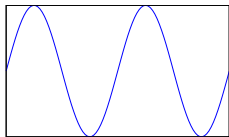Theory In
Software
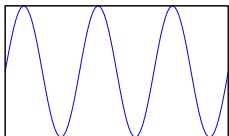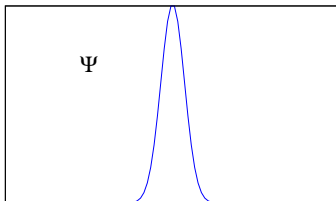
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Kohn-Sham Theory:

$$E^* = \inf_{\rho \in \mathcal{P}} \left\{ E^{\mathrm{KS}}[\rho] \big| \int d\mathbf{r}\, \rho = N, \langle \phi_i | \phi_j \rangle = \delta_{ij} \right\}$$

Kohn-Sham (Euler-Lagrange) equations:

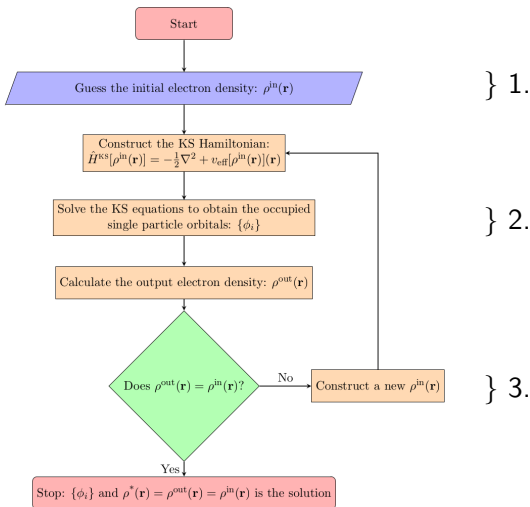$$\left(-\frac{1}{2}\nabla^2 + v^{\mathrm{ext}} + v^{\mathrm{h}} + v^{\mathrm{xc}} \right) \phi_i = \epsilon_i \phi_i$$

Plane-waves

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Guess the initial electron density: $\rho^{\text{in}}(\mathbf{r})$

$\left.\right\}$ 1.

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Calculate the output electron density: $\rho^{\text{out}}(\mathbf{r})$

Does $\rho^{\text{out}}(\mathbf{r}) = \rho^{\text{in}}(\mathbf{r})$?

No → Construct a new $\rho^{\text{in}}(\mathbf{r})$

$\left.\right\}$ 3.

Yes

Stop: $\{\phi_i\}$ and $\rho^*(\mathbf{r}) = \rho^{\text{out}}(\mathbf{r}) = \rho^{\text{in}}(\mathbf{r})$ is the solution

The Initial Guess

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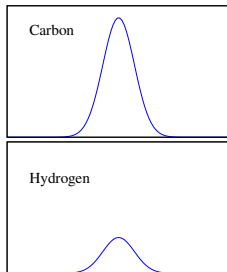Nick Woods

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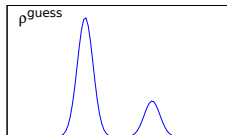Orbitals

3. Self-
Consistency

Goal: Find the (occupied) eigenfunctions of H^{KS}

1. Need an initial guess of the density ρ^{guess} in order to calculate the Hartree and XC potentials,

$$v_{\mathrm{h}}(\mathbf{r}) = \int d\mathbf{r}' \, \frac{\rho(\mathbf{r}')}{|r - r'|}$$

$$v_{\mathrm{xc}} = v_{\mathrm{xc}}[\rho](\mathbf{r})$$

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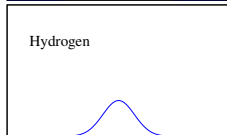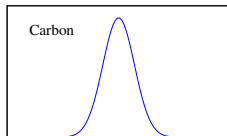
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The Initial Guess

Identify species at positions $\mathbf{R}_\mu$ C — H

The Initial Guess

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Identify species at positions $\mathbf{R}_\mu$ C — H

Run (pseudopotential) DFT to
obtain the electron density of
each *isolated* species

The Initial Guess

Identify species at positions $\mathbf{R}_\mu$

C — H

Carbon

Run (pseudopotential) DFT to obtain the electron density of each *isolated* species

Hydrogen

Place at $\mathbf{R}_\mu$ and add:
$$\rho^{\text{guess}} = \sum \rho_i^{\text{isolated}}$$

ρ^{guess}

The Naive Method

- Construct

$$\langle \mathbf{G} | H^{\mathrm{KS}} | \mathbf{G}' \rangle = \begin{pmatrix} \cdots & \cdots & \cdots & \\ \vdots & \ddots & & \\ \vdots & & \ddots & \\ \vdots & & & \end{pmatrix}$$

- Expanded in $\{|\mathbf{G}\rangle\}$ basis – labels plane-waves.

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• Typical (smallish) calculation $\sim \mathcal{O}(100,000)$ plane-waves.

$$RAM = 16 \times 100000^2 = 160GB$$

Bytes per entry (double precision $\mathbb{C}$) $\#$ entries

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Eigendecomposition of a Hermition $\mathbb{C}$ matrix scales $\sim \mathcal{O}(N^3)$

If it takes $\sim 1s$ to find eigenvectors and values of a 1000×1000 matrix

Our system takes:

$$t = \frac{(100000)^3}{(1000)^3} \times 1s \approx 12\text{days}$$

• Only want $\sim$ as many eigenfunctions as we have electrons

• Frame as an optimisation problem:

$$\epsilon(\phi_i) = \frac{\phi_i^* H^{\mathrm{KS}} \phi_i}{|\phi_i|^2}$$

is a function minimised by the ground state eigenvector, which evaluates to the ground state eigenvalue.

Solve

$$\min \left\{ \epsilon(\phi_i) \mid i \in [1, N_b], \langle \phi_i | \phi_j \rangle = \delta_{ij} \right\}$$

where

$$\frac{d\epsilon(\phi_i)}{d\phi_i} = 0$$

at eigenvectors.

Steepest descent

1) Generate an initial guess 'subspace': $\{\phi_i\}$

2) Compute gradient ('descent direction'): $\delta_i = \frac{d\epsilon(\phi_i)}{d\phi_i}$

3) Orthogonalise $\{\delta_i\}$

4) Update: $\phi_i^{\mathsf{new}} = \phi_i^{\mathsf{old}} + \delta_i$.

5) Terminate when $|\delta_i| = 0$.

Circumventing the Eigendecomposition

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CASTEP uses Davidson...

"The Iterative Calculation of a Few of the Lowest Eigenvalues
and Corresponding Eigenvectors of Large Real-Symmetric
Matrices"

Similar procedure, but particularly suited to KS DFT
calculations:

- Parallelisable
- Works well for diagonally dominant matrices (kinetic energy)

Circumventing the Eigendecomposition

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Source of the scaling in DFT: 'orthogonalise'

Approximately scales with
$N^3 = (\# \text{ eigenfunctions})^3 \approx (\# \text{ electrons})^3$

Eigendecomposition now takes $t \sim 10 \text{seconds}$ instead of 12
days.

No longer need to diagonalise, but in order to evaluate our optimisation function

$$\epsilon(\phi_i) = \frac{\phi_i^* H^{\text{KS}} \phi_i}{|\phi_i|^2}$$

we still need to construct H^{KS}; requires 160GB of RAM.

Circumventing Constructing H^{KS}

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Only require the *application* of H^{KS} on ϕ_i

Clever switching between Fourier (plane-wave) space and real space allows $(H^{\mathrm{KS}}\phi_i)$ to be calculated with just a series of vector-vector products.

What does CASTEP do?

Need to evaluate $H^{\mathrm{KS}}\phi_i = \chi_i$:

$$\left(-\frac{1}{2}\nabla^2 + v^{\mathsf{ext}} + v^{\mathsf{h}} + v^{\mathsf{xc}}\right)\phi_i$$
$$= \phi^{\mathsf{kinetic}} + \phi^{\mathsf{ext}} + \phi^{\mathsf{h}} + \phi^{\mathsf{xc}} = \chi_i$$

Kinetic energy

In plane-wave space, the matrix elements of the Hamiltonian
are diagonal:

$$\langle \mathbf{G} | -\frac{1}{2}\nabla^2 | \mathbf{G} \rangle = \frac{1}{2}|G|^2 \delta_{\mathbf{G}\mathbf{G}'}$$

Easy to construct, just populate a vector with $1/2|G|^2$,
multiply with ϕ_i to obtain $\phi_i^{\text{kinetic}}(G)$.

Circumventing Constructing H^{KS}

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Hartree potential

Requires an integral over all $\mathbf{r}'$ – costly

$$v_{\text{h}}(\mathbf{r}) = \int d\mathbf{r}' \, \frac{\rho(\mathbf{r}')}{|r - r'|}$$

but...

$$\mathcal{F}(v_{\text{h}}(\mathbf{r})) \sim \frac{\rho(\mathbf{G})}{|G|^2} = v_h(G)$$

Hartree potential

1. $\text{FFT}(\rho(\mathbf{r}))$

2. Construct $v_h(G)$

3. $\text{FFT}^{-1}(v_h(G)) = v_h(\mathbf{r})$

4. Multiply $\phi_i^h(\mathbf{r}) = v_h(\mathbf{r})\phi_i$

Other (local) potentials

Easy to construct in real-space, and apply in real-space:

$$\phi^{\mathsf{loc}}(\mathbf{r}) = v^{\mathsf{loc}}(\mathbf{r})\phi_i$$

(ignoring how pseudopotentials work)

Circumventing Constructing H^{KS}

We now have $\{\phi^{\mathsf{kinetic}}(G),\ \phi_i^h(\mathbf{r}),\ \phi_i^{xc}(\mathbf{r}),\ \phi_i^{ext}(\mathbf{r})\}$

Finally, add them all together *in the same space*:

$$FFT^{-1}(\phi^{\mathsf{kinetic}}(G)) + \phi_i^h(\mathbf{r}) + \phi_i^{xc}(\mathbf{r}) + \phi_i^{ext}(\mathbf{r}) = \chi_i$$

and we have applied H^{KS} to a vector, without constructing it, efficiently.

Savings...

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RAM requirements: $160GB \rightarrow \sim 4GB$

Time requirements: 12 days $\rightarrow \sim 10$ seconds

Self-Consistency

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Calculated correct (occupied) eigenfunctions $\{\phi_i\}$ from Davidson

Compute $\rho^{\text{out}}(\mathbf{r}) = \sum_{k,i} |\phi_i|^2$

Not the same as the guess density we used to construct H^{KS} in the beginning, ρ^{in}

Updating the Density

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

How do we update ρ such that they are $\sim$ equal?

The Naive Method

$$\rho^{\mathsf{in}} = \rho^{\mathsf{out}}$$

and start the process again...

- Diverges on most systems

- 'Damping' the iterations: guaranteed to converge for a small enough 'damping parameter'

- Can take $\mathcal{O}(1000)$ iterations (1000+ calculations of eigenfunctions...)

Updating the Density

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What does CASTEP do?

Pulay's method – 'discrete inversion in the iterative subspace'

$$\rho^{\text{new}} = \rho^{\text{old}} + \delta\rho$$

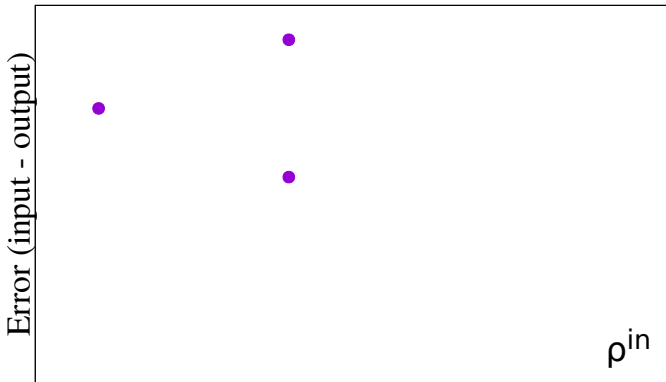Error: $\rho^{\text{in}} - \rho^{\text{out}}$

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Error (input - output)

ρ^{in}

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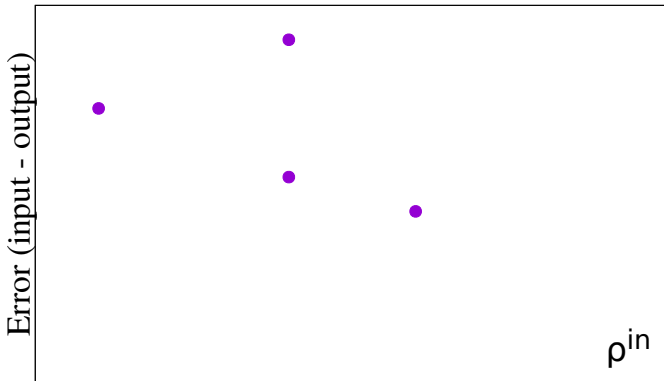of Occupied
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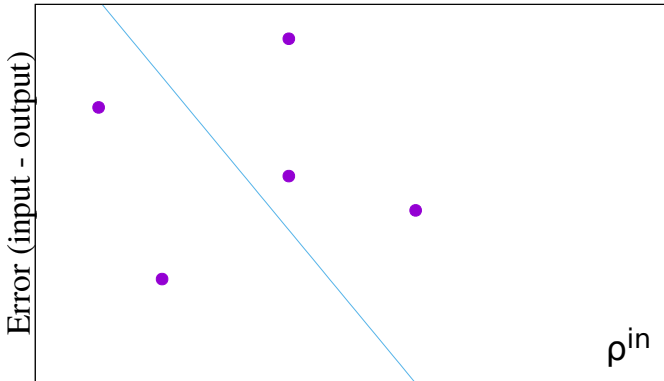
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Error (input - output)

ρ^{in}

Divergent or $\mathcal{O}(1000)$ iterations $\rightarrow$ $\mathcal{O}(10)$ iterations

Conclusion

Methods and Algorithms in CASTEP

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1. Initial Guess

2. Calculation of Occupied Orbitals

3. Self-Consistency

- Diagonalise iteratively as an optimisation problem

- FFTs switch between spaces to avoid storing large matrices

- Accelerated mixing allows the computation to converge

- Scaling saving: $\sim \mathcal{O}(N_{plane-waves}^3) \rightarrow \sim \mathcal{O}(N_{electrons}^3)$