Hybrid Time-Dependent Density Functional Theory in CASTEP

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Castep is...

- A general-purpose 'first principles' atomistic modelling program
- Based on density functional theory
- Used on many HPC machines, including HECToR

Written in

- Fortran 95
- BLAS/LAPACK for linear algebra
- FFT libraries (where available)
- MPI for parallel communication

Portable and well optimised

Castep can...

- Compute the electronic density
- Determine the groundstate atomic configuration and cell
- Simulate molecular dynamics (path-integrals, variable cell)
- Calculate band-structures and density of states
- Compute various spectra (optical, IR, Raman, NMR, XANES...)
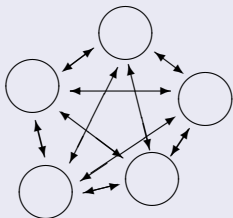- plus linear response, population analysis, ELF, etc.

What can't it do?

Excited states

- Optical properties
- Excited state MD
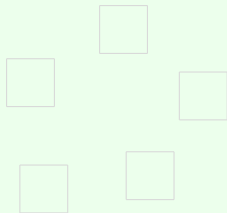- Excitons
- Catalytic reactions
- Low-Loss EELS

DFT overview

From this. . .

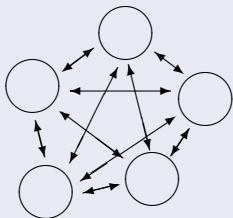### . . . to this

Lots of interacting particles in a potential.

Independent (fictitious) particles in an effective potential.

DFT overview

From this. . .

Lots of interacting particles in a potential.

. . . to this

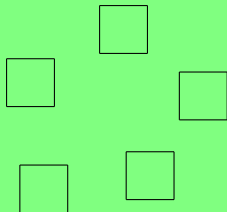Independent (fictitious) particles in an effective potential.

Castep Basics

Castep solves a set of Schrödinger equations,

$$\mathrm{H}_k[n]\psi_{bk}\left(\mathbf{r}\right) = \epsilon_{bk}\psi_{bk}\left(\mathbf{r}\right)$$

where n is the electronic density and $\{\psi_{bk}\}$ are the *bands*.

$$n\left(\mathbf{r}\right) = \sum_{bk} 2w_k \left|\psi_{bk}\left(\mathbf{r}\right)\right|^2$$
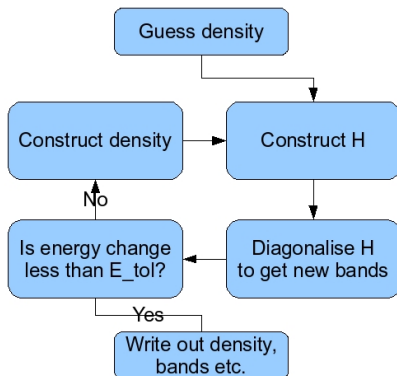
Self-consistency

$$H_k[n]\psi_{bk}(\mathbf{r}) = \epsilon_{bk}\psi_{bk}(\mathbf{r})$$

- H_k depends on $n(\mathbf{r})$
- $n(\mathbf{r})$ depends on $\{\psi_{bk}\}$

We need to solve this eigenvalue equation iteratively until we have *self-consistency*.

How Castep Works

A useful basis set

We expand ψ_{bk} in a plane-wave (Fourier) basis,

$$\psi_{bk}(\mathbf{r}) = \sum_G c_{Gbk} e^{i(\mathbf{G}+\mathbf{k}).\mathbf{r}}$$

The fundamental data object in CASTEP is the wavefunction data type, which stores the complex coefficients c_{Gbk} for all bands at all k-points:
wvfn%coeffs(1:nG,1:nbands,1:nkpts)
Thus for a given k-point, any band is just a vector of length N_G and the Hamiltonian $\hat{H}_k$ is a $N_G \times N_G$ matrix.

A useful basis set

$$\psi_{bk}\left(\mathbf{r}\right) = \sum_{G} c_{Gbk} e^{i(\mathbf{G}+\mathbf{k}).\mathbf{r}}$$

If we increase the size of our simulation system:

- The size of the smallest **G**-vector decreases
- The number of **G**-vectors, N_G, *increases*
- On HPC machines N_G might be O(100,000)

The **k**-points

The vectors $\{\mathbf{k}\}$ sample the region of reciprocal-space
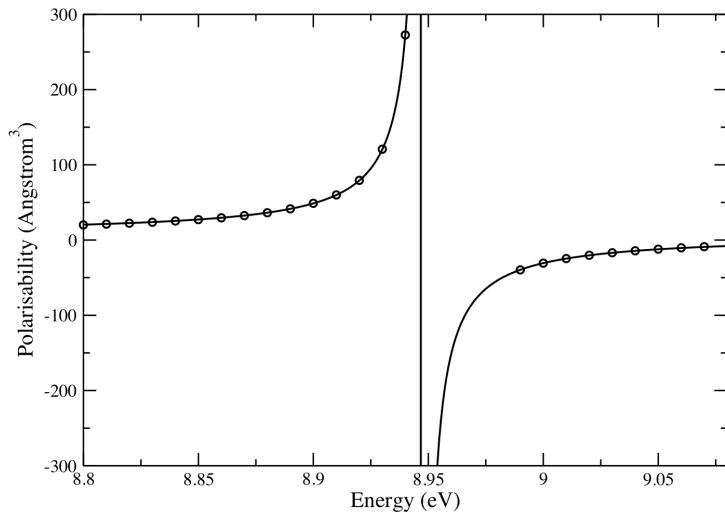
$$|\mathbf{k}| < \frac{1}{2}\,|\mathbf{G}_{smallest}|\,.$$

We increase the **k**-point density until our calculation converges.
If we increase the size of our simulation system:

- The size of the smallest **G**-vector decreases
- The number of **k**-points we need *decreases*
- On HPC machines N_k might be O(1)

- Analogous to DFT
- Density is now dependent on time: $n(\mathbf{r}, t)$
- Can be solved with a perturbative approach
- Excitation energies ω are poles of:

$$\sum_{i,j=1}^{N} \left(H\delta_{ij} - \epsilon_{ij} \right) \left| \Phi_j^{\{\pm\}} \right\rangle + P_c V^{\{\pm\}}(\pm\omega) \left| \Phi_i^{\{0\}} \right\rangle = \mp\omega \left| \Phi_i^{\{\pm\}} \right\rangle$$

Methane results

Eigenvalue problem

- Poles of the earlier equation can be found directly by solving a Hermitian eigenvalue problem.

- $(A + B) \left| \Phi^{\{\pm\}} \right\rangle = \omega \left| \Phi^{\{\pm\}} \right\rangle$

- $A \left| \Phi^{\{\pm\}} \right\rangle = (H - \epsilon) \left| \Phi^{\{\pm\}} \right\rangle$

- $B \left| \Phi^{\{\pm\}} \right\rangle = P_c V^{\{1\}}[n^{\{1\}}] \left| \Phi^{\{0\}} \right\rangle$
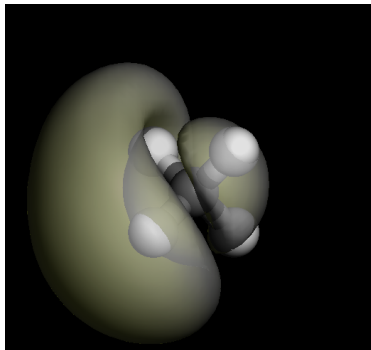
Self-consitent

- B depends on $n^{\{1\}}$
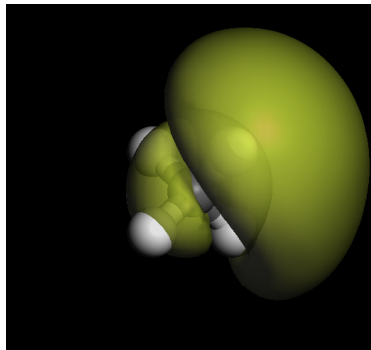- $n^{\{1\}}$ depends on $\left|\Phi^{\{\pm\}}\right\rangle$

Need an iterative method to solve.

- Initially start with canned serial library.
- ARPACK – Arnoldi method
- HSL EA19 – Rayleigh quotients with conjugate gradients and preconditoning
- Both have reverse communication interface

Methane response density

From

To

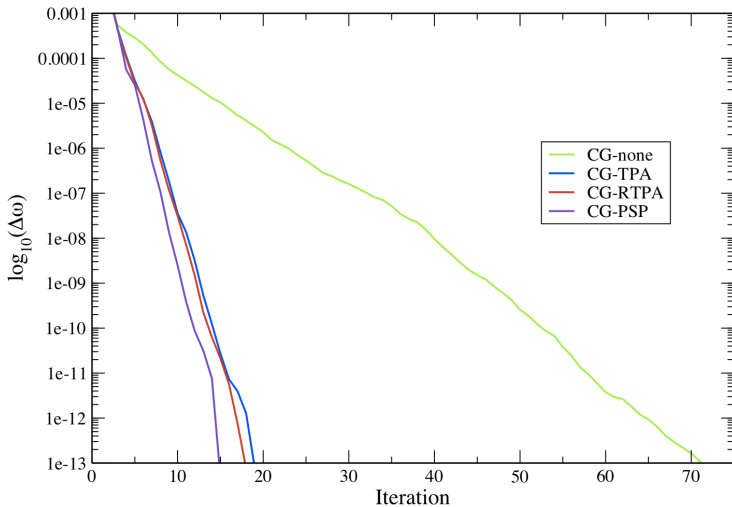## Numerical results

Methane (numbers in eV)

- Scan through frequency 9.09
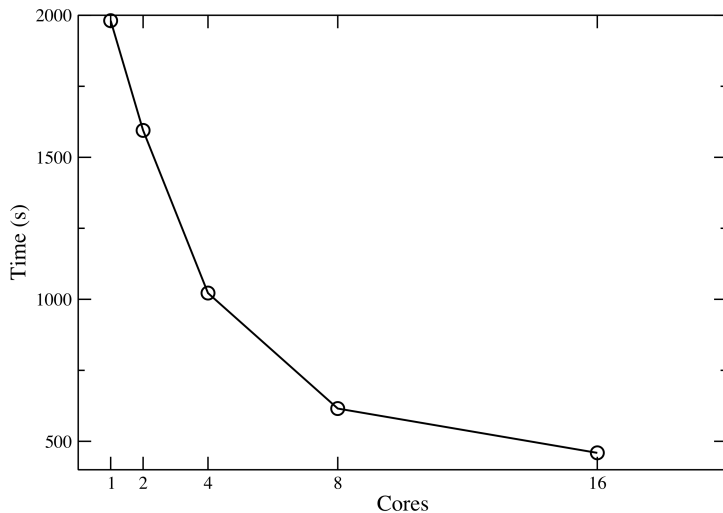- Tamm-Dancoff 9.09
- Literature 9.05

Formaldehyde

- Scan through frequency 3.91
- Tamm-Dancoff 1st 3.91 2nd 5.81
- Literature 1st 3.65 2nd 5.90

- Conjugate gradients
- Preconditioning
- Trivial to parallelise over G-vectors

Preconditioning

Scaling

What's next

- Davidson sovler
- Include k-points
- Include spin

- Forces
- Hybrid functionals