Introduction to first-principles modelling and CASTEP

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Introduction to DFT + CASTEP

Atomistic Simulations

If we know what the bonding in a material is beforehand, then we can often find good expressions for the forces between atoms, e.g.

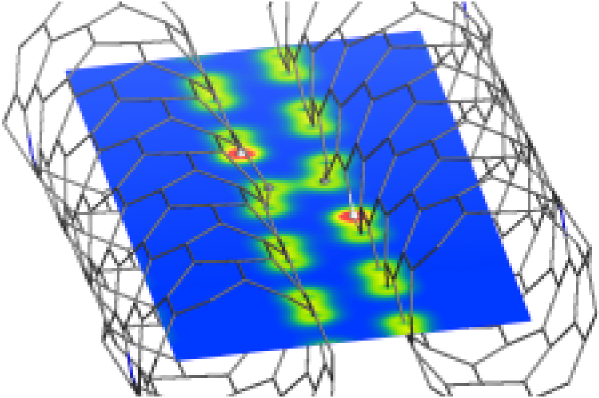
- Ionic $\Rightarrow$ electrostatic potentials
- Covalent $\Rightarrow$ directional potentials, e.g. Stillinger-Weber
- Metallic $\Rightarrow$ Bond Order Potentials, EAM...
- Van der Waals $\Rightarrow$ Born-Mayer, Lennard-Jones...

These potentials can do a good job of computing the mechanical properties of materials.

Atomistic Simulations

These ‘forcefield’ potentials do have problems:

- Usually parameterised for bulk equilibrium behaviour
- Parameterised for particular class of materials
- Cannot handle bond breaking or formation
- Cannot provide electronic information, so no predictions of
  - Resistance
  - Thermal conductivity
  - Colour



First Principles Simulations

We want to be able to predict what atoms will do from *first principles*, without needing to know what they'll do beforehand! We can do this using quantum mechanics.

Unfortunately, quantum mechanics is difficult!

Electronic Structure Simulations

We want to solve the Schrödinger equation. For 1-particle it's:

$$\left(-\frac{\hbar^2}{2m}\nabla^2+\hat{V}\right)\Psi\left(\mathbf{r},t\right)=i\hbar\frac{\partial\Psi\left(\mathbf{r},t\right)}{\partial t}$$

Now we just have to solve it for a real material.

How hard can it be?

The horror.... the horror...

For *M* nuclei and *N* electrons:

$$\left\{-\frac{\hbar^2}{2}\left(\frac{\nabla^2_{n1}}{m_1}+\ldots+\frac{\nabla^2_{nM}}{m_M},\frac{\nabla^2_{e1}}{m}+\ldots+\frac{\nabla^2_{eN}}{m}\right)\right.$$
$$\left.+\hat{V}\left(\mathbf{R}_1,\ldots,\mathbf{R}_M,\mathbf{r}_1,\ldots,\mathbf{r}_N,t\right)\right\}\Psi\left(\mathbf{R}_1,\ldots,\mathbf{R}_M,\mathbf{r}_1,\ldots,\mathbf{r}_N,t\right)$$
$$=i\hbar\frac{\partial\Psi\left(\mathbf{R}_1,\ldots,\mathbf{R}_M,\mathbf{r}_1,\ldots,\mathbf{r}_N,t\right)}{\partial t}$$

How big are *M* and *N*?

The horror.... the horror...

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$$\left.+\hat{V}\left(\mathbf{R}_1,...,\mathbf{R}_M,\mathbf{r}_1,...,\mathbf{r}_N,t\right)\right\}\Psi\left(\mathbf{R}_1,...,\mathbf{R}_M,\mathbf{r}_1,...,\mathbf{r}_N,t\right)$$
$$=i\hbar\frac{\partial\Psi\left(\mathbf{R}_1,...,\mathbf{R}_M,\mathbf{r}_1,...,\mathbf{r}_N,t\right)}{\partial t}$$

How big are *M* and *N*? For a few grams of material:

- $M \sim 100,000,000,000,000,000,000,000$
- $N \sim 1000,000,000,000,000,000,000,000$

The horror.... the horror...

For *M* nuclei and *N* electrons:

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How big are *M* and *N*? For a few grams of material:

- $M \sim 100,000,000,000,000,000,000,000$
- $N \sim 1000,000,000,000,000,000,000,000$

Oh dear.

Electronic Structure Simulations

How can we make quantum mechanics easier for ourselves?

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QM for the electrons

- Nuclei are heavy, slow and boring
  $\longrightarrow$ no QM for nuclei
- Electrons are light, quick and interesting
  $\longrightarrow$ Nuclei appear static
  $\longrightarrow$ No explicit time-dependence for electrons

This is the Born-Oppenheimer approximation.

$$\Psi\left(\mathbf{R}_1, ..., \mathbf{R}_M, \mathbf{r}_1, ..., \mathbf{r}_N, t\right) \longrightarrow \psi\left(\mathbf{r}_1, ..., \mathbf{r}_N\right)$$

Now we can solve the time-independent Schrödinger equation.

Electronic Structure Simulations

$$\left\{-\frac{\hbar^2}{2m}\left(\nabla_1^2+\ldots+\nabla_N^2\right)+\hat{V}\left(\mathbf{R}_1,\ldots,\mathbf{R}_M,\mathbf{r}_1,\ldots,\mathbf{r}_N\right)\right\}$$
$$\psi\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\right)=E\psi\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\right)$$

Hmm, looks a bit like an eigenvalue problem...
Still have $N \sim 10^{23}$ though.

Electronic Structure Simulations

How can we make quantum mechanics easier for ourselves?

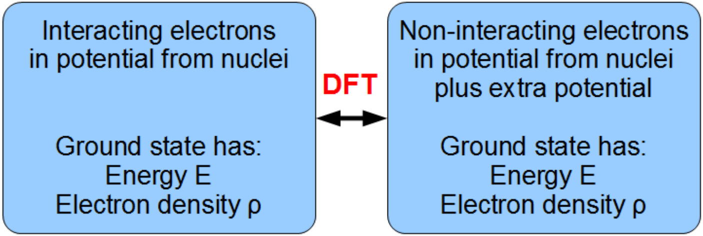
- Only use QM for the electrons✓
- Concentrate on the groundstate
- Exploit periodicity of crystals
- Get a computer to do it

Concentrate on the groundstate

- Materials' properties are dominated by the groundstate
- For the groundstate we can use a different form of QM
  Density Functional Theory

Density Functional Theory

The groundstate energy E and density $\rho(\mathbf{r})$ of electrons are exactly the same as those of *non-interacting* particles in a specially modified potential.



Interacting electrons in potential from nuclei

Ground state has:
Energy E
Electron density ρ

DFT

Non-interacting electrons in potential from nuclei plus extra potential

Ground state has:
Energy E
Electron density ρ

Density Functional Theory

Solve N non-interacting Schrödinger equations:

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V\left[\rho\right]\left(\mathbf{r}\right)\right\}\psi_j\left(\mathbf{r}\right) = \epsilon_j\psi_j\left(\mathbf{r}\right)$$

$V\left[\rho\right]$ is a *density functional*.

$$\rho(\mathbf{r}) = \sum_{j=1}^{N}\left|\psi_j(\mathbf{r})\right|^2$$

We don't know $V\left[\rho\right]$ exactly, but there are reasonable approximations available.

Density Functional Theory

We know the classical contributions to $V[\rho]$, e.g.

$$E_H[\rho](\mathbf{r}) \quad = \quad \frac{1}{2}\iint \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

but what about QM exchange and electron correlation? We have to approximate this exchange-correlation functional:

- Local density approximation (LDA)
  Tends to over-bind.
  In your param file use `xc_functional : LDA`
- Generalised gradient approximations (GGAs) PBE is the most popular. Tends to under-bind.
  In your param file use `xc_functional : PBE`

These approximations do not handle dynamic correlation well, e.g. no van der Waal's or Cooper pairs...

The story so far...

- Started with time-dependent 10^{23}-electron-nuclear wavefunction
- Born-Oppenheimer approximation
  $\longrightarrow$ time-independent, 10^{23}-electron wavefunction
- DFT $\longrightarrow$ 10^{23} 1-electron wavefunctions

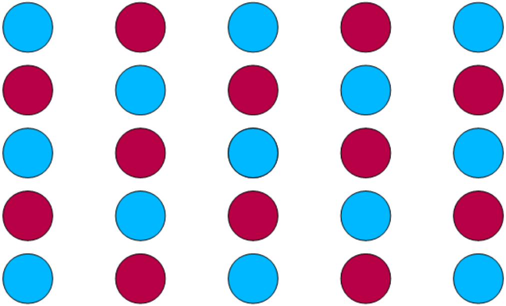
Electronic Structure Simulations

How can we make quantum mechanics easier for ourselves?

- Only use QM for the electrons✓
- Concentrate on the groundstate✓
- Exploit periodicity of crystals
- Get a computer to do it

Crystals and Unit Cells

In the solid state, most materials like to have their atoms arranged in some kind of regular, repeating pattern, e.g.



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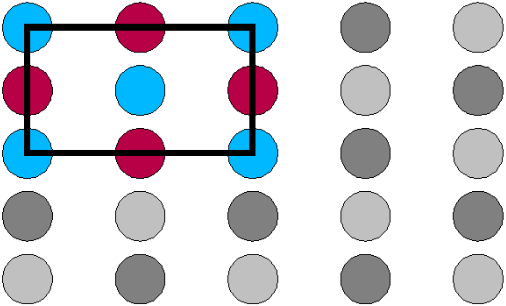


Bloch's Theorem

If the nuclei are arranged in a periodically repeating pattern, their potential acting on the electrons must also be periodic.

$$V(\mathbf{r}+\mathbf{L}) = V(\mathbf{r})$$

where **L** is any lattice vector.

What does this mean for the density and wavefunction?

Bloch's Theorem

If the potential is periodic, then so is the density:

$$\rho(\mathbf{r}+\mathbf{L}) = \rho(\mathbf{r})$$

What about the wavefunction?

Bloch's Theorem

If the potential is periodic, then so is the density:

$$\rho(\mathbf{r} + \mathbf{L}) = \rho(\mathbf{r})$$

What about the wavefunction?

$$\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$$

i.e. if $\rho(\mathbf{r})$ is periodic, so is the magnitude of the wavefunction.

Remember wavefunctions are complex; their magnitude is periodic, but their phase can be anything.

Bloch's Theorem

Bloch's theorem: in a periodic potential, the density has the same periodicity. The possible wavefunctions are all 'quasi-periodic':

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} u_k(\mathbf{r}),$$

where $u_k(\mathbf{r}+\mathbf{L}) = u_k(\mathbf{r})$, and $e^{i\mathbf{k}.\mathbf{r}}$ is an arbitrary phase factor.

Brillouin zone sampling

There are solutions for any **k** ⇒ general solution is integral over Brillouin zone.

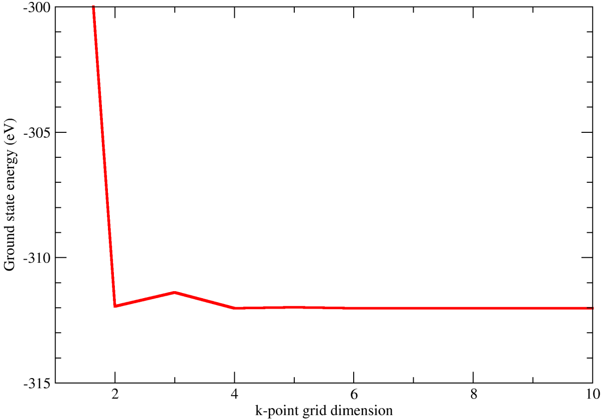
We approximate this integral by a sum over discrete **k**; these 'k-points' form a regular 3D grid in reciprocal space.

In your cell file use one of:

```
kpoint_mp_grid 5 5 5
kpoint_mp_spacing 0.04
```

Always need to ensure we have enough k-points to approximate the integral well.

k-point convergence



Exploiting periodicity

- Only compute $\psi_j(\mathbf{r})$ and $\rho(\mathbf{r})$ in a single unit cell
- No longer have 10^{23} wavefunctions, more like 10^2
- Now computing energy *per unit cell*

In fact because we've exploited the periodicity, in some ways we're now calculating for an *infinite* number of electrons!

Electronic Structure Simulations

How can we make quantum mechanics easier for ourselves?

- Only use QM for the electrons✓
- Concentrate on the groundstate✓
- Exploit periodicity of crystals✓
- Get a computer to do it

Basis sets

We need to choose a suitable basis set to represent our wavefunctions, but what should we choose...

- Points on a grid?
- Polynomials?
- Gaussians?
- Atomic orbitals?

None of these reflect the periodicity of our problem.

Plane-waves

Since $\psi(\mathbf{r})$ is periodic, we express it as a 3D Fourier series

$$\psi(\mathbf{r}) = \sum_{G} c_G e^{i\mathbf{G}.\mathbf{r}}$$

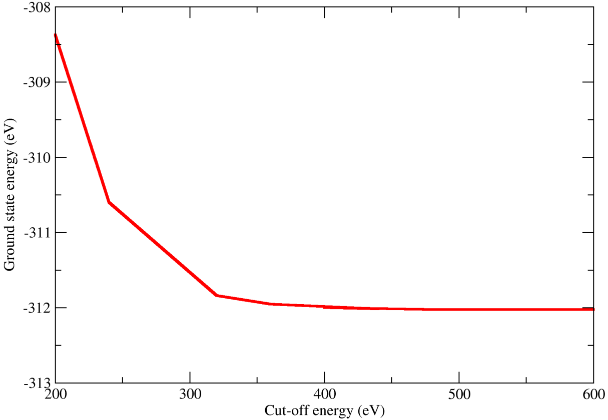
where c_G are complex Fourier coefficients, and the sum is over all wavevectors (spatial frequencies) with the right periodicity.

Each ψ is now a vector of coefficients c_G.

Cut-off Energy

- $e^{i\mathbf{G}.\mathbf{r}}$ is a plane-wave travelling perpendicular to **G**
- There are an infinite number of allowed **G**
- As $|\mathbf{G}| \rightarrow \infty$, $|c_G| \rightarrow 0$
  $\Rightarrow$ can truncate the Fourier expansion safely
- In your param file:
  `cut_off_energy :  420 eV`

Cut-off Energy



An Eigenvalue Problem

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V\left[\rho\right]\left(\mathbf{r}\right)\right\}\psi_j\left(\mathbf{r}\right) = \epsilon_j\psi_j\left(\mathbf{r}\right)$$

- ψ_j is a vector of `num_pw` Fourier coefficients
- The $\{...\}$ is a `num_pw`×`num_pw` matrix
- ⟶ just an eigenvalue problem!

$$\mathrm{H}\psi_j = \epsilon_j\psi_j$$

A *Large* Eigenvalue Problem

Solve using the variational principle:

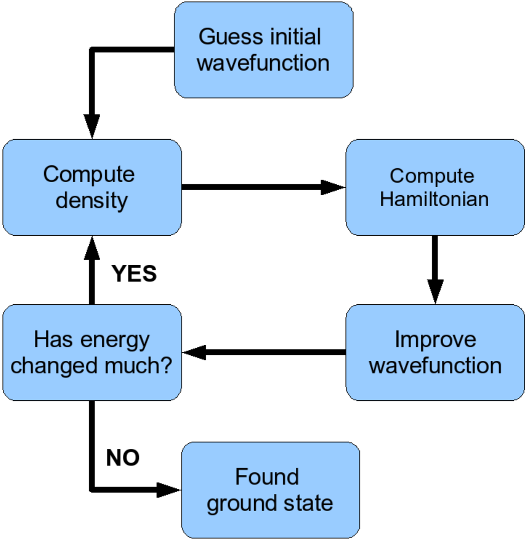
- The groundstate energy E_0 is the lowest possible energy
- Any wavefunction has energy $E \geq E_0$
  $\longrightarrow$ guess a wavefunction ψ (c_G)
  $\longrightarrow$ compute $E = \psi^\dagger H \psi$
  $\longrightarrow$ tweak c_G to lower E
- When we can't lower E any more,
  ψ is the groundstate!

Steepest Descent Diagonalisation

- Starting with ψ_j, compute ϵ_j
- Compute the gradient $\frac{\delta\epsilon_j}{\delta\psi_j^\dagger}$
- This is the change to c_G that *increases* ϵ_j quickest
- We want to *decrease* ϵ_j, so use $-\frac{\delta\epsilon_j}{\delta\psi_j^\dagger}$.
- Make a new guess eigenstate, $\psi_j^{new} = \psi_j - \lambda\frac{\delta\epsilon_j}{\delta\psi_j^\dagger}$
- Vary λ until we've found the lowest ϵ_j in this direction. This procedure is often called a *line search*.

There are better methods than steepest descent, e.g. conjugate gradients.

Finding the Groundstate



Guess initial wavefunction

Compute density

Compute Hamiltonian

Improve wavefunction

Has energy changed much?

YES

NO

Found ground state

Sample CASTEP output

Valence electrons and pseudopotentials

Core electrons do not affect material's properties.

- Compute core electronic states for isolated atom
- Treat nucleus and core electrons as single 'ion' $\longrightarrow$ replace nuclear potential with ionic pseudopotential.

In your cell file:

```
%block species_pot
Co Co_00.usp
Mn Mn_00.usp
Si Si_00.usp
%endblock species_pot
```

Fame and fortune

- Now have all the tools we need
- Can find solve DFT eq. for lowest N eigenstates $\longrightarrow$ get energy and electron density
- Can now predict:
  - Crystal and molecular structure
  - Bond breaking and formation
  - IR spectra
  - Reactivities
  - Colour, X-ray absorption, NMR spectra
  - ... and much more!

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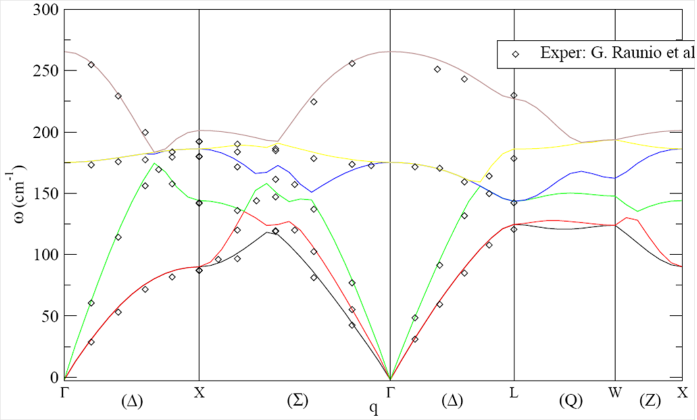
Summary
CASTEP



Summary

- Predictive materials simulations need QM calculations
- DFT reduces QM to a large, simple eigenvalue problem
- Use periodicity and pseudopotentials to improve speed
- Need to converge wrt **k**-points and cut-off energy

With these tools we can predict a vast range of properties for all kinds of materials and chemicals.

cell file

Your simulation system; important keywords are:

- Lattice

```
%block lattice_abc
2.4 2.4 3.5
90 90 120
%endblock lattice_abc
```

or specify fully (as *row vectors*)

```
%block lattice_cart
1.2000000 -2.0784610 0.0000000
1.2000000 2.0784610 0.0000000
0.0000000 0.0000000 3.0000000
%endblock lattice_cart
```

cell file

- Atomic positions

  ```
  %block positions_frac
  C 0.000000 0.00000 0.5
  C 0.333333 0.66667 0.5
  %endblock positions_frac
  ```

  (or `%block positions_abs` for absolute Cartesian coordinates; length units specified on 1st line)
- Pseudopotentials

  ```
  %block species_pot
  C C_00.recpot
  %endblock species_pot
  ```

cell file

- **k**-points

  ```
  kpoint_mp_grid nkx nky nkz
  ```

  or

  ```
  kpoint_mp_spacing k-dist unit
  ```

  or

  ```
  %block kpoint_mp_list
  kx ky kz weight
  %endblock kpoint_mp_list
  ```

cell file

- Symmetry

  ```
  symmetry_generate
  snap_to_symmetry
  ```

- Geometry optimisation

  ```
  fix_all_ions :  false
  ```

  Do not fix the ionic positions.

  ```
  fix_all_cell :  false
  ```

  Do not fix the cell lattice parameters.

param file

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What you want to do. Important keywords are:

- Task

```
task:  energy
task:  geometryoptimisation
task:  elnes
```

- Calculation

```
spin_polarized :  true
nextra_bands :  25
```

- Approximations

```
xc_functional :  lda
cut_off_energy :  500 eV
```

More information

- http://www.castep.org
  Lots of information including talks, tutorials and documentation.
- http://www.jiscmail.ac.uk/lists/CASTEP.html
  The CASTEP email list (website includes archives).
- `castep -help <castep keyword>`
  Returns information about that particular CASTEP keyword (if it exists).
- `castep -help search <any word>`
  Searches the CASTEP keyword descriptions for all occurrences of the word.