Density-functional theory

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Outline

- Atomistic black boxes
- Peeking inside the black box: a bit of theory
- What can DFT do for me?
- Getting started: practical considerations

Atomistic simulations

In atomistic simulations, the fundamental modelling units are *atoms*. As opposed to:

- Finite-element analysis (typically divide by small volumes of solid or liquid)
- Coarse-grained simulations (protein, polymer units)
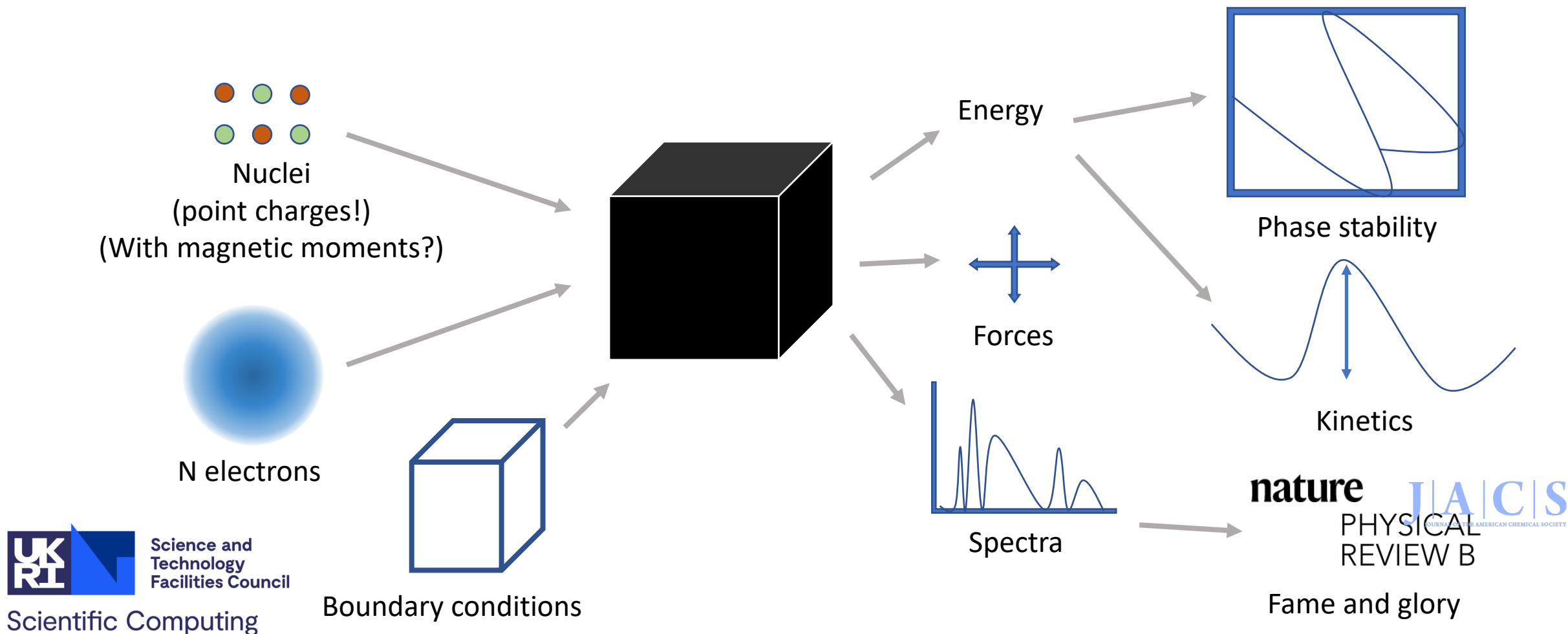- Subatomic particle physics

We can loosely group atomistic simulations into:

- Interatomic force fields (parametrised models, atom positions)
- Electronic structure (solve behaviour of electrons)

A few electronic structure approaches exist: while simplified semi-empirical and tight-binding methods have their uses, the "workhorse" DFT is *ab initio*
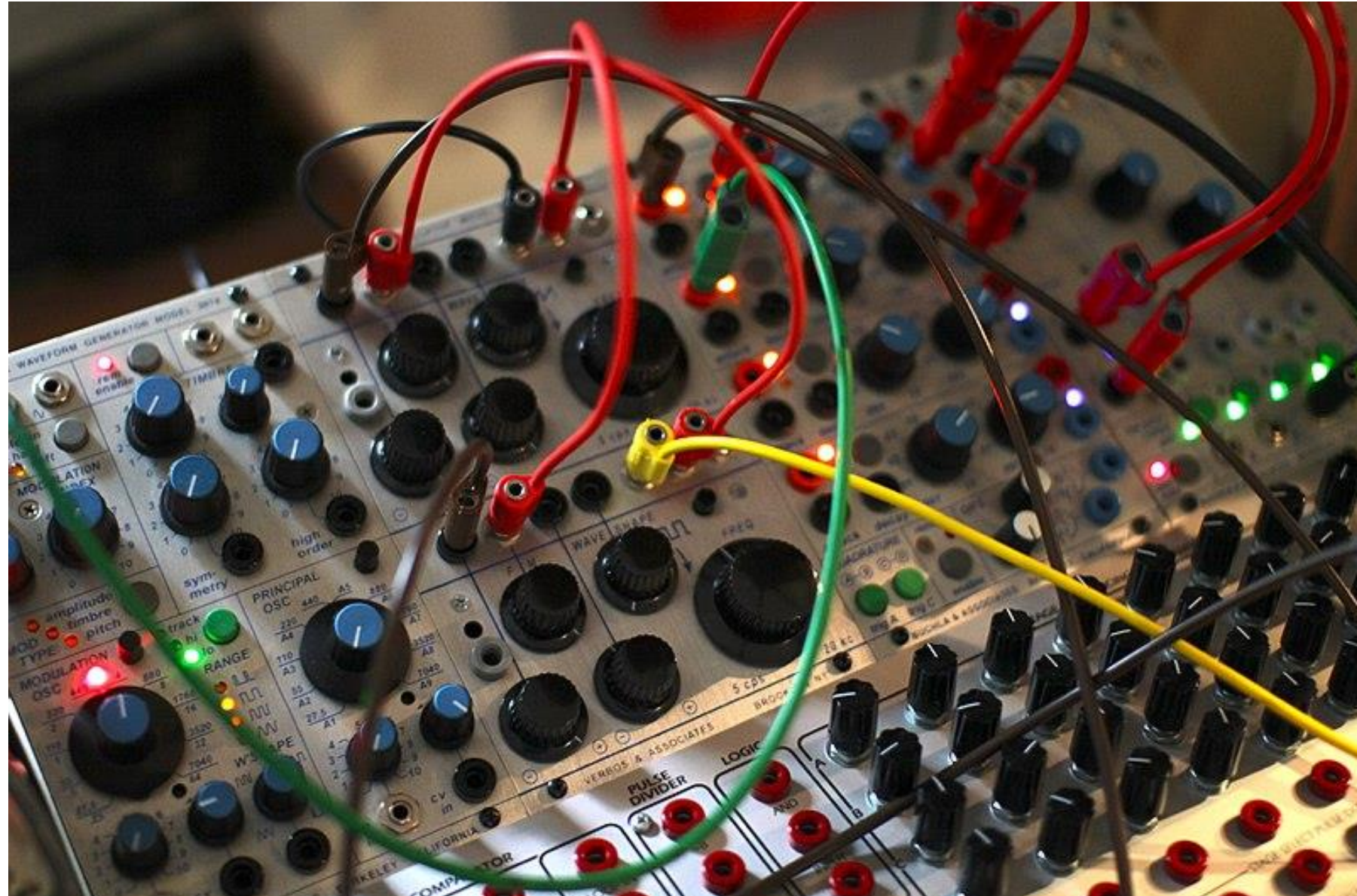
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An *ab initio* black box

"Ab initio" calculations are based on fundamental physics; they don't need special information about your system. How do we interact with these methods?
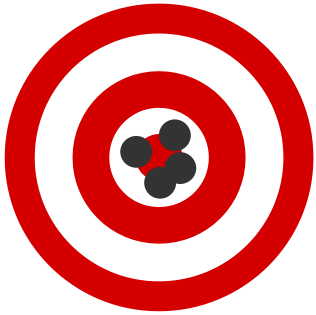

Nuclei
(point charges!)
(With magnetic moments?)

N electrons

Boundary conditions

Energy

Forces

Spectra

Phase stability

Kinetics

Fame and glory

The reality of *ab initio* methods

There seem to be quite a lot of parameters to play with...

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Precision and accuracy

High precision,
high accuracy

High precision,
low accuracy

Low precision,
high accuracy

Low precision,
low accuracy

- Some parameters concern numerical precision and can be systematically improved towards a "correct" result
  - E.g. numerical grid sizes
  - Usually a compromise with computational cost

- Other parameters will affect overall accuracy
  - E.g. physics approximations
  - effects are less predictable
  - May require more knowledge of problem, testing, system-dependence

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Inside the black box: electronic structure methods

$$E\Psi = \hat{\mathcal{H}}\Psi$$

- Looking to solve the time-independent Schrödinger equation (above)
- The nuclei define some Coulomb interactions in the Hamiltonian operator
- Solve eigenvalue problem for energy states (eigenvalues) and electronic wavefunctions (eigenvectors)
- For one nucleus and one electron, solutions give hydrogen-like orbitals
- Born–Oppenheimer approximation: nuclei are slow compared to electrons

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Inside the black box: electronic structure methods

$$E\Psi = \hat{\mathcal{H}}\Psi$$

- Things get more tricky when dealing with multiple electrons
  - Work with a set of one-electron wavefunctions to keep maths tractable (Hartree approximation)
  - Let electrons respond to a "mean field" of other electrons
- As well as Coulombic interactions, electrons interact through an anti-symmetry property related to Pauli exclusion principle

$$\Psi(\ldots, \mathbf{r}_1, \mathbf{r}_2, \ldots) = -\Psi(\ldots, \mathbf{r}_2, \mathbf{r}_1, \ldots)$$

- Putting this together yields the Hartree–Fock method: solve iteratively by minimising energy sum over occupied orbitals.

$$\epsilon_a \psi_a = \left[h + \sum_{b \neq a} \mathcal{I}_b - \sum_{b \neq a} \mathcal{X}_b \right] \psi_a$$

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Inside the black box:
Problems with Hartree–Fock

$$\epsilon_a \psi_a = \left[h + \sum_{b \neq a} \mathcal{I}_b - \sum_{b \neq a} \mathcal{X}_b \right] \psi_a$$

- Somewhat expensive $O(n^4)$
- Biggest problem is the neglect of *correlation:* mean-field sum over other electrons assumes they are independent
- Various "post-HF" methods address this by building further calculations on top of a HF starting-point. They are expensive and have their uses, but for most of the applications discussed in this lecture DFT is preferred.
- Alternatively we can work towards a similar Hamiltonian including corrections:

$$\mathcal{H}\Psi = \left(-\frac{1}{2}\nabla^2 + \mathcal{U}_{\text{ext}} + \mathcal{U}_{\text{H}} + \mathcal{U}_{\text{X}} + \mathcal{U}_{\text{C}} \right) \Psi = E\Psi$$

Density functionals

A landmark paper by Hohenberg & Kohn (1964) proves that every external potential (i.e. arrangement of nuclei) yields a unique electron density field ρ(***r***).
- Therefore each density defines a unique external potential
- Therefore density defines the Hamiltonian and all ground-state properties

$$E, E', \cdots = F\left[\rho(\mathbf{r})\right]$$

- Operators like *F* are a function on a function: known as a *functional*
- The good news: ρ(**r**) is a 3–D field, however many electrons we have
- The bad news: H–K tell us nothing about the form of these functionals

Kohn–Sham DFT

The Kohn–Sham method introduces density functionals while still using single-electron "orbitals" for some purposes.

$$\mathcal{H} = -\frac{1}{2}\nabla^2 + \mathcal{U}_{\text{ext}} + \mathcal{U}_{\text{H}} + \mathcal{U}_{\text{XC}}$$

$$E = -\frac{1}{2}\sum_i \phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r}) + E_{\text{ext}}(\rho(\mathbf{r})) + E_{\text{H}}(\rho(\mathbf{r})) + E_{\text{XC}}(\rho(\mathbf{r}))$$

These orbitals ϕ_i are variously described "auxiliary", "fictitious" or "non-interacting". They are summed to create a density and differentiated to obtain a kinetic energy.

$E_{\text{XC}}(\rho(\mathbf{r}))$ is the "exchange-correlation functional"

XC functionals

The XC functional's job is to correct for all the other errors and give correct results!

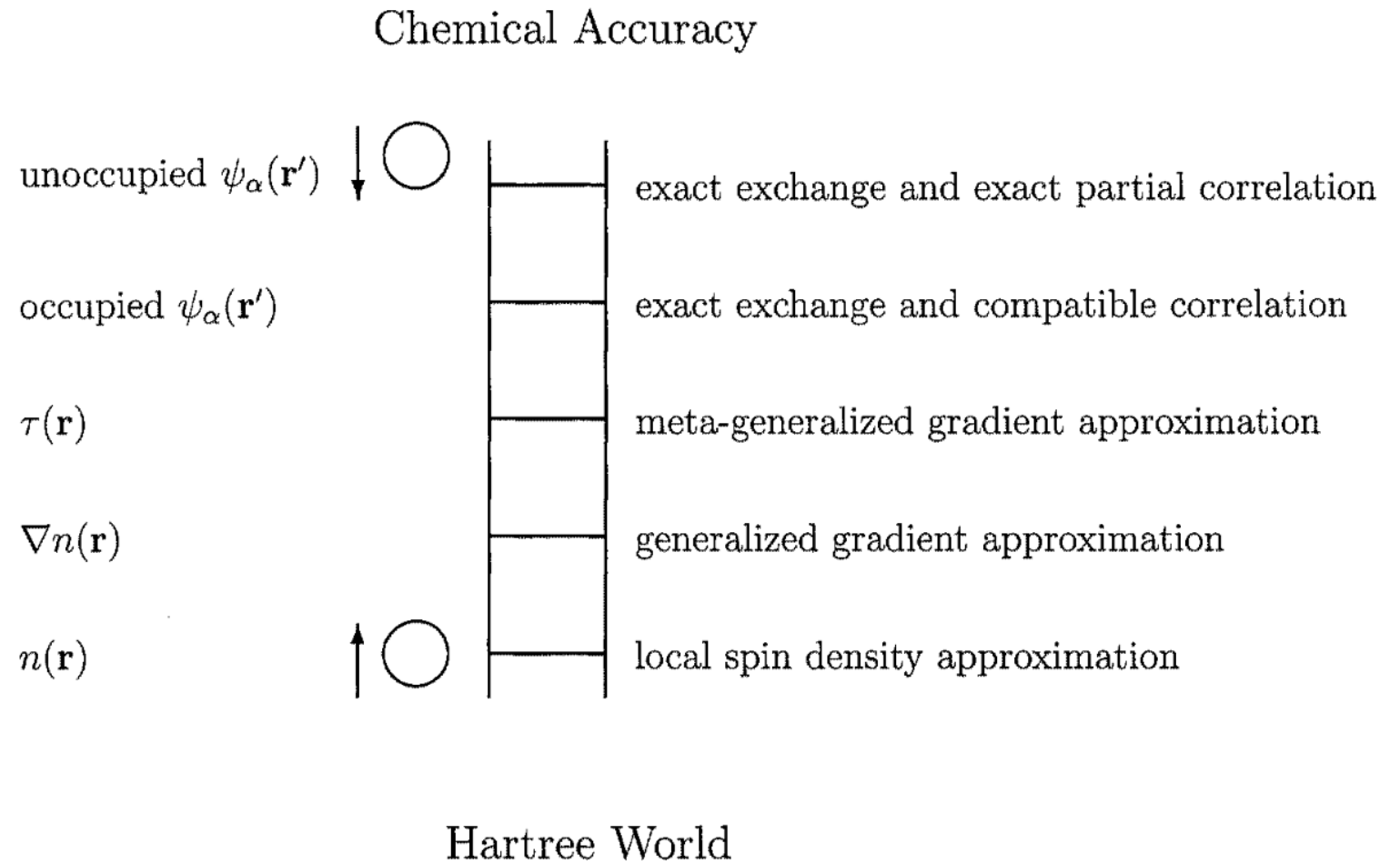Based on local density and derivative terms… as we move up the ladder we gain more parameters and make more choices

Chemical Accuracy

unoccupied $\psi_\alpha(\mathbf{r}')$	exact exchange and exact partial correlation
occupied $\psi_\alpha(\mathbf{r}')$	exact exchange and compatible correlation
$\tau(\mathbf{r})$	meta-generalized gradient approximation
$\nabla n(\mathbf{r})$	generalized gradient approximation
$n(\mathbf{r})$	local spin density approximation

Hartree World

FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.

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XC functionals

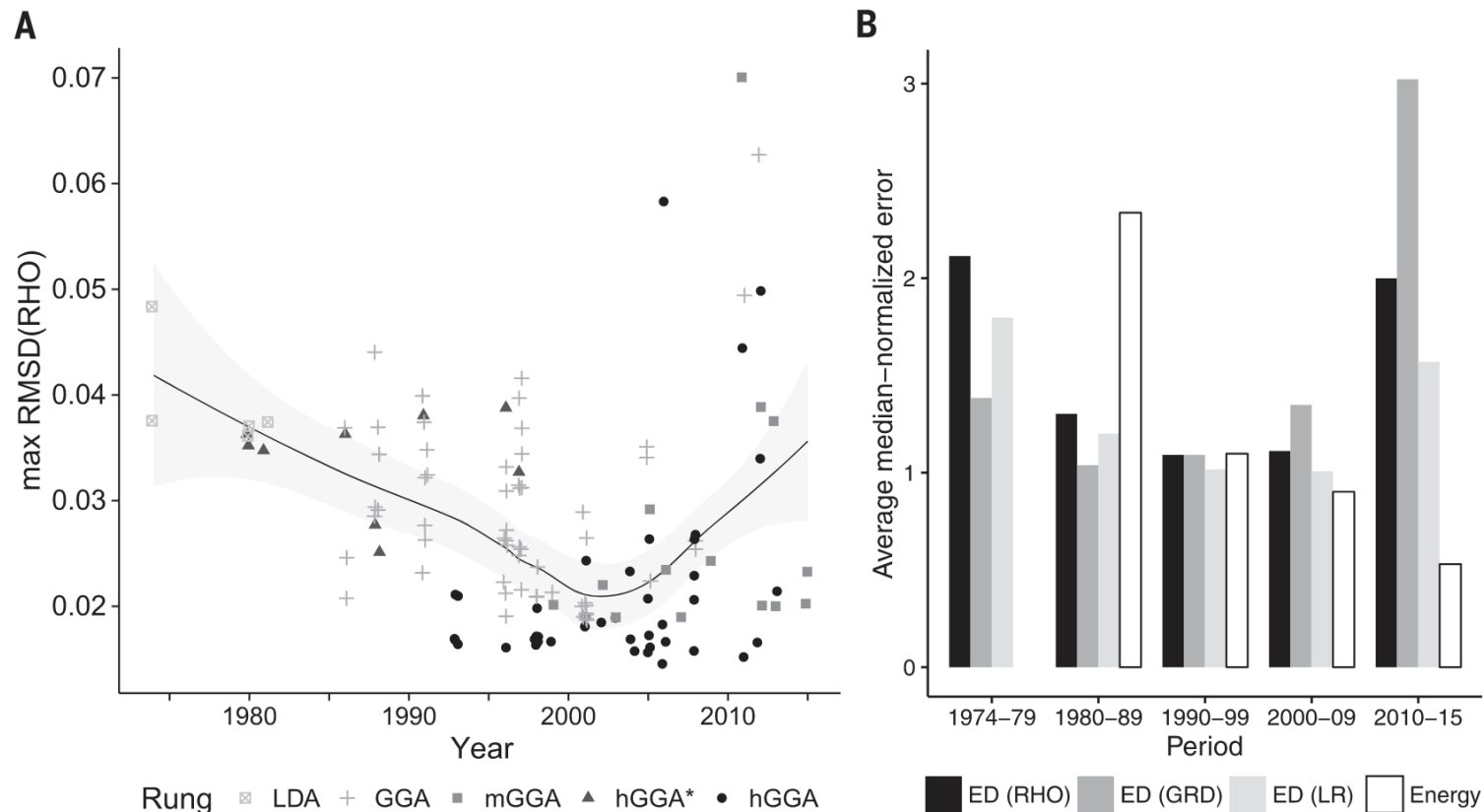XC functional design can be seen as a parameter optimisation

e.g. recent paper *"What is the optimal mGGA exchange functional for solids?"*
P. Kovács, F. Tran, P. Blaha, G. K. H. Madsen (2022) *J. Chem. Phys.* **157**, 094110
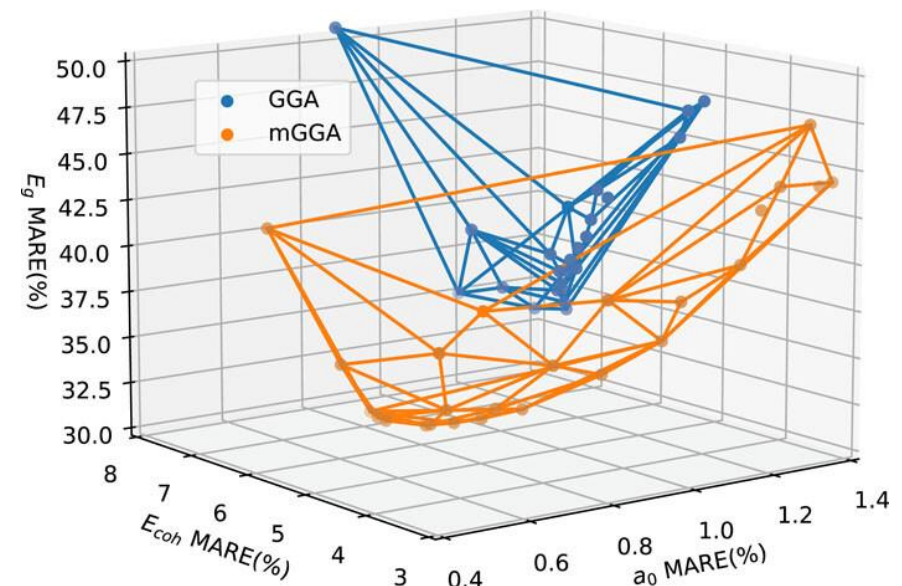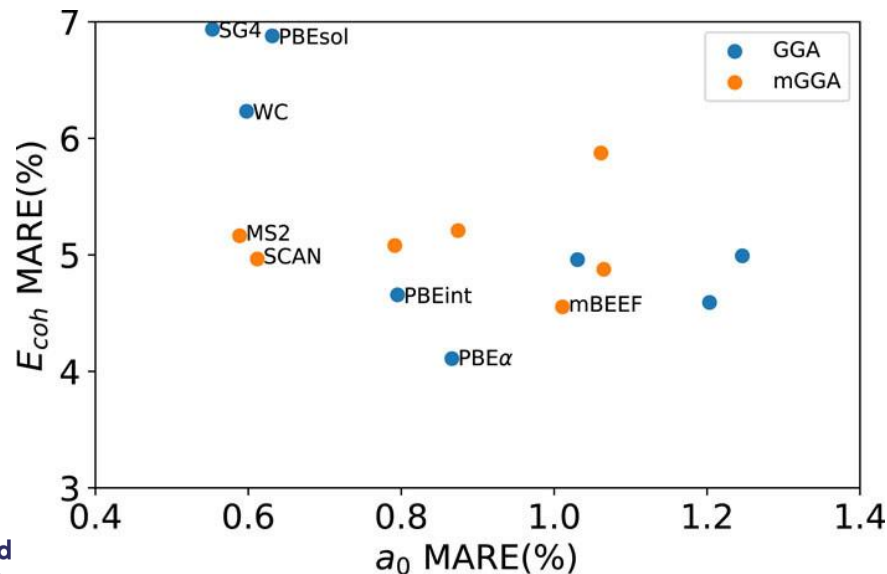
XC functionals

But we should also beware of overfitting to certain properties: controversial paper *"Density functional theory is straying from the path toward the exact functional"* finds energy predictions getting better over time, but density getting worse!

M G. Medvedev I. S. Bushmarinov, J. Sun, J, P. Perdew, K. A. Lyssenko (2017) *Science* **355** (6320) 49

Fig. 1. The historical trends in maximal deviation of the density produced by various DFT methods from the exact one. (**A**) The line shows the average deviation, with the light gray area denoting its 95% confidence interval; hGGA* denotes 100% exact exchange-based methods. (**B**) The bars denote averages of DFT functionals' median-normalized absolute error for energy [open bars, Truhlar's data (4)] and electron density with its derivatives (solid bars, this work) per publication decade.

Periodic systems: Bloch's theorem

Infinite crystals are described with periodic boundary conditions.

Long-range wavefunctions can be described using Bloch waves: product of a periodic function (unit-cell-sized!) and plane wave.

With enough **k**-points, properties should converge…

Periodic potential

$$u(\mathbf{r}, \mathbf{k})$$

$$\psi(\mathbf{r}, \mathbf{k}), \mathbf{k} = \left(\tfrac{1}{2}\right)$$

$$\psi(\mathbf{r}, \mathbf{k}), \mathbf{k} = \left(\tfrac{1}{8}\right)$$
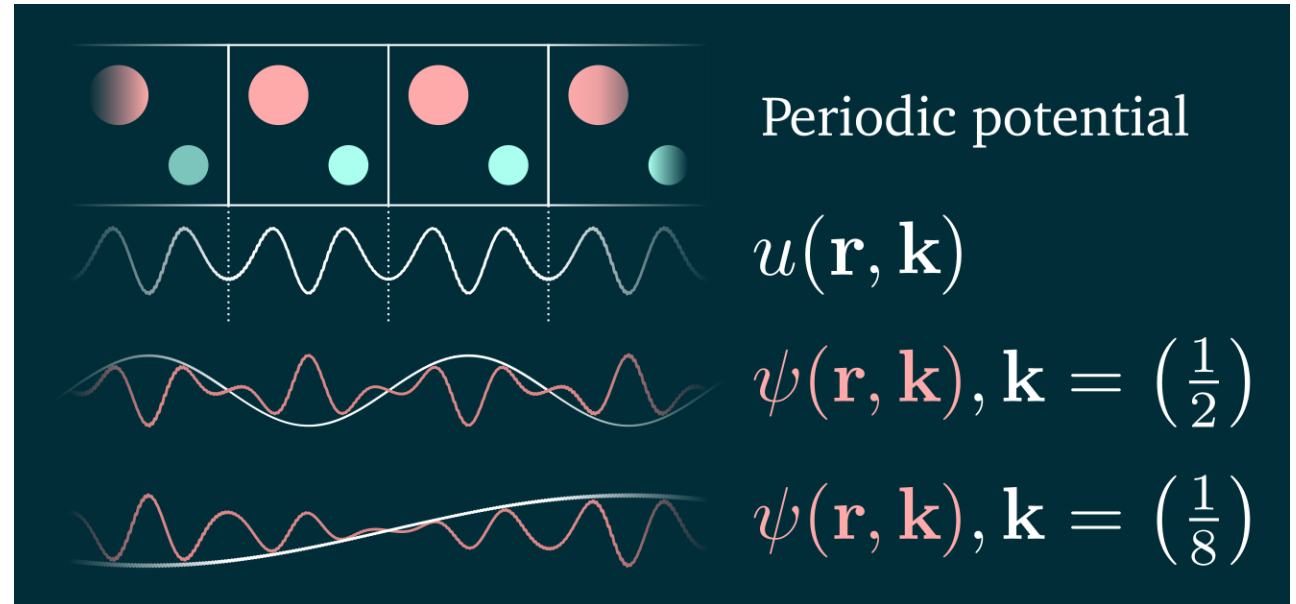
Basis sets

How do we actually represent Ψ or ϕ?

- It's difficult to solve for an unknown *function*
- It's easy to solve for a linear combination of components
- Represent unknown function as a linear combination of known functions: a *basis set*

Many different basis sets are used in DFT; technical choice.

Basis sets: pros/cons

Regular grid points

 SPARC

Local orbitals

Plane waves

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That's a lot of options!

There are a lot of DFT codes and some questions about the accuracy of some technical choices: basis sets, pseudopotentials etc.

So a study was performed across many different codes, performing equivalent equation-of-state calculations for solids.

Result: they agree pretty well!
(for more recent code versions)
(if you know what you are doing)

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RESEARCH ARTICLE

Reproducibility in density functional theory calculations of solids

KURT LEJAEGHERE, GUSTAV BIHLMAYER, TORBJÖRN BJÖRKMAN, PETER BLAHA, STEFAN BLÜGEL, VOLKER BLUM, DAMIEN CALISTE, IVANO E. CASTELLI, STEWART J. CLARK, ANDREA DAL CORSO, STEFANO DE GIRONCOLI, THIERRY DEUTSCH, JOHN KAY DEWHURST, IGOR DI MARCO, CLAUDIA DRAXL, MARCIN DUŁAK, OLLE ERIKSSON, JOSÉ A. FLORES-LIVAS, KEVIN F. GARRITY, LUIGI GENOVESE, PAOLO GIANNOZZI, MATTEO GIANTOMASSI, STEFAN GOEDECKER, XAVIER GONZE, OSCAR GRÅNÄS, E. K. U. GROSS, ANDRIS GULANS, FRANÇOIS GYGI, D. R. HAMANN, PHIL J. HASNIP, N. A. W. HOLZWARTH, DIANA IUŞAN, DOMINIK B. JOCHYM, FRANÇOIS JOLLET, DANIEL JONES, GEORG KRESSE, KLAUS KOEPERNIK, EMINE KÜÇÜKBENLI, YAROSLAV O. KVASHNIN, INKA L. M. LOCHT, SVEN LUBECK, MARTIJN MARSMAN, NICOLA MARZARI, ULRIKE NITZSCHE, LARS NORDSTRÖM, TAISUKE OZAKI, LORENZO PAULATTO, CHRIS J. PICKARD, WARD POELMANS, MATT I. J. PROBERT, KEITH REFSON, MANUEL RICHTER, GIAN-MARCO RIGNANESE, SANTANU SAHA, MATTHIAS SCHEFFLER, MARTIN SCHLIPF, KARLHEINZ SCHWARZ, SANGEETA SHARMA, FRANCESCA TAVAZZA, PATRIK THUNSTRÖM, ALEXANDRE TKATCHENKO, MARC TORRENT, DAVID VANDERBILT, MICHIEL J. VAN SETTEN, VERONIQUE VAN SPEYBROECK, JOHN M. WILLS, JONATHAN R. YATES, GUO-XU ZHANG, AND STEFAAN COTTENIER   fewer   Authors Info & Affiliations

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What can DFT do for me? Energies

The most direct output of a DFT calculation is a "total energy".

- These are not directly useful: need to compare with other energies
- Be careful comparing energies from calculations with different settings
- **Do not compare total energies from different XC functionals**
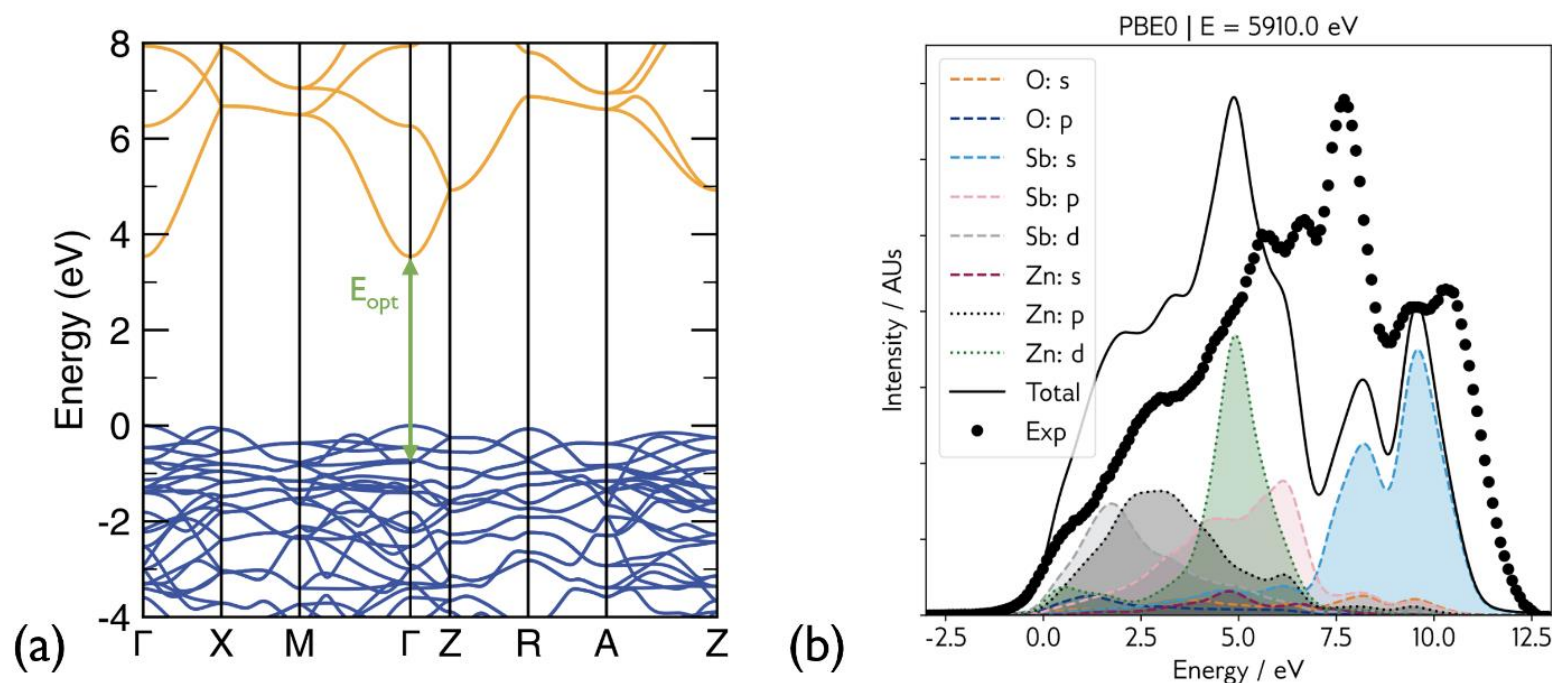- DFT energies are "athermal"; neglect vibrations, even ZPE

With a large set of energies, we can predict phase stability, choose between magnetic / ionic ordering, estimate heat of reaction…

Try https://materialsproject.org for a database of existing solid-state data
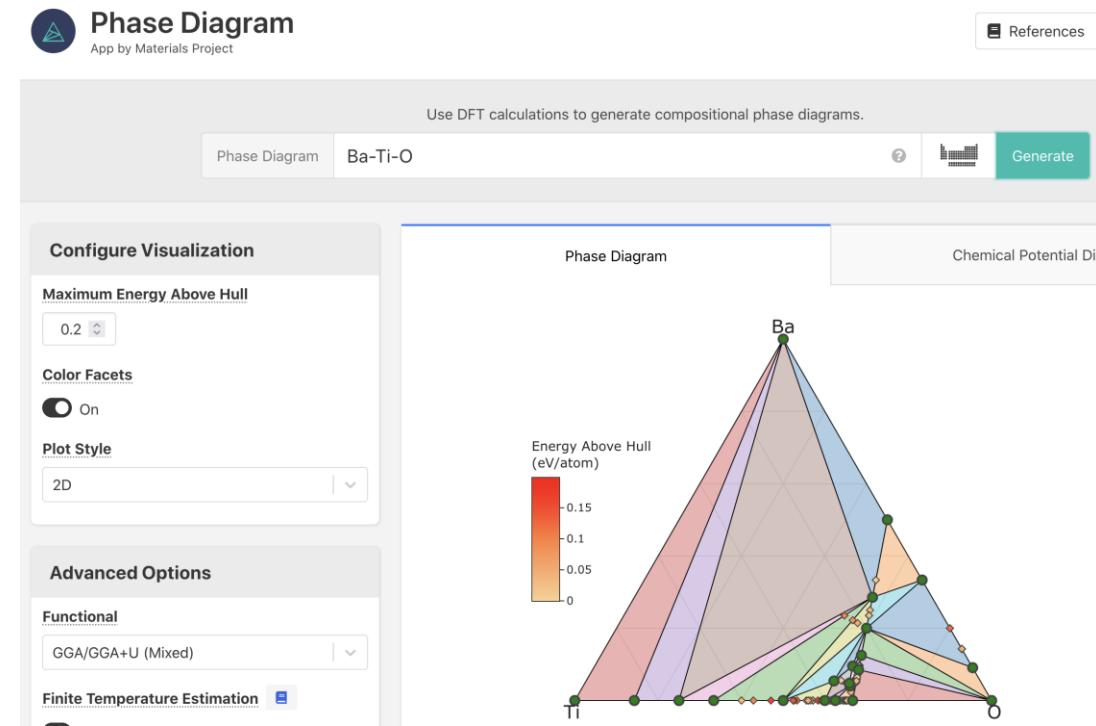
What can DFT do for me? Orbital energies

If we examine the shapes and energies of Kohn–Sham orbitals, we get pretty reasonable-looking information about electronic structure.

LDA, GGA tend to under-estimate electronic bandgap
Hartree–Fock tends to over-estimate it
"Hybrid" functionals fall somewhere in the middle

This isn't really supposed to work;
K–S theory doesn't promise it will.
But in practice results very useful...

What can DFT do for me? Forces

The Hellmann–Feynman theorem allows forces to be calculated quite inexpensively.

Typically structures are optimised by adjusting positions and lattice parameters to minimise the energy; this is *much* more efficient when forces are available.

This information also helps explore the "potential energy landscape" searching for transition states (i.e. reaction barriers ➜ kinetics)
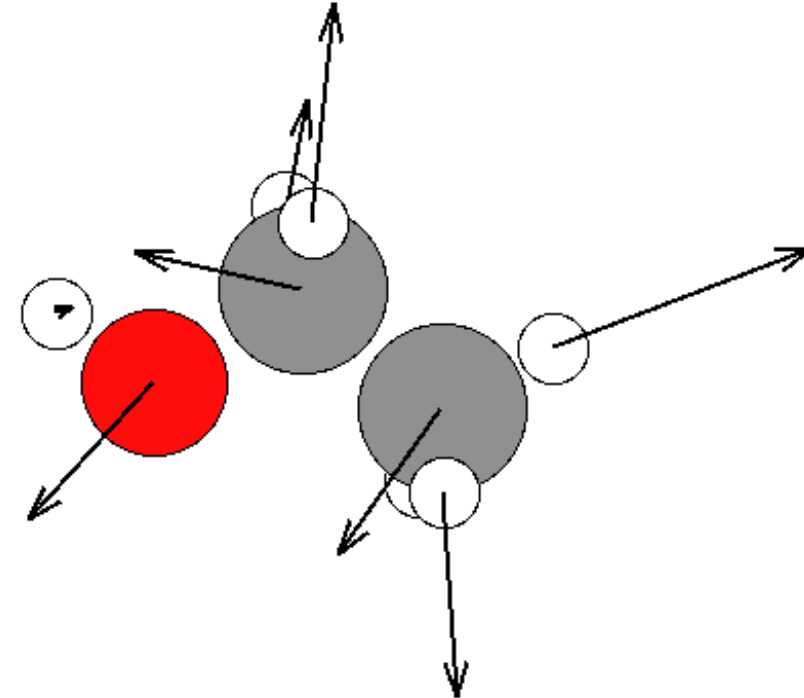
Ethanol molecule optimization with LBFGS algorithm

What can DFT do for me? Vibrations

In the *harmonic approximation*, vibrations are driven by linear spring-like interactions between each pair of molecules. This can be collected as a matrix of *force constants*.

$$E = T + E_0 + \Phi_i u_i + \frac{1}{2!}\Phi_{ij}u_i u_j + \frac{1}{3!}\Phi_{ijk}u_i u_j u_k + \cdots$$

$$F = -\frac{\partial E}{\partial u_i} = -\Phi_i - \Phi_{ij}u_j - \frac{1}{2!}\Phi_{ijk}u_j u_k - \cdots$$
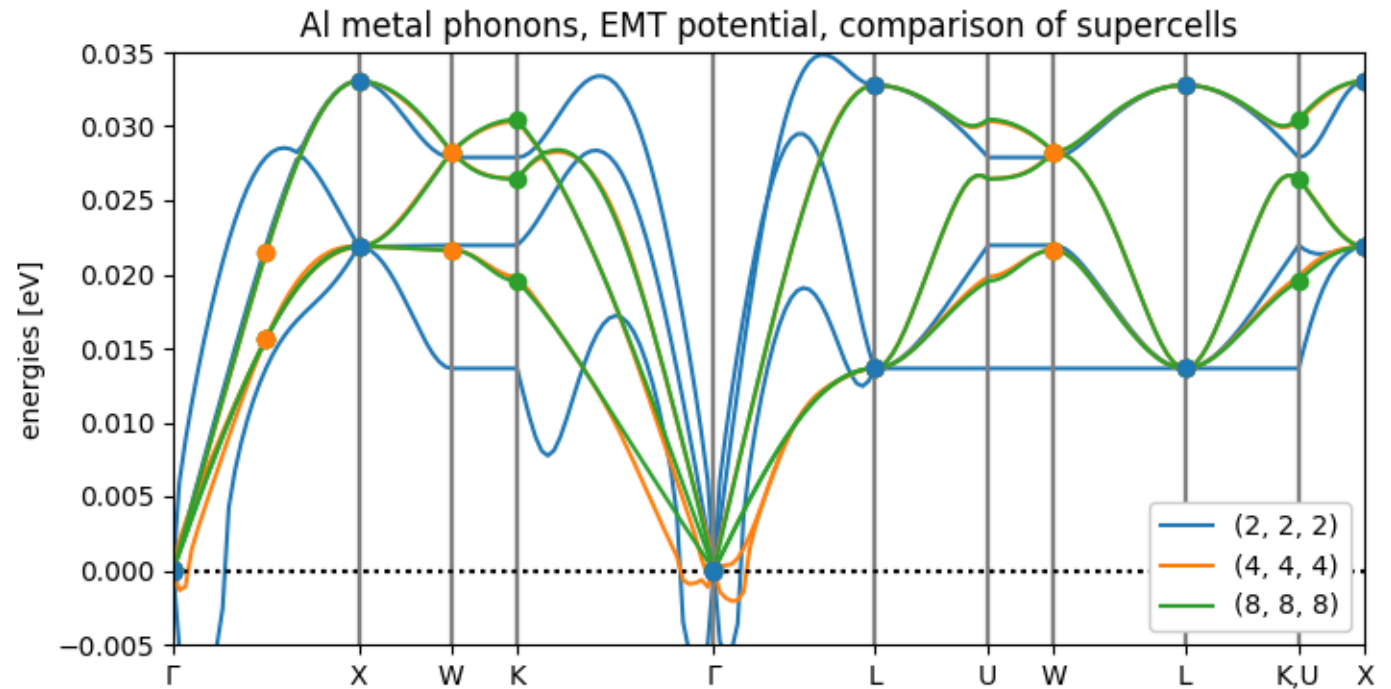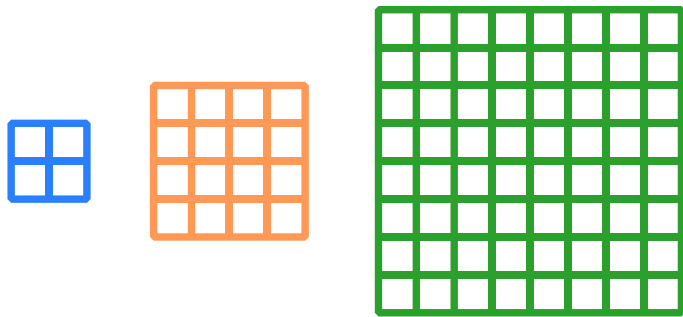
Zero for "relaxed" structure

Anharmonic terms
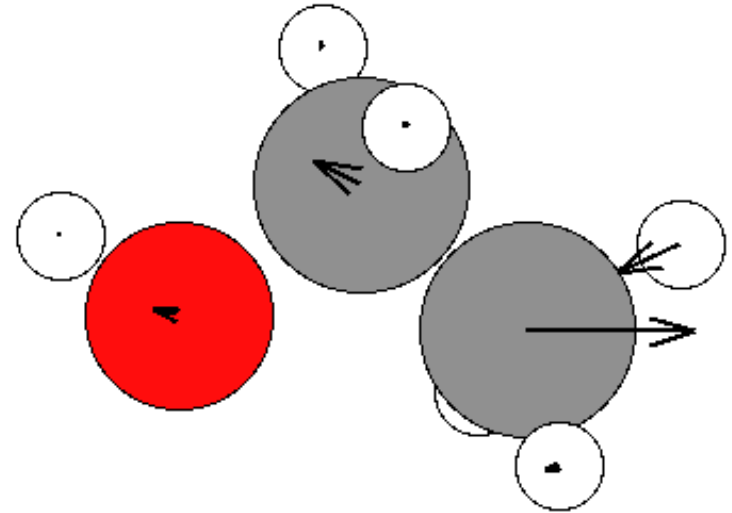
Force constant matrix Φ_{ij} can be filled in a row at a time by making small displacements along each degree of freedom

What can DFT do for me? Phonons

For a periodic system the same principle applies, but we may need to use a large "supercell" to avoid self-interaction and get correct information about low-symmetry q-points

Interactive visualisations:

http://henriquemiranda.github.io/phononwebsite/phonon.html

What can I do with these phonons?

Codes developed at ISIS for simulation of inelastic neutron scattering spectra

AbINS: incoherent approximation, DOS-like analytic powder-averaging, instrumental resolution functions, multi-phonon scattering (Good for molecular crystals)

Euphonic: coherent scattering, single-crystal and numerical powder-averaging, simple broadening (Good for solids, inorganic)
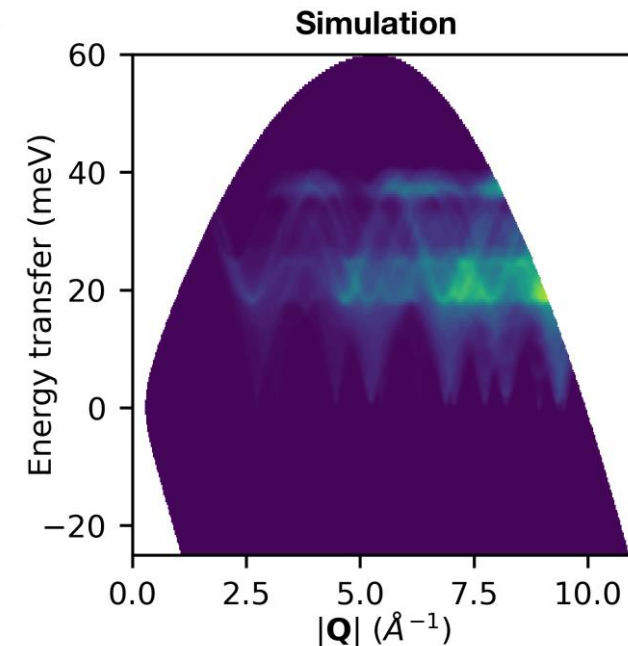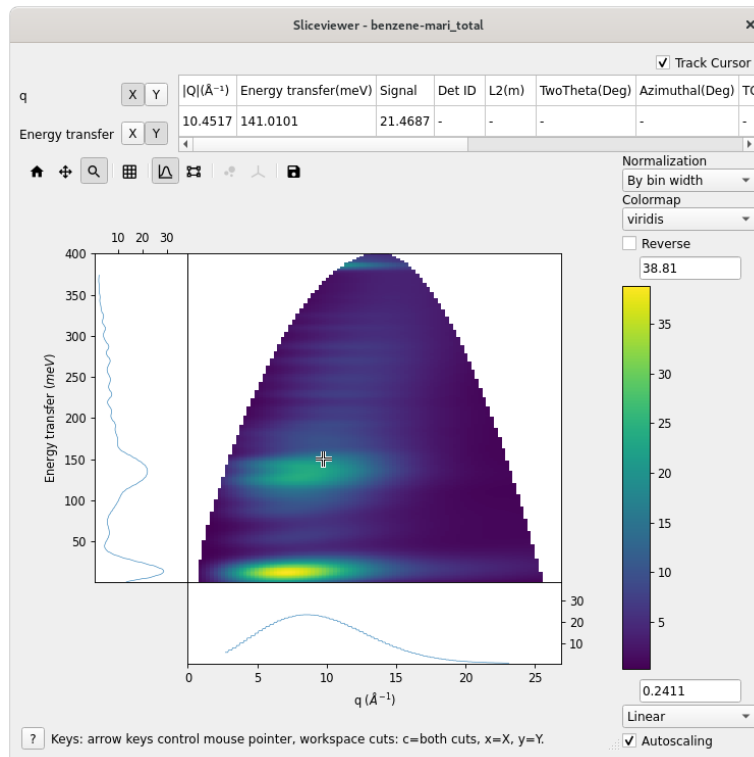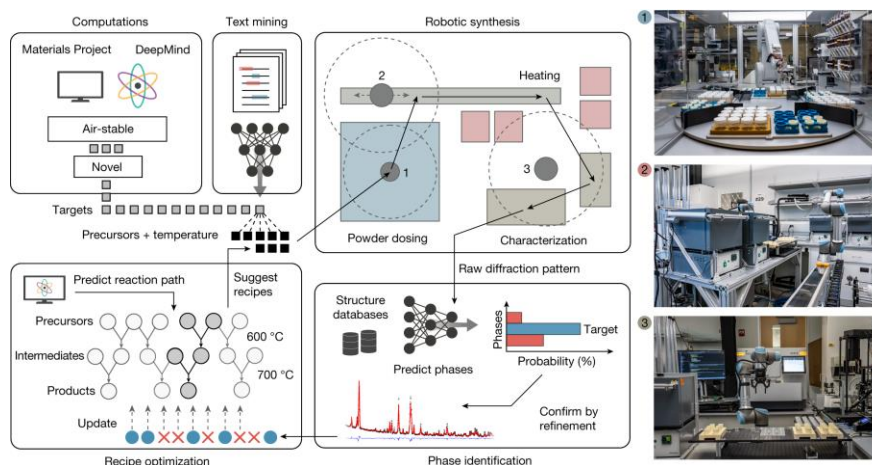
Ok, sounds great. What do I need?

- A suitable problem

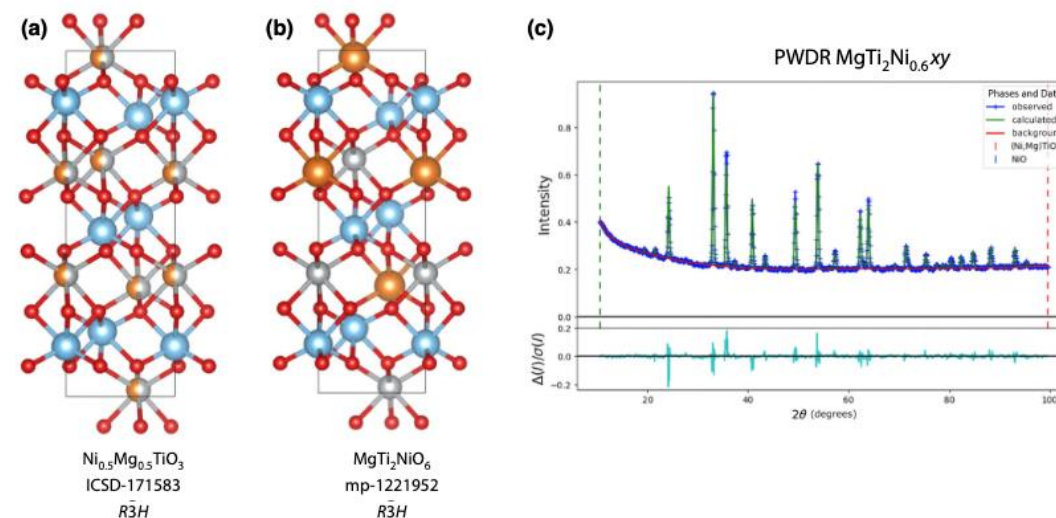- Software

- Computers

- Guidance

A suitable problem

- **Atomic positions** need to come from somewhere
  - Hypothesised structure
  - Diffraction data (x-ray or neutron)
    - Hydrogen may be missing
    - Average sites may differ from ground state
    - Fractional occupancy is a problem

"A-Lab" project, *Nature* paper claimed to discover 41 novel compounds
DOI:10.1038/s41586-023-06734-w

Critics observed that XRD cannot distinguish the majority of these from known disordered phases
DOI:10.1103/PRXEnergy.3.011002

A suitable problem

- **Atomic positions** need to come from somewhere
  - Hypothesised structure
  - Diffraction data (x-ray or neutron)
    - Hydrogen may be missing
    - Average sites may differ from ground state
    - Fractional occupancy is a problem

  - "Global optimisation" algorithm
    - A more expensive problem…
- **Magnetic (dis)order** can break symmetry and expand the unit cell
- **Known properties** can guide selection of parameters such as XC functional
  - e.g. lattice parameters, optical bandgap, bulk modulus, …

Software

There are many atomistic "codes"

- Some based on different technical choices *(e.g. theory, basis set, parallelism)*
- Some emerging from different communities *(target systems, code interfaces)*
- A lot of "not invented here syndrome" and licensing issues…
  (open vs commercial vs evolved-from-a-1980s-PhD-project)

Most of them are capable of decent precision, so in practice choose based on

- Required features *(periodicity, XC functionals, spin-orbit coupling, dispersion)*
- Computational performance *(scaling for small or large systems, GPU support)*
- Usability *(documentation quality, included tools, compatibility with external)*
- Access *(licensing, friendly developers, helpful post-docs)*

https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software

These matrices can be useful: keep in mind they don't tell which features work *simultaneously*

Software

A few codes come with graphical user interfaces that run on Windows (Materials Studio, GaussView) but this costs $$$ and may limit available functionality.
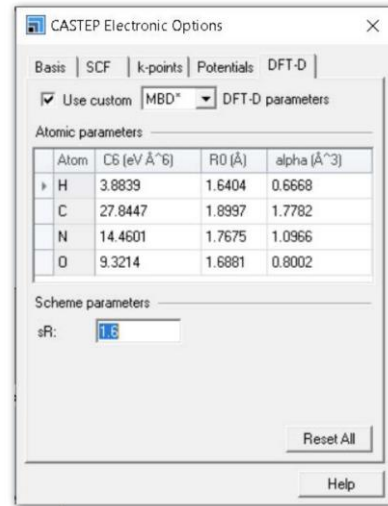
vs

Most codes are developed for use in a Linux(-like) command-line environment. To write input files, automate groups of calculations and compile codes from source code, it is recommended to:

- Get a bit of familiarity with the Bash shell
- Learn how to use a text editor effectively
- (Optional) use Python for more advanced manipulation and plotting

Computers

Modern DFT codes will run on a laptop, a 750,000-core supercomputer, or most things in-between.

- Personal computers can generally handle tens of atoms with GGA functionals.
- A high-end workstation will go slightly bigger… or run a lot of those calculations more quickly and reliably.
- Academic clusters become necessary when going to larger unit cells, heavy elements, hybrid DFT, spin-orbit coupling…

UK national supercomputer: ARCHER2

2x cores only means 2x faster if your problem breaks down very well! Check scaling efficiency and test parallelism options.

Guidance

This was just an overview!
- Find out what codes people in your field are using for similar systems
- See if you can get a copy of their parameter files and understand what options were chosen and what implications they have
- Talk to experts to see if what you are trying to do is reasonable: DFT is not always a practical option
  - For larger simulation regions, the practical options might be *trained* against a set of smaller DFT calculations
  - Some systems are known to be tricky: highly-correlated materials, liquids and glasses, unstable phases, excited states…

Recap: how to read a DFT methods section

- "We used DFT" is not enough information to reproduce a calculation!
- Neither is "we used CASTEP"
- Most important information are the "accuracy parameters" defining approximations made: XC functional, spin treatment, dispersion…
- Also useful are "precision" details: basis set, pseudopotentials, k-point sampling, convergence thresholds
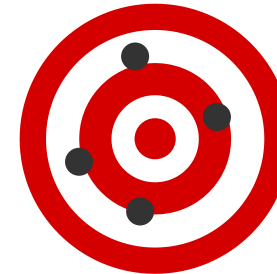- Best practice: include parameter files in the SI!

High precision, high accuracy
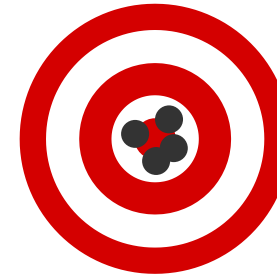
High precision, low accuracy

Low precision, high accuracy

Low precision, low accuracy

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Thank you

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