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First Principles Materials Modelling (with CASTEP)

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Overview of lecture

- First Principles Computational Modelling
    - Motivation
    - Meaning
    - Applications

- NB Colour slides are available on the website

Why Computer Modelling?

Why?

- Computers get cheaper & more powerful every year
- Experiments tend to get more expensive each year
- **IF** computer simulation offers acceptable accuracy then at some point it should become cheaper than experiment.
  - This has already occurred in many branches of science and engineering.
  - **Is this possible for properties of materials?**

Motivation

- Computer simulation is now the “3rd way”
- Advantages
  - Precise control of system under study
    - Can interpret complex experimental data
  - Predict new materials / properties
  - Can do ‘what if’ experiments to reveal detailed underlying causes
  - Can do practically impossible experiments, e.g. extreme conditions – planetary cores
  - As well as saving time and money

… more motivation

- Disadvantages
  - Requires correct underlying theory
    - How well tested & developed is it?
  - And correct computer implementation
    - How well verified is the code?
  - And correct usage!
    - How competent is the user? Do they understand the limitations of the theory/code? Are they using appropriate method?

Test and Verification

- We shall be using the CASTEP code:
  - Based upon the Density Functional Theory (DFT) version of quantum mechanics
    - More on DFT in future lectures …
  - CASTEP has been tested on many different systems and compared to experiment
    - We now know where it can be used safely, and where it should be used with caution
  - And YOU are the users!
    - Hence need for some training …

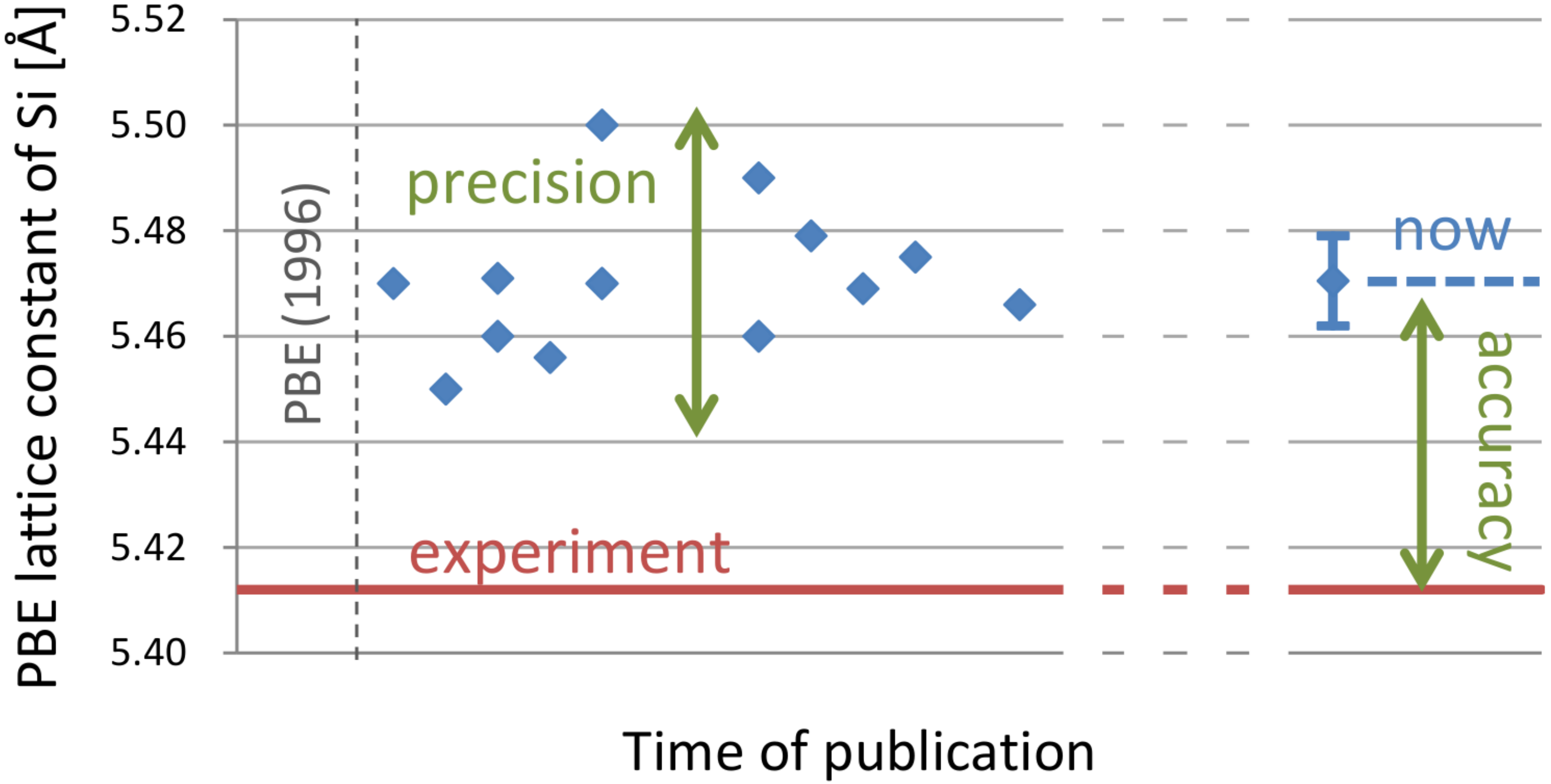
Example of test & verification

- CASTEP is one of a number of widely used DFT programs
  - Uses a common recipe of ‘plane waves and pseudopotentials’ – more on that soon
  - Traditionally test the ‘pseudopotential’ by comparing predict lattice constant of simple materials against experiment
    - Usually get ~few % error
    - But that is complicated by experimental error, finite temperature, material quality, etc
    - So hard to be definitive about HOW good it is …

Recent community project

- Recently the ‘delta-codes’ project made a detailed study of the effect of the pseudopot

https://molmod.ugent.be/deltacodesdft



Delta-codes project

- The study was careful to disentangle the effects of *accuracy* vs *precision*
  - Each code calculated an ‘energy-volume’ curve for each of 71 elements
  - Compared pseudopotential codes (e.g. CASTEP) against more computationally expensive codes that do not use pseudopotentials using the value of ‘delta’

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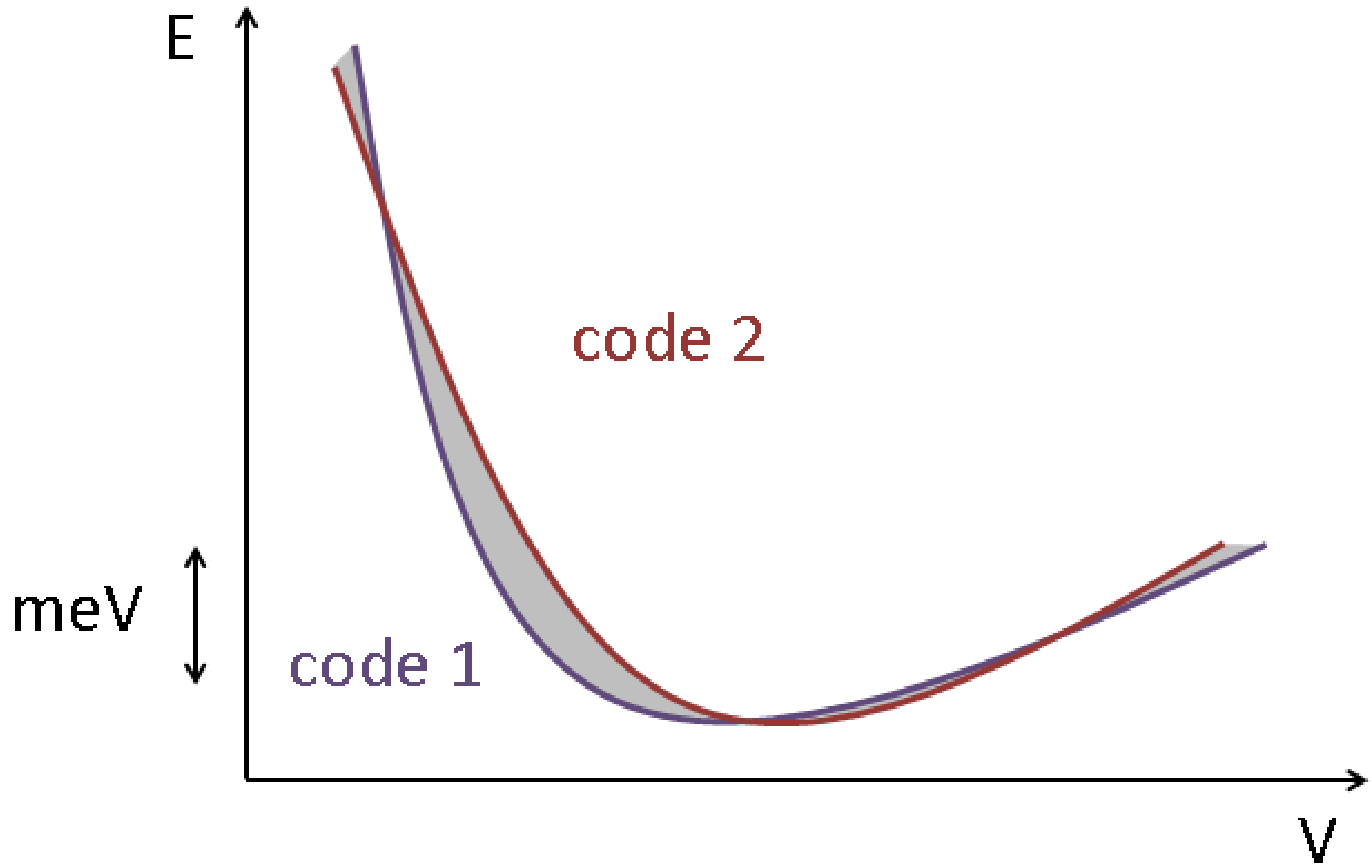
What is delta?



- Δ is the RMS difference between the E-V curves over ±6% interval around equilibrium

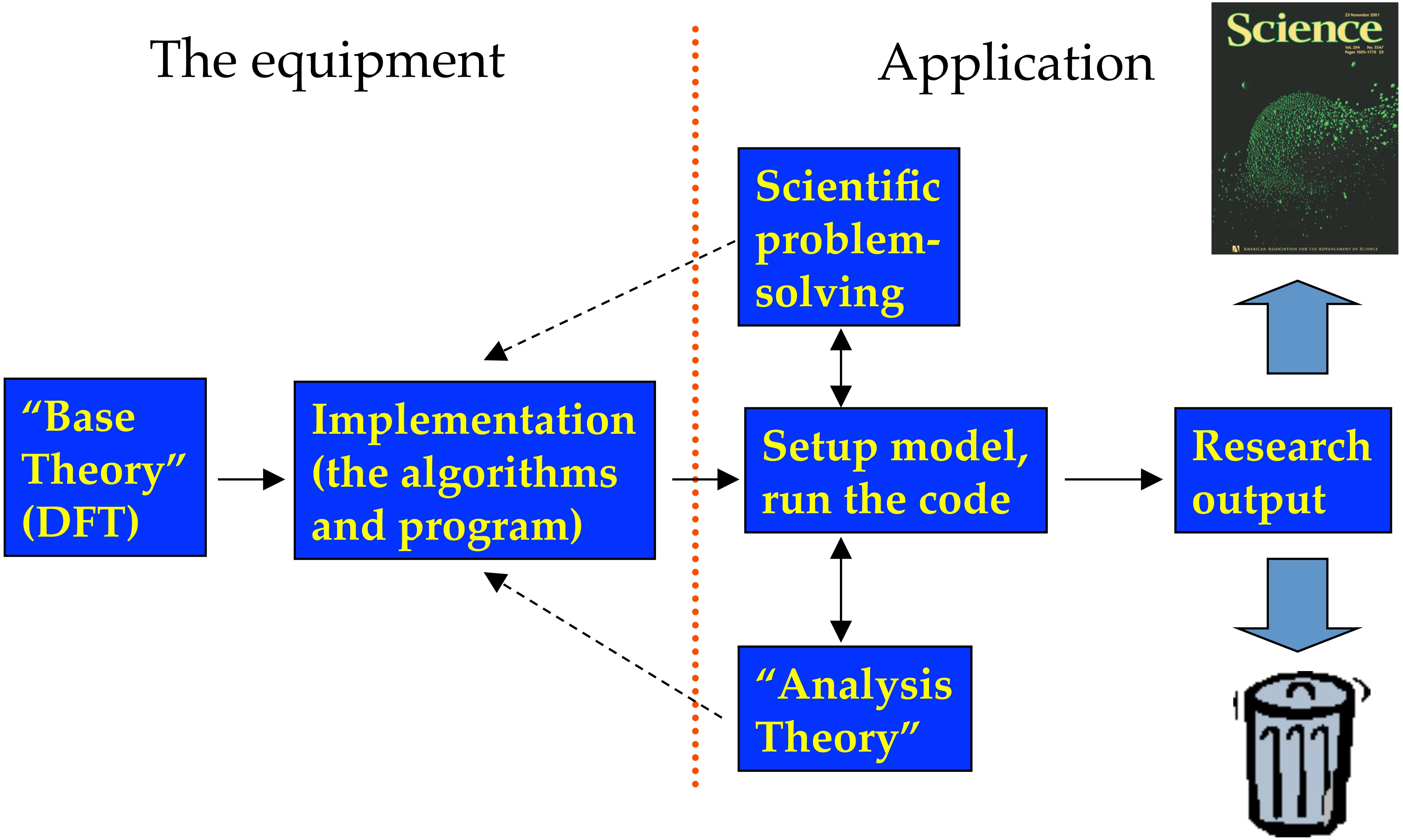
Delta-codes result

- Found that the error between modern high quality pseudopotentials (as used in CASTEP) and “all electron” codes is now SMALLER than experimental noise
- The result is a mega-paper “*Reproducibility in density functional theory calculations of solids*” Science **351** 6280 (2016)
  - 69 co-authors, 15 codes, 7 pages main text + 165 pages of ‘supplementary information’

Implication

- All these independent codes now agree with each other to a high degree of *precision*
  - Hence correct implementation of basic DFT in different codes
  - This was **not** the case 10 years ago – some codes gave consistently worse answers
- But the results are **not** same as experiment
  - This is the *accuracy* issue
  - See later lectures for why and how to fix

Work flow



The equipment

Application

"Base Theory" (DFT)

Implementation (the algorithms and program)

Scientific problem-solving

Setup model, run the code

"Analysis Theory"

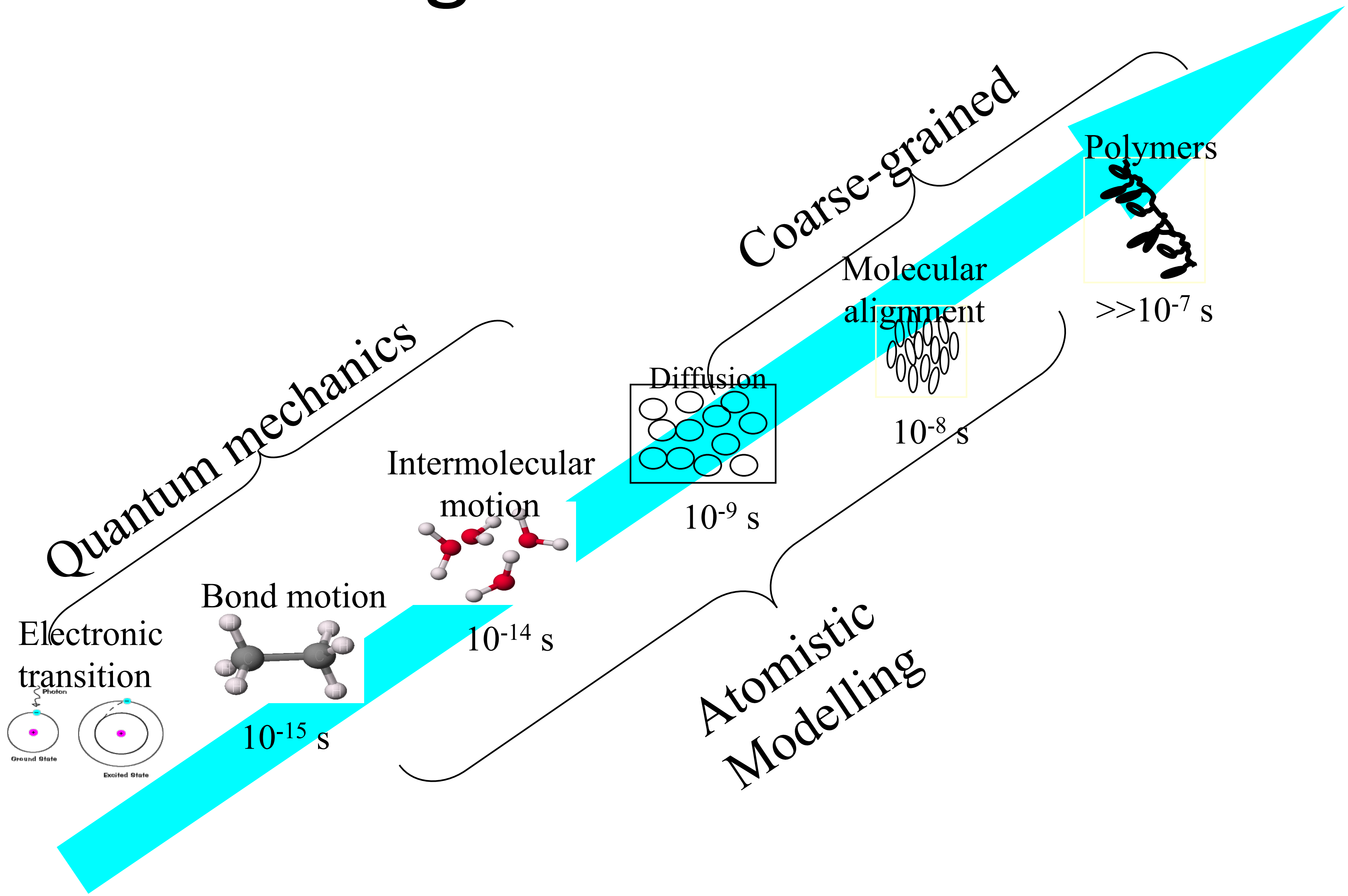
Research output

What about “First Principles”?

Meaning

- “First principles” means we rely only on fundamental laws of science
  - In this case, quantum mechanics and not on empirical fits
    - Hence should be accurate
- We can use QM to calculate the properties of electrons – can we do this for real solids or liquids or molecules or surfaces or …
- Limitations are finite computer speed & memory

Length and time scales



Quantum mechanics

Coarse-grained

Atomistic Modelling

Electronic transition

10^{-15} s

Bond motion

Intermolecular motion

10^{-14} s

Diffusion

10^{-9} s

Molecular alignment

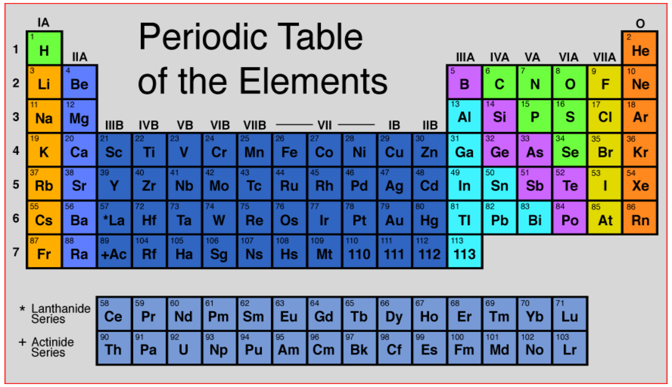
10^{-8} s

Polymers

$>>10^{-7}$ s

Basic idea

1. Take atomic numbers/elements as input



Periodic Table of the Elements

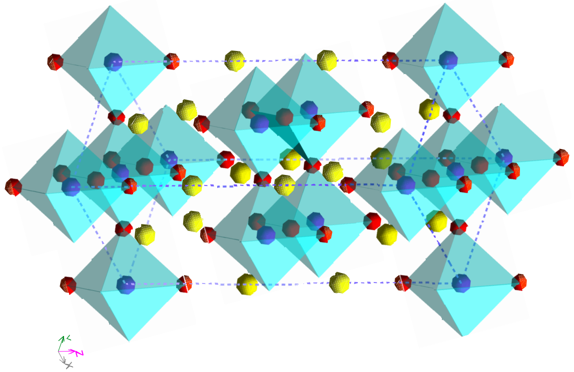
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII	VII	VII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112	113 113					

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

2. Solve QM equations

$$\hat{T}\Psi_{MB} + \hat{V}\Psi_{MB} = -i\frac{d\Psi_{MB}}{dt}$$

3. Predict physical and chemical properties



Quantum Mechanics

- Unfulfilled promise:
  - For the first 50 years of QM, just about every solution was for a single particle
- Claim:
  - It was claimed (by Dirac) that the Schrödinger equation explained all of chemistry, biology, materials science, etc.
- BUT:
  - The mathematics of many-particle QM is too complicated – and too computationally expensive – to apply to realistic systems

Density Functional Theory

- DFT is a reformulation of QM in terms of the electronic charge density
  - A big simplification over many-body wavefunction – and an observable!
- 1964: The foundations of density functional theory (the Hohenberg-Kohn Theorem)
- 1965: The Kohn-Sham equations (practical method for performing calculations)

Practical DFT

- DFT then languished until …
- 1981: A good local density approximation
- 1985: The Car-Parrinello method

1987: first version CASTEP

- 1991: Implementation on parallel computers

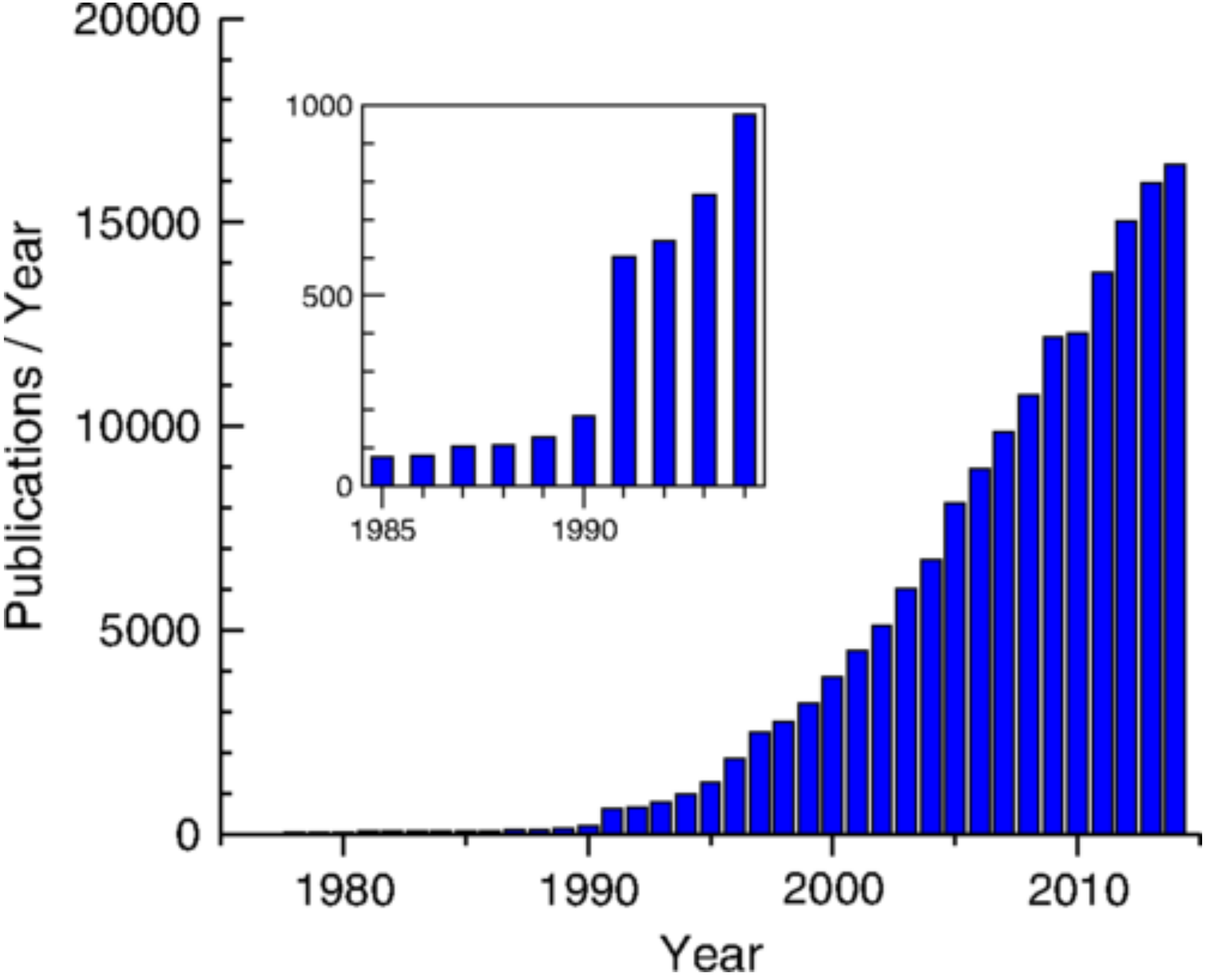
- a version of CASTEP called CETEP

- 1998: Nobel prize (in chemistry) for DFT

1999 – 2001: total rewrite of CASTEP

- … DFT now creating >15,000 papers / year

DFT publications



R.O. Jones, Rev. Mod. Phys. **87**, 897 (2015)

RMP Examples

- Using DFT to study the origins of life:

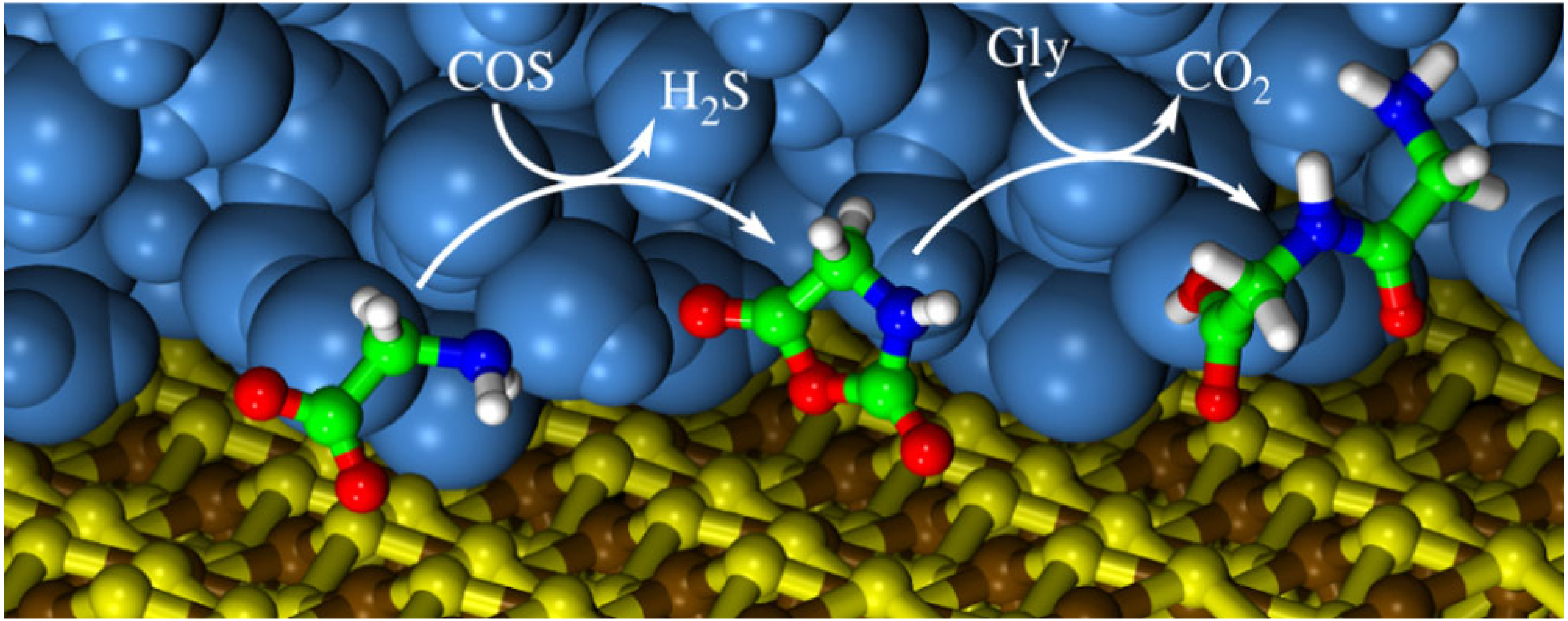


FIG. 7 (color online). Glycine (left), activated glycine (center), and the glycine-glycine dipeptide (right) between an FeS_2 surface (below) and water. COS: carbonyl sulfide.

RMP Examples

- Phase change materials for BlueRay DVD:

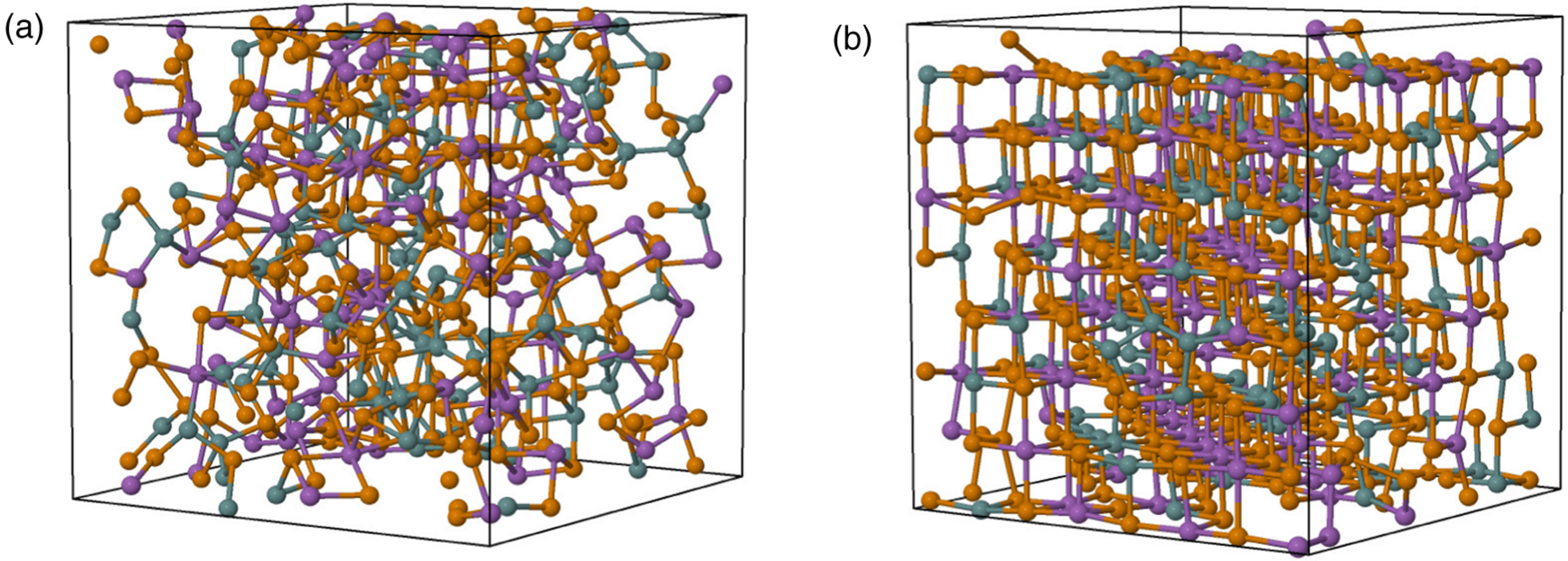


FIG. 8 (color online). Crystallization in GST alloy at 600 K. (a) Amorphous structure after 215 ps, (b) crystalline structure after 1045 ps.

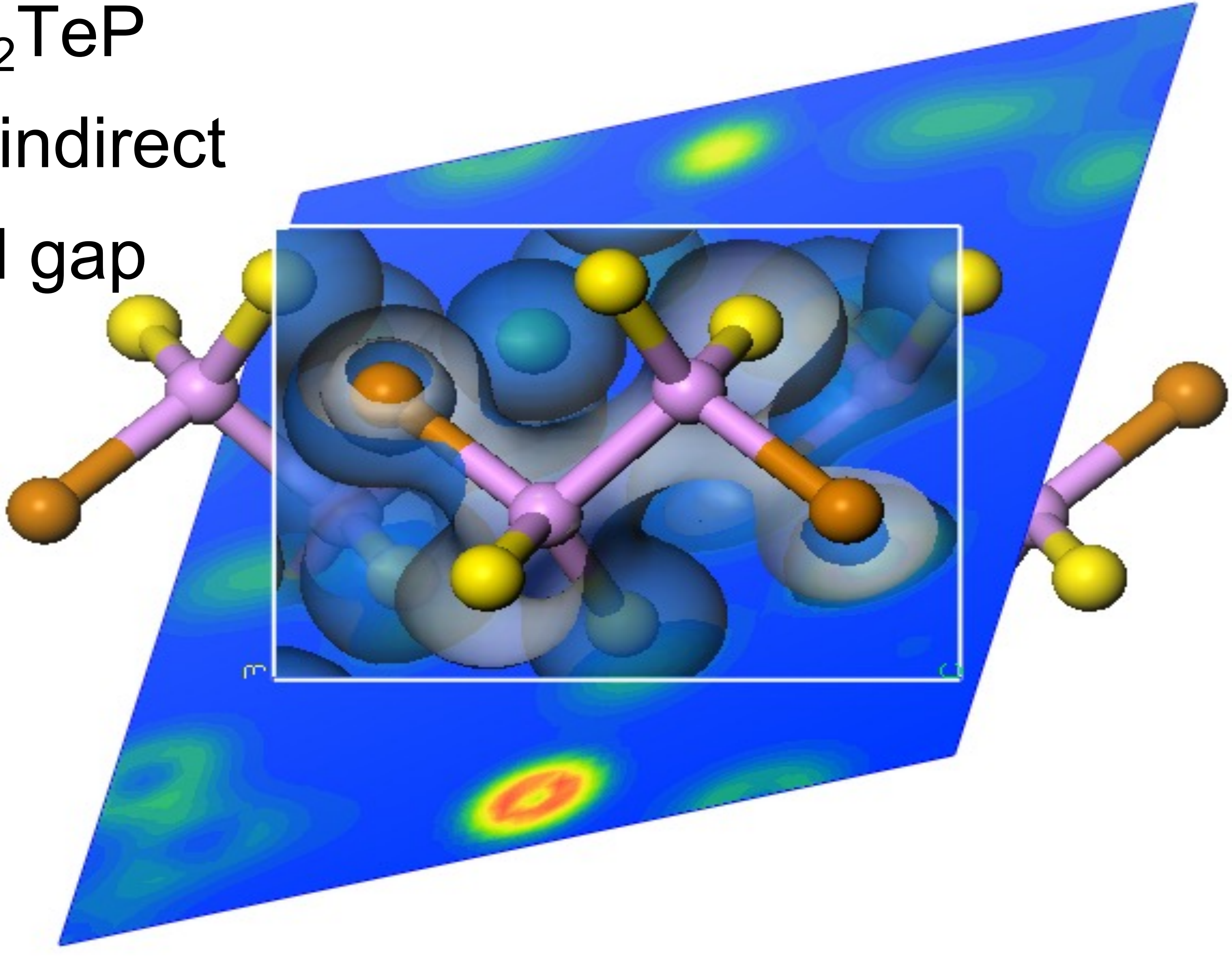
What is CASTEP?

What is CASTEP?

CaS_2TeP

2eV indirect

band gap



Introducing CASTEP

- CASTEP is a general-purpose DFT code
  - uses plane-wave basis set (position independent, easy to improve accuracy)
  - use pseudopotentials (replaces nuclei and inner electrons with pseudo-ion)
  - is parallel (can run on single core PC or largest supercomputer)
  - can calculate wide range of properties …

CASTEP abilities

- Total energies
    - forces and stresses with LDA/GGA/mGGA/sX/hybrid/LDA+U/vdW/S-O etc.
- Electronic structure
    - electronic charge, potential, band structure, DOS, atomic populations
- Geometry Optimisation
    - atomic positions, cell parameters, external pressure/stress
- Molecular dynamics
    - finite temperature, zero-point and non-equilibrium properties
- Transition state searches
    - chemical reaction pathways, diffusion barriers
- Phonons
    - Band structure, DOS, quasi-harmonic thermodynamics
- Electric field response
    - polarisability, dielectric constants, Born charges, LO/TO splitting
- Magnetic Response
    - NMR, Chemical shifts, electric field gradients, hyperfine constants, etc.
- ELNES, EELS, Raman, IR, Wannier Functions, electron-phonon coupling, elastic constants, deformation potential, and more …

CASTEP developers

- CASTEP is developed by a core team of UK academics + collaborators:
    - Stewart Clark (University of Durham)
    - Phil Hasnip (University of York)
    - Chris Pickard (University of Cambridge)
    - Matt Probert (University of York)
    - Keith Refson (STFC)
    - Jonathan Yates (University of Oxford)
- Plus many PhD students + postdocs

CASTEP responsibilities

- Each developer is responsible for a different part of the code - principally:
  - Stewart Clark = XC functionals
  - Phil Hasnip = ground state energy
  - Chris Pickard = pseudopotentials
  - Matt Probert = geometry optimisation + MD
  - Keith Refson = phonons
  - Jonathan Yates = NMR
- Plus other areas too!

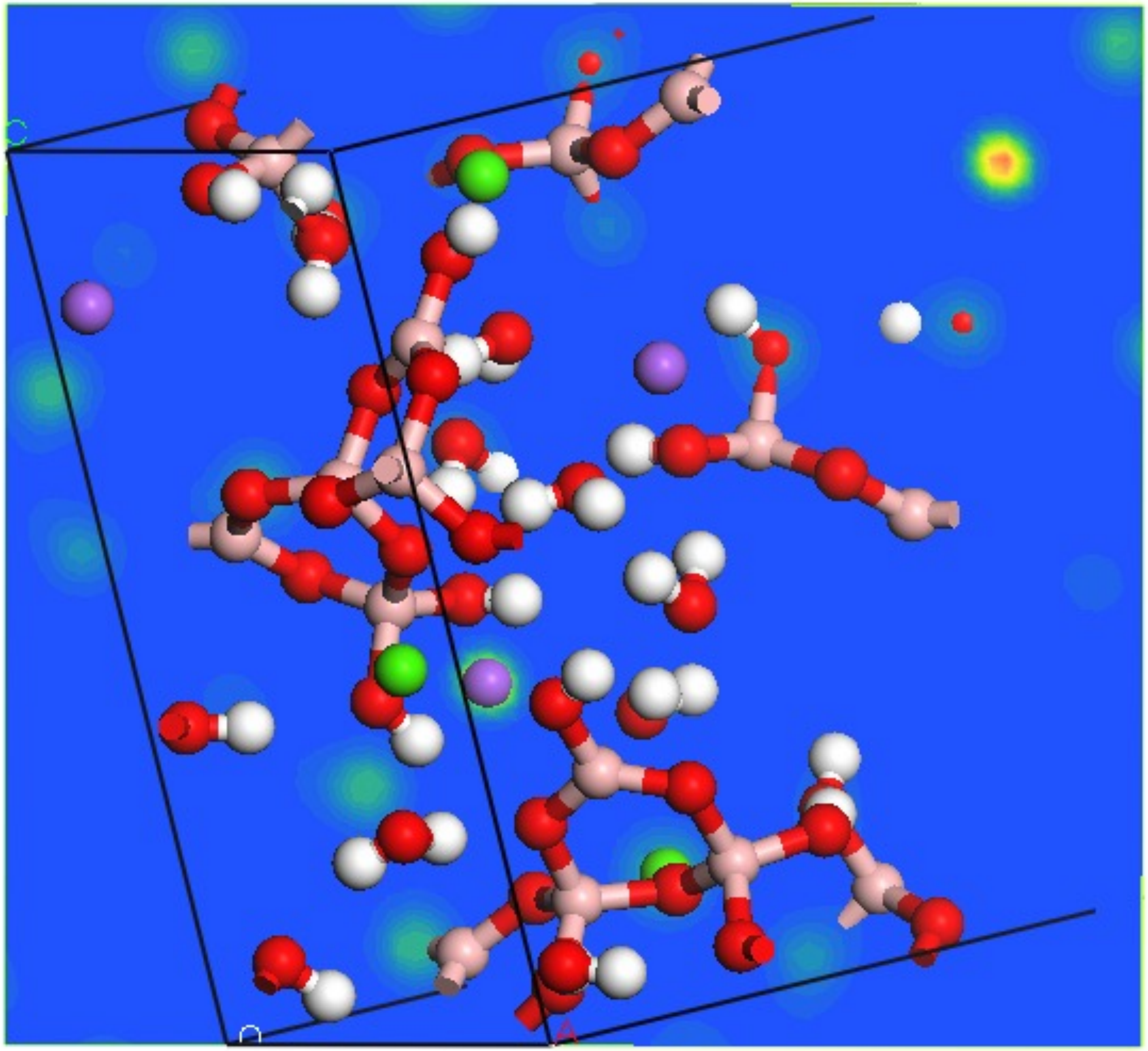
What can it do
for my research?

CASTEP applications

- Can use CASTEP for a purely theoretical study
  - To elucidate underlying mechanism of a reaction or process, or to study materials under extreme conditions, or …
- Or in collaboration with experimentalists
  - To help interpret experiments, predict spectra, or ...
- Or …

Can you guess?

NaCaB5O7(OH)4.
3(H2O)
{z=4}
124 ions
512 electrons
Egap ~ 5 eV



Basic energy minimization took 36 secs on 72 cores …

Also known as …

Examples of things I work on

- Thermoelectrics – Heusler alloys & novel 2D
- AFM materials for spintronics
- 2D materials, e.g. graphene, MoS2, ribbons
- High pressure – quartz + shock waves
- Biophysics – DNA + amines
- Superconductivity – metallic carbides
- Hydrogen – quantum diffusion, phase diagram

… all with same first principles approach!

Application Example

Water-Hydroxyl Overlayers on Metal Surfaces

Phys. Rev. Lett. **104**, 066102 (2010)

Xin-Zheng Li, Matt Probert, Ali Alavi, and Angelos Michaelides

Water-hydroxyl layers

- In many systems, the initial wetting layer is not pure water, but a water-hydroxyl mix
  - Bond lengths/angles unusual due to “pinning” with hydrogen-bonds formed to surface atoms
- Transition metal surfaces have been well-characterised
  - Pt(111) has large lattice constant and so inter-molecule distance ~ 2.83 Å
  - Ni(111) has much smaller distance ~2.50 Å

Water problem

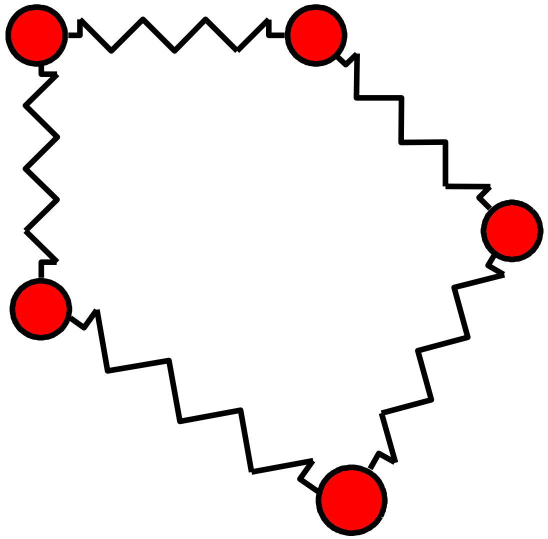
- In bulk ice have typical O-O distance ~ 2.8Å
- At high pressures (>70 GPa) ice has typical O-O distance of ~2.3 Å
  - No longer a molecular crystal
  - Have delocalised protons between O nuclei
- Low T (160 K) measurements of hydrogen diffusion on metal surfaces suggests that quantum tunnelling important
  - Hence need full QM treatment for hydrogen!

Ab initio Molecular Dynamics

- Use classical mechanics to move the atoms
  - Born-Oppenheimer approximation decouples nucleus and electrons and have electrons always relaxed onto the instantaneous B-O surface
  - Using forces and stresses derived from the electronic wavefunction – hence *ab initio* MD
  - Can use to study dynamical properties or to simulate a thermal equilibrium
- But the nucleus is always treated classically
  - Hence no quantum fluctuations, tunneling, zero point motion, etc.

Path Integral MD

- Use Feynman Path Integral formulation of Quantum Mechanics for the nucleus
  - now includes ZPM etc
  - important for light defects and/or low temperatures
  - "beads on springs" view with imaginary time axis
  - computationally expensive!
  - Use task-farming – one value of $i\tau$ per farm



Path integral view of a single quantum particle.

Nickel PIMD Movie

Platinum PIMD Movie

Summary

Summary

- QM of materials is hard
  - Many interacting particles
- DFT makes QM of materials feasible
  - Need to know about the approximations
- CASTEP is a robust and reliable implementation of DFT for periodic systems
  - Wide feature set
  - User friendly for theory and experimentalists
  - Fast and scalable

Useful References

- Hohenberg & Kohn, Phys. Rev. B **136**, 864 (1964)
- Kohn & Sham, Phys. Rev. A **140**, 1133 (1965)
- MC Payne *et al*, Rev. Mod. Phys **64**, 1045 (1992)
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- V Milman, K Refson, SJ Clark, CJ Pickard, JR Yates, S-P Gao, PJ Hasnip, MIJ Probert, A Perlov and MD Segall, "*Electron and vibrational spectroscopies using DFT, plane waves and pseudopotentials: CASTEP implementation*", J. Molec. Structure: THEOCHEM (2010)