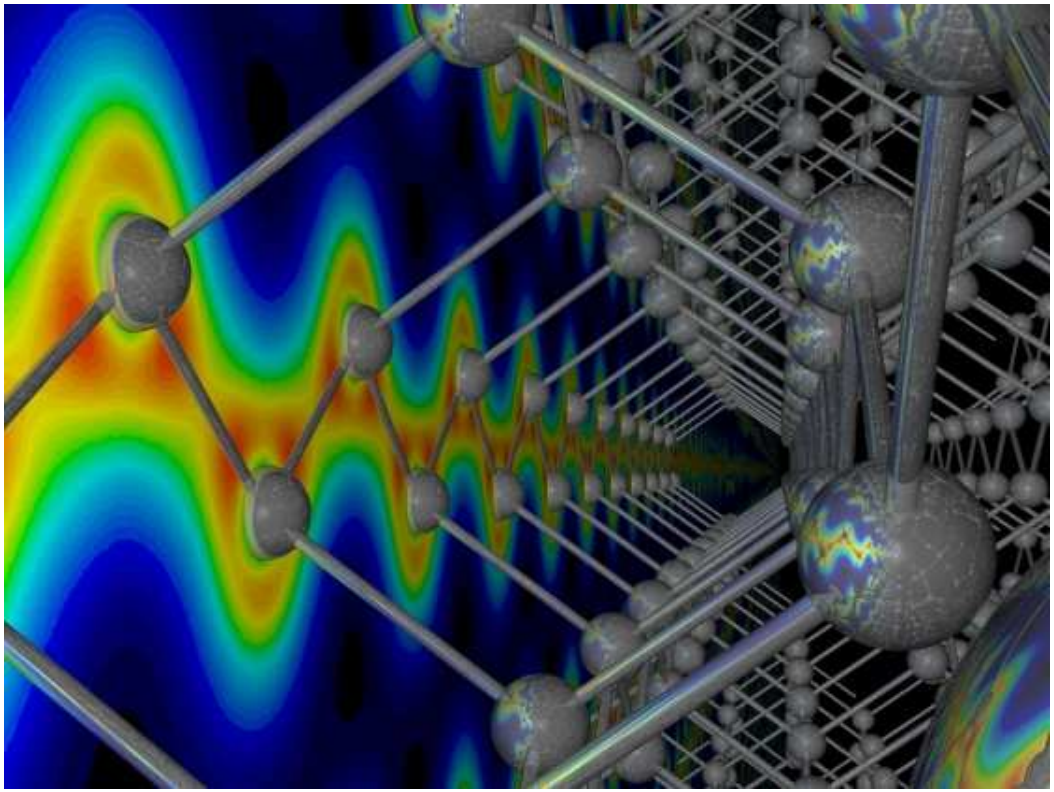
TCM/CUC3/Earth Sciences

Introduction to the Electronic Structure Discussion Group



Mike Towler

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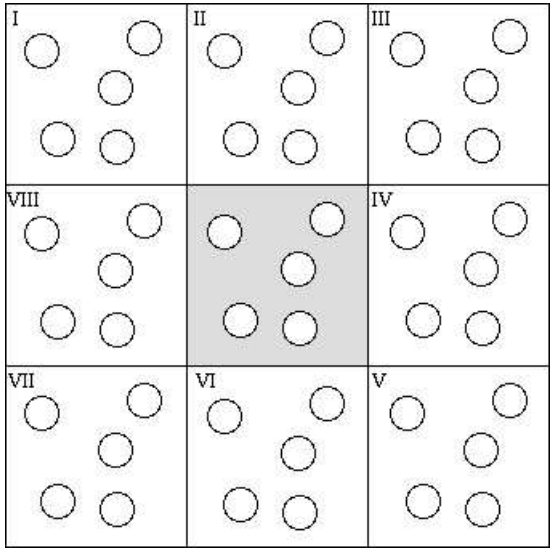
ESDG on the web: www.tcm.phy.cam.ac.uk/∼mdt26/esdg.html

FIRST PRINCIPLES CALCULATIONS



Atomic numbers

↓

Solve the quantum mechanical equations for the electrons

↓

(Follow the time evolution of the nuclei)

↓

Understand and predict physical and chemical properties of the system

Electronic Structure Theory

Justification for existence

Electronic structure calculations of materials designed to *complement* experiments, by

- helping to understand results of real experiments,
- calculating things that are experimentally inaccessible or cost money,
- providing an atomic scale resolution beyond most experiments,
- calculating things which don't exist (in experiments usually stuck with lowest free energy phase unless there is large activation energy so that metastable phases can be studied),

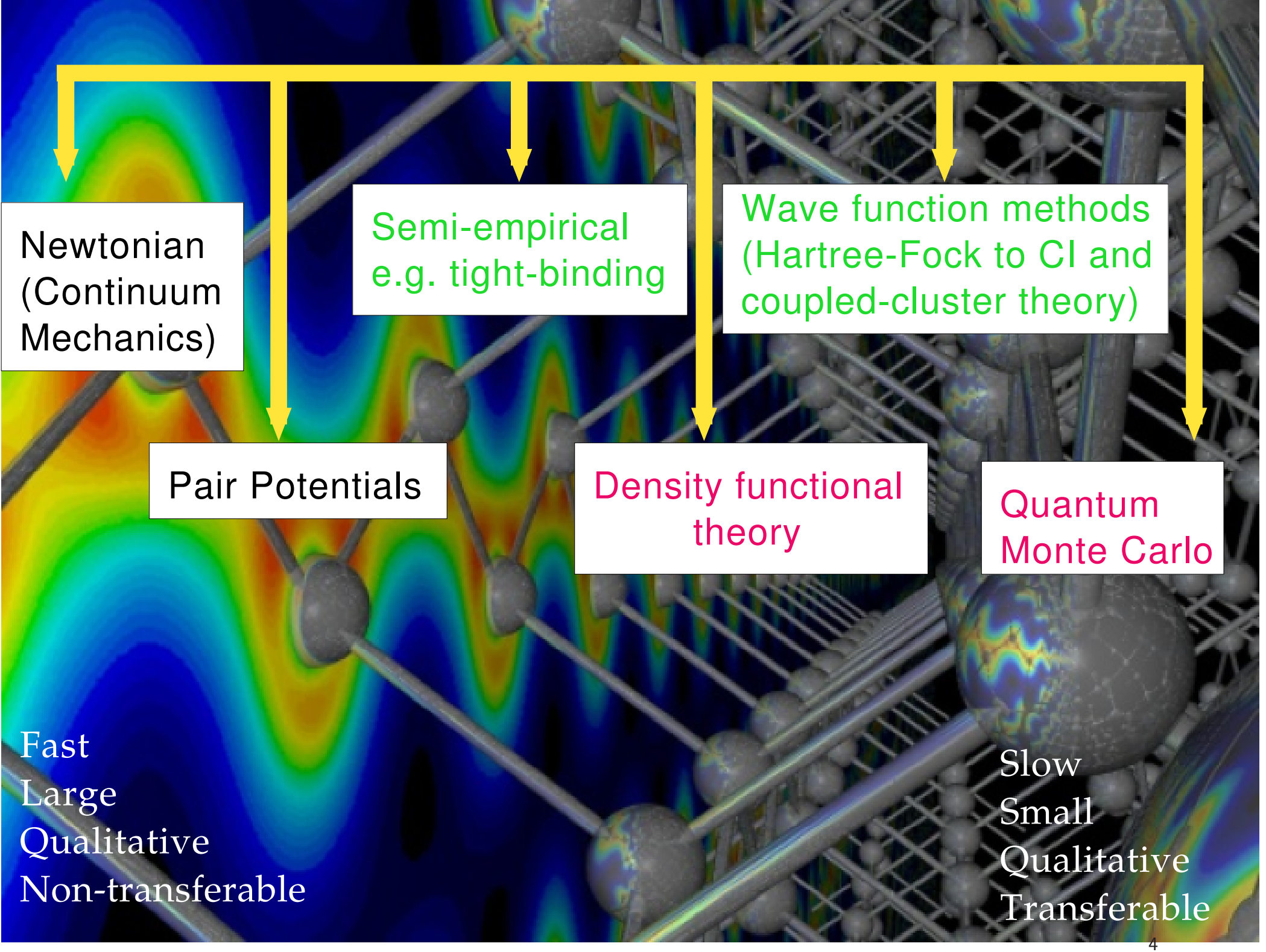
by "solving the Schrödinger equation" entirely from first principles with no adjustable parameters.

PLUS since we can only do this approximately, we try to

- improve the approximations to get better accuracy,
- improve the speed and scaling behaviour of the algorithms,
- work out how to use the theory to calculate new things

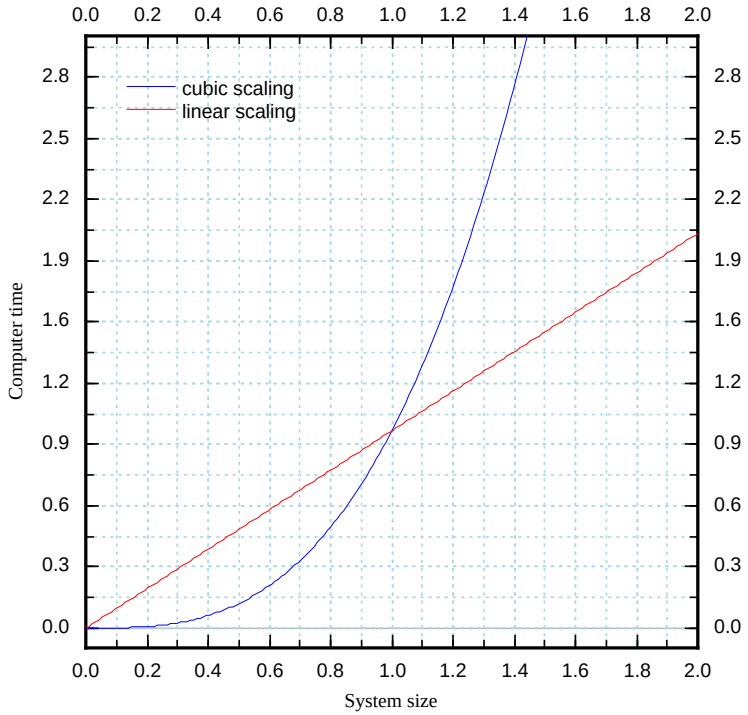
PLUS, as a service to the scientific community,

- we write generally applicable computer codes which do all of the above.


Newtonian (Continuum Mechanics)
Semi-empirical e.g. tight-binding
Wave function methods (Hartree-Fock to CI and coupled-cluster theory)
Pair Potentials
Density functional theory
Quantum Monte Carlo
Fast
Large
Qualitative
Non-transferable
Slow
Small
Qualitative
Transferable

Density functional theory

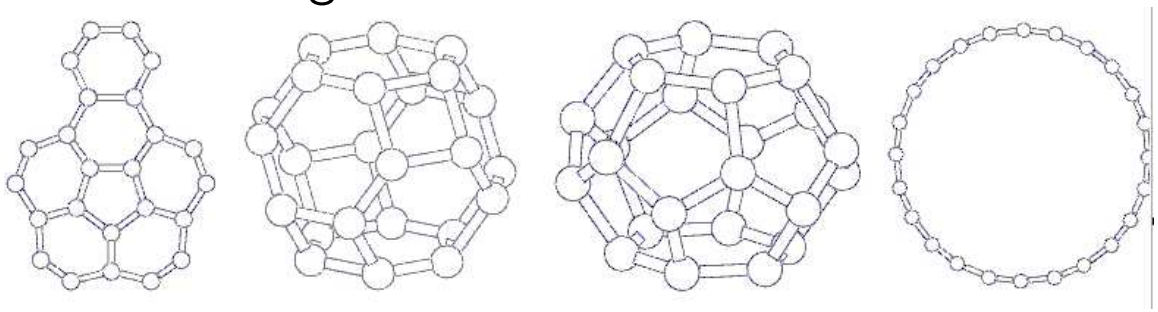
- Modern reformulation of quantum mechanics for large scale accurate microscopic calculations.
- Total energy from the density of electrons
- Favourable ratio accuracy versus computational cost
- Interdisciplinary applications
- combined with molecular dynamics
- 1998 Nobel prize to DFT inventor Walter Kohn and to John Pople



METHODS

Quantum Monte Carlo

• In some situations, *DFT is not accurate enough* due to limitations in currently available exchange-correlation functionals.



• Important alternative to DFT for situations where accuracy is paramount is quantum Monte Carlo, which is a stochastic (i.e. random sampling) technique using explicit many-particle wave functions. Very accurate! Quite a bit more expensive than DFT but not prohibitively so.

• Advantages over accurate quantum chemistry methods:
- Applicable to solids as well as molecules.
- Applicable to large systems (currently 2000 electrons/cell in a solid).
- Scales as N^3 with system size just like standard DFT, compared to N^6 or above for best quantum chemistry methods. Possibility of quadratic scaling- and even linear scaling for some cases - without crossover.

• Essentially independent of basis set.

Computer programs

CASINO

CASINO is the world's first and still only general quantum Carlo code (QMC for solids largely pioneered in Cambridge). Growing interest from international collaborators (see Mike Towler/Richard Needs).

CASINO web page: www.tcm.phy.cam.ac.uk/∼mdt26/casino.html

CASTEP

New modern rewrite of the original TCM DFT plane-wave code, which is widely used throughout the world. Marketed commercially by Accelrys (MSI). (see Chris Pickard)

ONES

Experimental linear scaling DFT code (see Peter Haynes/Chris Skylaris/Arash Mostofi)

Other codes used in TCM for applications

- CPMD - DFT ab initio molecular dynamics (Car-Parrinello)
- CRYSTAL - DFT/Hartree-Fock local basis set code
- PARATEC - DFT plane wave code
- SIESTA - Linear scaling DFT code
- GAUSSIAN - Huge quantum chemistry package

Electronic Structure Discussion Group

A forum to discuss all the above and more

Wednesday 11.15am-12.15pm

- BIG TALKS (35-45 minutes) : about electronic structure - current research/review of a field/speculative ideas followed by discussion.

- LITTLE TALKS (5-10 minutes) : about anything - people tend to choose electronic structure again but philosophical, artistic, literary or historical topics are welcome. Anything you think people will find interesting.

www.tcm.phy.cam.ac.uk/∼mdt26/esdg.html

Don't forget to send me your overheads (URL or ps/pdf file) for inclusion on the web site!

More information

Web sites

- TCM main page : www.tcm.phy.cam.ac.uk
- CUC3 : www-theor.ch.cam.ac.uk
- Earth Sciences : www.esc.cam.ac.uk
- Materials Science : www.msm.cam.ac.uk
- QMC group research : www.tcm.phy.cam.ac.uk/∼mdt26/casino.html

Emails of useful people

- Richard Needs : rn11 at cam.ac.uk
- Mike Payne : mcp1 at phy.cam.ac.uk
- Emilio Artacho : emilio at esc.cam.ac.uk
- Peter Haynes : pdh1001 at cam.ac.uk
- Chris Pickard : cjp20 at phy.cam.ac.uk
- Mike Towler : mdt26 at cam.ac.uk

Useful articles

QMC : www.tcm.phy.cam.ac.uk/∼mdt26/downloads/qmc_review.pdf

PW DFT/molecular dynamics : publish.aps.org/abstract/RMP/v64/p1045

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