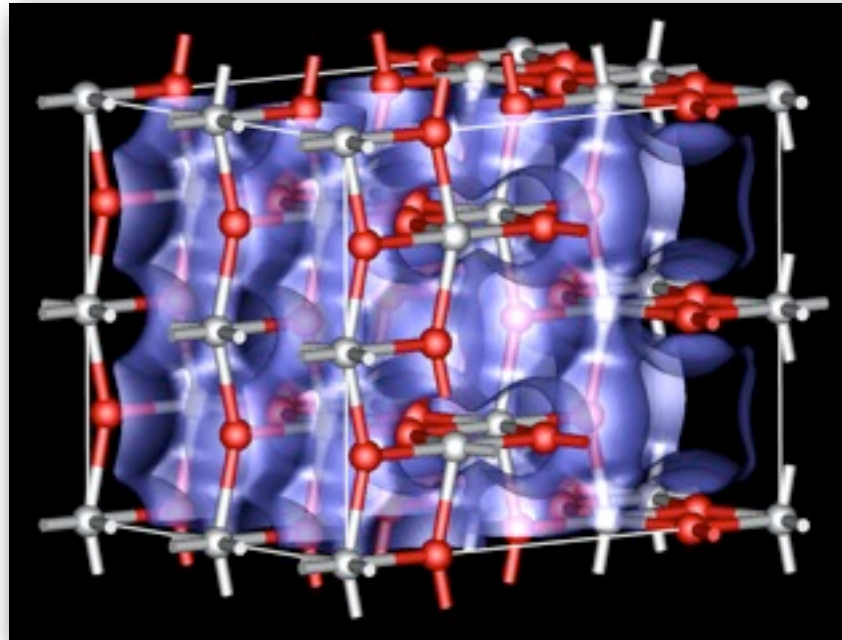


A Gentle Introduction to Electronic Structure Theory



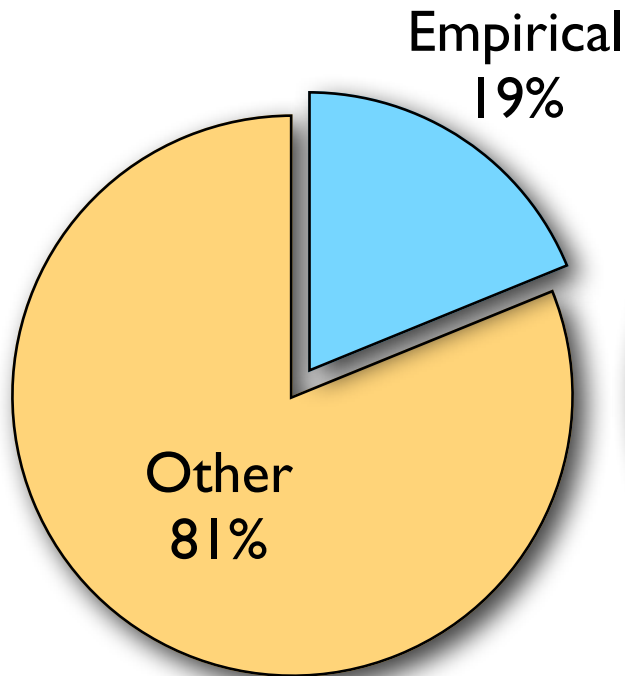
Paul R. C. Kent

<http://www.ornl.gov/~pk7>

Support: CDP Energy Frontier Research Center,
US DOE, Office of Science. Computers: NERSC, OLCF

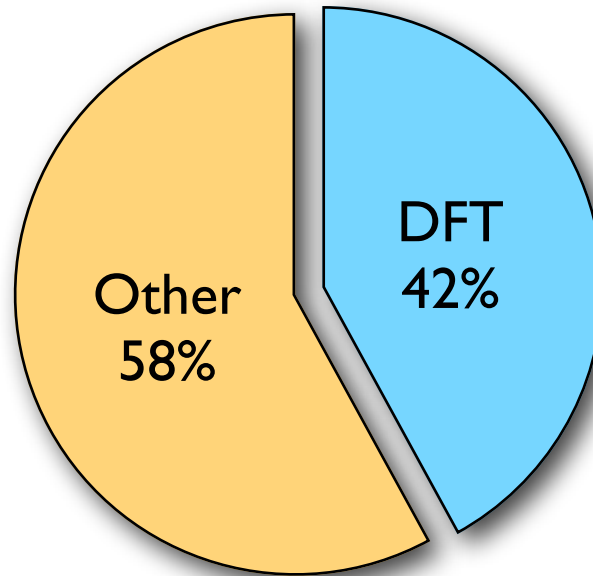
My background

- Distribution of papers by method (non-exclusive)



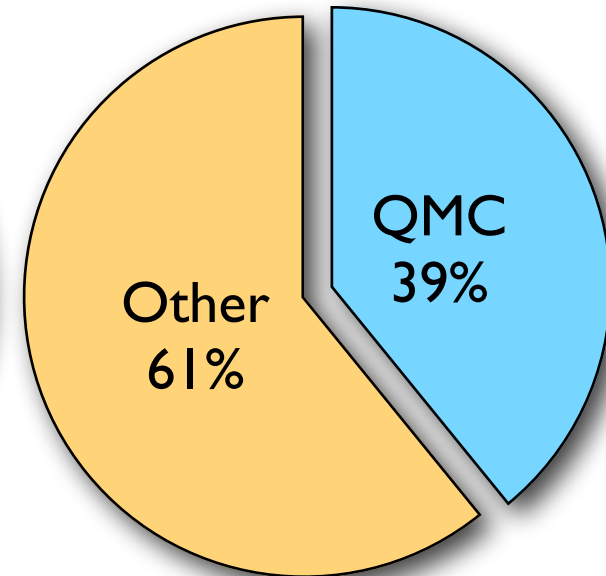
Empirical Potentials

Fastest, cheapest
Very limited
transferability



Density Functional Theory

Somewhat expensive
Reasonable applicability
and transferability

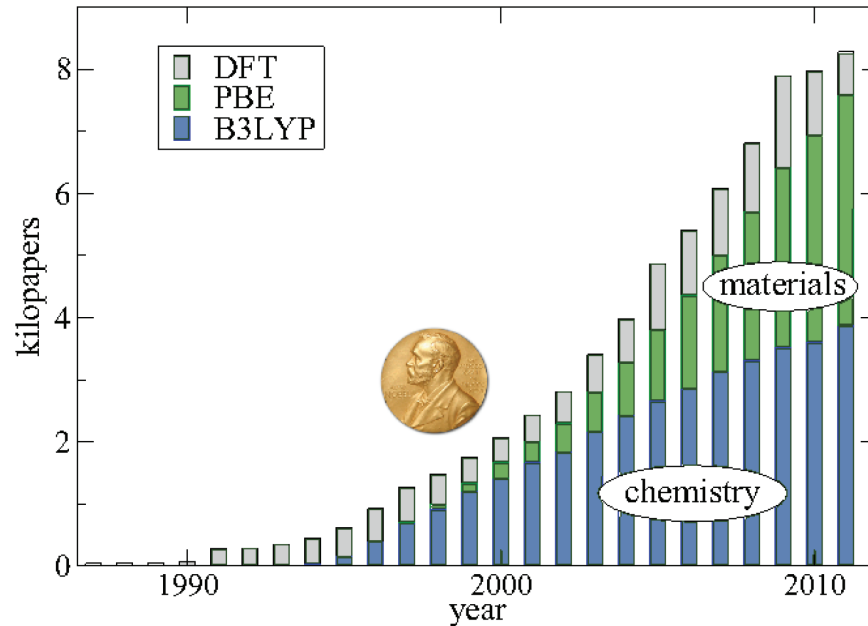


Quantum Monte Carlo

Most expensive (by far)
Most accurate

Background

- Density functional theory has become a very popular technique for obtaining the structure, energies, and properties of materials, molecules, and nanosystems

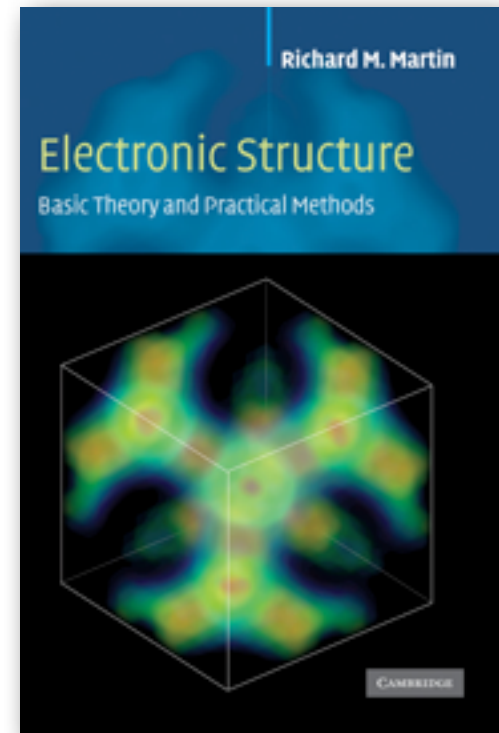


K. Burke, JCP 136 150901 (2012)

- Increasing ease of use and computational affordability will drive even more usage
- Significant problems remain for chemicals and materials

Key references

- “Electronic structure”,
Richard M. Martin, Cambridge
University Press (2004)
 - Excellent and ~complete DFT
introduction
 - Little discussion of classical MD
or multiscale modeling



INSTITUTE OF PHYSICS PUBLISHING MODELLING AND SIMULATION IN MATERIALS SCIENCE AND ENGINEERING
Modelling Simul. Mater. Sci. Eng. 13 (2005) R1–R31 doi:10.1088/0965-0393/13/1/R01

TOPICAL REVIEW

Designing meaningful density functional theory calculations in materials science—a primer

Ann E Mattsson¹, Peter A Schultz¹, Michael P Desjarlais²,
Thomas R Mattsson² and Kevin Leung³

¹ Computational Materials and Molecular Biology, Sandia National Laboratories Albuquerque,
NM 87185, USA

² HEDP Theory/ICF Target Design, Sandia National Laboratories Albuquerque, NM 87185, USA

³ Biomolecular Materials and Interfaces, Sandia National Laboratories Albuquerque,
NM 87185, USA

E-mail: aematts@sandia.gov, paschal@sandia.gov, mpdesja@sandia.gov, trmatts@sandia.gov
and kleung@sandia.gov

Received 9 July 2004, in final form 8 October 2004

Published 18 November 2004

Online at stacks.iop.org/MSMSE/13/R1

- A. E. Mattsson et al.
Modelling Simul. Mater.
Sci. Eng. 13 R1 (2005)
 - The art & craft of real
calculations
 - Recommendations

Outline

1. **A density functional theory primer**
2. **A visit to the “zoo” of density functionals**
 - Why so many? How are they related?
 - What are the evolutionary pressures and are they helping materials science?
3. **Practical computations**
 - What is feasible using the most popular plane wave pseudopotential approach?
 - Motivations for alternative approaches and implementations
4. **Summary**

Questions are welcome

Outline

- 1. A density functional theory primer**
- 2. A visit to the “zoo” of density functionals**
 - Why so many? How are they related?
 - What are the evolutionary pressures and are they helping materials science?
- 3. Practical computations**
 - What is feasible using the most popular plane wave pseudopotential approach?
 - Motivations for alternative approaches and implementations
- 4. Summary**

We aim to solve the many-body Schrodinger equation

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

$$\hat{H} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right) + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{Z_i Z_j}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$$

- **All electrons interact with all other electrons**
 - The electron-atom interactions are simple within the Born-Oppenheimer approximation
- **Finding the ground state is exponentially difficult**
 - Claimed to be NP hard M. Troyer PRL **94** 170201 (2005)

Formal density functional theory

- **Hohenberg-Kohn theorem(s)** Phys Rev **76** B6062 (1964)

$$E = F[\rho]$$

- The ground state energy is uniquely determined via the minimum of a universal Functional of the density
 - A massive simplification: one density instead of N electrons
 - Only an existence proof. Exact.
- **Kohn and Sham derived a coupled set of single particle Shrodinger equations enabling the density to be found**

$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{XC}[\rho(\mathbf{r})] + \dots$$

$$T_s[\rho(\mathbf{r})] = -\frac{1}{2} \sum_{i=1}^N \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r}$$

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$$

Functional

- **This is numerically tractable**

Phys Rev **140** A1133 (1965)

Summary

- **DFT provides a formally exact and equivalent way of solving the Schrodinger equation**
- **It leads to sets of equations that are numerically tractable**
- **However, the formal derivations give little guidance in the choice of Functional**

Outline

1. A density functional theory primer
2. A visit to the “zoo” of density functionals
 - Why so many? How are they related?
 - What are the evolutionary pressures and are they helping materials science?
3. Practical computations
 - What is feasible using the most popular plane wave pseudopotential approach?
 - Motivations for alternative approaches and implementations
4. Summary

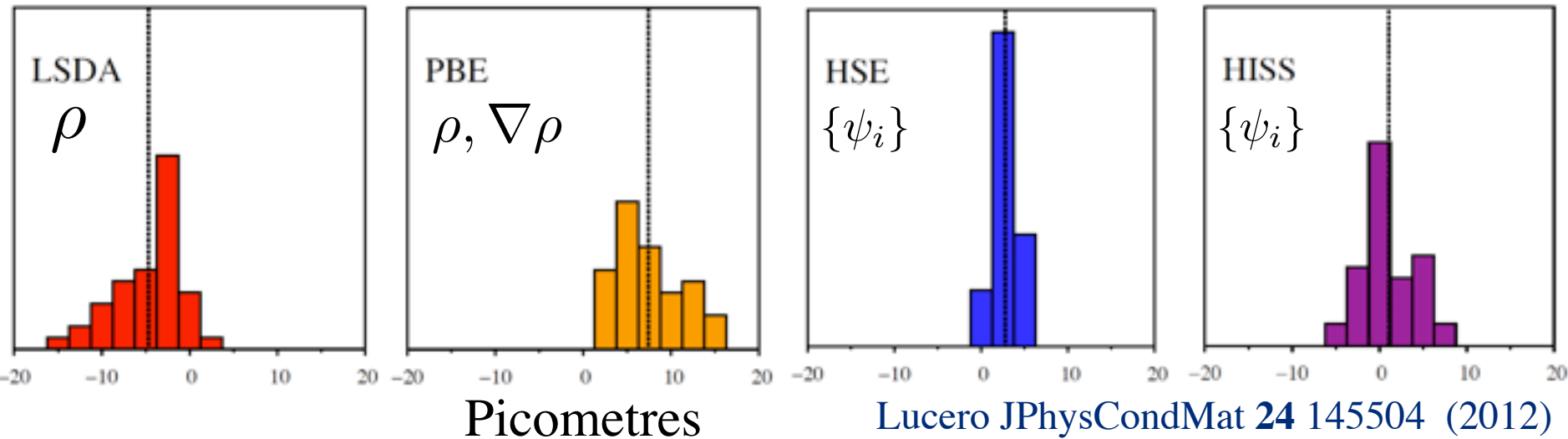
The zoo of functionals



- Size of word ~ a recent (unscientific) measure of popularity
- After 30+ years of development there are hundreds of functionals...
- ...but many are designed for chemistry and fail badly for materials. e.g. B3LYP fails for metals.
- In practice, we have to test the quantities of interest

Performance

- For simplicity, will look at histograms of lattice constant errors. In principle we should consider all properties of interest. Are trends correct?



- Test set is 40 common semiconductor systems “SC40”
- HSE shows less scatter than older cheaper functionals (LDA, PBE), but mean error is not dramatically improved

Performance

Lattice constants:

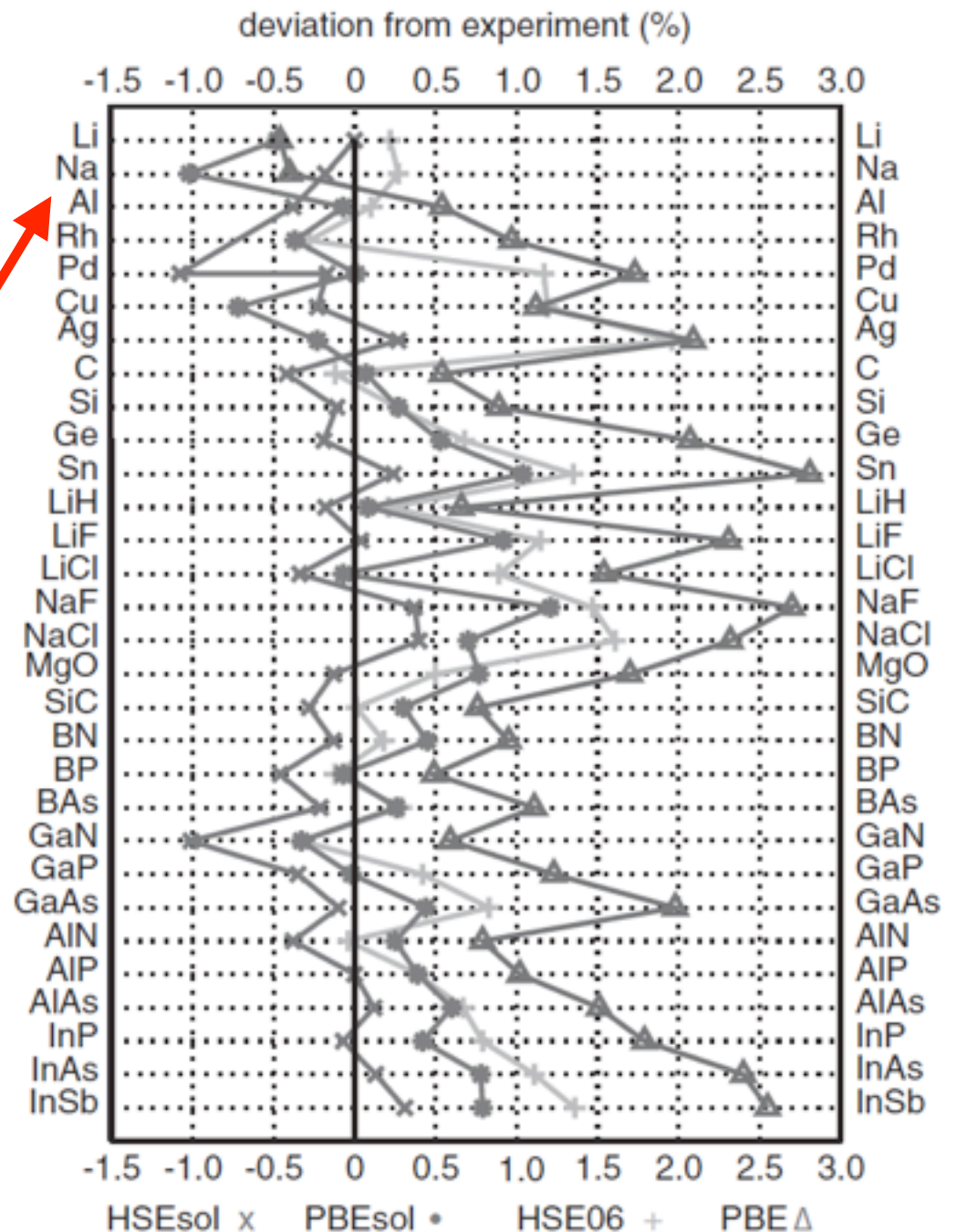
Scale is $O(1\%)$

No simple story even for metals

Hybrids (HSE...) consistently better in semiconductors

Some trends visible in related materials

Schimka JCP **134** 024116 (2011)



The zoo of functionals

- **Derivations of DFT do not sufficiently strongly guide choice of functionals**
 - Exact limiting behaviours can be/are included
- **Fitting a few parameters to data sets is increasingly common**
 - Different data sets lead to different functionals
 - Materials are rarely included in the fitting sets (!)
 - Need more “selective pressure” here from materials scientists
- **There is a popular belief that adding increased orbital (& gradient) dependence to the method will give increased accuracy**
 - Must be true eventually
 - Does not guarantee improvement along the way...

Jacob's Ladder of Functionals

- An organizing principle suggested by John Perdew



“Jacob’s Dream” by Marc Chagall via M. Marques

“Heaven of chemical accuracy”

All orbitals (gen. RPA)

Occupied orbitals

$\rho, \nabla\rho, \tau$ metaGGA

$\rho, \nabla\rho$ GGA

ρ LSDA

J. Tao et al. PRL **91** 146401 (2003)
(TPSS paper) and refs within

- **Problems: could easily move up a rung and lose accuracy for some material/property. Ladder is as much driven by complexity (cost) as accuracy. Many possible ladders/routes to improvement...**

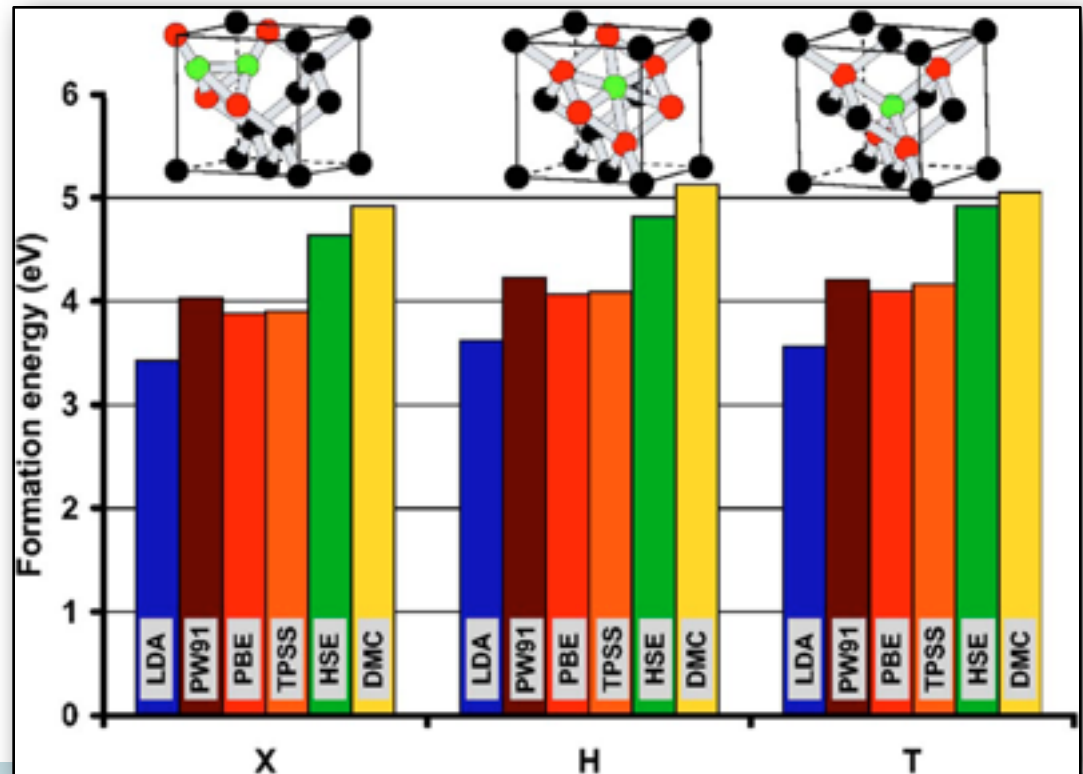
Key problems of DFT in practice

1. **“The method does not converge to the right answer”**
 - The theory is not systematically improvable. No easily accessible small parameter to converge. The formal derivations of DFT do not sufficiently guide functional development
 - Physical insight helps, but only to a certain extent
 - Difficulty of making consistent improvements invites empiricism
2. **Electrons interact with themselves, “self-interaction”**
 - A special case of #1
 - Extremely problematic for localized d,f electrons
 - Helped to some extent by orbital dependent functionals
3. **Dispersion interactions are not well described**
 - A special case of #1
 - Van der Waals functionals are making great progress...
 - ...but have yet to be fully integrated with developments for #2

Example: Defects in Si

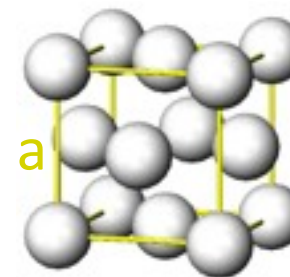
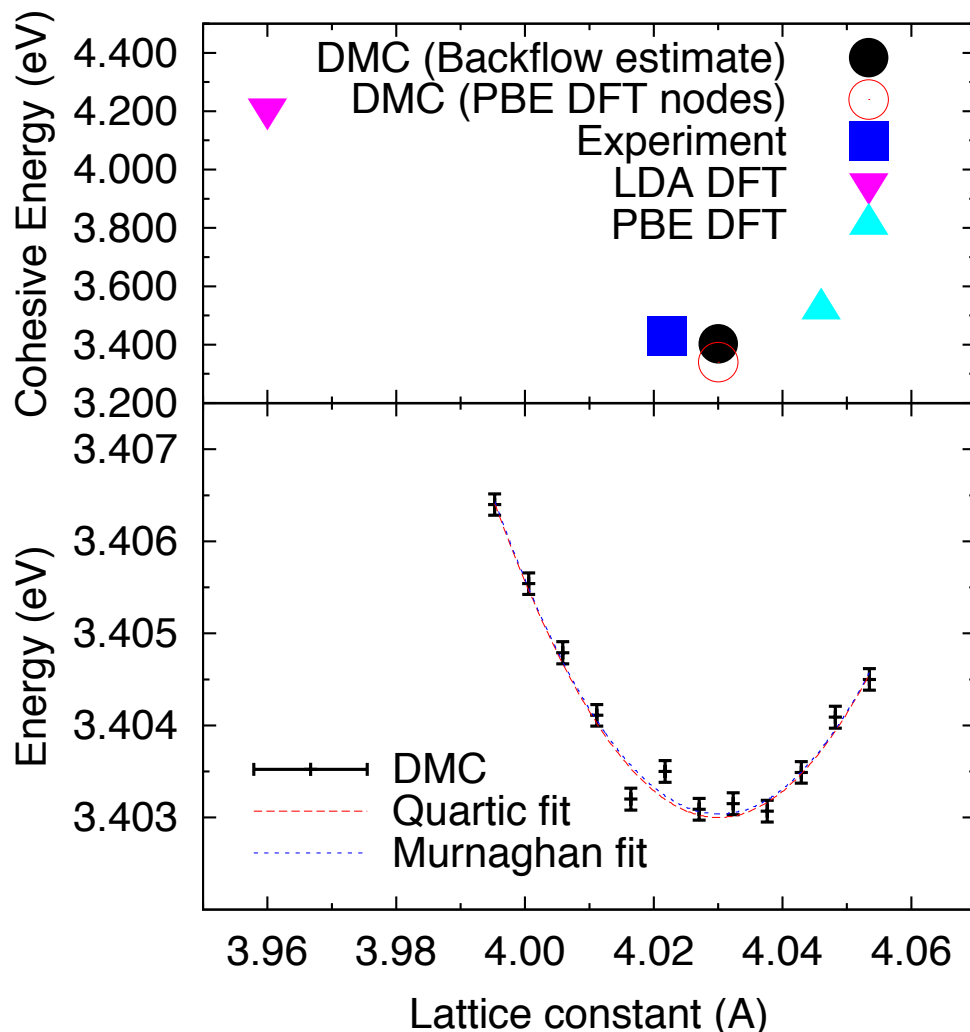
- Problem: LDA and GGA DFT predict self-diffusion activation energies 1/1.5eV lower than experiment
- The first QMC calculations on defects (1999) found defect formation energies much closer to experiment.
- More recent calculations (2006) confirm this and also find newer DFT functionals give better results
- But HSE is expensive
 - N^4 vs N^3 scaling

Leung et al. PRL **83** 2351 (1999)
Batista et al. PRB **74** 121102 (2006)



Diffusion QMC bulk fcc aluminium

With twisted-boundary conditions and extrapolation to infinite supercell

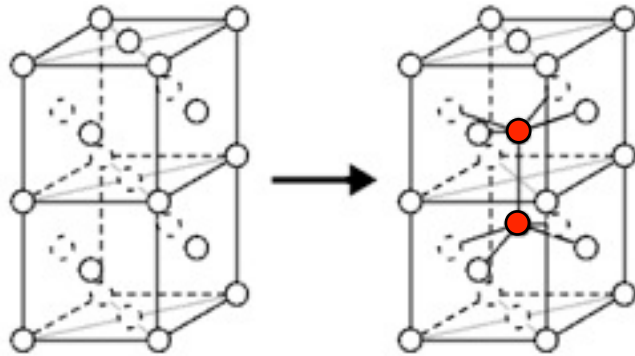


DMC differs by 0.008 \AA (0.2 %) and $<30\text{meV}$ from experiment

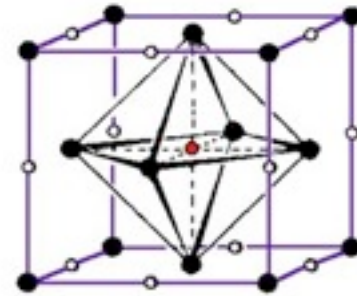
Likely improveable with additional backflow.

Hood et al. PRB **85**
134109 (2012)

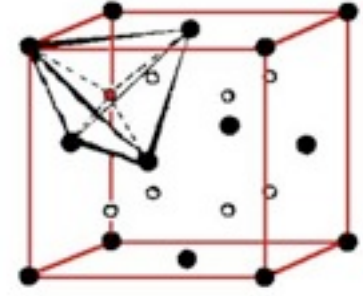
Self-interstitials in fcc aluminium



<100>-dumbbell



octahedral site



tetrahedral site

Increasing relaxation volume Ω_{rel}



Formation Energy (eV)

Relaxation volume (Ω_o)

	GGA (PBE)	DMC	Experiment	Ω_{rel} (calc.)	Experiment
<100>-dumbbell	2.70	2.94	3.0, 3.2(5)	2.29	1.9(4), 1.7(4)
octahedral	2.91	3.13		2.42	
tetrahedral	3.23	3.56		2.52	

Typical GGA DFT error for defects in Al ~ a few 0.1 eVs / 1000s K

Hood et al. PRB **85** 134109 (2012)

Density functionals poll (!?)

- A new functional that contains and weights all the functionals by popularity was constructed...
 - ...which performed worse than the best Truhlar functionals! (M06)
- ➔ Improving density functionals is no easy task



Outline

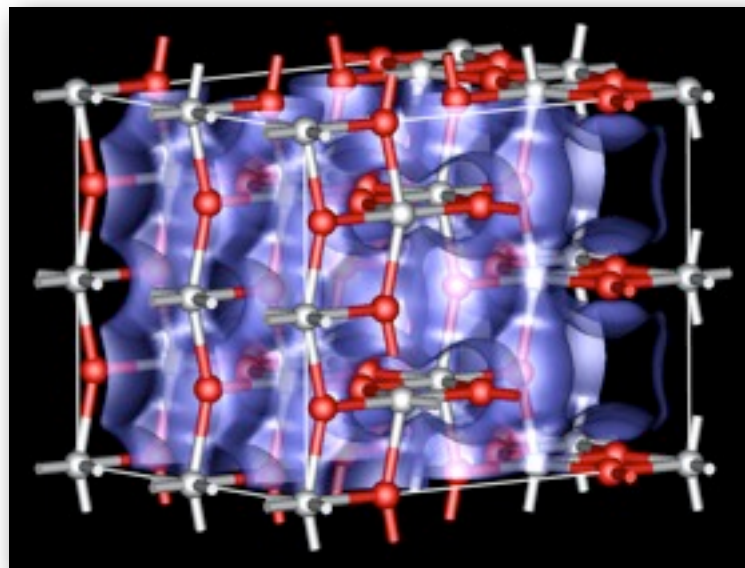
1. A density functional theory primer
2. A visit to the “zoo” of density functionals
 - Why so many? How are they related?
 - What are the evolutionary pressures and are they helping materials science?
3. Practical computations
 - What is feasible using the most popular plane wave pseudopotential approach?
 - Motivations for alternative approaches and implementations
4. Summary

Plane wave pseudopotential method

- A highly practical and popular method, fast enough for molecular dynamics, with many implementations:
 - ABINIT, CASTEP, PWSCF/Espresso, QBox, Socorro, VASP,...
 - Formally N^3 scaling with system size for local functionals
- Key choices:
 - Replace core electrons by an effective potential (pseudopotential)
 - Avoids requirement to represent core electrons in a basis
 - Avoids requirement to orthogonalize to core electrons
 - ➔ Far simpler and cheaper numerics than all electron calculations
 - Represent orbitals/wavefunctions by a Fourier series
 - Easily convergable by increasing the frequency (energy) of the plane wave cutoff
- Problems:
 - Sometimes core electrons are required (NMR, Xray spectra...)
 - Can be difficult to reproduce the all electron result
 - Many practitioners do not check vs all electron results

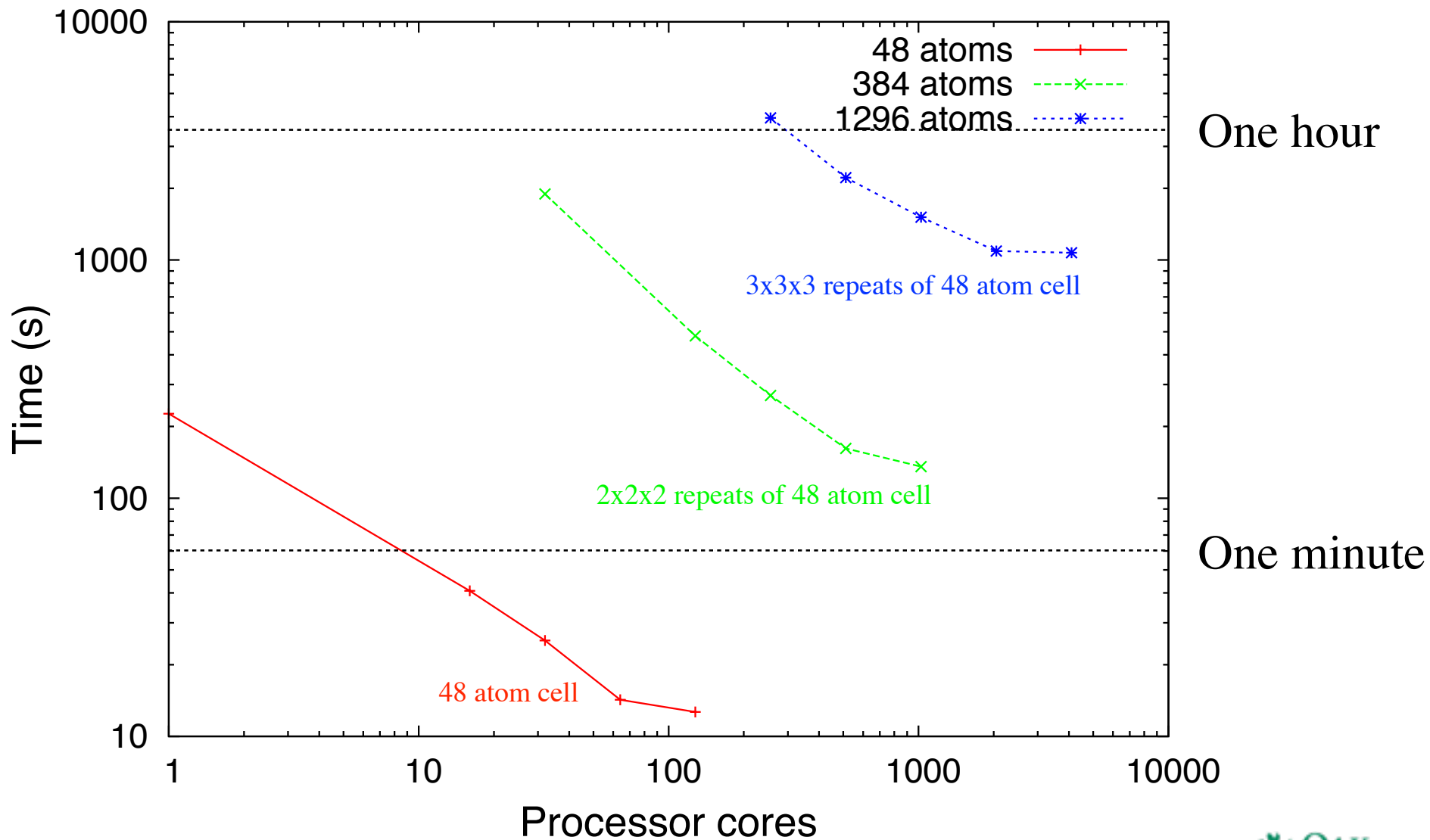
Example: Bulk TiO₂

- A simple wide band gap oxide.
- Time to converge wavefunctions, total energy, then calculate forces and stress. Finding the ground state structure requires many of these ionic steps.
- Reported performance is believed to be representative, not optimal. 2x improvement achievable, not 10x.
- Details:
 - PBE functional, lattice constants
 - 12 valence electron Ti, 6 electron O PAW potentials
 - 0.00001eV convergence
 - Gamma point sampling only
 - Reasonable choices for other parameters. Publishable.



16 TiO₂ units/48 atoms and charge density

TiO2 Scaling

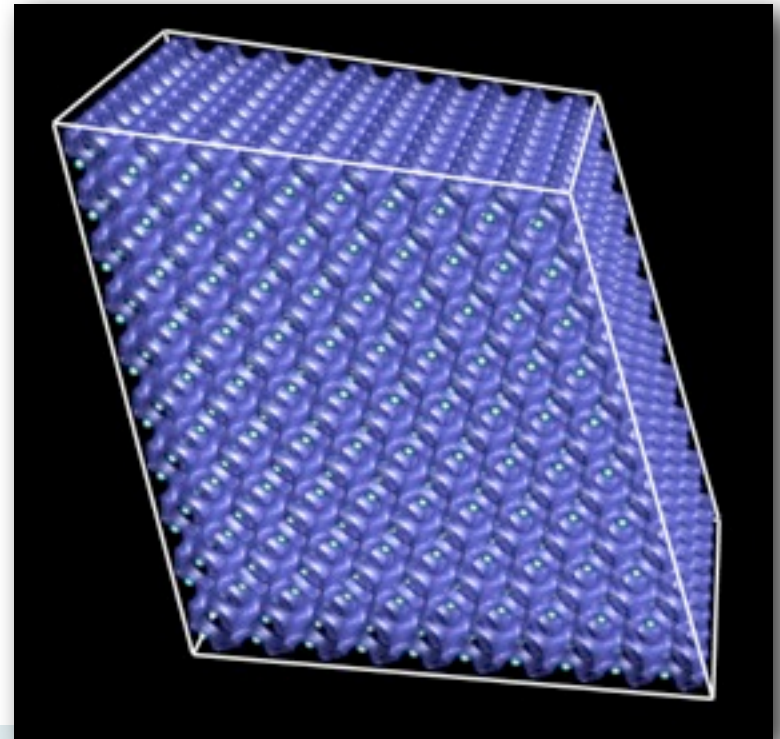


Remarks

- **<100 atoms are very affordable, may facilitate “design of materials” and “screening” of properties**
- **Moving from 48 to 1296 atoms (27x) only increases linear distances by 3x, but increases computational cost by 4400x ($^{2.5}$ scaling, not the formal cubic cost)**
- **Parallel scaling is never 100% efficient**
- **In practice, larger systems take longer to run**

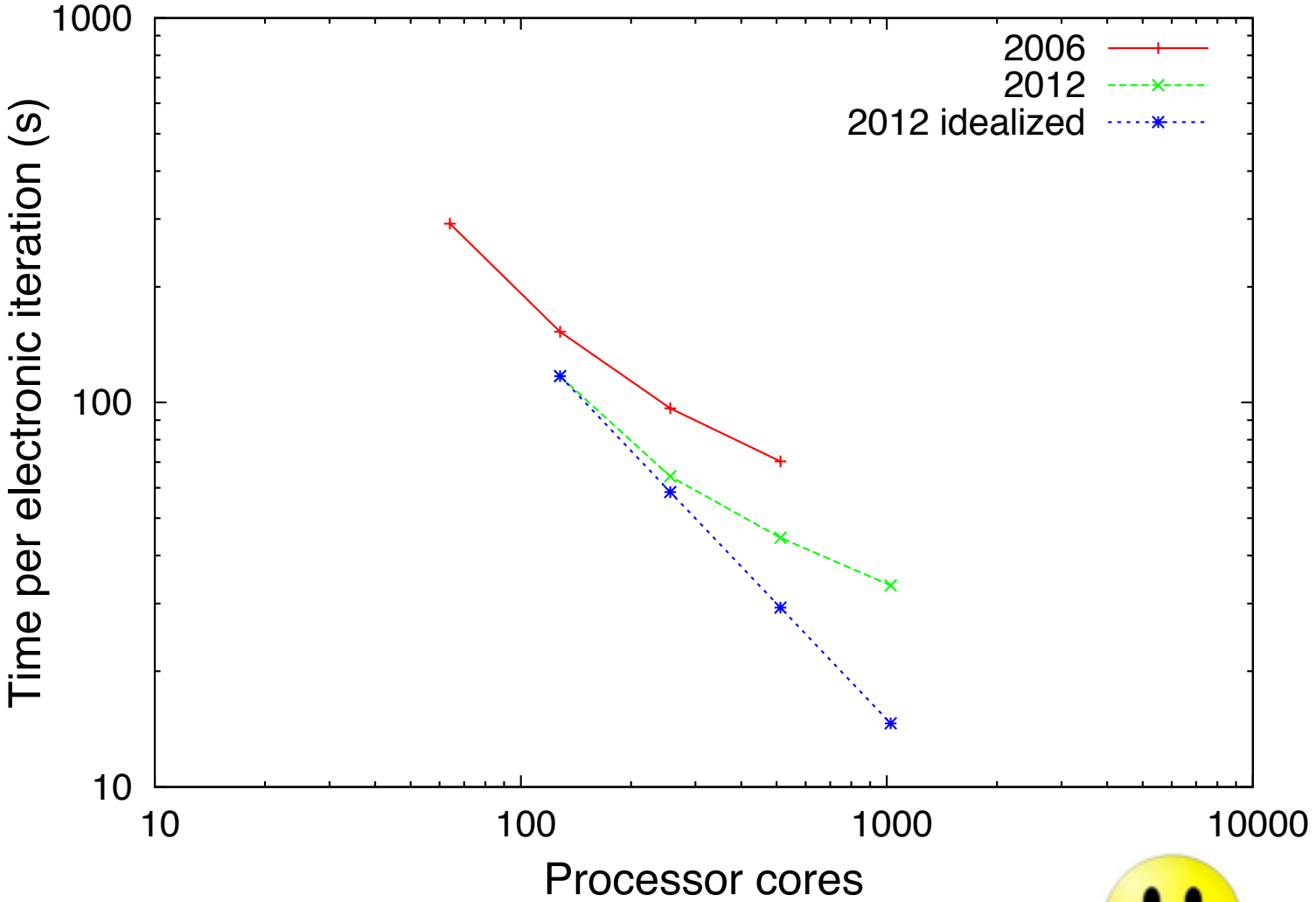
Quiz: 1000 atoms Mo bulk

- Time for each electronic iteration (~15 required for electronic convergence)
- I have data from 2006, ran on then jaguar at Oak Ridge
- Q. How much faster can we do the calculation today, using the latest version of jaguar with newer processors and a better interconnect?
 - Code etc. is identical



1000 Mo atoms and charge density

History lesson: Mo scaling



There are numerous ways to interpret this data...



A motivation for alternative methods

- **Data shows better scalability and performance but less than 2x improvement over ~6 years. Holds for numerous other runs (bulk, nanoparticles etc.) The speedup is useful but far from revolutionary.**
- **The cost of the computers has decreased considerably**
- **The modest improvements motivate methods that:**
 - **Exploit newer architectures better (CPUs, GPUs, MIC...)**
 - **Have much better scalability, e.g. are linear scaling, even at the expense of some generality or accuracy**
- **Some of these methods already exist**
- **Ideas win out over hardware**
- **Alternative methods still require good functionals**

Summary

- **DFT is a formally exact and very powerful approach to electronic structure, but we lack procedures for systematically improving the functionals**
- **Significant improvements have been made for chemical systems, but for materials problems progress is less clear. Careful testing and “design of experiments” is required**
- **Developments in computing will motivate changes in implementation, but the central DFT questions will remain**