The golden age of electronic structure theory

Kieron Burke and friends,
All papers available from
http://dft.uci.edu
(see especially *DFT in a nutshell*)

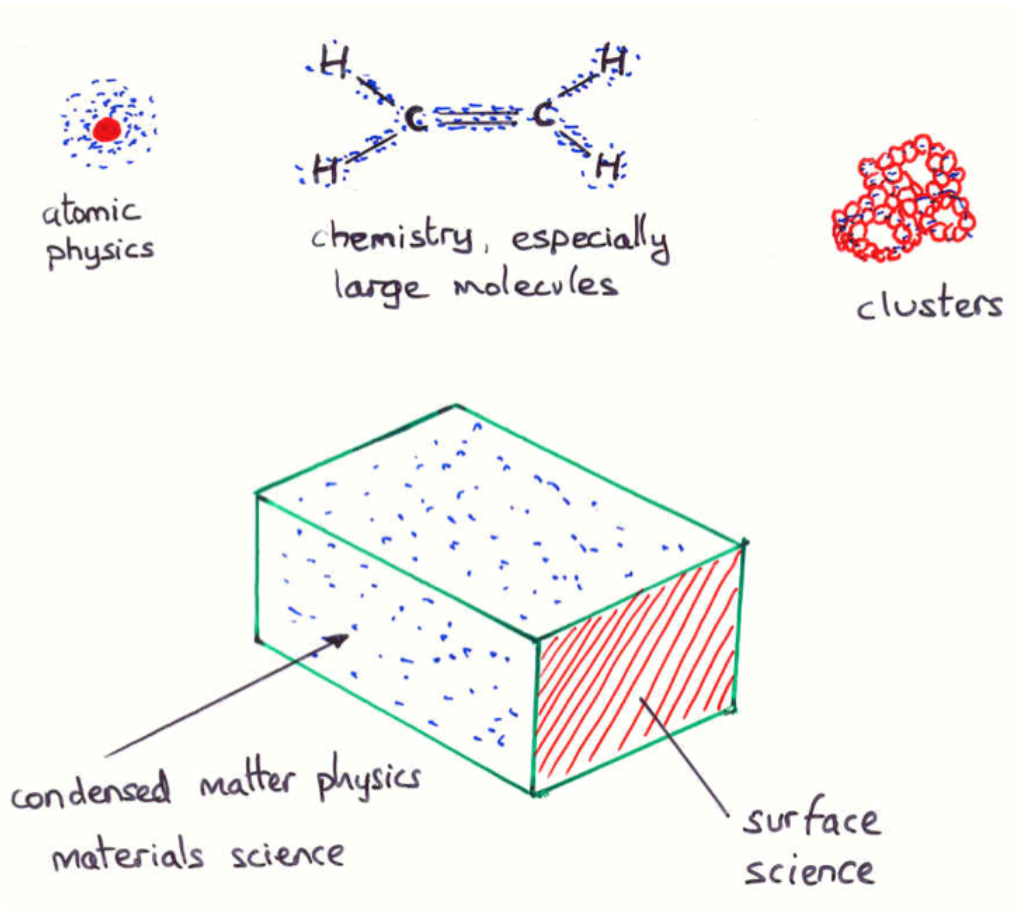
Outline

- Some basics and notation
- Practicalities and applications
- Challenges at present
- Looking back over last 20 years
- What might come in next 5 years
- Summary

Basics and notation

Electronic structure problem

What atoms, molecules, and solids exist, and what are their properties?



Multidisciplinary problem

- Chemistry
- physics
- Biochemistry
- Geology
- materials science
- plasma physics
- …

DFT is very different!

- We believe Schrödinger equation, but it's too expensive to solve
- DFT is an alternative
- Direct solution is more controllable but more expensive
- CI,CC, MPn, etc in quantum chemistry
- Green's function methods in physics

Kohn-Sham equations (1965)

$$\left[-\frac{1}{2}\nabla^2 + \mathrm{v}_s[n](\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\,\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{i=1}^{N}\left|\phi_i(\mathbf{r})\right|^2 =$$

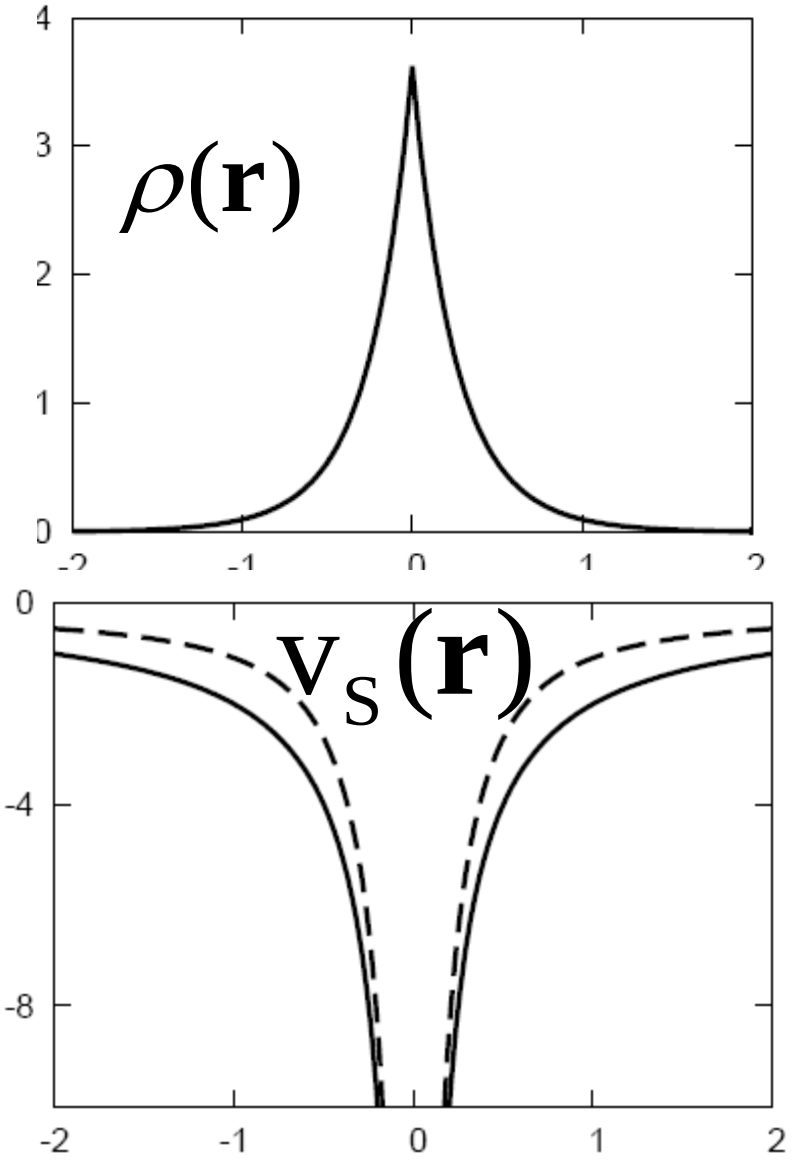
ground-state density of interacting system

$$\mathrm{v}_s(\mathbf{r}) = \mathrm{v}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + \mathrm{v}_{\mathrm{xc}}[n](\mathbf{r})$$

$$E_0 = T_S + V + U + E_{XC}[n]$$

$$\mathrm{v}_{\mathrm{xc}}[n](\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

He atom in Kohn-Sham DFT



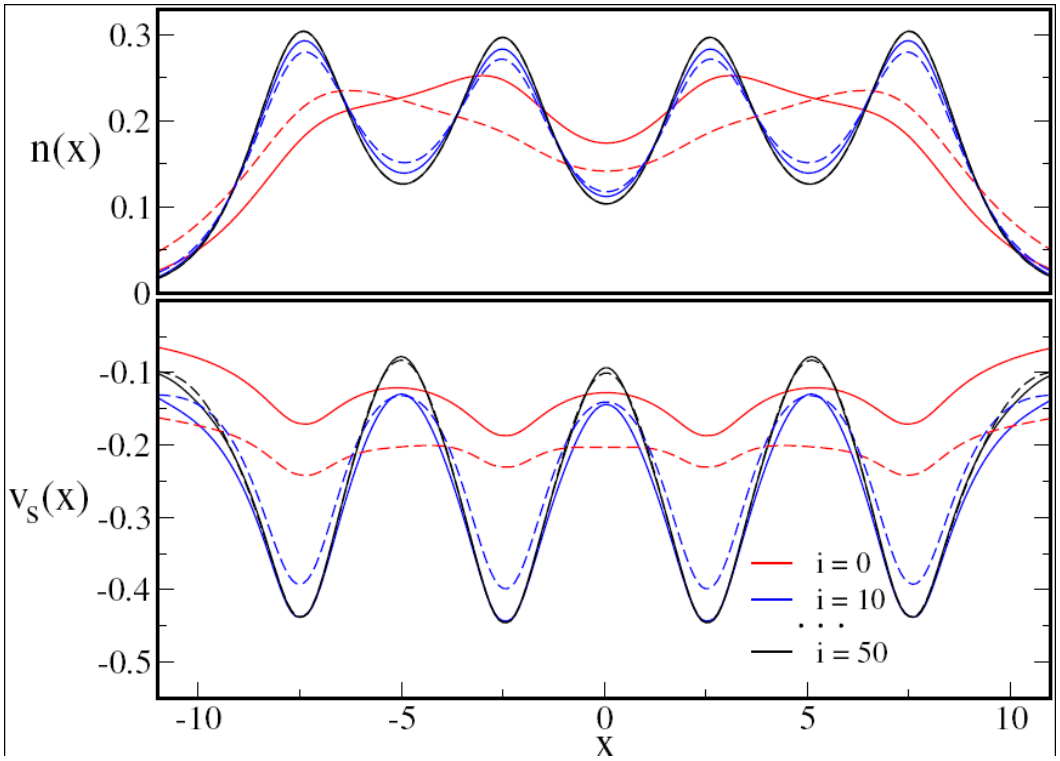
Everything has (at most) one KS potential

Dashed-line:

EXACT KS potential

First ever KS calculation with exact $E_{XC}[n]$

- Used DMRG (density-matrix renormalization group)
- 1d H atom chain
- Miles Stoudenmire, Lucas Wagner, Steve White
- On arXiv 1107.2394



DFA

In reality…

- Must approximate a small unknown piece of the functional, the exchange-correlation energy $E_{xc}[n]$.

- 70's-90's: Much work (Langreth, Perdew, Becke, Parr) going from gradient expansion (slowly-varying density) to produce more accurate functionals.

- Early 90's:
  - Approximations became accurate enough to be useful in chemistry
  - 98 Nobel to Kohn and Pople

The standard functionals

- Local density approximation (LDA) $E_{\mathrm{X}}^{\mathrm{LDA}}[n] = A_{\mathrm{X}} \int d^3r \; n^{4/3}(\mathbf{r})$
  - Uses only density at a point. $A_{\mathrm{X}} = -(3/4)(3/\pi)^{1/3} = -0.738$

- Generalized gradient approx (GGA)
  - Uses both density and its gradient
  - Should be more accurate, corrects overbinding of LDA
  - Examples are PBE and BLYP

- Hybrid:
  - Mixes some fraction of Hartree-Fock exchange
  - Examples are B3LYP and PBE0

Standard codes and functionals

- Chemistry – B3LYP in Gaussian
- Solids – PBE in VASP (see also quantum espresso, abinit, ELK, etc.)
- Chemists use localized basis functions (usually Gaussians on atoms)
- Physicists use plane waves and pseudopotentials

DFT – the only quantum game in town

- If you need chemically-useful accuracy for a few hundred atoms, DFT is your only man.
- Focused on ground-state only.
- More accurate, controllable methods produce benchmarks and tests on smaller systems.
- Not for use when underlying physics is not understood
- Useful when hundreds of folks need to perform same basic calculation in different contexts.

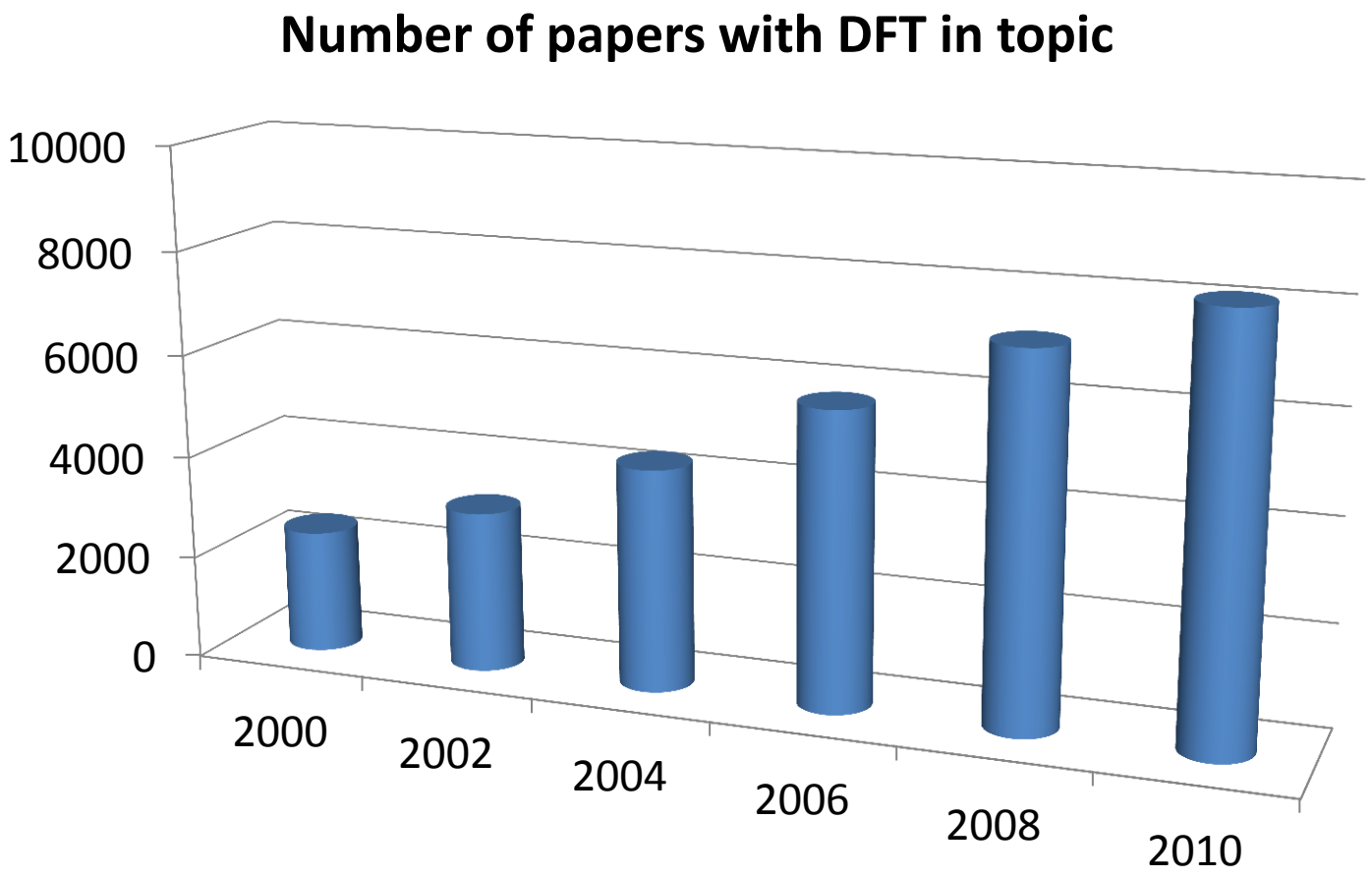
Weak versus strong correlation

- Mostly, DFA work well for weakly correlated systems
- Most systems in chemistry are weakly correlated, but need to get very high accuracy, e.g. transition state barriers
- Much of condensed matter is focused on strongly correlated systems, eg superconductivity, superfluidity, quantum Hall effect, topological insulators, etc.

About 20 years ago

- Revolution in chemistry beginning to happen
- 1993: Important paper showing GGA's accurate enough, and hybrids even better.
- 1998: Nobel prize for Pople and Kohn.

Rise in use of DFT



Incredible breadth

1. Title: Potential functions for hydrogen bonds in protein stru prediction and design
Author(s): Morozov AV, Kortemme T
Source: **PEPTIDE SOLVATION AND H-BONDS** Volume: **72** Pages: **1-+** Published: **2006**

2. Title: Ab initio study of high-pressure phases of gallium nitr
Author(s): Saib S, Bouarissa N
Source: **IEE PROCEEDINGS-OPTOELECTRONICS** Volume: Issue: **4** Pages: **179-182** Published: **AUG 2006**

3. Title: Transmission electron microscopy and theoretical analysis of AuCu nanoparticles: Atomic distribution and dynamic behavior
Author(s): Ascencio JA, Liu HB, Pal U, et al.
Source: **MICROSCOPY RESEARCH AND TECHNIQUE** Volur **69** Issue: **7** Pages: **522-530** Published: **JUL 2006**

4. Title: Dissolution and re-crystallization processes in multipl silicon stabilized tricalcium phosphate
Author(s): Tuck L, Astala R, Reid JW, et al.
Source: **JOURNAL OF MATERIALS SCIENCE-MATERIALS IN MEDICINE** Volume: **19** Issue: **2** Pages: **917-927** Published: **FEB 2008**

Source: **JOURNAL OF MATERIALS SCIENCE-MATERIALS IN MEDICINE** Volume: **19** Issue: **2** Pages: **917-927** Published: **FEB 2008**

5. Title: Sulphate adsorption at the Fe(hydr)oxide-H2O interface: comparison of cluster and periodic slab DFT predictions
Author(s): Paul KW, Kubicki JD, Sparks DL
Source: **EUROPEAN JOURNAL OF SOIL SCIENCE** Volume: **58** Issue: **4** Pages: **978-988** Published: **AUG 2007**

6. Title: Two new sarasinosides from the sponge Melophlus sarasinorum
Author(s): Santalova EA, Denisenko VA, Dmitrenok PS, et al.
Source: **NATURAL PRODUCT COMMUNICATIONS** Volume: **1** Issue: **4** Pages: **265-271** Published: **2006**

7. Title: Density functional calculations of the properties of silicon-substituted hydroxyapatite
Author(s): Chappell HF, Bristowe PD
Source: **JOURNAL OF MATERIALS SCIENCE-MATERIALS IN MEDICINE** Volume: **18** Issue: **5** Pages: **829-837** Published: **MAY 2007**

8. Title: He conductivity in cool white dwarf atmospheres
Author(s): Mazevet S, Challacombe M, Kowalski PM, et al.
Source: **ASTROPHYSICS AND SPACE SCIENCE** Volume: **307** Issue: **1-3** Pages: **273-277** Published: **JAN 2007**

9. Title: A TD-DFT investigation of the visible spectra of fluoro-anthraquinones
Author(s): Preat J, Jacquemin D, Perpete EA
Source: **DYES AND PIGMENTS** Volume: **72** Issue: **2** Pages: **185-191** Published: **2007**

10. Title: How metals bind: The deformable-jellium model with correlated electrons
Author(s): Tran HT, Perdew JP
Source: **AMERICAN JOURNAL OF PHYSICS** Volume: **71** Issue: **10** Pages: **1048-1061** Published: **OCT 2003**

Better Li batteries from Materials Genome

Opportunities and challenges for first-principles materials design and applications to Li battery materials

Gerbrand Ceder

This article is based on the MRS Medal presentation given by Gerbrand Ceder (Massachusetts Institute of Technology) on December 1, 2009, at the Materials Research Society Fall Meeting in Boston. Ceder was awarded the Medal "for pioneering the high-impact field of first-principles thermodynamics of batteries materials and for the development of high-power density Li battery compounds."

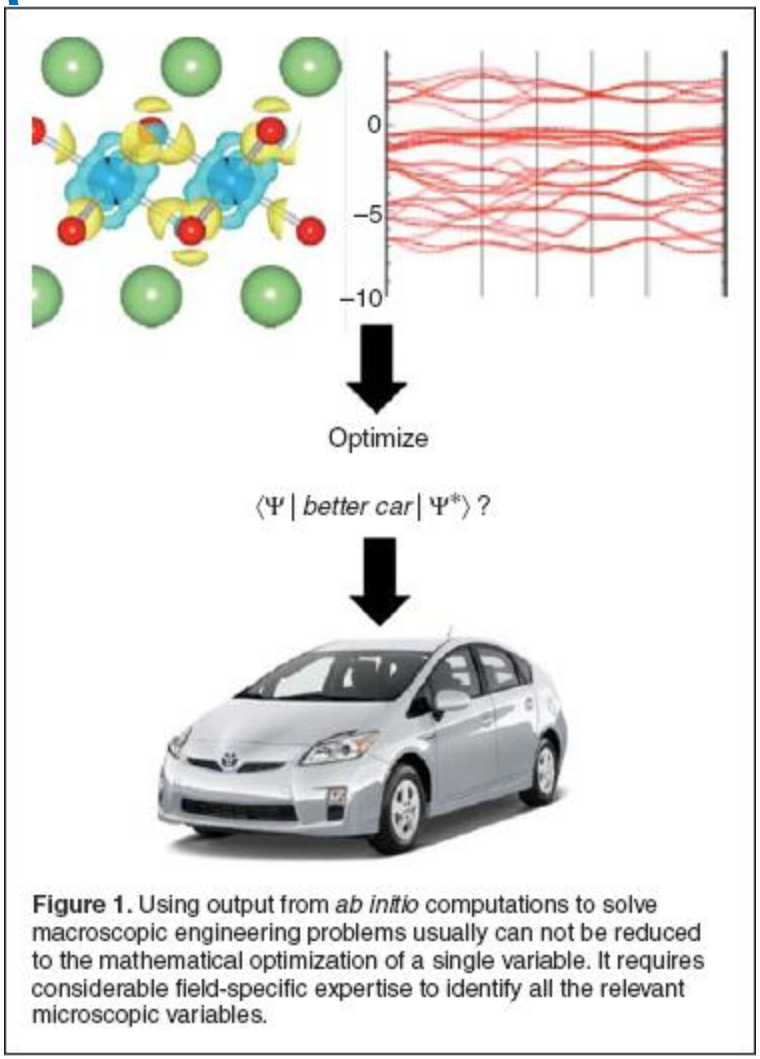


Figure 1. Using output from *ab initio* computations to solve macroscopic engineering problems usually can not be reduced to the mathematical optimization of a single variable. It requires considerable field-specific expertise to identify all the relevant microscopic variables.

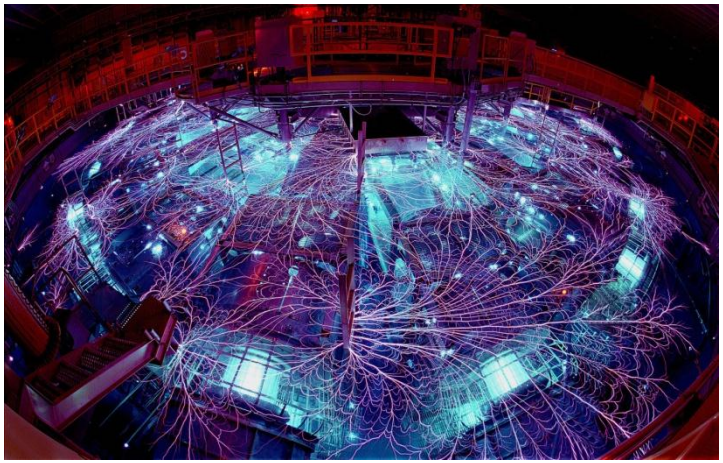
AMP: Advanced Manufacturing Partnership

- Obama announced $500 million about 2 weeks ago.
- Like the nano initiative
- Theory plays important role.

PRL 105, 085501 (2010) PHYSICAL REVIEW LETTERS week ending 20 AUGUST 2010

Shock Compression of a Fifth Period Element: Liquid Xenon to 840 GPa

Seth Root,* Rudolph J. Magyar, John H. Carpenter, David L. Hanson, and Thomas R. Mattsson
Sandia National Laboratories, Albuquerque, New Mexico 87185, USA
(Received 12 April 2010; published 17 August 2010)

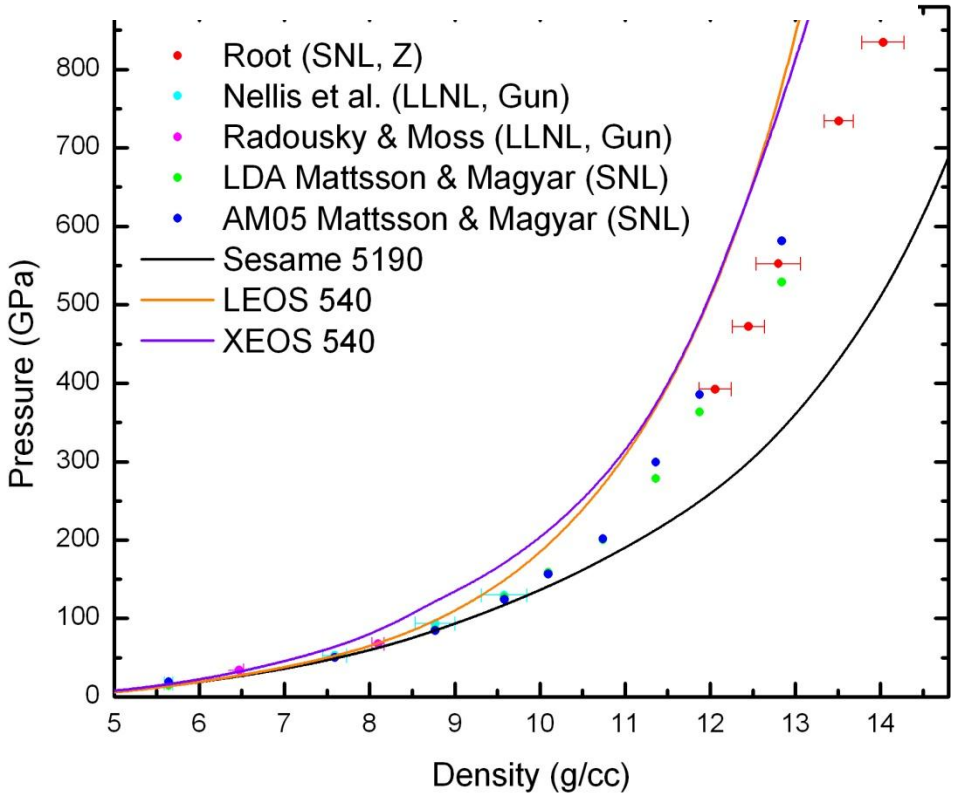


Z-pinch Pulsed Power System

- **Millions of amperes for less than 100 nanoseconds**
- **Peak temperature 3.7 GK or 6.6 billion °F, a world record**
- **Propelled small plates at 34 km/sec, 4x faster than a speeding bullet.**
- **Pressures 70,000 to 120,000 atm (7 to 12 Gpa).**

DFT-MD

- **Move classical nuclei in thermal quantum electrons**
- **VASP code (Georg Kresse, Vienna, Austria)**
- **World's tenth fastest computer**



Liquid Xenon Hugoniot

Submitted to PRL Root, Magyar, Carpenter, Hanson, Mattsson (2010).
DFT first published: Magyar and Mattsson CP1195, Shock Compression of Condensed Matter, 797 (2009).

The infidels

- Chemistry – most folks develop wavefunction-based methods, but use DFT for useful calculations
- Physics – most folks use model Hamiltonians that capture the relevant physics, but get parameters from DFT calculations
- Generic materials properties versus specific: *"If I want to know T_C for a superconductor, I ask an experimentalist. Why bother calculating it?"*

Challenges at present


outnow.ch

Materials genome from first principles?

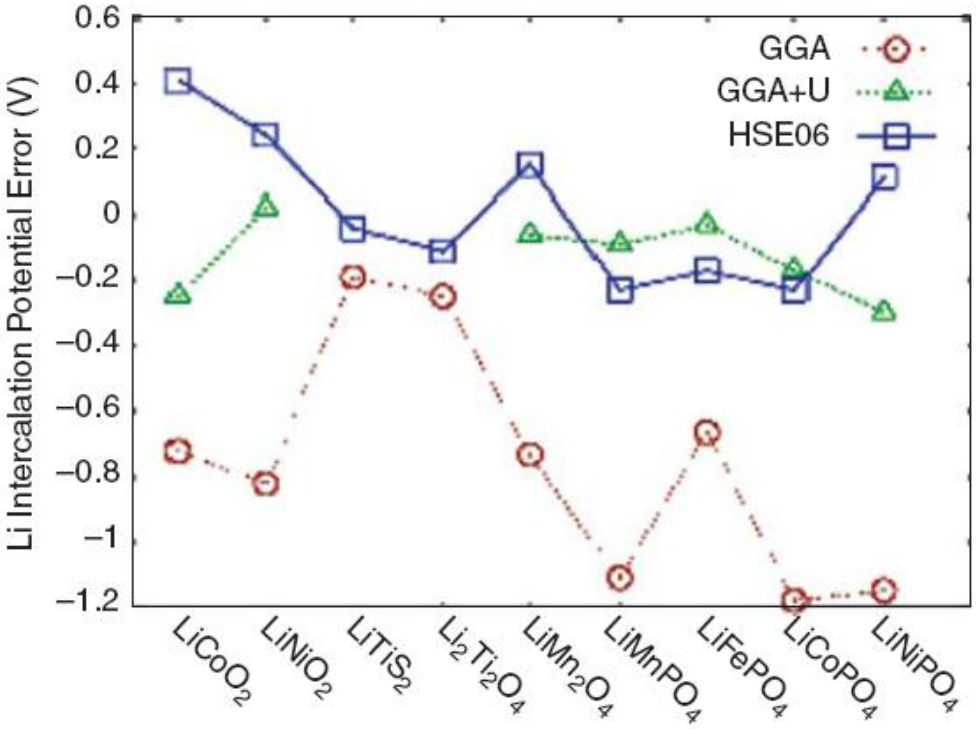


Figure 3. Error on calculated Li-insertion voltages for a series of cathode materials in standard GGA, GGA+U, and HSE approximation. GGA, generalized gradient approximation; GGA+U includes Hubbard "U"; HSE, Heyd-Scuseria-Ernzerhof screened exchange functional.

Things users despise about DFT

- No simple rule for reliability
- No systematic route to improvement
- If your property turns out to be inaccurate, must wait several decades for solution
- Complete disconnect from other methods
- Full of arcane insider jargon
- Too many functionals to choose from
- Can only be learned from a DFT guru

Things developers love about DFT

- No need to be reliable
- No route to systematic improvement
- If a property turns out to be inaccurate, can spend several decades looking for solution
- No need to connect other methods
- Lots of lovely arcane insider jargon
- Oh so many functionals to choose from
- Everyone needs their own DFT guru

Alphabet soup – Peter Elliott

A crisis for DFT

CECAM workshop: **How to Speed Up Progress and Reduce Empiricism in Density Functional Theory**

Location : ACAM, Dublin, Ireland

June 20, 2011 - June 24, 2011

Looking back 20 years

Problems from 20 years ago.

- Poor gaps
- Transition state barriers not good enough
- Strongly correlated systems
- Missing van der Waals
- No generic method for excitations
- Overestimation of conductance of molecular wires

Gap problem

- LDA and GGA give accurate KS gaps, but not accurate fundamental gaps (I-A)

- HSE06 (Heyd, Scuseria, Ernzerhof)
  - Range-separated hybrid
  - Based on Savin's range-separation (well-founded)
  - Gives good gaps for many semiconductors using generalized Kohn-Sham scheme (well-founded)
  - Please do not adjust the separation parameter!

Including weak interactions

- Van der Waals
  - Langreth-Lundquist functional (Dion 04)
  - Grimme method for molecules (DFT-D)
  - TS method is almost non-empirical and can be applied to any functional
  - Very hot area of research

Excitations

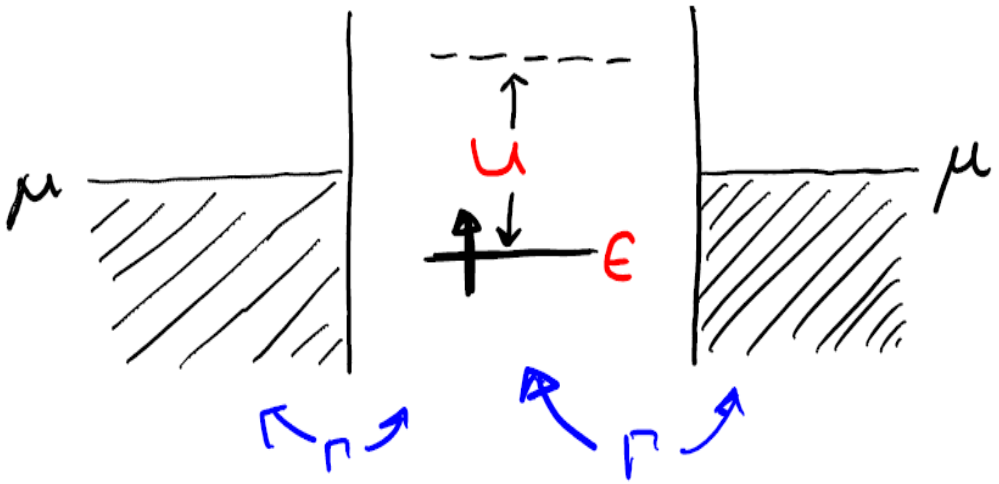
- TDDFT general method for extracting excitations for molecules
  - Less accurate than gs theory, but excellent properties in excited states
  - Quantum chemical methods difficult even for small molecules
  - In all standard packages now
  - Issues for solids, charge-transfer, strong fields, etc.

Challenges: Strong correlation

- Many energy-relevant materials are *oxides*
- A bit too strongly correlated for standard methods (see Saha-Dasgupta); KS gaps far too small.
- Paradigm is stretched H_2; many recent papers from Yang group

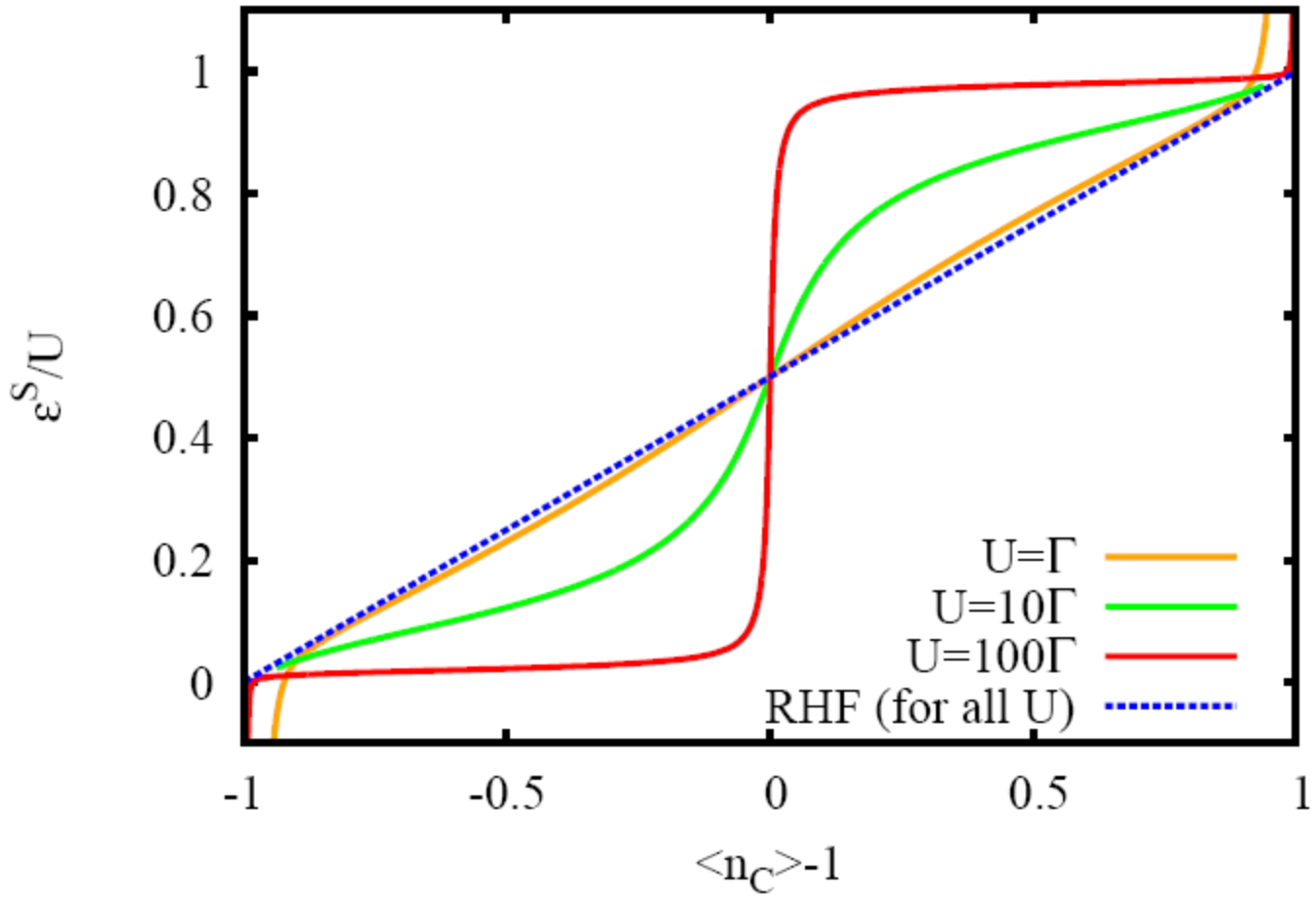
Example: Anderson junction

- Simple model of molecular conductance
- Lead chemical potential μ
- Single level ε in molecule
- Hubbard U
- Coupling to leads Γ
- Bergfield, Liu, Burke, and Stafford, arXiv 1106.3104

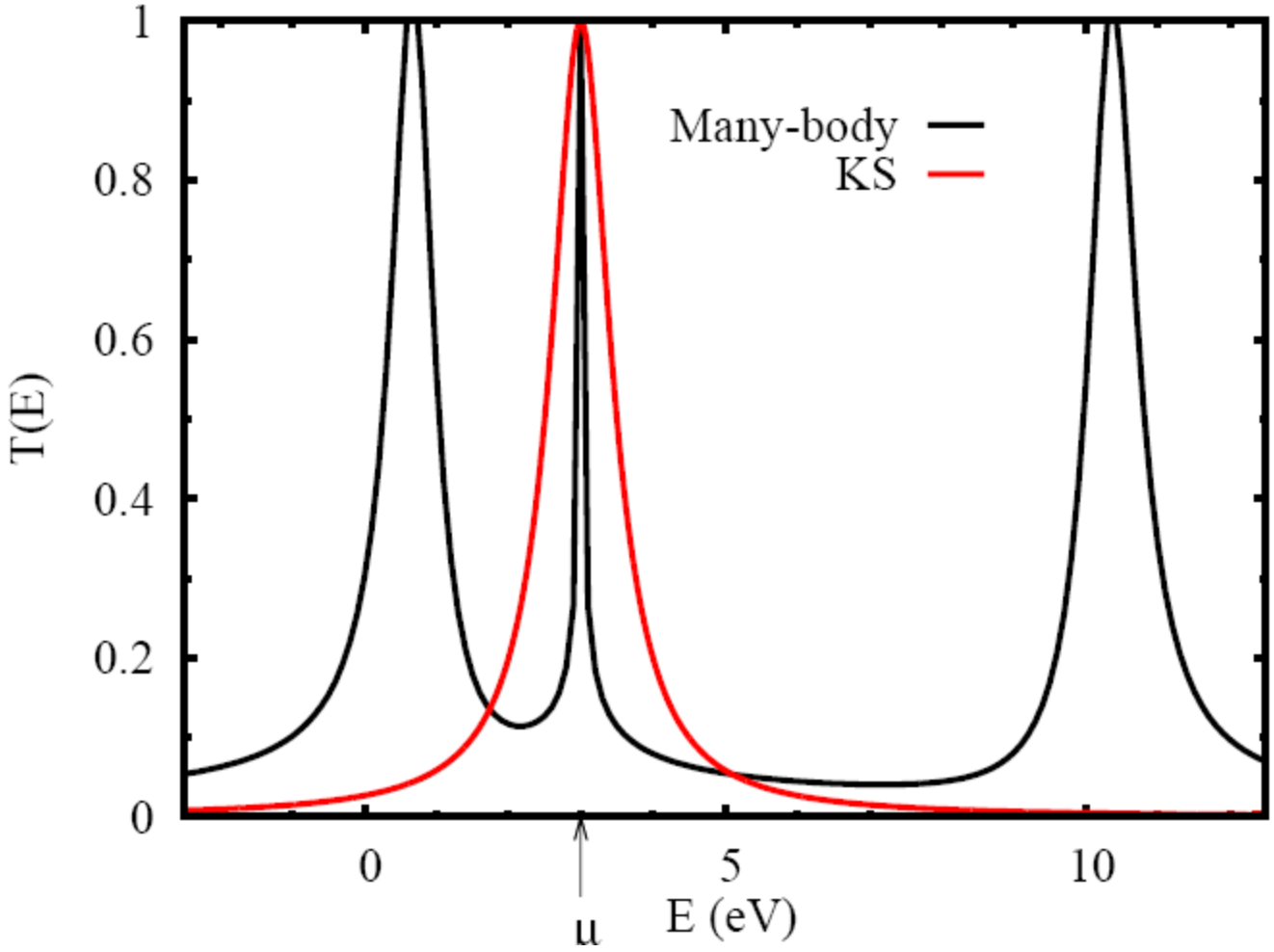


Γ >> U => covalent bonding to leads, weak correlation;
U >> Γ => weak coupling to leads, strong correlation

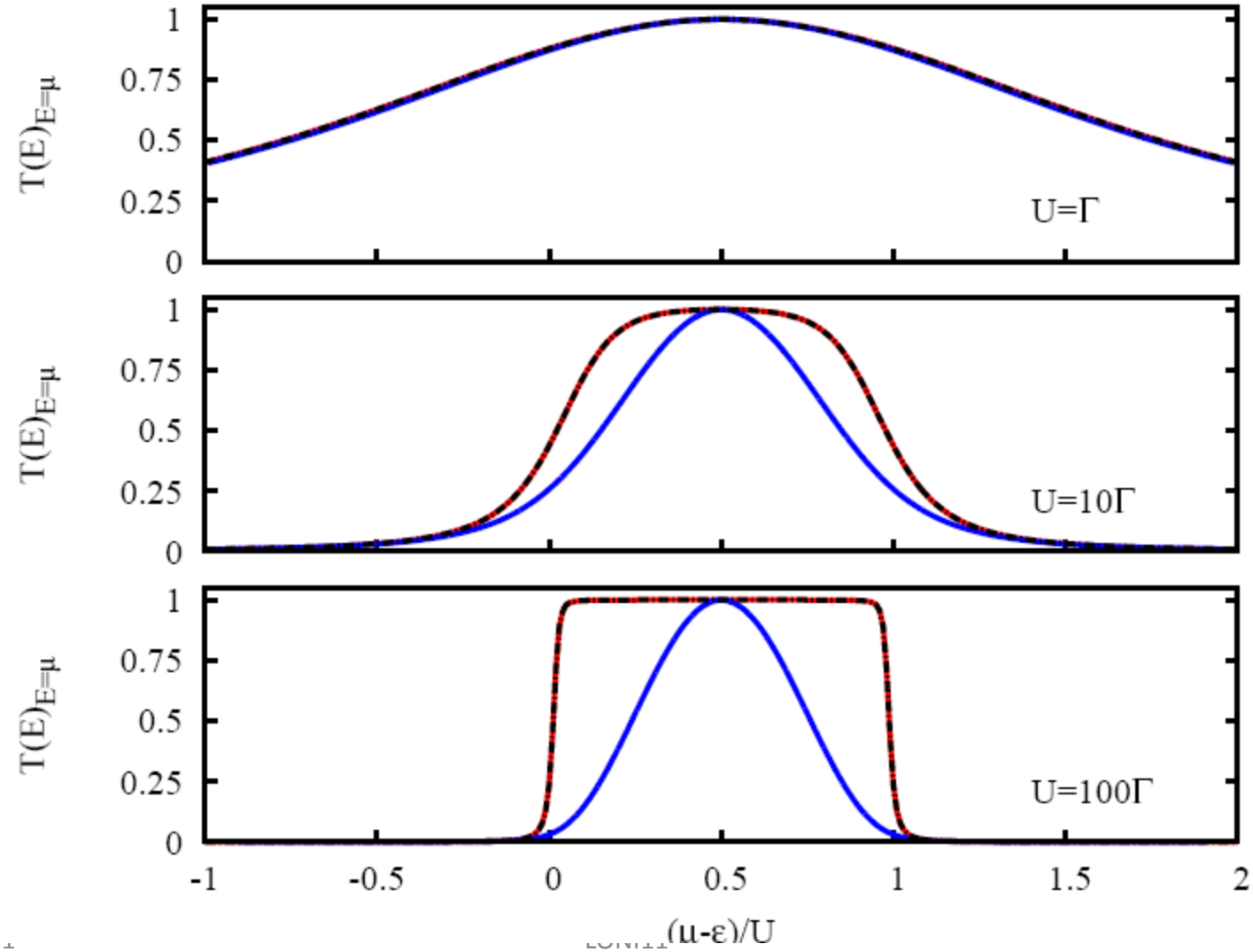
KS potential as function of U



Exact spectrum from BA and from KS system



Transmission in HF and exact



Progress in molecular electronics

- Greatly overestimate conductance in organic molecules
- Sorting out materials effects, e.g. recent work of Narasimhan with Sanvito.
- Looks like mostly error of ground-state functional, NOT methodology (see Quek et al, 2009 onwards).

Things I think will happen I next 5 years

- Explanation of ¼ in hybrids, beyond energetics
- Merging of generalized Kohn-Sham scheme with regular KS
- Unless more progress is made in understanding approximations, empiricism will undermine our field.
- Progress in strongly correlated system – what does exact functional buy you?

Non-exotic materials science

- Great strides in understanding weakly correlated materials
  - Magnetism (Narasimhan)
  - Alloys
  - Impurities

Liquid state

- Improved theory of embedding
  - New formalism: Density Functional Partition Theory, developed by Adam Wasserman (see his website)
- Improved methods for rare-event sampling.
- Excited state AIMD using TDDFT on firmer basis

For the longer term…

Time for a paradigm shift?

- 64/65 papers produced such a shift
  - Formal basis for DFT
  - Exact KS scheme (orbitals in DFT)
  - General purpose approximation (LDA)
- New starting point:
  - Generalized KS scheme?
  - RPA?
  - Reduced density matrix functional theory?
  - Dynamical mean field theory?

Semiclassical origins of DFT

- Ongoing project in my group
- Many implications for DFT
- Basic idea
  - In a semiclassical limit, LDA dominates for all matter
  - Next corrections are due to quantum oscillations, not slowly varying gradients
  - Expansion is asymptotic, so sometimes only first term is useful
- Short-term results
  - PBEsol improves lattice constants relative to LDA and PBE
  - Orbital-free calculations now possible for atoms
- Long-term goals
  - Systematic non-empirical construction of approximations
  - Unification of DFT with Green's function methods
  - General orbital-free calculations

Summary

- The future is *multidisciplinary*
- DFA is different from DFT
- Exact $E_{XC}[n]$ only gives ground-state E and n(**r**)
- Expect (soon)
  - further development of generalized KS scheme
  - more understanding and modeling of strong correlation
  - Standardized treatment of vdW
  - Standardized embedding for QM/MM
- Possible paradigm shift to escape accuracy wall
- Thanks to students and NSF and DOE