

## Density Functional Theory successes and failures

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<http://dft.uci.edu>

## Schedule

- Meet on four days:
  - Tues (9<sup>th</sup>) and Thurs (11<sup>th</sup>)
  - Tues (16<sup>th</sup>) and Thurs (18<sup>th</sup>)
- Meeting time: 14.15-18.00
- Each period
  - 30 mins HW discussion (14.15-14.45)
  - 90 mins lecture+questions (14.45-16.15)
  - 15 mins break (16.15-16.30)
  - 90 mins 2<sup>nd</sup> lecture (16.30-18.00)
- Office hours: After 18.00 in a pub with good ale.

## Syllabus

### First week: Basics

- Overview of course and introduction to DFT
- Elementary ground-state DFT
- Advanced ground-state DFT
- Elementary TDDFT

### Second week: Advanced topics

- Molecular electronics
- Semiclassical analysis
- Strong correlation
- Advanced TDDFT
- Thermal DFT and warm dense matter
- Density functionals from machine learning

## Homework

- For everyone
- mandatory for those registered
- HW at end of each class, due to be discussed at start of next class.
- Mostly done with pencil and paper and a lot of thought
- Just like quantum mechanics, you cannot learn DFT without doing problems

## Background needed to follow lectures

- Audience is mixture of condensed matter physics, electronic structure calculators, materials science, chemistry, etc.
- Both graduate and undergraduate students welcome.
- Vital: Excellent working knowledge of basics of quantum mechanics (e.g. Griffiths)
- Helpful: Vague or better idea of standard approaches to the problem, such as Hartree-Fock, coupled-cluster, ...

## Flavor of this course

- We keep everything as simple as possible.
- We show illustrations of everything.
- We are interested in first principles results, i.e. predicting materials-specific properties with no input from specific system.
- We cover only electronic DFT.
- We do not include
  - Careful math discussion
  - Second quantized notation
  - Proofs of anything (except HK)
  - How to run a specific code

## Background material on DFT

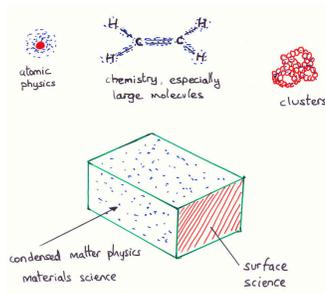
- Good books:
  - Primer in DFT (ed Marques)
  - TDDFT (ed. Marques)
  - Engel and Dreizler, Dreizler and Gross, Parr and Yang, Koch and Holthausen
- From my website
  - DFT in a nutshell (an intro, with Lucas)
  - Perspective on DFT (snapshot)
  - ABC of DFT (in bad shape, but has exercises)

## Today's lecture

- Overview of modern DFT
- Simple illustration of what a density functional is.
- Follows chapter 1 of ABC.

## Electronic structure problem

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



## Properties from Electronic Ground State

- Make Born-Oppenheimer approximation
- Solids:
  - Lattice structures and constants, cohesive energies, phonon spectra, magnetic properties, ...
- Liquids:
  - Can do AIMD, ab initio (DFT) molecular dynamics
- Molecules:
  - Bond lengths, bond angles, rotational and vibrational spectra, bond energies, thermochemistry, transition states, reaction rates, (hyper)-polarizabilities, NMR, ...

## Why is it so hard?

- Must solve to about 1 part in 10<sup>5</sup>
- Schrödinger equation: Coupled

$$\left\{ -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i < j} \frac{1}{|r_i - r_j|} + \sum_i V_{\text{ext}}(r_i) \right\} \Psi = E_0 \Psi$$

- Or variational principle:

$$E_0 = \min_{\Psi} \left\langle \Psi \left| -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i < j} \frac{1}{|r_i - r_j|} + \sum_i V_{\text{ext}}(r_i) \right| \Psi \right\rangle$$

## Traditional approaches

- All approximate solutions to Schrödinger equation
- Solid-state Physics
  - Many-body methods: GW
  - Wavefunction methods: QMC
- Chemistry
  - Variational methods: HF, CI, CC, CASSCF, ...
  - Perturbative: MP2, MP4, CISD(T), ...

## Traditional approaches

- Must solve the Schrödinger equation to find ground-state energy and wavefunction.
- Tough differential equation, with nuclear-electron attraction and electron-electron repulsion, coupling 3N coordinates.
- Chemistry (*ab initio*)
  - Variational methods: HF, CI, CC, CASCF,...
  - Perturbative: MP2, MP4, CISD(T),...
- Solid-state physics
  - Many-body methods: GW
  - Wavefunction methods: QMC

## DFT in modern practice

## Kohn-Sham equations (1965)

$$\left[ -\frac{1}{2}\nabla^2 + v_s[\rho](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

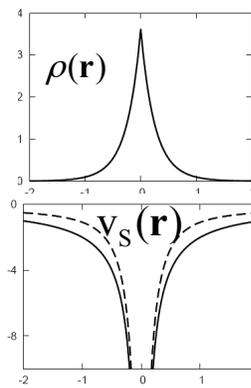
$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 = \text{ground-state density of interacting system}$$

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}[\rho](\mathbf{r})$$

$$E_0 = T_S + V + U + E_{\text{xc}}[\rho]$$

$$v_{\text{xc}}[\rho](\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}$$

## He atom in Kohn-Sham DFT



Everything has (at most) one KS potential

Dashed-line: EXACT KS potential

## In reality...

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

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## Commonly-used functionals

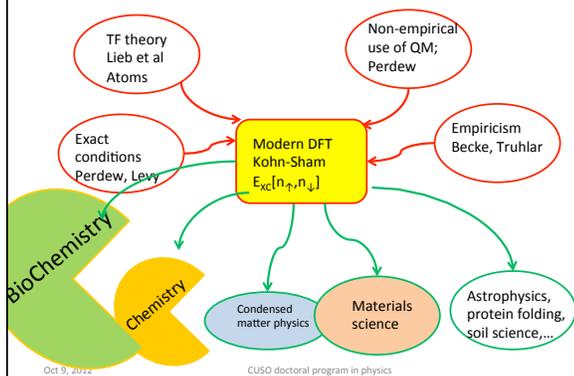
- Local density approximation (LDA)  $E_x^{LDA}[\rho] = A_x \int d^3r n^{1/3}(\mathbf{r})$ 
  - Uses only  $\rho(\mathbf{r})$  at a point.  $A_x = -(3/4)(3/\pi)^{1/3} = -0.738$
- Generalized gradient approx (GGA)
  - Uses both  $\rho(\mathbf{r})$  and  $|\nabla\rho(\mathbf{r})|$
  - Should be more accurate, corrects overbinding of LDA
  - Examples are PBE and BLYP and AM05
- Hybrid:
  - Mixes some fraction of HF
  - Examples are B3LYP and PBE0

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## Big picture



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## Incredible breadth

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

1. Title: Potential functions for hydrogen bonds in protein *in situ* prediction and design  
Author(s): Morozov AV, Kortemme T  
Source: PEPTIDE SOLVATION AND H-BONDS Volume: 72 Pages: 1-4 Published: 2006
2. Title: *Ab initio* study of high-pressure phases of gallium nitride  
Author(s): Saito S, Bouassria N  
Source: IEEE 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 Volume: 69 Issue: 7 Pages: 522-530 Published: JUL 2006
4. Title: Dissolution and re-crystallization processes in multi-silicon stabilized tricalcium phosphate  
Author(s): Tsui 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
5. Title: Sulphate adsorption at the FeHydroxide-H2O interface: comparison of cluster and periodic slab DFT predictions  
Author(s): Paulkay, Pabreja, G, Sengupta D  
Source: EUROPEAN JOURNAL OF SOIL SCIENCE Volume: 58 Issue: 4 Pages: 978-988 Published: AUG 2007
6. Title: Two new new sarsininsides from the sponge *Melophagus sarsinorum*  
Author(s): Santalova EA, Denisenko VA, Dehterov 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, Brisbane 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, Challaconba M, Kozakaki PM, et al  
Source: ASTROPHYSICS AND SPACE SCIENCE Volume: 307 Issue: 3-4 Pages: 293-297 Published: JAN 2006
9. Title: A TD-DFT investigation of the visible spectra of fluoro-antraquinones  
Author(s): Breat, Choummin O, 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): Train HT, Perdew JP  
Source: AMERICAN JOURNAL OF PHYSICS Volume: 71 Issue: 10 Pages: 1048-1061 Published: OCT 2003

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## Better Li batteries?

### 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 battery materials and for the development of high-power density Li battery compounds."*

MRS BULLETIN • VOLUME 35 • SEPTEMBER 2010 • www.mrs.org/bulletin ■ 693

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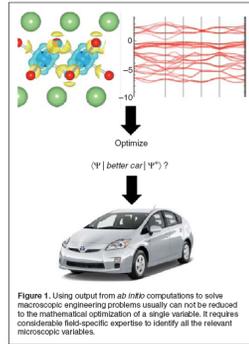


Figure 1. Using output from *ab initio* computations to solve macroscopic engineering problems usually can not be reduced to the mathematical optimization of a single variable. It requires considerable field-specific expertise to identify all the relevant microscopic variables.

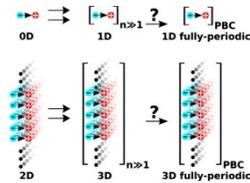
## Survey of some applications

- Picked at random from literature
- No endorsement of the actual science is intended or implied.
- Any resemblance to physical reality is purely accidental.

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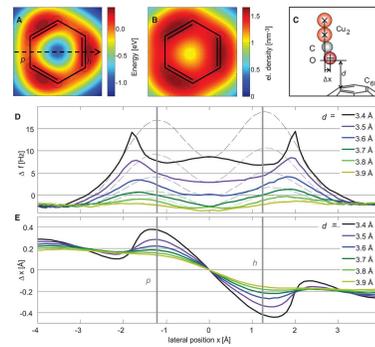
Ferdinand Rissner, Amir Natan, David A. Egger, Oliver T. Hofmann, Leonor Kronik, Egbert Zojer

Dimensionality effects in the electronic structure of organic semiconductors consisting of polar repeat units

Organic Electronics null 2012 null

<http://dx.doi.org/10.1016/j.orgel.2012.09.003>

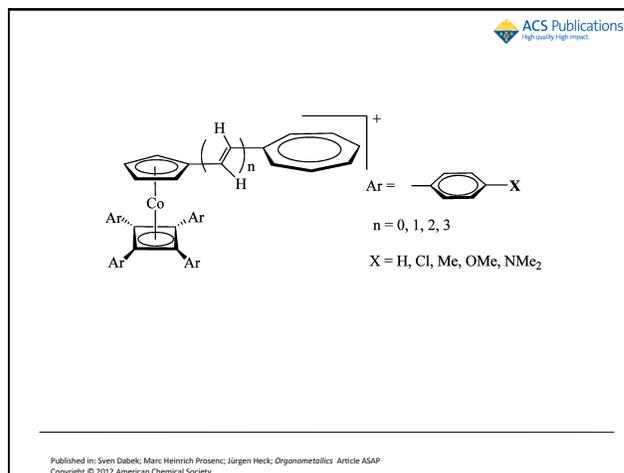
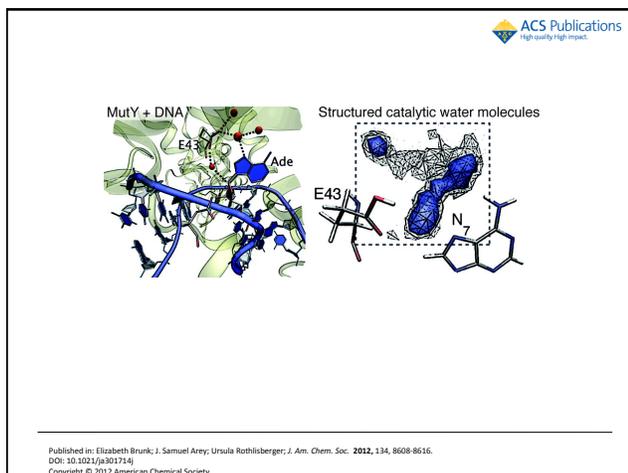
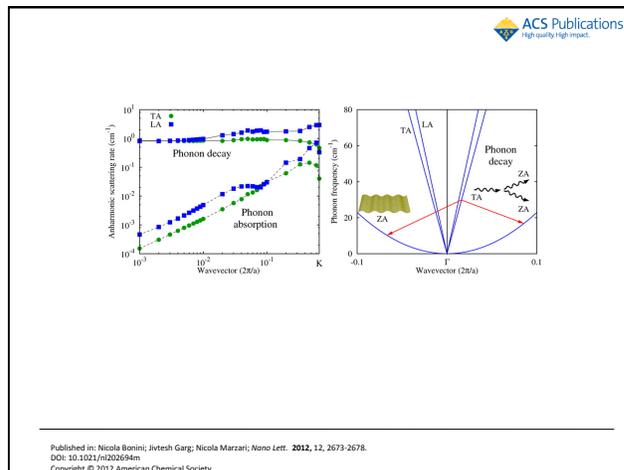
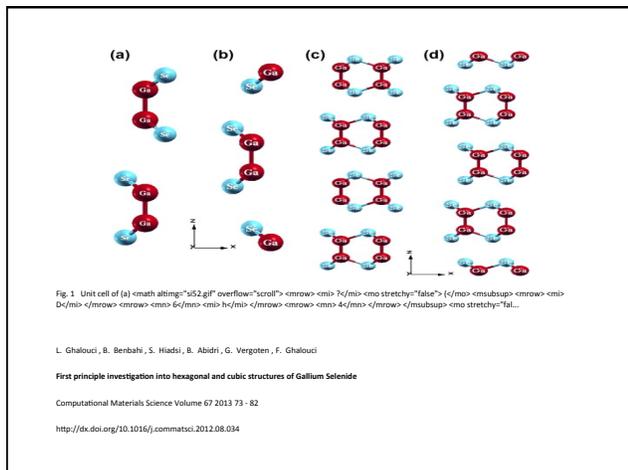
Fig. 2 Density functional theory calculations on C60.



L. Gross et al. Science 2012;337:1326-1329

Published by AAS

Science  
AAAS







## Perspective on DFT

THE JOURNAL OF CHEMICAL PHYSICS 136, 150901 (2012)

### Perspective on density functional theory

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(Received 21 December 2011; accepted 2 April 2012; published online 17 April 2012)

Density functional theory (DFT) is an incredible success story. The low computational cost, combined with useful (but not yet chemical) accuracy, has made DFT a standard technique in most branches of chemistry and materials science. Electronic structure problems in a dazzling variety of fields are currently being tackled. However, DFT has many limitations in its present form: too many approximations, failures for strongly correlated systems, too slow for liquids, etc. This perspective reviews some recent progress and ongoing challenges. © 2012 American Institute of Physics.

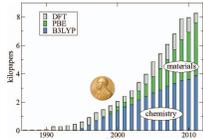


FIG. 1. Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).

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## 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

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## 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

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## Alphabet soup – Peter Elliott



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# Materials genome from first principles?

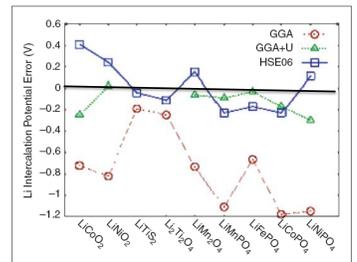


Figure 3. Error on calculated Li-insertion voltages for a series of cathode materials in standard GGA, GGA+U, and HSE approximation. GGA, generalized gradient approximation; GGA+U includes Hubbard "U"; HSE, Heyd-Scuseria-Ernzerhof screened exchange functional.

# Illustration

# Particle in a box

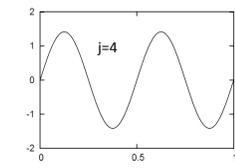
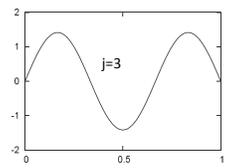
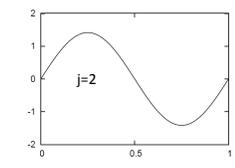
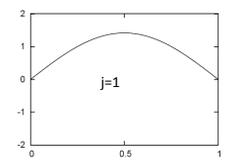
- Usual formula

$$E_j = \frac{h^2 j^2}{8mL^2}, \quad j = 1, 2, 3, \dots$$

- Atomic units, box length 1:

$$E_j = \frac{\pi^2}{2} j^2, \quad j = 1, 2, 3, \dots$$

# Wavefunctions



### Particles in a box: $n(x) = \sum |\phi_j(x)|^2$

TCD06 45

### Simple example: Flat box

- Potential  $v=0$  with hard walls at  $x=0$  and  $1$
- Exact density (sum of  $\sin^2(j\pi x)$ ) for  $N=4$

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### Kinetic energy in 1d

- Approximate kinetic energy by local functional:
 
$$T_s = \frac{1}{2} \int dx \sum_j \left( \frac{d\varphi_j}{dx} \right)^2$$

$$T_s^{loc} = \int dx f(\rho(x))$$
- Dimensional analysis gives:
 
$$T_s^{loc} = a_s \int dx \rho^3(x)$$
- Minimize, by spreading, to find:
 
$$\rho(x) = \frac{N}{L}$$

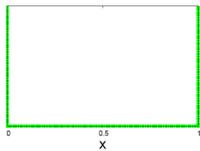
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### Simple example: Flat box

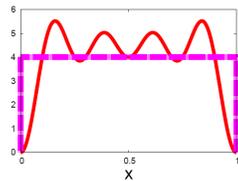
- Potential  $v=0$  with hard walls at  $x=0$  and  $1$
- TF density,  $n = \text{constant} = 4$

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### Simple example: Flat box



- Potential  $v=0$  with hard walls at  $x=0$  and  $1$



- TF density misses quantum oscillations and violates boundary conditions

### Setting the constant

- Exact formula:  $E(N) = \frac{\pi^2}{2L^2} \sum_{j=1}^N j^2 = \frac{\pi^2}{2L^2} N(N+1)\frac{2N+1}{6}$
- For large N:  $\frac{E(N)}{N} \rightarrow \frac{\pi^2 N^2}{6L^2}$

- Choose  $A_s = \pi^2/6$  to make exact in this limit.

- Remarkably,  $T_s^{loc}$  is exact for ALL bounded problems as N gets large

N	$T_s$	$T_s^{loc}$
1	4.934	4.112
2	24.67	21.79
3	69.09	62.92

### Accuracy of local approximation

- Exact formula:  $E(N) = \frac{\pi^2}{2L^2} \sum_{j=1}^N j^2 = \frac{\pi^2}{6L^2} N(N+1/2)(N+1)$
- For large N:  $\frac{E(N)}{N} \rightarrow \frac{\pi^2 N^2}{6L^2}$
- Choose  $a_s = \pi^2/6$  to make exact in this limit.  $T_s^{loc} = \frac{\pi^2}{6} \int dx \rho^3(x)$

- Remarkably,  $T_s^{loc}$  is exact for ALL bounded problems as N gets large

N	$T_s$	$T_s^{loc}[\rho^{loc}]$
1	4.93	1.64
2	24.7	13.2
3	69.1	44.4
4	148.0	105.3

### Survey of advanced topics

- Note: CECAM program next week on van der Waals.

## Strongly correlated systems

- Study basic phenomena and failures of all functionals for strong correlation
- Relation between lattice Hamiltonians and real-space.
- Very important for oxides and other energy-related materials.
- Dynamical mean field theory doing very well here.

## Molecular electronics

- Should we expect DFT calculations of current through molecules to be accurate?
- A perfect case study in understanding DFT
- Right on the border between weak methods and strong methods.
- Recent breakthroughs showing exactness of KS current for Anderson junction

## Semiclassical origins of approximate functionals

- From day 1, semiclassical methods were used to derive functionals
- Much harder to see in KS formalism.
- Last 7 years, we've been studying connection.
- Very fruitful, led to PBEsol, and fundamentals of potential functional theory.
- Much deeper understanding of functional performance than in literature.

## Fundamentals of TDDFT

- TDDFT has even weirder logic than ground-state DFT.
- We'll understand role of memory effects, biggest source of error (maybe) in present TDDFT
- Applications to low-energy electron scattering
- Representation problems and new results overturning some foundational papers.

### Finding functionals with machines

- Combine powerful new methodology from computer science (machine learning) with DFT to find functionals.
- For a toy problem, we produced the most accurate DFT approximation ever.
- Violates almost everything taught in week 1.
- Can even predict when it is accurate.

### Thermal DFT

- Much recent interest in warm dense matter
  - National ignition facility
  - Planetary interiors
  - Z machine
- Basic theorem by Mermin
- Development of temperature-dependent functionals.

### Vote

- A. Strong correlation
- B. Molecular electronics
- C. Semiclassical analysis
- D. Advanced TDDFT
- E. Density functionals from machine learning
- F. Thermal DFT and warm dense matter