Density Functional Theory
successes and failures

Kieron Burke
Departments of Physics and of Chemistry
UC Irvine
http://dft.uci.edu

Schedule
• Meet on four days:
  – Tues (9th) and Thurs (11th)
  – Tues (16th) and Thurs (18th)
• 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 2nd lecture (16.30-18.00)
• Office hours: After 18.00 in a pub with good ale.

Syllabus
First week: Basics
A. Overview of course and introduction to DFT
B. Elementary ground-state DFT
C. Advanced ground-state DFT
D. Elementary TDDFT

Second week: Advanced topics
A. Molecular electronics
B. Semiclassical analysis
C. Strong correlation
D. Advanced TDDFT
E. Thermal DFT and warm dense matter
F. 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 $10^5$
- Schrödinger equation: Coupled

\[
\left\{ -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{ij} \frac{1}{r_{ij}} - \sum_i V_{\text{ext}}(r_i) \right\} \Psi = E \Psi
\]

- Or variational principle:

\[
E_0 = \min \left\{ \left\langle \Psi \left| -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{ij} \frac{1}{r_{ij}} - \sum_i V_{\text{ext}}(r_i) \right| \Psi \right\}
\]

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, CASSCF,...
  – Perturbative: MP2, MP4, CISD(T),...
• Solid-state physics
  – Many-body methods: GW
  – Wavefunction methods: QMC

Kohn-Sham equations (1965)

\[
\begin{align*}
\left[-\frac{1}{2}\nabla^2 + v_{xc}(\rho)(\mathbf{r})\right] \psi(\mathbf{r}) &= E \psi(\mathbf{r}) \\
\rho(\mathbf{r}) &= \sum_i |\psi_i(\mathbf{r})|^2 \\
v_{\psi}(\mathbf{r}) &= v_{\psi\psi}(\mathbf{r}) + \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\rho}(\rho)(\mathbf{r}) \\
E_0 &= T_S + V(U + E_{xc}[\rho])
\end{align*}
\]

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

Commonly-used functionals

• Local density approximation (LDA) $E_{LDA} = T + E_{xc} - \int_0^\infty \frac{d}{dr} \left[ \rho(r) \right] \left( \frac{\rho(r)}{2\pi} \right) dr$
  – Uses only $\rho(r)$ at a point.

• Generalized gradient approx (GGA)
  – Uses both $\rho(r)$ and $|\nabla\rho(r)|$
  – 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

Incredible breadth
Better Li batteries?

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

Gerhard Calster

This text is focused on the development of materials for use in Li battery technology. It discusses the challenges and opportunities in first-principles materials design for Li battery applications.

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.

Fig. 2 Density functional theory calculations on C60.

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

Published by AAAS
Fig. 1. Unit cell of (a) hexagonal, (b) tetragonal, (c) orthorhombic, and (d) cubic GaSe. The Ga-Se bonds are shown in red, and the Se-Se bonds are shown in blue.


http://dx.doi.org/10.1016/j.commatsci.2012.08.034

Published in: Nicola Bonini, Jivtesh Garg, Nicola Marzari, Nano Lett. -2012, 12, 2673R2678. DOI: 10.1021/nl202694m

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Figure 1. The Leu46 hydrophobic pocket is highly conserved across MIF species.

http://www.plosone.org/article/info:doi/10.1371/journal.pone.0045024

More diverse applications

Fig. 8. Conceptual drawing of reverse flood reservoir management. Contours illustrate stripping of CO2-free CO2 from supercritical CO2.

Vassiliki R. Alexiou K, Peter McGrail H, Todd Nichol
Molecular interactions of CO2-free CO2 with carbonate minerals under re-sequstration conditions: A combined experimental and theoretical study.
Geochimica et Cosmochimica Acta Volume 92 2012 265-274
http://dx.doi.org/10.1016/j.gca.2012.06.015
Dentistry functional theory

Fig. 8: Optimized PBE1PBE/6-31G(d,p) geometries for the most stable ICs at 1:1 SRT/Cd, IV/VIII and 1:2 SRT/Cd.

Joel J. Passos, Frederico B. De Sousa, Ivana S. Lula, Elison A. Barreto, Juliana Fedoce Lopes, Wagner B. De A...

Multi-equilibrium system based on antitrip and 1-cycloadders supramolecular complexes in aqueuous solution


http://dx.doi.org/10.1016/j.ijpharm.2011.09.026

Not everything is rosy

Fig. 5: Anisotropies (directional differences ellipticity): translation + translation + translation + rotation - rotation - rotation + rotation + rotation (chiral) (a) CaTiO\textsubscript{3} and (b) SrTiO\textsubscript{3}.

K.C. Bhamu, Alpa Dashora, Gunjan Arora, B.L. Ahuja

Nature of bonding in CaTiO\textsubscript{3} and SrTiO\textsubscript{3}: A Compton scattering study


http://dx.doi.org/10.1016/j.radphyschem.2012.04.010
Perspective on DFT

THE JOURNAL OF CHEMICAL PHYSICS

Perspective on density functional theory

Kieron Burke

September 2012; 137(18) Annual Section I, University of California, Los Angeles, CAM Post MDI

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 chemistry today. On the other hand, the PBE GGA (Ref. 5) for inventing density matrix renormalization group (DMRG), has been adapted for use in DFT. The LDA and GGA approximations have become a much used tool in most branches of chemistry and materials science.

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
Materials genome from first principles?

![Graph showing energy levels for different materials.](image)

Illustration

Particle in a box

- Usual formula
  \[ E_j = \frac{\hbar^2 j^2}{8mL^2}, \quad j = 1,2,3,... \]
- Atomic units, box length 1:
  \[ E_j = \frac{\pi^2}{2} j^2, \quad j = 1,2,3,... \]

Wavefunctions

- \( j=1 \)
- \( j=2 \)
- \( j=3 \)
- \( j=4 \)
Particles in a box: \( n(x) = \sum |\phi_j(x)|^2 \)

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 \( N=4 \)

Kinetic energy in 1d
- Approximate kinetic energy by local functional:
  \[ T_r = \frac{1}{2} \int dx \sum \left( \frac{dp_j}{dx} \right)^2 \]
  \[ T^{loc}_r = \int dx \ f(\rho(x)) \]
  \[ T^{loc}_s = a \int dx \ \rho^2(x) \]
- Dimensional analysis gives:
- Minimize, by spreading, to find:
  \[ \rho(x) = \frac{N}{L} \]
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:
  \[ E(N) = \frac{\pi^2}{2L} \sum j^2 = \frac{\pi^2}{2L} N(N + 1) \frac{L}{\lambda_N} \]
- For large $N$:
  \[ E(N) = \frac{\pi^2 N^2}{6L} \]
- Choose $A = \frac{\pi^2}{6}$ to make exact in this limit.
- Remarkably, $T_s^{\text{loc}}$ is exact for ALL bounded problems as $N$ gets large

Accuracy of local approximation

- Exact formula:
  \[ E(N) = \frac{\pi^2}{2L} \sum j^2 = \frac{\pi^2}{6L} N(N + 1) / (N + 1) \]
- For large $N$:
  \[ E(N) = \frac{\pi^2 N^2}{6L} \]
- Choose $A = \frac{\pi^2}{6}$ to make exact in this limit.
- Remarkably, $T_s^{\text{loc}}$ is exact for ALL bounded problems as $N$ gets large

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