Tutorial: Ground-state DFT basics

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Outline

A. Electronic structure

B. Basics of DFT

C. Chemistry versus materials

D. XC functionals

E. Summary

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Basic problem

- Non-relativistic
- Born-Oppenheimer approximation
- No external B field
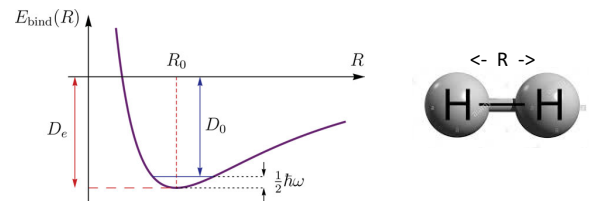- First principles
- Ab initio?

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Basic Electronic Structure Problem

- Just want E(R), mostly (fixed nuclei, electrons in ground state):

$E_{\rm bind}(R)$, R_0, R, D_e, D_0, $\frac{1}{2}\hbar\omega$

<- R ->

H   H

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Dominance of ground-state energy

- Determines which molecules and solids exist and many of their most basic properties
- Bond lengths / lattice parameters
- Vibrational frequencies / phonons
- Reaction rates via transition-state barriers
- Vital in chemistry, increasingly so in materials
- Often care more about response properties in physics

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Hamiltonian for N electrons in the presence of external potential $v(\mathbf{r})$:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V},$$

where the kinetic and elec-elec repulsion energies are

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2, \qquad \hat{V}_{ee} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

and difference between systems is N and the one-body potential

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i)$$

Often $v(\mathbf{r})$ is electron-nucleus attraction

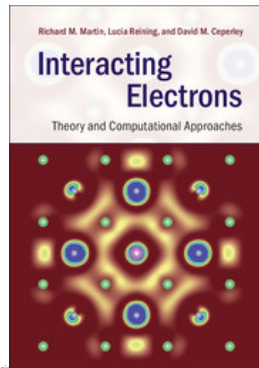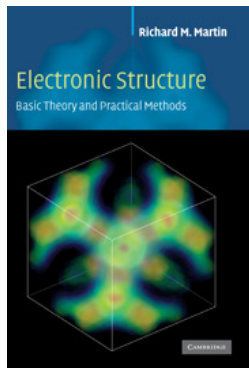$$v(\mathbf{r}) = -\sum_{\alpha}\frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|}$$

where α runs over all nuclei, plus weak applied $\mathbf{E}$ and $\mathbf{B}$ fields.

$$\{\hat{T} + \hat{V}_{ee} + \hat{V}\}\Psi = E\Psi. \qquad E = \min_{\Psi}\langle\Psi|\hat{T} + \hat{V}_{ee} + \hat{V}|\Psi\rangle$$

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Useful books for materials

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B. DFT (ground-state)

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Useful intro for anyone

DFT in a Nutshell

Kieron Burke[a,b] and Lucas O. Wagner*[a,b]

The purpose of this short essay is to introduce students and other newcomers to the basic ideas and uses of modern electronic density functional theory, including what kinds of approximations are in current use, and how well they work (or not). The complete newcomer should find it orients them well, while even lo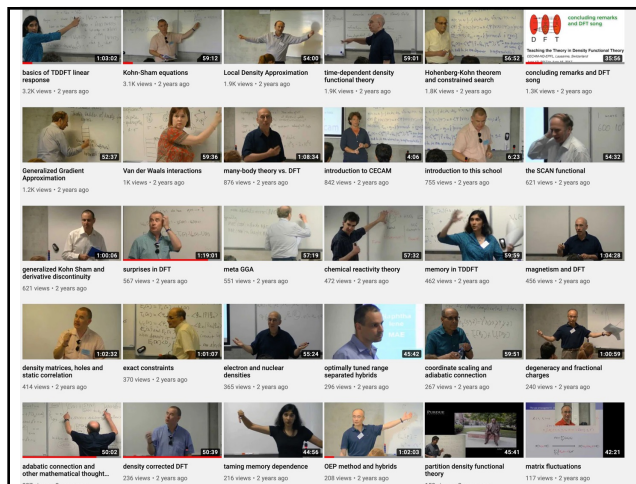ngtime users and aficionados might find something new outside their area. Important questions varying in difficulty and effort are posed in the text, and are answered in the Supporting Information. © 2012 Wiley Periodicals, Inc.

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DFT on Coursera

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Thomas/Fermi Theory 1927

- Derived in 1926 without Schrodinger eqn.

  The Calculation of Atomic Fields
  L. H. Thomas (Proc. Camb. Phil. Soc. 23, p. 542–548)
  Trinity College
  [Received 6 November, read 22 November 1926.]

- Thomas-Fermi Theory (TF):
    - $T \approx T^{TF}$
    - $V_{ee} \approx U$ = Hartree energy
    - $V = \int d\mathbf{r}\, \rho(\mathbf{r})\, v(\mathbf{r})$
    - $E_0 = T + V_{ee} + V$
    - Minimize $E_0[n]$ for fixed N

    $$T_s^{loc} = \frac{3(3\pi)^{2/3}}{10} \int d^3r\, n^{5/3}(r)$$

    $$U = \frac{1}{2}\int d^3r \int d^3r' \frac{n(r)n(r')}{|r-r'|}$$

- Properties:
    - Typical error of order 10%
    - Teller's unbinding theorem: Molecules don't bind.

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Hohenberg-Kohn theorems (1964)

- HK I:1-1 between n(**r**) and v(**r**)

- HK II: F[n] is independent of v(**r**) [universal]

- HK III: Minimize F+V for fixed N to find n(**r**)

- Constrained searc

$$E = \min_{\Psi}\langle\Psi|\hat{T}+\hat{V}_{ee}+\hat{V}|\Psi\rangle$$
$$= \min_{n}\left\{F[n]+\int d^3r\ v(\mathbf{r})n(\mathbf{r})\right\}$$
where
$$F[n] = \min_{\Psi\to n}\langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle$$

- TF a crude approximation to exact theory

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KS equations (1965)

Define *fictitious* non-interacting electrons satisfying:

$$\left\{-\frac{1}{2}\nabla^2+v_{\text{s}}(\mathbf{r})\right\}\phi_j(\mathbf{r})=\epsilon_j\phi_j(\mathbf{r}), \qquad \sum_{j=1}^N|\phi_j(\mathbf{r})|^2=n(\mathbf{r}).$$
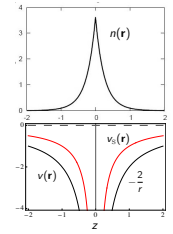
where $v_{\text{s}}(\mathbf{r})$ is *defined* to yield $n(\mathbf{r})$.
Define T_{s} as the kinetic energy of the KS electrons, U as their Hartree energy and

$$F = T + V_{ee} = T_{\text{s}} + U + E_{\text{XC}}$$

the remainder is the exchange-correlation energy.
Most important result of exact DFT:

$$v_{\text{s}}(\mathbf{r})=v(\mathbf{r})+\int d^3r\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+v_{\text{XC}}[n](\mathbf{r}), \qquad v_{\text{XC}}(\mathbf{r})=\frac{\delta E_{\text{XC}}}{\delta n(\mathbf{r})}$$
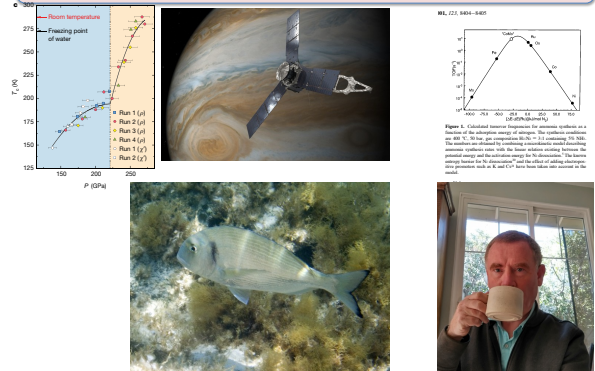
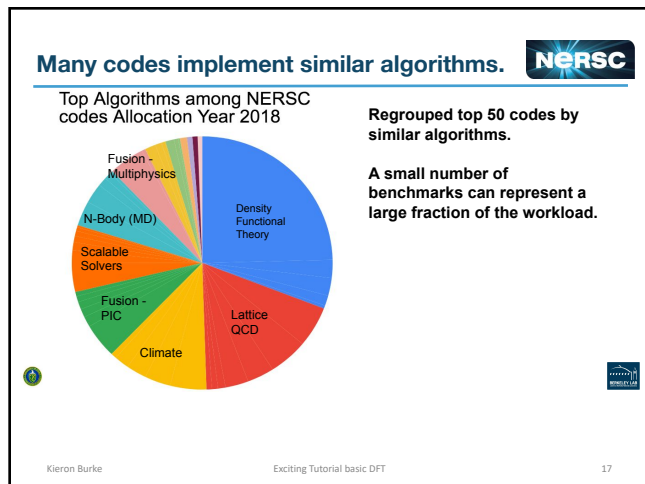Knowing $E_{\text{XC}}[n]$ gives closed set of self-consistent equations.

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XC approximations 20 yrs ago

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

- Generalized gradient approx (GGA) $E_{\text{XC}}^{\text{GGA}}=\int d^3r\ e_{\text{XC}}^{\text{GGA}}(n(\mathbf{r}),|\nabla n(\mathbf{r})|)$
  - Uses both n(**r**) and |∇n(**r**)|
  - Should be more accurate, corrects overbinding of LDA
  - Examples are PBE and BLYP

- Hybrid (global): $E_{\text{XC}}^{\text{hyb}}=a\left(E_{\text{x}}-E_{\text{x}}^{\text{GGA}}\right)+E_{\text{XC}}^{\text{GGA}}$
  - Mixes some fraction of HF with GGA
  - Examples are B3LYP and PBE0

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Cool DFT applications

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Many codes implement similar algorithms. NeRSC

Top Algorithms among NERSC codes Allocation Year 2018

Regrouped top 50 codes by similar algorithms.

A small number of benchmarks can represent a large fraction of the workload.

- Fusion - Multiphysics
- N-Body (MD)
- Scalable Solvers
- Fusion - PIC
- Climate
- Density Functional Theory
- Lattice QCD

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Basic successes ground-state DFT

- Local, semi-local, hybrid, vdw-corrected approximations yield useful accuracy for weakly correlated systems
- Works for both solids and molecules
- Some find functionals from general rules of quantum mechanics (eg Perdew), some from fitting databases (eg Truhlar)
- Perdew functionals work comparably well for solids and molecules simultaneously
- Many fitted functionals work only for molecules, but more accurate for those cases.

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C. Differences in subjects

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Chemistry versus physics

- Primary focus in physics: Response properties
  - Optical versus photoemission, etc.
- Primary focus in quantum chemistry: Ground-state energies to high accuracy
  - Tells you what bonds are formed and reaction rates
  - Chemical accuracy (1 kcal/mol)
  - CCSD(T) fails for multireference systems
  - Accuracy for weak bonds 0.1 kcal/mol
- Materials science needs both

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Molecules versus materials

- Traditionally, molecular codes distinct from materials codes
- Free boundaries versus periodic BCs
- Molecular codes usually use Gaussians centered on atoms
- Solid state codes often use plane waves
- Chemists have many databases, and can compare with highly accurate quantum chemical calculations
- Very little reference data for solids
- Basis sets in chemistry downloadable, allowing 10 digit replication of energies with different codes

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Reproducibility and benchmarking

- In quantum chemistry, Pople created the concept of a 'model chemistry'
- Model chemistry=a method plus a basis set
- Can get the same result to about 10 digits anywhere, anytime, with any professional-level code.
- The G2 data set is benchmark experimental and calculated data agreeing within 0.05 eV.
- In famous 1993 paper, Pople et al showed DFT could yield about 0.15 eV accuracy for covalent bond energies.

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GMTNK55

- Super database of 55 databases

- About 1500 numbers

- New methods routinely tested against it

- Many numbers at CCSD(T) level

- Beginning to see CCSD(T) no longer accurate enough

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Cost

- With GGA, KS cheaper than HF, scales N^3

- CCSD(T) scales N^7

- Moderate cluster, a week for CCSD(T) 20 atoms

- Decent desktop, a morning for 200 atoms HF or DFT.

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Performance

- Most cases, CCSD(T) gives chemical accuracy (error < 1 kcal/mol) for main group chemistry if converged

- Gives signal if there are known unknowns

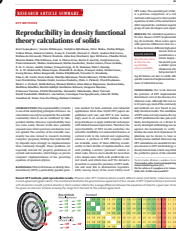- Dissociates H_2 correctly, but not N_2 because of single-reference starting point

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Solids

- Much harder to do calculations
- Much harder to guarantee convergence
- See Science article 2016
- No real databases
- Much benchmark data from expt

RESEARCH ARTICLE SUMMARY

Reproducibility in density functional theory calculations of solids

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D Modern functional approximation

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Heart of commonly-used XC approximations

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

  $$A_{\mathrm{x}} = -(3/4)(3/\pi)^{1/3} = -0.738$$

- Generalized gradient approx (GGA) $E_{\mathrm{xc}}^{\mathrm{GGA}} = \int d^3r \; e_{\mathrm{xc}}^{\mathrm{GGA}}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$
  - Uses both $n(\mathbf{r})$ and $|\nabla n(\mathbf{r})|$
  - Should be more accurate, corrects overbinding of LDA
  - Examples are PBE and BLYP

- Hybrid (global): $E_{\mathrm{xc}}^{\mathrm{hyb}} = a\,(E_{\mathrm{x}} - E_{\mathrm{x}}^{\mathrm{GGA}}) + E_{\mathrm{xc}}^{\mathrm{GGA}}$
  - Mixes some fraction of HF with GGA
  - Examples are B3LYP and PBE0

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Exact conditions on E_{XC}

- Can deduce many exact properties satisfied by E_{XC}

- $E_X[n_\gamma] = \gamma \, E_X[n]$ where $n_\gamma(\mathbf{r}) = \gamma^3 \, n(\gamma \, \mathbf{r})$

- $E_X[n_\uparrow, n_\downarrow] = E_X[n_\uparrow, 0] + E_X[0, n_\downarrow]$

- $I = -\varepsilon_{HOMO}$

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Perdew approach

- Write approximate form

- Use exact conditions to fix parameters in form

- Choose conditions to ensure reasonable performance on molecules and solids

- Nowadays, include appropriate norms (eg H atom, uniform gas) but no covalent bonds

- At each level, find a single functional for all systems

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Jacob's ladder
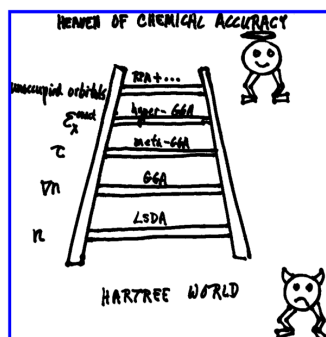
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Toulouse book chapter

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Head-Gordon and Mardirossian review

MOLECULAR PHYSICS, 2017
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https://doi.org/10.1080/00268976.2017.1333644

TOPICAL REVIEW · OPEN ACCESS

Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals

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Density functional theory; DFT; benchmark; chemistry database; density functionals

ABSTRACT
In the past 30 years, Kohn–Sham density functional theory has emerged as the most popular electronic structure method in computational chemistry. To assess the ever-increasing number of approximate exchange-correlation functionals, this review benchmarks a total of 200 density functionals on a molecular database (MGCDB84) of nearly 5000 data points. The database employed, provided as Supplemental Data, is comprised of 84 data-sets and contains non-covalent interactions, isomerization energies, thermochemistry, and barrier heights. In addition, the evolution of non-empirical and semi-empirical density functional design is reviewed, and guidelines are provided for the proper and effective use of density functionals. The most promising functional considered is ωB97M-V, a range-separated hybrid meta-GGA with VV10 nonlocal correlation, designed using a combinatorial approach. From the local meta-GGAs, B97-D3, revPBE-D3, and BLYP-D3 are recommended, while from the local meta-GGAs, B97M-rV is the leading choice, followed by MS1-D3 and M06-L-D3. The best hybrid GGAs are ωB97X-V, ωB97X-D3, and ωB97X-D, while useful hybrid meta-GGAs (besides ωB97M-V) include ωM05-D, M06-2X-D3, and MN15. Ultimately, today's state-of-the-art functionals are close to achieving the level of accuracy desired for a broad range of chemical applications, and the principal remaining limitations are associated with systems that exhibit significant self-interaction/delocalisation errors and/or strong correlation effects.

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Different approximations

- Almost all materials calculations use a functional created by Perdew et al

- Moderate accuracy for both materials and molecules

- Most chemical user calculations do not
  – B3LYP, old but standard
  – wB97-V is very accurate for GMTNK55 databases
  – Use D3 or D4 dispersion

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GS energy is 99% of everything

- Successes (and failures) of GS DFT do not automatically mean TDDFT will 'work'
- Almost all applications of gsDFT focus solely on E and its derivatives
- A KS calculation also yields gs density and KS eigenvalues/eigenvectors, both occ and unocc
- Density is rarely looked at; usually, but not always, 'pretty' good
- Eigenvalues are usually 'very bad', unless fixed

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Exact conditions

- Most chemistry functionals ignore exact conditions. Yet do very well on databases.
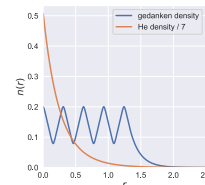- How come?

FIG. 1. An unpolarized ground-state gedanken density with 2 electrons whose correlation energy is -17 mH in PBE, but +37 mH in LYP. For reference, the He atom density (divided by 7) is plotted.

Reassessing the role of exact conditions in density functional theory R. Pederson and K. Burke, (2023). arXiv: 2303.01766

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Summary

- Ground-state DFT is successful on a vast scale, covering many areas

- Typically delivers useful accuracy

- Big differences between chemical and material communities

- Perdew functionals interpolate between solids and molecules

- Thanks to you, students and collaborators, and NSF

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