

Tutorial: Slightly advanced DFT

Kieron Burke and friends
UC Irvine
Physics & Astronomy and Chemistry

Kieron Burke

Exciting Tutorial advanced DFT

1

1

Topics

- Ground-state DFT:
 - DCDFD
 - Strong correlation
 - Semiclassics: orbital free
- Excitations:
 - optical versus quasiparticle
 - GKS versus KS
 - Ensemble DFT
 - Connection to GF
- Warm dense matter

Kieron Burke

Exciting Tutorial advanced DFT

2

2

A. ground-state DFT

Kieron Burke

Exciting Tutorial advanced DFT

3

3

DC-DFT

- True error: functional error plus density-driven error
- Find many molecular cases where density-driven error dominates.
- Often simply use HF density instead.
- Led by Eunji Sim, Yonsei University
- About 20 papers showing benefits (reducing errors)

Kieron Burke

Exciting Tutorial advanced DFT

4

4

JACS *DC-DFT*
 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
 publications.jacs.org

Improving Results by Improving Densities: Density-Corrected Density Functional Theory
 Eunji Sim,^{1*} Suhwan Song, Stefan Vuckovic, and Kieron Burke

Cite This: *J. Am. Chem. Soc.* 2022, 144, 6625–6639

Read Online

The abstract features three main plots: (1) Energy profile vs. H₂O number for a water cluster, showing DC-DFT (red) and BL1p (green) curves. (2) Energy profile vs. reaction coordinate for the reaction P⁺ + Cl₂Q → Cl₂P + Q⁺, comparing DFT (blue), DC-DFT (red), and BL1p (green). (3) Binding energy vs. distance for a halogen bonding transition state system, comparing DFT (blue), DC-DFT (red), and BL1p (green). A central diagram shows the 'Density Corrected DFT (DC-DFT)' method being applied to 'Water cluster', 'Reaction coordinate', and 'Halogen bonding transition state system'.

Kieron Burke

5

HF-R2SCAN-DC4

The abstract contains six subplots: (a) Interaction energy for nucleobases interaction, comparing SC-Lipt (red) and HF-R2SCAN-DC4 (blue). (b) Relative energy for water hexamer isomers, comparing SC-RSCAN-DC4 (red) and HF-R2SCAN-DC4 (blue). (c) Relative energy for water 27 vs. sensitivity, comparing SC-RSCAN-DC4 (red) and HF-R2SCAN-DC4 (blue). (d) Relative energy for water 20-mers isomers, comparing SC-RSCAN-DC4 (red) and HF-R2SCAN-DC4 (blue). (e) Interaction energy for water-opsin (structures from MD), comparing SC-RSCAN-DC4 (red) and HF-R2SCAN-DC4 (blue). (f) Mean absolute error for GMKNSS inter & intra HCl, comparing HF-R2SCAN-DC4 (blue) and SC-Lipt (red).

Extending density functional theory with near chemical accuracy beyond pure water. S. Song, S. Vuckovic, Y. Kim, H. Yu, E. Sim, and K. Burke, *Nature Communications* 14, 799 (2023). DOI: 10.1038/s41467-023-36094-y

Kieron Burke

6

Weak versus strong correlation

- Weakly correlated materials typically have exact spectral function looking quite like KS spectral function
- Often overlap of true wavefunction with KS wavefunction about 0.9 (per cell).
- For strongly correlated system, this is no longer true.
- But this does not necessarily imply gsDFT is with standard approximations fails.

Kieron Burke

Exciting Tutorial advanced DFT

7

7

Strong correlation

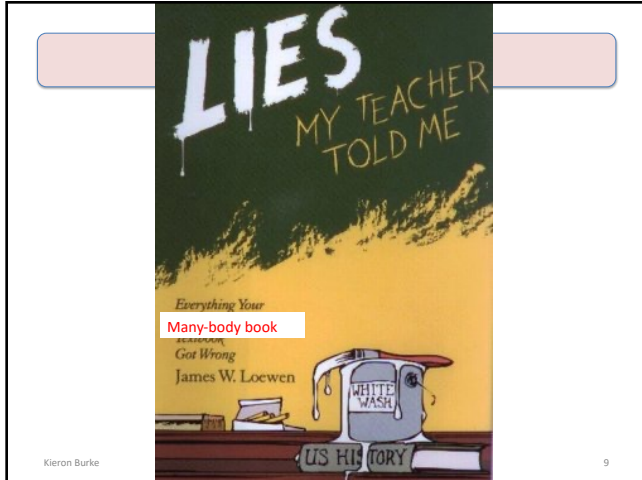
- Many materials are strongly correlated, especially those DOE cares about.
- Traditional functionals appear to fail in such cases. Maybe.
- Most molecules at equilibrium are weakly correlated.
- As you stretch any molecule, its correlations become strong.
- Often DFT will break symmetry, see recent work of Zunger and Perdew

Kieron Burke

Exciting Tutorial advanced DFT

8

8



9

Understanding the KS idea

- Correl 21 book chapter

Lies My Teacher Told Me About Density Functional Theory: Seeing Through Them with the Hubbard Dimer K. Burke and J. Kozłowski in: E. Pavarini and E. Koch (eds.) *Simulating Correlations on Computers: Modeling and Simulation*, Vol. 11, Verlag des Forschungszentrum Jülich (2021). ISBN 978-3-95808-529-1
- Ground-state review:

The Hubbard dimer: a density functional case study of a many-body problem D J Carrascal, D.J., Ferrer, J., Smith, J. and KB 2015 *J. Phys.: Condens. Matter* **27** 393001
- Linear-response TDDFT review:

Linear response time-dependent density functional theory of the Hubbard dimer Carrascal D.J., Ferrer, J., Maitra, N. and KB. Linear response time-dependent density functional theory of the Hubbard dimer. *Eur. Phys. J. B* **91**, 142 (2018).
- General intro to DFT in real-space:

DFT in a nutshell, Kieron Burke, Lucas O. Wagner, *Int. J. Quant. Chem.* **113**, 96-101 (2013).

10



11

Fundamental gap

$$I = E(N-1) - E(N)$$

$$A = E(N) - E(N+1)$$

$$\dots$$

$$E_g = I - A,$$

$$\epsilon^{\text{HOMO}} = -I,$$

$$E_g = E_{gs} + \Delta_{xc}$$

FIG. 11. Plot of $-I$, $-I$, ϵ^{HOMO} , and ϵ^{LUMO} as a function of Δv with $U=1$ and $2I=1$.

FIG. 12. Plot of $-I$, $-I$, ϵ^{HOMO} , and ϵ^{LUMO} as a function of Δv with $U=5$ and $2I=1$.

12

Conditional Probability-DFT

- Alternative to KS-DFT
- Calculate the pair-density at every point in system by finding conditional probability at each point via a KS



Bypassing the Energy Functional in Density Functional Theory: Direct Calculation of Electronic Energies from Conditional Probability Densities S. McCarthy, D. Perchak, R. Pederson, R. Evans, Y. Qiu, S. White, and K. Burke, *Phys. Rev. Lett.* **125**, 266401 (2020).

- Gets uniform gas right for all temperatures
- Dissociates H₂ and any H chain correctly

Correlation energy of the uniform gas determined by ground state conditional probability density functional theory D. Perchak, R. McCarthy, and K. Burke, *Phys. Rev. B* **105**, 165143 (2022).

Conditional probability density functional theory S. Pederson, J. Chen, S. White, and K. Burke, *Phys. Rev. B* **105**, 245138 (2022).

Kieron Burke Exciting Tutorial advanced DFT

13

Orbital-free DFT

- If we knew T_S[n] and its functional derivative, we could by-pass the need to solve KS equations.
- Likely limiting cost becomes Poisson solver
- TF theory has this form
- In 100 years, no-one has been able to do this
- Harder than XC, as T_S much bigger and need to create quantum shell structure
- See recent papers with Michael Berry.

Kieron Burke Exciting Tutorial advanced DFT

14

Orbital-free DFT in 3D

- Use slabs that are uniform in perp direction
- Analysis is more complicated but straightforward
- Poschl-Teller slab with filled bands



Pavel Okun

M	μ/D	\mathcal{T}	Error					$\mathcal{T}^{(2)}$
			T^{TF}	$T^{TF}[\rho]$	GEA	MGE2	$\mathcal{T}^{(2)}$	
1	0.41332	6.83530	0.69488	-0.35373	-0.09933	-0.02556	0.04840	
2	0.63054	26.98627	0.76086	-0.47493	-0.08953	0.02224	0.05235	
3	0.79775	57.49820	0.63855	-0.49398	-0.05655	0.07031	0.03967	
4	0.91496	89.80096	0.43912	-0.46514	-0.02701	0.10005	0.01965	
5	0.98218	113.52877	0.26432	-0.42937	-0.01064	0.11079	0.00154	

- Orbital-free functional with sub-millihartree errors for slabs P. Okun, A. Cancio, and K. Burke, (2023), arXiv: 2304.11115

Kieron Burke Exciting Tutorial advanced DFT

15

15

B Excitations

Kieron Burke Exciting Tutorial advanced DFT

16

16

Excitations in electronic structure

- Optical excitations:
 - Eigenvalue differences of the N-electron system
 - See in light absorption spectrum
 - Poles of density-density response function
 - Linear response TDDFT gives access
- Quasiparticle excitations:
 - Transitions between N and N±1 electrons
 - See in photoemission/absorption spectrum
 - Poles of many-body Greens function
 - GW gives these (and BSE recovers optical spectrum)

17

KS excitations

- Imagine you do a gs DFT calculation with the exact functional
- Gives occupied and unoccupied eigenvalues
- Differences are KS transitions, yielding KS spectrum
- For weakly correlated systems, these look roughly like either optical or quasiparticles (except for gap)
- But need to convert to either optical or quasiparticle spectrum

18

Spectral functions, real and KS

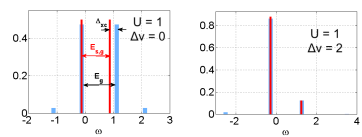


FIG. 9. Spectral function of the symmetric dimer for $U = 1$ and $\Delta v = 0$. The physical MI peaks are plotted in blue, the KS in red. Here $f = 0.1$, $A = -1.1$, and $\mu^0 = 0.0$.

FIG. 11. Same as Fig. 9, but now $U = 1$, $\Delta v = 2$. Here $f = 0.27$, $A = -1.27$, and $\mu^0 = 1.25$.

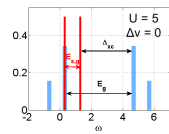


FIG. 10. Same as Fig. 9, but now $U = 5$. Here $f = -0.3$, $A = -0.1$, and $\mu^0 = 3.3$. Note that the KS gap remains unchanged by the alteration of U because $\Delta v = 0$ in both cases.

19

Three gaps: All 'HOMO-LUMO'

- Fundamental (or charge) gap: ($I=24.6$ eV for He)
 - Voltage needed to get solid to conduct.
 - Can also be found from I-A, but tricky for periodic codes
 - AKA quasiparticle gap, well-approximated by GW, seen in photoemission. experiments
- Optical gap: ($1s \rightarrow 2s$ singlet in He, 20.6 eV)
 - Lowest excitation by light, without changing N
 - Matches fundamental gap if no excitons
- Kohn-Sham gap: ($1s \rightarrow 2s$ in He, 20.3 eV)
 - Energy difference between KS HOMO and LUMO for neutral system
 - Typically a great underestimate of I-A for solids

20

Green's function approaches

- Exact Greens function gives quasiparticle excitations
- Start from non-interacting G
 - Add Hartree, gives G^{HF}
 - Add all many-body diagrams, get exact G
- For weakly-correlated systems:
 - Some flavor of GW
 - Green's function methods
- For strongly correlated systems:
 - Dynamical mean field theory
 - Poor man's version: DFT + U

Kieron Burke

Exciting Tutorial advanced DFT

21

21

Mott-Hubbard gap

- Classic prototype of condensed matter
- Infinite chain of H atoms
- When lattice spacing is large, must be an insulator
- But with one electron per site, always a band metal

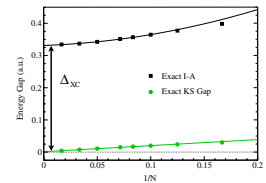


FIG. 3 (color online). Exact gaps for chains of N soft hydrogen atoms with atomic separation $\beta = 4$ (error bars are less than symbol sizes). The upper curve is a quadratic fit of exact gaps of the largest six systems and extrapolates to a finite value $E_g \approx 0.33$. The exact Kohn-Sham gaps, in contrast, extrapolate to zero showing that for $N \rightarrow \infty$ the true KS system is metallic (lower curve is a linear fit of exact KS gaps of the largest six systems).

One-Dimensional Continuum Electronic Structure with the Density-Matrix Renormalization Group and its Implications for Density-Functional Theory E.M. Stoudenmire, Lucas O. Wagner, Steven R. White, Kieron Burke, Phys. Rev. Lett. **109**, 056402 (2012).

Kieron Burke

Exciting Tutorial advanced DFT

22

22

KS versus GKS

- When dealing with orbital-dependent functionals, can treat as HF or pure KS (OEP)
- GKS treats as HF
- Both legitimate
- For ground-state energy, it typically makes almost no difference
- Makes large differences to eigenvalues spectrum!
- HSE gives good gaps in GKS

Kieron Burke

Exciting Tutorial advanced DFT

23

23

Ensemble DFT

$$\left\{ -\frac{1}{2}\nabla^2 + v_{s,w}[n_w](\mathbf{r}) \right\} \phi_{j,w}(\mathbf{r}) = \epsilon_{j,w} \phi_{j,w}(\mathbf{r}).$$

$$n_w(\mathbf{r}) = \sum_{m=0}^M w_m n_m(\mathbf{r}) = \sum_{m=0}^M w_m n_{s,m}(\mathbf{r}),$$

$$E_w[n] = T_{s,w}[n] + V[n] + E_H[n] + E_{xc,w}[n]$$

$$= \text{tr}\{\hat{D}_{s,w}\hat{T}\} + \int d^3r n(\mathbf{r})v(\mathbf{r})$$

$$+ E_H[n] + E_{xc,w}[n],$$

Solve KS equations self-consistently for each choice of weights; can repeat with first excitation only, then add next one, etc.

Kieron Burke

Exciting Tutorial advanced DFT

24

24

Does EDFT really work?

week ending
15 DECEMBER 2017

PHYSICAL REVIEW LETTERS

Hartree and Exchange in Ensemble Density Functional Theory:
PHYSICAL REVIEW LETTERS **123**, 016401 (2019)

PHYSICAL REVIEW LETTERS **130**, 106401 (2023)

Editorial Supplement Featured in Physics

Electronic Excited States in Extreme Limits via Ensemble Density Functionals

Tim Gould^{1*}
Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan, Queensland 4111, Australia

Derk P. Koc²
*Department of Chemistry and Pharmaceutical Sciences and Amsterdam Institute of Molecular and Life Sciences (AIMMS),
Faculty of Science, Vrije Universiteit, De Boelelaan 1083, 1081HV Amsterdam, Netherlands*

Paola Gori-Giorgi³
*Department of Chemistry and Pharmaceutical Sciences and Amsterdam Institute of Molecular and Life Sciences (AIMMS),
Faculty of Science, Vrije Universiteit, De Boelelaan 1083, 1081HV Amsterdam, Netherlands*

Stefano Pittalis⁴
CNR-Istituto Nanoscienze, Via Campi 213A, I-41125 Modena, Italy

(Received 17 May 2022; revised 14 October 2022; accepted 23 January 2023; published 8 March 2023)

¹Department of Physics, Arnold Sommerfeld Center for Theoretical Physics, Ludwig-Maximilians-Universität München, Theresienstrasse 37, 80333 München, Germany

²Munich Center for Quantum Science and Technology (MCQST), Schellingstrasse 4, 80799 München, Germany

³CNR-Istituto Nanoscienze, Via Campi 213A, I-41125 Modena, Italy

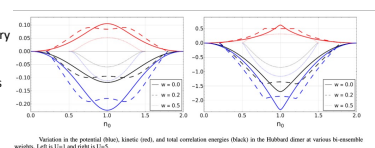
(Received 10 January 2021; revised 26 March 2021; accepted 2 June 2021; published 7 July 2021)

Kieron Burke




25

Exact conditions in ensemble DFT

- Establishing exact conditions for Ensemble Density functional theory (EDFT)
 - Including basic scaling inequalities
 - $T_{c,w}[n_\gamma] \leq \gamma^2 T_{c,w}[n]$,
 - $U_{c,w}[n_\gamma] \geq \gamma U_{c,w}[n]$,
 - $E_{c,w}[n_\gamma] \geq \gamma E_{c,w}[n]$,
 - ... and others!
- Check the satisfaction of these conditions on Hubbard dimer
- Evaluate the performance of perturbation theory and Hartree-Fock approximations



Variation in the ground (blue), kinetic (red), and total correlation energies (black) in the Hubbard dimer at various ensemble weights. Left to right and top to bottom.

Dr. Thais Scott John Kozłowski Prof Aurora Pribram-Jones

* Exact Conditions for Ensemble Density Functional Theory T. Scott, J. Kozłowski, S. Cristoforo, A. Pribram-Jones, and K. Burke, (2023). arXiv: 2307.00187

Kieron Burke Exciting Tutorial advanced DFT 26


26

Relation between DFT and GF

- Apply techniques of fluctuation dissipation theorem
- Subtract KS contribution to isolate XC
- Find Exc from G:

$$E_{XC} - \frac{V_{XC}}{2} = \lim_{\delta \rightarrow 0^+} \frac{-i}{2} \int \frac{d\omega}{2\pi} e^{i\omega\delta} \text{Tr}(\omega + \hat{T}) \Delta G,$$
- Gives an alternative view of XC from usual one in terms of XC hole (pair density).

$$E_{XC} = \lim_{t' \rightarrow t^+} -i \text{Tr} \left(\hat{T} \Delta G + \frac{1}{2} \Sigma_{XC} G \right)$$

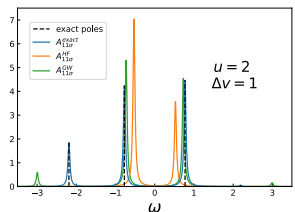


Steven Cristoforo

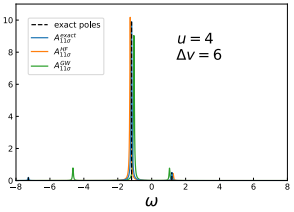
Kieron Burke Exciting Tutorial advanced DFT 27

27

HF and GW spectral functions



$u = 2$
 $\Delta v = 1$



$u = 4$
 $\Delta v = 6$

FIG. 4: The exact (blue), Hartree-Fock (orange), and GW (green) retarded spectral functions with $t = 1/2$.

Kieron Burke Exciting Tutorial advanced DFT 28

28

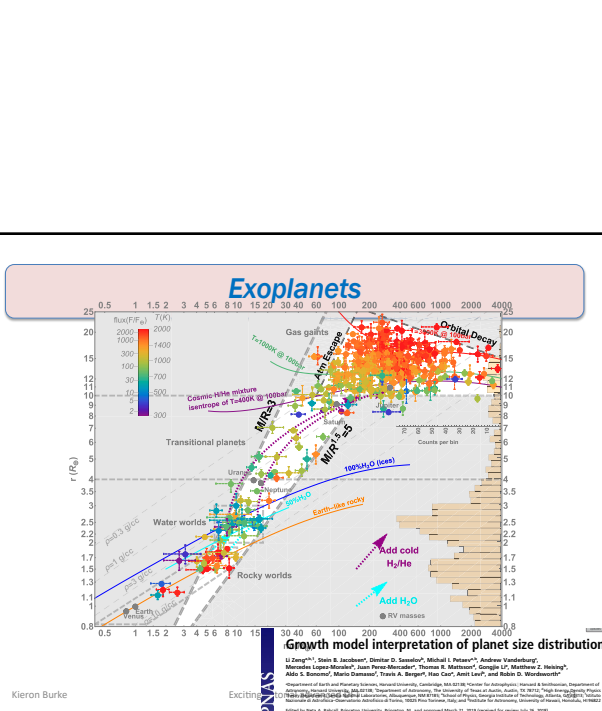
3. Warm dense matter

29

The significance of warm dense matter

- Field of WDM has been revolutionized by thermal DFT calculations over last 20 years.
- Applications include inertial confinement fusion, exoplanet equations of state, interiors of giant planets, shock experiments,...
- But just like TDDFT, folks use ground-state approximations, when they should use temperature-dependent XC.
- How important is the missing T-dependence?

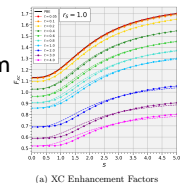
30



31

XC GGA for warm dense matter

- DFT applications dominate WDM, getting equilibrium free energy using Mermin theorem
- But all use zero-temperature XC functionals, ignoring temp dependence
- Even temp-dependence of uniform gas still being calculated via QMC
- We use CP-DFT to calculate temperature dependence of PBE



32

Summary

- gsDFT:
 - DCDFD improves energetics when density goes bad
 - Standard DFT may work better for strong correlation than we realize
 - CP-DFT is a new way to calculate energies for strong correlation
 - Orbital-free DFT may work as a potential functional (not density functional)
- Excitations:
 - optical and quasiparticles different, both differ from gsKS
 - GKS versus KS matters for excitations, not gs
 - Ensemble DFT is alternative to TDDFT
 - Can extract XC energy from GF
- Warm dense matter
 - Used CPDFT to generate temp dependence of PBE
- Thanks to NSF and DOE for support, and KAIST for sponsoring trip.

Kieron Burke

Exciting Tutorial advanced DFT

33

33

Exciting hands-on challenges

- 1) DC-DFT
Calculate e.g., the PBE energy evaluated on the LDA density for a bulk
- 2) CP-DFT
Do a CP-DFT calculation for an atom
- 3) EDFT
Do an ensemble DFT calculation for an optical excitation
- 4) thDFT
Calculate PBE free energy for bulk Al in its perfect crystalline structure at 30,000K by thermal occupation of KS orbitals.

Kieron Burke

Exciting Tutorial advanced DFT

34

34