Basics of electron structure DFT in chemistry, condensed-matter, and materials science:

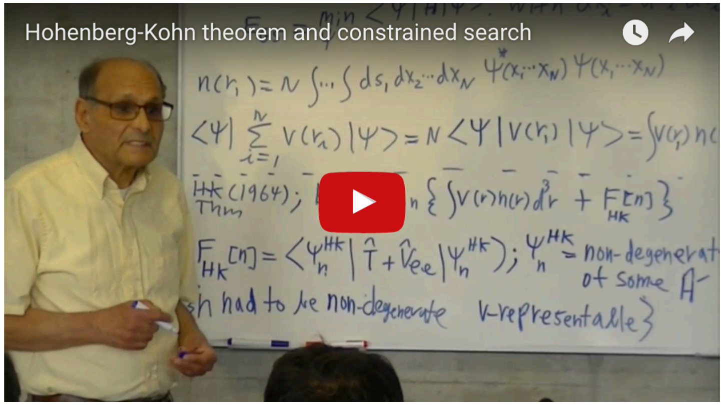
From the very fundamental to the very latest (machine-learning)

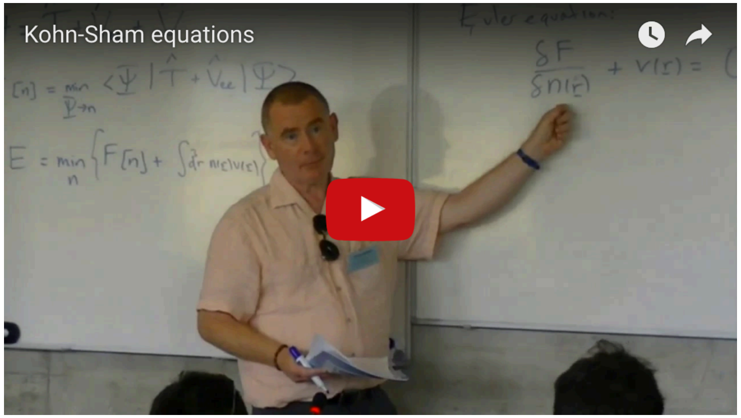
Kieron Burke and friends

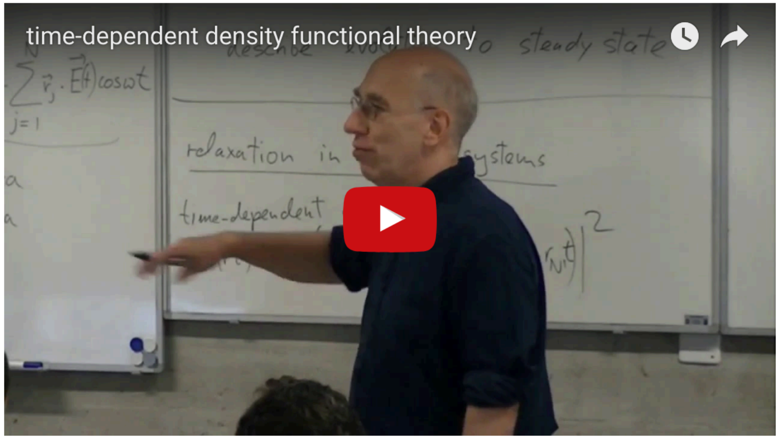
UC Irvine Physics & Chemistry

http://dft.uci.edu

https://www.cecam.org/workshop-9-1326.html







Plan

A. Introduction to electronic DFT
B. Exact conditions
C. Very fundamental stuff: Lieb-Simon limit
D. Machine-learning
E. Two recent papers in ML

A. What is density functional theory?

The electronic structure problem

- Use atomic units
- Born-Oppenheimer approximation
- Wavefunctions antisymmetric and normalized
- Only discuss ground-state electronic problem here, but many variations.
- All non-relativistic, non-magnetic here

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

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

where the kinetic and elec-elec repulsion energies are

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

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

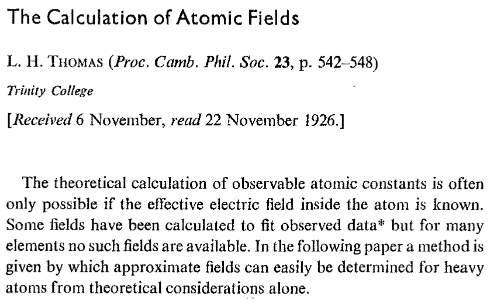
$$v(\mathbf{r}) = -\sum_{\alpha}\frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|}$$

where α runs over all nuclei, plus weak applied **E** and **B** fields.

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

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.]

The theoretical calculation of observable atomic constants is often only possible if the effective electric field inside the atom is known. Some fields have been calculated to fit observed data* but for many elements no such fields are available. In the following paper a method is given by which approximate fields can easily be determined for heavy atoms from theoretical considerations alone.

- Thomas-Fermi Theory (TF):
  - $T \approx T^{TF}$
  - $V_{ee} \approx U$ = Hartree energy
  - $V = \int dr\, \rho(\mathbf{r})\, v(\mathbf{r})$
  - $E_0 = T + V_{ee} + V$
  - 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.

Constrained search proof

1. Rewrite variational principle (Levy 79):

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

   where

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{\rm ee} | \Psi \rangle$$

   - The minimum is taken over all positive $n(\mathbf{r})$ such that $\int d^3r \; n(\mathbf{r}) = N$

2. The external potential $v(\mathbf{r})$ and the hamiltonian $\hat{H}$ are determined to within an additive constant by $n(\mathbf{r})$

- P. Hohenberg and W. Kohn, Phys. Rev. **136**, B 864 (1964).
- M. Levy, Proc. Natl. Acad. Sci. (U.S.A.) **76**, 6062 (1979).

KS equations (1965)

Define *fictitious* non-interacting electrons satisfying:

$$\left\{-\frac{1}{2}\nabla^2 + v_{\mathrm{S}}(\mathbf{r})\right\}\phi_j(\mathbf{r}) = \epsilon_j\phi_j(\mathbf{r}), \qquad \sum_{j=1}^{N}|\phi_j(\mathbf{r})|^2 = n(\mathbf{r}).$$

where $v_{\mathrm{S}}(\mathbf{r})$ is *defined* to yield $n(\mathbf{r})$.

Define T_{S} as the kinetic energy of the KS electrons, U as their Hartree energy and

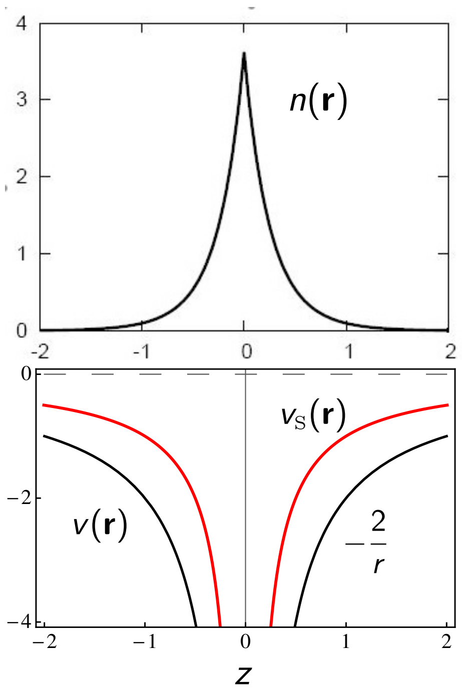
$$\boxed{F = T + V_{\mathrm{ee}} = T_{\mathrm{S}} + U + E_{\mathrm{XC}}}$$

the remainder is the exchange-correlation energy.

Most important result of exact DFT:

$$v_{\mathrm{S}}(\mathbf{r}) = v(\mathbf{r}) + \int d^3r\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\mathrm{XC}}[n](\mathbf{r}), \qquad v_{\mathrm{XC}}(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}}{\delta n(\mathbf{r})}$$

Knowing $E_{\mathrm{XC}}[n]$ gives closed set of self-consistent equations.



Today’s commonly-used functionals

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

$$A_{\rm X} = -(3/4)(3/\pi)^{1/3} = -0.738.$$

- Generalized gradient approx (GGA)
  - Uses both n(**r**) and |∇n(**r**)|
  - Should be more accurate, corrects overbinding of LDA
  - Examples are PBE and BLYP

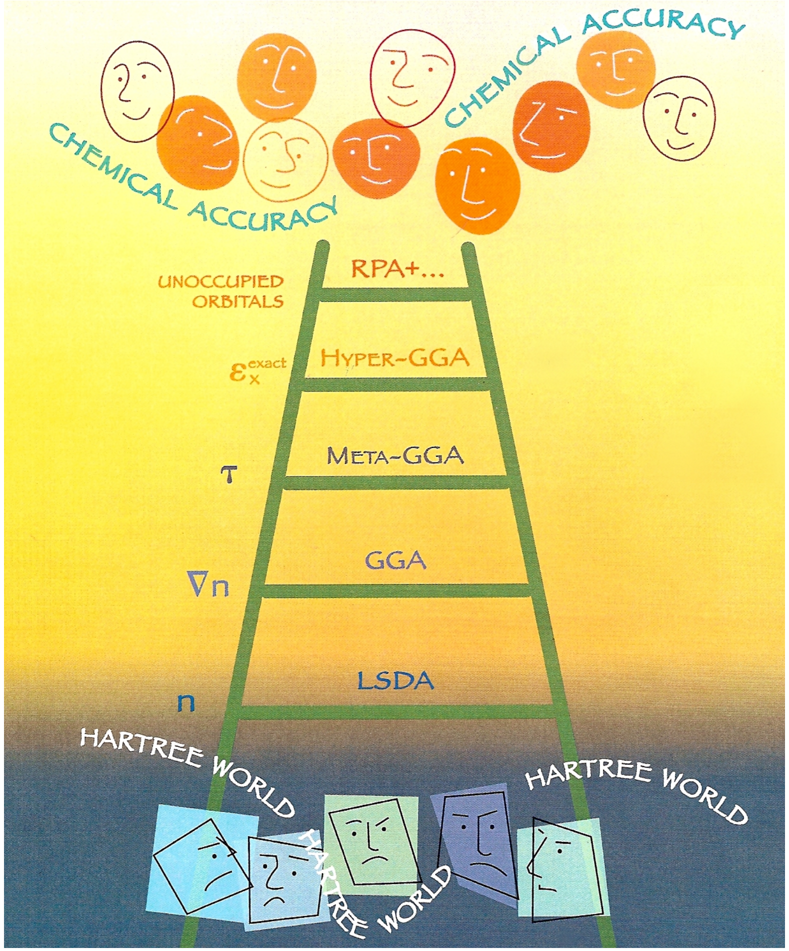
- Hybrid:
  - Mixes some fraction of HF
  - Examples are B3LYP and PBE0

A few recent applications

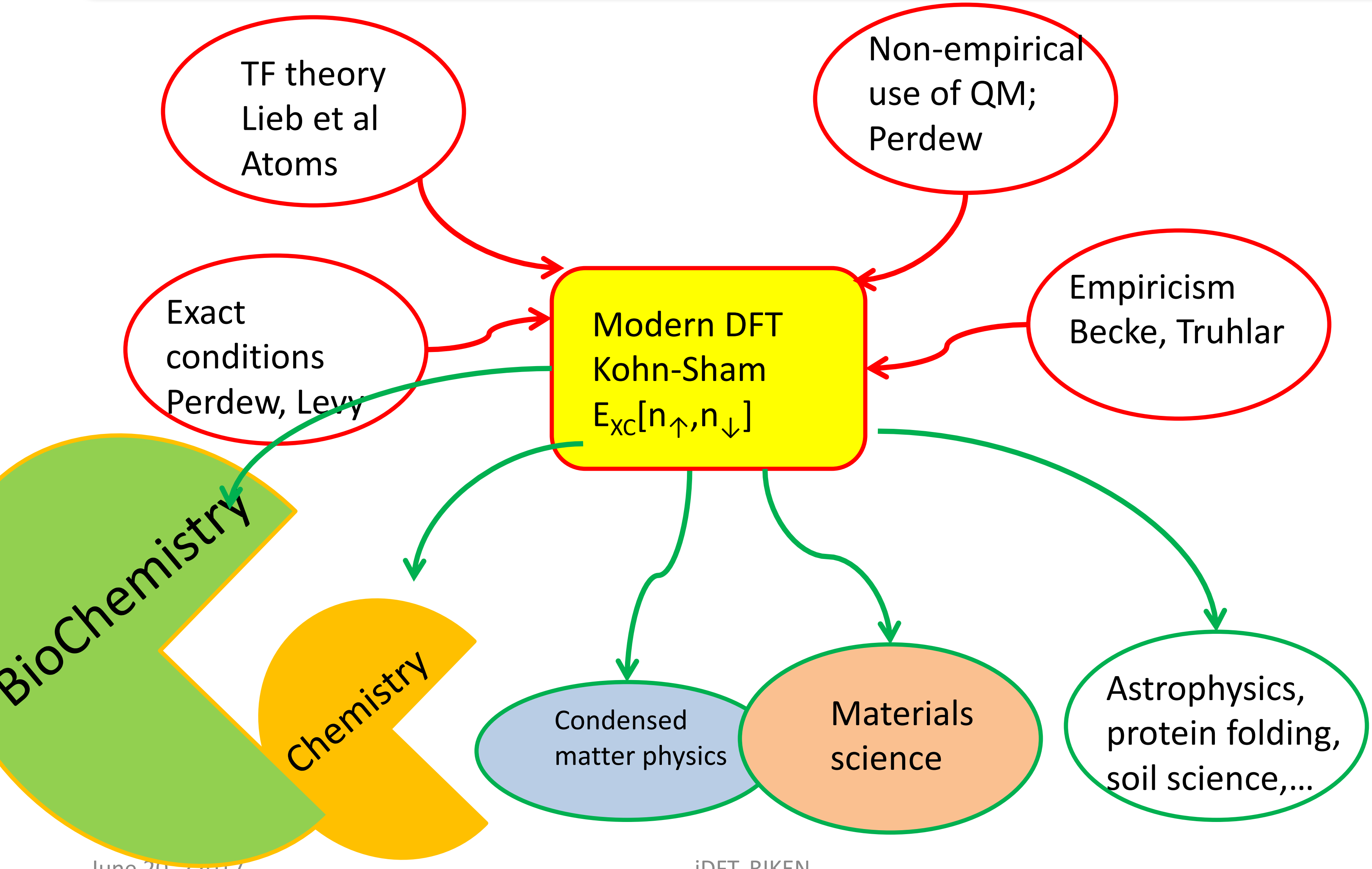
- Computers, codes, algorithms always improving
- Making bona fide predictions
- E.g., a new better catalyst for Haber-Bosch process (‘fixing’ ammonia from air) was predicted after about 25,000 failed experiments (Jens Norskov’s group)
- Now scanning chemical and materials spaces using big data methods for materials design (materials genome project).
- World’s hottest superconductor (203K) is hydrogen sulfide, predicted by DFT calculations, then made.

Perdew's systematic approach to XC

- Idea: Successively refine approximations
- Use exact conditions
- Avoid fitting of parameters to data sets
- Each rung is more sophisticated, but costs more



Big picture



TF theory
Lieb et al
Atoms

Non-empirical
use of QM;
Perdew

Exact
conditions
Perdew, Levy

Modern DFT
Kohn-Sham
$E_{XC}[n_{\uparrow},n_{\downarrow}]$

Empiricism
Becke, Truhlar

BioChemistry

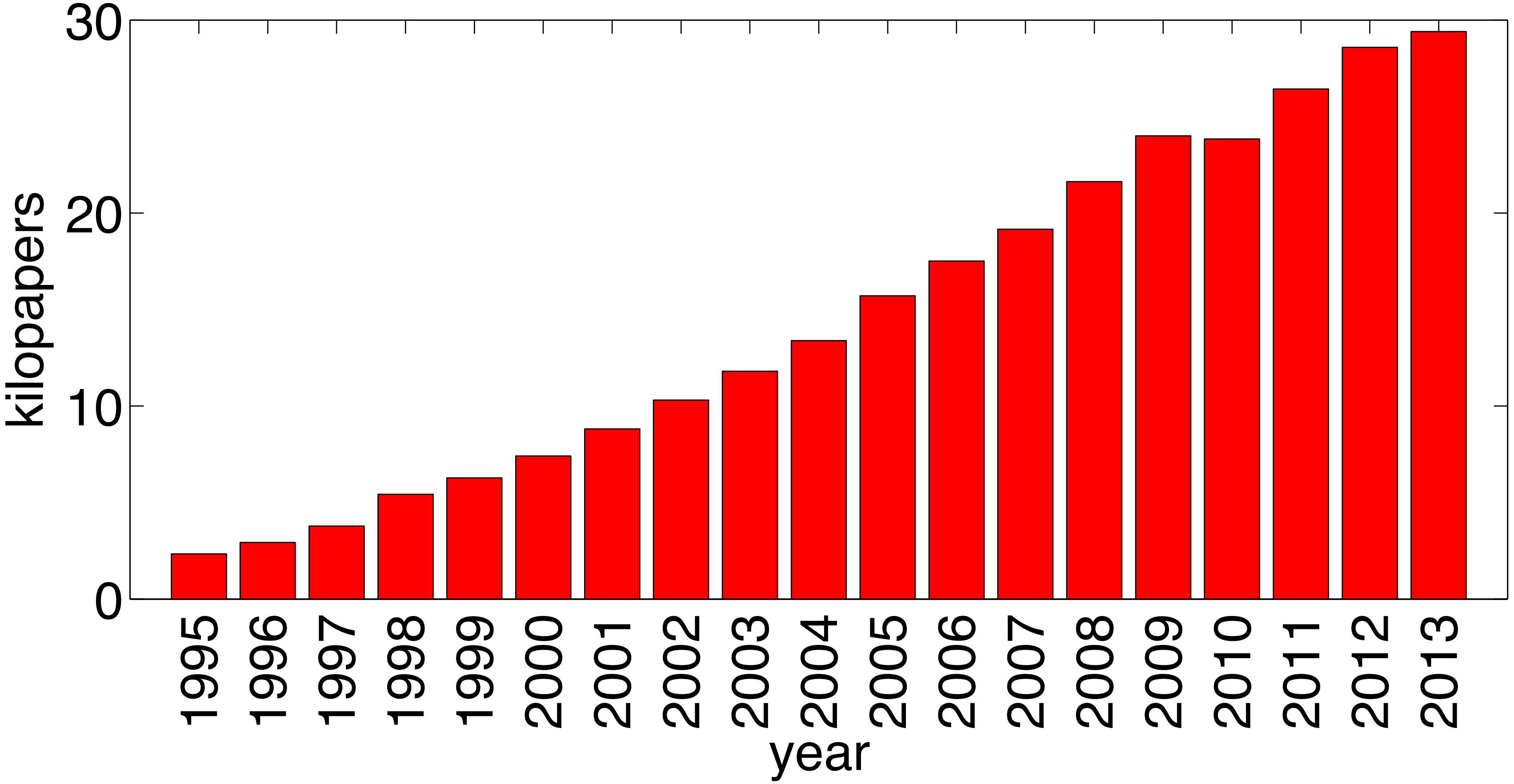
Chemistry

Condensed
matter physics

Materials
science

Astrophysics,
protein folding,
soil science,…

DFT papers



DFT: A Theory Full of Holes, Aurora Pribram-Jones, David A. Gross, Kieron Burke, Annual Review of Physical Chemistry (2014).

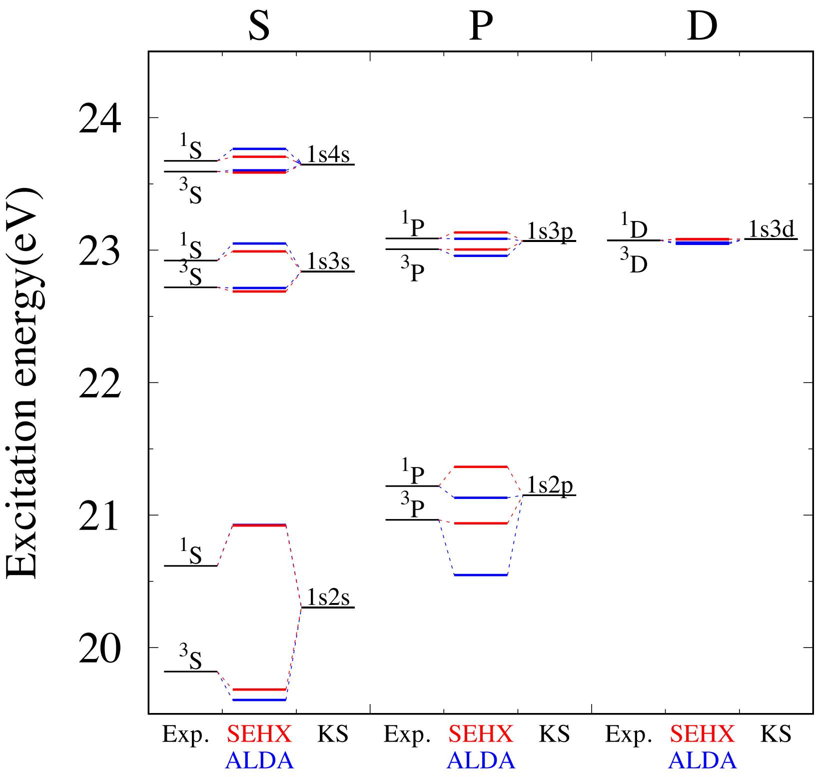
In reality…

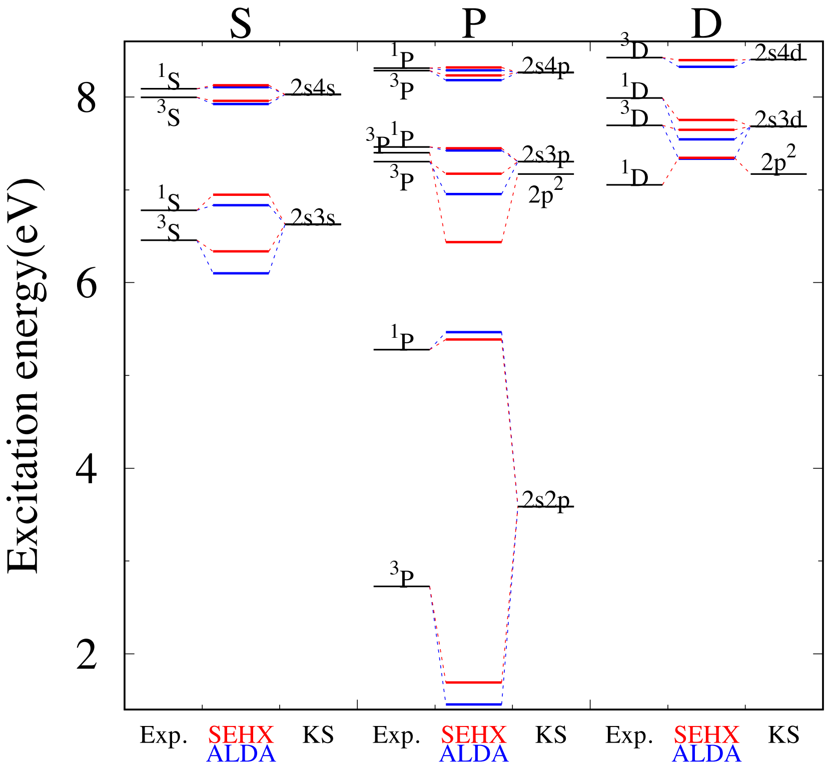

wB97
OBPW
LM81
X3LYP
PW92
SAOP
BNL05
PW91
EB08
M06-L
KMLYP
TLYP
PBE
LYP
V5LYP
LB9483
VP86
WC06
PBEsol
wB97XD
wB97X
MCY06
B2PLYP
BMK04
FT97
BOP
PBEOP
B97
WI
GL76
rPBE
B97-2
CS1
Bh3LYP
rB86
DK87
WL
TPSSh
GV09
HSE
vBH
M05-2X
BR89
KT2
B3LYP
EXX
OPTX
mPW
muB88
HL71
M06-HF
M05
revPBE
xPBE
M06-2X
HCTH
PKZB99
PBE0
muPBE
LRC-wPBE0
PL81
BP86
LG93
KCIS
KT1
lhf
wigner
VWN5
LSDA
O3LYP
SOGGA
RPA
LC-wPBE
B88
B95
BRC89
B97-D
PZ81
TPSS
PK06
BJ06
B86-mgc
EDF1
VS98
B94
AM05
GG99
PW86
B97-1
EDF2
mPBE
G96
CAM-B3LYP
wPBE
KT3
VWN1

Several DFT approaches to excited states

- Most popular: linear response TDDFT
- Ensemble DFT for ensembles of ground and excited states
- Delta SCF
- Min-max principle

Excitations from a `new' ensemble





[B180] Direct extraction of excitation energies from ensemble density-functional theory Zeng-hui Yang, Aurora Pribram-Jones, Kieron Burke, Carsten A. Ullrich, *Submitted* (2017).

Thermal DFT

- Created by Mermin, 1966.
- Can do constrained search over free energy to fiind equilibrium density at non-zero temperature
- Huge, rapid development for use in warm dense matter over the last 2 decades, such as modelling inertial confinement fusion.

[179] Warming Up Density Functional Theory, Justin C Smith, Francisca Sagredo, Kieron Burke, *Submitted.*

Simplest possible model?


Diego Carrascal (Oviedo)


Jaime Ferrer (Oviedo)


Justin Smith


IOP Publishing Journa
J. Phys.: Condens. Matter **27** (2015) 393001 (34pp) doi:10

Topical Review

The Hubbard dimer: a density functi case study of a many-body problem

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CrossMark

Abstract

This review explains the relationship between density functional theory and strongly correlated models using the simplest possible example, the two-site Hubbard model. The relationship to traditional quantum chemistry is included. Even in this elementary example, where the exact ground-state energy and site occupations can be found analytically, there is much to be explained in terms of the underlying logic and aims of density functional theory. Although the usual solution is analytic, the density functional is given only implicitly. We overcome this difficulty using the Levy–Lieb construction to create a parametrization of the exact function with negligible errors. The symmetric case is most commonly studied, but we find a rich variation in behavior by including asymmetry, as strong correlation physics vies with charge-transfer effects. We explore the behavior of the gap and the many-body Green's function, demonstrating the 'failure' of the Kohn–Sham (KS) method to reproduce the fundamental gap. We perform benchmark calculations of the occupation and components of the KS potentials, the correlation kinetic energies, and the adiabatic connection. We test several approximate functionals (restricted and unrestricted Hartree–Fock and Bethe ansatz local density approximation) to show their successes and limitations. We also discuss and illustrate the concept of the derivative discontinuity. Useful appendices include analytic expressions for density functional energy components, several limits of the exact functional (weak- and strong-coupling, symmetric and asymmetric), various adiabatic connection results, proofs of exact conditions for this model, and the origin of the Hubbard model from a minimal basis model for stretched H_2.

Keywords: density functional theory, Hubbard model, strongly correlated electron systems

(Some figures may appear in colour only in the online journal)

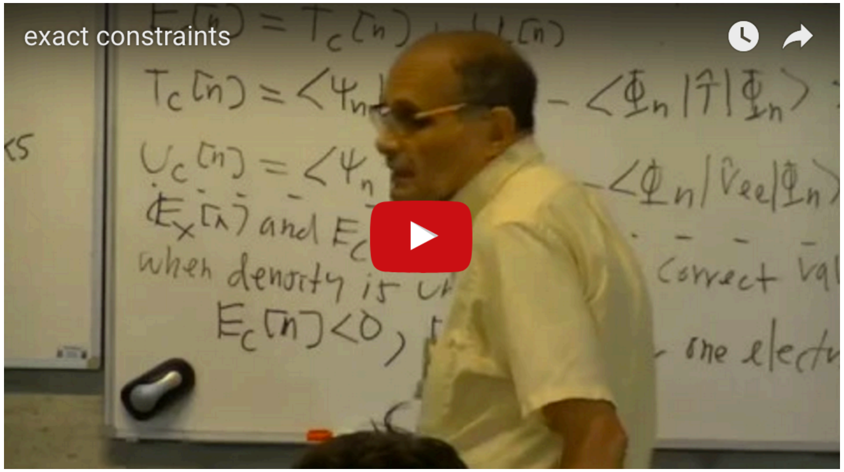
Maybe should be called: *The many-body theorists companion to DFT*

Orbital-free DFT

- An old dream of DFT
- Since $T_s[n]$ is also a density functional, if we knew it well-enough, we would not need to solve KS equations.
- Make everything much faster
- TF is this kind of theory
- No-one has found a universal approximation sufficiently accurate for this purpose.
- Most modern research focuses on XC
- Thermal DFT at higher temperature uses TF

B. Exact conditions in DFT

- Used to constrain good-quality approximations
- Some of the most powerful are very simple to deduce.
- See Mel Levy’s talk:



Kohn-Sham elementary facts

- T and $V_{\rm ee}$ are both positive, trying to rip system apart, but overcome by more negative V.
- Kinetic energies are positive, and $T > T_{\rm S}$ by definition.
- U is positive and dominates the electron-electron repulsion.
- $E_{\rm X}$ only has contributions from same-spin electrons and is negative. This part is given exactly by a HF calculation.
- The electron-electron repulsion of the KS wavefunction is just

$$\langle \Phi[n] | \hat{V}_{\rm ee} | \Phi[n] \rangle = U[n] + E_{\rm X}[n]$$

- $E_{\rm C}$ contains both kinetic and potential contributions:

$$\begin{aligned} E_{\rm C} &= \langle \Psi[n] | \hat{T} + \hat{V}_{\rm ee} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{V}_{\rm ee} | \Phi[n] \rangle \\ &= (T - T_{\rm S}) + (V_{\rm ee} - U - E_{\rm X}) = T_{\rm C} + U_{\rm C} \end{aligned}$$

Uniform coordinate scaling

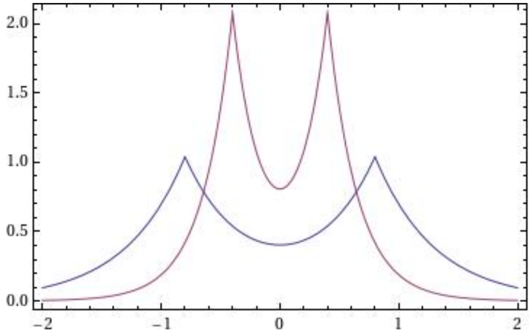


Figure: A one-dimensional density (blue) being squeezed by $\gamma = 2$ (red)

- A very handy way to study density functionals, especially in limits:

$$n_\gamma(\mathbf{r}) = \gamma^3\, n(\gamma \mathbf{r}), \qquad 0 \le \gamma \le \infty$$

  - For $\gamma > 1$, squeezes up the density, preserving norm; for $\gamma < 1$, stretches it out.

- Exchange: Require $E_{\rm X}[n_\gamma] = \gamma\, E_{\rm X}[n]$
- Correlation: $E_{\rm C}[n_\gamma] = B[n] + C[n]/\gamma + ...$ for high density limit of *finite* systems. (Violated by LDA!)

[172] Exact conditions on the temperature dependence of density functionals
Kieron Burke, Justin Smith, Paul E. Grabowski, Aurora Pribram-Jones, *Phys Rev B* **93**, 195132 (2016)

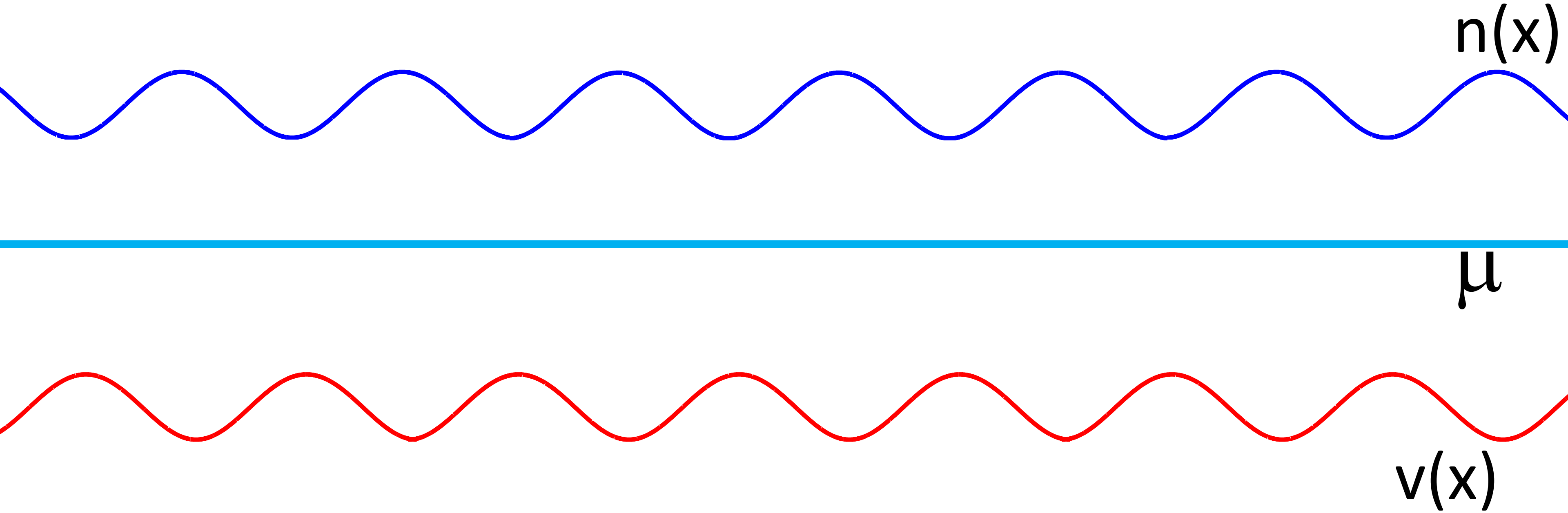
C. Very fundamental

- *In any event, the result is extraordinarily powerful, for it enables us to calculate (approximate) allowed energies without ever solving the Schrödinger equation, by simply evaluating one integral. The wave function itself has dropped out of sight.*

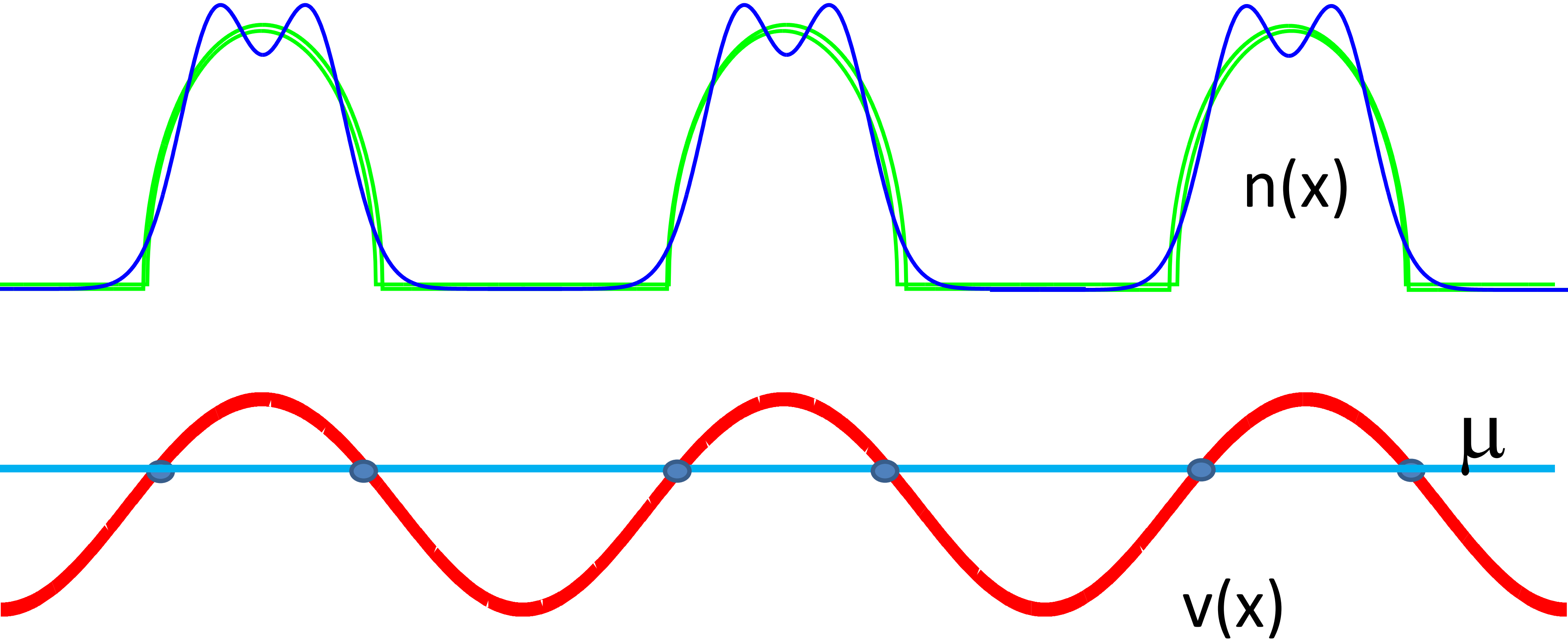
- Griffiths, *Quantum Mechanics*, about *semiclassical* approximations.

Original KS idea: Simple metals

WKB for one level=>sum over many=>TF theory
Corrections to WKB => sum over many => gradient expansion
As Ћ -> 0, TF becomes relatively exact (asymptotic expansion)



Chemistry and most materials



- TF theory STILL relatively exact in limit Ћ -> 0.
- Leading corrections come from turning points, yielding quantum oscillations.

Lieb-Simon limit

- Consider scaling to continuum limit:

$$v^{\zeta}(\mathbf{r}) = \zeta^{1+1/d}\, v(\zeta^{1/d}\mathbf{r})\ , \qquad N \to \zeta N.$$

  where d is spatial dimension.
- Lieb and Simon (1973) proved that Thomas-Fermi theory is relatively exact as $\zeta \to \infty$, i.e.,

$$\frac{E^{\mathrm{TF}} - E_0}{E_0} \to 0$$

- Equivalent to changing $Z = N$ for neutral atoms.
- Schwinger and Englert showed LDA exchange is relatively exact for atoms as $Z \to \infty$

KS version of Lieb-Simon statement

Almost certain that

- $E_{\rm xc}^{\rm LDA}$ is relatively exact in the $\zeta \to \infty$ limit

$$\lim_{\zeta\to\infty} \frac{\Delta E_{\rm xc}^{\rm LDA}}{E_{\rm XC}} = \frac{E_{\rm xc}^{LDA} - E_{\rm xc}}{E_{\rm XC}} = 0$$

Kieron’s instinct:

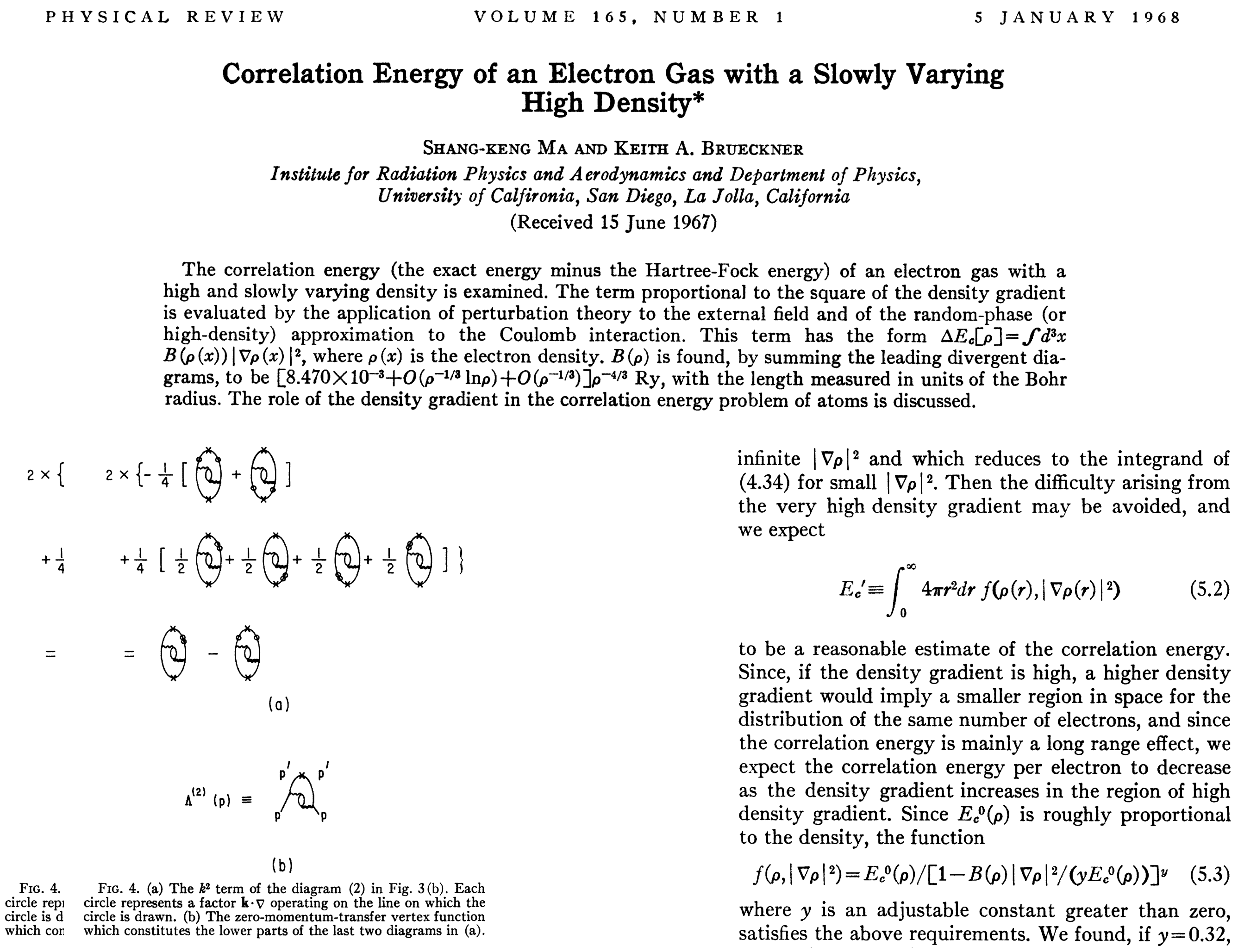
- Success of simple local-type approximations is because they are crude attempts to capture leading corrections to asymptotic limit (LDA)

[173] Locality of correlation in density functional theory Kieron Burke, Antonio Cancio, Tim Gould, Stefano Pittalis, The Journal of Chemical Physics **145**, 054112 (2016).

Motivation

- Local density approximation is semiclassical limit of all systems
- What are leading corrections in an expansion in hbar?
- Are these approximated by our GGA's, and is this why GGA's work?
- Gradient expansion of slowly-varying gas (discussed in HK and KS papers) is violated by most real systems, even metals.

Early work



PHYSICAL REVIEW VOLUME 165, NUMBER 1 5 JANUARY 1968

Correlation Energy of an Electron Gas with a Slowly Varying High Density*

Shang-keng Ma and Keith A. Brueckner
Institute for Radiation Physics and Aerodynamics and Department of Physics, University of Calfironia, San Diego, La Jolla, California

(Received 15 June 1967)

The correlation energy (the exact energy minus the Hartree-Fock energy) of an electron gas with a high and slowly varying density is examined. The term proportional to the square of the density gradient is evaluated by the application of perturbation theory to the external field and of the random-phase (or high-density) approximation to the Coulomb interaction. This term has the form $\Delta E_c[\rho]=\int d^3x\, B(\rho(x))|\nabla\rho(x)|^2$, where $\rho(x)$ is the electron density. $B(\rho)$ is found, by summing the leading divergent diagrams, to be $[8.470\times10^{-3}+O(\rho^{-1/3}\ln\rho)+O(\rho^{-1/3})]\rho^{-4/3}$ Ry, with the length measured in units of the Bohr radius. The role of the density gradient in the correlation energy problem of atoms is discussed.

FIG. 4.
circle repı
circle is d
which coı

FIG. 4. (a) The k^2 term of the diagram (2) in Fig. 3(b). Each circle represents a factor $\mathbf{k}\cdot\nabla$ operating on the line on which the circle is drawn. (b) The zero-momentum-transfer vertex function which constitutes the lower parts of the last two diagrams in (a).

infinite $|\nabla\rho|^2$ and which reduces to the integrand of (4.34) for small $|\nabla\rho|^2$. Then the difficulty arising from the very high density gradient may be avoided, and we expect

$$E_c'\equiv\int_0^\infty 4\pi r^2dr\, f(\rho(r),|\nabla\rho(r)|^2) \qquad (5.2)$$

to be a reasonable estimate of the correlation energy. Since, if the density gradient is high, a higher density gradient would imply a smaller region in space for the distribution of the same number of electrons, and since the correlation energy is mainly a long range effect, we expect the correlation energy per electron to decrease as the density gradient increases in the region of high density gradient. Since $E_c^0(\rho)$ is roughly proportional to the density, the function

$$f(\rho,|\nabla\rho|^2)=E_c^0(\rho)/[1-B(\rho)|\nabla\rho|^2/(yE_c^0(\rho))]^y \qquad (5.3)$$

where y is an adjustable constant greater than zero, satisfies the above requirements. We found, if $y=0.32$,

Hydrogenic atoms

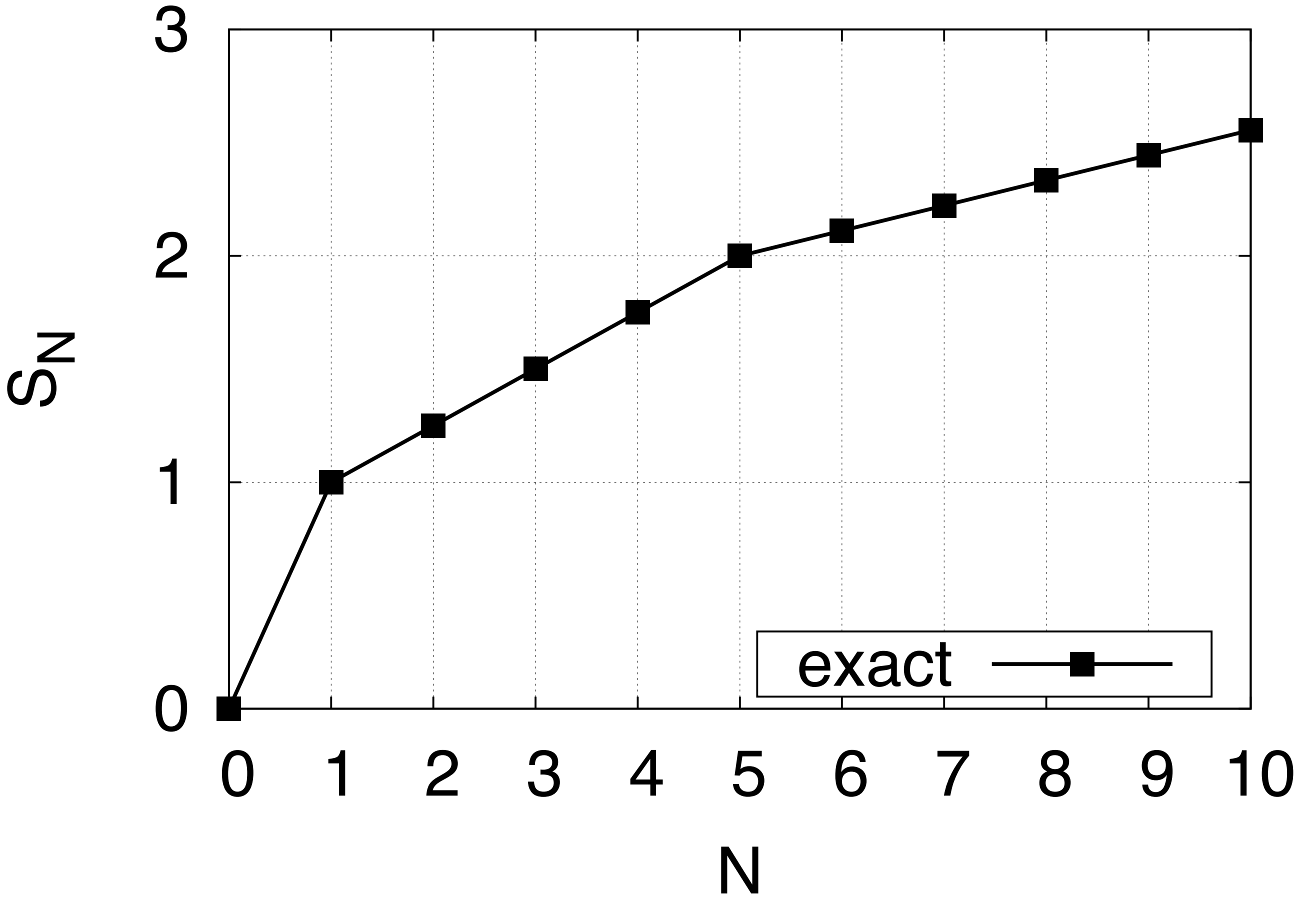
- Consider many same-spin `electrons’ in a -1/r potential
- Still fermions, satisfying exclusion principle
- Occupy 1s, 2s and 2p, 3s, 3p, 3d, etc.
- Kinetic energy = - total energy (virial theorem)
- $T = -(1+1/4+1/4+1/4+\ldots)/2$
- Example of $T_s[v]$.

Little math exercise

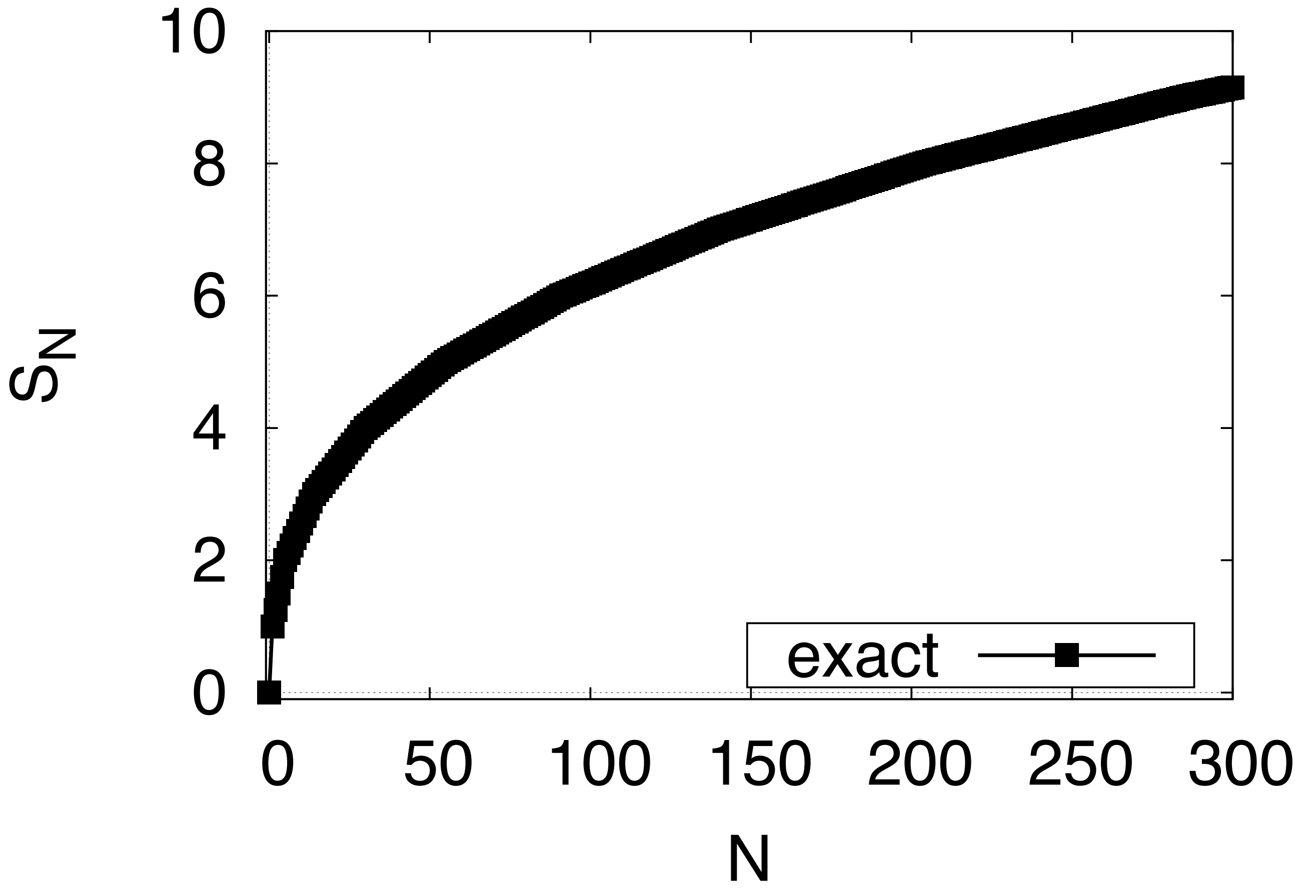
- Given a sequence: a_i
  - a_i=1, ¼, ¼, ¼, ¼, 1/9, 1/9, 1/9, 1/9, 1/9, 1/9, 1/9, 1/9, 1/9, 1/16,…

- Find partial sums of N terms S_N:
  - $S_N = \Sigma\, a_i$
  - S_N = 1,1.25,1.5,1.75,2,2.11111,2.2222,2.33333,…

Exact partial sums up to 10



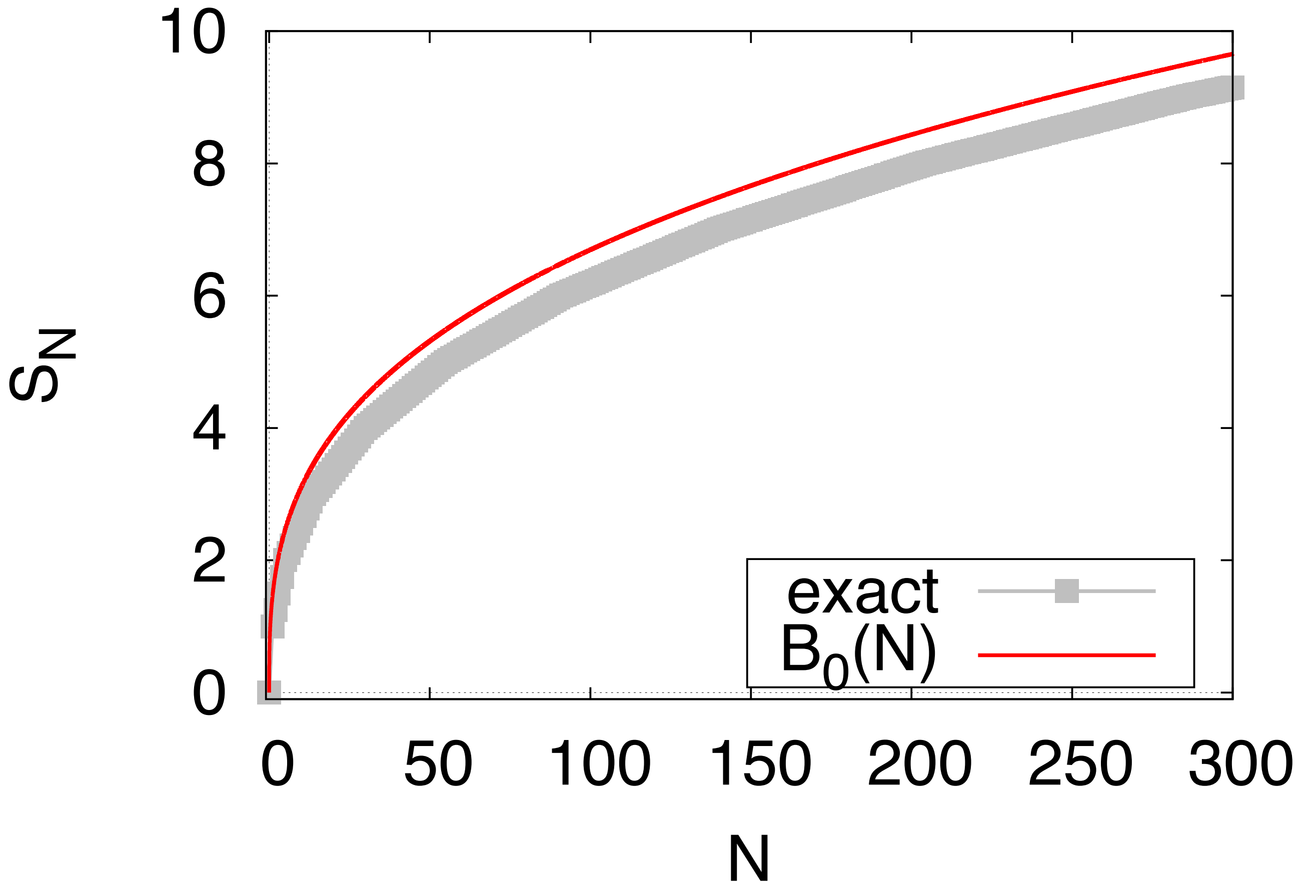
Exact partial sums up to 300



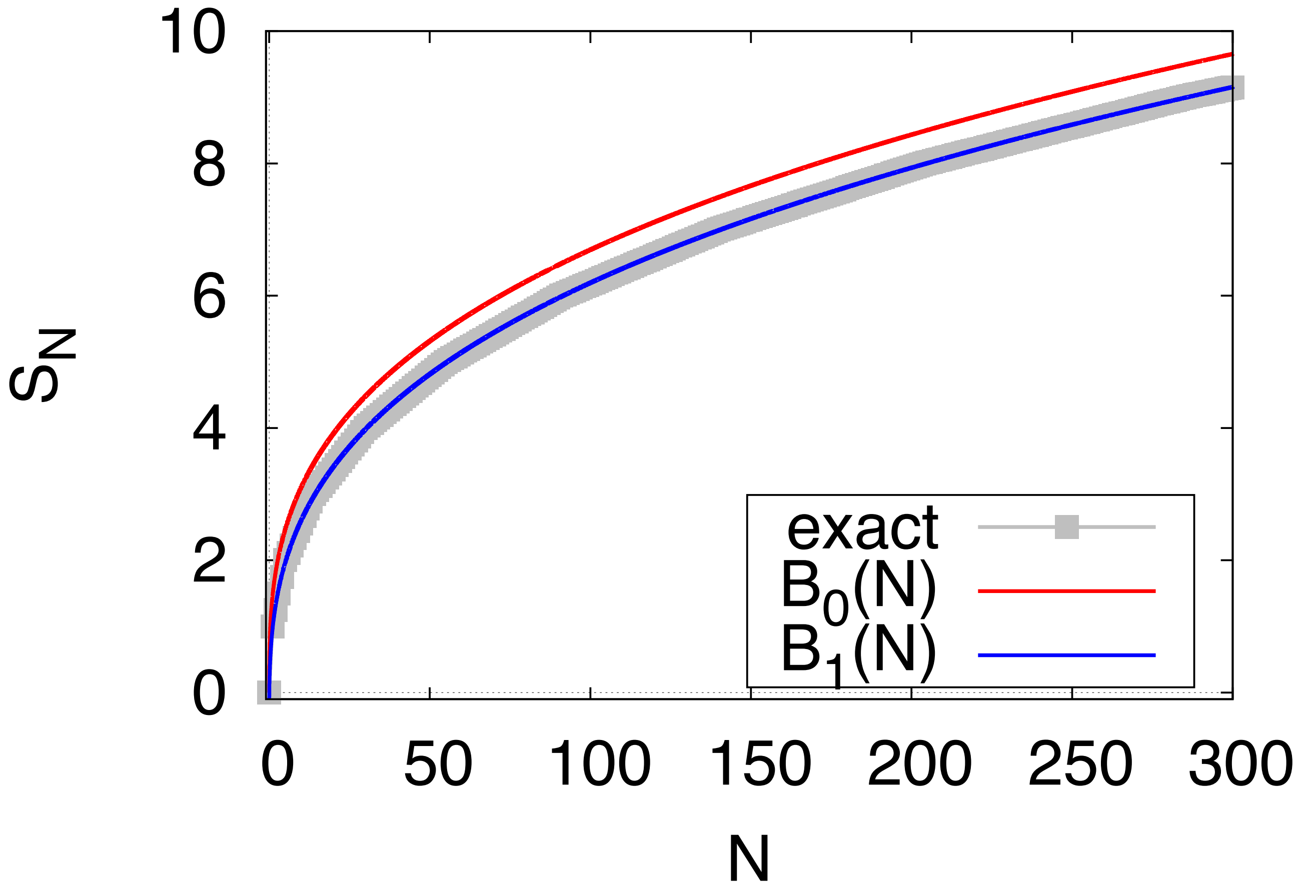
Expand for large N

- $S_N = B_0(N) + B_1(N) + B_2(N)+\ldots$
- Find $B_0(N) = (3N)^{1/3}$
- Find $B_1(N) = -1/2$
- …

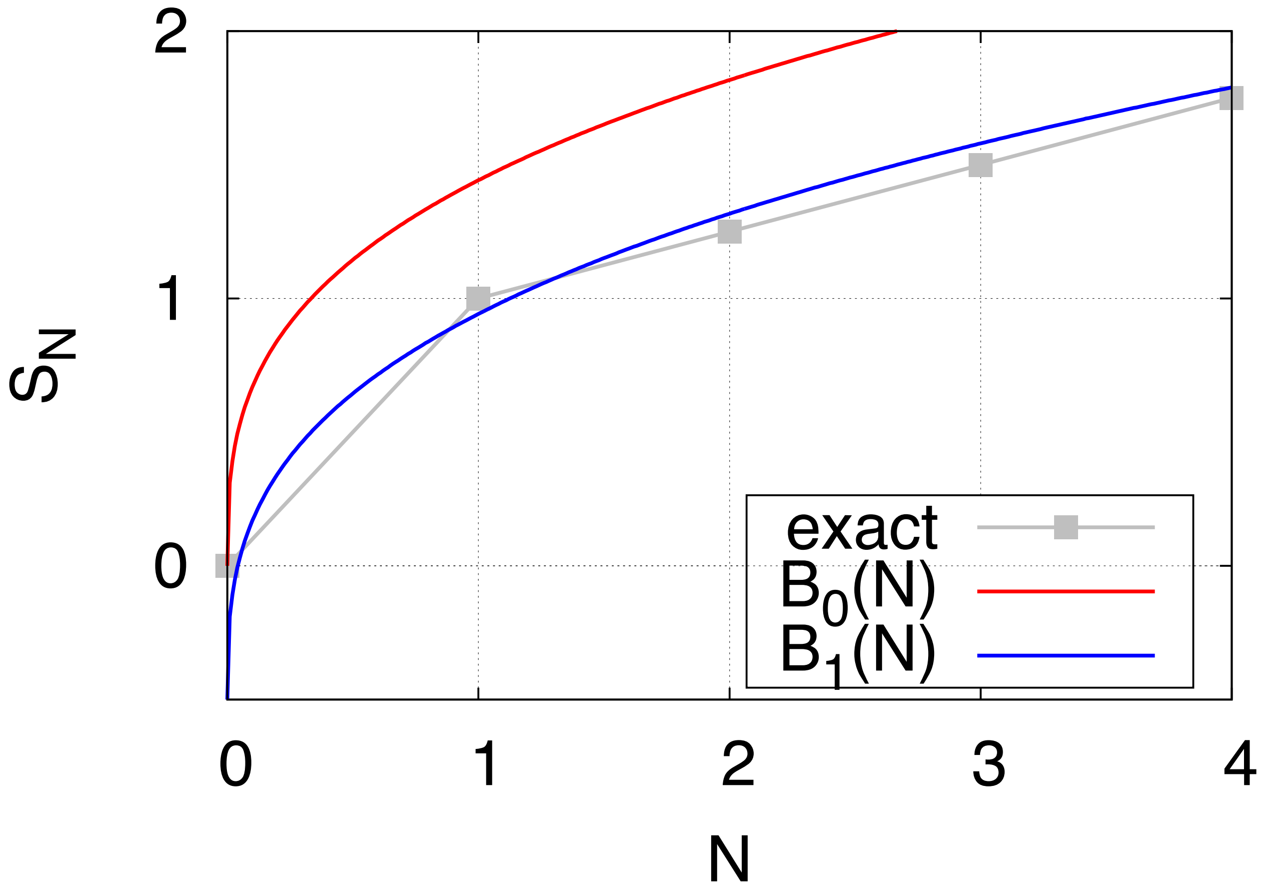
Leading large-N behavior



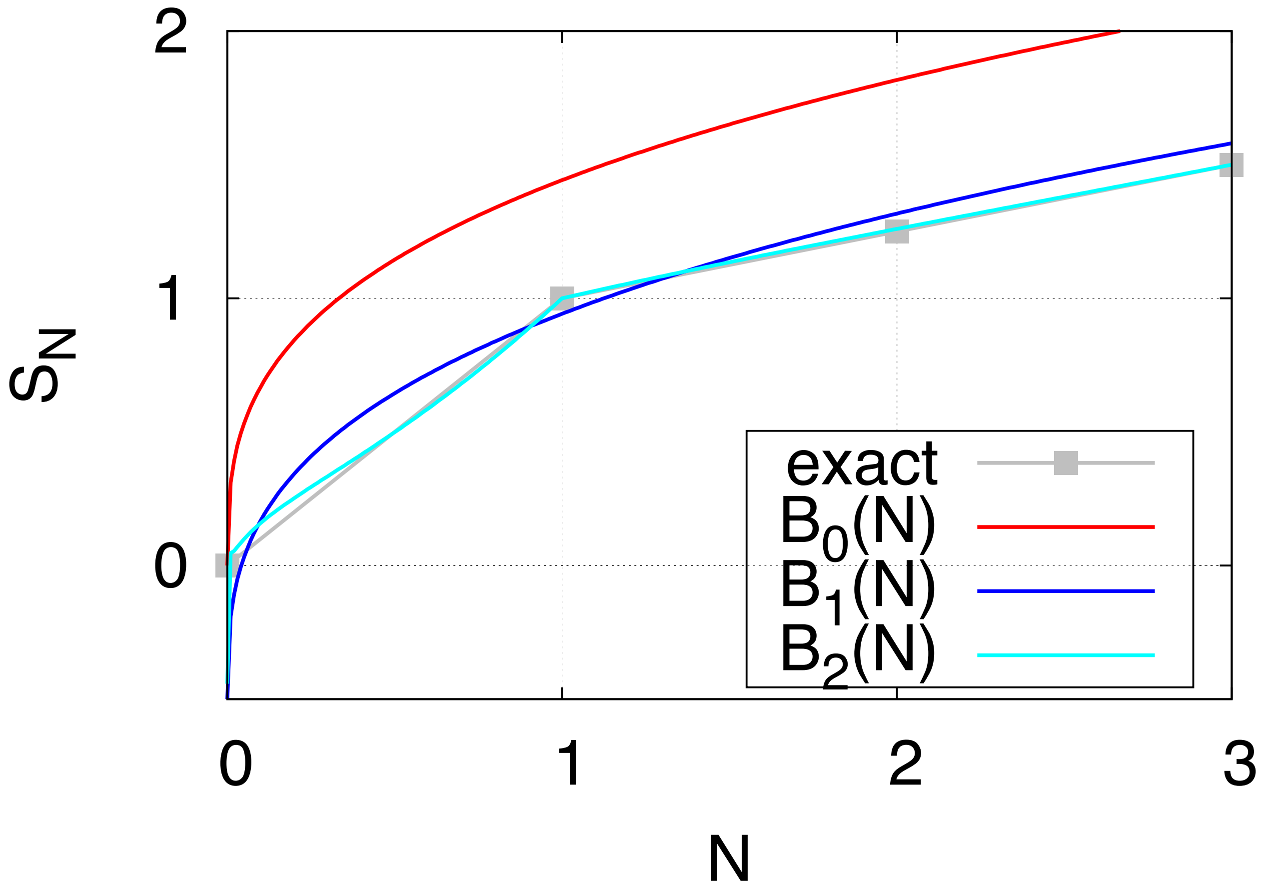
Leading plus first correction up to 300



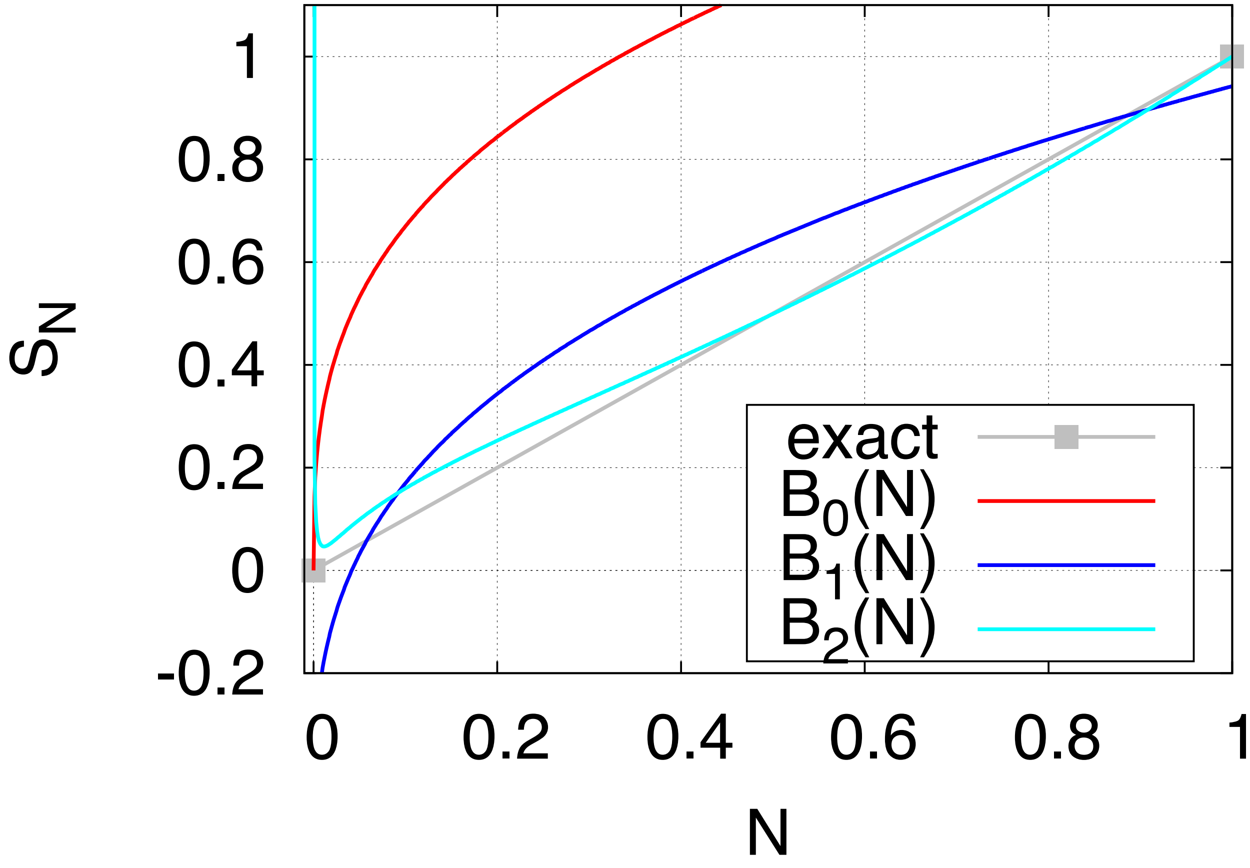
Leading plus first correction up to 4



Include 2nd correction up to 3



Include 2^{nd} correction up to 1



Results for expansion

- Performed expansion for N->infinity.
- For N=1:
  - S_1=1
  - B_0=1.442249570
  - B_0+B_1=0.9422495703
  - $B_0+B_1+B_2$=1.000029677
- TF theory yields B_0; first correction is Scott term
- No existing approximate density functional gets this and the slowly-varying gas right.

A new continuum

- Consider some simple problem, e.g., harmonic oscillator.
- Find ground-state for one particle in well.
- Add a second particle in first excited state, but divide ħ by 2, and resulting density by 2.
- Add another in next state, and divide ħ by 3, and density by 3
- …
- $\to\infty$

Continuum limit

Leading Corrections to the Local Density Approximation

Attila Cangi, Donghyung Lee, Peter Elliott, and Kieron Burke
Departments of Chemistry and of Physics, University of California, Irvine, CA 92697, USA

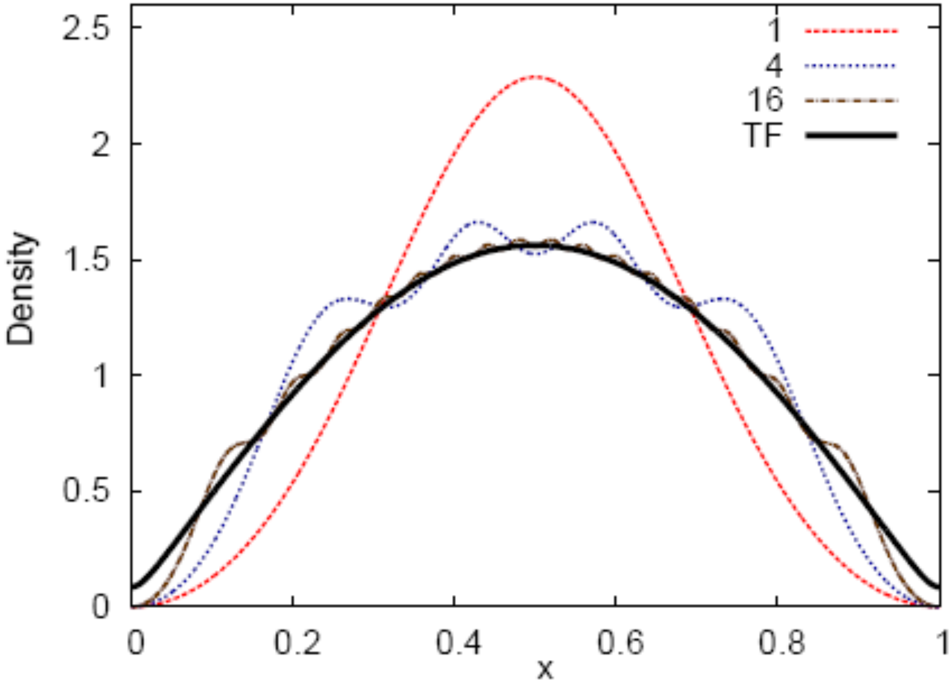


FIG. 2: TF and renormalized exact densities for $N' = 1, 4, \text{and} 16$ particles in $v(x) = -12\sin^2(\pi x), 0 \le x \le 1$, showing approach to continuum limit.

Leading corrections to local approximations Attila Cangi, Donghyung Lee, Peter Elliott, and Kieron Burke, Phys. Rev. B 81, 235128 (2010).

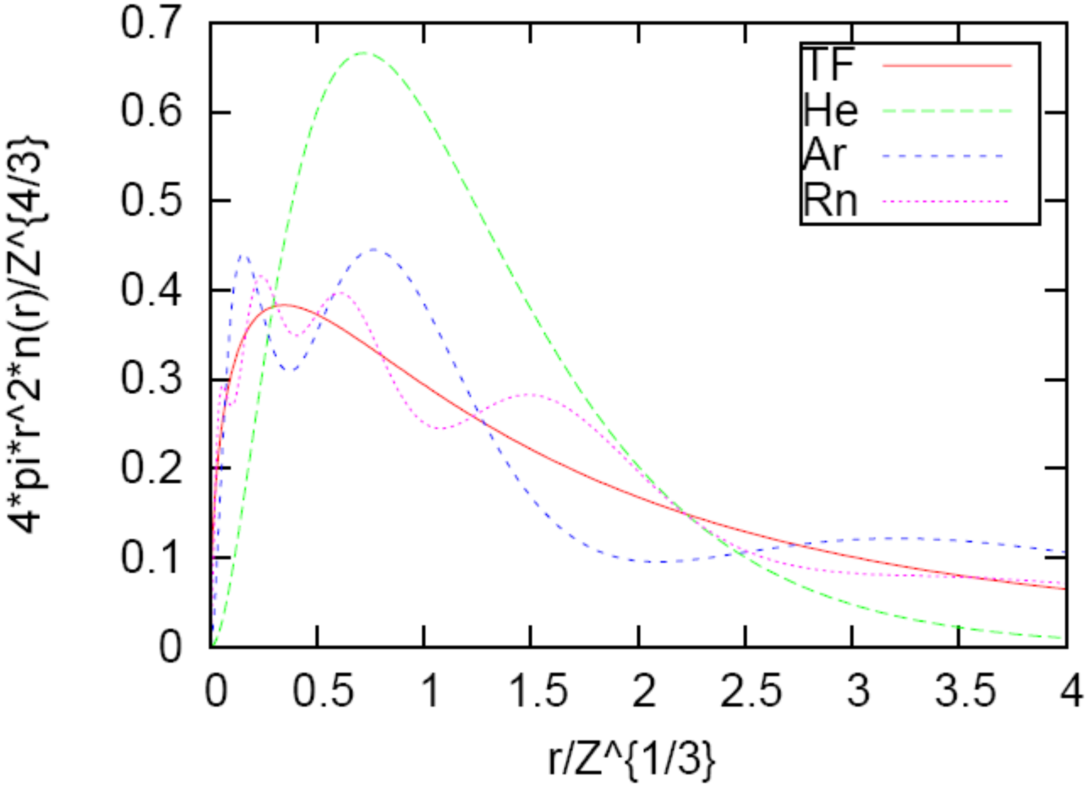
Attila Cangi

Getting to real systems

- Include real turning points and evanescent regions, using Langer uniformization
- Consider spherical systems with Coulombic potentials (Langer modification)
- Develop methodology to numerically calculate corrections for arbitrary 3d arrangements

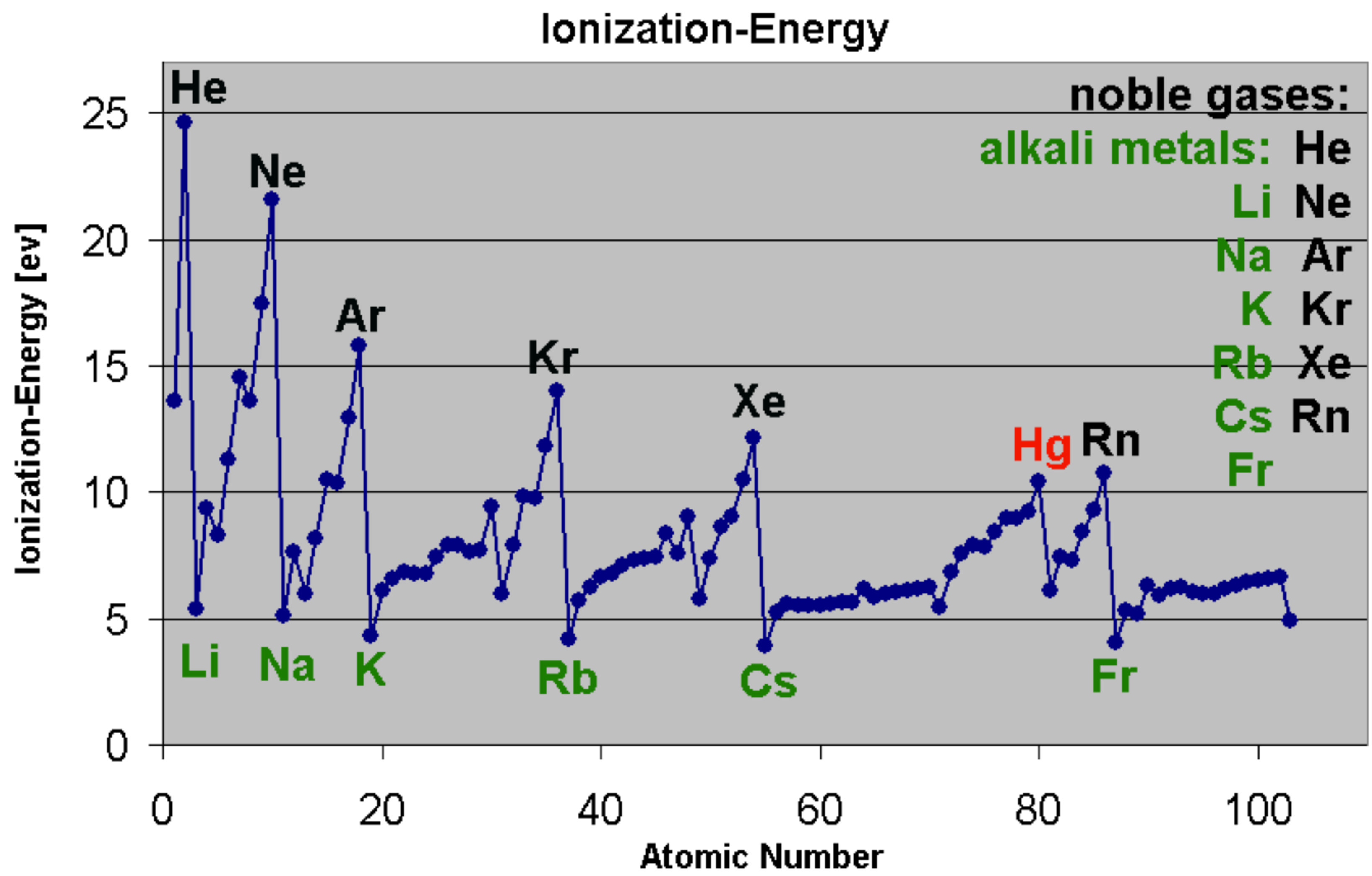
Classical limit for neutral atoms

- For interacting systems in 3d, increasing *Z* in an atom, keeping it neutral, approaches the classical continuum, ie same as ħ→0 (Lieb 81)



[158] Atomic correlation energies and the generalized gradient approximation, Kieron Burke, Antonio Cancio, Tim Gould, Stefano Pittalis, submitted and ArXiv:1409.4834 (2014)

What about energy differences?



- wikipedia

Z→∞ limit of ionization potential

- Shows even energy differences can be found
- Looks like LDA exact for E_X as Z-> ∞.
- Looks like finite E_C corrections
- Looks like extended TF (treated as a potential functional) gives some sort of average.
- Lucian Constantin, John Snyder, JP Perdew, and KB, JCP (2010).

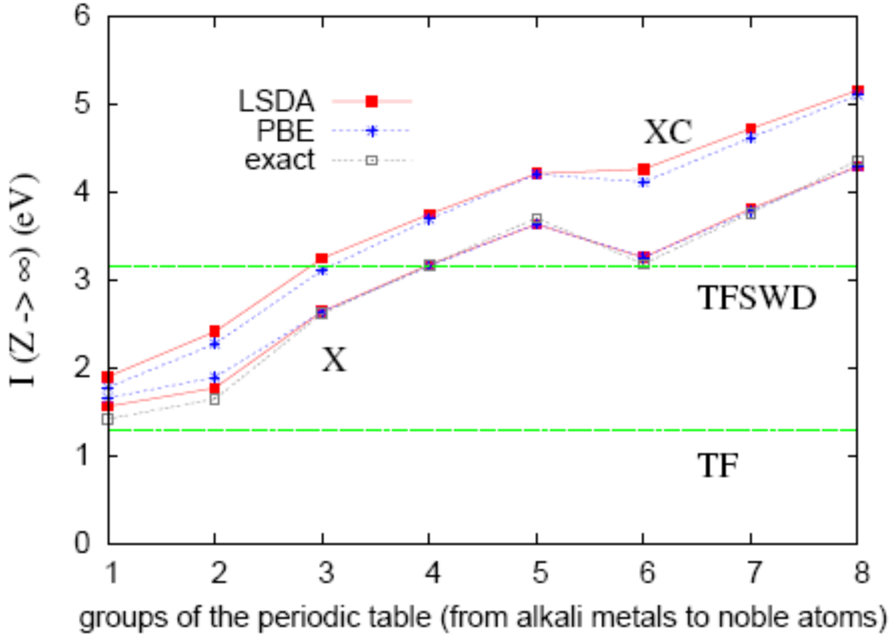


FIG. 1: Ionization potentials of the main groups in the limit of large row number of the periodic table, calculated using exact exchange, the local (spin) density approximation (LSD), and PBE. We also show the extended TF result.

Ionization density for large Z

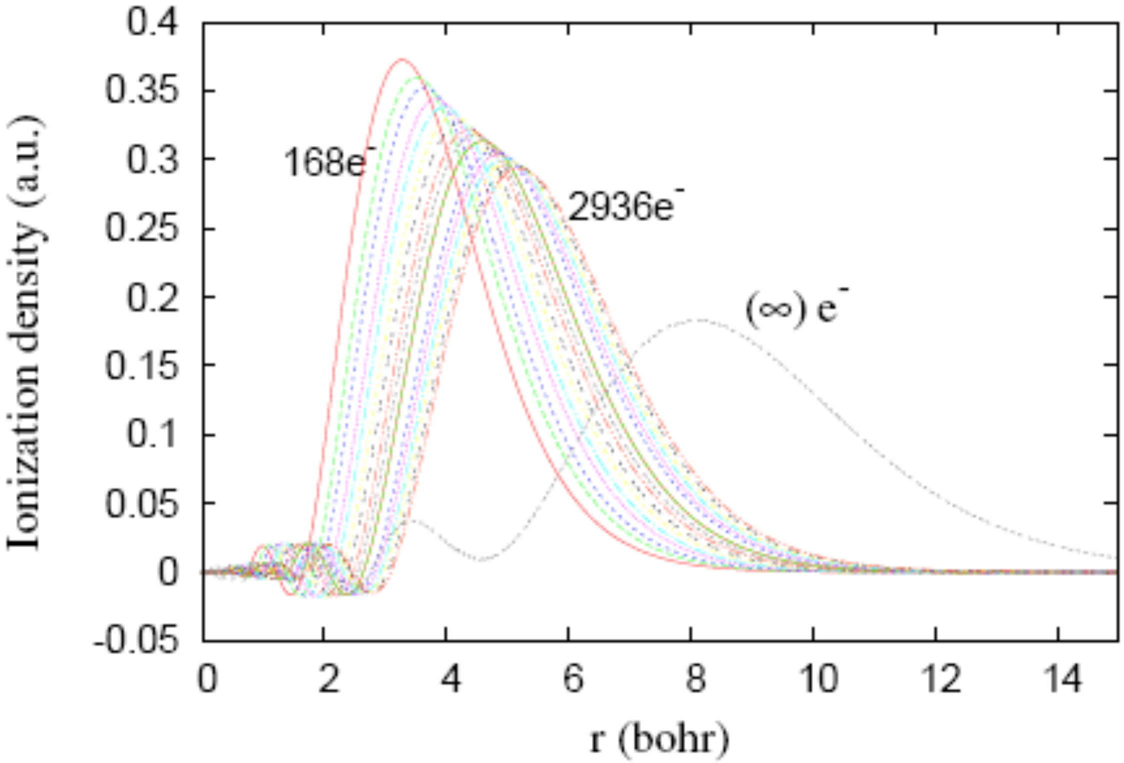
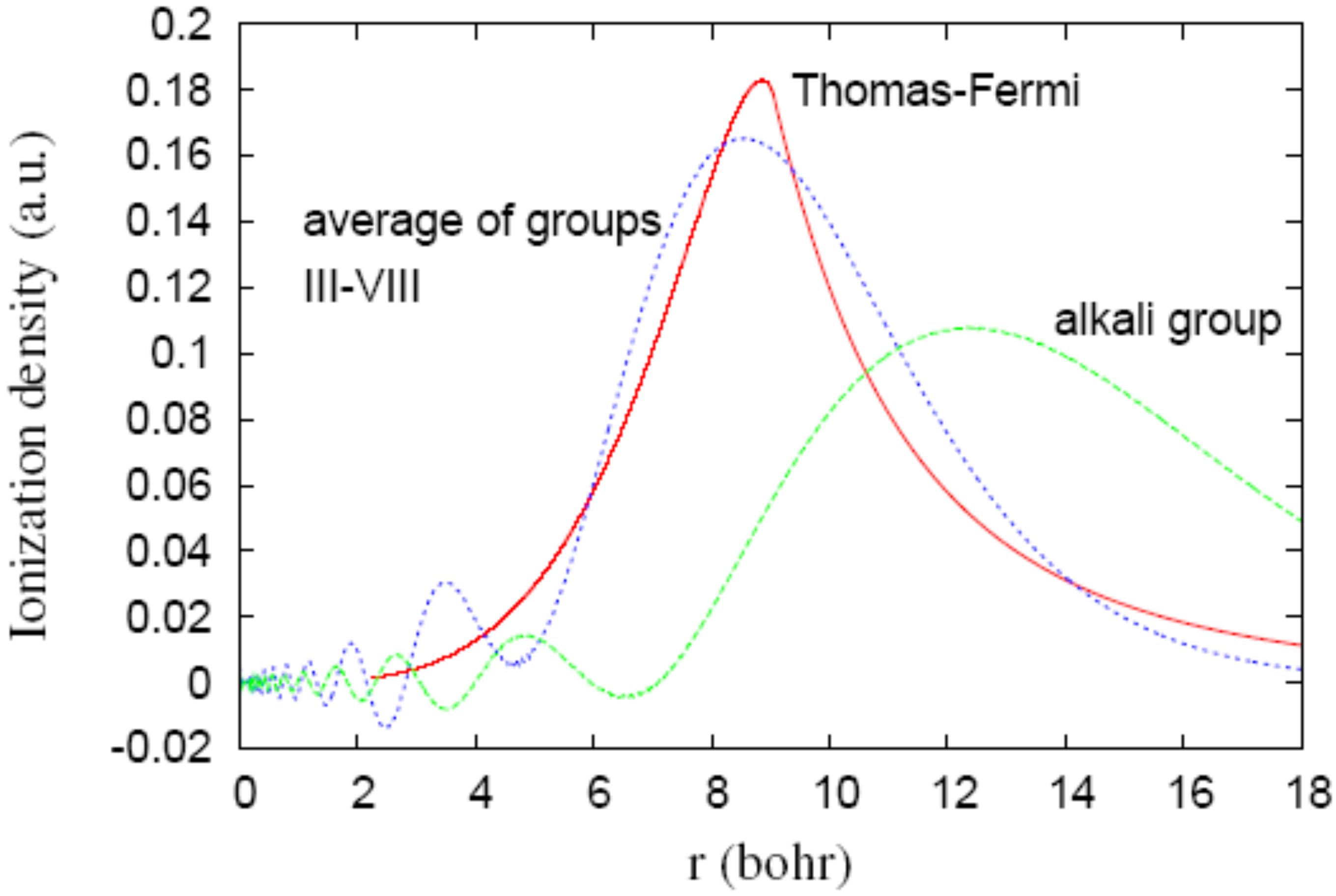


FIG. 4: Same as Fig. 3, but for the VIIIth or noble-gas column of the periodic table at various finite Z and in the limit $Z \to \infty$.

Ionization density as Z→∞



Leading corrections to n[v](**r**)

$$n^{\mathrm{sc}}(x) = \frac{p_{\mathrm{F}}(x)}{\hbar}\left[\left(\sqrt{z}\,\mathrm{Ai}^2(-z) + \frac{\mathrm{Ai}'^2(-z)}{\sqrt{z}}\right) + \left(\frac{\hbar\omega_F \csc[\alpha_F(x)]}{p_{\mathrm{F}}^2(x)} - \frac{1}{2z^{3/2}}\right)\mathrm{Ai}(-z)\ \mathrm{Ai}'(-z)\right]_{z=z_{\mathrm{F}}(x)}$$

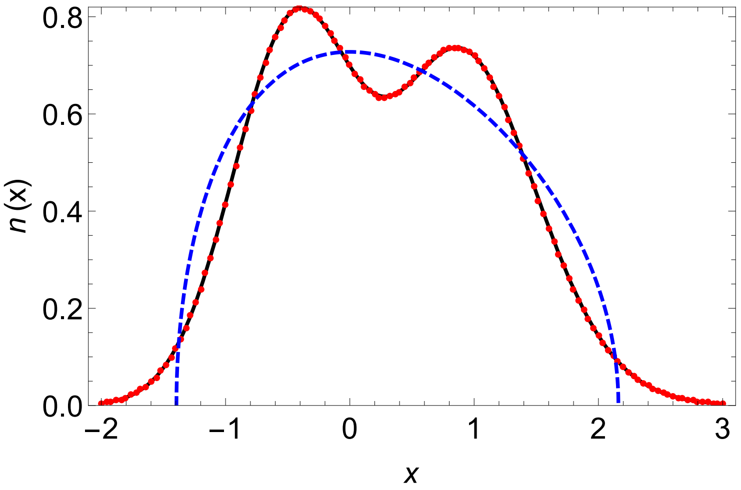


FIG. 1. Thomas-Fermi (dashed) and semiclassical (dotted) approximations to the density (solid) of 2 particles in a Morse potential, $v(x) = 15(e^{-x/2} - 2\,e^{-x/4})$.

Corrections to Thomas-Fermi Densities at Turning Points and Beyond Raphael F. Ribeiro, Donghyung Lee, Attila Cangi, Peter Elliott, Kieron Burke, *Phys. Rev. Lett.* **114**, 050401 (2015).

After a decade of work

[99] **Relevance of the Slowly Varying Electron Gas to Atoms, Molecules, and Solids** John P. Perdew, Lucian A. Constantin, Espen Sagvolden, Kieron Burke, *Phys. Rev. Lett.* **97**, 223002 (2006).

[108] **Restoring the Density Gradient Expansion for Exchange in Solids and Surfaces** John P. Perdew, Adrienn Ruzsinszky, Gábor I. Csonka, Oleg A. Vydrov, Gustavo E. Scuseria, Lucian A. Constantin, Xiaolan Zhou, Kieron Burke, *Phys. Rev. Lett.* **100**, 136406 (2008).

[111] **Semiclassical Origins of Density Functionals** Peter Elliott, Donghyung Lee, Attila Cangi, Kieron Burke, *Phys. Rev. Lett.* **100**, 256406 (2008).

[113] **Condition on the KohnSham kinetic energy and modern parametrization of the ThomasFermi density** Donghyung Lee, Lucian A. Constantin, John P. Perdew, Kieron Burke, *J. Chem. Phys.* **130**, 034107 (2009).

[118] **Nonempirical derivation of the parameter in the B88 exchange functional** Peter Elliott, Kieron Burke, *Canadian Journal of Chemistry* **87**, 14851491 (2009).

[125] **Leading corrections to local approximations** Attila Cangi, Donghyung Lee, Peter Elliott, Kieron Burke, *Phys. Rev. B* **81**, 235128 (2010).

[128] **Communication: Ionization potentials in the limit of large atomic number** Lucian A. Constantin, John C. Snyder, John P. Perdew, Kieron Burke, *The Journal of Chemical Physics* **133**, 241103 (2010).

[130] **Electronic Structure via Potential Functional Approximations** Attila Cangi, Donghyung Lee, Peter Elliott, Kieron Burke, E. K. U. Gross, *Phys. Rev. Lett.* **106**, 236404 (2011).

[146] **Potential functionals versus density functionals** Attila Cangi, E. K. U. Gross, Kieron Burke, *Phys. Rev. A* **88**, 062505 (2013).

[157] **Almost exact exchange at almost no computational cost in electronic structure** Peter Elliott, Attila Cangi, Stefano Pittalis, E. K. U. Gross, Kieron Burke, *Phys. Rev. A* **92**, 022513 (2015).

[158] **Atomic correlation energies and the generalized gradient approximation** Kieron Burke, Antonio Cancio, Tim Gould, Stefano Pittalis, *submitted and ArXiv:1409.4834* (2014).

[159] **Corrections to Thomas-Fermi Densities at Turning Points and Beyond** Raphael F. Ribeiro, Donghyung Lee, Attila Cangi, Peter Elliott, Kieron Burke, *Phys. Rev. Lett.* **114**, 050401 (2015).

[170] **Uniform semiclassical approximations for one-dimensional fermionic systems** Raphael F. Ribeiro, Kieron Burke, *submitted and ArXiv:1510.05676* (2015).

Summary

- Underlying success of DFT approximations is because they are semiclassical.
- I defy you to find semiclassical approximations in your many-body book (this specific limit).
- Very difficult to generate general forms:
  - Standard methods often useful only in 1d
  - Often fail in presence of Coulomb potentials
  - Can reverse-engineer to deduce forms, but very difficult.

Holy grail?

- What formulation of QM might directly yield expressions for density functionals?
- Within such a formulation, it should be natural to show LDA exact in Lieb-Simon limit.
- It should be possible to isolate leading corrections.
- It may be possible to capture essential features with simple density functionals.

D Machine learning

- An entirely different approach to finding approximate density functionals.

Machine learning

- Powerful branch of artificial intelligence
- Essentially fitting and interpolating
- Maps problem into much higher-dimension feature space, using a simple kernel
- Higher-dimension often means more linear
- Perform regression in feature space
- Project back to original problem

Kernel ridge regression

- Kernel ridge regression (KRR). Given $\{\mathbf{x}_j, f_j\}$

$$\hat{f}(\mathbf{x}) = \sum_{j=1}^{M} \alpha_j k(\mathbf{x}_j, \mathbf{x})$$

length scale

$$k(\mathbf{x}, \mathbf{x}') = \exp(-\|\mathbf{x} - \mathbf{x}'\|^2/(2\sigma^2))$$

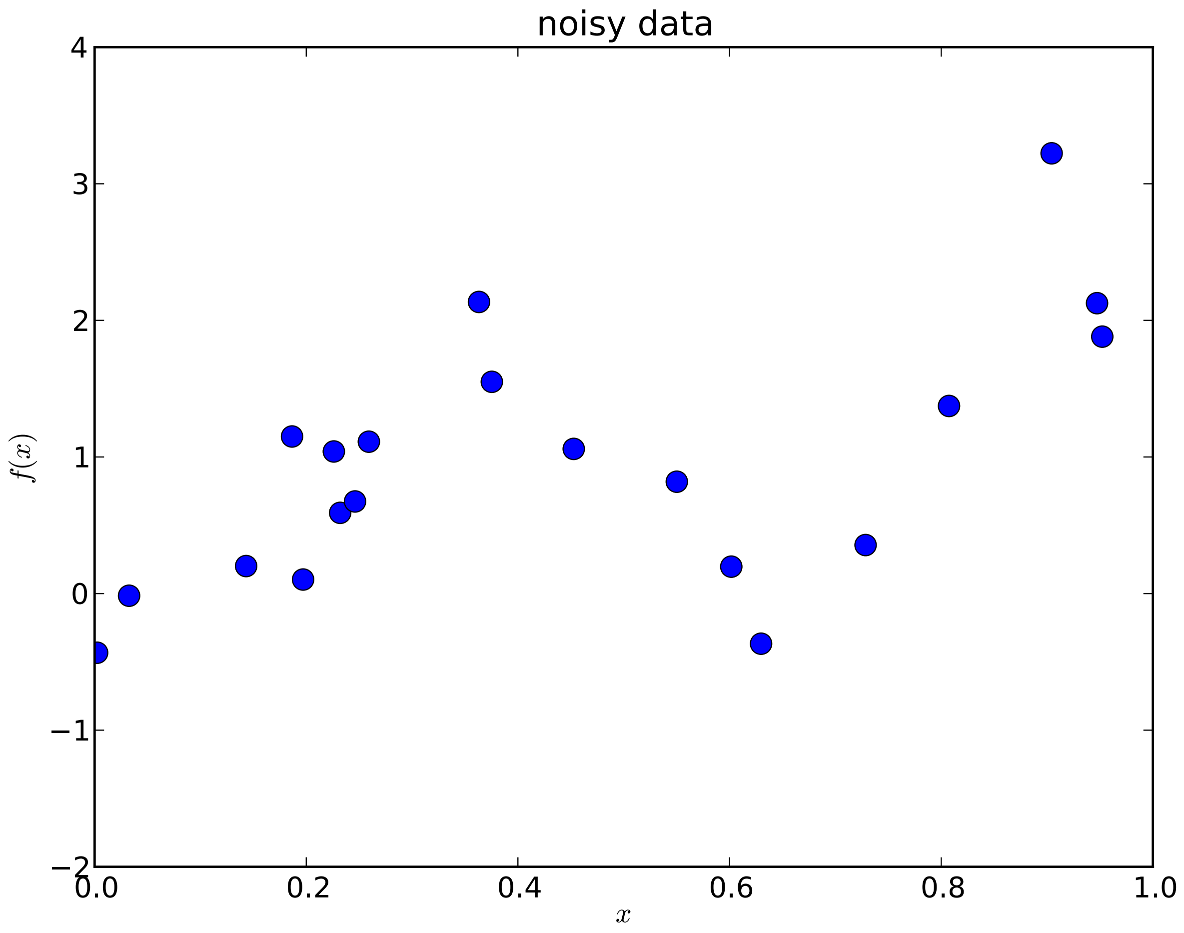
- Minimize:

$$\mathcal{C}(\boldsymbol{\alpha}) = \sum_{j=1}^{M} (\hat{f}(\mathbf{x}_j) - f_j)^2 + \lambda^2 \|\alpha\|^2$$

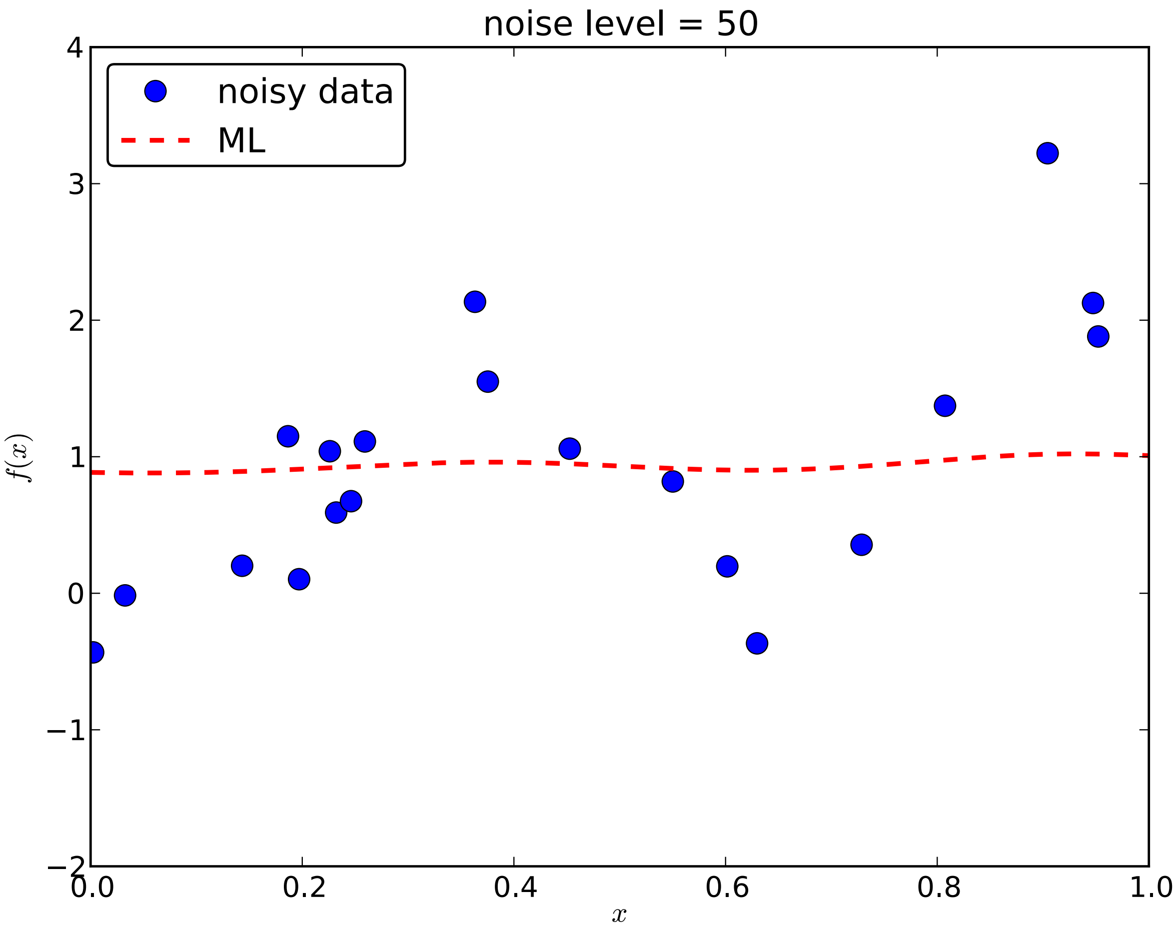
noise level

$$\boldsymbol{\alpha} = (K + \lambda^2 I)^{-1} \mathbf{f}$$

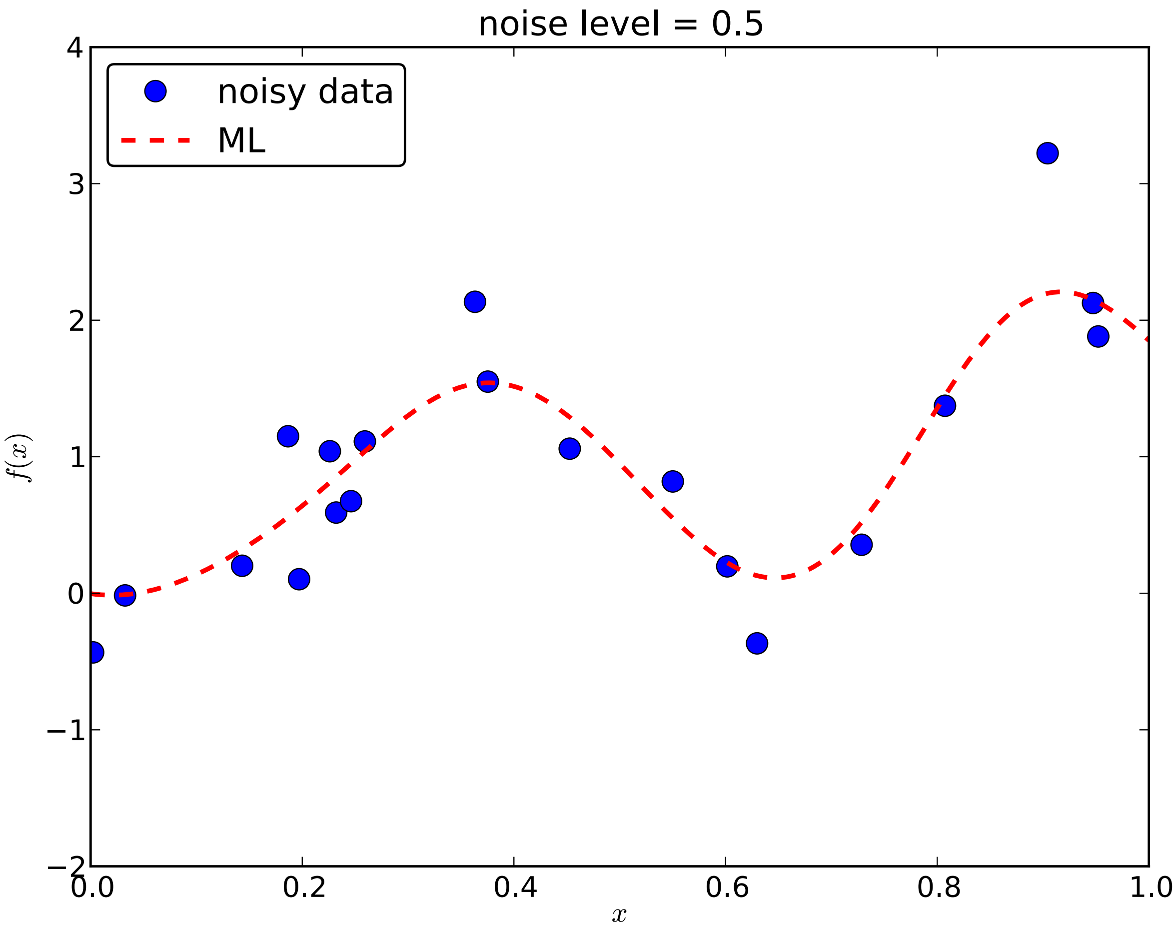
Fitting a simple function



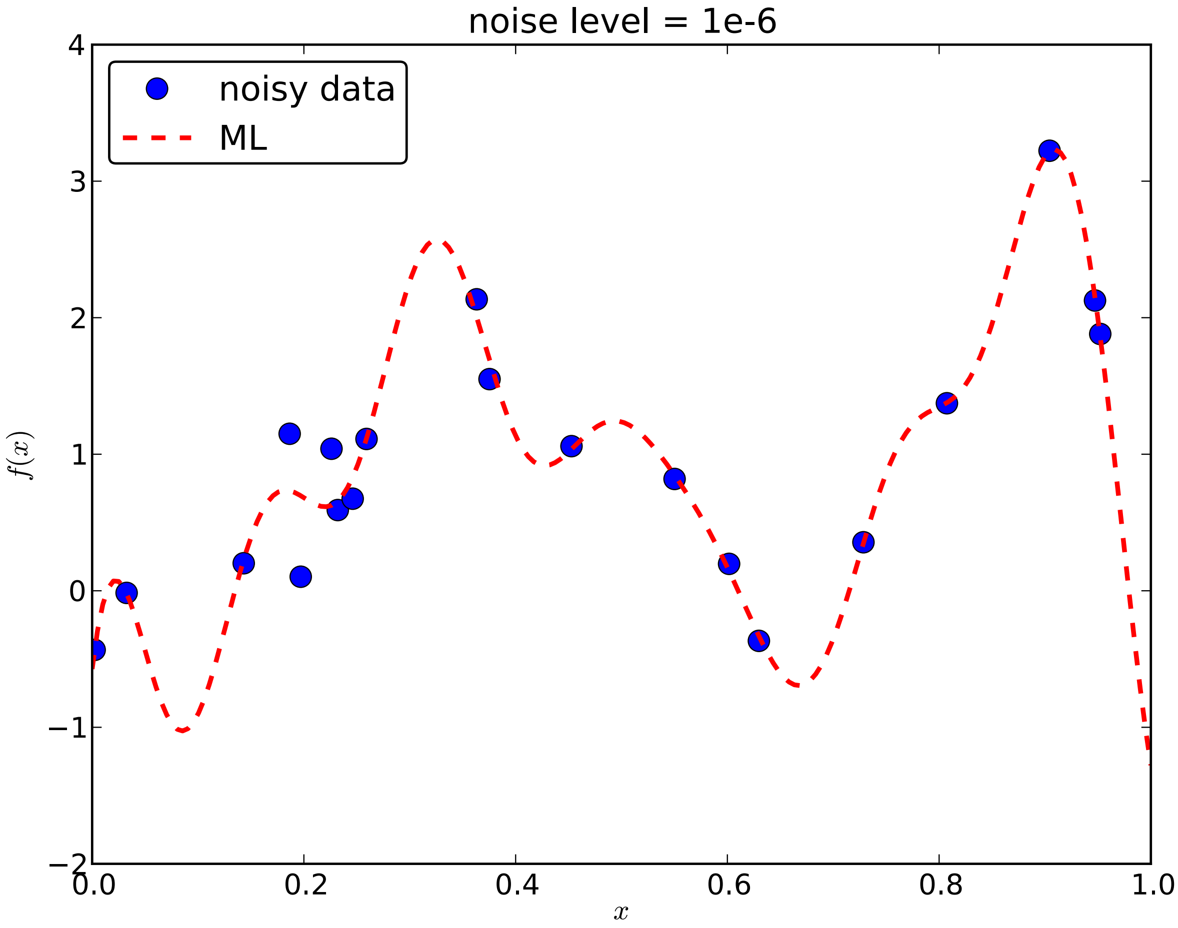
Too high noise level: underfit



Medium noise level

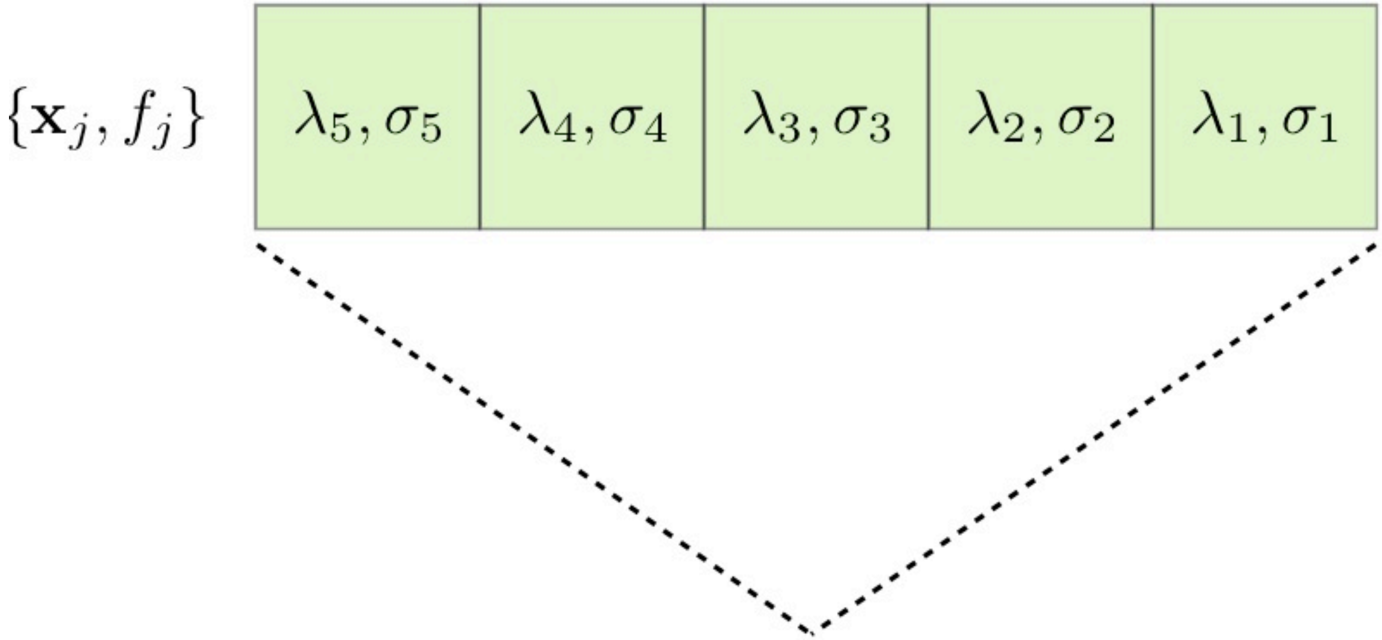


Small noise level: overfit



Average over samples

- Always optimize on samples *not* in the training set

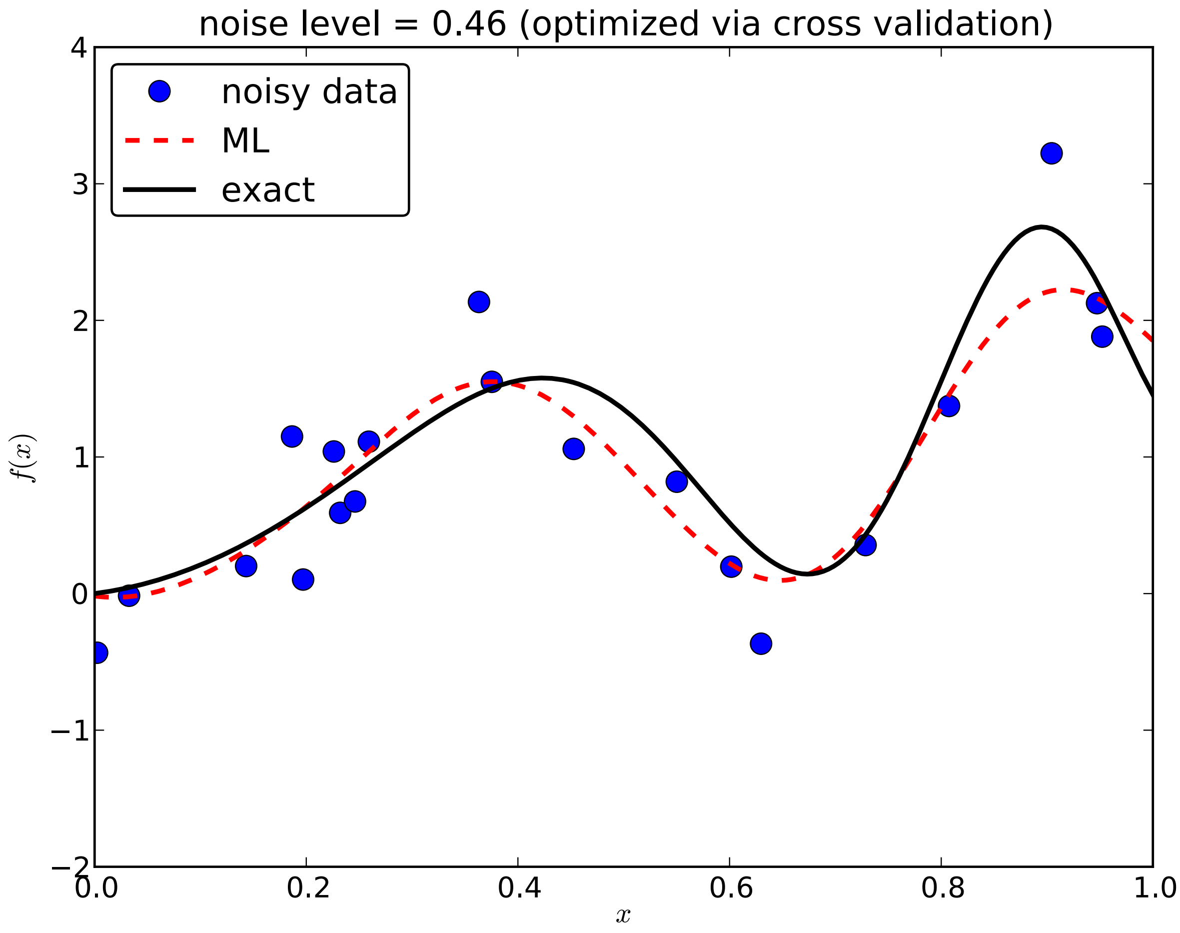


$\{\mathbf{x}_j, f_j\}$

λ_5, σ_5 | λ_4, σ_4 | λ_3, σ_3 | λ_2, σ_2 | λ_1, σ_1

$$\lambda, \sigma = \text{median}_j \{\lambda_j, \sigma_j\}$$

Exact function and best fit



Basic idea

- For a limited variety of one-body potentials, construct functionals via ML that are sufficiently accurate to do the job.
- Typically, require accuracy of 1 kcal/mol =0.0015 Ha.
- For kinetic energy, also need functional derivative.
- Most useful when multiple slightly different uses of DFT, eg during an MD run.
- Functional could be disposable, i.e., thrown away at end of run.
- Totally irrelevant that it does not apply to other systems.
- Is completely non-local in general, so best advantage when bonds break, as local functionals fail.

ML applications in electronic structure

- Most with Klaus Mueller of TU Berlin, computer science.


Klaus-Robert Müller

- ML now being applied directly to, e.g., molecular energies from geometries for drug design, many by Matthias Rupp (FHI Berlin).


Matthias Rupp

- Our efforts are focused on finding $T_s[n]$ from examples, work by John Snyder (Humboldt fellow at TU Berlin/MPI Halle)


John Snyder

Demo problem in DFT

- *N* non-interacting same-spin fermions confined to 1d box

- Define class of potential:

$$v(x) = -\sum_{i=1}^{3} a_i \exp(-(x-b_i)^2/(2c_i^2))$$

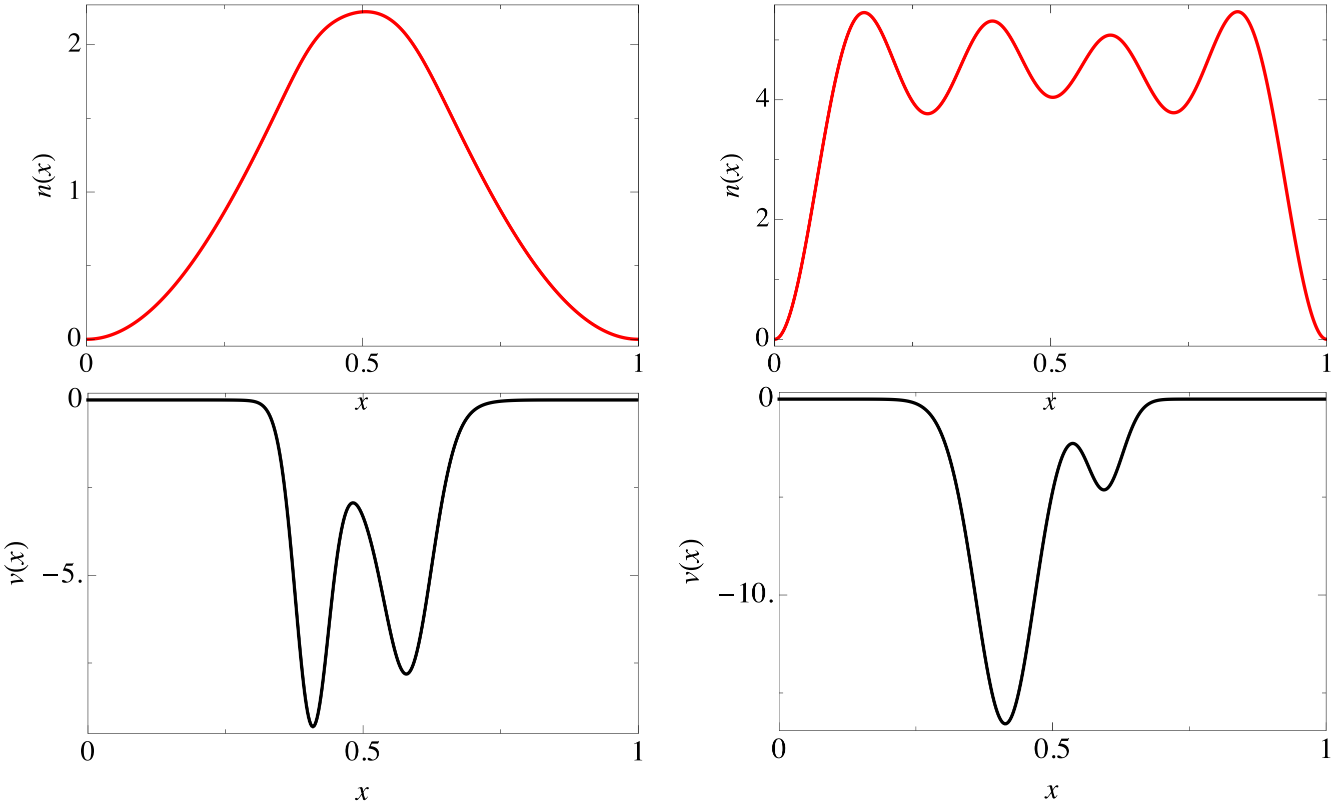
- Represent the density on a grid with spacing $\Delta x = 1/(G-1)$

- ML-DFA for KE:

$$\hat{T}(\mathbf{n}) = \bar{T} \sum_{j=1}^{M} \alpha_j k(\mathbf{n}_j, \mathbf{n})$$

Dataset

Generate 2000 potentials. Solve for up to 4 electrons.



Performance for T_s

kcal/mol

N	M	λ	σ	$\overline{\lvert\Delta T\rvert}$	$\lvert\Delta T\rvert^{\mathrm{std}}$	$\lvert\Delta T\rvert^{\mathrm{max}}$
1	40	2.4×10^{-5}	238	3.3	3.0	23.
	60	1.0×10^{-5}	95	1.2	1.2	10.
	80	6.7×10^{-6}	48	0.43	0.54	7.1
	100	3.4×10^{-7}	43	0.15	0.24	3.2
	150	2.5×10^{-7}	33	0.060	0.10	1.3
	200	1.7×10^{-7}	28	0.031	0.053	0.65
2	100	1.3×10^{-7}	52	0.13	0.20	1.8
3	100	2.0×10^{-7}	74	0.12	0.18	1.8
4	100	1.4×10^{-7}	73	0.078	0.14	2.3
1-4†	400	1.8×10^{-7}	47	0.12	0.20	3.6

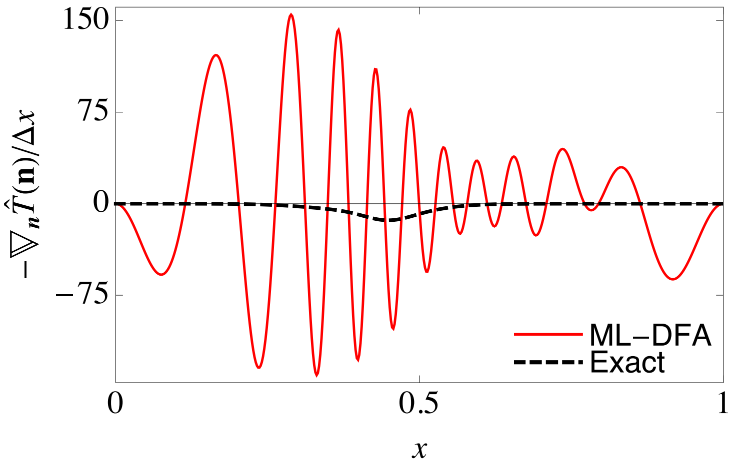
LDA ~ 223 kcal/mol, Gradient correction ~ 159 kcal/mol

functional derivative?

Exact **ML-DFA**

$$\frac{\delta T[n]}{\delta n(x)} = \mu - v(x) \longleftrightarrow \frac{1}{\Delta x}\nabla_{\mathbf{n}}\hat{T}(\mathbf{n}) = \sum_{j=1}^{M} \alpha'_j(\mathbf{n}_j - \mathbf{n})k(\mathbf{n}_j, \mathbf{n})$$

$$\alpha'_j = \alpha_j/(\sigma^2 \Delta x)$$



- Functionals are defined on infinite-dimensional spaces
- With finite interpolation, can always find bad directions
- Can we make a cruder definition that will work for our purposes?

Principal component analysis

$$X = (\mathbf{n}_{j_1} - \mathbf{n}, \ldots, \mathbf{n}_{j_m} - \mathbf{n})^\top$$

$$C = \frac{1}{m} X^\top X$$

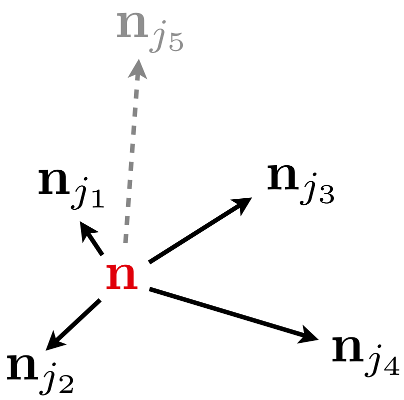
$$\downarrow$$

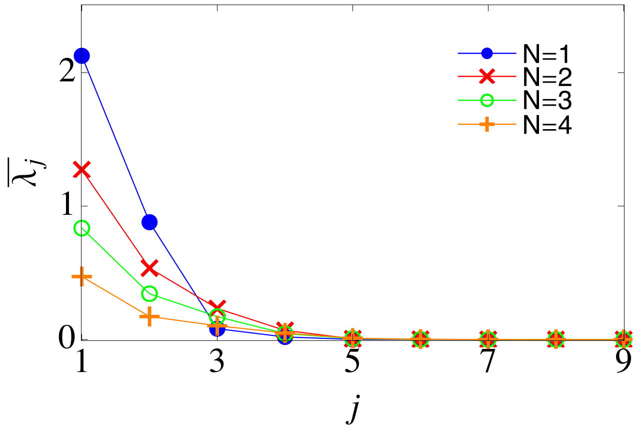
$$\lambda_j, \mathbf{x}_j$$

$$\downarrow$$

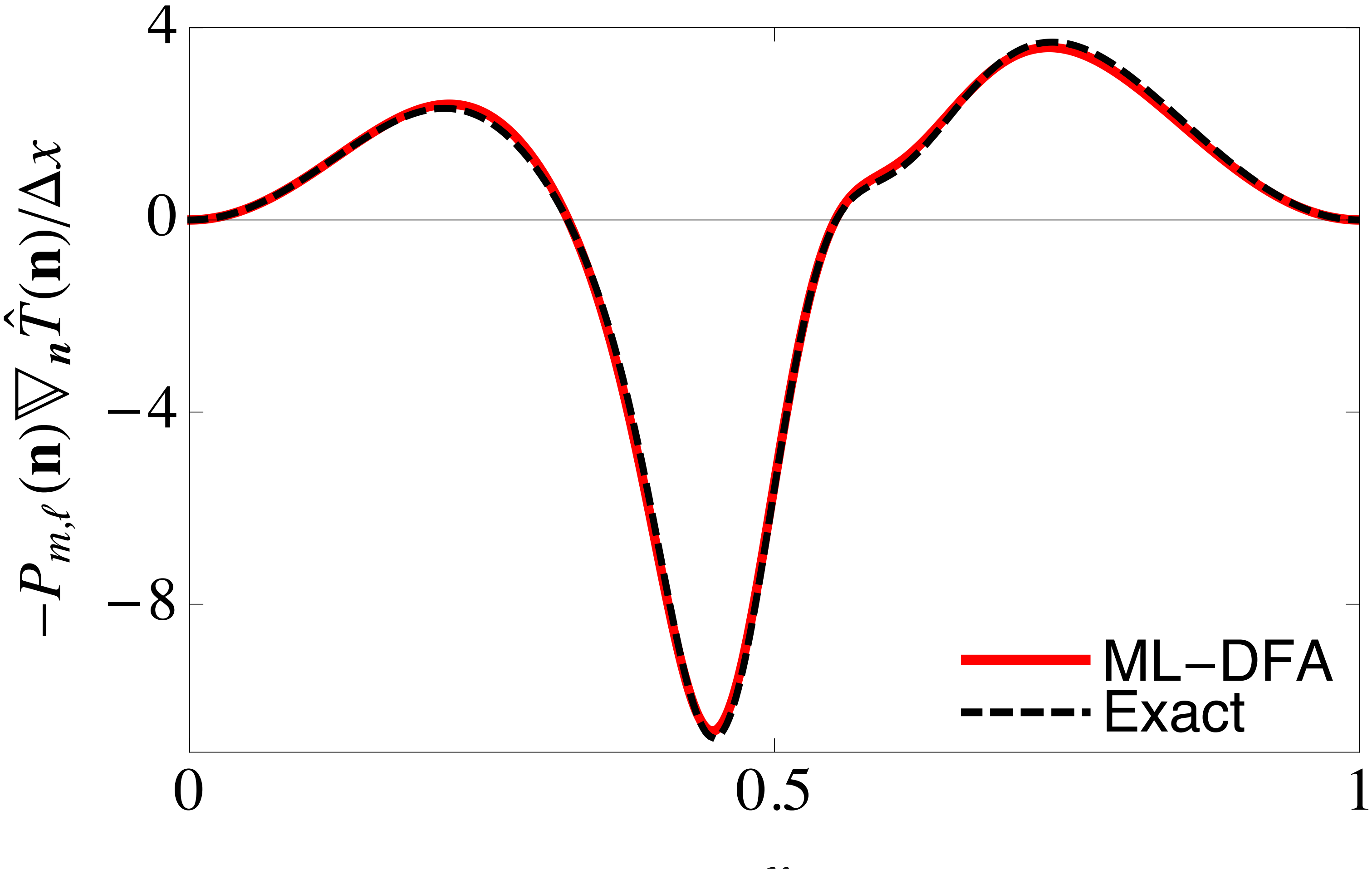
$$P_{m,\ell}(\mathbf{n}) = V^\top V$$

$$V = (\mathbf{x}_1, \ldots, \mathbf{x}_\ell)^\top$$





Projected functional derivative



First ‘ML makes a functional’ paper

26	−22.3897314906413	3.751807395744921	0.0852624107335768	0.4453450848668749	7.559337237177321	0.05840909867970421	0.4990223467101435	4.729884445483556	0.0929218712306724	0.5590503374710945
27	5.595799173773367	4.522456026868127	0.03620201946841309	0.5050210060676815	1.885091277540955	0.06521780385848891	0.4961601035955842	9.47421945496329	0.0556740133396159	0.4834045749740091
28	1.94645582566549	2.751346713386582	0.0948195528516815	0.4901204212506473	7.863592227266858	0.0951797983951825	0.5196620049802691	9.51608680035275	0.07785377315463609	0.5806015592262945
29	−1.105559822533069	5.725277193011525	0.03097303116261406	0.5511177785567803	7.988513342309234	0.0928323179868588	0.5146415116367569	1.101098863639624	0.0882939028519791	0.5265108634130272
30	−3.886381532577754	4.95871172966177	0.06823254438777603	0.5645951313008806	9.08135225317634	0.04472856905840844	0.4299117124064201	8.24973637849809	0.08854431361856	0.5416193648861009
31	−1.341930696378109	6.451869235304859	0.05482804889270922	0.5694170176403242	4.416924333519995	0.04212208612720639	0.5897125000677342	8.86521100790565	0.0866581794842557	0.5311744230227635
32	−10.16467121571373	6.705508349541454	0.0934749698077619	0.4420693171728495	2.858371131410651	0.03722557506068529	0.4216580500297413	6.670274811535954	0.0977332470946321	0.538756085129185
33	−1.107633246744663	7.390220519784453	0.07970661674181083	0.5081940602224835	3.815123656821275	0.04965529863397879	0.497023655525965	9.69945245311718	0.07039341131023045	0.4990744291774679
34	10.39451871866851	1.478170300165134	0.03602109509210016	0.5799113381048154	2.105782960173057	0.0861928382367878	0.4812528298377607	7.010226383015251	0.03535327789989237	0.4969989664577149
35	−0.139925361351959	4.045190240200832	0.03579955552582782	0.5678362348598895	9.32386837735074	0.0858648976559044	0.5698752996855582	9.81895903799508	0.04704020956533079	0.5708692337579542
36	3.656124569605117	4.944179742822627	0.0931916525333049	0.4834640277977335	9.3847979419491	0.0840810063497973	0.4090254720704045	3.673880603434117	0.07158934023489803	0.5598196803643543
37	8.06734679112684	2.988178201634472	0.07482186947515447	0.4950144569660614	1.910770315838324	0.03877152903045122	0.5786659568499292	4.285706479098184	0.05940487550770145	0.4844513368813702
38	0.3011566621835722	8.78996207364355	0.04833452393773747	0.459203937360375	9.93467757777873	0.0973964303071365	0.4280349684453508	4.931948094146255	0.0969410287755626	0.4560660353529726
39	−0.2469178958324283	6.242957525364009	0.0989568314234112	0.4205662570527381	4.73983230004983	0.0450110225161678	0.559400017887981	9.11978947943194	0.06189826031162779	0.493100819449519
40	−5.704905642148452	4.447521595114223	0.06770523205457797	0.5047965897298675	3.987888630073714	0.03595136615254331	0.5929011044925536	5.22121823715344	0.04029431905467698	0.514129411681418
41	0.1425795779687519	6.919606258393273	0.0821756368975312	0.5976799418614426	8.04099037018168	0.03129262110881438	0.4686530881925831	3.421695873368174	0.05166215779587051	0.4208560803818513
42	0.6843702894502789	8.27200587323167	0.0547013388431661	0.4453254786423237	7.433883810628654	0.04612202343826998	0.5269730370279639	8.3641619521824	0.07996879390804805	0.5036755718396144
43	−14.06571757369153	6.220712308892191	0.04765956545437692	0.4898959293071353	8.72249431241257	0.05059967705235588	0.4421274052875277	2.416276423317733	0.07373660930828208	0.5403850652535799
44	8.32346109443768	9.29716067662943	0.0656810603414827	0.4960066859011466	6.796263459296078	0.04037116107097755	0.4389885737869158	2.206183147865627	0.0804910989081056	0.5806221323132373
45	−5.252317079780442	3.424683176707511	0.0867529985575643	0.4322548560407479	6.859255296971943	0.0955962752949951	0.517620399931194	5.826144942819697	0.0910408442631135	0.4167014408128501
46	6.18641388898792	3.789578783769164	0.07617326304382499	0.5418490045761073	1.363177133649232	0.03197249245240319	0.5284999992906743	4.9879001955338	0.04126125322920861	0.4895167206754735
47	0.4821906326173532	1.195769022526768	0.04928749082970199	0.5286859472378347	8.76714063033632	0.0870852412295278	0.5989638152903285	2.489565114307663	0.05568685410478115	0.5787056957942209
48	5.707663438868804	4.058614230578957	0.04743875933294599	0.4981149890354436	1.015171237842736	0.085826684646538	0.5470349320774566	6.343764732282688	0.0878769436185823	0.5449452367497044
49	−0.1857958679022612	5.159763617905121	0.0850570422587659	0.5311491284465588	7.238990148015965	0.05867048711393652	0.5662410781222187	8.70600609334284	0.04088387548046445	0.5305143392409284
50	2.321594443893878	3.319181325761367	0.05391080867981007	0.5914435434600773	9.11776045377491	0.03583354001918901	0.4669413688494417	6.117669336479262	0.04553014156422459	0.4131324263527175
51	2.451069994722774	4.005247740100538	0.07620861067494449	0.5759225433332955	6.743529978394792	0.0967347280360008	0.4980631985926895	5.505849306951131	0.0971440363586883	0.45173467721102
52	−0.961350897030818	7.710615861039985	0.07131617125307138	0.4007362522722102	3.372061685311945	0.04579335436967417	0.4845503268496217	8.6021995929235	0.0634681851083368	0.4207242810824543
53	−10.67971490671366	4.728468083127391	0.06509200806253813	0.4959400801351127	9.81266481664175	0.0951346706530719	0.5047212015277842	3.180268423645401	0.06891913385037023	0.5758580789792047
54	1.375998039323297	2.740626958875014	0.06438323836566841	0.5077158168564866	1.813952930718781	0.0845523320869031	0.407247659218711	1.054506345314588	0.0998274789144316	0.5956344420441539
55	−4.330863793299111	3.209443235555092	0.05150806767094947	0.5932432195310449	4.682408324655706	0.03641376226612134	0.4491940043173043	9.57800470422746	0.089704223465467	0.4702887735348434
56	6.961655278126058	3.013659237176324	0.0802684211883349	0.5733460791404235	7.441047648005995	0.0924462539370359	0.5216671466381739	8.15403131934562	0.05611934350568269	0.4910483719005932
57	−5.30540083281513	2.088882156026381	0.07464091227469428	0.4740072756248339	4.228694369663863	0.03993178348974601	0.4402946238148492	4.912298433960689	0.06528359492264517	0.4923580906843156
58	3.395104400983763	7.9733680986292	0.0911843583955236	0.5314007871406556	6.375772536276909	0.0933026364108379	0.447244215655568	7.387561983870292	0.0977643384454912	0.479824590293356
59	1.330224789015745	5.105339790874075	0.06331718284342962	0.5503804706506275	9.5740821641842	0.07463500644132846	0.5814481952546582	5.810342341443878	0.03327635127803191	0.5550216356360829
60	−0.2920604955263079	6.773414983805557	0.07595819905259191	0.5210834626114553	4.229974804881476	0.03532177545633547	0.5725615130215063	8.88452823254966	0.0932985710685446	0.5046388124857028
61	−26.41840990525562	6.41701161854283	0.06246944646172664	0.4258923441426071	1.379491105318868	0.06306367927818108	0.4531443030507202	2.189456974183496	0.098078005933584	0.5174384564079299
62	6.630393088825135	6.476325542442256	0.07599435647188182	0.4345528705798566	6.969363897694016	0.06669302037176108	0.517427894398595	3.961825639220393	0.0929115322244988	0.4621043570336795
63	3.065748817227897	1.300093759156537	0.06741885075599173	0.4866345116967513	6.942052331590217	0.07107963920756023	0.4930672781311588	7.834870626014938	0.06446115603870624	0.5367219218216266
64	−1.743105697039855	3.145607697855832	0.0415292						0.07636214080338054	0.4330291254331895
65	−1.631255302904965	3.121291975208031	0.0313356						0.0936192481138518	0.4523240987335903
66	−9.50982692642515	7.367027947839741	0.0739810						0.04986976063479617	0.5394709698394433
67	−4.496736421068983	8.56498650586069	0.0870950						0.05651923264880363	0.4832351547748815
68	−1.002977917543076	9.43121814362608	0.0368989						0.05983735955021298	0.4837560035001434
69	−9.23106545170694	8.47929696159459	0.0547214						0.06892772167363432	0.5908529311844791
70	14.99926304831282	4.708917711658332	0.0907364						0.05825558914206748	0.566434199642786
71	4.189181104505013	7.583635162152007	0.0936829						0.04763840334231468	0.5010633160850224
72	8.328371188138842	3.414315967033806	0.05054048464274665	0.5043307410524706	3.070996567281799	0.06968276328974509	0.5702669702356848	5.360783854112533	0.0388888383066967	0.5784155467566237
73	−21.84200888491582	1.625552430388586	0.04546236831654488	0.5426078576324179	4.091176923293506	0.03836885039652842	0.504879512949007	4.527748284314512	0.05975894102927981	0.4670598506496871
74	6.604738977945651	3.42187897931262	0.0894449950697187	0.4941485628974172	4.96749741331263	0.06031151123783582	0.4119028637456998	4.581927607849956	0.0871948963692279	0.4176805754532423
75	15.27988423246628	6.229538426957454	0.0821521091215863	0.4118748449252315	2.377028497509498	0.0963110933106458	0.4746736556808109	5.398545541594487	0.0822574656780643	0.5258947233190487

Finding Density Functionals with Machine Learning John C. Snyder, Matthias Rupp, Katja Hansen, Klaus-Robert Müller, Kieron Burke, Phys. Rev. Lett. **108**, 253002 (2012)

Lessons

- Exact noise-free data infinitely available for $T_s[n]$, every cycle of every KS calculation in the world provides examples.
- Need very accurate derivatives to get accurate density from Euler equation.
- Can find ways to bypass this.
- Functionals can be made arbitrarily accurate with sufficient data.

E.Recent results

- All on arXiv

Felix Brockherde

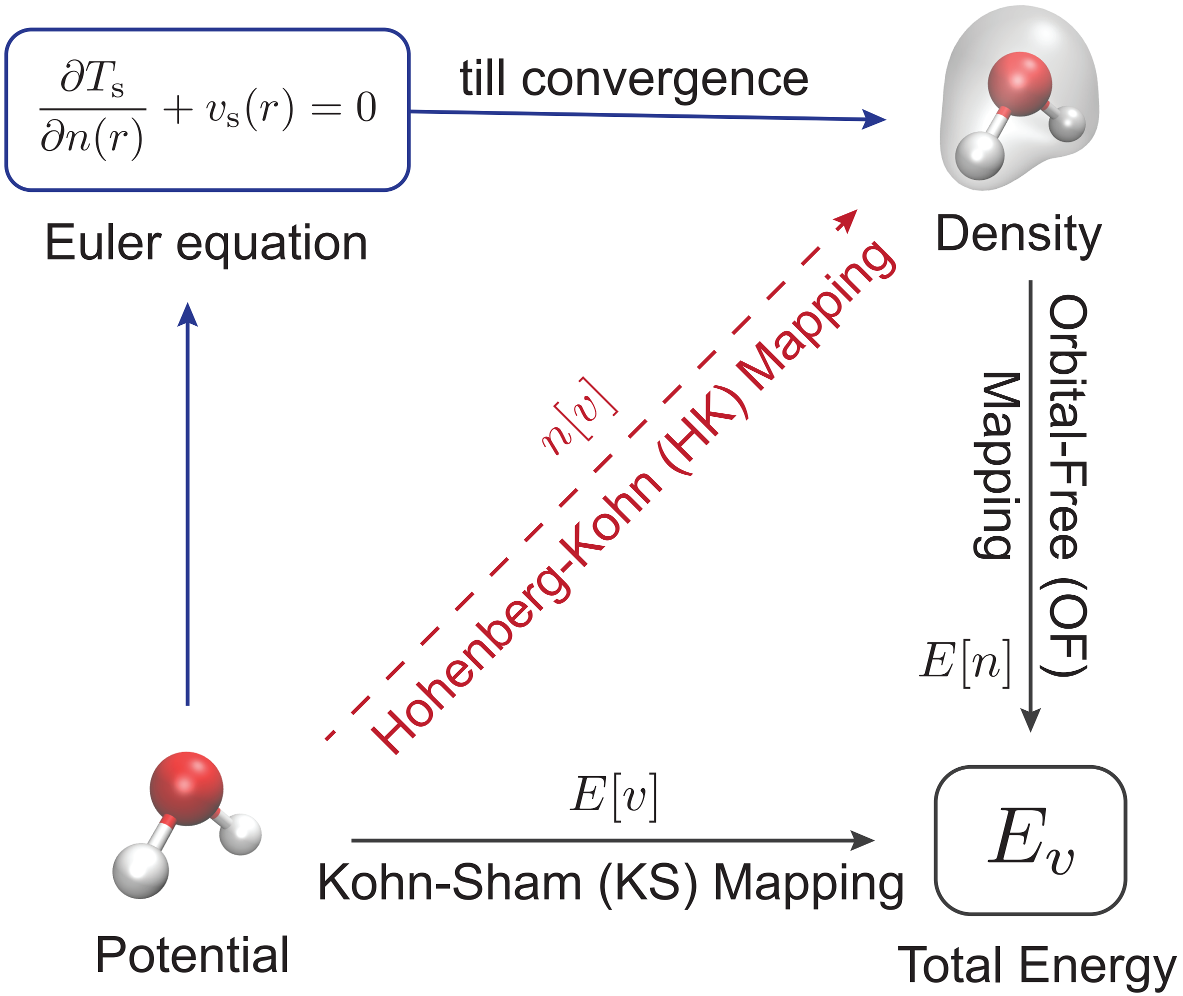
Li Li

Thomas E. Baker

2 new papers

- *By-passing the KS equations with ML (on arXiv)*
  - Felix Brockherde, Li Li, Klaus Muller, KB,…
  - Avoids functional derivative
  - Applied in 3D
  - Still doing KS problem, $T_s[n]$
- *Pure Density Functional for Strong Correlations and the Thermodynamic Limit Using Machine Learning. in Phys Rev B.*
  - Li Li, Thomas E. Baker, Steven R. White and KB
  - Do interacting functional (ie. Exact Exc)
  - Do strong correlation
  - Do thermodynamic limit
  - Still in 1d

By-passing KS



$$\frac{\partial T_{\mathrm{s}}}{\partial n(r)} + v_{\mathrm{s}}(r) = 0$$

Euler equation

till convergence

Density

Orbital-Free (OF) Mapping

$E[n]$

$n[v]$

Hohenberg-Kohn (HK) Mapping

Potential

$E[v]$

Kohn-Sham (KS) Mapping

$$\boxed{E_v}$$

Total Energy

Performance of ML for HK map

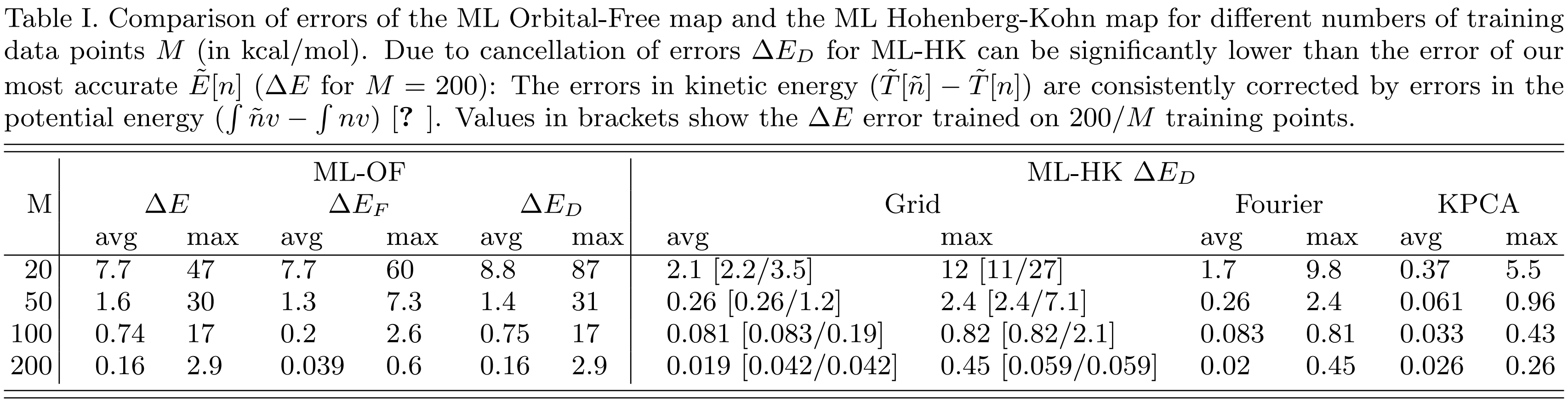
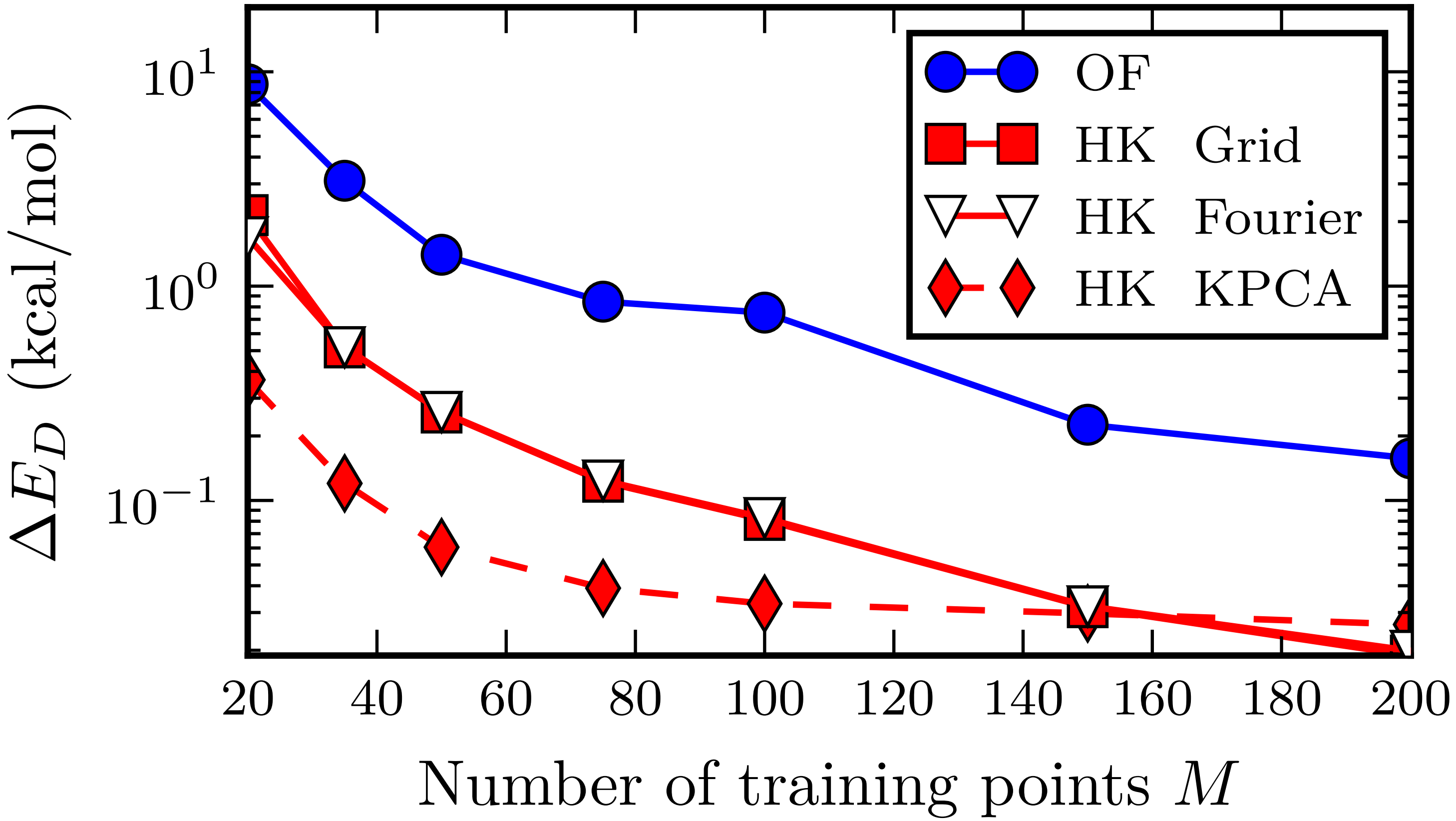


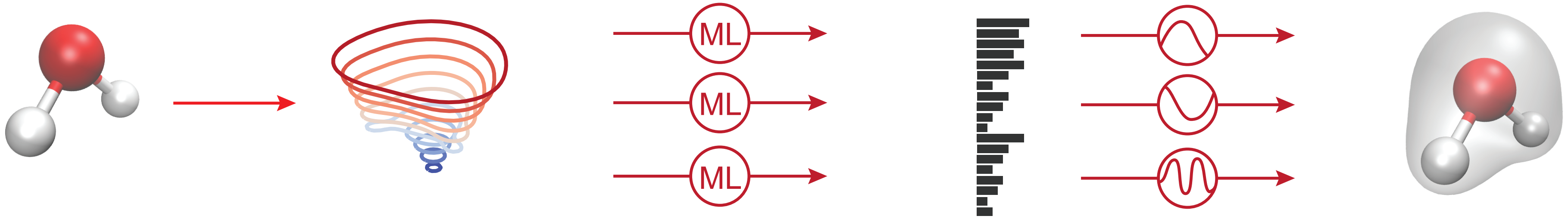
Table I. Comparison of errors of the ML Orbital-Free map and the ML Hohenberg-Kohn map for different numbers of training data points M (in kcal/mol). Due to cancellation of errors ΔE_D for ML-HK can be significantly lower than the error of our most accurate $\tilde{E}[n]$ (ΔE for $M = 200$): The errors in kinetic energy ($\tilde{T}[\tilde{n}] - \tilde{T}[n]$) are consistently corrected by errors in the potential energy ($\int \tilde{n}v - \int nv$) [**?**]. Values in brackets show the ΔE error trained on $200/M$ training points.

	ML-OF						ML-HK ΔE_D					
M	ΔE		ΔE_F		ΔE_D		Grid		Fourier		KPCA	
	avg	max	avg	max	avg	max	avg	max	avg	max	avg	max
20	7.7	47	7.7	60	8.8	87	2.1 [2.2/3.5]	12 [11/27]	1.7	9.8	0.37	5.5
50	1.6	30	1.3	7.3	1.4	31	0.26 [0.26/1.2]	2.4 [2.4/7.1]	0.26	2.4	0.061	0.96
100	0.74	17	0.2	2.6	0.75	17	0.081 [0.083/0.19]	0.82 [0.82/2.1]	0.083	0.81	0.033	0.43
200	0.16	2.9	0.039	0.6	0.16	2.9	0.019 [0.042/0.042]	0.45 [0.059/0.059]	0.02	0.45	0.026	0.26

Convergence of different HK maps



Non-interacting HK map



Potential

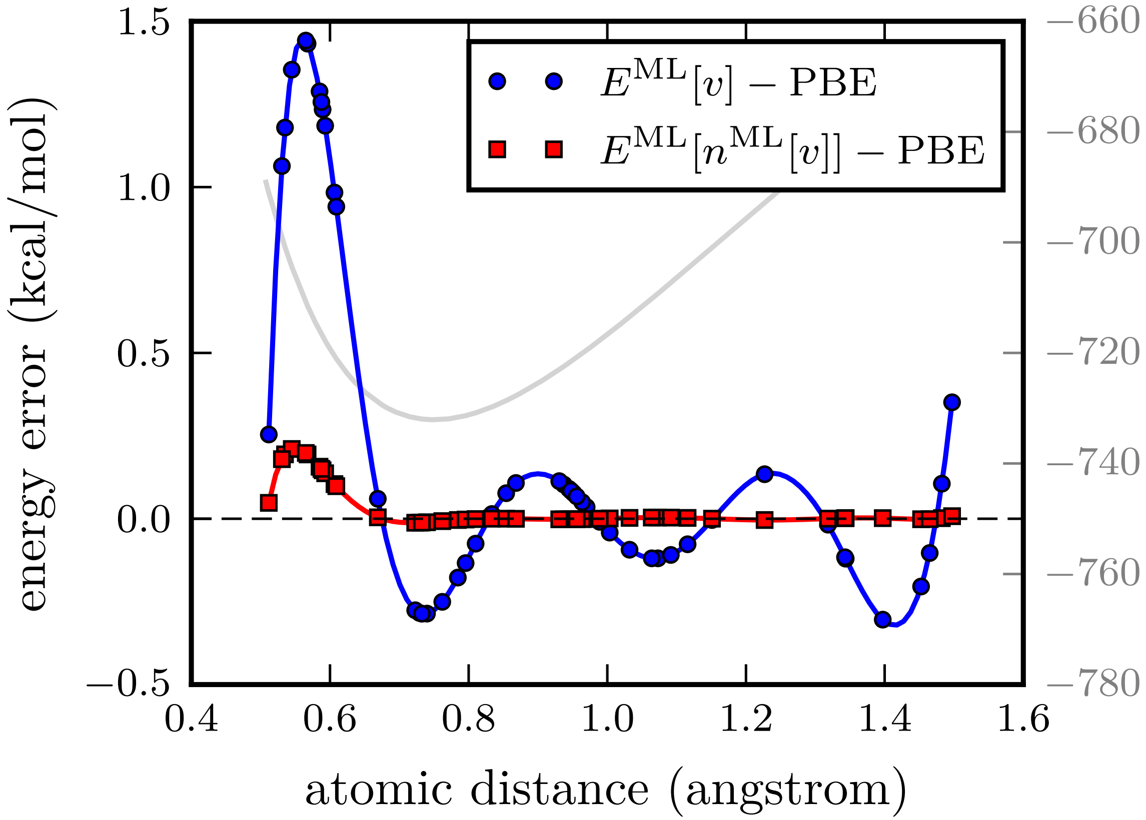
Potential as
Gaussian blobs

Independent
ML models

Data-driven and physicaly
motivated basis represen-
tations

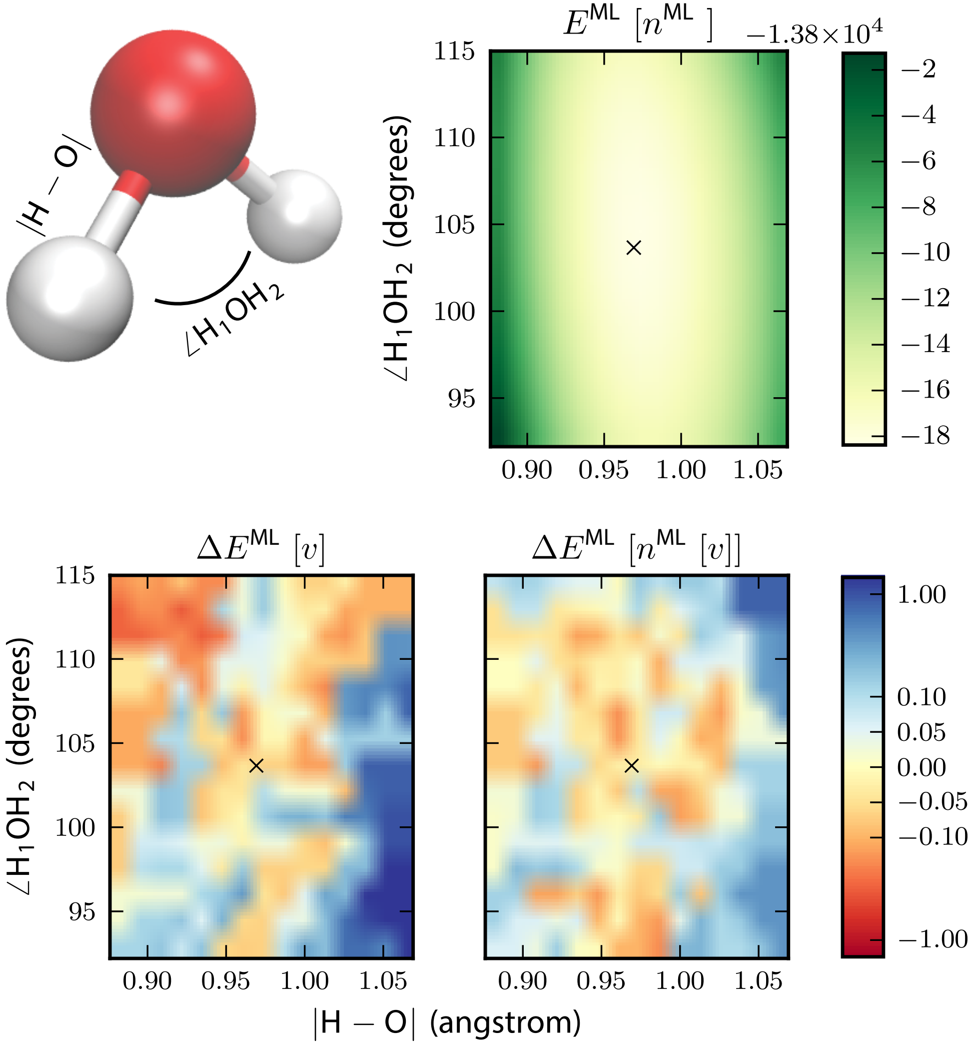
Density

Error for H_2

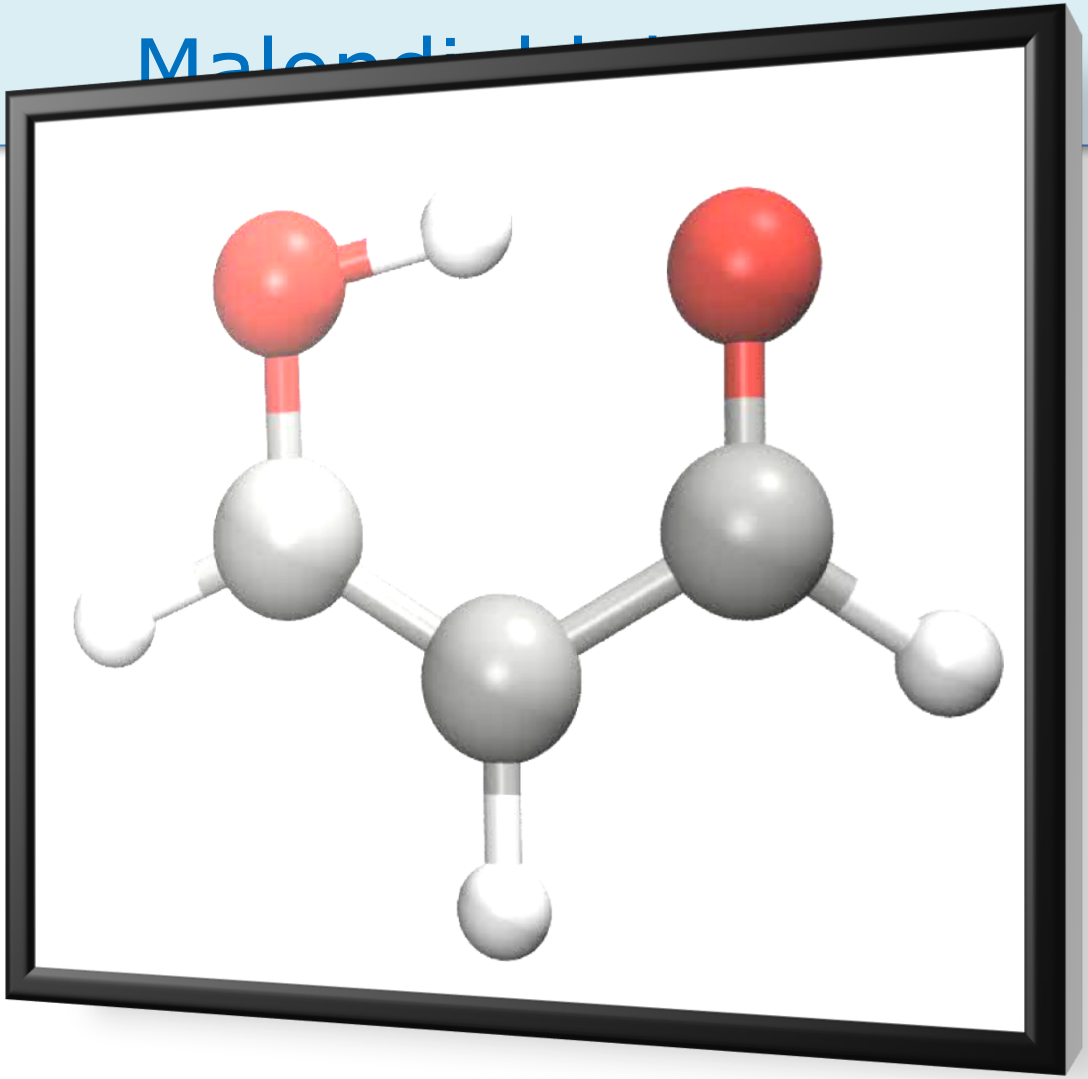


$E^{\mathrm{ML}}[v] - \mathrm{PBE}$
$E^{\mathrm{ML}}[n^{\mathrm{ML}}[v]] - \mathrm{PBE}$
energy error (kcal/mol)
atomic distance (angstrom)
1.5
1.0
0.5
0.0
−0.5
0.4
0.6
0.8
1.0
1.2
1.4
1.6
−660
−680
−700
−720
−740
−760
−780

H_2O


$|H-O|$
$\angle H_1OH_2$
$E^{ML}[n^{ML}]$
-1.38×10^4
115
110
105
100
95
$\angle H_1OH_2$ (degrees)
0.90
0.95
1.00
1.05
−2
−4
−6
−8
−10
−12
−14
−16
−18
$\Delta E^{ML}[v]$
$\Delta E^{ML}[n^{ML}[v]]$
1.00
0.10
0.05
0.00
−0.05
−0.10
−1.00
$|H-O|$ (angstrom)

Malondi



B175: By-passing the Kohn-Sham equations with machine learning Felix Brockherde, Leslie Vogt, Li Li, Mark E Tuckerman, Kieron Burke, Klaus-Robert Müller, *(submitted)* (2016).

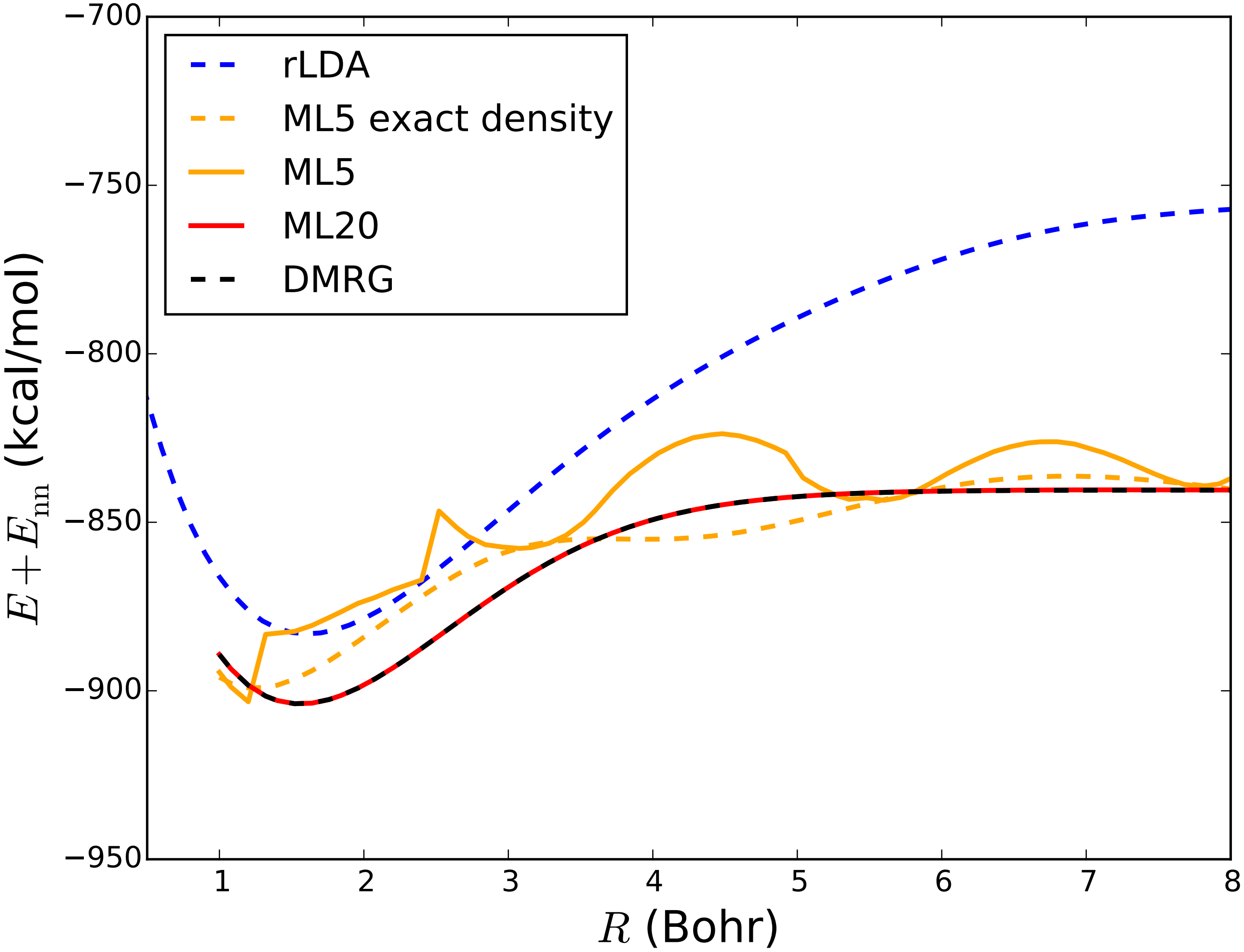
2nd paper: ML of exact functionals

- Use DMRG to solve continuum problems in 1d.
- Much success in past, showing failures of DFT approximations for strong correlation.
- Here use DMRG to generate much data of exact densities and energies
- All restricted to 1d.
- We train and test a machine learning F[n], the universal part of the electronic density functional, to within quantum chemical accuracy. We (a) bypass the standard Kohn-Sham approach, (b) include the strong correlation of highly-stretched bonds and (c) create a model for the infinite chain limit.

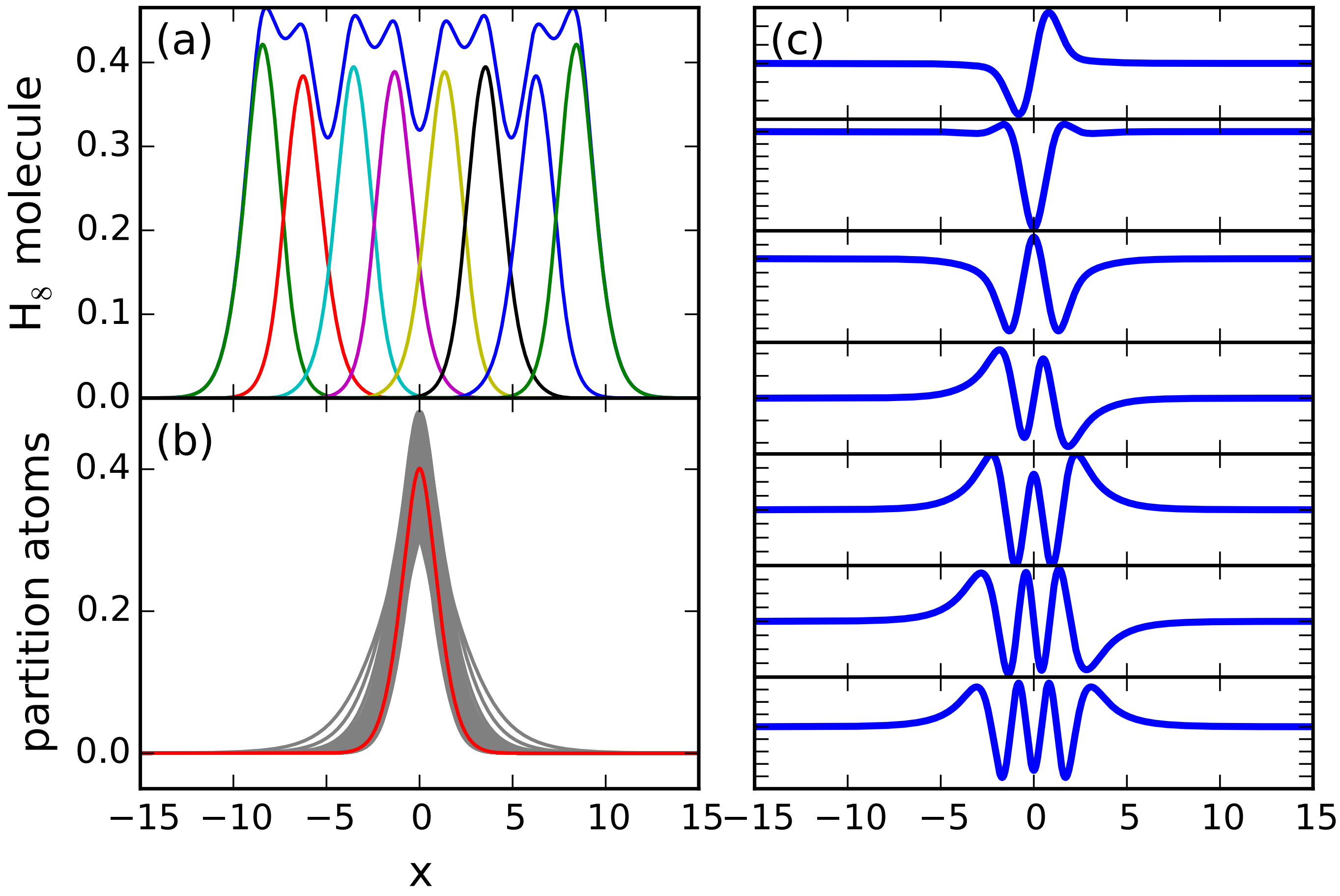
Guaranteed Convergence of the Kohn-Sham Equations Lucas O. Wagner, E. M. Stoudenmire, Kieron Burke, Steven R. White, Phys. Rev. Lett. **111**, 093003 (2013).

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

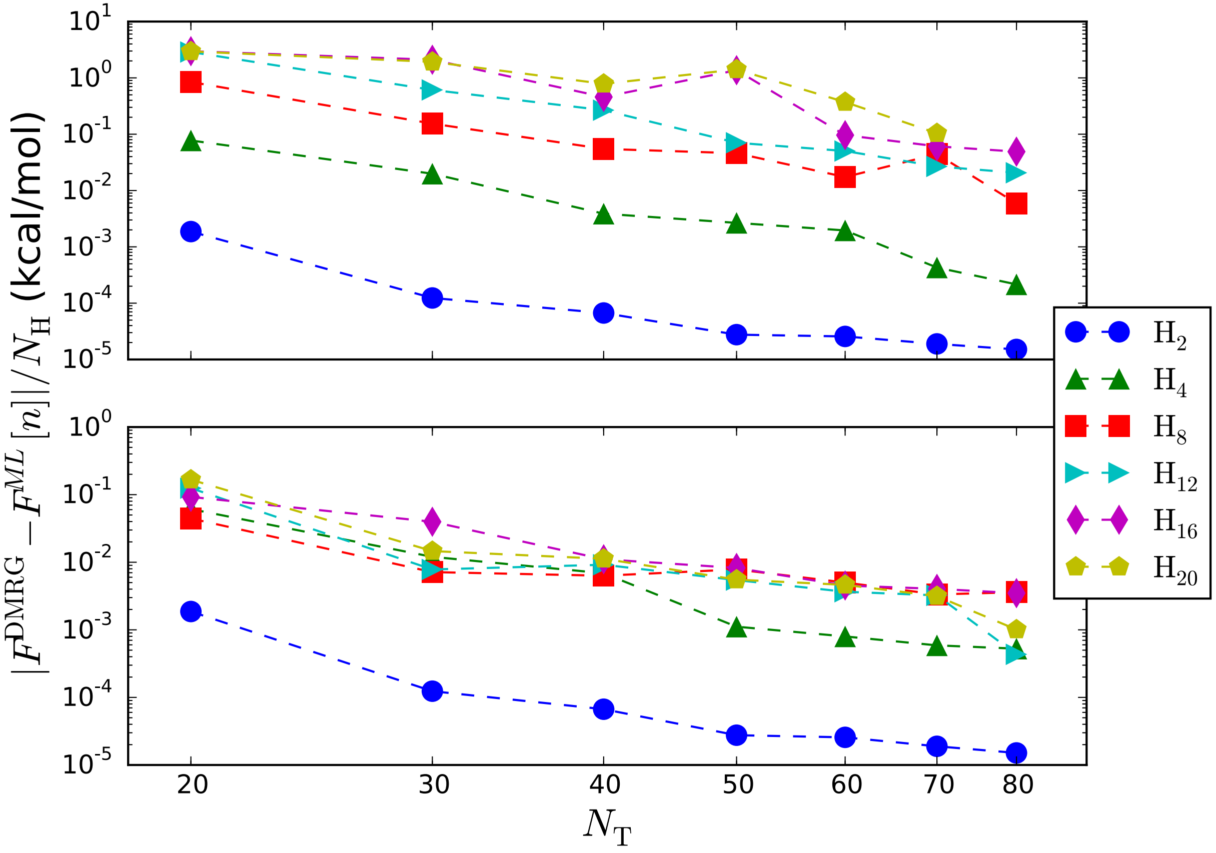
Convergence for H_2



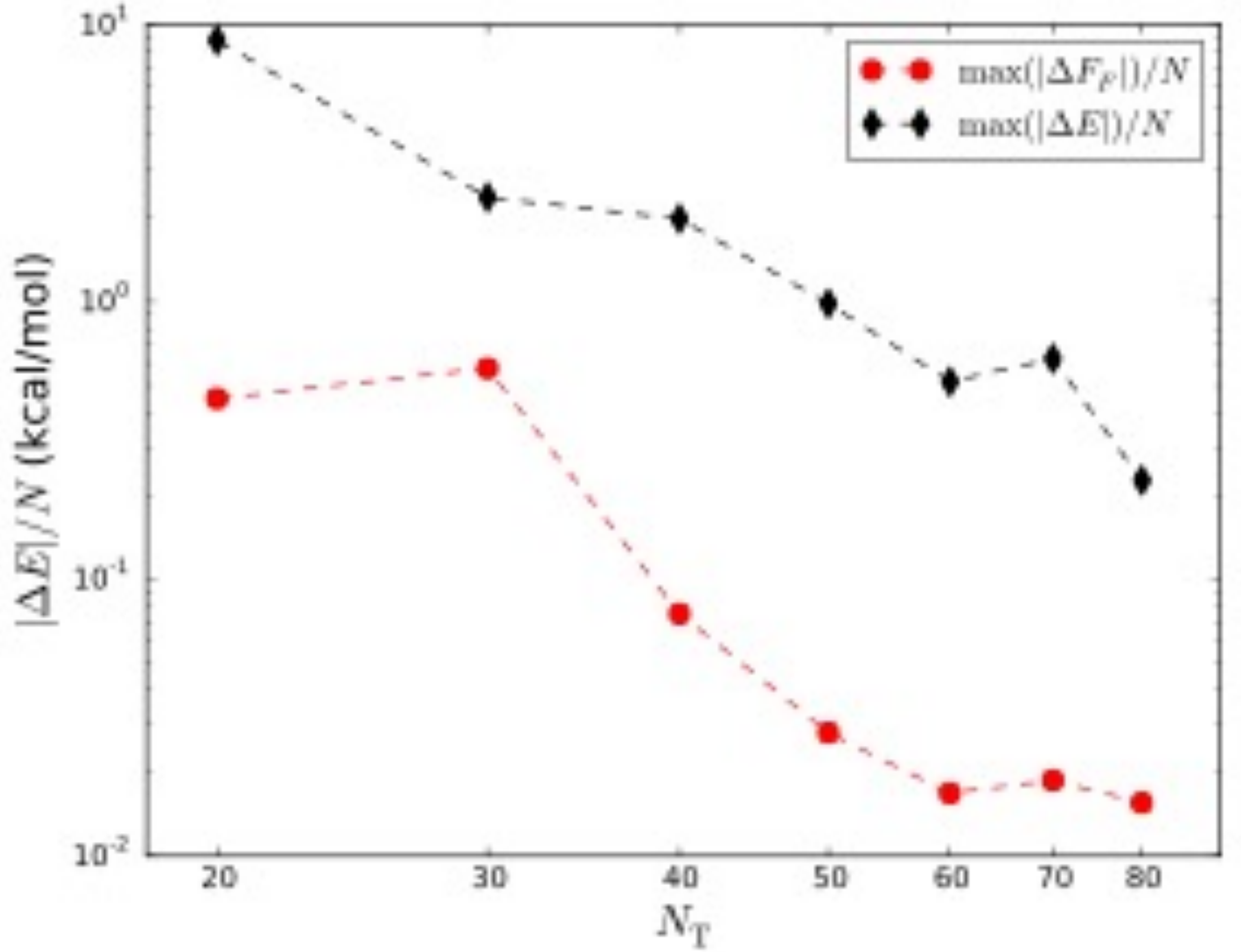
PCA basis for atomic densities



Improved convergence from basis



Origin of error for chain



Convergence for infinite chain

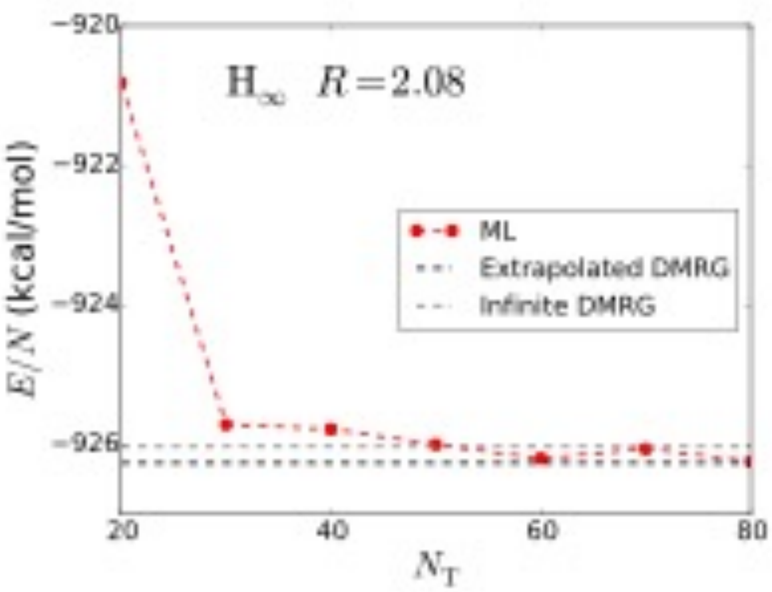


FIG. 1. (Color online) Electronic energy of infinite chain from model learned from extrapolated chain densities and energies. The accurate value was calculated with infinite DMRG (see text).

Pure density functional for strong correlations and the thermodynamic limit from machine learning Li Li, Thomas E. Baker, Steven R. White, Kieron Burke, to appear Phys Rev B.

Lessons

- Can learn exact functional from exact data.
- Can learn F[n] instead of T_s[n] so accurately you can even get density.
- Created a new data-driven basis by using atoms in molecules; greatly reduced computational cost.
- Extrapolate to infinite chain limit to within 1 kcal/mol.
- No problem in principle to do in 3d.

Papers (all on dft.uci.edu)

Nonlinear gradient denoising: Finding accurate extrema from inaccurate functional derivatives John C. Snyder, Matthias Rupp, Klaus-Robert Müller, Kieron Burke, *International Journal of Quantum Chemistry* **115**, 1102--1114 (2015).

Understanding kernel ridge regression: Common behaviors from simple functions to density functionals Kevin Vu, John C. Snyder, Li Li, Matthias Rupp, Brandon F. Chen, Tarek Khelif, Klaus-Robert Müller, Kieron Burke, *International Journal of Quantum Chemistry* **115**, 1115--1128 (2015).

Understanding machine-learned density functionals Li Li, John C. Snyder, Isabelle M. Pelaschier, Jessica Huang, Uma-Naresh Niranjan, Paul Duncan, Matthias Rupp, Klaus-Robert Müller, Kieron Burke, *International Journal of Quantum Chemistry* n/a--n/a (2015).

Kernels, Pre-Images and Optimization John C. Snyder, Sebastian Mika, Kieron Burke, Klaus-Robert Müller, *Chapter in Empirical Inference - Festschrift in Honor of Vladimir N. Vapnik* (2013).

Orbital-free Bond Breaking via Machine Learning John C. Snyder, Matthias Rupp, Katja Hansen, Leo Blooston, Klaus-Robert Müller, Kieron Burke, *J. Chem. Phys.* **139**, 224104 (2013).

Finding Density Functionals with Machine Learning John C. Snyder, Matthias Rupp, Katja Hansen, Klaus-Robert Müller, Kieron Burke, *Phys. Rev. Lett.***108**, 253002 (2012).

Summary

- DFT is a great physics success story
- Although very useful, DFT has lots of issues
- ML functionals can even
  - find accurate densities
  - break bonds
  - Do the full functional for solids (in 1d)
  - Can now do KS-MD for small molecules in 3d
- Thanks to
  - Funders: NSF from chem, DMR, math