

Density functional theory: A great physics success story?

Kieron Burke and friends
UC Irvine
Chemistry & Physics

<http://dft.uci.edu>

Questions I will raise

- Is DFT interesting physics?
- What are the leading corrections to the local density approximation?
- Where can I find the Poisson equation inside the Schrodinger equation?
- For potentials that are $v(\mathbf{r})$, what is special about the quantum mechanics?

The electronic structure problem

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

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

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

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.

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

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.]

- Thomas-Fermi Theory (TF):

- $T \approx T^{\text{TF}}$

- $V_{\text{ee}} \approx U = \text{Hartree energy}$

- $V = \int d\mathbf{r} \rho(\mathbf{r}) v(\mathbf{r})$

- $E_0 = T + V_{\text{ee}} + V$

- Minimize $E_0[n]$ for fixed N

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

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

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.

- Properties:

- Typical error of order 10%

- Teller's unbinding theorem: Molecules don't bind.

HK theorem (1964)

- Makes TF an approximation to an exact theory
- Can find both ground-state density and energy via Euler equation

- 1 Rewrite variational principle (Levy 79):

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

where

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

- ▶ 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:

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

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

Define T_S as the kinetic energy of the KS electrons, U as their Hartree energy and

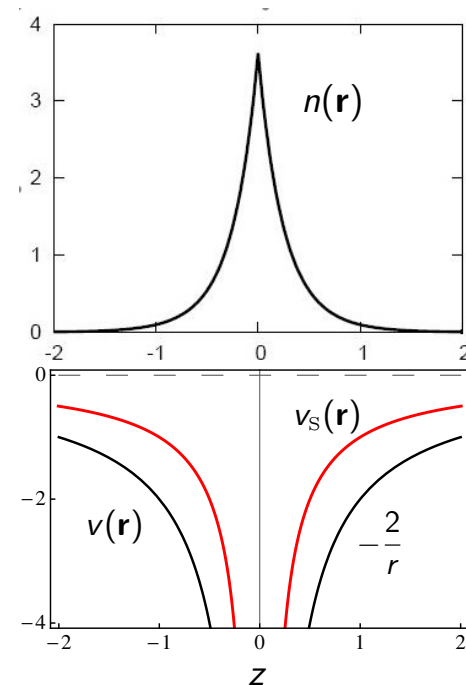
$$F = T + V_{ee} = T_S + U + E_{XC}$$

the remainder is the exchange-correlation energy.

Most important result of exact DFT:

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

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



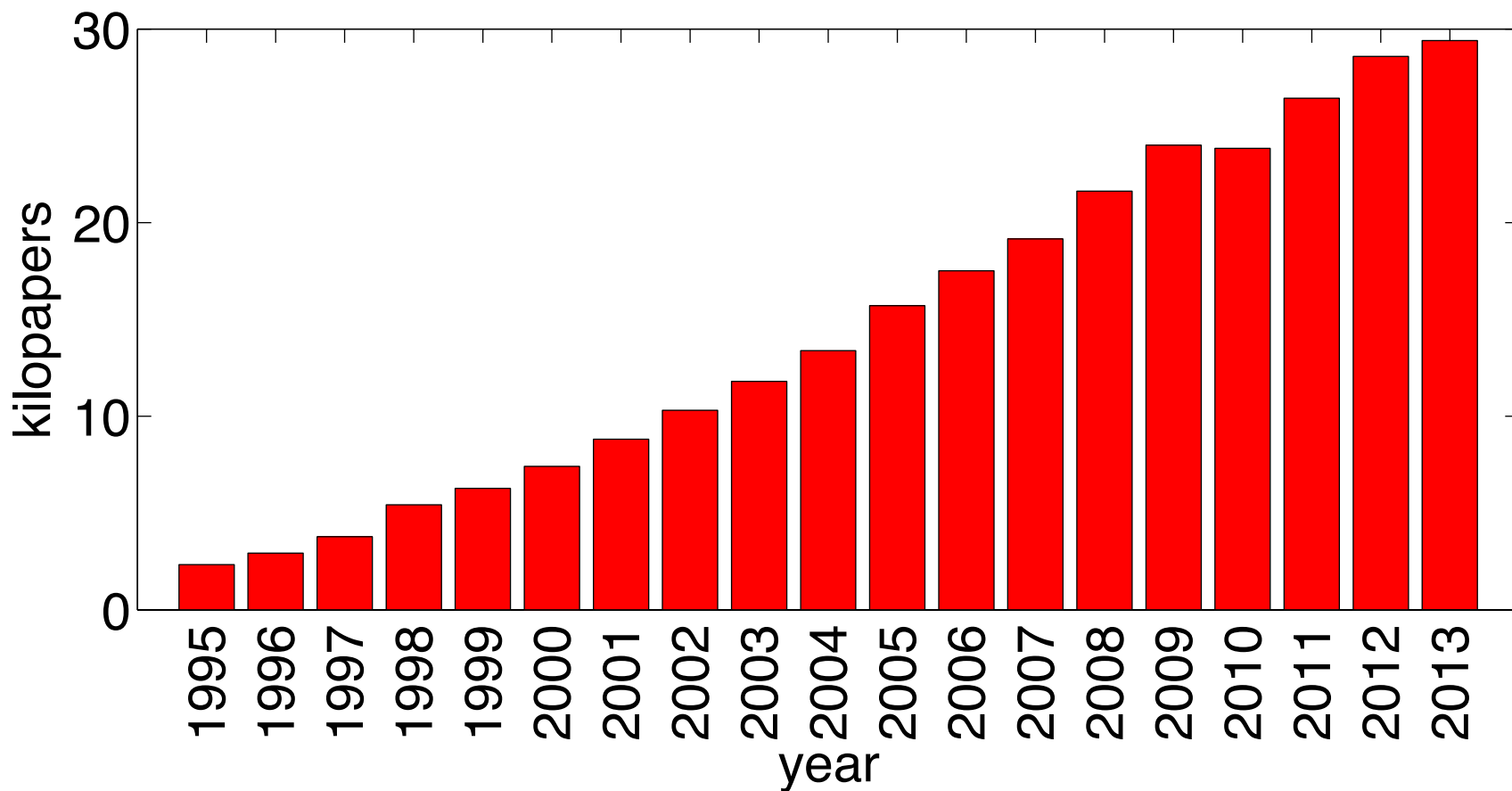
Today's commonly-used functionals

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

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.
- Latest generation of intel chips (needed for Mac airbook) is half-size and Pb-free with help of DFT calcs.

DFT papers



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

In reality...



Important points

- DFT 'works' for both molecules and materials
- There are too many different approximations on the market, but in fact at least 70% of all calculations use only a half-dozen approximations.
- Electronic structure in chemistry and materials dominated by need for useful accuracy for very small energy differences; physics more concerned with response functions.
- Starts with local density approximations:
 - Pure DFT: Local approximation for $T_S[n]$
 - KS DFT: LDA for $E_{XC}[n]$.

B. Random sampling of modern DFT development

- Many different directions
- Many different people
 - Study exact functional
 - New XC approximations
 - New solution methods
 - Strong correlation
 - Extensions beyond ground state

Exact KS-DFT

- Derive conditions that $E_{xc}[n]$ must satisfy
 - Scaling relations, derivative discontinuity,...
- Solve electronic problem highly accurately
 - Reverse-engineer to find $E_{xc}[n]$ and $v_{xc}[n](r)$.
- Results used for
 - Building new approximations
 - Testing existing ones

Guaranteed convergence

$$\eta \equiv \frac{1}{N^2} \int d^3 r (n'(\mathbf{r}) - n(\mathbf{r}))^2.$$

$$n_\lambda(\mathbf{r}) = (1 - \lambda)n(\mathbf{r}) + \lambda n'(\mathbf{r}),$$

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

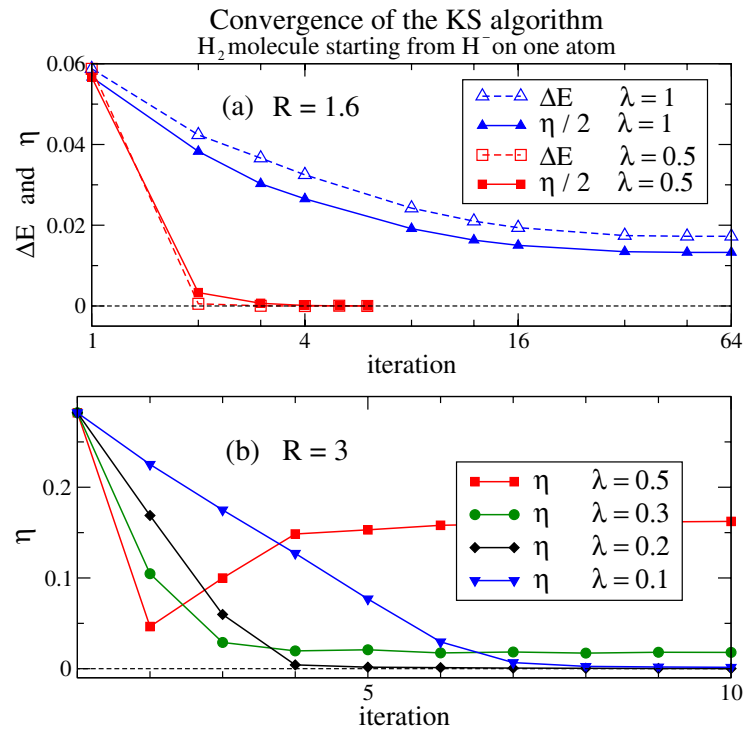


FIG. 3 (color online). Differences in the density η using Eq. (4) and the energy with $\Delta E = E_v[n'] - E_v^{gs}$, for an H₂ molecule with (a) $R = 1.6$ and (b) $R = 3$. In (b), the ΔE curves are omitted for clarity, but are like those in (a).

New DFT approximations

- Originally based on XC hole
 - Either non-empirical (Perdew) or mildly so (Becke)
- SCAN – Perdew group meta-GGA
- vdW
 - Langreth-Lundqvist, Grimme, Tkatchenko-Scheffler
- RPA – use KS orbitals
- LCSF
 - Truhlar
- ML: machine learning

Failures for strong correlation

- Local approximations go bad as bonds are stretched.
- Importance of $T[n]$ less relative to $V_{ee}[n]$.
- E.g., $U/2t \rightarrow$ infinity in Hubbard model

The Hubbard dimer: a density functional case study of a many-body problem D J Carrascal, J Ferrer, J C Smith, K Burke, *J Physics: Cond Mat* **27**, 393001 (2015)

Infamous limitation

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).

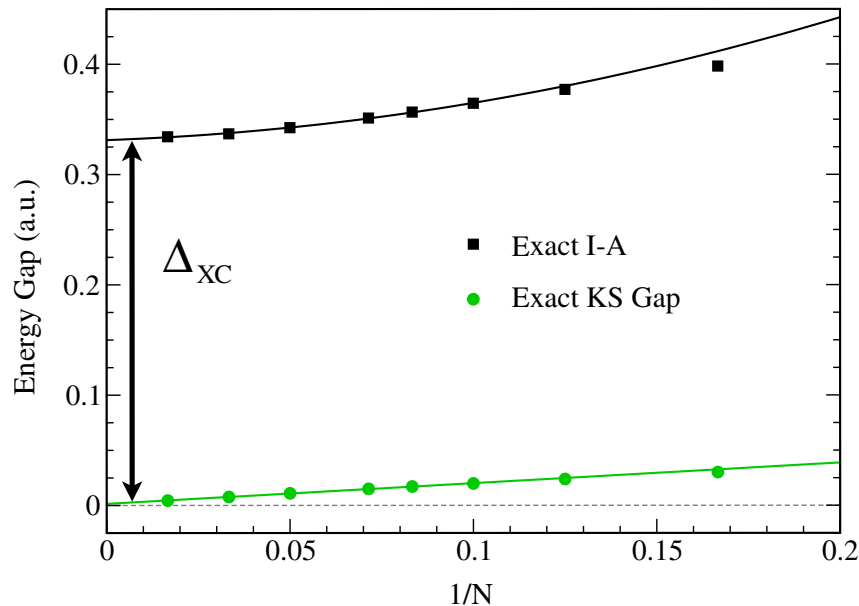
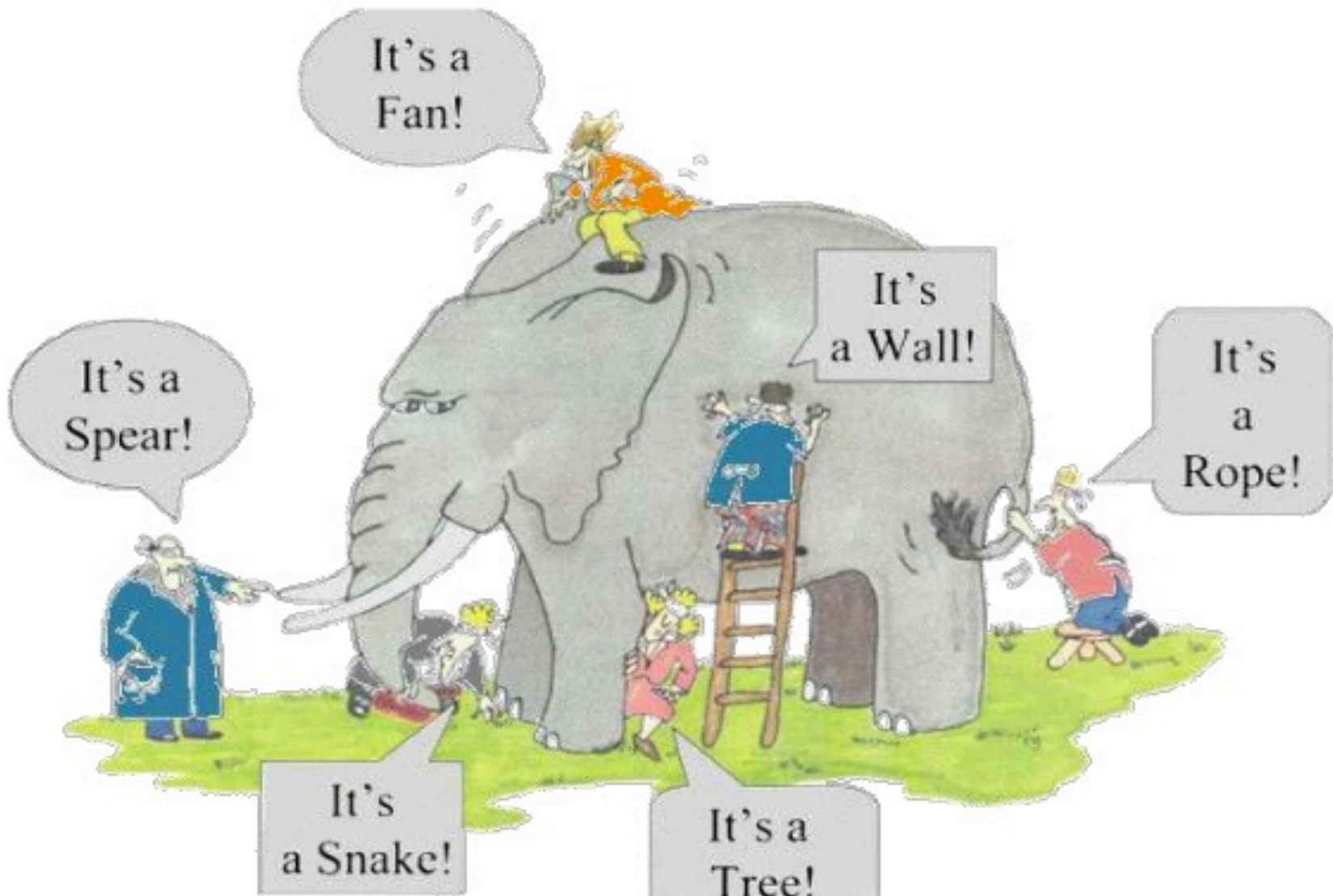


FIG. 3 (color online). Exact gaps for chains of N soft hydrogen atoms with atomic separation $b = 4$ (error bars are less than symbol sizes). The upper curve is a quadratic fit of exact gaps of the largest six systems and extrapolates to a finite value $E_g \simeq 0.33$. The exact Kohn-Sham gaps, in 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).



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Aside: DFT beyond ground state

- Time-dependent DFT (TDDFT)
 - Yields electronic excitations
- Ensemble DFT (eDFT)
 - Alternative route to excitations
 - 2 recent papers with Aurora Pribram-Jones
- Thermal DFT (thDFT)
 - Applies to warm dense matter (hot electrons)
 - 4 recent papers with Aurora Pribram-Jones

Message:

- This is a very bizarre way to do quantum mechanics.



Important quote

- *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.

$$\int dx \sqrt{2(E - v(x))} = \pi \left(j + \frac{1}{2} \right)$$

C. Grand challenge: Systematic approach

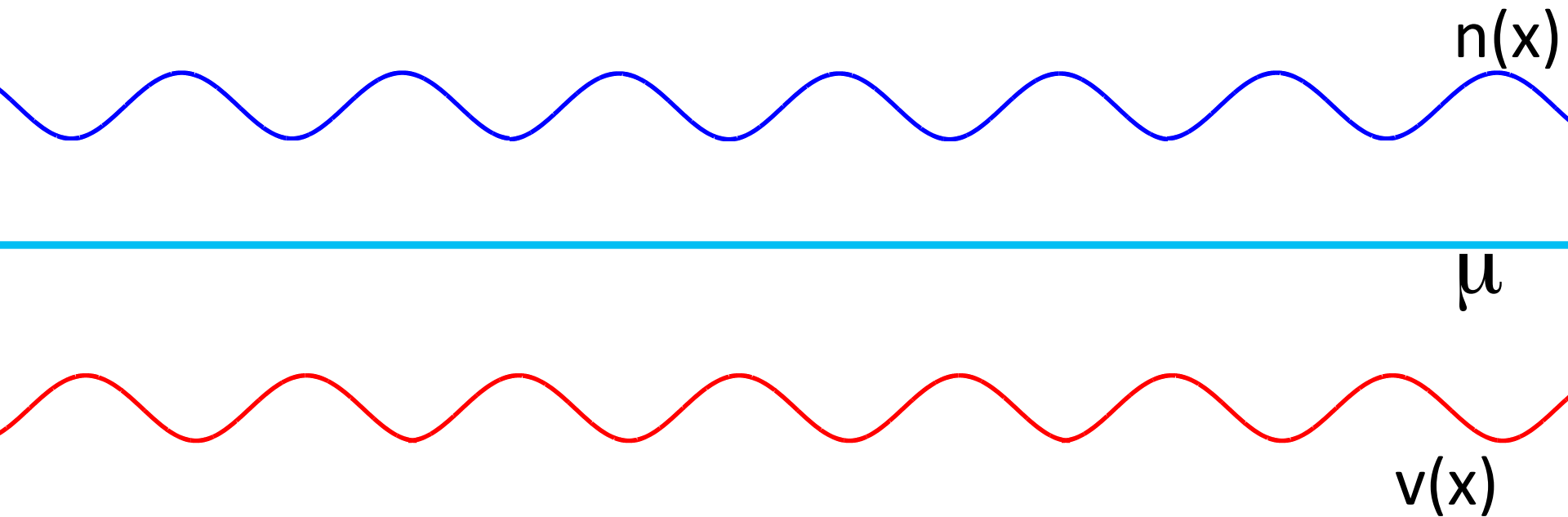
- Is there a systematic approach to constructing density functional approximations?
- Answer: I believe they are a very specific expansion in powers of \hbar , but we don't know how to do this expansion.

Original KS idea: Simple metals

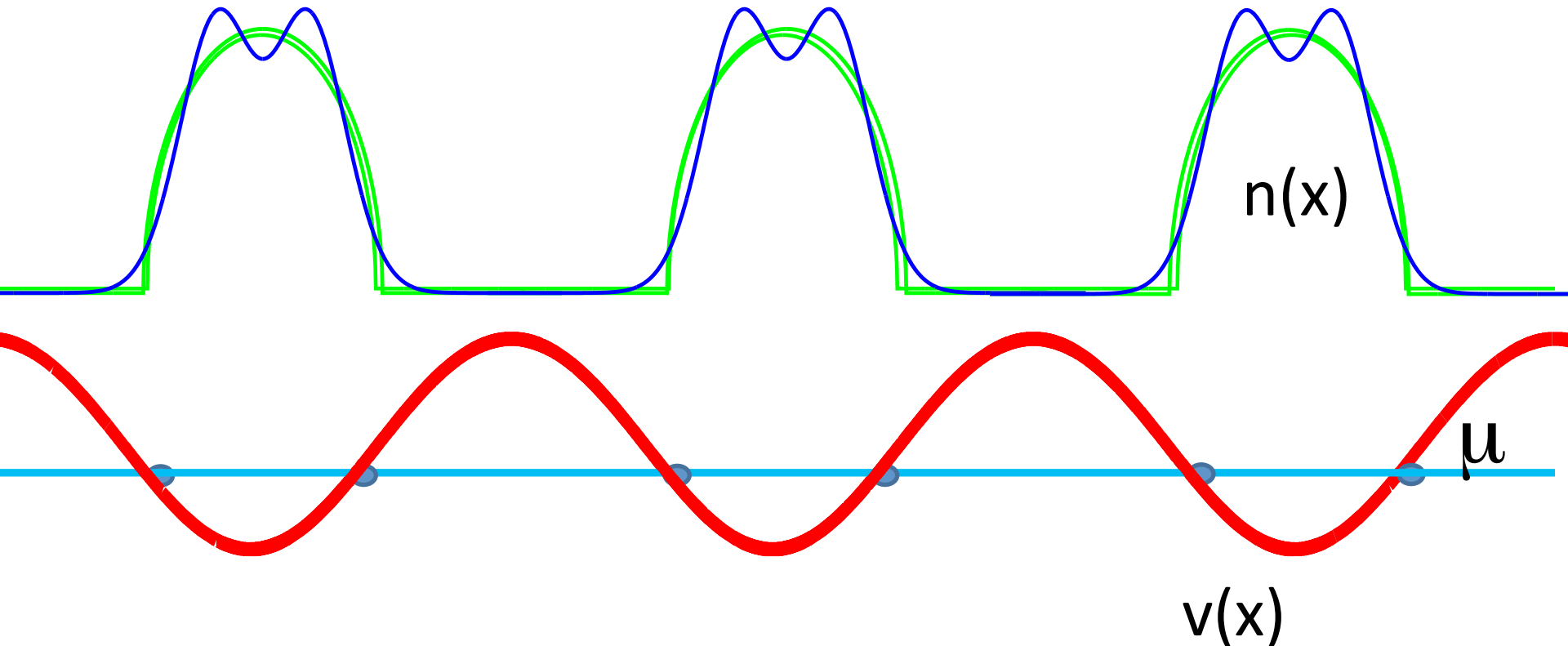
WKB for one level \Rightarrow sum over many \Rightarrow TF theory

Corrections to WKB \Rightarrow sum over many \Rightarrow gradient expansion

As $\hbar \rightarrow 0$, TF becomes relatively exact (asymptotic expansion)



Chemistry and most materials



- TF theory STILL relatively exact in limit $\hbar \rightarrow 0$.
- Leading corrections come from turning points, yielding quantum oscillations.

Lieb-Simon limit

- Consider scaling to continuum limit:

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

where d is spatial dimension.

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

$$\frac{E^{\text{TF}} - E_0}{E_0} \rightarrow 0$$

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

KS version of Lieb-Simon statement

Almost certain that

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

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

Kieron's instinct:

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

Atomic correlation energies and the generalized gradient approximation, Kieron Burke, Antonio Cancio, Tim Gould, Stefano Pittalis, J Chem Phys, 2016.

Leading corrections

$$n^{\text{sc}}(x) = \frac{p_F(x)}{\hbar} \left[\left(\sqrt{z} \text{Ai}^2(-z) + \frac{\text{Ai}'^2(-z)}{\sqrt{z}} \right) + \left(\frac{\hbar \omega_{FCSC}[\alpha_F(x)]}{p_F^2(x)} - \frac{1}{2z^{3/2}} \right) \text{Ai}(-z) \text{Ai}'(-z) \right]_{z=z_F(x)}$$

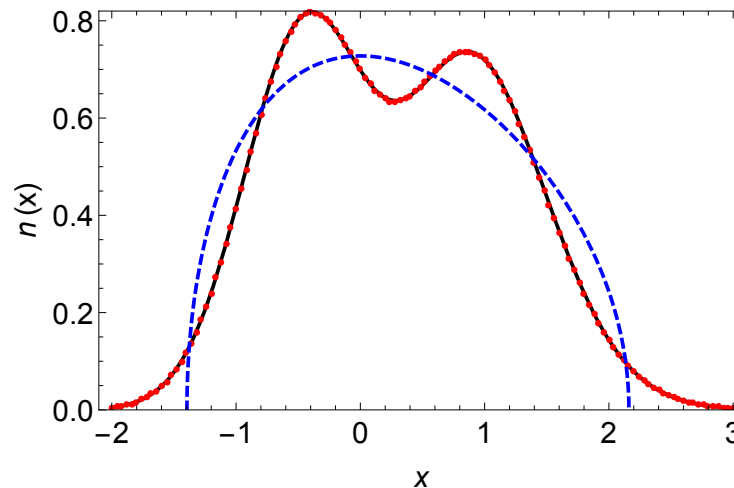


FIG. 1. Thomas-Fermi (dashed) and semiclassical (dotted) approximations to the density (solid) of 2 particles in a Morse potential, $v(x) = 15(e^{-x/2} - 2e^{-x/4})$.

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).

Lesson

- 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.
- Almost all successes and failures of local density functionals can be understood in this way.

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 Kohn-Sham kinetic energy and modern parametrization of the Thomas-Fermi density** Donghyung Lee, Lucian A. Constantin, John P. Perdew, Kieron Burke, *J. Chem. Phys.* **130**, 034107 (2009).
- [118] **Non-empirical derivation of the parameter in the B88 exchange functional** Peter Elliott, Kieron Burke, *Canadian Journal of Chemistry* **87**, 1485-1491 (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:1409.1884 (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).

A subtle mystery

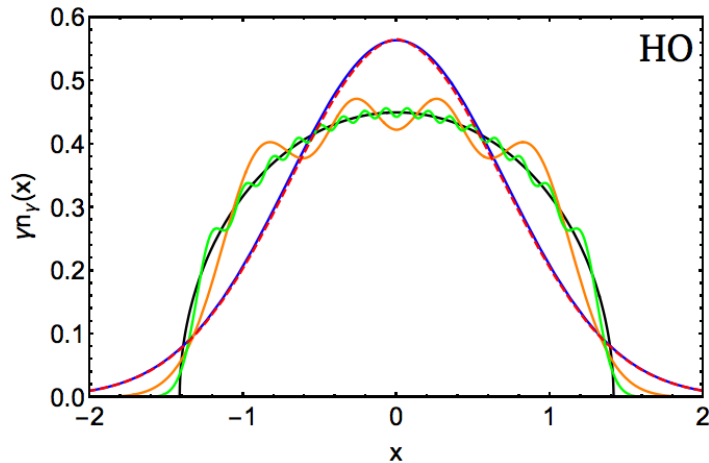


FIG. 1. $\gamma n_\gamma(x)$ for $N = 1$ harmonic potential where $\gamma = 1$ (blue, with semiclassical approximation dashed red), $1/4$ (orange), $1/16$ (green), and TF (black).

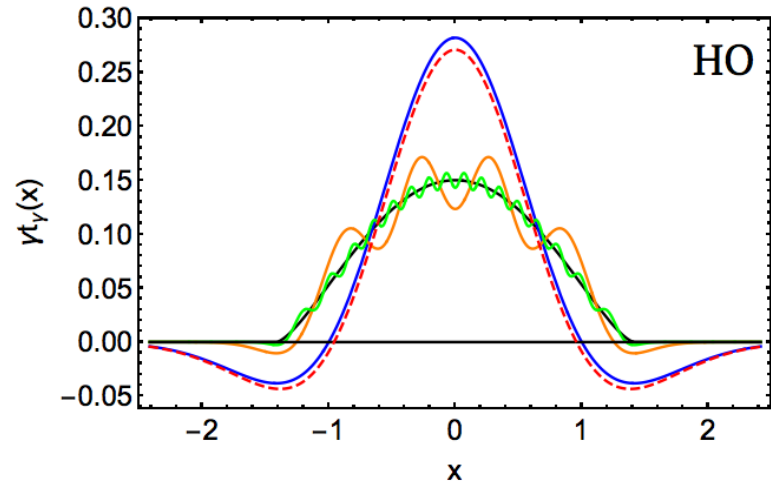


FIG. 4. Same as Fig. 1, but for the kinetic energy density.

Leading corrections to local approximations II (with turning points),
Raphael F. Ribeiro and Kieron Burke, *submitted to Phys Rev B*

Summary

- Introduction
 - DFT incredibly successful in terms of applications
 - DFT incredibly annoying in terms of derivations
- Modern DFT research
 - Studies of exact functional
 - As many approaches as practitioners
- My Perspective
 - We are missing the semiclassical chapter in our quantum many-body books.
 - Suggests there's another way to formulate QM

Thanks to NSF and students