

# *Semiclassical origins of density functional approximations*



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Physics & Chemistry

<http://dft.uci.edu>

# Outline

A. Background in DFT

B. Connection to semiclassics

C. Our work in (a little) detail, and cry for help

# A. The electronic structure problem

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

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

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

# Thomas/Fermi Theory 1927

$$T[n] \approx T_s^{\text{LDA}}[n] = \frac{3(3\pi)^{2/3}}{10} \int d^3r n^{5/3}(\mathbf{r})$$

$$V_{\text{ee}}[n] \approx U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$E^{\text{TF}} = \min_n \left\{ T_s^{\text{LDA}}[n] + U[n] + \int d^3r v(\mathbf{r}) n(\mathbf{r}) \right\}$$

# Walter Kohn (1923-2016)



# Hohenberg-Kohn theorem (1965)

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

# 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

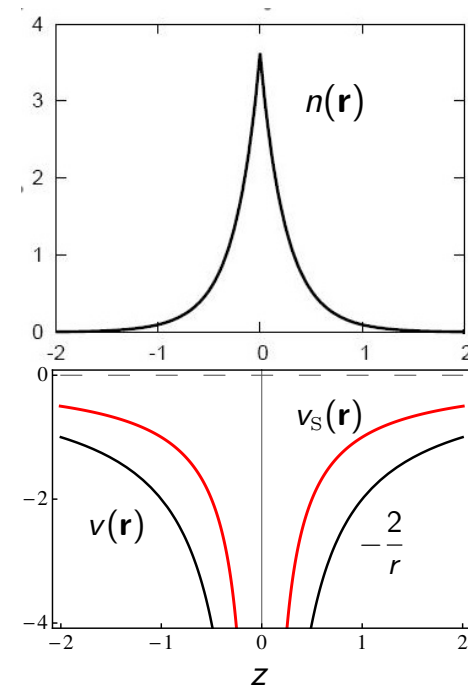
$$F = T + V_{ee} = T_S + U + E_{XC}$$

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.



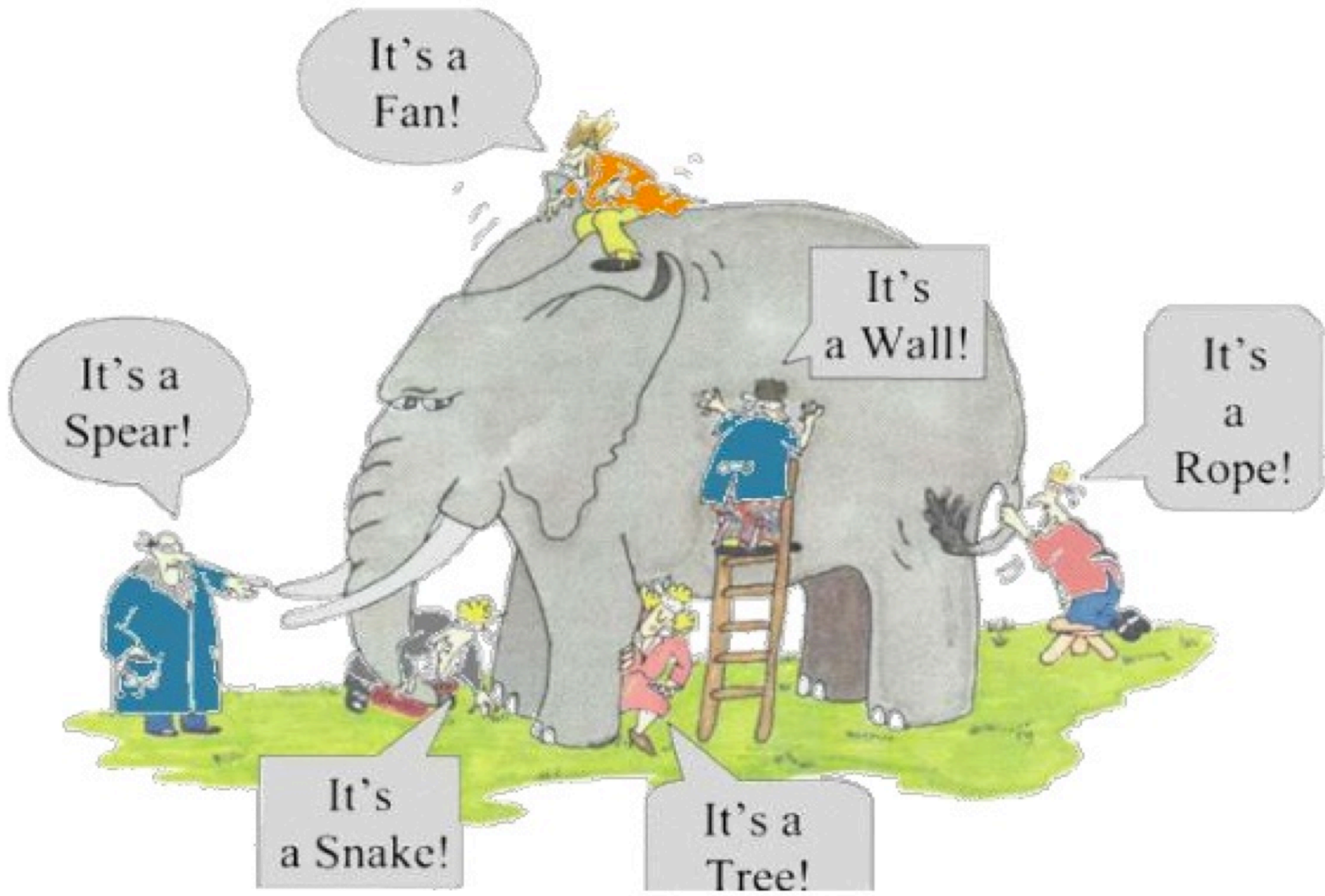
# Today's commonly-used functionals

- **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)**  $E_{XC}^{\text{GGA}} = \int d^3r e_{XC}^{\text{GGA}}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$ 
  - Uses both  $n(\mathbf{r})$  and  $|\nabla n(\mathbf{r})|$
  - Should be more accurate, corrects overbinding of LDA
  - Examples are PBE and BLYP
- **Hybrid:**  $E_{XC}^{\text{hyb}} = a (E_X - E_X^{\text{GGA}}) + E_{XC}^{\text{GGA}}$ 
  - Mixes some fraction of HF with GGA
  - Examples are B3LYP and PBE0



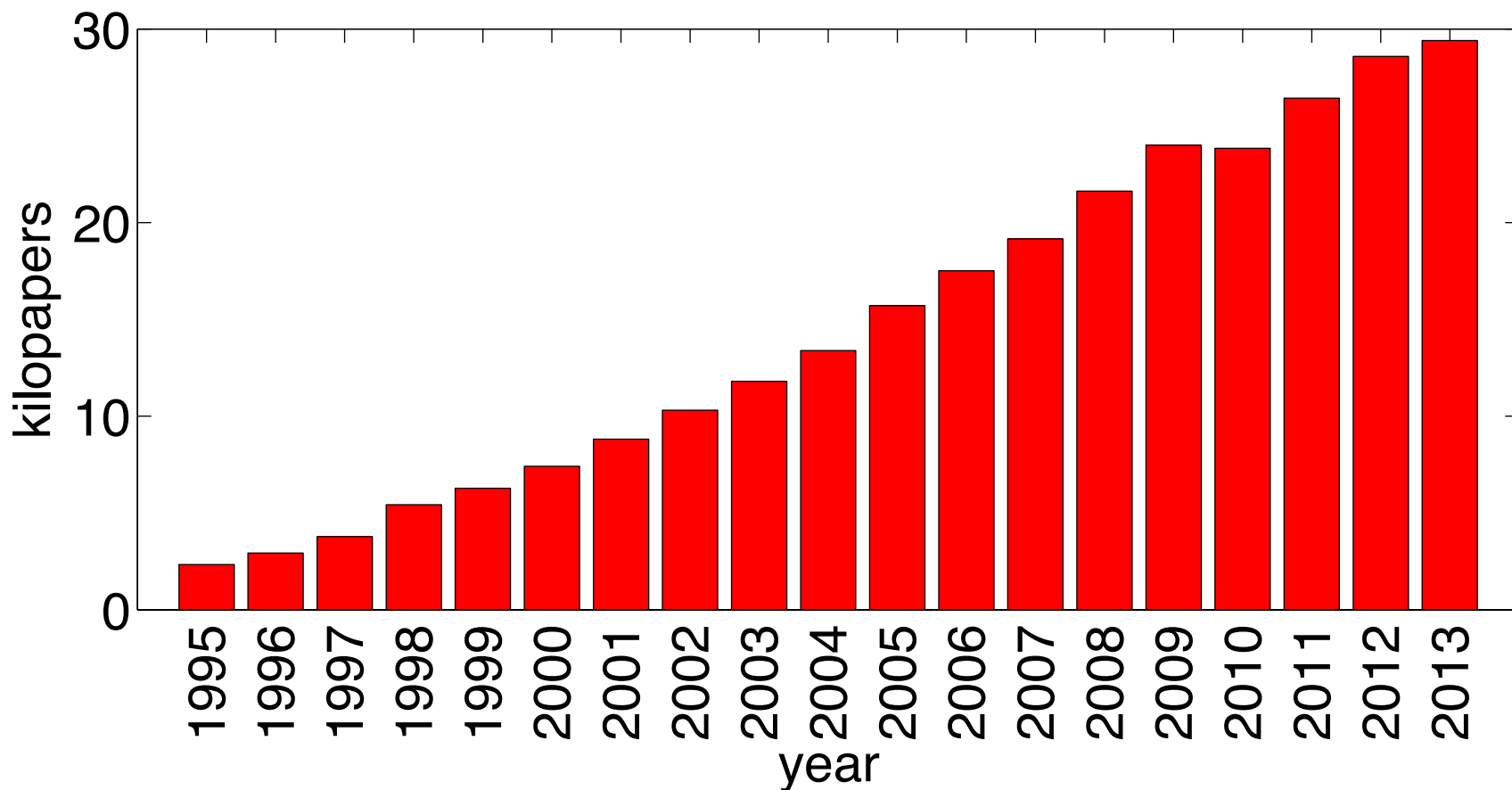
# Applications

- 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, made in 2015.
- Latest generation of intel chips (needed for Mac airbook) is half-size and Pb-free with help of DFT calcs.
- Can also extract excitations via time-dependent DFT.



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# DFT papers



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

# Important points

- DFT 'works' for both molecules and materials
- There are too many different approximations on the market.
- The 'best' ones are made by Perdew and Becke.
- Always starts with local approximations
  - In TF theory, local approx for kinetic energy
  - In KS method, local approx for XC energy

# Message:

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



## **B. How is DFT related to semiclassics?**

## 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.

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

# Semiclassical connection to DFT

- **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)
- **Semiclassical Origins of Density Functionals** Peter Elliott, Donghyung Lee, Attila Cangi, Kieron Burke, *Phys. Rev. Lett.* **100**, 256406 (2008).
- **Electronic Structure via Potential Functional Approximations** Attila Cangi, Donghyung Lee, Peter Elliott, Kieron Burke, E. K. U. Gross, *Phys. Rev. Lett.* **106**, 236404 (2011).
- **Potential functionals versus density functionals** Attila Cangi, E. K. U. Gross, Kieron Burke, *Phys. Rev. A* **88**, 062505 (2013).

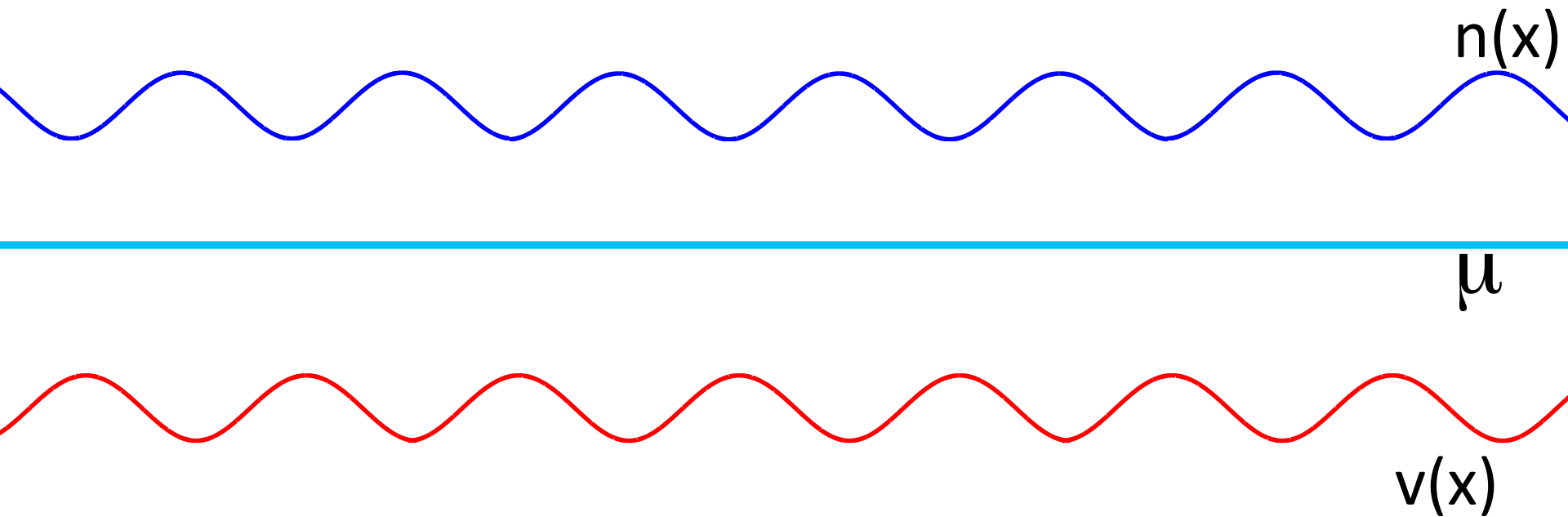


# Original KS idea: Simple metals

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)



# 1d TF for no interaction

$$n(x) \approx \int_{-\infty}^{E_F} \frac{dE}{\pi \hbar} |\phi_E(x)|^2 = \frac{k_F(x)}{\pi}, \quad k(x) = p(x)/\hbar,$$

$$t(x) \approx \int_{-\infty}^{E_F} \frac{dE}{\pi \hbar} [E - v(x)] |\phi_E(x)|^2 = \frac{\hbar^2 k_F^3(x)}{6\pi}.$$

- Both  $n(x)$  and  $t(x)$  are determined solely by  $v(x)$  and  $E_F$ , i.e., local approximation in  $v(x)$ .
- Global condition to get  $E_F$  is normalization of  $n(x)$ :

$$\int dx n(x) = N \quad \text{or} \quad \theta_F(\infty) = N\pi.$$

# Lieb-Simon limit

- Consider scaling to continuum limit:

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

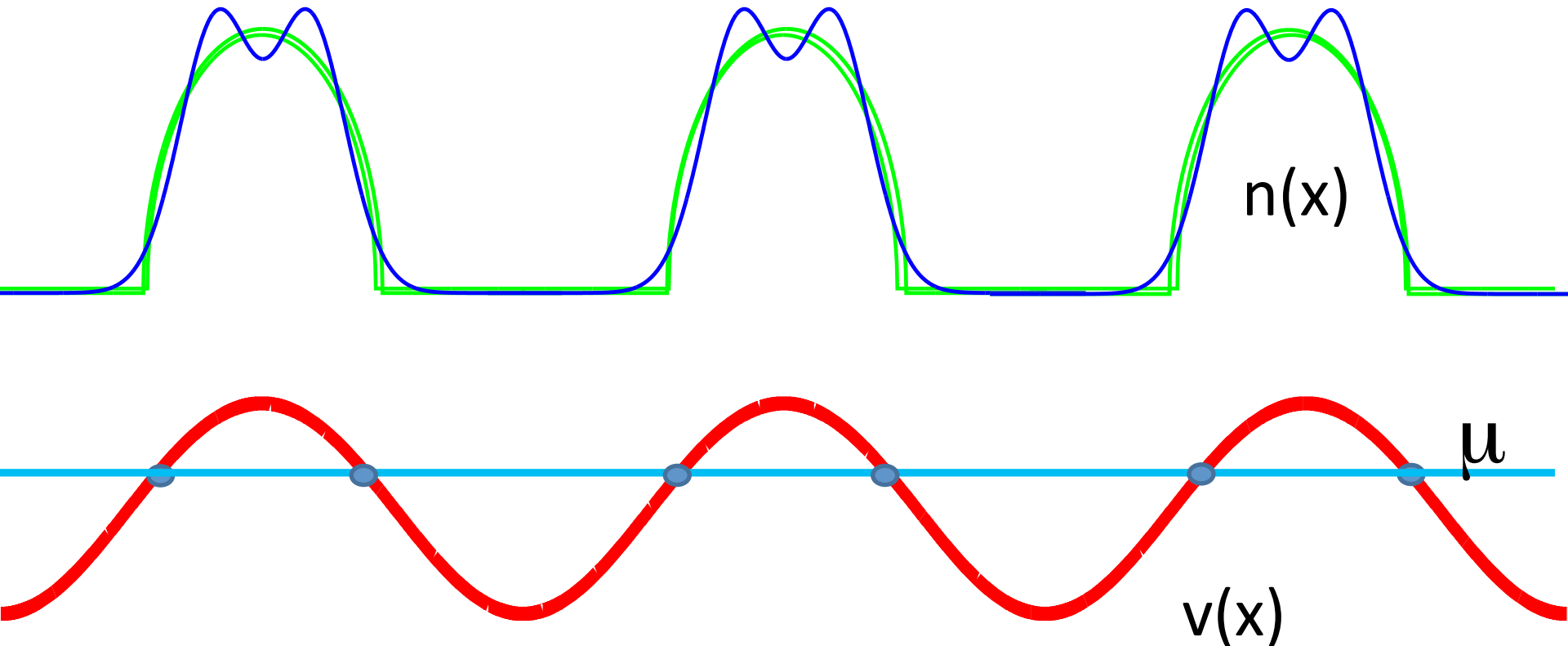
where  $d$  is spatial dimension.

- 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  $Z \rightarrow \infty$

# Chemistry and most materials



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

# 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.*

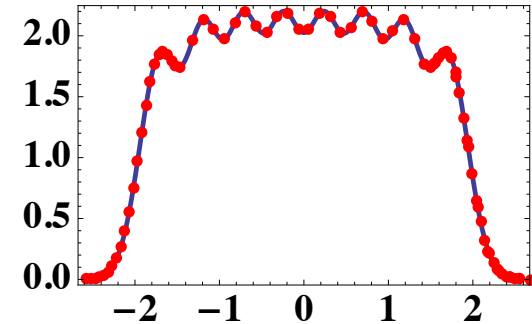
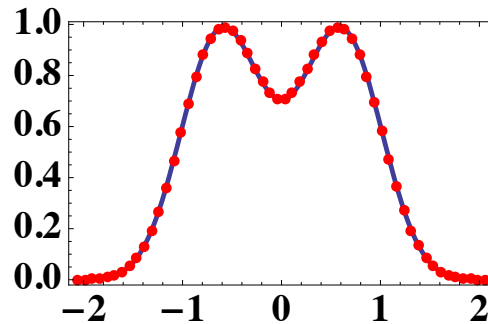
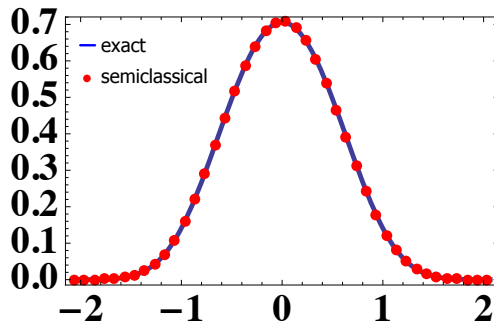
# 1d derivations

- **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)
- **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).
- **Uniform semiclassical approximations for one--dimensional fermionic systems** Raphael F. Ribeiro, Kieron Burke, *submitted and ArXiv:1510.05676* (2015).
- **Leading corrections to local density approximations II: The case with turning points** Raphael F. Ribeiro, Kieron Burke, to appear in *Phys Rev B.* and [arXiv:1611.00881](https://arxiv.org/abs/1611.00881).

## C. Recent work in 1d

# Performance of uniform approximations

- Quartic oscillator densities



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).



# Turning points

- “The Poisson sum formula seems to be the appropriate mathematical device to use in problems involving sums over discrete values of a variable which classically can assume any value” (MV Berry, 66)

$$n(x, N) = \sum_{j=0}^{N-1} |\phi_j(x)|^2 = \sum_{m=-\infty}^{\infty} \int_{-1/2}^{N-1/2} |\phi_\lambda(x)|^2 e^{2\pi i m \lambda} d\lambda$$

- Airy uniform approximation:

$$\phi_\lambda(x) = 2 \frac{\omega_\lambda \left( 3/(2\hbar) \int_{x_\lambda}^x p_\lambda(x') dx' \right)^{2/3}}{p_\lambda(x)} \text{Ai} \left[ - \left( \frac{3}{2\hbar} \int_{x_\lambda}^x p_\lambda(x') dx' \right)^{2/3} \right]$$

- WKB density of states

$$\frac{1}{2\pi} \oint p_\lambda(x') dx' = \left( n + \frac{1}{2} \right) \hbar$$

# Leading corrections

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

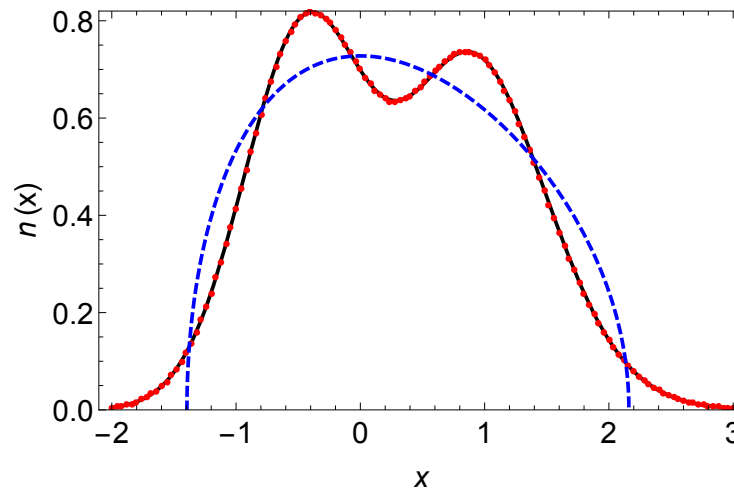


FIG. 1. Thomas-Fermi (dashed) and semiclassical (dotted) approximations to the density (solid) of 2 particles in a Morse potential,  $v(x) = 15(e^{-x/2} - 2e^{-x/4})$ .

**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).

# To appear in PRB

PHYSICAL REVIEW B **00**, 005100 (2017)

## **Leading corrections to local approximations. II. The case with turning points**

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Quantum corrections to Thomas-Fermi (TF) theory are investigated for noninteracting one-dimensional fermions with known uniform semiclassical approximations to the density and kinetic energy. Their structure is analyzed, and contributions from distinct phase space regions (classically-allowed versus forbidden at the Fermi energy) are derived analytically. Universal formulas are derived for both particle numbers and energy components in each region. For example, in the semiclassical limit, exactly  $(6\pi\sqrt{3})^{-1}$  of a particle leaks into the evanescent region beyond a turning point. The correct normalization of semiclassical densities is proven analytically in the semiclassical limit. Energies and densities are tested numerically in a variety of one-dimensional potentials, especially in the limit where TF theory becomes exact. The subtle relation between the pointwise accuracy of the semiclassical approximation and integrated expectation values is explored. The limitations of the semiclassical formulas are also investigated when the potential varies too rapidly. The approximations are shown to work for multiple wells, except right at the mid-phase point of the evanescent regions. The implications for density functional approximations are discussed.

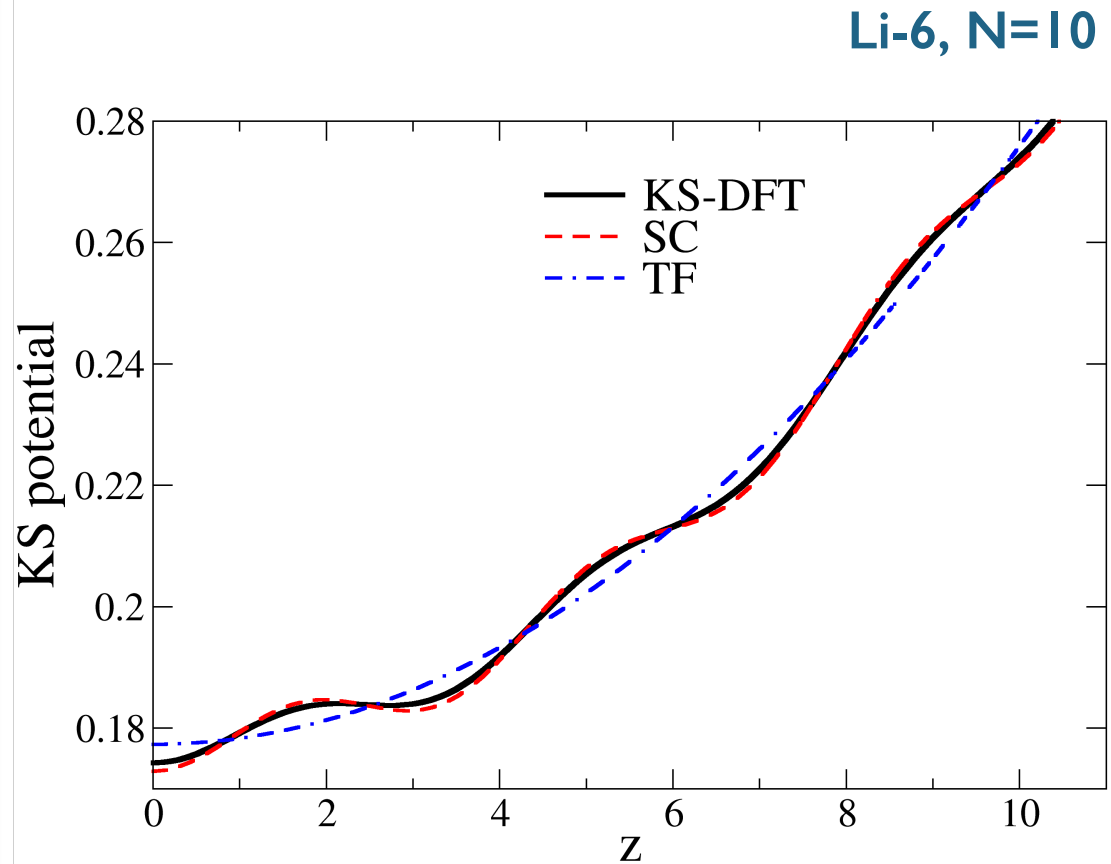
DOI: [10.1103/PhysRevB.00.005100](https://doi.org/10.1103/PhysRevB.00.005100)

# In the real world

- **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)
- **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).
- **Non-empirical derivation of the parameter in the B88 exchange functional** Peter Elliott, Kieron Burke, *Canadian Journal of Chemistry* **87**, 1485-1491 (2009).
- **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).
- **Atomic correlation energies and the generalized gradient approximation** Kieron Burke, Antonio Cancio, Tim Gould, Stefano Pittalis, *arXiv:1409.4834* (2014) and *J Chem Phys*, 2016.

# In three dimensions

Recent application to FATS from Attila Cangi



# 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).
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- [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 this specific semiclassical approximations in your many-body book.
- 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.



# A few open semiclassical questions

- Can we construct an explicit functional (of potential or of density) that yields the leading correction to local approximation as  $\hbar \rightarrow 0$  for bound problems?
- Examples of other problems
  - 1d band structure from WKB?
  - Generalization to 3d
  - Changes for Coulomb interactions
  - Application to exchange energy: generalize to density matrices
  - Path integral formulation

# How different theorists fail differently

- Electronic structure theorists:
  - Physics, chemistry, materials science
  - Excellent at computation, useless at derivation
- Many-body theorists in condensed matter:
  - Do not care about high accuracy numbers or materials-specific properties
- Quantum chemists
  - Cannot stand this DFT stuff
- Applied mathematicians
  - Don't have a strong feeling for quantum mechanics
- Mathematical physicists:
  - Need to prove things, not derive them.

# Summary

- Introduction
  - DFT incredibly successful in terms of applications
  - DFT incredibly annoying in terms of derivations
- Connection to semiclassics
  - TF theory becomes relatively exact in Lieb-Simon limit
  - Relation is obscured by KS scheme
- My perspective
  - We are missing the semiclassical chapter in our quantum many-body books.
  - I could use help on the derivations
  - Maybe there's another way to formulate QM?

Thanks to NSF and students