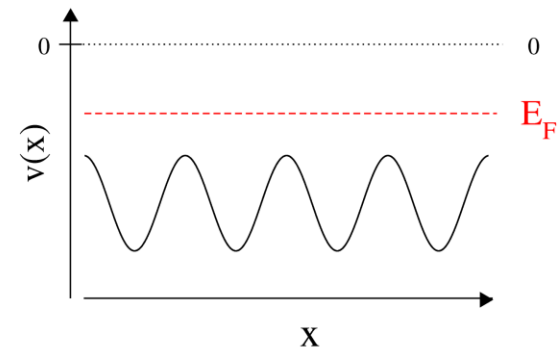
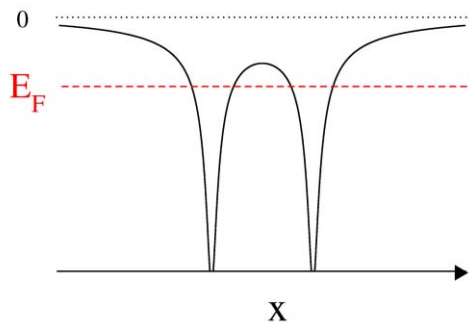


The unreasonable utility of asymptotic estimates: Why density functional theory works

Kieron Burke and friends

UC Irvine Chemistry and Physics

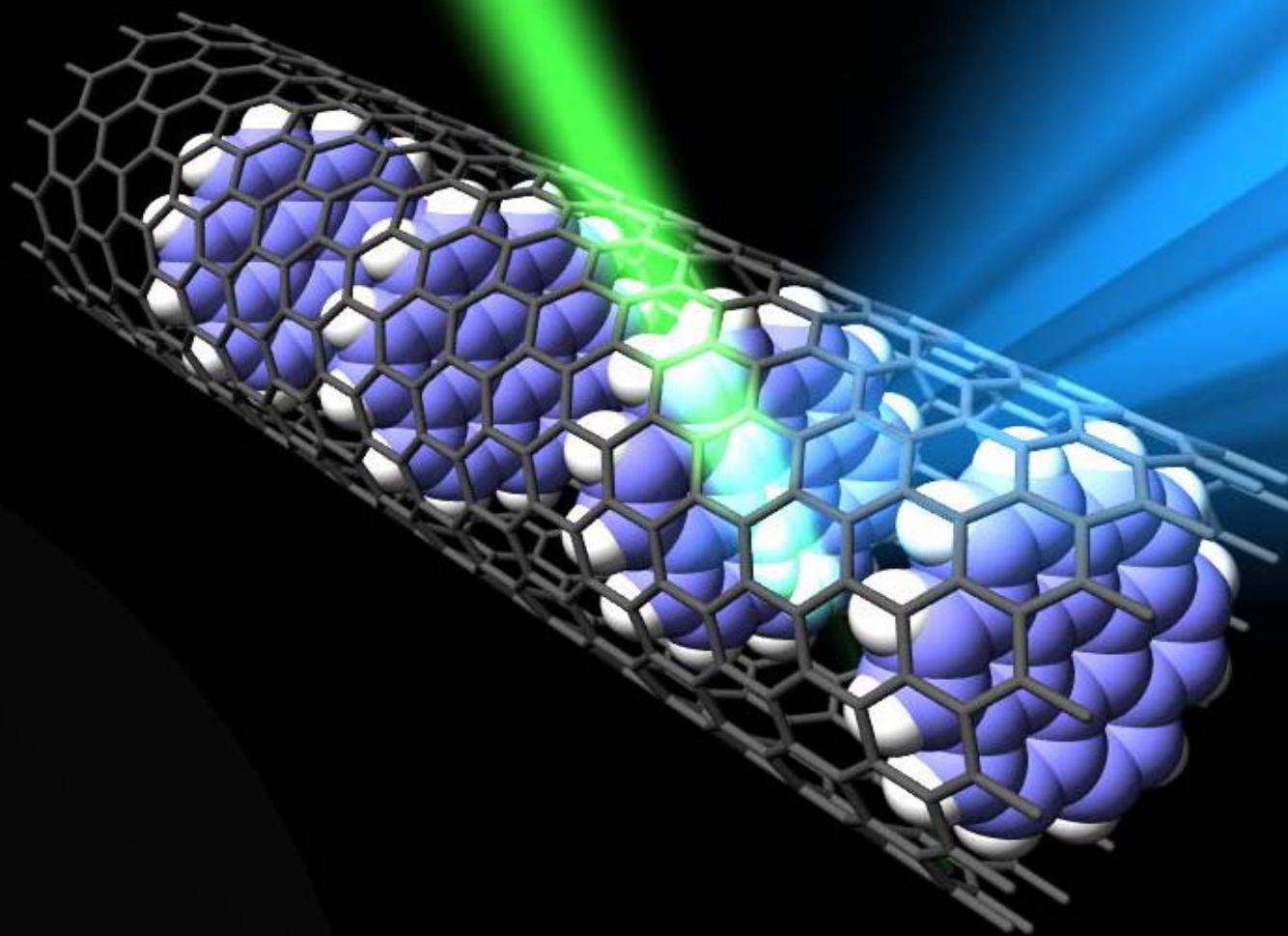


<http://dft.uci.edu>

Various subjects being covered

- Solid-state physics
 - Weakly correlated
 - Strongly correlated
- Atomic and molecular physics
- Mathematical physics
- Semiclassical physics
- Quantum Information
- Chemistry

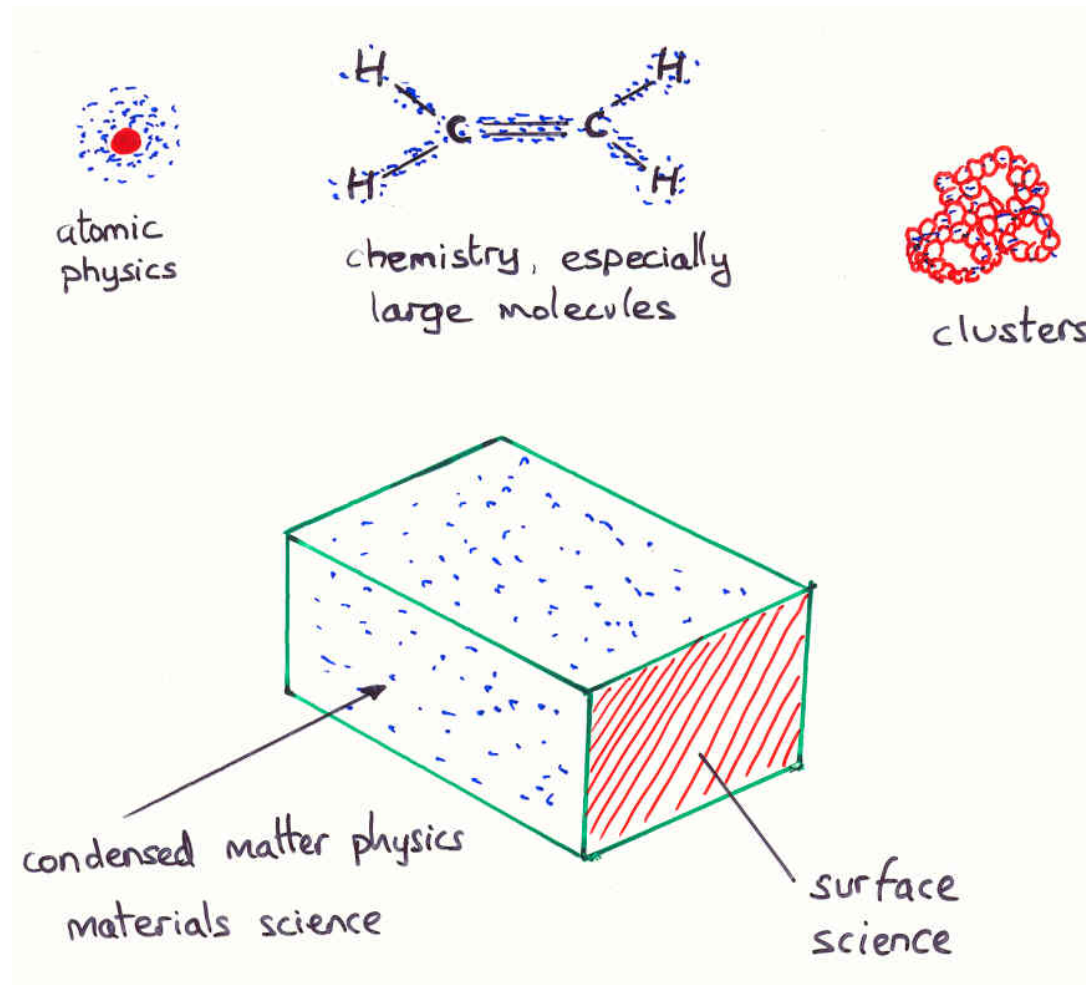
Modern density functional theory in a nutshell



Nano-
Hybrids

Electronic structure problem

What atoms, molecules, and solids exist, and what are their properties?



Properties from Electronic Ground State

- Make Born-Oppenheimer approximation
- Solids:
 - Lattice structures and constants, cohesive energies, phonon spectra, magnetic properties, ...
- Molecules:
 - Bond lengths, bond angles, rotational and vibrational spectra, bond energies, thermochemistry, transition states, reaction rates, (hyper)-polarizabilities, NMR, ...

Traditional approaches to electronic structure

- Quantum chemistry: Start from HF (Hartree-Fock) and either do perturbation theory or add more configurations variationally.
- Quantum chemical accuracy: errors below 1 kcal/mol = 0.05 eV
- Many-body physics: Truncate some expansion for the Green's function.

Thomas/Fermi Theory 1926

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.

- Around since 1926, before QM
- Exact energy: $E_0 = T + V_{ee} + V$
 - T = kinetic energy
 - V_{ee} = electron-electron repulsion
 - V = All forces on electrons, such as nuclei and external fields
- Thomas-Fermi Theory (TF):
 - $T \approx T^{TF} = 0.3 (3\pi)^{2/3} \int dr n^{5/3}(r)$
 - $V_{ee} \approx U = \text{Hartree energy} = \frac{1}{2} \int dr \int dr' n(r) n(r') / |\mathbf{r}-\mathbf{r}'|$
 - $V = \int dr n(\mathbf{r}) v(\mathbf{r})$
 - Minimize $E_0[n]$ for fixed N
- Properties:
 - Exact for neutral atoms as Z gets large (Lieb+Simon, 73)
 - Typical error of order 10%
 - Teller's unbinding theorem: Molecules don't bind.

Modern Kohn-Sham era

- 40's and 50's: John Slater began doing calculations with orbitals for kinetic energy and an approximate density functional for $E_{xc}[n]$ (called $X\alpha$)
- 1964: Hohenberg-Kohn theorem proves an *exact* $E_0[n]$ exists
- 1965: Kohn-Sham produce formally exact procedure and suggest LDA for $E_{xc}[n]$

Kohn-Sham equations (1965)

$$\left[-\frac{1}{2} \nabla^2 + v_s[n](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

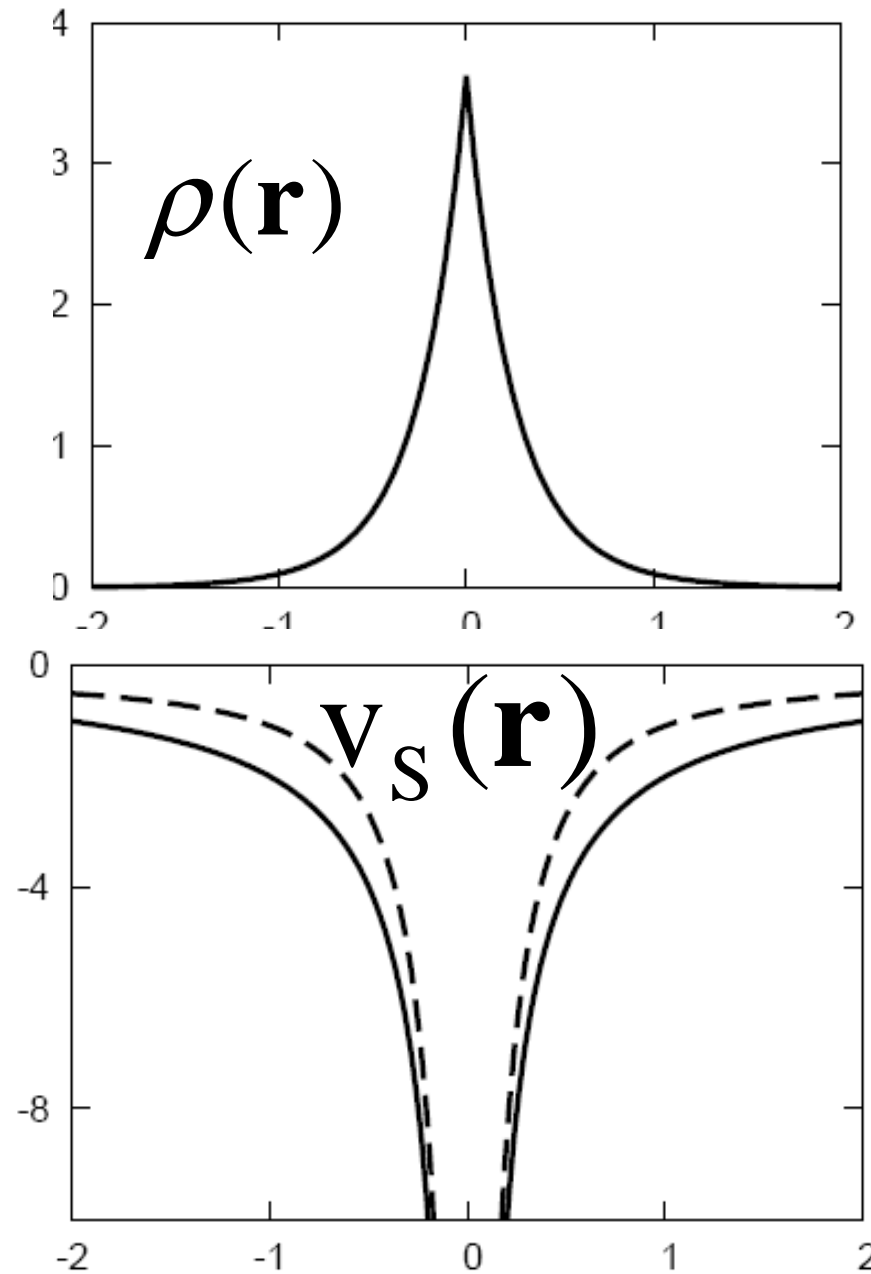
$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 = \text{ground-state density of interacting system}$$

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}[n](\mathbf{r})$$

$$E_0 = T_S + V + U + E_{\text{XC}}[n]$$

$$v_{\text{xc}}[n](\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}$$

He atom in exact Kohn-Sham DFT



Everything
has (at
most) one
KS potential

Dashed-line:
EXACT KS potential

Recipe for exact $E_{xc}[n]$

- Given a trial density $n(\mathbf{r})$
 - Find the $v(\mathbf{r})$ that yields $n(\mathbf{r})$ for interacting electrons
 - Find the $v_s(\mathbf{r})$ that yields $n(\mathbf{r})$ for non-interacting electrons
 - Find $v_H(\mathbf{r})$ (easy)
 - $v_{xc}(\mathbf{r}) = v_s(\mathbf{r}) - v(\mathbf{r}) - v_H(\mathbf{r})$
 - Can also extract $E_{xc} = E - T_s - V - U$
- Much harder than solving Schrödinger equation.
- In fact, QMA hard (Schuch and Verstraete. Nature Physics, **5**, 732 (2009).)

Local (spin)density approximation

- Write $E_{xc}[n]=\int d^3r e_{xc}(n(\mathbf{r}))$, where $e_{xc}(n)$ is XC energy density of uniform gas.
- Workhorse of solid-state physics for next 25 years or so.
- Uniform gas called reference system.
- Most modern functionals begin from this, and good ones recover this in limit of uniformity.

Subsequent development

- Must approximate a small unknown piece of the functional, the exchange-correlation energy $E_{xc}[n]$.
- 70's-90's: Much work (Langreth, Perdew, Becke, Parr) going from gradient expansion (slowly-varying density) to produce more accurate functionals, called generalized gradient approximations (GGA's).
- Early 90's:
 - Approximations became accurate enough to be useful in chemistry
 - 98 Nobel to Kohn and Pople

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

Successes and failures of PBE

- PBE based on simple exact conditions of quantum mechanics, no empirical parameters.
- Reduces LDA overbinding in all chemically bonded systems.
- LDA underestimates most bond lengths. PBE stretches them, but often by too much.
- Still has (in general) self-interaction errors, poor gaps, etc.

Is this useful?

Record 1 of 30

KOHN, W; SHAM, LJ. 1965. SELF-CONSISTENT EQUATIONS INCLUDING EXCHANGE AND CORRELATION EFFECTS. *PHYSICAL REVIEW* 140 (4A): 1133-&..

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Record 2 of 30

Perdew, JP; Burke, K; Ernzerhof, M. 1996. Generalized gradient approximation made simple. *PHYSICAL REVIEW LETTERS* 77 (18): 3865-3868..

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CEPERLEY, DM; ALDER, BJ. 1980. GROUND-STATE OF THE ELECTRON-GAS BY A STOCHASTIC METHOD. *PHYSICAL REVIEW LETTERS* 45 (7): 566-569..

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YABLONOVITCH, E. 1987. INHIBITED SPONTANEOUS EMISSION IN SOLID-STATE PHYSICS AND ELECTRONICS. *PHYSICAL REVIEW LETTERS* 58 (20): 2059-2062..

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BARDEEN, J; COOPER, LN; SCHRIEFFER, JR. 1957. THEORY OF SUPERCONDUCTIVITY. *PHYSICAL REVIEW* 108 (5): 1175-1204..

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Record 7 of 30

FANO, U. 1961. EFFECTS OF CONFIGURATION INTERACTION ON INTENSITIES AND PHASE SHIFTS. *PHYSICAL REVIEW* 124 (6): 1866-&..

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Record 8 of 30

CAR, R; PARRINELLO, M. 1985. UNIFIED APPROACH FOR MOLECULAR-DYNAMICS AND DENSITY-FUNCTIONAL THEORY. *PHYSICAL REVIEW LETTERS* 55 (22): 2471-2474..

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WEINBERG, S. 1967. A MODEL OF LEPTONS. *PHYSICAL REVIEW LETTERS* 19 (21): 1264-&..

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Record 10 of 30

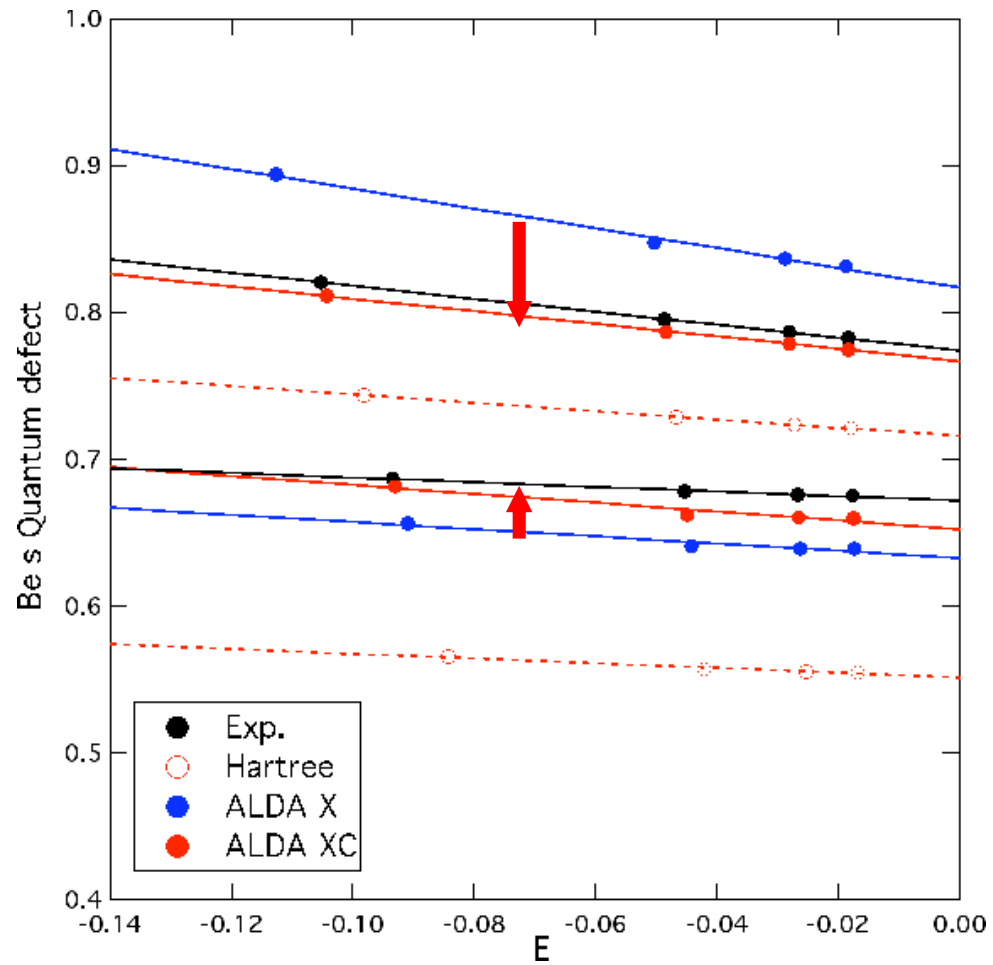
ANDERSON, PW. 1958. ABSENCE OF DIFFUSION IN CERTAIN RANDOM LATTICES. *PHYSICAL REVIEW* 109 (5): 1492-1505..

Times Cited: 4554

Performance for H atom

- Exact total energy: -13.6058 eV
- L(S)DA: -12.99 eV
- PBE: -13.6056 eV

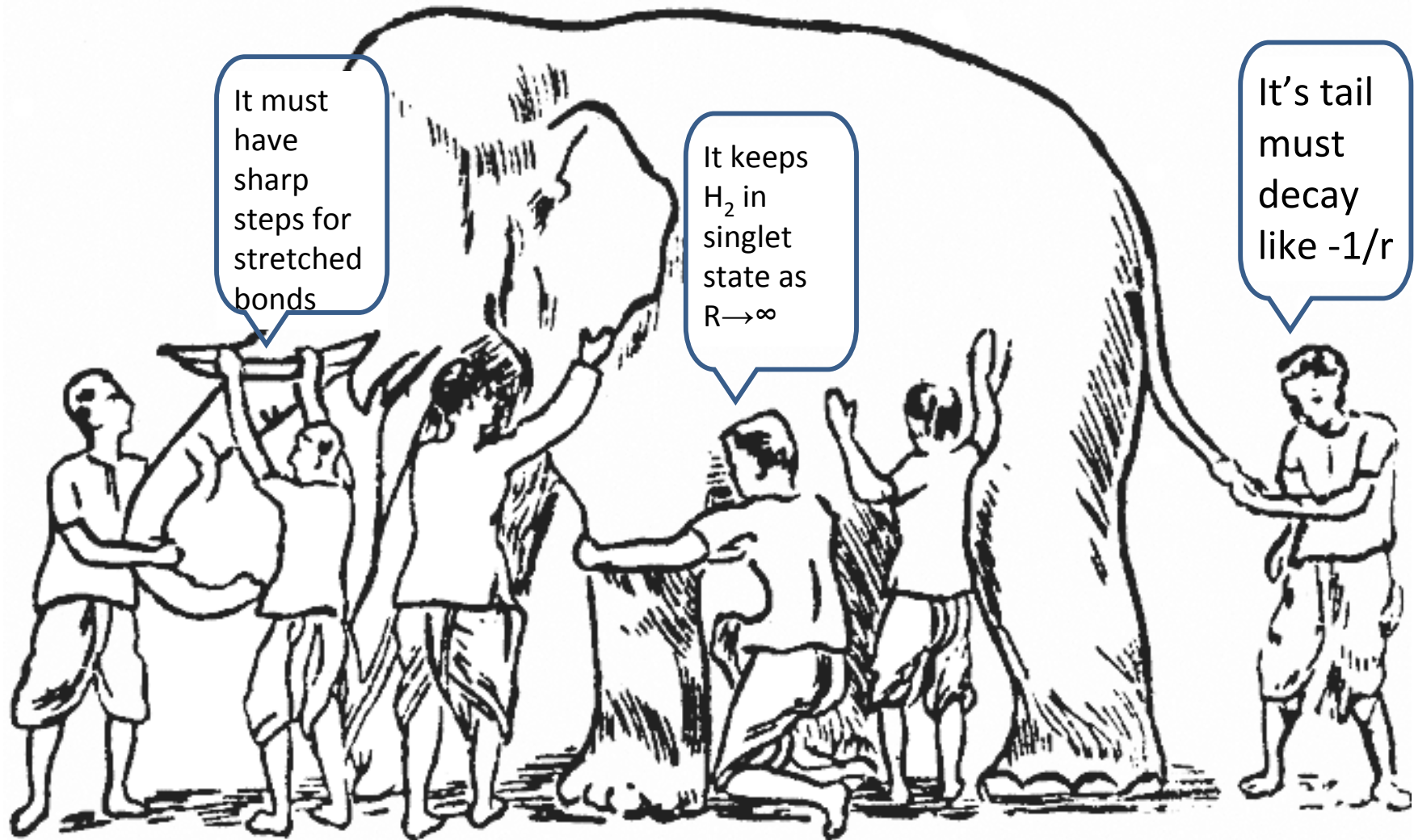
Be s quantum defect: ALDA



Paradigm of strong correlation

- When H_2 (or any bond) is stretched, true wavefunction approaches Heitler-London (1927) form = 2 Slater determinants, not one.
- Somehow exact KS still has doubly occupied molecular orbital, with $\frac{1}{2} \uparrow$ electron and $\frac{1}{2} \downarrow$ electron on each atom, but energy of two hydrogen atoms.
- No standard functional (or HF) reproduces this.

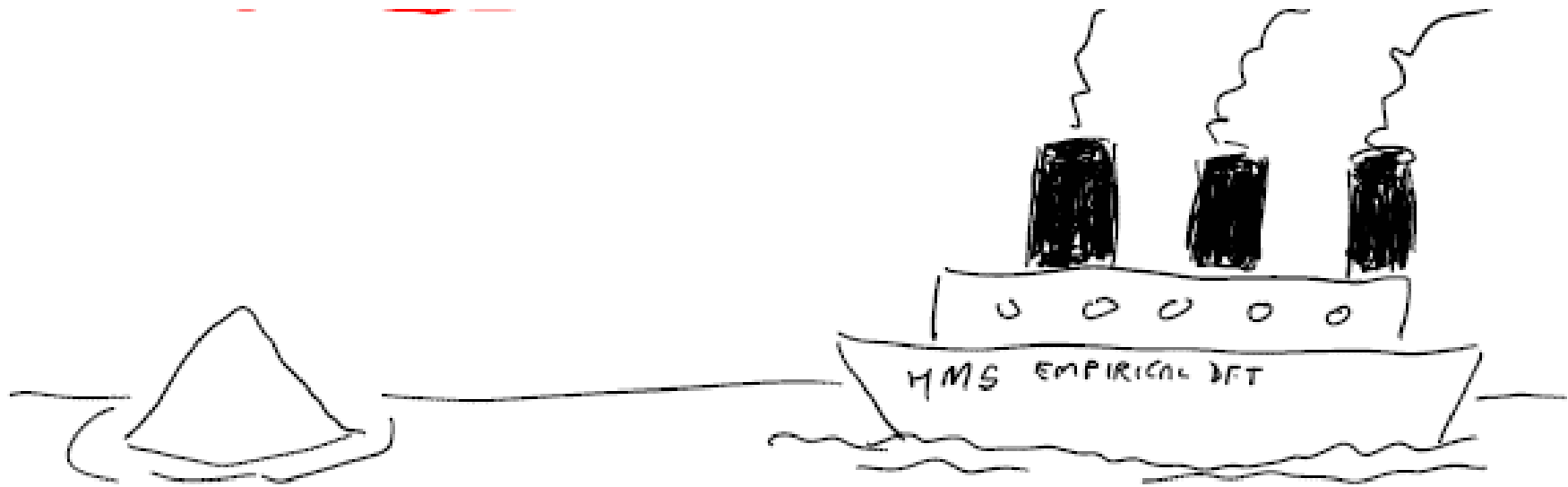
Modern DFT development



Too many functionals



Disaster looms?



The simplest example of a density functional

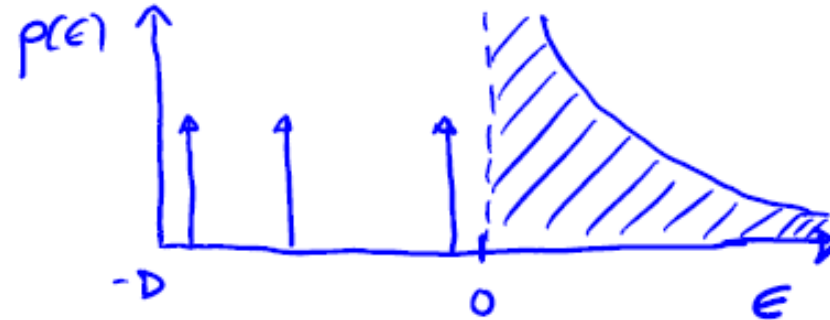
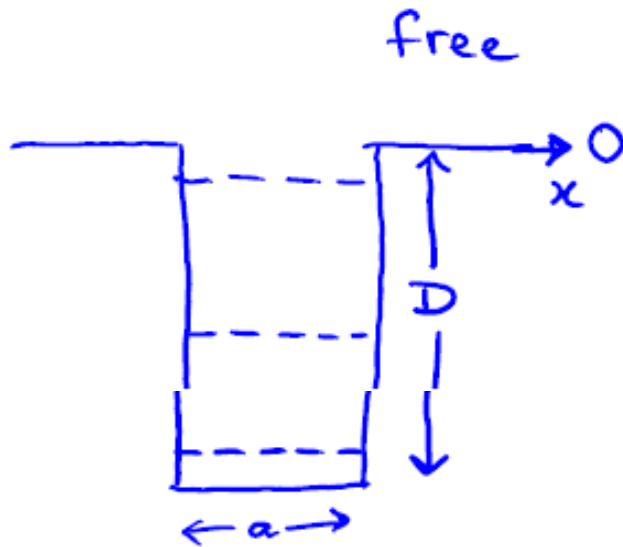
Power of the method

- “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

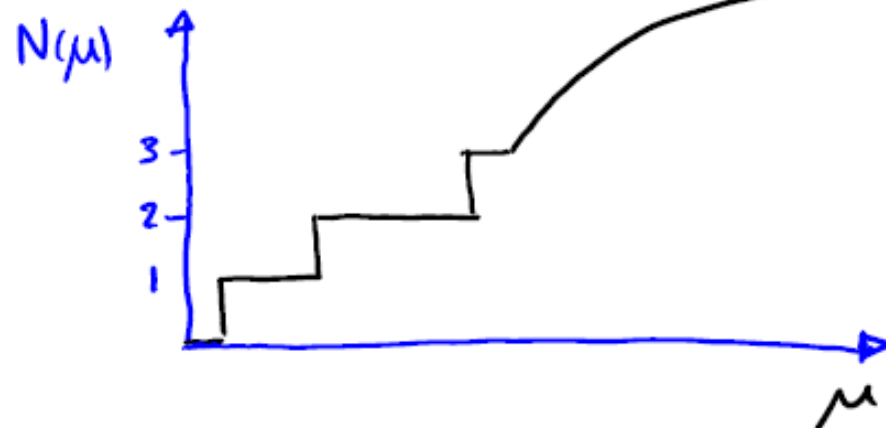
Gross simplification

- Avoid interaction: Just look at kinetic energy
- Avoid Coulomb attraction: Consider only smooth potentials
- Avoid 3d: Reduce to 1d
- Avoid spin: Make all particles same spin
- Avoid real turning points: Use box boundaries

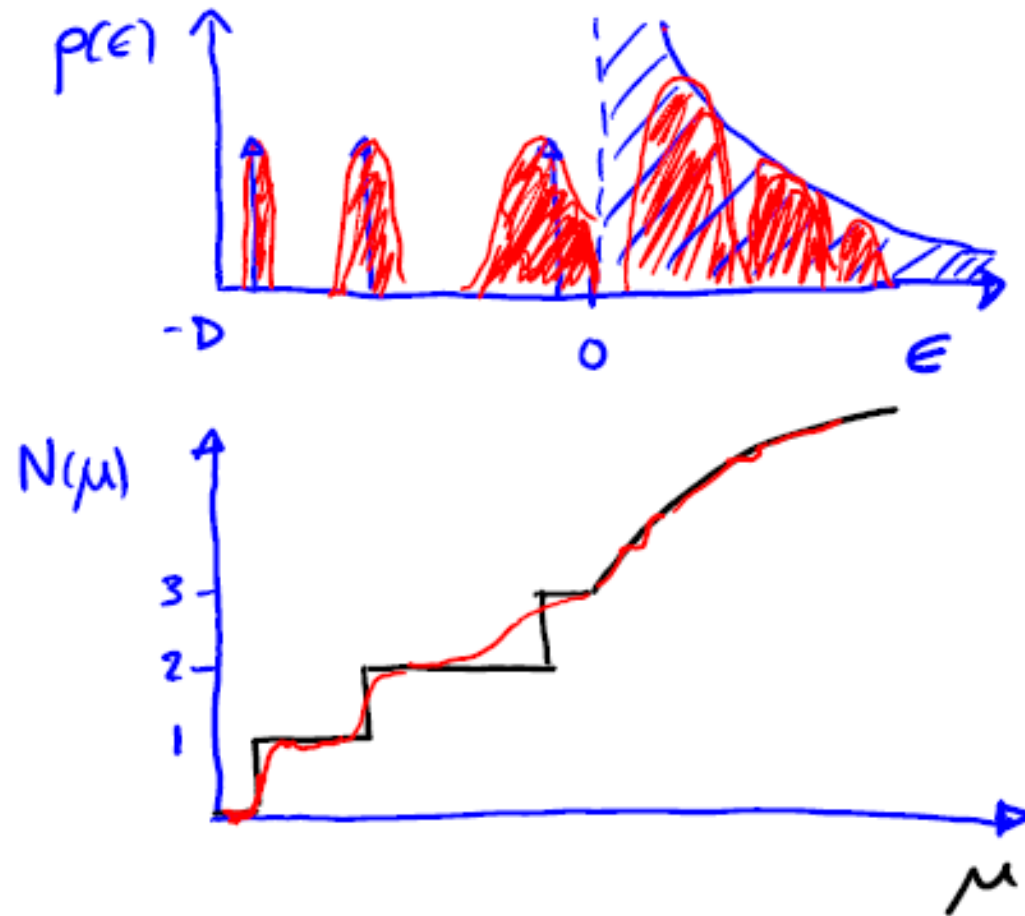
Free continuum



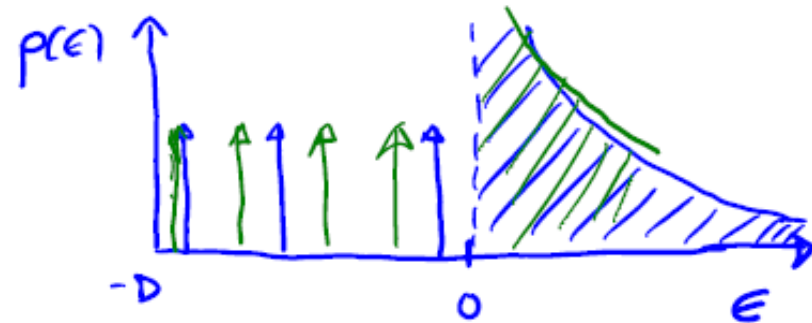
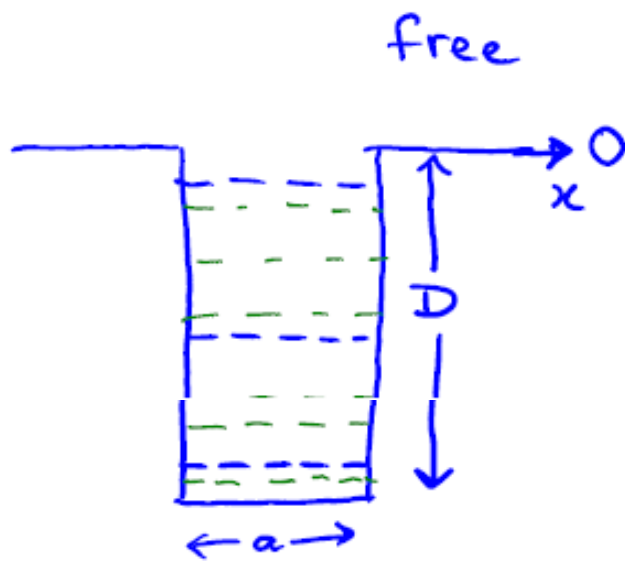
$$N(\mu) = \int_{-\infty}^{\mu} d\epsilon p(\epsilon)$$



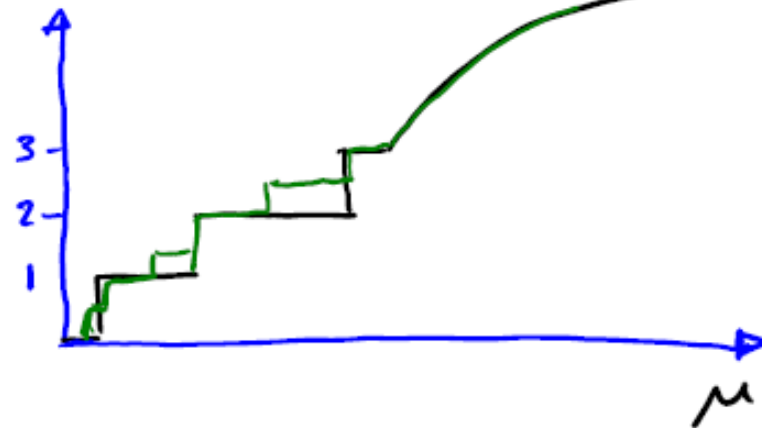
Bulk continuum



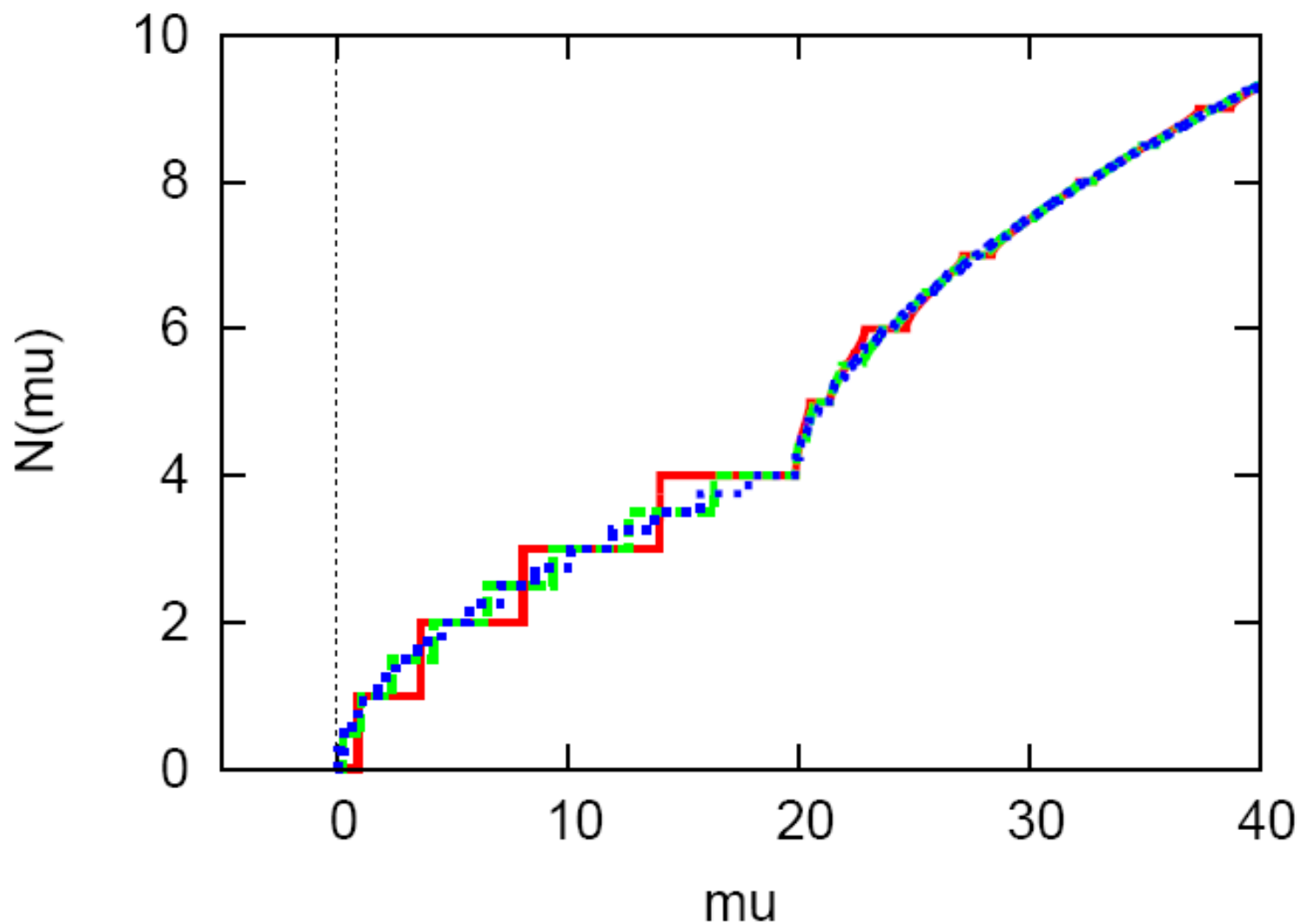
A third one: The classical continuum ($\hbar \rightarrow \gamma \hbar$), $\gamma < 1$



$$\check{N}(\mu) = \gamma N(\mu)$$



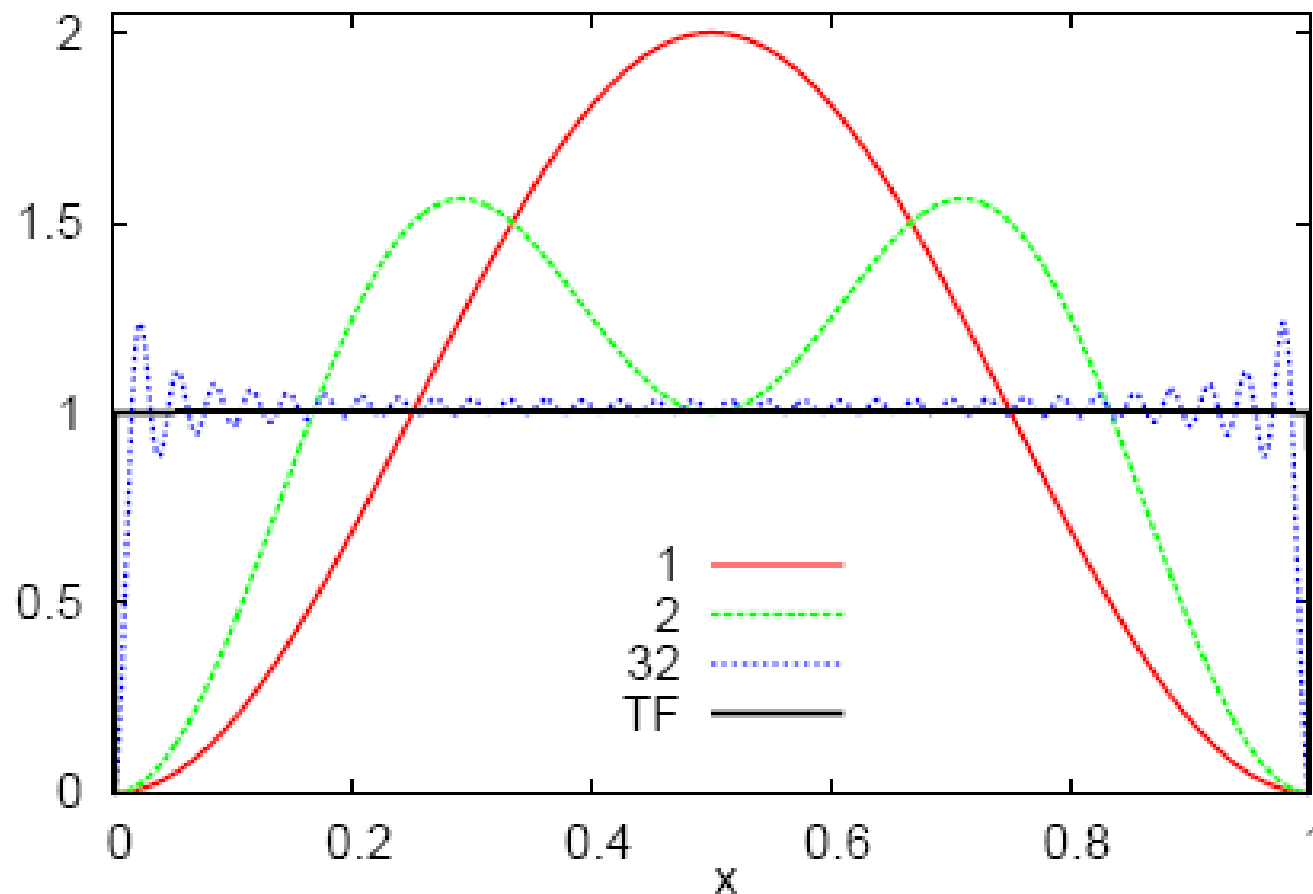
Renormalized integrated DOS for finite well as $\gamma \rightarrow 0$



Approach to classical continuum limit

$$\tilde{n}_\gamma(x) = \frac{N}{N'} n_\gamma(x)$$

Thomas-Fermi limit for particles in a flat box



Origin of quantum oscillations

- Take WKB wavefunctions, satisfying correct boundary conditions:

$$n^{\text{semi}}(\mu, x) = \sum_{j=1}^{N(\mu)} \frac{1 - \cos 2\theta(\epsilon_j, x)}{k(\epsilon_j, x)\tau(\epsilon_j, L)}$$

- Find dominant contributions to integrals.
 - First term is TF result
 - Second term is non-uniform correction.

Semiclassical density for 1d box

$$n^{\text{semi}}(x) = \frac{k_F(x)}{\pi} - \frac{\sin 2\Theta_F(x)}{2T_F k_F(x) \sin \alpha(x)}$$

Classical momentum: $k(x) = \sqrt{2(\mathcal{E} - v(x))}$

Classical phase: $\Theta(x) = \int_0^x dx' k(x')$

Fermi energy: $\Theta_F(L) = (N + \frac{1}{2})/\pi$

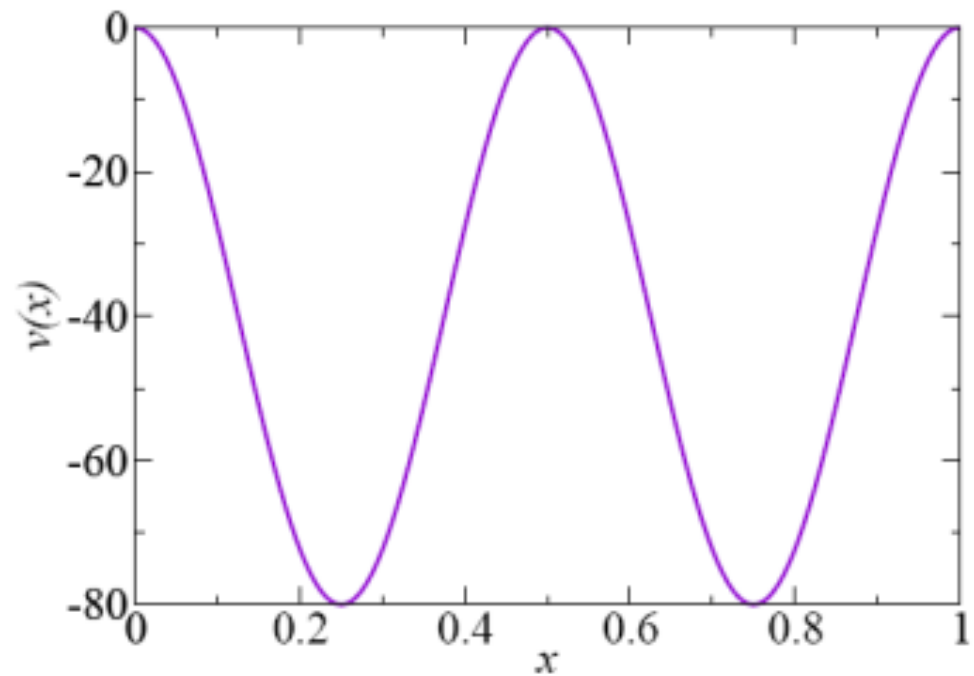
Classical transit time: $\tau_F(x) = \int_0^x dx' / k_F(x')$

$$T_F = \tau_F(L) \quad \alpha(x) = \pi\tau_F(x)/T_F$$

Severe test of semiclassical density

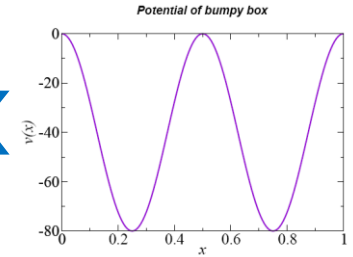
- A very bumpy potential:

Potential of bumpy box

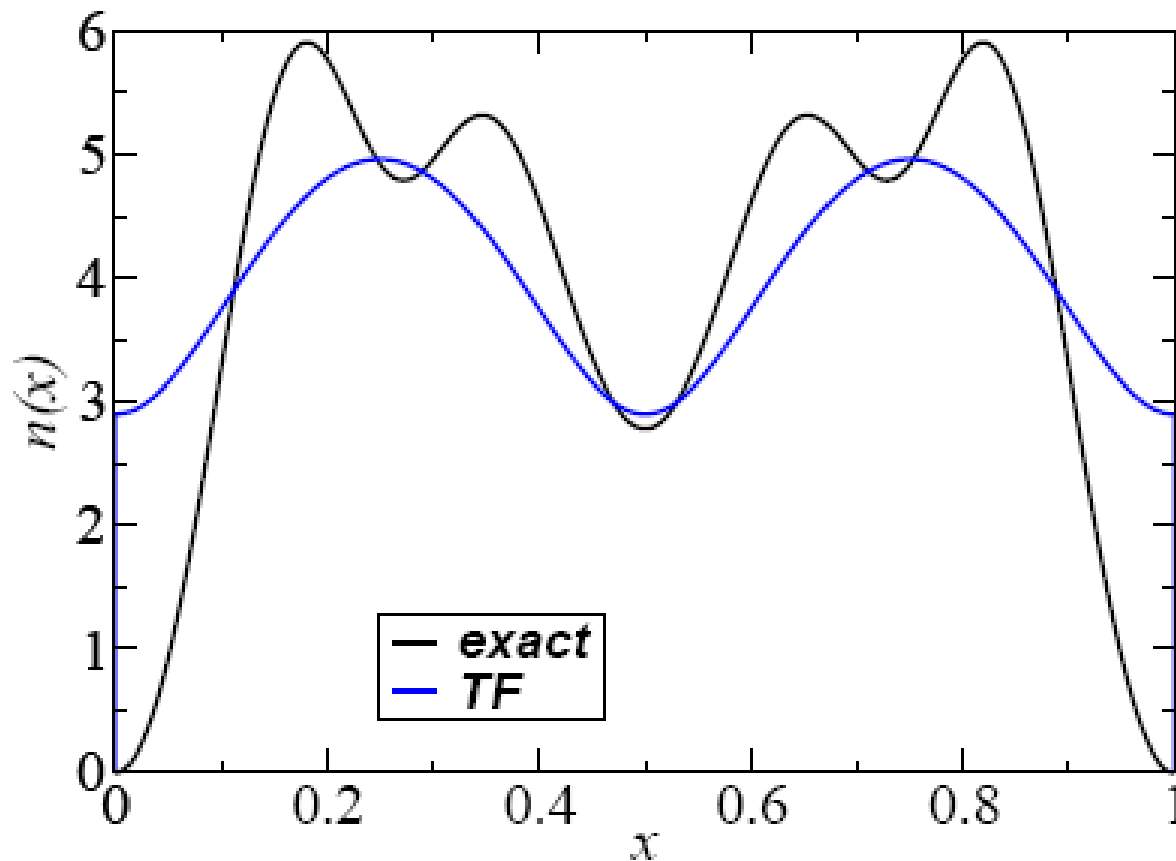


- Orbital energies:
– $\varepsilon_i = -46, -42, 10, 37$

Density in bumpy box



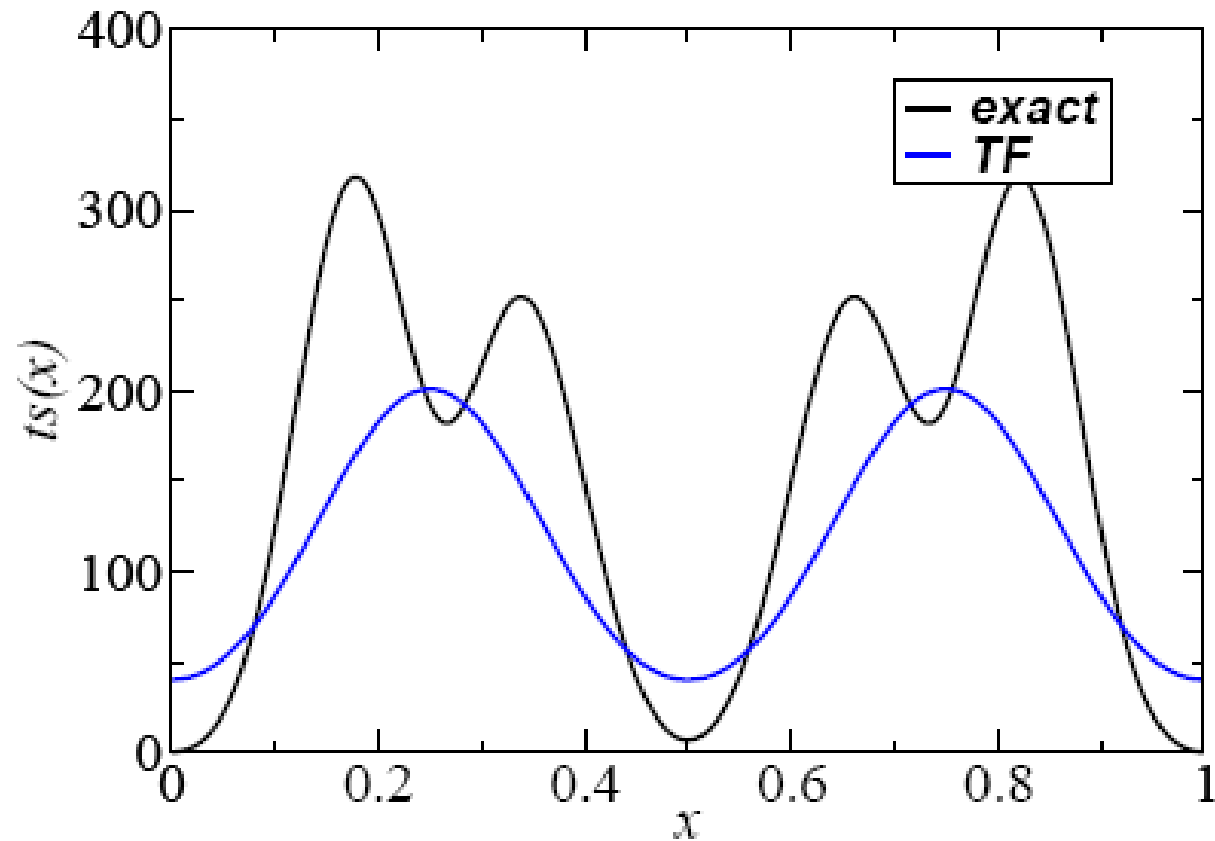
4 spinless Fermions in a bumpy box



- Exact density:
 - $T^{\text{TF}}[n]=153.0$
- Thomas-Fermi density:
 - $T^{\text{TF}}[n^{\text{TF}}]=115$
- Semiclassical density:
 - $T^{\text{TF}}[n^{\text{semi}}]=151.4$
 - $\Delta N < 0.2\%$

Kinetic energy density in bumpy well

4 spinless Fermions in a bumpy box



Elliott, Lee,
Cangi and KB,
PRL 2008

- Kinetic energy:
 - T^{TF} is 115, T^{exact} is 157.2
 - T^{semi} is 156.2

Even evanescent regions right

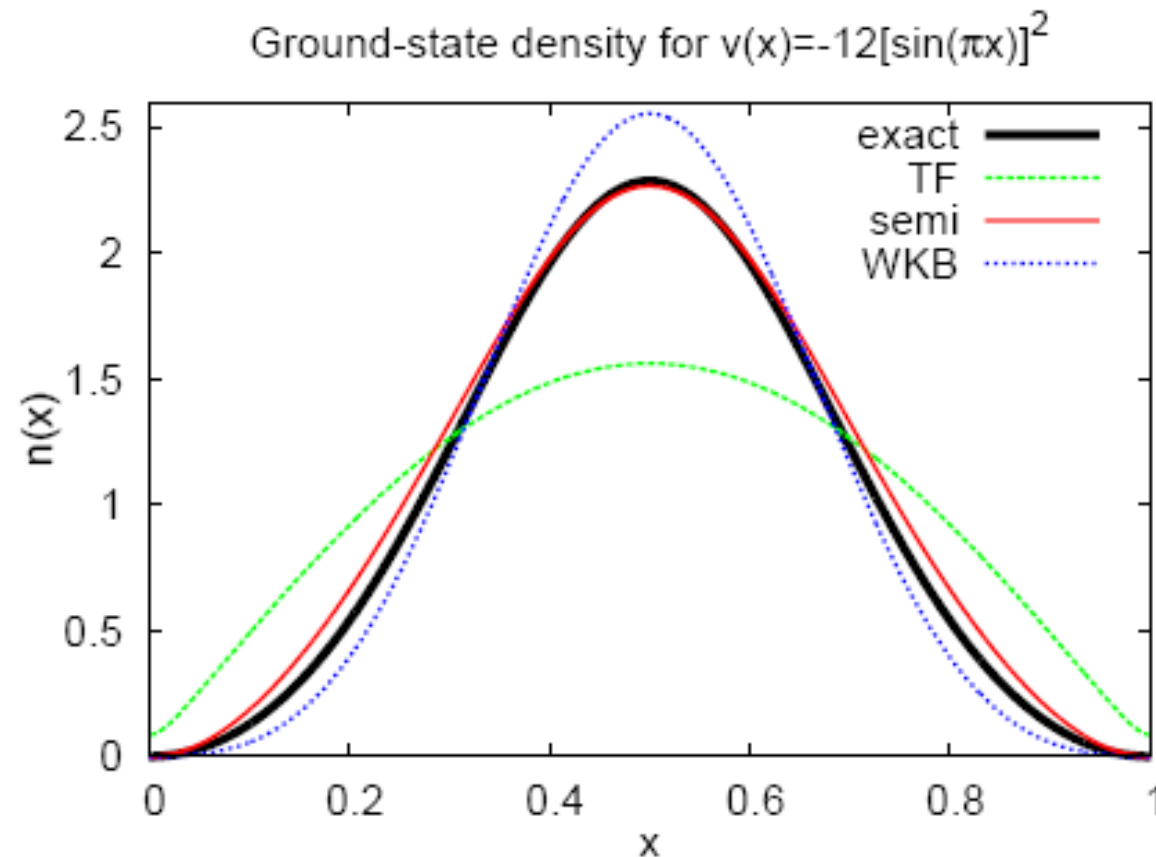


FIG. 1 Exact and approximate densities in $v(x) = -10 \sin^2(\pi x)$ with hard walls at $x = 0$ and $x = 1$.

Very evanescent density

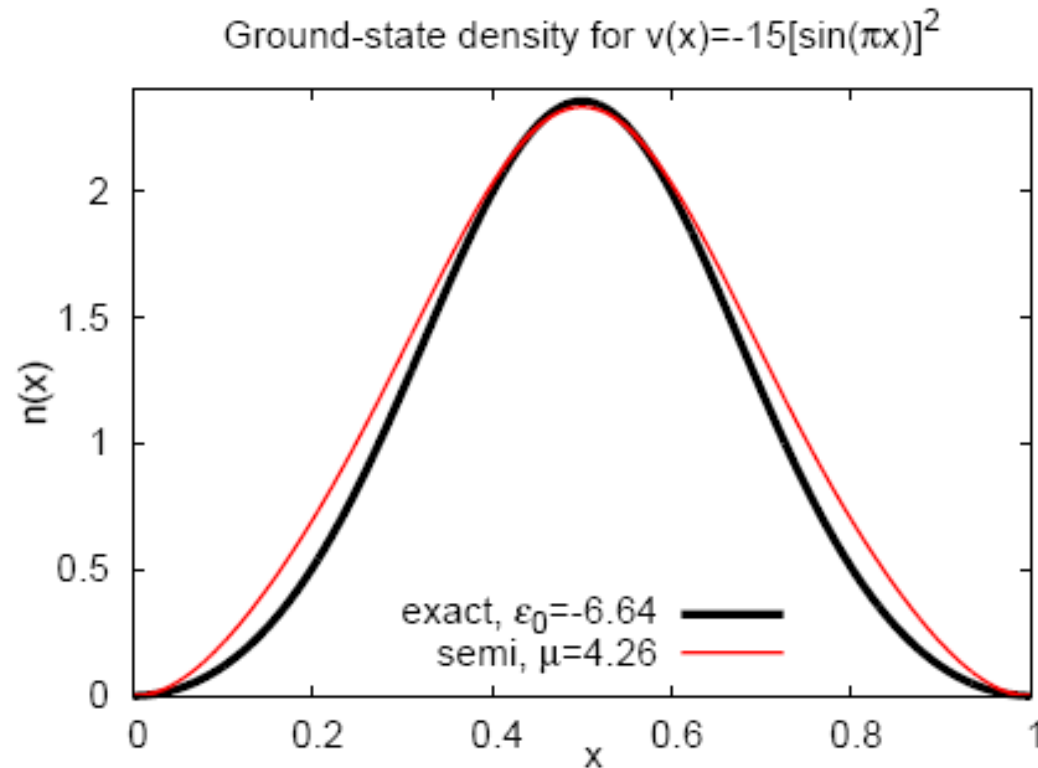


FIG. 4 Exact and approximate ground-state densities for $v(x) = -15 \sin^2(\pi x)$ with hard walls at $x = 0$ and $x = 1$. The lowest eigenvalue is $\epsilon_0 = -6.64$ and therefore has turning points and evanescent regions, and $\mu = 4.26$.

Lessons

- Dominant terms are local in $v(x)$
- Write $t(x)$ in terms of $v(x)$, $v(x)$ in terms of $n(x)$, to get $t^{\text{TF}}(n(x))$
- TF dominates as $N \rightarrow \infty$, so local approx becomes exact for ALL potentials.
- Quantum corrections depend on boundaries, turning points, etc.
- Inclusion of quantum corrections make asymptotically exact to high order.

Implications for reality

Leading corrections to local approximations

- Schwinger and Englert: Neutrals as $Z \rightarrow \infty$
 - $E(Z) = -0.768745 Z^{7/3} + \frac{1}{2} Z^2 - 0.269900 Z^{5/3} + \dots$
- Unreasonably accurate, e.g., only 10% error for H
- First term is exact in TF theory.
- This is the same expansion:
 - $E(\gamma) = -0.768745 + \frac{1}{2} \gamma^{1/3} - 0.269900 \gamma^{2/3} + \dots$

Lieb

- Lieb (RMP, 1981) showed TF becomes relatively exact for all quantum matter (non-relativistic, etc.)
- This is same limit!

A. The $Z \rightarrow \infty$ limit for the energy and density

Let us first concentrate on the energy; later on we shall investigate the meaning of $\rho(x)$. For simplicity the number of nuclei is fixed to be k ; it is possible to derive theorems similar to the following if $k \rightarrow \infty$ in a suitable way (e.g., a solid with periodically arranged nuclei), but we shall not do so here. In TF theory the relevant scale length is $Z^{-1/3}$ and therefore we shall consider the following limit.

Fix $\{\underline{z}^0, \underline{R}^0\} = \{z_j^0, R_j^0\}_{j=1}^k$ and $\lambda > 0$. For each $N = 1, 2, \dots$, define a_N by $\lambda a_N = N$, and in H_N , replace z_j by $a_N z_j^0$ and R_j by $a_N^{-1/3} R_j^0$. Thus $\lambda = Z^0 N / Z$, and a_N is the scale parameter. The TF quantities scale as [Eq. (2.24)]:

$$\begin{aligned} E_{\lambda a}(a \underline{z}^0, a^{-1/3} \underline{R}^0) &= a^{7/3} E_{\lambda}(\underline{z}^0, \underline{R}^0), \\ \rho_{\lambda a}(a^{-1/3} x, a \underline{z}^0, a^{-1/3} \underline{R}^0) &= a^2 \rho_{\lambda}(x, \underline{z}^0, \underline{R}^0). \end{aligned} \quad (5.2)$$

In this limit the nuclear spacing decreases as $a_N^{-1/3} \sim N^{-1/3} \sim Z^{-1/3}$. This should be viewed as a refinement rather than as a necessity. If instead the R_j are fixed $= R_j^0$, then in the limit one has isolated atoms. All that really matters are the limits $N^{1/3} |R_i - R_j|$.

Theorem 5.1 (LS Sec. III). *With $N = \lambda a_N$ as above*

$$\lim_{N \rightarrow \infty} a_N^{-7/3} E_N^Q(a_N \underline{z}^0, a_N^{-1/3} \underline{R}^0) = E_{\lambda}(\underline{z}^0, \underline{R}^0).$$

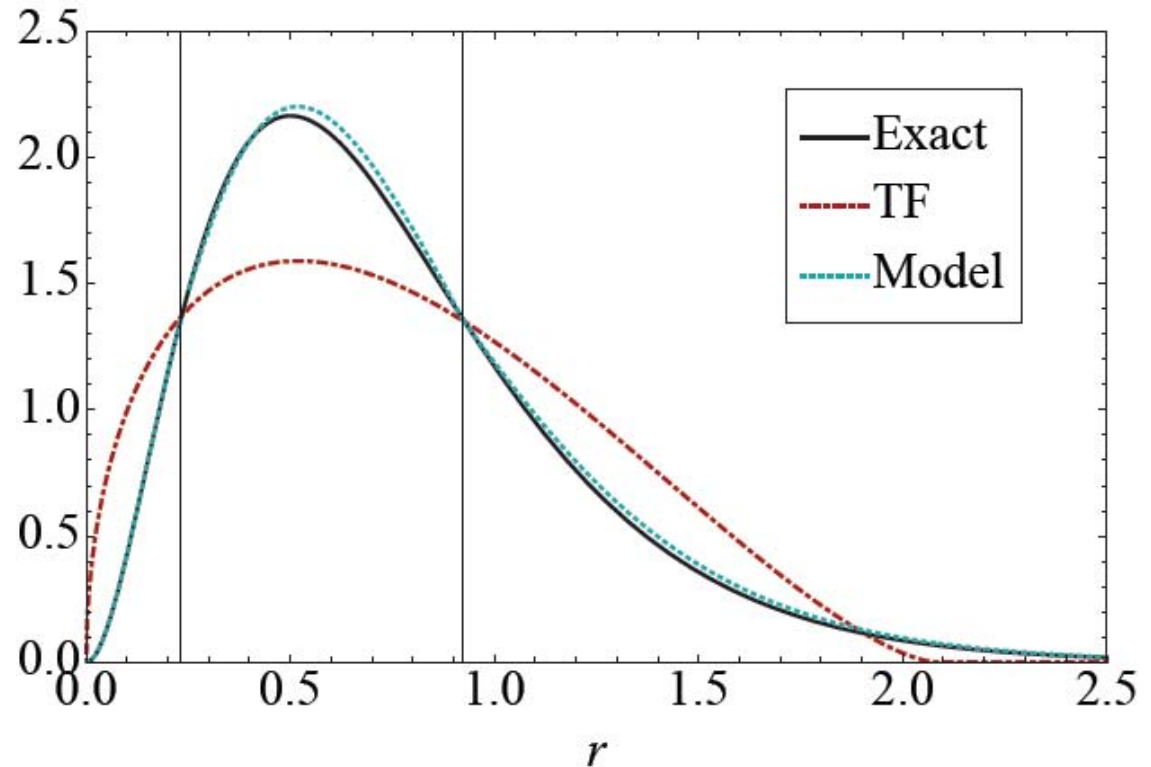
The proof is via upper and lower bounds for E_N^Q . The upper bound is greater than the Hartree-Fock energy, which therefore proves that Hartree-Fock theory is correct to the order we are considering, namely $N^{7/3}$.

H from asymptotic corrections to Bohr atoms

- From Ovadia's thesis:

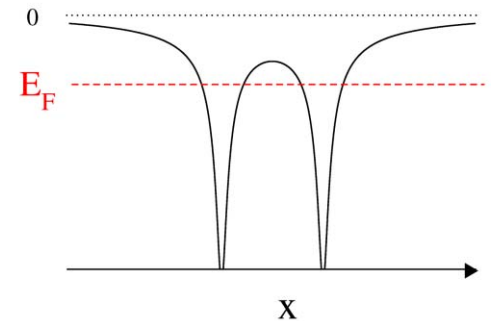
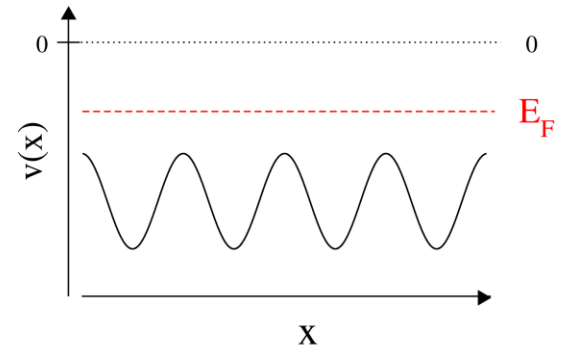
	Exact	TF	Model
E_X^{PBE}	-1.223	-1.353	-1.245
E_X^{exact}		-1.25	

Figure 4: Our 3-region model captures the quantum correction to the Thomas-Fermi density in the Bohr atom as well as the correct limiting behavior as $r \rightarrow 0$ and $r \rightarrow \infty$.



What is role of gradient expansion?

- If system has no edges and no turning points at Fermi energy, then NO quantum corrections
- Gradient expansion yields correct next-order
- But this is special case of more general semiclassical small \hbar expansion, which applies to ALL cases, and includes quantum oscillations which dominate over gradient corrections.
- We've done it just to leading order. In next order, get leading gradient correction plus quantum gradient corrections.



Return to stretched H_2

- Consider $v_s(r)$ as function of bond length R
- For exact KS potential, new turning points occur at about $R=3.3 \text{ \AA}$
- Coulson-Fischer point (where spontaneous symmetry is broken) is 3.3 \AA in LDA
- Beyond that point (i.e., for strongly correlated systems), there is a different non-universal asymptotic expansion!
- Failure of local-type approximations for strongly-correlated systems.

Quantum chemistry

- Even the most fitted functionals do not produce mean average errors less than 2 kcal/mol.
- There are also wild outliers, where the errors are much bigger.
- Almost all chemical electronic structure calculations today (> 95%) are DFT, not wavefunction calculations.

E_x for neutral atoms

- $E_x = -0.2208 Z^{5/3} - .195 Z + \dots$
- Schwinger proved first term exact for LDA exchange.
- With GEA, get almost exactly $\frac{1}{2}$ second coefficient
- All commonly-used GGA's get second coefficient about right!
- Assuming equal contributions, Becke's parameter in B88: $\beta = 5 / (216 (6\pi^5)^{1/3}) = .00378$
- compare with .0042 from Becke's fit

PBEsol

- Most important idea: Restore gradient expansion for exchange!
- Correlation fixed from jellium surface energy.
- Screws up typical atomization energies, but reduces overcorrection of bond length.
- AM05 gives comparable result with very different derivation.

Students doing all the work

Attila Cangi,
Peter Elliott,
Donghyung
Lee



Lessons for DFT

- As $\hbar \rightarrow 0$, local approximations become relatively exact for all systems.
- The local density approximation is a *limit* of *all* electronic systems.
- That expansion is not uniformly convergent in space
- The well-defined gradient expansion is the correct asymptotic expansion for simple metals
- Quantum corrections for finite systems are larger than gradient corrections.

- What does the existence of an asymptotic expansion mean for quantum information theory?
- The solution to which differential equation will generally give me my leading corrections to local approximations?
- Can this be used in other contexts?
- Thanks to NSF.

Broader questions