Semiclassical origins of density functional approximations

Kieron Burke
& many friends
UC Irvine Physics and Chemistry

INSTITUTE FOR PURE AND APPLIED MATHEMATICS
Los Angeles, California
Semiclassical Origins of Density Functional Approximations
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http://dft.uci.edu

Idea behind workshop

- DFT is now used worldwide to simulate and find new materials and drugs.
- Conjecture: The reason for its success is very poorly understood, and reflects power of asymptotic semiclassical expansions.
- Different groups approach this problem from different angles.
- Try to find unifying themes and create practical framework for improving DFT.

Participants

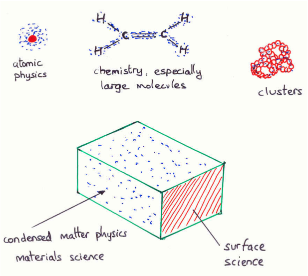
- All speakers carefully chosen
- Represent a wide range of disparate interests
- About half have made direct contributions to this subject (not necessarily recently)
- Others are working with various techiques of great relevance, e.g., semiclassics, multiple length scales, etc.
- Challenge: Find common language.

Contents

- Introduction to electronic structure problem
- My rosetta stone: Particles in a 1d box
- Back to chemical reality and KS world
- A new formalism: Potential functional theory
- Some current projects
- Conclusions

Electronic structure problem

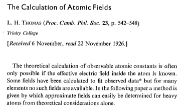
What atoms, molecules, and solids exist, and what are their properties?



Traditional first-principles approaches

- Make Born-Oppenheimer approximation
- Must solve the Schrödinger equation for electrons to find ground-state energy
- Huge number of material-specific properties (e.g., geometries, vibrations, bond energies, reaction rates, etc.) available
- Tough differential equation, with nuclear-electron attraction and electron-electron repulsion, coupling 3N coordinates.
- Chemistry
  - Variational methods: HF, CI, CC, CASSCF,…
  - Perturbative: MP2, MP4, CISD(T),…
- Solid-state physics
  - Many-body methods: GW
  - Wavefunction methods: QMC

First DFT: Thomas-Fermi Theory



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.

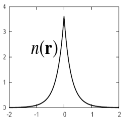
- Around since 1926, before *Schrödinger* energy: $E_0 = T + V_{ee} + V$
  - T = kinetic energy
  - V_{ee} = electron-electron repulsion
  - V = All forces on electrons, such as nuclei and external fields
- Thomas-Fermi Theory (TF):
  - $T \approx T^{TF} = 0.3\,(3\pi)^{2/3}\int d\mathbf{r}\; n^{5/3}(\mathbf{r})$
  - $V_{ee} \approx U$ = Hartree energy = $\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\; n(\mathbf{r})\, n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$
  - $V = \int d\mathbf{r}\; n(\mathbf{r})\, v(\mathbf{r})$
  - 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.

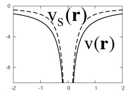
Kohn-Sham equations (1965)

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

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

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





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

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

Also introduced local density approximation for $E_{xc}[n]$

The present

- KS DFT ubiquitous in quantum chemistry, materials science,..
- More than 10,000 paper/ year.
- Codes available for free or small charge
- But an abundance of approximations
- Annoyances:
  - ● No simple rule for reliability
  - ● No systematic route to improvement
  - ● If your property turns out to be inaccurate, must wait several decades

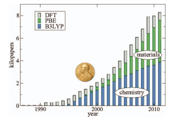
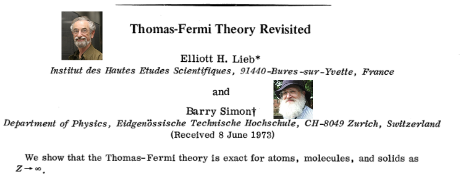


FIG. 1. Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).

Perspective in J. Chem. Phys. 2012

Essential questions

- When do local density approximations become relatively exact for quantum system?
- What is nature of expansion?
- What are leading corrections?
- Lieb/Simon proved true for TF theory as Z->∞
- Schwinger/Englert demonstrated true for LDA for XC in atoms.
- Best modern GGA's constructed to 'improve' over LDA



Thomas-Fermi Theory Revisited

Elliott H. Lieb*
Institut des Hautes Etudes Scientifiques, 91440-Bures-sur-Yvette, France

and

Barry Simon†
Department of Physics, Eidgenössische Technische Hochschule, CH-8049 Zurich, Switzerland
(Received 8 June 1973)

We show that the Thomas-Fermi theory is exact for atoms, molecules, and solids as $Z \to \infty$.

ROSETTA STONE:
1d particles in wavy box

One particle in 1d

- WKB wavefunction has first two powers of $\hbar$:

$$\phi_E^{WKB}(x) \approx \frac{1}{\sqrt{p(x)}}\, e^{\pm i\,\theta(x)} ,$$

where ($m = e^2 = 1$):

$$p(x) = \sqrt{2(E - v(x))} \qquad \theta(x) = \int_0^x dx'\, p(x')/\hbar .$$

- Exact for flat potential, $v(x) = 0$.
- Highly accurate for a slowly-varying potential.

N fermions in 1d

Suppose I have N (same-spin) fermions, and occupy the first N levels of the system. Is there a way to make a direct semiclassical approximation to *sums* over occupied orbitals? For example,

$$n(x) = \sum_{i=1}^{N} |\phi_i(x)|^2 , \qquad t(x) = -\frac{\hbar^2}{2} \sum_{i=1}^{N} \phi_i^*(x)\phi_i''(x) ,$$

the density and kinetic energy density ($\phi'(x) = d\phi/dx$),

$$N = \int dx\, n(x) , \qquad T = \int dx\, t(x) ,$$

Rough sums

$$n(x) \approx \int_{-\infty}^{E_{\rm F}} \frac{dE}{\pi\hbar}\, |\phi_E(x)|^2 = \frac{k_{\rm F}(x)}{\pi} , \qquad k(x) = p(x)/\hbar ,$$

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

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

$$\int dx\, n(x) = N \quad \textit{or} \quad \theta_{\rm F}(\infty) = N\pi .$$

Inversion

One can invert the density equation and insert into $t(x)$ equation to find:

$$t^{\rm loc}(x) = \frac{\pi^2\hbar^2}{6}\, n^3(x),$$

which is the *local density approximation* to the non-interacting kinetic energy in 1d.
Knowing $T^{\rm loc}[n]$, one could solve the Euler equation:

$$\frac{\pi^2\hbar^2}{2}\, n^2(x) + v(x) = \mu ,$$

forgetting derivation of $T^{\rm loc}$.

Next order: gradient expansion for slowly varying potentials

- Continuing the expansion to higher power of $\hbar$, we find, e.g.,

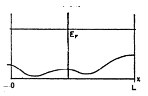
$$n(x) = \frac{k_{\rm F}(x)}{\pi}\left(1 + \frac{\hbar^2\, v''(x)}{48[E_{\rm F} - v(x)]^2} + ...\right) ,$$

$$t(x) = \frac{\hbar^2 k_{\rm F}^3(x)}{6\pi}\left(1 + \frac{\hbar^2\, v''(x)}{16[E_{\rm F} - v(x)]^2} + ...\right) .$$

- Notice that expansion becomes accurate when $\hbar \to 0$ or $N \to \infty$, or $v(x)$ becomes constant.
- Inversion leads to the *gradient expansion* for T:

$$T^{GE}[n] = \frac{\pi^2\hbar^2}{6}\int dx\, n^3(x) - \frac{\hbar^2}{24}\int dx \frac{n'(x)^2}{n(x)} + ...$$

Wavy boxes



- Simplest example: Insert hard walls at $x = 0$ and $x = L$.
- WKB traveling wavefunction no longer correct, even for flat box.
- Need to impose boundaries: choose $\pm$ combination so that $\phi(0) = \phi(L) = 0$.
- Even yields simple condition for bound states, $\int dx\, p(x) = j\pi\hbar$, j an integer.
- Works well even for not-too-bumpy box or high enough, i.e., $E \to \infty$, or $\hbar \to 0$ or $v(x)$ flat.

Semiclassical density for 1d box

$$\boxed{n^{\mathrm{TF}}(x) = \frac{k_{\mathrm{F}}(x)}{\pi} - \frac{\sin 2\Theta_{\mathrm{F}}(x)}{2T_{\mathrm{F}}\, k_{\mathrm{F}}(x) \sin\alpha(x)}}$$

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

Classical phase: $\Theta(x) = \int_0^x \mathrm{d}x'\, k(x')$

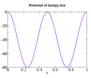
Fermi energy: $\Theta_F(L) = (N + \frac{1}{2})/\pi$

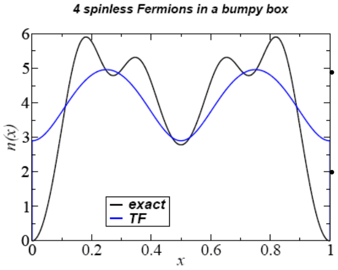
Classical transit time: $\tau_{\mathrm{F}}(x) = \int_0^x \mathrm{d}x'/k_{\mathrm{F}}(x')$

$$T_{\mathrm{F}} = \tau_{\mathrm{F}}(L) \qquad \alpha(x) = \pi\tau_{\mathrm{F}}(x)/T_{\mathrm{F}}$$

Elliott, Cangi, Lee, KB, PRL 2008

Density in bumpy box





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

A different continuum

1. Scattering states:
   For a finite system, E > 0
2. Solid-state: Thermodynamic limit
   For a periodic potential, have continuum bands
3. Classical 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
   - …
   - →∞

Classical Continuum limit

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

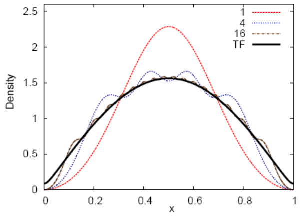
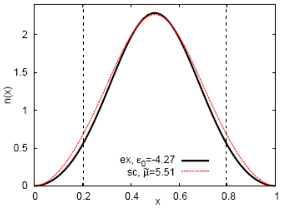


FIG. 2: TF and renormalized exact densities for $N' = 1, 4, \text{and} 16$ particles in $v(x) = -12\sin^2(\pi x), 0 \leq x \leq 1$, showing approach to continuum limit.

Attila Cangi

Example of utility of formulas

- Worst case (*N*=1)
- Note accuracy outside of turning points
- No evanescent contributions in formula

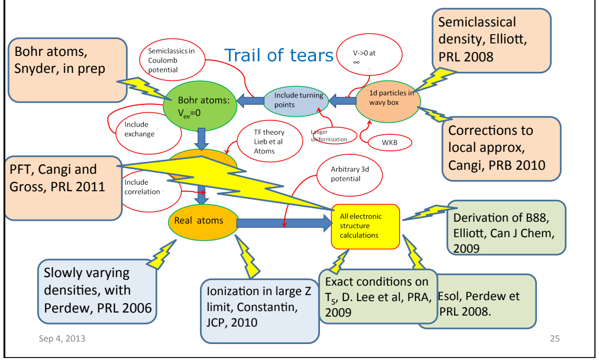


$$n^{\mathrm{semi}}(x) = \frac{k_{\mathrm{F}}(x)}{\pi} - \frac{\sin 2\Theta_{\mathrm{F}}(x)}{2T_{\mathrm{F}}\, k_{\mathrm{F}}(x) \sin\alpha(x)}$$

FIG. 9: Exact and approximate ground-state densities for $v(x) = -12\sin^2(\pi x)$, where $0 \leq x \leq 1$. The lowest eigenvalue is $\epsilon_0 = -6.64$ and $\tilde{\mu} = 4.26$. The position of the turning points is indicated by dashed lines.

BACK TO REALITY:

Many aspects of this problem



Bohr atoms, Snyder, in prep

Semiclassics in Coulomb potential

Trail of tears

V->0 at ∞

Semiclassical density, Elliott, PRL 2008

Bohr atoms: $V_{ee}=0$

Include turning points

1d particles in wavy box

Include exchange

TF theory Lieb et al Atoms

Langer uniformization

WKB

Corrections to local approx, Cangi, PRB 2010

PFT, Cangi and Gross, PRL 2011

Include correlation

Arbitrary 3d potential

Real atoms

All electronic structure calculations

Derivation of B88, Elliott, Can J Chem, 2009

Slowly varying densities, with Perdew, PRL 2006

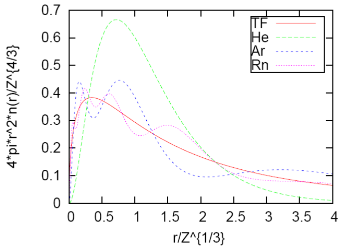
Ionization in large Z limit, Constantin, JCP, 2010

Exact conditions on T_S, D. Lee et al, PRA, 2009

Esol, Perdew et PRL 2008.

Classical continuum limit for neutral atoms

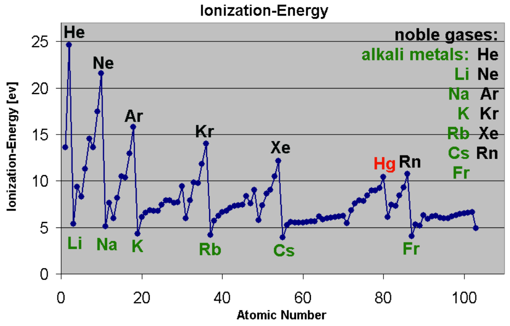
- For interacting systems in 3d, increasing *Z* in an atom, keeping it neutral, approaches the classical continuum, i.e. same as ħ→0
- Can study E_x as Z→∞, *find universal limit*



A major ultimate aim: $E_{XC}[n]$

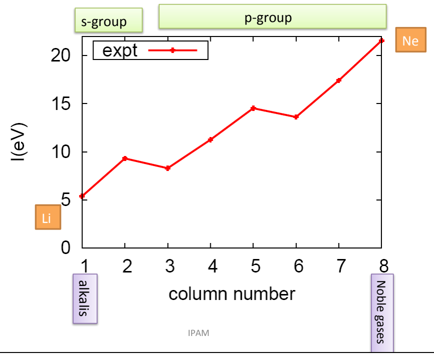
- Explains why gradient expansion needed to be generalized (*Relevance of the slowly-varying electron gas to atoms, molecules, and solids* J. P. Perdew, L. A. Constantin, E. Sagvolden, and K. Burke, Phys. Rev. Lett. 97, 223002 (2006).)
- Derivation of β parameter in B88 (*Non-empirical 'derivation' of B88 exchange functional* P. Elliott and K. Burke, Can. J. Chem. 87, 1485 (2009).).
- PBEsol *Restoring the density-gradient expansion for exchange in solids and surfaces* J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008))
  - fixes failure of PBE for lattice constants (but at cost of good thermochemistry)

What about energy differences?

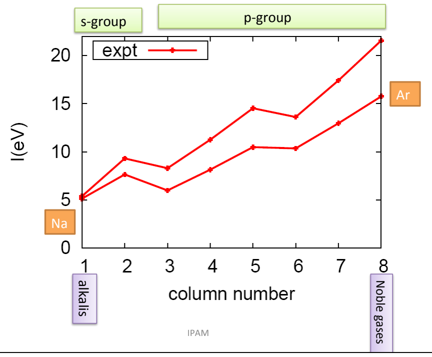


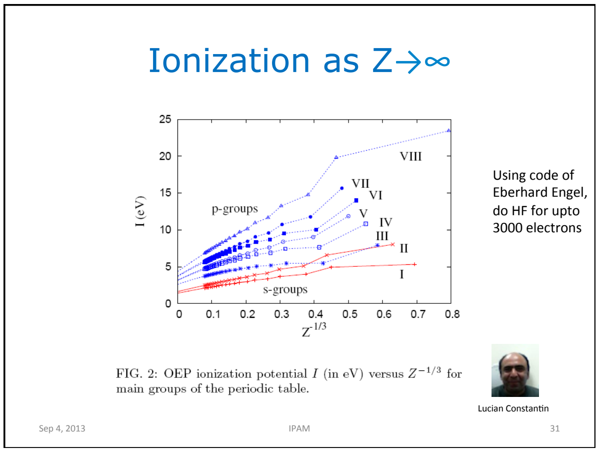
- wikipedia

I along first row



I along first and second rows





Ionization as Z→∞

Using code of Eberhard Engel, do HF for upto 3000 electrons

FIG. 2: OEP ionization potential I (in eV) versus $Z^{-1/3}$ for main groups of the periodic table.

Lucian Constantin

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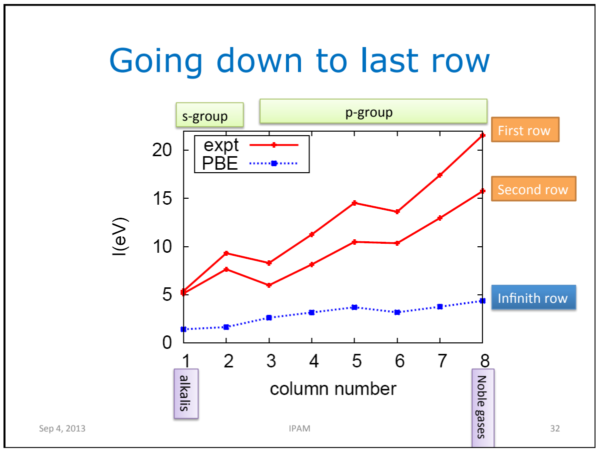

Going down to last row

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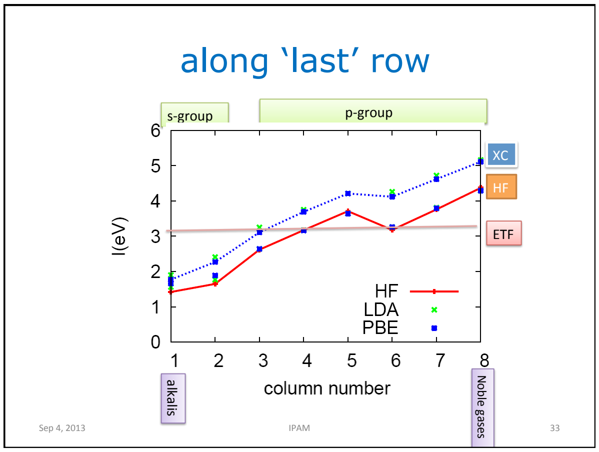

along 'last' row

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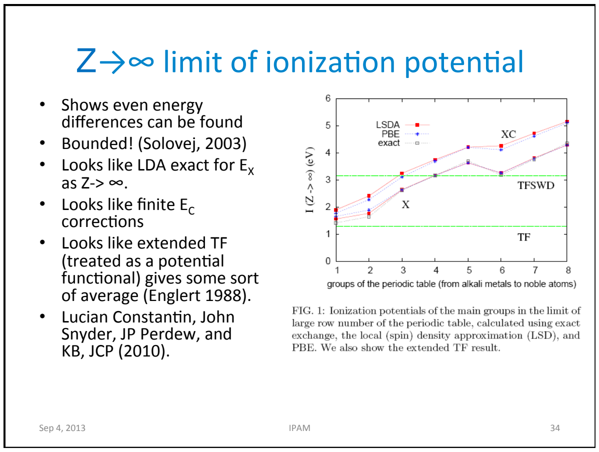

Z→∞ limit of ionization potential

- Shows even energy differences can be found
- Bounded! (Solovej, 2003)
- 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 (Englert 1988).
- 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.

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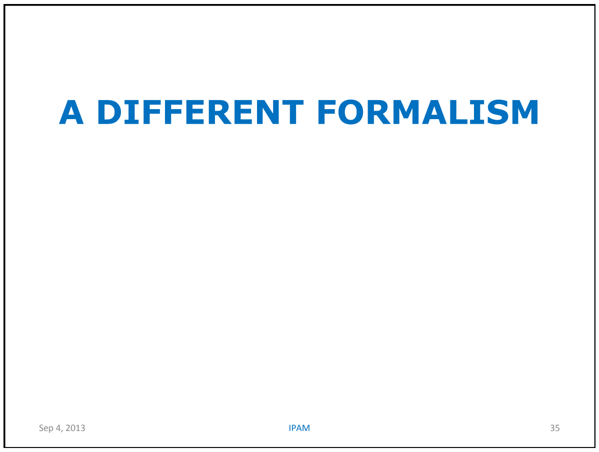

A DIFFERENT FORMALISM

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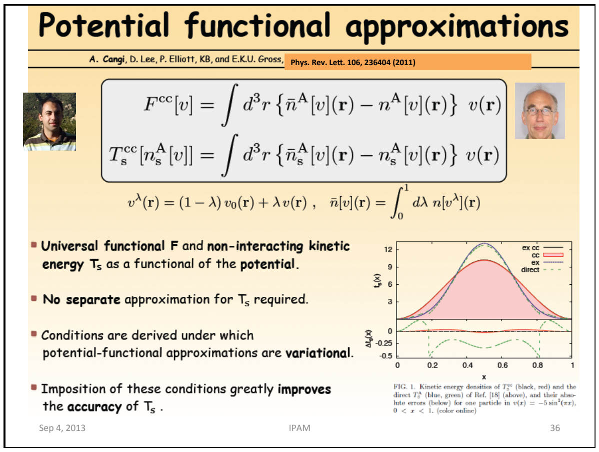

Potential functional approximations

A. Cangi, D. Lee, P. Elliott, KB, and E.K.U. Gross, Phys. Rev. Lett. 106, 236404 (2011)

$$F^{\rm cc}[v] = \int d^3r\,\{\bar{n}^{\rm A}[v](\mathbf{r}) - n^{\rm A}[v](\mathbf{r})\}\ v(\mathbf{r})$$

$$T_{\rm s}^{\rm cc}[n_{\rm s}^{\rm A}[v]] = \int d^3r\,\{\bar{n}_{\rm s}^{\rm A}[v](\mathbf{r}) - n_{\rm s}^{\rm A}[v](\mathbf{r})\}\ v(\mathbf{r})$$

$$v^\lambda(\mathbf{r}) = (1-\lambda)\,v_0(\mathbf{r}) + \lambda\,v(\mathbf{r})\ ,\quad \bar{n}[v](\mathbf{r}) = \int_0^1 d\lambda\ n[v^\lambda](\mathbf{r})$$

- **Universal functional F** and **non-interacting kinetic energy** T_s as a functional of the **potential**.
- **No separate** approximation for T_s required.
- Conditions are derived under which potential-functional approximations are **variational**.
- Imposition of these conditions greatly **improves** the **accuracy** of T_s .

FIG. 1. Kinetic energy densities of T_s^{cc} (black, red) and the direct T_s^A (blue, green) of Ref. [18] (above), and their absolute errors (below) for one particle in $v(x) = -5\sin^2(\pi x)$, $0 < x < 1$. (color online)

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New results in PFT

- Universal functional of v(**r**):

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

- Direct evaluation of energy:

$$E_v^{\rm A,dir} = F^{\rm A}[v] + \int d^3r\, n^{\rm A}[v](\mathbf{r})\, v(\mathbf{r})$$

Coupling constant:

$$v^\lambda(\mathbf{r}) = (1-\lambda)\, v_0(\mathbf{r}) + \lambda\, v(\mathbf{r})$$

- New expression for F:

$$F[v] = \int d^3r\, \{\bar{n}[v](\mathbf{r}) - n[v](\mathbf{r})\}\; v(\mathbf{r})$$

Variational principle

$$E^{\rm A,var} = \min_{\tilde{v}} \left\{ F^{\rm A}[\tilde{v}] + \int d^3r\, n^{\rm A}[\tilde{v}](\mathbf{r})\, v(\mathbf{r}) \right\}$$

- Necessary and sufficient condition for same result:

$$\chi^{\rm A}[v](\mathbf{r}, \mathbf{r}') = \delta n^{\rm A}[v](\mathbf{r}) / \delta v(\mathbf{r}')$$

$$\chi^{\rm A}[v](\mathbf{r}, \mathbf{r}') = \chi^{\rm A}[v](\mathbf{r}', \mathbf{r})$$

All you need is n[v](**r**)

- Any approximation for the non-interacting density as a functional of v(**r**) produces immediate self-consistent KS potential and density

$$v_{\rm s}(\mathbf{r}) = v(\mathbf{r}) + \int {\rm d}^3r' \frac{n[v_{\rm s}](\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\rm XC}[n[v_{\rm s}]](\mathbf{r})$$

Evaluating the energy

- With a pair T_s^A[v] and n_s^A[v](**r**), can get E two ways:

$$E_v^{\rm A} = T_{\rm S}^{\rm A}[v] + \int d^3r\, n_{\rm S}^{\rm A}[v](\mathbf{r})\, v(\mathbf{r})$$

$$E_v^{\rm A\prime} = \min_{\tilde{v}} \left\{ T_{\rm S}^{\rm A}[\tilde{v}] + \int d^3r\, n_{\rm S}^{\rm A}[\tilde{v}](\mathbf{r})\, v(\mathbf{r}) \right\}$$

- Both yield same answer if

$$\frac{\delta T_{\rm S}^{\rm A}[v]}{\delta v(\mathbf{r})} = -\int d^3r'\; v(\mathbf{r}') \frac{\delta n_{\rm S}^{\rm A}[v](\mathbf{r}')}{\delta v(\mathbf{r})} .$$

Coupling constant formula for energy

- Choose any reference (e.g., v_0(**r**)=0) and write

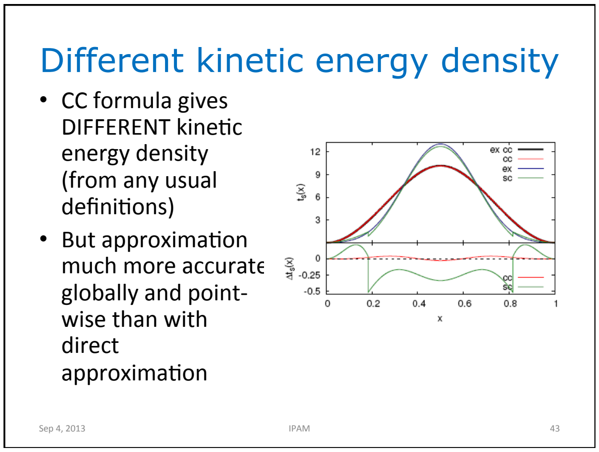
$$v^\lambda(\mathbf{r}) = (1-\lambda)\, v_0(\mathbf{r}) + \lambda\, v(\mathbf{r}) .$$

- Do usual Pauli trick

$$E_v = E_0 + \int_0^1 d\lambda \int d^3r\; n[v^\lambda](\mathbf{r})\, \Delta v(\mathbf{r})$$

- Yields T_s[v] directly from n[v]:

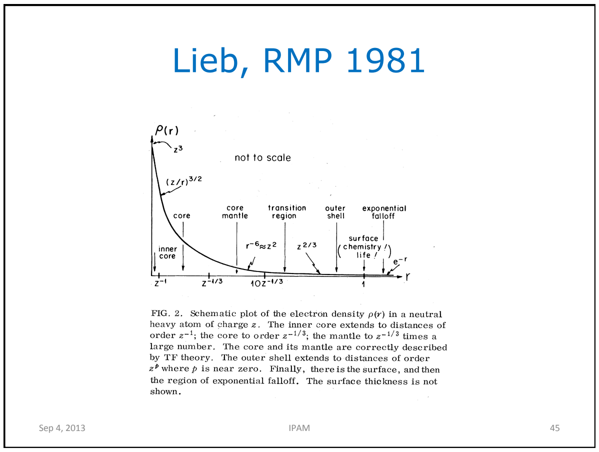
$$T_{\rm S}^{\rm cc}[v] = \int d^3r\, \{\bar{n}_{\rm S}^{\rm A}[v](\mathbf{r}) - n_{\rm S}^{\rm A}[v](\mathbf{r})\}\; v(\mathbf{r})$$



Different kinetic energy density

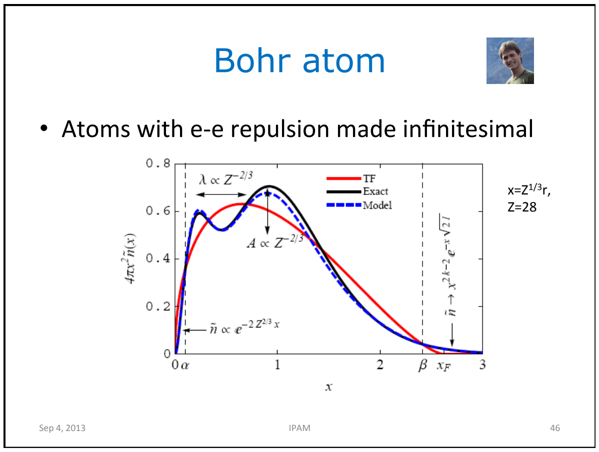
- CC formula gives DIFFERENT kinetic energy density (from any usual definitions)
- But approximation much more accurate globally and point-wise than with direct approximation

AREAS WE'RE WORKING ON



Lieb, RMP 1981

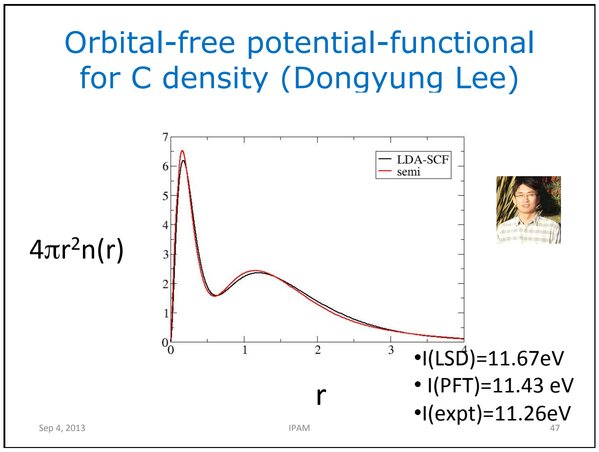
FIG. 2. Schematic plot of the electron density $\rho(r)$ in a neutral heavy atom of charge z. The inner core extends to distances of order z^{-1}; the core to order $z^{-1/3}$; the mantle to $z^{-1/3}$ times a large number. The core and its mantle are correctly described by TF theory. The outer shell extends to distances of order z^p where p is near zero. Finally, there is the surface, and then the region of exponential falloff. The surface thickness is not shown.



Bohr atom

- Atoms with e-e repulsion made infinitesimal

$x=Z^{1/3}r$, $Z=28$



Orbital-free potential-functional for C density (Dongyung Lee)

$4\pi r^2 n(r)$

r

- I(LSD)=11.67eV
- I(PFT)=11.43 eV
- I(expt)=11.26eV

Selected other projects in motion

- In 1d
  - Exchange energies from semiclassical density matrix
  - Results for 1d systems with proper turning points
  - Orbital energies and densities by subtraction
- Beyond 1d
  - Long paper on potential functional theory (arXiv)
  - Is LDA exact for E_c in large Z limit? (Pittalis)
  - Path integral formulation of problem (Cangi)

Need help

- Asymptotic analysis
- Semiclassical theory, including periodic orbits
- Boundary layer theory
- Path integrals
- Green's functions for many-body problems
- Random matrix theory(?)

Simple questions

- Do universal corrections exist, as functionals of the potential, at least for each class of problem?
- Can they be identified for a general 3D potential, even just numerically?
- Are they useful as necessary limits of density functionals, or should we simply replace DFT with PFT?
- A general procedure for even just $T_S[n]$ would revolutionize all DFT calculations!

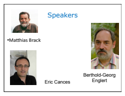
Harder questions

- What is relation between gradient expansion to all orders and expansion in terms of smooth and oscillating pieces?
- Can all corrections be extracted from semiclassical approximate methods, especially in more than 1D?
- How does correlation fit into this picture?

Conclusions

- For T_S:
  - Strongly suggests orbital-free calculations should use potential not density
  - Now have improved formula for getting T directly from any n[v](r)
  - Developing path-integral formulation
- For E_{XC}:
  - Already have bits and pieces
  - Beginning assault on $E_X[n]$
- Only 7th year of project, but Rome was not burnt in a day
- Thanks to students, collaborators, and NSF

Now let's hear from the smart people

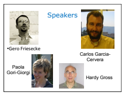


Speakers

•Matthias Brack

Eric Cances

Berthold-Georg Englert



Speakers

•Gero Friesecke

Carlos Garcia-Cervera

Paola Gori-Giorgi

Hardy Gross

Speakers

Elliott Lieb

•Eric Heller

Lin Lin

Ann Mattsson

William Miller

Speakers

Jan-Michael Rost

Qian Niu

Thierry Paul

Francis Nier

Speakers

Michael Seidl

Barry Simon

Jan Philip Solovej

Maciej Zworski