

DFT Master Class: Advanced Topics

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Outline

- 1 Self-interaction error
- 2 Including orbital effects
- 3 Static correlation
- 4 Why hybrids work for thermochemistry
- 5 Present-day developments

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With local approximations, each electrons repels itself

- For any one-electron density $n(\mathbf{r})$:

$$E_x[n] = -U[n], \quad E_c[n] = 0 \quad (N = 1)$$

- Standard functionals all unable to cancel the self-Hartree energy.
- Real trouble is unbalanced nature of effect.
- Stretched H_2^+ is an extreme case as local-type functionals have huge error as $R \rightarrow \infty$.
- Violated by most semilocal functionals (unless artificially built in).
- Particularly problematic for localized and f electrons in solids.

At the edge of all matter...

To understand asymptotic behavior:

- Each subshell of orbitals decays with characteristic length, depending on binding
- In the tail of a density, most loosely bound electron dominates, so its a one-electron region.
- leads to severe constraint on XC potential:

$$v_{\text{XC}}(\mathbf{r}) \rightarrow -v_{\text{H}}^{N=1}(r) = -\frac{1}{r} \quad (r \rightarrow \infty)$$

- Also determines decay of KS potential, since nuclear and Hartree contributions cancel for a neutral system, so

$$v_{\text{S}}(\mathbf{r}) \rightarrow v_{\text{XC}}(r) = -\frac{1}{r} \quad (r \rightarrow \infty)$$

The LDA (or GGA or hybrid) potentials decay too rapidly

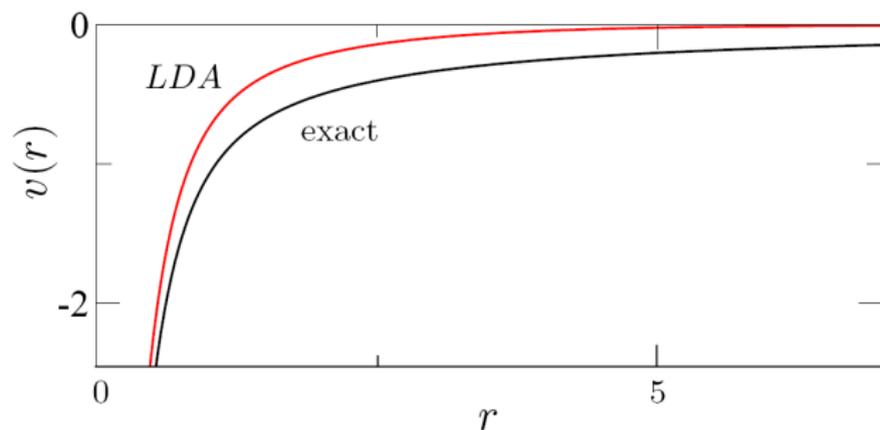


FIG. 3: Exact and LDA KS potentials for the He atom. While

- Accurate densities from QMC calculations:
 - ▶ C. J. Umrigar and X. Gonze, *Phys. Rev. A* **50**, 3827 (1994).
- So how come it produces a good density?
 - ▶ Unambiguous exchange-correlation energy density K. Burke, F.G. Cruz, and K.C. Lam, *J. Chem. Phys.* **109**, 8161 (1998).

Koopmans' theorem is *exact* in KS-DFT

- From many-body wavefunction, can prove asymptotic decay of the density

$$\sqrt{n(\mathbf{r})} \rightarrow Ar^\beta e^{-\sqrt{2I}r}$$

- The KS system must reproduce this behavior exactly, but decay is determined by HOMO.
- So this determines KS HOMO:

$$\epsilon_{\text{HOMO}} = -I$$

As a function of N , the energy is a sequence of straight line segments

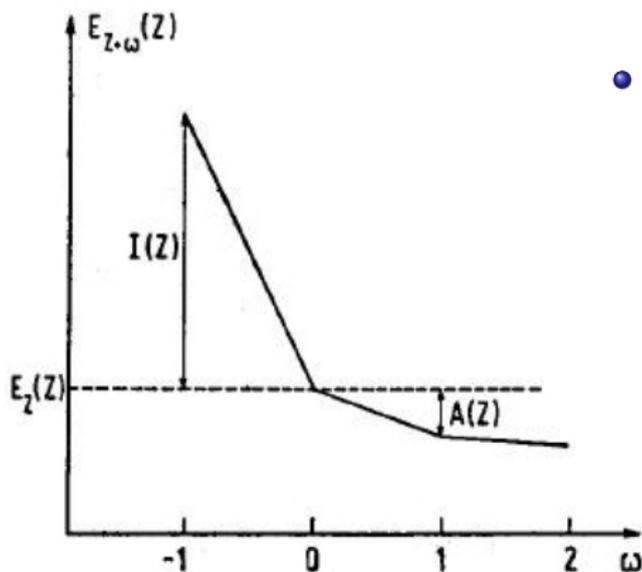


Fig. 2.2. Ground state energy of an atom with nuclear charge Z and $(Z+\omega)$ electrons

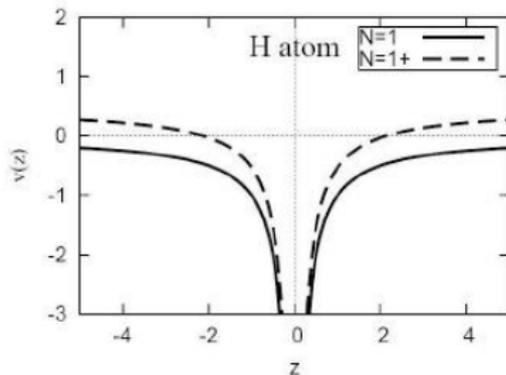
- R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).

$$\mu = \frac{\partial E}{\partial N} = - \begin{cases} I, & N \leq Z \\ A, & N > Z \end{cases}$$

The KS potential jumps suddenly as N crosses an integer

- When you add a tiny fraction of an electron to a system, the KS potential shifts uniformly, since before, $\epsilon_{\text{HOMO}}(N) = -I$, but now, $\epsilon_{\text{HOMO}}(N + \delta) = -A$
- Thus $v_{\text{S}}(\mathbf{r})$ must jump by

$$\Delta_{\text{XC}} = (I - A) + (\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}) = -\epsilon_{\text{LUMO}} - A$$



- Very important in DFT calculations of:
 - ▶ molecules approaching each other, before they bond covalently.
 - ▶ single-molecule transport if molecule is weakly bound to leads.

The KS HOMO-LUMO gap is not the fundamental gap

- The fundamental gap of any system
 - ▶ $\Delta = I - A$ (= 24.6 eV for He)
- The exact Kohn-Sham gap:
 - ▶ $\Delta_S = \epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}$ (= $\epsilon_{1s} - \epsilon_{2s} = 21.16$ eV for He)
- These gaps are *not* the same!
- KS gap is typically smaller than Δ
- Most notorious case: bulk Si
- The *exact* ground-state $E_{\text{XC}}[n]$ produces a KS gap different from the fundamental gap.

There are sharp steps in the KS potential between separated systems

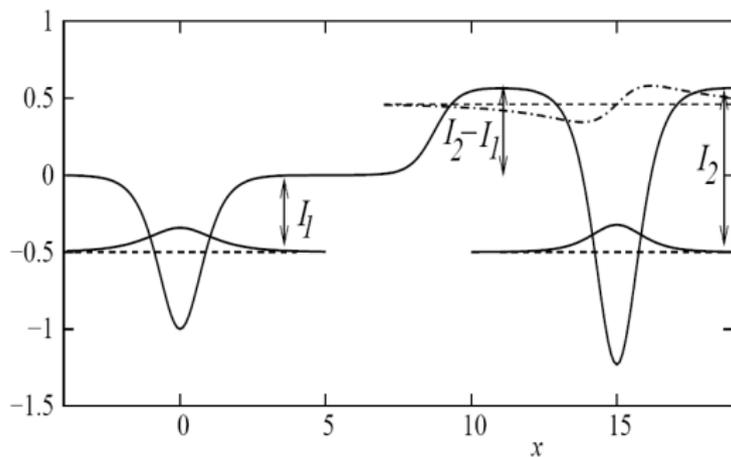


Figure: Cartoon of step in KS potential between two well-separated open-shell fragments.

- N. T. Maitra, J. Chem. Phys. 122, 234104 (2005).

Energy as a function of electrons transferred for a stretched bond

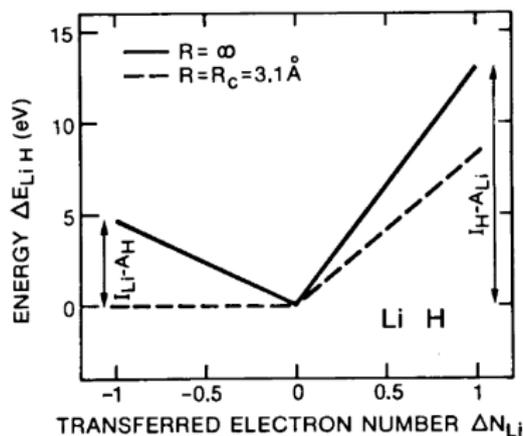


Figure: Total energy of separated LiH as a function of the number of electrons transferred from Li to H.

- *What do the Kohn-Sham orbitals mean? How do atoms dissociate?*, J.P. Perdew, in *Density Functional Methods in Physics*, edited by R.M. Dreizler and J. da Providencia (Plenum, NY, 1985), p. 265.

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Orbital dependence

- Much of deficiencies in common functionals are due to their explicit local (or semi-local) density dependence.
- There are many effects due to discrete orbitals that are missed.
- Some of these effects are seriously **weird**, but are important to know about.

Perdew-Zunger Self-Interaction Correction, 1981

- Perdew-Zunger found a way to correct for self-interaction:

$$E_{\text{HXC}}^{\text{SIC}}[n] = E_{\text{HXC}}[n] - \sum_{j=1}^N E_{\text{HXC}}[|\phi_j|^2]$$

- Exact for any one electron system, for both X and C
- Improves LDA results, especially those with strong SI error.
- Does not generally improve GGA or hybrid
- Sadly, not invariant under unitary transformation of occupied orbitals, so not a proper functional.
- Very useful for localized electrons, where LDA fails badly, but must choose which orbitals.
- For bulk system, correction vanishes if KS orbitals are used, but generally correct when orbitals are localized.

Separated LiH with approximations and SIC

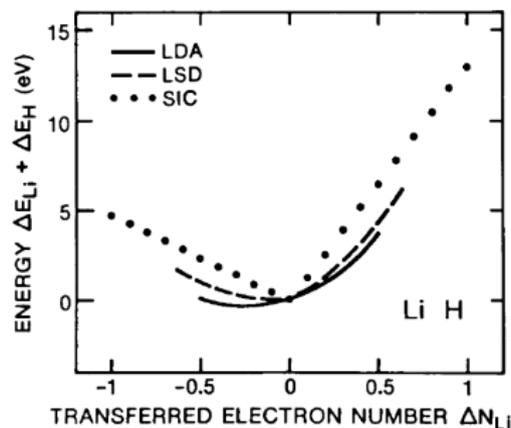


Figure: Total energy of separated LiH as a function of the number of electrons transferred in various approximations.

- *What do the Kohn-Sham orbitals mean? How do atoms dissociate?*, J.P. Perdew, in *Density Functional Methods in Physics*, edited by R.M. Dreizler and J. da Providencia (Plenum, NY, 1985), p. 265.

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Static correlation is not the same as strong correlation

- Effect of small gaps in molecules, if they dissociate into open shells.
- Worsens as bond length increases, producing unbalanced error.
- Called *static* correlation as there's no analog in, eg, uniform gas.
- Very slight in total energy, still small in dissociation energy, but causes GGA errors of order 10 kcal/mol.
- Biggest effect in multiple bonds, e.g., N_2 .
- Worst cases are Cr_2 at equilibrium, or stretched H_2 .
- Can understand how mixing exact exchange improves energetics when static correlation is present.
- Explains accuracy of hybrids for bonds and transition state barriers.

Stretched H_2

- Consider H_2 as $R \rightarrow \infty$:

- ▶ e.g. Yang et. al, 8 August 2008 *Science* **321** (5890), 792

$$E(R) \rightarrow 2E(H), \quad R \rightarrow \infty$$

- But Ψ is *always* a singlet, for large but finite R , have 1/2 electron of each spin on each atom.
- Single-reference wavefunction has one doubly-occupied molecular orbital, but Ψ becomes Heitler-London wavefunction, which is completely different.
- Any single-reference theory gives spin-unpolarized H atoms that are wrong in energy.
- **Symmetry dilemma**: Can allow spin-symmetry to break, and get right energetics, but then no longer a spin eigenstate.
- Coulson-Fischer point is R when symmetry spontaneously breaks in approximate treatment

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Adiabatic connection and relation to scaling

Write XC energy as integral over coupling constant, $n(\mathbf{r})$ fixed:

$$E_{\text{XC}}^\lambda[n] = \lambda^2 E_{\text{XC}}[n_{1/\lambda}], \quad E_{\text{XC}}[n] = \int_0^1 d\lambda \frac{dE_{\text{XC}}^\lambda}{d\lambda} = \int_0^1 d\lambda U_{\text{XC}}^\lambda[n]$$

- D.C. Langreth and J.P. Perdew, *Solid State Commun.* 17, 1425 (1975).
- O. Gunnarsson and B.I. Lundqvist, *Phys. Rev. B* 13, 4274 (1976).

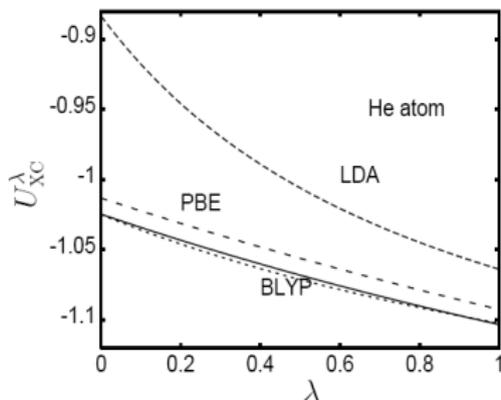


Figure: Adiabatic connection curve for He in various approximations

Static correlation shows up in adiabatic connection

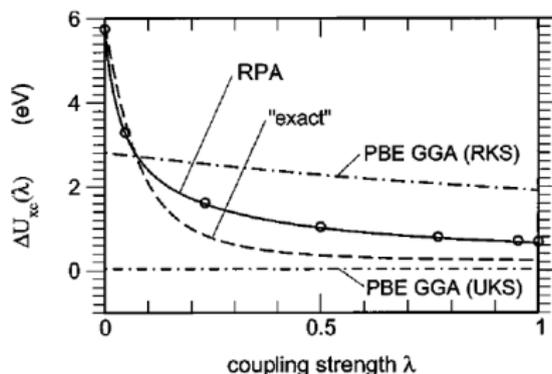


FIG. 3. Same as Fig. 1, but for $R=5$ bohrs, i.e., beyond the Coulson–Fisher point. The RPA results are based on the *total* density of a unrestricted EXX KS calculation. Also shown are the adiabatic connections for the PBE GGA applied in the restricted KS formalism (RKS), yielding poor energetics, and in the unrestricted KS formalism (UKS), yielding better energetics but artificially breaking inversion symmetry.

Figure: Adiabatic connection in various approximations for H_2 at 5\AA .

- M. Fuchs, Y.-M. Niquet, X. Gonze, and K. Burke, *J. Chem. Phys.* **122**, 094116 (2005)

Adiabatic connection for dissociation energy of N_2

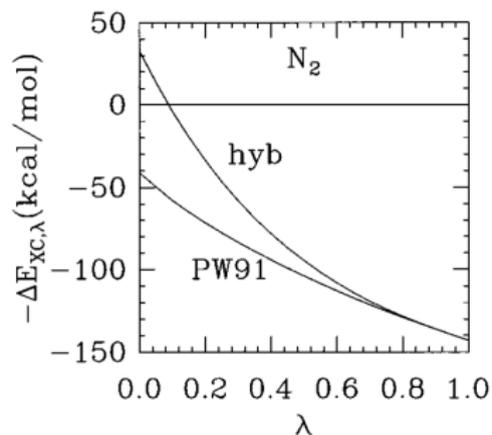


Figure: Adiabatic decomposition of XC energy difference between N_2 and 2 N atoms

You can 'derive' the $\frac{1}{4}$ mixing of exact exchange in PBE0.

- J.P. Perdew, M. Ernzerhof, and K. Burke, *J. Chem. Phys.* **105**, 9982 (1996).

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If a GGA is physical, is a meta-GGA metaphysical?

- Basic idea: If you are doing KS, you already have an indicator of non-locality, the KS kinetic energy density:
- Formula:

$$E_{\text{XC}} = \int d^3r f(n, \nabla n, \tau)$$

where

$$\tau(\mathbf{r}) = \sum_J^{\text{occ}} \frac{1}{2} |\nabla \phi_j|^2 = \text{positive KE density}$$

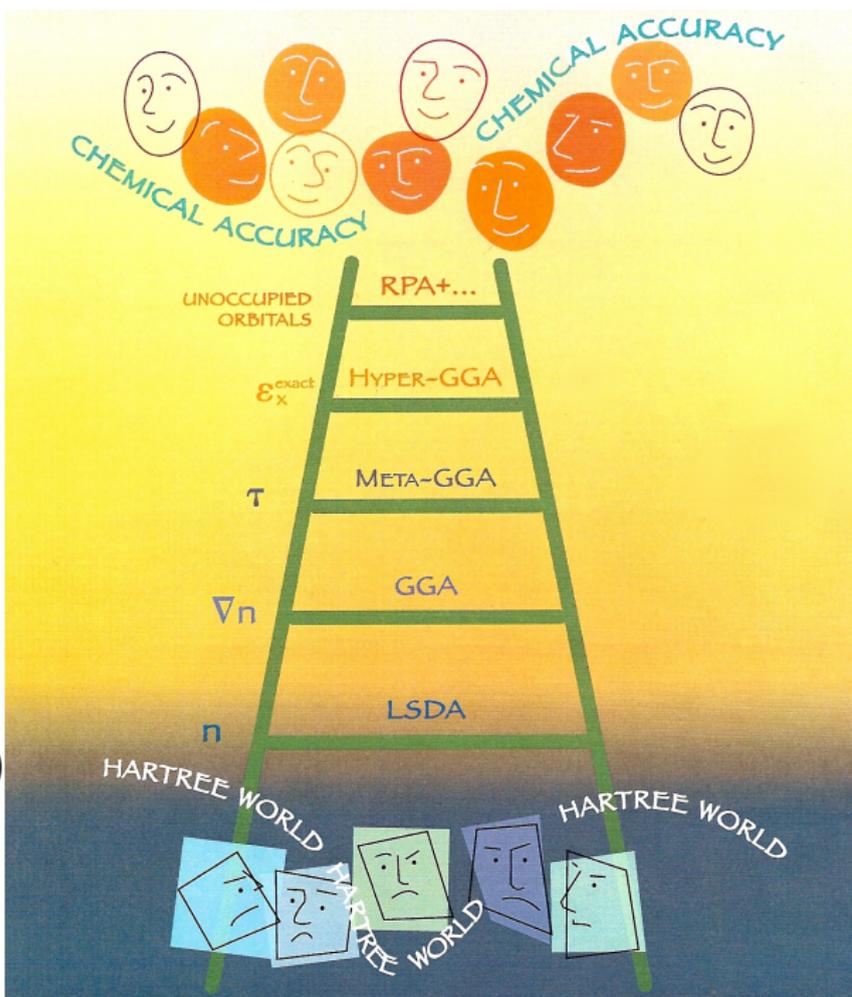
- Attempt to get accuracy of hybrids *without* having to do HF.

Jacob's ladder to DFT heaven (or hell?)

Increasingly sophisticated
and expensive density
functional
approximations.

$$E_{\text{XC}} = \int d^3r f(n, \nabla n, \tau, \dots)$$

- JCTC 2009 Vol. 5, Iss. 4.



How to handle orbital-dependence in KS DFT

Use the **Optimized Effective Potential (Method)**

- Way to handle orbital-dependent functionals in KS scheme, i.e., with single multiplicative KS potential
- Still density functionals, since orbitals uniquely determined by density
- Several schemes to implement, all much more expensive than regular KS-DFT
- Improves many properties:
 - ▶ No self-interaction error
 - ▶ Potentials and orbital energies much better
 - ▶ Approximates derivative discontinuity
- But don't have compatible correlation
 - ▶ Stephan Kümmel and Leor Kronik, Rev. Mod. Phys. 80, 3 (2008)

What's the difference between HF and EXX?

- HF minimizes $E_x[\{\phi_j\}]$ over all possible wavefunctions
- EXX includes additional constraint of common potential (i.e., KS)
- Yields almost identical total energies, with HF an eesty bit lower
- Occupied orbital energies very similar, but big difference in unoccupied orbitals
- Reports of good gaps with hybrids use HF scheme mixed with KS (generalized KS scheme), so *not* getting a 'good' KS gap.

Van der Waals forces

- Very important for soft Coulomb matter
- Can show $E \rightarrow -C_6/R^6$ for large R between two fragments
- But GGA's use $n(\mathbf{r})$ and $|\nabla n|$, so E decays exponentially with R .
- Many attempts to include in DFT
 - ▶ Add empirical corections to DFT results, eg DFT-D
 - ★ Grimme,LW
 - ▶ Langreth and Lundquist: RPA treatment leading to explicit non-local functional.
 - ★ M. Dion et al, Phys. Rev. Lett. **92**, 246401 (2004).
 - ▶ Exchange hole used to get C_6 .
 - ★ Axel D. Becke and Erin R. Johnson J. Chem. Phys. **127**, 154108 (2007)
- LL functional now widely coded and being applied to many systems.

Lessons from this part

- **Self-interaction error** is a nebulous error that can be somewhat cured by SIC.
- KS potentials have definite features (steps, decay at large r) related to line-segment nature of $E(N)$.
- Some things are just **not included** in common functionals, e.g., dispersion forces, neutral fragmentation, etc.
- Good thermochemistry of hydrides can be **partially rationalized** using adiabatic connection.
- **Many things are not correct.**
- Thanks to students and NSF.

Density functional theory: A great physics success story

Kieron Burke

UC Irvine Physics & Chemistry

<http://dft.uci.edu>

What is DFT?

PREPRINT FROM THE BURKE GROUP ARCHIVES

dft.uci.edu

DFT in a nutshell - v1.1

Kieron Burke and Lucas Wagner

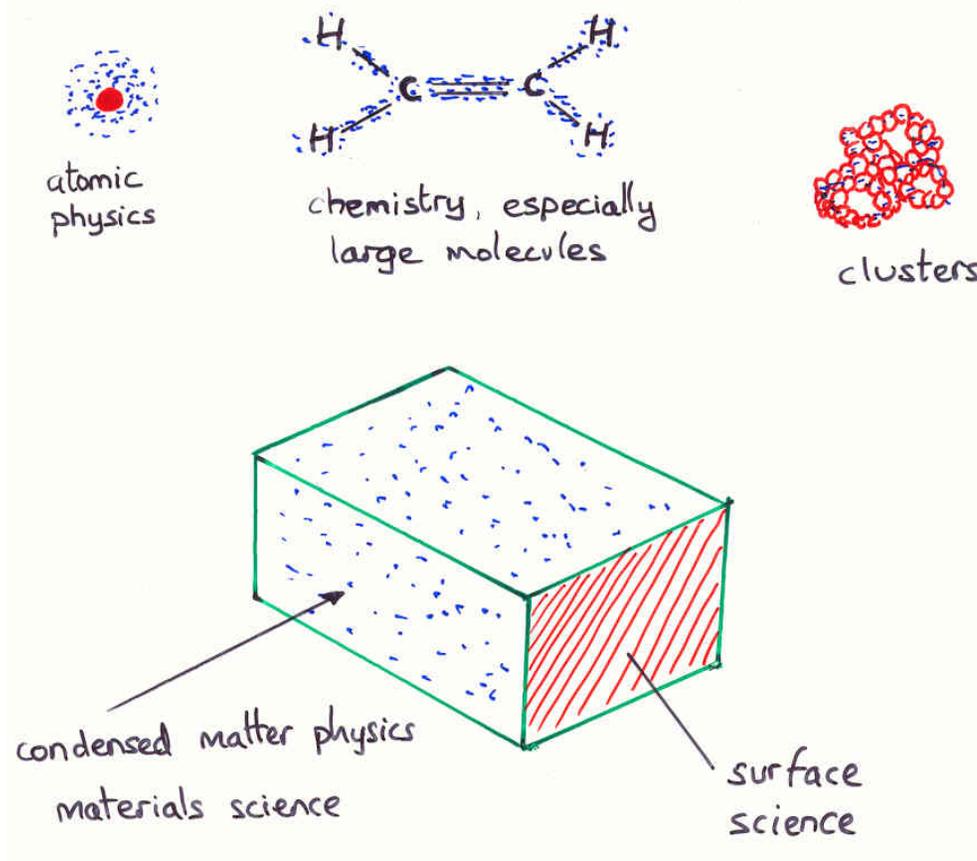
Departments of Chemistry and of Physics, University of California, Irvine, CA 92697, USA

(Dated: December 13, 2010)

The purpose of this short essay is to introduce students and other newcomers to the basic ideas and uses of modern electronic density functional theory (DFT), including what kinds of approximations are in current use, and how well they work (or not). The complete newcomer should find it orients them well, while even longtime users and aficionados might find something new outside their area. To check you've followed the essay, you should certainly try the conceptual questions at the end. If you wish to master the material, you should work through the problems.

Electronic structure problem

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



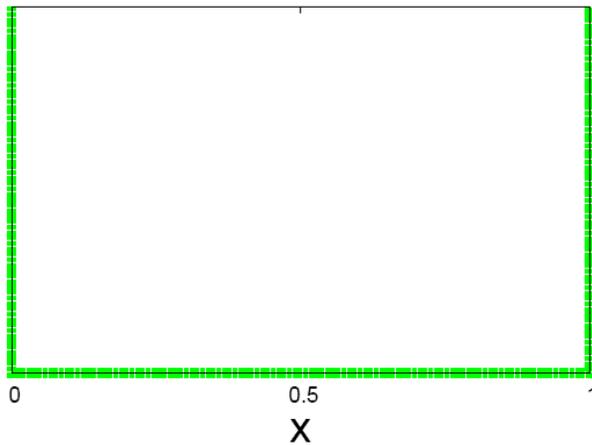
Properties from Electronic Ground State

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

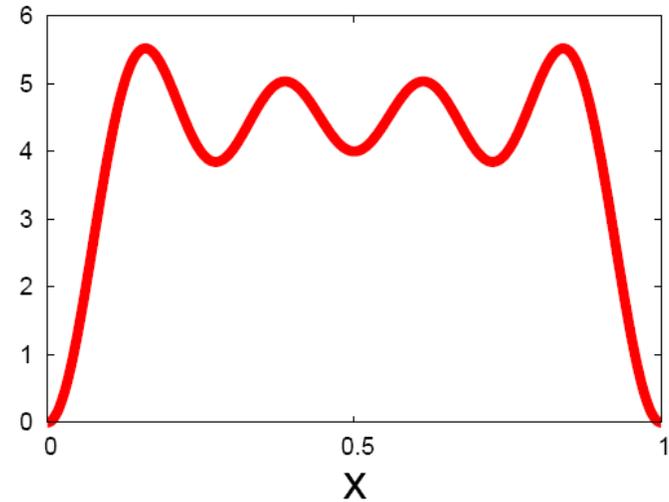
Traditional approaches

- Must solve the Schrödinger equation to find ground-state energy and wavefunction.
- 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

Simple example: Flat box



- Potential $v=0$ with hard walls at $x=0$ and 1



- Exact density (sum of $\sin^2(j\pi x)$) for $N=4$

Kinetic energy in 1d

- Approximate kinetic energy by local functional:



$$T_s = \frac{1}{2} \int dx \sum_j \left(\frac{d\varphi_j}{dx} \right)^2$$

$$T_s^{loc} = \int dx f(\rho(x))$$

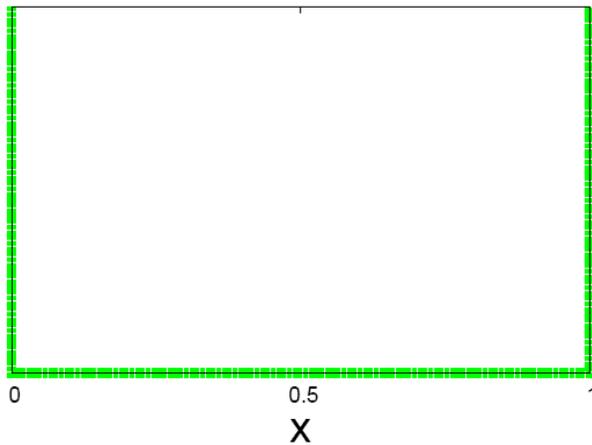
- Dimensional analysis gives:

$$T_s^{loc} = a_s \int dx \rho^3(x)$$

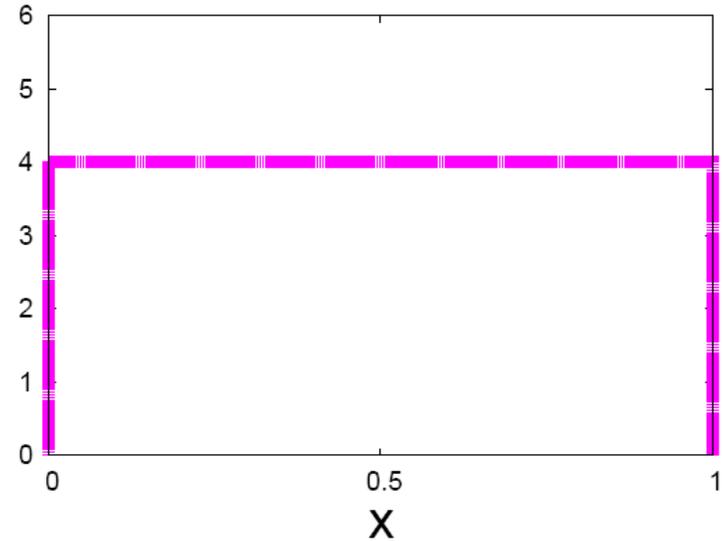
- Minimize, to find:

$$\rho(x) = \frac{N}{L}$$

Simple example: Flat box

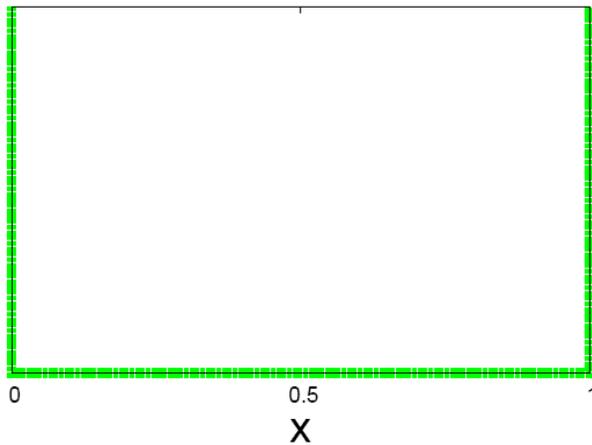


- Potential $v=0$ with hard walls at $x=0$ and 1

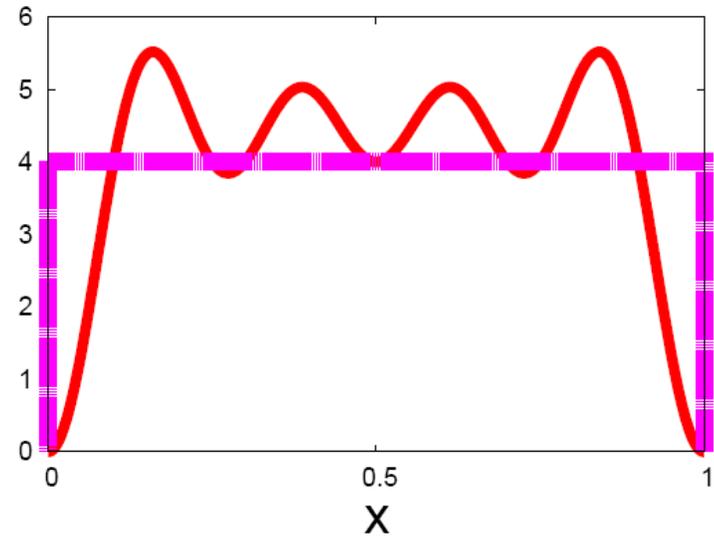


- TF density, $n=\text{constant}=4$

Simple example: Flat box



- Potential $v=0$ with hard walls at $x=0$ and 1



- TF density misses quantum oscillations and violates boundary conditions

Accuracy of local approximation

- Exact formula:
$$E(N) = \frac{\pi^2}{2L^2} \sum_{j=1}^N j^2 = \frac{\pi^2}{6L^2} N(N+1/2)(N+1)$$

- For large N:
$$\frac{E(N)}{N} \rightarrow \frac{\pi^2 N^2}{6L^2}$$

- Choose $a_s = \pi^2/6$ to make exact in this limit.
$$T_s^{loc} = \frac{\pi^2}{6} \int dx \rho^3(x)$$

- Remarkably, T_s^{loc} is exact for **ALL** bounded problems as N gets large

N	T_s	$T_s^{loc}[\rho^{loc}]$
1	4.93	1.64
2	24.7	13.2
3	69.1	44.4
4	148.0	105.3

Thomas/Fermi Theory 1927

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.

- Derived in 1926 without Schrodinger equation
- 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):
 - $T \approx T^{TF}$
 - $V_{ee} \approx U$ = Hartree energy
 - $V = \int dr \rho(\mathbf{r}) v(\mathbf{r})$
 - Minimize $E_0[\rho]$ 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.

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

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

DFT in modern practice

Kohn-Sham equations (1965)

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

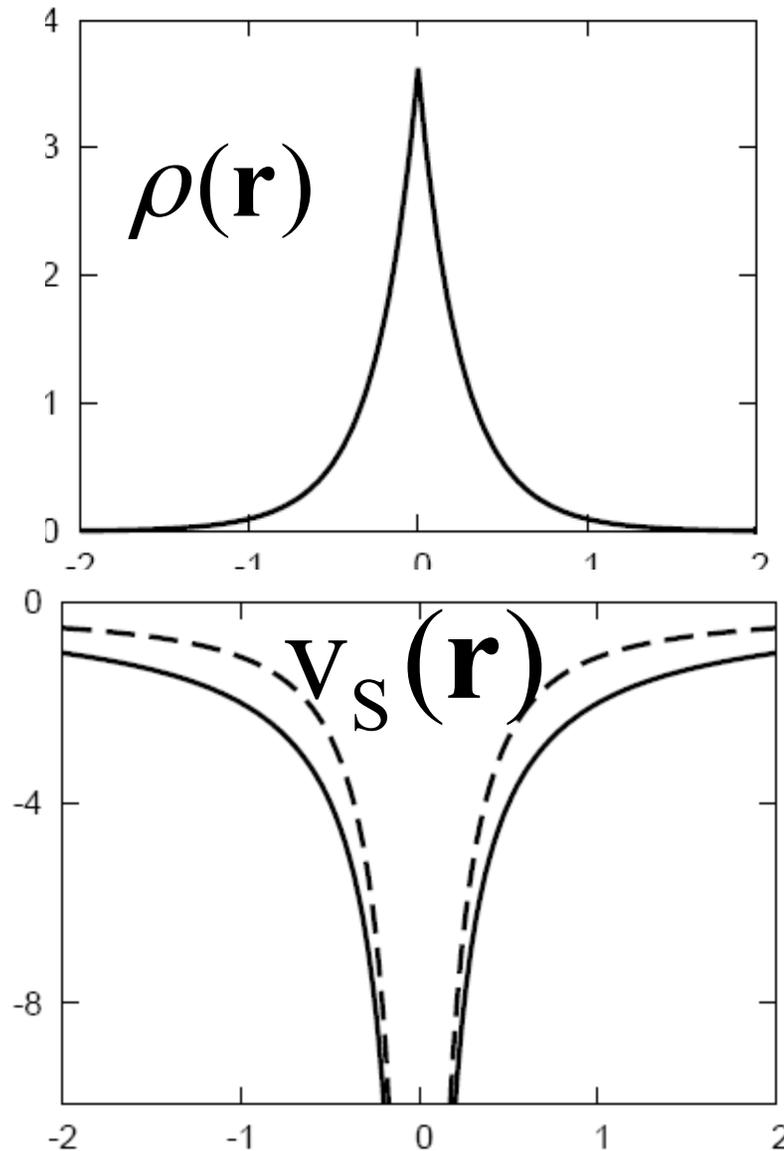
$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 = \text{ground-state density of interacting system}$$

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

$$E_0 = T_S + V + U + E_{\text{xc}}[\rho]$$

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

He atom in Kohn-Sham DFT



Everything
has (at
most) one
KS potential

Dashed-line:
EXACT KS potential

Commonly-used functionals

- Local density approximation (LDA) $E_X^{\text{LDA}}[n] = A_X \int d^3r n^{4/3}(\mathbf{r})$
 - Uses only $\rho(\mathbf{r})$ at a point.
$$A_X = -(3/4)(3/\pi)^{1/3} = -0.738.$$
- Generalized gradient approx (GGA)
 - Uses both $\rho(\mathbf{r})$ and $|\nabla\rho(\mathbf{r})|$
 - 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

Perspective on density functional theory

Perspective on DFT

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(Dated: January 19, 2012)

Density functional theory (DFT) is an incredible success story. The low computational cost, combined with useful (but not yet chemical) accuracy, has made DFT a standard technique in most branches of chemistry and materials science. Electronic structure problems in a dazzling variety of fields are currently being tackled. However, DFT has many limitations in its present form: Too many approximations, failures for strongly correlated systems, too slow for liquids, etc. This perspective reviews some recent progress and ongoing challenges.

I. INTRODUCTION

Over the past 20 years, DFT has become a much used tool in most branches of chemistry. Many experimental investigations in organic and inorganic chemistry routinely include such calculations, using a popular code, a standard basis, and a standard functional approximation [1]. A similar transformation is now underway in materials science where, in the past decade, improvements in both hardware and codes have made it possible to perform systematic comparisons with experiment across large ranges of materials, learning which approximations work and why, and allowing for true first-principles predictions of properties. Among notable recent successes are the prediction of new catalysts [2] and new Li battery materials [3] in the Materials Genome Project. A complementary aspect of this story is shown in Fig. 1, which plots the number of papers given by Web of Knowledge when DFT is searched as a topic (grey bars). This will soon reach 10,000 per year, vindicating the 1998 Nobel prize in chemistry, which went to Walter Kohn [4] for inventing the theory and to John Pople [5] for making it accessible through popular computational packages. The figure also marks the fraction of papers citing B3LYP [6–8], currently the most popular approximation in chemistry, and PBE [9], the most popular approximation in materials. Clearly, applications to materials will soon outstrip those in chemistry.

This perspective is for a general audience, and focuses on fundamental general aspects of DFT, rather than detailed computational procedures and results for specific systems. Because DFT is now applied so broadly, no such article can hope to be comprehensive. The topics covered here are designed to give a flavor of how the field works, and are mostly those I have personally worked in. Great longer reviews exist for experts [10–12] and for

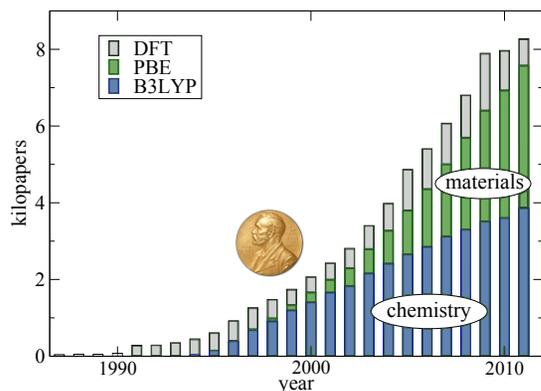


FIG. 1. Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).

ory, a generalization [17].

II. A BRIEF HISTORY

Our story begins in 1926 with the creation of Thomas-Fermi theory [18, 19], an approximate method for finding the electronic structure of atoms using just the one-electron ground-state density, $\rho(\mathbf{r})$, but too crude to bind molecules [20]. In the 50's, Slater [21] intuitively combined this idea with Hartree's orbital method [22] in the $X\alpha$ scheme. Later, the Hohenberg-Kohn (HK) theorem [23] proved that an exact method based on $\rho(\mathbf{r})$ exists in principle. The modern version in use today is Kohn-

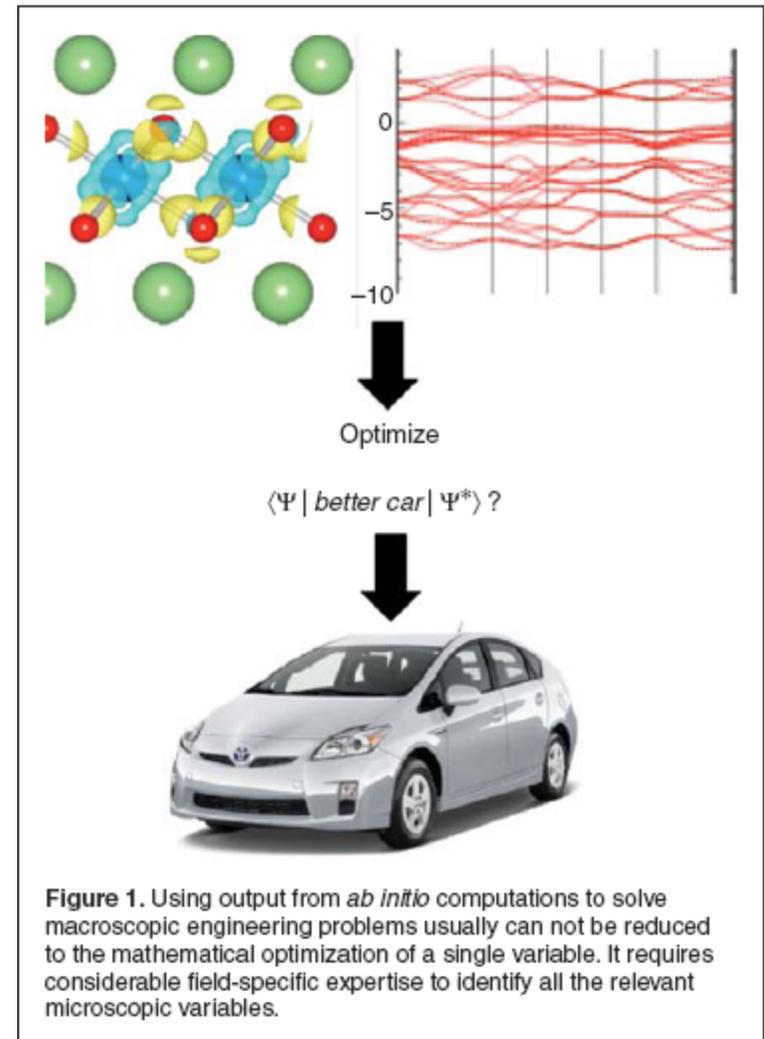
Better Li batteries?

Opportunities and challenges for first-principles materials design and applications to Li battery materials

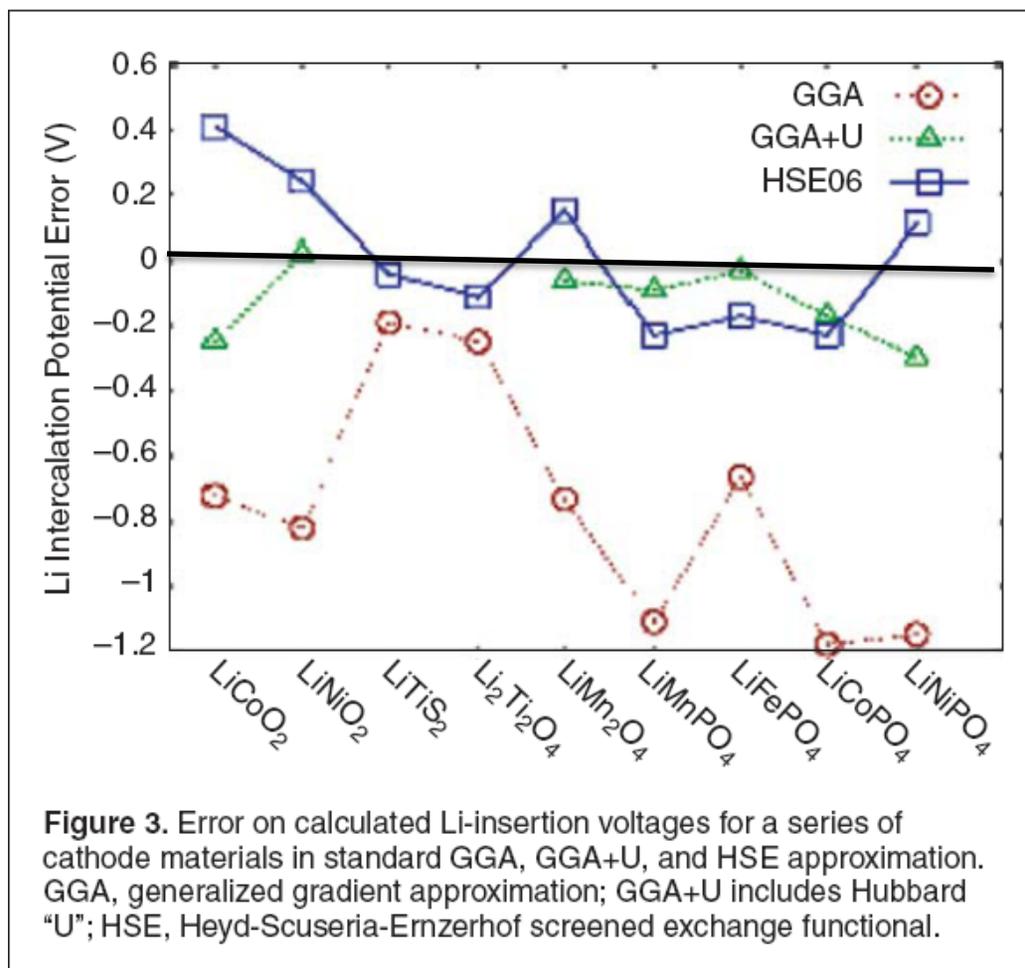
Gerbrand Ceder

This article is based on the MRS Medal presentation given by Gerbrand Ceder (Massachusetts Institute of Technology) on December 1, 2009, at the Materials Research Society Fall Meeting in Boston. Ceder was awarded the Medal "for pioneering the high-impact field of first-principles thermodynamics of batteries materials and for the development of high-power density Li battery compounds."

MRS BULLETIN • VOLUME 35 • SEPTEMBER 2010 • www.mrs.org/bulletin ■ 693



Materials genome from first principles?



Quiz

- Students/postdocs only:
 - Why is a Kohn-Sham DFT calculation so fast compared to traditional *ab initio* methods?
- Professors only:
 - Give the XC energy of a uniform electron gas with $\rho=1$ in atomic units
 - » to 6 significant digits.

Outline

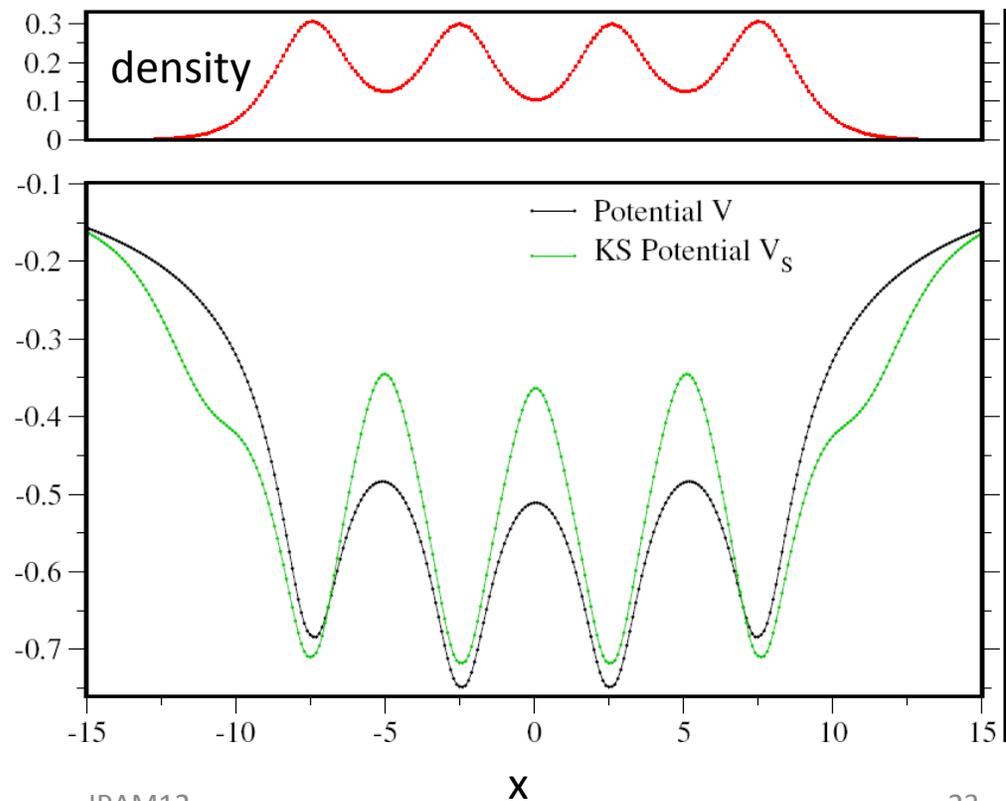
- Background
 - Difference between traditional approaches and density functional theory (DFT)
 - Generality of electronic structure problem
 - A brief history of DFT through modern era
- Breadth
 - A random survey of projects I'm involved in
- Depth
 - A look into my biggest challenge

Breadth

Exactness of DFT?

First ever KS calculation with *exact* $E_{xc}[n]$

- Used DMRG (density-matrix renormalization group)
- 1d H atom chain
- Miles Stoudenmire, Lucas Wagner, Steve White, arXiv



Comparing DMRG and LDAX

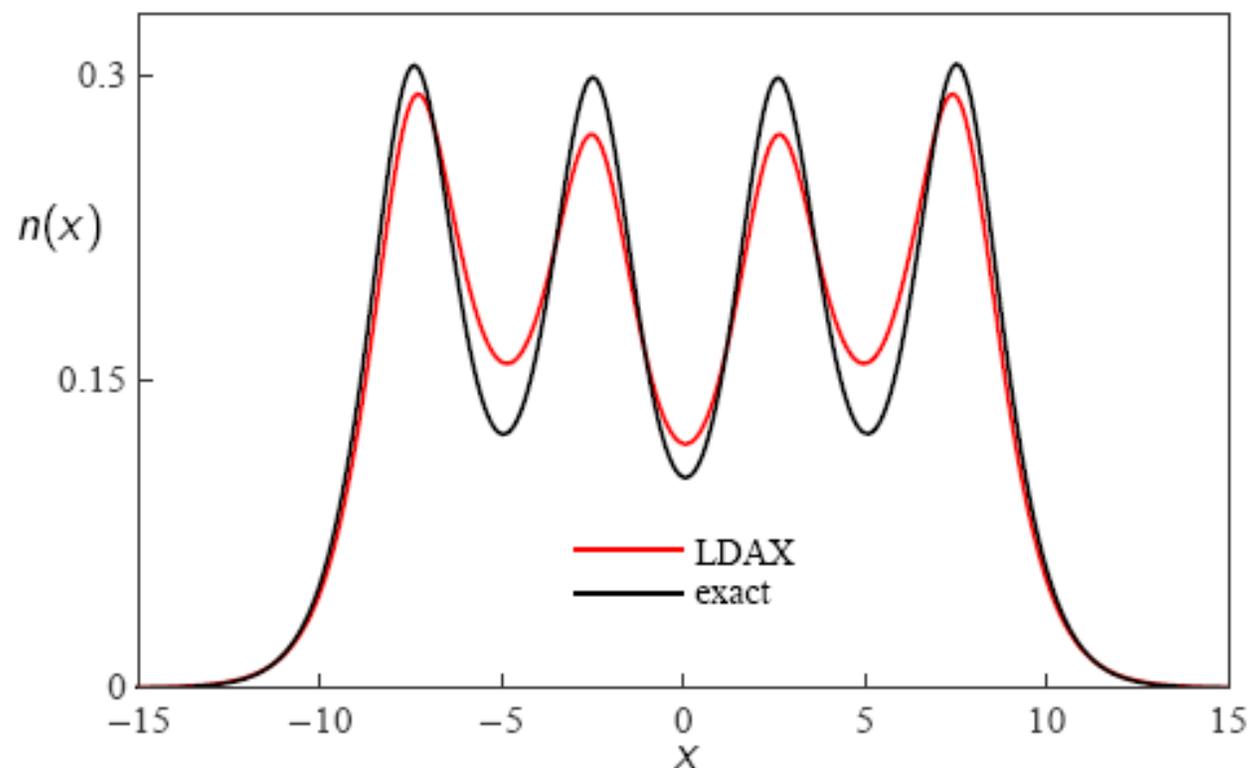


Figure: Comparison of LDAX and DMRG densities for four electrons. The exact functional took 5 hours to converge, whereas LDAX took a few minutes.

Transport through single molecules

Accuracy of DFT calculations of current



- Justin Bergfield, Zhenfei Liu and Charles Stafford (U. Arizona)
- Are errors in DFT calculations of transport due to errors in approximations, or need we go beyond gs-DFT+Landauer?



Exact results for Anderson junction

- At zero bias and zero temperature, exact ground-state KS DFT recovers exact conductance, including Kondo plateau!
- Suggests accurate results from DFT with accurate approximations
- **Phys. Rev. Lett. 108, 066801 (2012)**

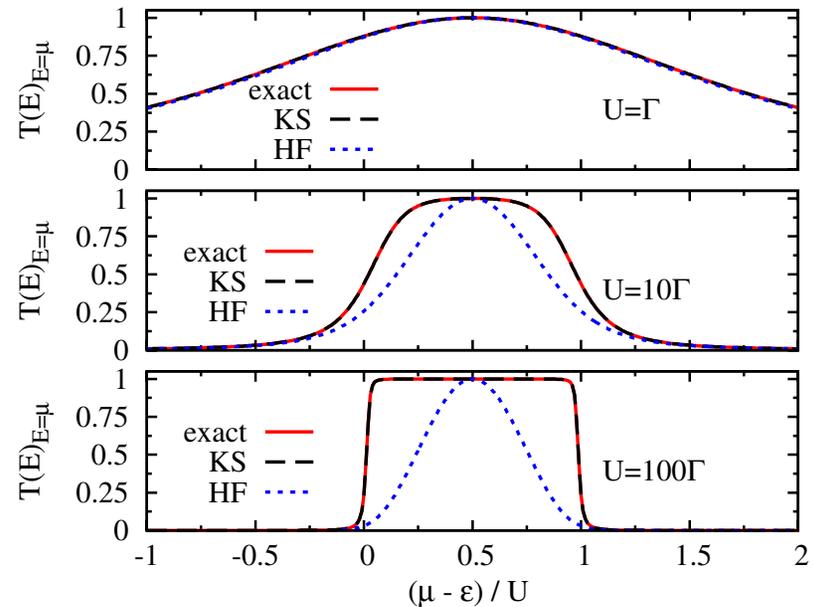
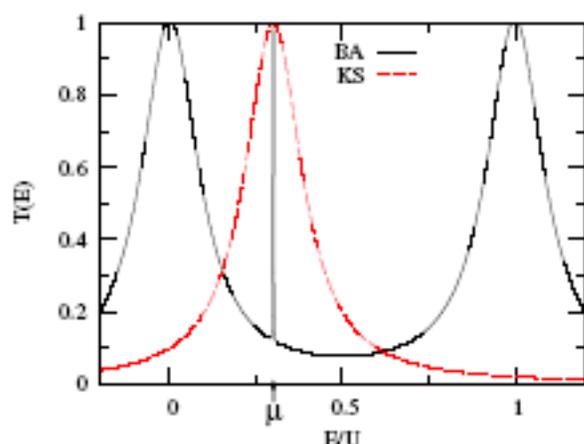


FIG. 1 (color online). Zero-temperature transmission of an Anderson junction as a function of ε using Bethe ansatz (BA), Kohn-Sham DFT (KS), and (spin-restricted) Hartree-Fock (HF). As U increases, HF misses the sharp structure, but the KS transport is always the same as that from BA.

Generalization

In finite bias, $I = \int_{\mu_1}^{\mu_2} dE \mathcal{T}(E)$.

Fix μ , calculate $\mathcal{T}(E)$:



Kohn-Sham DFT:
 $\mathcal{T}(E)_{E=\mu}$ right,
 all other $\mathcal{T}(E)$ wrong.

Finite temperature $T > T_K$,
 the Kondo peak goes away.

Conclusion

At finite bias or temperature,
 Kohn-Sham conductance \neq real conductance.

Testing approximations

PREPRINT FROM THE BURKE GROUP ARCHIVES

dft.uci.edu

Accuracy of density functionals for molecular electronics: the Anderson junction

Zhen-Fei Liu, Justin P. Bergfield, and Kieron Burke

Departments of Chemistry and of Physics, University of California, Irvine, California 92697, USA

Charles A. Stafford

Department of Physics, University of Arizona, 1118 East Fourth Street, Tucson, Arizona 85721, USA

(Dated: January 10, 2012)

The exact ground-state exchange-correlation functional of Kohn-Sham density functional theory yields the exact transmission through an Anderson junction at zero bias and temperature. The exact impurity charge susceptibility is used to construct the exact exchange-correlation potential. We analyze the successes and limitations of various types of approximations, including smooth and discontinuous functionals of the occupation, as well as symmetry-broken approaches.

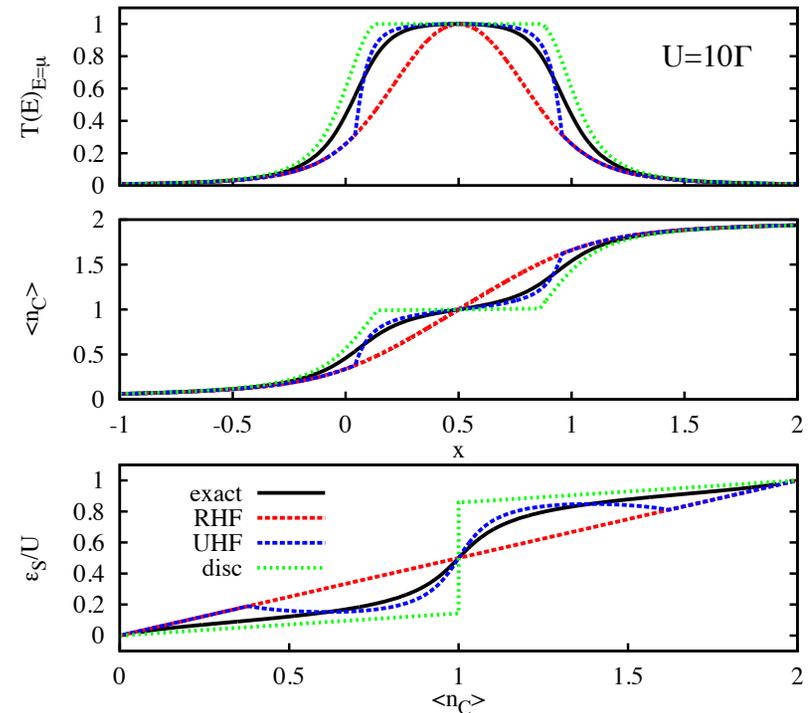
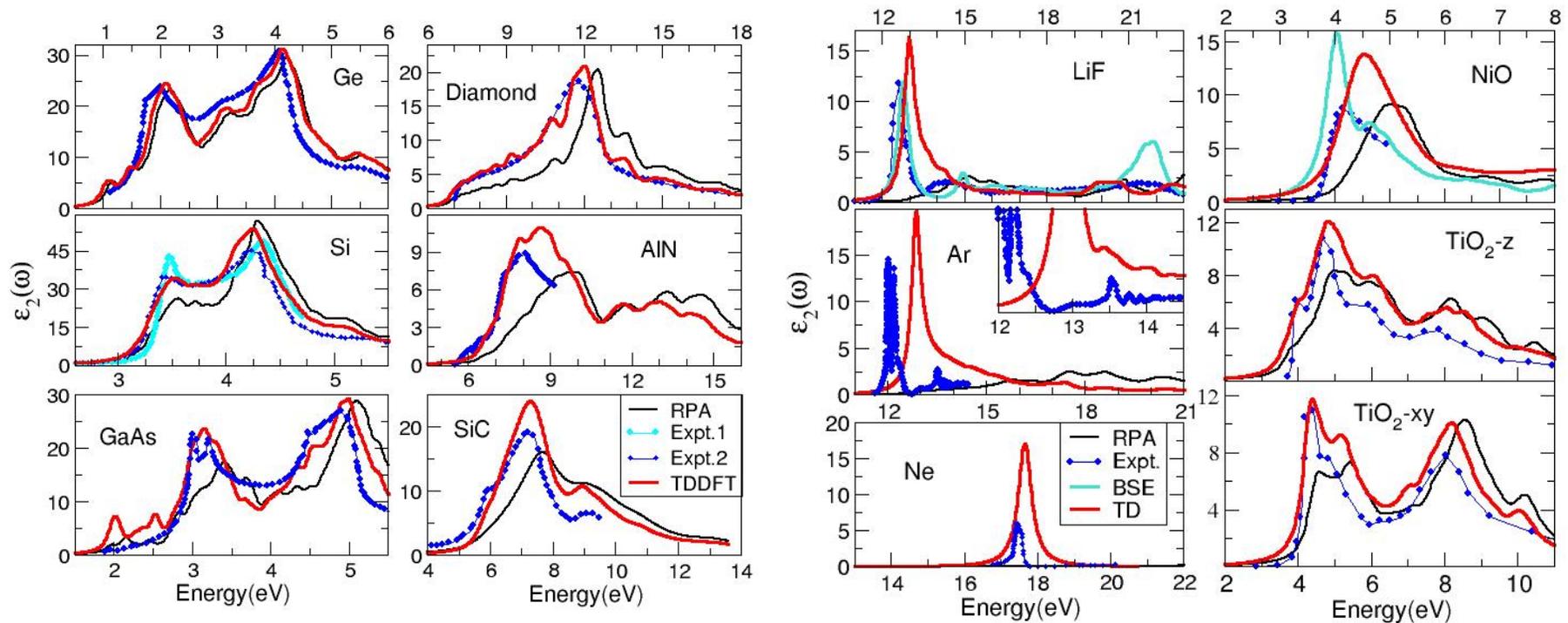


FIG. 4. Upper panel: transmission as a function of $x = (\mu - \epsilon)/U$; middle panel: occupation as a function of x ; lower panel: KS potential as a function of occupation. Results are shown for Bethe ansatz or exact KS DFT (exact), restricted Hartree-Fock (RHF), unrestricted Hartree-Fock (UHF), and discontinuous approximation [disc, Eq. (10)]. $U = 10\Gamma$ in all cases.

Excitations from TDDFT

Extension to time-dependent quantum mechanics, allowing calculation of electronic excitations

Excitons in solids: Bootstrap approximation for exchange-correlation kernel



$$f_{xc}(q,\omega) = \epsilon^{-1}(q,0) / \chi_0(0,0)$$

$$\epsilon^{-1}(q,\omega) = 1 + v(q)\chi_0(q,\omega) / \{1 - [v(q) + f_{xc}(q,\omega)]\chi_0(q,\omega)\}$$

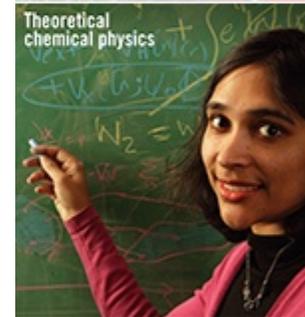
Sharma, Dewhurst, and Gross. Phys. Rev. Lett. **107**, 186401 (2011)

Role of cusps in TD QM

- Zenghui Yang, and KB



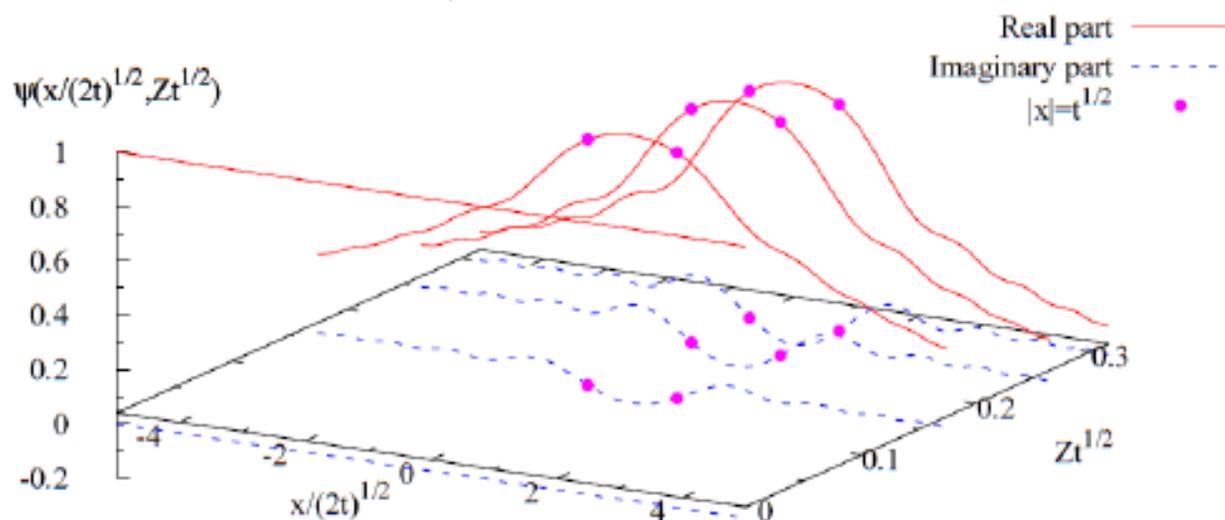
- Collaborator: Prof Neepa Maitra, Hunter College, NY



- Shakes (but does not destroy) the foundations of TDDFT
- **Phys. Rev. Lett. 108, 063003 (2012)**

Zooming into the cusp region

$$\bar{\mathbf{r}} = \mathbf{r}/\sqrt{2t}, \quad s = Z\sqrt{t}.$$



$$\nabla_{\bar{\mathbf{r}}}^2 \psi(\bar{\mathbf{r}}, s) - \frac{4s^2}{Z^2} V(\bar{\mathbf{r}}, s) \psi(\bar{\mathbf{r}}, s) + 2i \left\{ s \frac{\partial \psi(\bar{\mathbf{r}}, s)}{\partial s} - \bar{\mathbf{r}} \cdot \nabla_{\bar{\mathbf{r}}} \psi(\bar{\mathbf{r}}, s) \right\} = 0.$$

3d H in E-field: Solving the differential equation

Asymptotic series for $\exp[S(\bar{r})]\bar{z}$

$$a_4\bar{z} \left(\bar{r}^3 + \frac{9i\bar{r}}{2} - \frac{9}{4\bar{r}} + \frac{3i}{8\bar{r}^3} \right) + b_4\bar{z} \frac{e^{i\bar{r}^2}}{\bar{r}^8} \left[1 + \sum_{m=0}^{\infty} \frac{(-i)^{m+1}(m+4)(2m+6)!}{(m+1)!2^{2m+5} \cdot 9\bar{r}^{2m+1}} \right]$$

Borel resummation

$$a_4\bar{z} \left(\bar{r}^3 + \frac{9i\bar{r}}{2} - \frac{9}{4\bar{r}} + \frac{3i}{8\bar{r}^3} \right) + b_4\bar{z} \frac{1+i}{72\bar{r}^3} \left[(2+2i)e^{i\bar{r}^2}(4\bar{r}^5 + 16i\bar{r}^3 - 3\bar{r}) - \sqrt{2\pi}(3i - 18\bar{r}^2 + 36i\bar{r}^4 + 8\bar{r}^6) \operatorname{erfc} \left(\frac{1-i}{\sqrt{2}}\bar{r} \right) \right]$$

Eine kleine chemistry



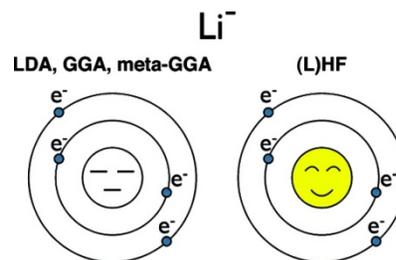
Calculating electron affinities with DFT and Koreans

- Old work on atoms



Accuracy of Electron Affinities of Atoms in Approximate Density Functional Theory Donghyung Lee, Filipp Furche and Kieron Burke, *J. Phys. Chem. Lett.*, 1, [pp 2124–2129](#) (2010).

- *Finding electron affinities with approximate density functionals* D. Lee and K. Burke, *Mol. Phys.*, 108, [2687](#) (2010).



- New work on molecules

- Min Cheol Kim and Eunji Sim and KB, *J Chem Phys*, **2011**



Mol.	EA	$\Delta\text{EA}(\text{MBS})$		$\Delta\text{EA}(\text{HF-DFT})$		$-\epsilon_{\text{HOMO}}$	
	expt.	PBE	B3LYP	PBE	B3LYP	B3LYP	HF
CH	1.24	0.29	0.04	0.22	-0.03	-1.3	2.1
CH ₂	0.65	0.13	0.06	0.05	0.02	-1.3	1.3
CH ₃	0.08	0.00	-0.05	-0.04	-0.09	-1.7	0.6
NH	0.38	0.17	0.02	0.04	-0.07	-2.1	0.1
NH ₂	0.77	0.06	-0.11	-0.01	-0.15	-1.7	1.3
OH	1.83	0.12	-0.09	0.00	-0.16	-1.1	3.0
SiH	1.28	0.12	-0.08	0.10	-0.12	-0.8	1.5
SiH ₂	1.12	0.17	-0.01	0.13	-0.06	-1.0	1.3
SiH ₃	1.41	0.01	-0.06	0.01	-0.05	-0.3	1.8
PH	1.03	0.04	-0.01	0.02	-0.01	-1.1	0.9
PH ₂	1.27	-0.02	-0.09	-0.01	-0.08	-1.0	1.2
HS	2.36	-0.03	-0.11	-0.04	-0.11	-0.2	2.6
O ₂	0.44	0.00	0.03	-0.08	-0.02	-2.2	2.4
NO	0.02	0.27	0.26	0.16	0.14	-2.3	2.5
PO	1.09	0.18	0.11	0.14	0.07	-1.1	2.0
S ₂	1.66	-0.07	-0.04	-0.04	-0.02	-0.5	2.2
Cl ₂	2.39	0.27	0.40	0.26	0.38	1.9	4.7
MAE	0.00	0.11	0.09	0.08	0.09	2.2*	0.8*
ME	0.00	0.10	0.02	0.05	-0.02	-2.2*	0.8*

* Based on Koopman's theorem, mean absolute errors and mean errors are obtained by comparing the differences between $-\epsilon_{\text{HOMO}}$ and EA.

EAs of G2-1 set

- ΔEA : Electron affinity error
- ϵ_{HOMO} : eigen value of anion's HOMO orbital
- $\text{EA} \approx -\epsilon_{\text{HOMO}}$ [anion] (Koopman's theorem)
- HF-PBE: smallest MAE, but not much difference
- Still...
 - $\epsilon_{\text{HOMO}}[\text{HF}]$ is negative (MAE & ME same sign)
 - $\epsilon_{\text{HOMO}}[\text{B3LYP}]$ positive (MAE & ME opposite sign)

QM/MM

Partition DFT



- Created by Morrel Cohen and Adam Wasserman (Prof Purdue, chem)
- Very elegant approach to atoms in molecules
- Many possible applications:
 - Embedding
 - $O(N)$ methods
 - QM/MM etc.
- See Wasserman website

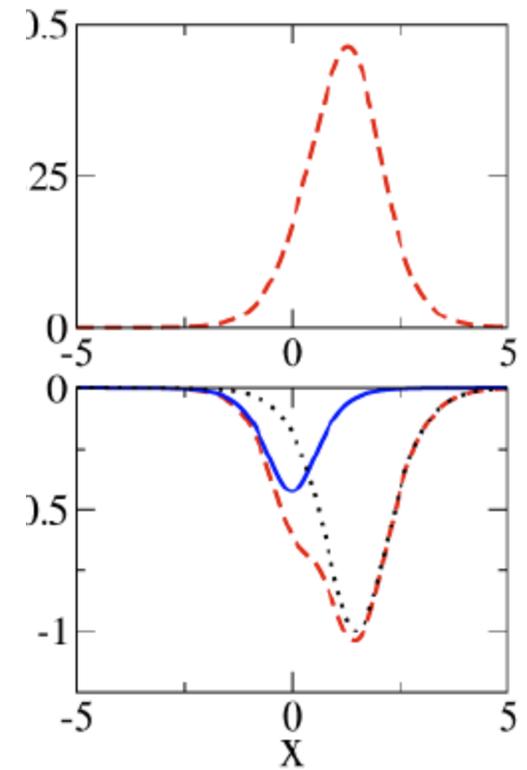
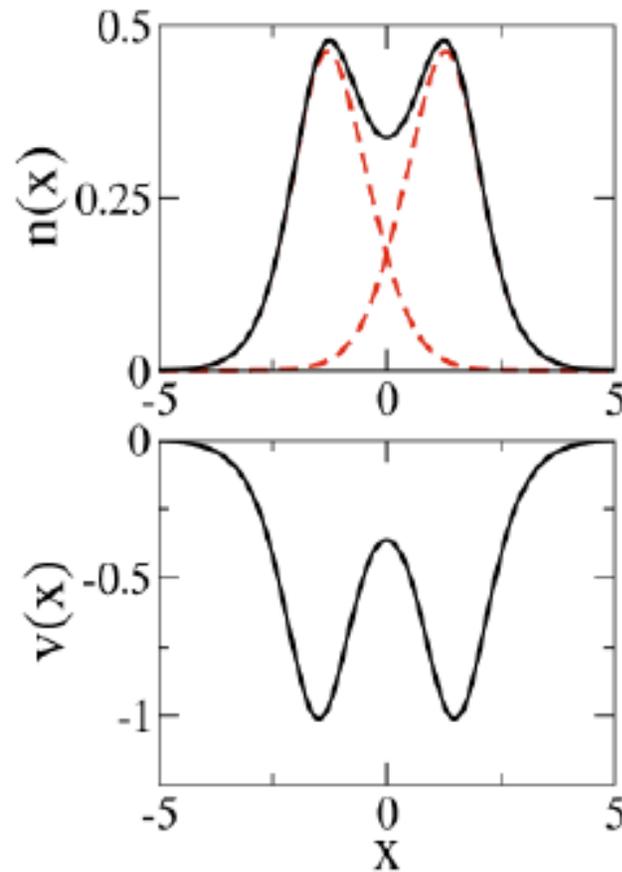
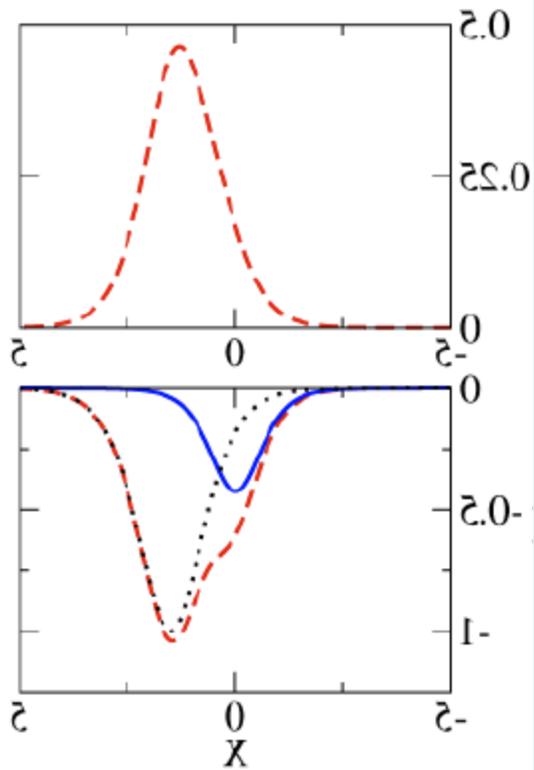
Basics: Partition potential

- How to find minimum? Use Lagrange multipliers:

$$\mathcal{G} = E_f + \int d^3r v_p(\mathbf{r}) \left(n(\mathbf{r}) - \sum_{\alpha=1}^{N_f} n_{\alpha}(\mathbf{r}) \right)$$

- Lagrange multiplier is called partition potential, $v_p(\mathbf{r})$, a global property of the molecule

Example: Partition potential



Finite T

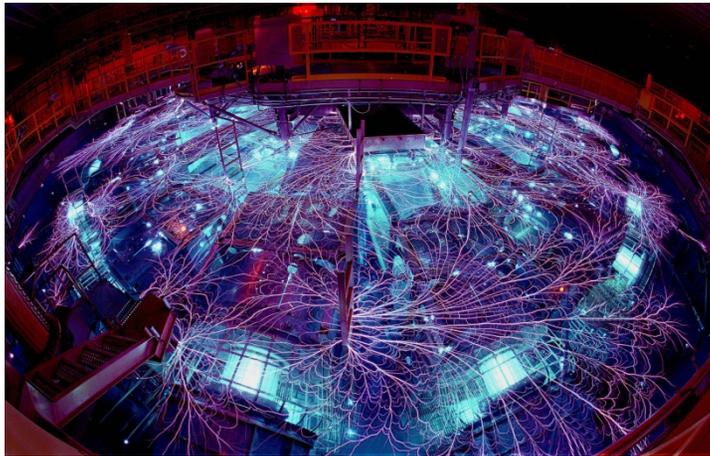


Shock Compression of a Fifth Period Element: Liquid Xenon to 840 GPa

Seth Root,* Rudolph J. Magyar, John H. Carpenter, David L. Hanson, and Thomas R. Mattsson

Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

(Received 12 April 2010; published 17 August 2010)

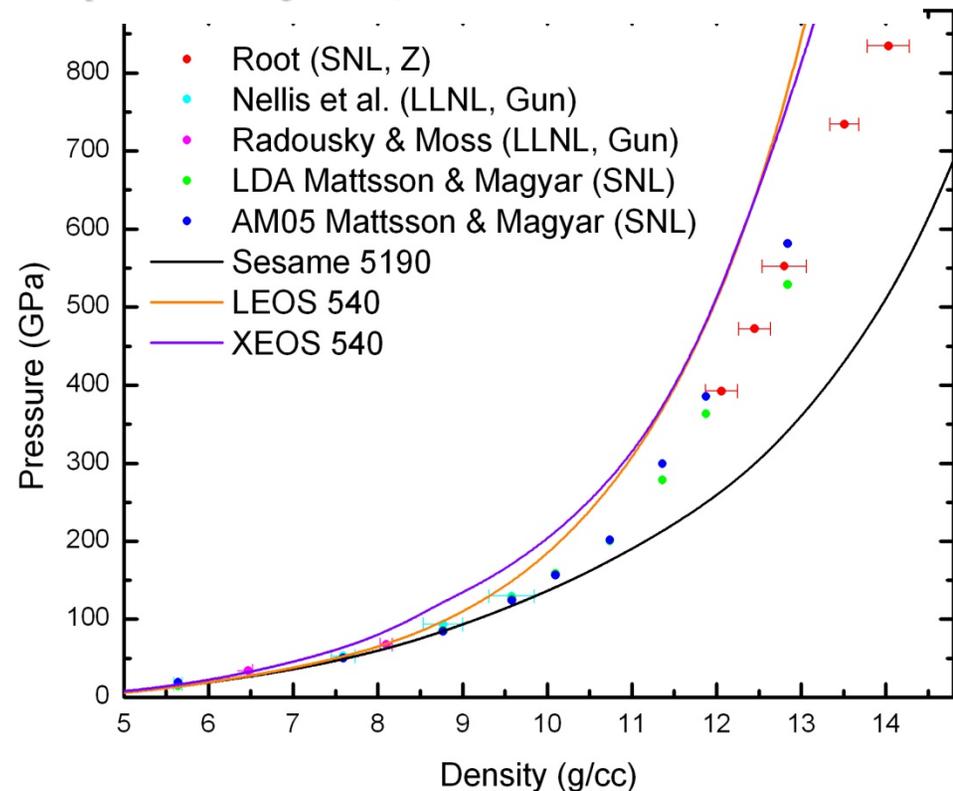


Z-pinch Pulsed Power System

- Millions of amperes for less than 100 nanoseconds
- Peak temperature 3.7 GK or 6.6 billion °F, a world record
- Propelled small plates at 34 km/sec, 4x faster than a speeding bullet.
- Pressures 70,000 to 120,000 atm (7 to 12 Gpa).

DFT-MD

- Move classical nuclei in thermal quantum electrons
- VASP code (Georg Kresse, Vienna, Austria)
- World's tenth fastest computer



Liquid Xenon Hugoniot

Submitted to PRL Root, Magyar, Carpenter, Hanson, Mattsson (2010)
DFT first published: Magyar and Mattsson CP1195, Shock Compression
Condensed Matter, 797 (2009).





Andrea Floris, Hardy Gross,
Cesar Proetto, Antonio Sanna



Finite temperatures

PRL **107**, 163001 (2011)

PHYSICAL REVIEW LETTERS

week ending
14 OCTOBER 2011

Exact Conditions in Finite-Temperature Density-Functional Theory

S. Pittalis,^{1,2,3,*} C. R. Proetto,^{2,3,4,†} A. Floris,^{2,3,‡} A. Sanna,^{3,4} C. Bersier,^{3,4} K. Burke,⁵ and E. K. U. Gross^{3,4}

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(Received 9 March 2011; published 12 October 2011)

Density-functional theory (DFT) for electrons at finite temperature is increasingly important in condensed matter and chemistry. The exact conditions that have proven crucial in constraining and constructing accurate approximations for ground-state DFT are generalized to finite temperature, including the adiabatic connection formula. We discuss consequences for functional construction.

vert the sense of Eq. (17), we can write:

$$F_S^{\tau'}[n] = \frac{\tau'}{\tau} F_S^\tau[n \sqrt{\tau/\tau'}], \quad (19)$$

i.e., knowledge of $F_S^\tau[n]$ at any one finite τ generates *its entire temperature dependence*. via scaling. Furthermore.

Functionals ex Machina

Machine learning meets DFT



- In collaboration with Klaus Mueller of TU Berlin, computer science.
- ML very successful in neuroscience, financial prediction, etc.
- ML now being applied directly to molecular energies from geometries for drug design.
- We applied it to particle-in-a-box kinetic energy functional

Results from ML

- Create a model functional that interpolates among training densities
- Contains about 10^6 parameters
- With enough training (about 100 samples), can get chemical accuracy (i.e., systematically improvable).
- Can get self-consistent densities of similar accuracy.
- Can predict errors within interpolation region.
- Fully non-local, avoids human biases.
- See arXiv or dft.uci.edu

Depth

Major ongoing project

- Semiclassical derivations of density functional approximations.
- Students: Peter Elliot (physics), Attila Cangi, Donghyung Lee, John Snyder (physics)
- Collaborators: John Perdew (Tulane), Gus Scuseria (Rice), Hardy Gross (MPI Halle, Germany).

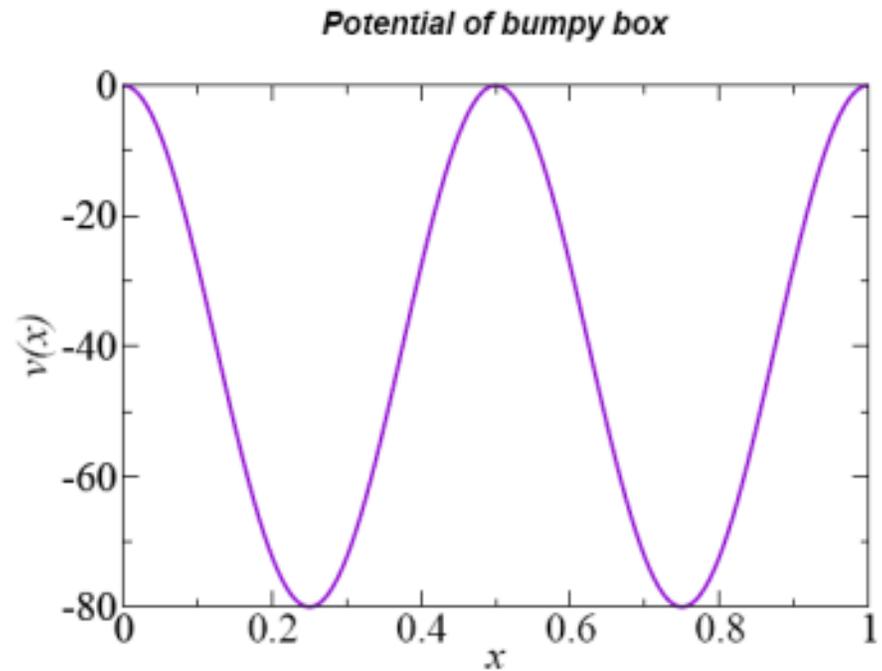
Semiclassical density for 1d box

$$n^{\text{TF}}(x) = \frac{k_{\text{F}}(x)}{\pi}$$

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

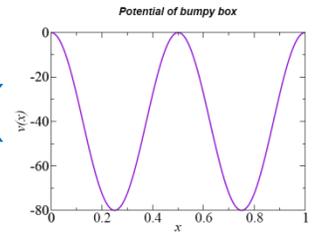
Severe test of semiclassical density

- A very bumpy potential:

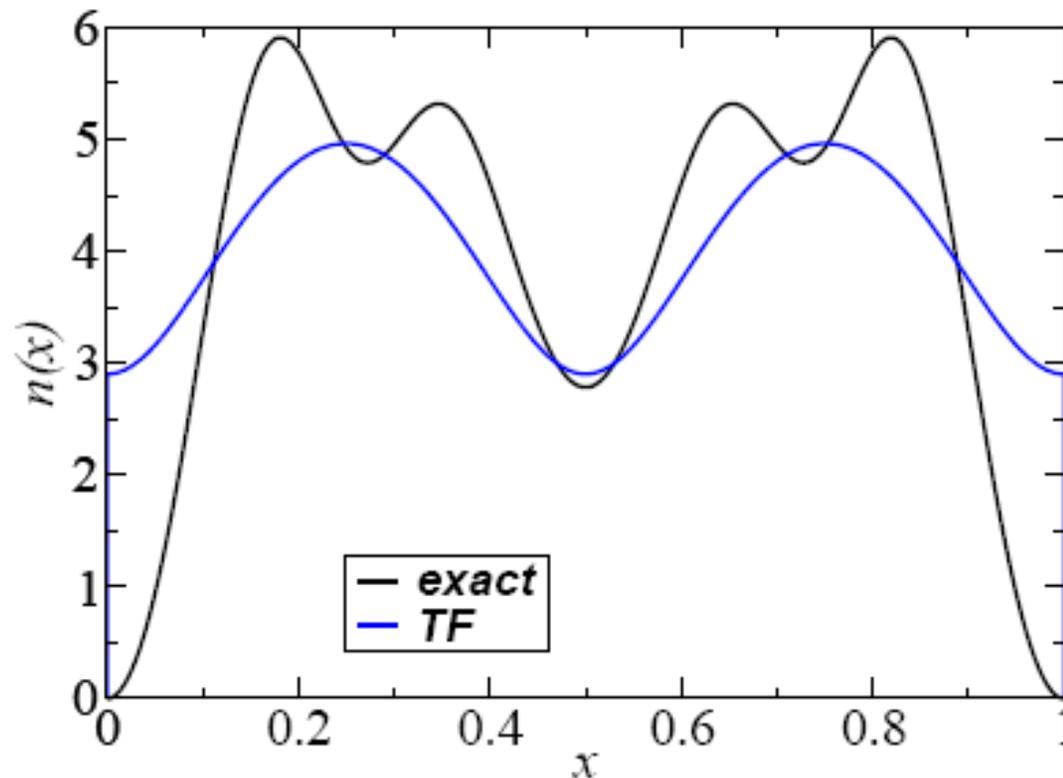


- Orbital energies:
– $\varepsilon_i = -46, -42, 10, 37$

Density in bumpy box



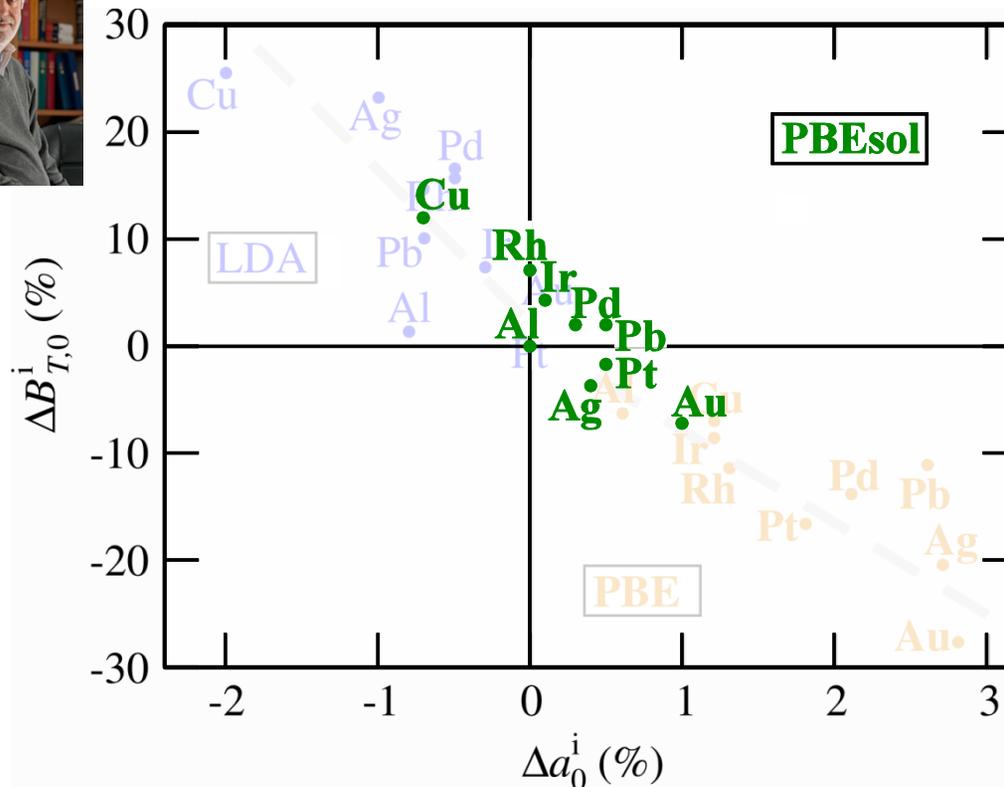
4 spinless Fermions in a bumpy box



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

Structural and Elastic Properties of solids

Errors in LDA/GGA(PBE)-DFT computed lattice constants and bulk modulus with respect to experiment



→ Fully converged results (basis set, k-sampling, supercell size)
 → Error solely due to xc-functional

→ GGA does not outperform LDA
 → characteristic errors of <3% in lat. const.
 < 30% in elastic const.
 → LDA and GGA provide bounds to exp. data
 → provide “ab initio error bars”

Blazej Grabowski, Dusseldorf

⇒ Inspection of several xc-functionals is critical to estimate predictive power and error bars!



$Z \rightarrow \infty$ limit of ionization potential of neutral atoms

- Shows even energy differences can be found
- Looks like LDA exact for E_x as $Z \rightarrow \infty$.
- 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

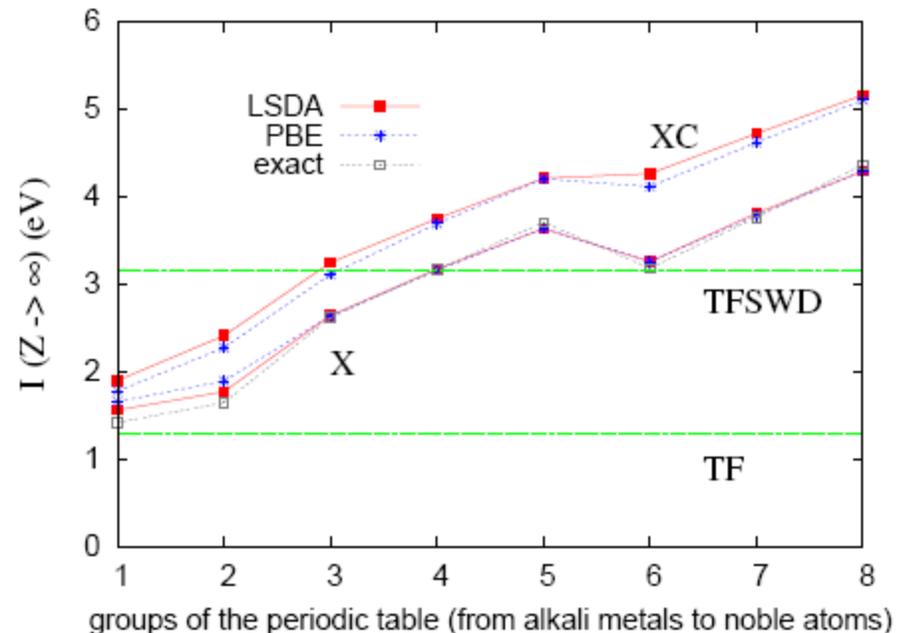


FIG. 1: Ionization potentials of the main groups in the limit of large row number of the periodic table, calculated using exact exchange, the local (spin) density approximation (LSD), and PBE. We also show the extended TF result.

Potential functional approximations

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



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

$$T_s^{\text{cc}}[n_s^{\text{A}}[v]] = \int d^3r \{ \bar{n}_s^{\text{A}}[v](\mathbf{r}) - n_s^{\text{A}}[v](\mathbf{r}) \} v(\mathbf{r})$$

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

- 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 .

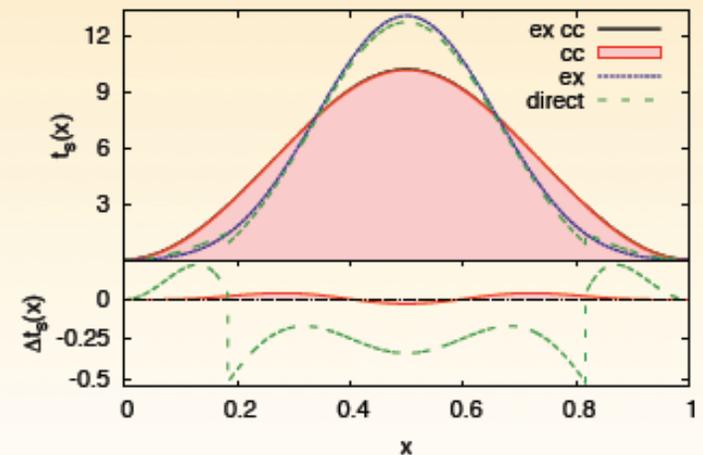
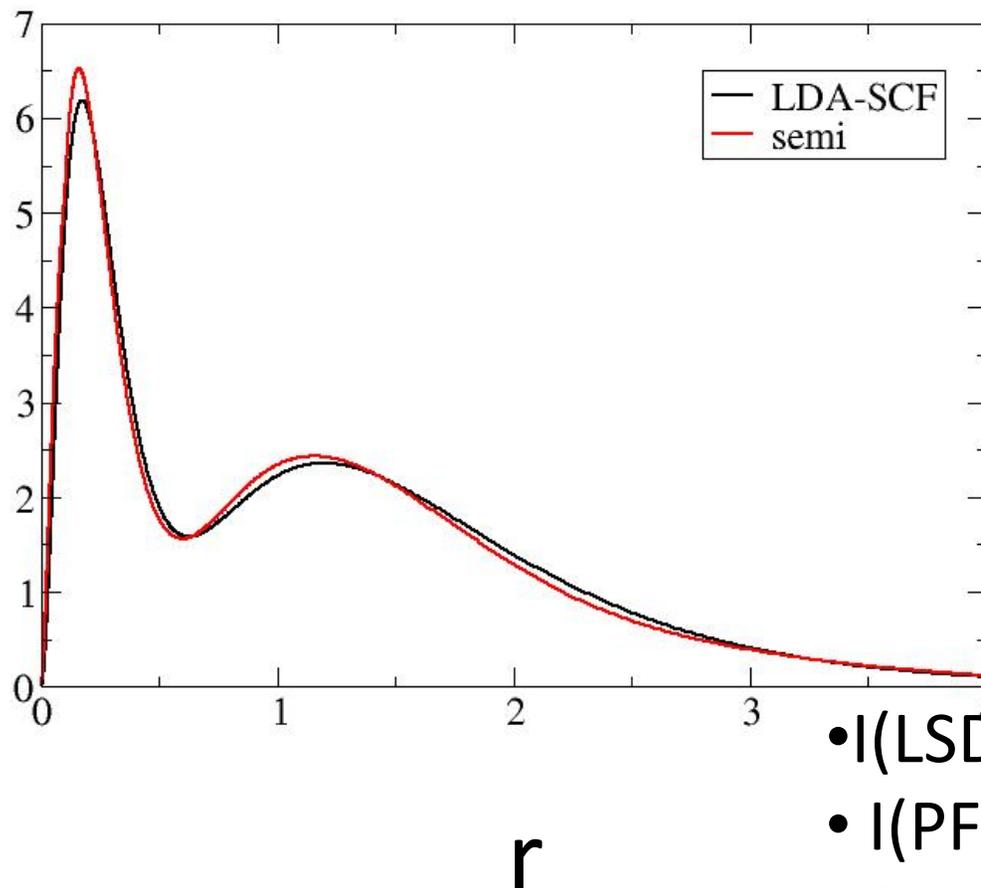


FIG. 1. Kinetic energy densities of T_s^{cc} (black, red) and the direct T_s^{A} (blue, green) of Ref. [18] (above), and their absolute errors (below) for one particle in $v(x) = -5 \sin^2(\pi x)$, $0 < x < 1$. (color online)

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

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



- $I(\text{LSD})=11.67\text{eV}$
- $I(\text{PFT})=11.43\text{ eV}$
- $I(\text{expt})=11.26\text{eV}$

Summary

- General:
 - DFT is a great physics success, driving more and more development in chemistry and materials
 - DFT is a simple crude way to approximate QM of many particles.
 - There is an exact XC functional, even for strongly correlated systems.
 - Present approximations limited in application.
- Breadth and depth:
 - Every new area has its own challenges
 - Still don't really understand why it works.
- Thanks to students and NSF and DOE