Benasque IV

Kieron Burke

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http://dft.uci.edu

Winning topics

A. Semiclassical origins of density functional approximations
B. Strong correlation in DFT
C. Using machine learning to find functionals
D. Transport through molecules
E. Density-corrected DFT (coming up)
F. Warm dense matter
G. Time-dependent density functional theory

Burke group

A. Semiclassical analysis

Semiclassical analysis and density functional theory

- Consider scaling to continuum limit:

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

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

  $$\frac{E^{\mathrm{TF}} - E_0}{E_0} \to 0$$

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

Conjecture on KS-DFT E_{xc}

Almost certain that

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

$$\lim_{\zeta \to \infty} \frac{\Delta E_{\mathsf{xc}}^{\mathrm{LDA}}}{E_{\mathrm{XC}}} = \frac{E_{\mathsf{xc}}^{LDA} - E_{\mathsf{xc}}}{E_{\mathrm{XC}}} = 0$$

Kieron's instinct:

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

Leading corrections to local approximations

- Can we define and find leading corrections to $E_{\mathrm{XC}}^{\mathrm{LDA}}$ in an expansion of the electronic energy as a function of particle number?
- Recent research has shown that at *least* for simple cases the answer is yes, but as explicit functionals of the *potential*, not density

Toy model: SNIFs

Same-spin **N**on**I**nteracting **F**ermions

- no internal interactions
- Pauli Principle: Occupy lowest N levels

Also limit to

- one dimension
- Dirichlet boundary conditions (box)
- Arbitrary (but smooth) potential $v(x)$

Semiclassical analysis of SNIFS

WKB theory for bound states

$$\phi_j^{\mathrm{WKB}}(x) = \frac{A}{\sqrt{k_j(x)}}\sin\theta_j(x)$$

$$k_j(x) = \sqrt{2(E_j - V(x))}$$

$$\theta_j(x) = \int_0^x k_j(x')\mathrm{d}x'$$

$$\Theta_j(E_j) = \int_0^L k_j(x')\mathrm{d}x' = j\pi$$

Semiclassics of sums over levels

$$n^{\mathrm{sc}}(x) = n^{\mathrm{TF}}(x) + n^{\mathrm{osc}}(x)$$

$$n^{\mathrm{sc}}(x) = \frac{k_F(x)}{\pi} - \frac{\sin 2\theta_F(x)}{2k_F(x)\tau_F(x)\sin[\alpha_F(x)]}$$

$$k_F(x) = \sqrt{E_F - V(x)}$$

$$\Theta_F(E_F) = \int_0^L k_F(x')\mathrm{d}x' = \left(N + \frac{1}{2}\right)\pi$$

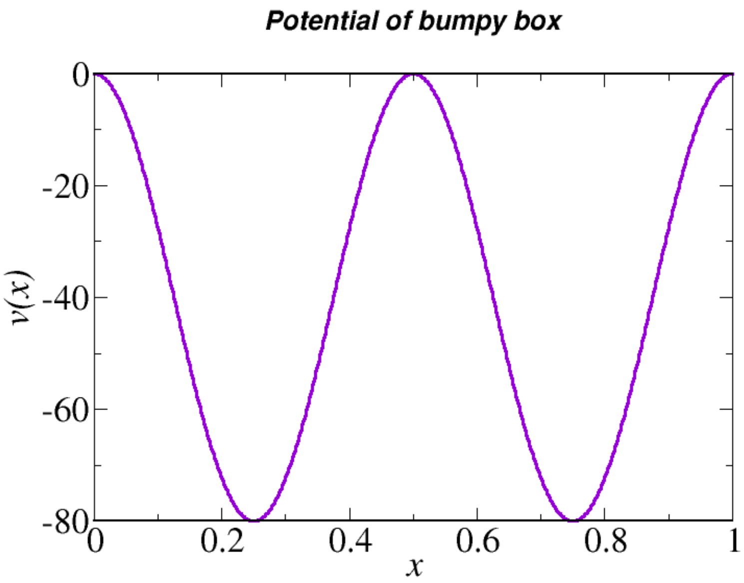
$$t_F(x) = \int_0^x \frac{\mathrm{d}x'}{k_F(x')}$$

Properties of semiclassical density

$$n^{\mathrm{semi}}(x) = \frac{k_{\mathrm{F}}(x)}{\pi} - \frac{\sin 2\theta_{\mathrm{F}}(x)}{2\tau_{\mathrm{F}}(L)\, k_{\mathrm{F}}(x) \sin\left(\frac{\pi \tau_{\mathrm{F}}(x)}{\tau_{\mathrm{F}}(L)}\right)} \,,$$

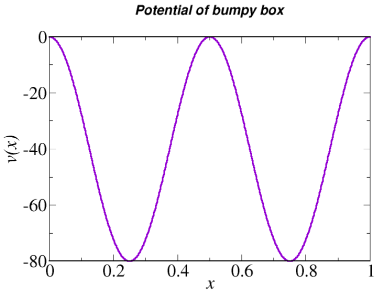
- Exact for $v = 0$, flat box.
- $\theta_{\mathrm{F}}(L) = 0$ required to make $n(L)$ vanish, but does not imply normalization.
- Highly non-local functional via E_{F}, and integrals of local functionals $\theta_{\mathrm{F}}(x)$ and $\tau_{\mathrm{F}}(x)$.
- TF theory retains only first term, E_{F} different.
- Only valid for $E_{\mathrm{F}} > v_{max}$, but works even if low-lying orbitals have turning points.

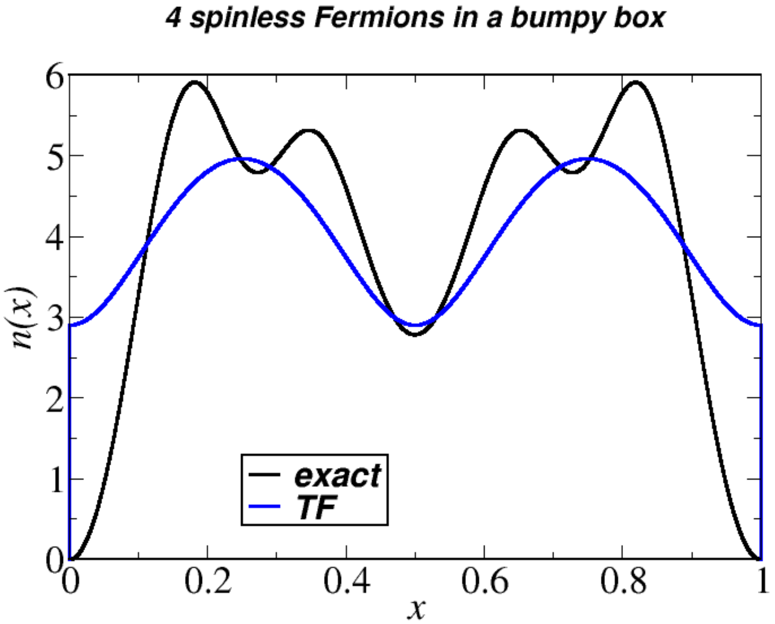
Bumpy box



- Choose double bump: $v(x) = -80\sin^2(2\pi x/L)$.
- Orbital energies: $-46, -42, 10, 37$, so almost degenerate first and second levels.

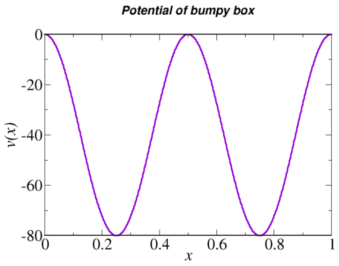
Density in bumpy box

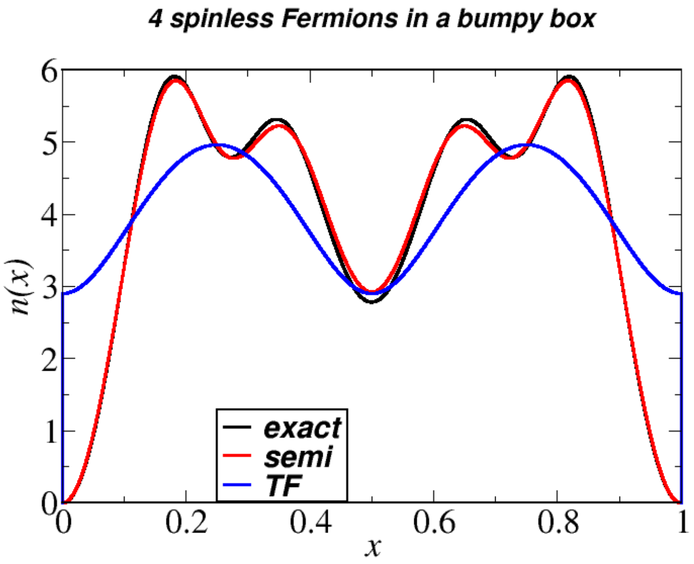




- Test quality of $n(x)$ by inserting into $T^{\mathrm{loc}}[n]$ and find:
- Self-consistent TF (local approx) yields 115.
- Exact answer is 153.0.

Semiclassical density in bumpy box

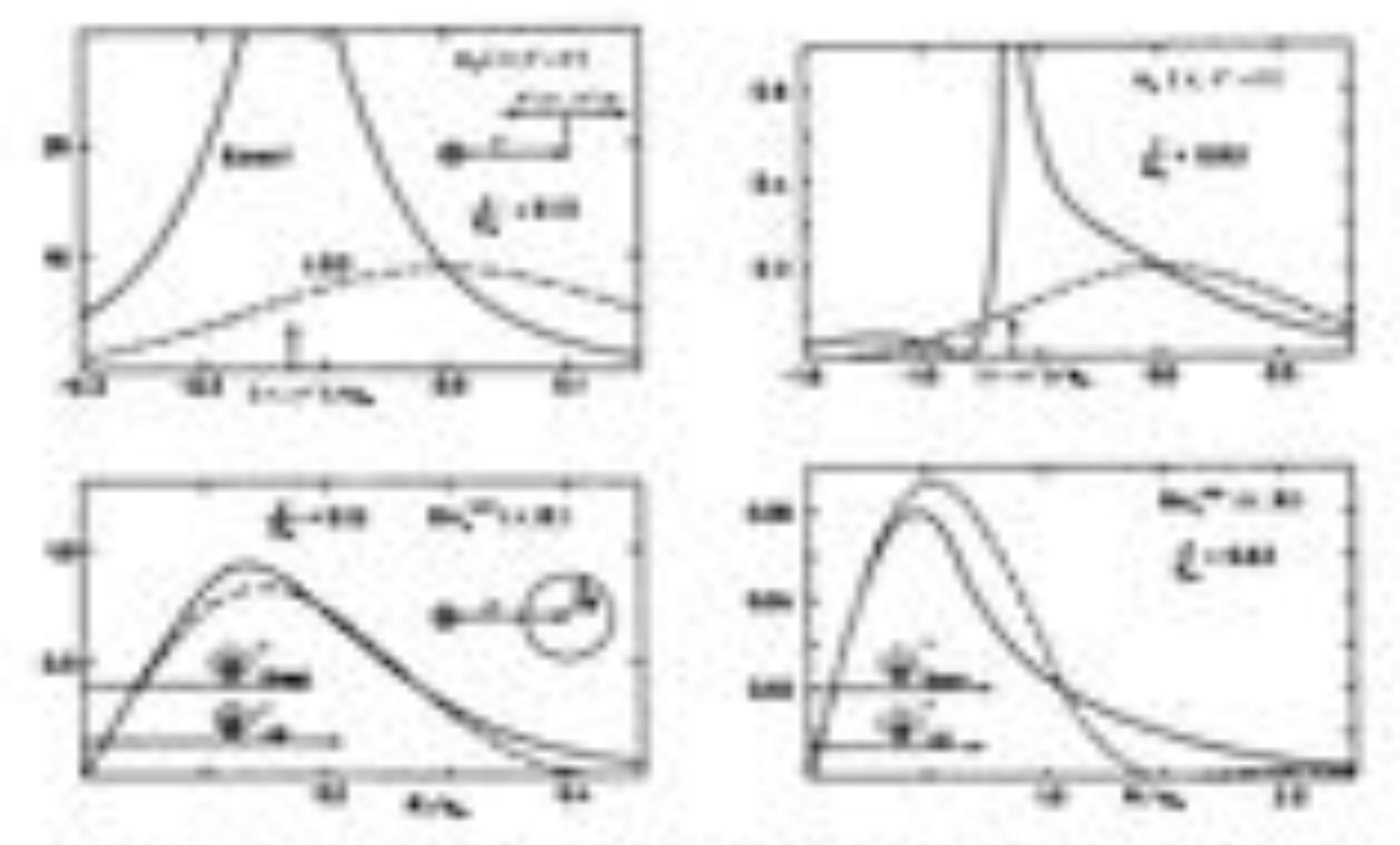




- Norm error $< 0.2\%$.
- Test quality of $n(x)$ by inserting into $T^{\rm loc}[n]$ and find:
- Self-consistent TF (local approx) yields 115.
- Semiclassical approximation yields 151.4.
- Exact answer is 153.0.

Latest preliminary results

Exchange holes in Ne



Jones and Gunnarsson, Reviews of Modern Physics, Vol. 61, No. 3, July 1989

GGA X hole

J. Chem. Phys., Vol. 109, No. 9, 1 September 1998

Ernzerhof and Perdew

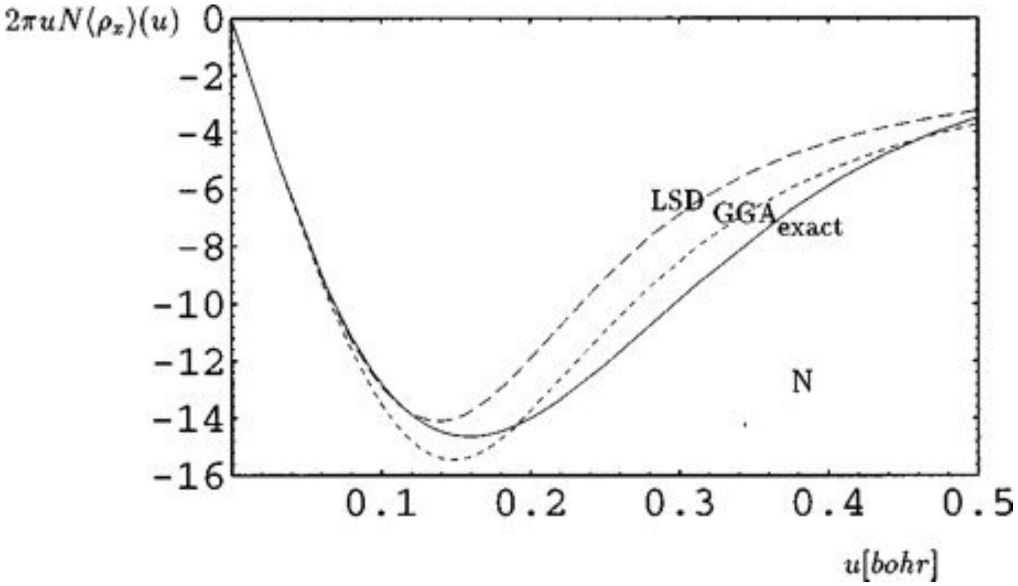
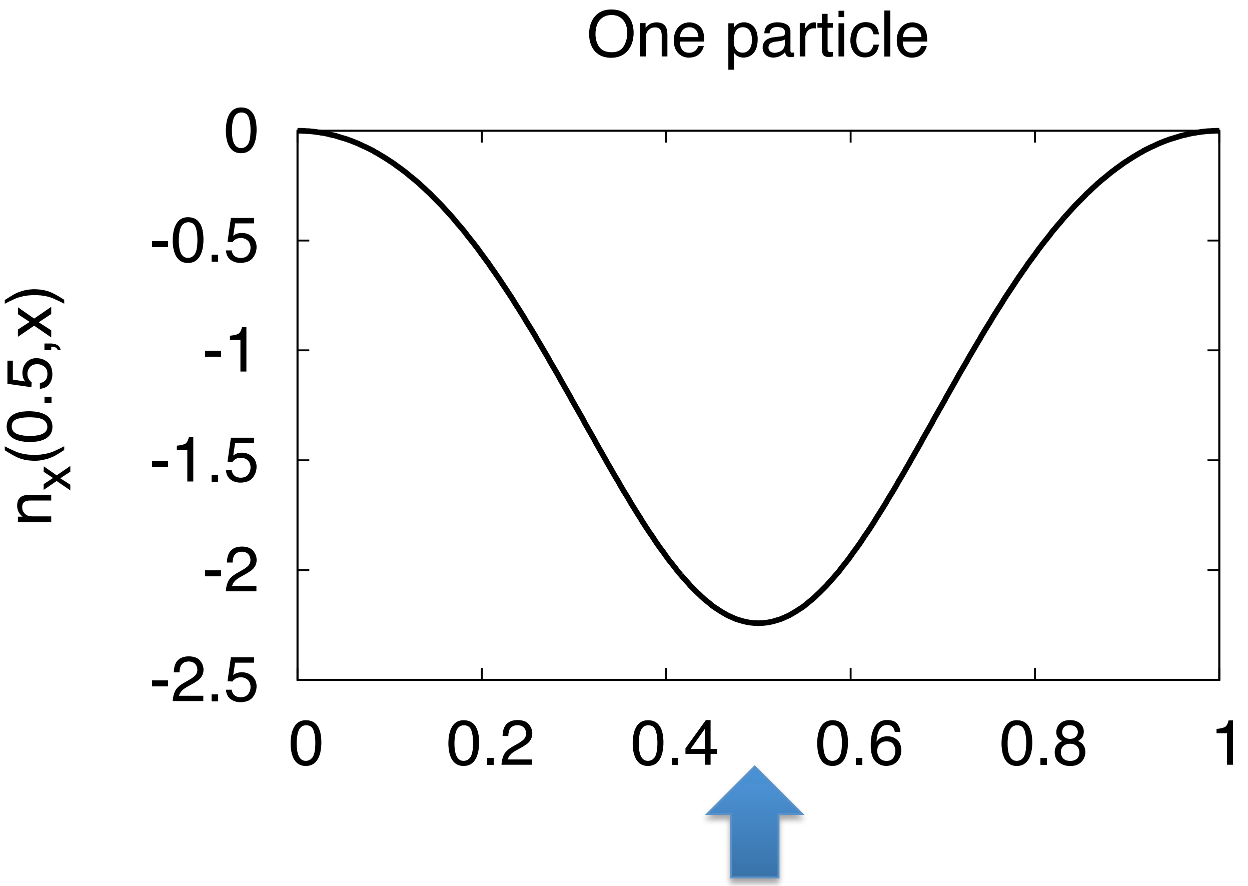


FIG. 3. Energy-weighted angle- and system-averaged exchange holes for the N atom in the core-dominated regime $u<0.5$ bohr. The solid line represents the exact result, the long dashes show LSD, and the short dashed line is the GGA curve.

Semiclassical results for 1d x hole

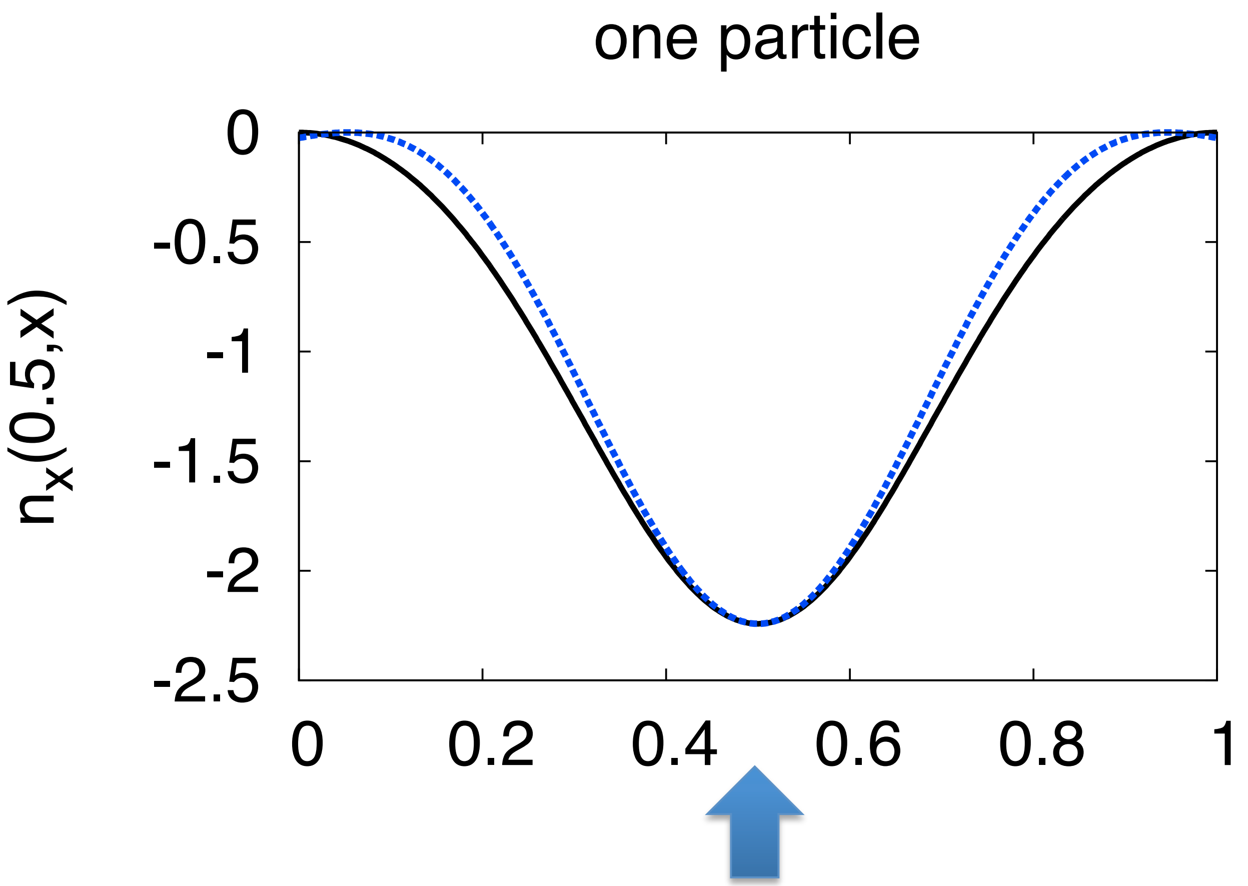
X hole in 1d box

Black=exact



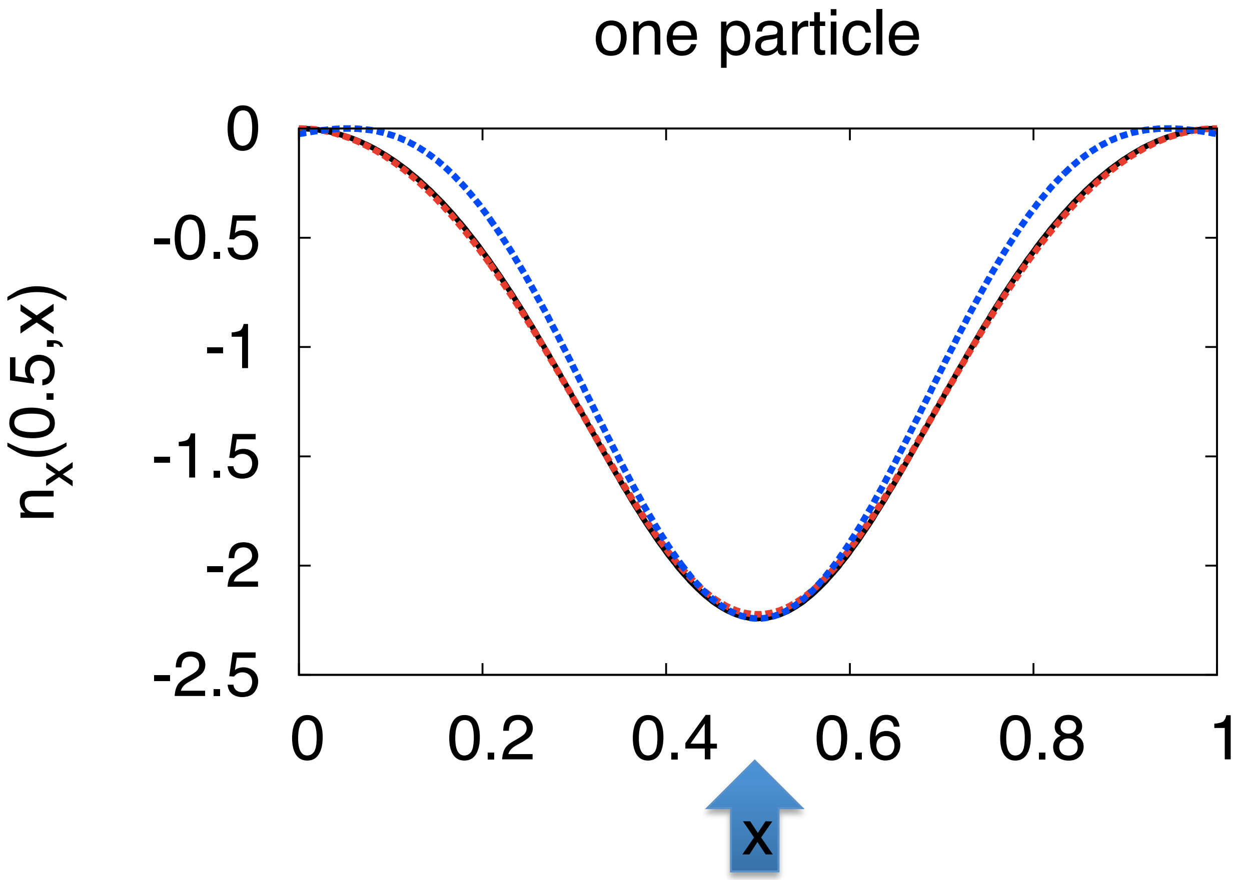
X hole in 1d box

Black=exact
Blue = LDA



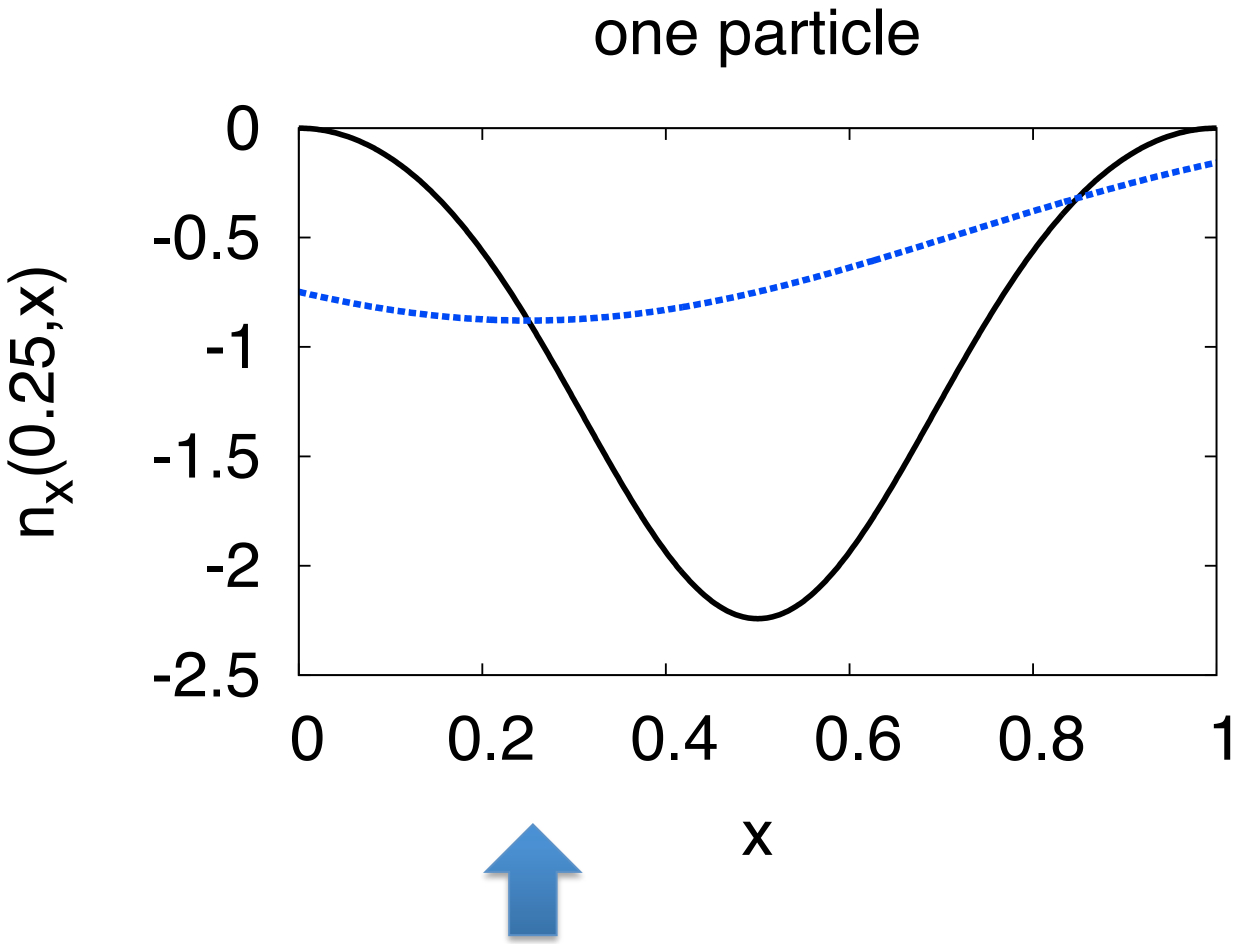
X hole in 1d box

Black=exact
Blue = LDA
Red = semiclass



X hole in 1d box

Black=exact
Blue = LDA



X hole in 1d box

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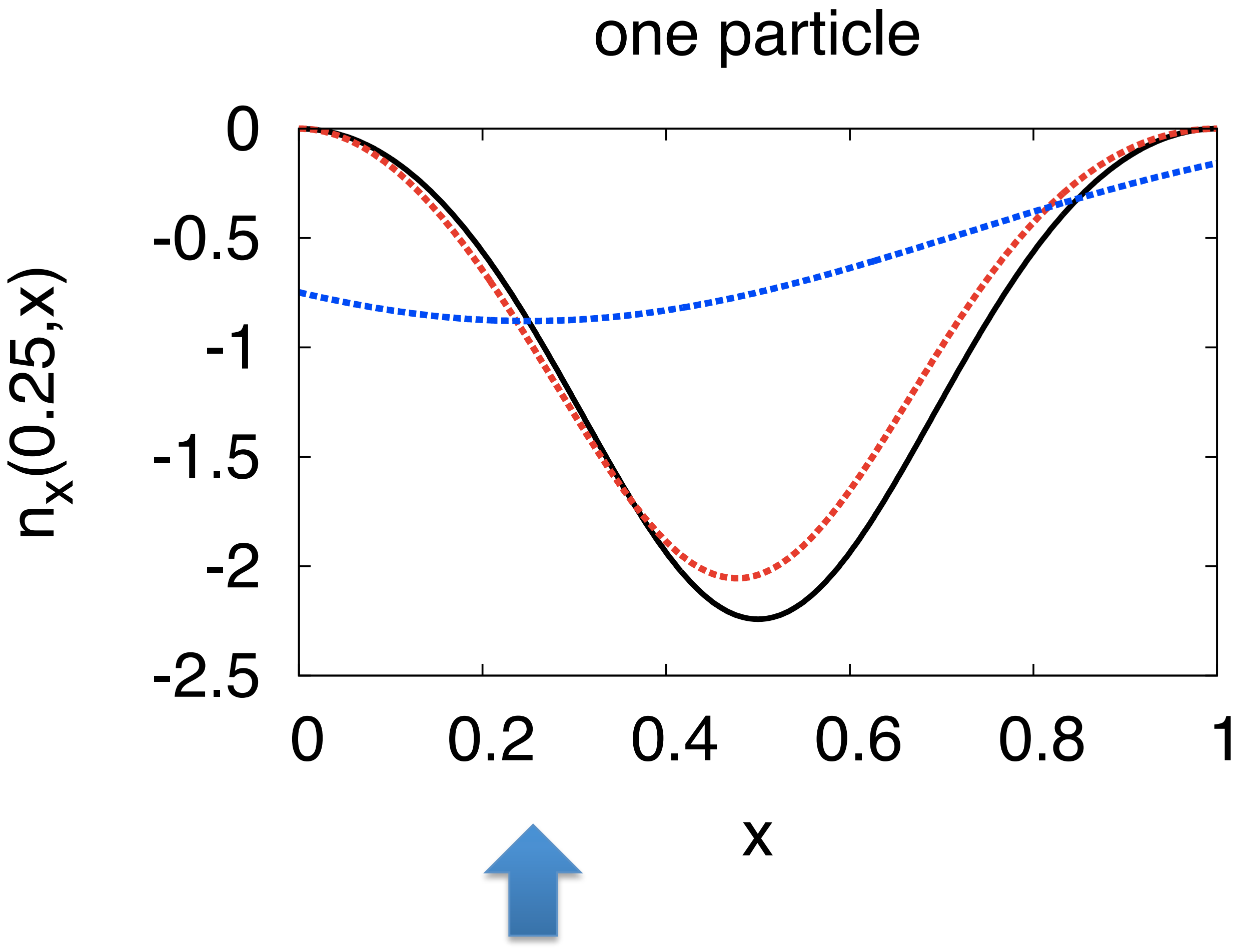

X hole in 1d box

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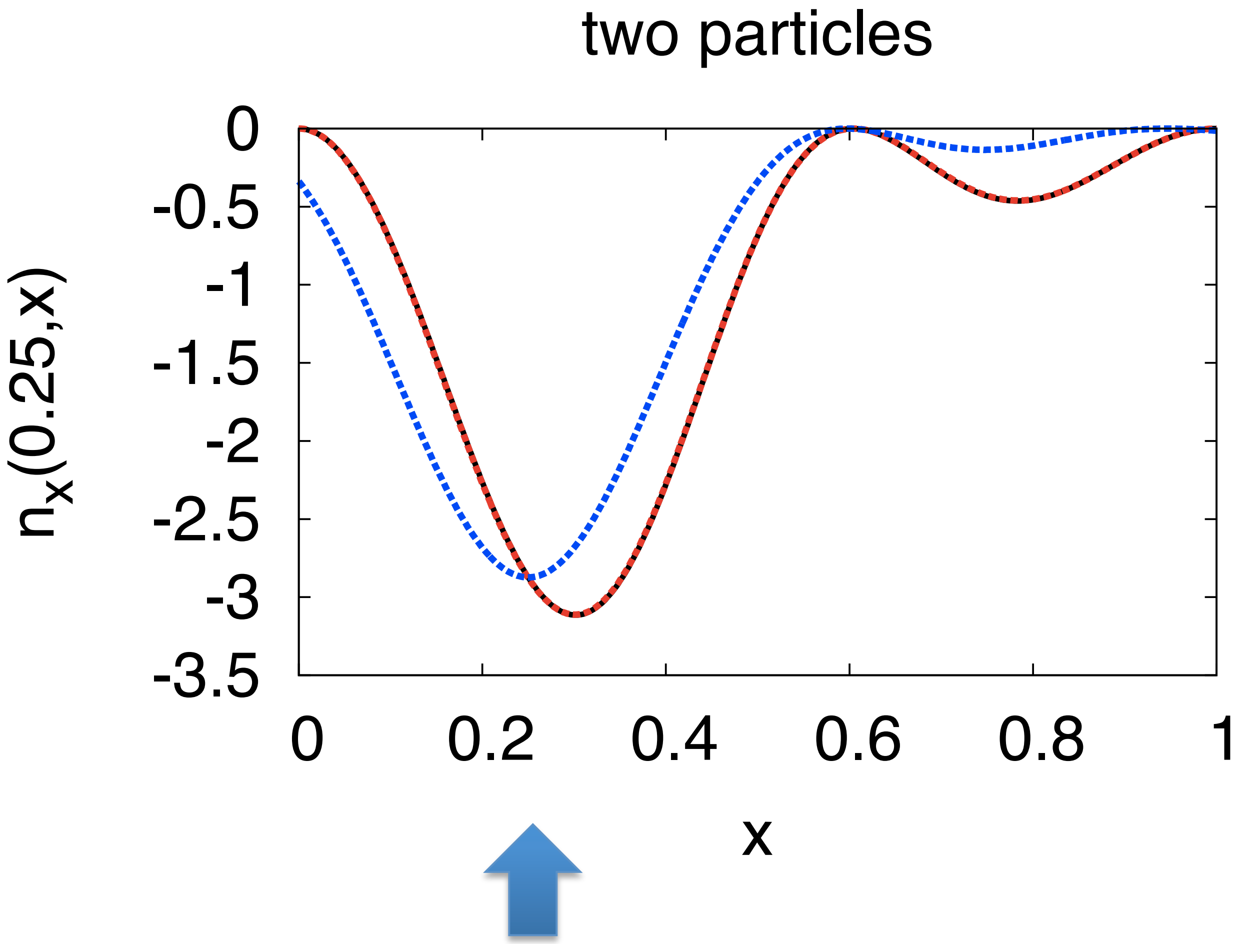

X hole in 1d box

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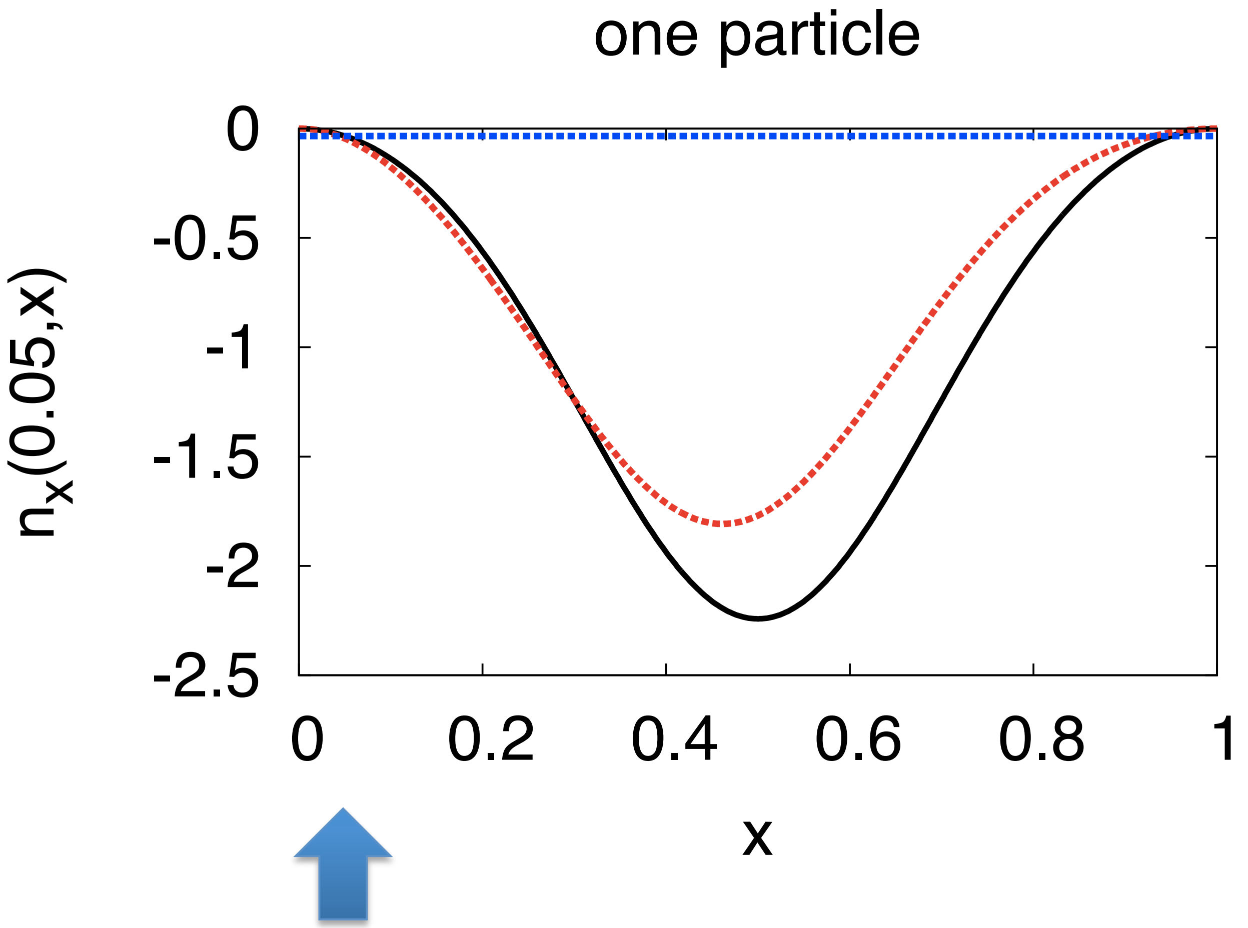
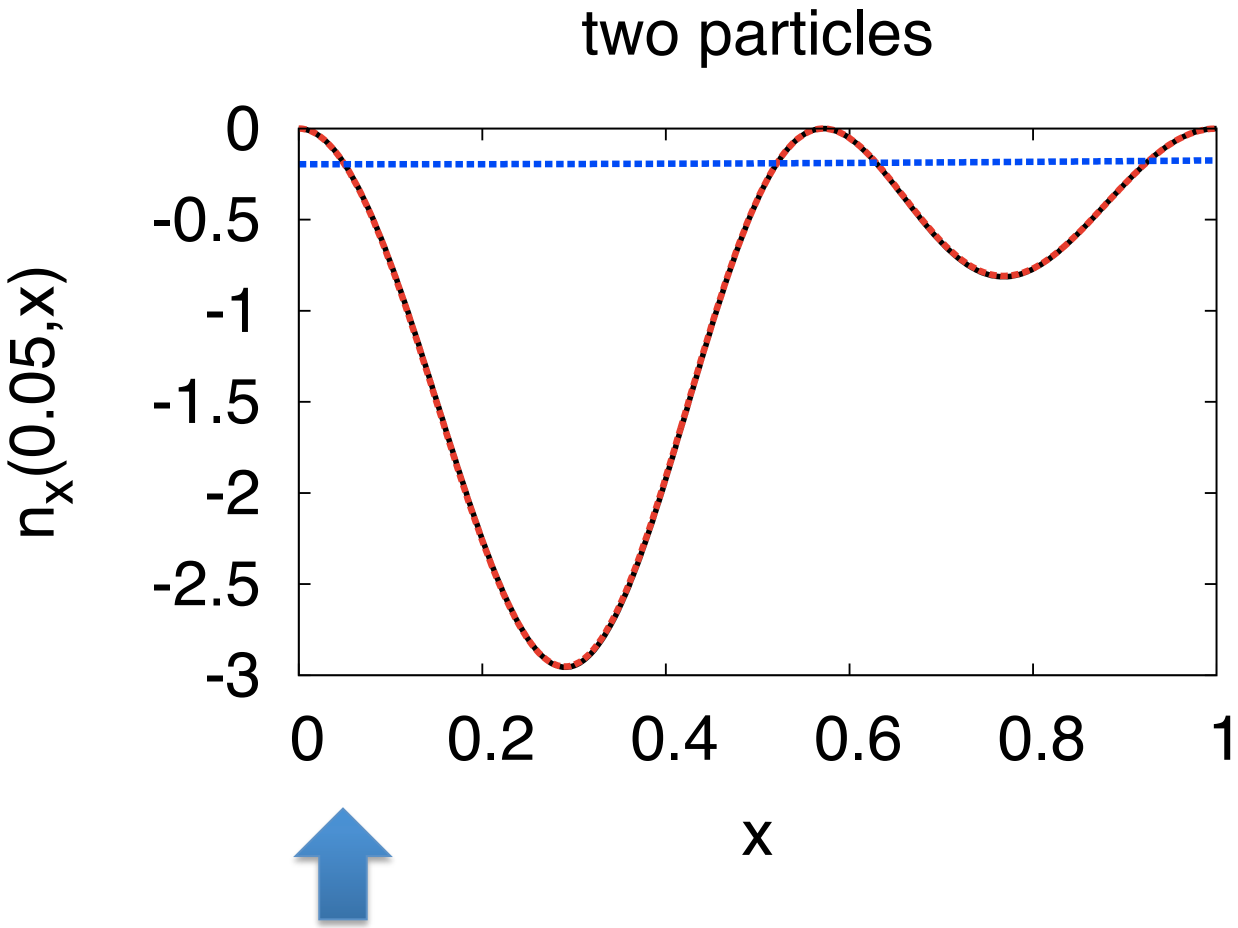


X hole in 1d box

Black=exact
Blue = LDA
Red = semiclass



Papers (formalism)

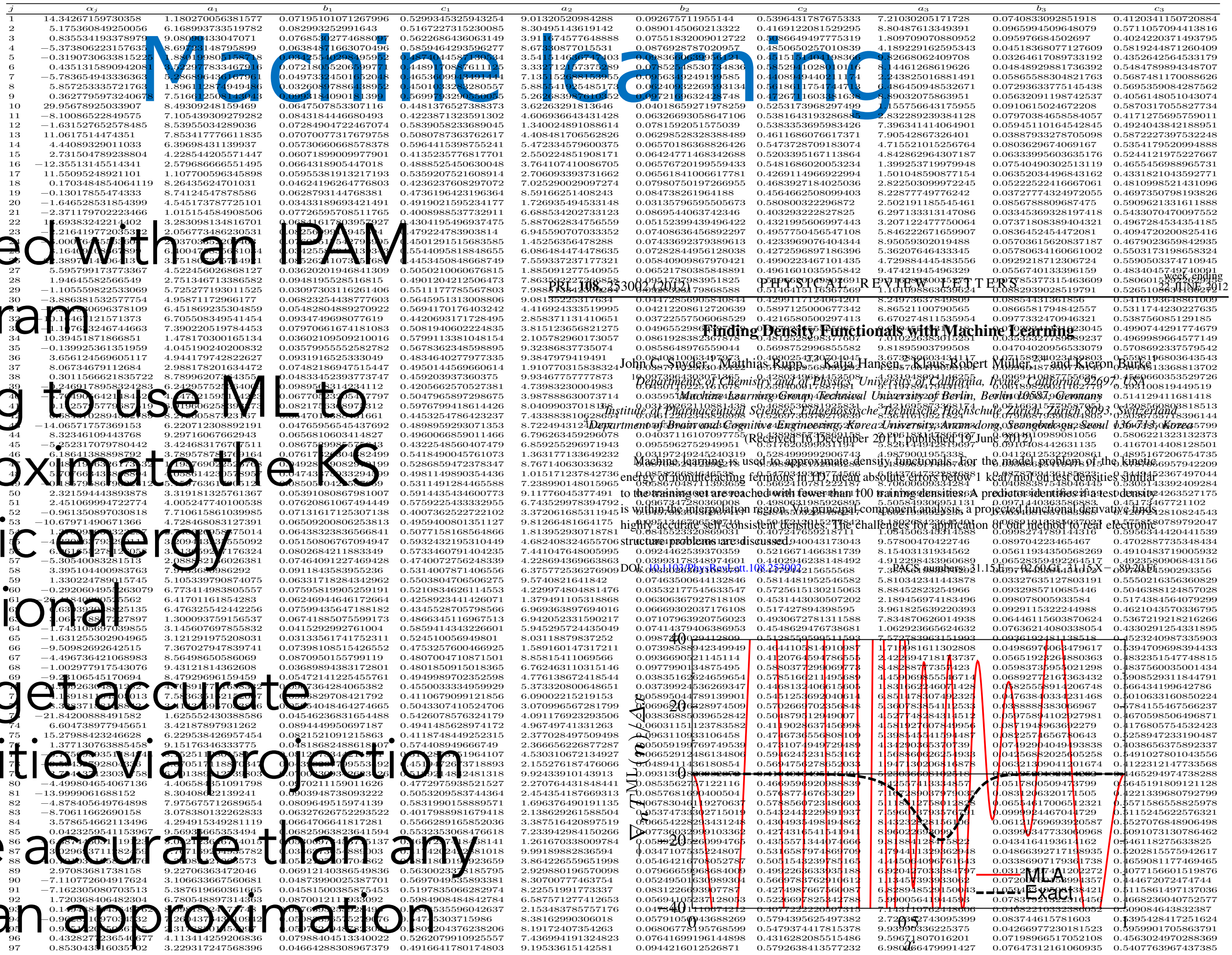
- *Semiclassical Origins of Density Functionals*, Peter Elliott, Donghyung Lee, Attila Cangi, KB, Phys. Rev. Lett. 100, 256406 (2008)
- *Leading corrections to local approximations*, Attila Cangi, Donghyung Lee, Peter Elliott, KB, Phys. Rev. B 81, 235128 (2010).
- *Electronic Structure via Potential Functional Approximations*, Attila Cangi, Donghyung Lee, Peter Elliott, KB, E. K. U. Gross, Phys. Rev. Lett. 106, 236404 (2011)
- *Potential functionals versus density functionals*, Attila Cangi, E. K. U. Gross, KB, to appear Phys. Rev. A (2013).
- ————-*In preparation* ————————
- *Semiclassical density from parition function*, A. Cangi and E. Sim.
- *Semiclassical exchange energies*, A. Cangi, P. Elliott, E.K.U. Gross.
- *Semiclassical density for finite wells*, R. Ribeiro.
- *Semiclassical densities in quasi-2D systems*, S. Pitallis, A. Cangi
- *Orbital-free orbital energies*, A. Cangi, E.K.U. Gross.

Papers (more practical)

- *Relevance of the slowly varying electron gas...* J. Perdew, L Constantin, E Sagvolden, KB, Phys. Rev. Lett. 97, 223002 (2006)
- *Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces*, J.P. Perdew et al. Phys. Rev. Lett. 100, 136406 (2008).
- *Non-empirical derivation of the parameter in the B88 exchange functional*, Peter Elliott, KB, Can J Chem 87, 1485-1491 (2009)
- *Condition on the Kohn-Sham kinetic energy and ..*, D Lee, L Constantin, J Perdew, KB, J. Chem. Phys. 130, 034107 (2009)
- *Ionization potentials in the limit of large atomic number*, L Constantin, J Snyder, J Perdew, KB, J Chem Phys 133, 241103 (2010).
- ————-*In preparation* ————————
- *Ionization potentials and exchange energies for Bohr atoms*, J. Snyder, S. Pitallis.
- *Correlation energy in semiclassical limit*, S. Pitallis.

Machine Learning

- Started with an IPAM program
- Trying to use ML to approximate the KS kinetic energy functional
- Can get accurate densities via projection
- More accurate than any human approximation



PRL 108, 253002 (2012) PHYSICAL REVIEW LETTERS week ending 22 JUNE 2012

Finding Density Functionals with Machine Learning

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(Received 16 December 2011; published 19 June 2012)

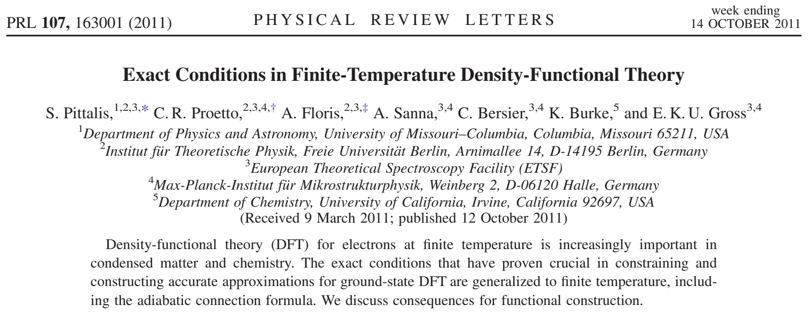
Machine learning is used to approximate density functionals. For the model problem of the kinetic energy of noninteracting fermions in 1D, mean absolute errors below 1 kcal/mol on test densities similar to the training set are reached with fewer than 100 training densities. A predictor identifies if a test density is within the interpolation region. Via principal component analysis, a projected functional derivative finds highly accurate self-consistent densities. The challenges for application of our method to real electronic structure problems are discussed.

DOI: 10.1103/PhysRevLett.108.253002 PACS numbers: 31.15.E−, 02.60.Gf, 31.15.X−, 89.20.Ff

FIG. 3 (color online). Functional derivative of $T^{\rm ML}$, evaluated on the density of Fig. 2.

Warm dense matter

- Much interest in performing DFT calculations at high pressure and temperature
- Do we need thermal corrections to XC?
- What are the rules?
- Book chapter ➔ on our website.



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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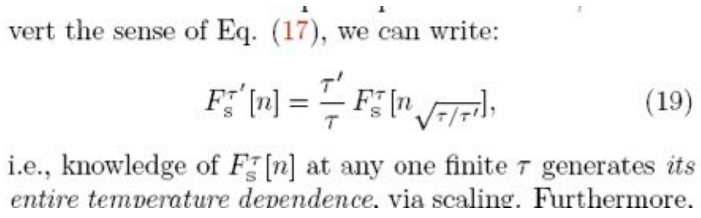
(Received 9 March 2011; published 12 October 2011)

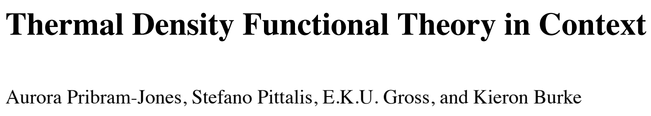
Density-functional theory (DFT) for electrons at finite temperature is increasingly important in condensed matter and chemistry. The exact conditions that have proven crucial in constraining and constructing accurate approximations for ground-state DFT are generalized to finite temperature, including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



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

$$F_s^{\tau'}[n] = \frac{\tau'}{\tau} F_s^{\tau}[n_{\sqrt{\tau/\tau'}}], \tag{19}$$

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



Thermal Density Functional Theory in Context

Aurora Pribram-Jones, Stefano Pittalis, E.K.U. Gross, and Kieron Burke

‘True’ self-interaction error

Anions

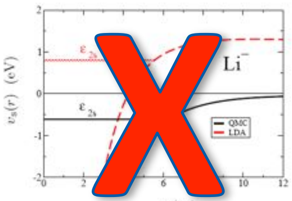


FIG. 1: Comparison of KS potentials of Li^-. The black line is essentially exact, using a density from quantum Monte Carlo. The red (dashed) line is the LDA potential on that density. The horizontal lines mark the HOMO (2s orbital) energies.

Barriers

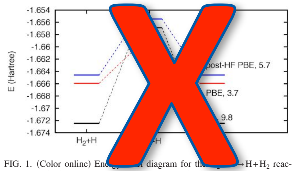


FIG. 1. (Color online) En[illegible] diagram for th[illegible] $\to$ H+H_2 reaction. PBE (red), post-HF PBE, and high-level (HL) *ab initio* calculations. Classical reaction barriers (kcal/mol) are given in the labels; other details are in the text.

Crazy Hemibonds
in solution

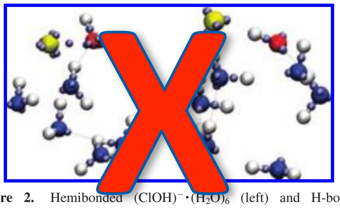
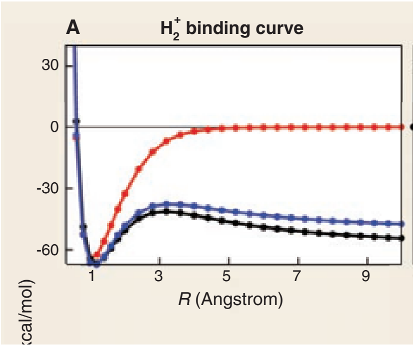
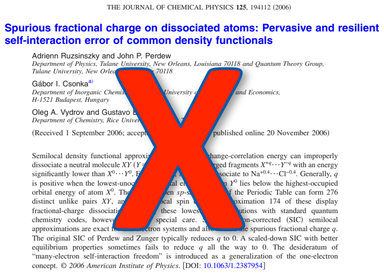


Figure 2. Hemibonded $(ClOH)^-\bullet(H_2O)_6$ (left) and H-bonded $OHCl^-\bullet(H_2O)_6$ (right) cluster geometries observed in simulations without and with the SIC, respectively. Water oxygens are depicted in blue, OH oxygen in red, hydrogens in white, and chlorine in yellow, and the gray spheres represents the WFCs (see text).

Dissociating H_2^+



Elongated molecules



THE JOURNAL OF CHEMICAL PHYSICS **125**, 194112 (2006)

Spurious fractional charge on dissociated atoms: Pervasive and resilient self-interaction error of common density functionals

Adrienn Ruzsinszky and John P. Perdew
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Gábor I. Csonka[a)]
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Department of Chemistry, Rice Univer[illegible]

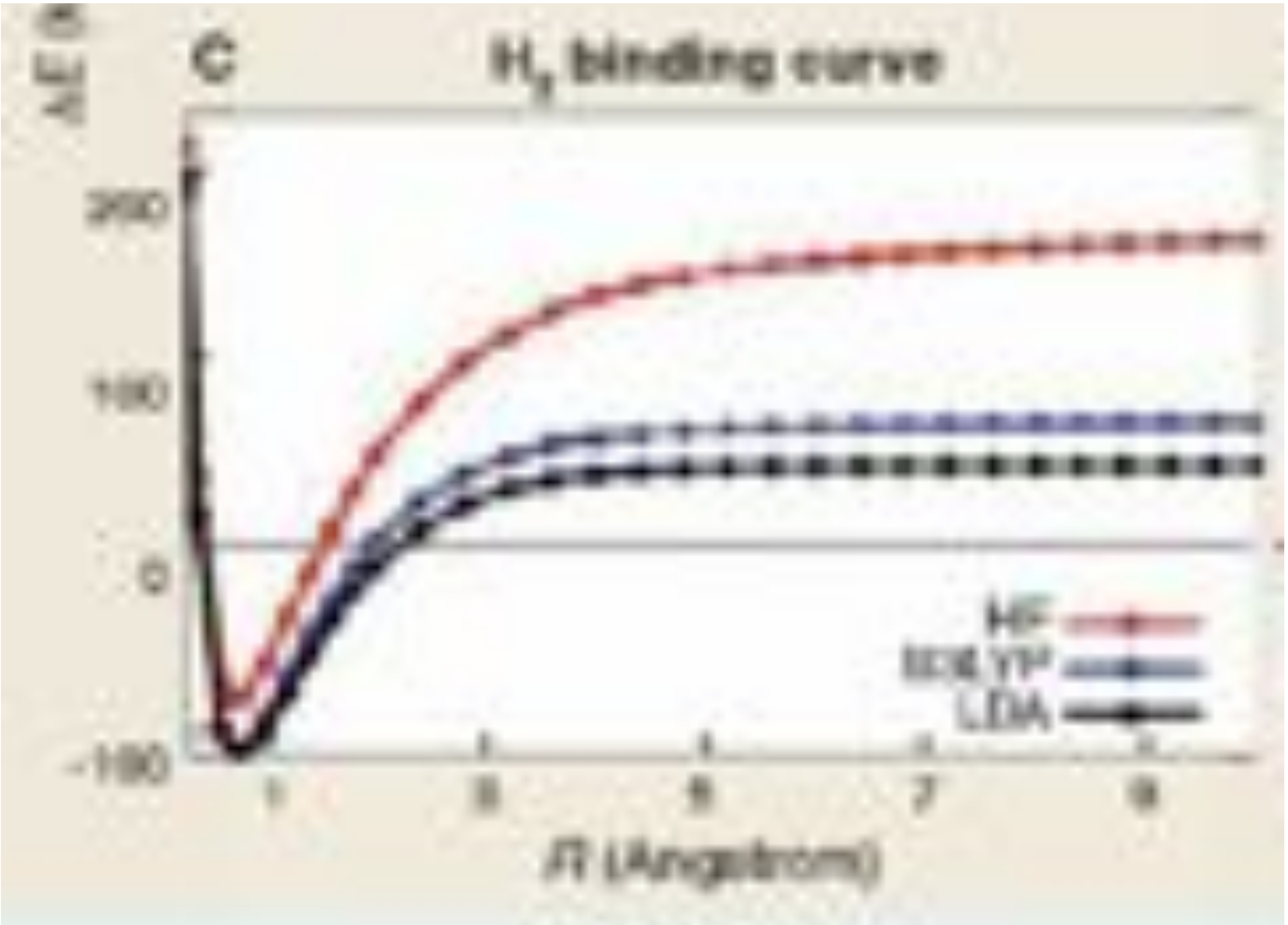
(Received 1 September 2006; accept[illegible] published online 20 November 2006)

Semilocal density functional approxi[illegible]change-correlation energy can improperly dissociate a neutral molecule XY (Y[illegible]rged fragments $X^{+q}\cdots Y^{-q}$ with an energy significantly lower than $X^0\cdots Y^0$. F[illegible]sociate to $Na^{+0.4}\cdots Cl^{-0.4}$. Generally, q is positive when the lowest-unoc[illegible]tal e[illegible] Y^0 lies below the highest-occupied orbital energy of atom X^0. The[illegible]en sp-s[illegible] the Periodic Table can form 276 distinct unlike pairs XY, an[illegible]ocal spin [illegible]oximation 174 of these display fractional-charge dissociati[illegible] these lowes[illegible]tions with standard quantum chemistry codes, howeve[illegible] special care. [illegible]on-corrected (SIC) semilocal approximations are exact f[illegible]ectron systems and als[illegible] the spurious fractional charge q. The original SIC of Perdew and Zunger typically reduces q to 0. A scaled-down SIC with better equilibrium properties sometimes fails to reduce q all the way to 0. The desideratum of “many-electron self-interaction freedom” is introduced as a generalization of the one-electron concept. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2387954]

Understanding and reducing errors in density functional calculations Min-Cheol Kim, Eunji Sim, Kieron Burke, Phys. Rev. Lett. 111, 073003 (2013).

B. Strong correlation

Errors in standard DFT approximations

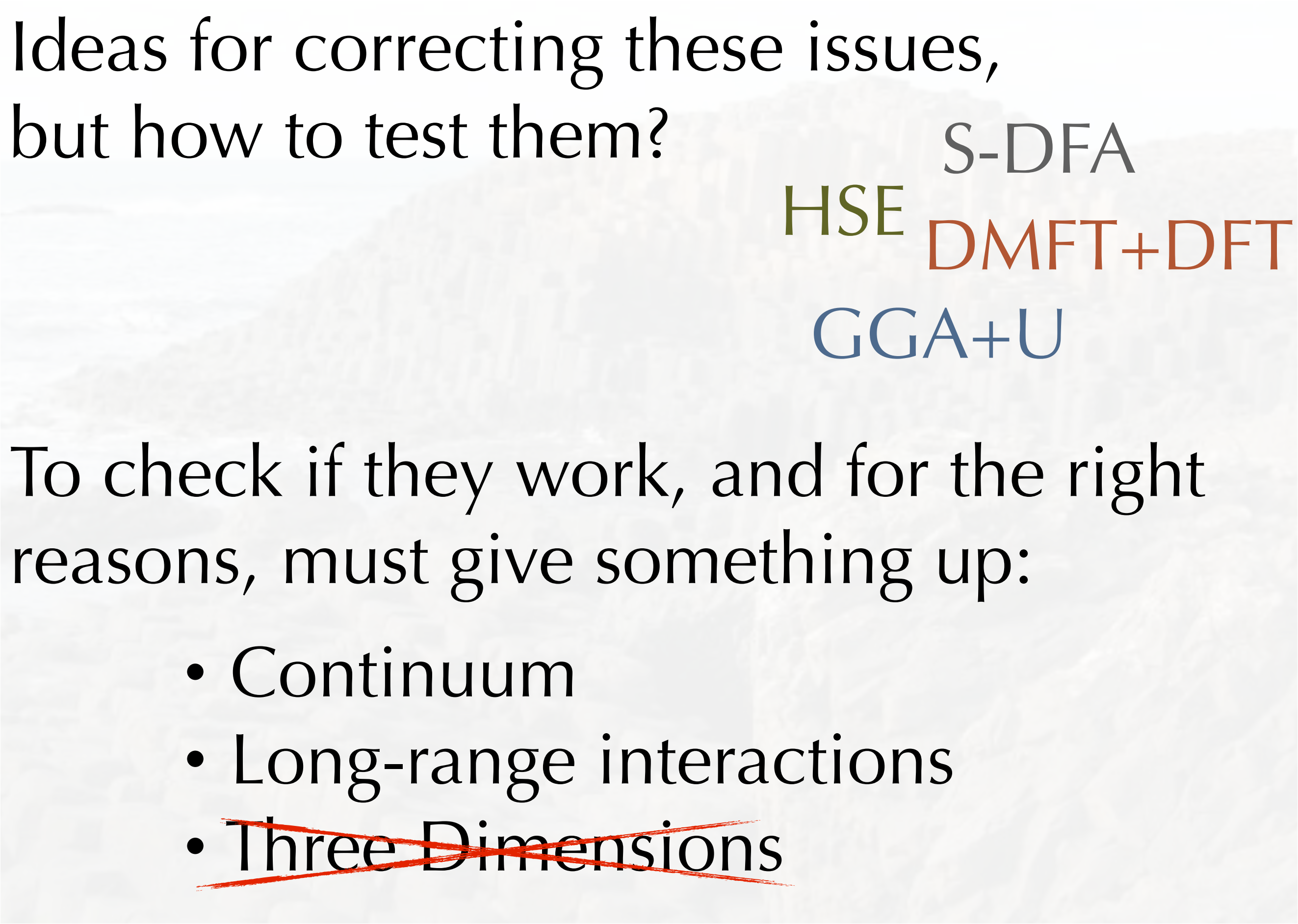


: A.J. Cohen, P. Mori-Sánchez, W. Yang, *Science* **321**, 792 (2008).

DMRG

- Extremely efficient exact solver for 1d problems
- Traditionally applied to model Hamiltonians, e.g., 2000 site Hubbard chain
- Works well when correlation is so strong that nothing starting from HF can work.

Basic ingredients



Ideas for correcting these issues, but how to test them?

S-DFA

HSE

DMFT+DFT

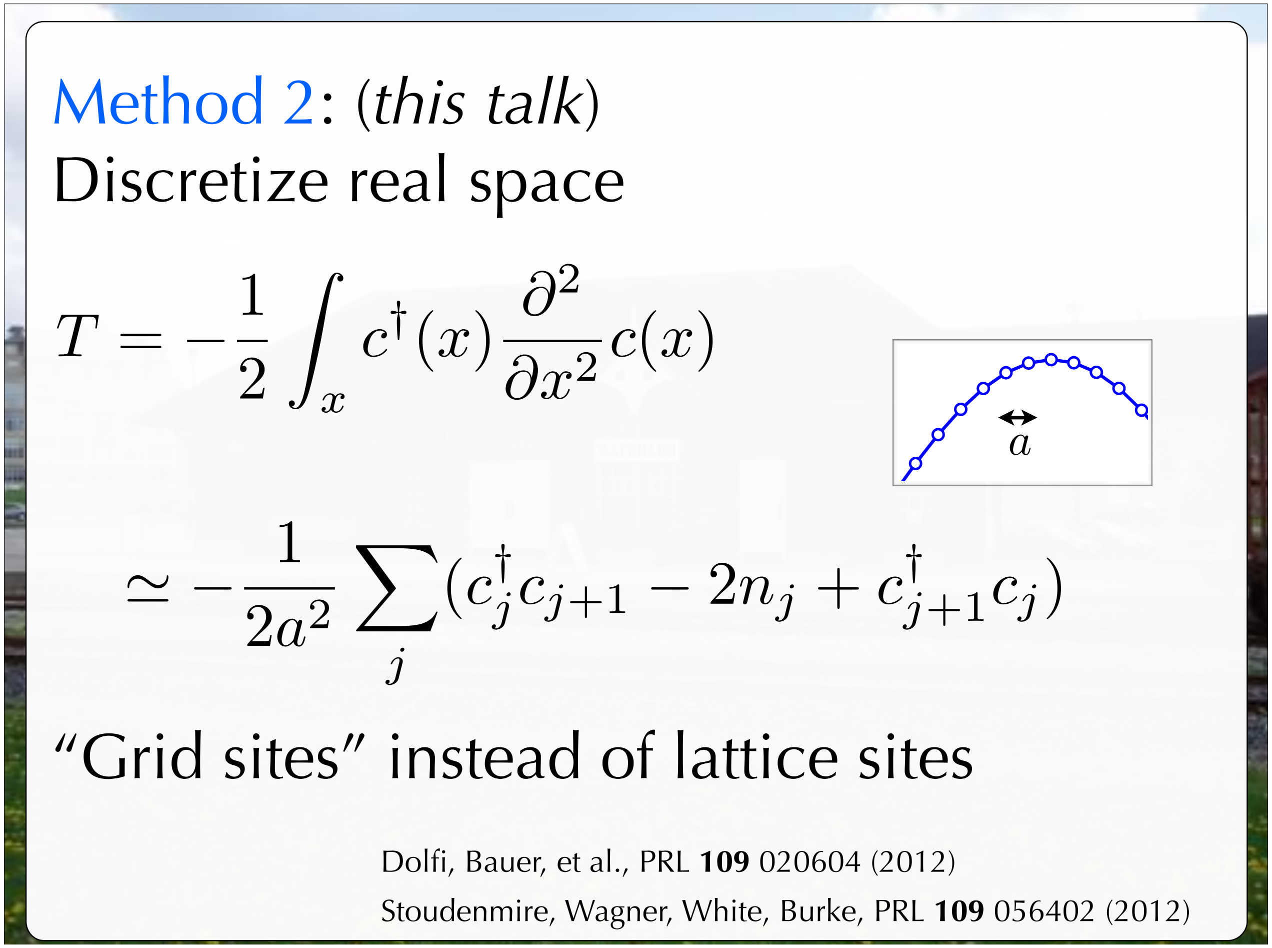
GGA+U

To check if they work, and for the right reasons, must give something up:

- Continuum
- Long-range interactions
- ~~Three Dimensions~~

Using an exact numerical solver for 1d systems (known as DMRG), we can learn more about density functional theory (DFT) and find ways to make it better

From Miles



Method 2: (*this talk*)

Discretize real space

$$T = -\frac{1}{2}\int_x c^\dagger(x)\frac{\partial^2}{\partial x^2}c(x)$$

$$\simeq -\frac{1}{2a^2}\sum_j (c_j^\dagger c_{j+1} - 2n_j + c_{j+1}^\dagger c_j)$$

“Grid sites” instead of lattice sites

Dolfi, Bauer, et al., PRL **109** 020604 (2012)

Stoudenmire, Wagner, White, Burke, PRL **109** 056402 (2012)

Three levels of activity

Three levels of application to DFT:

Level I: compare exact results to DFT approximations

● Easier

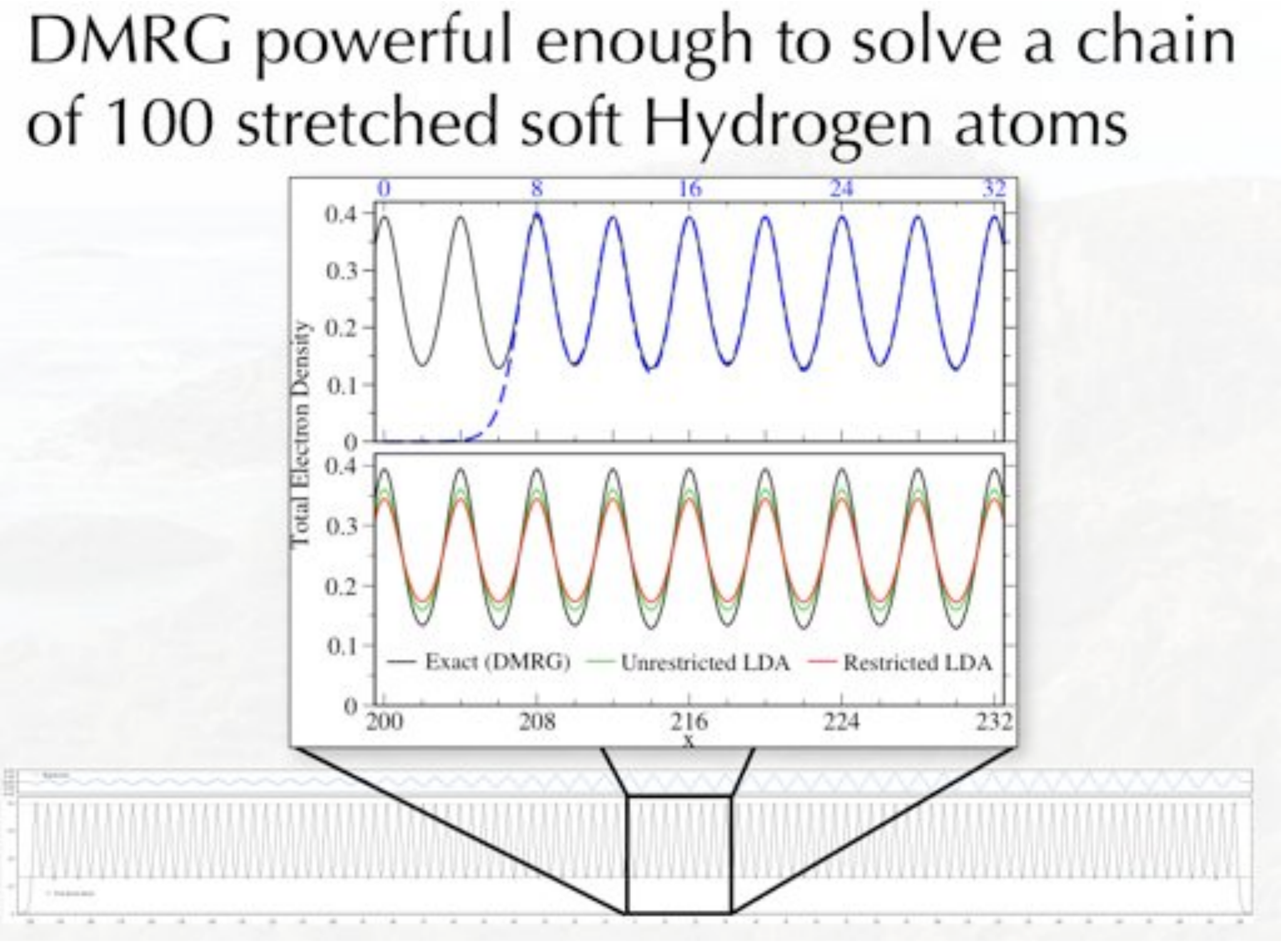
Level II: study the exact Kohn-Sham system

■ More Difficult

Level III: self-consistent KS calculation with the exact functional

◆◆ Most Difficult: Use Extra Caution

Example of long chains



DMRG powerful enough to solve a chain of 100 stretched soft Hydrogen atoms

Easier

Spontaneous dimerization

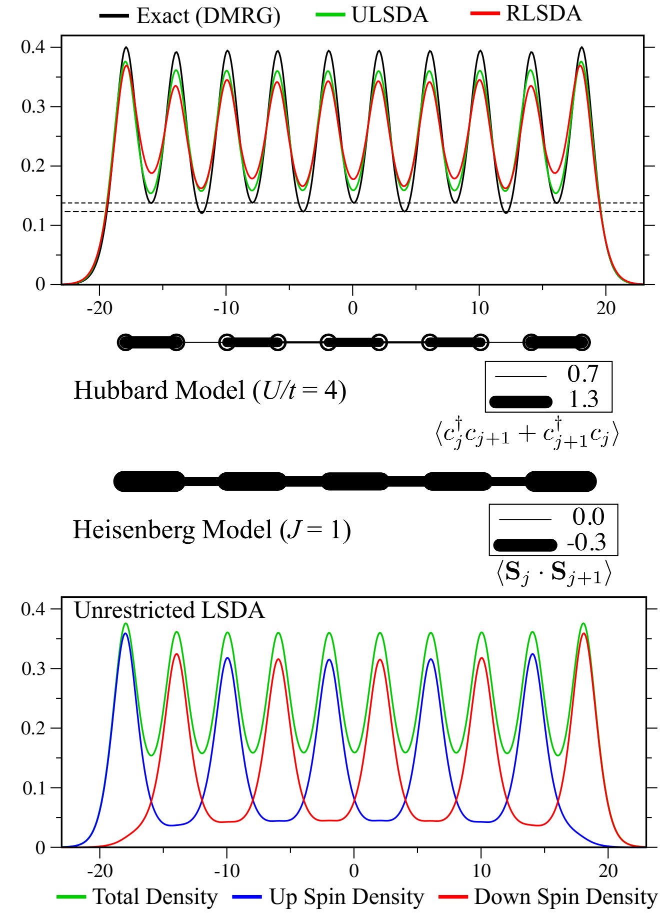


FIG. 2 (color online). Spontaneous dimerization of the density for a chain of 10 soft hydrogen atoms with interatomic spacing $b = 4$ (dashed lines are a guide to the eye). The upper panel compares the densities predicted by DFT within the LSDA; the lower panel shows the spin densities for unrestricted LSDA. Also shown is the expectation value of the kinetic energy $\langle c_j^\dagger c_{j+1} + c_{j+1}^\dagger c_j \rangle$ for a Hubbard model with $U/t = 4$ and the exchange energy $\langle \mathbf{S}_j \cdot \mathbf{S}_{j+1} \rangle$ for the Heisenberg model on 10 lattice sites. The thickness of the lines indicates the magnitude of these quantities on each bond.

Mott-Hubbard gap

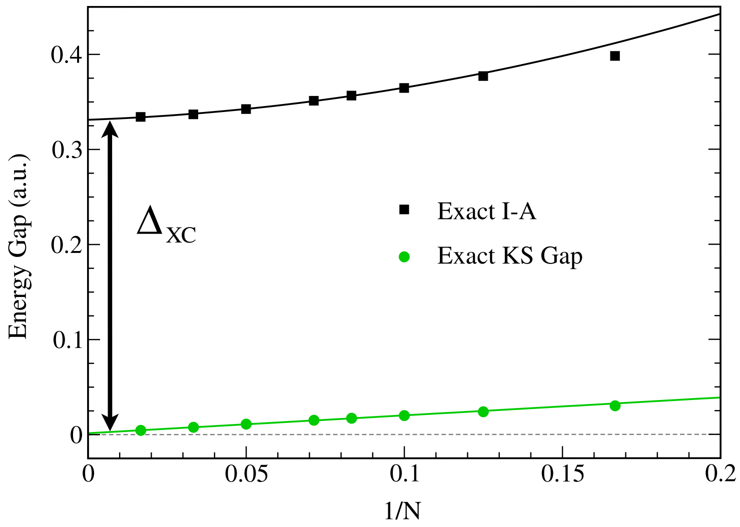
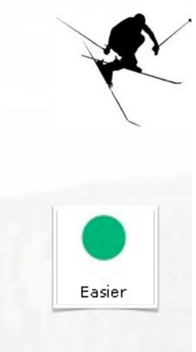
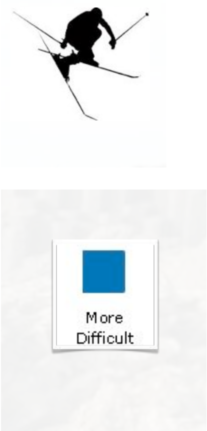


FIG. 3 (color online). Exact gaps for chains of N soft hydrogen atoms with atomic separation $b = 4$ (error bars are less than symbol sizes). The upper curve is a quadratic fit of exact gaps of the largest six systems and extrapolates to a finite value $E_g \simeq 0.33$. The exact Kohn-Sham gaps, in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

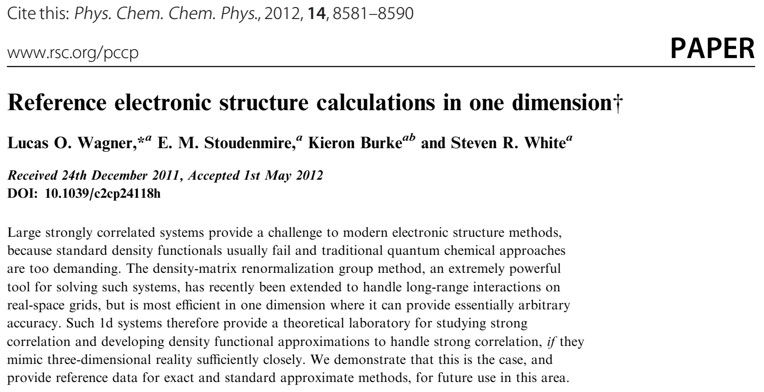
BENCHMARKS





H_2

- Extract KS potential from exact density
- A non-interacting inversion



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www.rsc.org/pccp **PAPER**

Reference electronic structure calculations in one dimension†

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Large strongly correlated systems provide a challenge to modern electronic structure methods, because standard density functionals usually fail and traditional quantum chemical approaches are too demanding. The density-matrix renormalization group method, an extremely powerful tool for solving such systems, has recently been extended to handle long-range interactions on real-space grids, but is most efficient in one dimension where it can provide essentially arbitrary accuracy. Such 1d systems therefore provide a theoretical laboratory for studying strong correlation and developing density functional approximations to handle strong correlation, *if* they mimic three-dimensional reality sufficiently closely. We demonstrate that this is the case, and provide reference data for exact and standard approximate methods, for future use in this area.

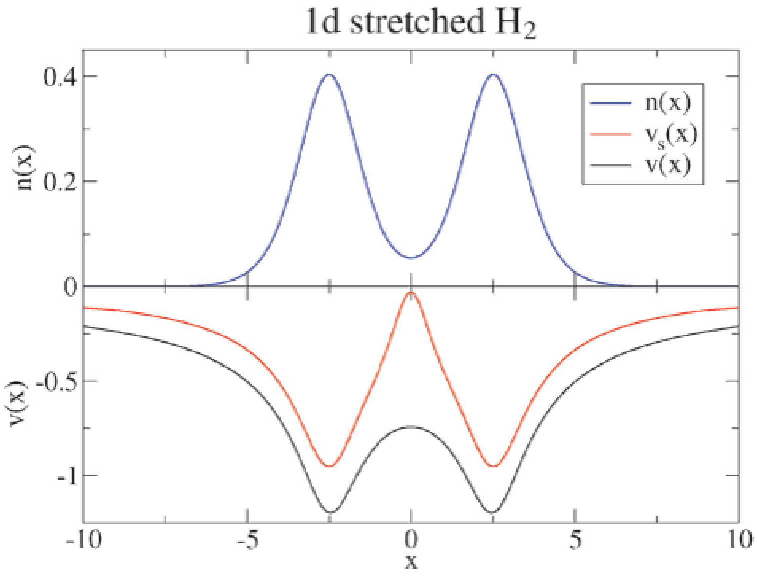


Fig. 1 The KS potential for a stretched hydrogen molecule found from interacting electrons in 1d.

LDA for soft Coulomb

- Get uniform gas inputs from QMC for 1d soft-Coulomb gas, by Nicole Helbig et al

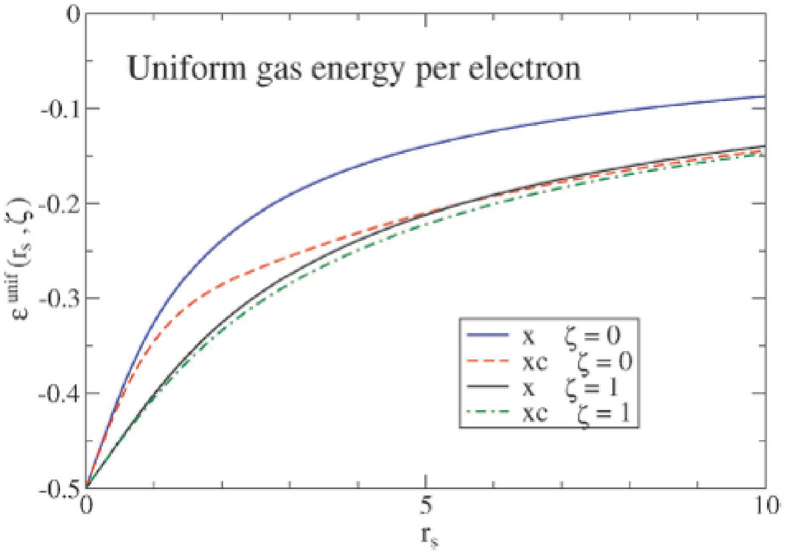


Fig. 2 Parametrization of the LDA exchange and exchange–correlation energy densities per electron for polarized $\zeta = 1$ and unpolarized $\zeta = 0$ densities.[18]

Comparing 1d and 3d

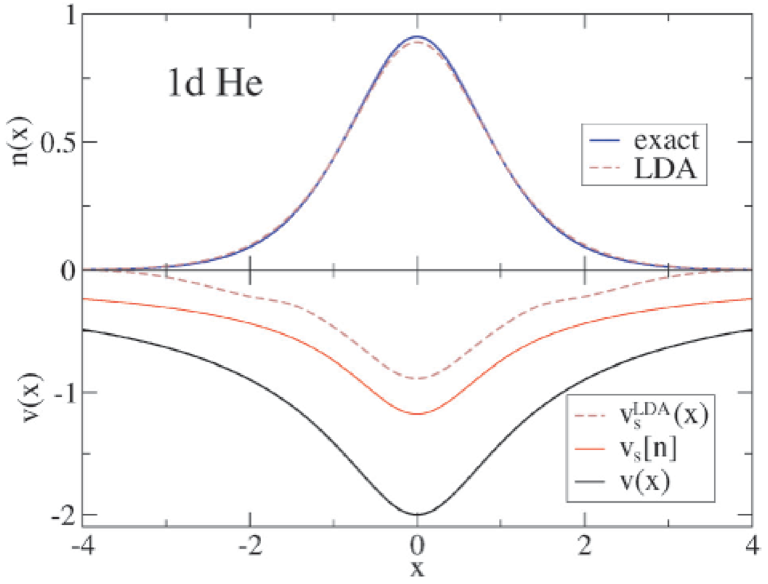


Fig. 4 The exact KS potential for a model helium density found from interacting electrons in 1d, as well as the LDA density and LDA KS potential found self-consistently.

Table 3 Exact and HF two-electron atoms and ions, in 1- and 3-d (exact data from ref. 20, Li^+ is fit quadratically to surrounding elements, and HF data from ref. 36 and 37)

System	T	V	V_{ee}	E	E^{HF}	E_C^{QC}
H^-	0.115	−1.326	0.481	−0.731	−0.692	−0.039
He	0.290	−3.219	0.691	−2.238	−2.224	−0.014
Li^+	0.433	−5.084	0.755	−3.896	−3.888	−0.008
Be^{++}	0.556	−6.961	0.790	−5.615	−5.609	−0.006
3d H^-	0.528	−1.367	0.311	−0.528	−0.488	−0.042
3d He	2.904	−6.753	0.946	−2.904	−2.862	−0.042
3d Li^+	7.280	−16.13	1.573	−7.280	−7.236	−0.043
3d Be^{++}	13.66	−29.50	2.191	−13.66	−13.61	−0.044

Classic DFT errors

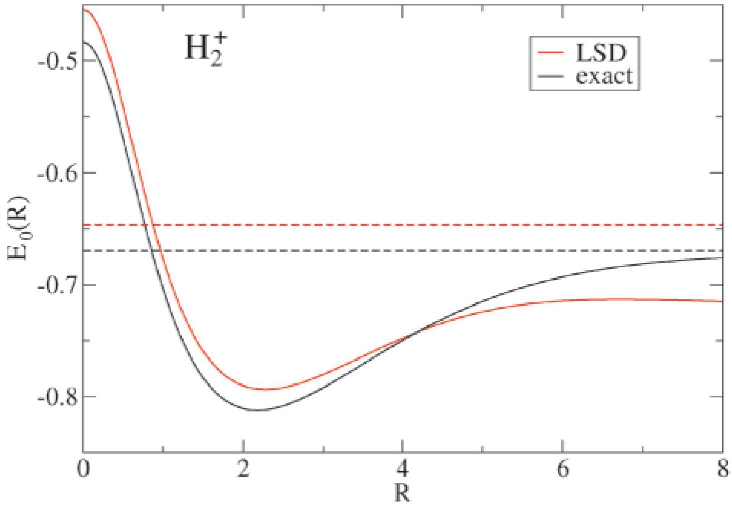


Fig. 8 The binding energy curve for our 1d model $H_2{}^+$, shown with an absolute energy scale, and with nuclear separation *R*; horizontal dashed lines indicate the energy of a single H atom.

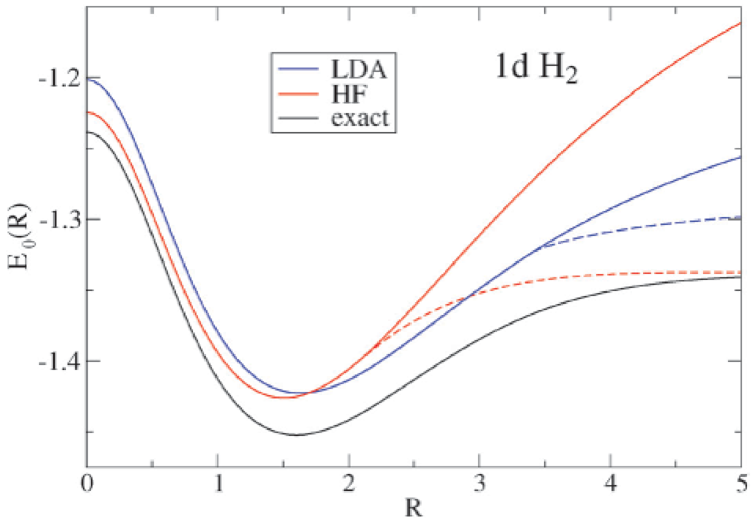


Fig. 9 The binding energy curve for our 1d model H_2, shown on an absolute energy scale, with nuclear separation *R*. Dashed curves represent unrestricted calculations.

CONVERGENCE

Interacting inversion

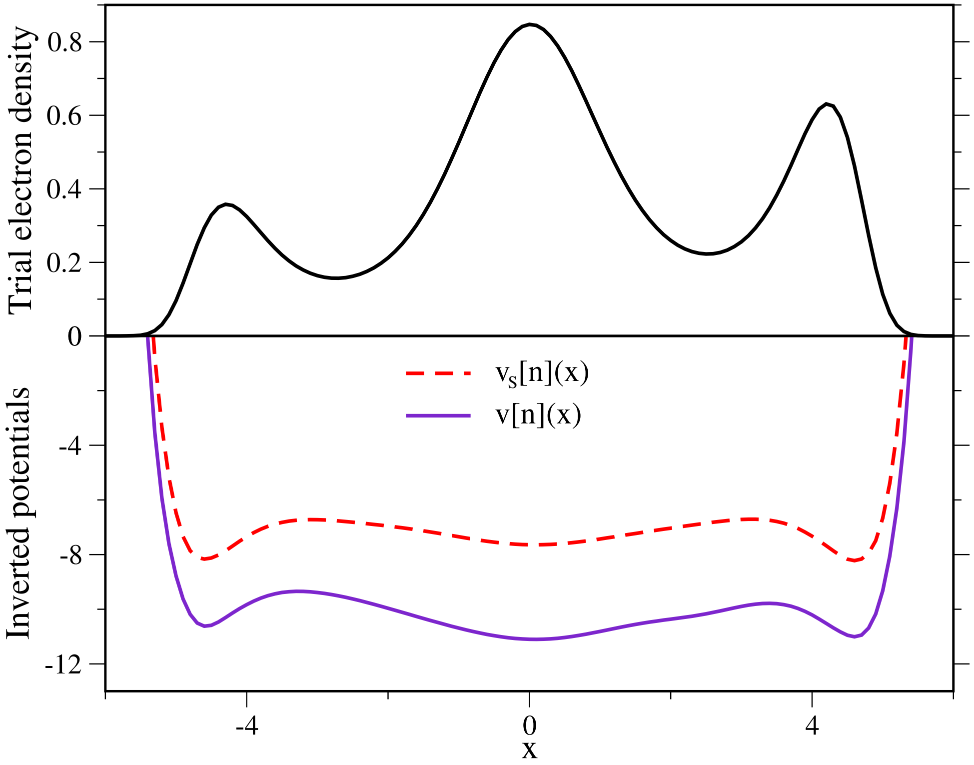
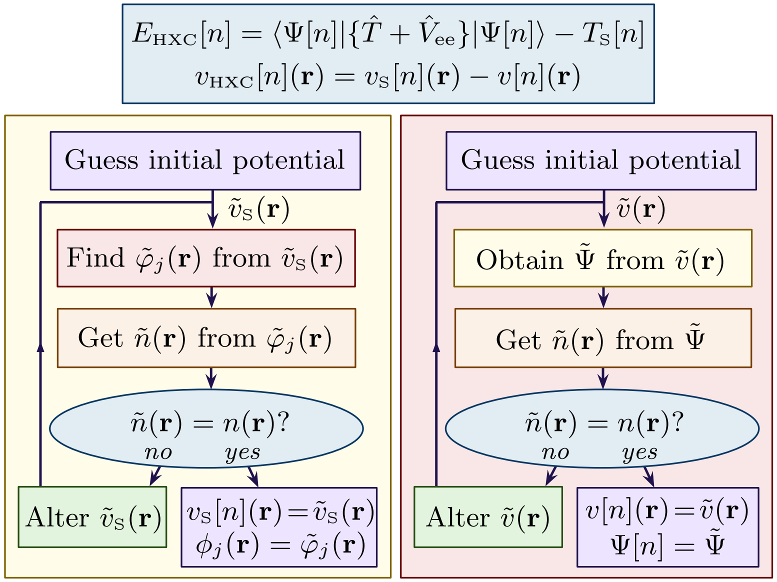


FIG. 2. Arbitrary density inversion for non-interacting and interacting potentials.

KS with exact XC



$$E_{\mathrm{HXC}}[n] = \langle \Psi[n] | \{\hat{T} + \hat{V}_{\mathrm{ee}}\} | \Psi[n] \rangle - T_{\mathrm{S}}[n]$$

$$v_{\mathrm{HXC}}[n](\mathbf{r}) = v_{\mathrm{S}}[n](\mathbf{r}) - v[n](\mathbf{r})$$

Guess initial potential

$\tilde{v}_{\mathrm{S}}(\mathbf{r})$

Find $\tilde{\varphi}_j(\mathbf{r})$ from $\tilde{v}_{\mathrm{S}}(\mathbf{r})$

Get $\tilde{n}(\mathbf{r})$ from $\tilde{\varphi}_j(\mathbf{r})$

$\tilde{n}(\mathbf{r}) = n(\mathbf{r})$?

no *yes*

Alter $\tilde{v}_{\mathrm{S}}(\mathbf{r})$

$v_{\mathrm{S}}[n](\mathbf{r}) = \tilde{v}_{\mathrm{S}}(\mathbf{r})$
$\phi_j(\mathbf{r}) = \tilde{\varphi}_j(\mathbf{r})$

Guess initial potential

$\tilde{v}(\mathbf{r})$

Obtain $\tilde{\Psi}$ from $\tilde{v}(\mathbf{r})$

Get $\tilde{n}(\mathbf{r})$ from $\tilde{\Psi}$

$\tilde{n}(\mathbf{r}) = n(\mathbf{r})$?

no *yes*

Alter $\tilde{v}(\mathbf{r})$

$v[n](\mathbf{r}) = \tilde{v}(\mathbf{r})$
$\Psi[n] = \tilde{\Psi}$

FIG. 3. To determine the $E_{\mathrm{HXC}}[n]$ and $v_{\mathrm{HXC}}[n](\mathbf{r})$: Our exact calculation requires a computationally demanding inversion algorithm to find the one-body potential $v[n](\mathbf{r})$ of the interacting system whose density is $n(\mathbf{r})$, in addition to a non-interacting inversion to find $v_{\mathrm{S}}[n](\mathbf{r})$. In case of degeneracy, mixed-states should be used instead of pure-state wavefunctions in both non-interacting and interacting inversions [5, 51].

Definitions

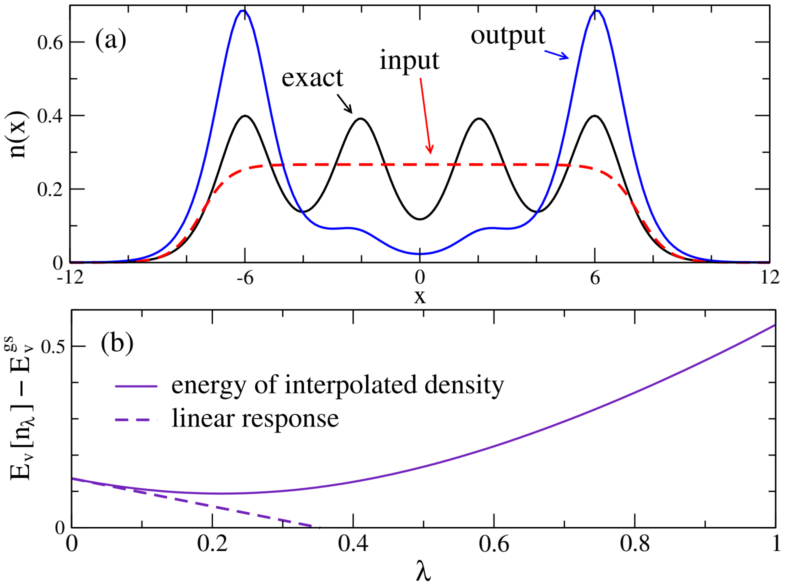
- n(**r**) is some given density
- n'(**r**) is output from one KS step
- λ is a mixing parameter
- η is a measure of closeness of 2 densities
- ΔE is energy above true ground-state

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

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

One KS step

FIG. 1 (color online). (a) The input and output densities for a single step of the Kohn-Sham scheme, as well as the exact density, of a one-dimensional, strongly correlated four atom, four electron system. (b) The energy of the system which interpolates between the input and output densities $E_v[n_\lambda]$, measured from the ground-state energy E_v^{gs}. Also shown is the linear-response approximation with slope given by Eq. (12).



Convergence of chain

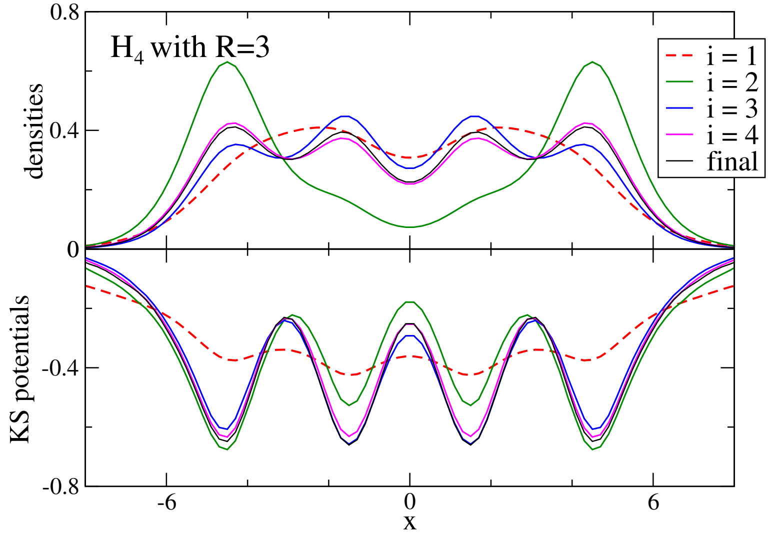


FIG. 2 (color online). KS procedure for a moderately correlated four-electron system (four hydrogen atoms with $R = 3$), showing the first few iterations. Using a fixed $\lambda = 0.30$, we converge to $\eta < 10^{-6}$ using Eq. (4) within 13 iterations.

Rate of convergence

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

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

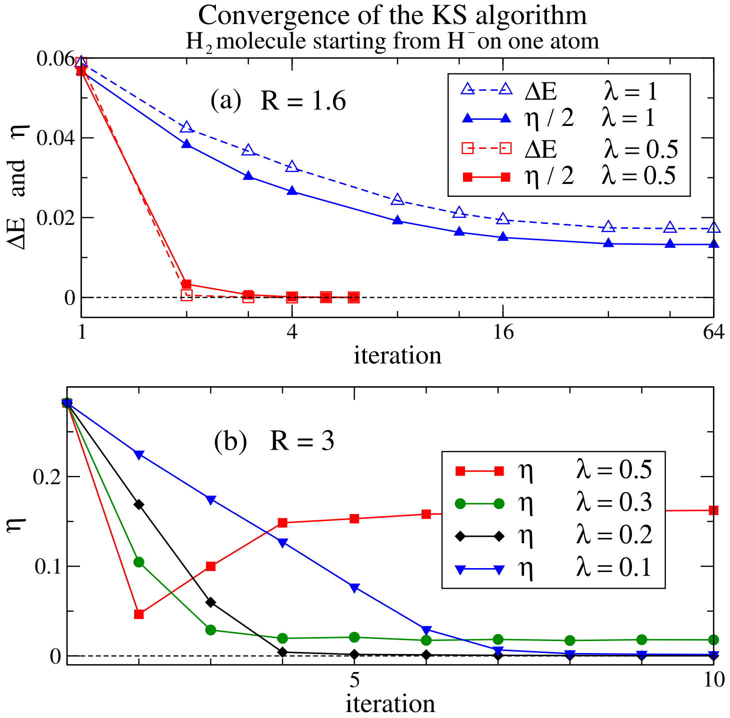
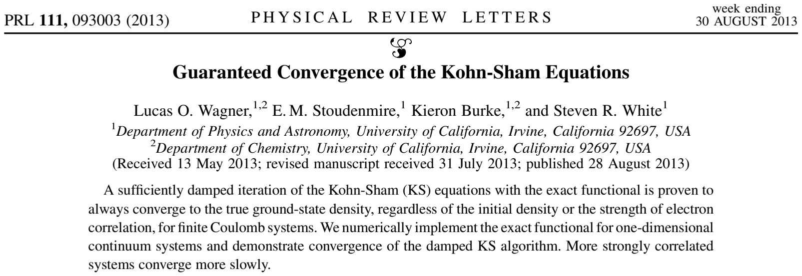


FIG. 3 (color online). Differences in the density η using Eq. (4) and the energy with $\Delta E = E_v[n'] - E_v^{\mathrm{gs}}$, for an H_2 molecule with (a) $R = 1.6$ and (b) $R = 3$. In (b), the ΔE curves are omitted for clarity, but are like those in (a).

Spin polarization



PRL **111,** 093003 (2013) PHYSICAL REVIEW LETTERS week ending 30 AUGUST 2013

Guaranteed Convergence of the Kohn-Sham Equations

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A sufficiently damped iteration of the Kohn-Sham (KS) equations with the exact functional is proven to always converge to the true ground-state density, regardless of the initial density or the strength of electron correlation, for finite Coulomb systems. We numerically implement the exact functional for one-dimensional continuum systems and demonstrate convergence of the damped KS algorithm. More strongly correlated systems converge more slowly.

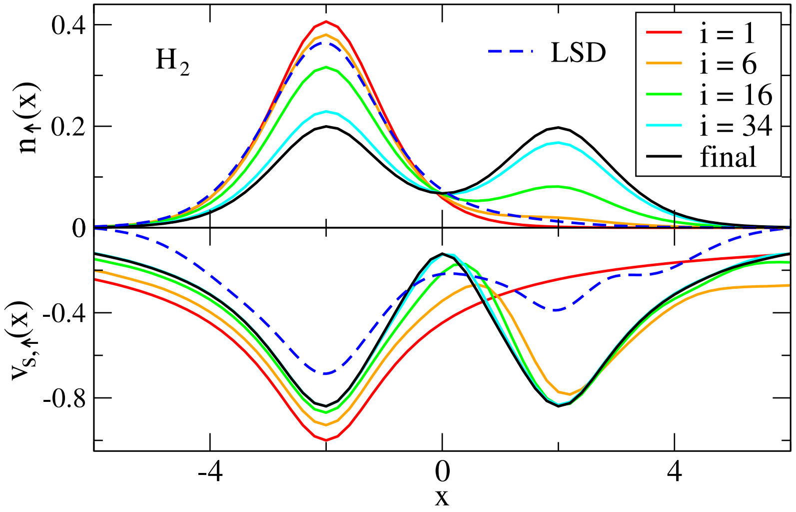


FIG. 4 (color online). Starting an exact KS calculation of stretched H_2 with a spin-polarized density still converges (with $\lambda = 0.5$) to the correct spin-singlet density. For the same initial density, the KS calculation with the local spin-density (LSD) approximation [47] converges to the broken spin-symmetry solution shown.

LONG PAPER (in prep)

KS steps when weakly correlated

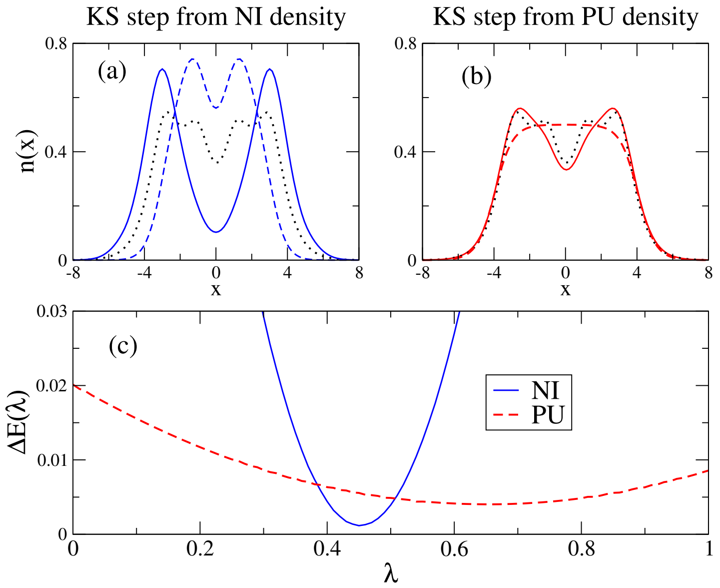


FIG. 6. A single step in the KS scheme for a weakly correlated system (H_4 with $R = 2$) away from two different initial densities: non-interacting electrons in the external potential (NI) and a pseudouniform electron density (PU). These initial densities are the dashed curves in (a) and (b), and the solid curves are the output densities for each KS step; for comparison the dotted curve is the exact density. The lower panel plots Eq. (22), the energy of the system as it interpolates from the input to the output density.

Single step for strong correlation

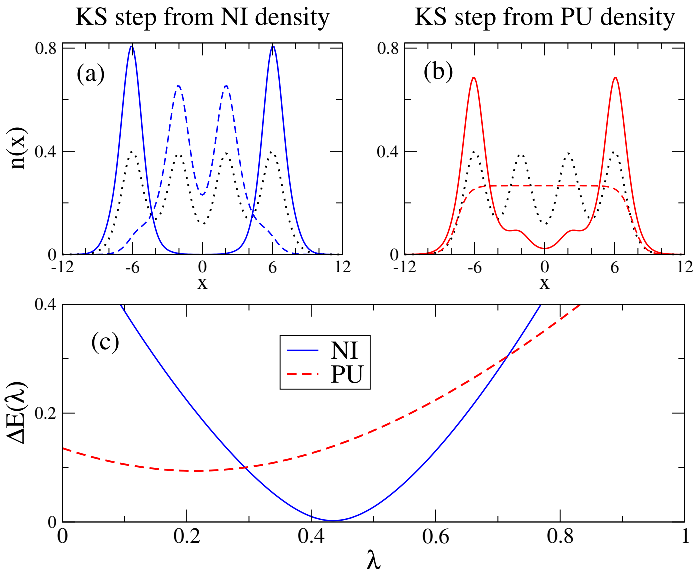


FIG. 7. A single step in the KS scheme for a strongly correlated system (H_4 with $R = 4$) away from two different initial densities: non-interacting electrons in the external potential (NI) and a pseudouniform electron density (PU). These initial densities are the dashed curves in (a) and (b), and the solid curves are the output densities for each KS step; for comparison the dotted curve is the exact density. The lower panel plots Eq. (22), the energy of the system as it interpolates from the input to the output density.

KS step when close to gs

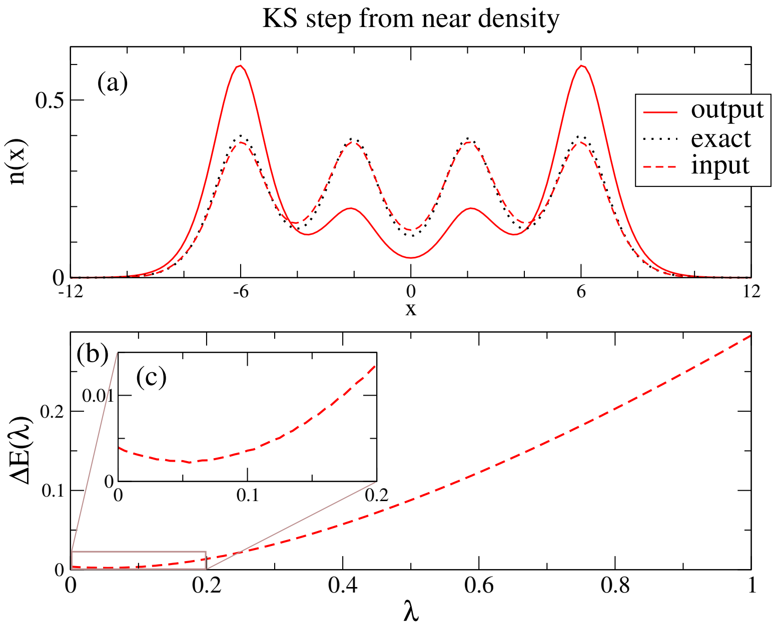


FIG. 8. Taking a second step in the KS scheme for a strongly correlated system (H_4 with $R = 4$). Panel (a) shows the input density which is near to the exact density (the $\lambda = 42\%$ density of the NI input density of Fig. 7) and the resulting output density, which is far from the ground-state. The lower panel (b) plots Eq. (22), and the inset (c) magnifies the small λ region.

No of iterations vs R

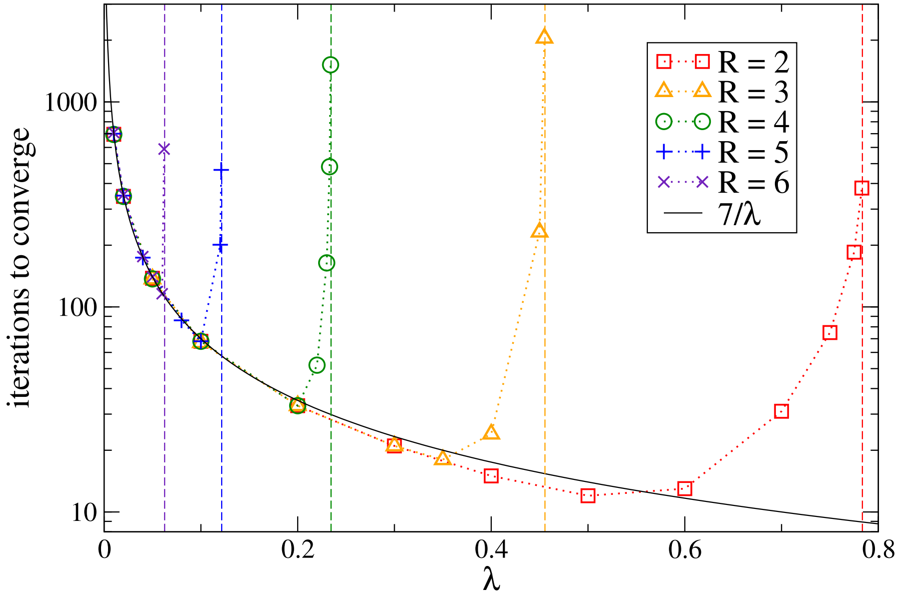


FIG. 10. The number of iterations required to converge an LDA calculation to $\eta < 10^{-8}$ (12), as a function of λ, for various bond-lengths R of the H_2 molecule, starting with an initial density of H^- on the left atom. The asymptotic form for small λ can be well-approximated by $7/\lambda$ for the data shown.

Convergence vs bond length

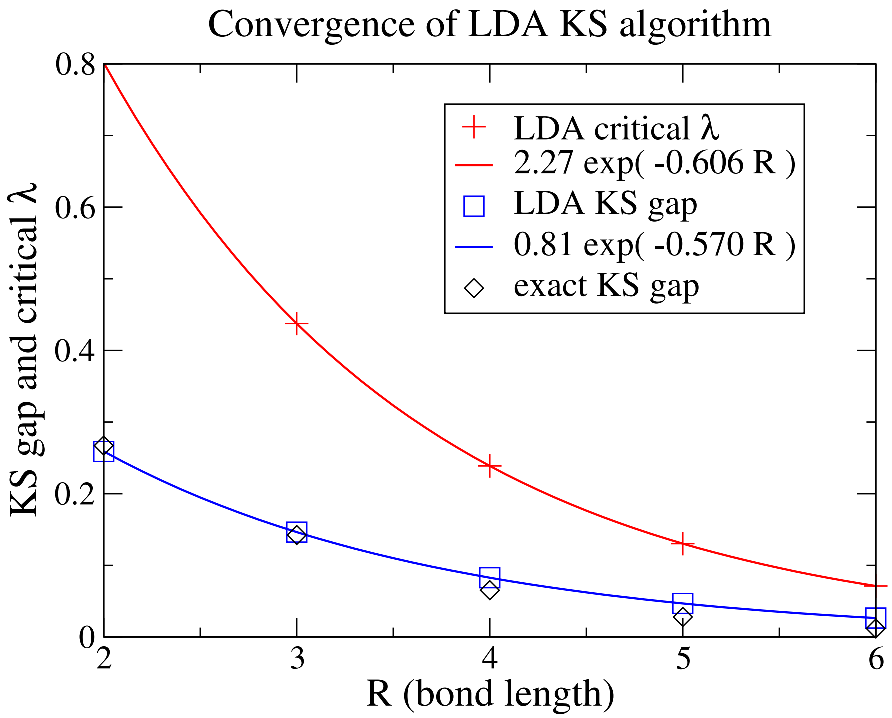
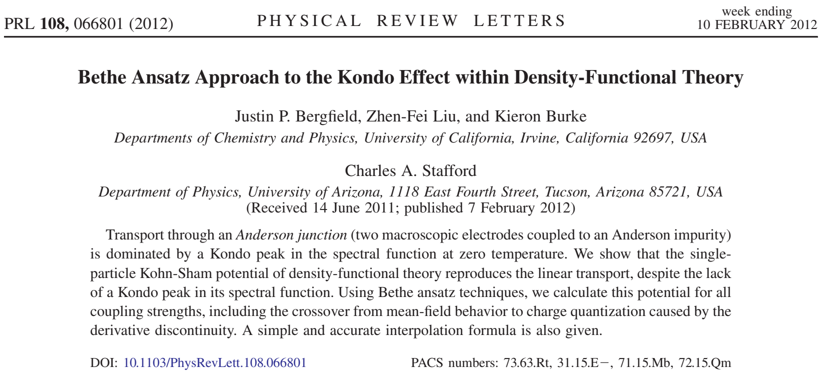


FIG. 11. Plotting the convergence-critical λ for an LDA calculation, as a function of the bond length R of a stretched hydrogen molecule, starting with the exact H^- density on one atom, as well as KS gaps for both the LDA and exact systems.

Transport through single molecules

- Are DFT calculations generally accurate for current?
- For weak bias and zero temperature, surprising answer is yes, but only with accurate XC
- Present XC approxs miss important steps in potential



PRL **108,** 066801 (2012) PHYSICAL REVIEW LETTERS week ending 10 FEBRUARY 2012

Bethe Ansatz Approach to the Kondo Effect within Density-Functional Theory

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(Received 14 June 2011; published 7 February 2012)

Transport through an *Anderson junction* (two macroscopic electrodes coupled to an Anderson impurity) is dominated by a Kondo peak in the spectral function at zero temperature. We show that the single-particle Kohn-Sham potential of density-functional theory reproduces the linear transport, despite the lack of a Kondo peak in its spectral function. Using Bethe ansatz techniques, we calculate this potential for all coupling strengths, including the crossover from mean-field behavior to charge quantization caused by the derivative discontinuity. A simple and accurate interpolation formula is also given.

DOI: 10.1103/PhysRevLett.108.066801 PACS numbers: 73.63.Rt, 31.15.E−, 71.15.Mb, 72.15.Qm

$$\varepsilon_{\mathrm{XC}} \simeq \frac{U}{2}\left[1-\langle n_{\mathrm{C}}\rangle-\frac{2}{\pi}\tan^{-1}\left[\frac{\pi^2 U(1-\langle n_{\mathrm{C}}\rangle)}{8\Gamma}\right]\right],$$

Summary: semiclassics

- DFT is extremely popular because if it so powerful.
- Too much ambiguity in choice of approximation
- Semiclassical analysis holds hope of systematic approach with powerful new approximations.
- DFT works because LDA is semiclassical
- Thanks to NSF.

Summary: strong correlation

- Have a new tool for studying KS DFT in 1d, especially good for strong correlation.
- Relies on efficiency of DMRG in 1d.
- Have shown KS equations can always be made to converge
- Convergence slows with strength of correlation
- Thanks to US DOE for funding.