Failures of density functional theory for strongly correlated systems using density-matrix renormalization group

Kieron Burke, Lucas Wagner, Miles Stoudenmire
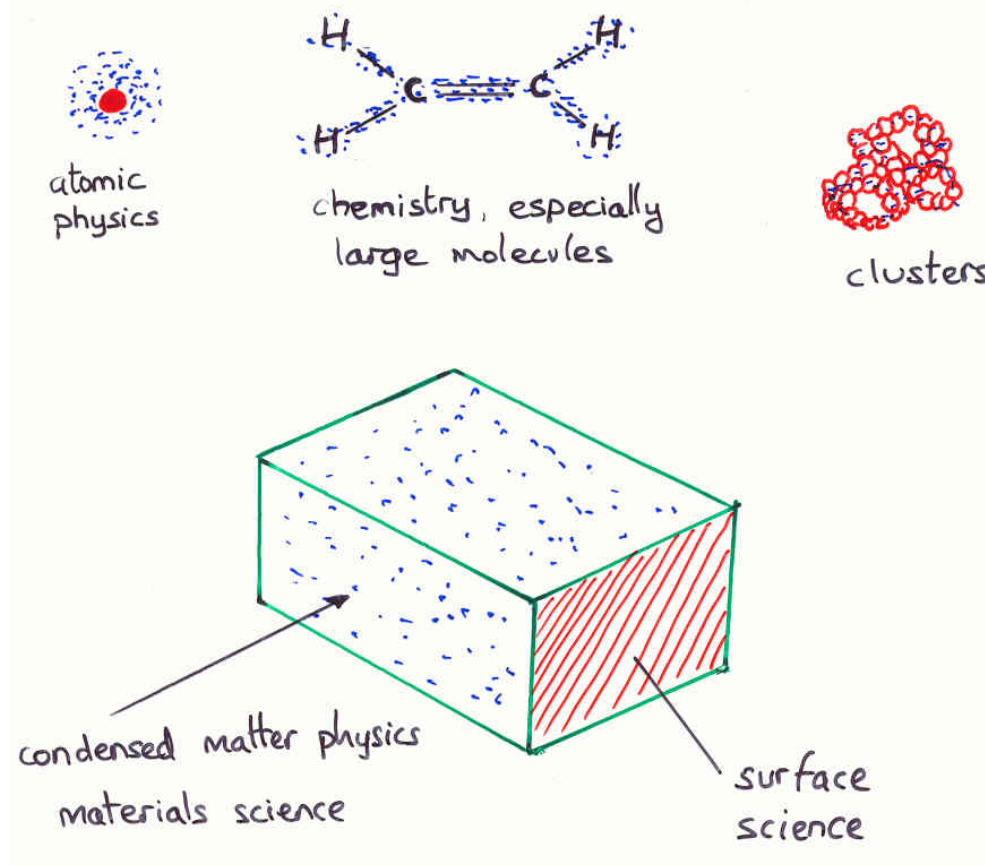
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http://dft.uci.edu

INTRODUCTION

Electronic structure problem

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

atomic physics

chemistry, especially large molecules

clusters

condensed matter physics
materials science

surface science

Kohn-Sham equations (1965)

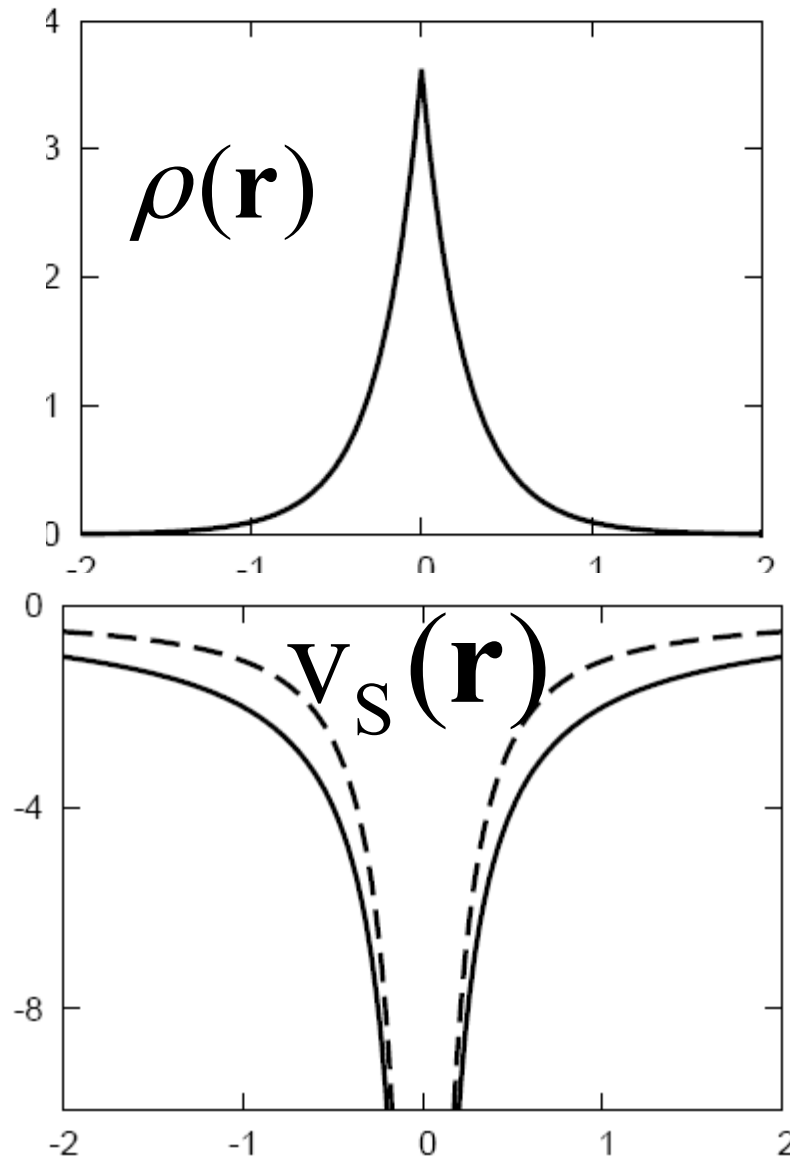$$\left[-\frac{1}{2}\nabla^2 + v_s[\rho](\mathbf{r}) \right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

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

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

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

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

# He atom in Kohn-Sham DFT

$\rho(\mathbf{r})$

$v_S(\mathbf{r})$

Everything
has (at
most) one
KS potential

Dashed-line:

EXACT KS potential

Commonly-used functionals`

- Local density approximation (LDA)
  - Uses only $\rho(\mathbf{r})$ at a point.

$$E_{\mathrm{X}}^{\mathrm{LDA}}[n] = A_{\mathrm{X}} \int d^3r \ n^{4/3}(\mathbf{r})$$

$$A_{\mathrm{X}} = -(3/4)(3/\pi)^{1/3} = -0.738$$

- 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

Errors in standard DFT approximations

H_2 binding curve

HF
B3LYP
LDA

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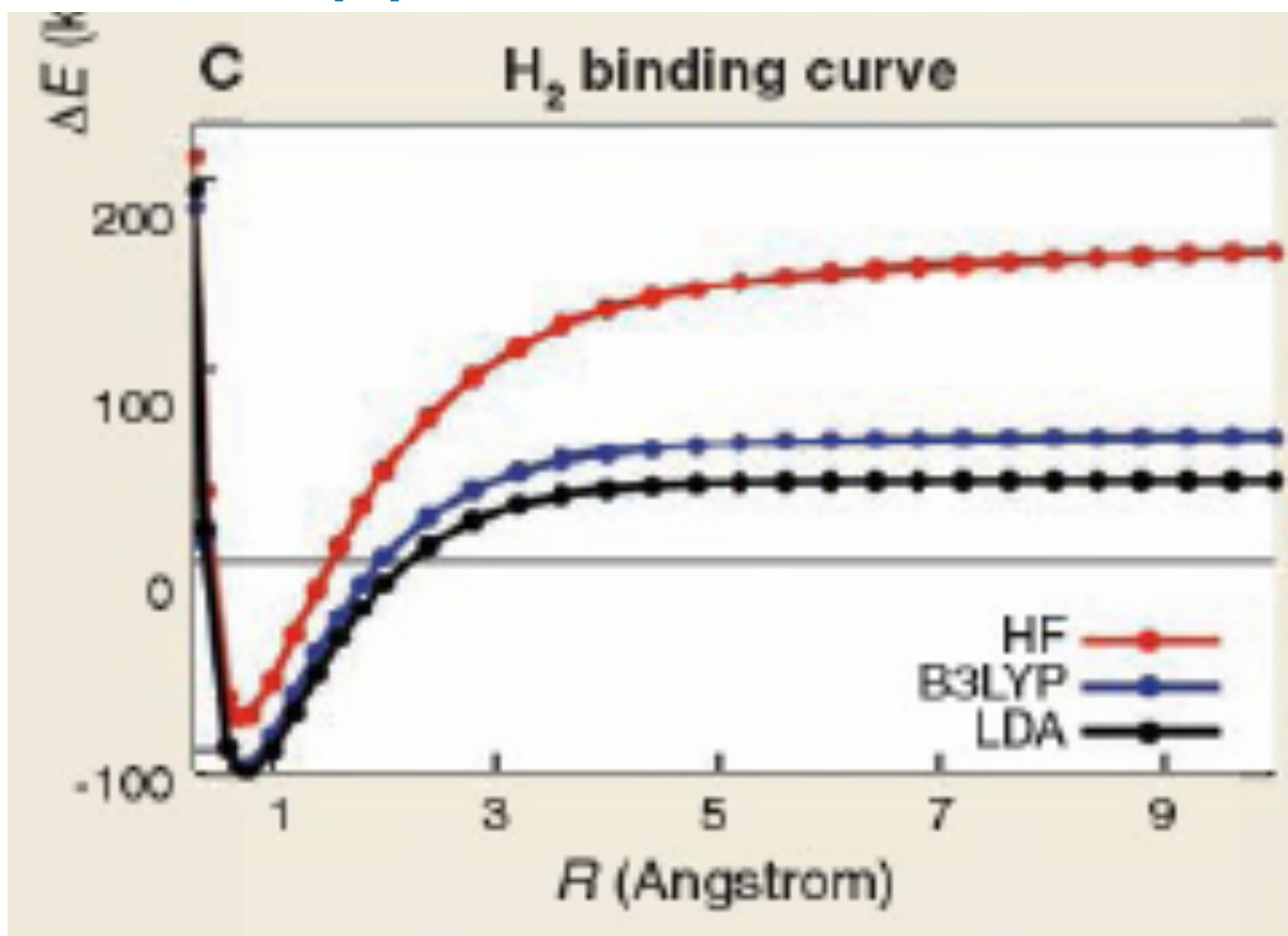
n: A.J. Cohen, P. Mori-Sánchez, W. Yang, *Science* **321**, 792 (2008).

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.

Problems with DFT

Density functional theory (DFT) is an efficient method that works extremely well for molecules and materials....

...except when it doesn't

Basic ingredients

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

S-DFA

HSE DMFT+DFT

GGA+U

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

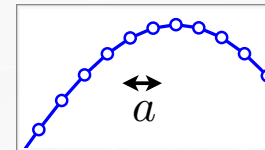To check if they work, and for the right reasons, must give something up:

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

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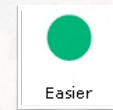
Dolfi, Bauer, et al., PRL **109** 020604 (2012)

Stoudenmire, Wagner, White, Burke, PRL **109** 056402 (2012)
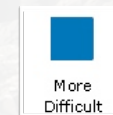
Three levels of activity

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

SET UP

How to do this

One-Dimensional Continuum Electronic Structure with the Density-Matrix Renormalization Group and Its Implications for Density-Functional Theory

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(Received 12 July 2011; revised manuscript received 5 January 2012; published 1 August 2012)

We extend the density matrix renormalization group to compute exact ground states of continuum many-electron systems in one dimension with long-range interactions. We find the exact ground state of a chain of 100 strongly correlated artificial hydrogen atoms. The method can be used to simulate 1D cold atom systems and to study density-functional theory in an exact setting. To illustrate, we find an interacting, extended system which is an insulator but whose Kohn-Sham system is metallic.

Example of long chains

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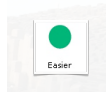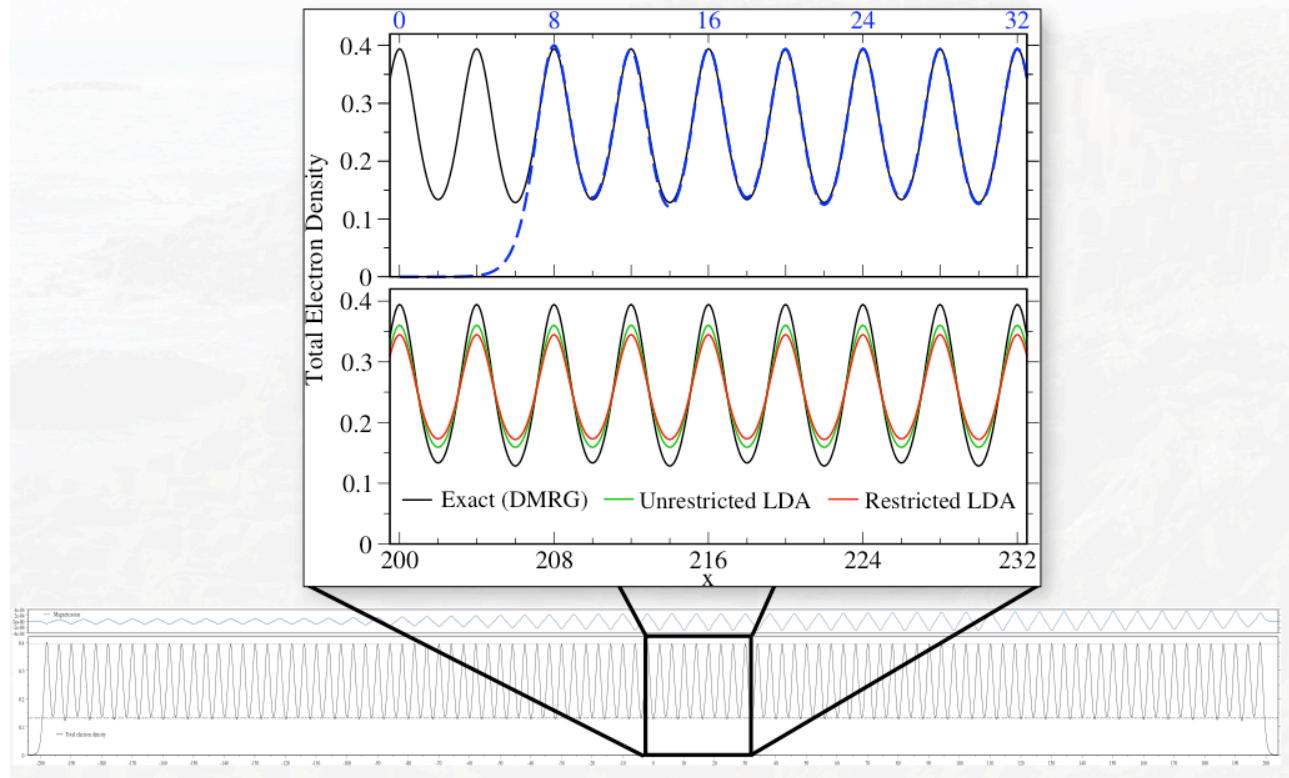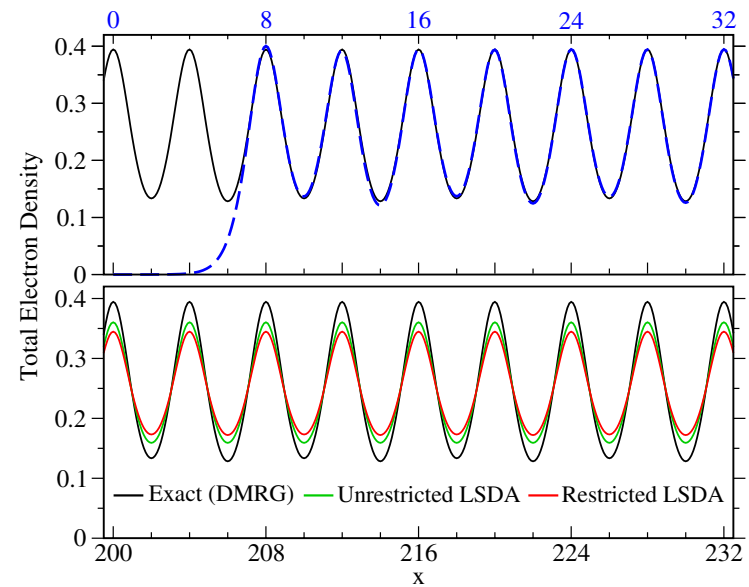
Densities of long chains

FIG. 1 (color online). The exact ground state density of a chain of 100 widely separated (strongly correlated) artificial atoms. The total length of the system is $L = 420$ in atomic units (4200 grid sites with a spacing of 0.1). The upper panel shows the electron density of a central region superimposed with the density at the left edge (the dashed blue curve with corresponding x above). The lower panel compares the exact electron density to DFT predictions within the local spin density approximation.

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.
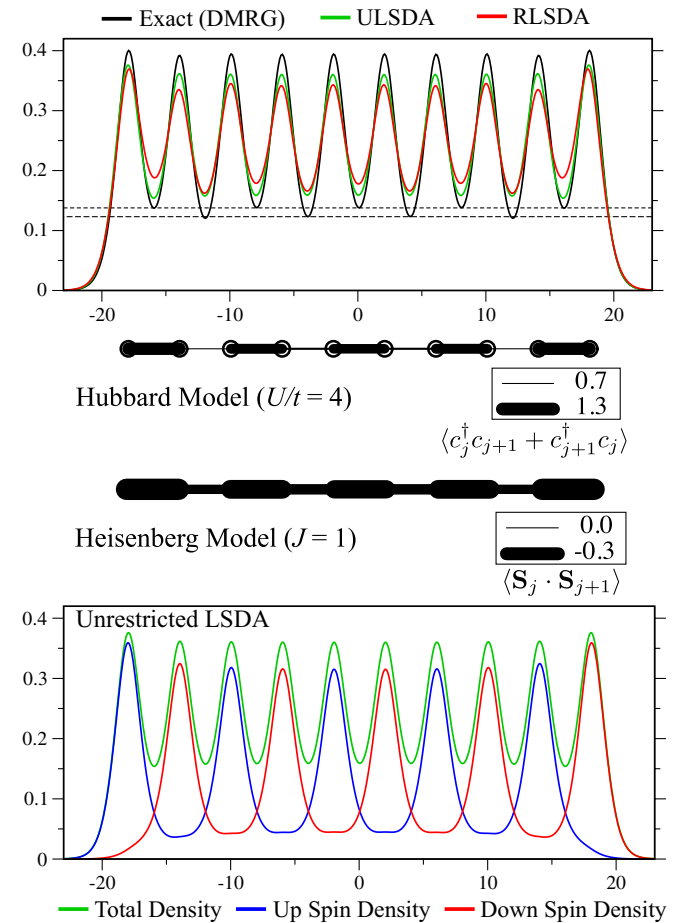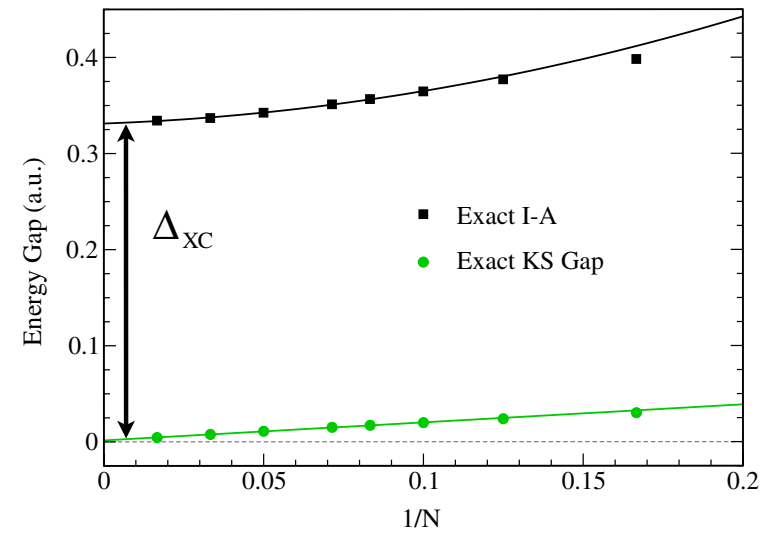
Mott-Hubbard gap

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 $N \to \infty$ the true KS system is metallic (lower curve is a linear fit of exat KS gaps of the largest six systems).
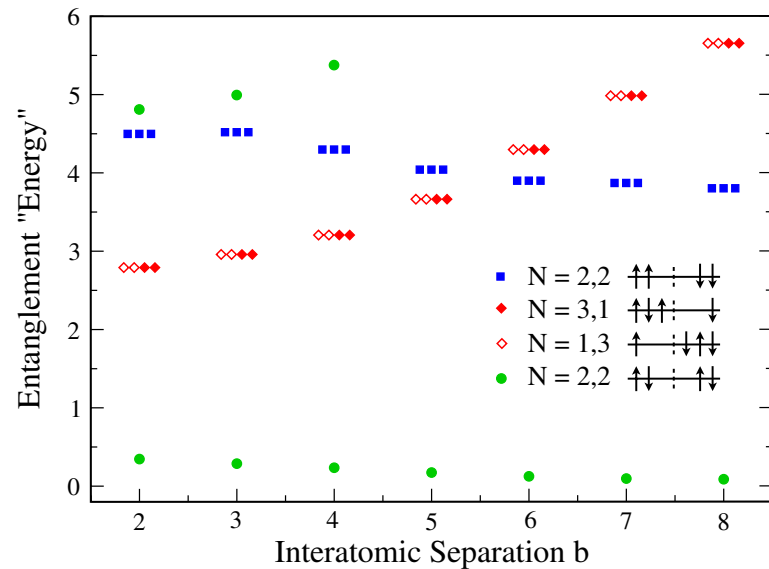
Entanglement spectrum

FIG. 4 (color online). Entanglement spectrum at the center of interacting 4-atom chains with various interatomic separations b. $N = (N_L, N_R)$ refers to the number of electrons to the left and right of the cut for each density matrix eigenstate. The states with $N_L = 3, 1$ primarily correspond to charge fluctuations while those with $N_L = 2$ to spin fluctuations.

BENCHMARKS

Easier

More
Difficult
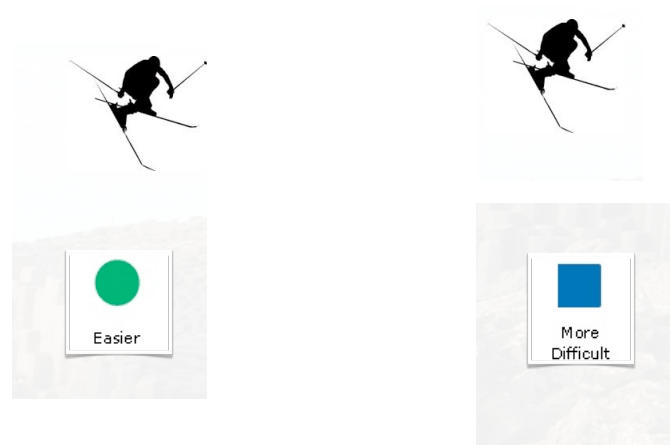
Benchmark DFT calculations

PAPER

Reference electronic structure calculations in one dimension†

Lucas O. Wagner,[*a] **E. M. Stoudenmire,**[a] **Kieron Burke**[ab] **and Steven R. White**[a]

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.

H$_2$

- Extract KS potential from exact density

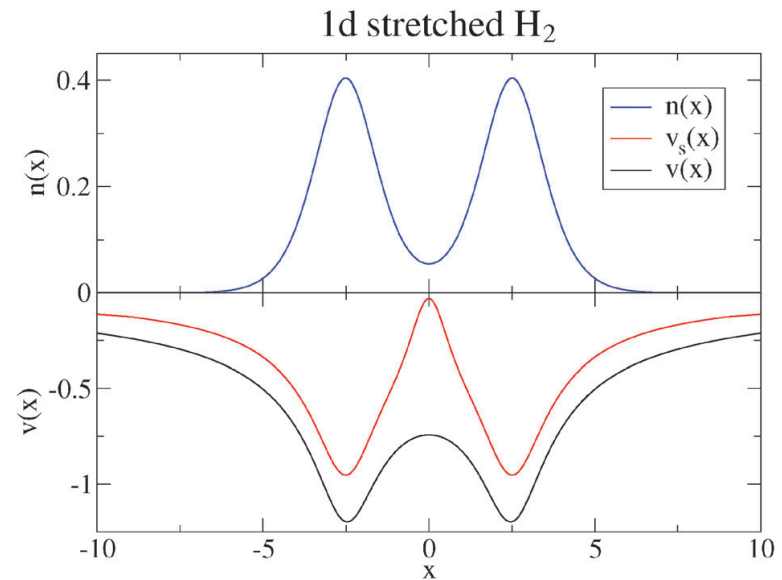- A non-interacting inversion

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

LDA for soft Coulomb

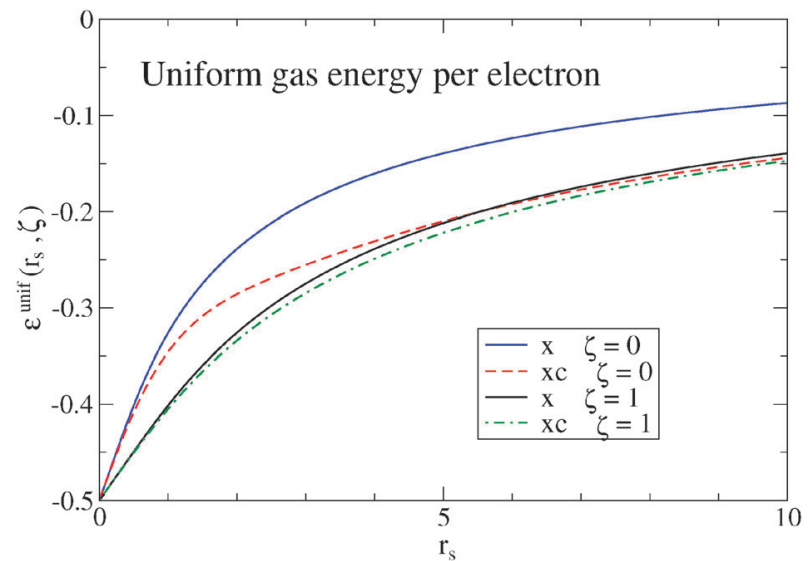- Get uniform gas inputs from QMC for 1d soft-Coulomb gas, by Nicole Helbig et al

Fig. 2 Parametrization of the LDA exchange and exchange–correlation energy densities per electron for polarized $\zeta = 1$ and unpolarized $\zeta = 0$ densities.[18]
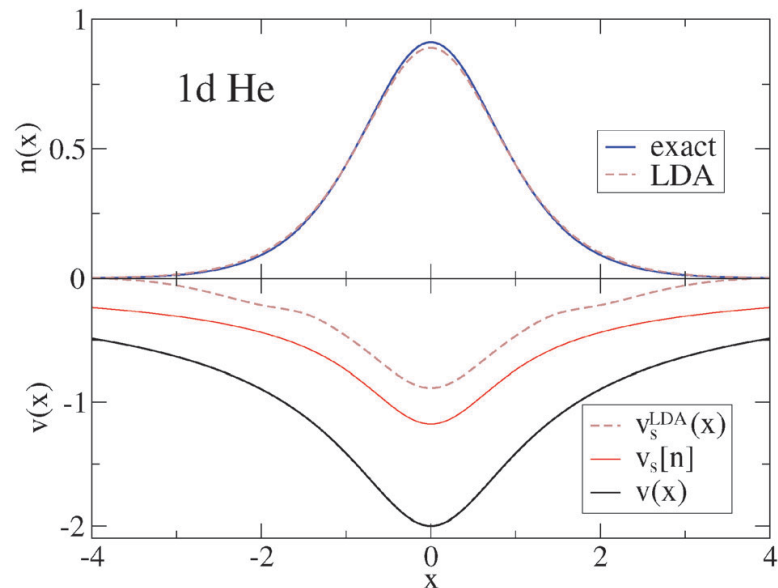
Comparing 1d and 3d

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)

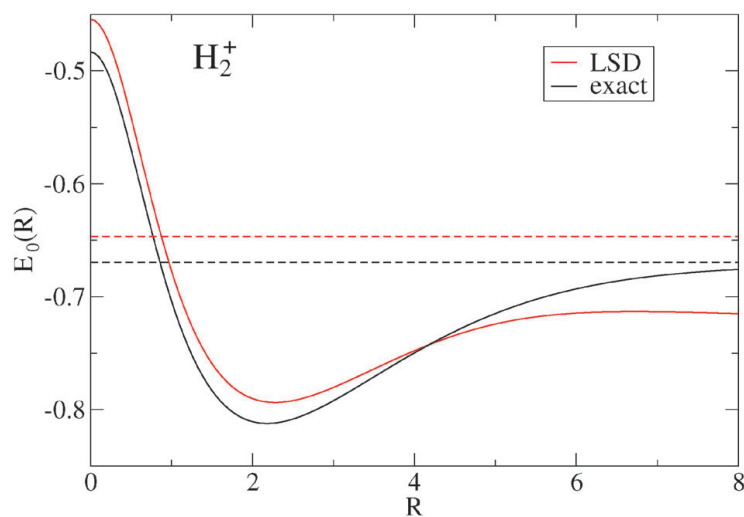| System	T	V	V_{ee}	E	E^{HF}	E_C^{QC}
H^-	0.115	−1.326	0.481	−0.731	−0.692	−0.039
He	0.290	−3.219	0.691	−2.238	−2.224	−0.014
Li^+	0.433	−5.084	0.755	−3.896	−3.888	−0.008
Be^{++}	0.556	−6.961	0.790	−5.615	−5.609	−0.006
3d H^-	0.528	−1.367	0.311	−0.528	−0.488	−0.042
3d He	2.904	−6.753	0.946	−2.904	−2.862	−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.
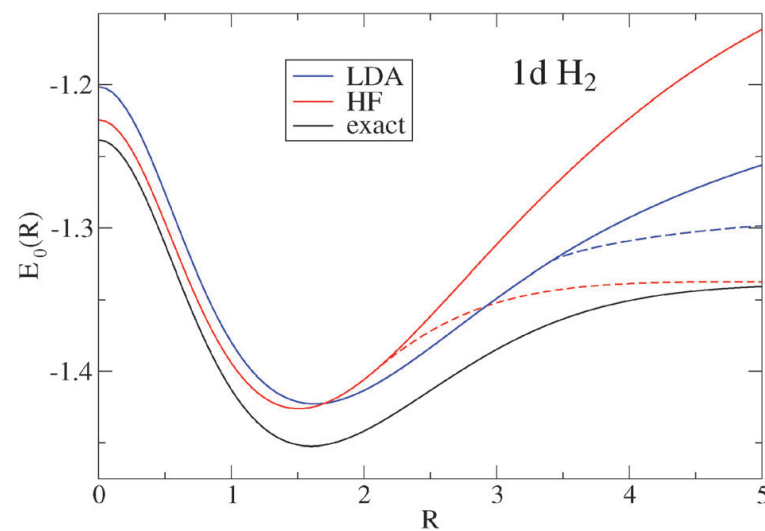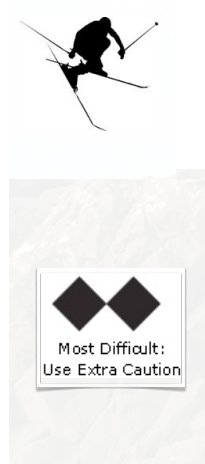
Fig. 9 The binding energy curve for our 1d model H_2, shown on an absolute energy scale, with nuclear separation R. Dashed curves represent unrestricted calculations.

CONVERGENCE

Convergence of KS equations

Guaranteed Convergence of the Kohn-Sham Equations

Lucas O. Wagner,[1,2] E. M. Stoudenmire,[1] Kieron Burke,[1,2] and Steven R. White[1]

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[2]*Department of Chemistry, University of California, Irvine, California 92697, USA*

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.
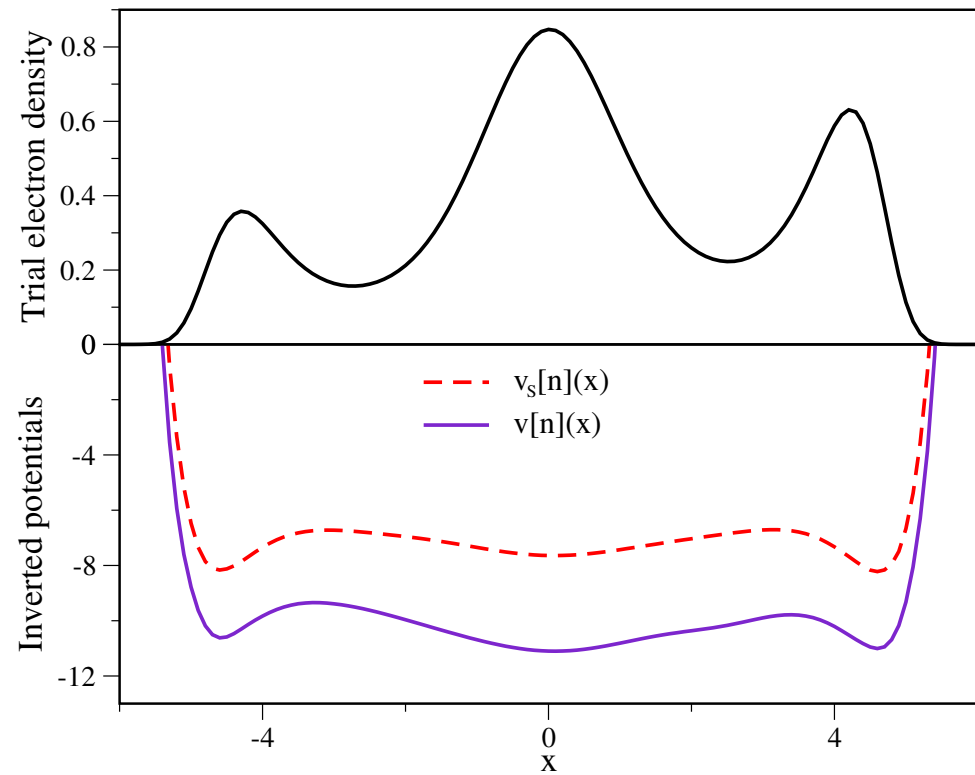
Interacting inversion

FIG. 2. Arbitrary density inversion for non-interacting and interacting potentials.
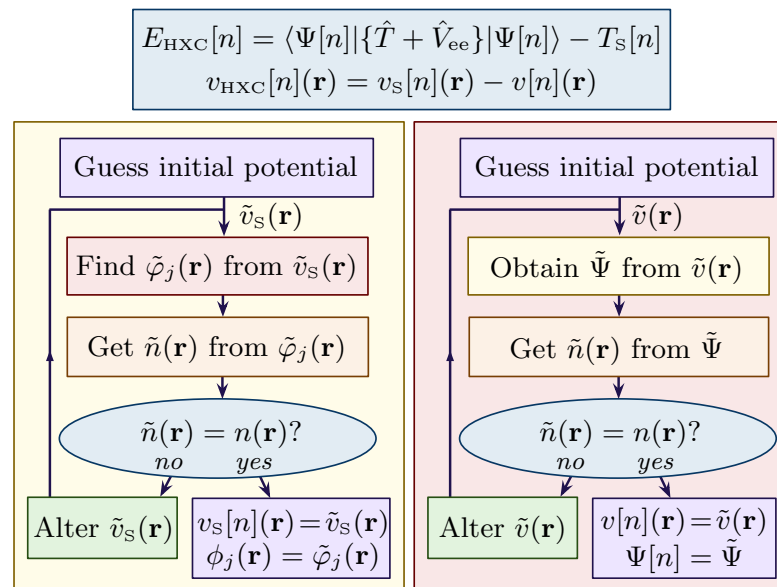
KS with exact XC

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

Left column (yellow):

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

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

Right column (pink):

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).
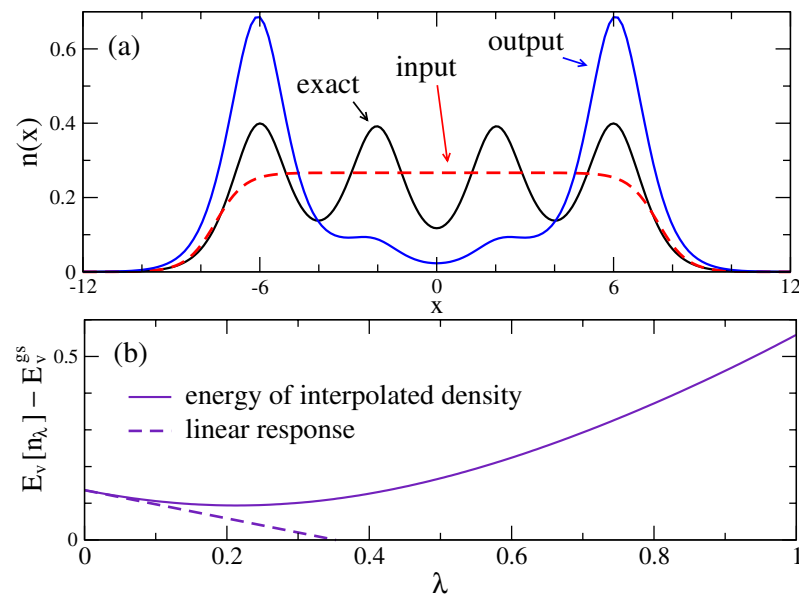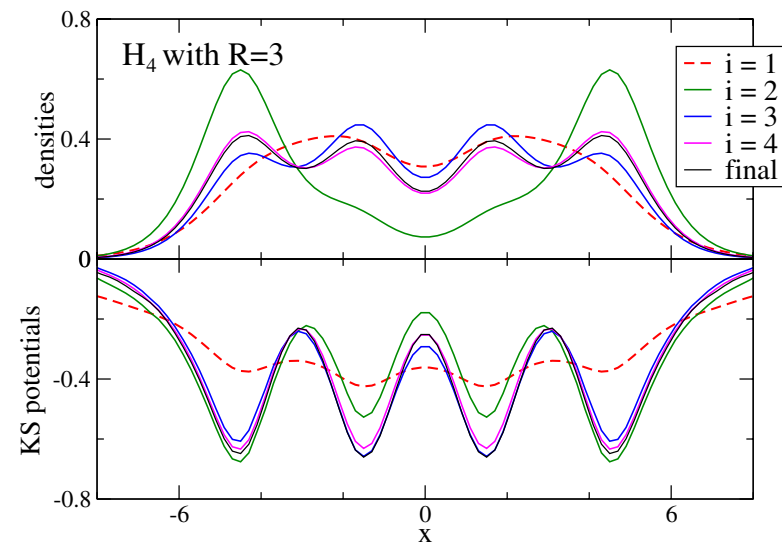
Convergence of chain

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

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

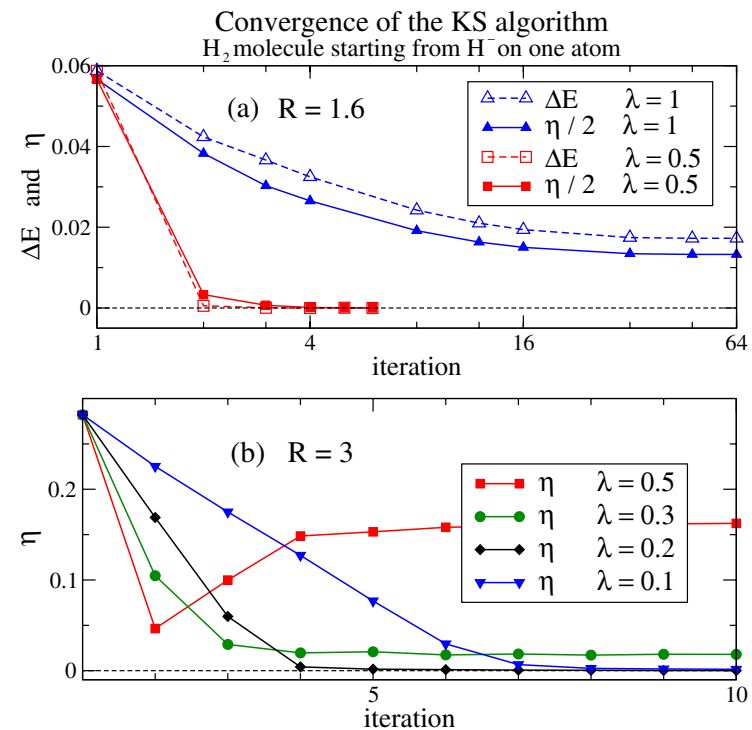$$n_\lambda(\mathbf{r}) = (1 - \lambda)n(\mathbf{r}) + \lambda n'(\mathbf{r}),$$

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).
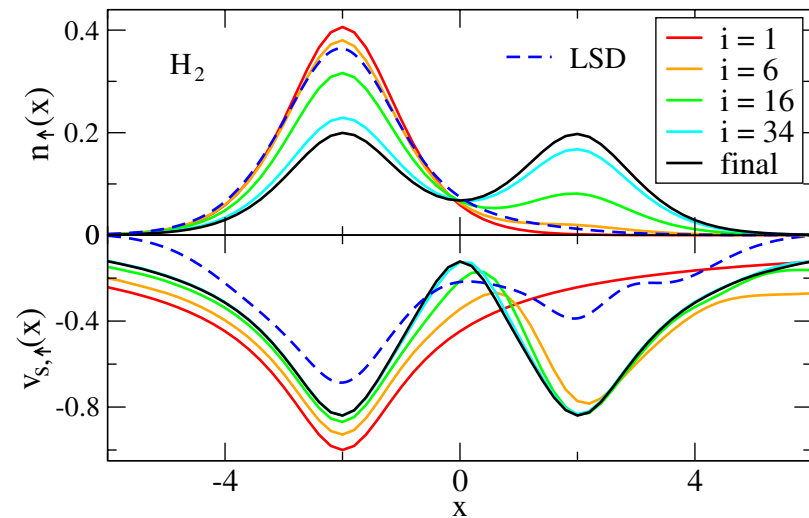
Spin polarization

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)
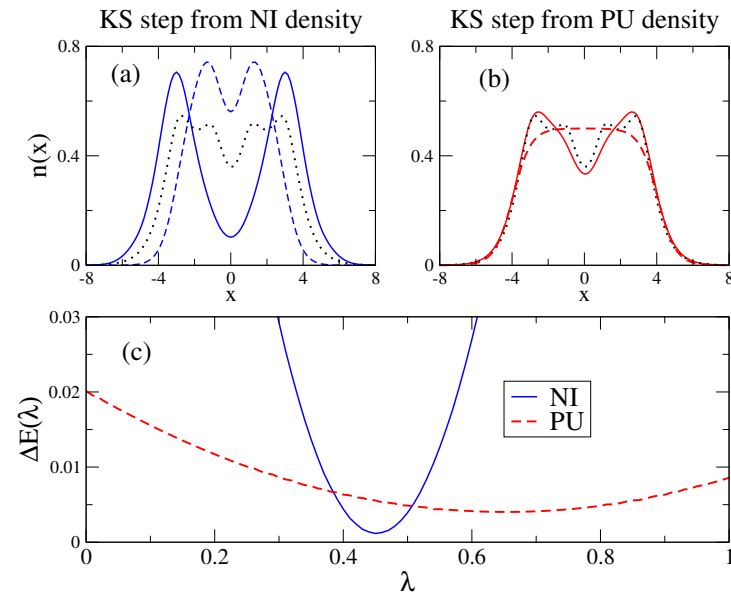
Cambridge 13

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.
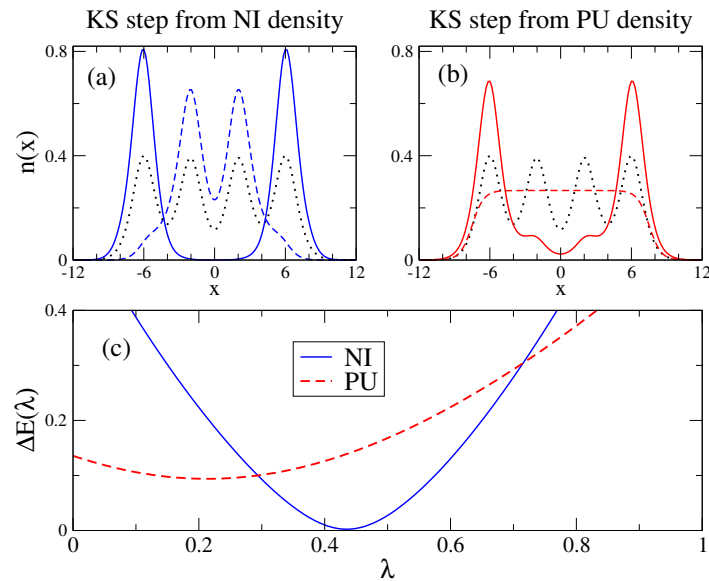
Single step for strong correlation

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.
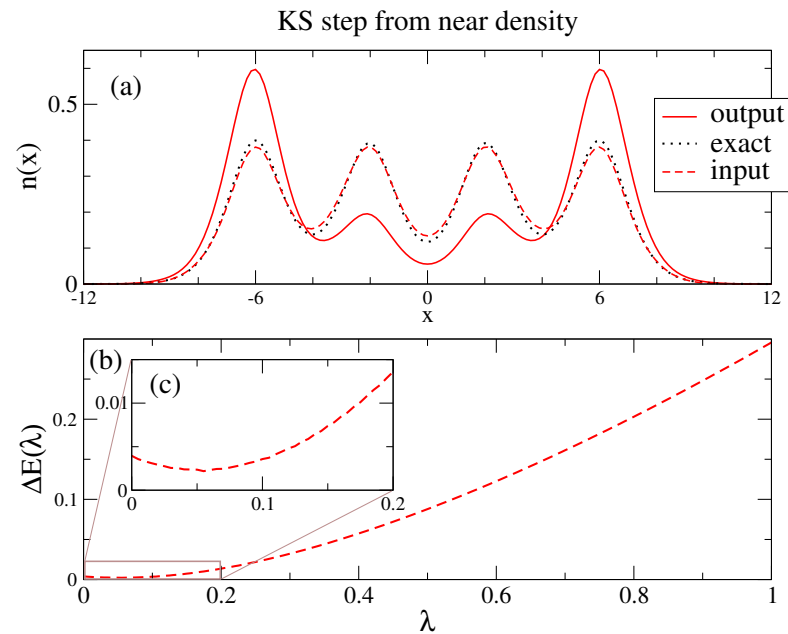
KS step when close to gs

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.
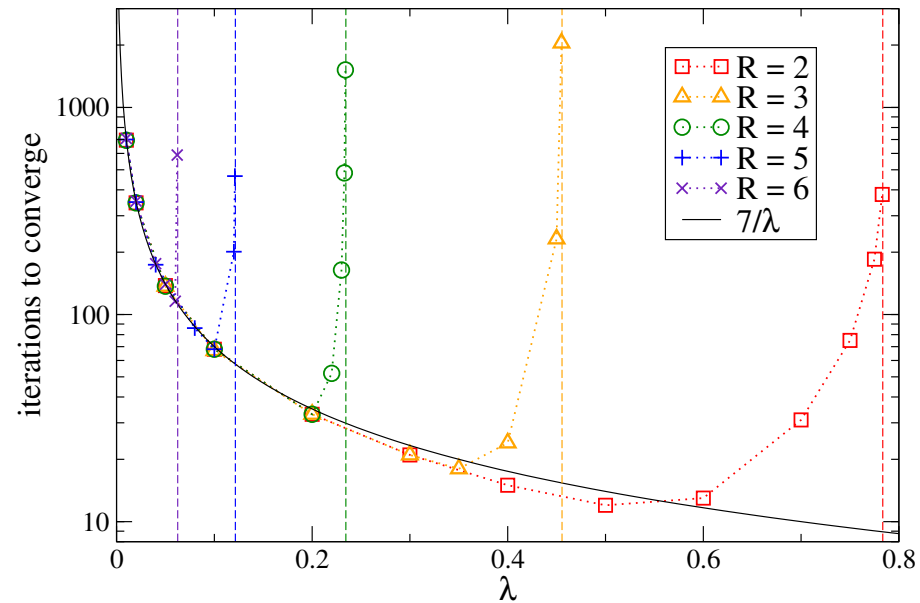
No of iterations vs b

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.
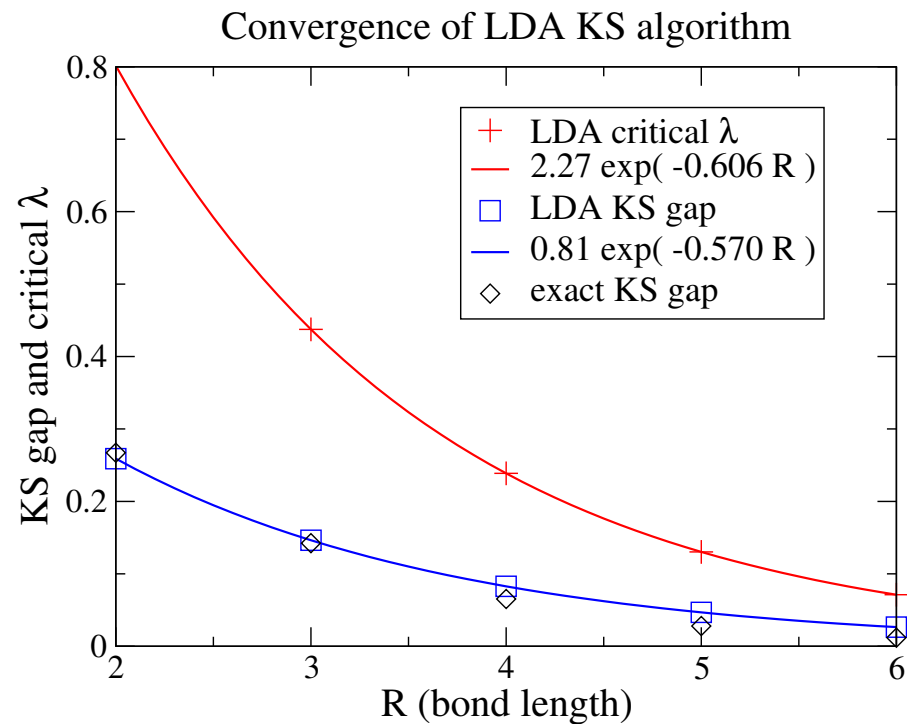
Convergence vs bond length

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.

GAPS FOR SOLIDS

Summary

- 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.