

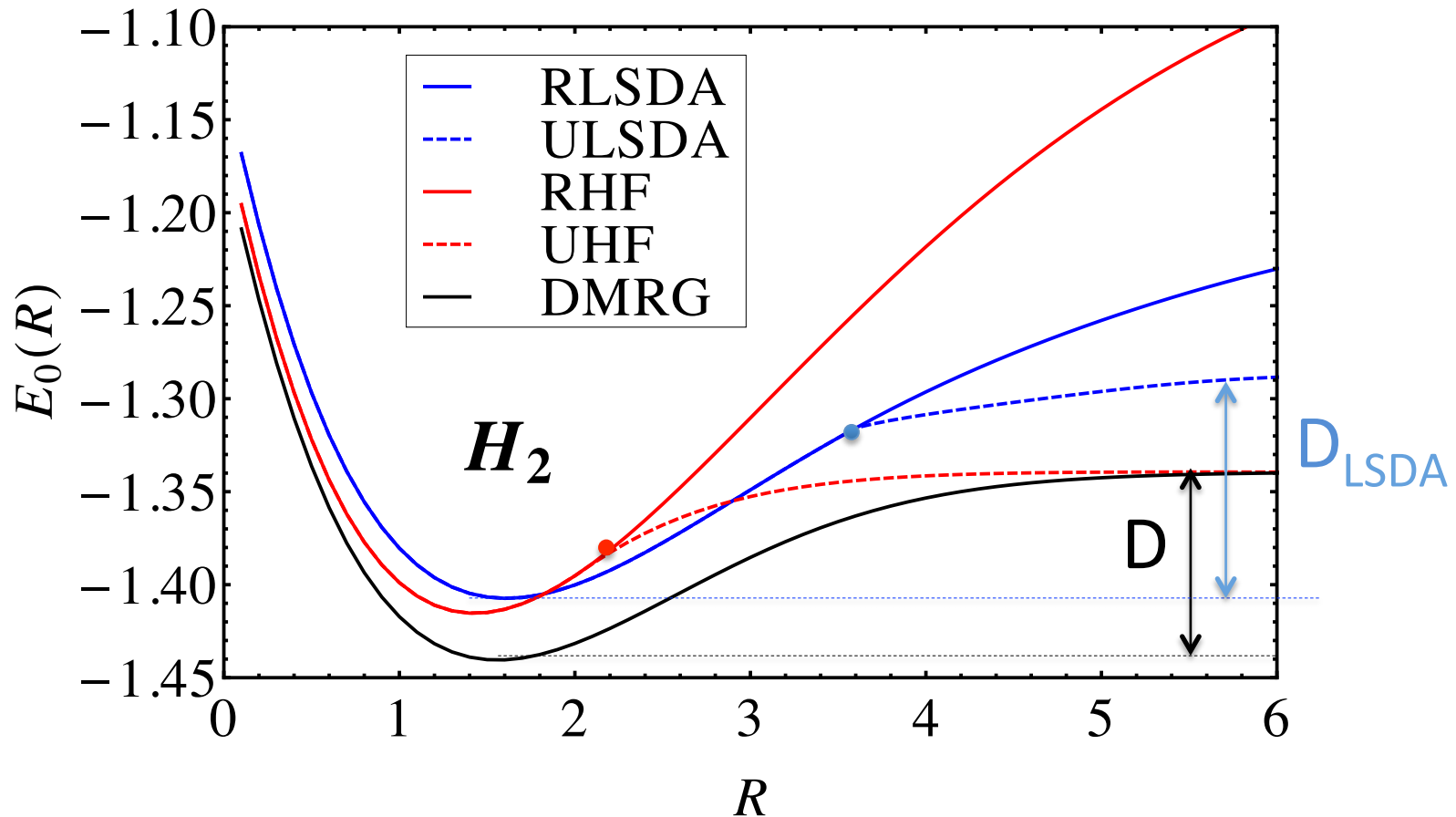
Failures of density functional theory for strongly correlated systems

Kieron Burke and friends
UC Irvine Physics & Chemistry

<http://dft.uci.edu>



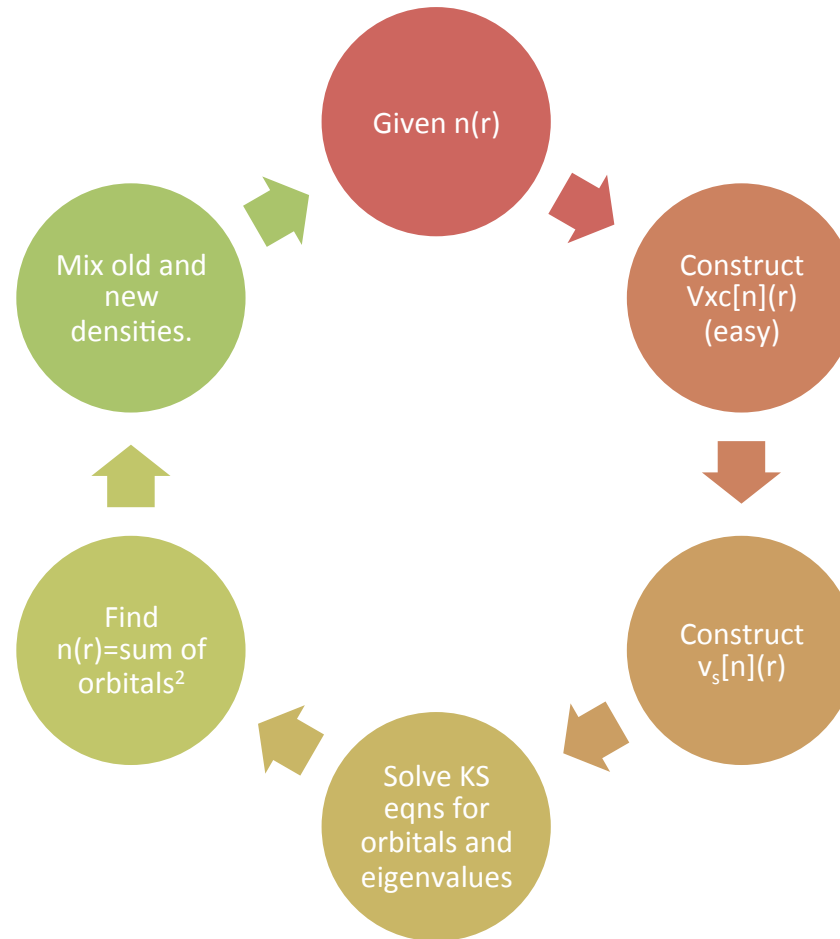
Prototype of Strong/static correlation



Basics of DFT

- There exists an exact XC functional that yields the exact ground-state energy and density.
- Semilocal approximations yield accurate ground-state energies and (usually) densities for weakly correlated systems.
- Condensed matter theorists usually care more about
 - Response properties
 - Thermal properties, eg phase transitions
 - More homogeneous systems

KS algorithm (standard)



Two opposite themes

- Part 1: Do DFT of lattice model
 - Shows what DFT methods actually do
 - Allows study of errors in very controlled situation
 - Not clear which lessons can be taken back to real space
- Part 2: Take lattice to continuum limit, converging to real-space solution
 - Real DFT approximations really tested.
 - Use powerful 'exact' solvers to study many features
 - Limited to 1d

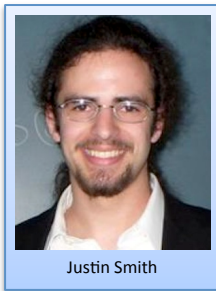
Part 1: DFT of a lattice



Diego Carrascal (Oviedo)



Jaime Ferrer (Oviedo)



Justin Smith

The Hubbard Dimer: A density functional case study of a many-body problem

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(Dated: February 10, 2015)

This review explains the relationship between density functional theory and strongly correlated models using the simplest possible example, the two-site Hubbard model. The relationship to traditional quantum chemistry is included. Even in this elementary example, where the exact ground-state energy and site occupations can be found analytically, there is much to be explained in terms of the underlying logic and aims of Density Functional Theory. Although the usual solution is analytic, the density functional is given only implicitly. We overcome this difficulty using the Levy-Lieb construction to create a parametrization of the exact function with negligible errors. The symmetric case is most commonly studied, but we find a rich variation in behavior by including asymmetry, as strong correlation physics vies with charge-transfer effects. We explore the behavior of the gap and the many-body Green's function, demonstrating the 'failure' of the Kohn-Sham method to reproduce the fundamental gap. We perform benchmark calculations of the occupation and components of the KS potentials, the correlation kinetic energies, and the adiabatic connection. We test several approximate functionals (restricted and unrestricted Hartree-Fock and Bethe Ansatz Local Density Approximation) to show their successes and limitations. We also discuss and illustrate the concept of the derivative discontinuity. Useful appendices include analytic expressions for Density Functional energy components, several limits of the exact functional (weak- and strong-coupling, symmetric and asymmetric), the Kohn-Sham hopping energy functional for 3 sites, various adiabatic connection results, proofs of exact conditions for this model, and the origin of the Hubbard model from a minimal basis model for stretched H₂.

PACS numbers: 71.15.Mb, 71.10.Fd, 71.27.+a

1. INTRODUCTION

In condensed matter, the world of electronic structure theory can be divided into two camps: the weakly and the strongly correlated. Weakly correlated solids are almost always treated with density-functional methods as a starting point for ground-state properties (Burke, 2012; Burke and Wagner, 2013; Capelle, 2006; Dreizler and Gross, 1990; Kohm, 1999). Many-body (MB) approximations such as GW might then be applied to find properties of the quasi-particle spectrum, such as the gap (Aryasetiawan and Gunnarsson, 1998; Pollen *et al.*, 1998; Verdozzi *et al.*, 1995). This approach is 'first-principles', in the sense that it uses the real-space Hamiltonian for the electrons in the field of the nuclei, and produces a converged result that is independent of the basis set, once a sufficiently large basis set is used. Density functional theory (DFT) is known to be exact in principle, but the usual approximations often fail when correlations become strong (Cohen *et al.*, 2008b).

On the other hand, strongly correlated systems are most

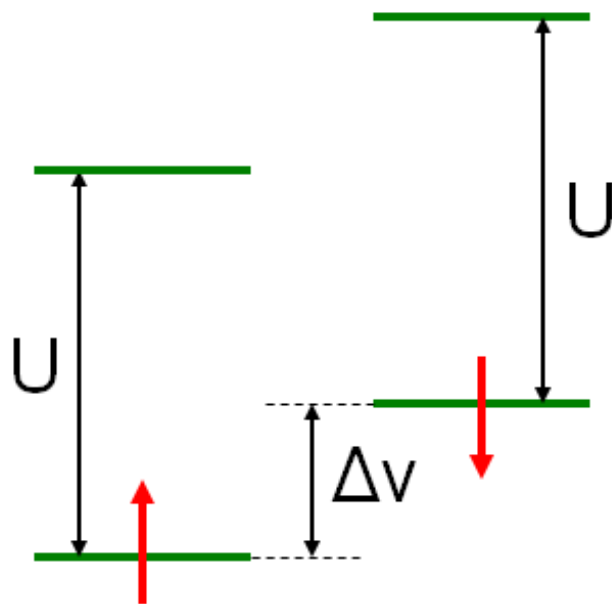
often treated via lattice Hamiltonians with relatively few parameters (Dagotto, 1994; Korepin and Essler, 1994). These simplified Hamiltonians can be easier to deal with, especially when correlations are strong (Dagotto, 1994; Essler *et al.*, 1992). Even approximate solutions to such Hamiltonians can yield insight into the physics, especially for extended systems (Solov'yev, 2008). However, such Hamiltonians can rarely be unambiguously derived from a first-principles starting point, making it difficult (if not impossible) to say how accurate such solutions are quantitatively or to improve on that accuracy. Moreover, methods that yield approximate Green's functions are often more focused on response properties or thermal properties rather than on total energies in the ground-state.

On the other hand, the ground-state energy of electrons plays a much more crucial role in chemical and material science applications (Martin, 2004; Parr and Yang, 1989). Very small energy differences determine geometries and sometimes qualitative properties, such as the nature of a transition state in a chemical reaction (Feller and Peterson,

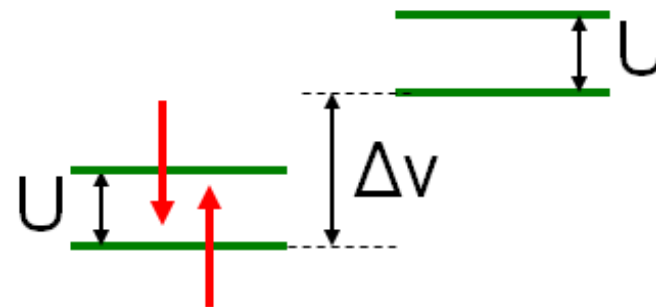
Maybe
should be
called: *The
many-body
theorists
companion
to DFT*

arXiv:1502.02194v1 [cond-mat.str-el] 7 Feb 2015

Asymmetric 2-site Hubbard

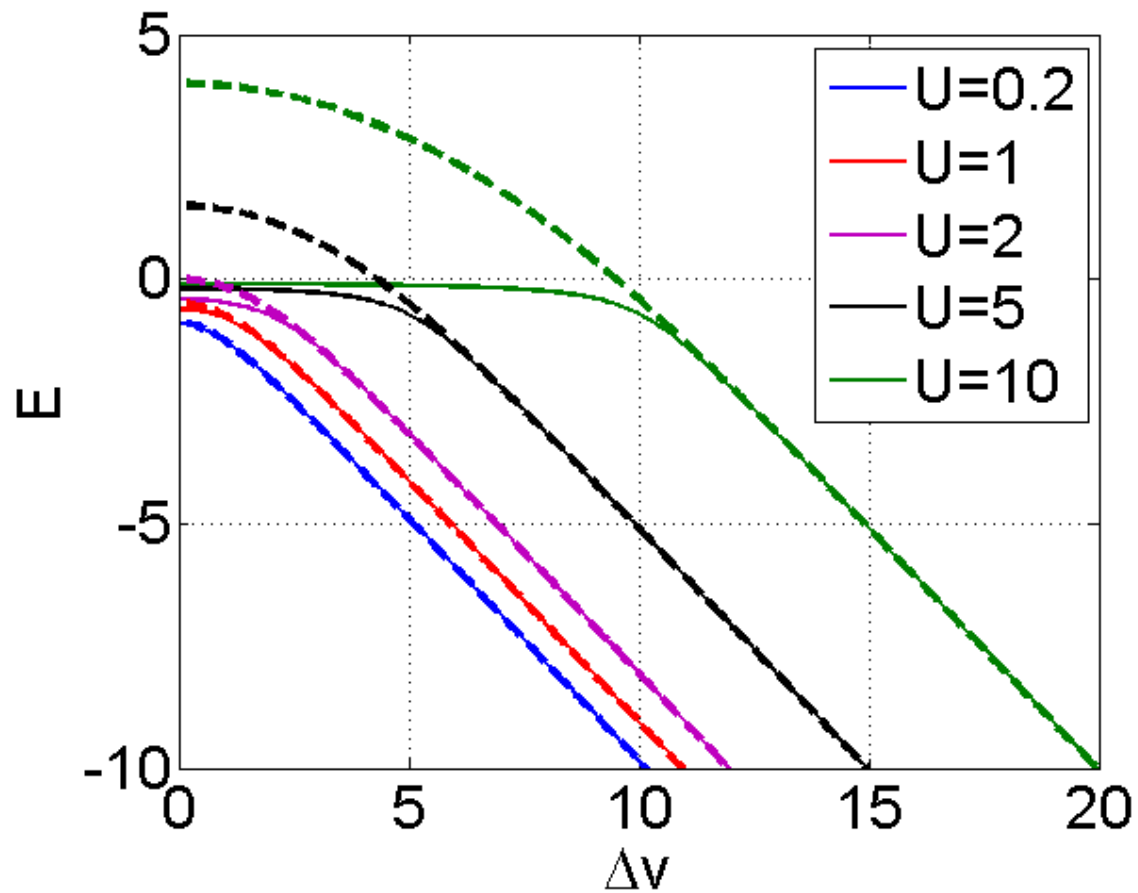


Mott-Hubbard

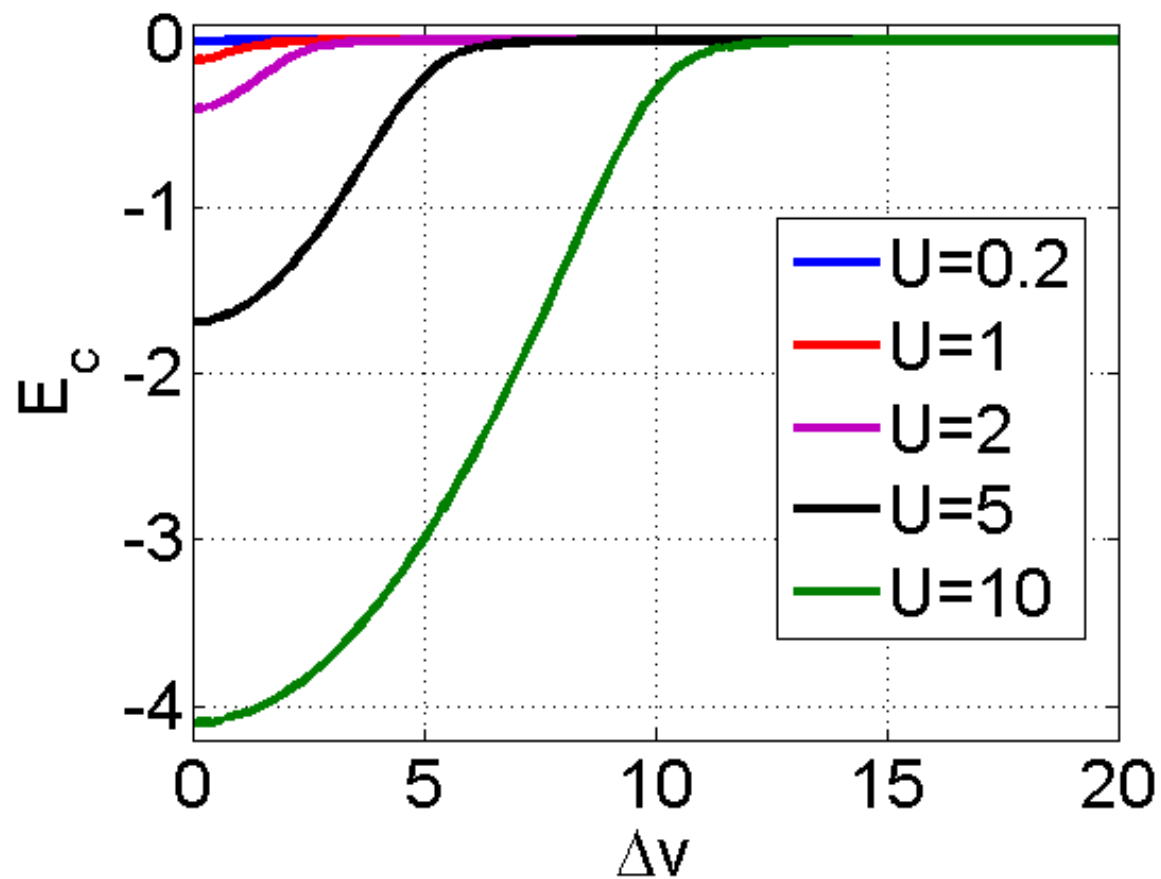


Charge-Transfer

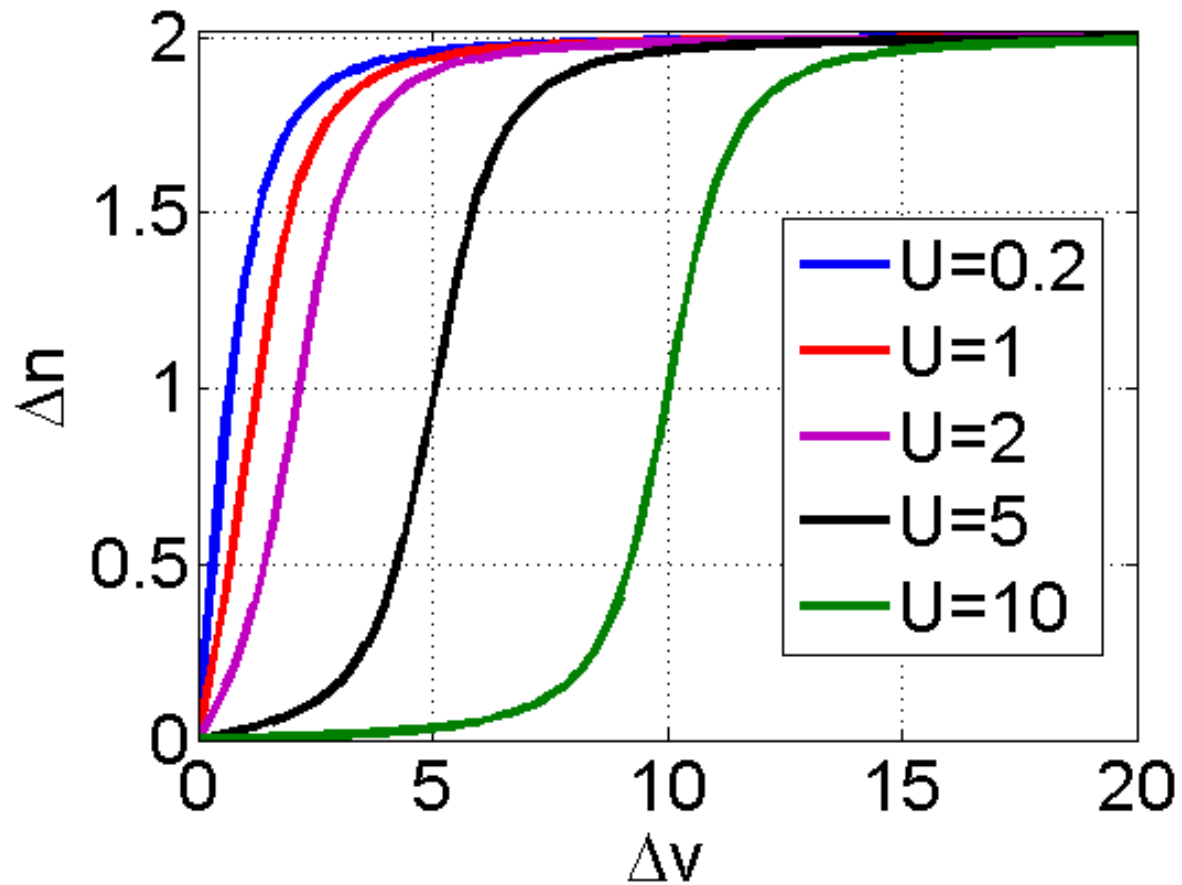
Ground-state energy (exact and RHF)



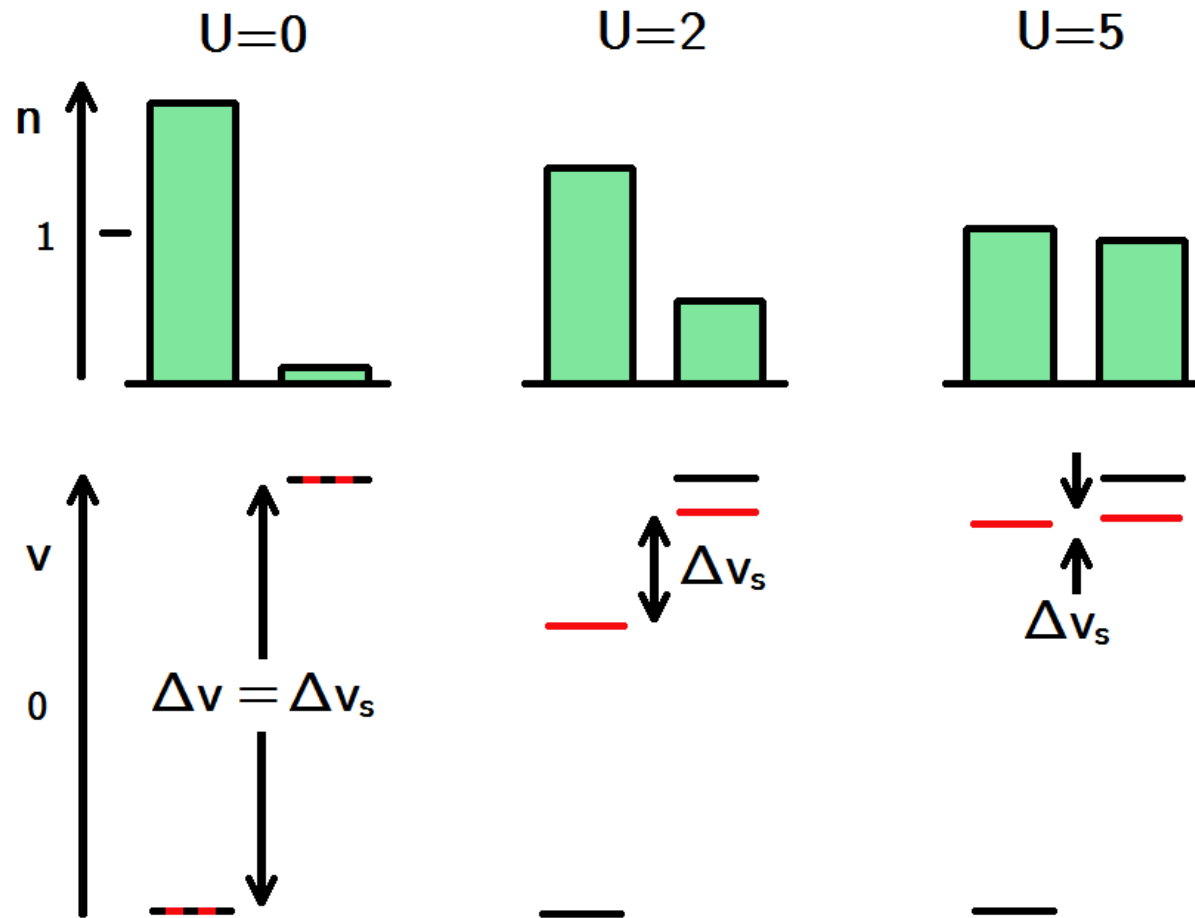
Correlation energy



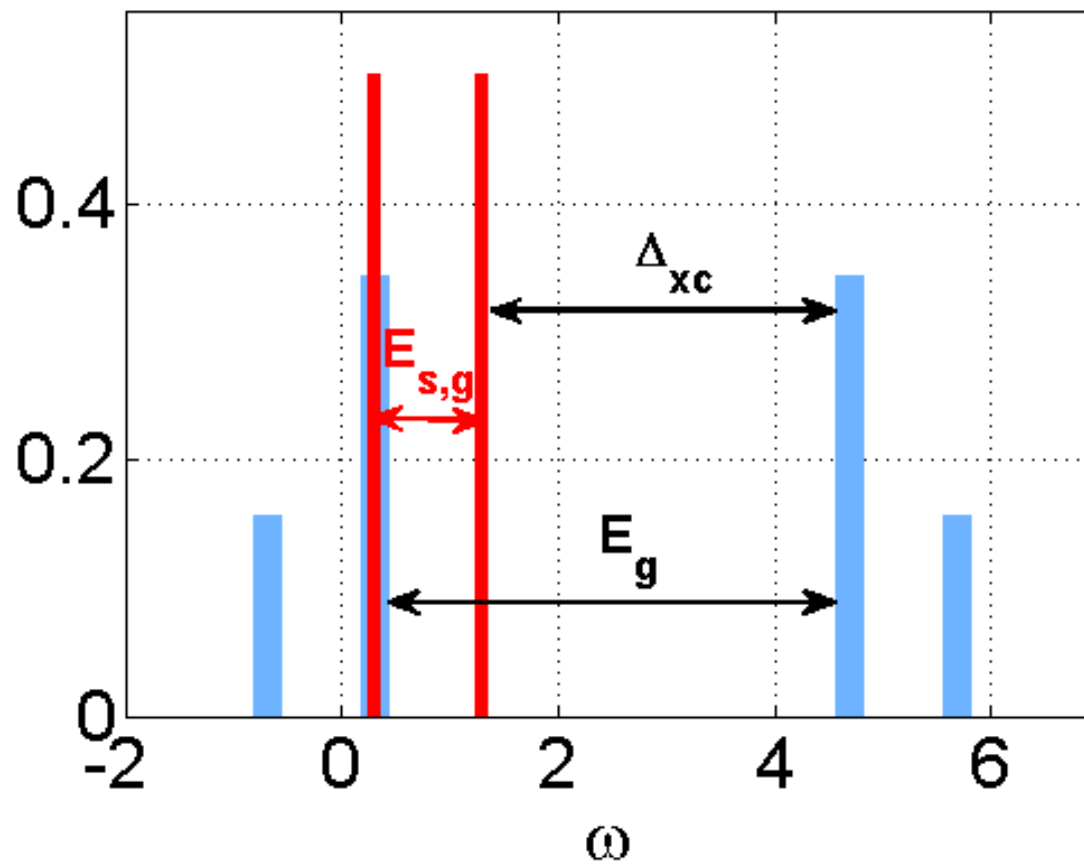
Density as a function of Δv



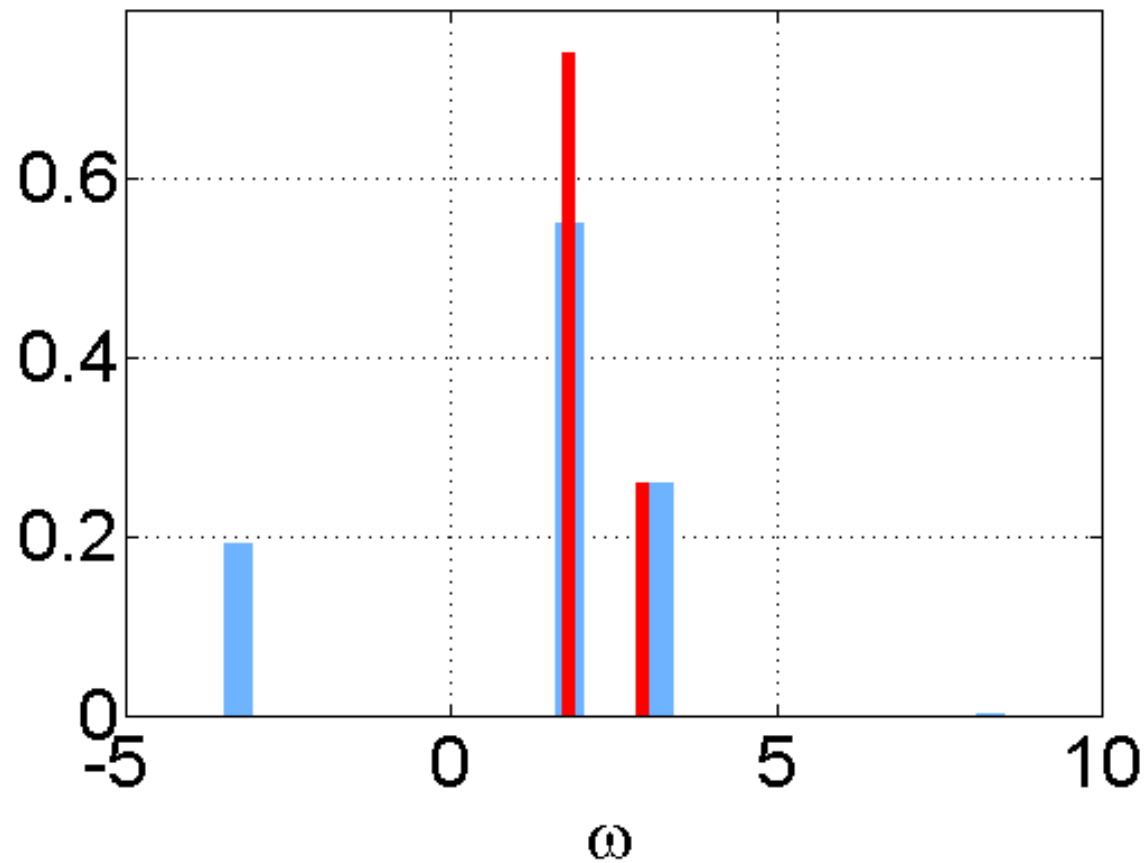
KS version



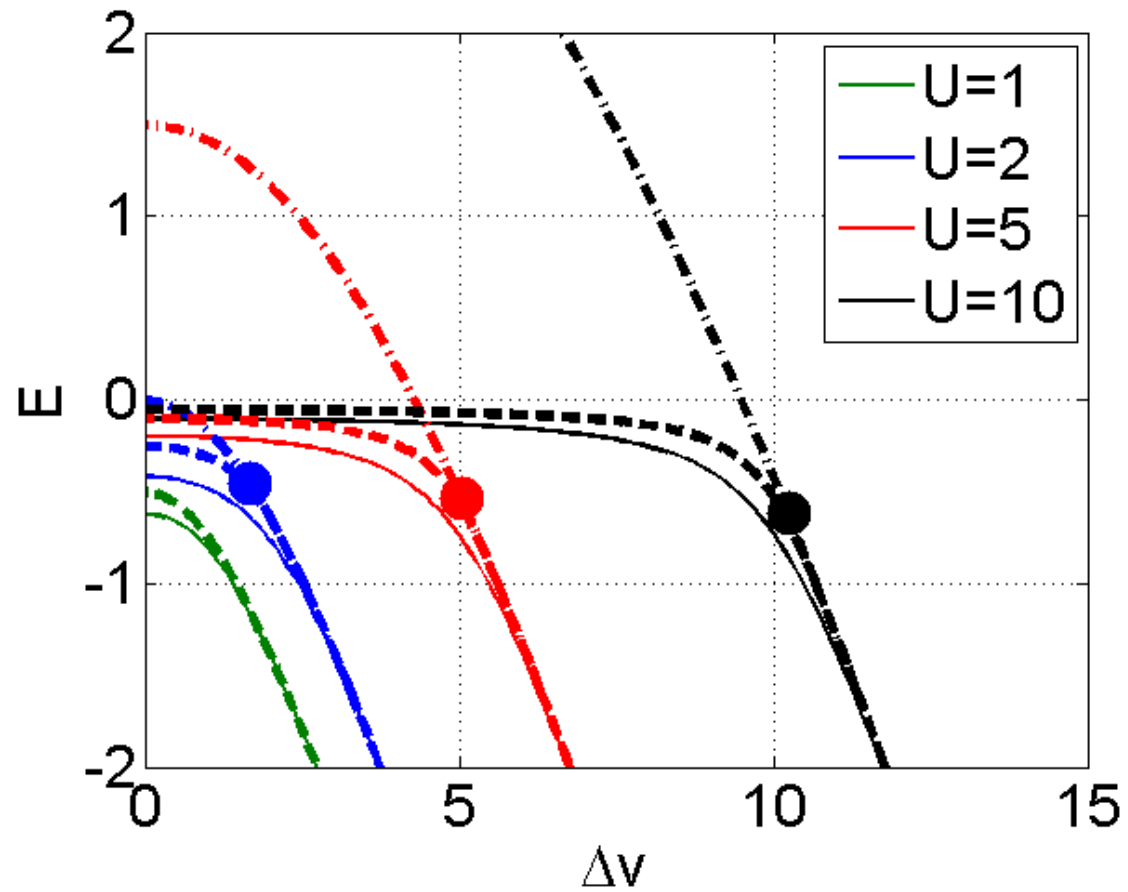
Spectral function (sym, $U=5$)



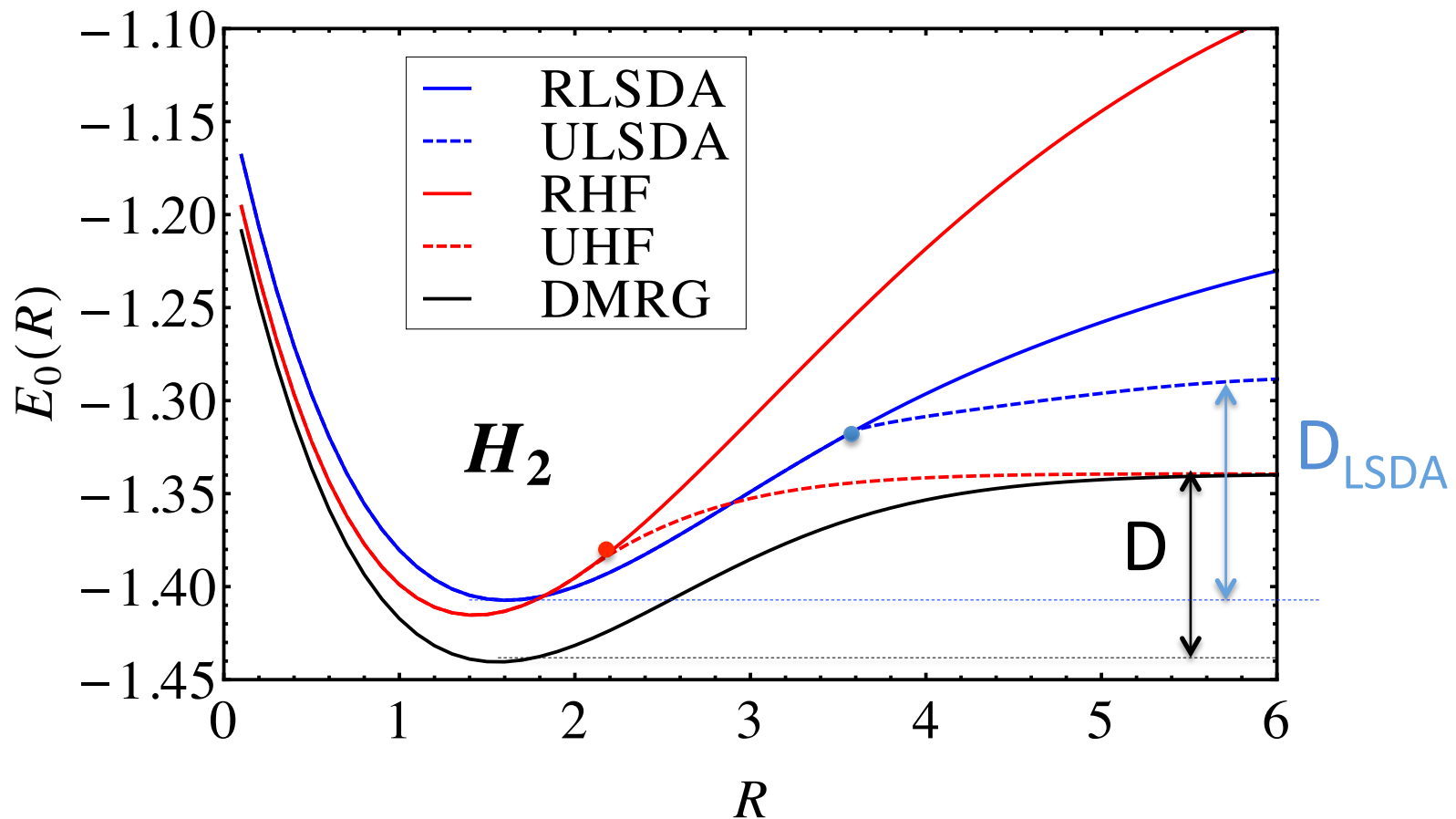
Spectral function ($\Delta v=5, U=5$)



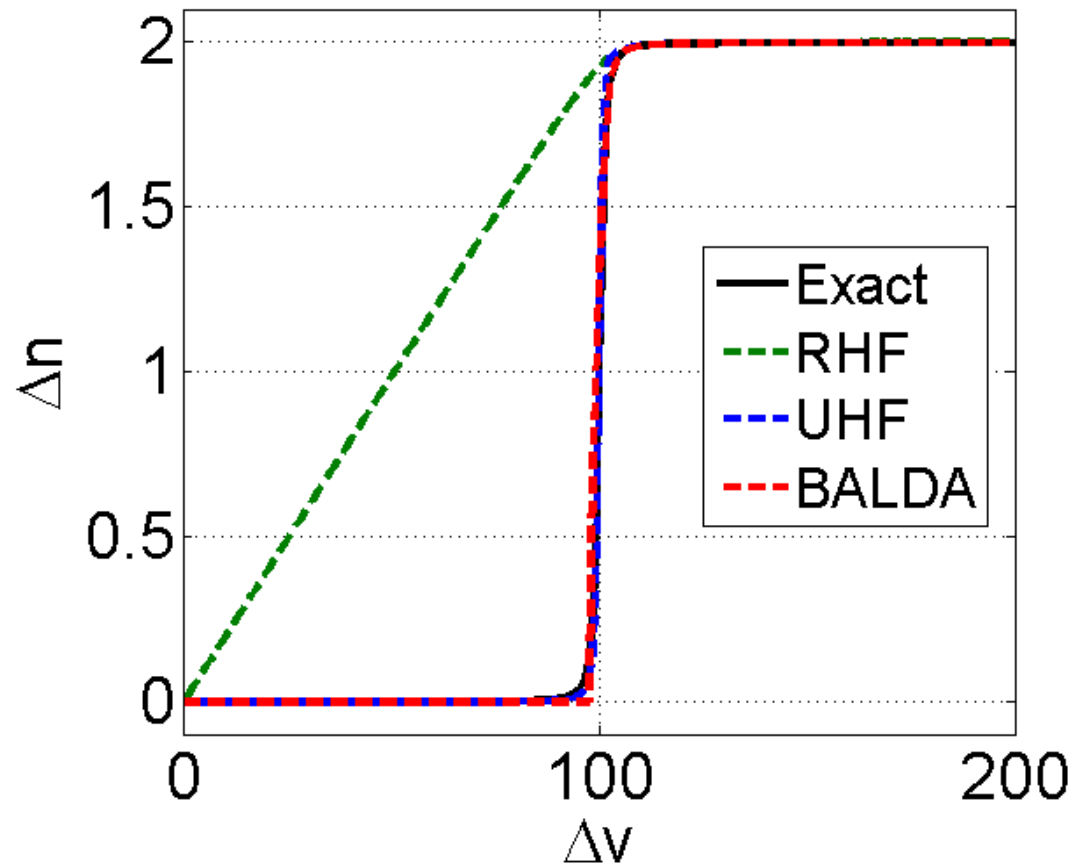
Ground-state energy in UHF



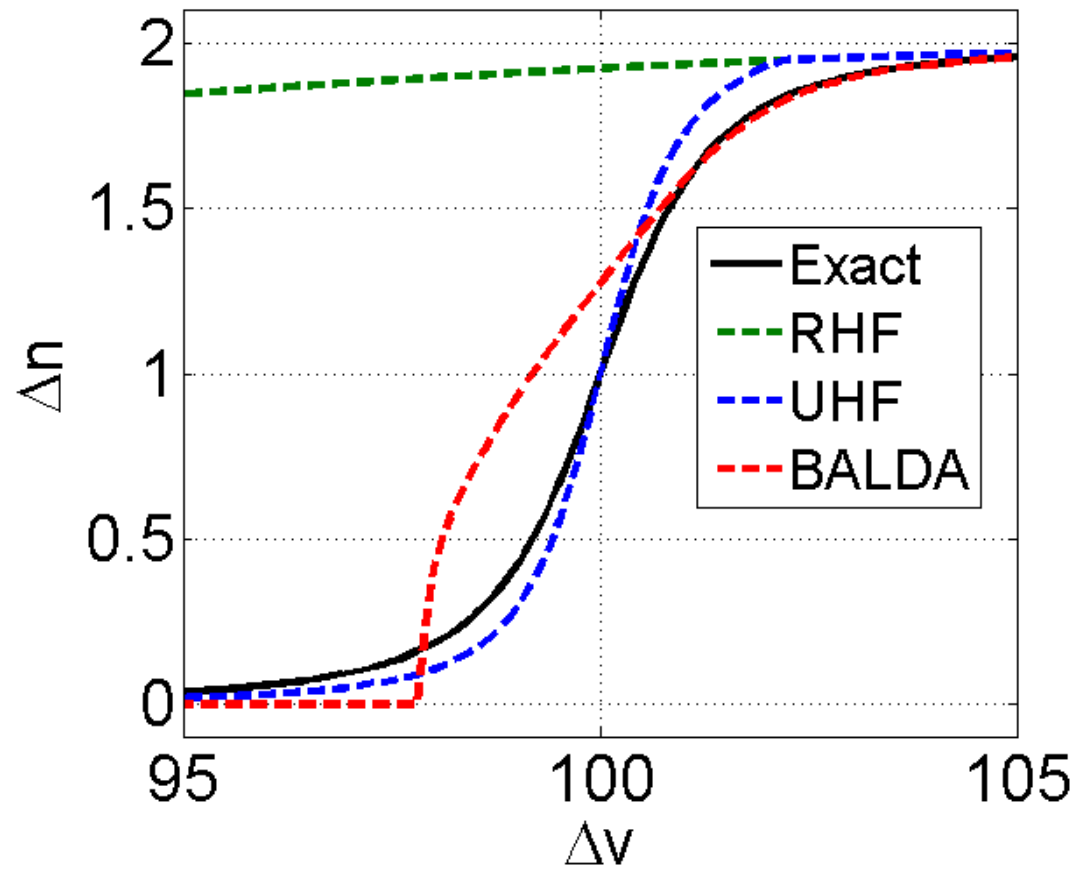
Prototype of Strong/static correlation



Density for $U=100$



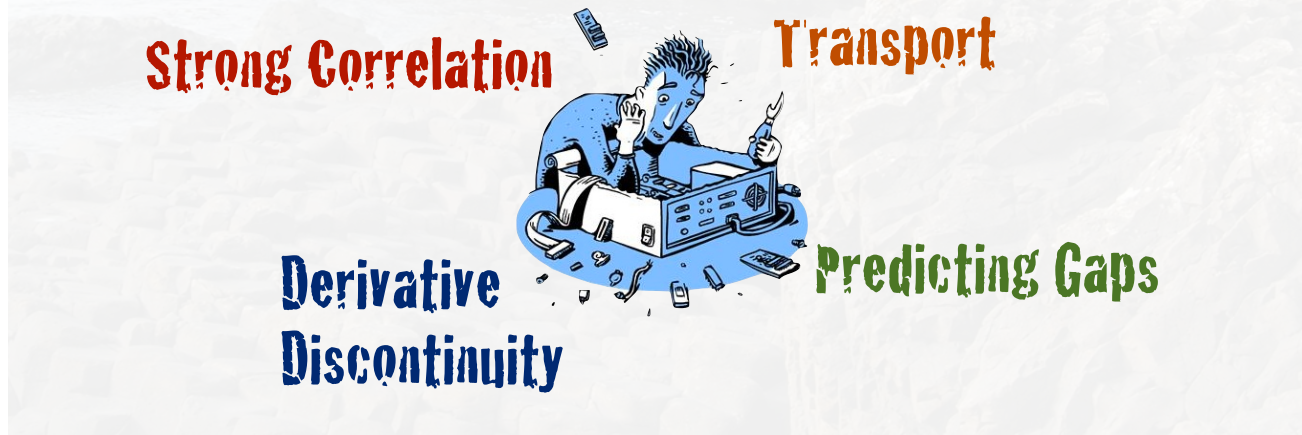
Zoom in density ($U=100$)



Part II: 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

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

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

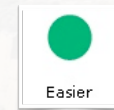
Using an exact numerical solver for 1d systems (known as DMRG), we can learn more about density functional theory (DFT) and find ways to make it better

Three levels of activity

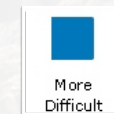
Three levels of application to DFT:



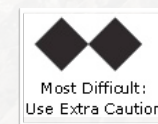
Level I: compare exact results to
DFT approximations



Level II: study the exact
Kohn-Sham system

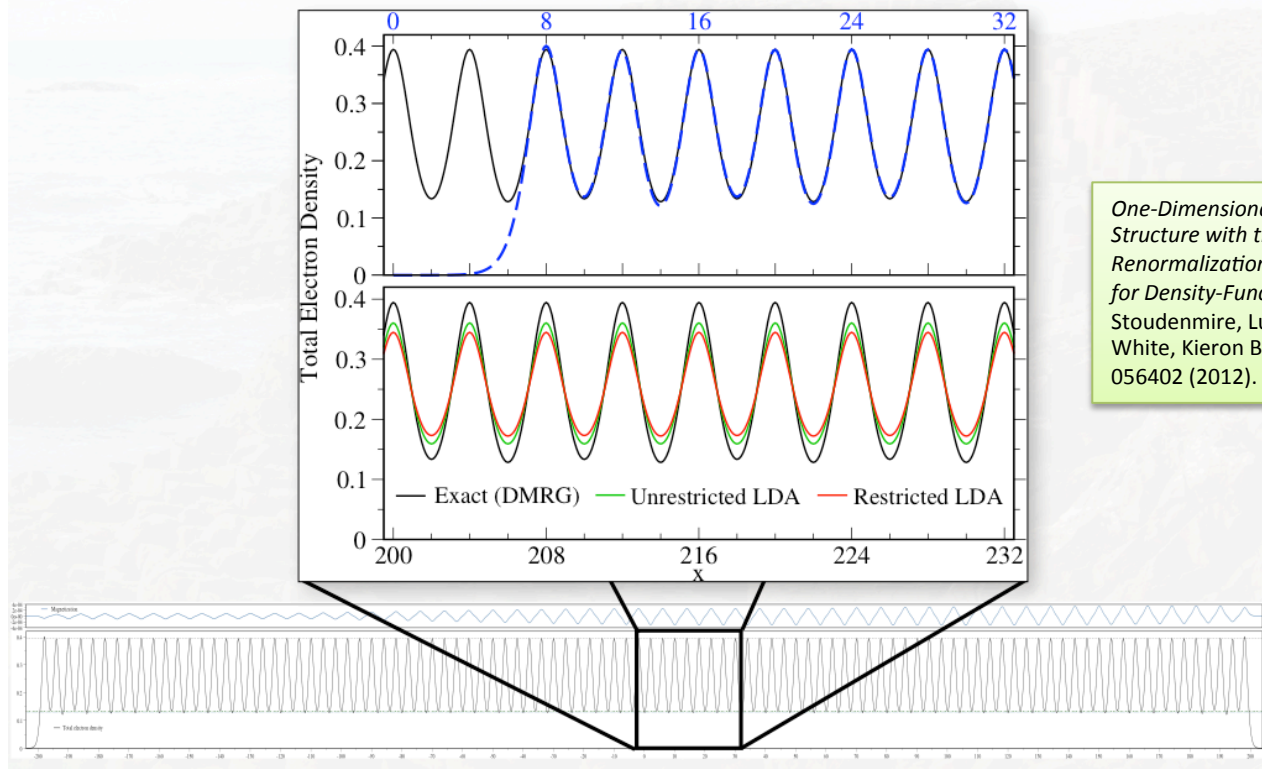


Level III: self-consistent KS
calculation with the
exact functional



Example of long chains

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



*One-Dimensional Continuum Electronic Structure with the Density-Matrix Renormalization Group and Its Implications for Density-Functional Theory E.M. Stoudenmire, Lucas O. Wagner, Steven R. White, Kieron Burke, Phys. Rev. Lett. **109**, 056402 (2012).*



Mott-Hubbard gap



- Classic prototype of condensed matter
- Infinite chain of H atoms
- When lattice spacing is large, must be an insulator
- But with one electron per site, always a band metal

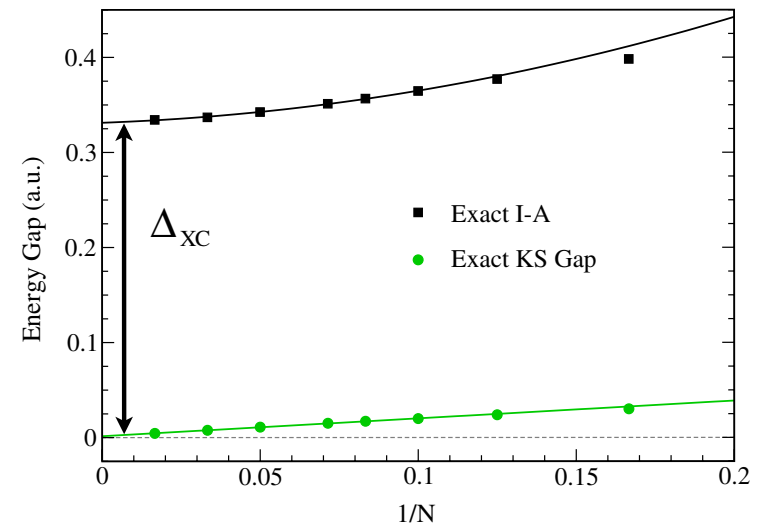


FIG. 3 (color online). Exact gaps for chains of N soft hydrogen atoms with atomic separation $b = 4$ (error bars are less than symbol sizes). The upper curve is a quadratic fit of exact gaps of the largest six systems and extrapolates to a finite value $E_g \approx 0.33$. The exact Kohn-Sham gaps, in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

Benchmark DFT calculations

Cite this: *Phys. Chem. Chem. Phys.*, 2012, **14**, 8581–8590

www.rsc.org/pccp

PAPER

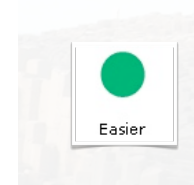
Reference electronic structure calculations in one dimension†

Lucas O. Wagner,^{*a} E. M. Stoudenmire,^a Kieron Burke^{ab} and Steven R. White^a

Received 24th December 2011, Accepted 1st May 2012

DOI: 10.1039/c2cp24118h

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.



Possible problems with KS calculations for strongly correlated systems

- Uniqueness of the KS potential
 - No problem, because of HK
- Existence of KS potential
 - Uniqueness does not guarantee existence, and neither HK nor Levy/Lieb prove this.
 - Always find it exists for all systems we've looked at.
- Convergence
 - Even if a unique KS exists, what if you can never find it?
 - What if you get stuck in an endless limit cycle?

Interacting inversion (insanity)

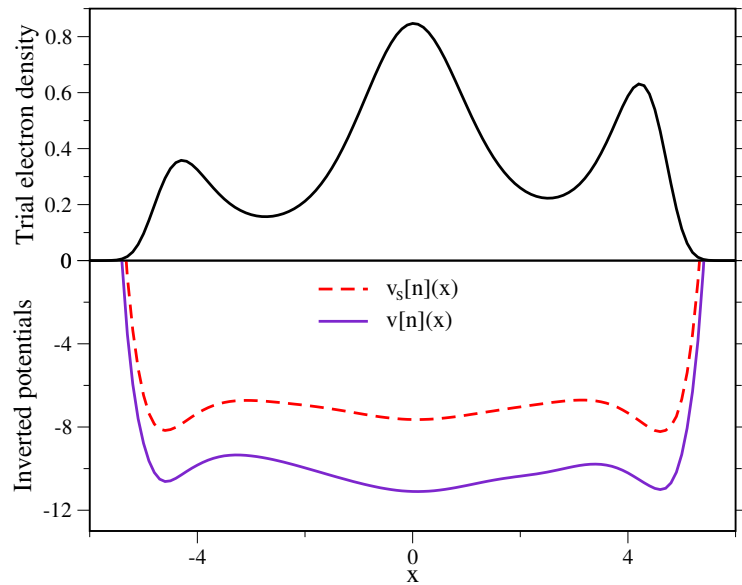
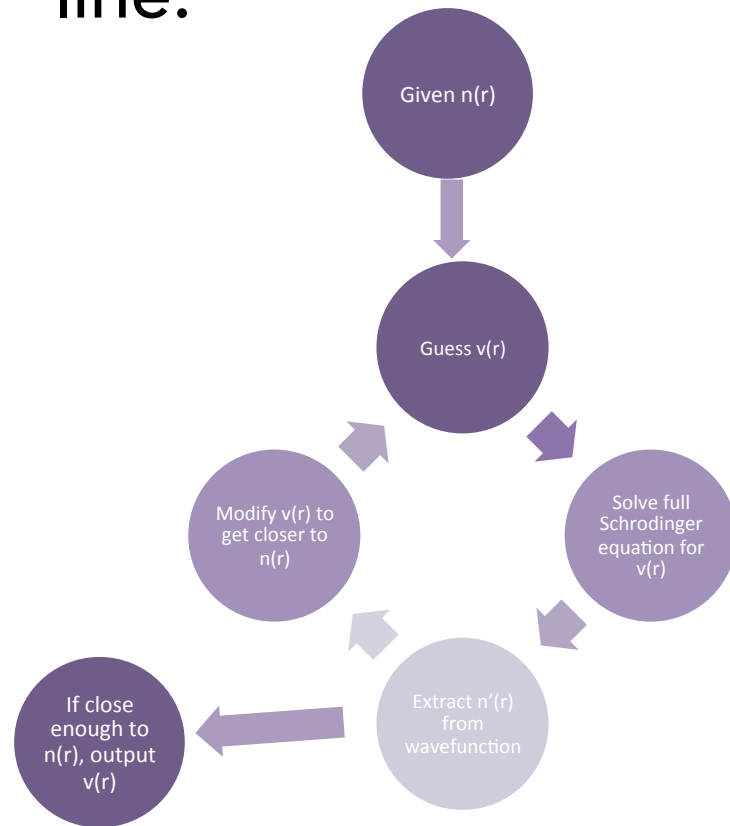


FIG. 2. Arbitrary density inversion for non-interacting and interacting potentials.

- To find the purple line:



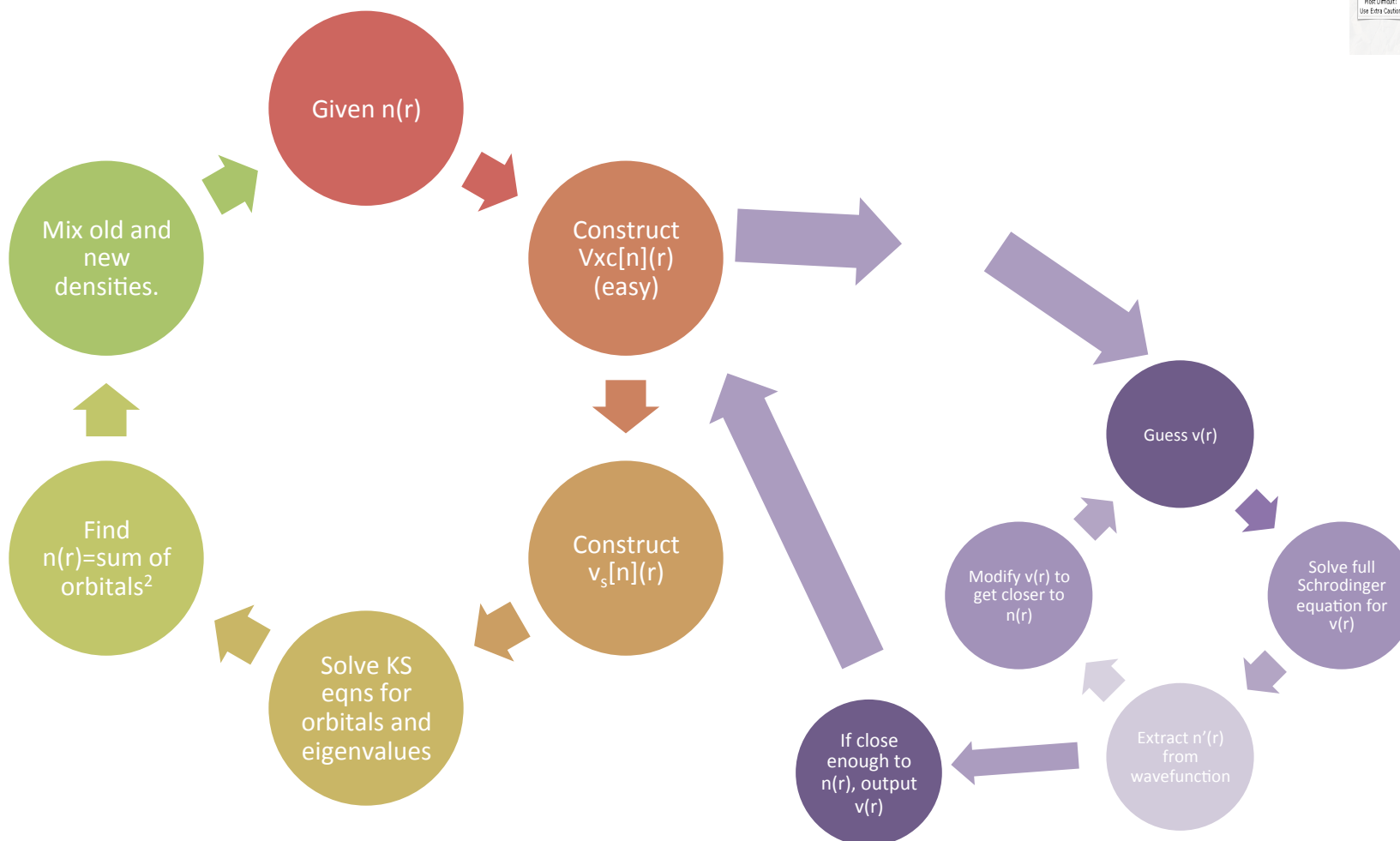
Definitions

- $n(\mathbf{r})$ is some given density
- $n'(\mathbf{r})$ 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

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

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

KS algorithm (with exact XC)

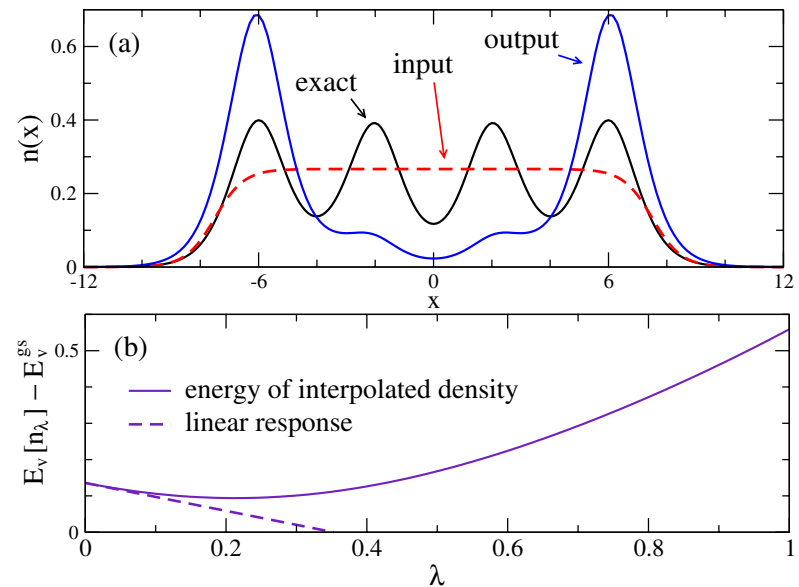


Actual calculations

- Sometimes with exact functional
- Sometimes with LDA
- Start from some well-defined density, often chosen to be far from end point, e.g., H^- density centered at one nucleus, or pseudo uniform density
- Chose a fixed tolerance in η and a given λ
- Can always find finite λ so that it converges to ground state.

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

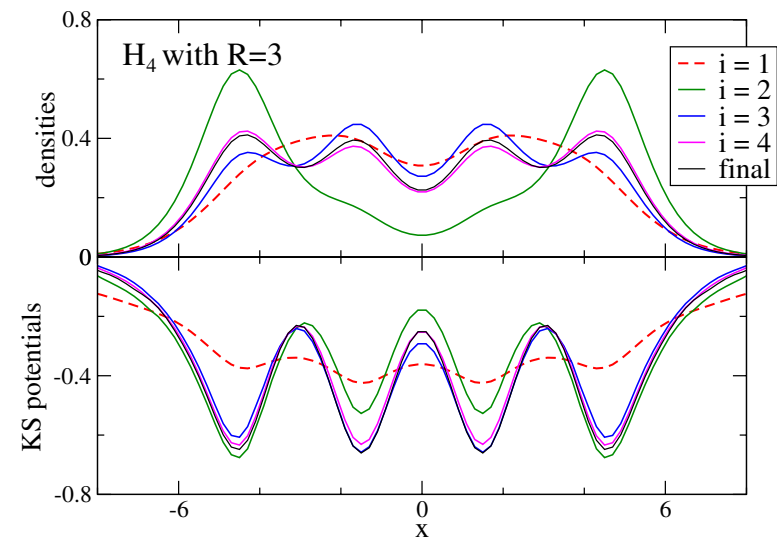


FIG. 2 (color online). KS procedure for a moderately correlated four-electron system (four hydrogen atoms with $R = 3$), showing the first few iterations. Using a fixed $\lambda = 0.30$, we converge to $\eta < 10^{-6}$ using Eq. (4) within 13 iterations.

Proof of convergence

- Lemma: $\int d^3r (v[n'](\mathbf{r}) - v[n](\mathbf{r}))(n'(\mathbf{r}) - n(\mathbf{r})) < 0$.
- Oops: Already proven by Gritsenko and Baerends (2005) – see our erratum.
- Consequence: take one step for some
 - $dE/d\lambda$ always < 0 at ends of curve
 - Guarantees a minimum
 - Can prove always converges for $\lambda < \lambda_c$
 - Assume Hilbert space finite

Guaranteed Convergence of the Kohn-Sham Equations Lucas O. Wagner, E. M. Stoudenmire, Kieron Burke, Steven R. White, Phys. Rev. Lett. **111**, 093003 (2013).

Rate of convergence

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

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

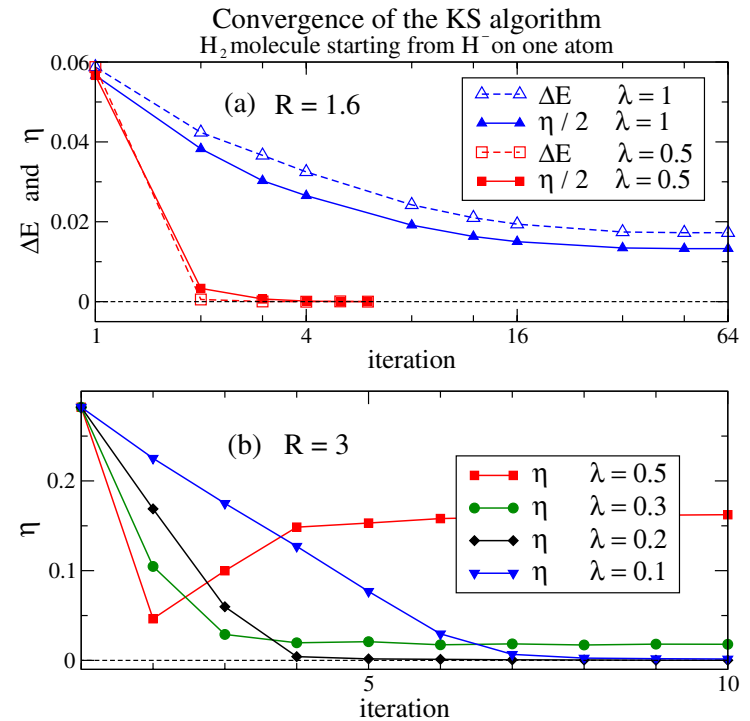


FIG. 3 (color online). Differences in the density η using Eq. (4) and the energy with $\Delta E = E_v[n'] - E_v^{gs}$, for an H₂ molecule with (a) $R = 1.6$ and (b) $R = 3$. In (b), the ΔE curves are omitted for clarity, but are like those in (a).



Kohn-Sham calculations with the exact functional

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(Received 5 May 2014; revised manuscript received 20 June 2014; published 9 July 2014)

As a proof of principle, self-consistent Kohn-Sham calculations are performed with the *exact* exchange-correlation functional. Finding the exact functional for even one trial density requires solving the interacting Schrödinger equation many times. The density matrix renormalization group method makes this possible for one-dimensional, real-space systems of more than two interacting electrons. We illustrate and explore the convergence properties of the exact KS scheme for both weakly and strongly correlated systems. We also explore the spin-dependent generalization and densities for which the functional is ill defined.



Thomas E. Baker



Lucas Wagner



Miles Stoudenmire



Steve White

Tom's original introduction

Four score and seven years ago, our physics forebears [1, 2] brought into this world a new theory, conceived in simplicity, and dedicated to the proposition that although all particles are waves [3], their density can be simply calculated [1, 2]. Now we are engaged in a great electronic structure debate, testing whether Kohn–Sham theory [4], or any density functional theory [5] so conceived and so dedicated, can endure in the face of strongly correlated systems. We have come to dedicate a portion of this paper, as a final convergence proof [6] for those who have dedicated their lives to developing the constrained search [7] and approximations thereto [8–10]. It is altogether fitting and proper that we should prove this.

KS steps when weakly correlated

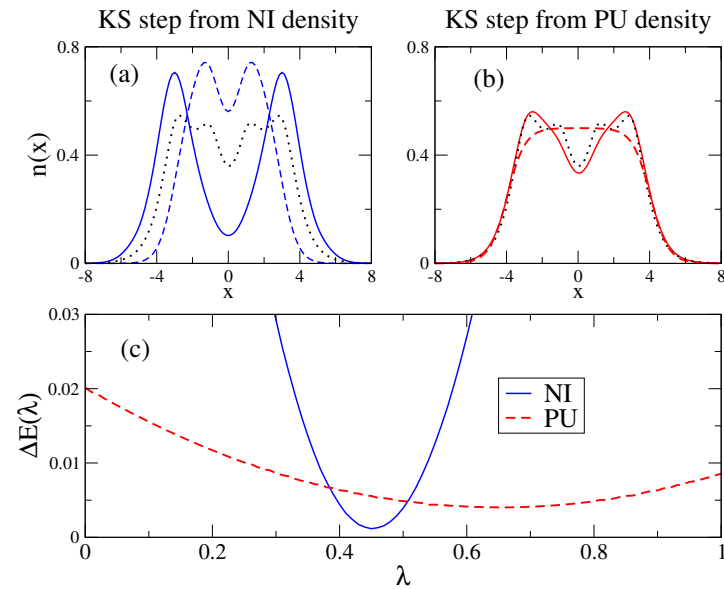


FIG. 6. A single step in the KS scheme for a weakly correlated system (H_4 with $R = 2$) away from two different initial densities: non-interacting electrons in the external potential (NI) and a pseudouniform electron density (PU). These initial densities are the dashed curves in (a) and (b), and the 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

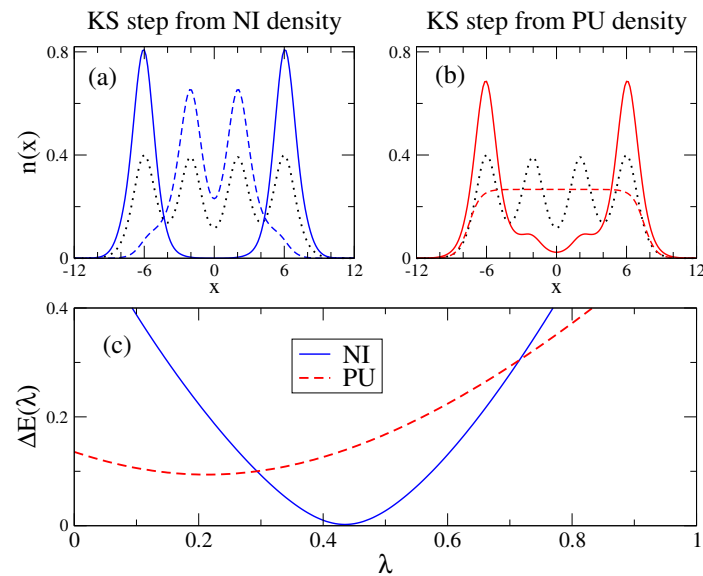


FIG. 7. A single step in the KS scheme for a strongly correlated system (H_4 with $R = 4$) away from two different initial densities: non-interacting electrons in the external potential (NI) and a pseudouniform electron density (PU). These initial densities are the dashed curves in (a) and (b), and the 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

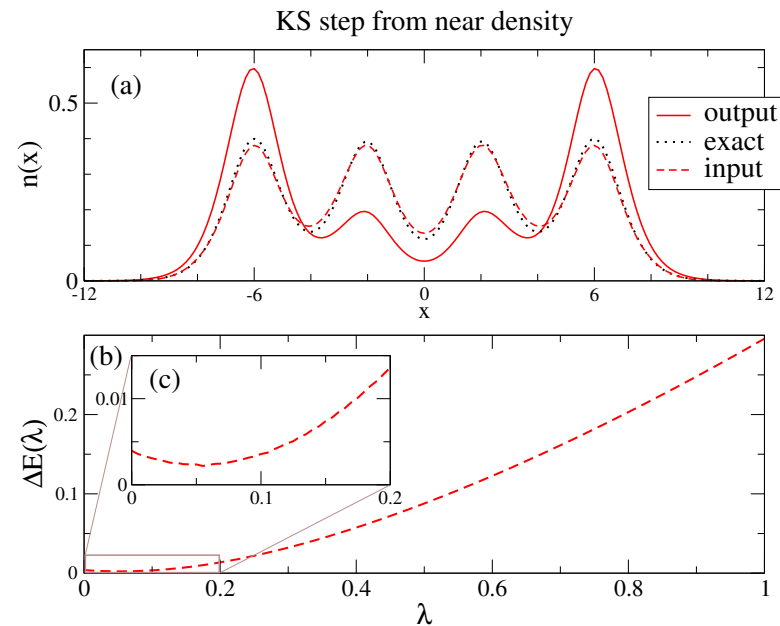


FIG. 8. Taking a second step in the KS scheme for a strongly correlated system (H_4 with $R = 4$). Panel (a) shows the input density which is near to the exact density (the $\lambda = 42\%$ density of the NI input density of Fig. 7) and the resulting output density, which is far from the ground-state.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

No of iterations vs b

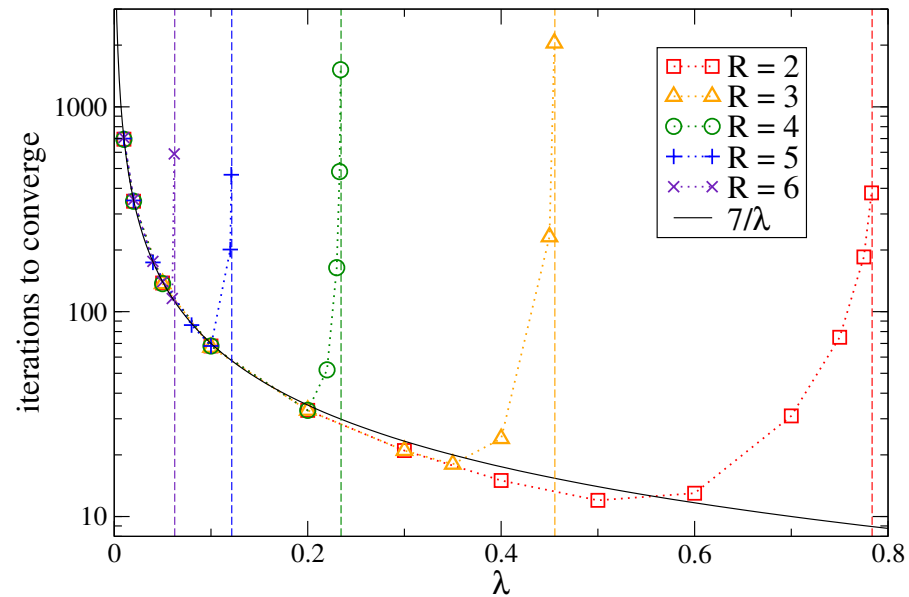


FIG. 10. The number of iterations required to converge an LDA calculation to $\eta < 10^{-8}$ (12), as a function of λ , for various bond-lengths R of the H_2 molecule, starting with an initial density of H^- on the left atom. The asymptotic form for small λ can be well-approximated by $7/\lambda$ for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

Convergence vs bond length

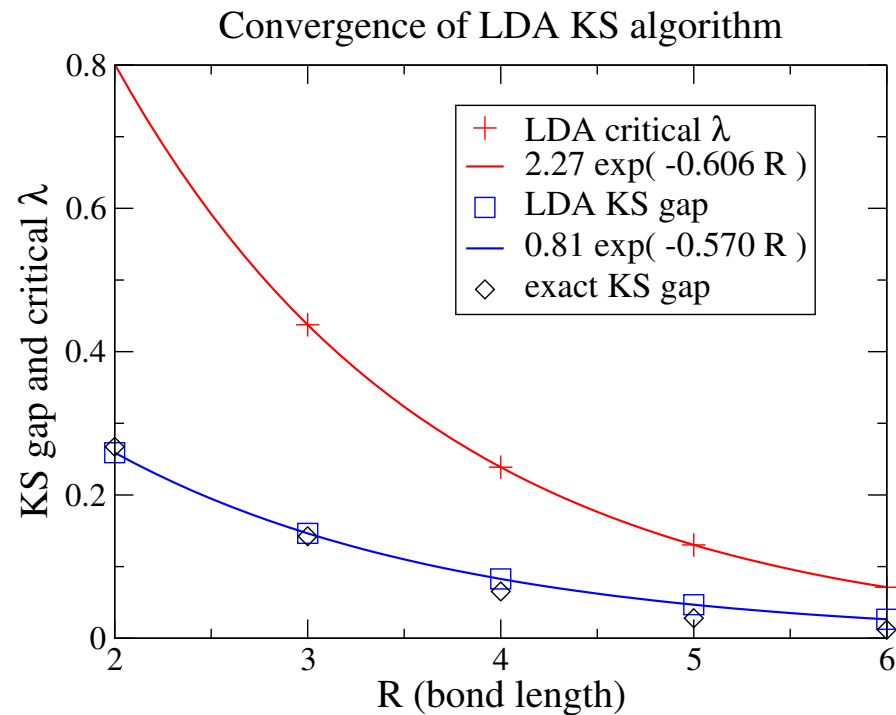
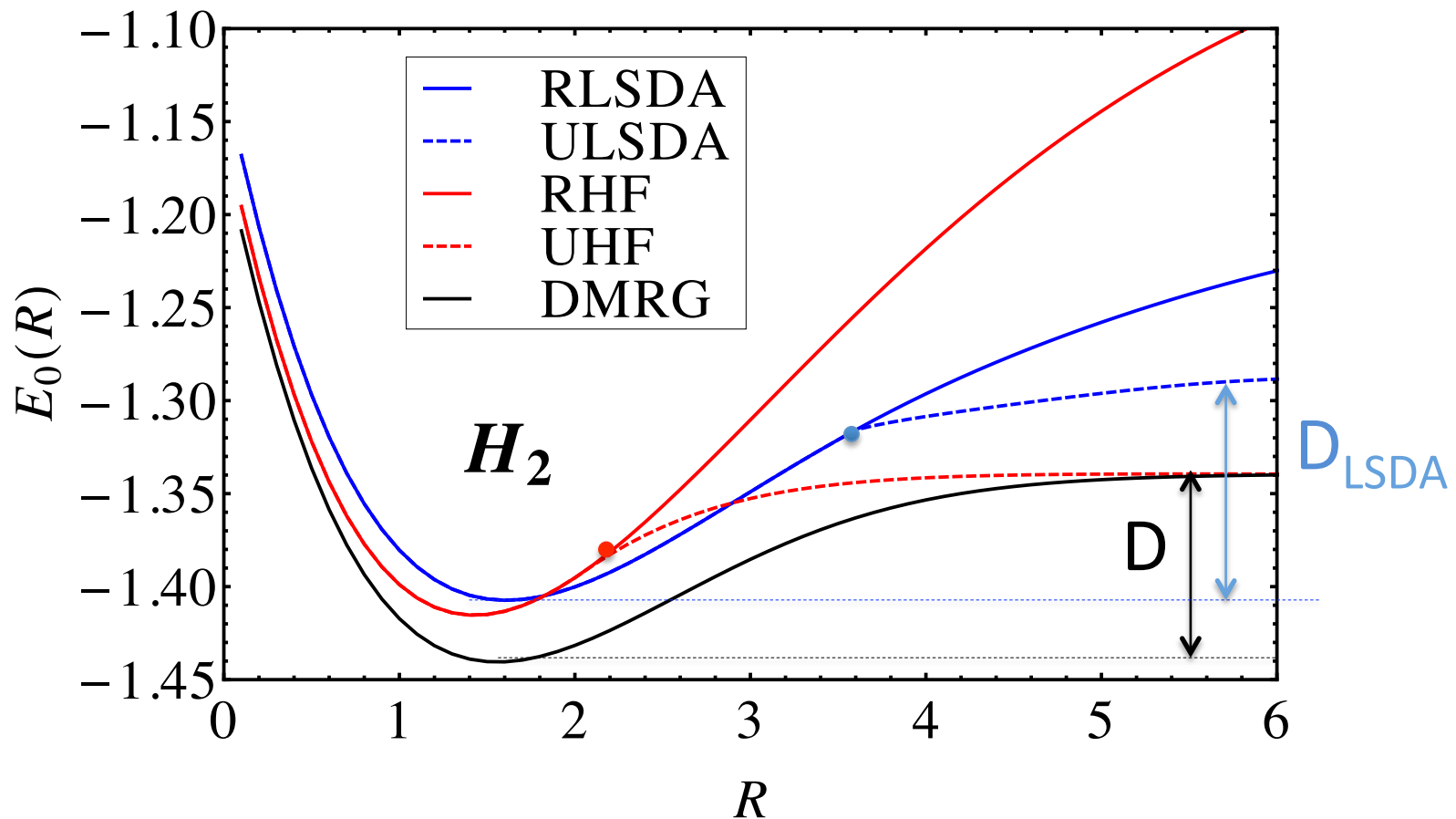


FIG. 11. Plotting the convergence-critical λ for an LDA calculation, as a function of the bond length R of a stretched hydrogen molecule, starting with the exact H^- density on one atom, as well as KS gaps for both the LDA and exact systems.

Prototype of Strong/static correlation



Summary

- Part I: See arXiv for *Companion to DFT*.
- Part II: Have a new tool for studying KS DFT in 1d, especially good for strong correlation.
 - Relies on efficiency of DMRG in 1d.
 - Can get to thermodynamic limit.
 - Have shown KS equations can always be made to converge (with exact functional).
 - Convergence slows with strength of correlation.
- Thanks to US DOE for funding.