Exact Solution to 1D Hydrogen, Hubbard Model, and Time-Dependent Density Functional Theory

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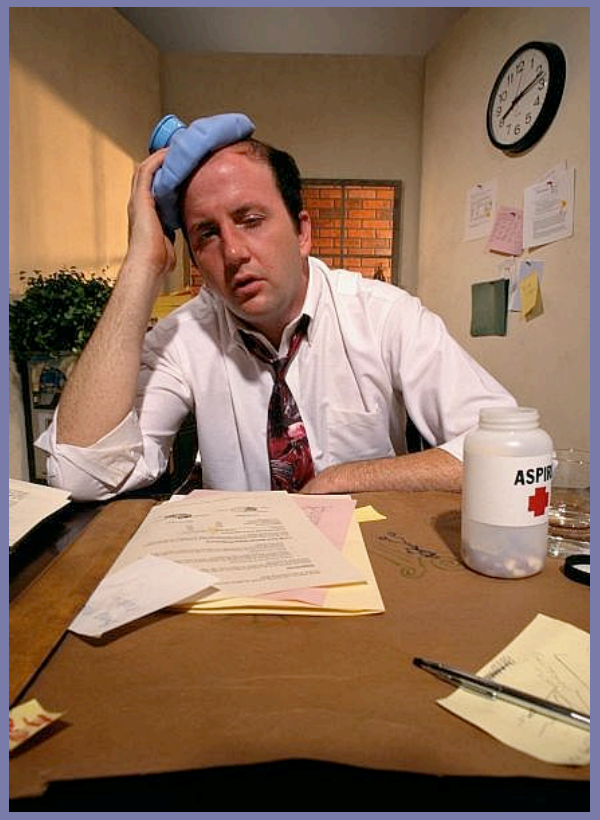
The Big Picture

- Predictive quantum many-body simulations of atoms, molecules, nano-systems, and bulk materials
- Ground-state: geometry, energy
- Excited-state: optical response, transport
- This requires big computers: DFT, GW, etc.
- But these methods are not perfect. . .

Headaches for DFT

- Self-interaction
- Long-ranged Coulomb tails
- Multi-reference (Maybe even a problem for GW)
- The Hydrogen atom!
- Stretched bonds.
- Dissociation.



Why Study Exact Model Systems

- Improving understanding
- Challenging our prejudices
- Examining features that are difficult to observe experimentally

1D Contact-Interaction

$$v_I(x_1 - x_2) = \lambda\delta(x_1 - x_2)$$

- Scales as the Coulomb interaction
- Short-ranged
- Exact-exchange DFT and HF theory are identical and are explicit theories in the particle density
- Used as a model interaction in strongly-correlated physics and for dense matter
- Many-body physics dominated by hard to model correlation effects

Diracium: One-Dimensional Helium

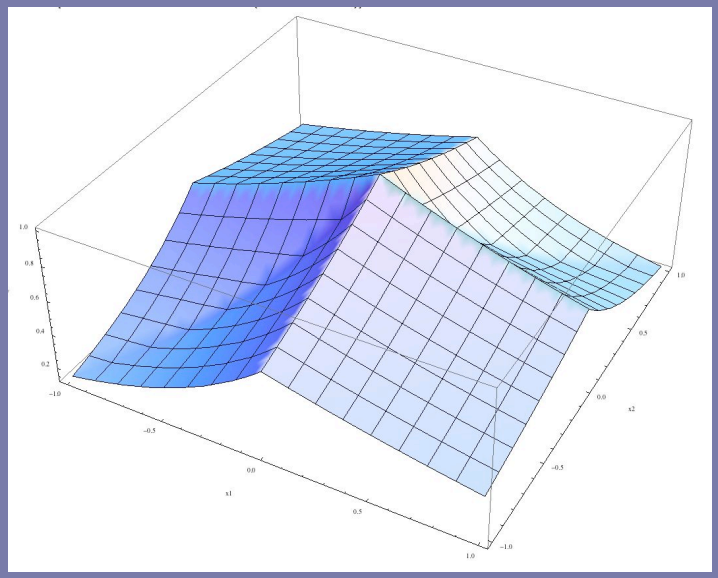
$$\hat{H} = \left[-\frac{1}{2}\frac{d^2}{dx^2{}_1} - \frac{1}{2}\frac{d^2}{dx^2{}_2} + \lambda\delta(x_1 - x_2) - Z\delta(x_1) - Z\delta(x_2) \right]$$

$$\hat{H}\Psi(x_1, x_2, \sigma_1, \sigma_2) = E\Psi(x_1, x_2, \sigma_1, \sigma_2)$$

- One-dimensional analog of Helium
- Atomic units
- x's denote position variables
- σ's denote spin-like labels, collinear spin
- The ground state is a singlet in spin
- Fully interacting system at λ=1
- Exactly solvable numerically
- *C. Rosenthal, J. Chem. Phys. 55, 2474 (1971)*

Method of Exact Solution

- Momentum space representation
- One-dimensional integral equation
- Gauss-Legendre integration
- Eigenvalue problem
- Search for solution with eigenvalue 1



Diracium:LDA Approach

- Effective single-particle equation
- Easy to handle numerically
- Stays bound where exact exchange unbinds
- Shooting method
- Self-consistency

Constructing a Local Density Functional

- $E_{HXC}^{LDA}[n]$ should give exact results when applied to a uniform interacting gas.
- This is the 1D delta-interacting Fermion system
- $E_{HXC}^{LDA}[n]$ is parameterized and written as an explicit functional of the density.

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Y.E. Kim, A.L. Zubarev Physics Letters A 327 397–403 (2004) Phys. Rev. A 70 033612 (2004).
Astrakharchik G E, Blume D, Giorgini S and Pitaevskii L P Phys. Rev. Lett. 93 050402 (2004).
Gao Xianlong, Marco Polini, M. P. Tosi, Vivaldo L. Campo, Klaus Capelle, and Marcos Rigol Physical Review B 73 165120 (2006).

Deltium: One-Dimensional Uniform Reference System

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\frac{d^2}{dx_i^2} + \lambda\sum_{i<j}\delta(x_i - x_j)$$

- Uniform system of N fermions in length L
- This model can be solved exactly using Bethe Ansatz methods.
- Perturbation theory in high density
- Renormalization group analysis in low density
- *M. Gaudin, Phys. Lett. 24A, 55 (1967).*
- *W. I. Friesen and B. Bergersen, J. Phys. C 13, 6627 (1980).*

Our Approximate Local Density Correlation Functional

$$E_{HX_C}^{LDA}[n,\zeta] = \int_{-\infty}^{\infty} dx\, n(x)\varepsilon_{HXC}(n(x))f(\zeta(x))$$

$$\varepsilon_H^{HD}(n) = \frac{\lambda}{2}n$$

$$\varepsilon_X^{HD}(n) = -\frac{\lambda}{2}n\left(1+\varsigma^2\right)$$

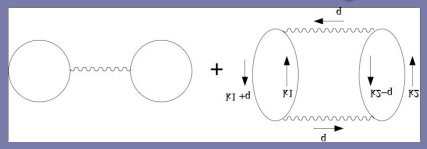
- Only opposite spins feel interaction to first order

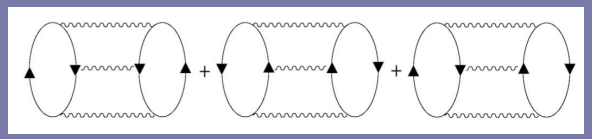
Our Approximate Local Density Correlation Functional

$$\varepsilon_C^{HD}(n) = -\frac{\lambda^2}{24} + \frac{\lambda^3 \zeta(3)}{2\pi^4 n} - \frac{\lambda^4 3\zeta(3)}{4\pi^6 n^2} + \ldots$$

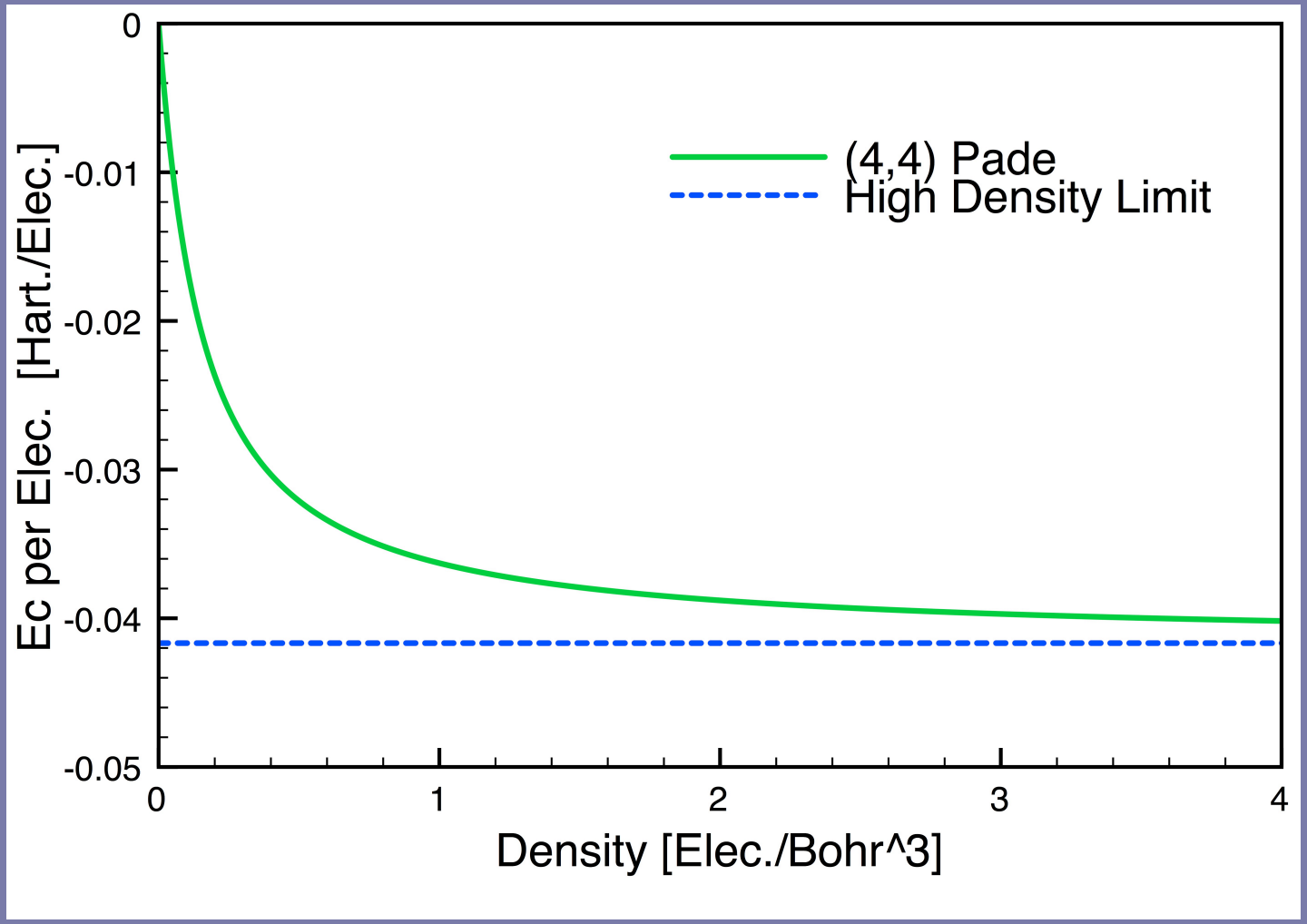
$$\varepsilon_C^{LD}(n) = -\frac{\lambda n}{4} + \frac{n\pi^2}{8} - \frac{n^2 2\pi^2 \ln 2}{3\lambda} + \ldots$$

- (4,4) Padé for numeric reasons
- Correct in both the high density and low density limits.
- High density: exchange-like
- Low density: kinetic-like





Deltium: Local Density vs. Bethe Ansatz Results



Exact-Exchange Kohn-Sham Equation

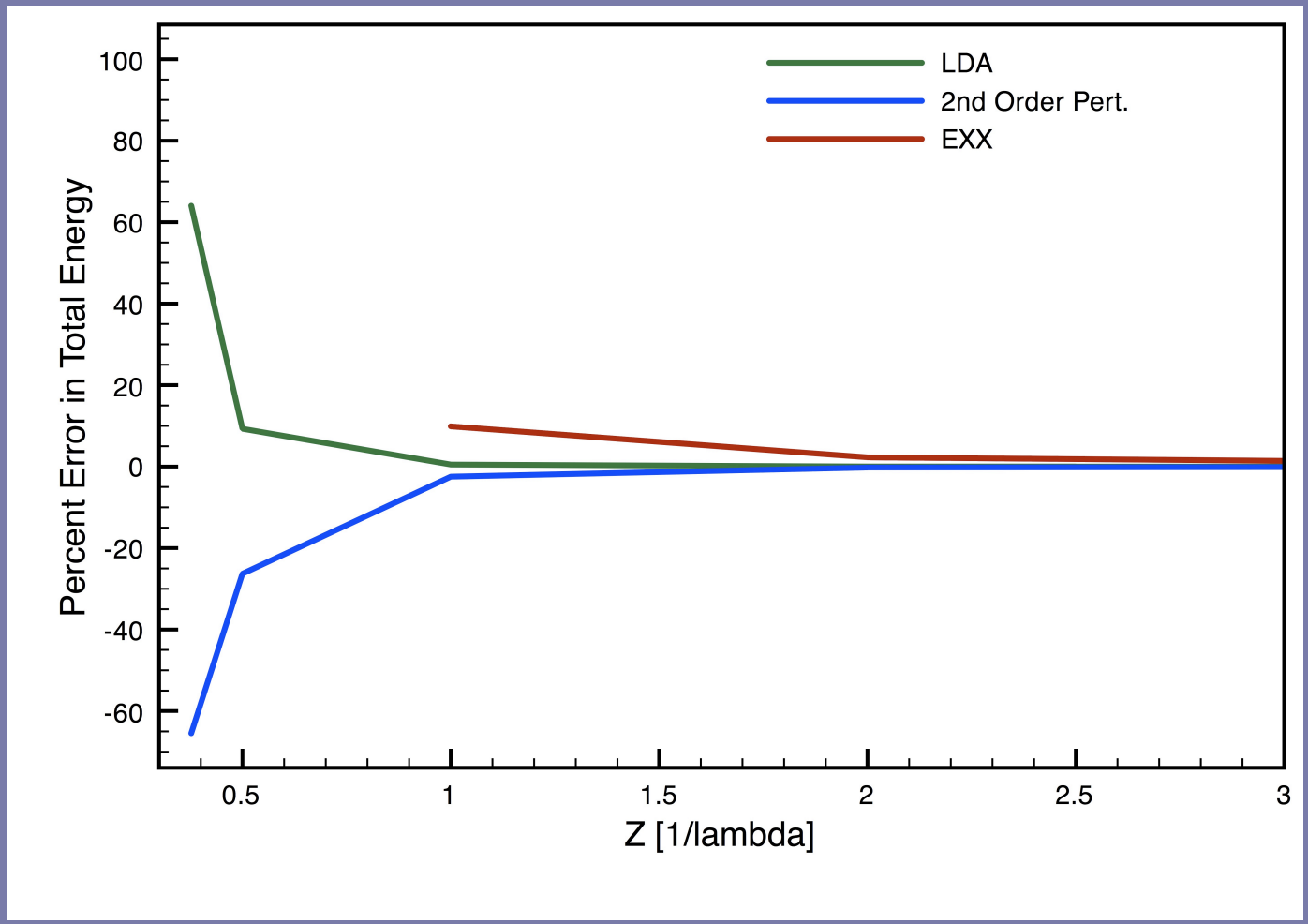
$$\left[-\frac{1}{2}\frac{d^2}{dx^2}+\lambda\,|\,\Phi_{KS}(x)\,|^2\,-Z\delta(x)\right]\Phi_{KS}(x)=\varepsilon_{KS}\Phi_{KS}(x)$$

$$\varepsilon_{KS}=-\frac{1}{2}\left(Z+\frac{\lambda}{2}\right)^2$$

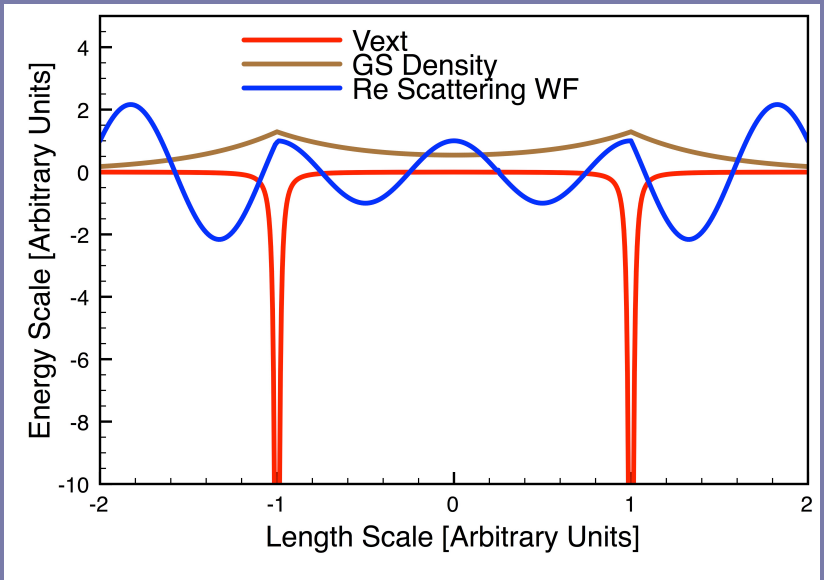
$$E_{EXX}=-Z^2\left(1-\frac{1}{2}\left(\frac{\lambda}{Z}\right)+\frac{1}{12}\left(\frac{\lambda}{Z}\right)^2\right)$$

- Typically, exact-exchange must be done numerically, but here we have an analytic result.
- Accurate for large Z
- Equivalent to Hartree Fock for this interaction
- Ionizes too easily

Errors in the Total Energy for Diracium



One-Dimensional Contact-Interacting Hydrogen (H_2)



- Admits exact numeric results.
- Reduces to known limits in the separate and united atom cases.
- Has a finite number of bound states.
- Allows for continuum solutions.
- Bonding and anti-bonding solutions.
- Self-correlation errors

Exact Results for 1D H_2

$$\hat{H} = -\tfrac{1}{2}\sum_{i=1}^{2}\frac{d^2}{d^2 x_i} + \lambda\delta(x_1 - x_2) - Z\sum_{i=1}^{2}\delta(x_i - a) - Z\sum_{i=1}^{2}\delta(x_i + a)$$

$$when\ \lambda = 0,\ \varepsilon_{\pm} = -\tfrac{1}{2}k_{\pm}^2$$

$$with\ k_{\pm} = Z + \tfrac{1}{2a}LambertW\left(\pm 2aZ\exp(-2aZ)\right)$$

Bonding and anti-bonding non-interacting orbitals

Non-interacting Two-Particle Solutions

State	1	2	Space	Spin	Interaction	E_0
S_0	S↑	S↓	Symmetric	Antisymm.	λ	$2\varepsilon_0$
S_1	S↑	A↓	Symmetric	Antisymm.	λ	$\varepsilon_0 + \varepsilon_1$
S_2	A↑	A↓	Symmetric	Antisymm.	λ	$2\varepsilon_1$
T_1	S↑	A↑	Antisymm.	Symmetric	0	$\varepsilon_0 + \varepsilon_1$

Exact EXX GS Solution

$$\phi_{EXX}(x) = \begin{cases} \sqrt{\frac{1-m}{2m-1}}\sqrt{\frac{2\varepsilon}{\lambda}}\,JacobiNC\left[\sqrt{\frac{2\varepsilon}{2m-1}}x, m\right], |x| < a \\ \sqrt{\frac{2\varepsilon}{\lambda}}\,Csch\left[\sqrt{2\varepsilon}x + x_0\right], |x| > a \end{cases}$$

- x_0 and m determined through continuity and discontinuity of the first derivatives at each well.
- ε determined through the unitary normalization of the wave-function.
- Note that $1/2 < m \leq 1$

Time-Dependent DFT in the Linear Response Formalism

- Method to give excited states in DFT
- Identify excited states with poles of the density response function
- Not well understood and difficult to improve upon
- Key inputs: ground-state result and f_{HXC}
- Adiabatic versus non-adiabatic
- A convenient scheme to extract excitation energies from ground-state orbitals
- Depends on the quality of the ground-state orbitals and f_{xc}

The Correlation Kernel: f_C

$$f_{HXC,\sigma\tau}^{ALDA}(x,x') = \frac{\delta^2}{\delta n_\sigma(x)\,\delta n_\tau(x')} E_{HXC}^{LDA}[n,\zeta]$$

$$n\varepsilon_C^{HD}(n) = -\frac{\lambda^2}{24}n + \frac{\lambda^3\zeta(3)}{2\pi^4} - \frac{\lambda^4 3\zeta(3)}{4\pi^6 n} + \ldots$$

- High density limit ($d^2/dn^2\, n\, \varepsilon_c$) not available in older LDA
- Third order contribution to $n\, \varepsilon_c$ must be accurate
- Adiabatic Approximation
- Reparameterized LDA needed

Two State Solution

$$\omega_S = \sqrt{(\varepsilon_1 - \varepsilon_0)\left[(\varepsilon_1 - \varepsilon_0) + 2\left(K_{\uparrow\uparrow} + K_{\uparrow\downarrow}\right)\right]}$$

$$\omega_T = \sqrt{(\varepsilon_1 - \varepsilon_0)\left[(\varepsilon_1 - \varepsilon_0) + 2\left(K_{\uparrow\uparrow} - K_{\uparrow\downarrow}\right)\right]}$$

$$K_{\sigma\tau} = \lambda(1 - \delta_{\sigma\tau}) \int_{-\infty}^{\infty} dx\, \phi_0^2(x)\phi_1^2(x)$$

$$+ \int_{-\infty}^{\infty} dx\, \phi_0^2(x)\phi_1^2(x) f_C(x, x', \omega)\phi_0^2(x')\phi_1^2(x')$$

Ignores continuum

Exact Solution

- Momentum space-representation
- Set of one-dimensional integral equations
- Entire bound-state spectrum calculable
- *R.J. Magyar Phys. Rev. B 79, 195127 (2009)*

Trace Functions

$$G_1(k) = \int_{-\infty}^{\infty} dy \exp(iky)\left[\psi(a,y) + \psi(-a,y)\right]$$

$$G_2(k) = i\int_{-\infty}^{\infty} dy \exp(iky)\left[\psi(a,y) - \psi(-a,y)\right]$$

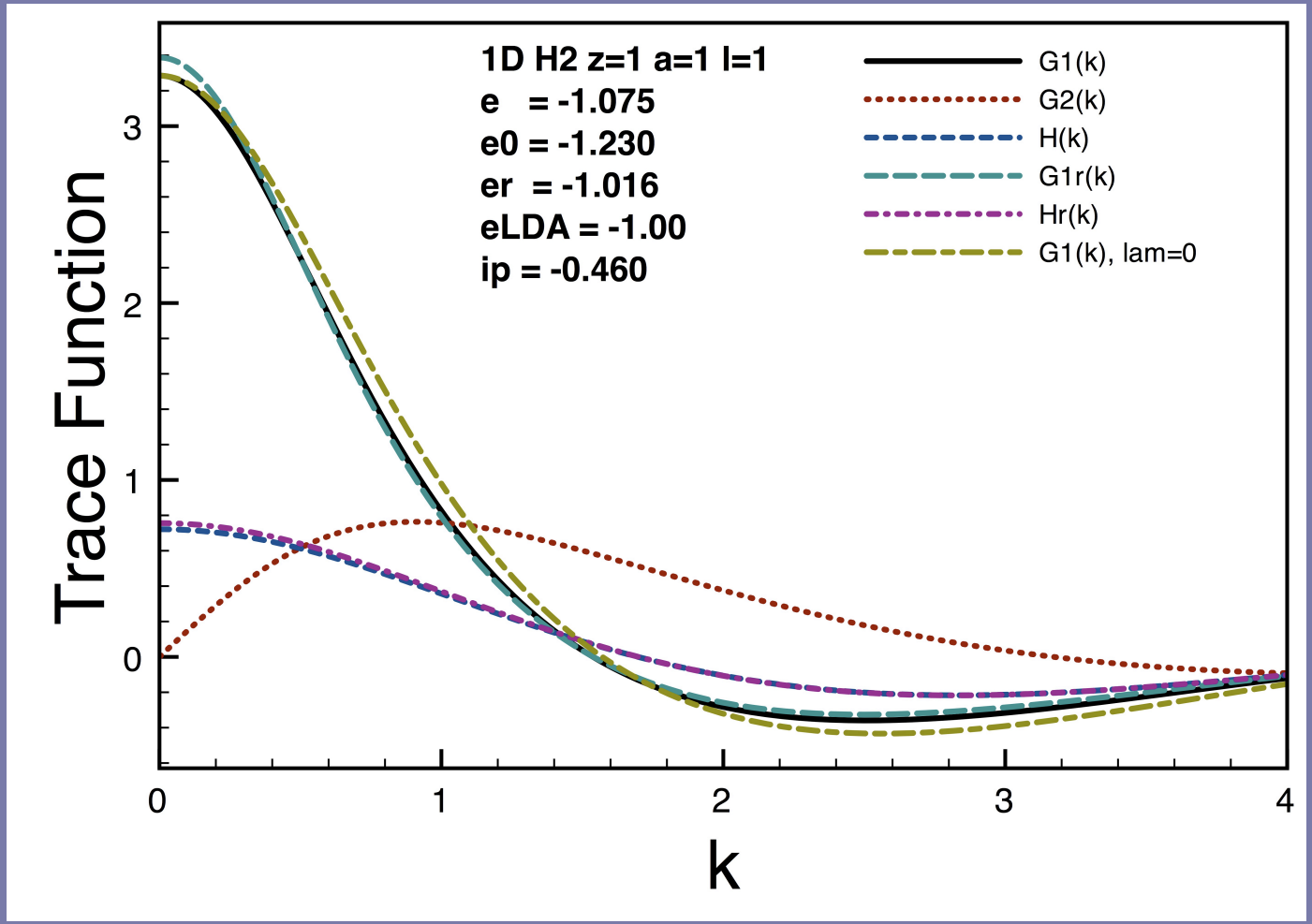
$$H(k) = \int_{-\infty}^{\infty} dy \exp(-iky)\psi(y,y)$$

Real Functions.

Exact and broken symmetries.

$G_2(k) \neq 0$ for the ground state

The Trace Functions



The Exact Numeric Solution

$$\begin{pmatrix} F_S \\ F_A \\ H \end{pmatrix} = \mu(p) \begin{pmatrix} M_{11} & M_{12} & \lambda M_{13} \\ M_{21} & M_{22} & \lambda M_{23} \\ M_{31} & M_{32} & 0 \end{pmatrix} \begin{pmatrix} F_S \\ F_A \\ H \end{pmatrix}$$

- Gauss-Legendre integration
- Matrix equation
- Oscillating integrands
- Ugly integral with a branch cut is handled numerically along the cut but probably can be reduced to known high order elliptical integrals
- Recursive iteration
- Search for p

Oscillating Integrals and the Gauss-Legendre Scheme

$$\int_0^\infty dk \frac{\cos(k)}{k^2 + p^2} G(k)$$

$$G(k) \approx \frac{\cos(k)}{k^2 + p^2/2}$$

- Asymptotic decay
- Break integration into regions π/2 wide
- Use Gauss-Legendre scheme in each region
- Weigh the number of points per region using approximate integral value of the region relative to the next.

The Density

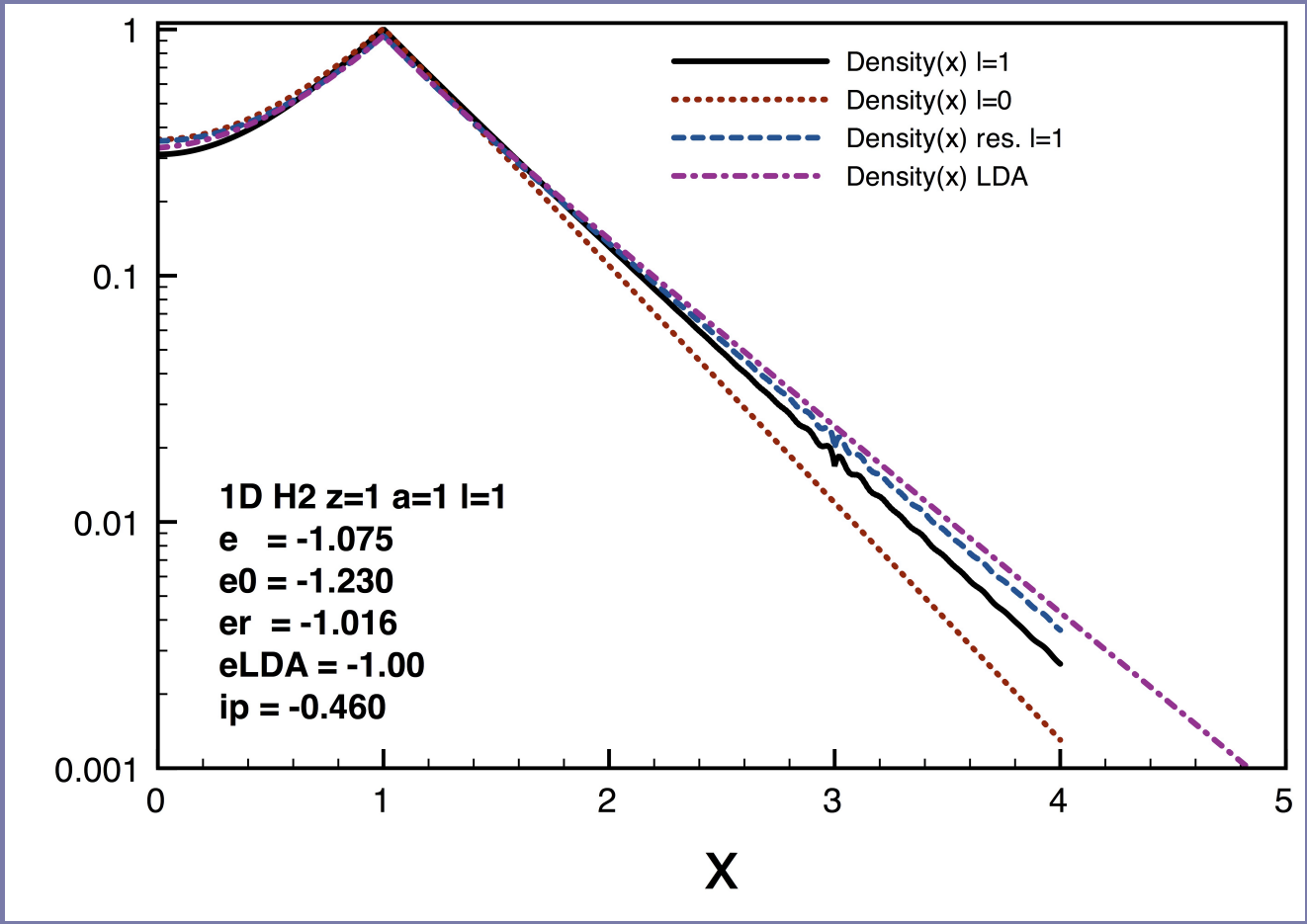
$$u_c(x,k_1) = \int_{-\infty}^{\infty} dk_2\, \Phi(k_1,k_2)\cos(x\,k_2)$$

$$u_s(x,k_1) = \int_{-\infty}^{\infty} dk_2\, \Phi(k_1,k_2)\sin(x\,k_2)$$

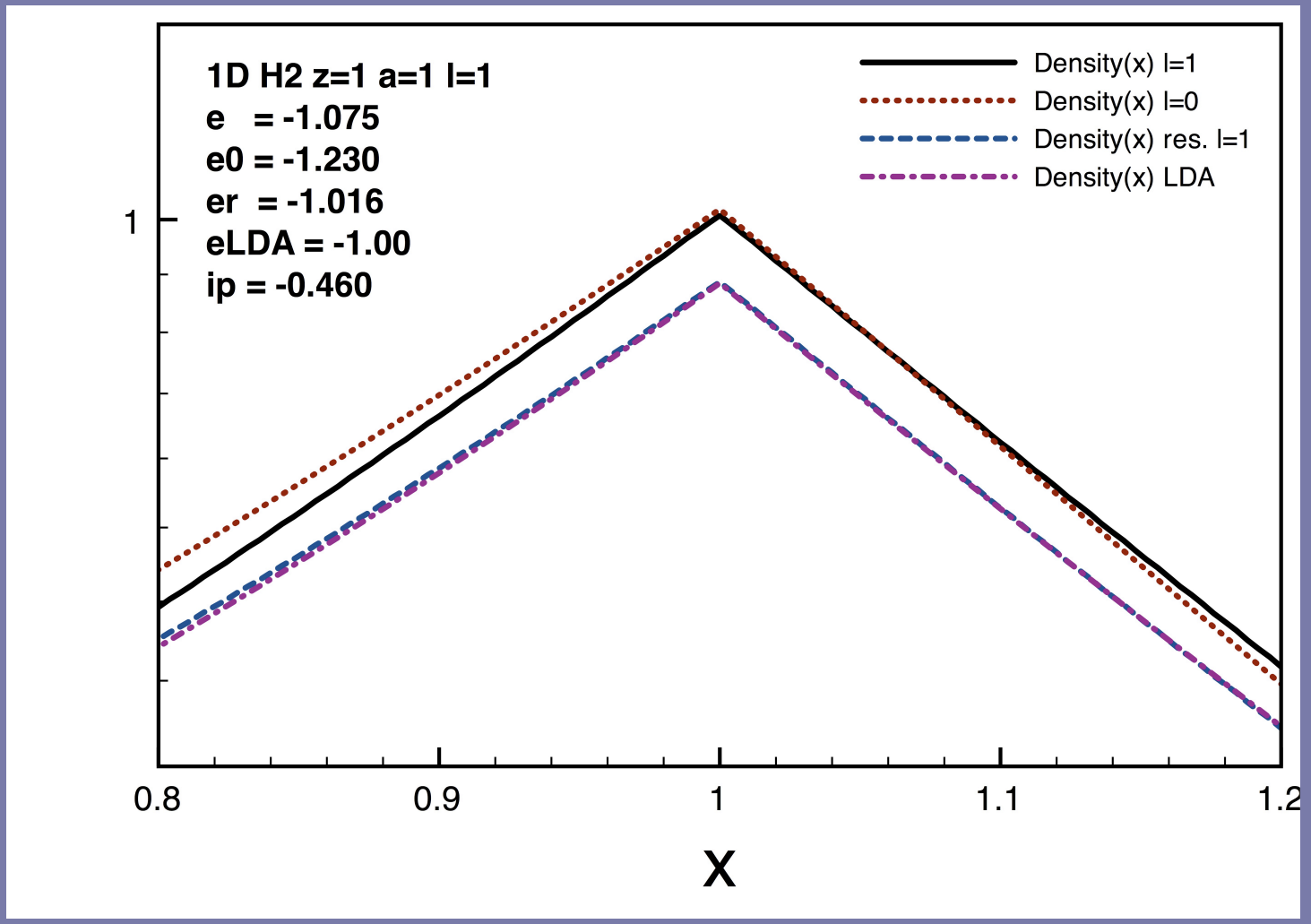
$$\rho(x) = \frac{1}{4\pi^3}\int_{-\infty}^{\infty} dk_1 \left(u_c^2(x,k_1) + u_s^2(x,k_1)\right)$$

- Double numerical integration
- Aliasing
- Asymptotes

Log of the Density



Near Cusp


1D H2 z=1 a=1 l=1
e = -1.075
e0 = -1.230
er = -1.016
eLDA = -1.00
ip = -0.460
Density(x) l=1
Density(x) l=0
Density(x) res. l=1
Density(x) LDA
1
0.8
0.9
1
1.1
1.2
X

2-Site Hubbard Model

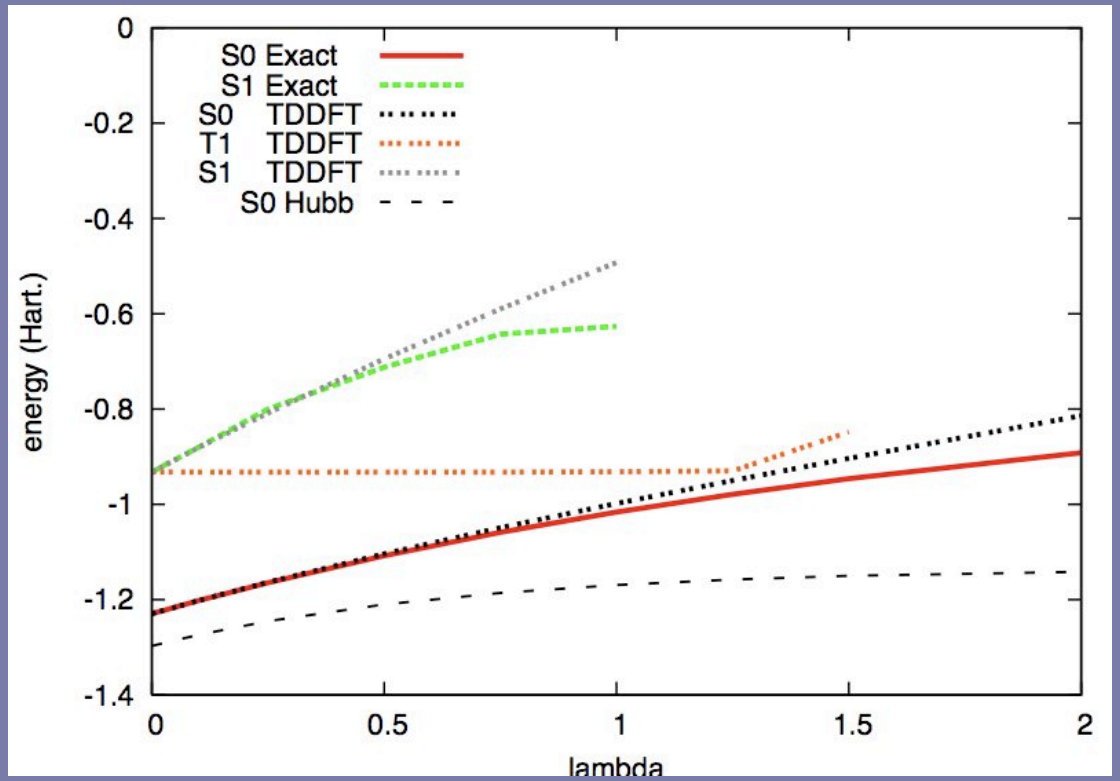
$$E = \begin{cases} 2\varepsilon + \frac{U}{2} - \frac{1}{2}\sqrt{16t^2 + U^2} \\ 2\varepsilon + U \\ 2\varepsilon + \frac{U}{2} + \frac{1}{2}\sqrt{16t^2 + U^2} \end{cases}$$

$$t = \tfrac{1}{2}\int dx \phi_R(x)\nabla^2\phi_L(x) = \tfrac{1}{4}\left(k_+^2 - k_-^2\right)$$

$$U_\varepsilon(\lambda) \approx 0.500\lambda - 0.163\lambda^2 + 0.017\lambda^3$$

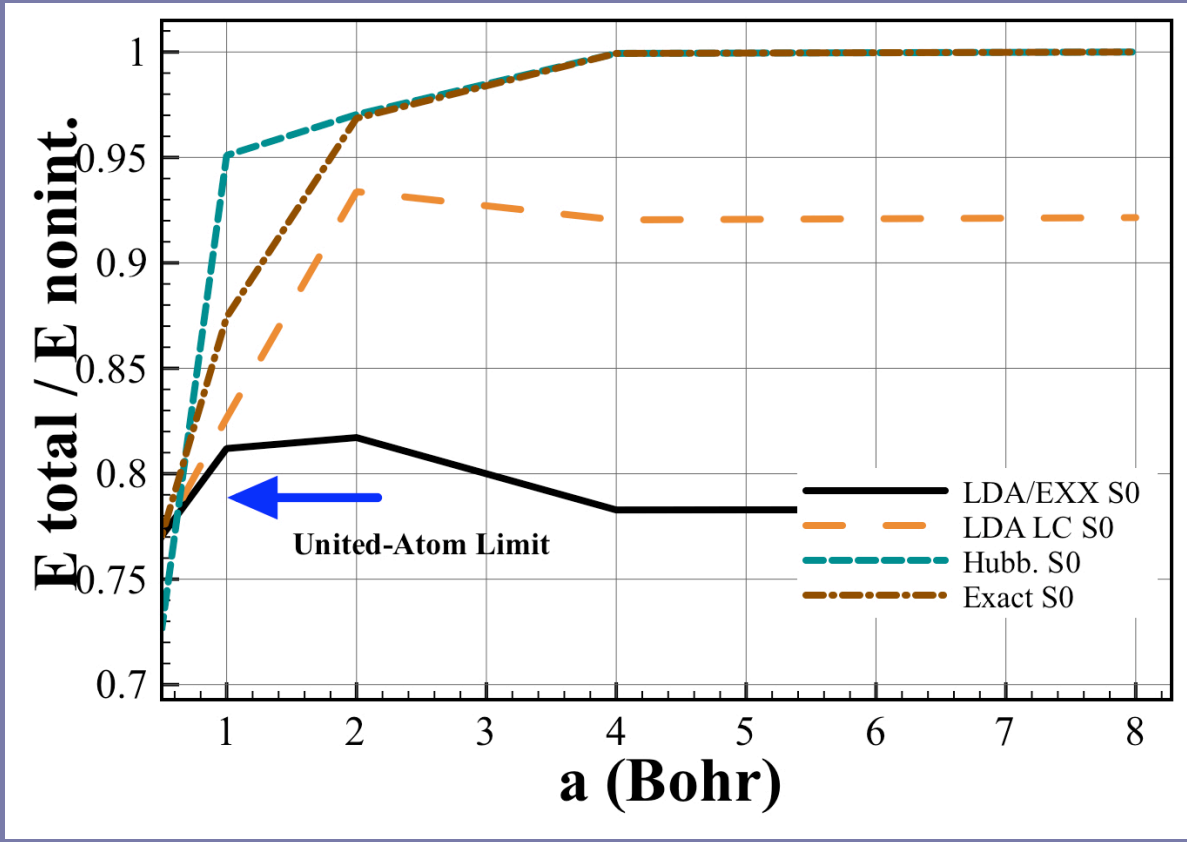
$$E_{S0} = -Z^2 - \frac{4Z^2}{U}e^{-2aZ}\ , a \to \infty$$

TDDFT Results



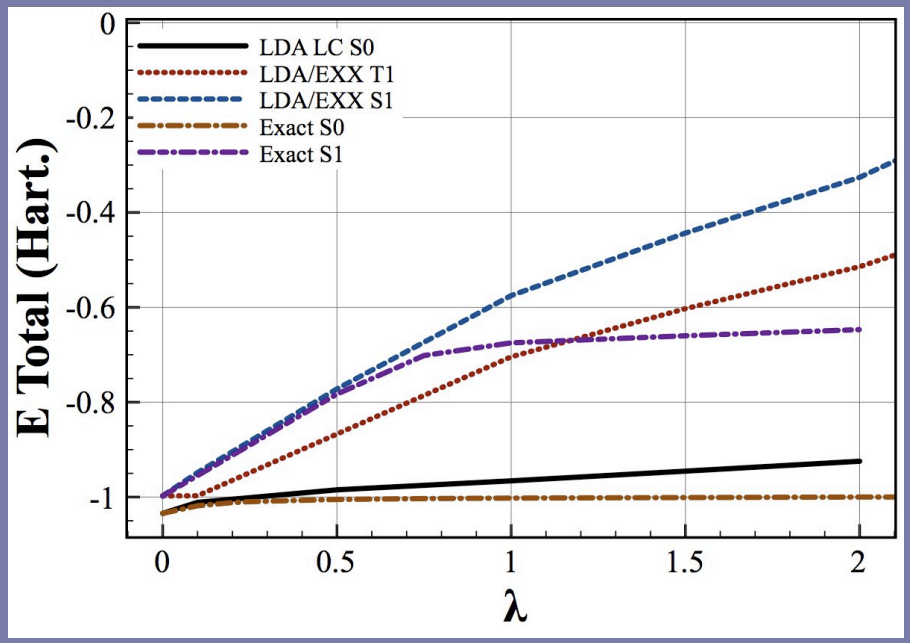
- Z=1, a=1
- Non-adiabatic approximation needed
- Level crossing
- Continuum contribution

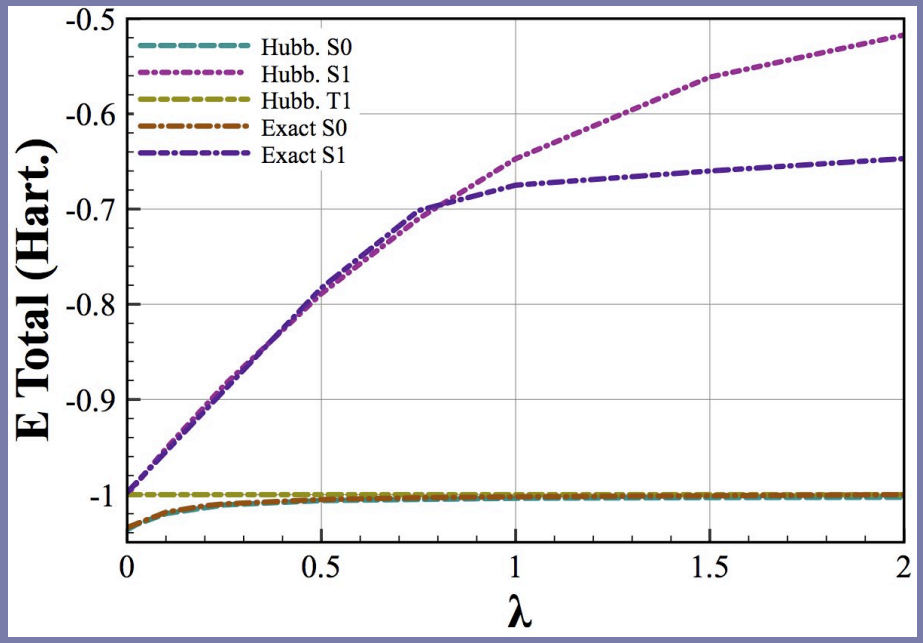
Stretching H_2



- Z=1, λ=1

Separated Limit

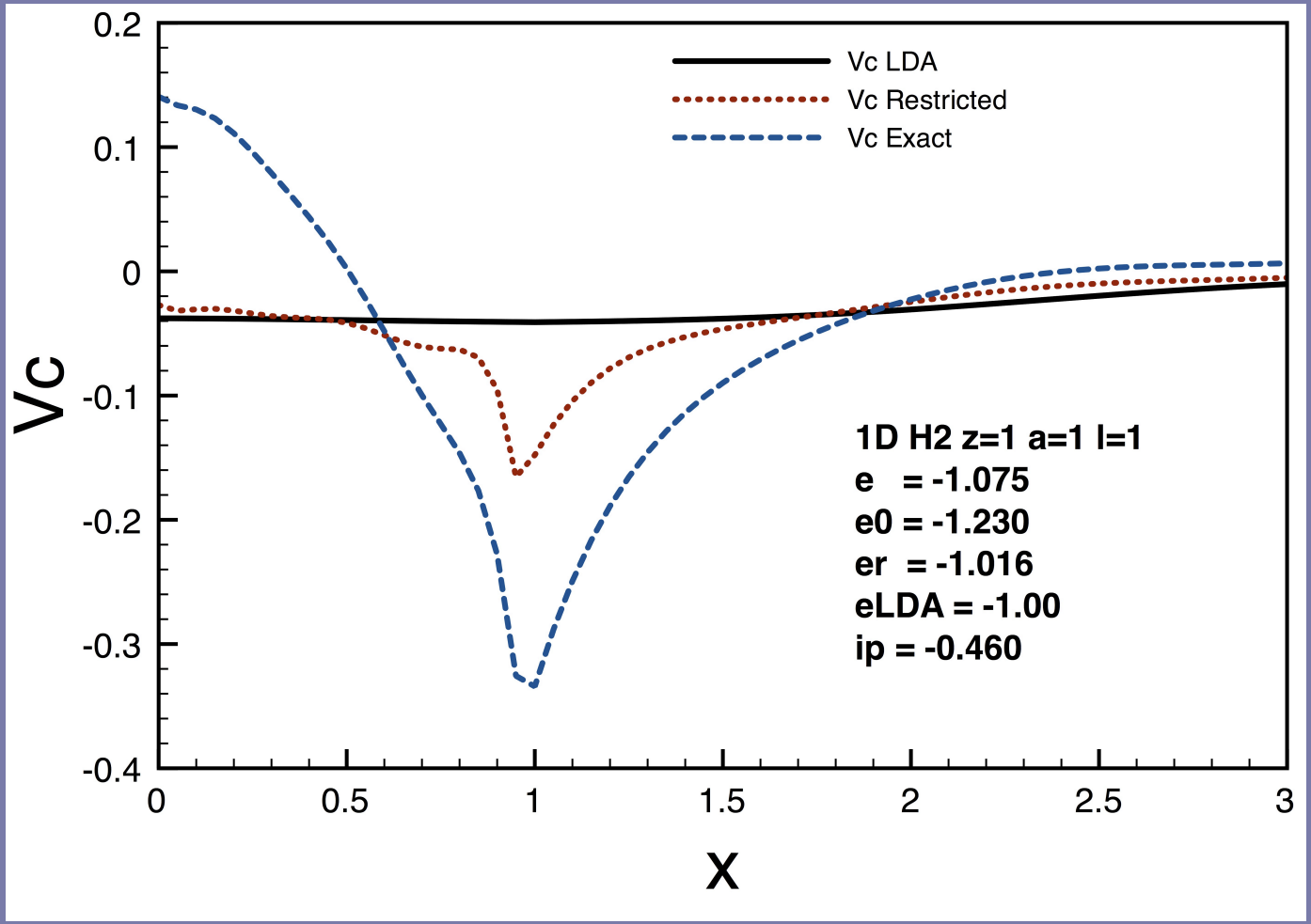




DFT Solution for Ground and Excited Bound States

- United-atom limit accurate
- Two-well limit accurate
- Stretched H_2 limit not well reproduced in LDA

Preliminary Result Alert: Exact KS potential



Time Propagation

$$i\frac{d}{dt}\Phi(k_1,k_2) = -\left(k_1^2 + k_2^2\right)\Phi(k_1,k_2)$$
$$+2\Big[\cos(k_1 a)G_1(k_2) + \cos(k_2 a)G_1(k_1)$$
$$+ \sin(k_1 a)G_2(k_2) + \sin(k_2 a)G_2(k_1) - \lambda H(k_1 + k_2)\Big]$$

The trace functions at the new time step can be calculated from momentum space wave-function.
The system can be perturbed via a vector potential switched on in time.
Depending on boundary conditions, this could be a model for transport.

Continuum Solutions

- Trace functions become complex
- Matrix Equation now real and imaginary terms
- Kappa integral has a modified analytic structure
- Good news is that a continuum range of energies will satisfy the integral equations.

Challenge

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\frac{d^2}{dx_i^2} + \lambda\sum_{i<j}\delta(x_i - x_j) - Z\sum_{i=1}^{N}\sum_{j=1}^{M}\delta\left(x_i - \frac{j}{ML}\right)$$

- Dirac comb with interactions
- Uniform gas of N fermions in length L with M evenly spaced attractive sites
- Can this model be solved exactly using Bethe Ansatz methods?

Conclusions

- Density functional theory is a powerful tool to understand electronic structure even in 1D with non-Coulombic interactions.
- The curious fact that exact-exchange in 1D is a local density functional allows the detailed analysis of correlation.
- With more work, this model can serve as a benchmark case for ideas that aim toward modeling transport.

Many thanks to …

- KITP
- The Organizers
- Sandia National Lab
- January, my wife