Lies my teacher told me: Understanding DFT with the Hubbard dimer

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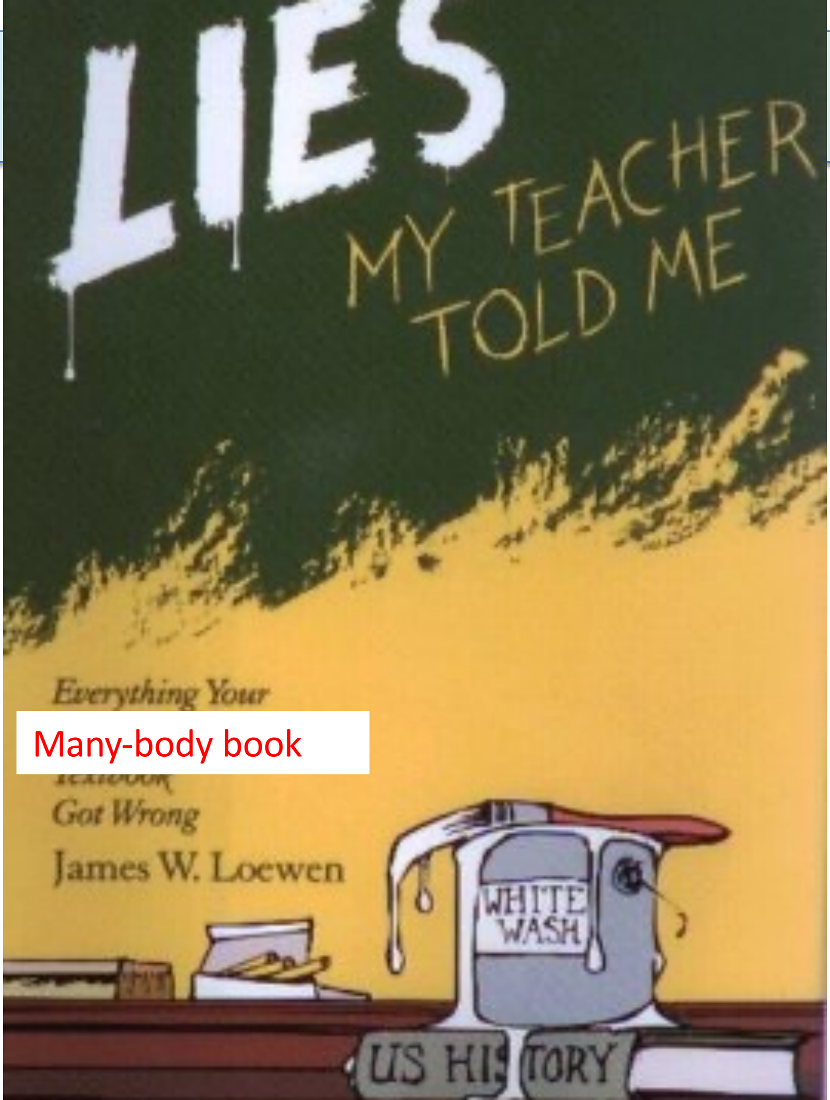


Many-body book

References

- Correl 21 book chapter
- Ground-state review:

The Hubbard dimer: a density functional case study of a many-body problem D J Carrascal D.J., Ferrer, J., Smith, J. *and KB* 2015 *J. Phys.: Condens. Matter* **27** 393001

- Linear-response TDDFT review:

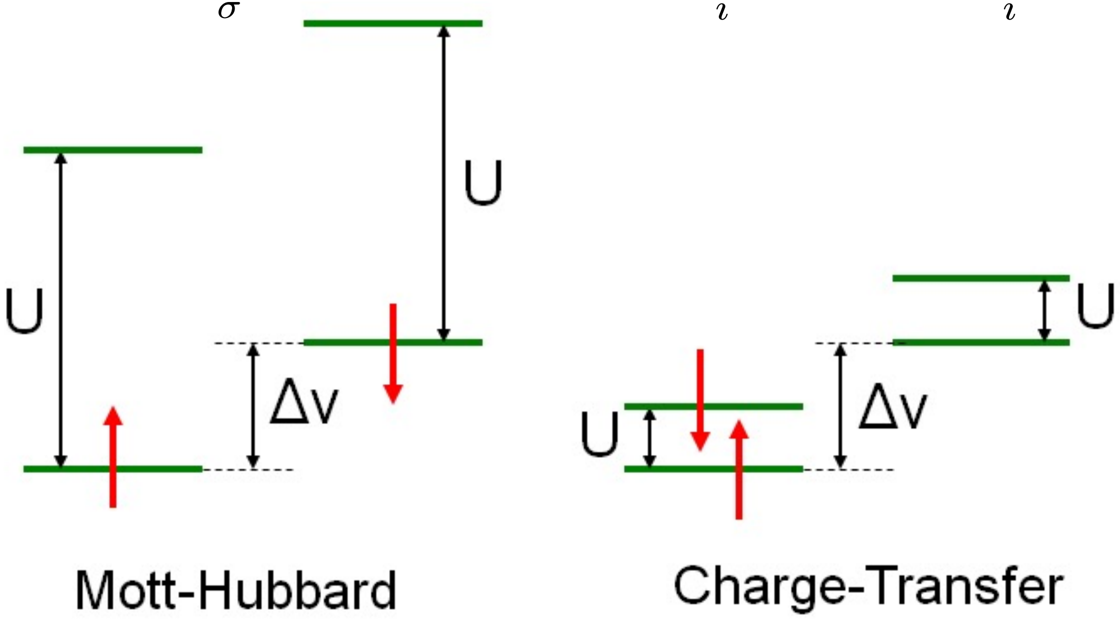
Linear response time-dependent density functional theory of the Hubbard dimer Carrascal, D.J., Ferrer, J., Maitra, N. *and KB.* Linear response time-dependent density functional theory of the Hubbard dimer. *Eur. Phys. J. B* **91,** 142 (2018).

- General intro to DFT in real-space:

DFT in a nutshell, Kieron Burke, Lucas O. Wagner, *Int. J. Quant. Chem.* **113**, 96-101 (2013).

Asymmetric 2-site Hubbard

$$\hat{H} = -t\sum_{\sigma}(\hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} + h.c) + U\sum_{i}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} + \sum_{i} v_i\hat{n}_i$$



E as function of Δv

- E(Δv) is analytic

- Symmetric

$$E = -\sqrt{1+(U/2)^2} + U/2, \qquad \Delta n = 0$$

- Tight-binding

$$E = -\sqrt{1+\Delta v^2}, \quad \Delta n = -2\,\frac{\Delta v}{\sqrt{1+\Delta v^2}} \qquad (U{=}0) \qquad \Delta v = \frac{\Delta n}{\sqrt{4-\Delta n^2}}$$

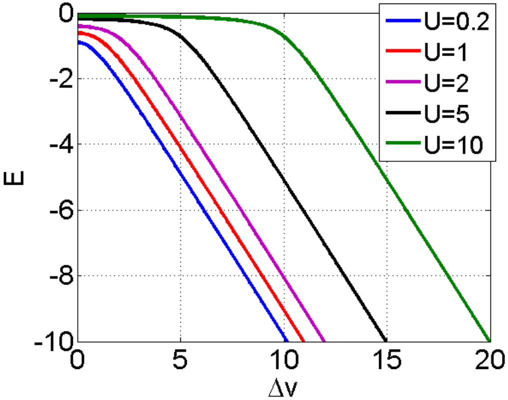
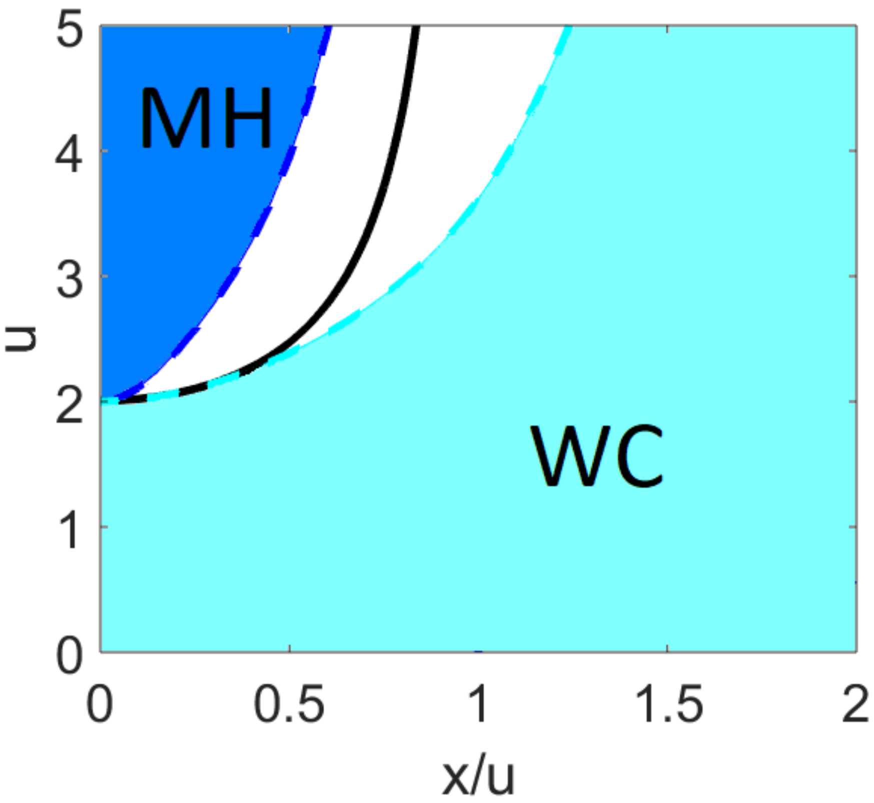


FIG. 2. Exact ground-state energy of the Hubbard dimer as a function of Δv for several values of U. The qualitative behavior changes as Δv passes through U.

Weak and strong correlation



Ground-state DFT

$$\hat{H} = \hat{T} + \hat{V}_{\mathrm{ee}} + \hat{V},$$

$$\hat{H} = -t \sum_{\sigma} \left(\hat{c}^{\dagger}_{1\sigma} \hat{c}_{2\sigma} + h.c. \right) + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \sum_{i} v_i \hat{n}_i \,.$$

HK I

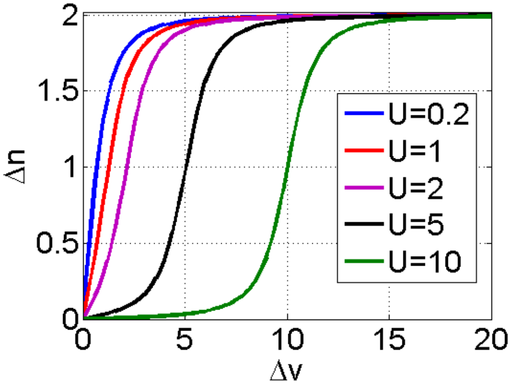


FIG. 3. Ground-state occupation of the Hubbard dimer as function of Δv for several values of U.

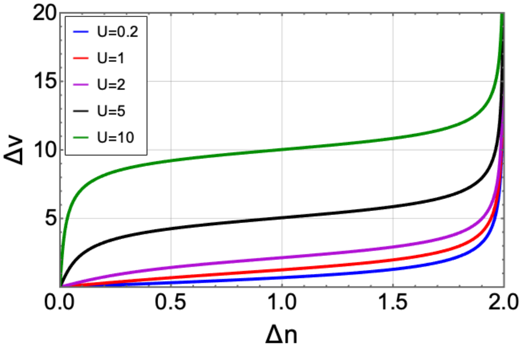


FIG. 4. Ground-state potential difference as a function of Δn for several values of U.

HK II: Part of E is universal

$$F_{\mathrm{U}}(n_1) = \min_{\Psi\rightarrow n_1} \langle\Psi|\hat{T} + \hat{V}_{\mathrm{ee}}|\Psi\rangle = \max_{\Delta v}\left\{E(\Delta v) - \Delta v \Delta n/2\right\}$$

- Simply means F independent of dv, i.e, is the same for every different v

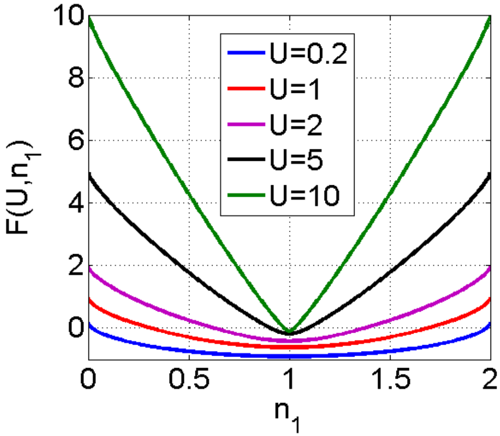


FIG. 5. Universal part of the energy function(al) of a Hubbard dimer as a function of n_1 for several values of U. As U increases, F tends to $U|1-n_1|$.

HK III: Density variational principle

$$E(\Delta v) = \min_{n_1} \left\{ F_{\mathrm{U}}(n_1) + \Delta v \Delta n/2 \right\}.$$

- Euler equation

$$\frac{dF_{\mathrm{U}}(n_1)}{dn_1} - \frac{\Delta v}{2} = 0,$$

KS DFT

- Consider fake unique non-interacting electrons with same density

$$F_{\rm U}(n_1) = T_{\rm S}(n_1) + U_{\rm H}(n_1) + E_{\rm XC}(n_1). \qquad U_{\rm H} = \frac{U}{2}(n_1^2 + n_2^2),$$

- Euler equation implies

$$v_{\rm S,i} = v_i + U n_i + \frac{\partial E_{\rm XC}}{\partial n_i}$$

KS DFT

- Can reconstruct total energy

$$E = T_{\rm S} + U_{\rm H} + E_{\rm XC} + V = \varepsilon - U_{\rm H} + E_{\rm XC} - \Delta v_{\rm XC} \Delta n/2\,,$$

- Given some XC[n], get approximate E for any electronic structure problem

$$F_{U=0}(n_1) = T_{\rm S}(n_1) = -\sqrt{n_1(2-n_1)}.$$

Exact definitions and an approx

$$E_{\mathrm{X}} = \langle \Phi_{\mathrm{S}} | \hat{V}_{\mathrm{ee}} | \Phi_{\mathrm{S}} \rangle - U_{\mathrm{H}}$$

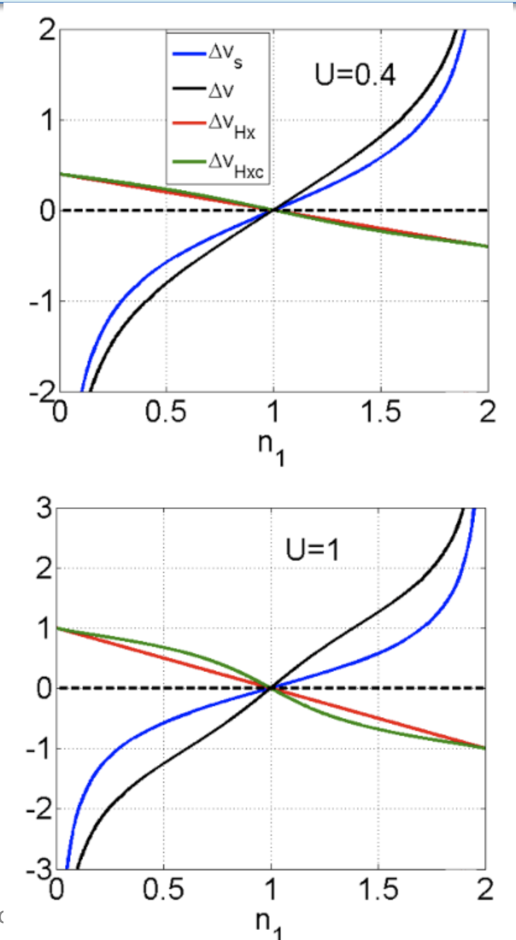
$$E_{\mathrm{C}} = \langle \Psi | \hat{H} | \Psi \rangle - \langle \Phi_{\mathrm{S}} | \hat{H} | \Phi_{\mathrm{S}} \rangle$$

- HF approximation

$$F^{\mathrm{HF}} = T_{\mathrm{S}} + \frac{1}{2} U_{\mathrm{H}}$$

$$E_{\mathrm{XC}}^{\mathrm{HF}} = -U_{\mathrm{H}}/2$$

KS potential components



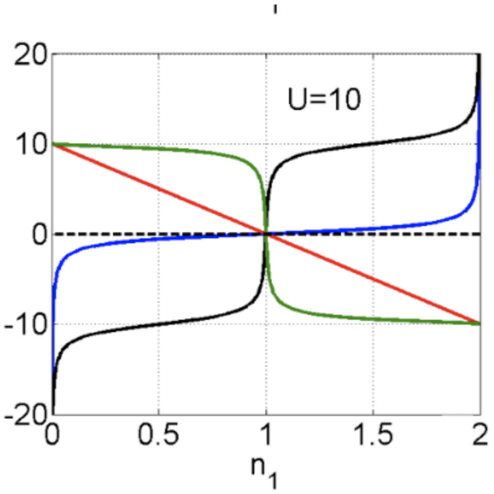


FIG. 7. Plots of Δv_S (blue) and its components, the one-body potential Δv (black), the Hartree plus exchange potentials, $U\Delta n/2$ (red), and the same with correlation added, $U\Delta n/2 + \Delta v_C$ (green) plotted against n_1 for various values of U.

Comments

- Ground-state DFT is a machinery for extracting ground-state electronic energies
- Almost all calculations use KS scheme plus approximate XC
- 99% of all applications of gsDFT are to find E as function of nuclear coordinates
- Even the density can be extracted from E
- Uses about 30% of NSERC's supercomputers

KS equations (1965)

Define *fictitious* non-interacting electrons satisfying:

$$\left\{-\frac{1}{2}\nabla^2 + v_S(\mathbf{r})\right\}\phi_j(\mathbf{r}) = \epsilon_j\phi_j(\mathbf{r}), \qquad \sum_{j=1}^{N}|\phi_j(\mathbf{r})|^2 = n(\mathbf{r}).$$

where $v_S(\mathbf{r})$ is *defined* to yield $n(\mathbf{r})$.

Define T_S as the kinetic energy of the KS electrons, U as their Hartree energy and

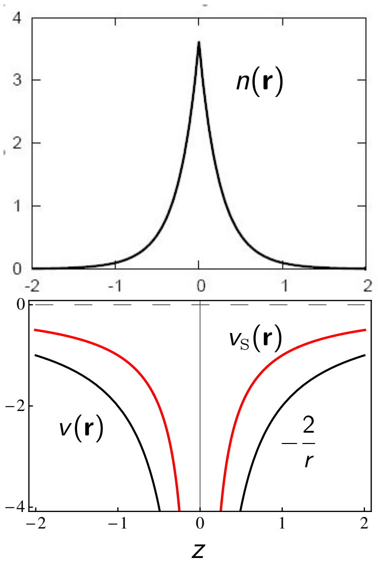
$$\boxed{F = T + V_{\rm ee} = T_S + U + E_{\rm XC}}$$

the remainder is the exchange-correlation energy.

Most important result of exact DFT:

$$v_S(\mathbf{r}) = v(\mathbf{r}) + \int d^3r\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\rm XC}[n](\mathbf{r}), \qquad v_{\rm XC}(\mathbf{r}) = \frac{\delta E_{\rm XC}}{\delta n(\mathbf{r})}$$

Knowing $E_{\rm XC}[n]$ gives closed set of self-consistent equations.



KS energy components

- The KS kinetic energy is the kinetic energy of the KS orbitals

$$T_{\mathrm{S}}[n] = \frac{1}{2} \sum_{i=1}^{N} \int d^3r \, |\nabla \phi_i(\mathbf{r})|^2 \qquad > 0$$

- The Hartree (aka Coulomb aka electrostatic) repulsive self-energy of a charge density is

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \, \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad > 0$$

- The exchange energy is

$$E_{\mathrm{X}} = -\frac{1}{2} \sum_{\sigma} \sum_{\substack{i,j \\ occ}} \int d^3r \int d^3r' \, \frac{\phi^*_{i\sigma}(\mathbf{r}) \phi^*_{j\sigma}(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}') \phi_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \qquad < 0$$

- E_{C} is everything else, $\quad < 0$

$E_C = (T - T_S) + (V_{ee} - U - E_X)$

Basic points

- In general, KS scheme yields E
- No formal meaning for KS eigenvalues
- KS eigenvalues are NOT quasiparticle excitations
- Often, KS DOS interpreteted as spectral function
- Often, this is roughly correct, with largest error at gap
- Exact formula relates E to Eval sum.
- Knowledge of exact Exc does NOT give non-gs properties, eg excitations

Simple points about KS calculations

- The total energy is *not* the sum of the orbital energies:

$$E \neq \sum_{i=1}^{N} \epsilon_i$$

- If some approximation is used for $E_{\rm XC}$, then energy can go *below* the exact ground-state energy.
- Any given formula for $E_{\rm XC}$, no matter where it came from, produces a *non-empirical* scheme for *all* electronic systems.
- The KS scheme, even with the exact functional, yields only E and $n(\mathbf{r})$ (and anything that can be deduced from them).
- In principle, from HK, *all* properties are determined by $n(\mathbf{r})$, but in reality, we only know one really well.

KS properties


MIND THE GAP

Fundamental gap

$$I = E(N-1) - E(N)$$

$$A = E(N) - E(N+1).$$

$$E_g = I - A,$$

$$\epsilon^{\mathrm{HOMO}} = -I,$$

$$E_g = E_{gs} + \Delta_{\mathrm{XC}}$$

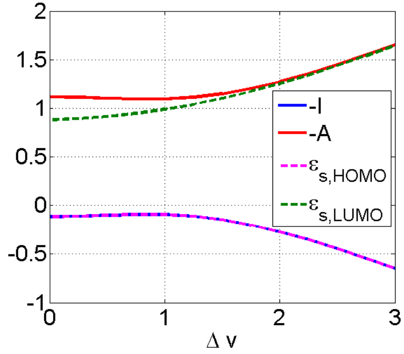


FIG. 11. Plot of $-A$, $-I$, ϵ^{HOMO}, and ϵ^{LUMO} as a function of Δv with $U = 1$ and $2t = 1$.

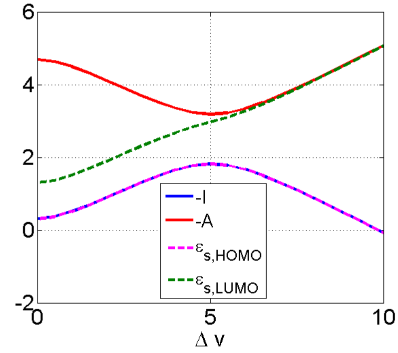


FIG. 12. Plot of $-A$, $-I$, ϵ^{HOMO}, and ϵ^{LUMO} as a function of Δv with $U = 5$ and $2t = 1$.

Spectral functions, real and KS

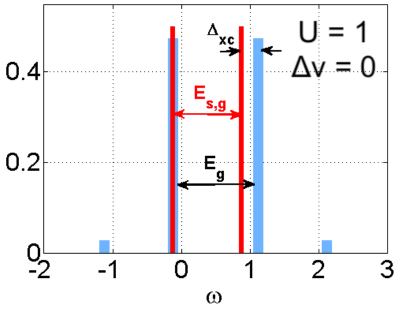


FIG. 9. Spectral function of the symmetric dimer for $U = 1$ and $\Delta v = 0$. The physical MB peaks are plotted in blue, the KS in red. Here $I = 0.1$, $A = -1.1$, and $\varepsilon^{\mathrm{LU}} = 0.9$.

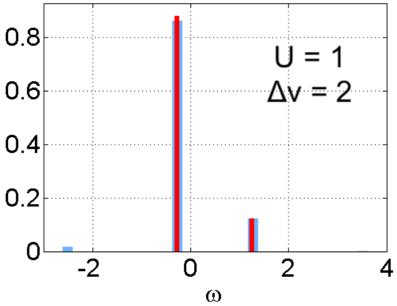


FIG. 11. Same as Fig. 9, but now $U = 1$, $\Delta v = 2$. Here $I = 0.27$, $A = -1.27$, and $\varepsilon^{\mathrm{LU}} = 1.25$.

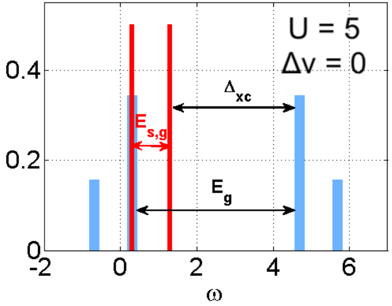


FIG. 10. Same as Fig. 9, but now $U = 5$. Here $I = -0.3$, $A = -4.7$, and $\varepsilon^{\mathrm{LU}} = 1.3$. Note that the KS gap remains unchanged by the alteration of U because $\Delta n = 0$ in both cases.

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

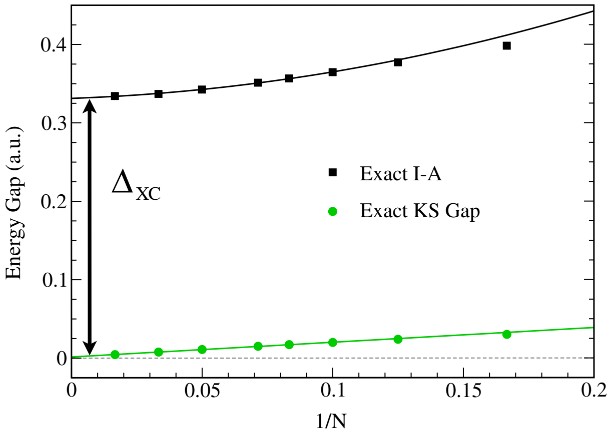


FIG. 3 (color online). Exact gaps for chains of N soft hydrogen atoms with atomic separation $b = 4$ (error bars are less than symbol sizes). The upper curve is a quadratic fit of exact gaps of the largest six systems and extrapolates to a finite value $E_g \simeq 0.33$. The exact Kohn-Sham gaps, in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

Ways to approximate Greens functions

Pina Romaniello

Hubbard Dimer in GW and Beyond

Robert Eder

Green Functions and Self-Energy Functionals

Václav Janiš

Green Functions in the Renormalized Many-Body Perturbation Theory

TDDFT

- Based on very different theorem (RG84)
- Applies to any time-dependent one-body perturbation
- In general, XC potential functional of initial-state and history of density
- Usually start from non-degenerate ground-state, so HK theorem says only depends on n(r,t)
- See work of Neepa Maitra (recent review).

Linear response TDDFT

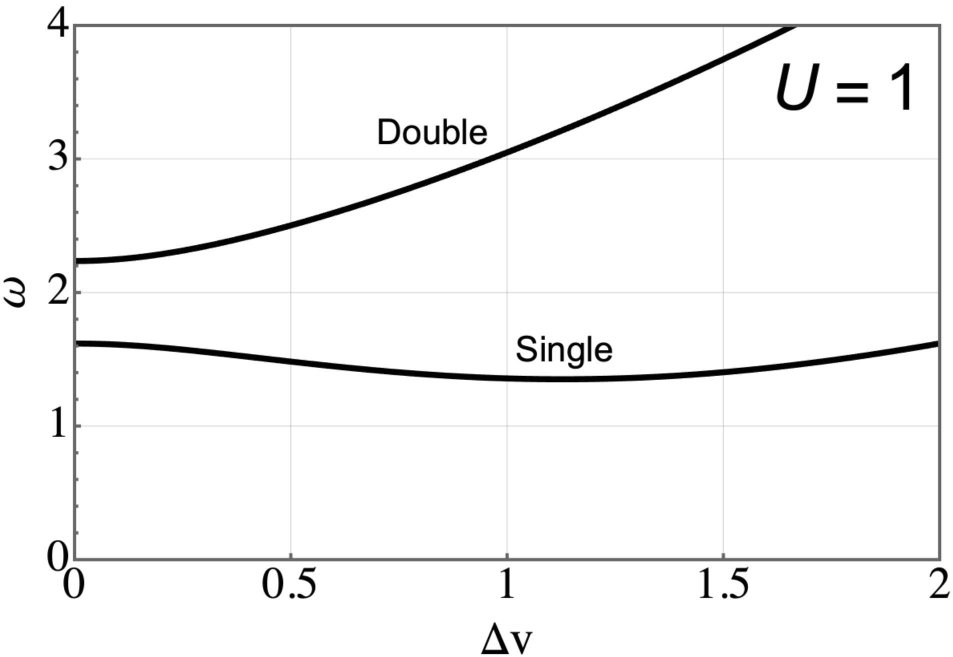
- Apply to weak external uniform E-field
- Yields Gross-Kohn formula for density-density response function

$$\chi(\omega) = \chi_{\mathrm{S}}(\omega) + \chi_{\mathrm{S}}(\omega) * (f_{\mathrm{H}} + f_{\mathrm{XC}}(\omega)) * \chi(\omega),$$

- Poles of response function are optical excitations
- Need XC kernel.
- For finite systems, ω=0 given by gsDFT.
- Used mostly to get low-lying single excitations of molecules (error about 0.3 eV)

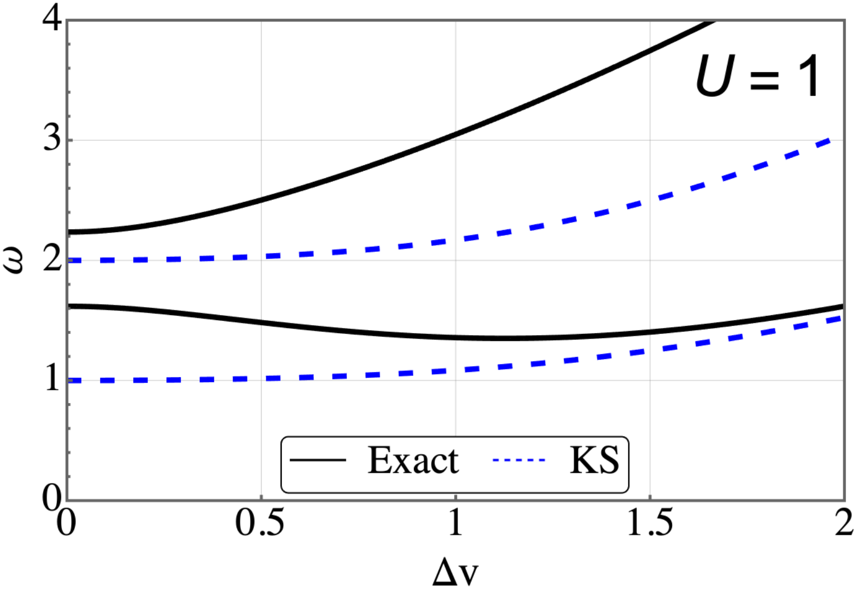
2 Exact optical excitations

$$\chi_n(\omega) = \frac{a_1}{\omega^2 - \omega_1^2} + \frac{a_2}{\omega^2 - \omega_2^2},$$

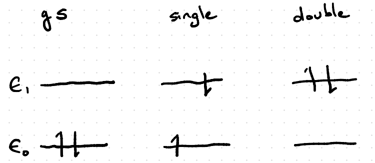


KS excitations

- Optical excitation of the KS ground-state



MO's for Hubbard dimer



ϵ_0 = doubly occupied KS orbital

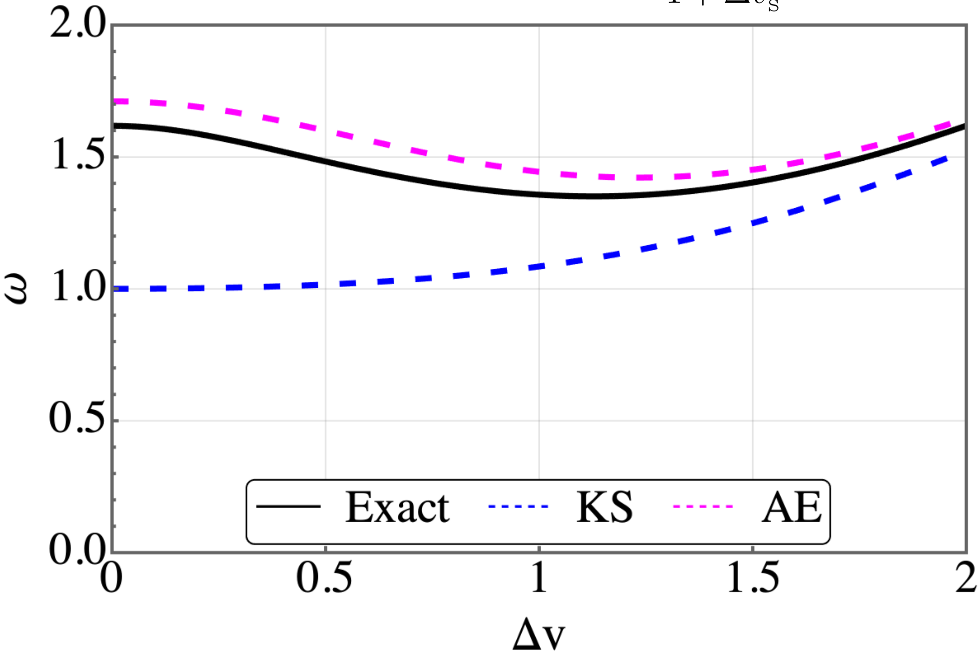
ϵ_1 = unoccupied KS orbital

$$\chi_S(\omega) = \frac{a_s}{\omega^2 - \omega_s^2}$$

Adiabatically exact TDDFT for single

- Use exact ground-state XC in KS-TDDFT

$$\omega^2 = \omega_S^2 + 2\omega_S\, f_{HXC}(\omega)\, \frac{2}{1+\Delta v_S^2}\,.$$



What this means

- Linear-response TDDFT yields optical excitations
- Can consider KS spectrum as excellent starting point for optical excitations (not quasiparticle excitations)
- Ground-state XC typically gives excellent correction to KS excitations
- But always small error due to missing frequency dependence

What happened to double excitation?

- Double (and higher order) excitations missing from adiabatic linear response KS TDDFT
- KS response function has zero numerator at double excitation pole
- No prediction in adiab TDDFT
- But must be present in exact response function
- Due to dynamic part of kernel, i.e., frequency-dependence, i.e., time-dependence
- Missed when TDDFT performed with gs XC

Can see exact frequency dependence

$$f_{\rm HXC}(\omega) = \chi_{\rm S}^{-1}(\omega) - \chi^{-1}(\omega)$$

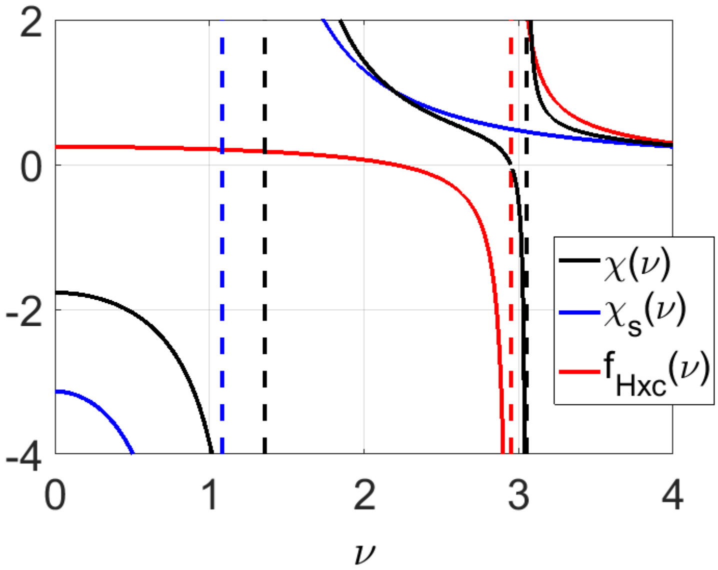


FIG. 16. Frequency dependence of exact (black) and Kohn-Sham susceptibilities (blue) and exchange-correlation kernel (red) for $U = \Delta v = 1$. Poles marked by dashed vertical lines, as a function of frequency ν. The red line shows the

Relatively unexplored territory

- Relatively little study of XC kernel for strong correlation
- See TDDFT review for approximate forms and interpolation from weak to strong
- Don’t know of general functional for this
- Could be tested on stretched molecules

Context of strongly correlated materials

- Often KS used as starting point for more sophisticated approaches, e.g., GGA+U or dynamical mean-field theory
- Often KS orbitals interpreted as quasi-particle excitations, i.e., approximations to peaks in spectral function.
- But results must depend on choice of XC approximation
- Most advances in DFT these days aimed at improving ground-state energy
- KS potentials in general highly inaccurate, but yield accurate densities

Eva Pavarini
Dynamical Mean-Field Theory for Materials

To really calculate G with TD

Gianluca Stefanucci
An Essential Introduction to NEGF Methods for Real-Time Simulations

`Lies’ in electronic structure

- Not actual lies, just misconceptions

- KS eigenvalues are quasiparticle excitations
- KS band gap should match true gap
- Good energies imply good potentials
- More accurate energies mean more accurate potentials and/or densities
- Our approximate functionals work for all external potentials

Summary

- You can learn a lot of the principles of DFT from studying simple models
- Does NOT yield insight into approximations, eg BALDA etc not real LDA.
- Fundamental issue: How much do DFT approximations effect many-body results? (Often not much for materials, I can guess why)
- Actually, in general HK fails on a lattice! See Penz and van Leeuwen arXiv:2106.15370

Q&A

1. State which aspect of Fig. 4 illustrates the HKI theorem.
2. What geometrical construction gives you the corresponding ground-state potential for a given n_1 in Fig. 5?
3. Study the extreme edges ($n_1 = 0$ and 2) of Fig. 5. What interesting qualitative feature is barely visible, and why must it be there?

More questions

4. What feature must always be present in Fig. 5 near $n_1 = 1$? Explain.
5. How can you be sure that, no matter how large U becomes, $F_{\rm U}(n_1)$ is never quite $U|1-n_1|$?
6. Assuming the blue line is essentially that of $U = 0$, use geometry on Fig. 3 to find $\Delta v_{\rm S}$ for $U = 5$.
7. What is the relation, if any, between each of the blue plots in the three panels of Fig. 7? Explain.
8. What is the relation, if any, between each of the red plots in the three panels of Fig. 7? Explain.
9. Why is the green line almost the mirror image of the black line in the $U = 10$ panel of Fig. 7? Could it be the exact mirror image? Explain.
10. From Fig. 8, using $E(N)$ about $N = 2$, determine the locations of the largest peaks of Fig. 9 and compute the gap between them.
11. Sketch how Fig. 8 must look if $U = 10$ and $\Delta v = 0$.
12. What is the relation between the two blue lines in Fig. 14? Explain.
13. Give a rule relating the numbers of vertical lines of different color in Fig. 16.
    Explain its significance.
14. Recall the definition of the kernel from section 4. Using this, derive $f_{\rm H}$ and $f_{\rm X}$, and draw them on Fig. 16. Explain where double excitations must come from for 2 electrons.
15. Using formulas and figures from both sections, deduce the results of Fig. 15 in the absence of correlation (Hint: You will need to solve the Hartree-Fock self-consistent equations), and comment on the relative errors. This is a little more work than the other exercises.