

Zero, one, many: the Hubbard dimer with two electrons in many-body perturbation theory

Abdallah El Sahili, Francesco Sottile, Lucia Reining
Palaiseau Theoretical Spectroscopy Group & Friends
Steve Guyot, Pina Romaniello



Zero, one, many: the Hubbard dimer with two electrons in many-body perturbation theory

- About the choice of a model: the symmetric Hubbard dimer
- Analysis of GW failures
- Approximate vertex corrections from TDDFT
- When an approximation yields (or not) exact results
- Illustration: symmetric Hubbard dimer
- Conclusions

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Why do we use models?

→ To simplify (part of) a real material
interfaces, pseudopotentials, Born-Oppenheimer,

We do this always.

*Sometimes this maps onto a well-established model
downfolding on low-energy subspace with effective interaction

*As a result of a general approximation
approx. of near-sighted local self-energy makes AIM appear

→ To gain insight that can be extrapolated to real materials
homogeneous electron gas to simple metals

→ To sharpen our (numerical) swords
2D Hubbard model Qin et al., Annual Review Cond. Matter Physics 13, 275 (2022)

→ To benchmark theoretical and numerical approaches
*because this is the only way we can do it

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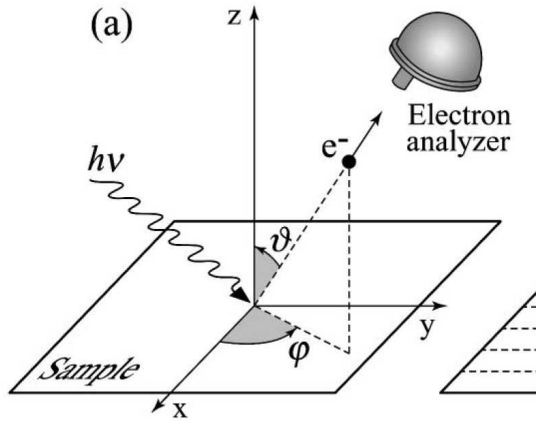
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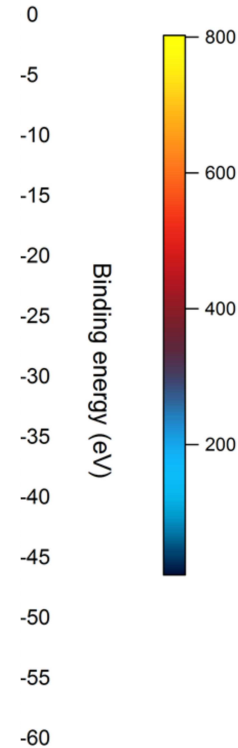
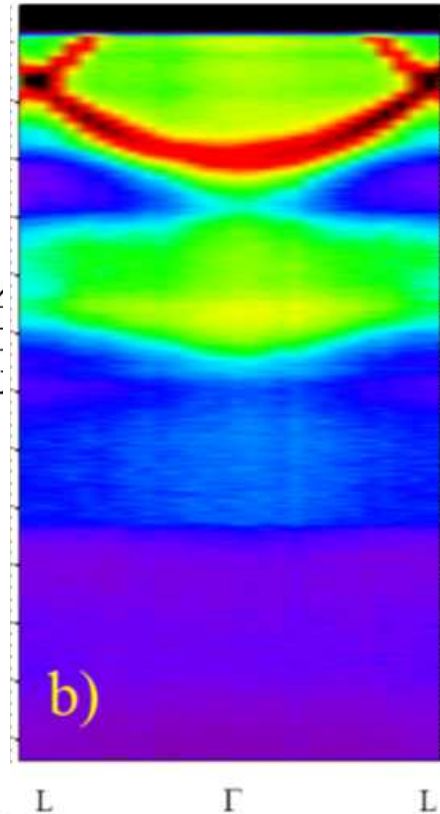
Photoemission of bulk aluminum

Experiment



Photoemission geometry

From Damascelli et al.,
RMP 75, 473 (2003)



Zhou, Reining, Nicolaou, Bendounan, Ruotsalainen, Vanzini, Kas, Rehr, Muntwiler, Strocov, Sirotti, Gatti,
PNAS 117 (46), 28596 (2020)

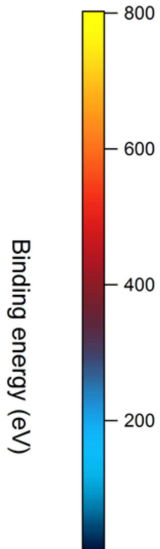
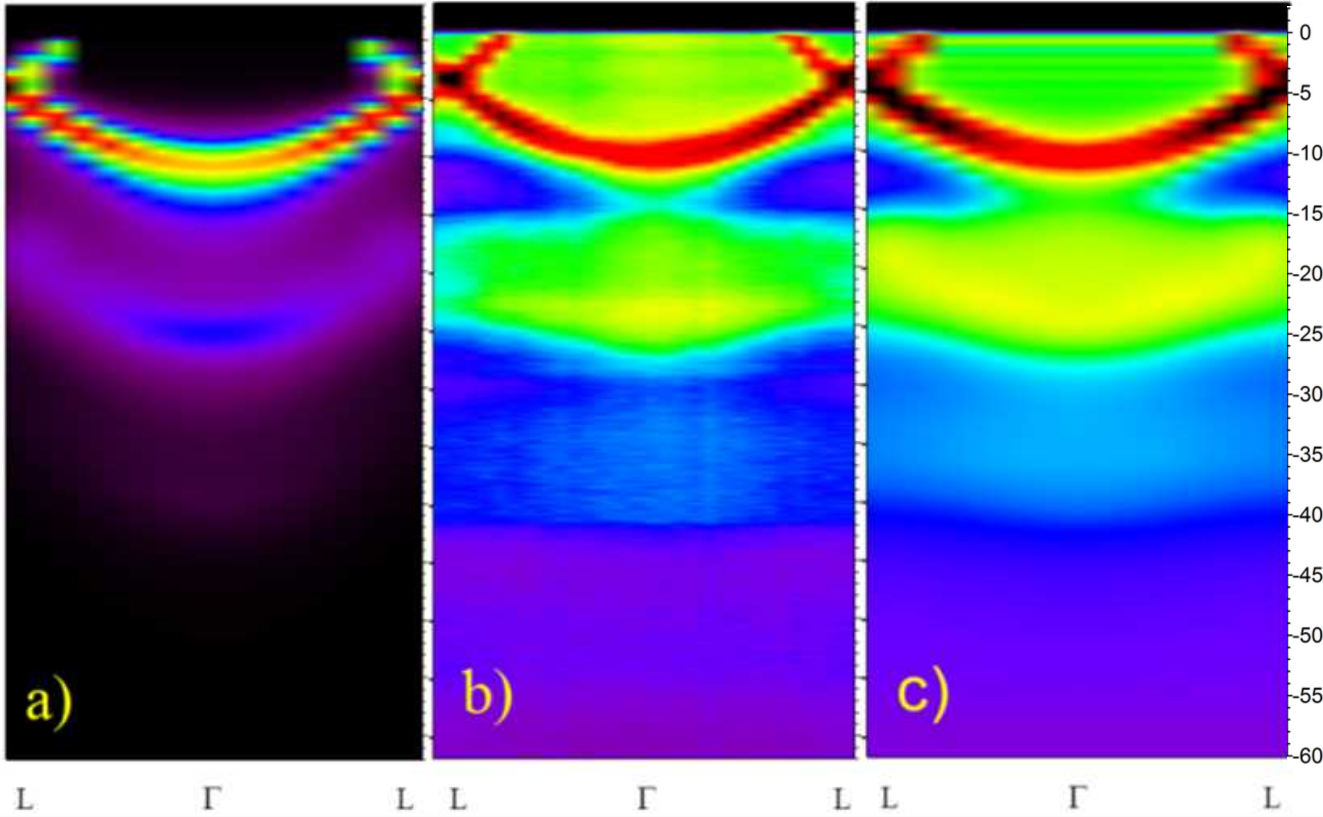
Photoemission of bulk aluminum

→ Temperature
→ extrinsic scattering

cumulant
GW+C spectrum

Experiment

GW+C++



Zhou, Reining, Nicolaou, Bendounan, Ruotsalainen, Vanzini, Kas, Rehr, Muntwiler, Strocov, Sirotti, Gatti, PNAS 117 (46), 28596 (2020)

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Periodic Hubbard model

$$\hat{H} = \sum_{i,\sigma} \epsilon_0 \hat{n}_{i\sigma} - \sum_{\langle i,j \rangle, i \neq j, \sigma} t \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

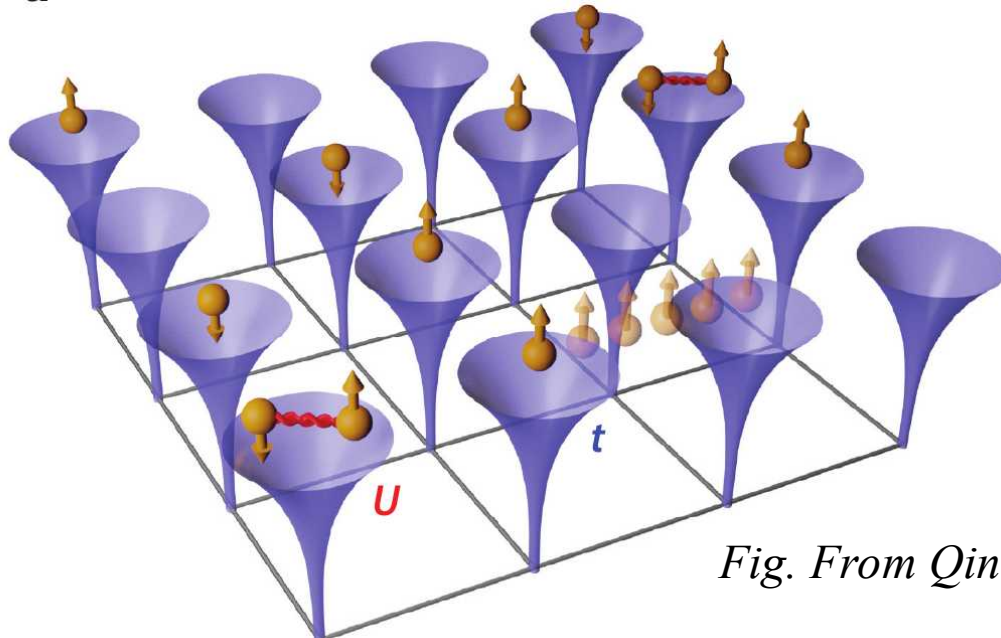


Fig. From Qin et al., ARCMP 13, 275 (2022)

- Hubbard J. 1963. *Proc. R. Soc. Lond. Ser. A* 276(1365):238–57
Kanamori J. 1963. *Prog. Theor. Phys.* 30(3):275–89
Gutzwiller MC. 1963. *Phys. Rev. Lett.* 10(5):159–62

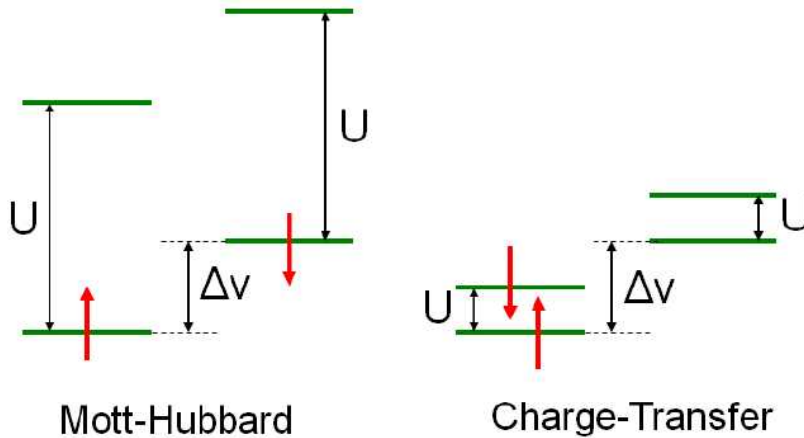
Symmetric Hubbard dimer: 2 sites

$$\hat{H} = \sum_{i,\sigma} \epsilon_0 \hat{n}_{i\sigma} - \sum_{\langle i,j \rangle, i \neq j, \sigma} t \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

$i=1,2$

Symmetric Hubbard dimer: 2 sites

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D J Carrascal et al 2015 J. Phys.: Condens. Matter 27 393001

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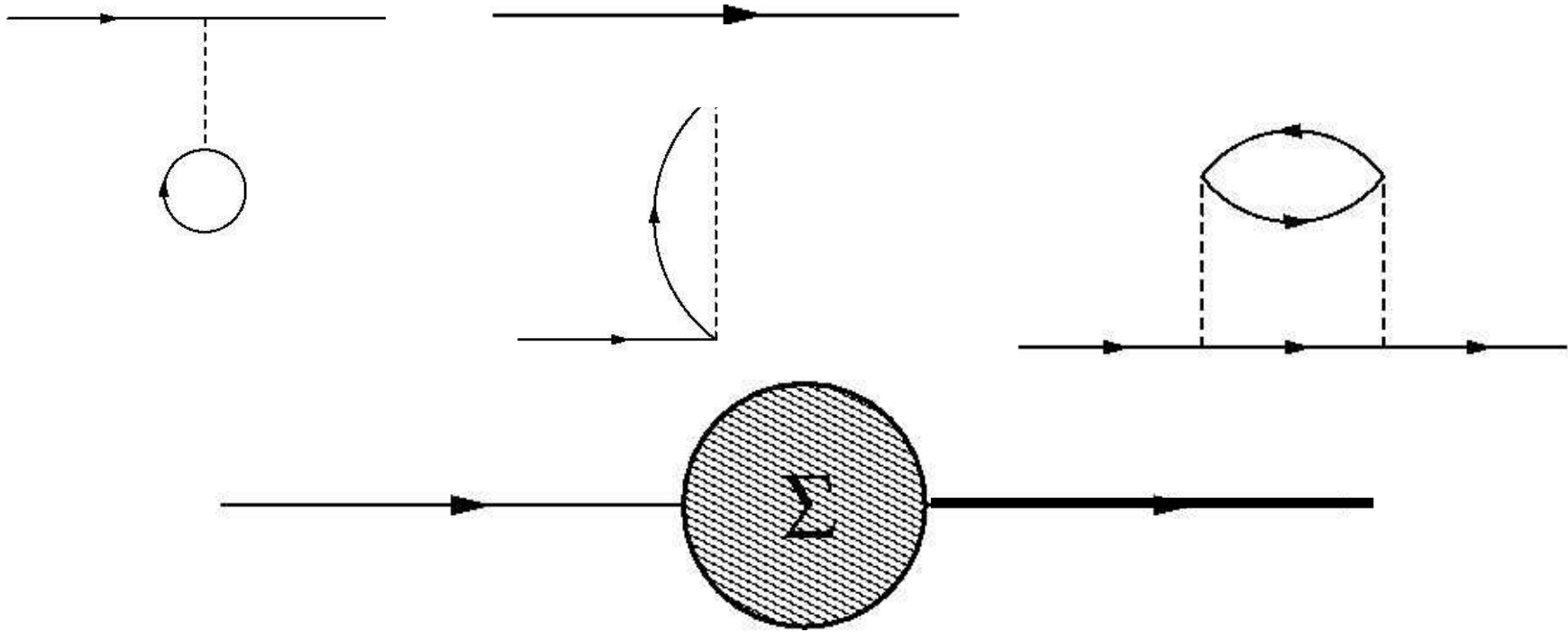
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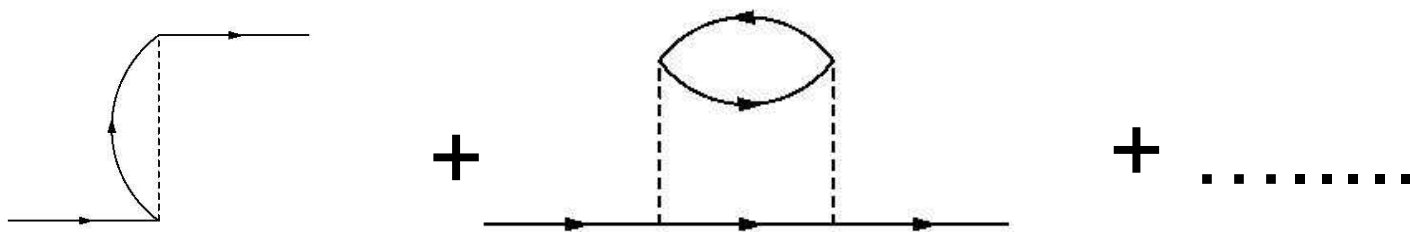
$$G(x_1, x'_1, t, t') = -i \langle N | T[\hat{\Psi}(x_1, t) \hat{\Psi}^\dagger(x'_1, t')] | N \rangle$$

Many things can happen to a particle that propagates in the middle of others.....



$$G = G_0 + G_0 \Sigma G$$

Typical GFFT approximation strategy



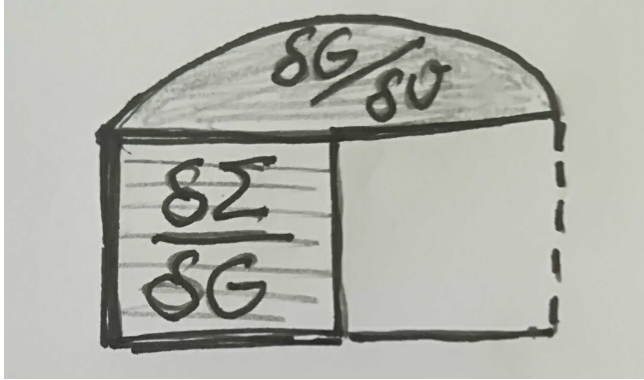
$$\rightarrow \Sigma \sim i GW$$

“GW”

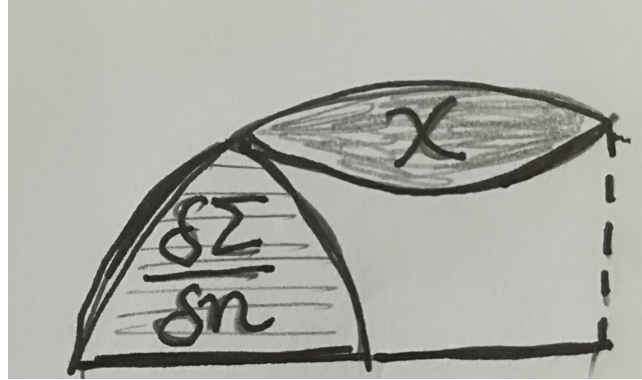
L. Hedin, Phys. Rev. 139:A796–823, 1965

$$W(\omega) = \epsilon(\omega)^{-1} v_c$$

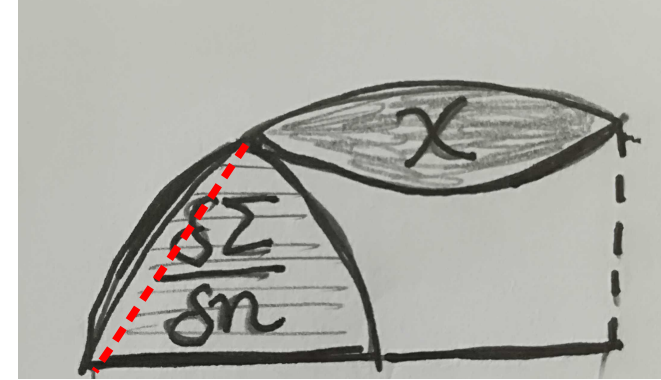
Correlation self-energy:



Martin, Reining, Ceperley
Interacting Electrons
(Cambridge 2016)

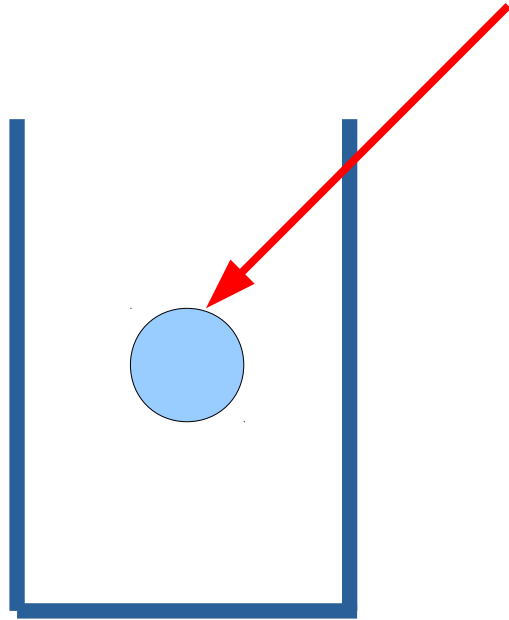


Bruneval, et al,
PRL 94, 186402 (2005)



GW
Hedin 1965

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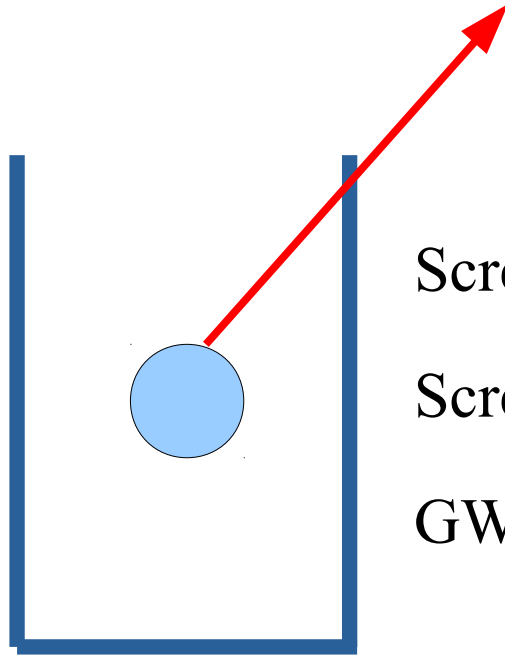


No screening

Fock cancels SI

GW=HF=OK

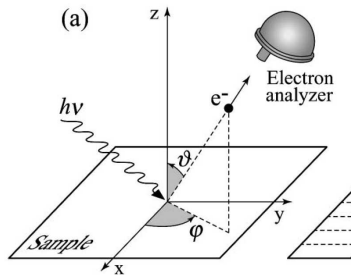
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Screening by $N=1$ electron

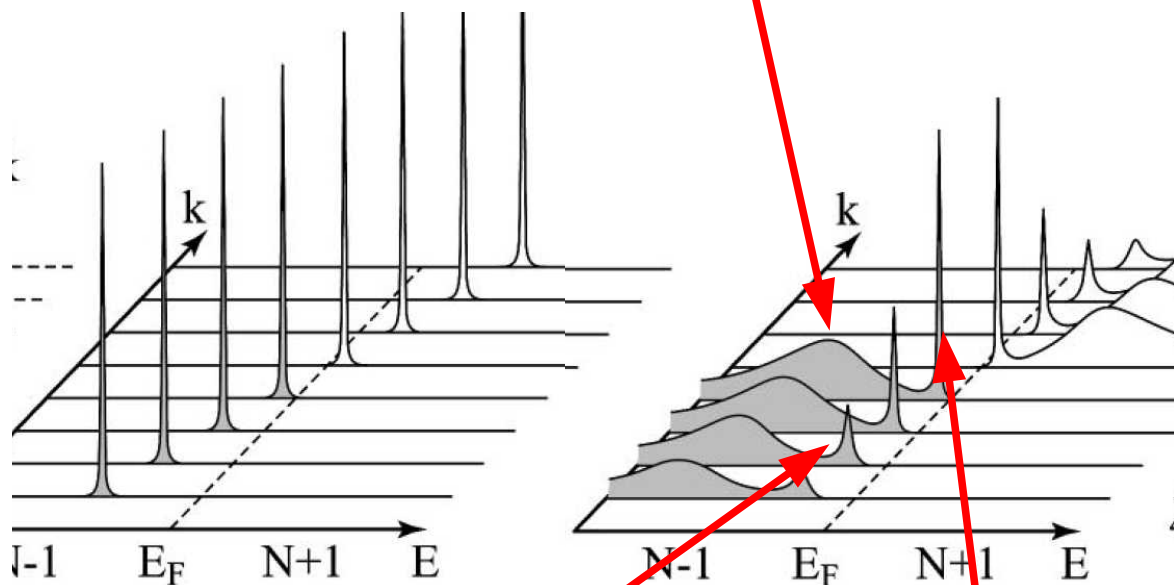
Screened Fock does not cancel SI

GW NOT OK



Photoemission geometry

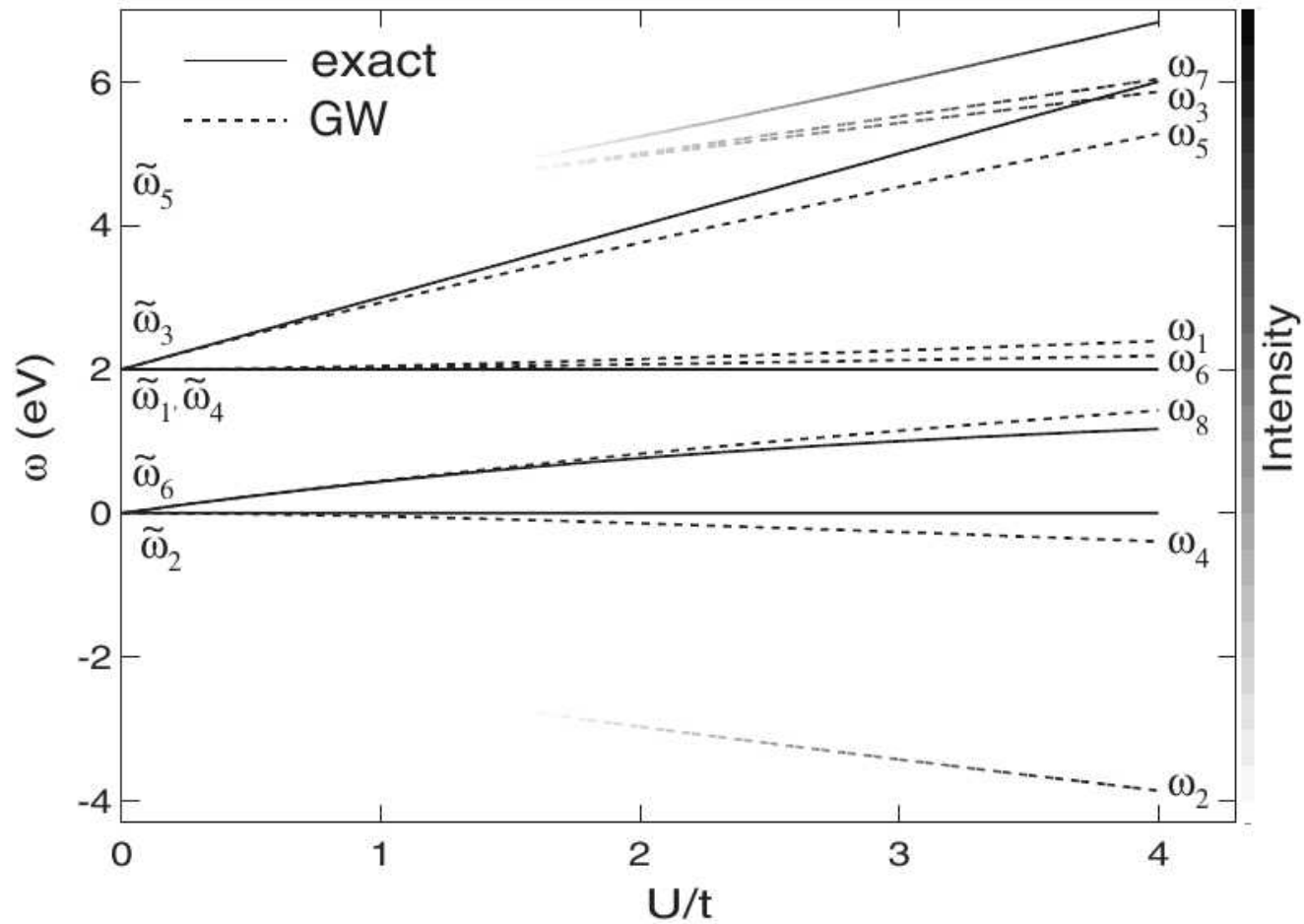
$$W(\omega) = \epsilon(\omega)^{-1} v_c$$



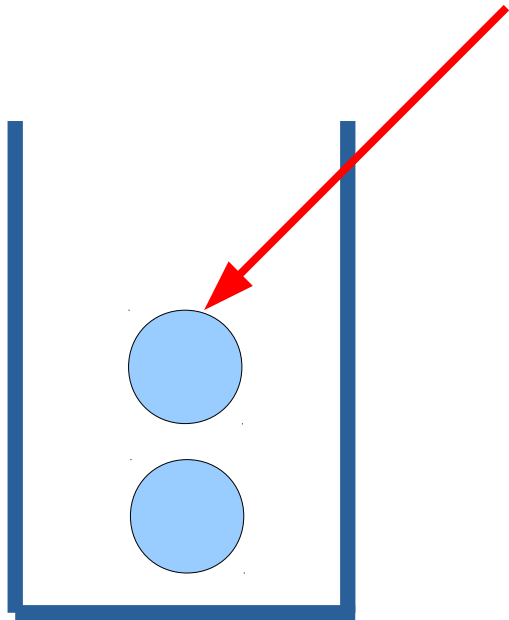
Satellite

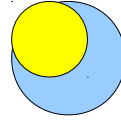
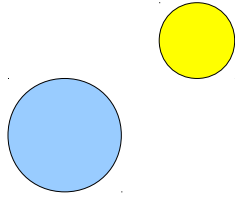
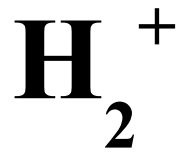
Broadening

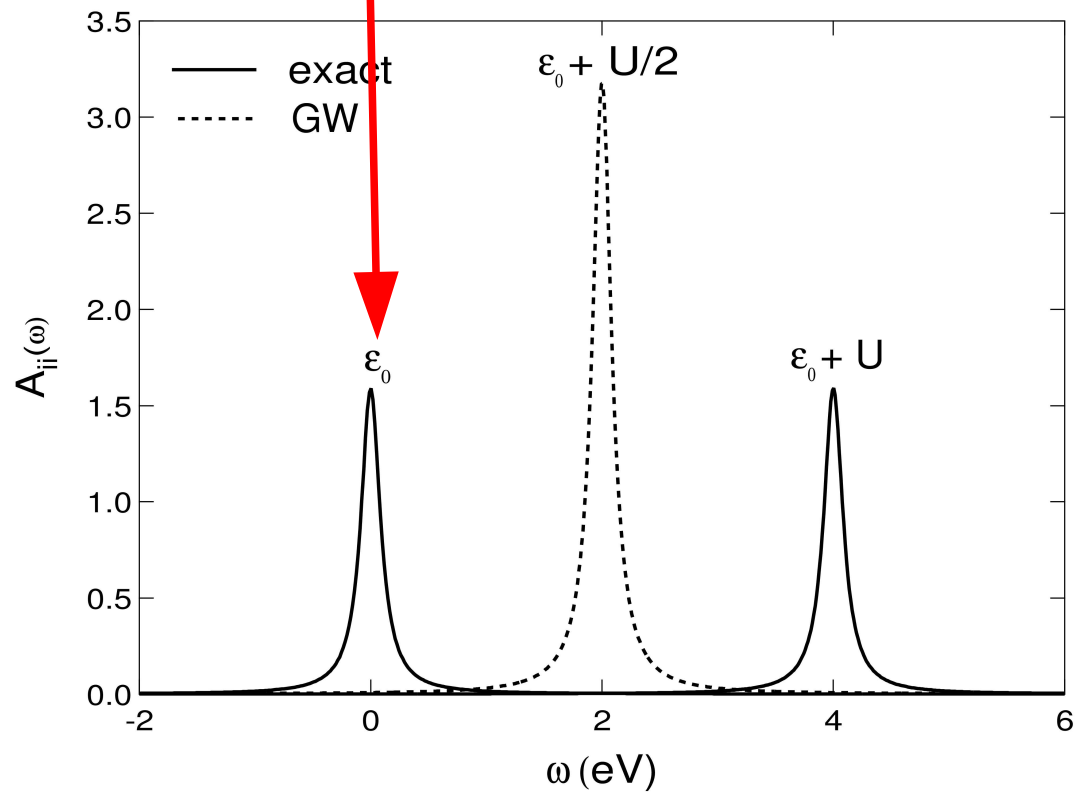
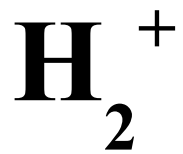
Renormalization

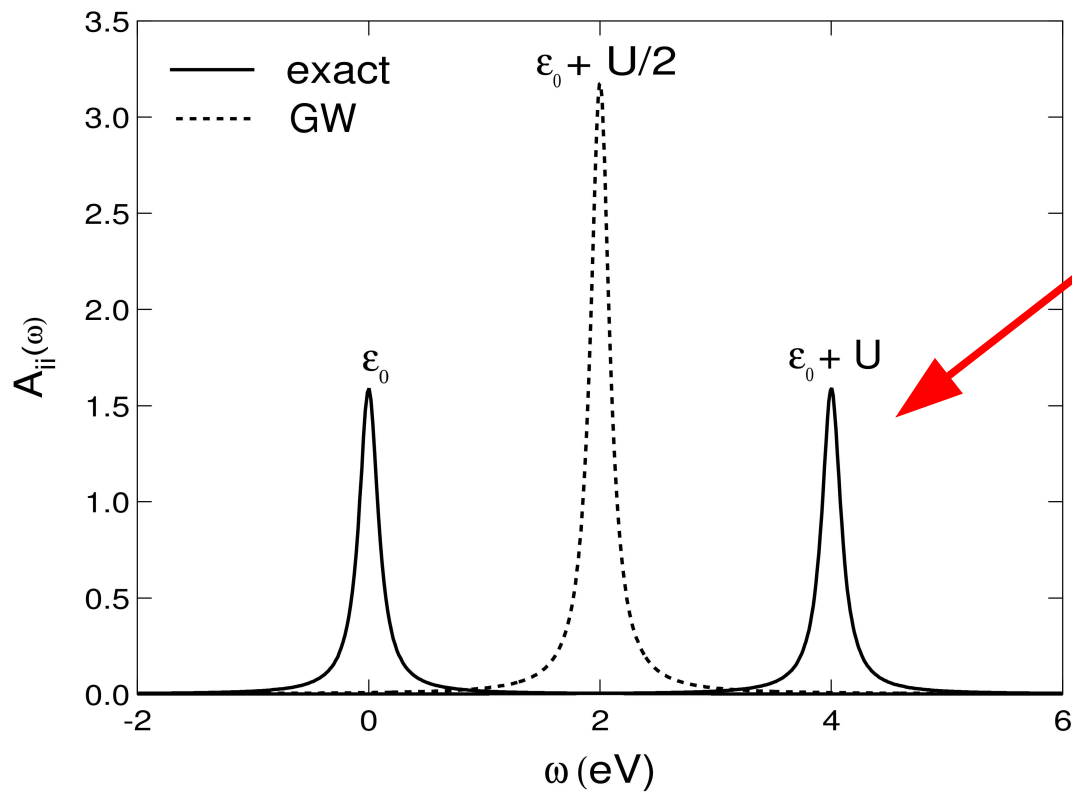


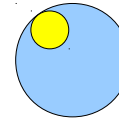
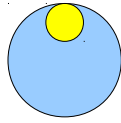
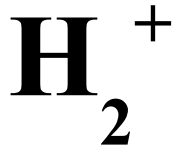
Romaniello, Guyot, Reining, *J. Chem. Phys.* 131, 154111 (2009)



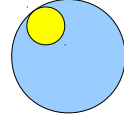
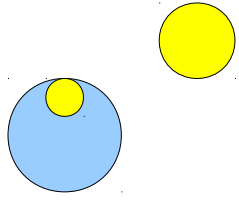
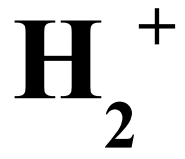


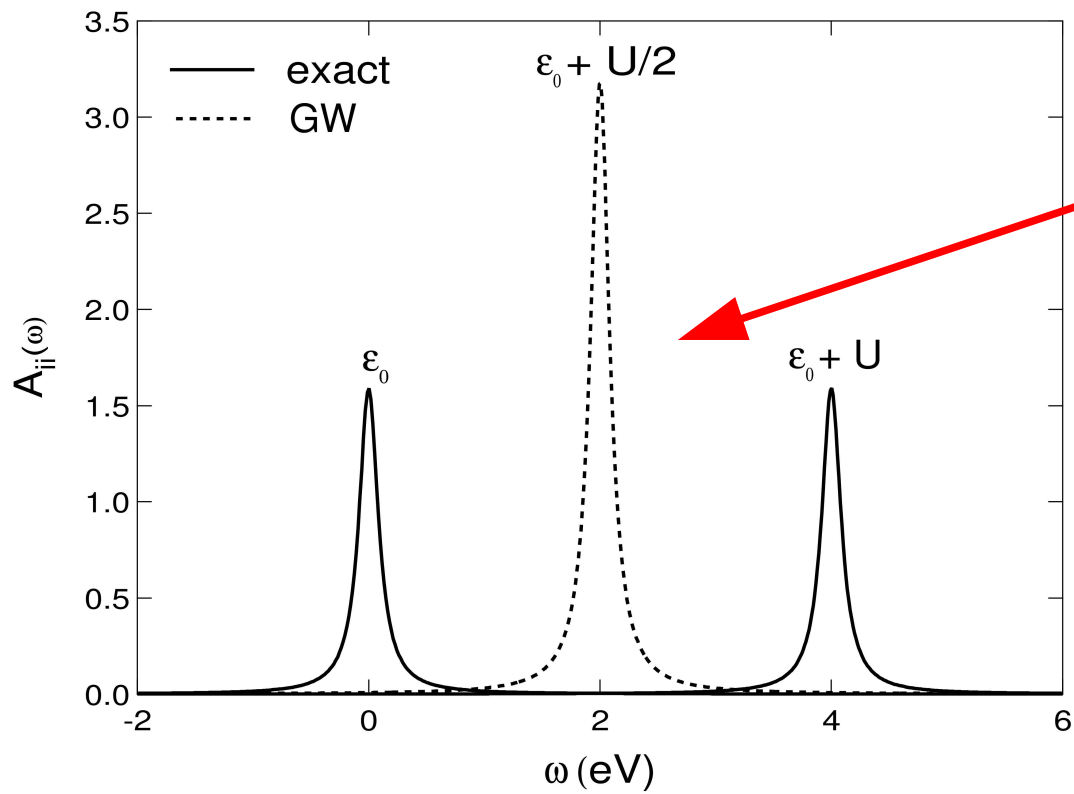
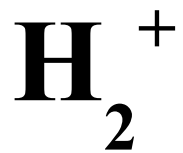


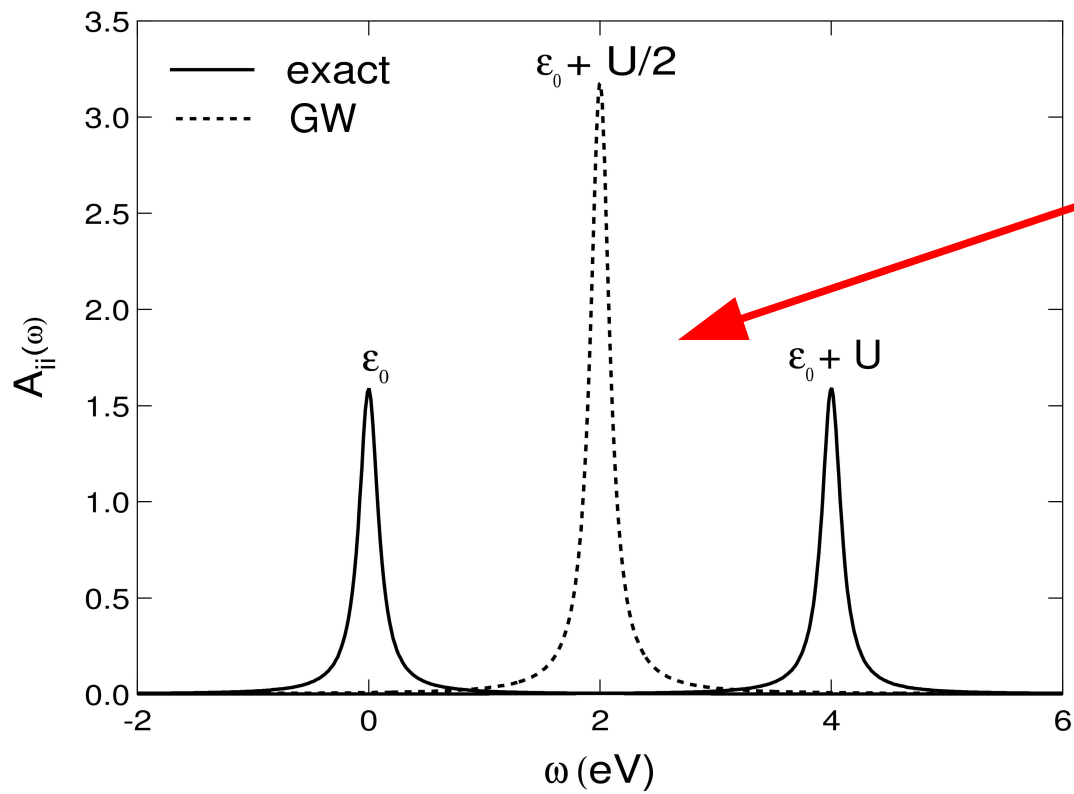
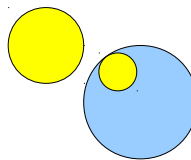
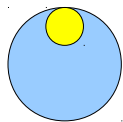
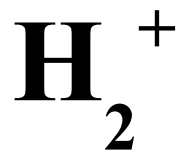


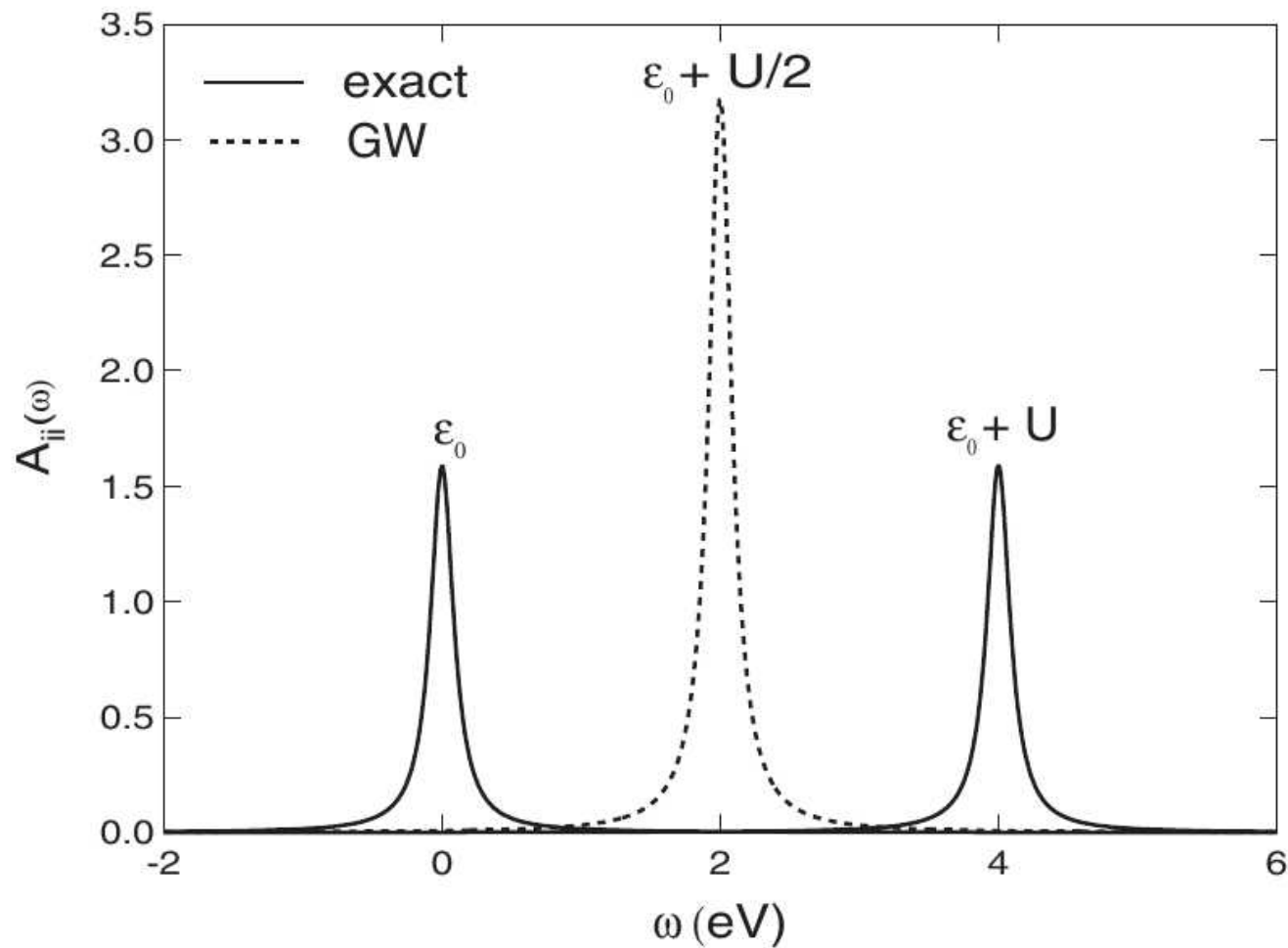


Mean field interpretation of the density: $\frac{1}{2} + \frac{1}{2}$



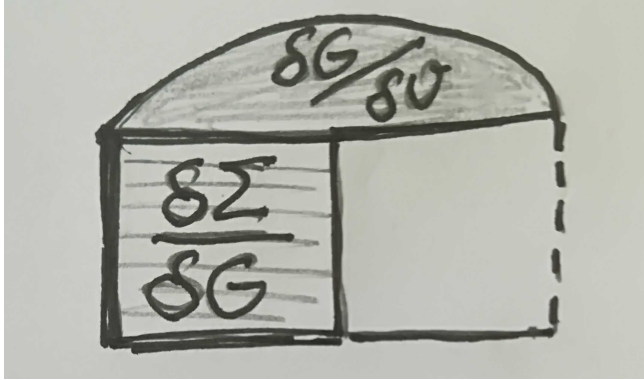




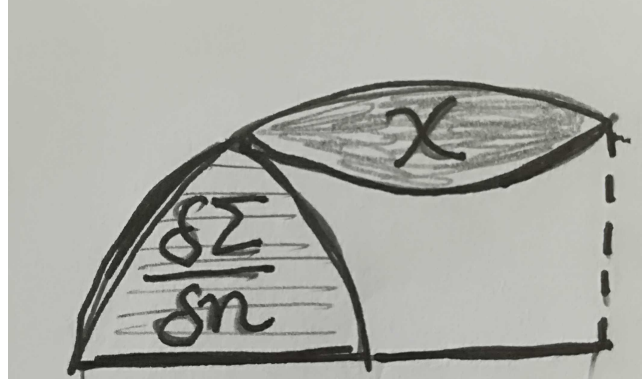


Romaniello, Guyot, Reining, J. Chem. Phys. 131, 154111 (2009)

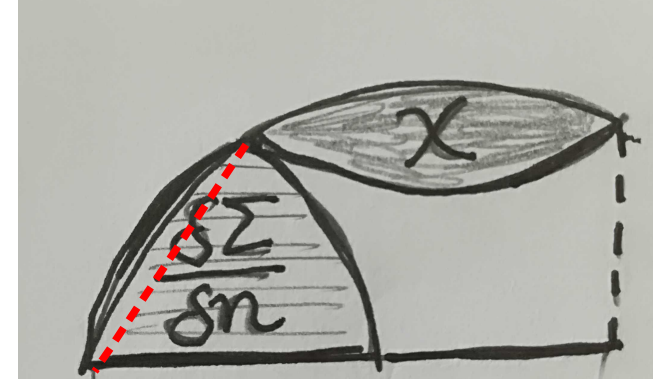
Correlation self-energy:



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Bruneval, et al,
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GW
Hedin 1965

Can we use TDDFT for better effective interactions?

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→ Approximate vertex corrections from TDDFT



Abdallah El Sahili

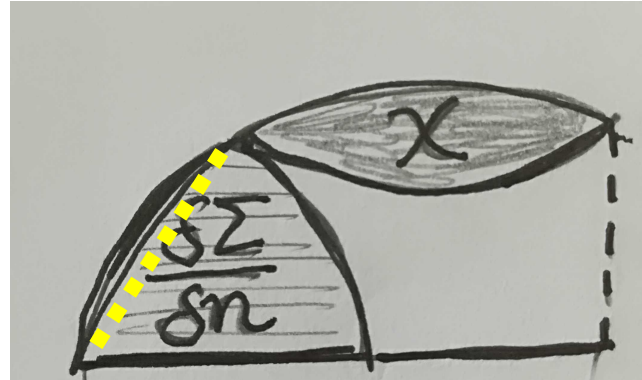
El Sahili, Sottile, Reining, JCTC 2024

→ Illustration: symmetric Hubbard dimer

→ Conclusions

An old idea for the correlation self-energy:

“G \tilde{W} ”




..... = $v_c + f_{xc}$

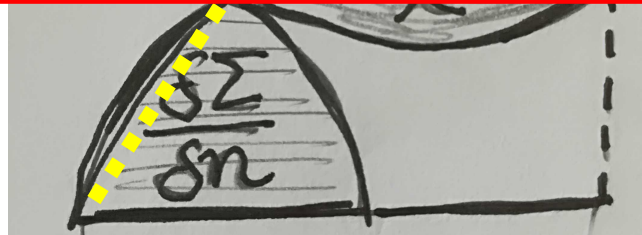
Beyond GW, approximate vertex from TDDFT: $i \frac{\delta \Sigma_{xc}}{\delta G} \rightarrow \frac{\delta v_{xc}}{\delta n} = f_{xc}$

Overhauser, PRB 3, 1888 (1971); Petrillo and Sacchetti, PRB 38, 3834 (1988);
 Mahan and Sernelius, PRL. 62, 2718 (1989); Hybertsen and Louie, PRB 34, 5390 (1986);
 Del Sole, Reining, and Godby, PRB 49, 8024 (1994); Hindgren and Almladh, PRB 56, 12832 (1997);
 Schmidt, Patrick, and Thygesen, PRB 96, 205206 (2017);
 Chen, Ambrosio, Miceli, and Pasquarello, PRL 117, 186401 (2016);
 Shishkin, Marsman, and Kresse, PRL 99, 246403 (2007).

An old idea for the correlation self-energy:

This will have errors from the procedure
and from approx. of f_{xc}


$$= v_c + f_{xc}$$



Beyond GW, approximate vertex from TDDFT: $i \frac{\delta \Sigma_{xc}}{\delta G} \rightarrow \frac{\delta v_{xc}}{\delta n} = f_{xc}$

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El Sahili, Sottile, Reining, JCTC 2024

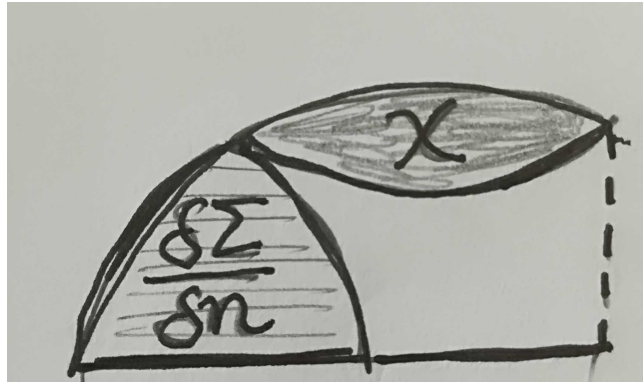


Abdallah El Sahili

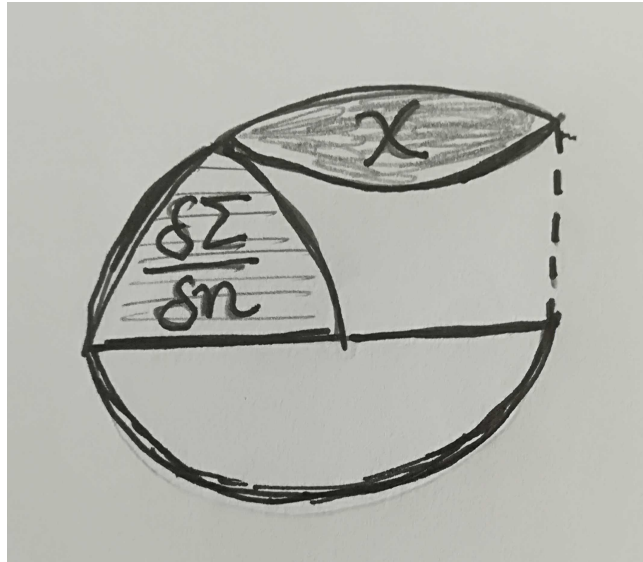
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Correlation energy (no kinetic contribution)



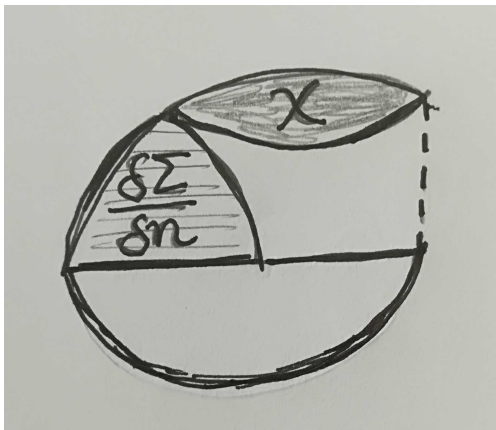
Correlation energy (no kinetic contribution)



V.M. Galitskii, A. M. JETP 1950, 7, 96

$$E_{xc} = -\frac{i}{2} \int dx_1 d2 \bar{\Sigma}_{xc}(1, 2) \bar{G}(2, 1^{++})$$

Correlation energy (no kinetic contribution)



A diagrammatic equation for the Bethe-Salpeter Equation (BSE). On the left is a rectangular box with horizontal lines, containing the fraction $\frac{SG}{S^0_{une}}$. This is followed by an equals sign, then two horizontal lines representing a pair of particles. To the right of this is a plus sign, followed by another pair of horizontal lines. The second pair of lines is enclosed in a rectangular box with horizontal lines, containing the fraction $\frac{\delta \Sigma}{\delta n}$ on the left and $\frac{SG}{S^0_{une}}$ on the right.

BSE

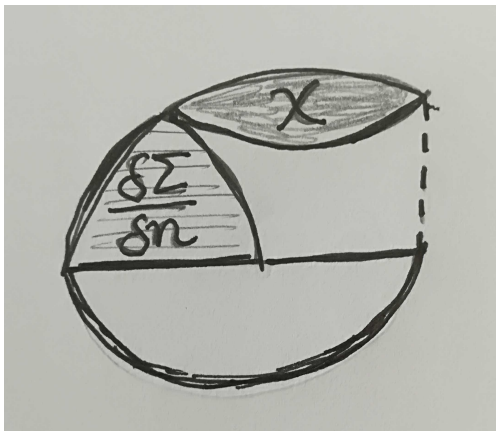
A diagrammatic equation for the BSE diagonal approximation. On the left is a shaded cap labeled with the Greek letter χ . This is followed by an equals sign, then an empty cap. To the right of this is a plus sign, followed by a cap divided vertically. The left half of this cap is shaded and labeled with the fraction $\frac{\delta \Sigma}{\delta n}$, and the right half is shaded and labeled with the Greek letter χ .

BSE
diagonal

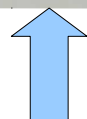
A diagrammatic equation for Time-Dependent Density Functional Theory (TDDFT). On the left is a shaded cap labeled with the Greek letter χ . This is followed by an equals sign, then a pink loop. To the right of this is a plus sign, followed by a pink loop with a shaded cap labeled with the Greek letter χ attached to its right side.

TDDFT

Correlation energy (no kinetic contribution)



A diagrammatic equation showing the correlation energy. On the left, a shaded cap labeled χ is connected to a shaded circle labeled χ . The connection is labeled $\frac{\delta \Sigma}{\delta n}$. This is equal to the sum of two terms: a loop with a shaded cap labeled χ and a shaded circle labeled χ connected by a pink double line, and a loop with a shaded circle labeled χ and a shaded cap labeled χ connected by a pink double line, minus a shaded circle labeled χ .



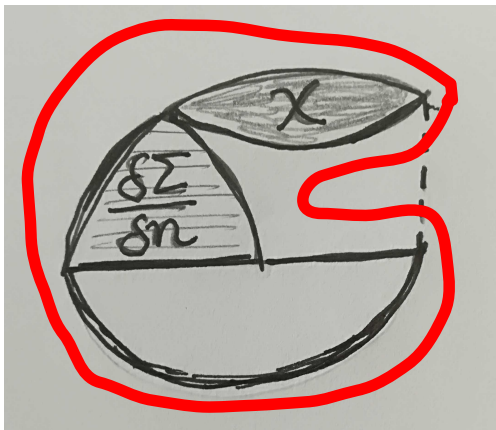
A diagrammatic equation labeled "BSE diagonal". On the left, a shaded cap labeled χ is equal to the sum of a shaded circle and a shaded cap labeled χ connected to a shaded circle labeled χ . The connection is labeled $\frac{\delta \Sigma}{\delta n}$.

BSE
diagonal

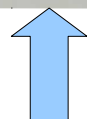
A diagrammatic equation labeled "TDDFT". On the left, a shaded cap labeled χ is equal to the sum of a loop with a shaded cap labeled χ and a loop with a shaded cap labeled χ and a shaded circle labeled χ connected by a pink double line.

TDDFT

Correlation energy (no kinetic contribution)



$$\chi \frac{\delta \Sigma}{\delta n} = \text{loop}(\chi, \text{pink wavy}) + \text{loop}(\text{white}, \text{pink wavy}) - \chi$$



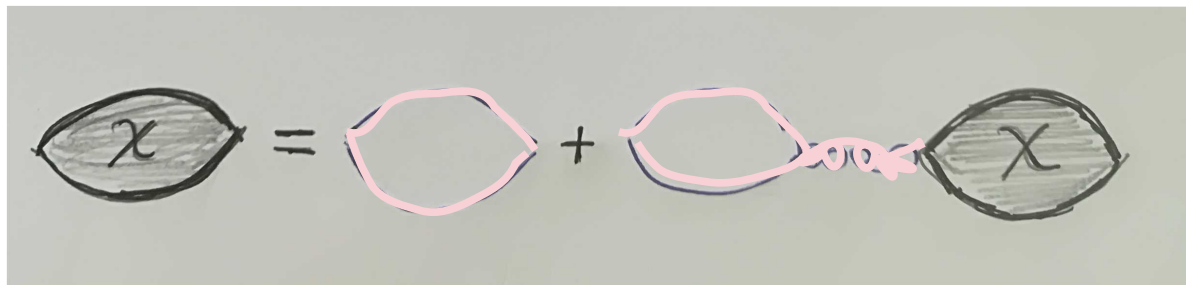
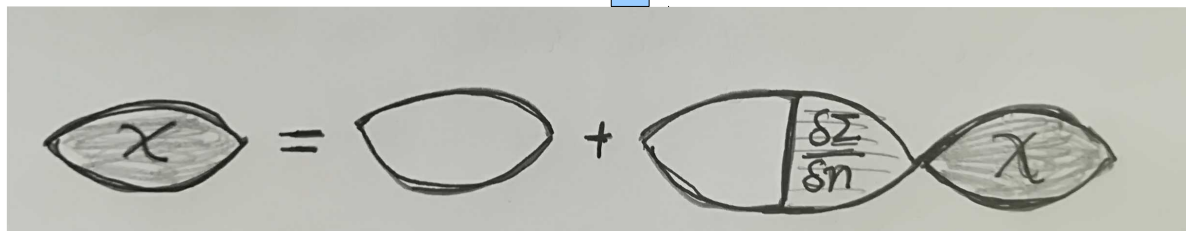
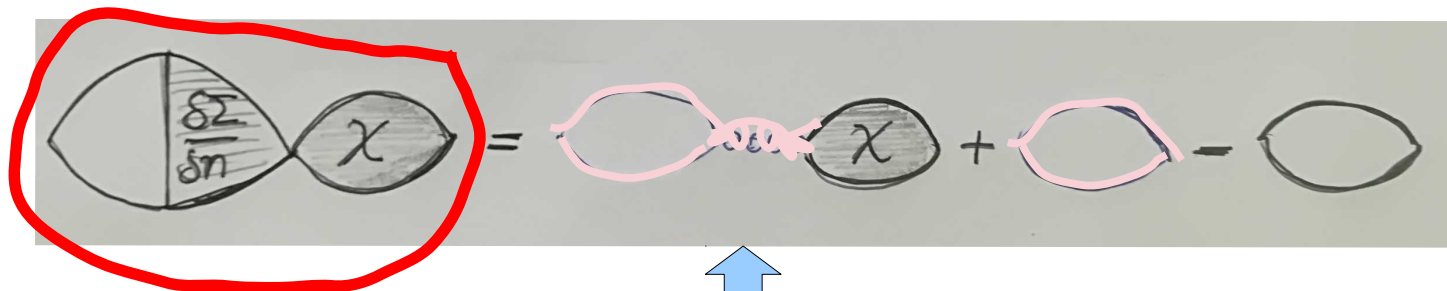
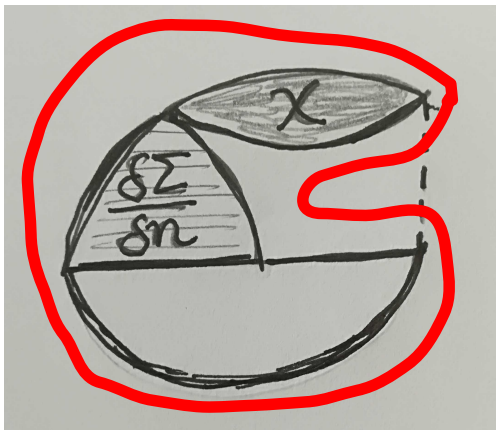
$$\chi = \text{white lobe} + \chi \frac{\delta \Sigma}{\delta n}$$

BSE
diagonal

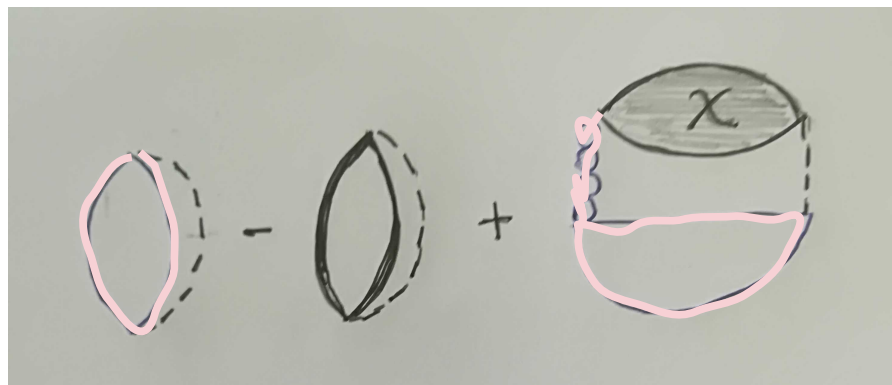
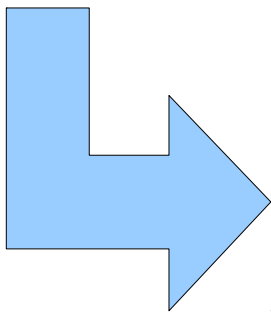
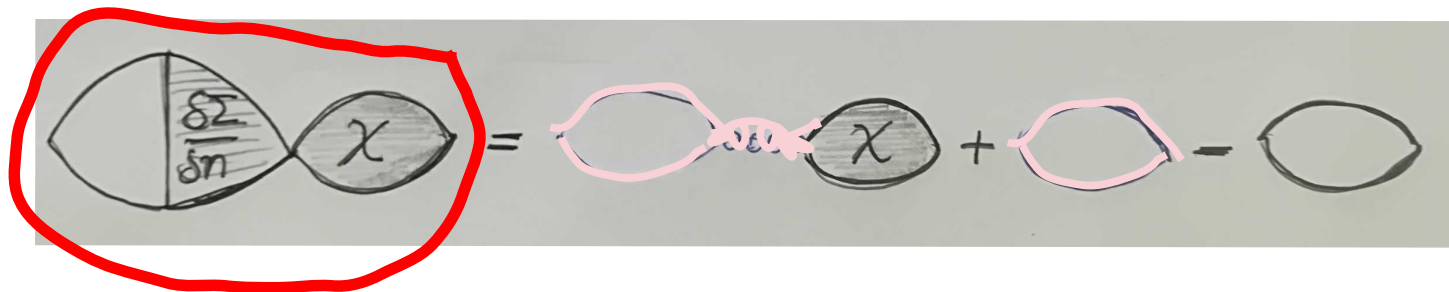
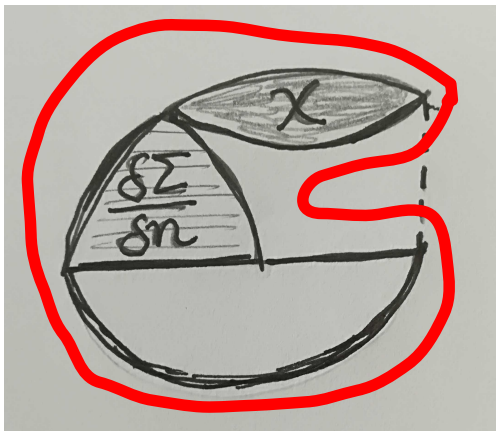
$$\chi = \text{white lobe} + \text{loop}(\chi, \text{pink wavy})$$

TDDFT

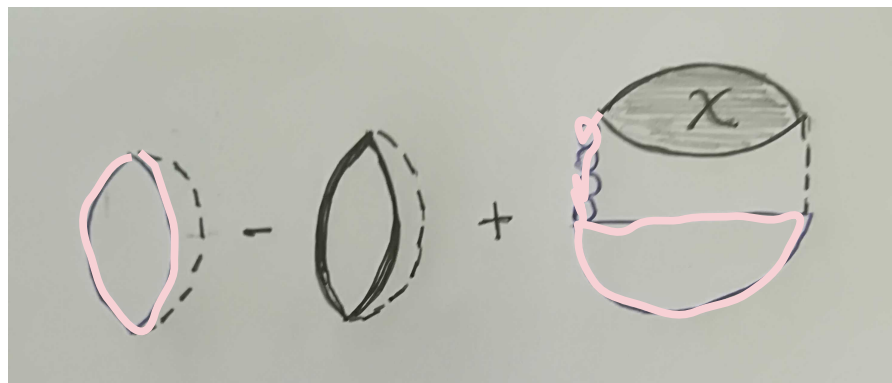
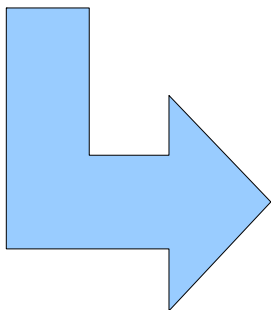
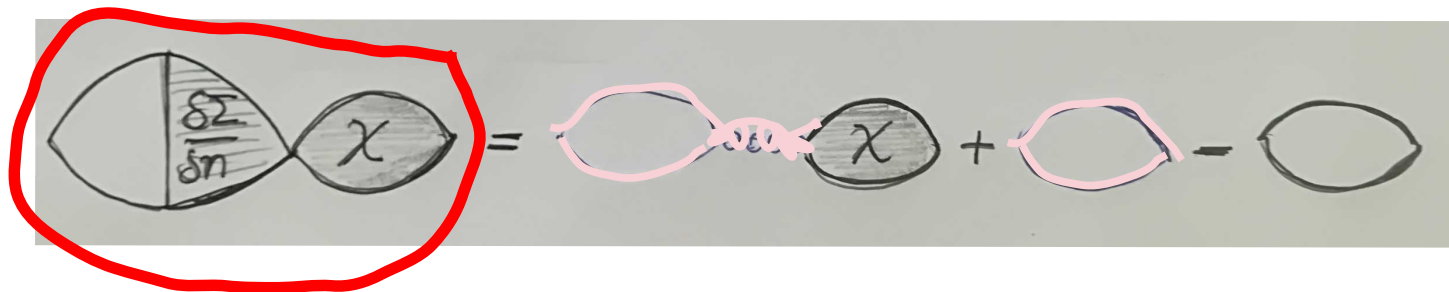
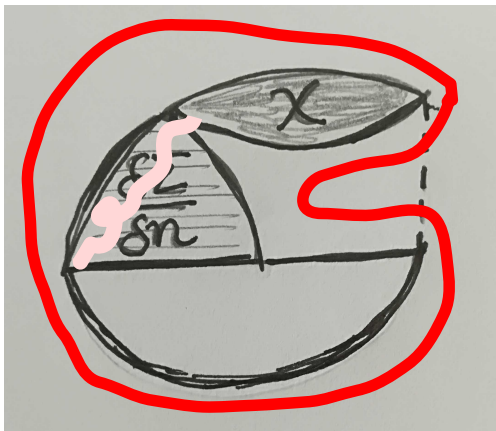
Correlation energy (no kinetic contribution)



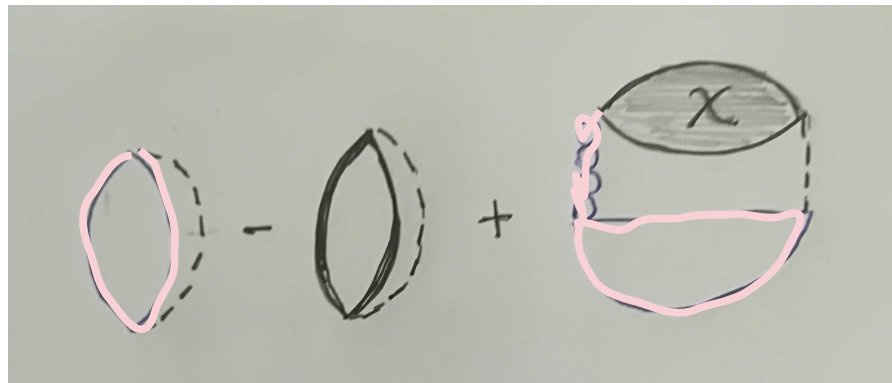
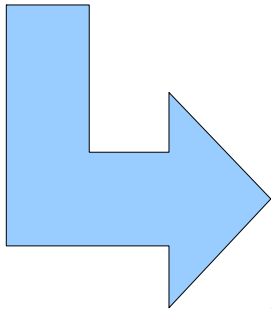
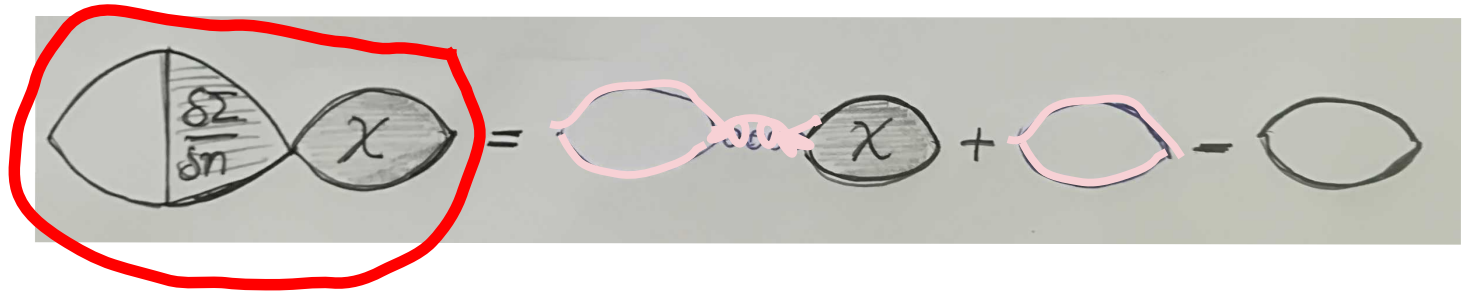
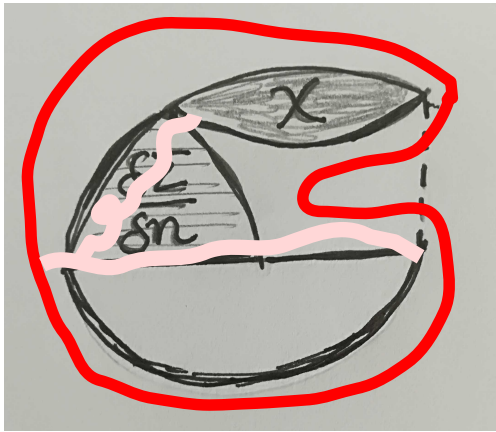
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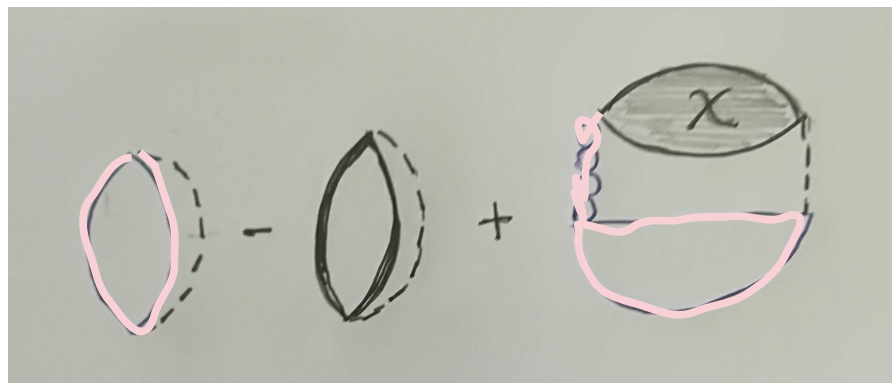
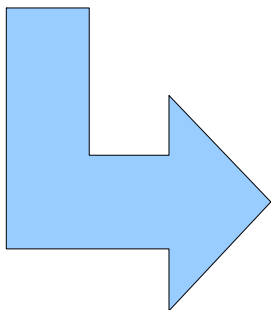
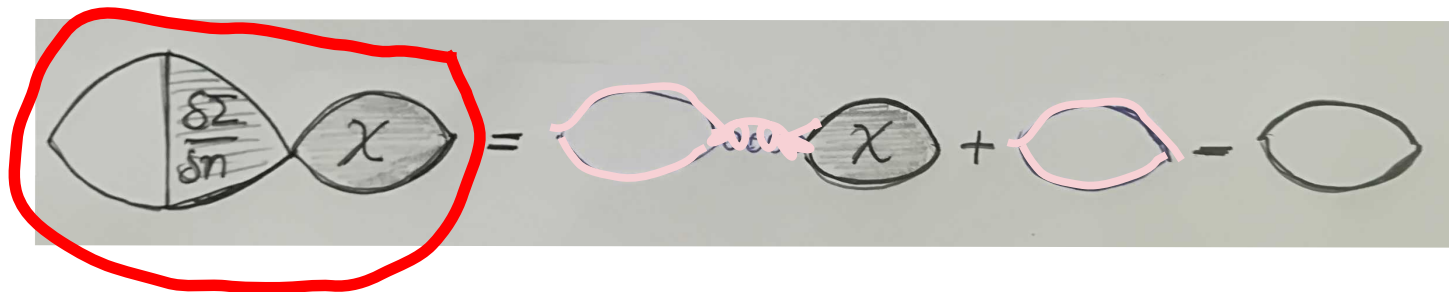
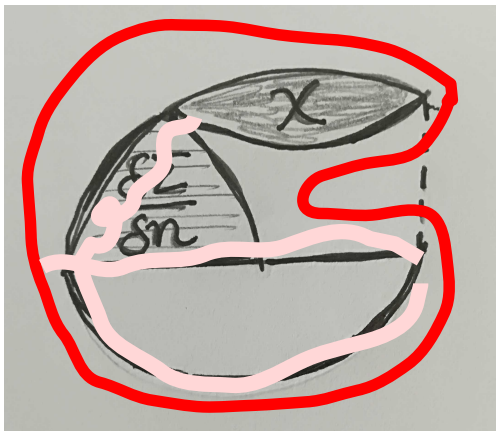
Correlation energy (no kinetic contribution)



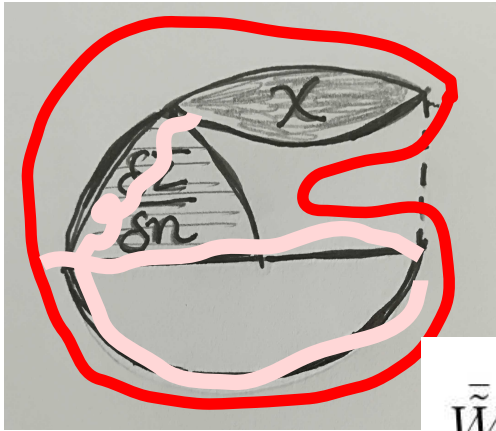
Correlation energy (no kinetic contribution)



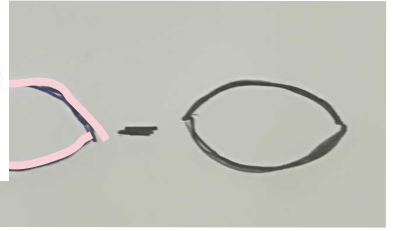
Correlation energy (no kinetic contribution)



Correlation energy (no kinetic contribution)

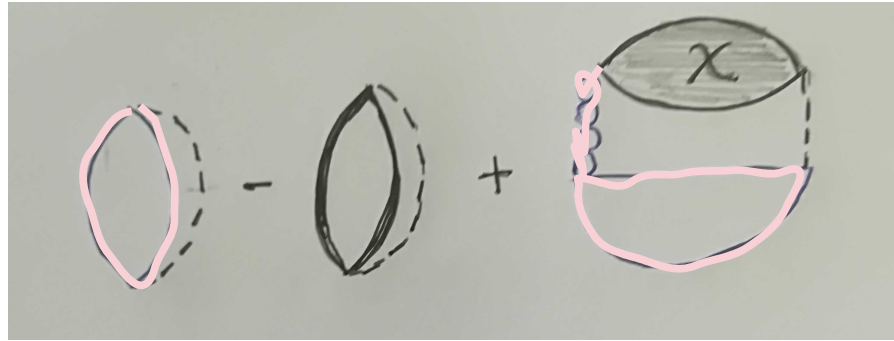
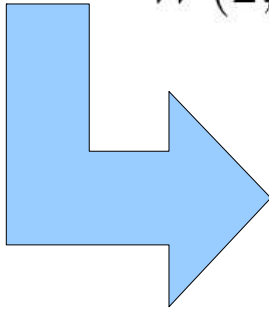


$$E_{\text{xc}} = -\frac{i}{2} \int dx_1 d2 \bar{\Sigma}_{\text{xc}}(1, 2) \bar{G}(2, 1^{++})$$

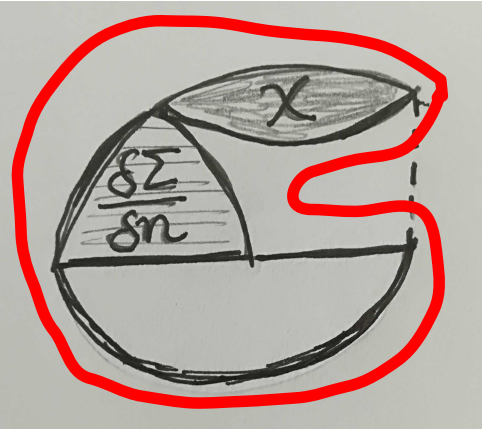


$$\bar{\Sigma}_{\text{xc}}(1, 2) \equiv i \bar{G}(1, 2) \bar{W}(2, 1^+)$$

$$\bar{W}(2, 1) = v_c(2, 1) + \int d(34) \left(v_c(2, 4) + \bar{f}_{\text{xc}}(1, 4) \right) \chi(4, 3^{++}) v_c(3, 1)$$

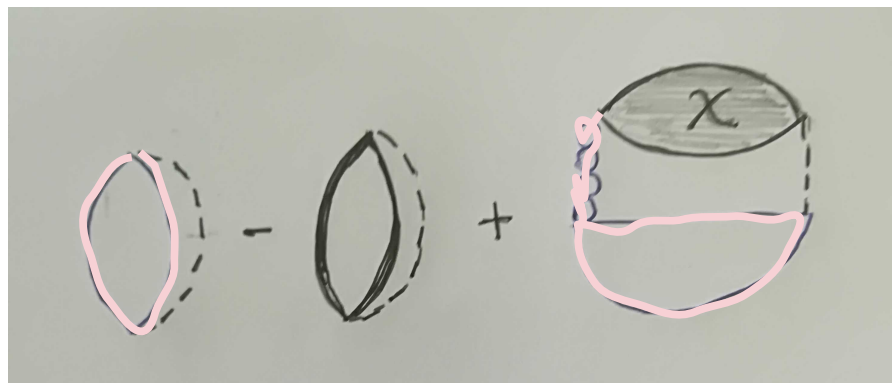
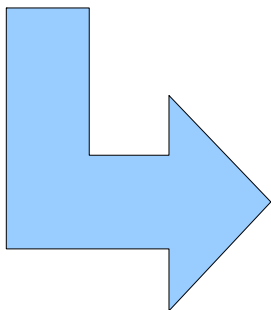
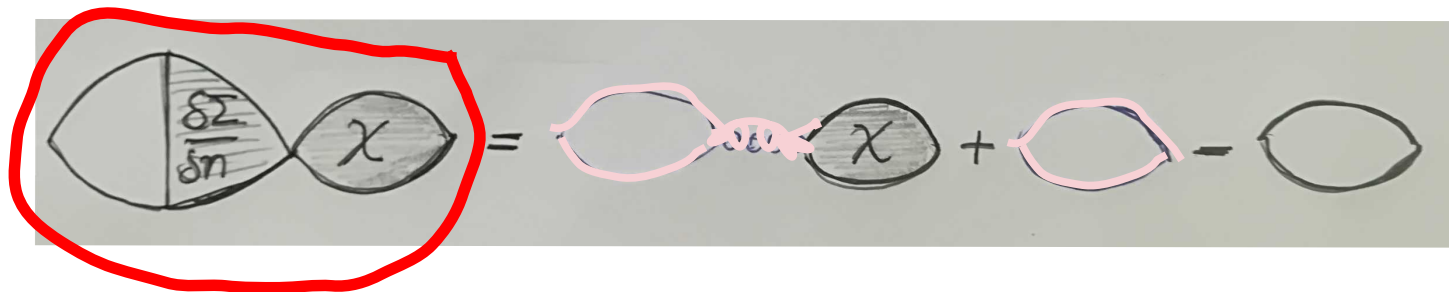
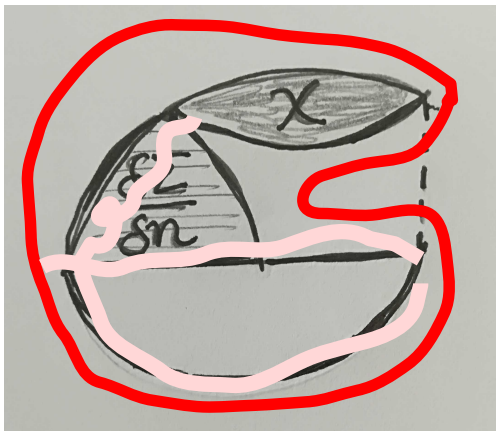


Correlation energy (no kinetic contribution)

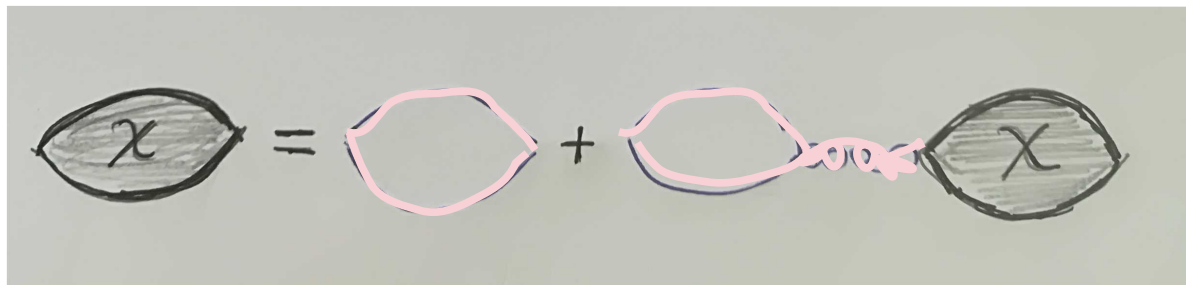
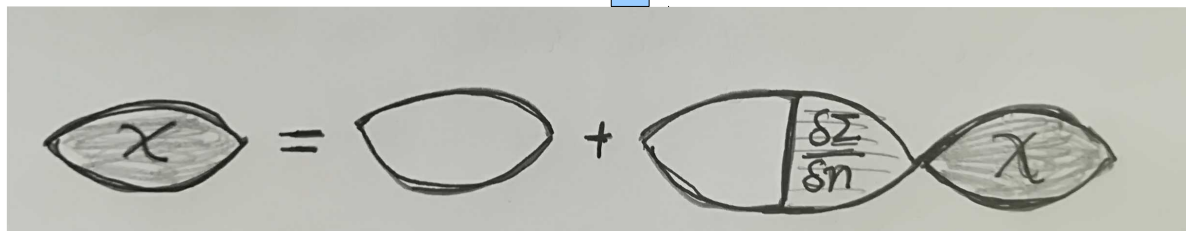
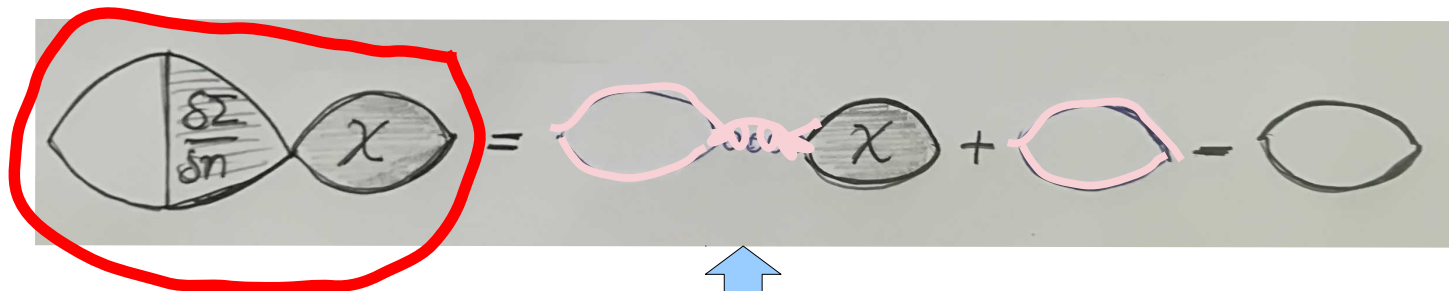
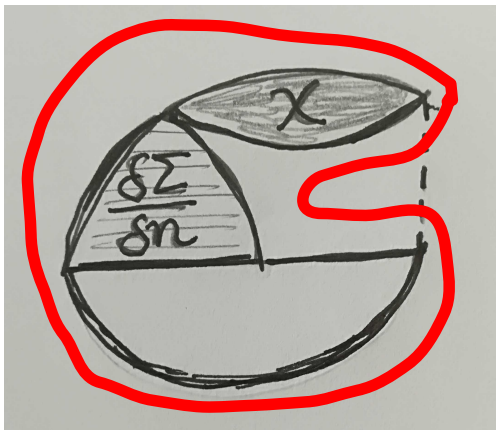


The (approximate!!!) $G\tilde{W}$ self-energy together with an xchange correction yields the exact correlation energy

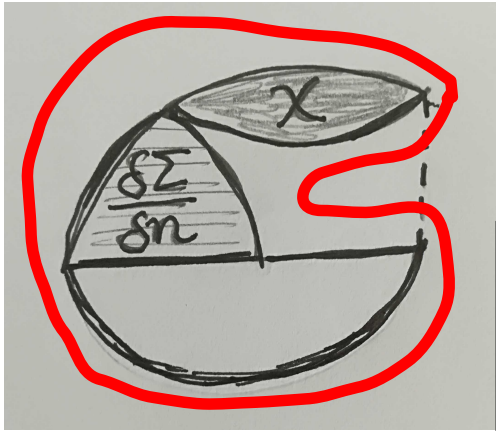
Correlation energy (no kinetic contribution)



Correlation energy (no kinetic contribution)



Correlation energy (no kinetic contribution)



The (approximate!!!) $G\tilde{W}$ self-energy together with an xchange correction yields the exact correlation energy

One of several choices: KS ingredients

The $G\tilde{W}$ approx. self-energies yield the exact xc energy if the density is exact
and if the expression is evaluated consistently

$$E_{\text{xc}} = -i\frac{1}{2} \int \Sigma_{\text{xc}}(1, 3)G(3, 1^{++}) \longrightarrow E_{\text{xc}} = -i\frac{1}{2} \int \bar{\Sigma}_{\text{xc}}(1, 3)\bar{G}(3, 1^{++})$$

Zero, one, many: the Hubbard dimer with two electrons in many-body perturbation theory

- About the choice of a model
- Analysis of GW failures
- Approximate vertex corrections from TDDFT



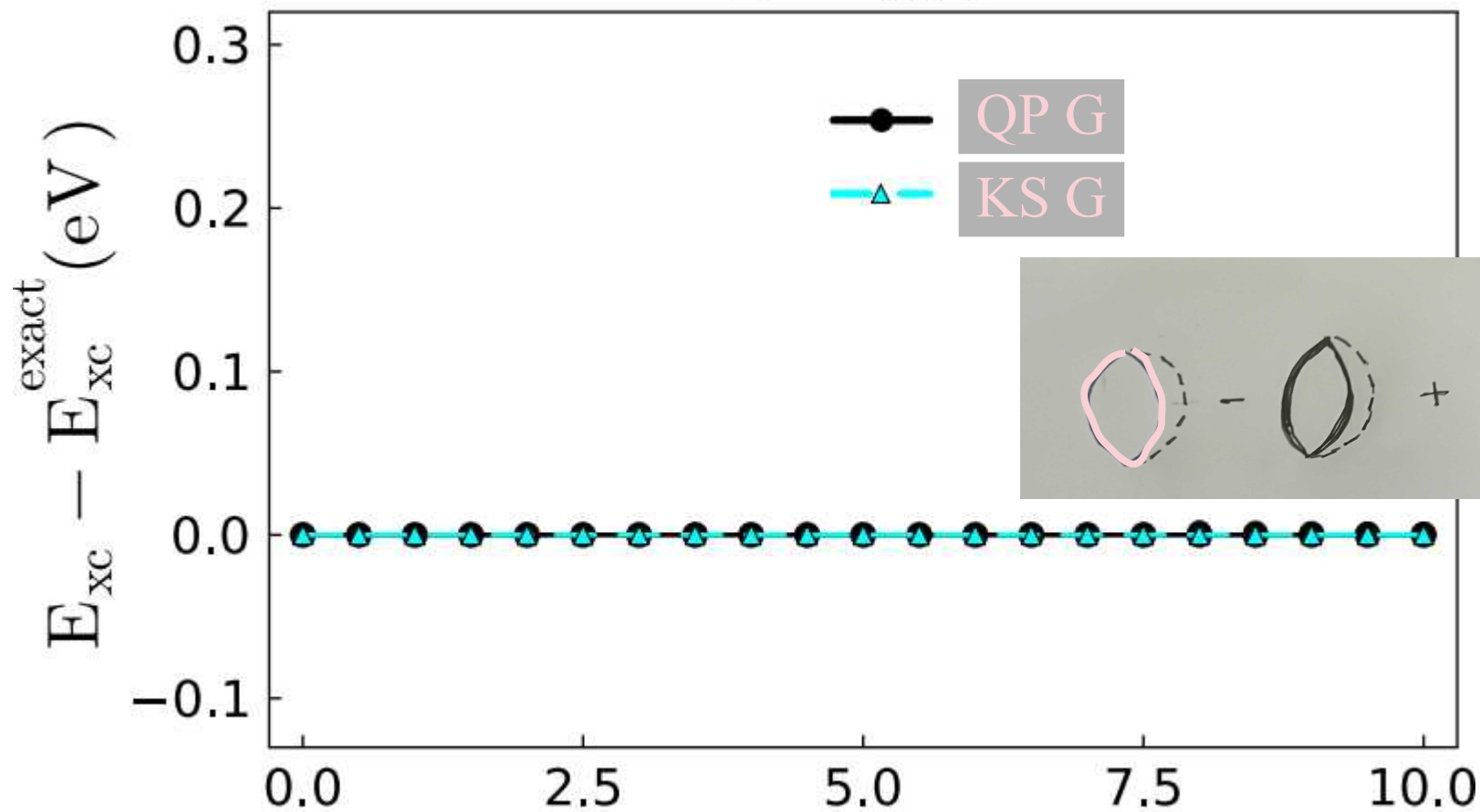
Abdallah El Sahili

El Sahili, Sottile, Reining, JCTC 2024

→ Illustration: symmetric Hubbard dimer

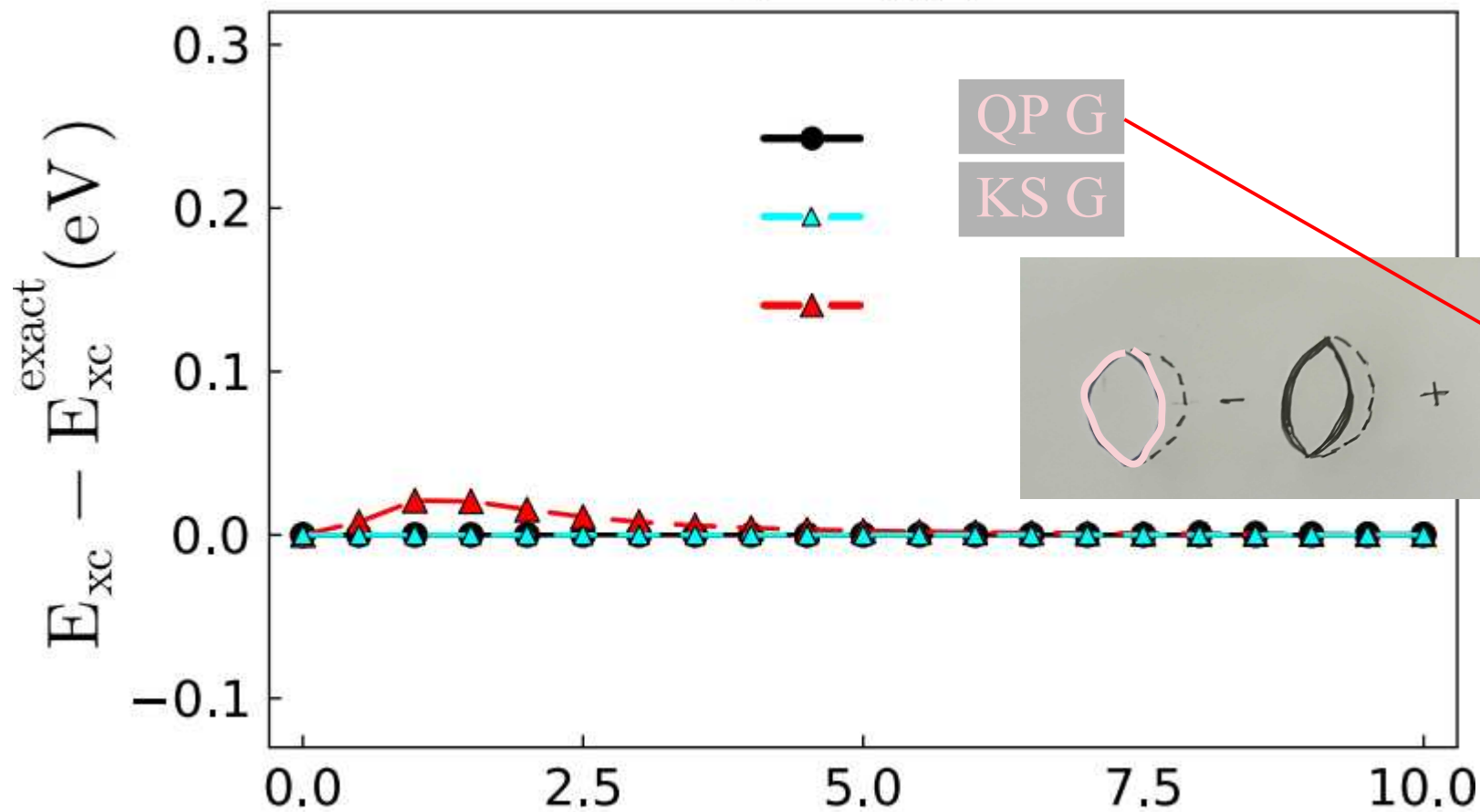
→ Conclusions

$U = 4\text{eV}$



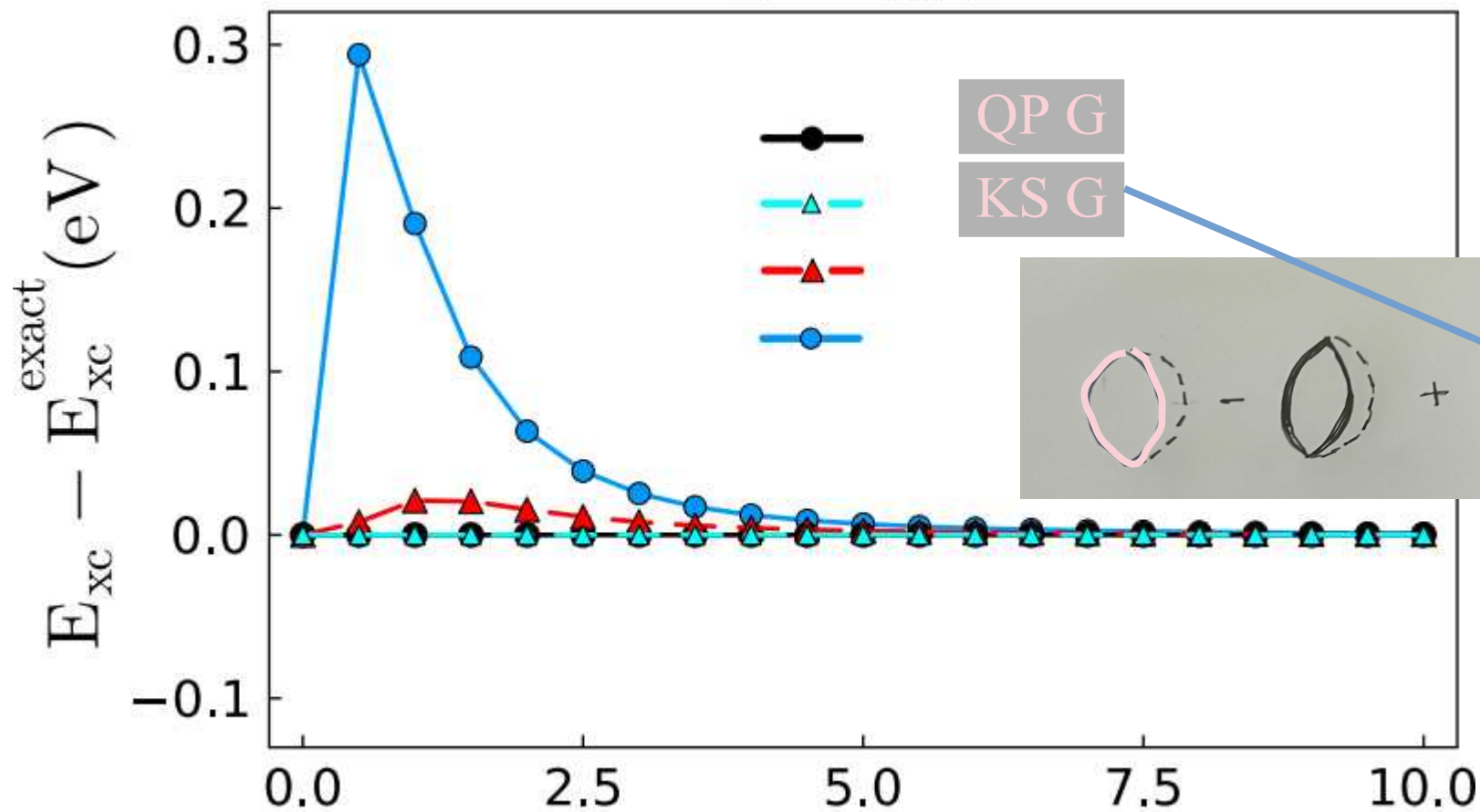
$$E_{xc} = -i\frac{1}{2} \int \Sigma_{xc}(1,3)G(3,1^{++}) \xrightarrow{t(\text{eV})} E_{xc} = -i\frac{1}{2} \int \bar{\Sigma}_{xc}(1,3)\bar{G}(3,1^{++})$$

$U = 4\text{eV}$



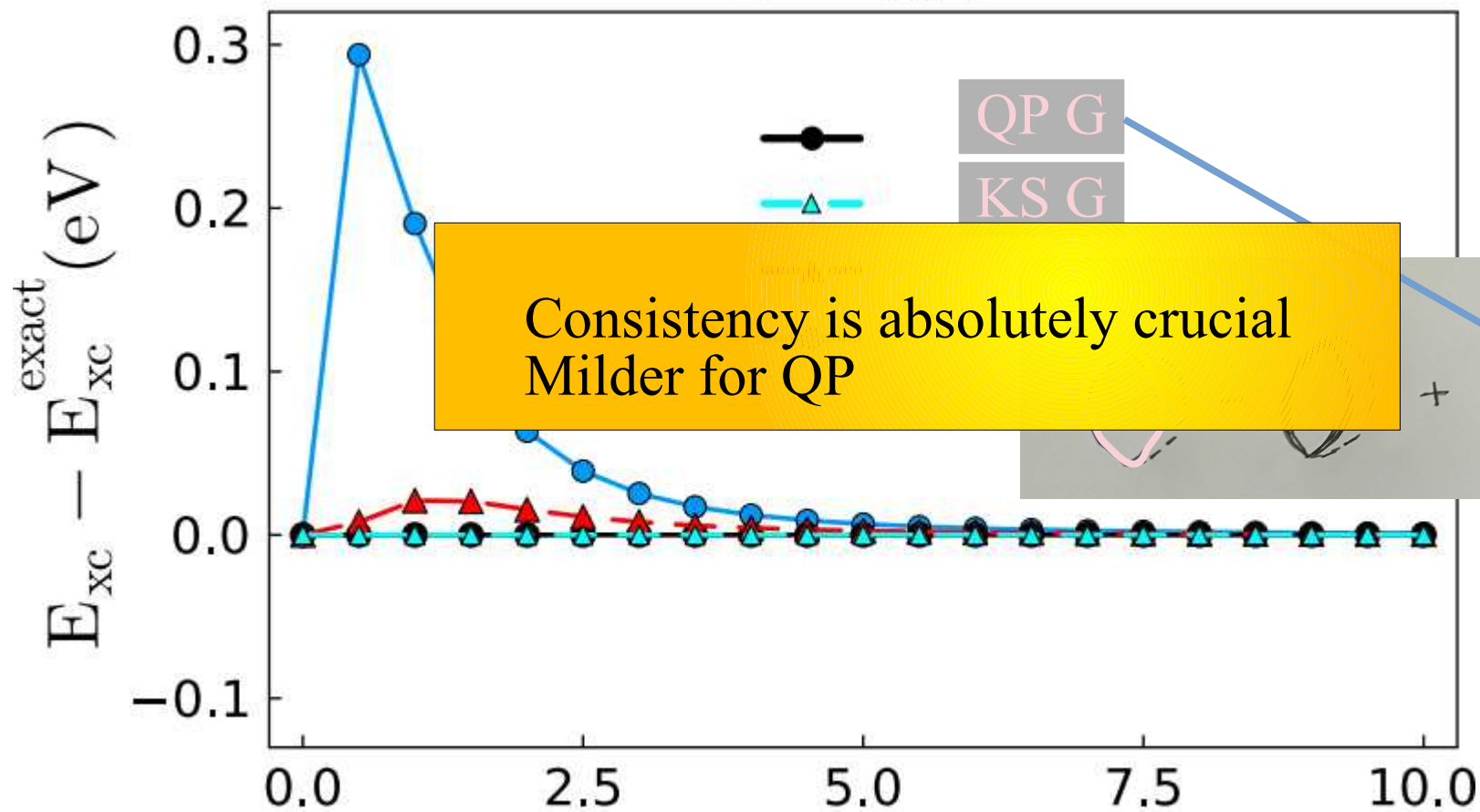
$$E_{\text{xc}} = -i\frac{1}{2} \int \Sigma_{\text{xc}}(1, 3)G(3, 1^{++}) \xrightarrow{t(\text{eV})} E_{\text{xc}} = -i\frac{1}{2} \int \bar{\Sigma}_{\text{xc}}(1, 3)\bar{G}(3, 1^{++})$$

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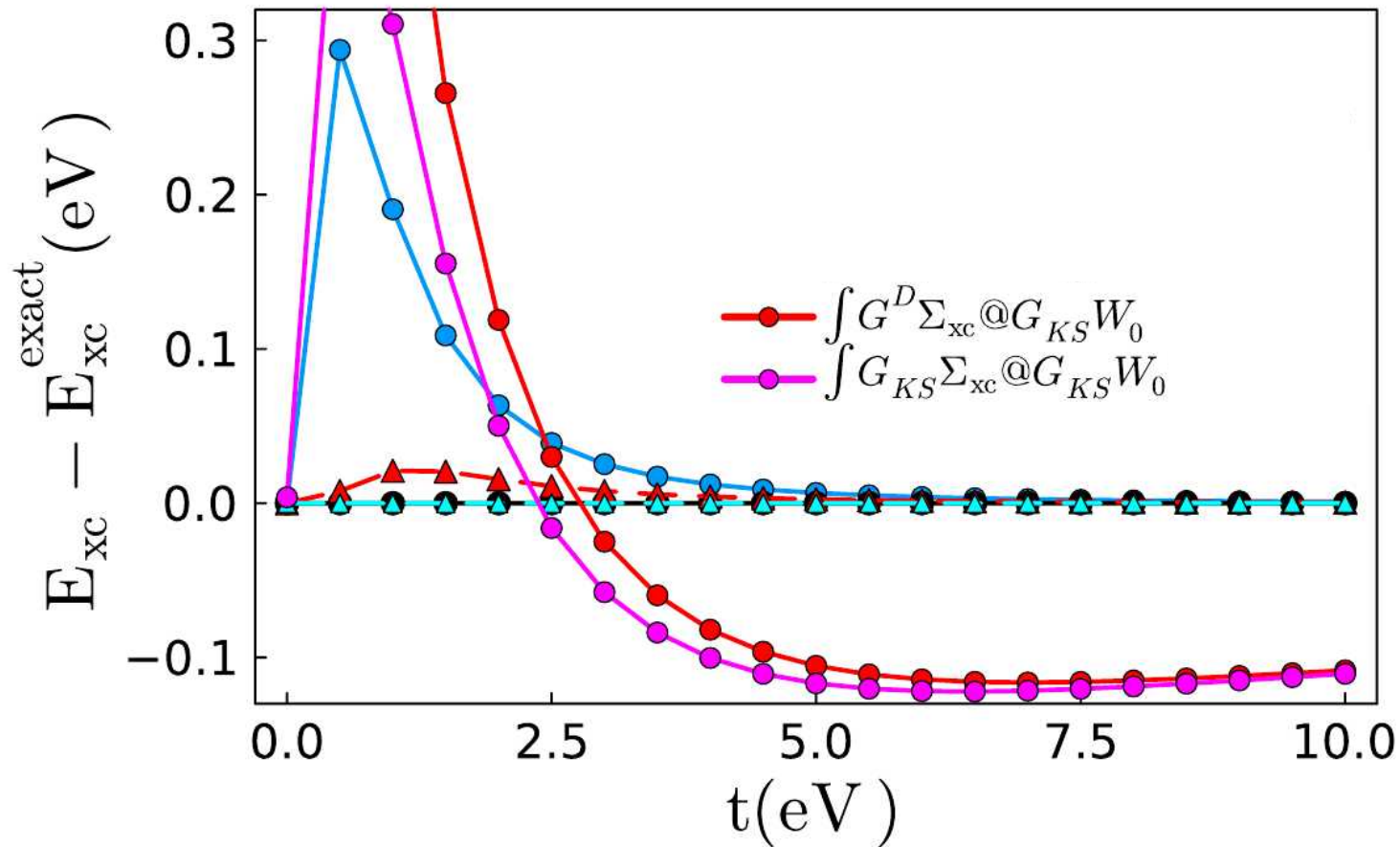
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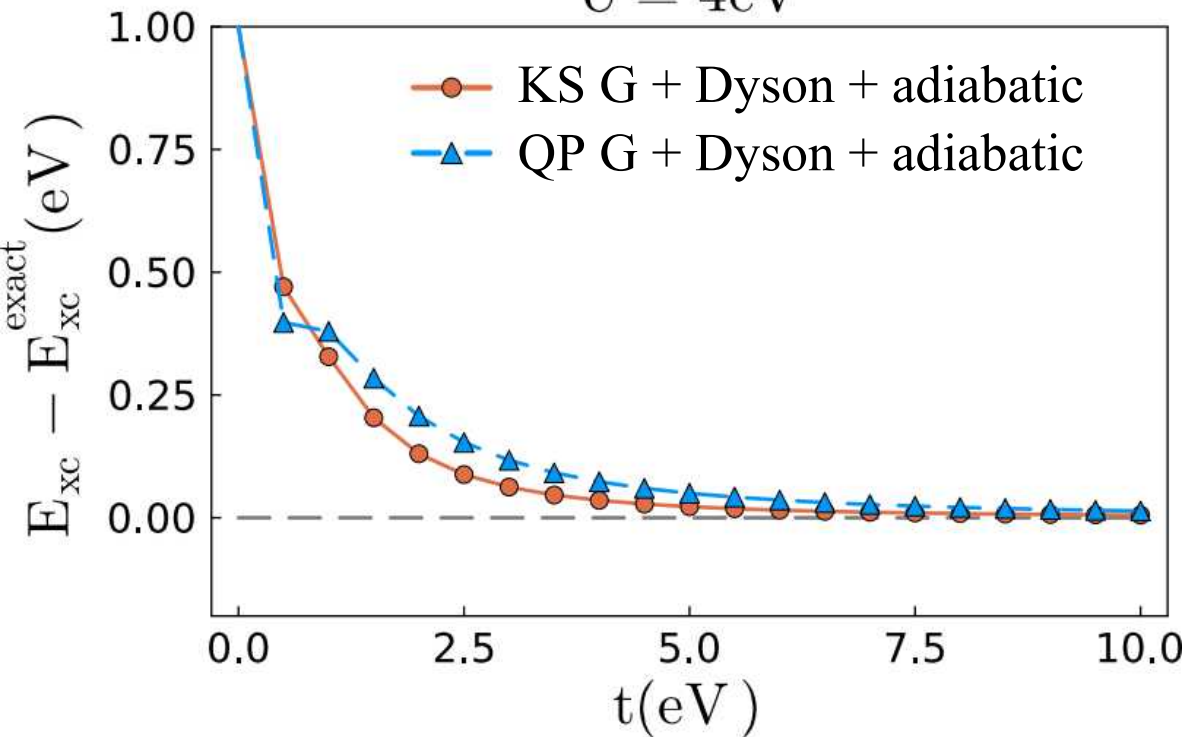
With TDDFT vertex, error much reduced wrt GW

$U = 4\text{eV}$

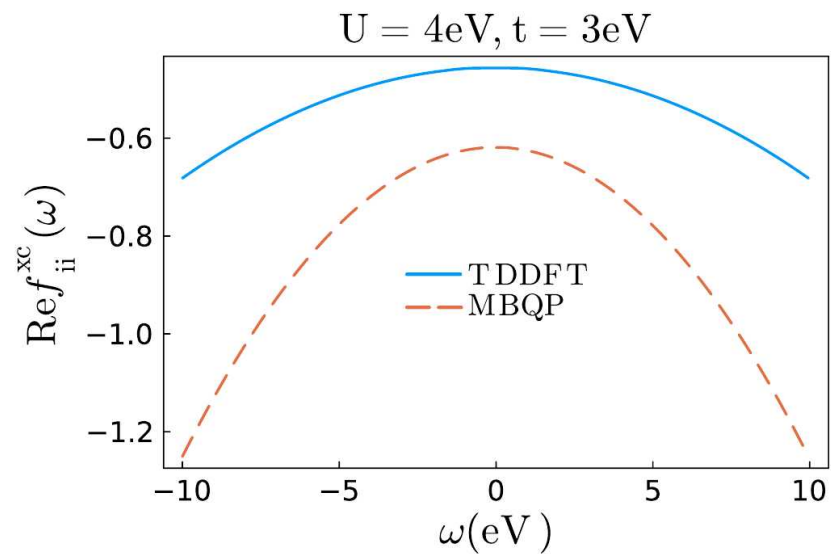
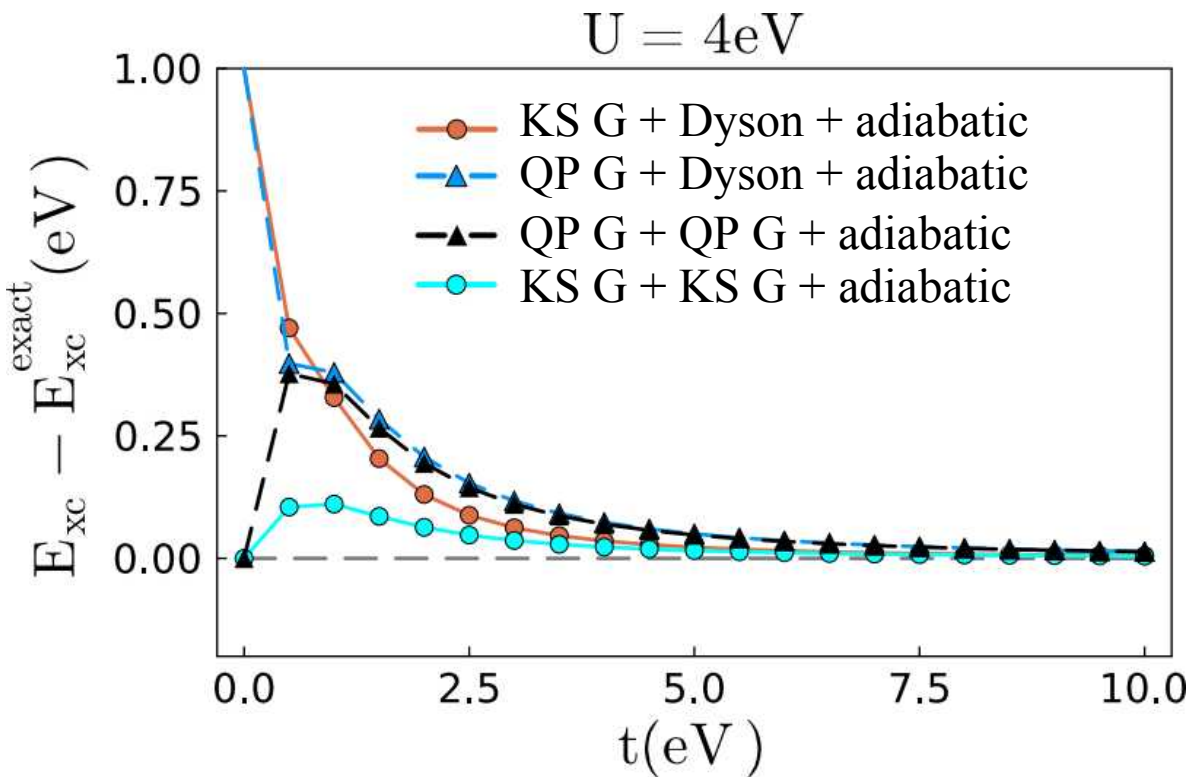


Adiabatic approx. for f_{xc}

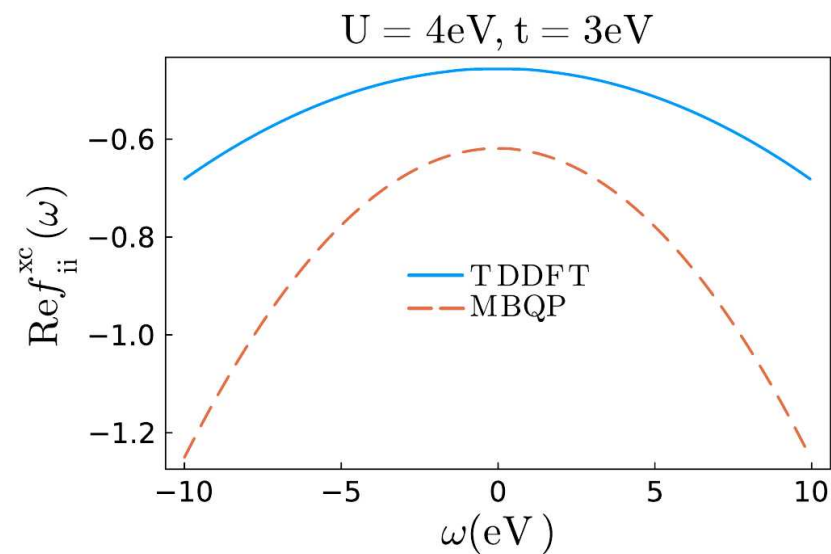
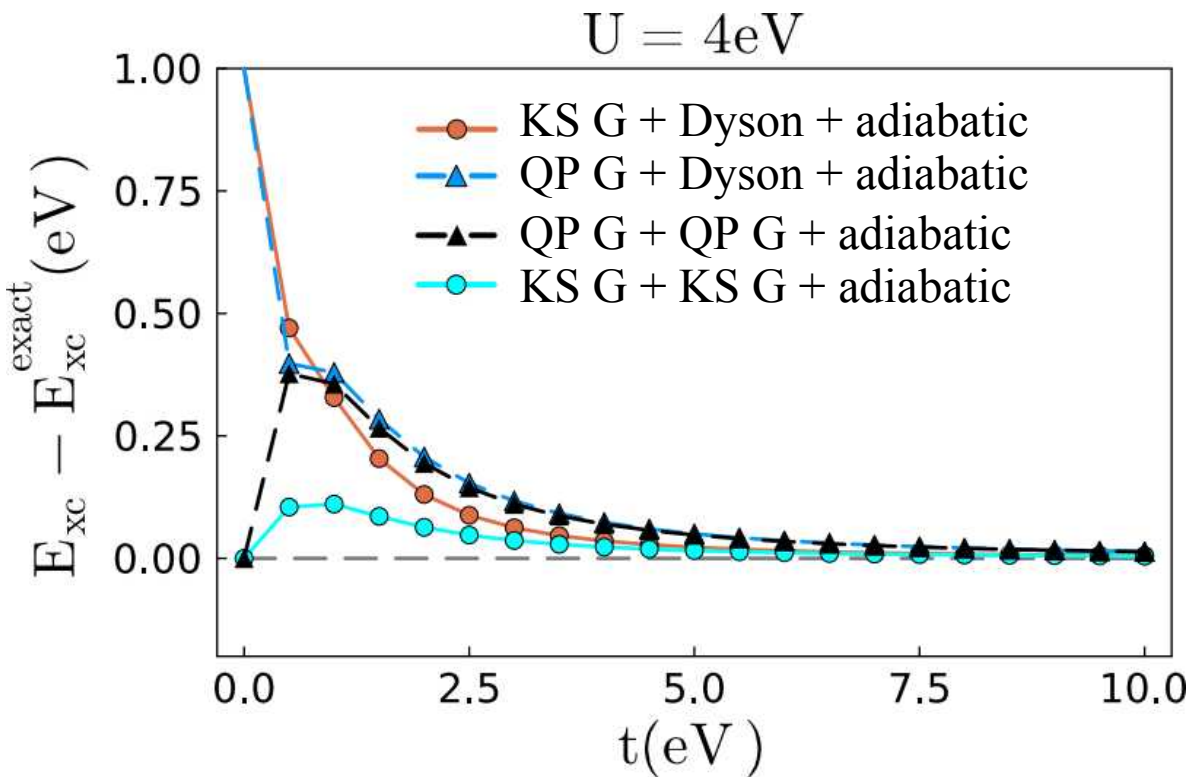
$U = 4\text{eV}$



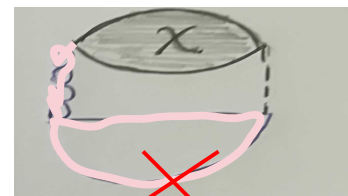
Adiabatic approx. for f_{xc}



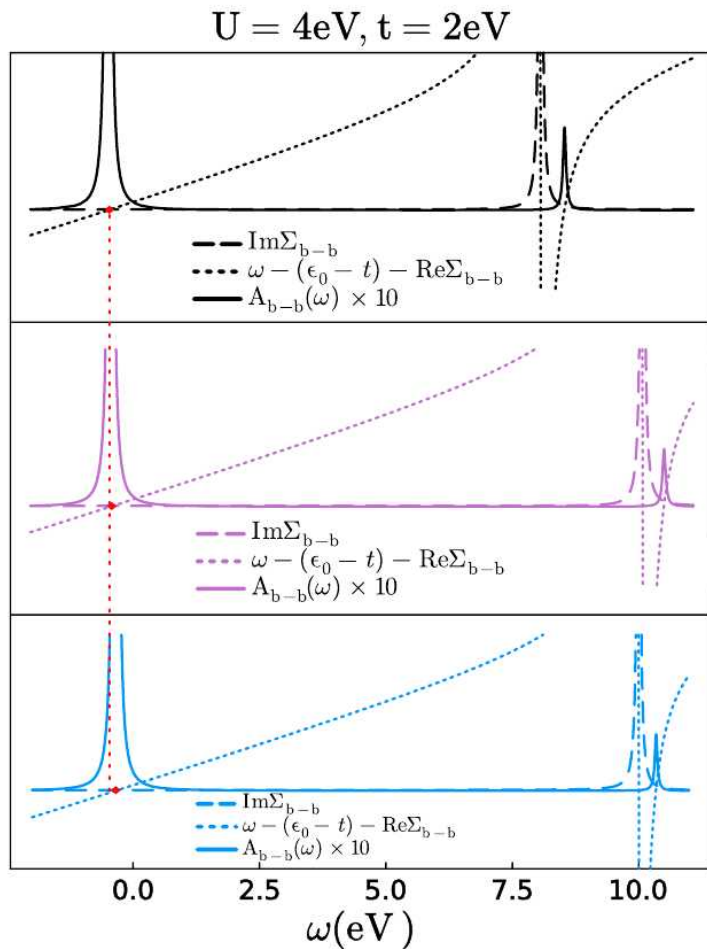
Adiabatic approx. for f_{xc} **OK, better for KS**



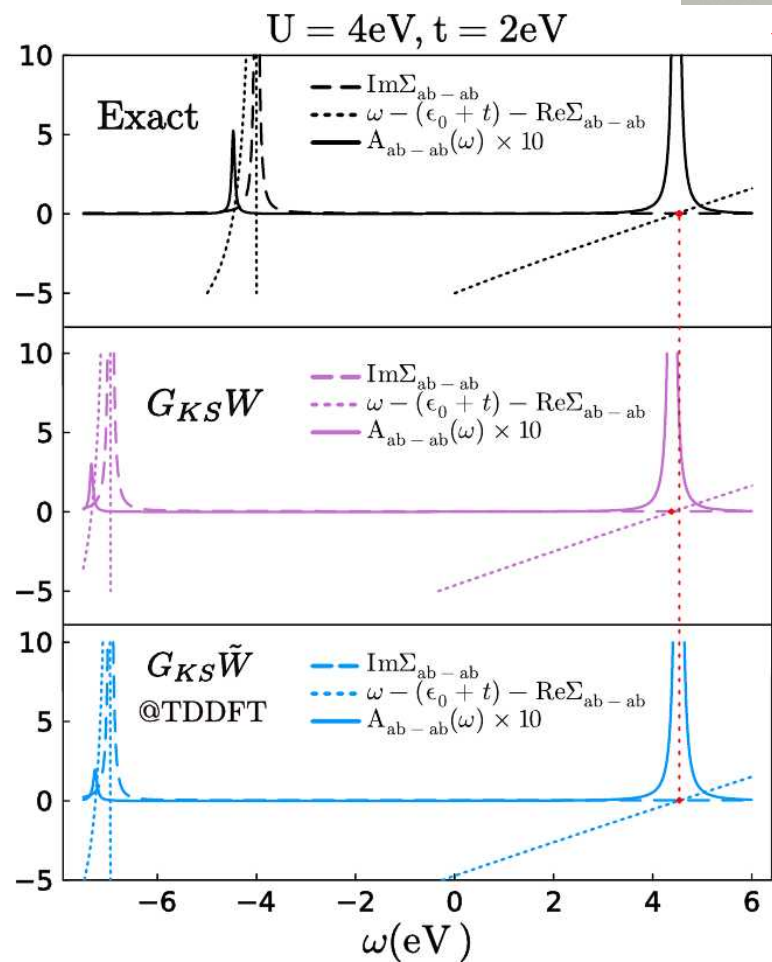
Spectral function with approximate self-energies



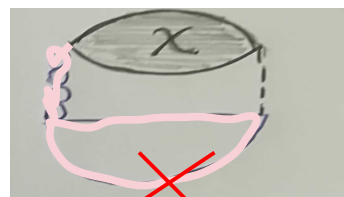
bonding



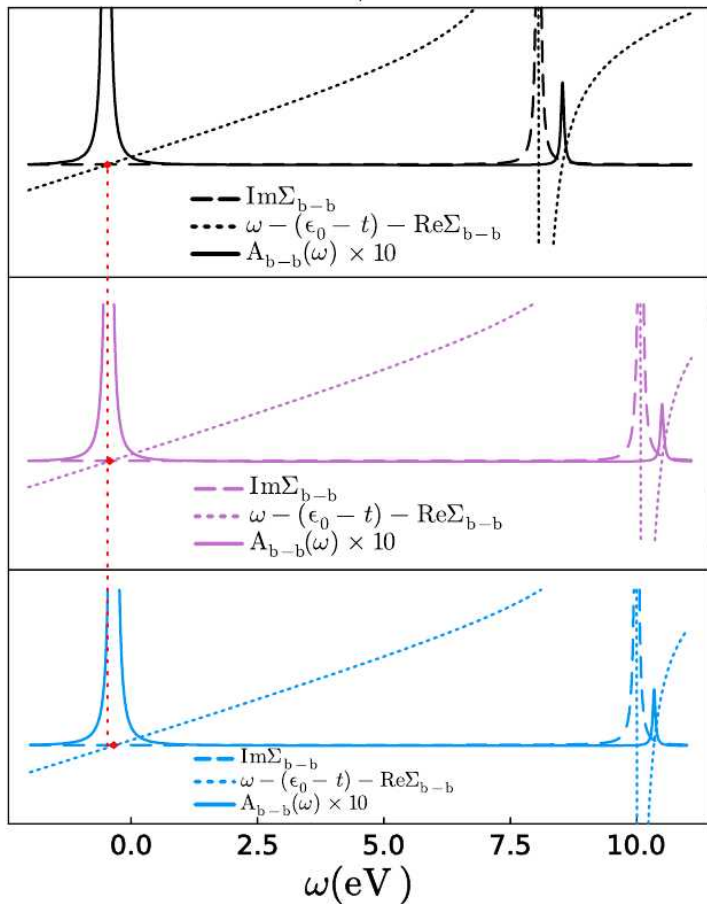
anti-bonding



Spectral function: QP quite ok

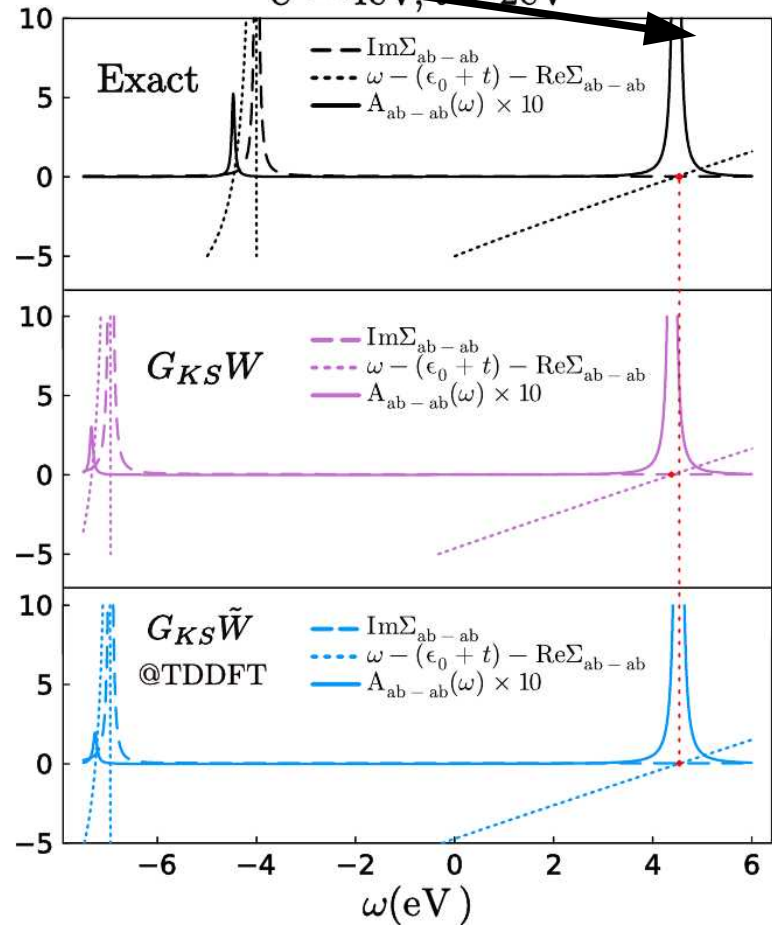


$U = 4\text{eV}, t = 2\text{eV}$



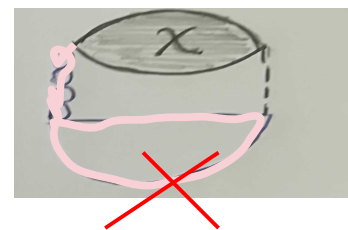
bonding

$U = 4\text{eV}, t = 2\text{eV}$

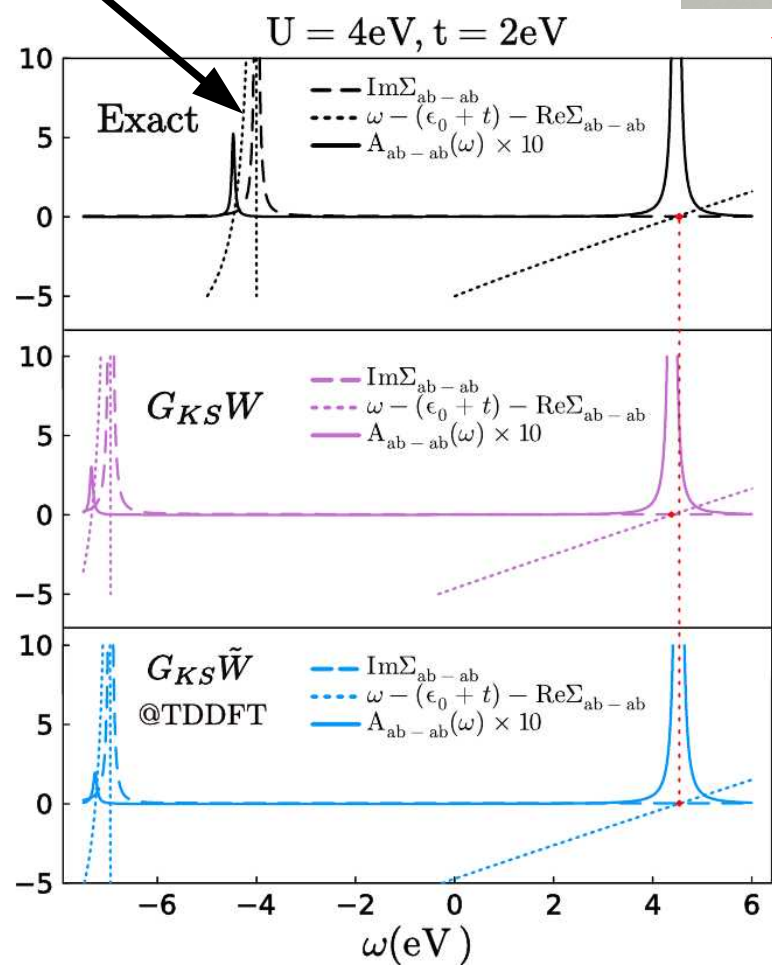
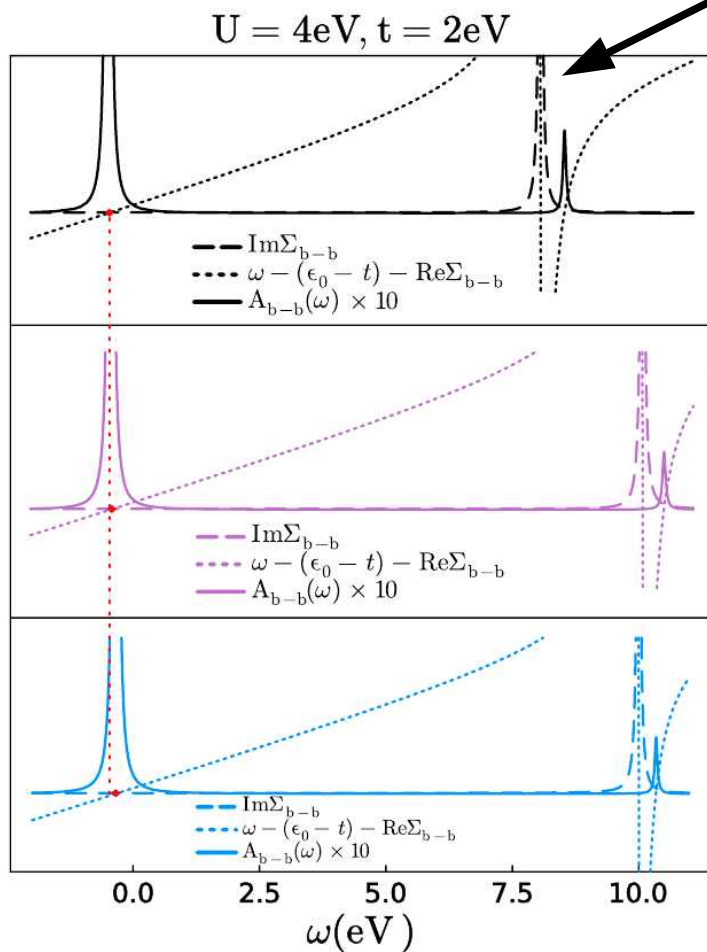


anti-bonding

Spectral function: QP quite ok, satellites bad.



bonding



anti-bonding

Spectral function: QP quite ok, **satellites bad.**

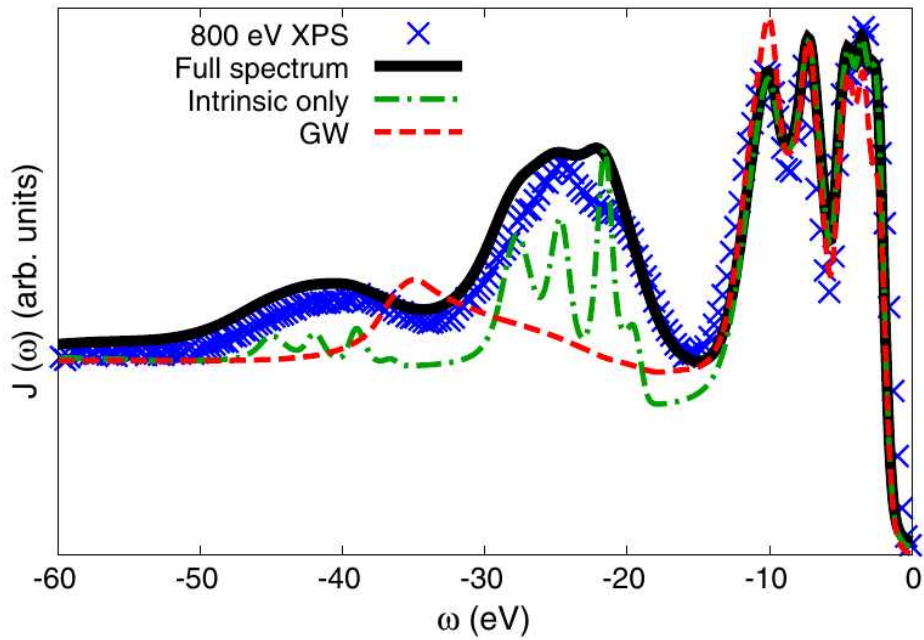
→ This is the worst error of $G\tilde{W}$

→ It is intrinsic to the use of TDDFT:

$$E_{N\pm 1,s} - E_N = \underbrace{E_{N\pm 1,s} - E_{N\pm 1}}_{\text{Excitations of charged system}} + \underbrace{E_{N\pm 1} - E_N}_{\text{Chemical potentials, 1}^{\text{st}} \text{ QP}}$$

GW and $G\tilde{W}$ put excitations of N electron system!

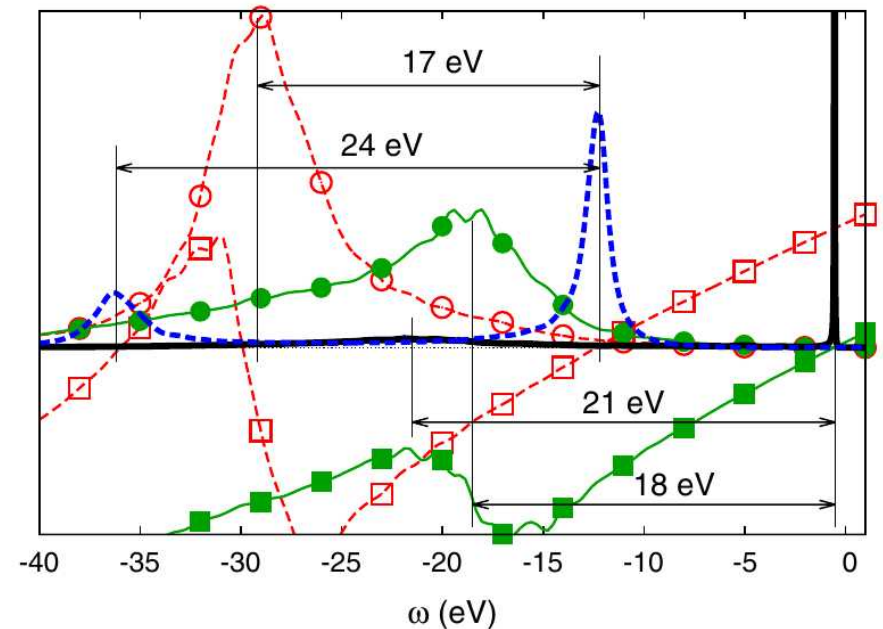
Need 2 frequency vertex to fix this (*or new effective W, thesis Abdallah*).



In an extended system,
the satellite position is another pb.

**Example where model has to be used
with caution!!!!**

Guzzo et al., PRL 107, 166401 (2011)



Zero, one, many: the Hubbard dimer with two electrons in many-body perturbation theory

- About the choice of a model
- Analysis of GW failures
- Approximate vertex corrections from TDDFT



Abdallah El Sahili

El Sahili, Sottile, Reining, JCTC 2024

→ Illustration: symmetric Hubbard dimer

→ Conclusions

The $G\tilde{W}$ approx. self-energies yield the exact xc energy if the density is exact
and if the expression is evaluated consistently

..... but not the exact G nor the exact density matrix nor kinetic energy!

- When the TDDFT input is exact, QPs are quite ok while sat.s are bad
- The adiabatic approximation to the xc kernel does ok, better when KS
- Consistency of the ingredients is most crucial for xc energy

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Much more to show.....

.....since simple Hubbard dimer allows us to explore quickly!

(but mind its limits)