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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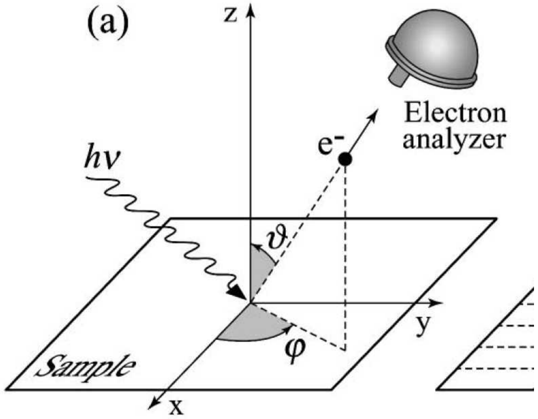
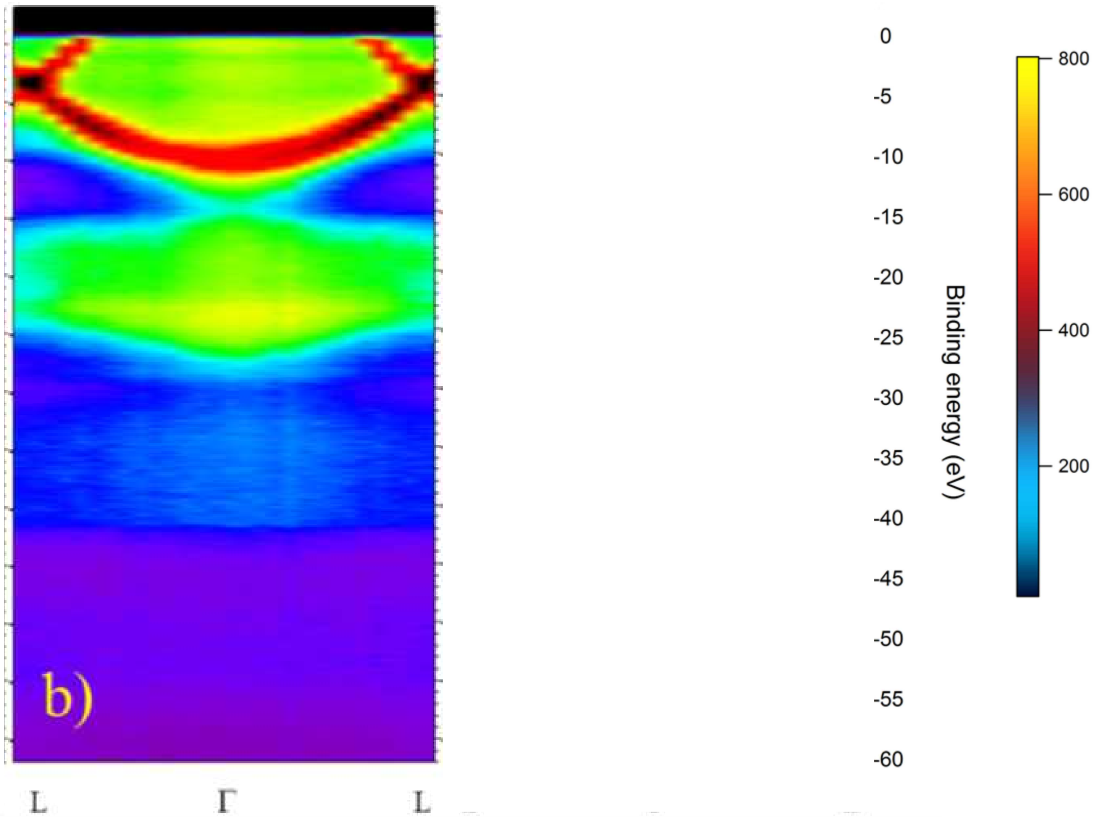
Photoemission of bulk aluminum



Photoemission geometry

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

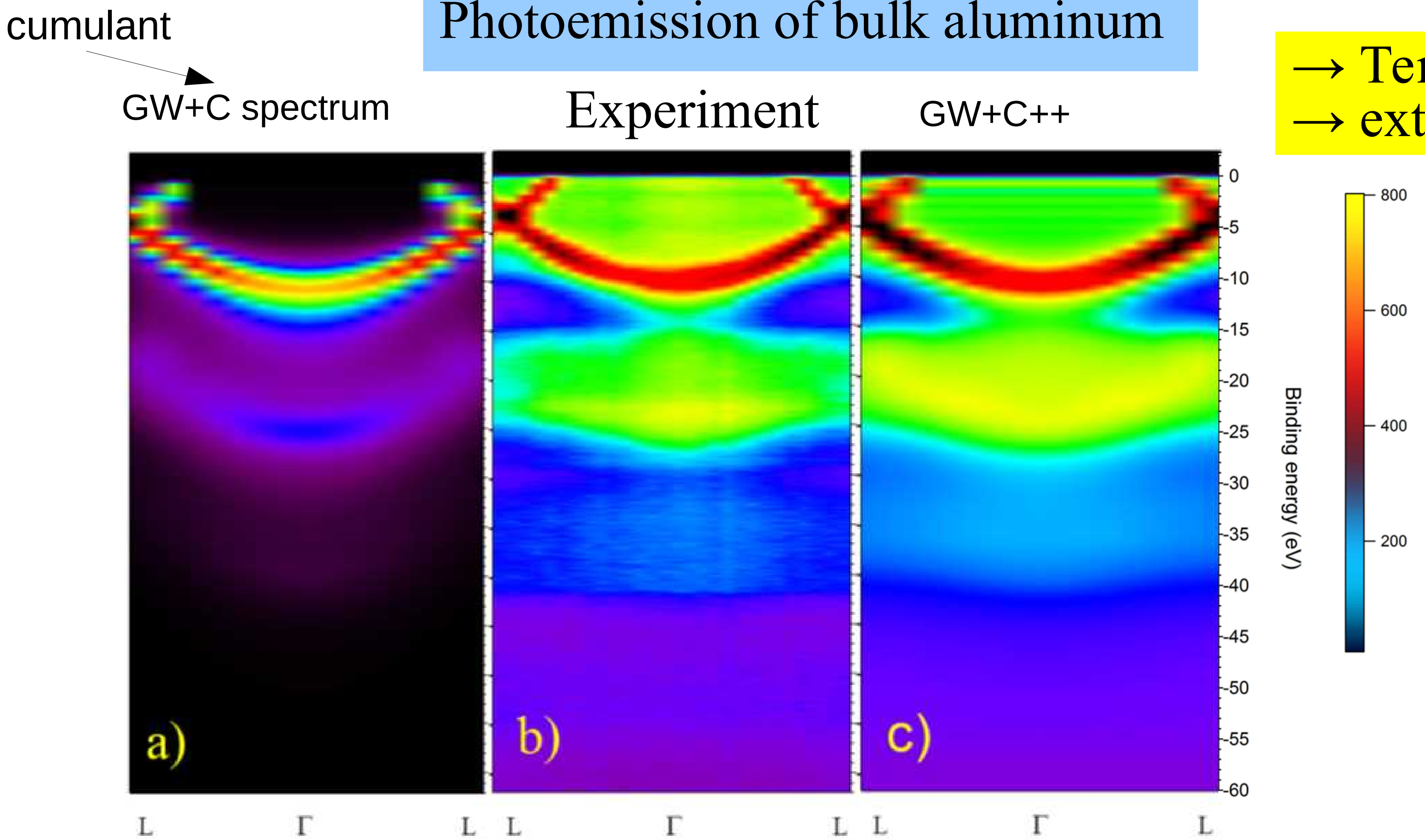
Experiment



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

Photoemission of bulk aluminum

→ Temperature
→ extrinsic scattering



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Periodic Hubbard model

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

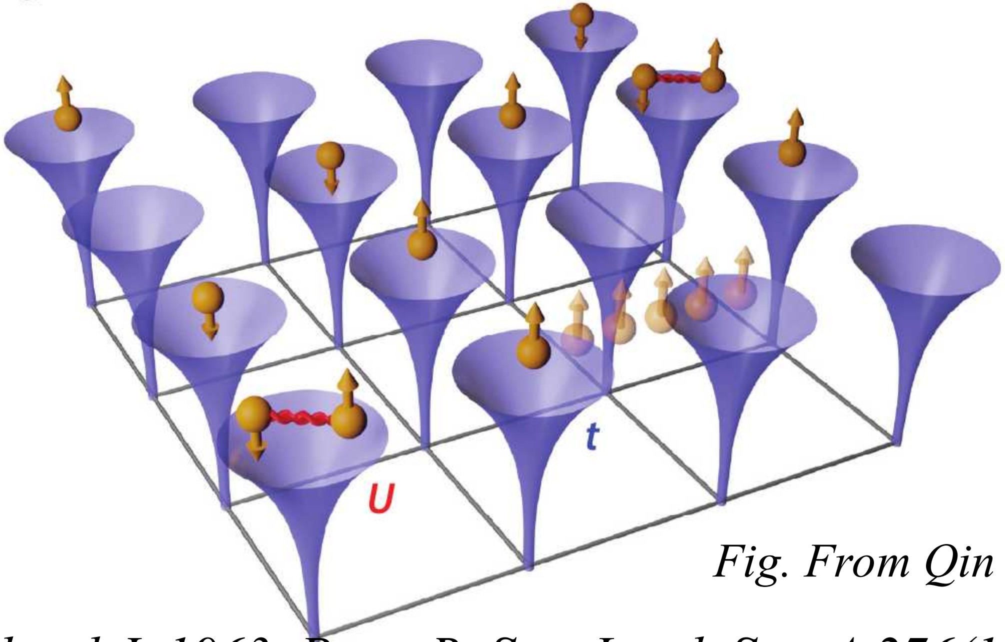

Fig. From Qin et al., ARCMP 13, 275 (2022)

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

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

i=1,2

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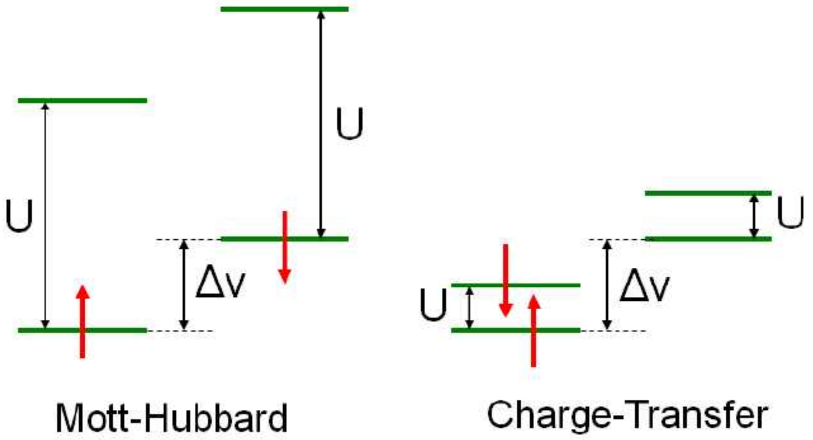

D J Carrascal et al 2015 J. Phys.: Condens. Matter 27 393001

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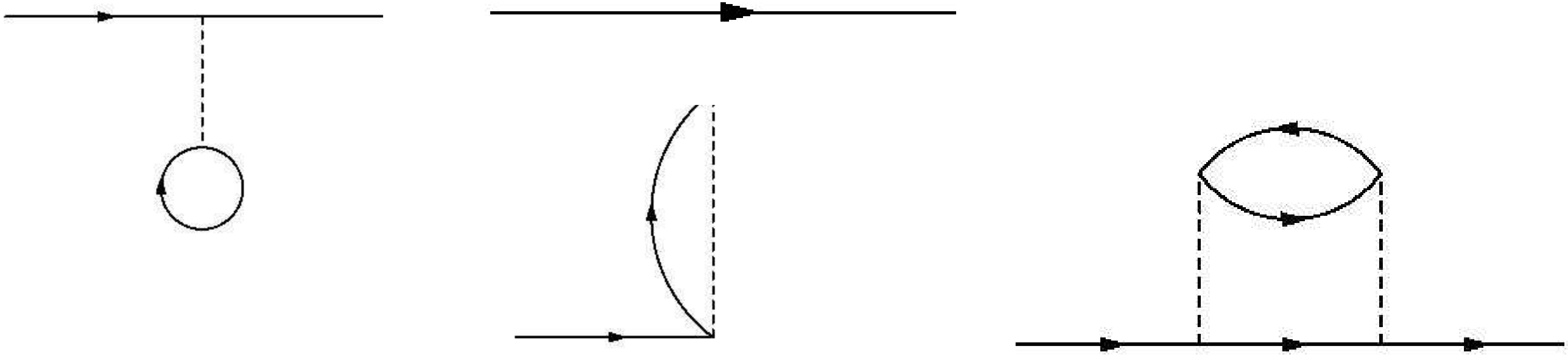
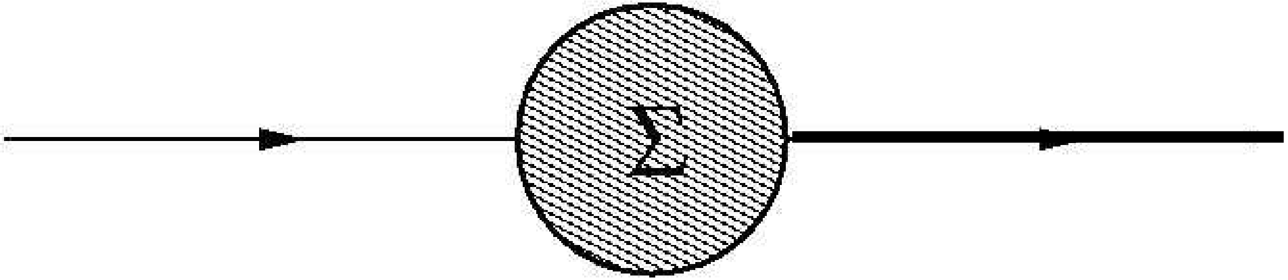
$$G(x_1, x_1', t, t') = -i\langle N|T[\hat{\Psi}(x_1, t)\hat{\Psi}^\dagger(x_1', t')]|N\rangle$$

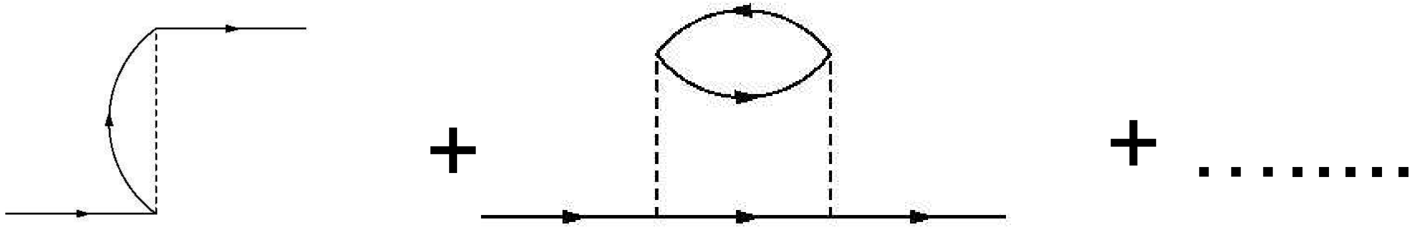
Many things can happen to a particle that propagates in the middle of others......





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

Typical GFFT approximation strategy

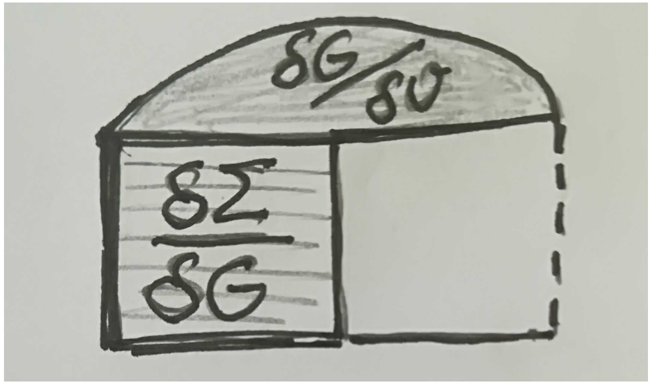


$$\rightarrow \Sigma \sim i\, GW$$ “GW”

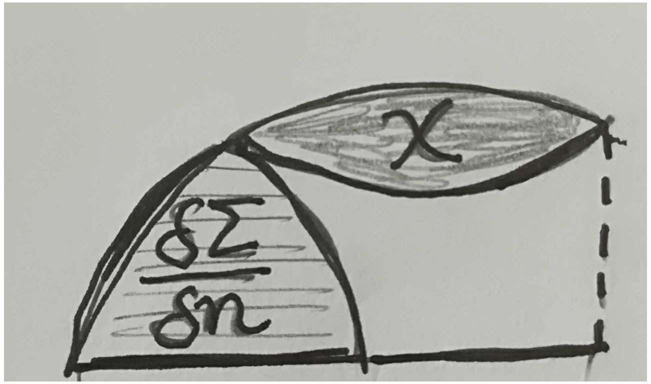
L. Hedin, Phys. Rev. 139:A796–823, 1965

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

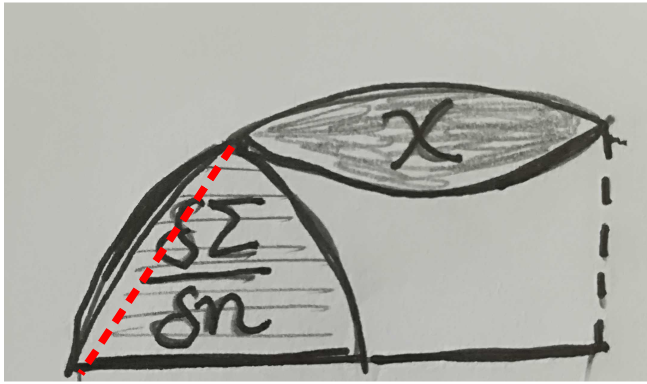
Correlation self-energy:



Martin, Reining, Ceperley
Interacting Electrons
(Cambridge 2016)

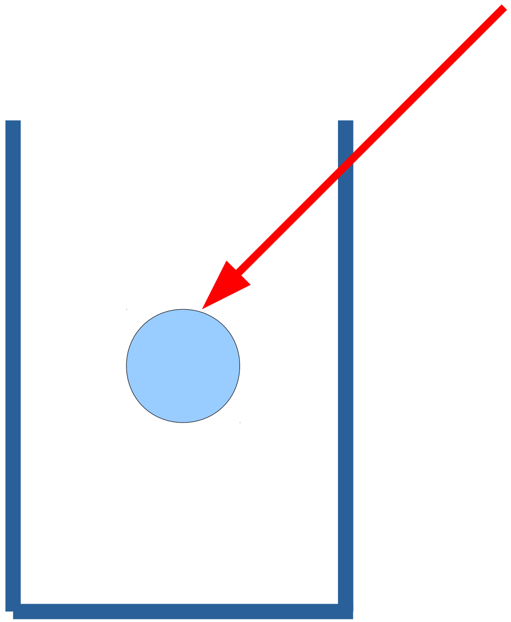


Bruneval, et al,
PRL 94, 186402 (2005)



GW
Hedin 1965

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

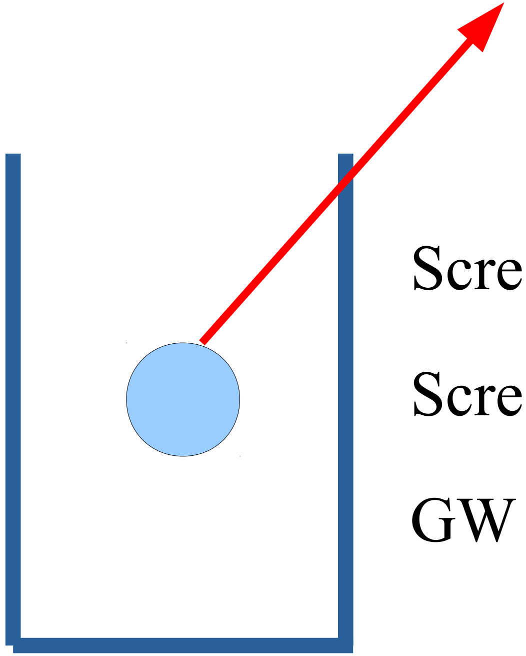


No screening

Fock cancels SI

GW=HF=OK

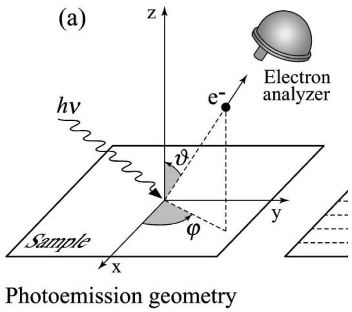
Zero, one, many: the Hubbard dimer with two electrons in many-body perturbation theory



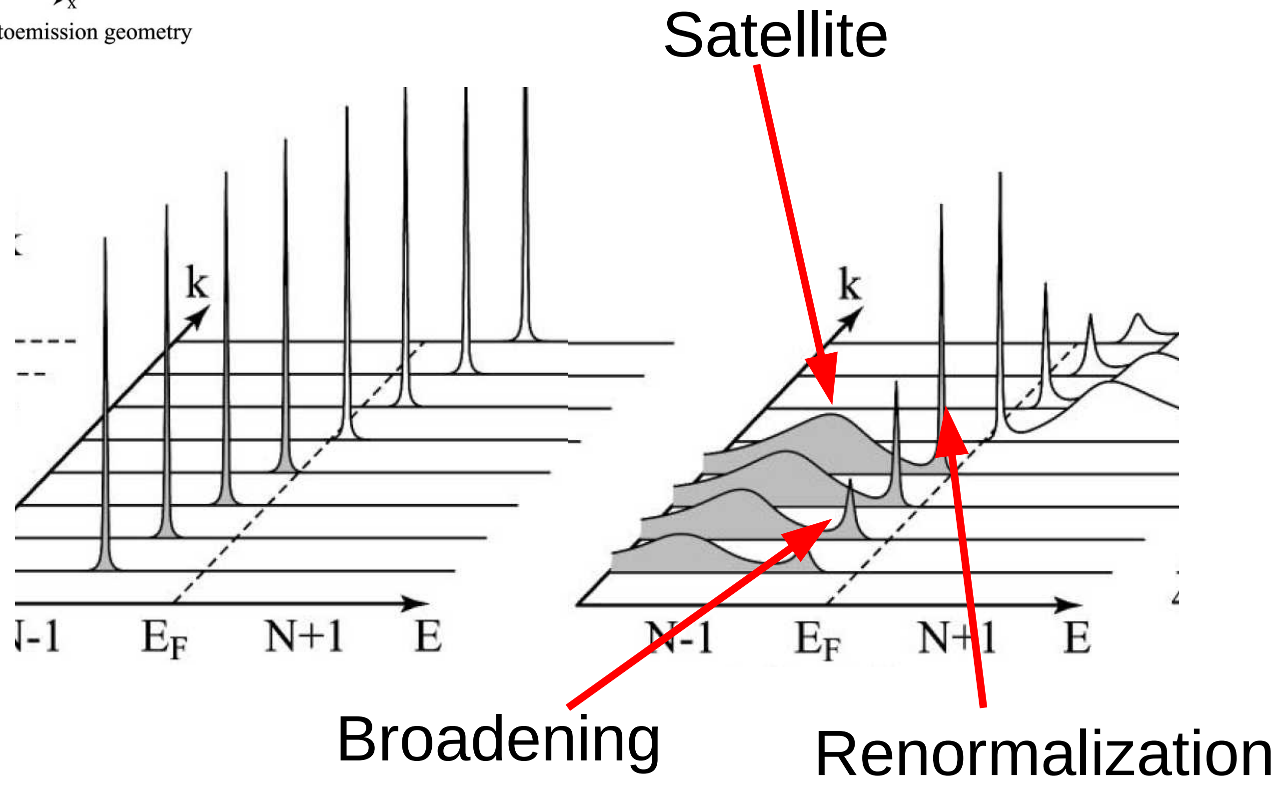
Screening by N=1 electron

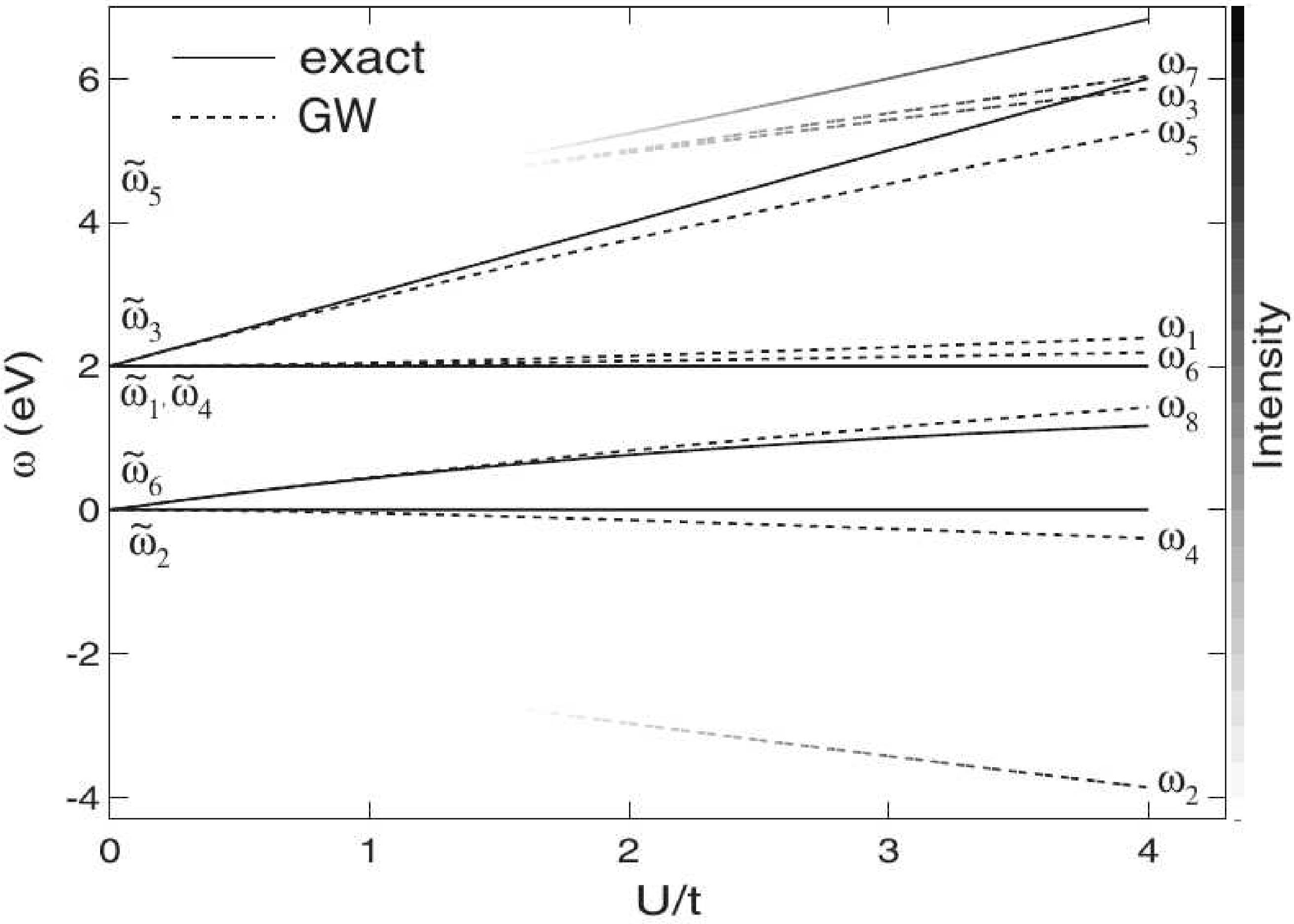
Screened Fock does not cancel SI

GW NOT OK

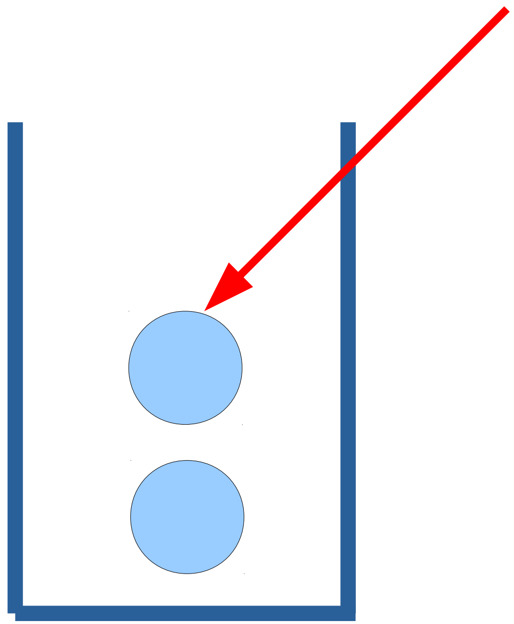


$$W(\omega) = \epsilon(\omega)^{-1} v_c$$

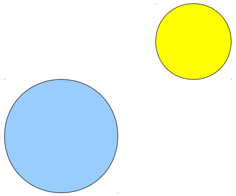


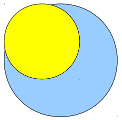


Romaniello, Guyot, Reining, J. Chem. Phys. 131, 154111 (2009)

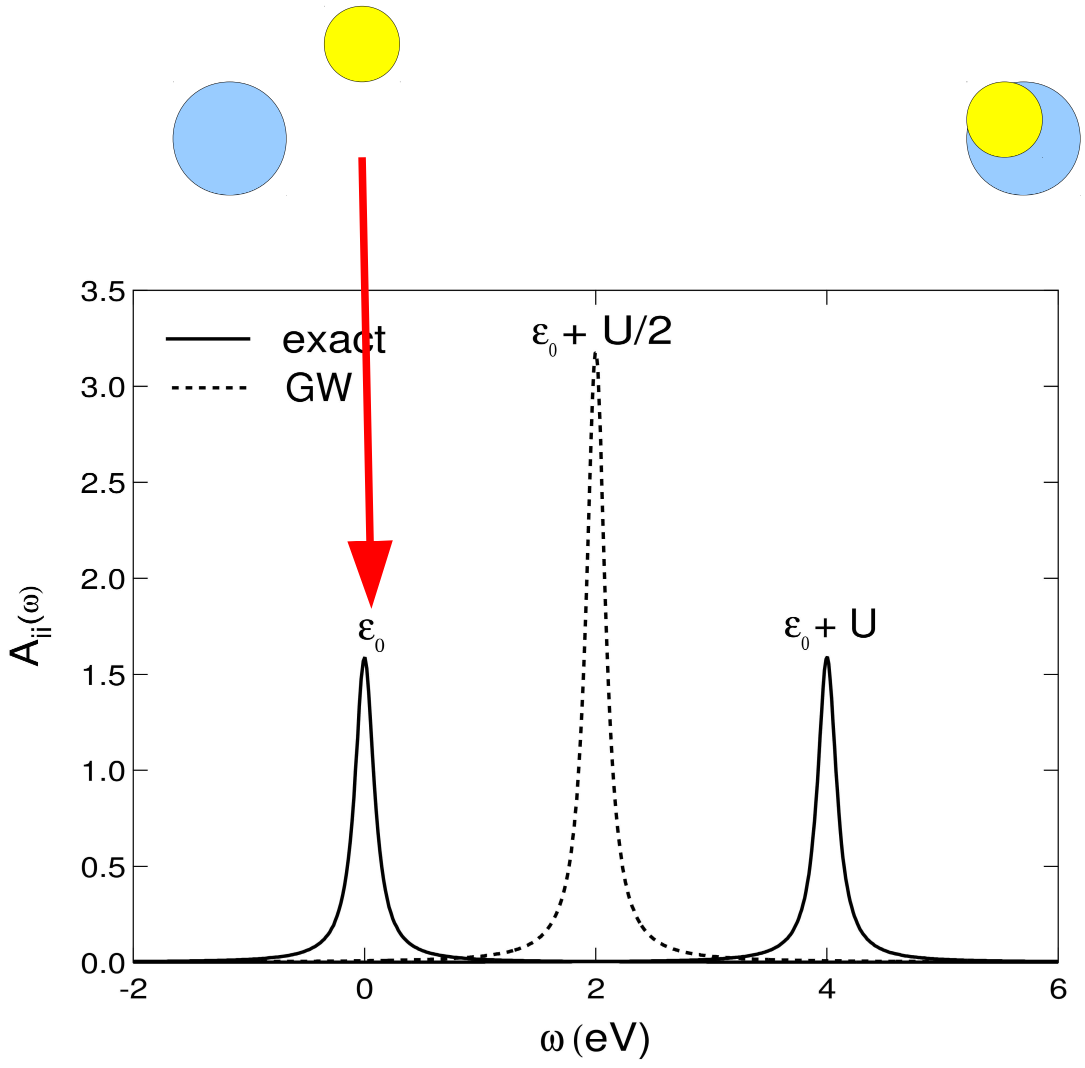


H_2^+





H_2^+



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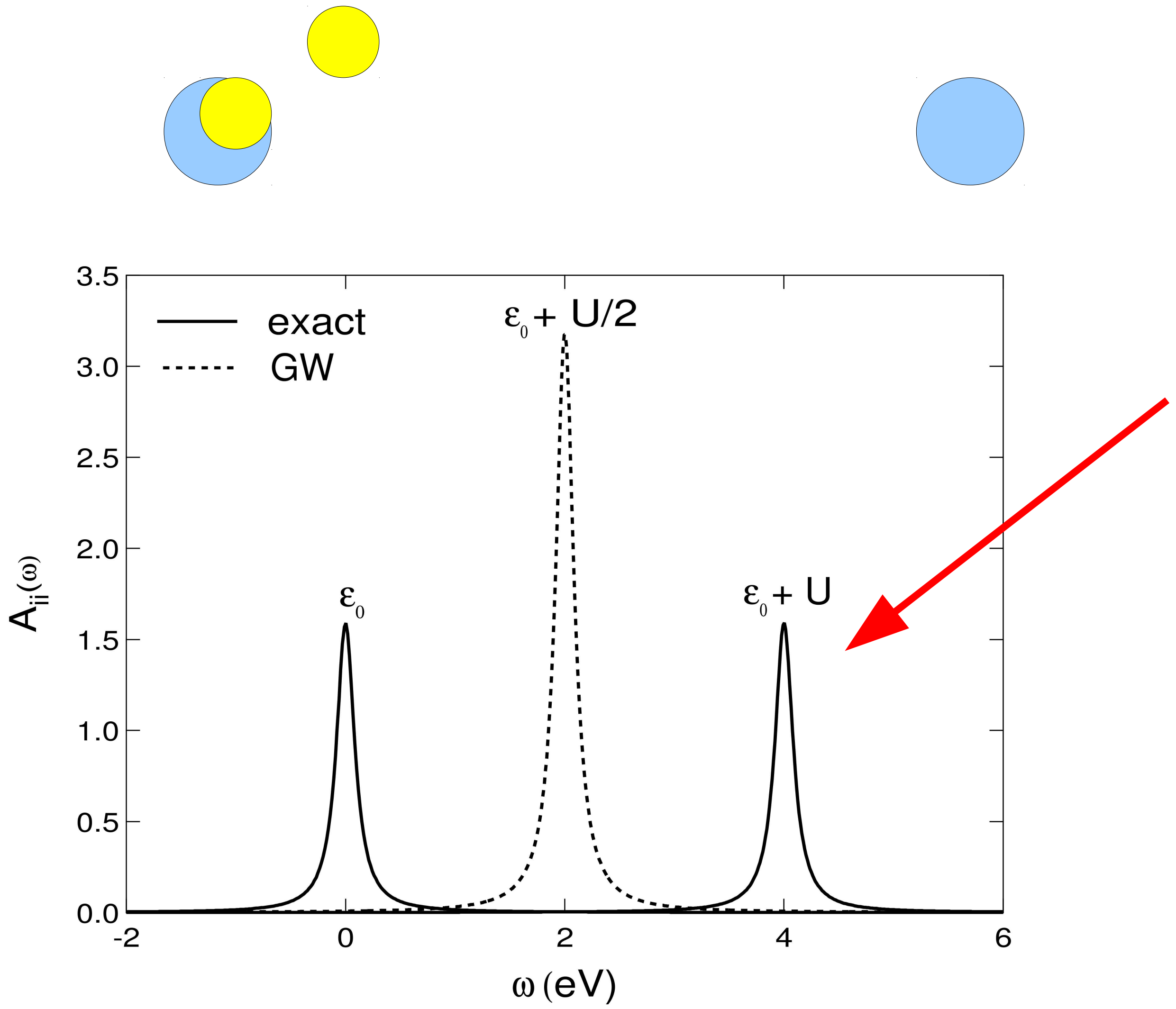
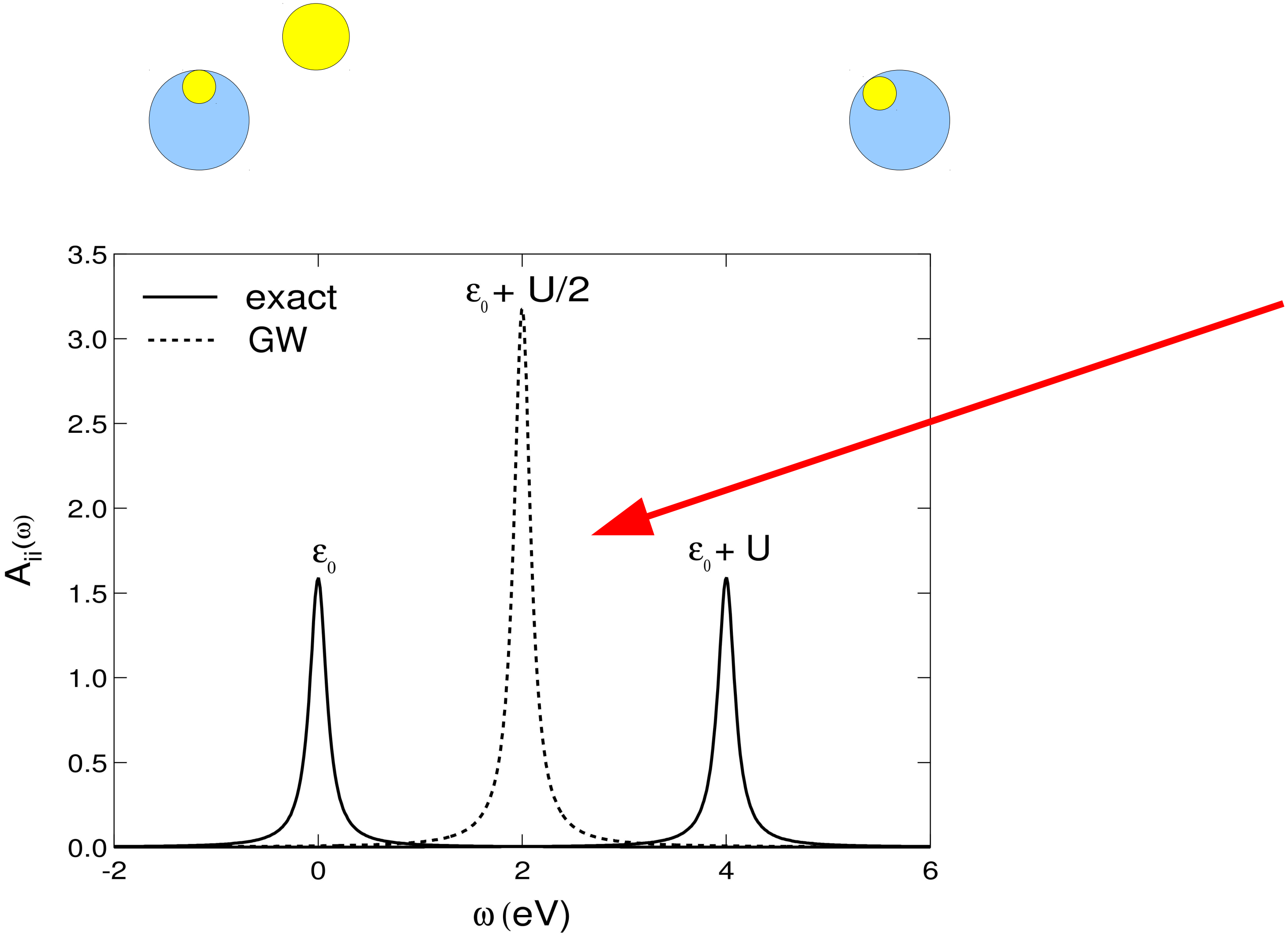


H_2^+

Mean field interpretation of the density: ½ + ½

H_2^+

H_2^+



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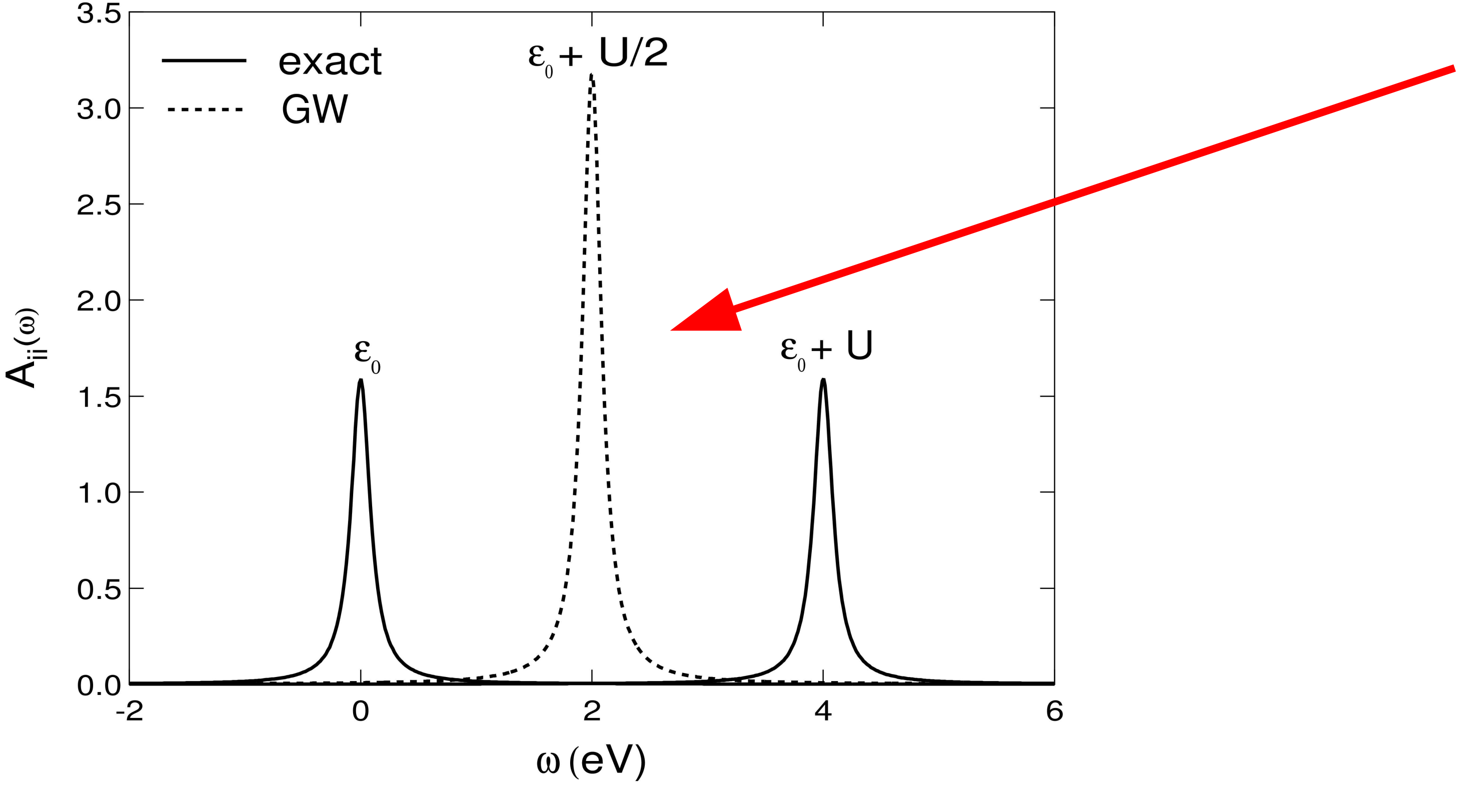
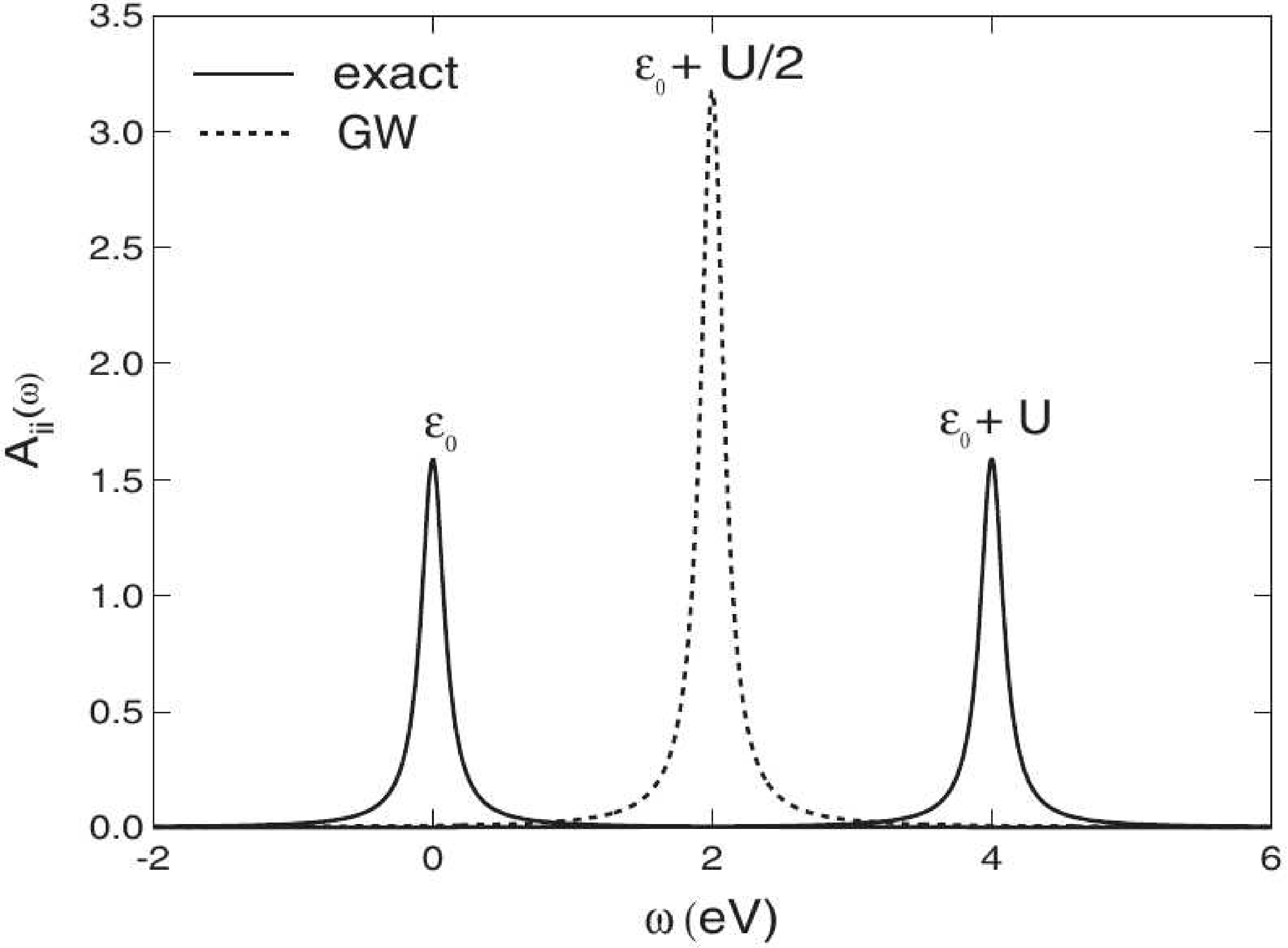
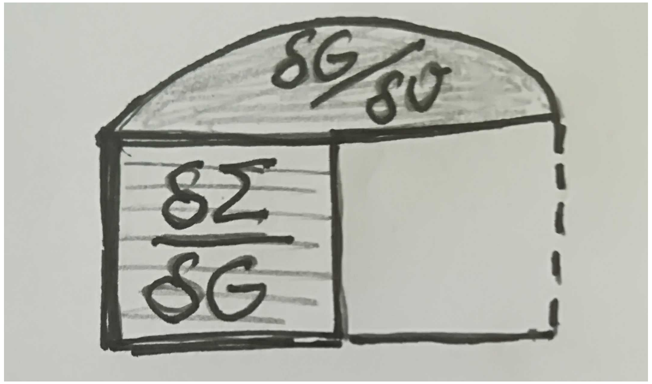


exact
GW
$\varepsilon_0 + U/2$
ε_0
$\varepsilon_0 + U$
$A_{ii}(\omega)$
ω (eV)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2
0
2
4
6



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

Correlation self-energy:



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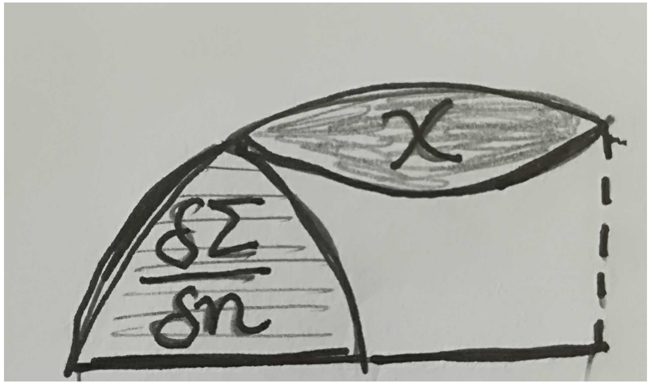

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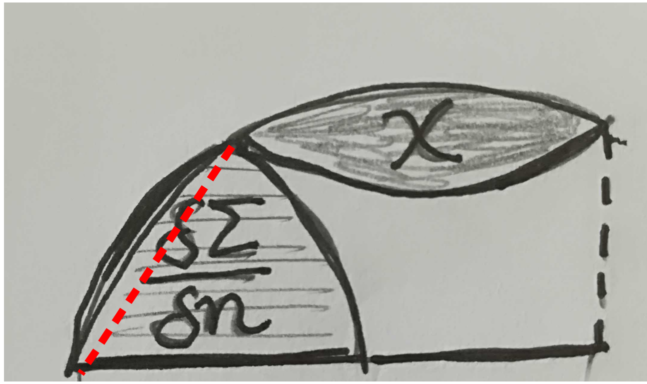

GW
Hedin 1965

Can we use TDDFT for better effective interactions?

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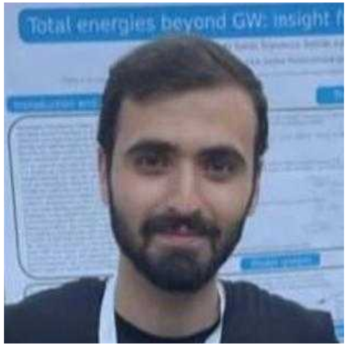
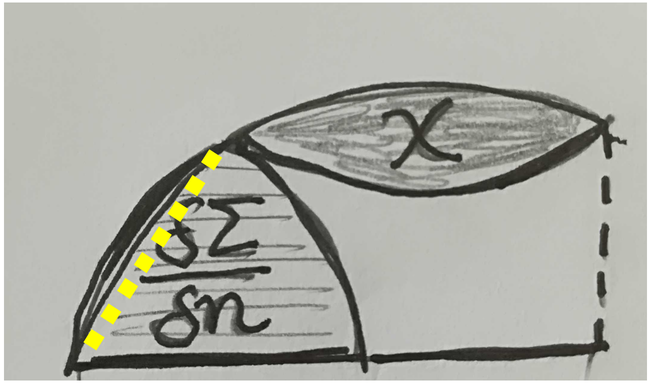


Abdallah El Sahili

El Sahili, Sottile, Reining, JCTC 2024

An old idea for the correlation self-energy:

"G$\widetilde{W}$"



$= v_c + f_{\rm xc}$

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

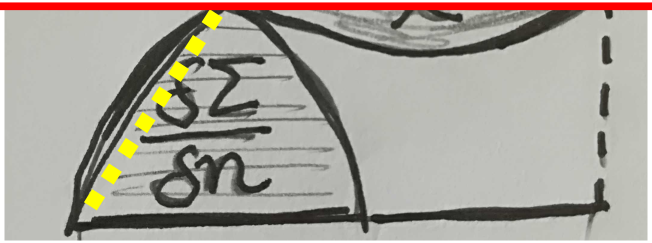
Overhauser, PRB 3, 1888 (1971); Petrillo and Sacchetti, PRB 38, 3834 (1988);
Mahan and Sernelius, PRL. 62, 2718 (1989); Hybertsen and Louie, PRB 34, 5390 (1986);
Del Sole, Reining, and Godby, PRB 49, 8024 (1994); Hindgren and Almbladh, PRB 56, 12832 (1997);
Schmidt, Patrick, and Thygesen, PRB 96, 205206 (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 $f_{\rm xc}$

$= v_c + f_{\rm xc}$



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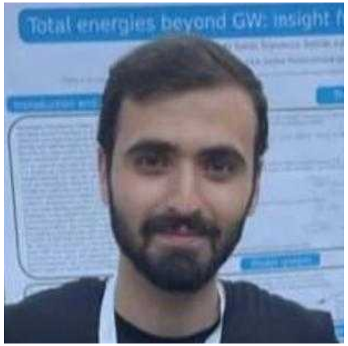

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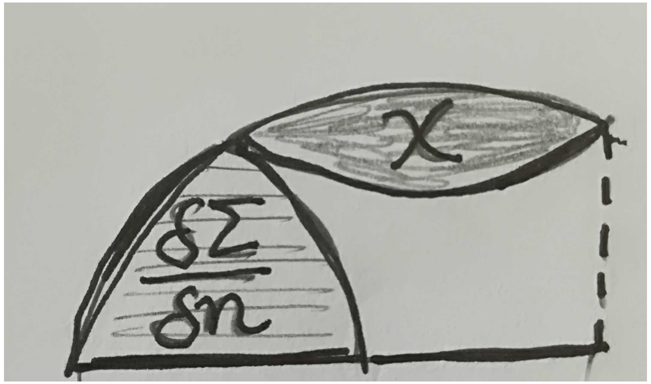
Correlation energy (no kinetic contribution)



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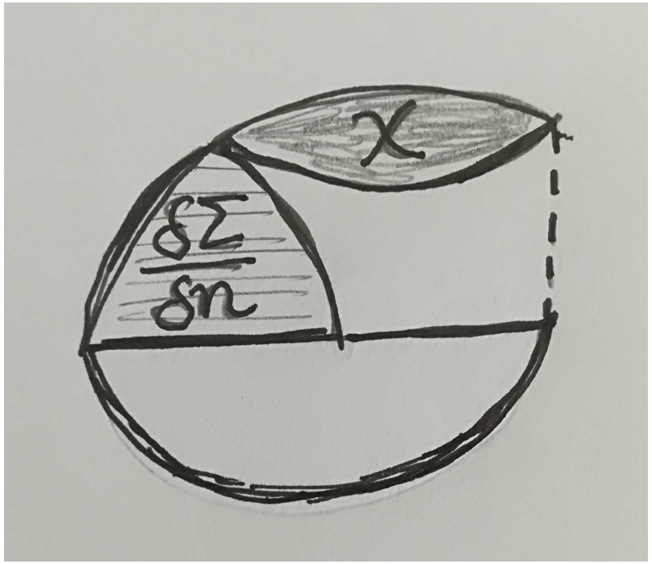

V.M. Galitskii, A. M. JETP 1950, 7, 96

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

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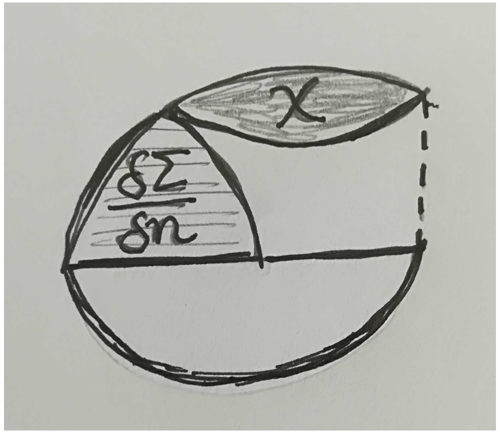
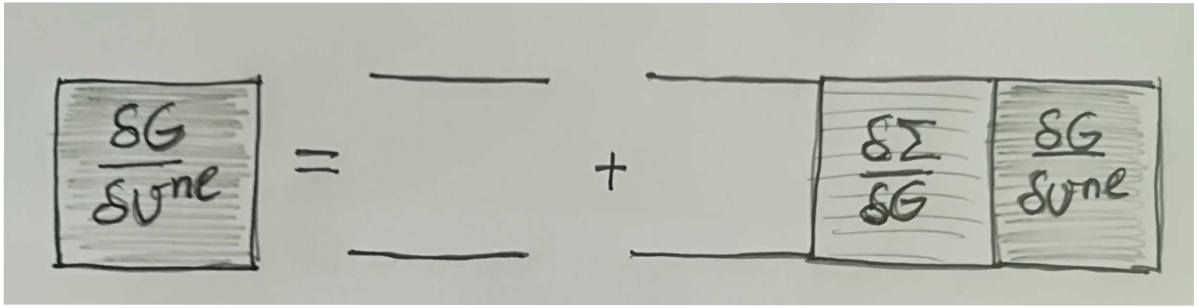
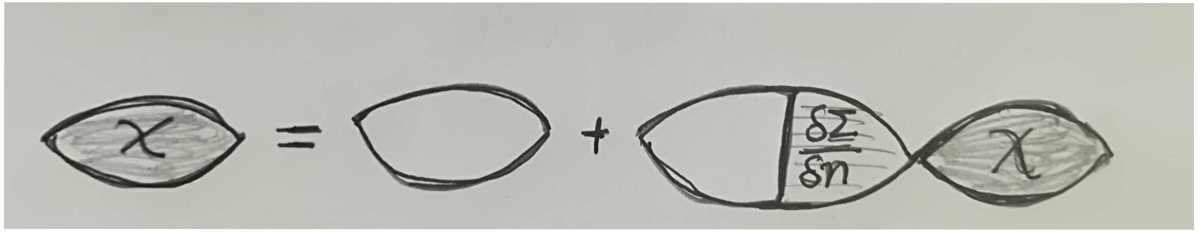
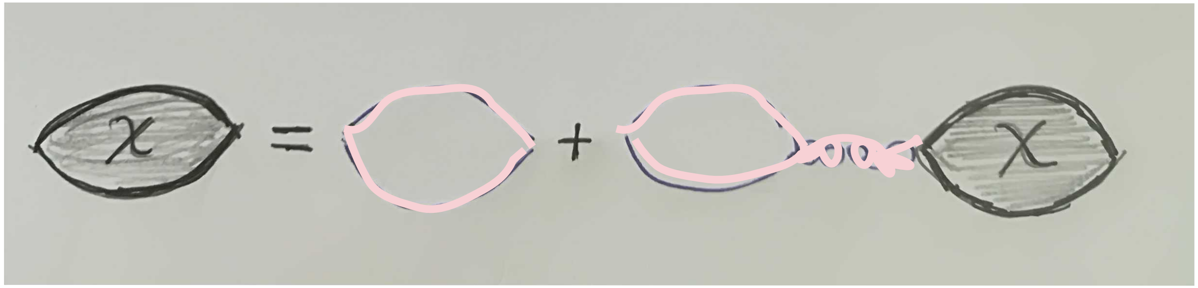




BSE

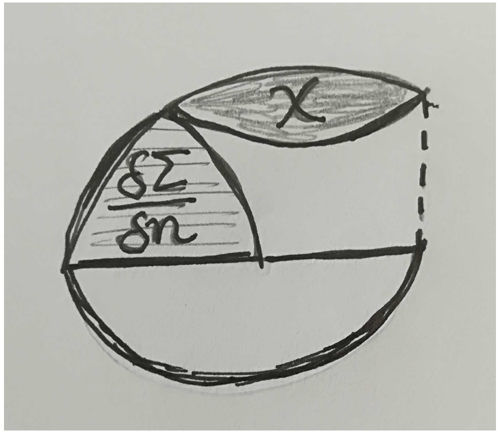


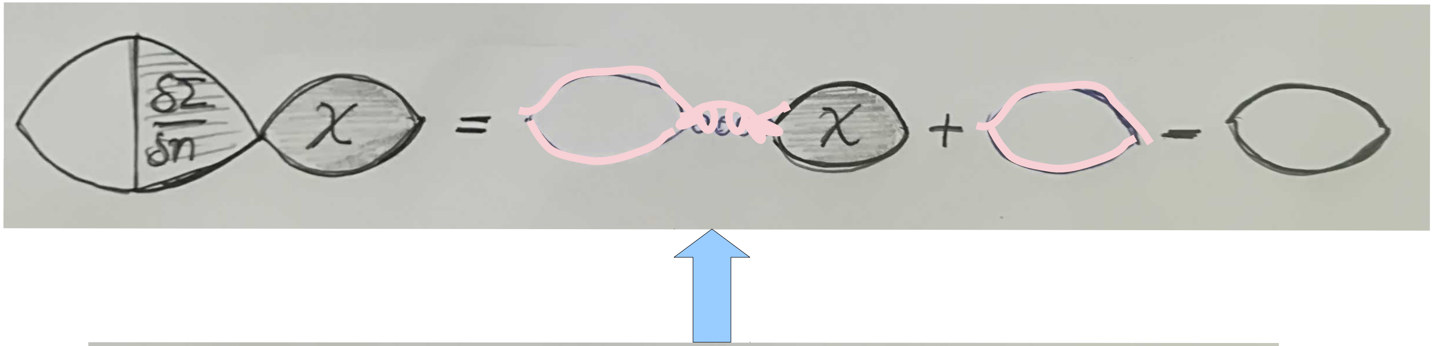
BSE diagonal

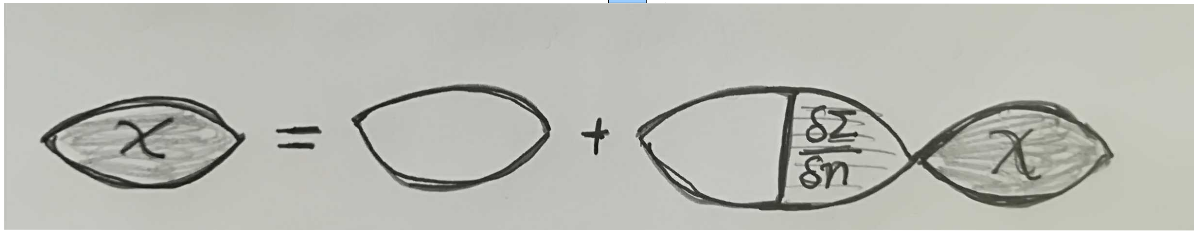


TDDFT

Correlation energy (no kinetic contribution)







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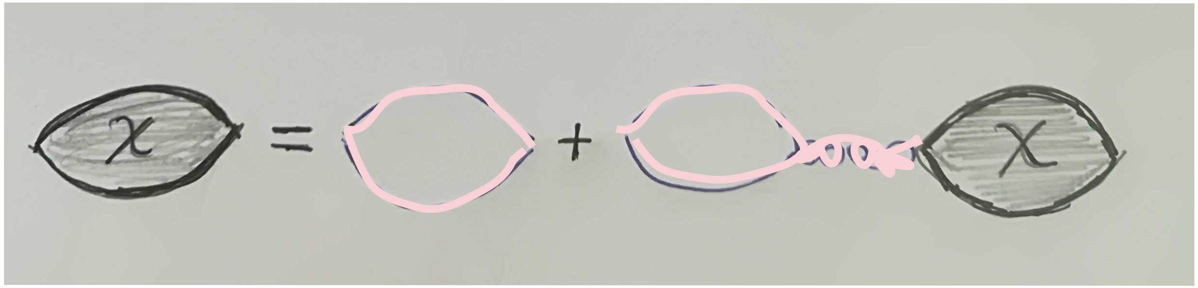

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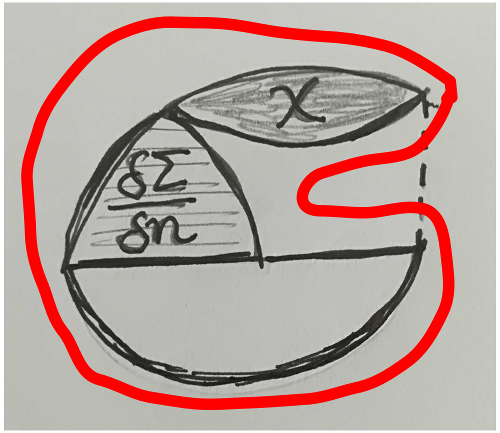

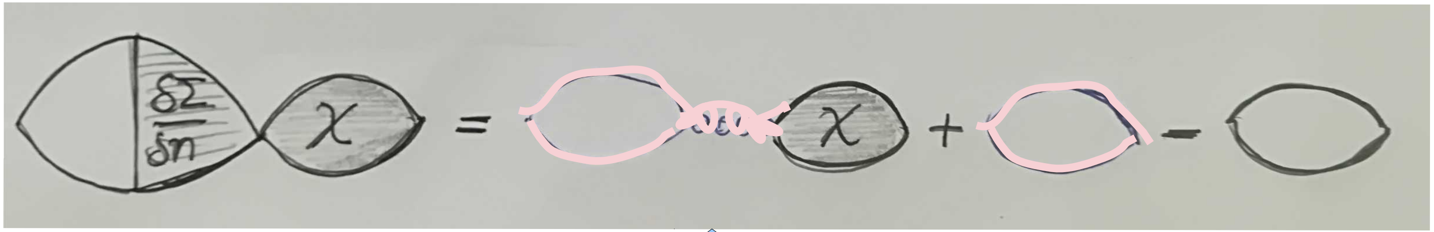

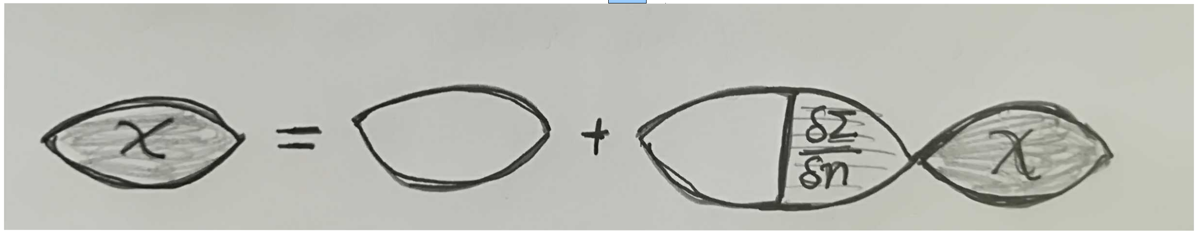

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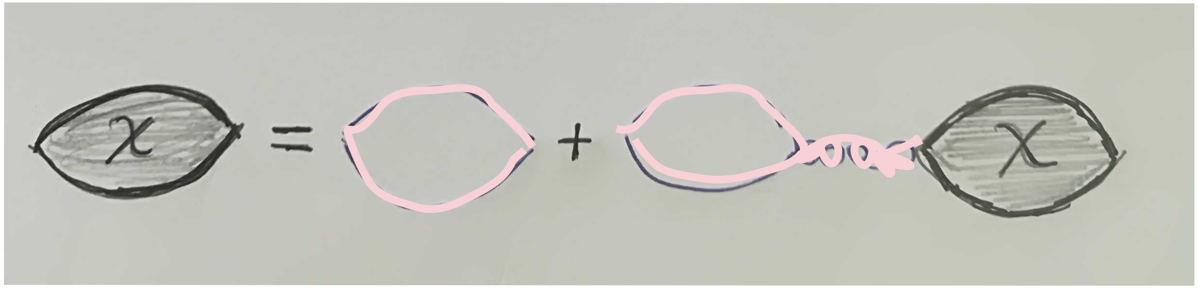

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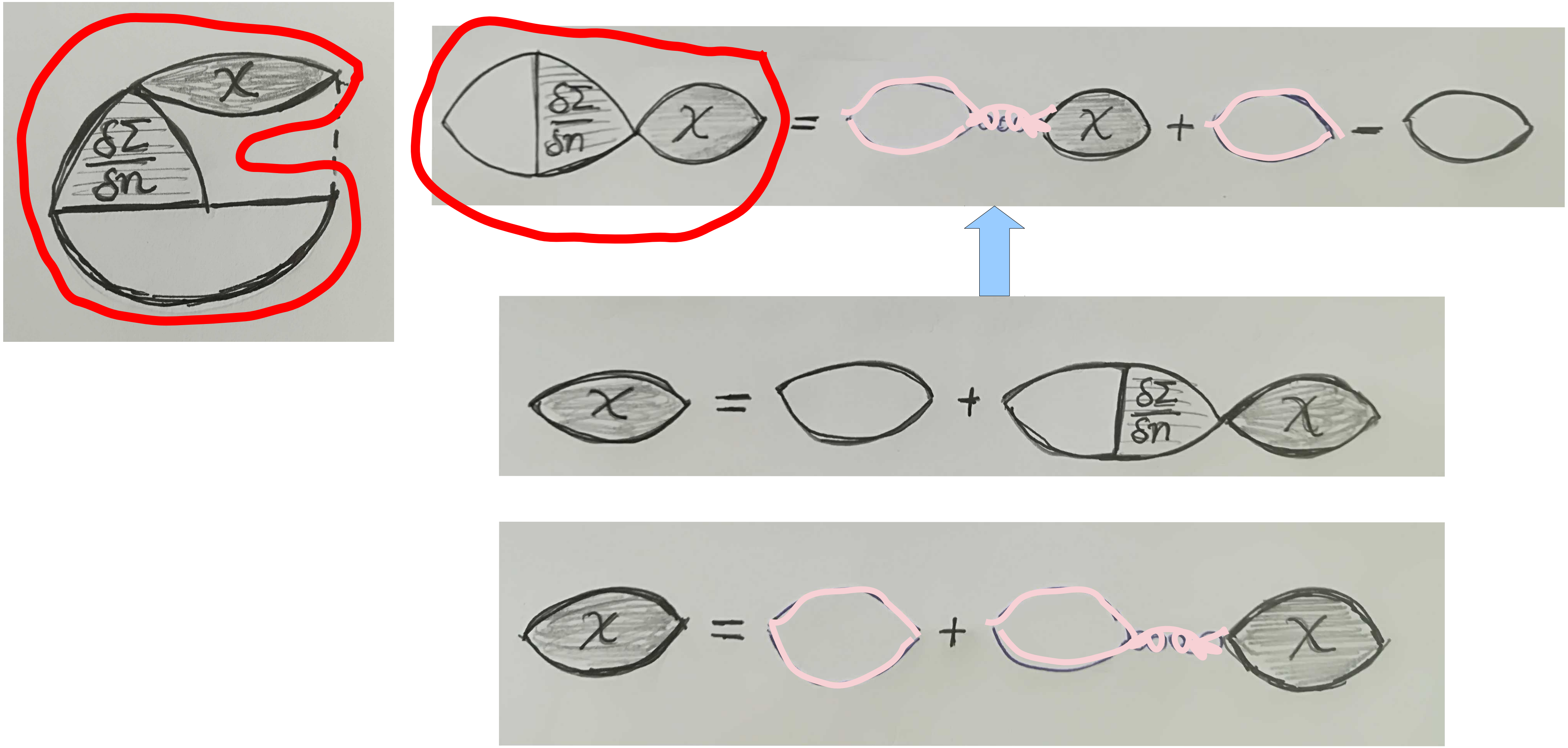

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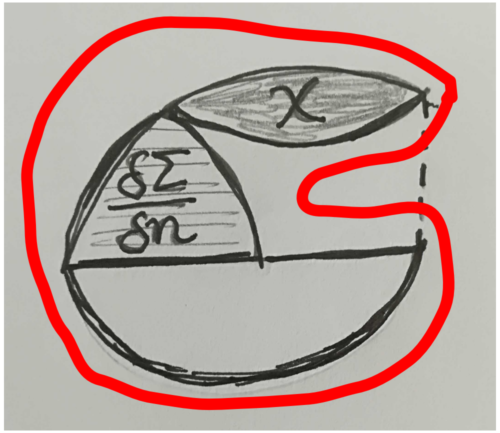

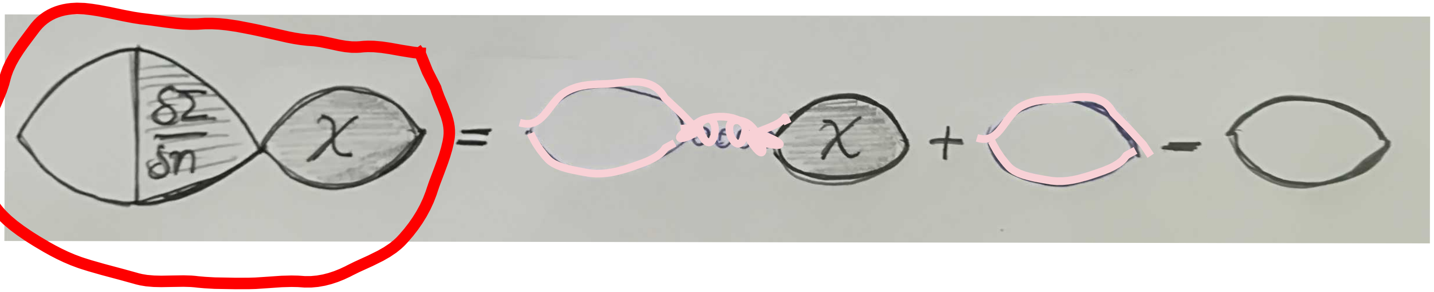

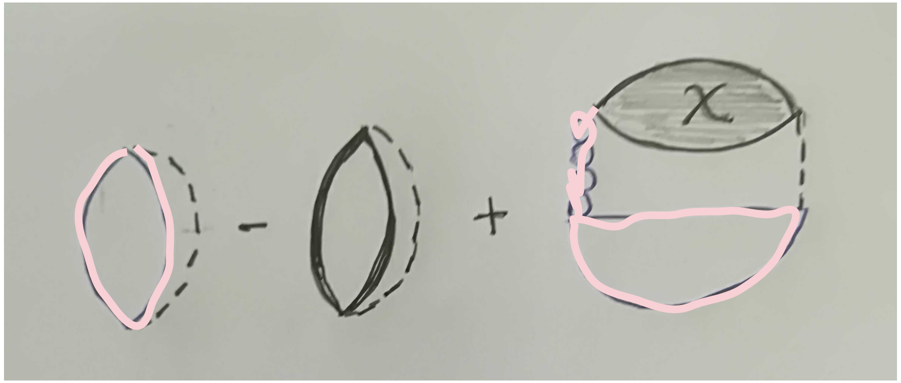

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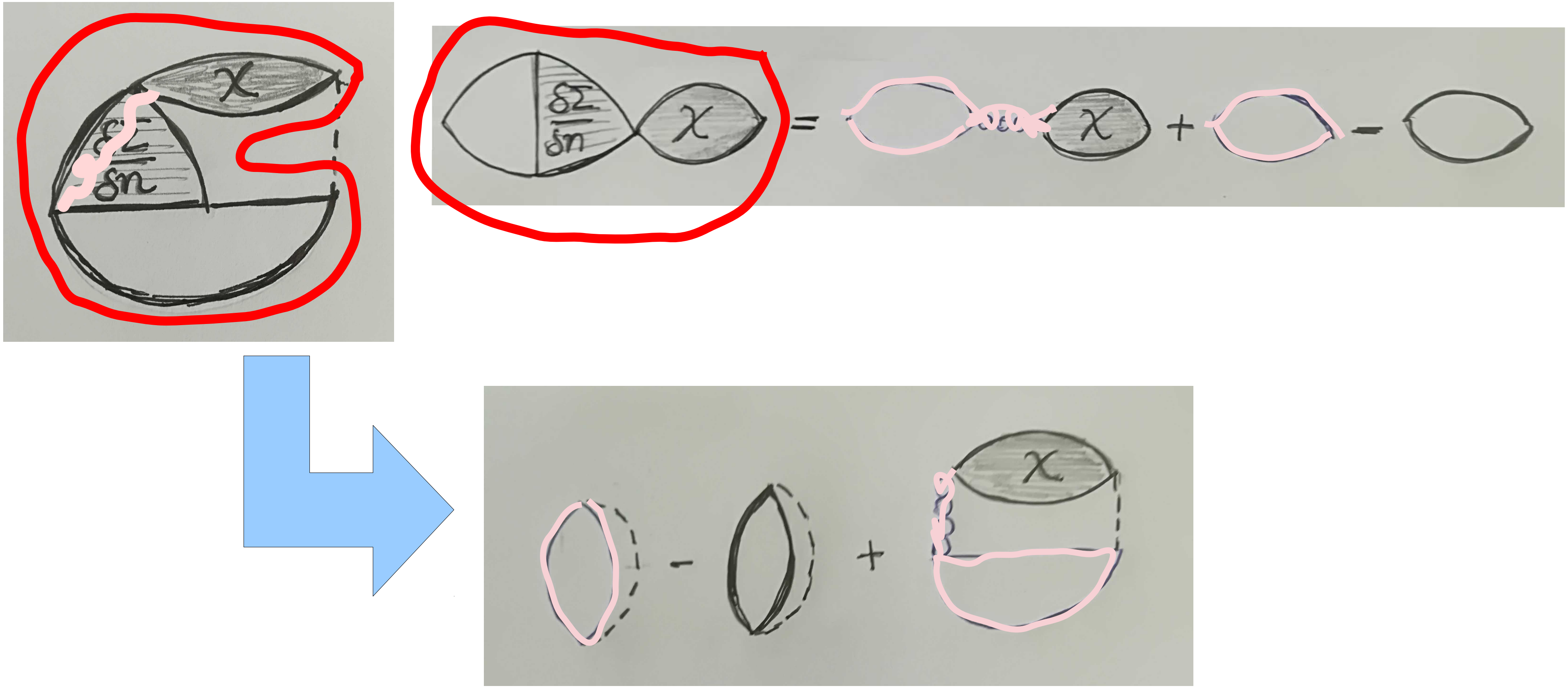
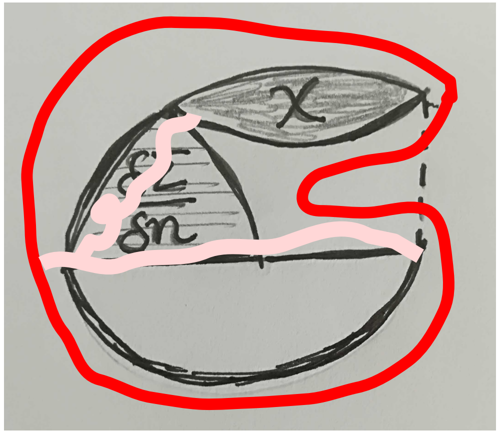
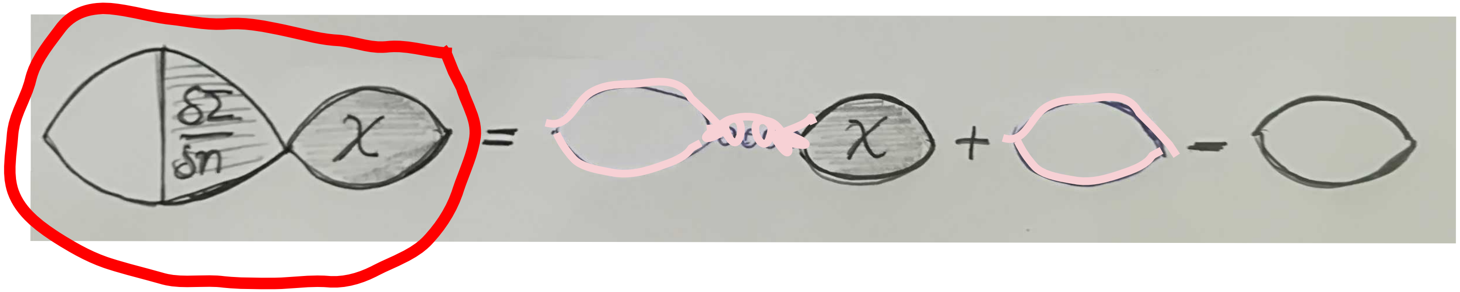
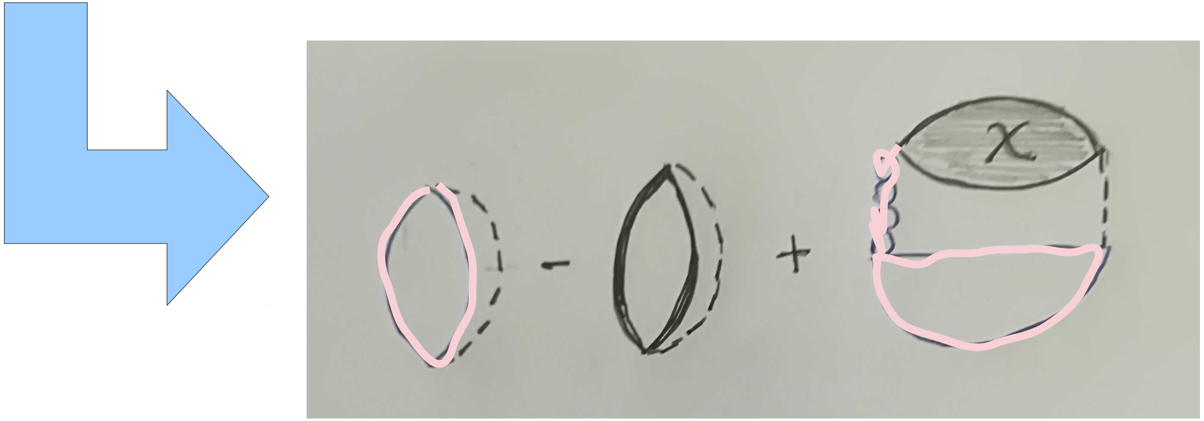


Correlation energy (no kinetic contribution)







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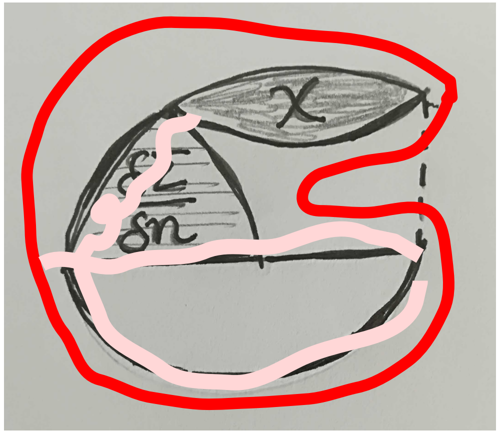

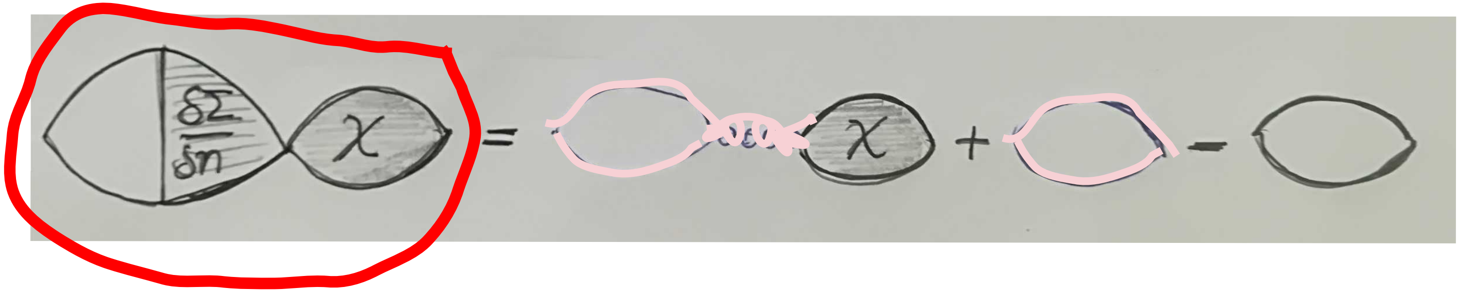

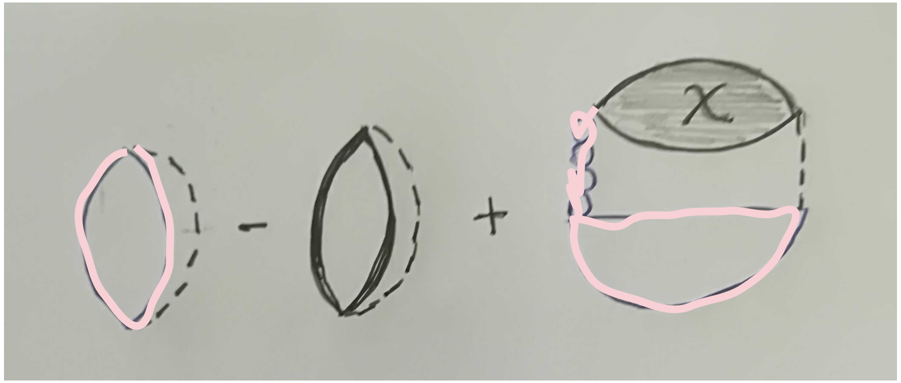

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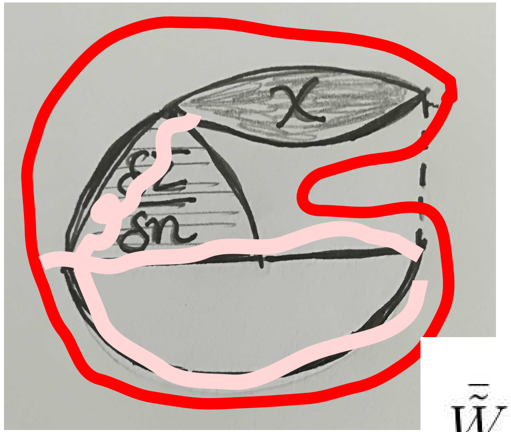
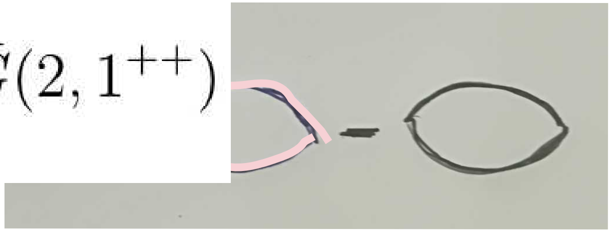
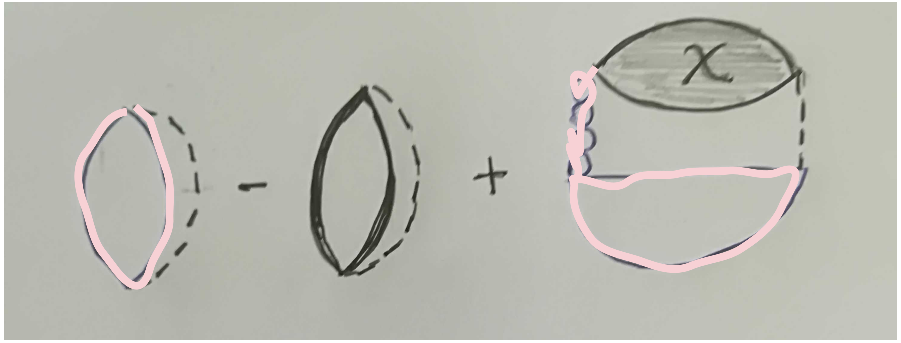


$$E_{xc} = -\frac{i}{2}\int dx_1 d2\, \bar{\Sigma}_{xc}(1,2)\bar{G}(2,1^{++})$$



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

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



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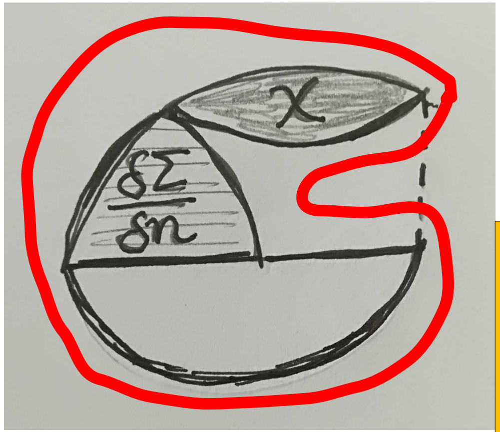

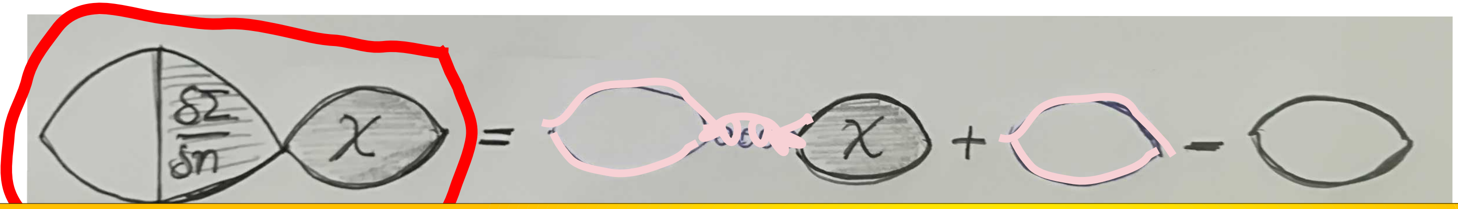

The (approximate!!!) $G\widetilde{W}$ self-energy together with an xchange correction yields the exact correlation energy

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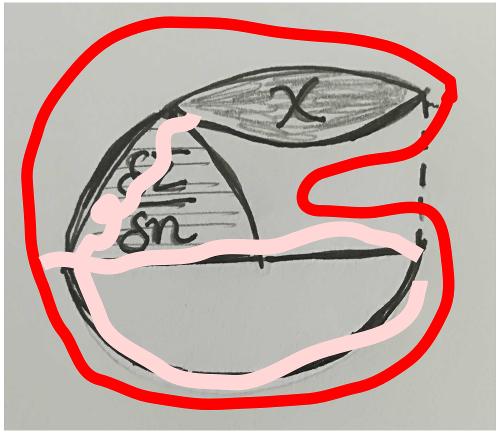

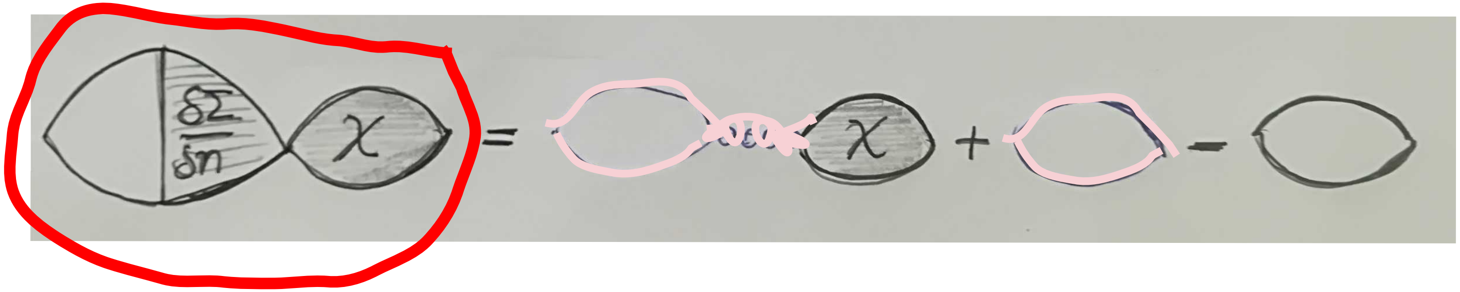

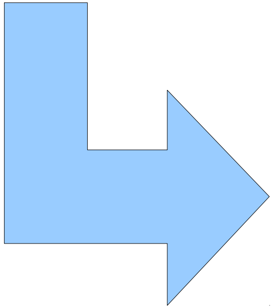

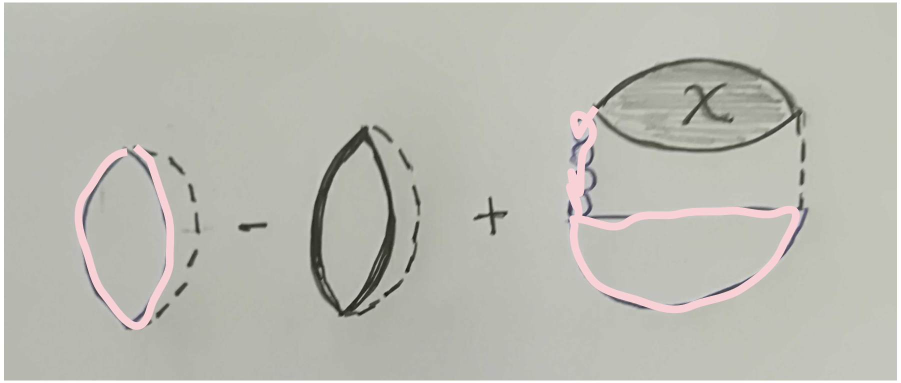

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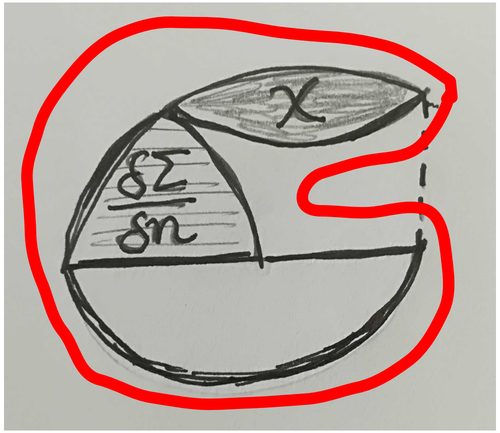

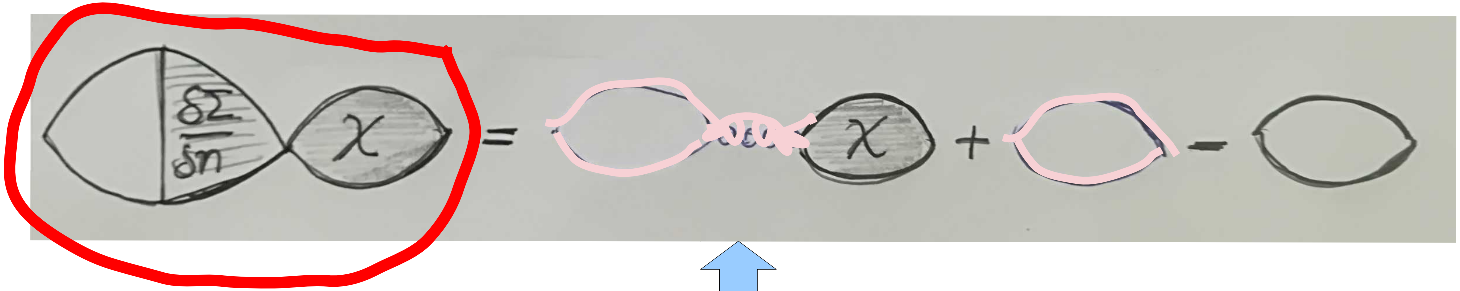

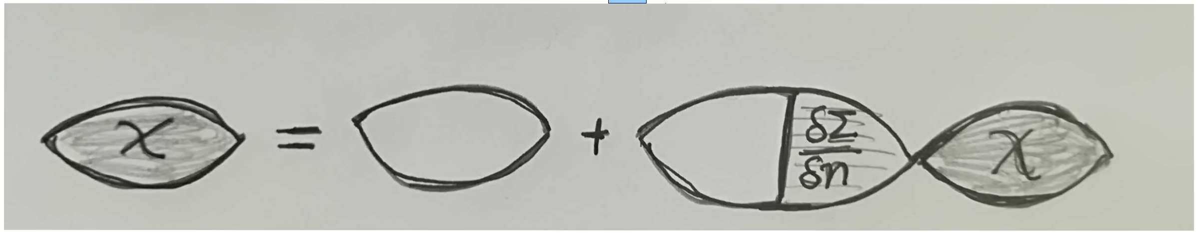

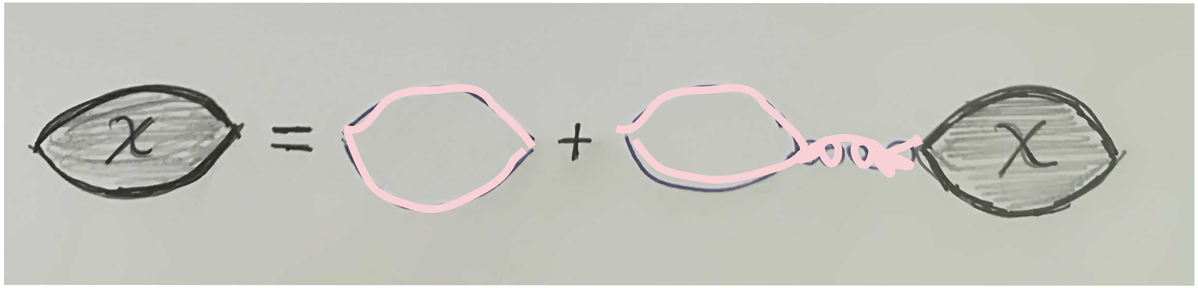

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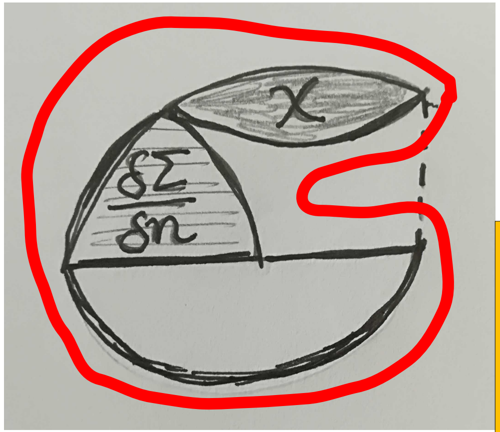

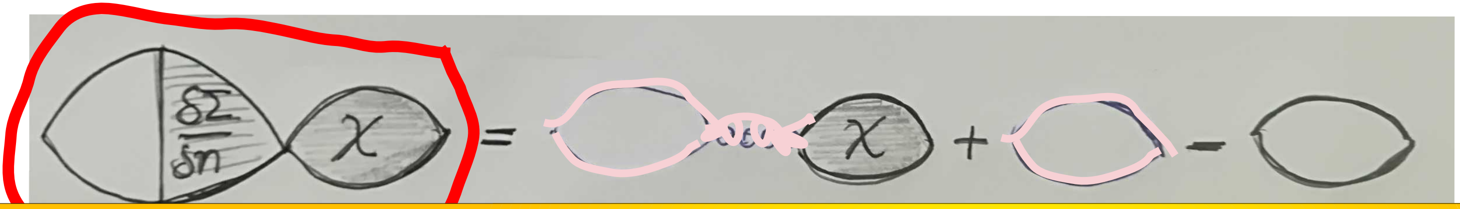

The (approximate!!!) $G\widetilde{W}$ self-energy together with an xchange correction yields the exact correlation energy

One of several choices: KS ingredients

The G$\widetilde{\mathrm{W}}$ approx. self-energies yield the exact xc energy if the density is exact

and if the expression is evaluated consistently

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

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

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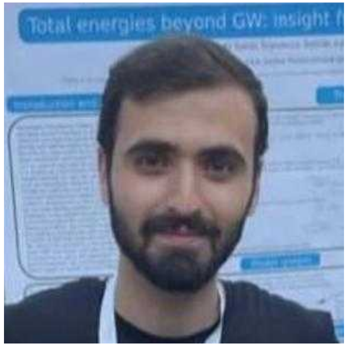
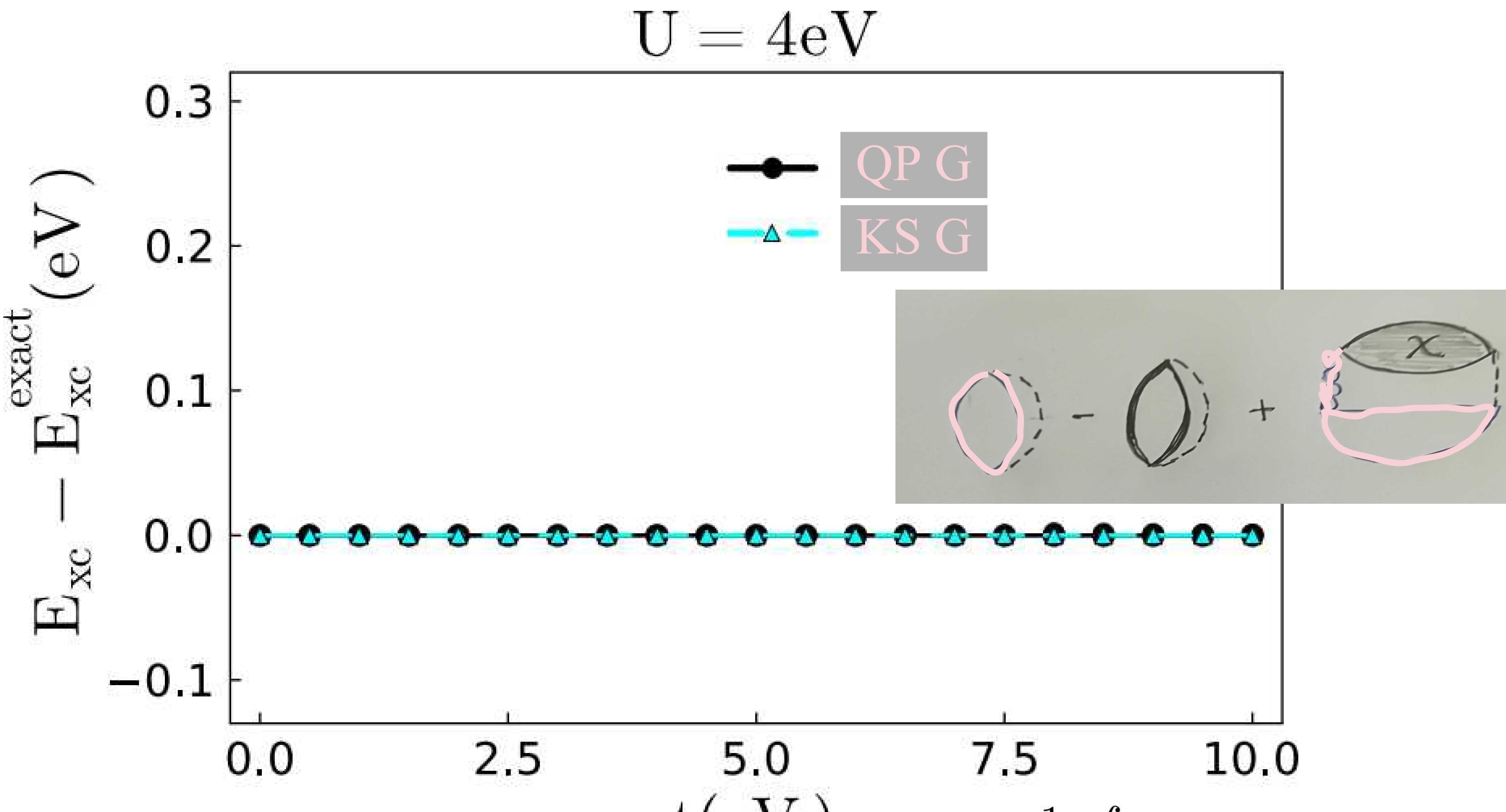


Abdallah El Sahili

El Sahili, Sottile, Reining, JCTC 2024

→ **Illustration: symmetric Hubbard dimer**

→ Conclusions



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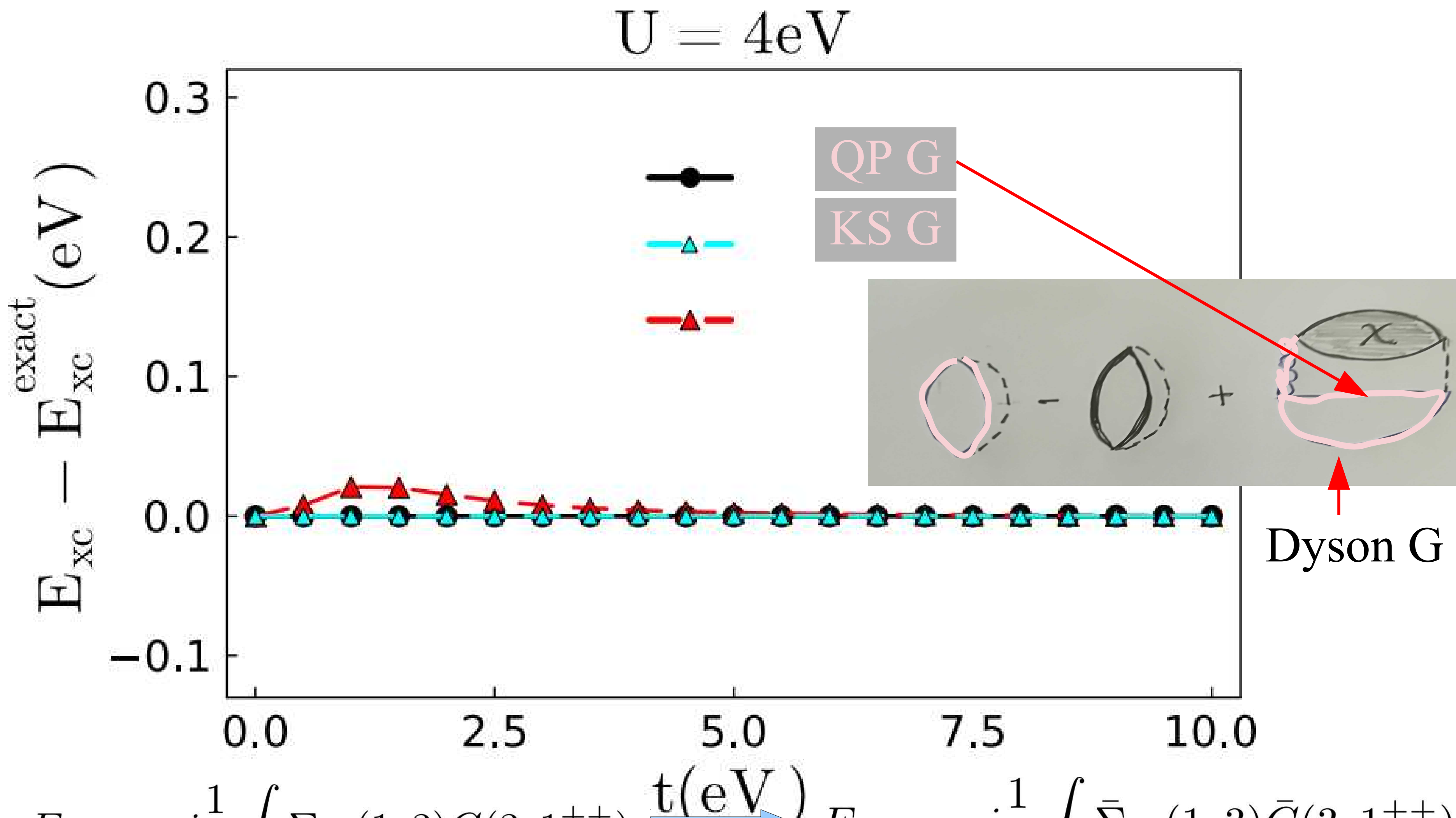

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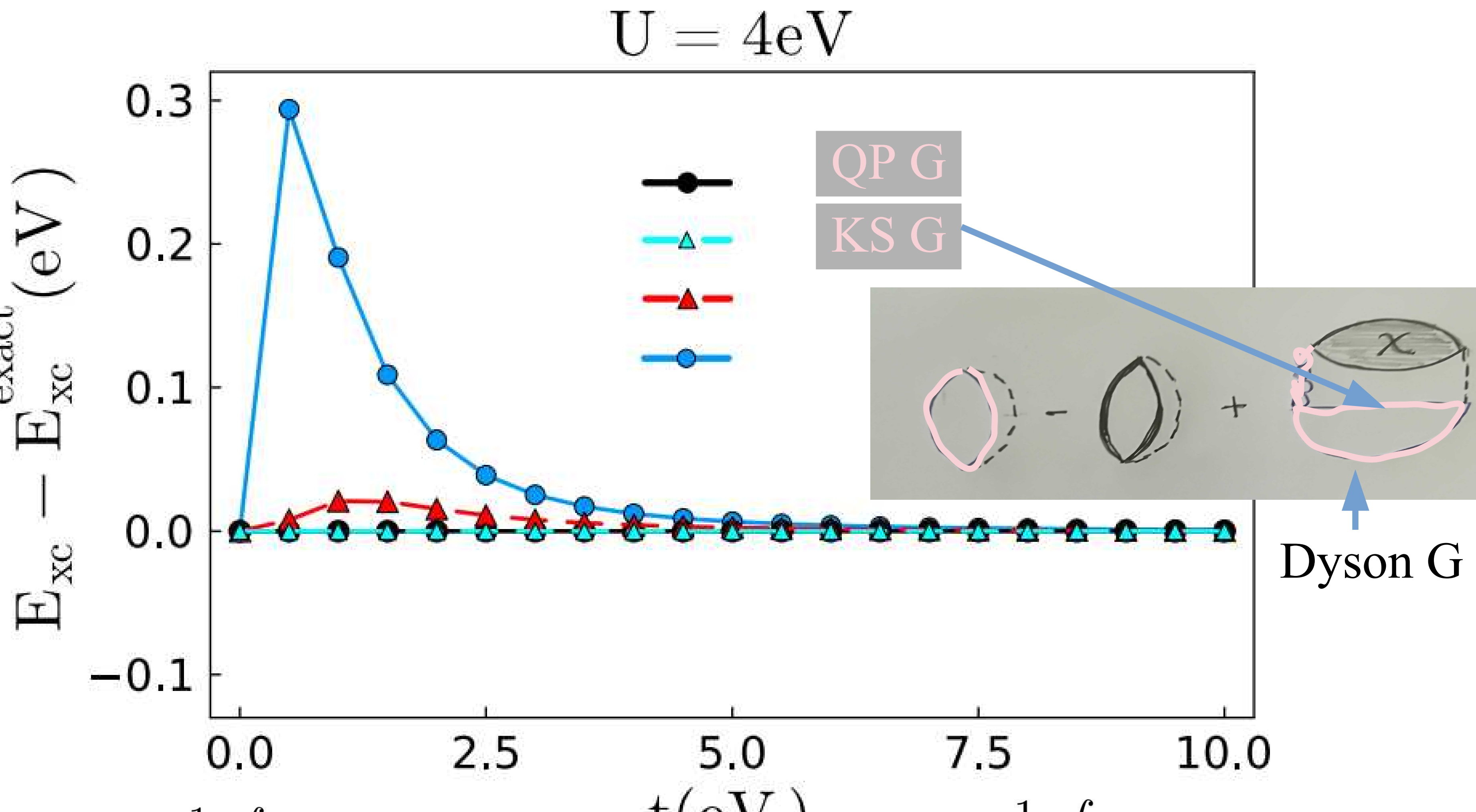

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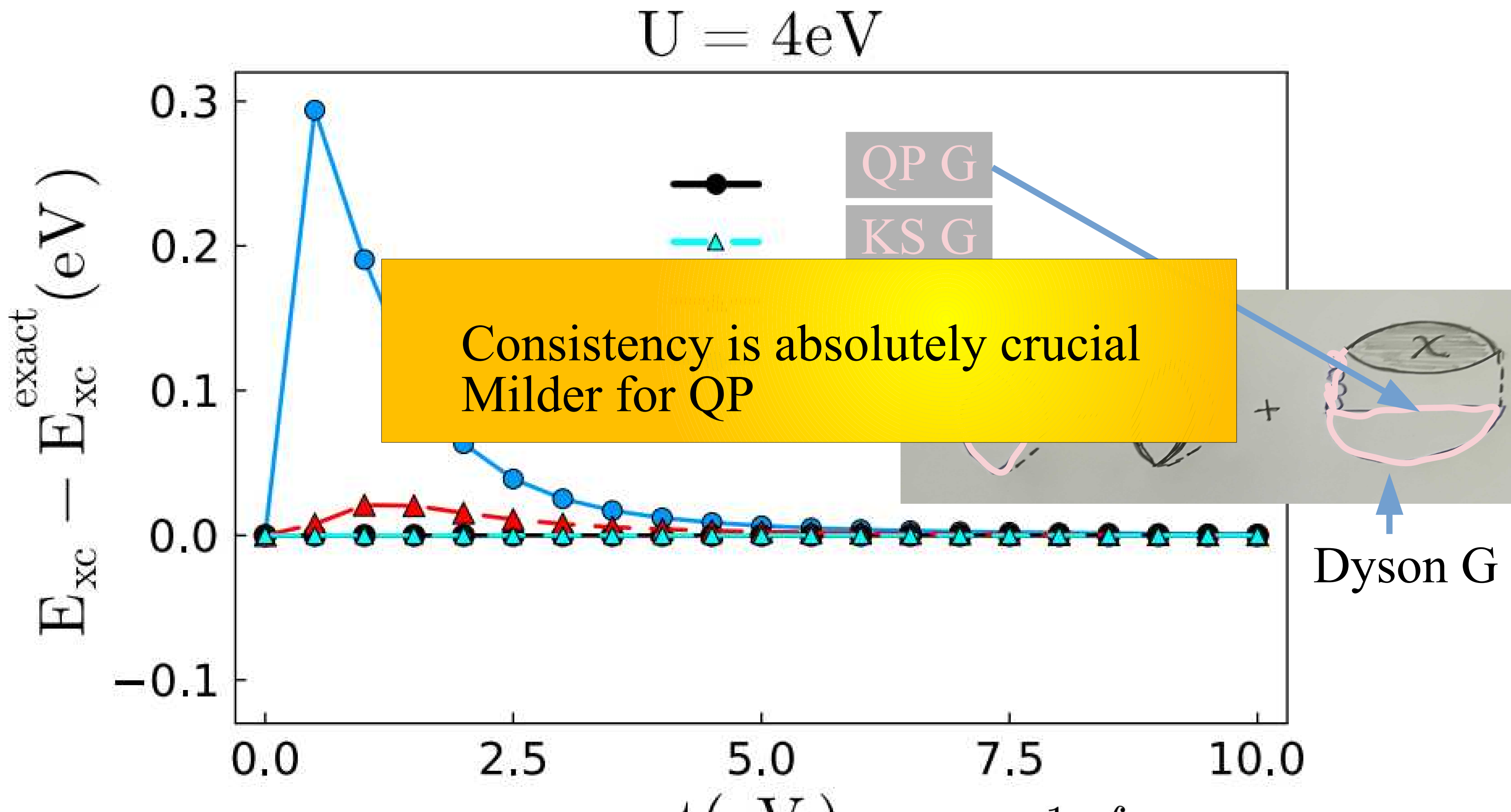
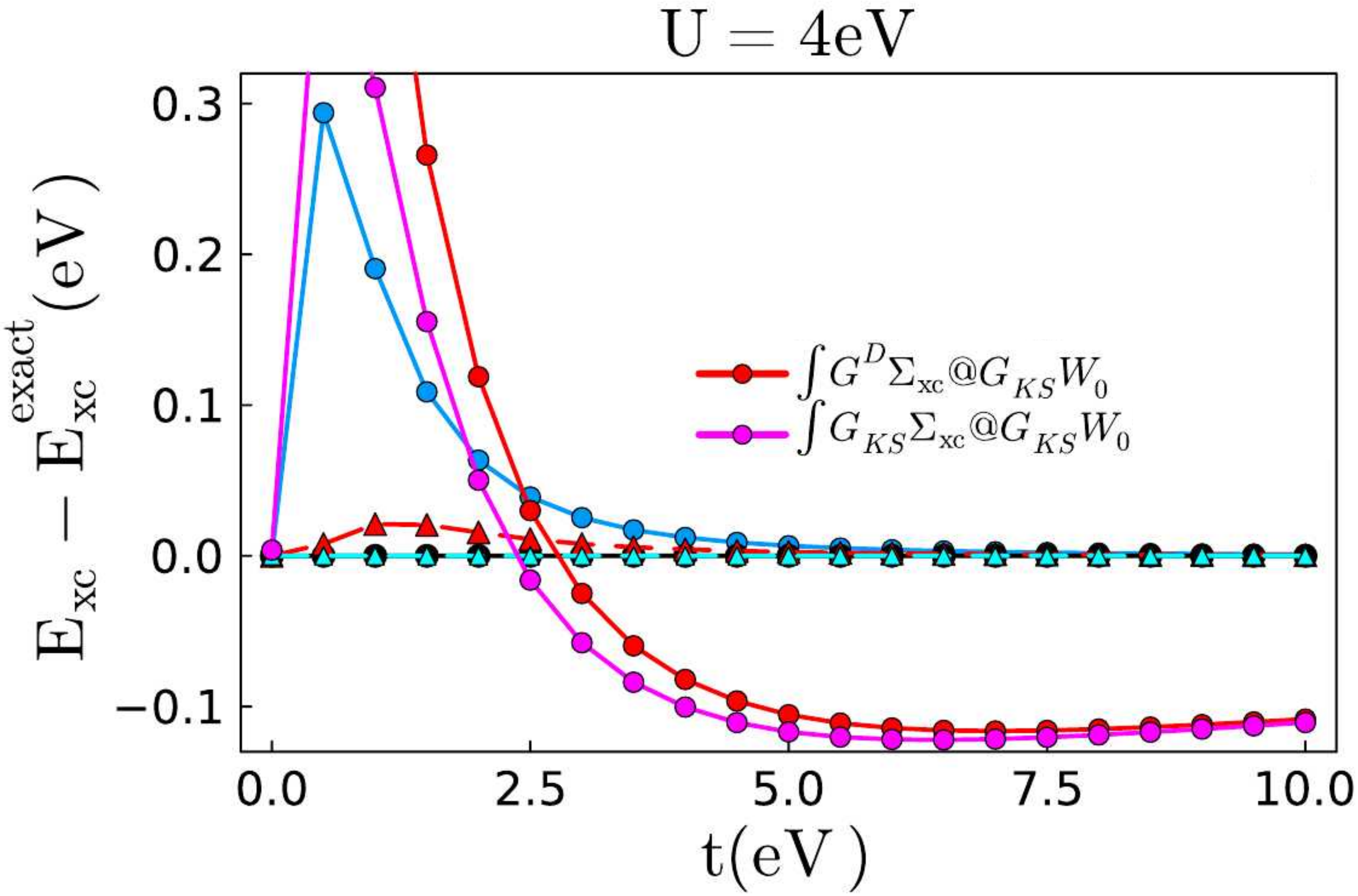


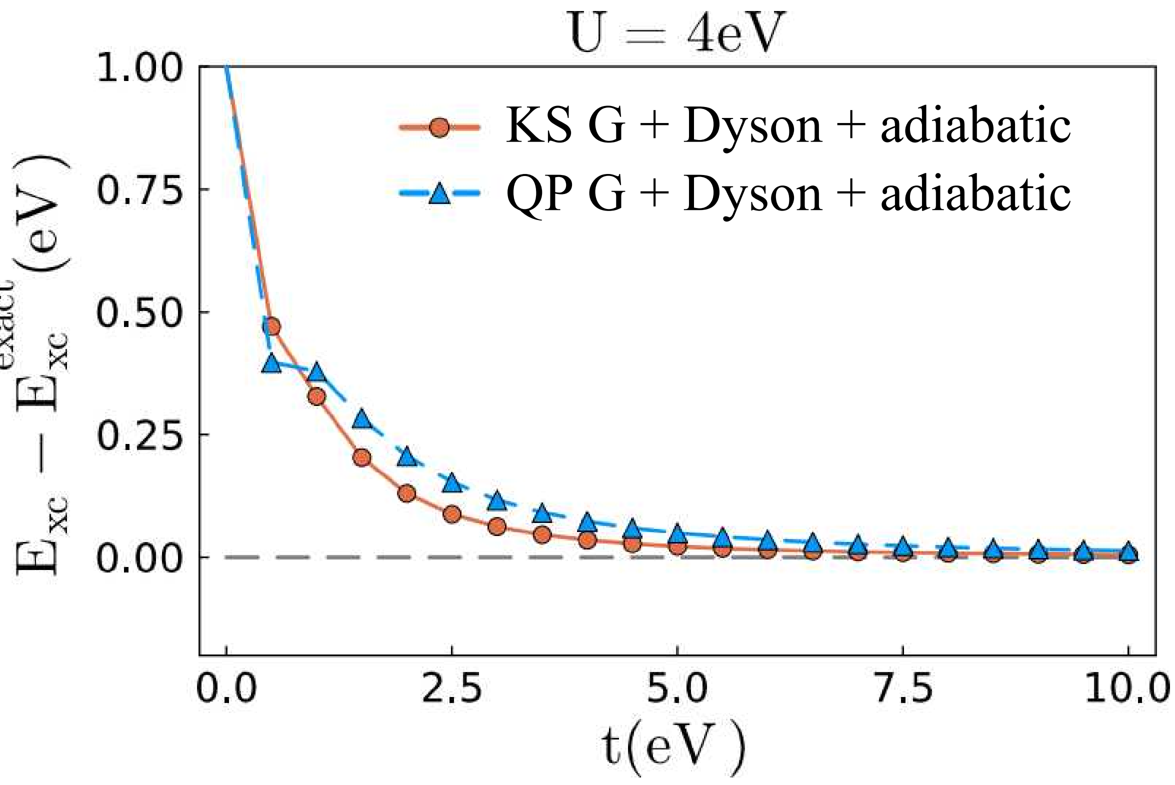
Consistency is absolutely crucial
Milder for QP

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

With TDDFT vertex, error much reduced wrt GW



Adiabatic approx. for f_{xc}



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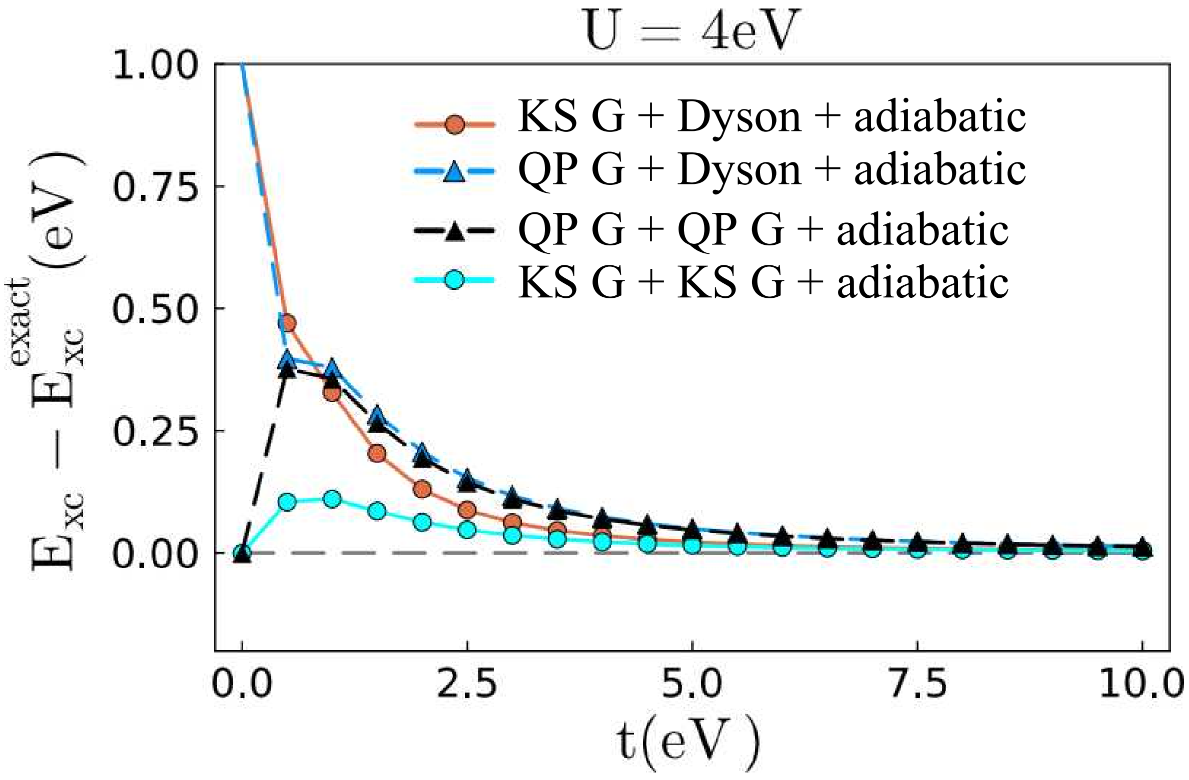
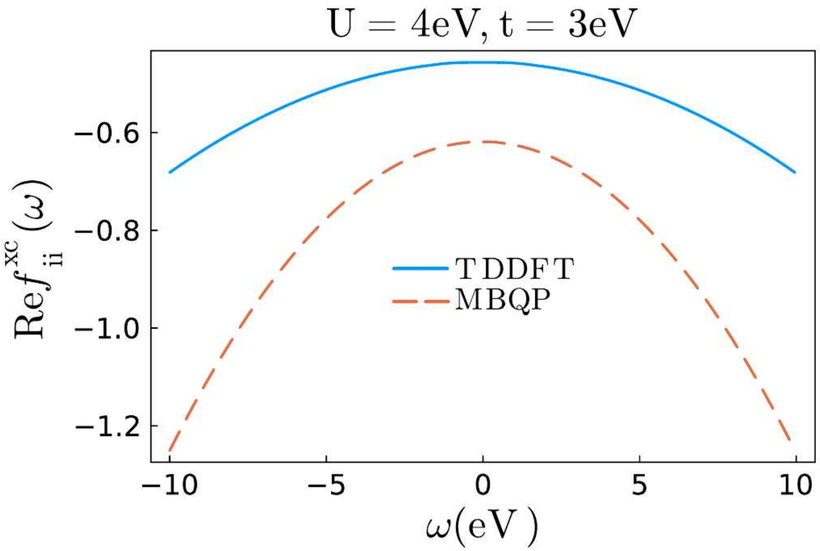
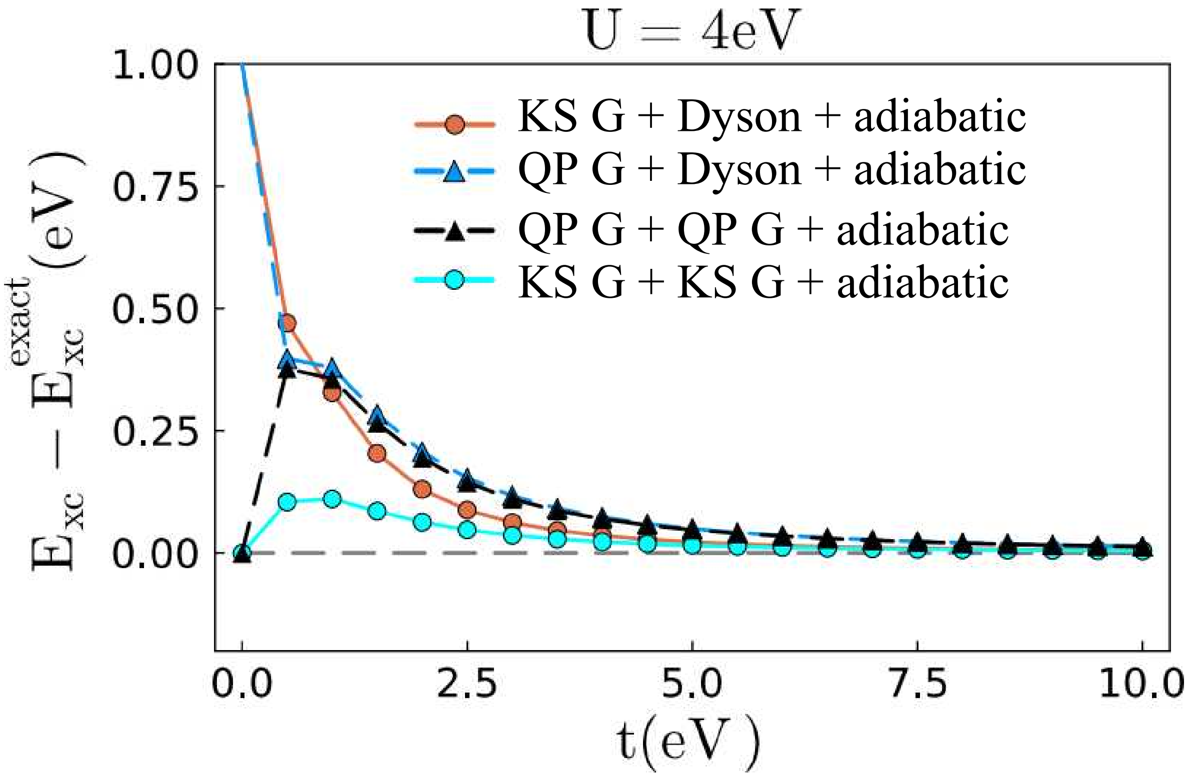
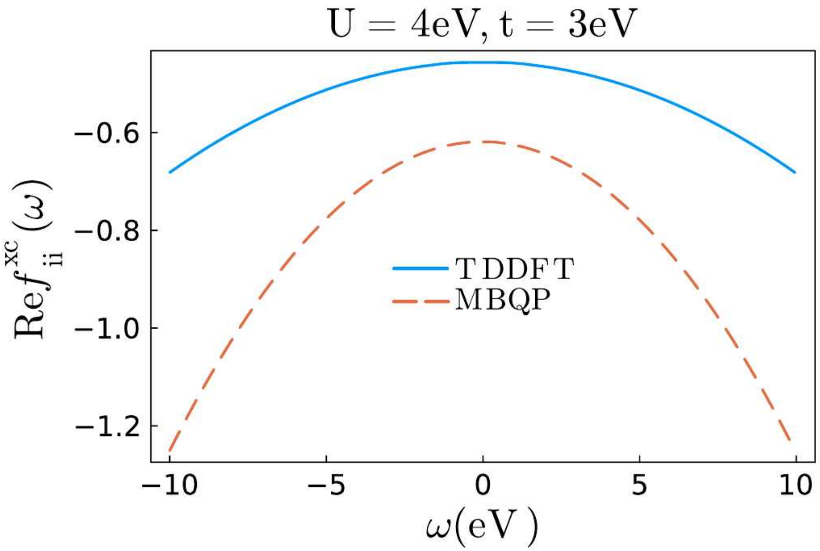


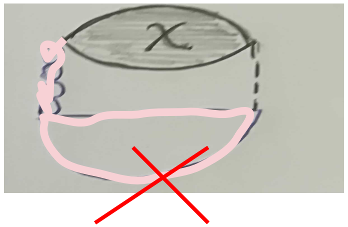


Adiabatic approx. for f_{xc} ***OK, better for KS***

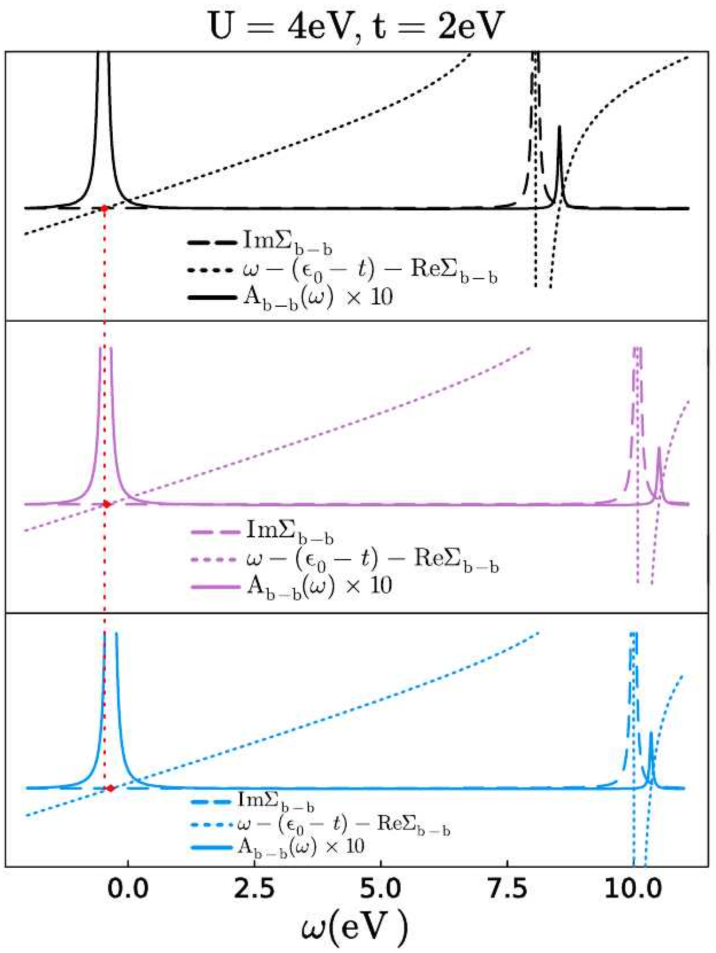


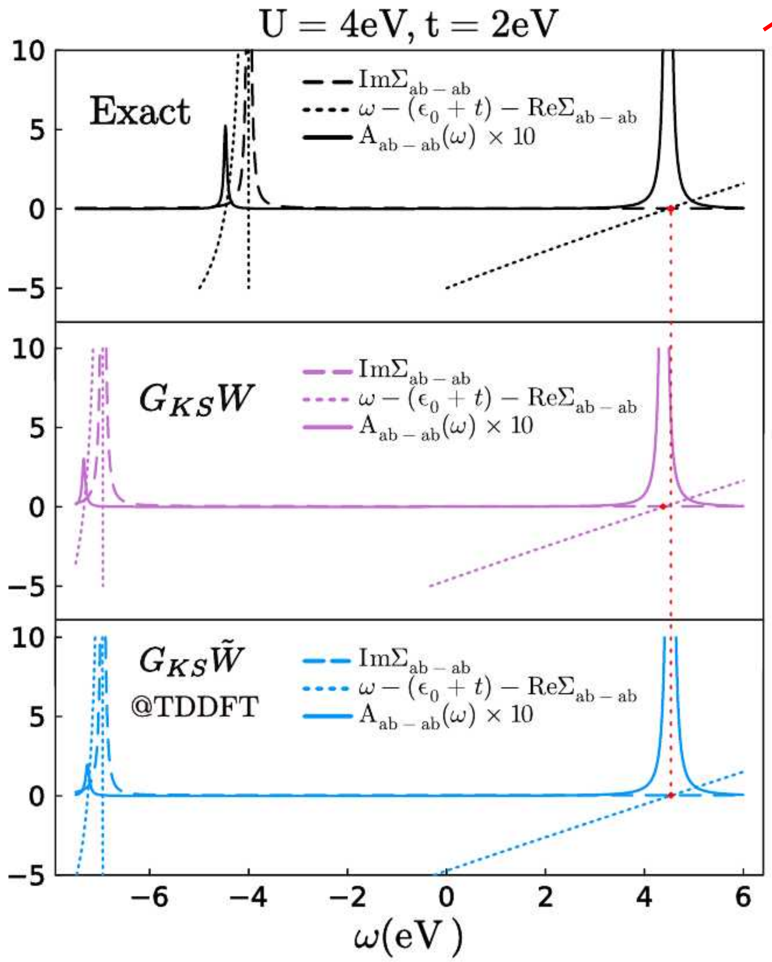


Spectral function with approximate self-energies



bonding

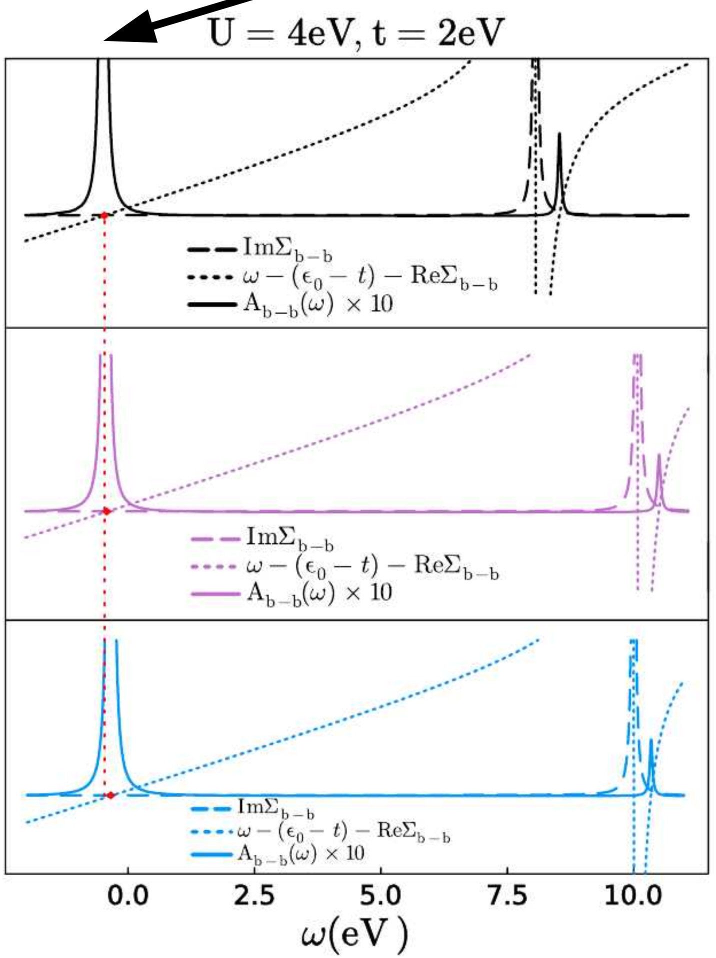


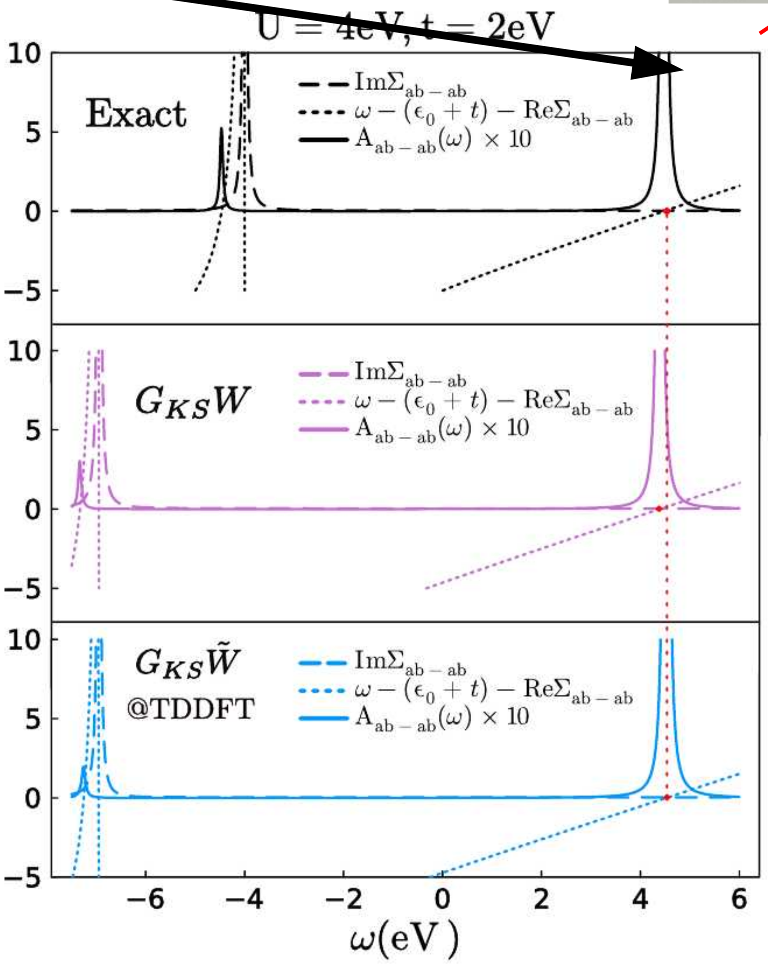


anti-
bonding

Spectral function: **QP quite ok**

bonding





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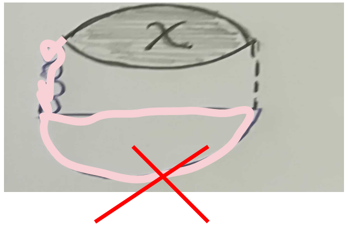
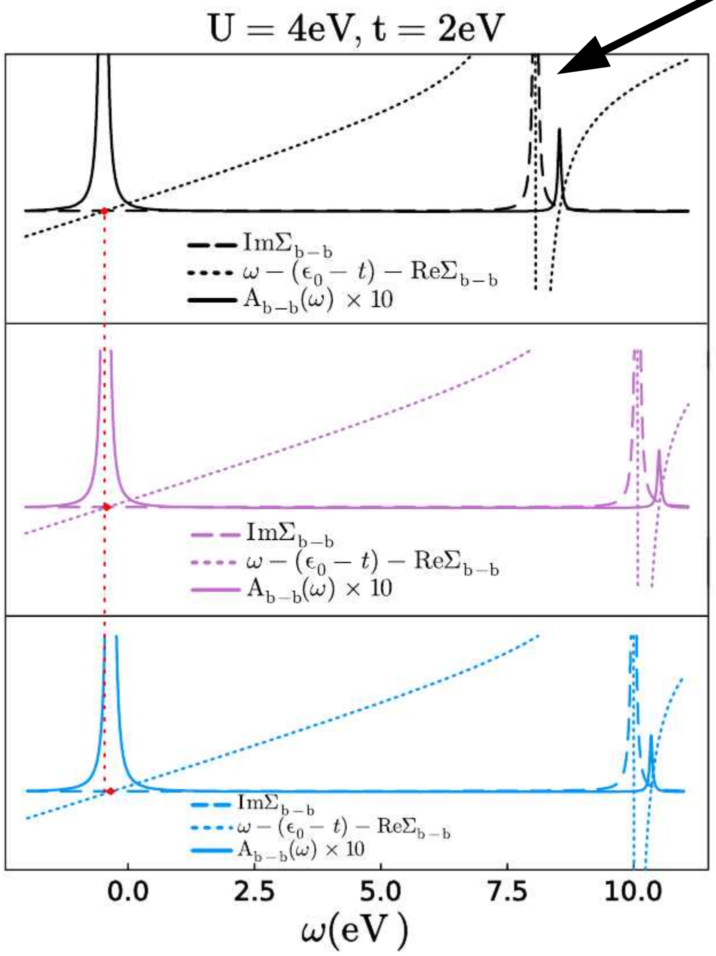
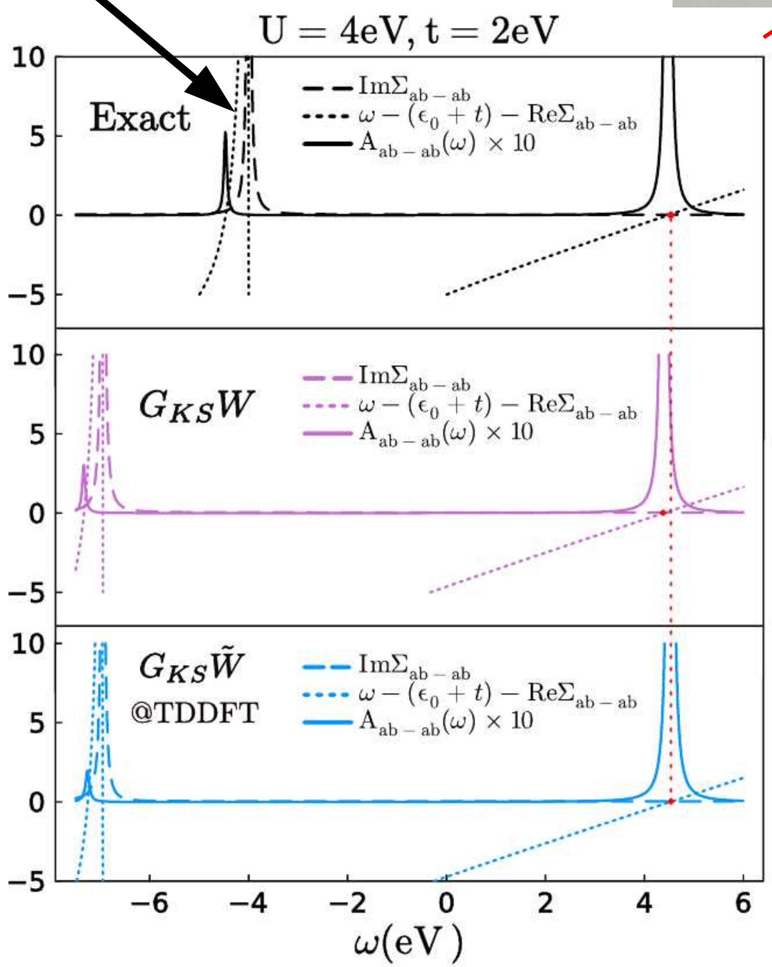


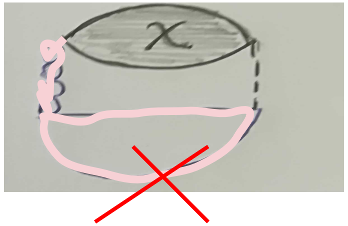
Spectral function: QP quite ok, **satellites bad**.

bonding





anti-bonding



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

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

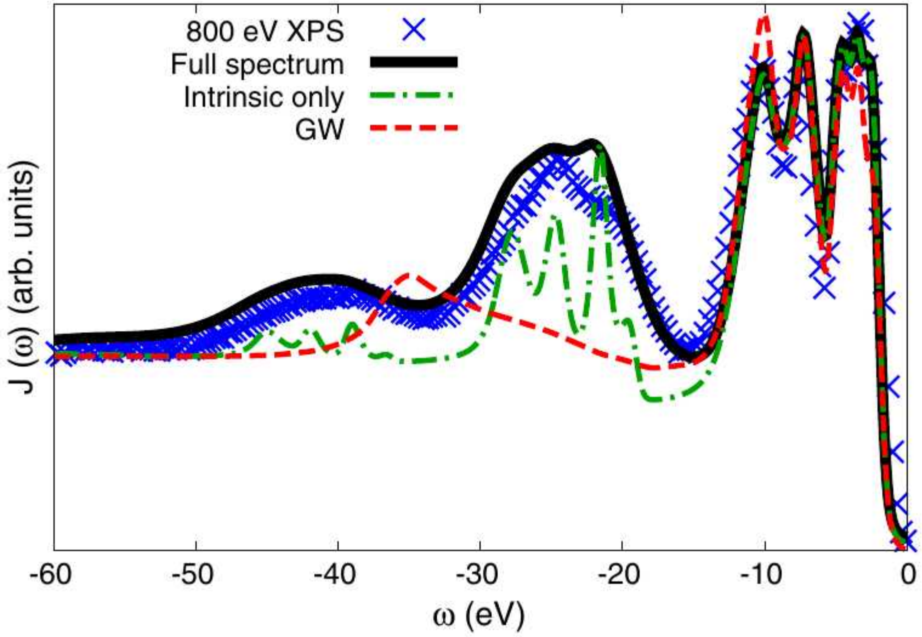
→ It is intrinsic to the use of TDDFT:

$$E_{N\pm1,s} - E_N = \underbrace{E_{N\pm1,s} - E_{N\pm1}}_{\text{Excitations of charged system}} + \underbrace{E_{N\pm1} - E_N}_{\text{Chemical potentials, 1st QP}}$$

Excitations of charged system

Chemical potentials, 1st QP

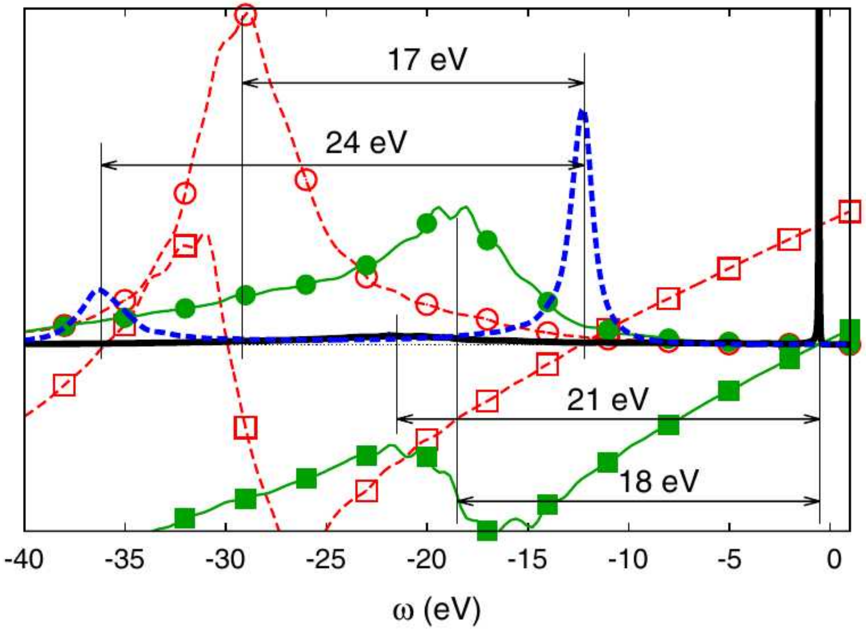
GW and G$\widetilde{W}$ put excitations of N electron system!
Need 2 frequency vertex to fix this *(or new effective W, thesis Abdallah)*.



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)



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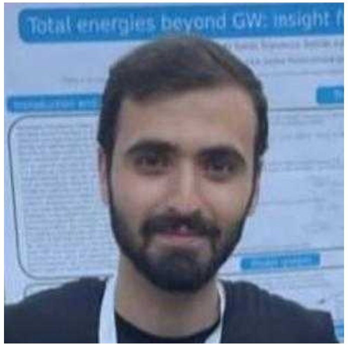

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→ Illustration: symmetric Hubbard dimer

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The $G\widetilde{W}$ 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 Hubard dimer allows us to explore quickly!

(but mind its limits)