The *GW* approximation in 2 x 90 minutes + additional time

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I. Introduction: going beyond DFT

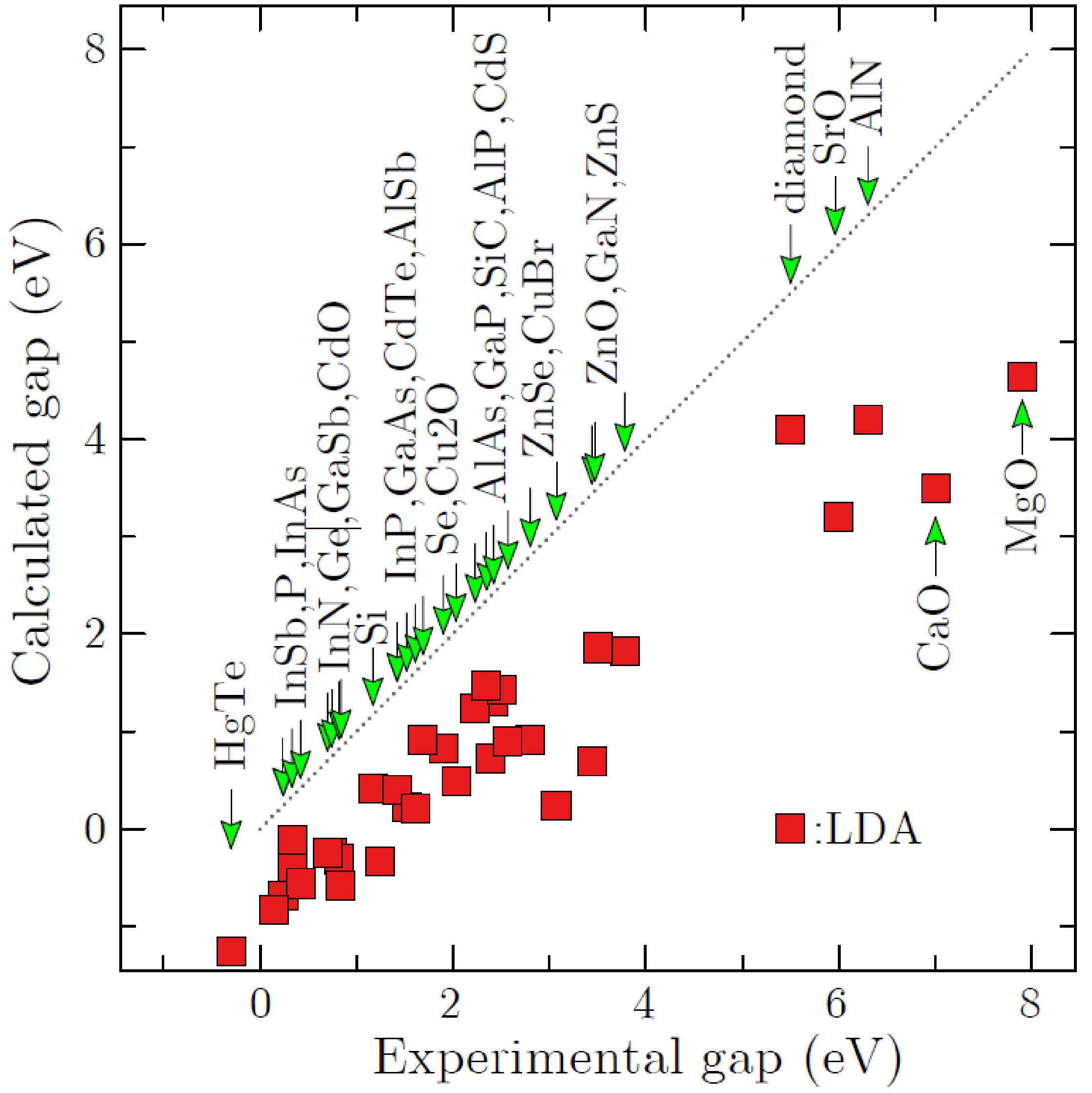
II. Introduction of the Green's function

III. Exact Hedin's equations and the *GW* approximation

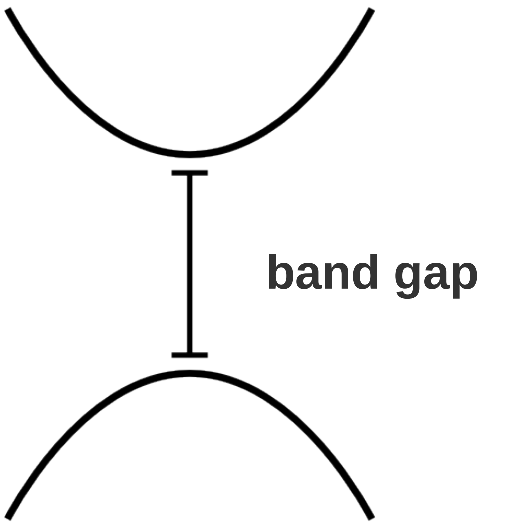
IV. Calculating the *GW* self-energy in practice

V. Applications

Standard DFT has unfortunately some shortcomings



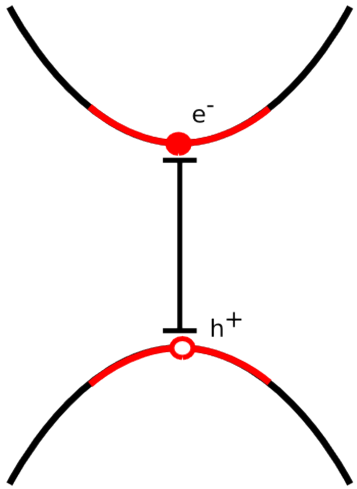
after van Schilfgaarde *et al* PRL **96** 226402 (2008)



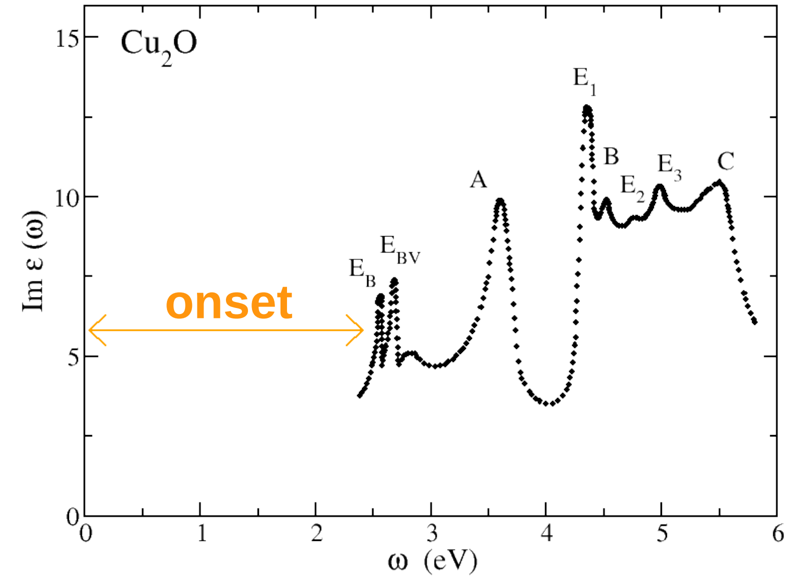
Band gap problem!

A pervasive problem

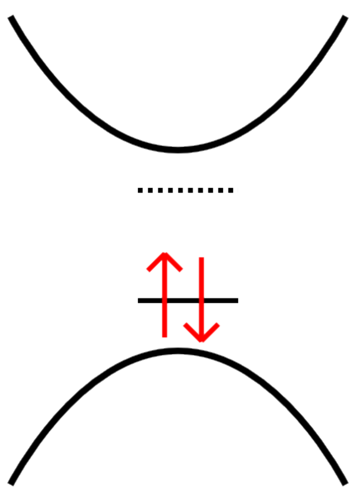
Effective masses
for transport in semiconductors



Optical absorption



Defect formation energy,
dopant solubility



Photoemission

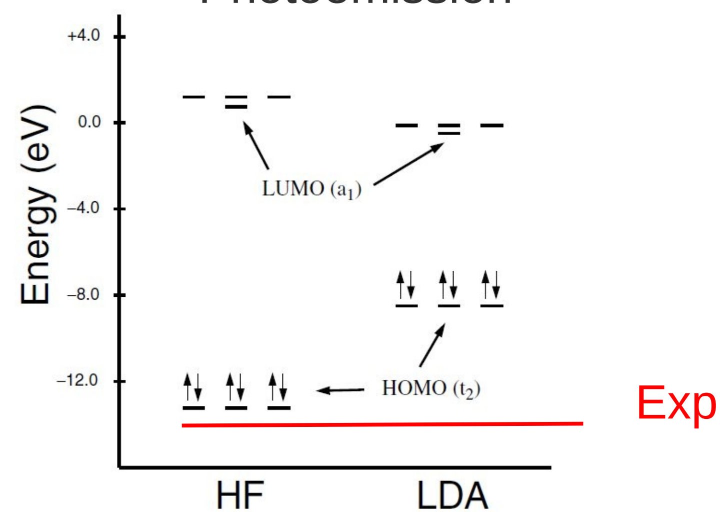


FIG. 1. Single-particle Hartree-Fock and local density approximation eigenvalue spectra (eV) for the SiH_4 molecule.

Gap re-normalization by a (metallic) substrate

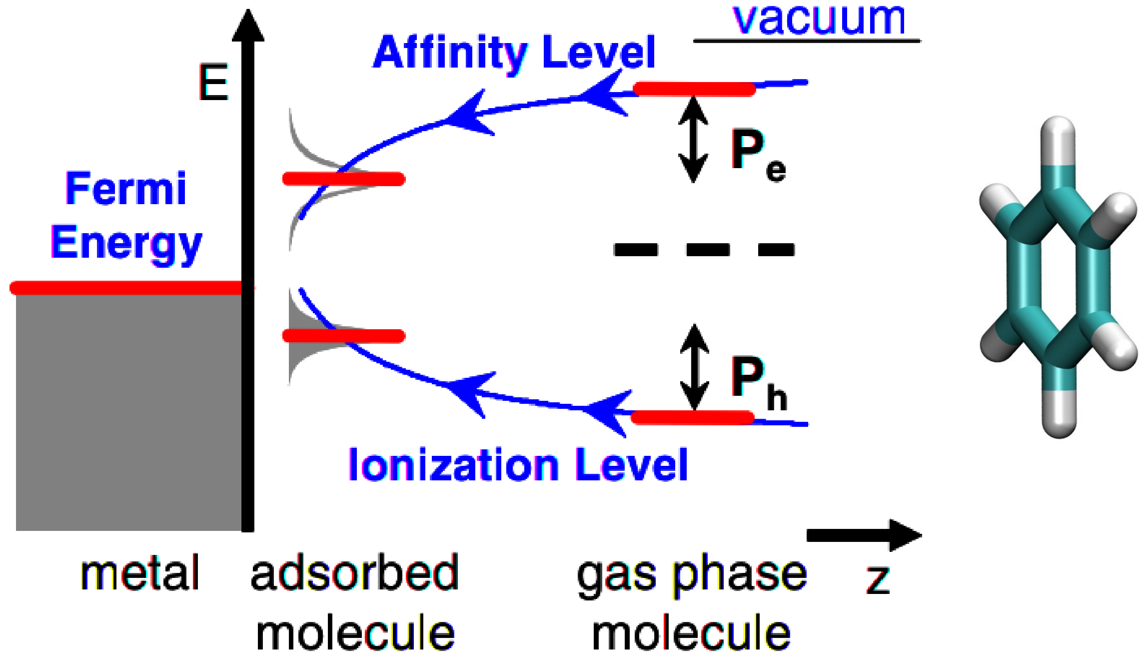


FIG. 1 (color online). Schematic energy level diagram indicating polarization shifts in the frontier energy levels (ionization and affinity) of a molecule upon adsorption on a metal surface.

Benzene deposited on copper, gold, graphite

Neaton, Hybertsen, Louie PRL (2006)

How do go beyond within the DFT framework?

Not easy to find improvement within DFT framework

- There is no such thing as a perturbative expansion
- Perdew's Jacob's ladder does not help for the band gap

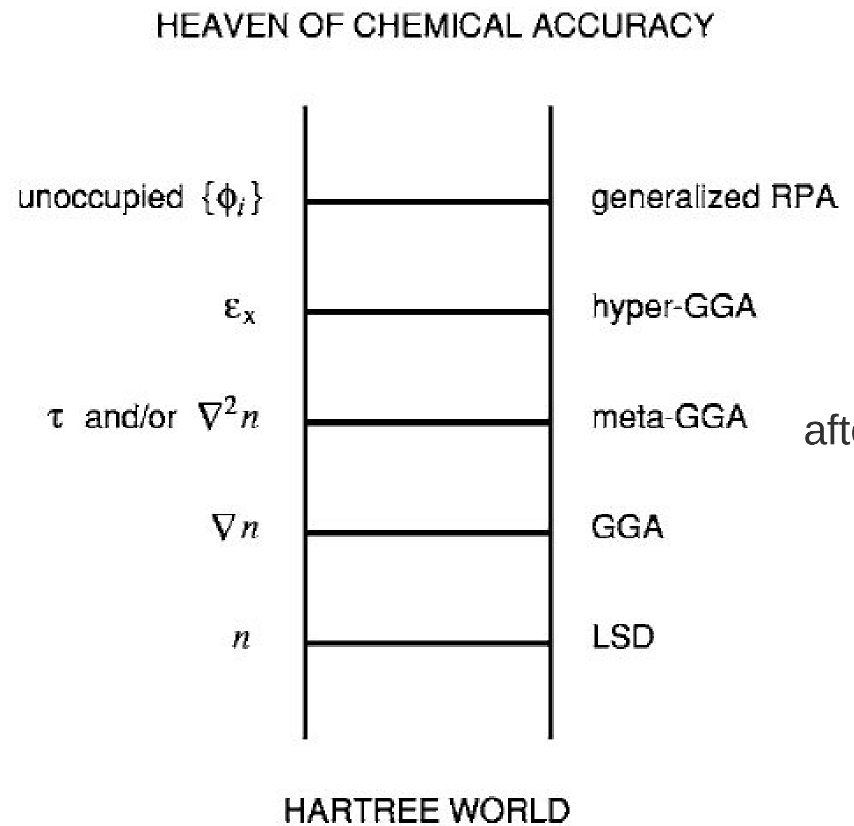


FIG. 1. Jacob's ladder of density functional approximations to the exchange-correlation energy.

after J. Perdew JCP (2005).

Need to change the overall framework!

Outline

I. Introduction: going beyond DFT

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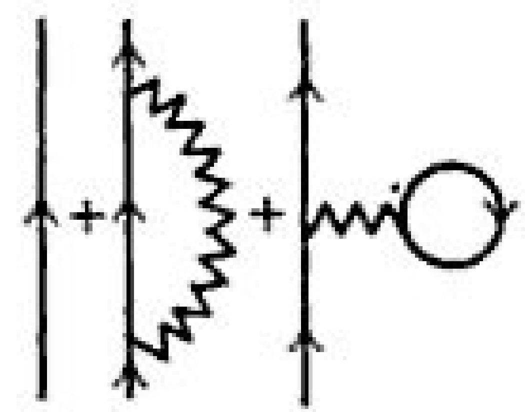
Many-body perturbation theory

Historically older than the DFT (from the 40-50's)!
Big names: Feynman, Schwinger, Hubbard, Hedin, Lundqvist

Green's functions
= propagator

$$G(\boldsymbol{r}t,\boldsymbol{r}'t')=$$



The Green's function

Exact ground state wavefunction: $\left| N,0 \right\rangle$

Creation, annihilation operator: $\Psi^{\dagger}(\boldsymbol{r}t), \; \Psi(\boldsymbol{r}t)$

1 $\Psi^{\dagger}(\boldsymbol{r}t)\left| N,0 \right\rangle$ is a (N+1) electron wavefunction not necessarily in the ground state

2 $\Psi^{\dagger}(\boldsymbol{r}'t')\left| N,0 \right\rangle$ is another (N+1) electron wavefunction

Let's compare the two of them!

Green's function definition

$$\underbrace{\langle N,0|\Psi(\boldsymbol{r}t)}_{1}\underbrace{\Psi^\dagger(\boldsymbol{r}'t')|N,0\rangle}_{2}$$

$$= i G^e(\boldsymbol{r}t, \boldsymbol{r}'t') \quad \text{for} \quad t > t'$$

Mesures how an extra electron propagates from (*r'*'*t'*) to (*rt*).

Green's function definition

$$\underbrace{\langle N,0 | \Psi^\dagger(\boldsymbol{r}'t')}_{2} \underbrace{\Psi(\boldsymbol{r}t) | N,0 \rangle}_{1}$$

$$= i\,G^h(\boldsymbol{r}'t',\boldsymbol{r}t) \qquad \text{for} \qquad t' > t$$

Mesures how a missing electron (= a hole) propagates from (rt) to ($r't'$).

Final expression for the Green's function

$$i G(\mathbf{r} t, \mathbf{r}' t') = \langle N, 0 | T \left[\Psi(\mathbf{r} t) \Psi^\dagger(\mathbf{r}' t') \right] | N, 0 \rangle$$

time-ordering operator

$$G(\mathbf{r} t, \mathbf{r}' t') = G^e(\mathbf{r} t, \mathbf{r}' t') - G^h(\mathbf{r}' t', \mathbf{r} t)$$

Compact expression that describes both the propagation of an extra electron and an extra hole

Lehman representation

$$iG(\boldsymbol{r},\boldsymbol{r}',t-t') = \langle N,0 | T[\Psi(\boldsymbol{r}t)\Psi^{+}(\boldsymbol{r}'t')] | N,0\rangle$$

Closure relation

$$\sum_{M,i} |M,i\rangle\langle M,i|$$

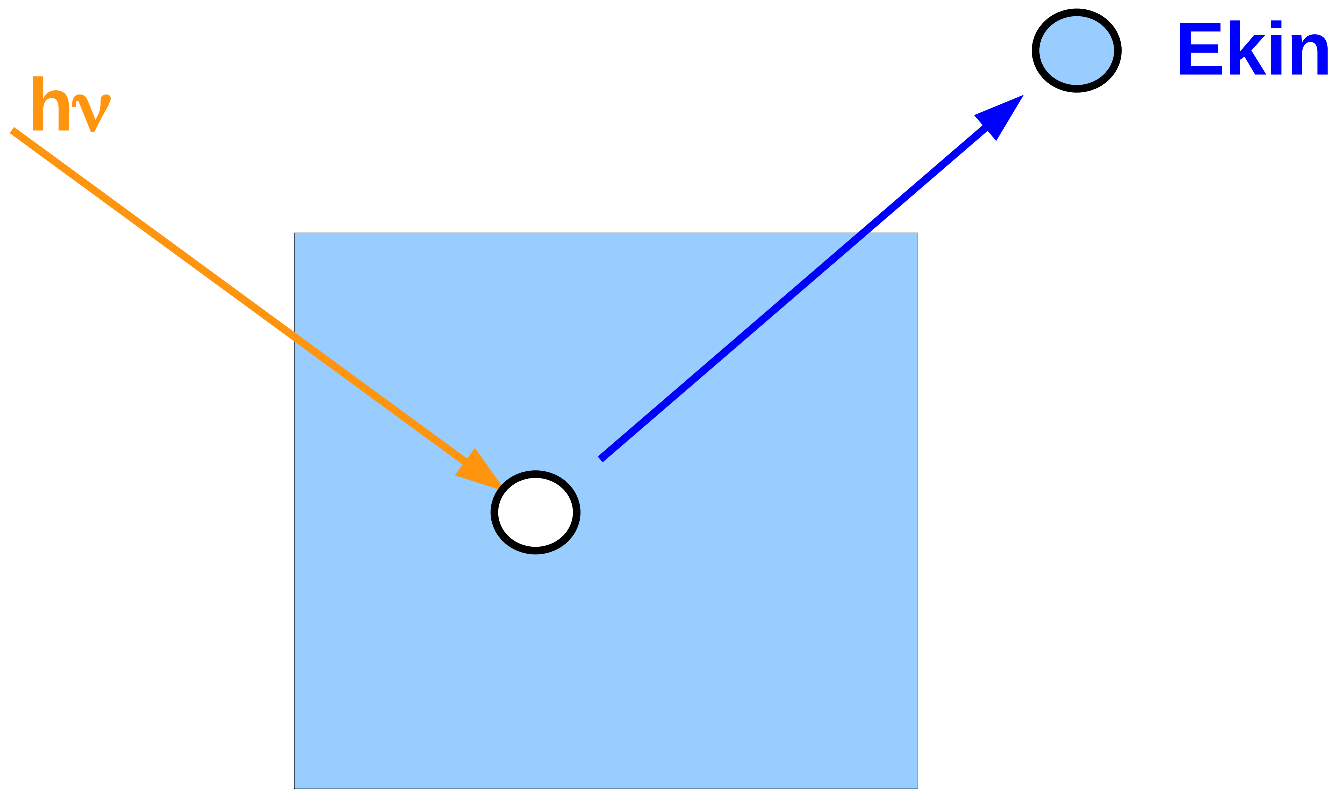
Lehman representation:

$$G(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_i \frac{f_i(\boldsymbol{r})\, f_i^{*}(\boldsymbol{r}')}{\omega - \epsilon_i \pm i\eta}$$

where $\epsilon_i = \begin{cases} E(N+1,i) - E(N,0) \\ E(N,0) - E(N-1,i) \end{cases}$

Exact excitation energies!

Related to photoemission spectroscopy

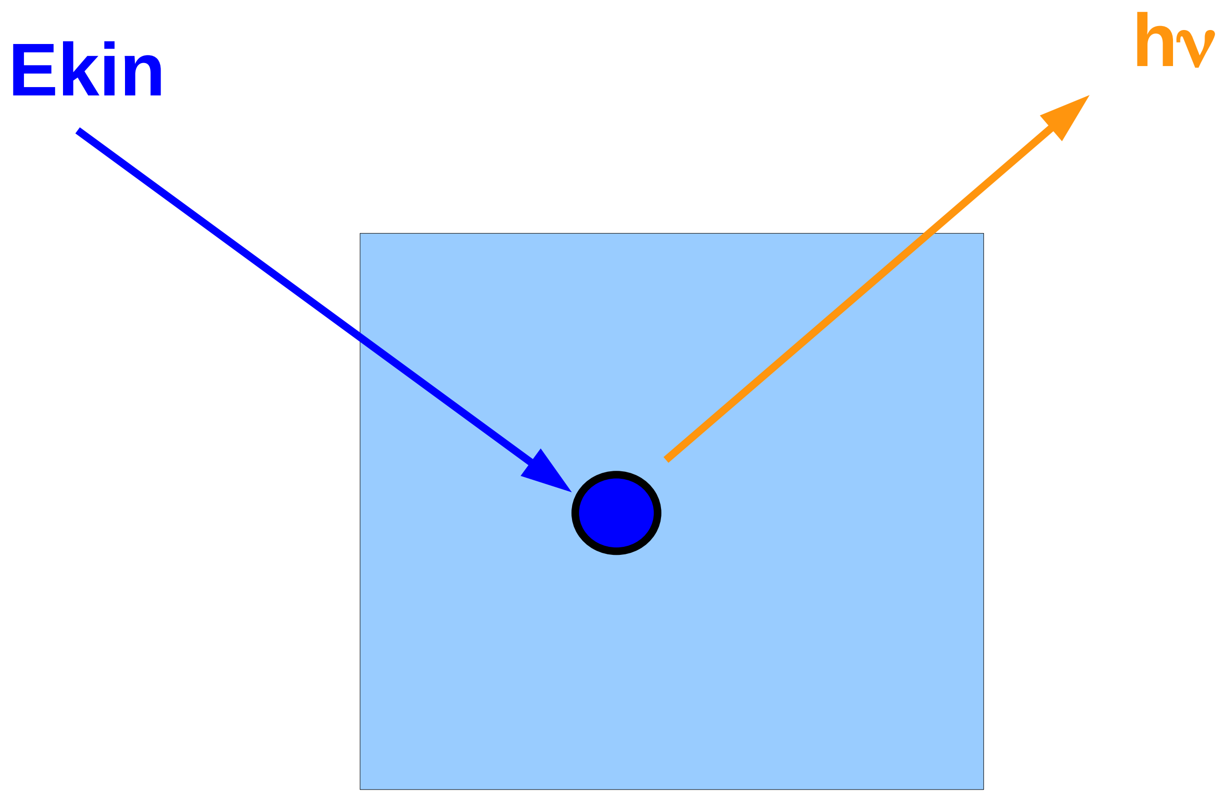


Energy conservation: before after

$$h\nu + E(N,0) = E_{kin} + E(N-1,i)$$

Quasiparticle energy: $$\epsilon_i = E(N,0) - E(N-1,i) = E_{kin} - h\nu$$

And inverse photoemission spectroscopy



Energy conservation: before after

$$E_{kin} + E(N,0) = h\nu + E(N+1,i)$$

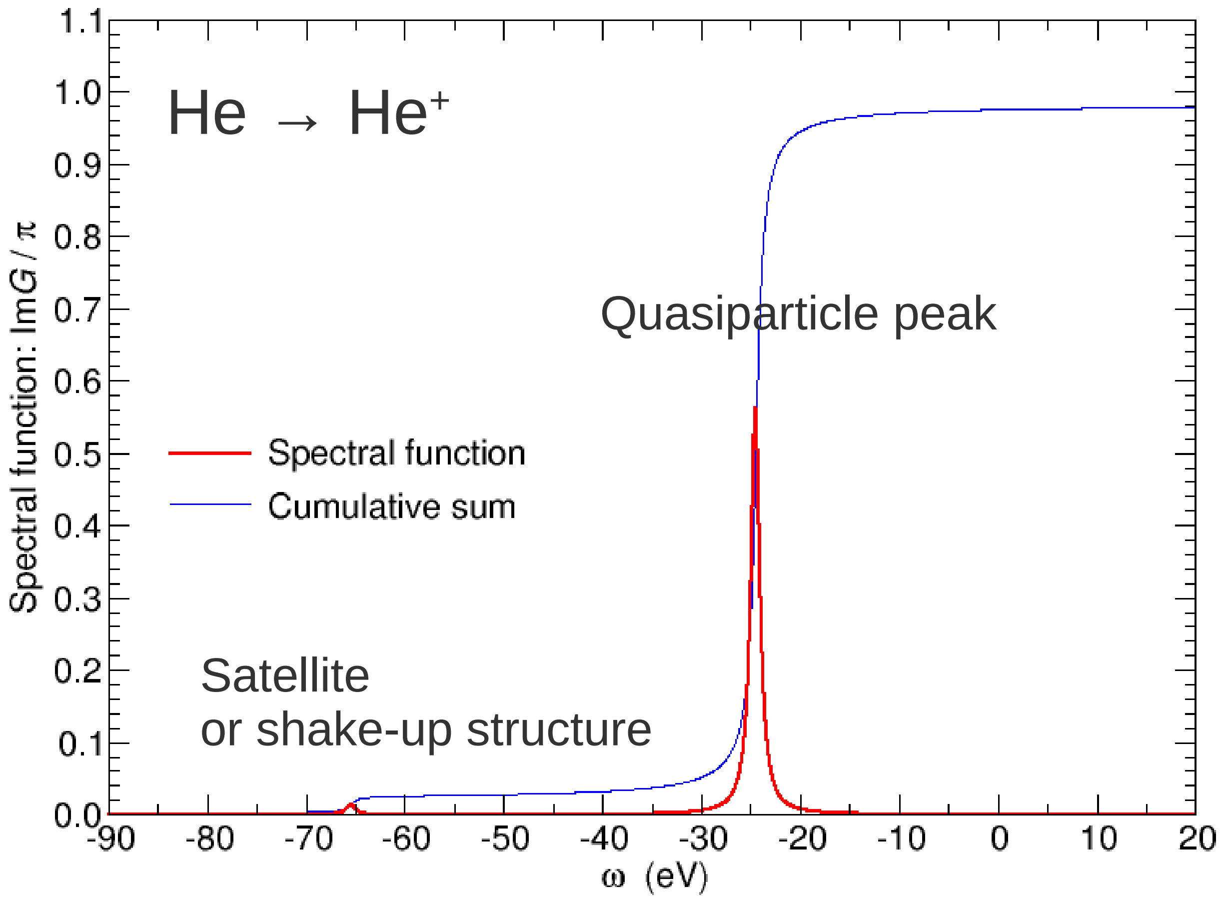
Quasiparticle energy: $$\epsilon_i = E(N+1,i) - E(N,0) = E_{kin} - h\nu$$

Exact realization of the Lehman decomposition

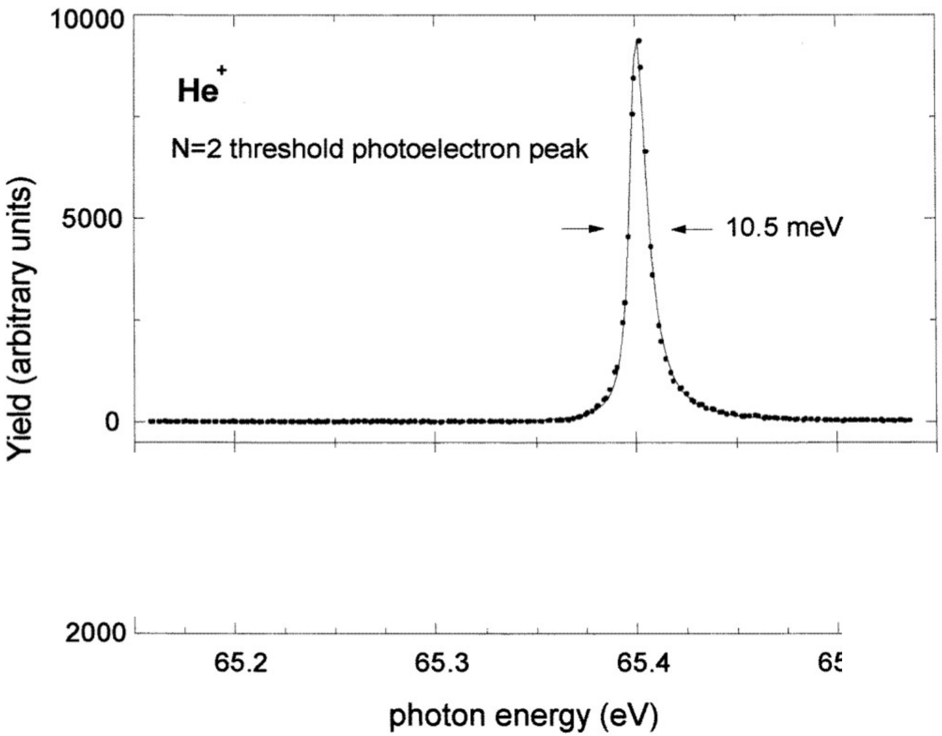
$$\langle m|G^h(\omega)|m\rangle = \sum_i \frac{\langle N\,0|\hat{c}_m^+|N-1\,i\rangle\langle N-1\,i|\hat{c}_m|N\,0\rangle}{\omega-\epsilon_i-i\eta}$$

$$N=2$$
$$N-1=1$$
$$m=1s$$

Obtained from FCI calculations



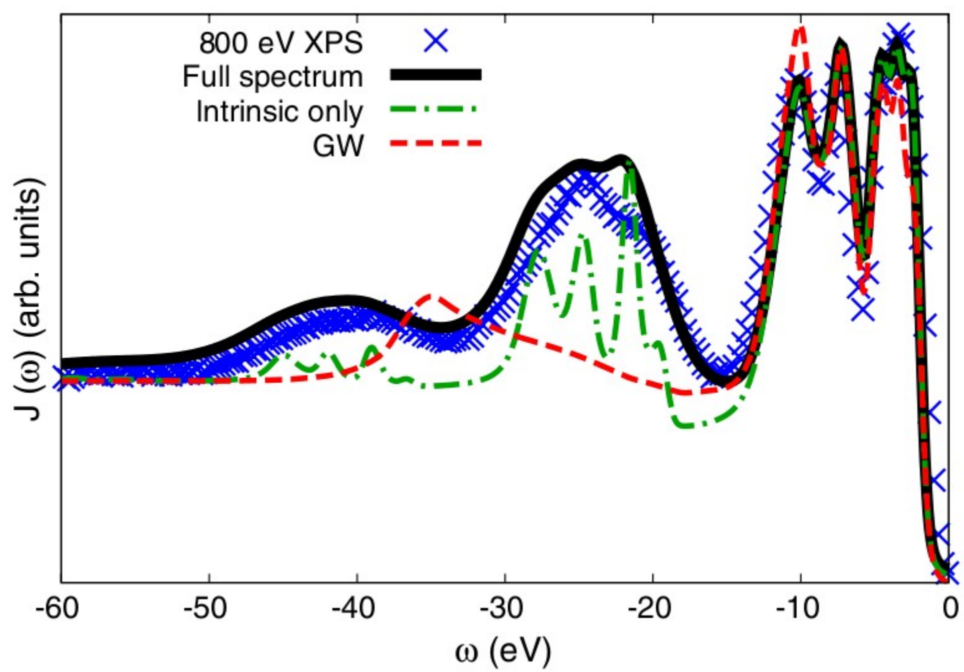
Satellites in reality?



Helium gas
Thompson *et al.*
J. Phys. B: At. Mol. Opt. Phys. 1998

Silicon crystal

Guzzo *et al.* PRL 2011



Other properties of the Green's function

Get the electron density:

$$\rho(\boldsymbol{r}) = -i\,G(\boldsymbol{r}t^{-}, \boldsymbol{r}, t)$$

Galitskii-Migdal formula for the total energy:

$$E_{total} = \frac{1}{\pi}\int_{-\infty}^{\mu} d\omega\, \mathrm{Tr}\left[\left(\omega - h_0\right) \mathrm{Im}\, G(\omega)\right]$$

Expectation value of any 1 particle operator (local or non-local)

$$\langle O \rangle = \lim_{t \to t'} Tr\left[O\,G\right]$$

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Equation of motion of Green's functions: Dyson equation

Let us start with a non-interacting Green's function G_0
corresponding to a hamiltonian h_0

$$\int d\,\mathbf{r_2}\,\delta(\mathbf{r_1}-\mathbf{r_2})\left[\omega-h_0(\mathbf{r_2})\right]G_0(\mathbf{r_2},\mathbf{r_3},\omega)=\delta(\mathbf{r_1}-\mathbf{r_3})$$

In short:

$$\left[\omega-h_0\right]G_0=1 \qquad \text{or} \qquad G_0^{-1}=\left[\omega-h_0\right]$$

Imagine h_0 is Hartree and h_{KS} is Kohn-Sham

$$\left[\omega-h_{\mathrm{KS}}\right]G_{\mathrm{KS}}=1$$

$$\left[\omega-h_0-v_{xc}\right]G_{\mathrm{KS}}=1$$

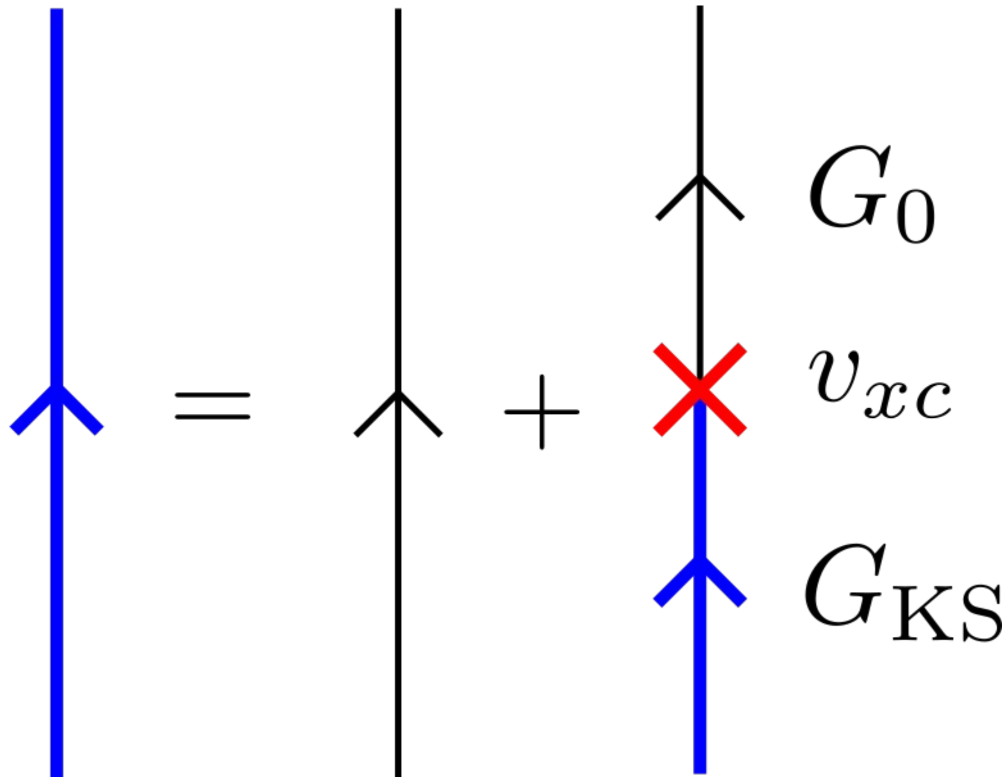
$$\left[G_0^{-1}-v_{xc}\right]G_{\mathrm{KS}}=1$$

$$G_{\mathrm{KS}}=G_0+G_0\,v_{xc}\,G_{\mathrm{KS}}$$

$$G_{\mathrm{KS}}=G_0 \;+\; G_0 v_{xc} G_0 \;+\; G_0 v_{xc} G_0 v_{xc} G_0 \;+\ldots$$

Exercice

A first contact with diagrams



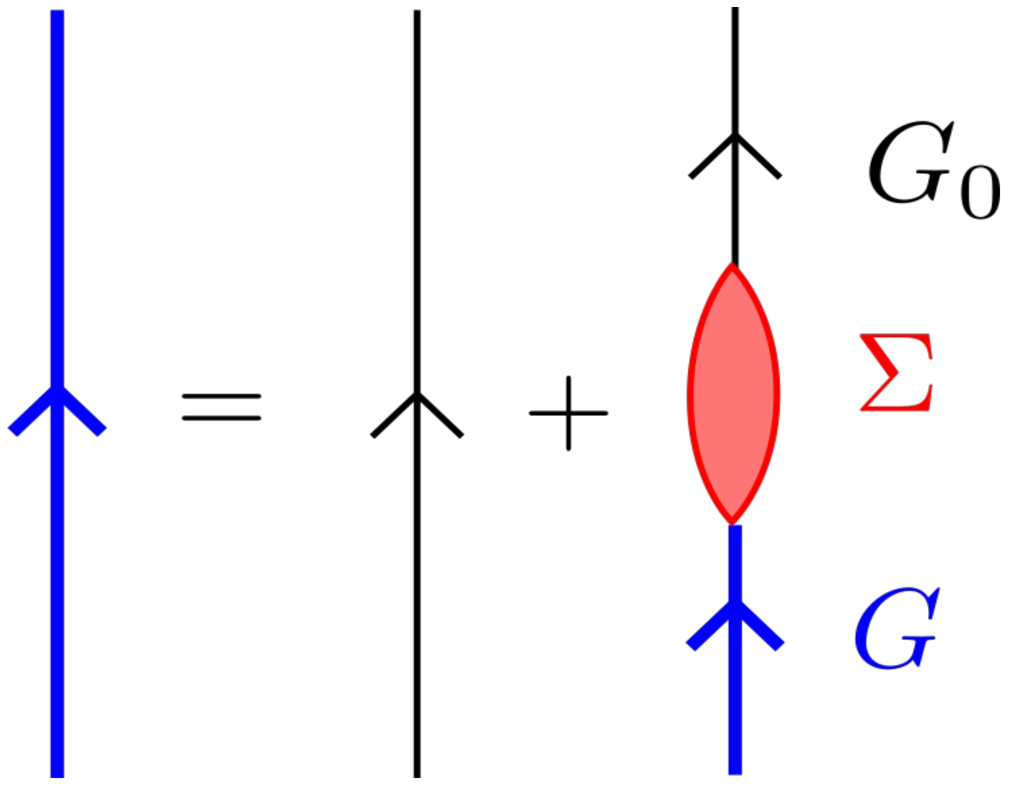
$$G_{\mathrm{KS}}(1,2) = G_0(1,2) + \int d3\, G_0(1,3)\, v_{xc}(3)\, G_{\mathrm{KS}}(3,2)$$

Dyson equation connects the Green's functions arising from different approximations

What about the **exact Green's function?**

Dyson equation for the exact Green's function

Imagine there exists an operator that generates the exact *G*



$$G(1,2) = G_0(1,2) + \int d(34)\, G_0(1,3)\,\Sigma(3,4)\,G(4,2)$$

This operator is the famous “self-energy”:
- non-local in space
- time-dependent
- non-Hermitian

Everything else now deals with finding expressions for the self-energy!

A hierarchy of equations of motion

In fact there is an exact expression for the self-energy as a function of the **two-particle Green's function**

$$\left[G_0^{-1} - \Sigma \right] G = 1$$

$$\left[G_0^{-1} - G_2 \right] G = 1$$

$$G_2(1,2;3,4) = \langle N,0 | T[\Psi(1)\Psi(2)\Psi^+(3)\Psi^+(4)] | N,0 \rangle$$

And try to guess the equation of motion for the two-particle Green's function?

$$G_2 \;\; \text{needs} \;\; G_3$$

$$G_3 \;\; \text{needs} \;\; G_4$$

$$G_4 \;\; \text{needs} \;\; G_5$$

$$\ldots\ldots\ldots\ldots\ldots$$

An expression for the self-energy

Trick due to Schwinger (1951):

• Introduce a small external potential *U* (that will be made equal to zero at the end)

• Calculate the variations of *G* with respect to *U*

$$G_2(1,3;2,3^+) = G(1,2)\,G(3,3^+) - \frac{\delta G(1,2)}{\delta U(3)}$$

Obtain a perturbation theory with basic ingredients *G* and *v*
1st order is Hartree-Fock
2nd order is MP2

However MP2 diverges for metals!

Trick due to Hubbard+Hedin (late 1950's – early 1960's):

• Introduce the electrostatic response *V* to *U*
• Calculate the variations of *G* with respect to *V*

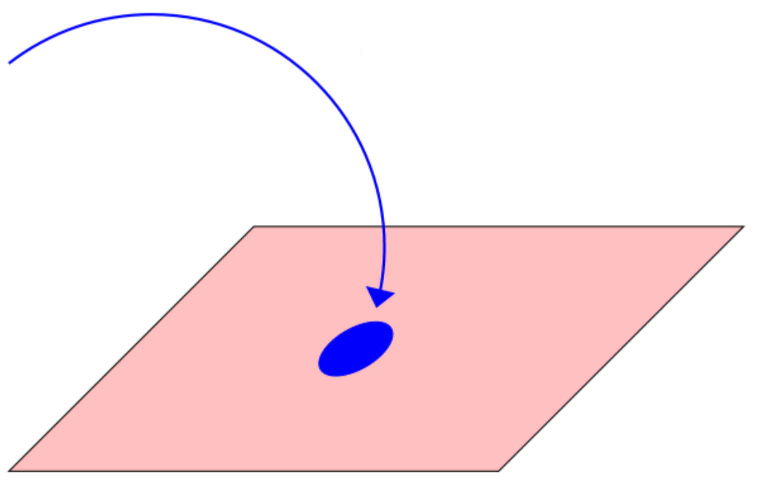
$$V(1) = U(1) - i\int d2\, v(1,2)\,\delta G(2,2)$$

Obtain **a new renormalized perturbation theory** with basic ingredients *G* and *W*

1st order is *GW*

Shifting from U to V

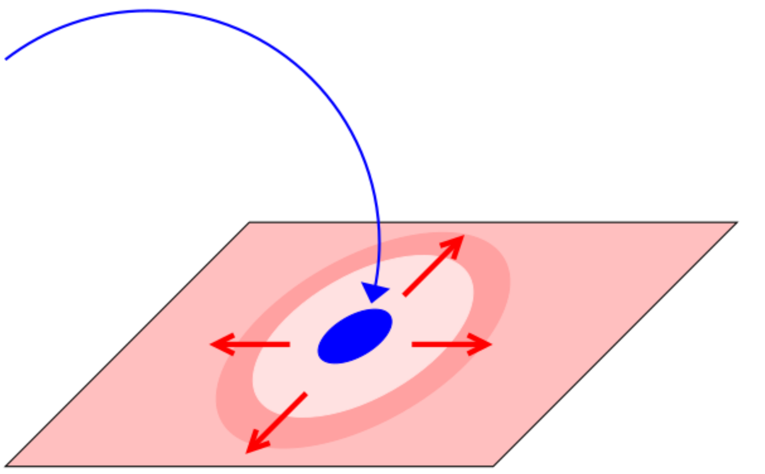
$$U(1) = \varepsilon\,\delta(\mathbf{r}-\mathbf{r_1})\,\delta(t-t_1)$$



Everything is functional of U

$$G[U]$$

$$U(1) = \varepsilon\,\delta(\mathbf{r}-\mathbf{r_1})\,\delta(t-t_1)$$



$$V(1) = U(1) + \int d\mathbf{r}\, v(r_1 - r)\,\delta\rho(\mathbf{r})$$

V also includes the electrostatic response

Everything is functional of V

$$G[V]$$

Hedin's coupled equations

5 coupled equations: $1=(\boldsymbol{r_1} t_1 \sigma_1)$ $2=(\boldsymbol{r_2} t_2 \sigma_2)$

$$G(1,2)=G_0(1,2)+\int d34\, G_0(1,3)\Sigma(3,4)G(4,2)$$

Dyson equation

$$\Sigma(1,2)=i\int d34\, G(1,3)W(1,4)\Gamma(4,2,3)$$

self-energy

$$\Gamma(1,2,3)=\delta(1,2)\delta(1,3)+\int d4567\, \frac{\delta\Sigma(1,2)}{\delta G(4,5)}G(4,6)G(5,7)\Gamma(6,7,3)$$

vertex

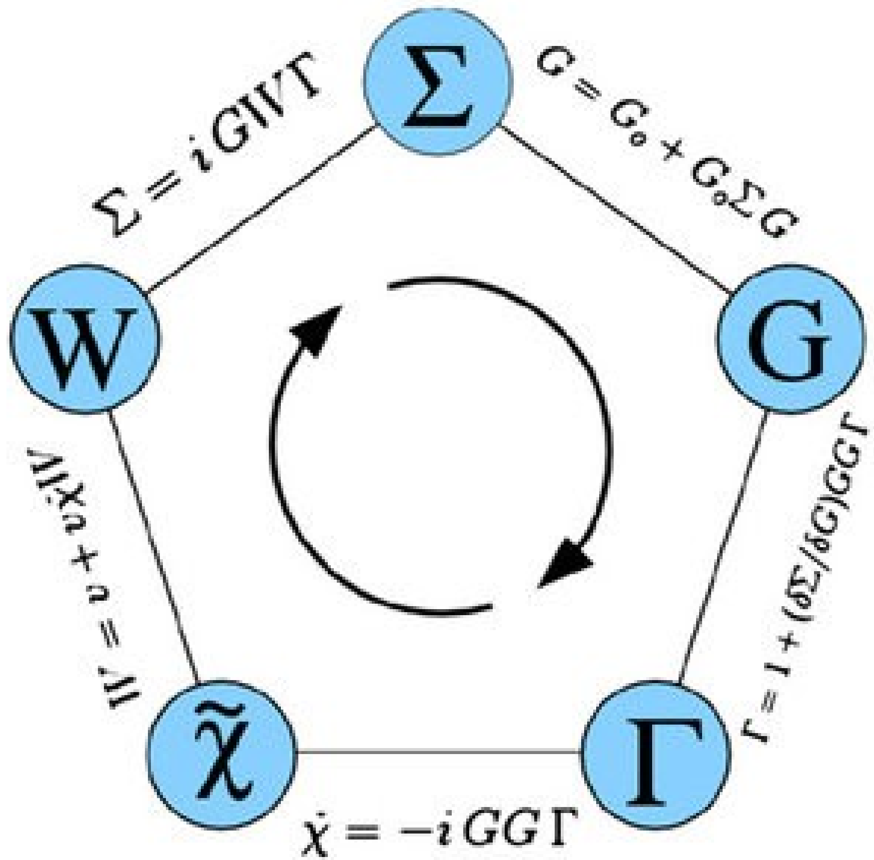
$$\chi_0(1,2)=-i\int d34\, G(1,3)G(4,1)\Gamma(3,4,2)$$

polarizability

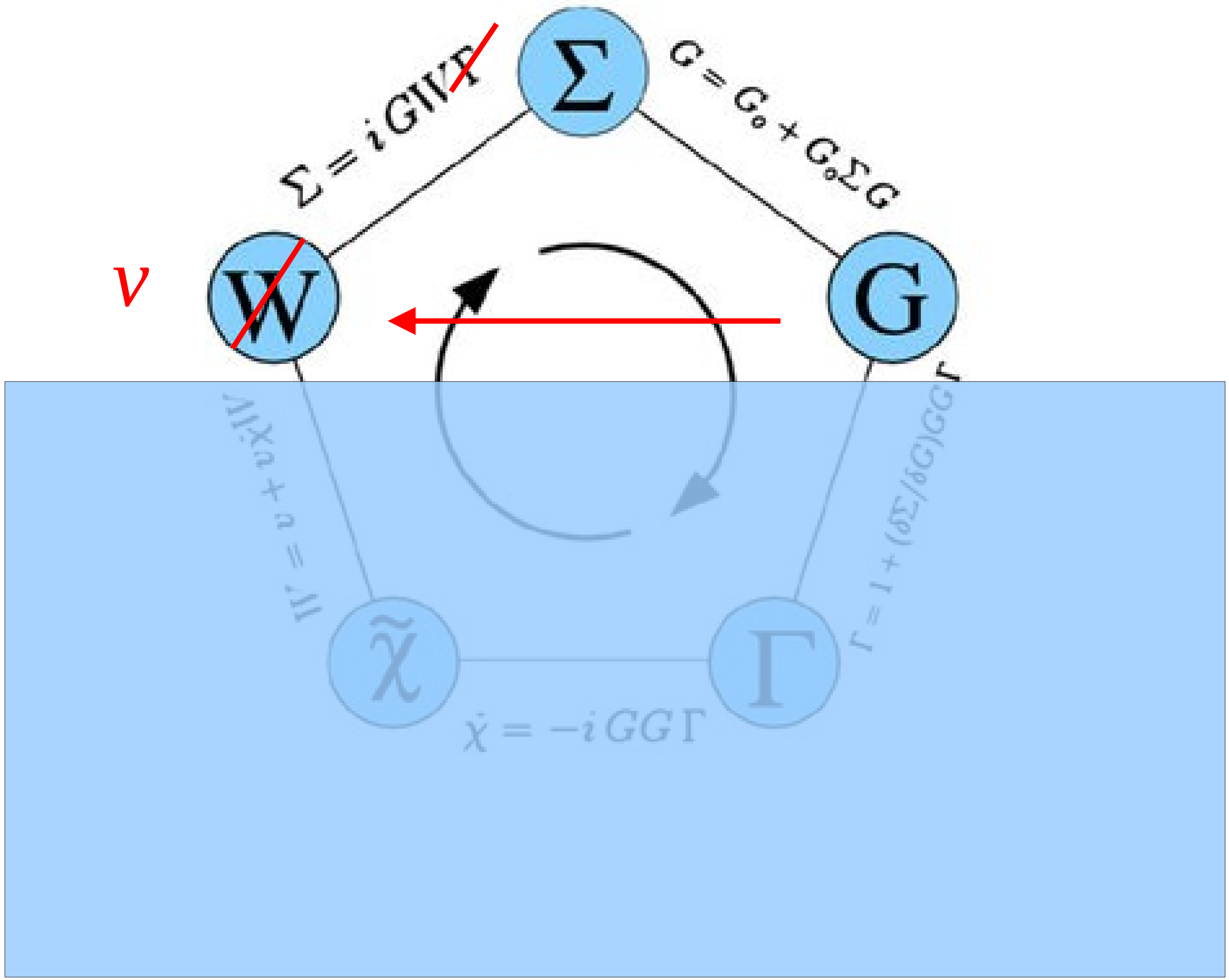
$$W(1,2)=v(1,2)+\int d34\, v(1,3)\chi_0(3,4)W(4,2)$$

screened Coulomb interaction

Hedin's pentagram

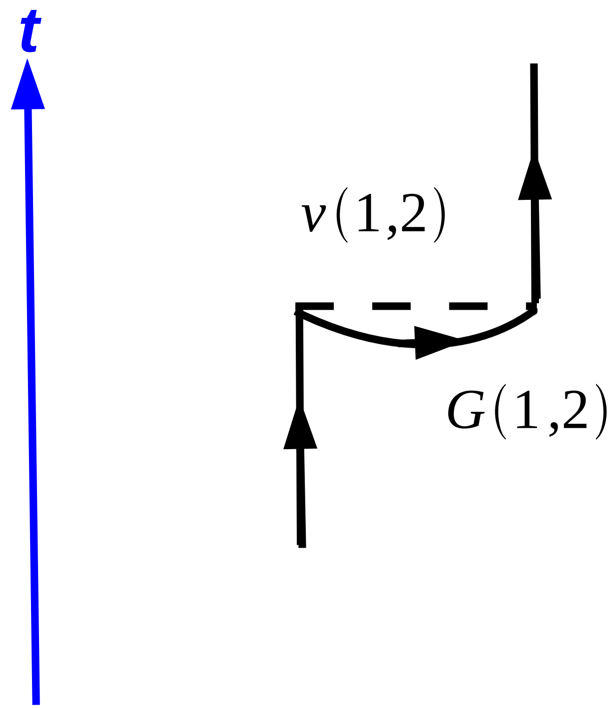


Hedin’s pentagram approximated



Simplest approximation

$$\Sigma(1,2) = iG(1,2)v(1^+,2)$$ ⇨ Fock exchange



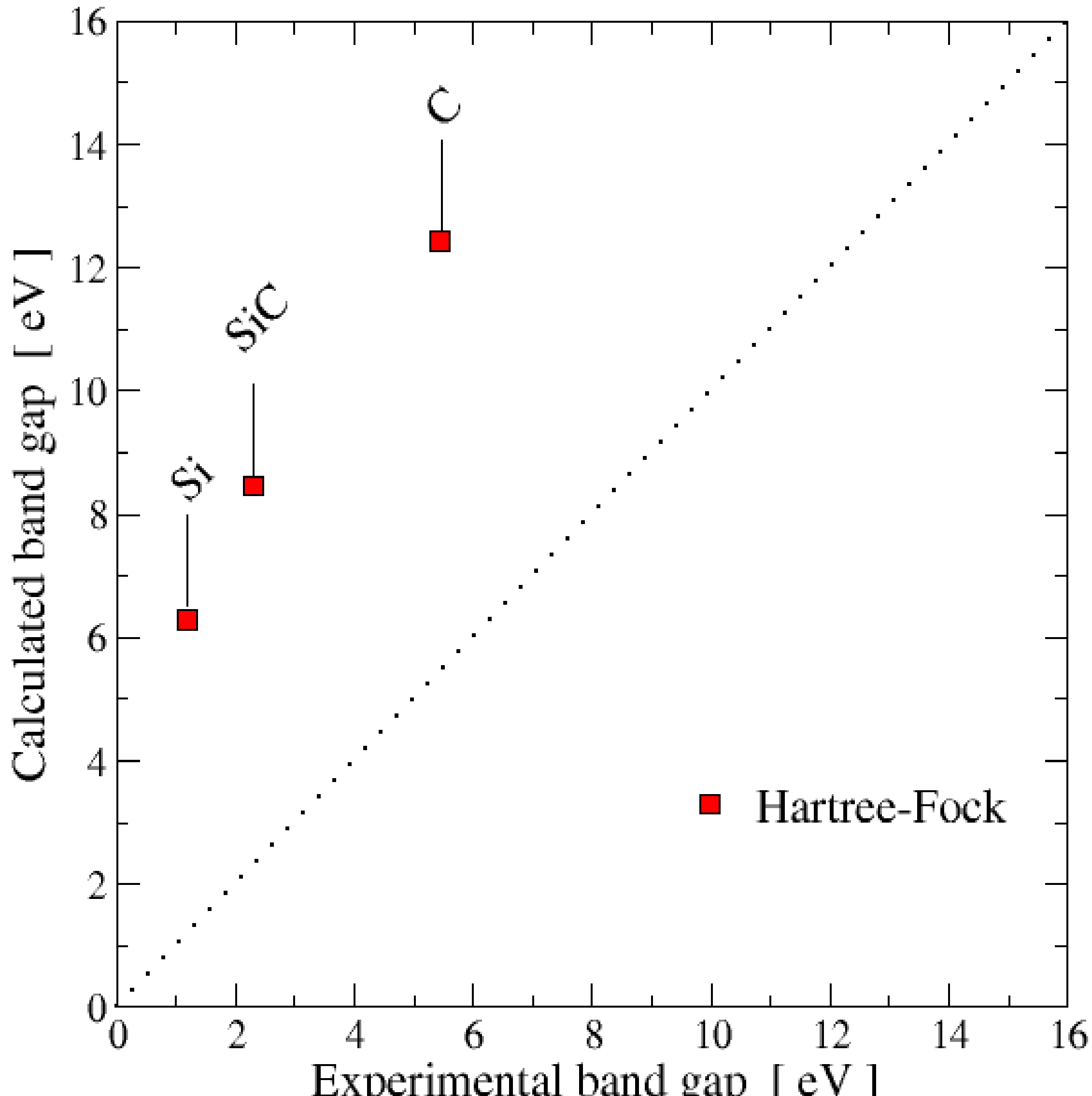
Dyson equation:

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

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

Not enough: Hartree-Fock is known to perform poorly for solids

Hartree-Fock approximation for band gaps



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Dyson equation

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self-energy

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \cancel{\int d4567 \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(5,7)\Gamma(6,7,3)}$$

vertex

$$\chi_0(1,2) = -i\int d34\, G(1,3)G(4,1)\Gamma(3,4,2)$$

polarizability

$$W(1,2) = v(1,2) + \int d34\, v(1,3)\chi_0(3,4)W(4,2)$$

screened Coulomb interaction

Hedin's coupled equations

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$$G(1,2)=G_0(1,2)+\int d34\,G_0(1,3)\,\Sigma(3,4)\,G(4,2)$$

Dyson equation

$$\Sigma(1,2)=i\,\cancel{\int d34}\,G(1,2)\,W(1,2)\,\cancel{\Gamma(4,2,3)}$$

self-energy

$$\Gamma(1,2,3)=\delta(1,2)\,\delta(1,3)+\cancel{\int d4567\,\frac{\delta\Sigma(1,2)}{\delta G(4,5)}\,G(4,6)\,G(5,7)\,\Gamma(6,7,3)}$$

vertex

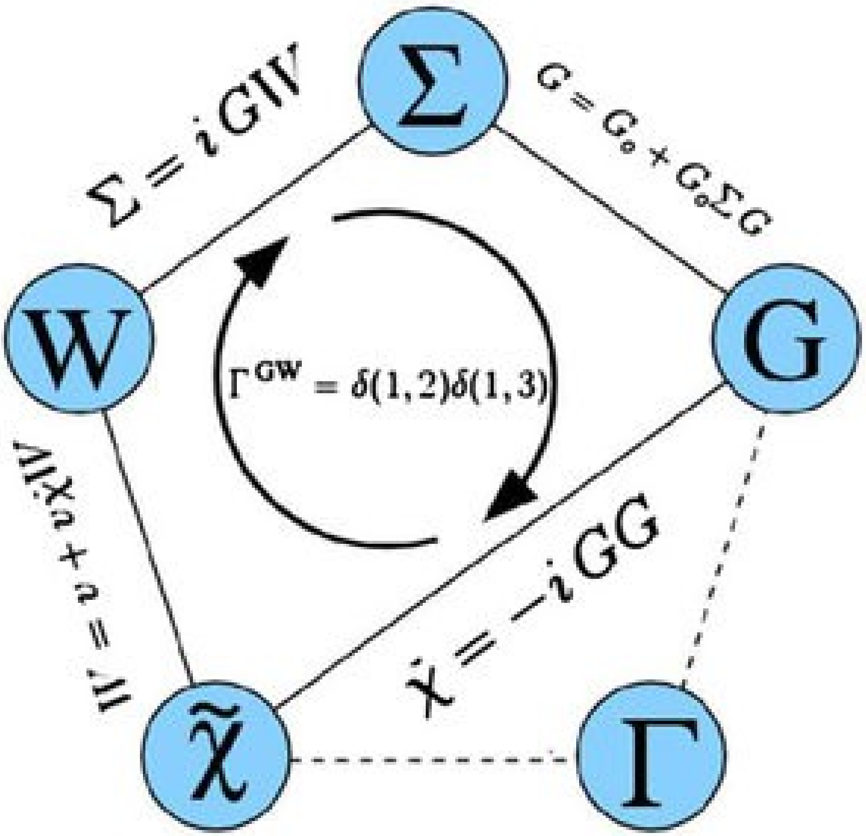
$$\chi_0(1,2)=-i\,\cancel{\int d34}\,G(1,2)\,G(2,1)\,\cancel{\Gamma(3,4,2)}$$

polarizability

$$W(1,2)=v(1,2)+\int d34\,v(1,3)\,\chi_0(3,4)\,W(4,2)$$

screened Coulomb interaction

Truncated Hedin's pentagram



short-cutting the vertex À

Here comes the *GW* approximation

$$\Sigma(1,2) = iG(1,2)W(1,2)$$ *GW* approximation

$$\chi_0(1,2) = -iG(1,2)G(2,1)$$ RPA approximation

$$W(1,2) = v(1,2) + \int d34\, v(1,3)\chi_0(3,4)W(4,2)$$ Dyson-like equation

Let us draw somes diagrams

$$\chi_0(1,2) = -i\,G(1,2)\,G(2,1)$$

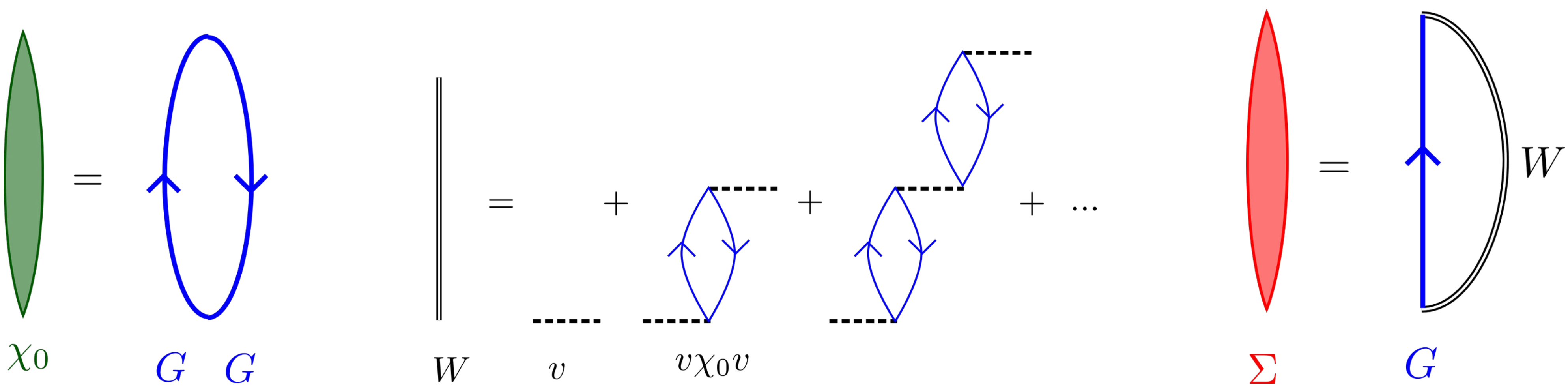
Infinite summation
over bubble (or ring) diagrams
electron-hole pairs

$$W = v + v\chi_0 W$$

$$= v + v\chi_0 v + v\chi_0 v\chi_0 v + \ldots$$

$$= \left[\sum_{n=0}^{\infty} (v\chi_0)^n\right] v \quad = [1 - v\chi_0]^{-1}\; v$$

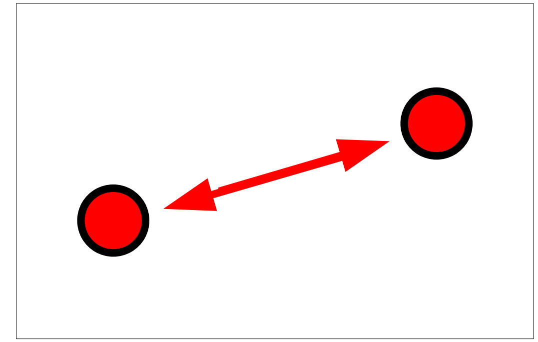
$$\Sigma(1,2) = i\,G(1,2)\,W(1,2)$$



What is W?

Interaction between electrons in vacuum:

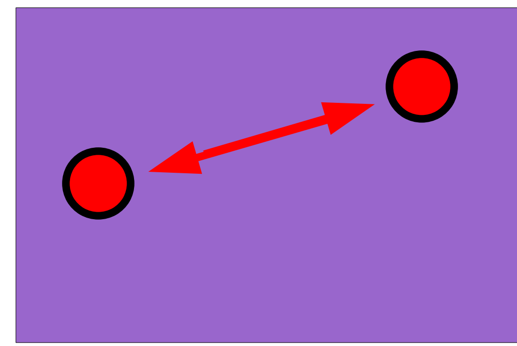
$$v(\boldsymbol{r},\boldsymbol{r}')=\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}$$



Interaction between electrons in a homogeneous polarizable medium:

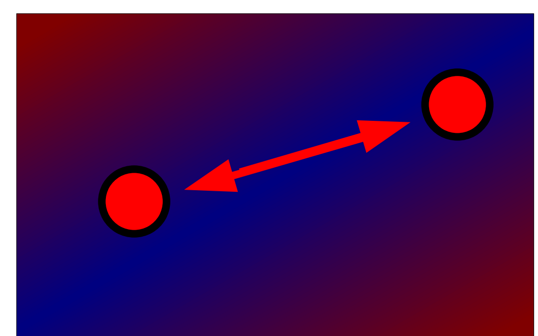
$$W(\boldsymbol{r},\boldsymbol{r}')=\frac{1}{4\pi\varepsilon_0\varepsilon_r}\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

Dielectric constant
of the medium



Dynamically screened interaction between electrons
in a general medium:

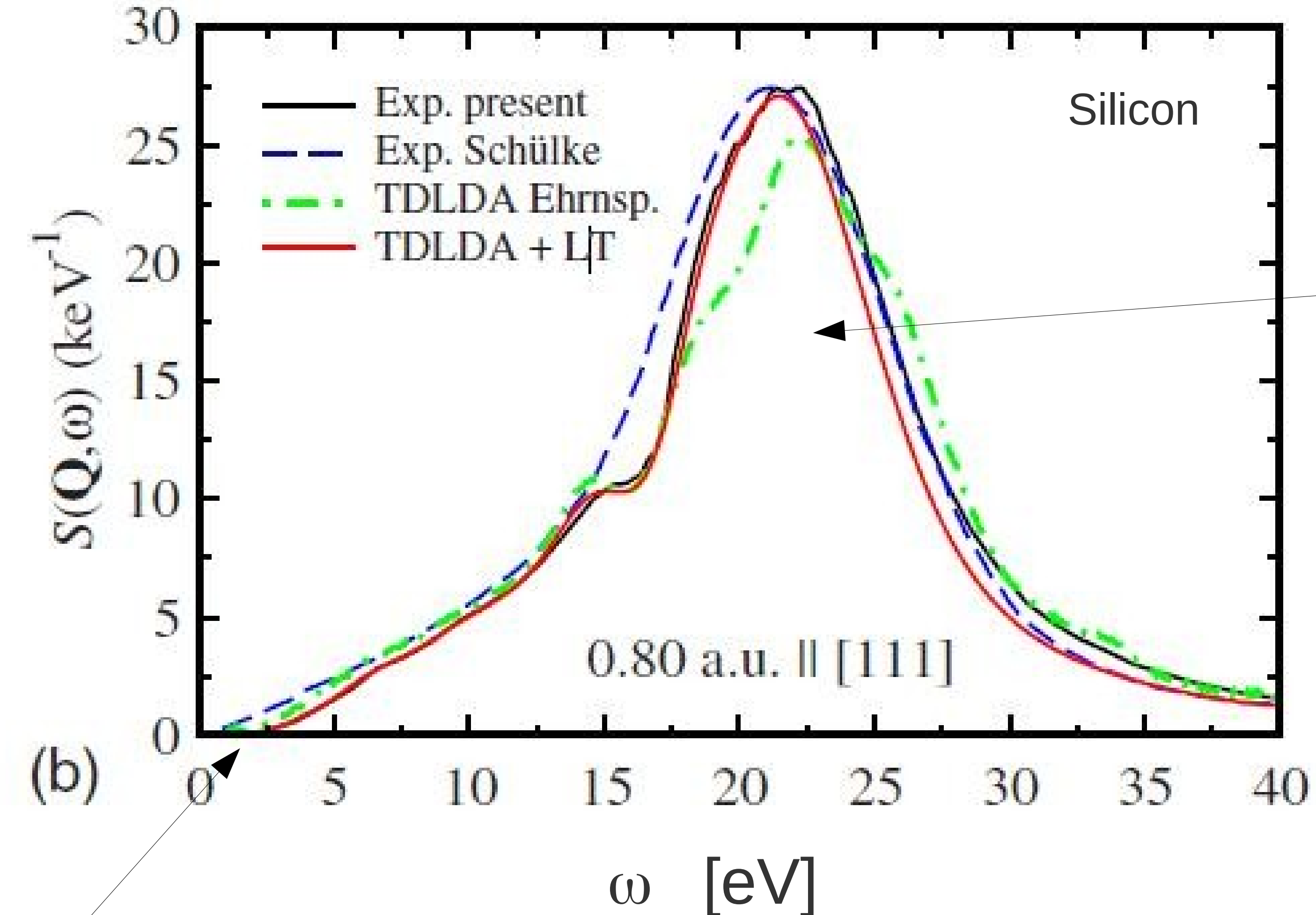
$$W(\boldsymbol{r},\boldsymbol{r}',\omega)=\frac{e^2}{4\pi\varepsilon_0}\int dr''\frac{\varepsilon^{-1}(\boldsymbol{r},\boldsymbol{r}'',\omega)}{|\boldsymbol{r}''-\boldsymbol{r}'|}$$



W is frequency dependent

W can measured directly by Inelastic X-ray Scattering

$$W(\boldsymbol{q} = 0.80\,\text{a.u}, \omega)$$



Zero below the band gap

H-C Weissker et al. PRB (2010)

Summary

GW viewed as a "super" Hartree-Fock

Hartree-Fock Approximation

$$\Sigma_x(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{i}{2\pi}\int_{-\infty}^{\mu} d\omega' G(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega') v(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

= bare exchange

GW Approximation

$$\Sigma_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega) = \frac{i}{2\pi}\int d\omega' G(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega+\omega') W(\boldsymbol{r}_2,\boldsymbol{r}_1,\omega')$$

Exercice

$$\Sigma_x(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

Bare exchange

$$\Sigma_c(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega)$$

+ correlation

Non Hermitian
dynamic

***GW* is nothing else but a "screened" version of Hartree-Fock.**

Summary: DFT vs *GW*

Electronic density | **Green's function**

$\rho(\boldsymbol{r})$ ⟺ $G(\boldsymbol{r}t,\boldsymbol{r}'t')$

Local and static

Non-local, dynamic
Depends onto empty states

exchange-correlation potential

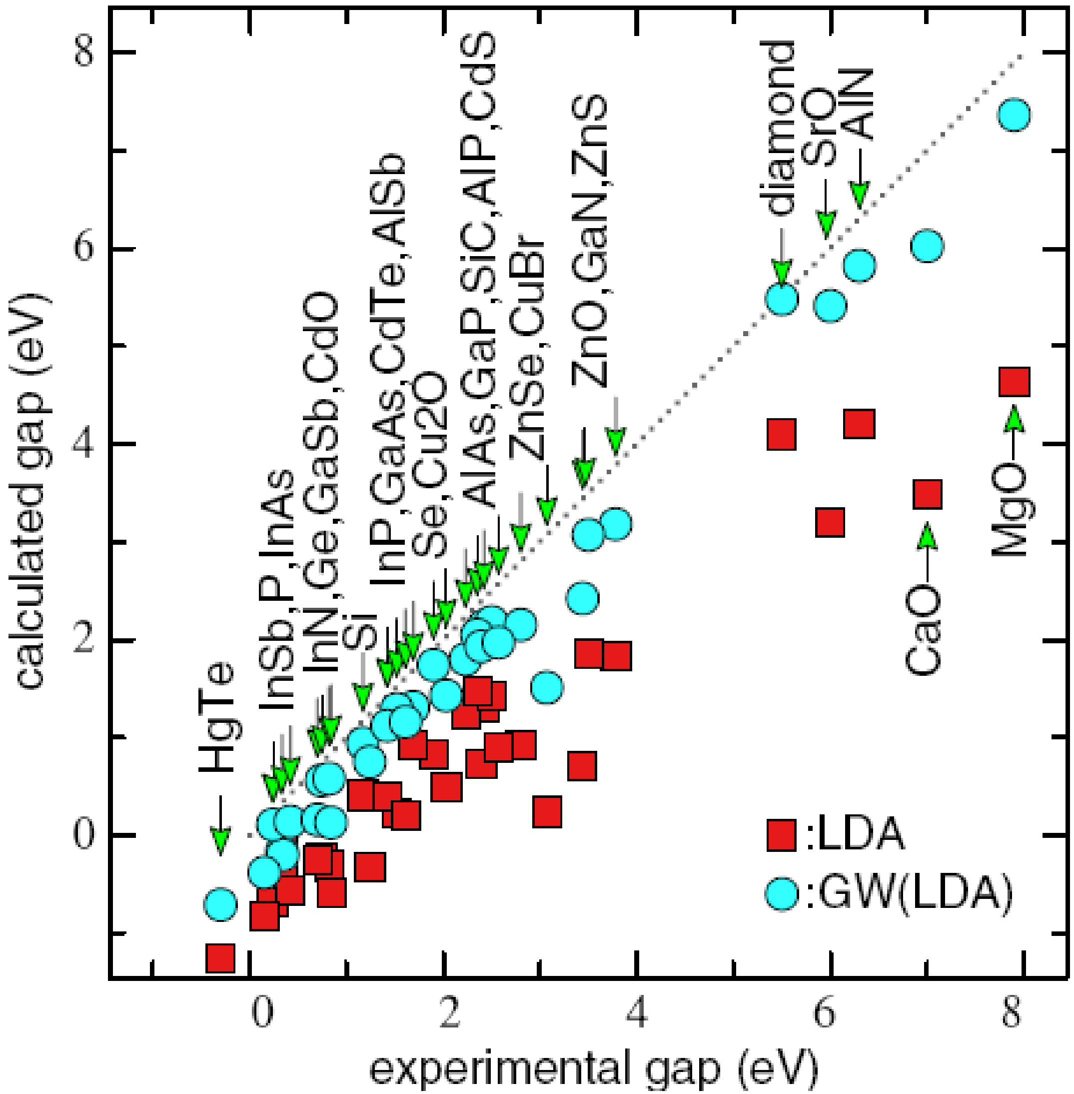
exchange-correlation operator
= self-energy

$v_{xc}(\boldsymbol{r})$ ⟺ $\Sigma_{xc}(\boldsymbol{r}t,\boldsymbol{r}'t')$

Approximations: LDA, GGA, hybrids | *GW* approximation

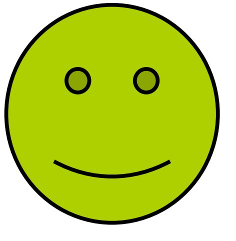
$$\boxed{\Sigma_{GW}(\boldsymbol{r}t,\boldsymbol{r}'t') = iG(\boldsymbol{r}t,\boldsymbol{r}',t')W(\boldsymbol{r}t,\boldsymbol{r}'t')}$$

GW approximation gets good band gap



after van Schilfgaarde *et al* PRL **96** 226402 (2008)

No band gap problem anymore!



Outline

I. Introduction: going beyond DFT

II. Introduction of the Green's function

III. Exact Hedin's equations and the *GW* approximation

IV. Calculating the *GW* self-energy in practice

V. Applications

Hedin's coupled equations

5 coupled equations: $1=(\boldsymbol{r_1} t_1 \sigma_1)$ $2=(\boldsymbol{r_2} t_2 \sigma_2)$

$$G(1,2) = G_0(1,2) + \int d34\, G_0(1,3)\Sigma(3,4)G(4,2)$$

Dyson equation

$$\Sigma(1,2) = i \cancel{\int d34}\, G(1,\cancel{3}\,\mathbf{2})\, W(1,\cancel{4}\,\mathbf{2})\, \cancel{\Gamma(4,2,3)}$$

self-energy

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \cancel{\int d4567 \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(5,7)\Gamma(6,7,3)}$$

vertex

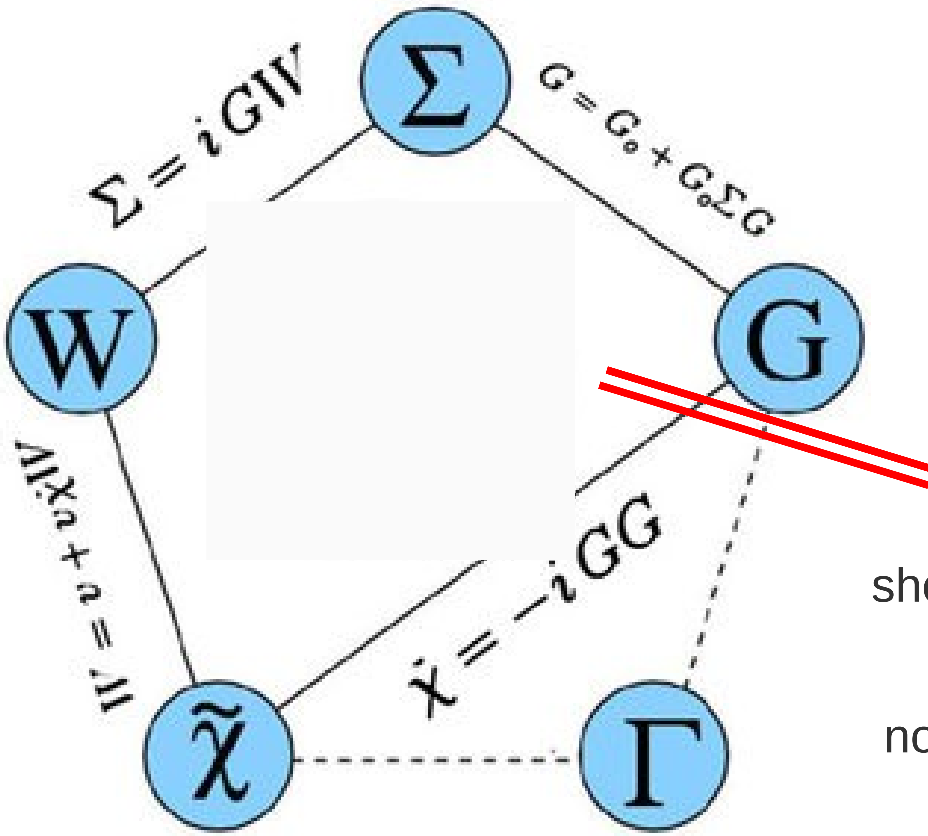
$$\chi_0(1,2) = -i \cancel{\int d34}\, G(1,\cancel{3}\,\mathbf{2})\, G(\cancel{4}\,\mathbf{2},1)\, \cancel{\Gamma(3,4,2)}$$

polarizability

$$W(1,2) = v(1,2) + \int d34\, v(1,3)\chi_0(3,4)W(4,2)$$

screened Coulomb interaction

Super-truncated Hedin's pentagram



short-cutting the vertex À

no self-consistency

Historical recap of *GW* calculations

- 1965: Hedin's calculations for the homogeneous electron gas
  Phys Rev **2201 citations**

- 1967: Lundqvist's calculations for the homogeneous electron gas
  Physik der Kondensierte Materie **299 citations**

- 1982: Strinati, Mattausch, Hanke for real semiconductors but within tight-binding
  PRB **154 citations**

- 1985: Hybertsen, Louie for real semiconductors with ab initio LDA
  PRL **711 citations** & PRB **1737 citations**

- 1986: Godby, Sham, Schlüter for real semiconductors to get accurate local potential
  PRL **544 citations** & PRB **803 citations**

- ~2001: First publicly available *GW* code in ABINIT

- 2003: Arnaud, Alouani for extension to Projector Augmented Wave
  PRB **102 citations**

- 2006: Shishkin, Kresse for extension to Projector Augmented Wave (again)
  PRB **256 citations**

GW approximation in practice

- For periodic solids: Abinit, BerkeleyGW, VASP, Yambo

based on plane-waves (with pseudo or PAW)

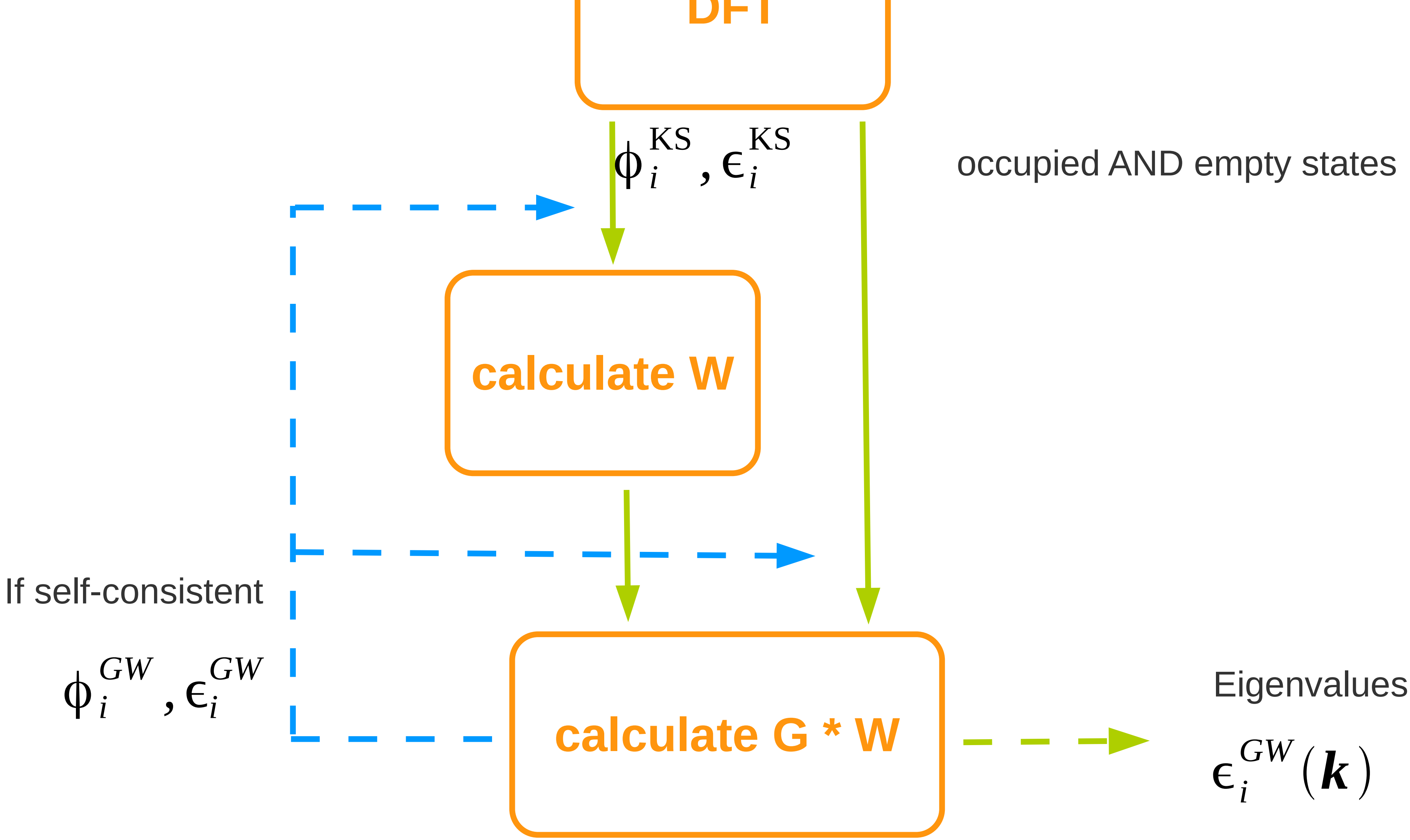
- For finite systems: MOLGW, Fiesta, FHI-AIMS

based on localized orbitals (Gaussians or Slater or other)

What is common to all implementations

Workflow of a typical *GW* calculation

$G_0 W_0$ vs GW



How to get *G*?

From Kohn-Sham DFT

Remember

$$\left[\omega - h_{\mathrm{KS}}\right] G_{\mathrm{KS}} = 1$$

Exercice

which means

$$G^{KS}(\boldsymbol{r}, \boldsymbol{r}', \omega) = \sum_i \frac{\phi_i^{\mathrm{KS}}(\boldsymbol{r})\, \phi_i^{\mathrm{KS}*}(\boldsymbol{r}')}{\omega - \epsilon_i^{\mathrm{KS}} \pm i\eta}$$

This expression will be used to get W and Σ

How to get *W*?

Exercice

From the RPA equation

$$\chi_0(1,2) = -i G(1,2) G(2,1)$$

which translates into

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_{\substack{i\,\text{occ} \\ j\,\text{virt}}} \phi_i(\mathbf{r}_1) \phi_i^*(\mathbf{r}_2) \phi_j(\mathbf{r}_2) \phi_j^*(\mathbf{r}_1) \times \left[\frac{1}{\omega - (\epsilon_j - \epsilon_i) - i\eta} - \frac{1}{\omega - (\epsilon_i - \epsilon_j) + i\eta} \right]$$

This is the Alder-Wiser formula or the SOS formula

It involves empty states!

Then $\chi_0(1,2)$ $\quad\longrightarrow\quad$ $W(1,2)$

differs with implementations

Diagonal self-energy correction approximation

Dyson equation: $$G^{-1} = G^{\mathrm{KS}\ -1} - \left(\Sigma - v_{xc}\right)$$

And remember: $$G^{\mathrm{KS}\ -1}(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathrm{i}} \phi_{\mathrm{i}}^{\mathrm{KS}}(\mathbf{r}) \left[\omega - \epsilon_{\mathrm{i}}^{\mathrm{KS}}\right] \phi_{\mathrm{i}}^{\mathrm{KS}\,*}(\mathbf{r}')$$

G^{KS} is **diagonal** in KS basis

$$G_{\mathrm{i\,j}}^{\mathrm{KS}\ -1}(\omega) = \delta_{\mathrm{ij}} \left(\omega - \epsilon_{\mathrm{i}}^{\mathrm{KS}}\right)$$

Approximation: $$\left\langle i \middle| \Sigma(\omega) - v_{xc} \middle| j \right\rangle \approx \delta_{ij} \left\langle i \middle| \Sigma(\omega) - v_{xc} \middle| i \right\rangle$$

Hence G is **diagonal** in KS basis

$$G_{ij}^{-1}(\omega) \approx \delta_{ij}\left(\omega - \epsilon_i^{\mathrm{KS}} - \left\langle i \middle| \Sigma(\omega) - v_{xc} \middle| i \right\rangle\right)$$

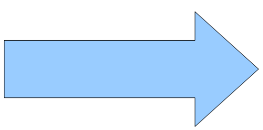
Diagonal self-energy correction approximation

G is **diagonal** in KS basis

$$G_{ij}^{-1}(\omega) \approx \delta_{ij}\left(\omega - \epsilon_i^{KS} - \langle i | \Sigma(\omega) - v_{xc} | i \rangle\right)$$

Excitation energies are the poles of *G* or the zeros of G^{-1}

$$G^{-1}(\epsilon_i^{GW}) = 0$$

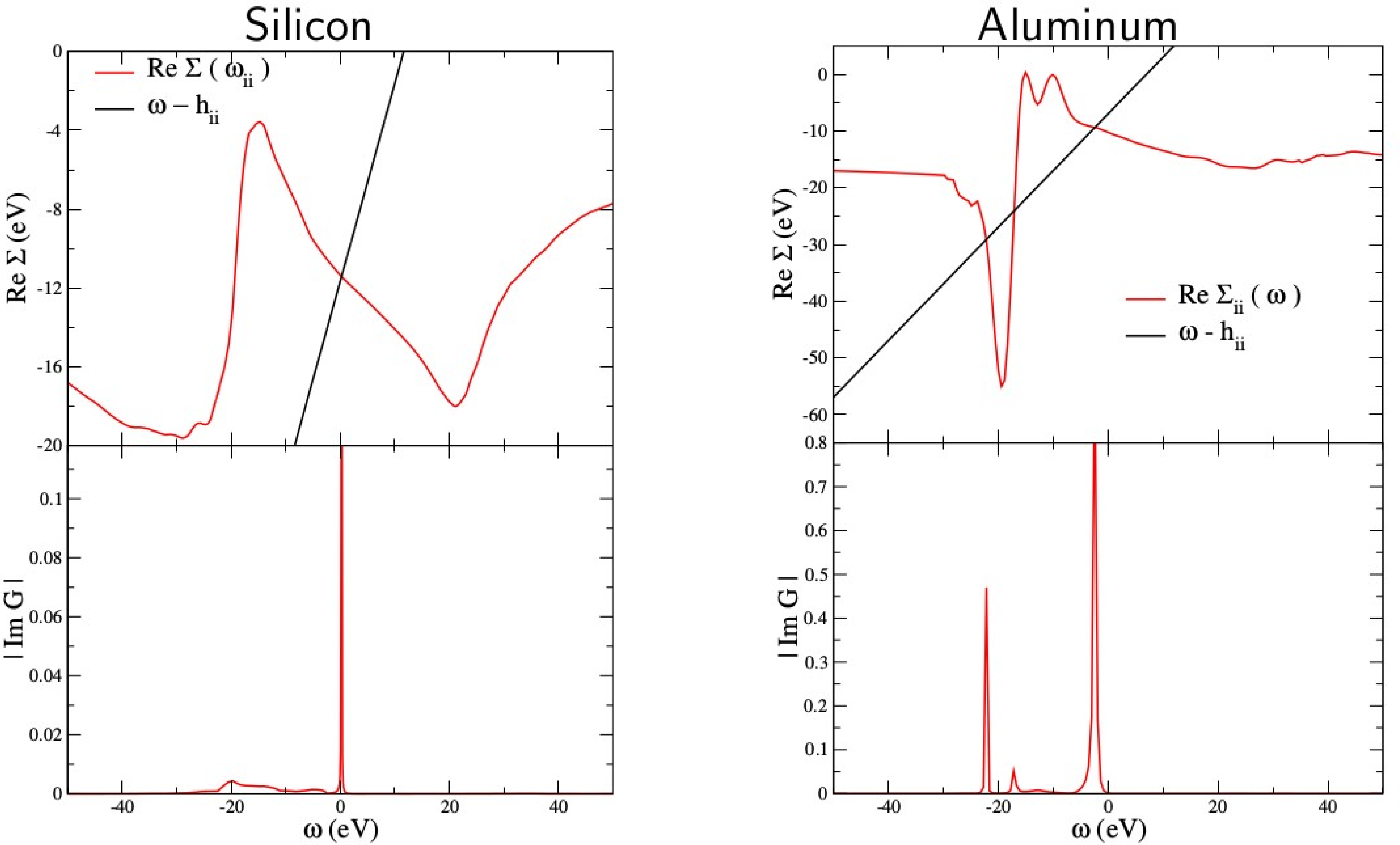


Quasiparticle energies:

$$\epsilon_i^{GW} = \epsilon_i^{KS} + \langle i | \Sigma(\epsilon_i^{GW}) - v_{xc} | i \rangle$$

Full quasiparticle solution

$$\epsilon_i^{GW} - \epsilon_i^{\mathrm{KS}} + \left\langle \phi_i^{\mathrm{KS}} \middle| v_{xc} \middle| \phi_i^{\mathrm{KS}} \right\rangle = \left\langle \phi_i^{\mathrm{KS}} \middle| \Sigma\left(\epsilon_i^{GW}\right) \middle| \phi_i^{\mathrm{KS}} \right\rangle$$



Linearization of the energy dependance

$$\epsilon_i^{GW} - \epsilon_i^{KS} = \langle \phi_i^{KS} | \left[\Sigma\left(\epsilon_i^{GW}\right) - v_{xc} \right] | \phi_i^{KS} \rangle$$

Not yet known

Taylor expansion:

$$\Sigma\left(\epsilon_i^{GW}\right) = \Sigma\left(\epsilon_i^{KS}\right) + \left(\epsilon_i^{GW} - \epsilon_i^{KS}\right) \frac{\partial \Sigma}{\partial \epsilon} + \ldots$$

Final result:

$$\boxed{\epsilon_i^{GW} = \epsilon_i^{KS} + Z_i \langle \phi_i^{KS} | \left[\Sigma\left(\epsilon_i^{KS}\right) - v_{xc} \right] | \phi_i^{KS} \rangle}$$

where $$Z_i = 1 / \left(1 - \langle i | \frac{\partial \Sigma}{\partial \epsilon} | i \rangle \right)$$

Quasiparticle equation

A typical ABINIT ouptput for Silicon at Gamma point

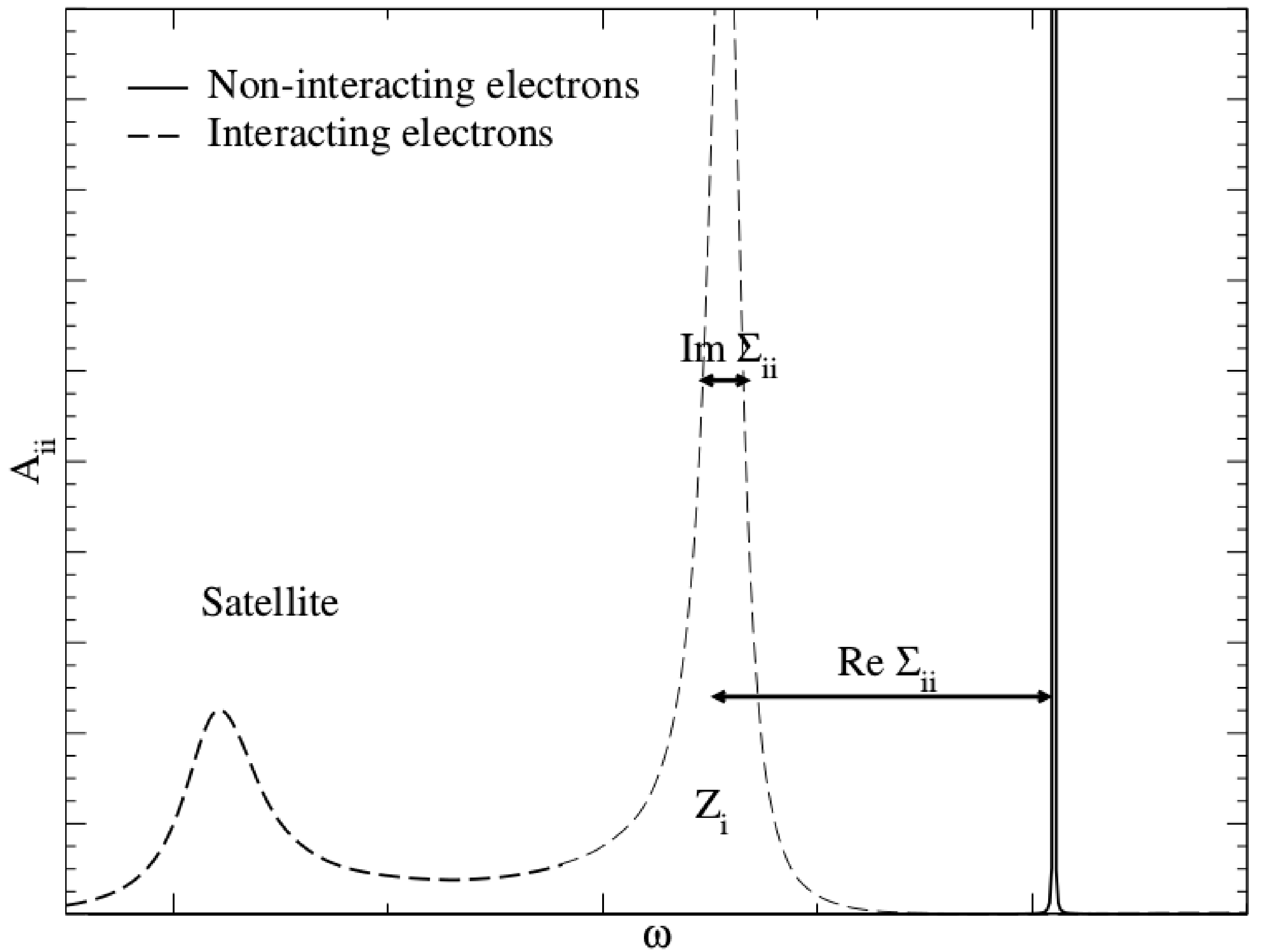
```
k =     0.000   0.000   0.000
Band      E0 <VxcLDA>   SigX SigC(E0)      Z dSigC/dE  Sig(E)    E-E0       E
   4   0.506 -11.291 -12.492   0.744   0.775   -0.291 -11.645  -0.354   0.152
   5   3.080 -10.095  -5.870  -3.859   0.775   -0.290  -9.812   0.283   3.363

E^0_gap          2.574
E^GW_gap         3.212
```

$$\epsilon_i^{GW} = \epsilon_i^{\mathrm{LDA}} + Z_i \left\langle \varphi_i^{\mathrm{LDA}} \middle| \left[\Sigma_{xc}(\epsilon_i^{\mathrm{LDA}}) - v_{xc}^{\mathrm{LDA}} \right] \middle| \varphi_i^{\mathrm{LDA}} \right\rangle$$

Spectral function

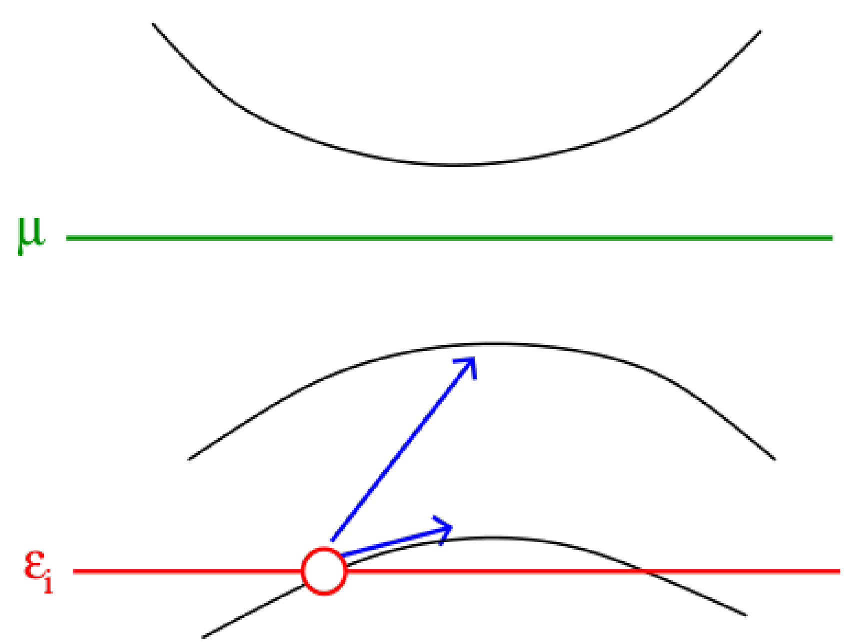
$$A(\omega) = |\mathrm{Im}\, G(\omega)| \;/\; \pi$$



Excitation lifetime

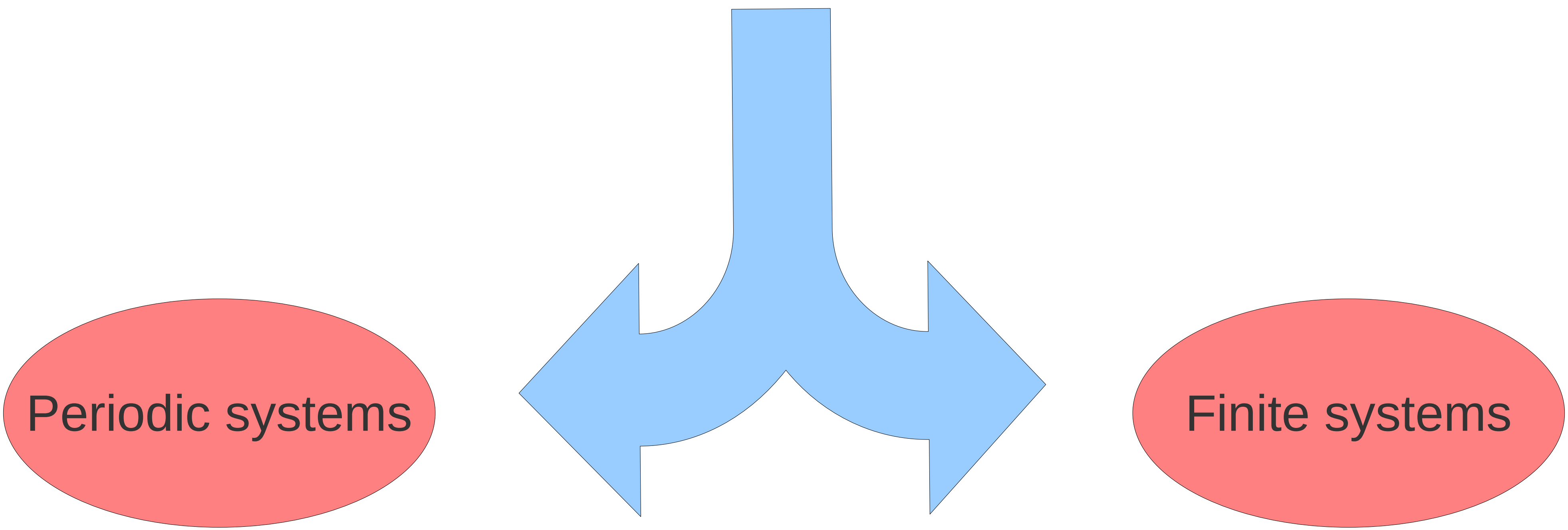
Hole self-energy:

$$\mathrm{Im}\{\langle i|\Sigma(\epsilon_i)|i\rangle\} = -\sum_{j\mathbf{qGG'}} M_{ij}(\mathbf{q}+\mathbf{G})M^*_{ij}(\mathbf{q}+\mathbf{G}') \times \mathrm{Im}(W-v)_{\mathbf{GG'}}(\mathbf{q},\epsilon_j-\epsilon_i) \times \theta(\mu-\epsilon_j)\theta(\epsilon_j-\epsilon_i)$$



When the paths split

$$\Sigma(\boldsymbol{r}_1, \boldsymbol{r}_2, \omega) = \frac{i}{2\pi} \int d\omega' G(\boldsymbol{r}_1, \boldsymbol{r}_2, \omega+\omega') W(\boldsymbol{r}_2, \boldsymbol{r}_1, \omega')$$



Self energy evaluation in *GW*

Correlation part of the GW self energy requires a convolution in frequency:

$$\Sigma_c(\omega) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega' \, G(\omega+\omega') \, W_p(\omega')$$

$$G(\omega) = \sum_i \frac{\phi_i(\boldsymbol{r})\phi_i^*(\boldsymbol{r}')}{\omega - \epsilon_i \pm i\eta}$$

?

How to deal with the frequency dependence in W?

How do we perform the convolution?
How do we treat the frequency dependence in *W*?

Dealing with two-point functions in reciprocal space

Remember 1-point functions are

$$\phi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{k}\boldsymbol{G}} c_{\boldsymbol{k}}(\boldsymbol{G}) e^{i(\boldsymbol{k}+\boldsymbol{G}).\boldsymbol{r}}$$

1 vector of coefficients per k-point in the Brillouin zone

Then 2-point functions are

$$W(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{\Omega} \sum_{\boldsymbol{q}\boldsymbol{G}\boldsymbol{G}'} e^{i(\boldsymbol{q}+\boldsymbol{G}).\boldsymbol{r}_1} W_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) e^{-i(\boldsymbol{q}+\boldsymbol{G}').\boldsymbol{r}_2}$$

a matrix of coefficients per q-point in the BZ due to translational symmetry:

$$W(\boldsymbol{r}_1,\boldsymbol{r}_2) = W(\boldsymbol{r}_1+\boldsymbol{R},\boldsymbol{r}_2+\boldsymbol{R})$$

W in plane-waves and frequency space

(1) $$\chi_0(\boldsymbol{r_1},\boldsymbol{r_2},\omega)=\sum_{\substack{i\,\text{occ}\\ j\,\text{virt}}}\phi_i(\boldsymbol{r_1})\phi_i^*(\boldsymbol{r_2})\phi_j(\boldsymbol{r_2})\phi_j^*(\boldsymbol{r_1})\times\left[\frac{1}{\omega-(\epsilon_j-\epsilon_i)-i\eta}-\frac{1}{\omega-(\epsilon_i-\epsilon_j)+i\eta}\right]$$

(2) $$\varepsilon(1,2)=\delta(1,2)-\int d3\,v(1,3)\,\chi_0(3,2)$$

(3) $$W(1,2)=\int d3\,\varepsilon^{-1}(1,3)\,v(3,2)$$

---

(1) $$\chi_{0\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q},\omega)=\sum_{\substack{\boldsymbol{k}\\ i\,\text{occ}\\ j\,\text{virt}}}\langle j\boldsymbol{k}-\boldsymbol{q}|e^{-i(\boldsymbol{q}+\boldsymbol{G}).\boldsymbol{r}_1}|i\boldsymbol{k}\rangle\langle i\boldsymbol{k}|e^{i(\boldsymbol{q}+\boldsymbol{G}').\boldsymbol{r}_2}|j\boldsymbol{k}-\boldsymbol{q}\rangle\times\left[\frac{1}{\omega-(\epsilon_j-\epsilon_i)-i\eta}-\frac{1}{\omega-(\epsilon_i-\epsilon_j)+i\eta}\right]$$

(2) $$\varepsilon_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q},\omega)=\delta_{\boldsymbol{G},\boldsymbol{G}'}-\sum_{G''}v_{\boldsymbol{G}\boldsymbol{G}''}(\boldsymbol{q})\,\chi_{0\boldsymbol{G}''\boldsymbol{G}'}(\boldsymbol{q},\omega)$$ ⟵ $$v_{\boldsymbol{G}\boldsymbol{G}''}(\boldsymbol{q})=\frac{4\pi}{|\boldsymbol{q}+\boldsymbol{G}|^2}\delta_{\boldsymbol{G},\boldsymbol{G}''}$$

(3) $$W_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q},\omega)=\varepsilon^{-1}_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q},\boldsymbol{G}')\,v_{\boldsymbol{G}'}(\boldsymbol{q})$$ ⟵ matrix inversion

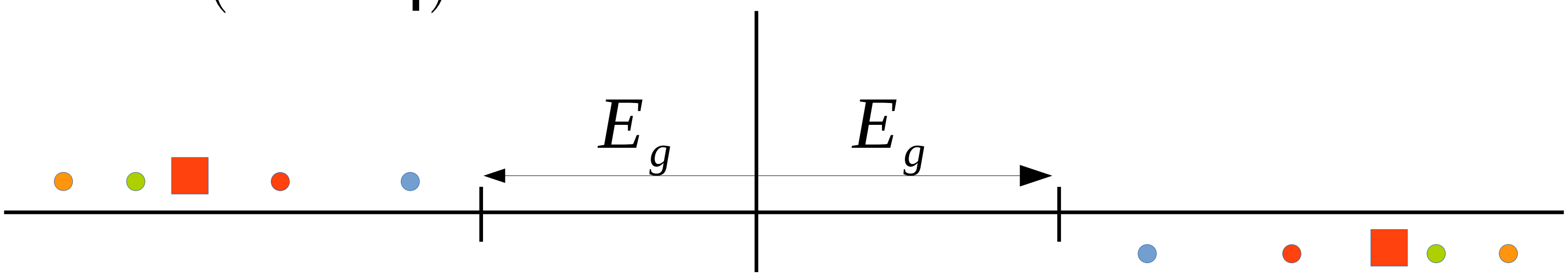
Analytic structure of $W(\omega)$

- Time ordered response function:

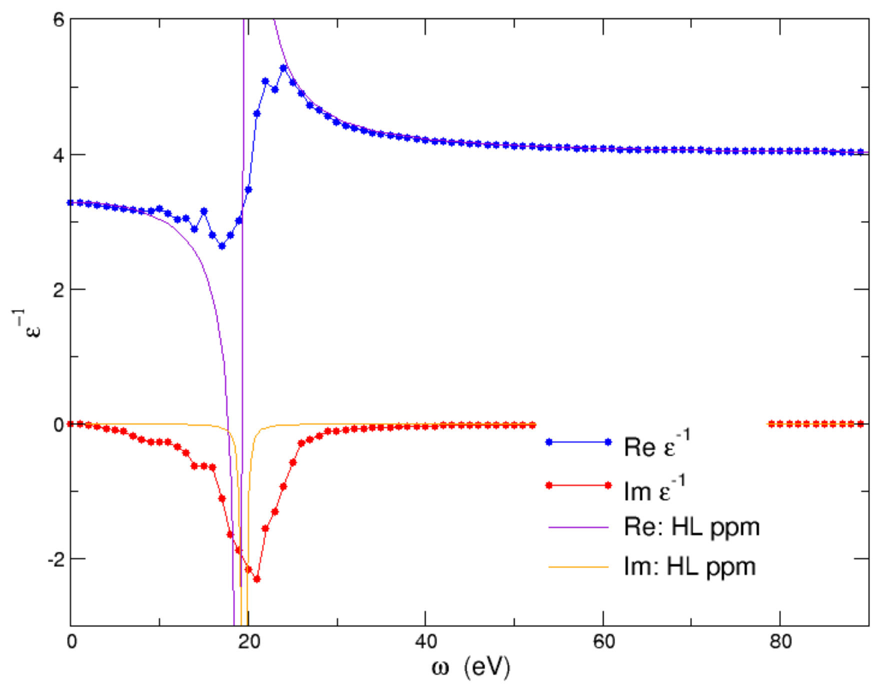
  Many poles which go by pairs: $\pm(\tilde{\omega}_i - i\,\eta)$

- Plasmon-pole model:
  One pair of poles: $\pm(\tilde{\omega} - i\,\eta)$

Complex plane:



Silicon:
For a given **q+G**:



Plasmon-Pole Models in *GW*

Correlation part of the GW self energy requires a convolution in frequency:

$$\Sigma_c(\omega) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega' \, G(\omega+\omega') \, W_p(\omega')$$

Generalized Plasmon-Pole Model:

$$\varepsilon^{-1}(\omega') - 1 = \frac{\Omega^2}{2\tilde{\omega}}\left[\frac{1}{\omega' - \tilde{\omega} + i\eta} - \frac{1}{\omega' + \tilde{\omega} - i\eta}\right]$$

Amplitude of the pole

Position of the pole

small real number

2 parameters need two constraints:

- Hybertsen-Louie (HL): $\varepsilon^{-1}(0)$ and f sum rule $\int_0^{+\infty} \omega \, \mathrm{Im}\,\varepsilon^{-1}(\omega) = -\frac{\pi}{2}\omega_p^2$
- Godby-Needs (GN): $\varepsilon^{-1}(0)$ and $\varepsilon^{-1}(i\omega)$

Silicon band gap with PPM

Silicon unit cell:

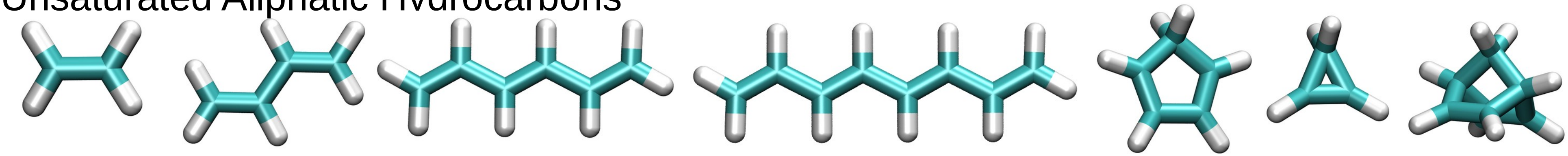
k-points:	5x5x5
bands:	190 empty states
cutoff energy for epsilon:	8 Ry

	HL	GN	Expt.
Γ_v	5.45	5.65	
Γ_c	8.71	8.87	
Direct Band gap	3.26	3.22	3.40 eV

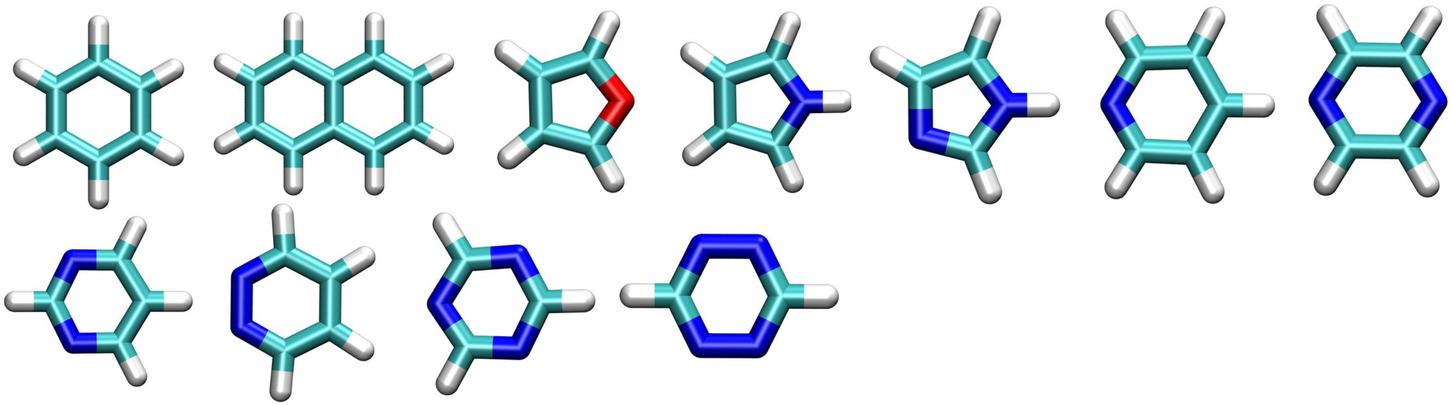
Band gaps are almost the same
However, the absolute positioning of the bands is not (**0.2 eV difference!**)

Molecular systems

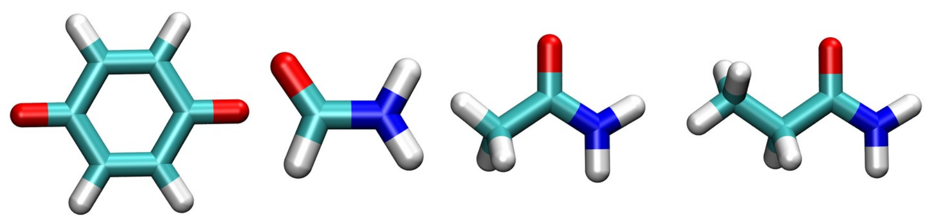
Unsaturated Aliphatic Hydrocarbons



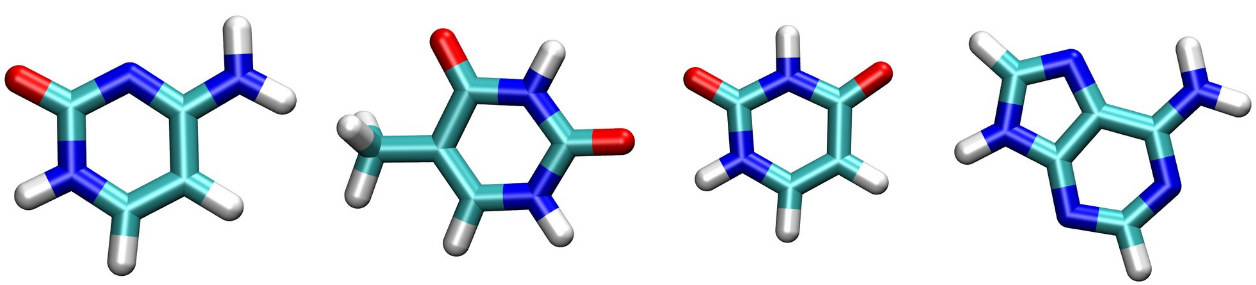
Aromatic Hydrocarbons and Heterocycles



Aldehydes, Ketones and Amides



Nucleobases



RPA in Linear Response

RPA screening equation:

$$W_p(\omega) \quad \text{needs} \qquad \chi(\omega) = \chi_0(\omega) + \chi_0(\omega)\, v\, \chi(\omega) \quad \Longleftrightarrow \quad \chi^{-1}(\omega) = \chi_0^{-1}(\omega) - v$$

In transition space:

$$\chi^{-1}(\omega) = \omega I + \underbrace{\begin{array}{cc} & |k\,l\rangle \\ \langle i\,j| & \begin{pmatrix} \epsilon_j - \epsilon_i & & \\ & \ddots & \\ & & \ddots \end{pmatrix} - \begin{pmatrix} (i\,j|\frac{1}{\boldsymbol{r}}|k\,l) \end{pmatrix} \end{array}}$$

Transition space:
if *i* is occupied, then *j* is empty
if *j* is occupied, then *i* is empty

Diagonalization instead of an inversion for each ω

Obtain left and right eigenvectors L_s , R_s
and excitation energies Ω_s

TD-DFT in Linear Response

TD-DFT screening equation:

$$\chi(\omega) = \chi_0(\omega) + \chi_0(\omega)\left(v + \boxed{f_{xc}}\right)\chi(\omega) \quad \Longleftrightarrow \quad \chi^{-1}(\omega) = \chi_0^{-1}(\omega) - v - \boxed{f_{xc}}$$

In transition space:

$$\chi^{-1}(\omega) = \omega I + \begin{array}{cc} & |k\,l\rangle \\ \langle i\,j| & \underbrace{\begin{pmatrix} \epsilon_j - \epsilon_i & & & & & \\ & \cdot & & & & \\ & & \cdot & & & \\ & & & \cdot & & \\ & & & & \cdot & \\ & & & & & \cdot \end{pmatrix} - \begin{pmatrix} \\ (i\,j|\frac{1}{\boldsymbol{r}}|k\,l) \\ \\ \end{pmatrix}} \end{array} \boxed{- \begin{pmatrix} \\ (i\,j|f_{xc}|k\,l) \\ \\ \end{pmatrix}}$$

Transition space:
if i is occupied, then j is empty
if j is occupied, then i is empty

Diagonalization instead of an inversion for each ω

Obtain left and right eigenvectors L_s , R_s
and excitation energies Ω_s

Bethe-Salpeter Equation in Linear Response

BSE screening equation:

$$\chi(\omega)=\chi_0(\omega)+\chi_0(\omega)(v-\boxed{W})\chi(\omega) \quad \Longleftrightarrow \quad \chi^{-1}(\omega)=\chi_0^{-1}(\omega)-v+\boxed{W}$$

In transition space:

$$\chi^{-1}(\omega)=\omega I + \underbrace{\begin{array}{cc} & |k\,l\rangle \\ \langle i\,j| & \begin{pmatrix} \epsilon_j-\epsilon_i & & \\ & \ddots & \\ & & \ddots \end{pmatrix} \end{array} - \begin{pmatrix} & & \\ & (i\,j|\frac{1}{\boldsymbol{r}}|k\,l) & \\ & & \end{pmatrix}} + \boxed{\begin{pmatrix} & & \\ & (i\,j|W|k\,l) & \\ & & \end{pmatrix}}$$

Transition space:
if *i* is occupied, then *j* is empty
if *j* is occupied, then *i* is empty

Diagonalization instead of an inversion for each ω

Obtain left and right eigenvectors L_s , R_s
and excitation energies Ω_s

Self energy evaluation in *GW*

Correlation part of the GW self energy requires a convolution in frequency:

$$\Sigma_c(\omega) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega' \, G(\omega+\omega') \, W_p(\omega')$$

$$G(\omega) = \sum_i \frac{\phi_i(\boldsymbol{r})\phi_i(\boldsymbol{r}')}{\omega - \epsilon_i \pm i\eta}$$

$$W_p(\omega) = \sum_s \frac{R_s(\boldsymbol{r}) R_s(\boldsymbol{r}')}{\omega - \Omega_s \pm i\eta}$$

Residue theorem yields the result straightforwardly.

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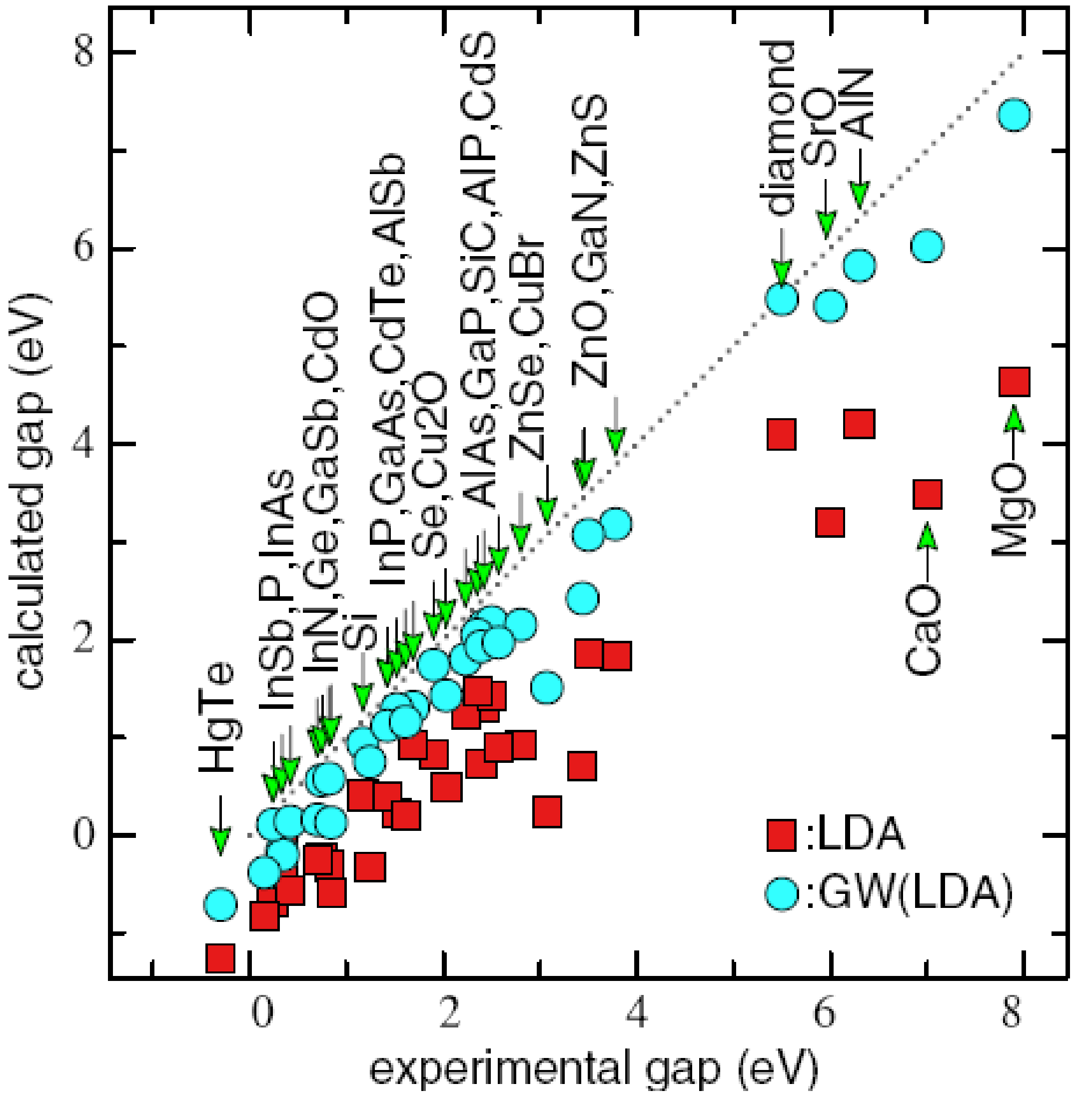
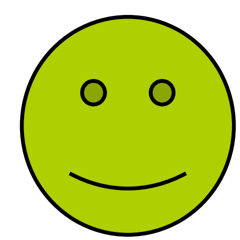
GW approximation gets good band gap



van Schilfgaarde *et al* PRL **96** 226402 (2008)

No more a band gap problem !

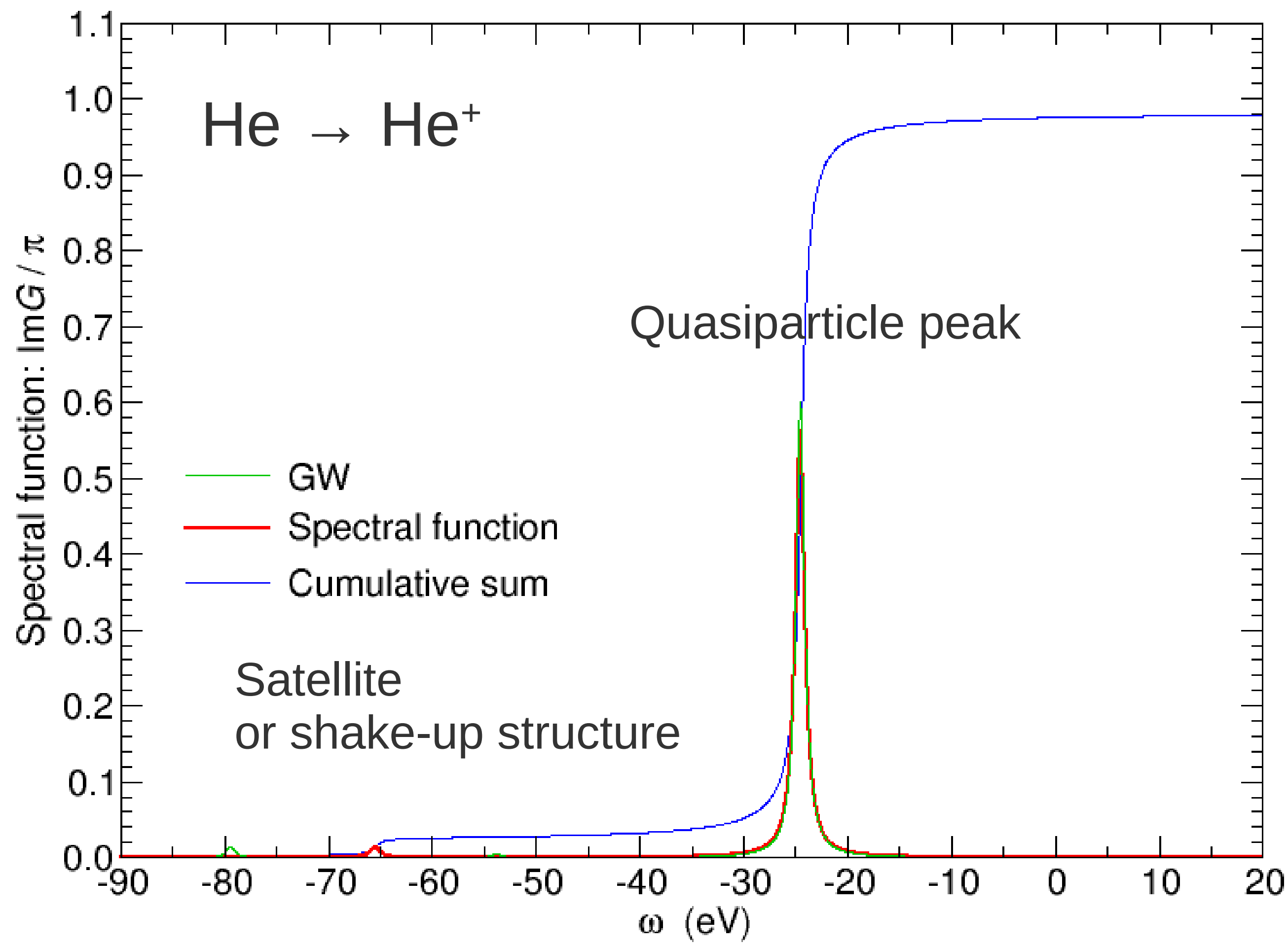


Exact realization of the Lehman decomposition

$$\langle m|G^h(\omega)|m\rangle = \sum_i \frac{\langle N\,0|\hat{c}_m^+|N-1\,i\rangle\langle N-1\,i|\hat{c}_m|N\,0\rangle}{\omega-\epsilon_i-i\eta}$$

$$N=2$$
$$N-1=1$$
$$m=1s$$

Obtained from FCI calculations



F. Bruneval

What is the best starting point for G_0W_0?

Ionization potential of 100 small molecules

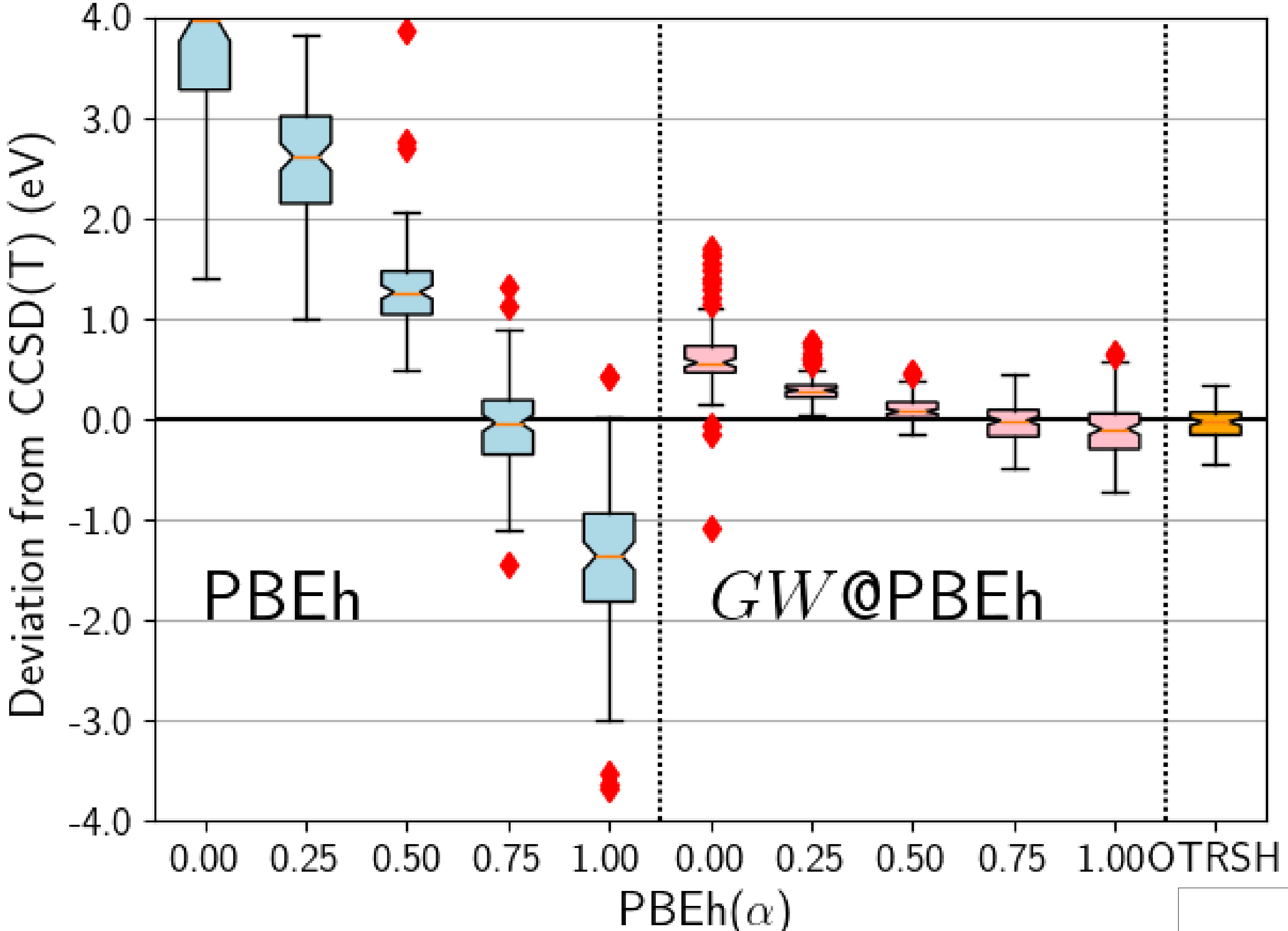
van Setten *et al.* JCTC (2015)

https://gw100.wordpress.com/

but containing difficult elements: Rb, Cs, Br, As etc...

GW versus Coupled-cluster

$$E_{\mathrm{CCSD(T)}}\left(\mathrm{X}^0\right) - E_{\mathrm{CCSD(T)}}\left(\mathrm{X}^+\right)$$

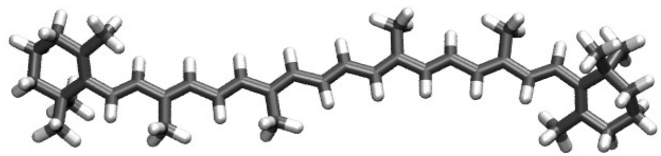


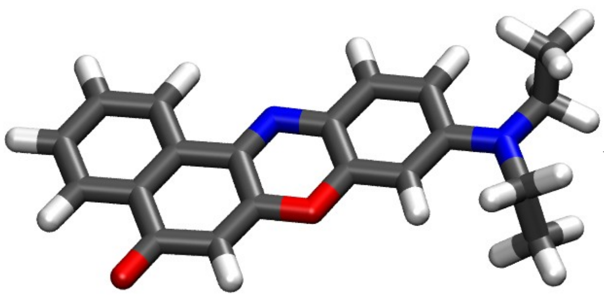
$$v_{xc} = \alpha \Sigma_x + \left(1 - \alpha\right) v_x^{\mathrm{PBE}} + v_c^{\mathrm{PBE}}$$

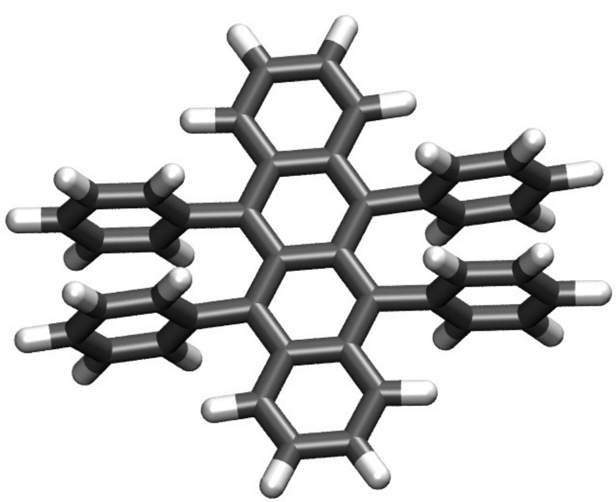
F. Bruneval, N. Dattani,
M. van Setten, Frontiers in Chemistry (2021)

Large acceptor/dye molecules

Bruneval *et al.* JCTC 2020





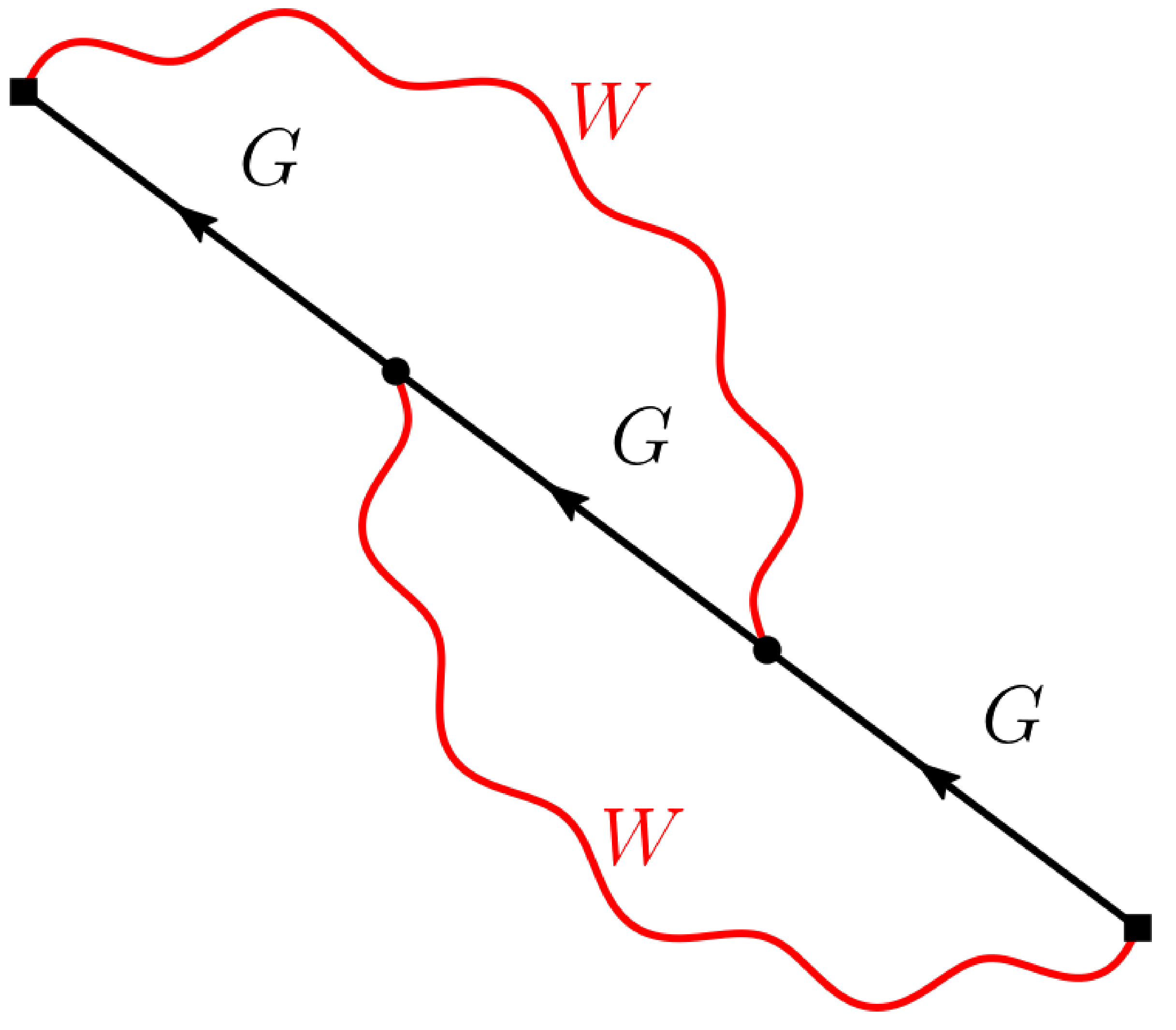


			IP (eV)		EA (eV)	
molecule	**formula**	**CAS number**	**GW@BHLYP**	**expt**	**GW@BHLYP**	**expt**
TCNQ	$C_{12}H_4N_4$	1518-16-7	9.87	9.61	3.52	2.80
F4-TCNQ	$C_{12}F_4N_4$	29261-33-4	10.27		4.05	
anthracene	$C_{14}H_{10}$	120-12-7	7.55	7.44	0.57	0.53
Nile red	$C_{20}H_{18}N_2O_2$	7385-67-3	7.35		1.47	
coronene	$C_{24}H_{12}$	191-07-18	7.37	7.21	0.69	0.47–
PTCDA	$C_{24}H_8O_6$	128-69-8	8.30	8.2	3.34	
pigment red 179	$C_{26}H_{14}N_2O_4$	5521-31-3	7.79		2.91	
β carotene	$C_{40}H_{56}$	7235-40-7	6.66	6.5	1.19	
rubrene	$C_{42}H_{28}$	517-51-1	6.36	6.41	1.52	
buckminsterfullerene	C_{60}	99685-96-8	7.66	7.6	2.61	2.70

0.1 - 0.2 eV accuracy wrt expt

Beyond GW: G3W2

Bruneval, Förster JCTC 2023



Beyond GW: G3W2

$$\Sigma_{pq}^{ooo}(\omega) = \sum_{ts}\sum_{ijk} \frac{w_t^{pi}\cdot w_t^{jk}\cdot w_s^{qk}\cdot w_s^{ij}}{(\omega - \epsilon_i + \Omega_t - 2i\eta)\cdot(\omega - \epsilon_j + \Omega_t + \Omega_s - 3i\eta)\cdot(\omega - \epsilon_k + \Omega_s - 2i\eta)} \tag{13a}$$

$$\Sigma_{pq}^{vvv}(\omega) = \sum_{ts}\sum_{abc} \frac{w_t^{pa}\cdot w_t^{bc}\cdot w_s^{qc}\cdot w_s^{ab}}{(\omega - \epsilon_a - \Omega_t + 2i\eta)\cdot(\omega - \epsilon_b - \Omega_t - \Omega_s + 3i\eta)\cdot(\omega - \epsilon_c - \Omega_s + 2i\eta)} \tag{13b}$$

$$\Sigma_{pq}^{voo+oov}(\omega) = \sum_{ts}\sum_{ajk} \frac{w_t^{pa}\cdot w_t^{jk}\cdot w_s^{qk}\cdot w_s^{aj}}{(\omega - \epsilon_k + \Omega_s - 2i\eta)\cdot(\Omega_s + \epsilon_a - \epsilon_j - 3i\eta)} \times \left[\frac{2}{(\omega - \epsilon_a - \Omega_t + 2i\eta} - \frac{2}{\omega - \epsilon_j + \Omega_s + \Omega_t - 3i\eta}\right] \tag{13c}$$

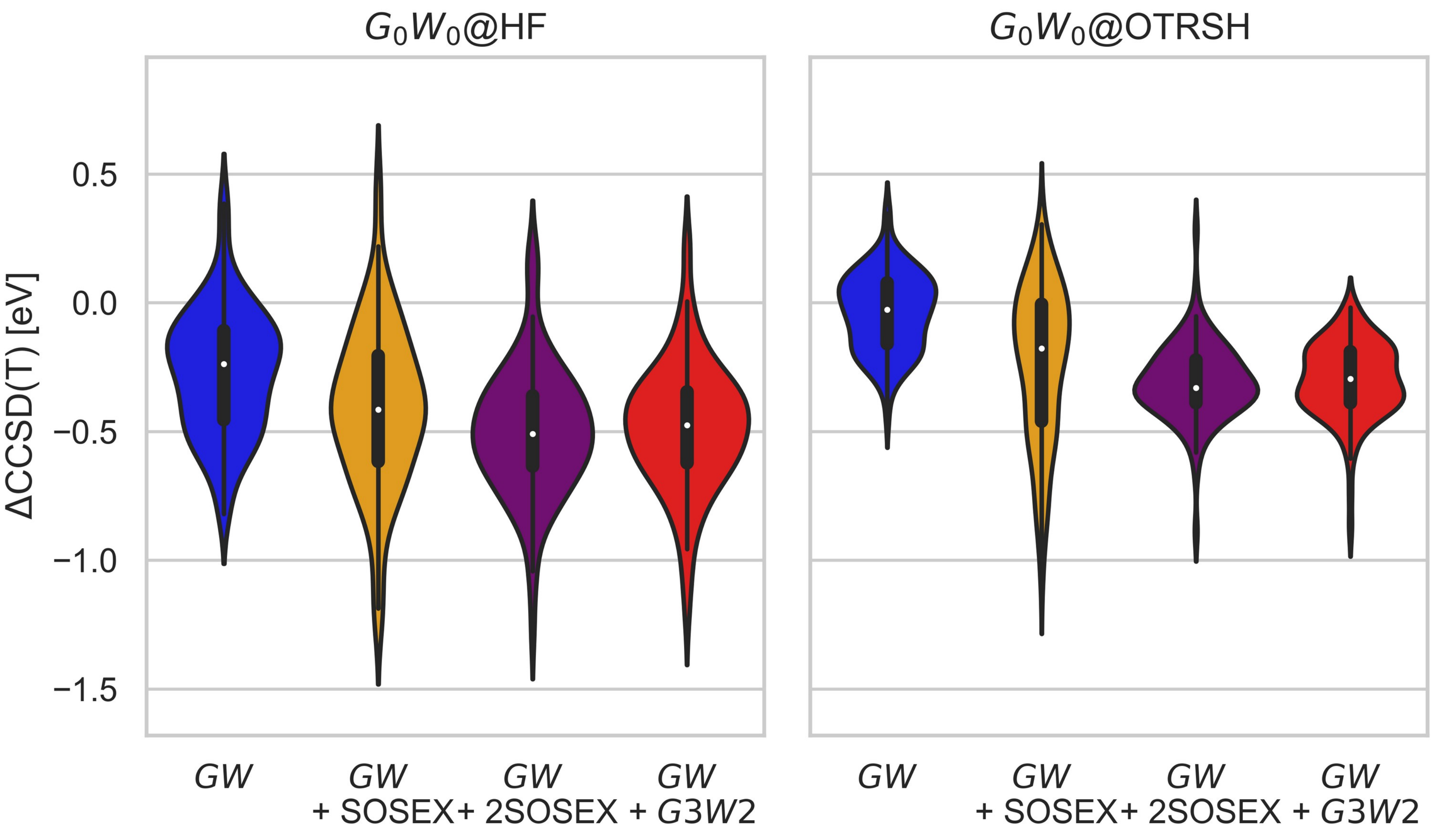
$$\Sigma_{pq}^{ovv+vvo}(\omega) = \sum_{ts}\sum_{ibc} \frac{w_t^{pi}\cdot w_t^{bc}\cdot w_s^{qc}\cdot w_s^{ib}}{(\omega - \epsilon_c - \Omega_s + 2i\eta)\cdot(\Omega_s - \epsilon_i + \epsilon_b - 3i\eta)} \times \left[-\frac{2}{\omega - \epsilon_i + \Omega_t - 2i\eta} + \frac{2}{\omega - \epsilon_b - \Omega_s - \Omega_t + 3i\eta}\right] \tag{13d}$$

$$\begin{aligned}\Sigma_{pq}^{ovo}(\omega) = \sum_{ts}\sum_{ibk} &\frac{w_t^{pi}\cdot w_t^{bk}\cdot w_s^{qk}\cdot w_s^{ib}}{\omega - \epsilon_i - \epsilon_k + \epsilon_b - 3i\eta} \\ &\times \left[\frac{2\epsilon_b - \epsilon_i - \epsilon_k + \Omega_t + \Omega_s}{(\omega - \epsilon_b - \Omega_t - \Omega_s + 3i\eta)\cdot(\Omega_s + \epsilon_b - \epsilon_i - 3i\eta)\cdot(\Omega_t + \epsilon_b - \epsilon_k - 3i\eta)}\right. \\ &\left.- \frac{2}{(\Omega_t + \epsilon_b - \epsilon_k - 3i\eta)\cdot(\omega - \epsilon_k + \Omega_s - 2i\eta)} - \frac{1}{(\omega - \epsilon_i + \Omega_t - 2i\eta)\cdot(\omega - \epsilon_k + \Omega_s - 2i\eta)}\right]\end{aligned} \tag{13e}$$

$$\begin{aligned}\Sigma_{pq}^{vov}(\omega) = \sum_{ts}\sum_{ajc} &\frac{w_t^{pa}\cdot w_t^{jc}\cdot w_s^{qc}\cdot w_s^{aj}}{\omega - \epsilon_a - \epsilon_c + \epsilon_j + 3i\eta} \times \left[\frac{2\epsilon_j - \epsilon_a - \epsilon_c - \Omega_t - \Omega_s}{((\omega - \epsilon_j + \Omega_t + \Omega_s - 3i\eta)\cdot(\Omega_s - \epsilon_j + \epsilon_a - 3i\eta)\cdot(\Omega_t - \epsilon_j + \epsilon_c - 3i\eta)}\right. \\ &\left.+ \frac{2}{(\Omega_t - \epsilon_j + \epsilon_c - 3i\eta)\cdot(\omega - \epsilon_c - \Omega_s + 2i\eta)} - \frac{1}{(\omega - \epsilon_a - \Omega_t + 2i\eta)\cdot(\omega - \epsilon_c - \Omega_s + 2i\eta)}\right]\end{aligned} \tag{13f}$$

Beyond GW: G3W2

Performance on GW100



Getting the density-matrix from GW

Electronic density:
$$\rho(\mathbf{r}) = \sum_i f_i \, \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r})$$

Density-matrix:
$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i f_i \, \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}')$$

An example: the kinetic energy is a explicit functional of $\gamma(\mathbf{r}, \mathbf{r}')$

$$T = -\frac{1}{2} \sum_i f_i \iint d\mathbf{r} d\mathbf{r}' \varphi_i^*(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \nabla^2_{\mathbf{r}'} \varphi_i^*(\mathbf{r}')$$

GW density matrix in ABINIT

$$\langle \mathbf{k}i | \Sigma^{GW}(\mu_F + i\omega) | \mathbf{k}j \rangle$$

$$\langle \mathbf{k}i | \gamma^{GW} | \mathbf{k}j \rangle = -\frac{1}{2\pi} \int d\omega \frac{\langle \mathbf{k}i | \Sigma^{GW}(\mu_F + i\omega) | \mathbf{k}j \rangle}{(\mu_F + i\omega - \epsilon_{\mathbf{k}i})(\mu_F + i\omega - \epsilon_{\mathbf{k}j})}$$

already available in ABINIT v9.4

Denawi, Bruneval, Torrent, Rodriguez-Mayorga PRB (2023)

Surprising facts with density-matrices 1

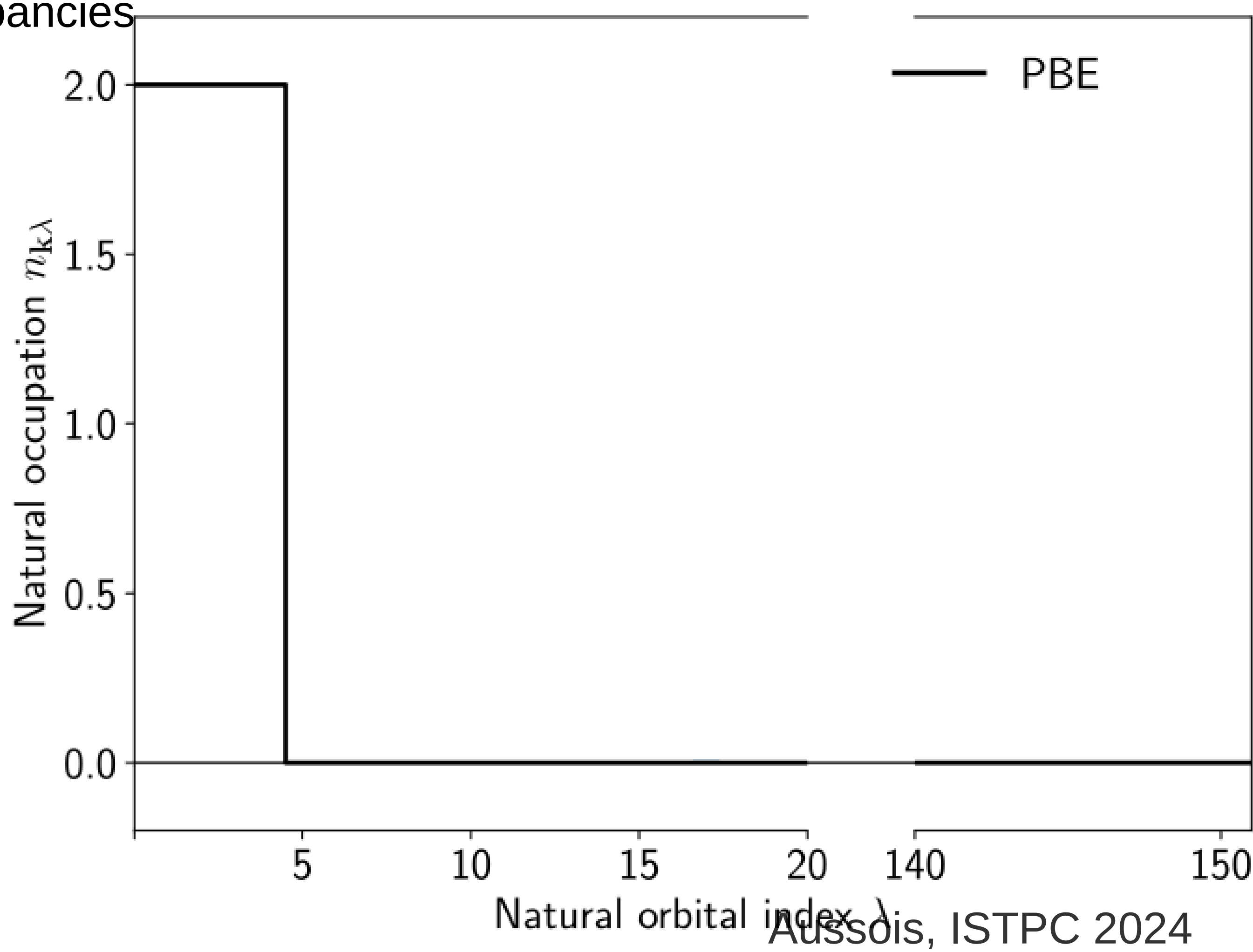
Diagonalization:

$$\sum_{j=1}^{N_b} \gamma_{\mathbf{k}ij} U_{\mathbf{k}j\lambda} = n_{\mathbf{k}\lambda} U_{\mathbf{k}i\lambda}$$

Natural orbitals, natural occupancies

$$\phi_{\mathbf{k}\lambda}(\mathbf{r}) = \sum_{i=1}^{N_b} U_{\mathbf{k}i\lambda} \varphi_{\mathbf{k}i}(\mathbf{r}).$$

Si



Surprising facts with density-matrices 1

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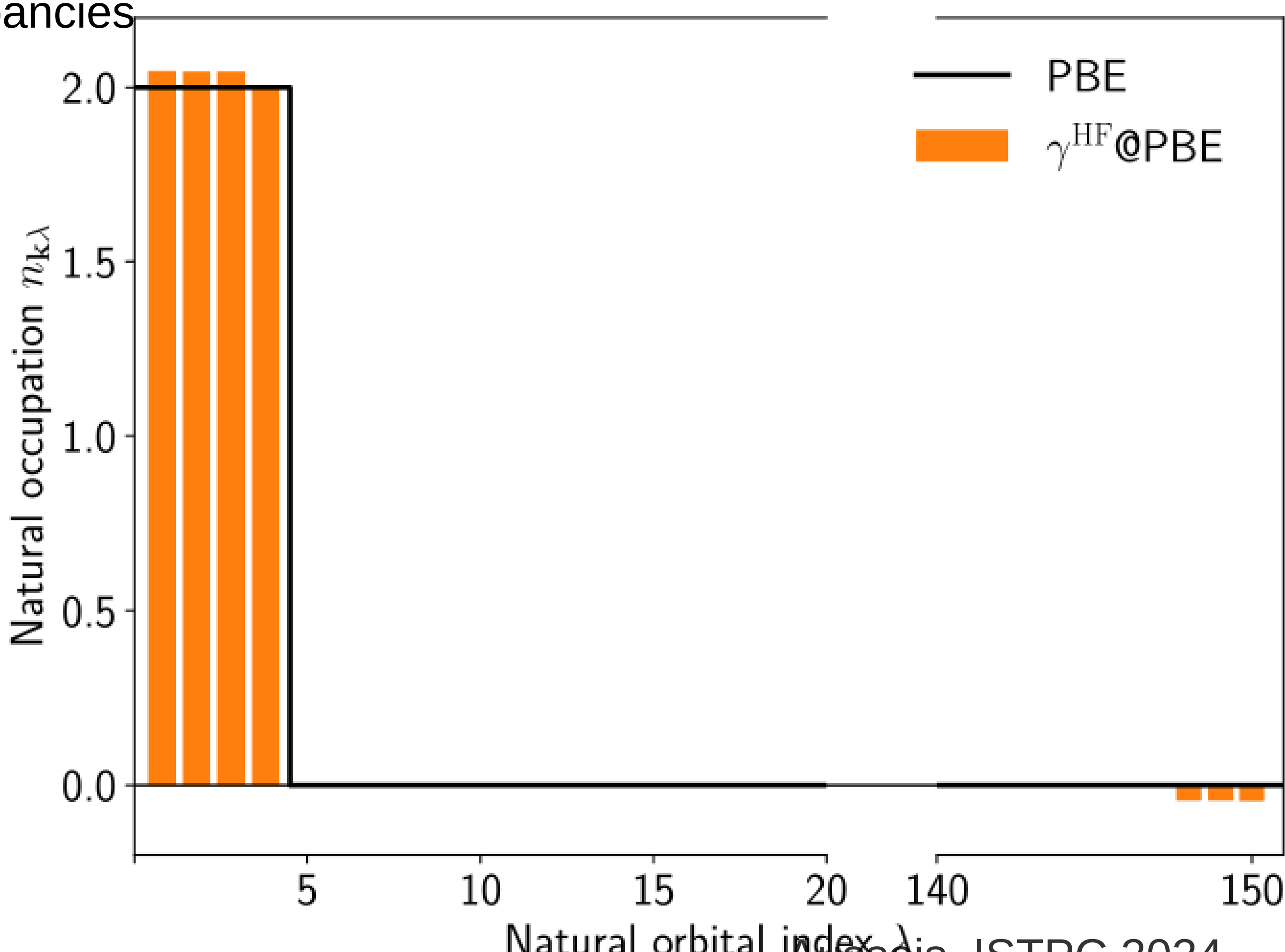
Si



Surprising facts with density-matrices 1

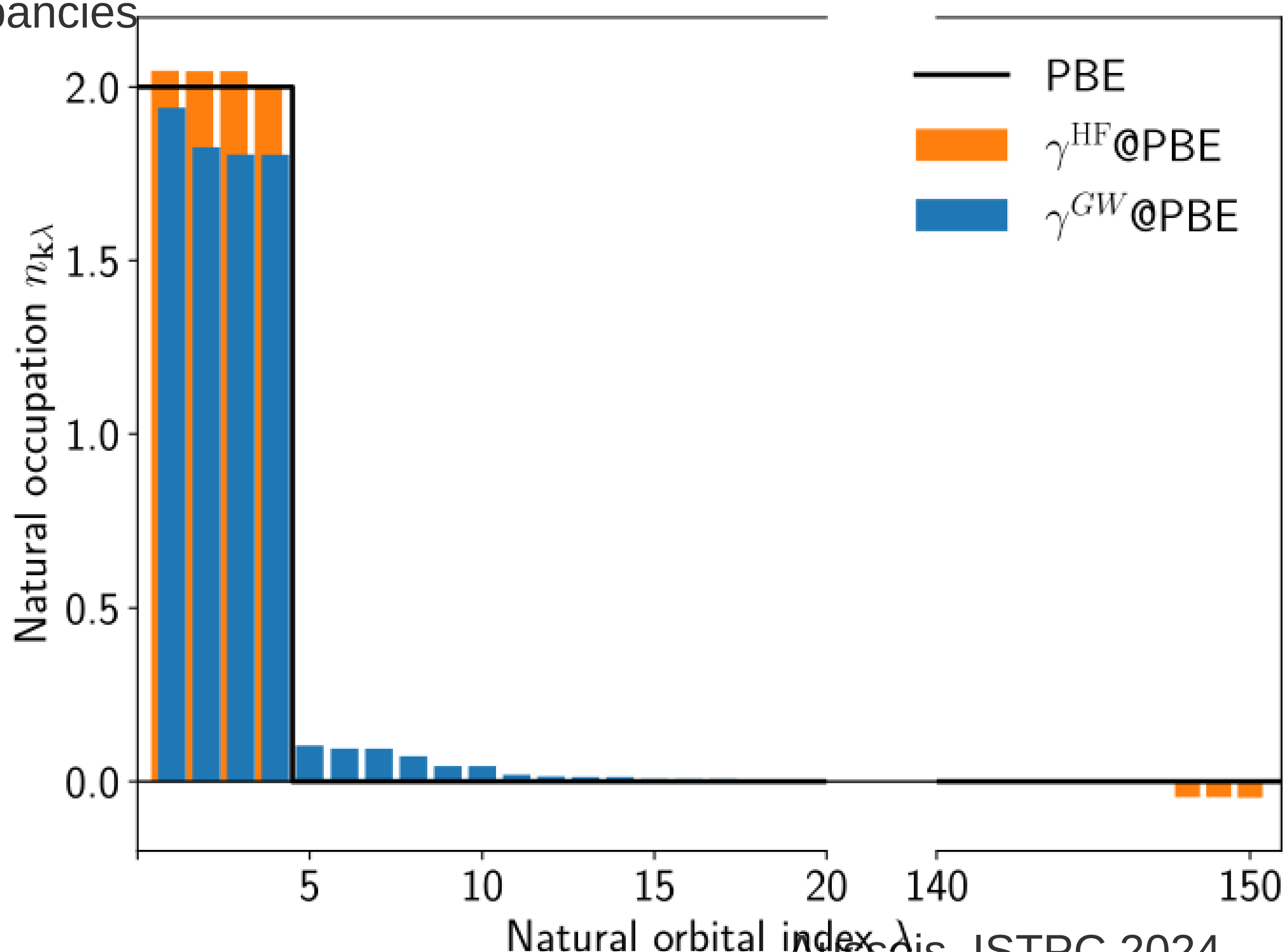
Diagonalization:

$$\sum_{j=1}^{N_b} \gamma_{\mathbf{k}ij} U_{\mathbf{k}j\lambda} = n_{\mathbf{k}\lambda} U_{\mathbf{k}i\lambda}$$

Natural orbitals, natural occupancies

$$\phi_{\mathbf{k}\lambda}(\mathbf{r}) = \sum_{i=1}^{N_b} U_{\mathbf{k}i\lambda} \varphi_{\mathbf{k}i}(\mathbf{r}).$$

Si

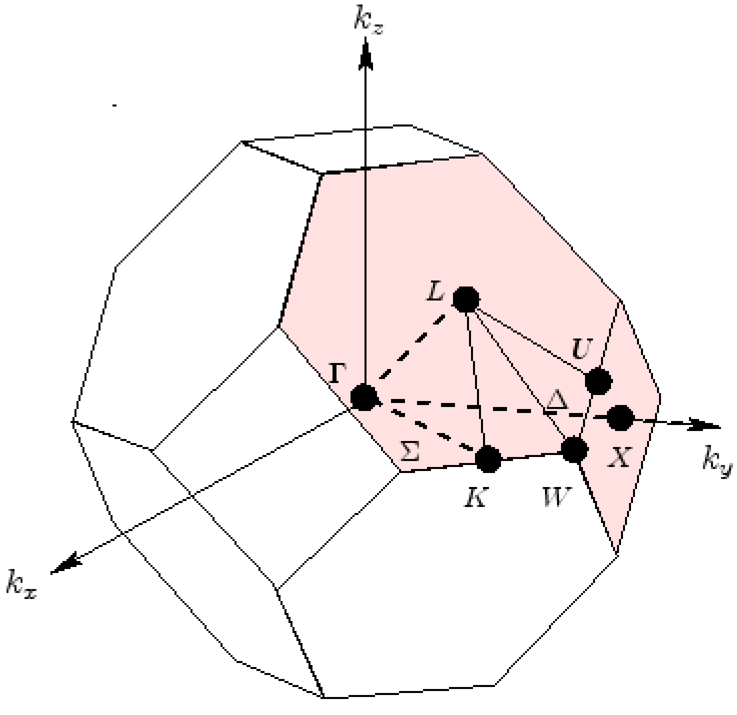


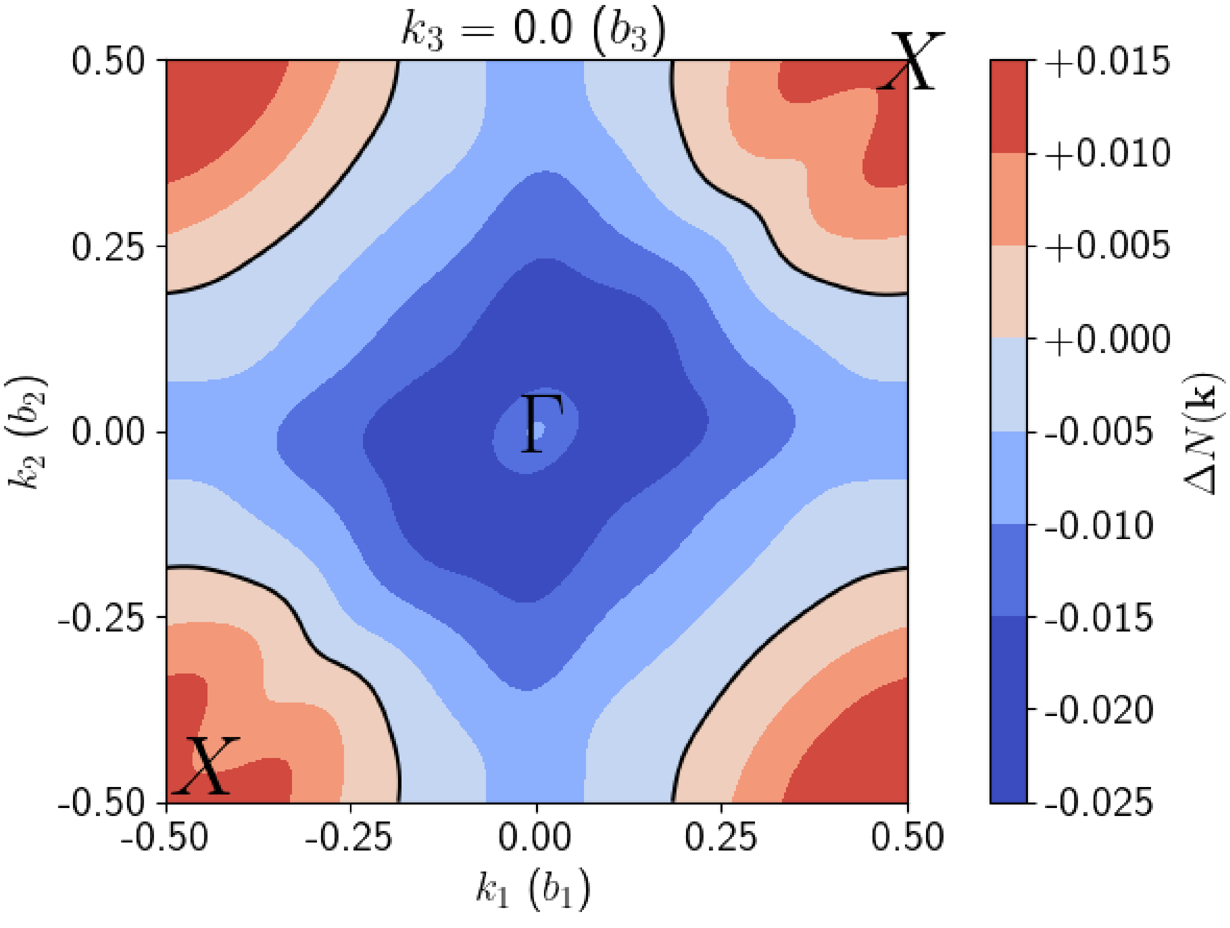
Surprising facts with density-matrices 2

Si

Electron count across the BZ

$$\sum_{\mathbf{k}} \sum_{\lambda} n_{\mathbf{k}\lambda} = N_e$$

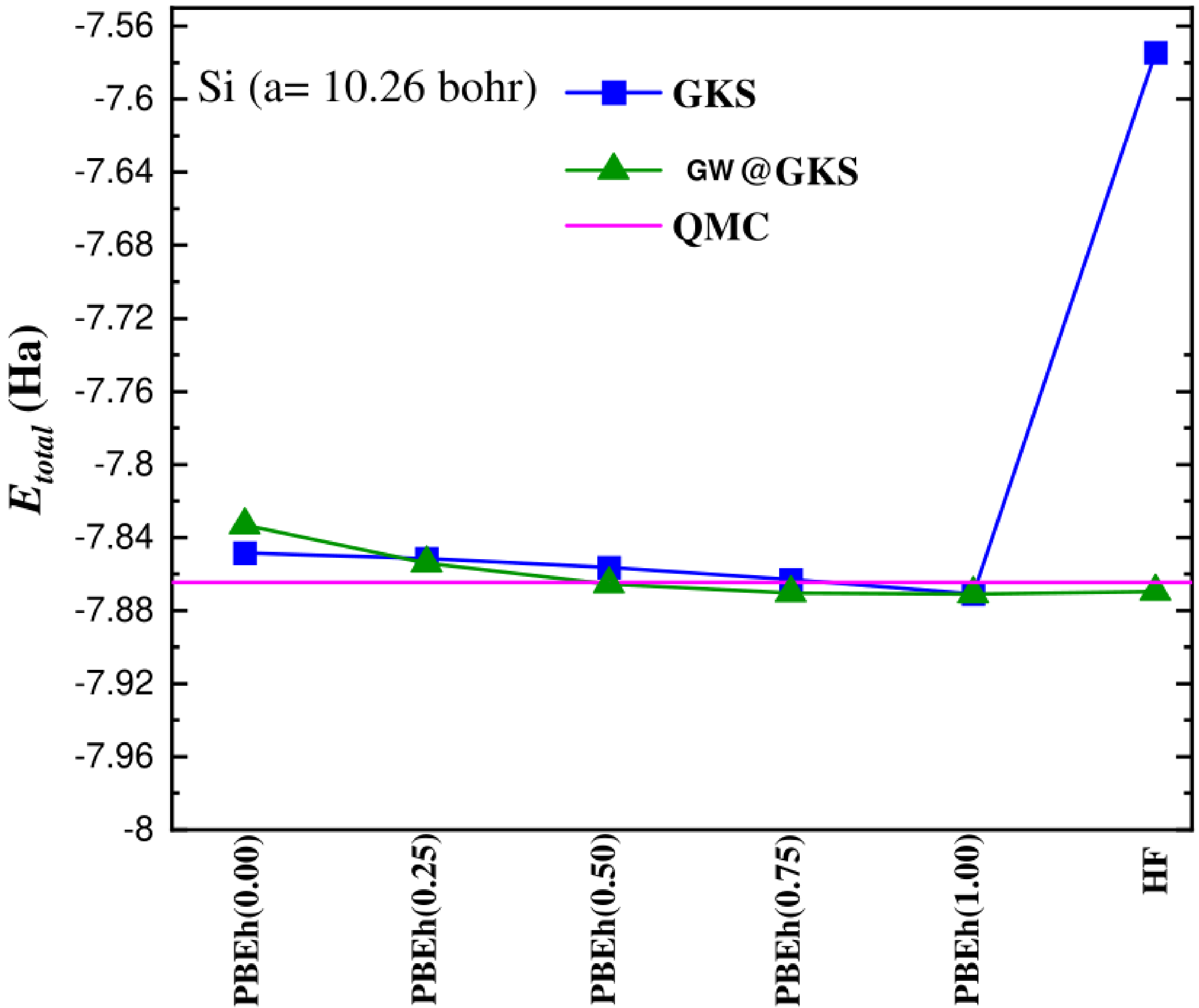




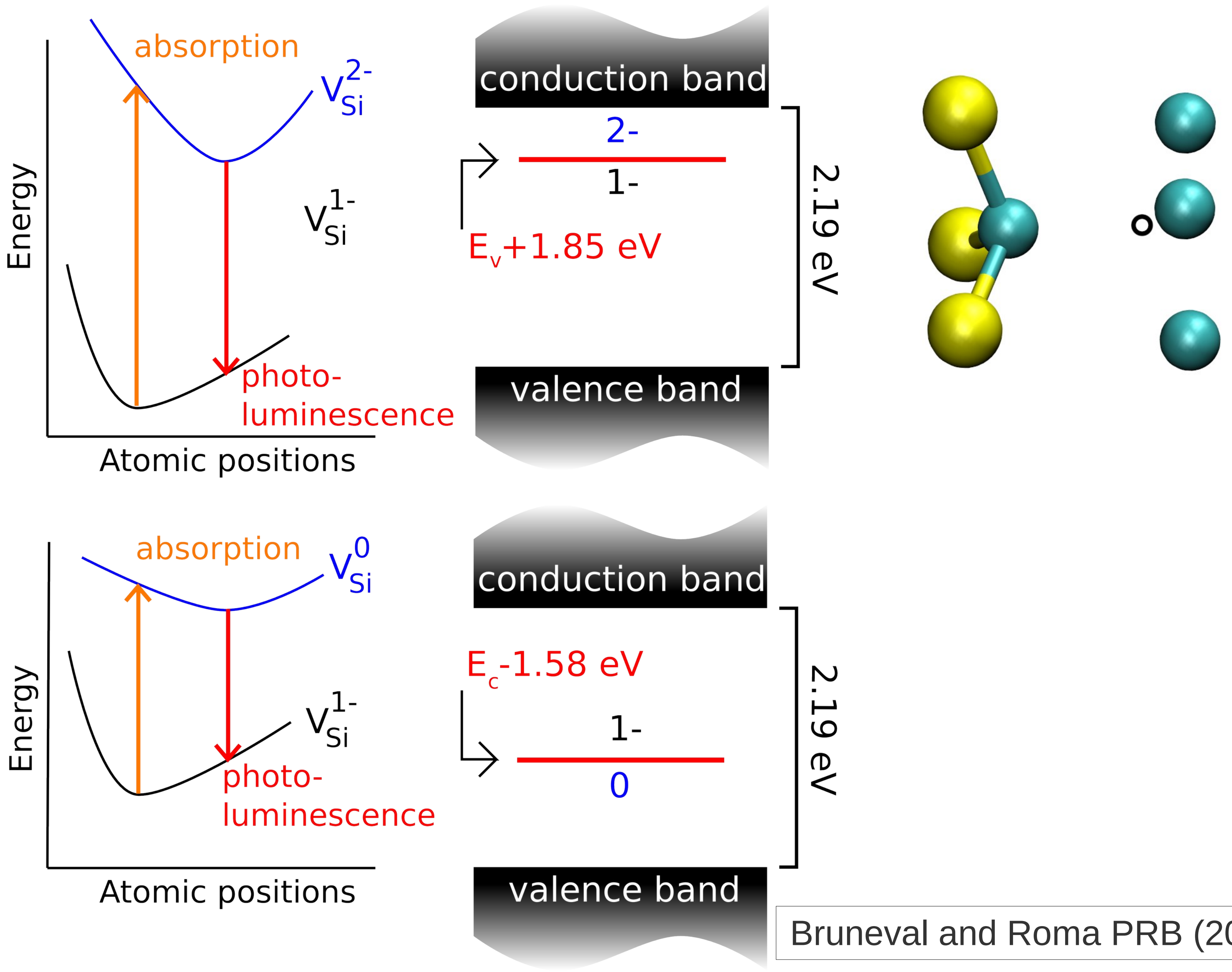
Varying number of electrons that sum up to the correct count!

Density matrix to estimate self-consistent GW energy

Denawi, Bruneval, Torrent, Rodriguez-Mayorga PRB (2023)



Photoluminescence of V_{Si}



Bruneval and Roma PRB (2011)

Summary

- The *GW* approximation **solves the band gap problem!**
- The calculations are extremely heavy, so that we resort to many additional technical approximations: **method named G_0W_0**
- The complexity comes from
  - Dependence upon empty states
  - Non-local operators
  - Dynamic operators that requires freq. convolutions

Reviews - Links

Reviews:

- L. Hedin, Phys. Rev. **139** A796 (1965).
- L. Hedin and S. Lunqdvist, in Solid State Physics, Vol. **23** (Academic, New York, 1969), p. 1.
- F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61** 237 (1998).
- W.G. Aulbur, L. Jonsson, and J.W. Wilkins, Sol. State Phys. **54** 1 (2000).
- G. Strinati, Riv. Nuovo Cimento **11** 1 (1988).

- F. Bruneval and M. Gatti, “Quasiparticle Self-Consistent GW Method for the Spectral Properties of Complex Materials”, Top. Curr. Chem (2014) 347: 99–136

Codes:

- http://www.abinit.org
- http://www.berkeleygw.org/
- https://github.com/bruneval/molgw

Exercice: H_2 in minimal basis: GW@HF

Find the location of the poles of the self-energy

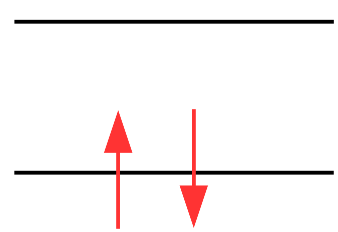
Szabo-Ostlung book chapter 3 teaches how to perform HF in this example:

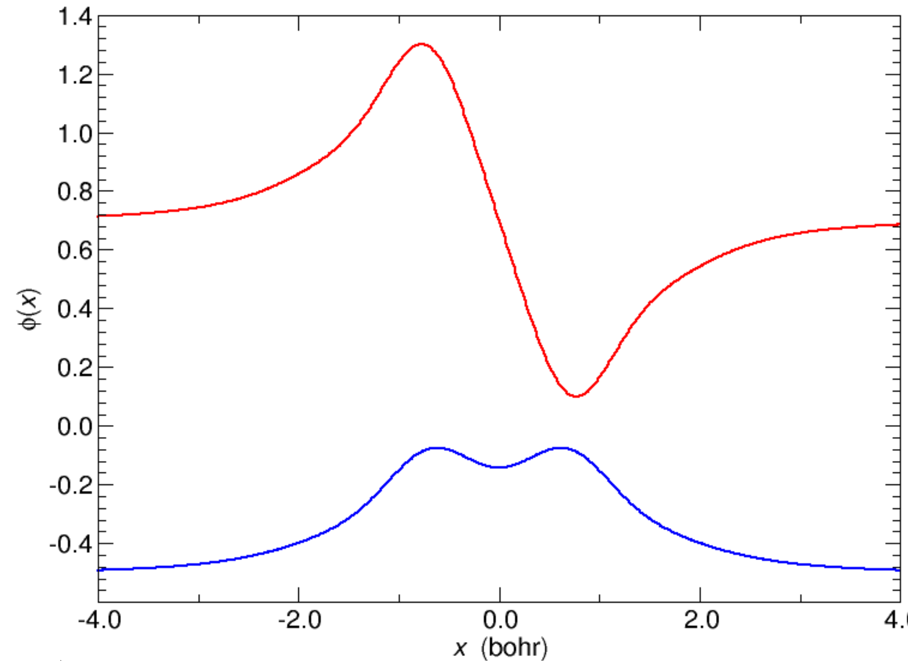
Basis: STO-3G r(H-H) = 1.4 bohr

2 basis functions → 2 eigenstates:

LUMO anti-bonding

HOMO bonding





In eigenvector basis:
Hamiltonian

$$C^T H C = \begin{pmatrix} -0.578 & 0 \\ 0 & 0.670 \end{pmatrix}$$

Coulomb interaction:

$$(11|\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}|11) = 0.675$$

$$(12|\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}|12) = 0.181$$

$$(22|\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}|22) = 0.697$$

Atomic units

Exercice: H_2 in minimal basis: GW@HF

Find the location of the poles of W

Diagonalize the RPA equation

$$\chi^{-1}(\omega) = \begin{array}{cc} & |k\,l\rangle \\ \langle i\,j| & \begin{pmatrix} \frac{\omega-(\epsilon_j-\epsilon_i)}{f_i-f_j} & & \\ & \ddots & \\ & & \ddots \end{pmatrix} \end{array} - \begin{pmatrix} (i\,j|\frac{1}{\boldsymbol{r}}|k\,l) \end{pmatrix}$$

$$\Delta\epsilon = \epsilon_2-\epsilon_1 = 1.248$$

$$v = (12|1/r|1\,2) = 0.181$$

$$\begin{array}{ccc} & |1\,2\rangle & |2\,1\rangle \\ \langle 1\,2| & \frac{\omega-\Delta\epsilon}{2} & 0 \\ \langle 2\,1| & 0 & \frac{\omega+\Delta\epsilon}{-2} \end{array} - \begin{pmatrix} v & v \\ v & v \end{pmatrix}$$

$$\Omega = \pm\sqrt{\Delta\epsilon^2+4v\,\Delta\epsilon} = \pm 1.569$$

Exercice: H_2 in minimal basis: GW@HF

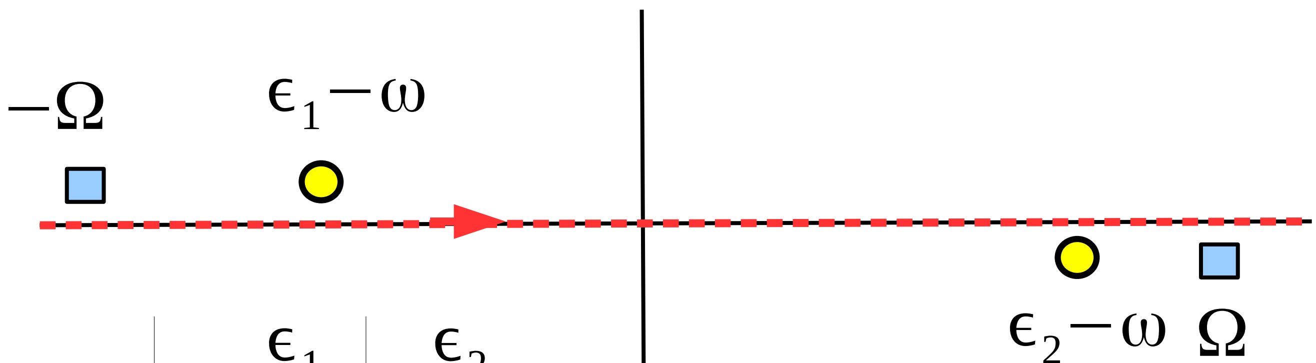
$$\Sigma_c(\omega) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega' \, G(\omega+\omega') \, W_p(\omega')$$

$$G(\omega) = \sum_i \frac{\phi_i(\boldsymbol{r})\phi_i(\boldsymbol{r}')}{\omega - \epsilon_i \pm i\eta}$$

$$W_p(\omega) = \sum_s \frac{R_s(\boldsymbol{r}) R_s(\boldsymbol{r}')}{\omega - \Omega_s \pm i\eta}$$

$$\Sigma_c(\omega) = \frac{i}{2\pi} \sum_{i \in \{1,2\}} \sum_{s \in \{1\to 2, 2\to 1\}} \int_{-\infty}^{+\infty} d\omega' \frac{\alpha}{\omega+\omega' - \epsilon_i \pm i\eta} \times \frac{\beta}{\omega' - \Omega \pm i\eta}$$

Integration in the complex plane:



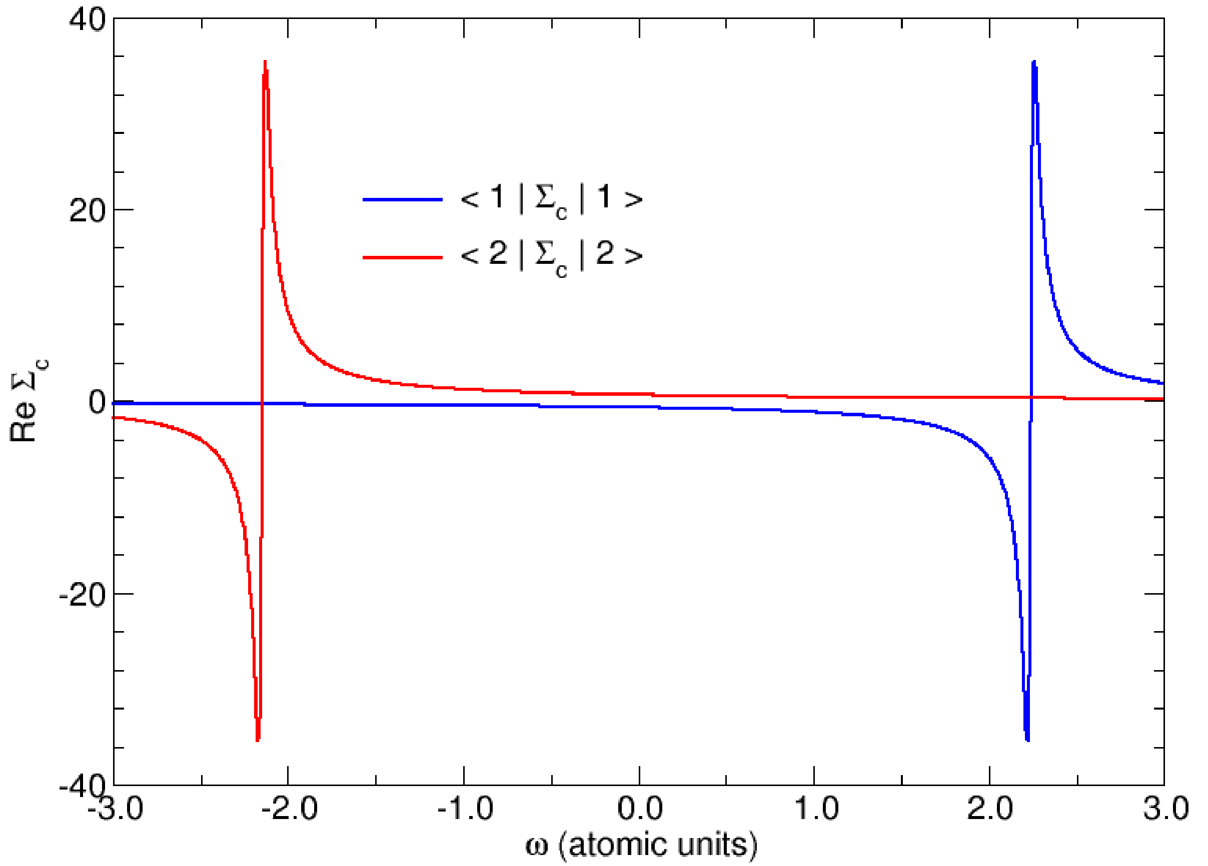
Pole table:

	ϵ_1	ϵ_2
$-\Omega$	$\times$	$\epsilon_2 + \Omega$
Ω	$\epsilon_1 - \Omega$	$\times$

Exercice: H_2 in minimal basis: GW@HF

$$\epsilon_2 + \Omega = 2.239$$
$$\epsilon_1 - \Omega = -2.147$$

Real part of
the self-energy
from MOLGW



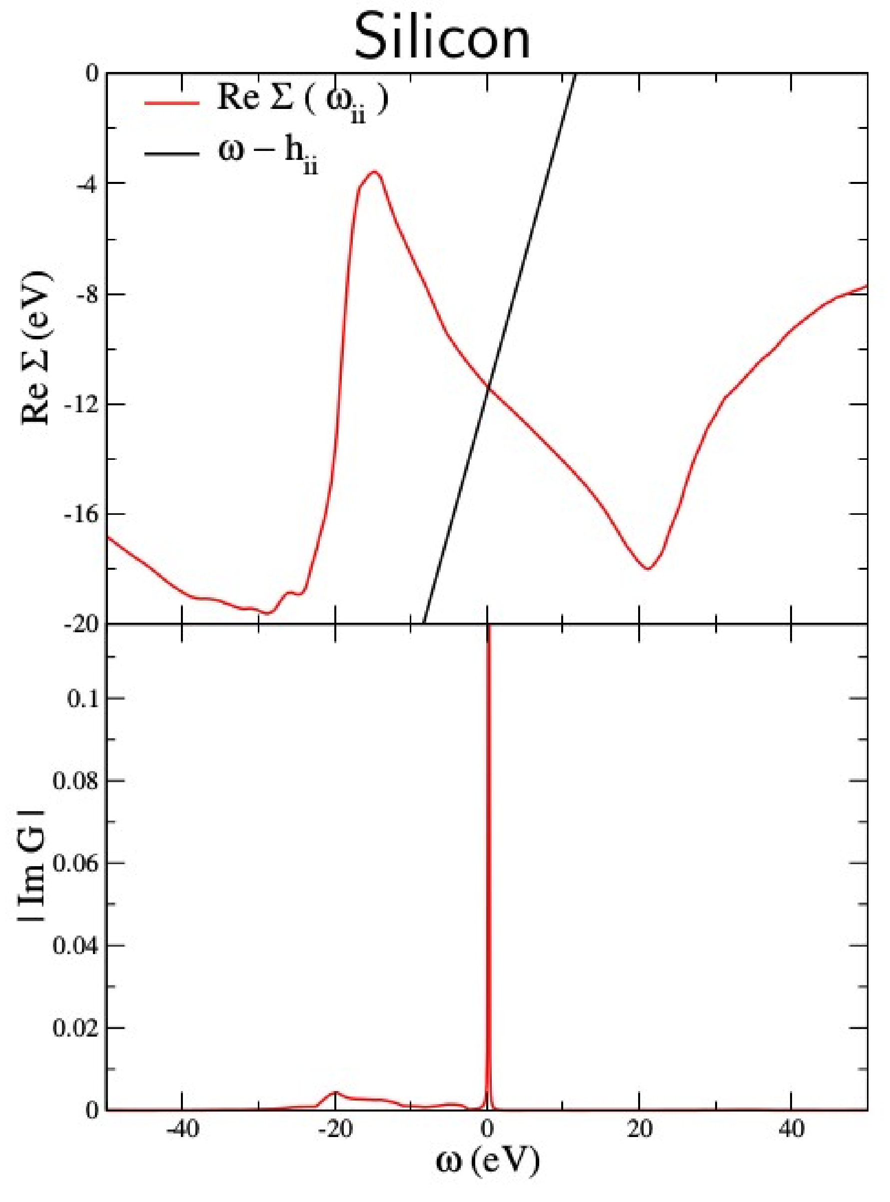
$$\epsilon^{GW}_{\mathrm{HOMO}} = -16.23 \quad \mathrm{eV}$$
$$\epsilon^{GW}_{\mathrm{LUMO}} = 18.74 \quad \mathrm{eV}$$

Exercice: H_2 in minimal basis: GW@HF

Same conclusions hold for
a many-state case:

Bulk silicon

Plasmon frequency ~ 17 eV
Occupied states ~ -5 - 0 eV
Empty states ~ +2 - … eV



Exercise 0: Where the spectral weight comes from?

Ex: A complex function made of single poles:

$$f(z) = \frac{A_1}{z - a_1} + \frac{A_2}{z - a_2} + \frac{A_3}{z - a_3} + \cdots = \sum_i \frac{A_i}{z - a_i}$$

poles : a_i Residus : A_i

$$(z - a_1) f(z) = A_1 + A_2 \frac{z - a_1}{z - a_2} + A_3 \frac{z - a_1}{z - a_3} + \cdots$$

$$\lim_{z \to a_1} (z - a_1) f(z) = A_1$$

Now with G $\quad \lim_{z \to a} (z - a) G(z) = \lim_{z \to a} \frac{z - a}{z - \epsilon - \Sigma(z)}$ $\quad \frac{0}{0}$ undetermined

$$G^{-1}(z) = G_0^{-1}(z) - \Sigma(z)$$
$$= z - \epsilon - \Sigma(z)$$

L'Hopital rule : $\lim_{x \to a} \frac{f(x)}{g(x)} = \lim_{x \to a} \frac{f'(x)}{g'(x)}$

$$= \lim_{z \to a} \frac{1}{1 - \Sigma'(z)} = \frac{1}{1 - \Sigma'(a)}$$

$$= Z(a)$$

spectral weight

Exercise 1

Green's function in frequency domain

$$iG(\boldsymbol{r_1}t_1,\boldsymbol{r_2}t_2)=\theta(t_1-t_2)\sum_{i\,\mathrm{virt}}\phi_i(\boldsymbol{r_1})\phi_i^*(\boldsymbol{r_2})e^{-i\epsilon_i(t_1-t_2)}$$
$$-\theta(t_2-t_1)\sum_{i\,\mathrm{occ}}\phi_i(\boldsymbol{r_2})\phi_i^*(\boldsymbol{r_1})e^{-i\epsilon_i(t_2-t_1)}$$

$$G(\boldsymbol{r_1},\boldsymbol{r_2},\omega)=\int d(t_1-t_2)\,e^{i\omega(t_1-t_2)}G(\boldsymbol{r_1}t_1,\boldsymbol{r_2}t_2)$$

$$G(\boldsymbol{r_1},\boldsymbol{r_2},\omega)=\sum_i\frac{\phi_i(\boldsymbol{r_1})\phi_i^*(\boldsymbol{r_2})}{\omega-\epsilon_i\pm i\eta}$$

Exercise 2:

Fock exchange from Green's functions

$$\Sigma_x(1,2) = iG(1,2)\,v(1^{\%+\%},2) \quad \longrightarrow \quad \Sigma_x(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega) = -\sum_{i\,\mathrm{occ}} \% \frac{\phi_i(\boldsymbol{r}_1)\,\phi_i^{\%*\%}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$

$$\Sigma_x(1,2) = i\,G(1,2)\,v(1^+,2)$$

$$v(1^+2) = v(r_1 t_1+\eta,\; r_2 t_2)$$

$$= \frac{1}{|r_1-r_2|}\,\delta(t_1+\eta-t_2)$$

$$\eta>0 \Rightarrow t_1-t_2<0$$

$$iG(12) = \Theta(t_1-t_2)\sum_a \phi_a(r_1)\,\phi_a^*(r_2)\,e^{-i\epsilon_a(t_1-t_2)}$$

$$- \Theta(t_2-t_1)\sum_i \phi_i(r_1)\,\phi_i^*(r_2)\,e^{-\epsilon_i(t_2-t_1)}$$

$$\Sigma_x(r_1,r_2,\omega) = \int d(t_1-t_2)\,e^{i\omega(t_1-t_2)}\,G(r_1t_1,r_2,t_2)$$

$$= -\frac{1}{|r_1-r_2|}\sum_i \phi_i(r_1)\,\phi_i^*(r_2)\,e^{-\epsilon_i\eta}$$

Exercise 3: let's play with Dyson equations

1) The multiple faces of the Dyson equation

$$[\omega - h_{\mathrm{KS}}] G_{\mathrm{KS}} = 1$$

$$[\omega - h_0 - v_{xc}] G_{\mathrm{KS}} = 1$$

$$[G_0^{-1} - v_{xc}] G_{\mathrm{KS}} = 1$$

$$G_{\mathrm{KS}} = G_0 + G_0 v_{xc} G_{\mathrm{KS}}$$

$$G_{\mathrm{KS}} = G_0 + G_0 v_{xc} G_0 + G_0 v_{xc} G_0 v_{xc} G_0 + \ldots$$

$$G_{\mathrm{KS}}^{-1} = G_0^{-1} - v_{xc}$$

2) Combining the Dyson equations

$$\left.\begin{aligned} G^{-1} &= G_0^{-1} - \Sigma \\ G_{\mathrm{KS}}^{-1} &= G_0^{-1} - v_{xc} \end{aligned}\right\} \quad G^{-1} = G_{\mathrm{KS}}^{-1} - (\Sigma - v_{xc})$$

$$1 = [G_{\mathrm{KS}}^{-1} - (\Sigma - v_{xc})] \; G$$

$$1 = [\omega - h_0 - \Sigma] \; G$$

Exercise 4

Derive the standard Adler-Wiser formula (1963):

$$\chi_0(1,2) = -i\,G(1,2)G(2,1)$$

$$\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega) \;=\; -\frac{i}{2\pi}\int d\omega'\,G(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega+\omega')G(\boldsymbol{r}_2,\boldsymbol{r}_1,\omega')$$

$$\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega) = \sum_{\substack{i\,\mathrm{occ}\\ j\,\mathrm{virt}}} \phi_i(\boldsymbol{r}_1)\phi_i^*(\boldsymbol{r}_2)\phi_j(\boldsymbol{r}_2)\phi_j^*(\boldsymbol{r}_1) \times\left[\frac{1}{\omega-(\epsilon_j-\epsilon_i)-i\eta}-\frac{1}{\omega-(\epsilon_i-\epsilon_j)+i\eta}\right]$$

Exercice 4: solution (1/3)

Definitions:

$$G(\omega) = \int d\tau \; G(\tau) \; e^{i\omega\tau} \qquad G(\tau) = \frac{1}{2\pi} \int d\omega \; G(\omega) \; e^{-i\omega\tau} \qquad \int d\omega \; e^{i\omega\tau} = 2\pi \, \delta(\tau)$$

$$\chi(\tau) = -i \; G(\tau) \; G(-\tau)$$

Exercice 4: solution (2/3)

$$\chi(\omega) = \int d\tau \, \chi(\tau)\, e^{i\omega\tau} = -\frac{i}{(2\pi)^2} \int d\tau \int d\omega_1 \, G(\omega_1)\, e^{-i\omega_1\tau} \int d\omega_2 \, G(\omega_2)\, e^{+i\omega_2\tau} \, e^{i\omega\tau}$$

$$= -\frac{i}{(2\pi)^2} \int d\omega_1 \int d\omega_2 \, G(\omega_1)\, G(\omega_2) \underbrace{\int d\tau \, e^{+i\tau(\omega+\omega_2-\omega_1)}}_{2\pi\,\delta(\omega+\omega_2-\omega_1)}$$

$$= -\frac{i}{2\pi} \int d\omega_2 \, G(\omega+\omega_2)\, G(\omega_2)$$

$$= -\frac{i}{2\pi} \int d\omega_2 \sum_p \frac{\phi_p(r)\,\phi_p^*(r')}{\omega+\omega_2 - \epsilon_p \pm i\eta} \times \sum_q \frac{\phi_q(r')\,\phi_q^*(r)}{\omega_2 - \epsilon_q \pm i\eta}$$

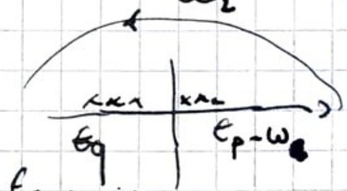
Exercice 4: solution (3/3)

$$\chi(\omega) = \int d\tau\, \chi(\tau)\, e^{i\omega\tau} = -\frac{i}{(2\pi)^2} \int d\tau \int d\omega_1\, G(\omega_1)\, e^{-i\omega_1\tau} \int d\omega_2\, G(\omega_2)\, e^{+i\omega_2\tau}\, e^{i\omega\tau}$$

$$= -\frac{i}{(2\pi)^2} \int d\omega_1 \int d\omega_2\, G(\omega_1)\, G(\omega_2) \underbrace{\int d\tau\, e^{+i\tau(\omega+\omega_2-\omega_1)}}_{2\pi\,\delta(\omega+\omega_2-\omega_1)}$$

$$= -\frac{i}{2\pi} \int d\omega_2\, G(\omega+\omega_2)\, G(\omega_2)$$

$$= -\frac{i}{2\pi} \int d\omega_2 \sum_p \frac{\phi_p(r)\,\phi_p^*(r')}{\omega+\omega_2 - \epsilon_p \pm i\eta} \times \sum_q \frac{\phi_q(r')\,\phi_q^*(r)}{\omega_2 - \epsilon_q \pm i\eta}$$



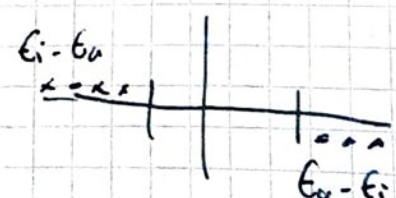
$$= \sum_{ia} \frac{\phi_i(r)\,\phi_i^*(r')\,\phi_a(r')\,\phi_a^*(r)}{\epsilon_i - \epsilon_a - \omega + 2i\eta}$$

pole $\omega_2 = \epsilon_p - \omega + i\eta$

pole: $\epsilon_q + i\eta$

$$+ \sum_{ia} \frac{\phi_a(r)\,\phi_a^*(r')\,\phi_i(r')\,\phi_i^*(r)}{\omega + \epsilon_i - \epsilon_a + 2i\eta}$$

$$= \sum_{ia} \frac{\phi\phi\phi\phi}{\omega - (\epsilon_a - \epsilon_i) + 2i\eta} - \sum_{ia} \frac{\phi\phi\phi\phi}{\omega - (\epsilon_i - \epsilon_a) - 2i\eta}$$



Exercise 5

Derive that the product in time becomes a convolution in frequency:

$$\Sigma(\mathbf{r_1},\mathbf{r_2},t_1-t_2)=iG(\mathbf{r_1},\mathbf{r_2},t_1-t_2)W(\mathbf{r_2},\mathbf{r_1},t_2-t_1)$$

$$G(\mathbf{r_1},\mathbf{r_2},\omega)=\int d(t_1-t_2)\,e^{i\omega(t_1-t_2)}G(\mathbf{r_1}t_1,\mathbf{r_2}t_2)$$

$$G(\mathbf{r_1},\mathbf{r_2},t_1-t_2)=\frac{1}{2\pi}\int d\omega\,e^{-i\omega(t_1-t_2)}G(\mathbf{r_1},\mathbf{r_2},\omega)$$

$$\Sigma(\mathbf{r_1},\mathbf{r_2},\omega)=\frac{i}{2\pi}\int d\omega'\,G(\mathbf{r_1},\mathbf{r_2},\omega+\omega')W(\mathbf{r_2},\mathbf{r_1},\omega')$$

Exercice 6: Feynman diagram drawing

a) Draw all the 1st order diagrams for the self-energy
b) Draw all the 2nd order diagrams for the self-energy
c) What is the difference between the proper and the improper self-energy
d) How self-consistency can simplify the expansion?

Self-energy diagram drawing rules:

1. Diagrams are combinations of arrows (Green’s function) and horizontal lines (Coulomb interaction).

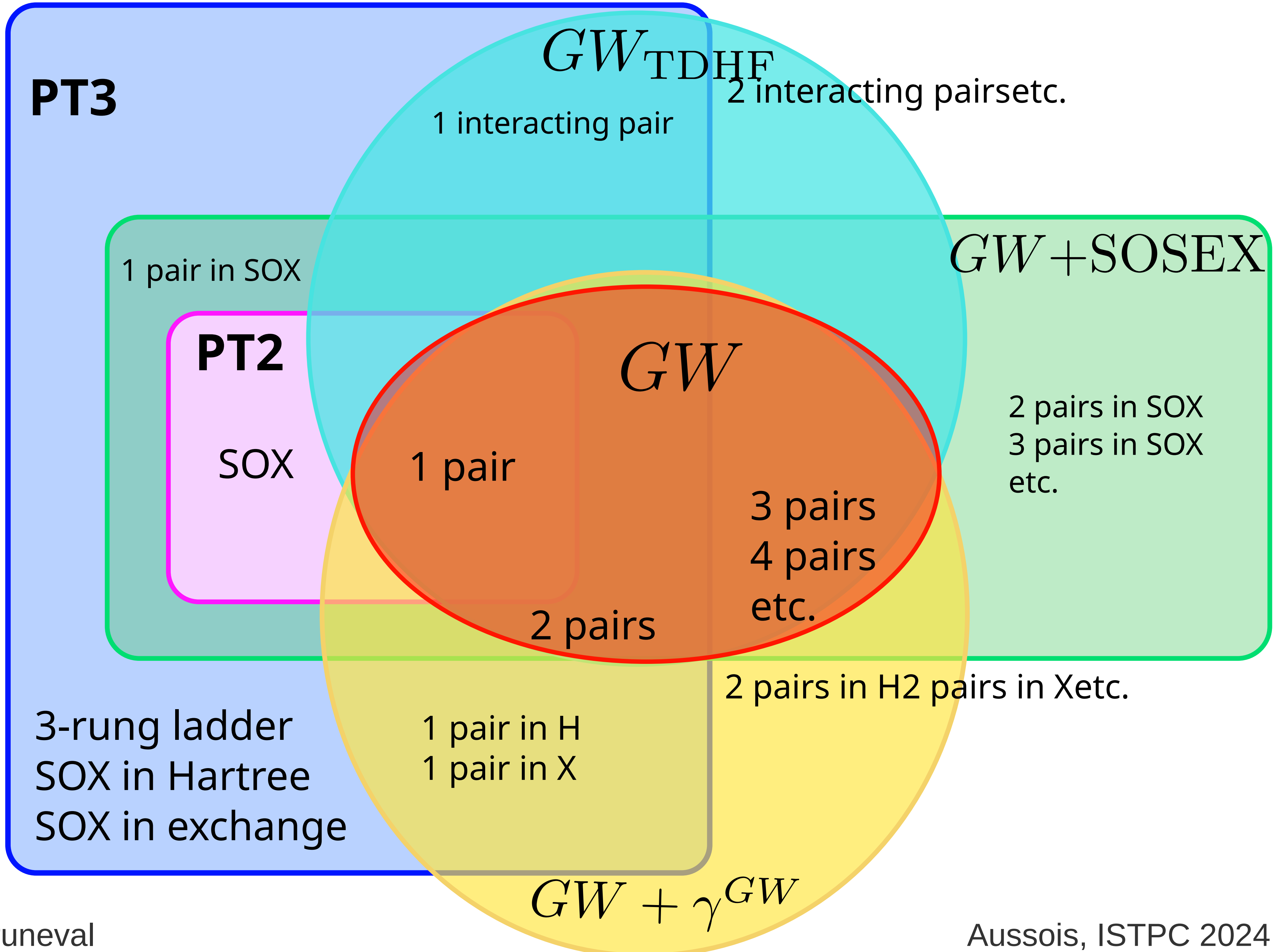
2. Diagrams should be connected.

3. Self-energy have an entry point and an exit point (possibly the same).

4. Each intersection (=vertex) should conserve the particle numbers.

5. A proper self-energy diagram cannot be cut (by removing an arrow) into another smaller self-energy.

Exercise 6:



PT3
GW_{TDHF}
1 interacting pair
2 interacting pairsetc.
1 pair in SOX
GW+SOSEX
PT2
SOX
GW
1 pair
2 pairs in SOX
3 pairs in SOX
etc.
3 pairs
4 pairs
etc.
2 pairs
2 pairs in H2 pairs in Xetc.
3-rung ladder
SOX in Hartree
SOX in exchange
1 pair in H
1 pair in X
$GW + \gamma^{GW}$

Perturbation theory up to third order

$$\Sigma_{pq}^{(3)}(\omega)=\sum_{I=1}^{6}(AI+CI+DI)$$

$$A1=-\sum\frac{(2V_{pkqj}-V_{pkjq})(2V_{jiab}-V_{jiba})V_{abki}}{(\varepsilon_j+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\varepsilon_k+\varepsilon_i-\varepsilon_a-\varepsilon_b)}$$

$$A2=\sum\frac{(2V_{pcqb}-V_{pcbq})(2V_{jiab}-V_{jiba})V_{jica}}{(\varepsilon_j+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\varepsilon_j+\varepsilon_i-\varepsilon_a-\varepsilon_c)}$$

$$A3=\sum\frac{(2V_{pcqj}-V_{pcjq})(2V_{jiab}-V_{jiba})V_{abci}}{(\varepsilon_j+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\varepsilon_j-\varepsilon_c)}$$

$$A4=\sum\frac{(2V_{pjqc}-V_{pjcq})(2V_{jiab}-V_{jiba})V_{abci}}{(\varepsilon_j+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\varepsilon_j-\varepsilon_c)}$$

$$A5=-\sum\frac{(2V_{pbqk}-V_{pbkq})(2V_{jiab}-V_{jiba})V_{ijka}}{(\varepsilon_j+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\varepsilon_k-\varepsilon_b)}$$

$$A6=-\sum\frac{(2V_{pkqb}-V_{pkbq})(2V_{jiab}-V_{jiba})V_{ijka}}{(\varepsilon_j+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\varepsilon_k-\varepsilon_b)}$$

$$C1=\sum\frac{(2V_{piab}-V_{piba})V_{abcd}V_{qicd}}{(\omega+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\omega+\varepsilon_i-\varepsilon_c-\varepsilon_d)}$$

$$C2=\sum\frac{(2V_{piab}-V_{piba})V_{abjk}V_{qijk}}{(\omega+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\varepsilon_j+\varepsilon_k-\varepsilon_a-\varepsilon_b)}$$

$$C3=\sum\frac{(2V_{pijk}-V_{pikj})V_{abjk}V_{qiab}}{(\omega+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\varepsilon_j+\varepsilon_k-\varepsilon_a-\varepsilon_b)}$$

$$C4=\sum\frac{(2V_{paij}-V_{paji})V_{ijbc}V_{qabc}}{(\omega+\varepsilon_a-\varepsilon_i-\varepsilon_j)(\varepsilon_i+\varepsilon_j-\varepsilon_b-\varepsilon_c)}$$

$$C5=\sum\frac{(2V_{pabc}-V_{pacb})V_{ijbc}V_{qaij}}{(\omega+\varepsilon_a-\varepsilon_i-\varepsilon_j)(\varepsilon_i+\varepsilon_j-\varepsilon_b-\varepsilon_c)}$$

$$C6=-\sum\frac{(2V_{pakl}-V_{palk})V_{klij}V_{qaij}}{(\omega+\varepsilon_a-\varepsilon_i-\varepsilon_j)(\omega+\varepsilon_a-\varepsilon_k-\varepsilon_l)}$$

$$D1=\sum\left\{\frac{V_{piab}\left[V_{ajic}(V_{qjcb}-2V_{qjbc})+V_{ajci}(V_{qjbc}-2V_{qjcb})\right]}{(\omega+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\omega+\varepsilon_j-\varepsilon_b-\varepsilon_c)}+\frac{V_{piba}\left[V_{ajic}(4V_{qjbc}-2V_{qjcb})+V_{ajci}(V_{qjcb}-2V_{qjbc})\right]}{(\omega+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\omega+\varepsilon_j-\varepsilon_b-\varepsilon_c)}\right\}$$

$$D2=\sum\left\{\frac{V_{pica}\left[V_{abij}(4V_{qbcj}-2V_{qbjc})+V_{abji}(V_{qbjc}-2V_{qbcj})\right]}{(\omega+\varepsilon_i-\varepsilon_a-\varepsilon_c)(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)}+\frac{V_{piac}\left[V_{abij}(V_{qbjc}-2V_{qbcj})+V_{abji}(V_{qbcj}-2V_{qbjc})\right]}{(\omega+\varepsilon_i-\varepsilon_a-\varepsilon_c)(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)}\right\}$$

$$D3=\sum\left\{\frac{V_{pcja}\left[V_{jicb}(V_{qiba}-2V_{qiab})+V_{jibc}(V_{qiab}-2V_{qiba})\right]}{(\omega+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\varepsilon_j+\varepsilon_i-\varepsilon_b-\varepsilon_c)}+\frac{V_{pcaj}\left[V_{jicb}(4V_{qiab}-2V_{qiba})+V_{jibc}(V_{qiba}-2V_{qiab})\right]}{(\omega+\varepsilon_i-\varepsilon_a-\varepsilon_b)(\varepsilon_j+\varepsilon_i-\varepsilon_b-\varepsilon_c)}\right\}$$

$$D4=\sum\left\{\frac{V_{pakj}\left[V_{jiab}(4V_{qikb}-2V_{qibk})+V_{jiba}(V_{qibk}-2V_{qikb})\right]}{(\omega+\varepsilon_a-\varepsilon_j-\varepsilon_k)(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)}+\frac{V_{pajk}\left[V_{jiab}(V_{qibk}-2V_{qikb})+V_{jiba}(V_{qikb}-2V_{qibk})\right]}{(\omega+\varepsilon_a-\varepsilon_j-\varepsilon_k)(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)}\right\}$$

$$D5=\sum\left\{\frac{V_{pibk}\left[V_{jiab}(V_{qajk}-2V_{qakj})+V_{jiba}(V_{qakj}-2V_{qajk})\right]}{(\omega+\varepsilon_a-\varepsilon_j-\varepsilon_k)(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)}+\frac{V_{pikb}\left[V_{jiab}(4V_{qakj}-2V_{qajk})+V_{jiba}(V_{qajk}-2V_{qakj})\right]}{(\omega+\varepsilon_a-\varepsilon_j-\varepsilon_k)(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)}\right\}$$

$$D6=-\sum\left\{\frac{V_{paki}\left[V_{ibaj}(4V_{qbkj}-2V_{qbjk})+V_{ibja}(V_{qbjk}-2V_{qbkj})\right]}{(\omega+\varepsilon_a-\varepsilon_i-\varepsilon_k)(\omega+\varepsilon_b-\varepsilon_j-\varepsilon_k)}+\frac{V_{paik}\left[V_{ibaj}(V_{qbjk}-2V_{qbkj})+V_{ibja}(V_{qbkj}-2V_{qbjk})\right]}{(\omega+\varepsilon_a-\varepsilon_i-\varepsilon_k)(\omega+\varepsilon_b-\varepsilon_j-\varepsilon_k)}\right\}$$

L.S. Cederbaum, W. Domcke (1977)

Exercice 6: effect of the other diagrams

Ionization potentials of the **GW100** benchmark (reference CCSD(T))