GW approximation in ABINIT

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Outline

I. Introduction: going beyond DFT

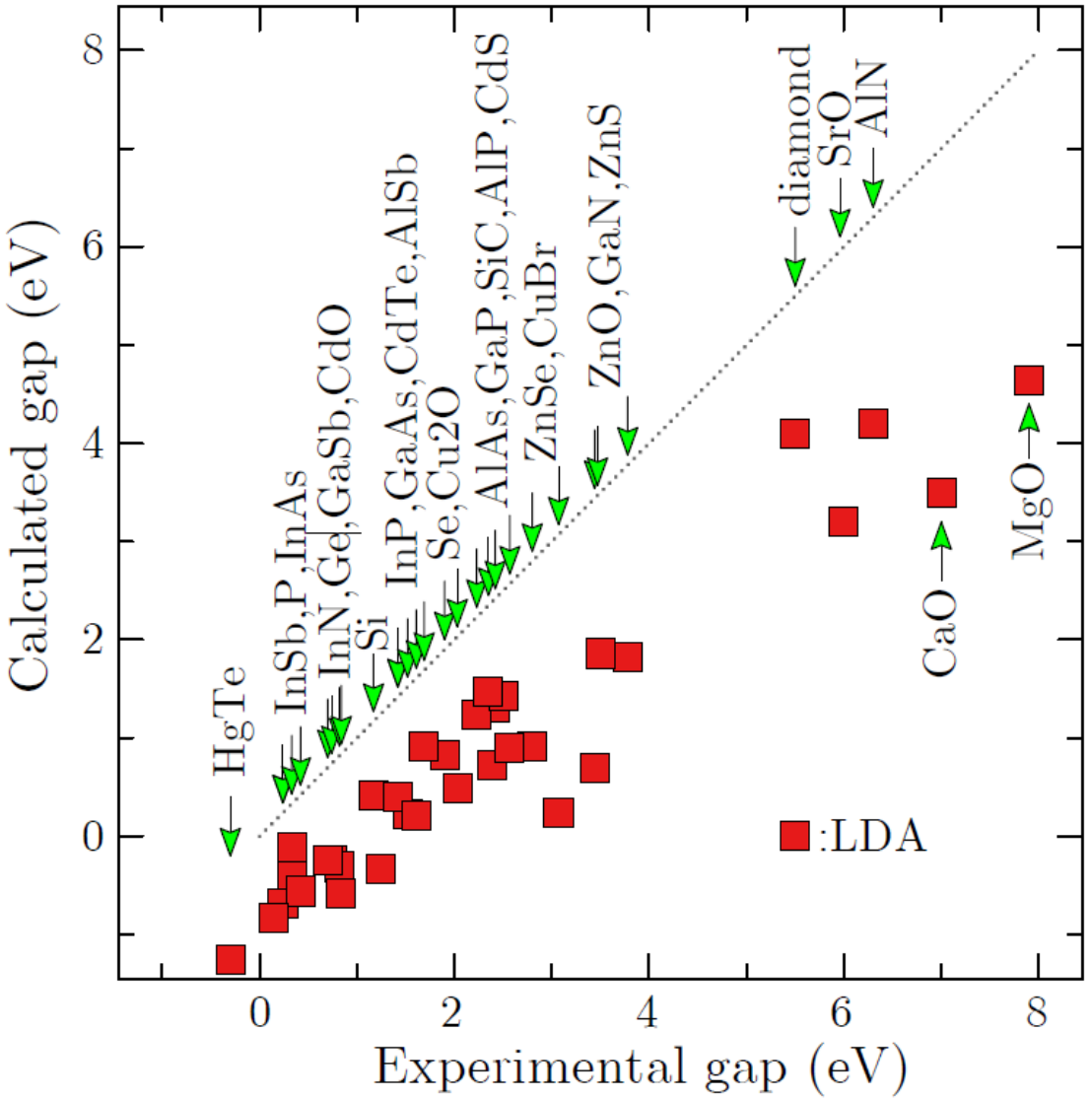
II. Introduction of the Green's function

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

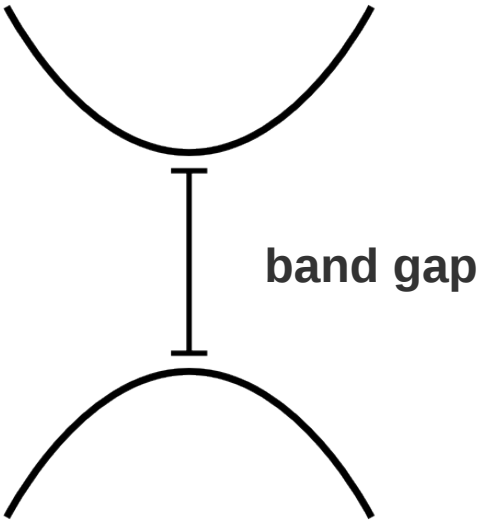
IV. Calculating the *GW* self-energy in practice

V. Applications

Standard DFT has unfortunately some shortcomings



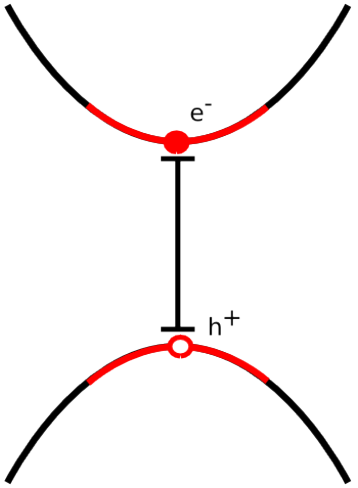
after van Schilfgaarde *et al* PRL **96** 226402 (2008)



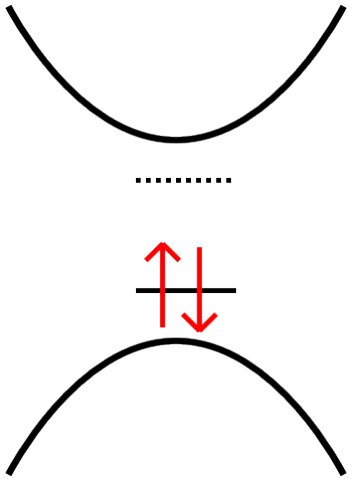
Band gap problem!

A pervasive problem

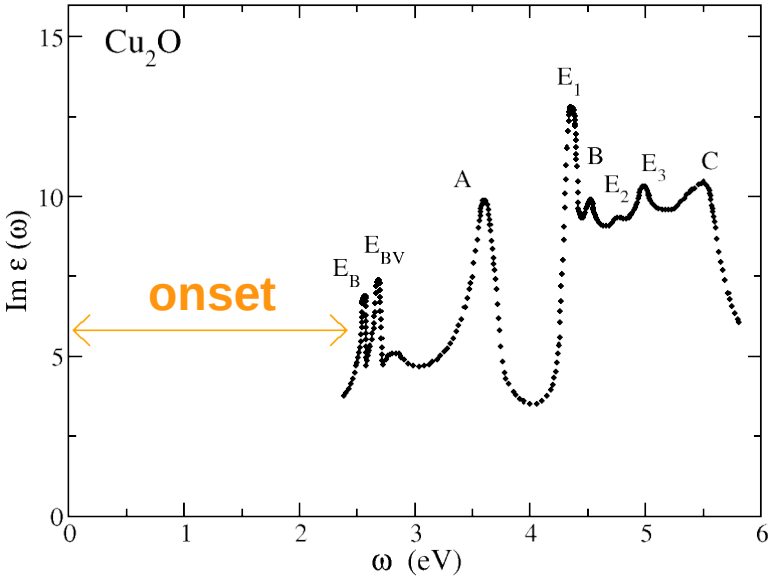
Conductivity for charge transport in semiconductors



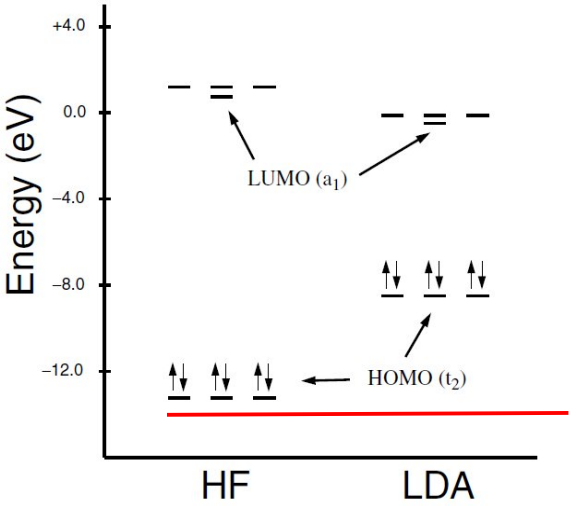
Defect formation energy
Charge transition level



Optical absorption



Photoemission



Exp.

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

Jouvence, Quantum Materials 2018

Gap re-normalization by a (metallic) substrate

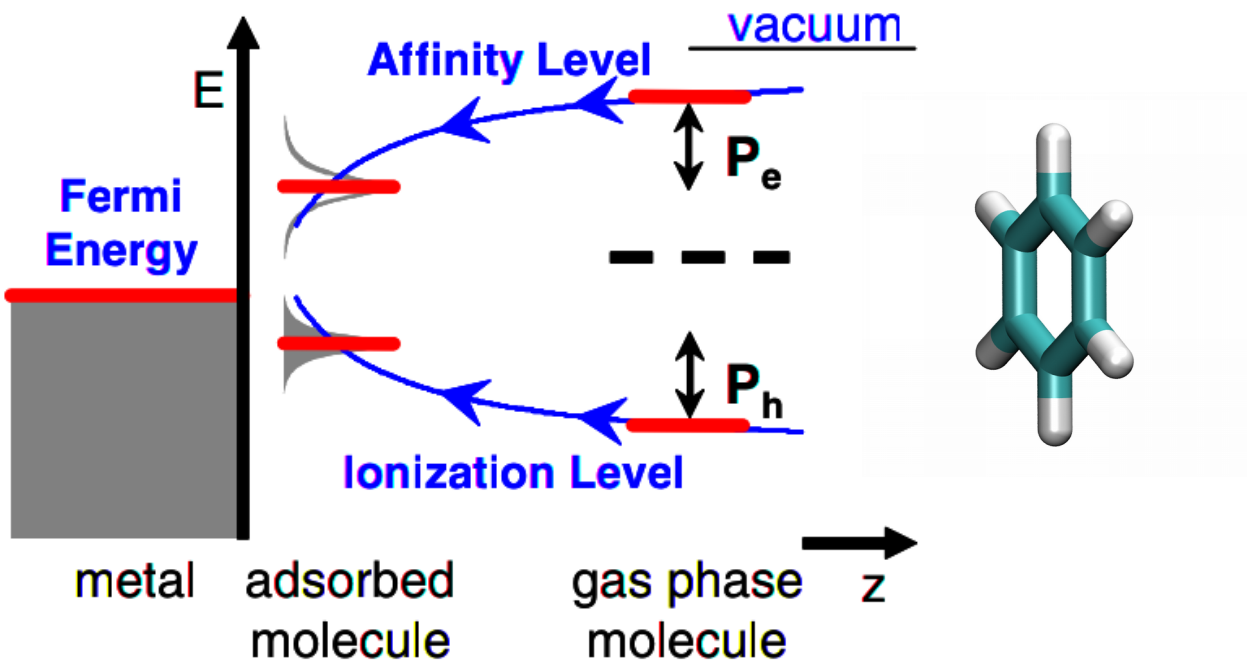


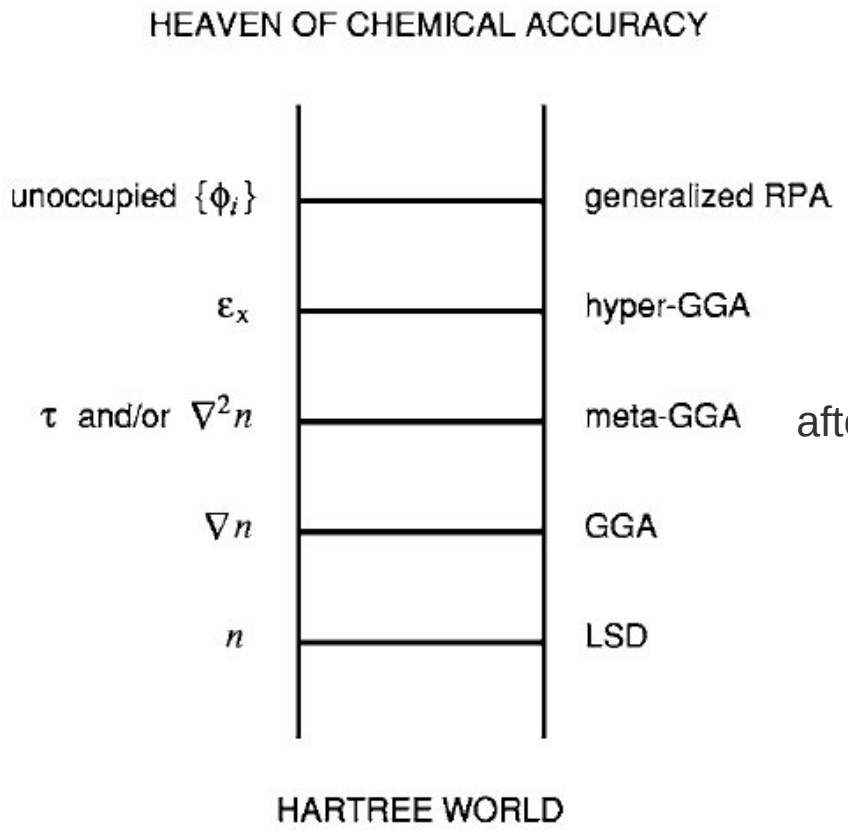
FIG. 1 (color online). Schematic energy level diagram indicating polarization shifts in the frontier energy levels (ionization and affinity) of a molecule upon adsorption on a metal surface.

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



after J. Perdew JCP (2005).

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

Need to change the overall framework!

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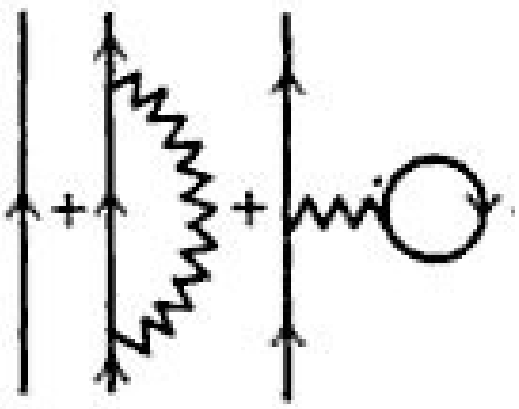
Many-body perturbation theory

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

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

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

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

Green's function definition

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

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

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

Final expression for the Green's function

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

time-ordering operator

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

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

Lehman representation

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

Closure relation

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

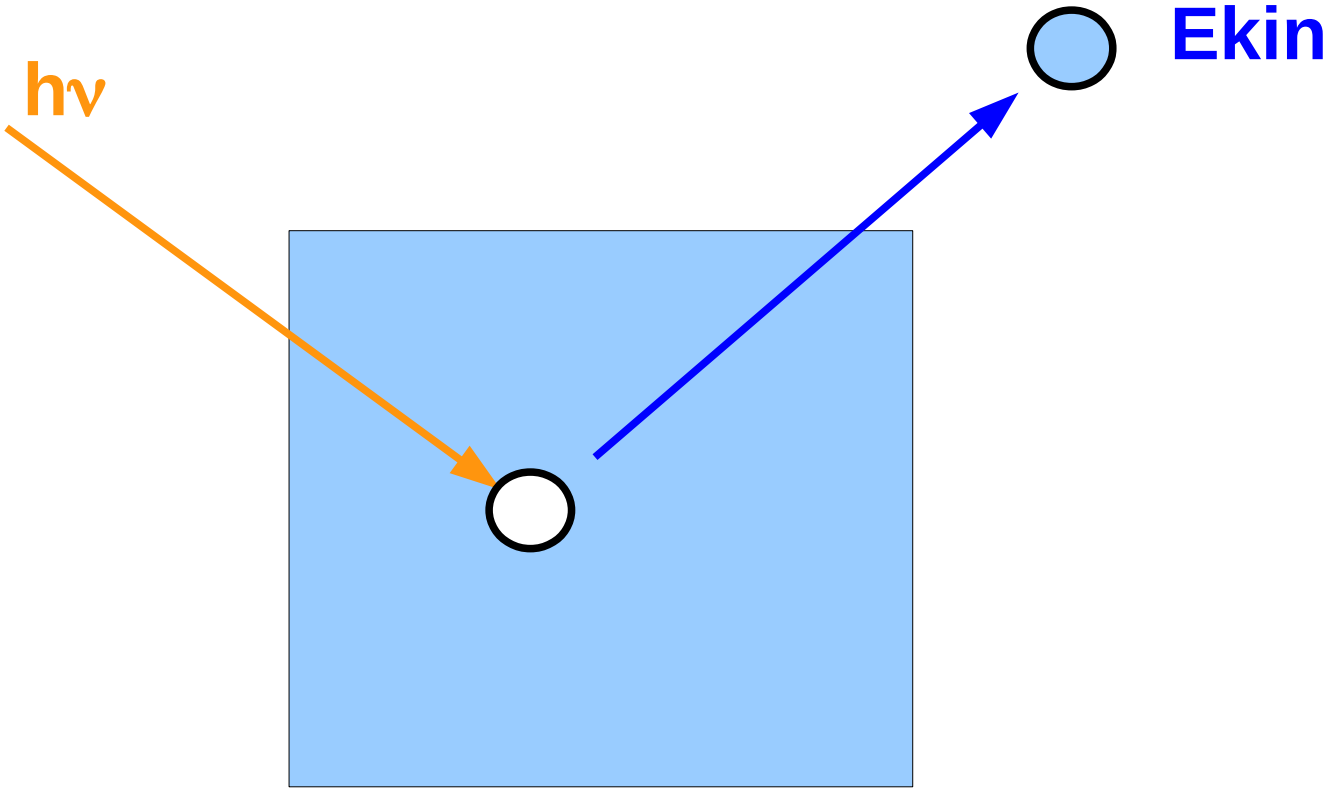
Lehman representation:

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

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

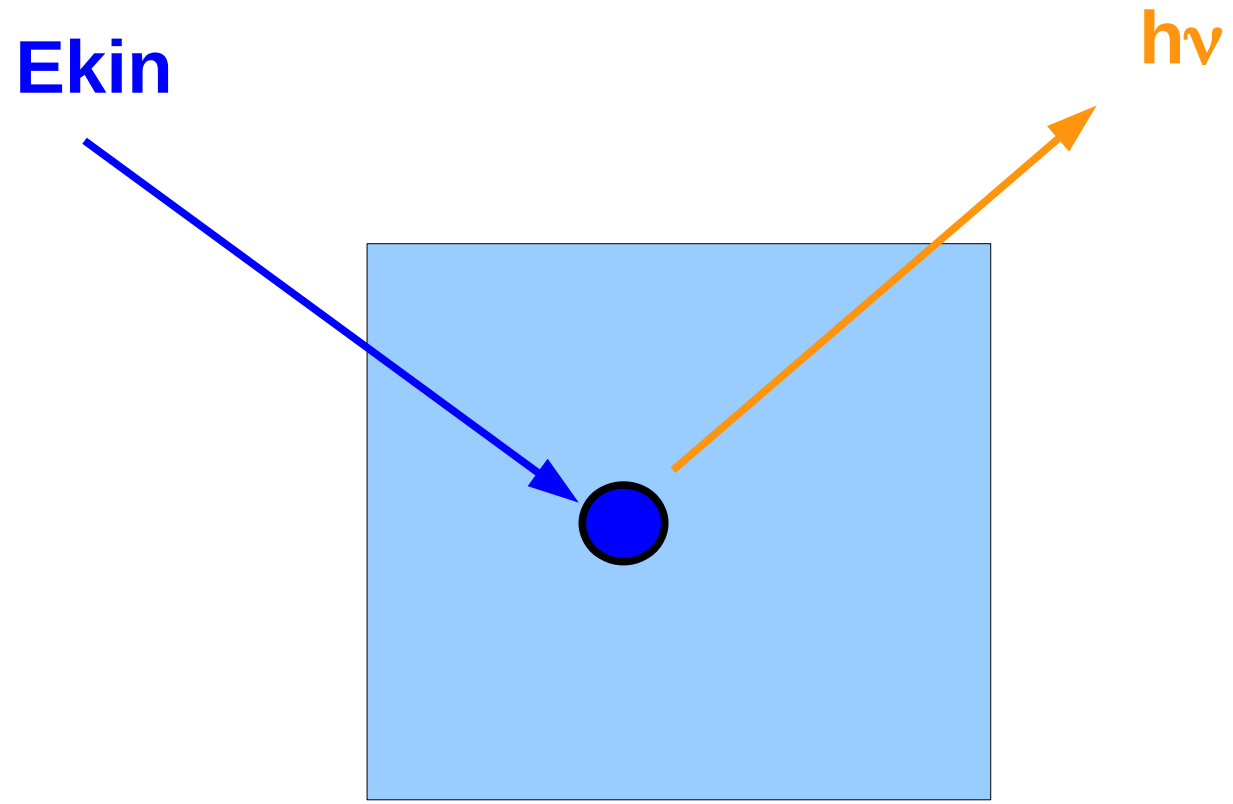


Energy conservation: before after

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

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

And inverse photoemission spectroscopy



Energy conservation: before after

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

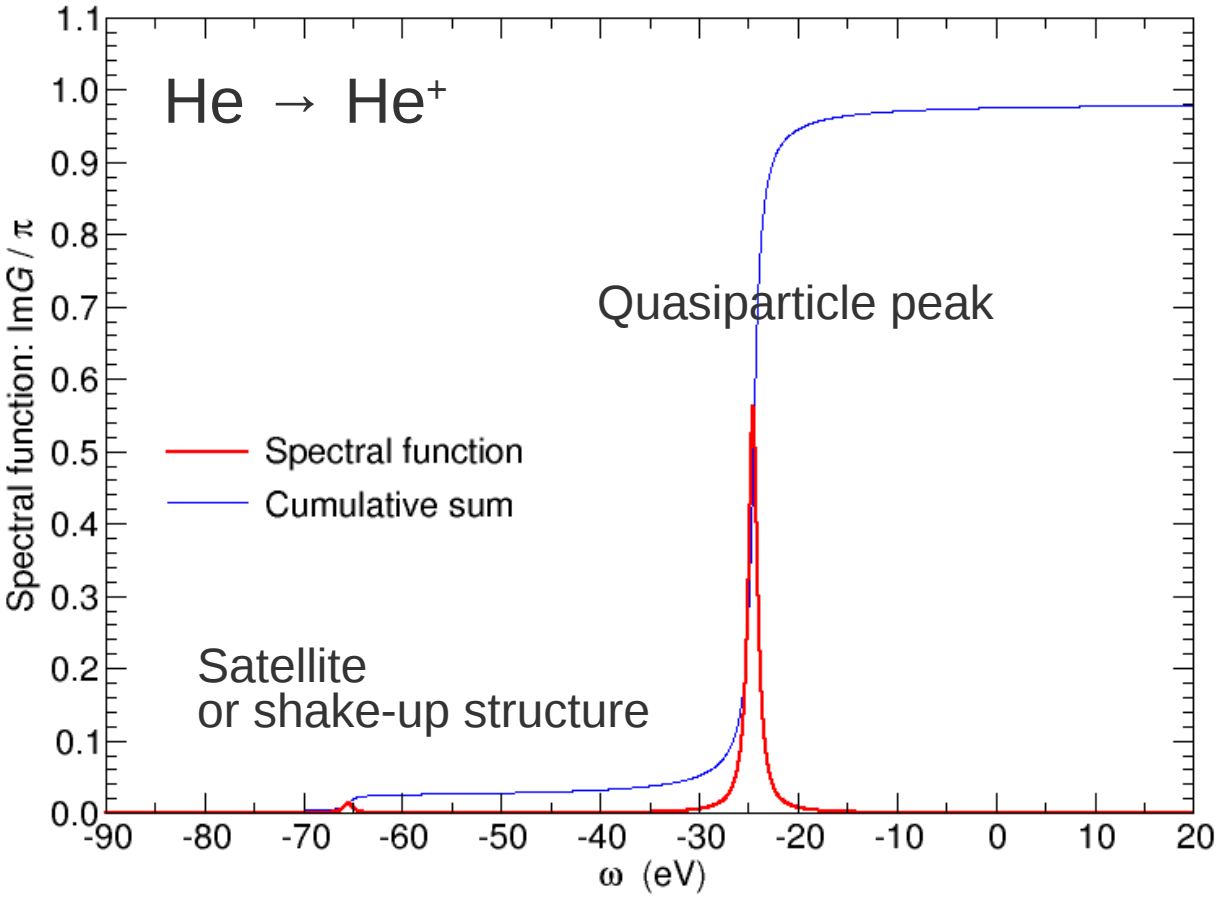
Quasiparticle energy: $$\epsilon_i = E(N+1,i) - E(N,0) = E_{kin} - h\nu$$

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



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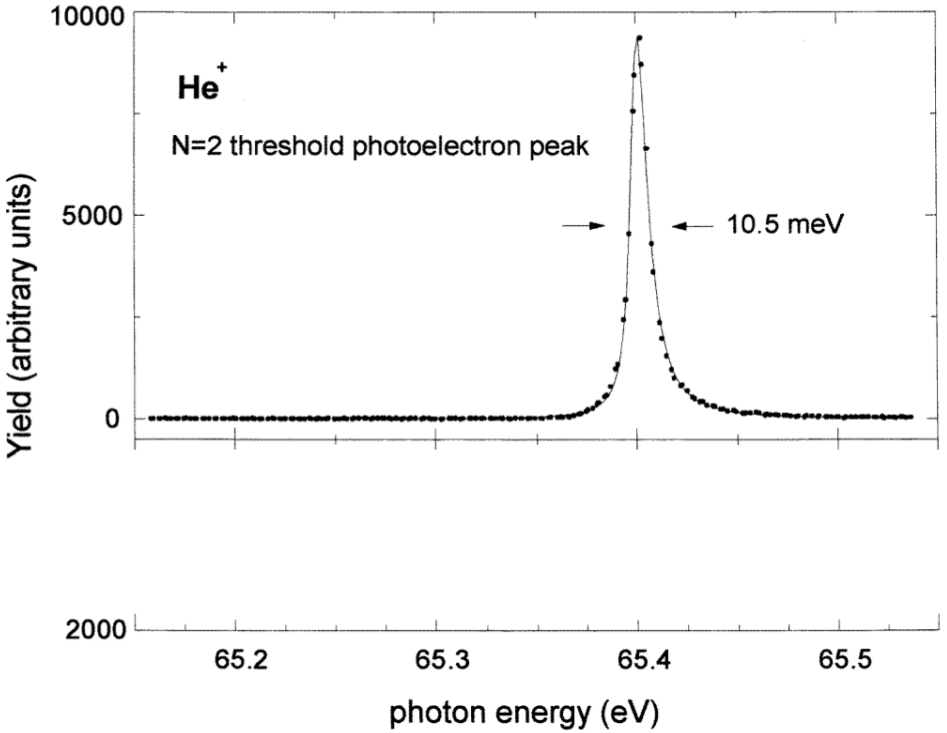
Satellites in reality?

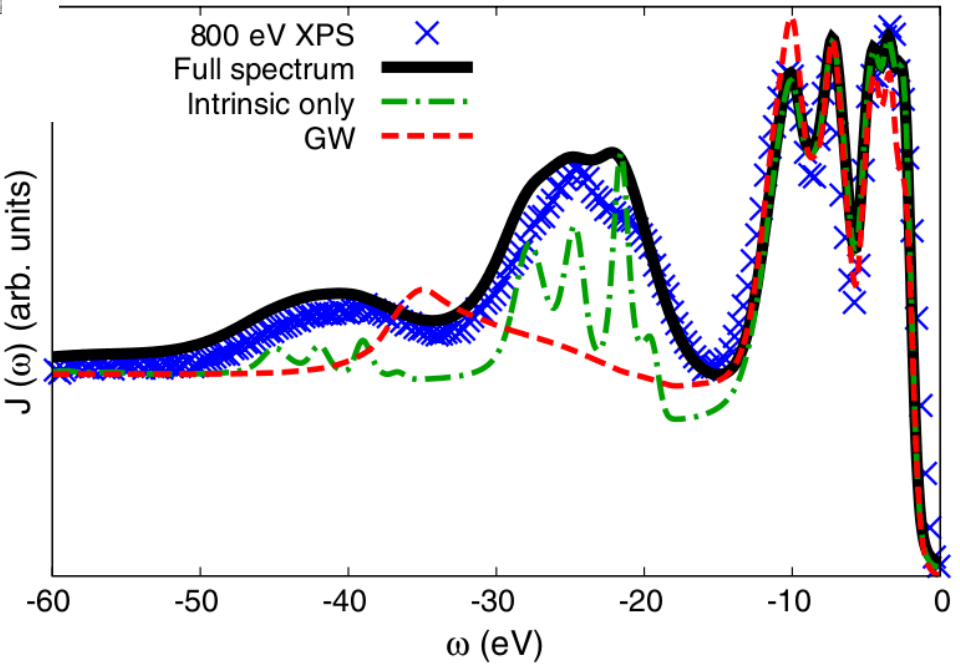


Helium gas

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:

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

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

$$\int d\,\boldsymbol{r}_2 \delta(\boldsymbol{r}_1-\boldsymbol{r}_2)\left[\omega-h_0(\boldsymbol{r}_2)\right]G_0(\boldsymbol{r}_2,\boldsymbol{r}_3,\omega)=\delta(\boldsymbol{r}_1-\boldsymbol{r}_3)$$

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

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

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

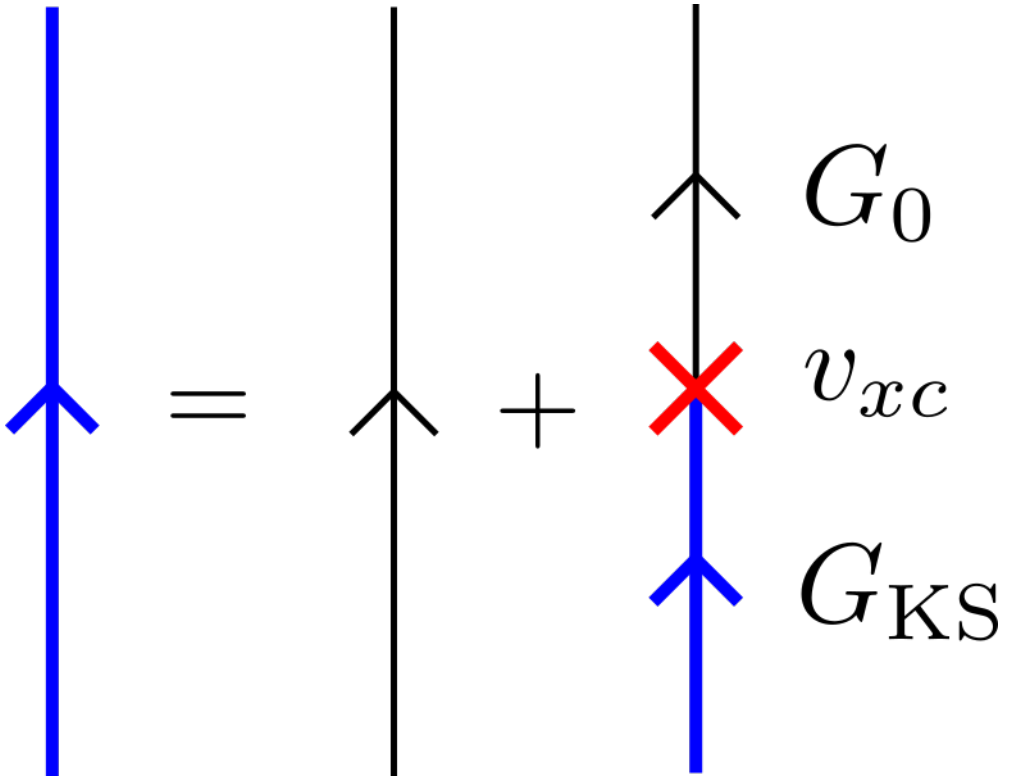
$$\hookrightarrow \quad \left[G_0^{-1}-v_{xc}\right]G_{\mathrm{KS}}=1$$

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

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

Exercice

A first contact with diagrams



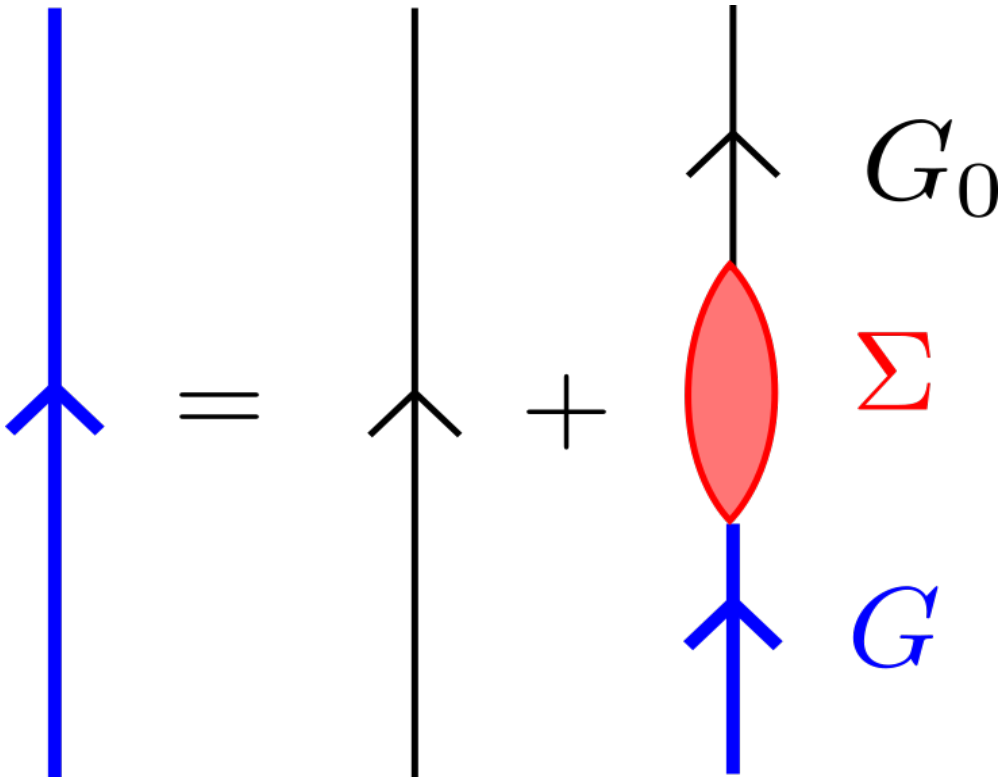
$$G_{\mathrm{KS}}(1,2) = G_0(1,2) + \int d3\, G_0(1,3) v_{xc}(3) G_{\mathrm{KS}}(3,2)$$

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?

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

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

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

.....

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*

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

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*

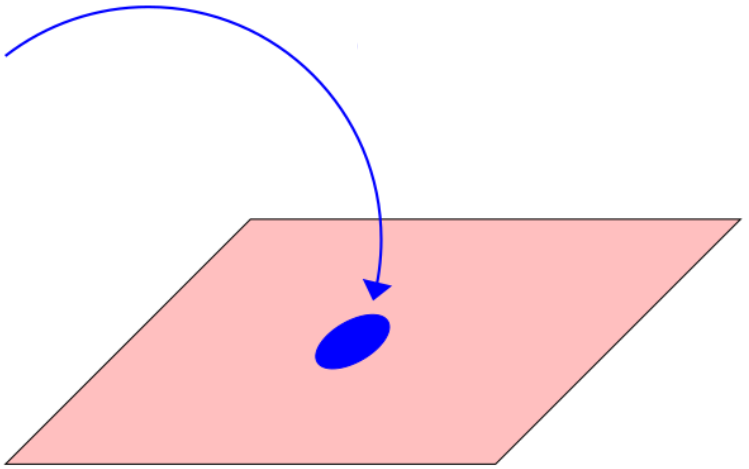
$$V(1) = U(1) - i\int d2\, v(1,2)\delta G(2,2)$$

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

1st order is *GW*

Shifting from *U* to *V*

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



Everything is functional of *U*

$$G[U]$$

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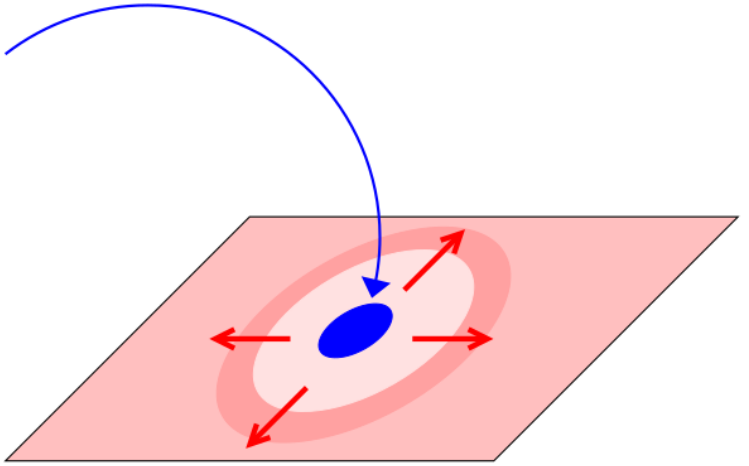


$$V(1) = U(1) + \int d\boldsymbol{r}\, v(r_1 - r)\,\delta\rho(\boldsymbol{r})$$

V also includes the electrostatic response

Everything is functional of *V*

$$G[V]$$

Hedin's coupled equations

6 coupled equations: $1=(\boldsymbol{r}_1 t_1 \sigma_1)$ $2=(\boldsymbol{r}_2 t_2 \sigma_2)$

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

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

$$\Gamma(1,2,3)=\delta(1,2)\delta(1,3)+\int d\,4567\frac{\delta\,\Sigma(1,2)}{\delta\,G(4,5)}G(4,6)G(5,7)\Gamma(6,7,3)$$ **vertex**

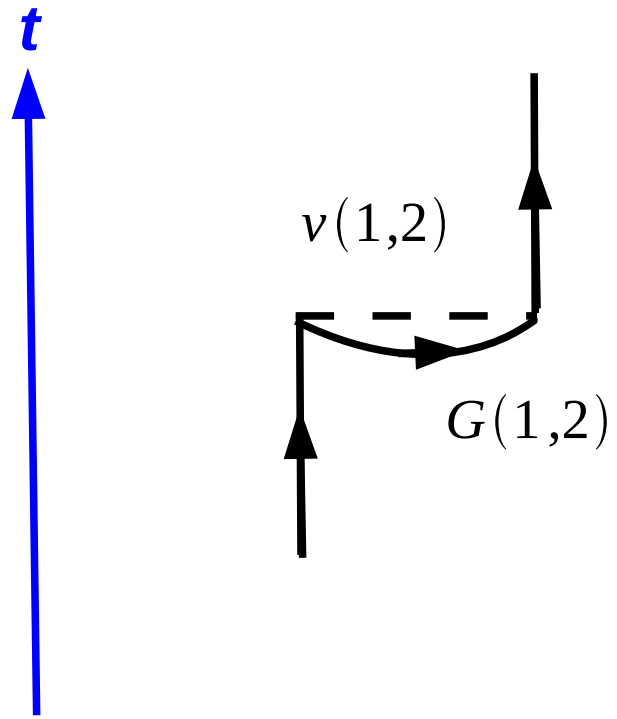
$$\chi_0(1,2)=-i\int d34\,G(1,3)G(4,1)\Gamma(3,4,2)$$ **polarizability**

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

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

Simplest approximation

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



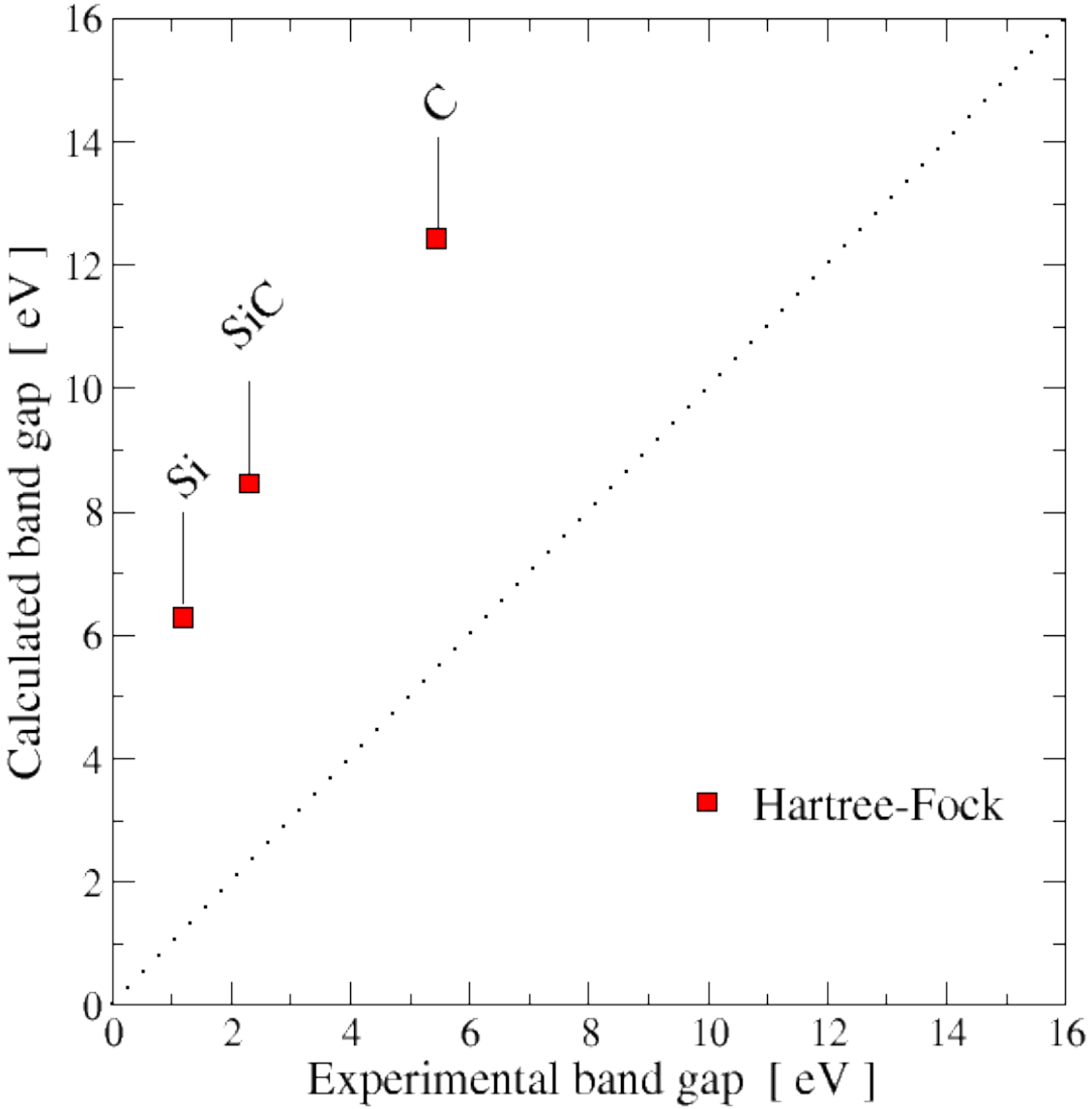
Dyson equation:

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

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

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

Hartree-Fock approximation for band gaps



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

$$\Gamma(1,2,3) = \delta(1,2)\,\delta(1,3) + \int d\,4567\,\frac{\delta\,\Sigma(1,2)}{\delta\,G(4,5)}\,G(4,6)\,G(5,7)\,\Gamma(6,7,3)$$

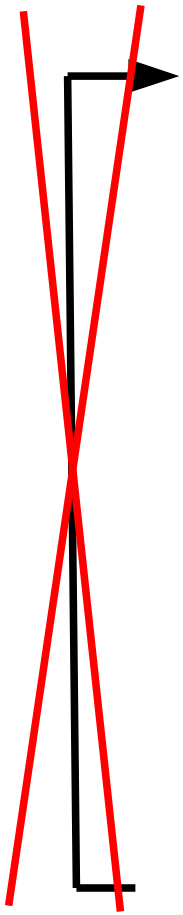
$$\chi_0(1,2) = -i\int d34\, G(1,3)\,G(4,1)\,\Gamma(3,4,2)$$

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

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

Hedin's coupled equations

6 coupled equations:



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

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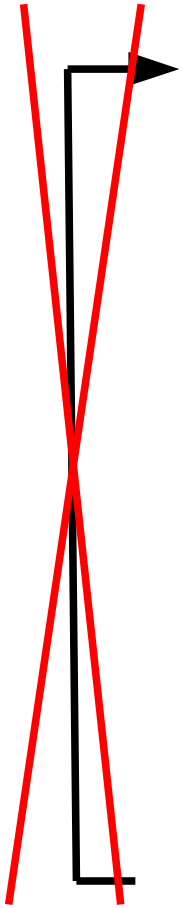
Hedin's coupled equations

6 coupled equations:



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

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

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

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

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

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

Let us play with diagrams

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

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

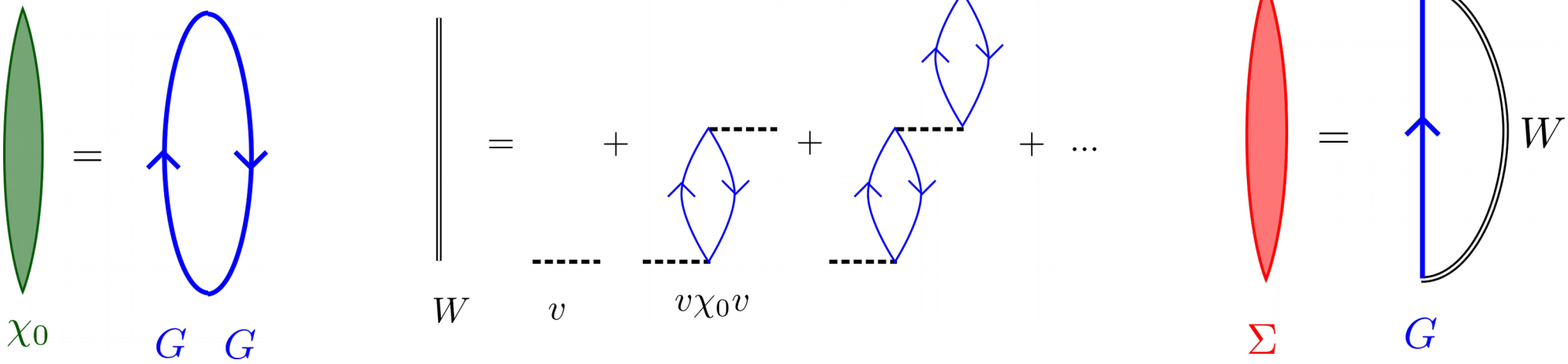
$$\varepsilon(1,2) = \delta(1,2) - \int d3\, v(1,3)\chi_0(3,2)$$

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

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

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

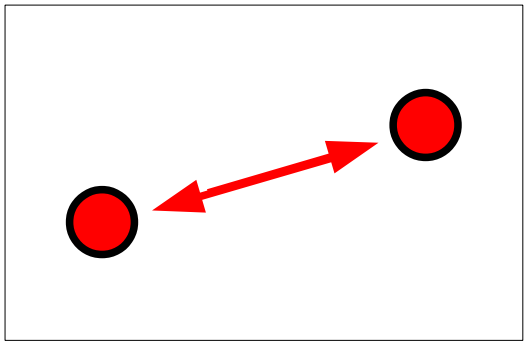
Infinite summation over bubble (or ring) diagrams



What is W?

Interaction between electrons in vacuum:

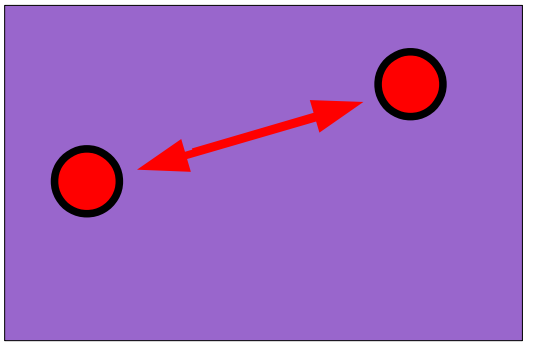
$$v(\boldsymbol{r},\boldsymbol{r}')=\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}$$



Interaction between electrons in a homogeneous polarizable medium:

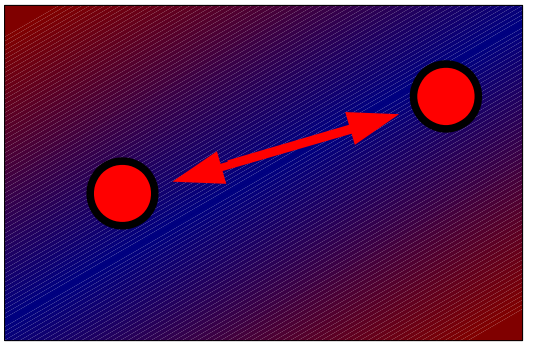
$$W(\boldsymbol{r},\boldsymbol{r}')=\frac{1}{4\pi\varepsilon_0\varepsilon_r}\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

Dielectric constant of the medium



Dynamically screened interaction between electrons in a general medium:

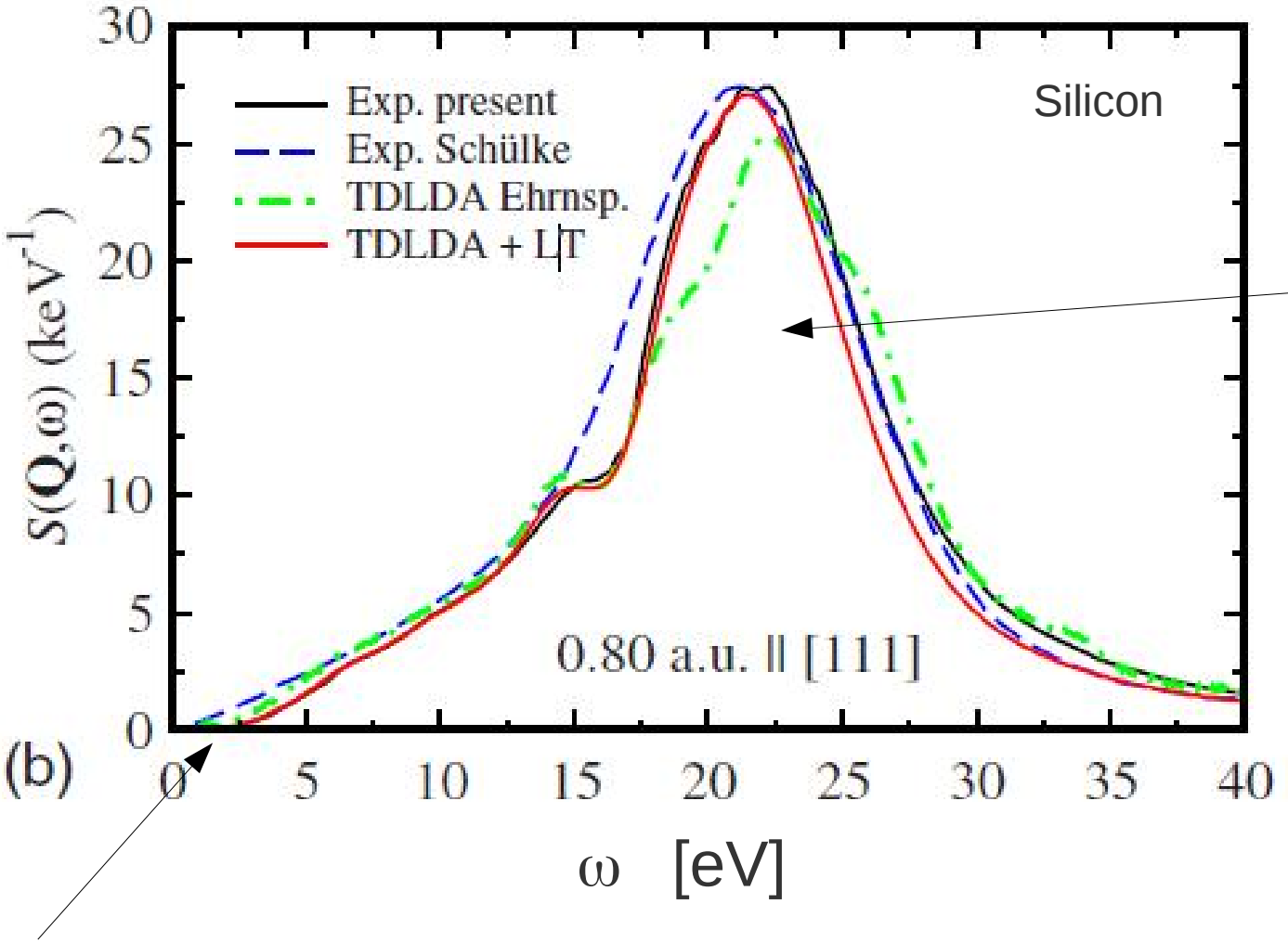
$$W(\boldsymbol{r},\boldsymbol{r}',\omega)=\frac{e^2}{4\pi\varepsilon_0}\int d\,r''\,\frac{\varepsilon^{-1}(\boldsymbol{r},\boldsymbol{r}'',\omega)}{|\boldsymbol{r}''-\boldsymbol{r}'|}$$



W is frequency dependent

W can measured directly by Inelastic X-ray Scattering

$$\mathrm{Im}\, W\left(\boldsymbol{q} = 0.80\,\mathrm{a.u}\,, \omega\right)$$



Plasmon frequency

Zero below the band gap

H-C Weissker et al. PRB (2010)

Summary

Summary: DFT vs Green's function

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 ⟺ HF, *GW* approximation

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

Jouvence, Quantum Materials 2018

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

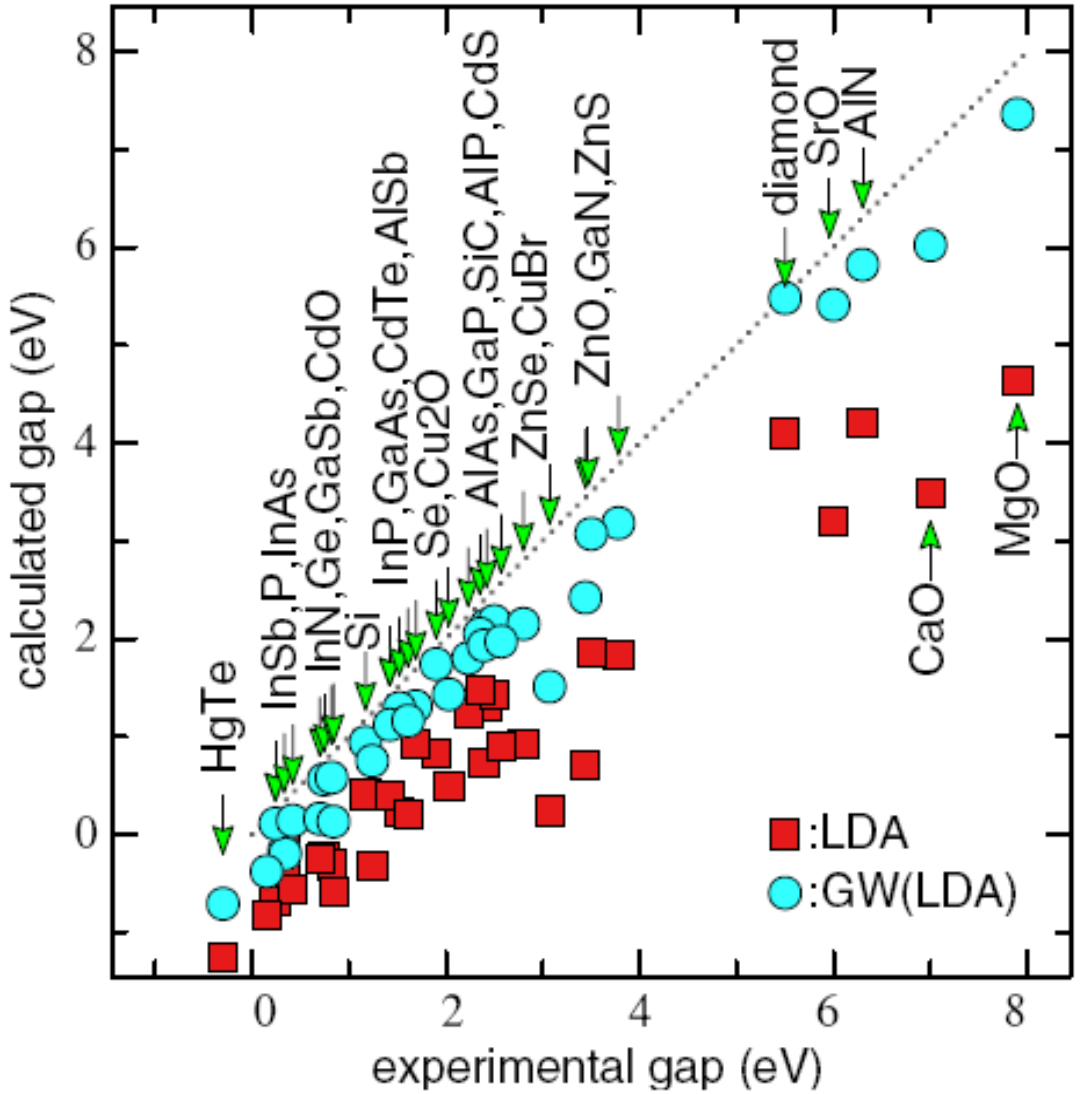
$\Sigma_c(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega)$

+ correlation

Non Hermitian dynamic

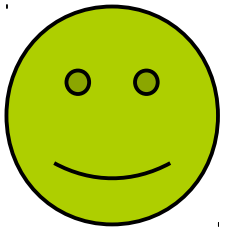
***GW* is nothing else but a “screened” version of Hartree-Fock.**

GW approximation gets good band gap



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

No band gap problem anymore!



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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

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 through the ABINIT project
- 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)

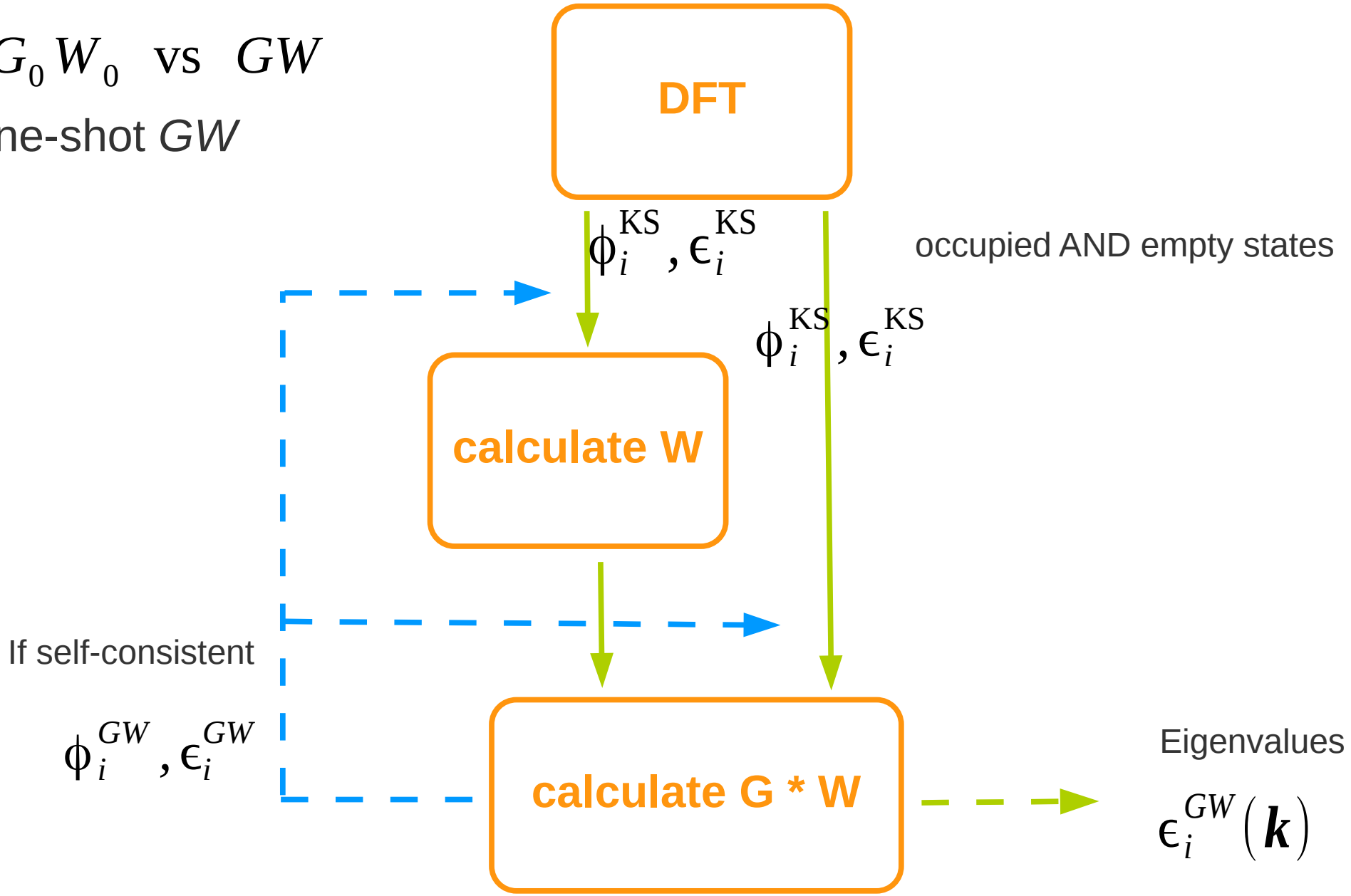
- For finite systems: MOLGW, Fiesta, FHI-AIMS

based on localized orbitals (Gaussians or Slater or other)

Workflow of a typical *GW* calculation

G_0W_0 vs GW

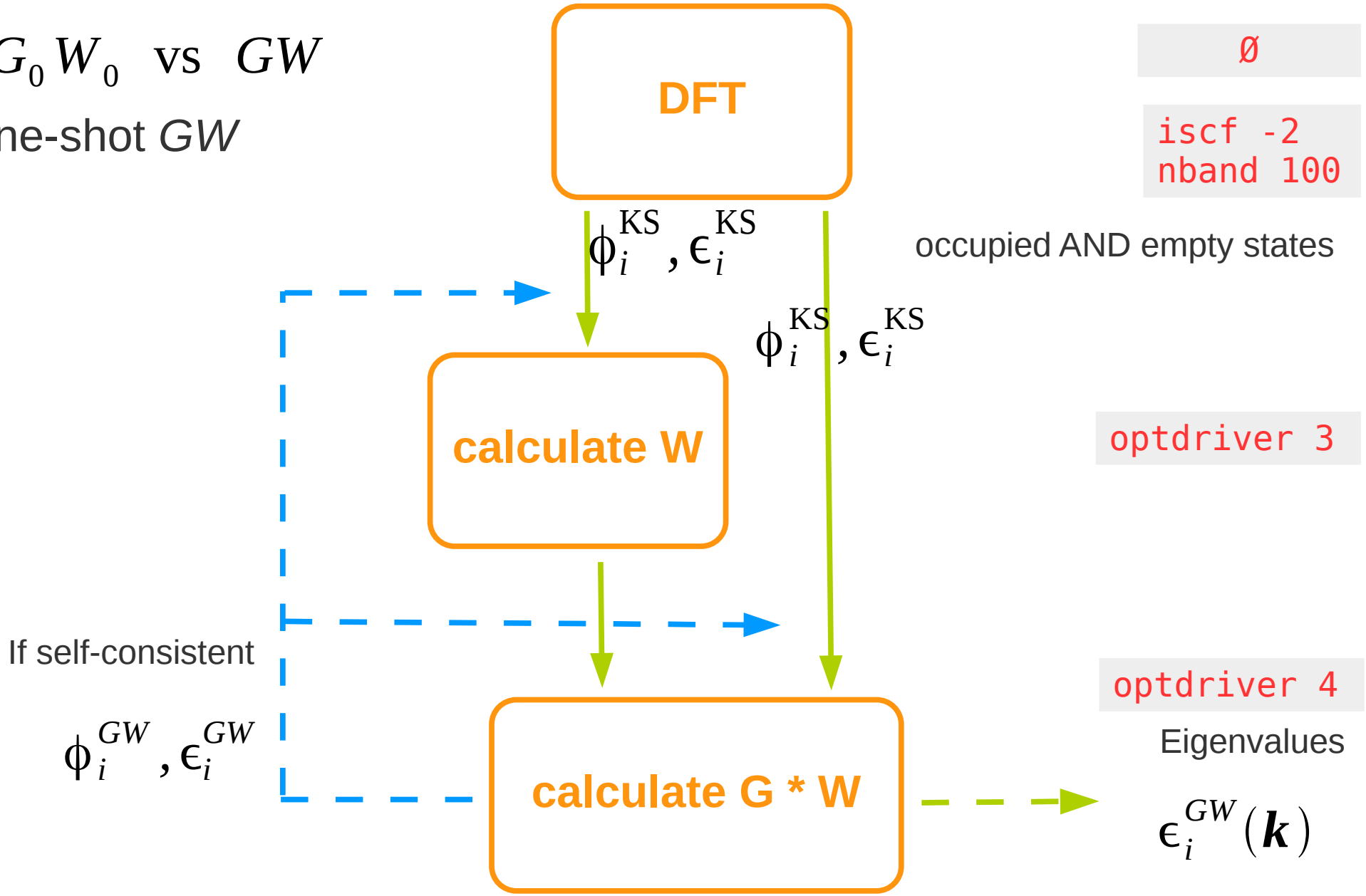
One-shot *GW*



Workflow of a typical *GW* calculation

G_0W_0 vs GW

One-shot *GW*




```
Ø
```

```
iscf -2
nband 100
```

```
optdriver 3
```

```
optdriver 4
```

How to get *G*?

From Kohn-Sham DFT

Remember

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

which means

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

This expression will be used to get W and Σ

How to get *W*?

From the RPA equation

$$\chi_0(1,2) = -iG_{\mathrm{KS}}(1,2)G_{\mathrm{KS}}(2,1)$$

which translates into

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

Exercice

This is the Alder-Wiser formula or the SOS formula

It involves empty states!

Then

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

$$W = (1-v\chi_0)^{-1} v$$

geometric series

Dealing with two-point functions in reciprocal space

Remember 1-point functions are

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

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) $$\chi_0(\boldsymbol{r_1},\boldsymbol{r_2},\omega)=\sum_{\substack{i\,\mathrm{occ}\\ j\,\mathrm{virt}}} \phi_i(\boldsymbol{r_1})\phi_i^*(\boldsymbol{r_2})\phi_j(\boldsymbol{r_2})\phi_j^*(\boldsymbol{r_1})$$

(2) $$\times\left[\frac{1}{\omega-(\epsilon_j-\epsilon_i)-i\,\eta}-\frac{1}{\omega-(\epsilon_i-\epsilon_j)+i\,\eta}\right]$$

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

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

---

(1) $$\chi_{0\boldsymbol{GG'}}(\boldsymbol{q},\omega)=\sum_{\substack{\boldsymbol{k}\\ i\,\mathrm{occ}\\ j\,\mathrm{virt}}} \left\langle j\boldsymbol{k}-\boldsymbol{q}\middle|e^{-i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r_1}}\middle|i\boldsymbol{k}\right\rangle\left\langle i\boldsymbol{k}\middle|e^{i(\boldsymbol{q}+\boldsymbol{G'})\cdot\boldsymbol{r_2}}\middle|j\boldsymbol{k}-\boldsymbol{q}\right\rangle$$

nband
ecuteps

(2) $$\times\left[\frac{1}{\omega-(\epsilon_j-\epsilon_i)-i\,\eta}-\frac{1}{\omega-(\epsilon_i-\epsilon_j)+i\,\eta}\right]$$

q the same regular grid as k but Γ-centered

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

$$W_{\boldsymbol{GG'}}(\boldsymbol{q},\omega)=\varepsilon^{-1}_{\boldsymbol{GG'}}(\boldsymbol{q},\boldsymbol{G'})v_{\boldsymbol{G'}}(\boldsymbol{q}) \quad\Leftarrow\quad \text{matrix inversion}$$

Self energy evaluation in *GW*

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

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

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

nband

?

How to deal with the frequency dependence in W?

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

Analytic structure of $W(\omega)$

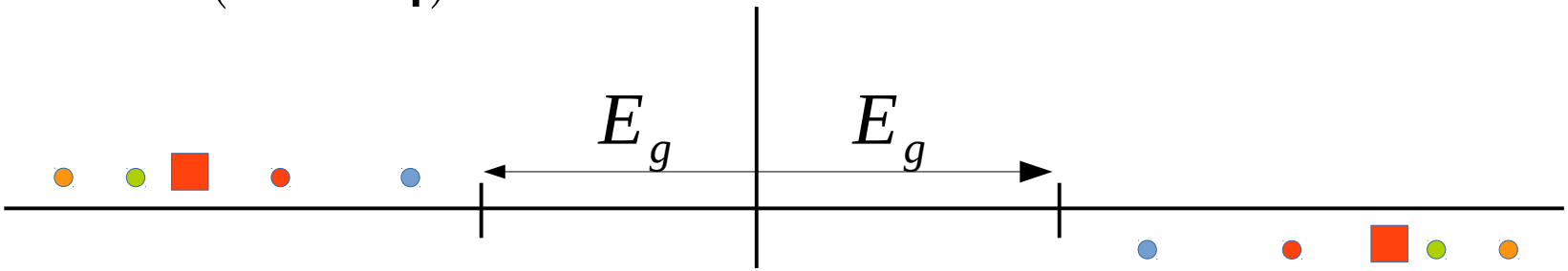
- Time ordered response function:

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

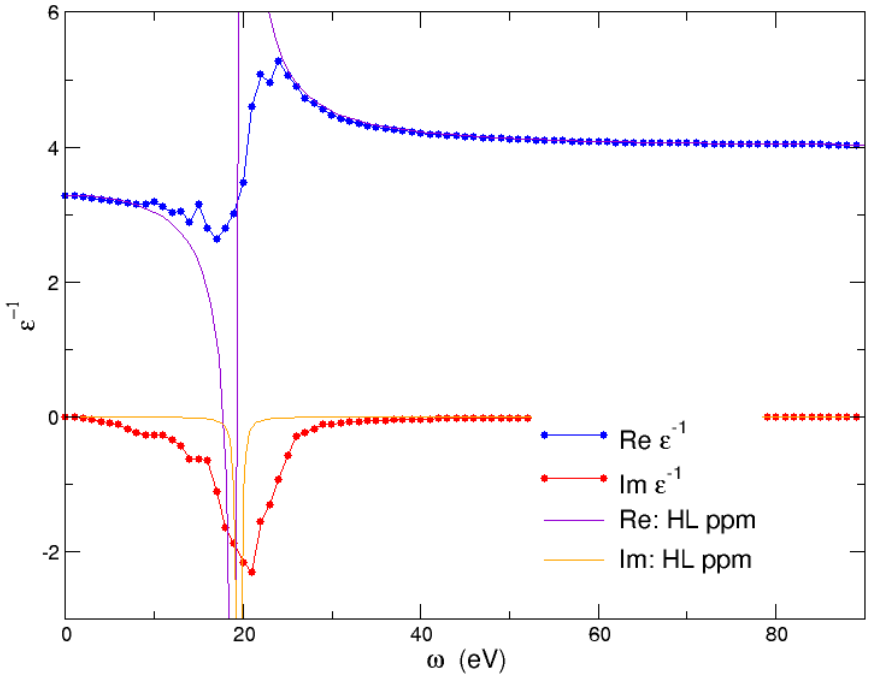
- Plasmon-pole model:

  One pair of poles: $\pm\left(\tilde{\omega} - i\,\eta\right)$

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:

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

`ppmodel`

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 $\varepsilon^{-1}(i\omega)$

`ppmfrq`

GW obtained as a first-order perturbation

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

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

$$\Rightarrow \quad G^{-1} = G_{\mathrm{KS}}^{-1} - (\Sigma - v_{xc})$$

Approximation : $\phi_i^{GW} \approx \phi_i^{\mathrm{KS}}$

$$G^{-1} = \sum_i |\phi_i\rangle (\omega - \epsilon_i^{GW}) \langle \phi_i|$$

$$G_{\mathrm{KS}}^{-1} = \sum_i |\phi_i\rangle (\omega - \epsilon_i^{\mathrm{KS}}) \langle \phi_i|$$

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

Linearization of the energy dependance

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

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:

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

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

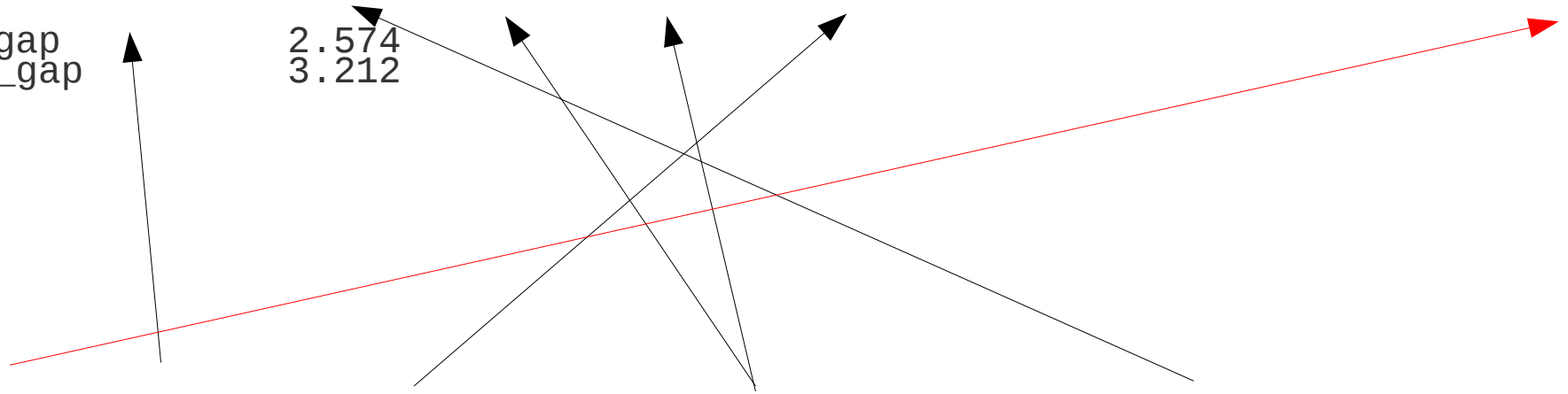
`nomegasrd`

Typical GW output in ABINIT

```
nkptgw  1
kptgw   0. 0. 0.
bdgw    4 5
```

```
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
```

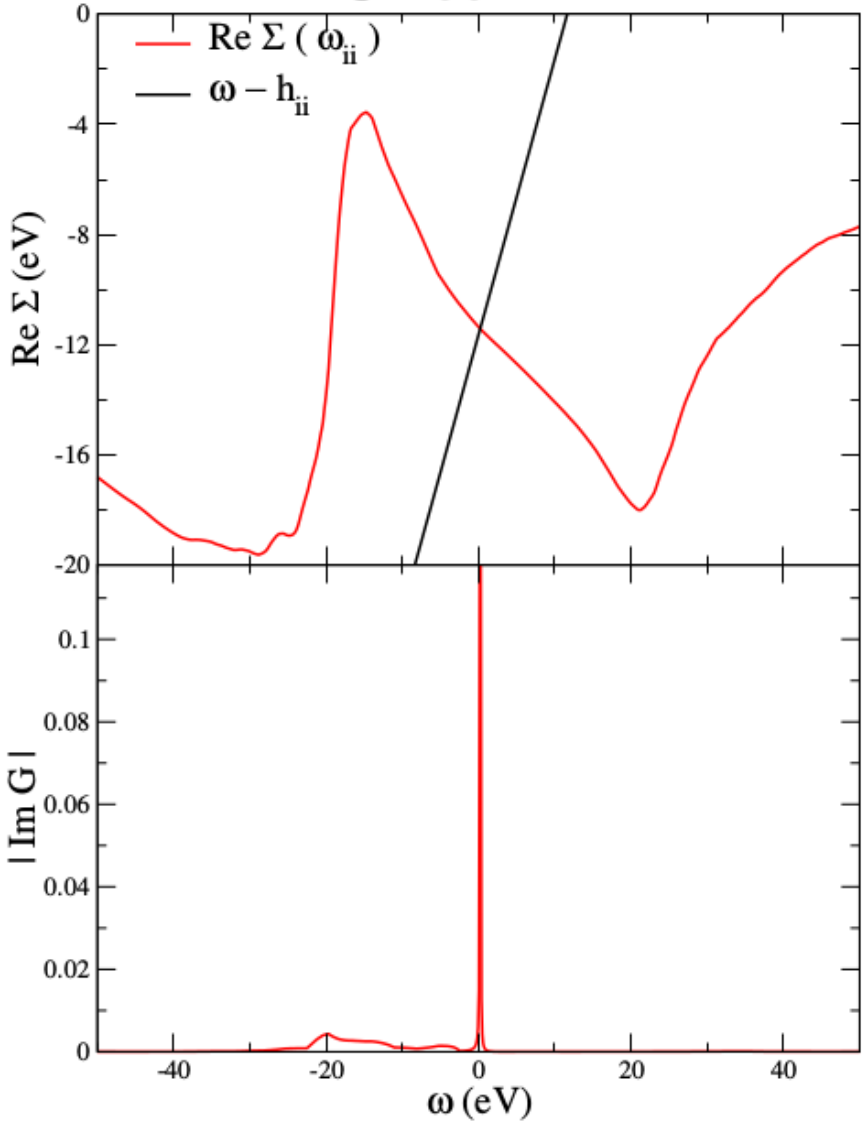


$$\epsilon_i^{GW} = \epsilon_i^{KS} + Z_i \left\langle \varphi_i^{KS} \middle| \Sigma_{xc}\left(\epsilon_i^{KS}\right) - v_{xc} \middle| \varphi_i^{KS} \right\rangle$$

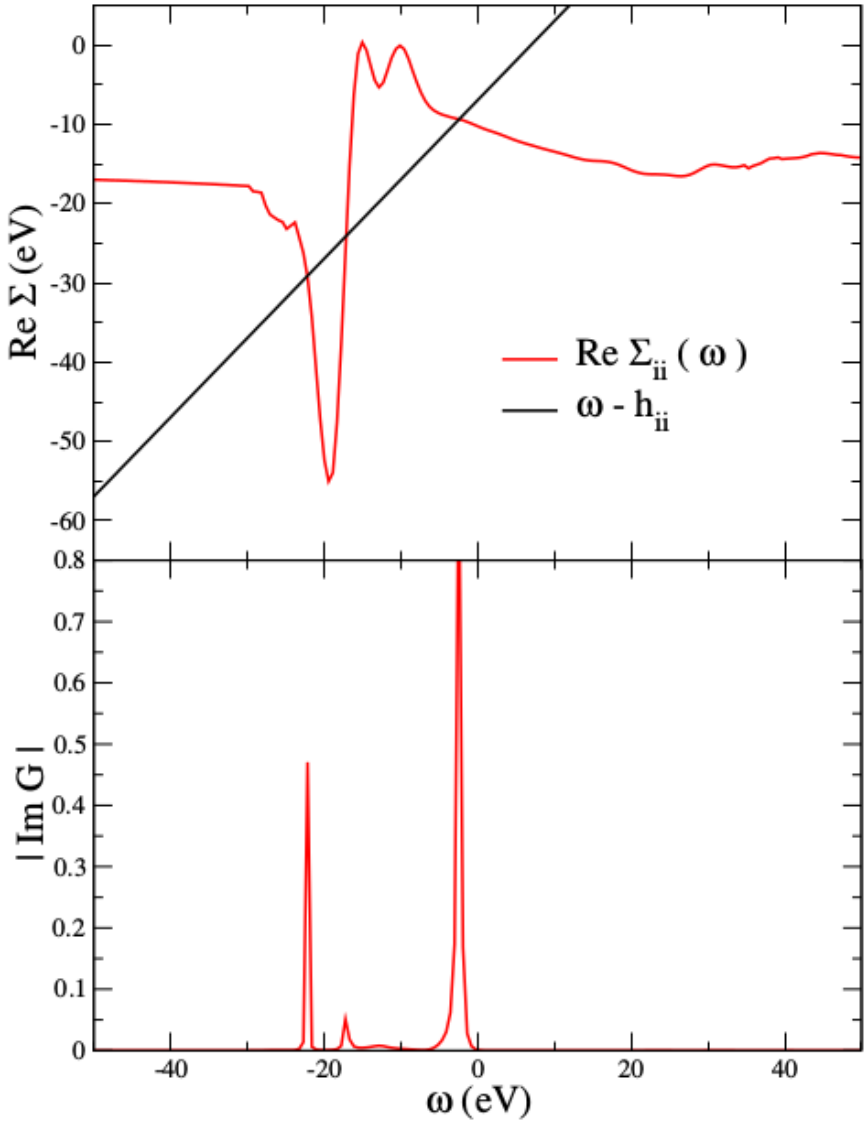
Full quasiparticle solution

$$A_{ii}(\omega) = \frac{1}{\pi}|\mathrm{Im}\,G(\omega)| = \frac{\mathrm{Im}\,\Sigma_{ii}(\omega)}{\left(\omega-\epsilon_i^{KS}+\mathrm{Re}\,\Sigma_{ii}(\omega)-v_{xc}\right)^2+\mathrm{Im}\,\Sigma_{ii}(\omega)^2}$$

Silicon



Aluminum



F. Bruneval

Jouvence, Quantum Materials 2018

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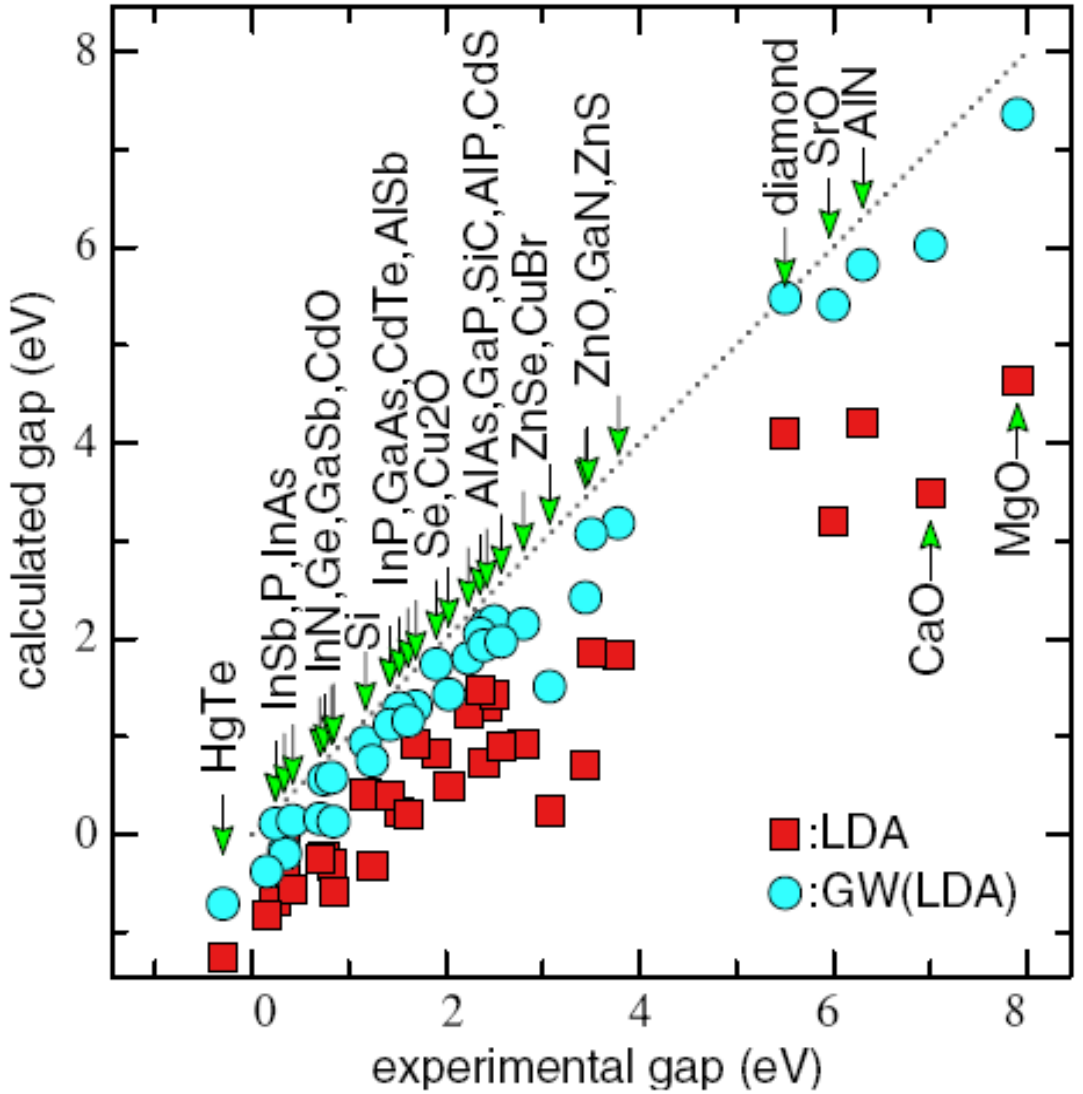
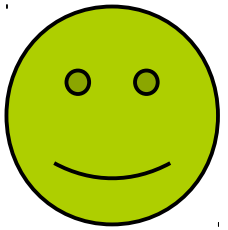
GW approximation gets good band gap



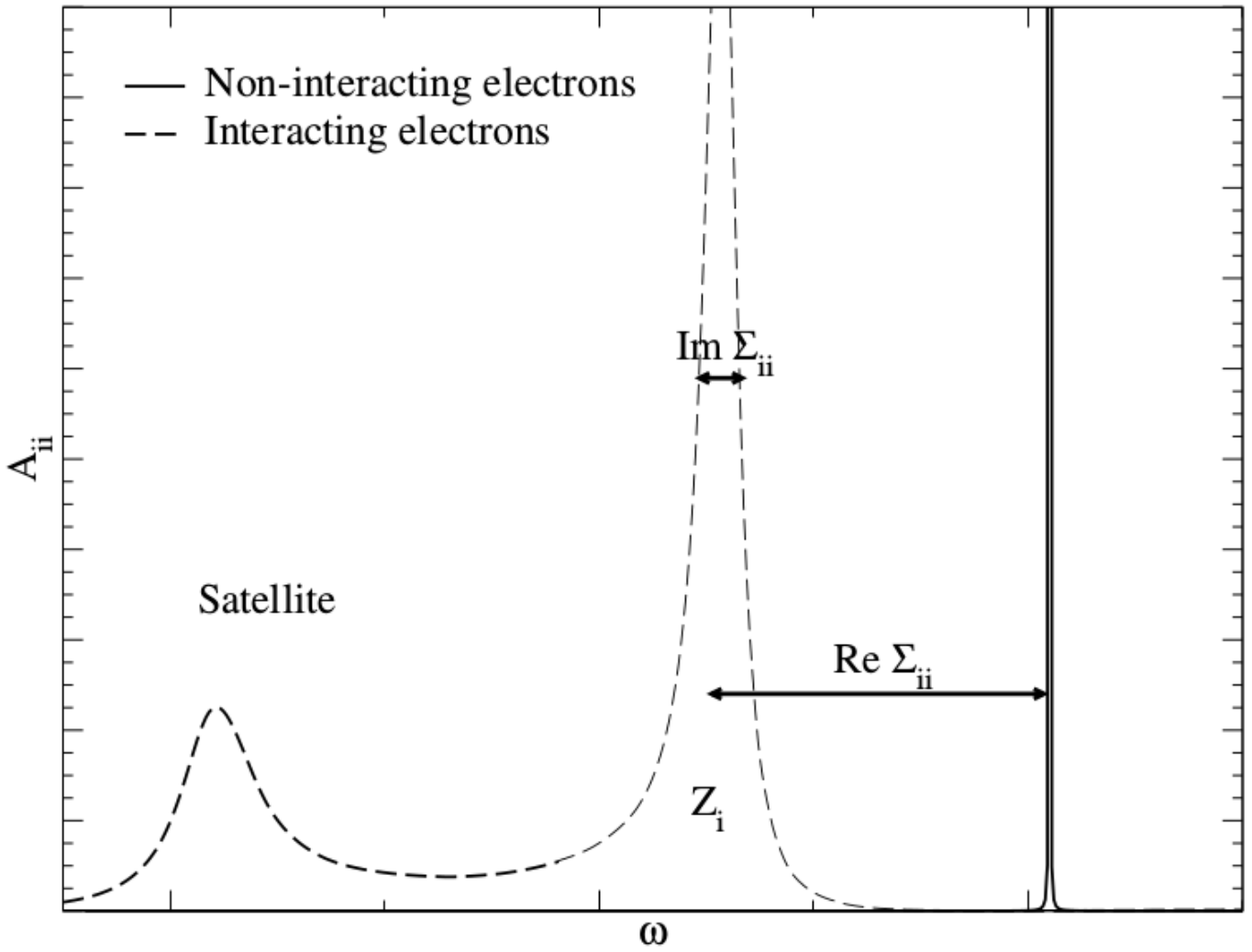
van Schilfgaarde *et al* PRL **96** 226402 (2008)

No more a band gap problem !



Spectral function

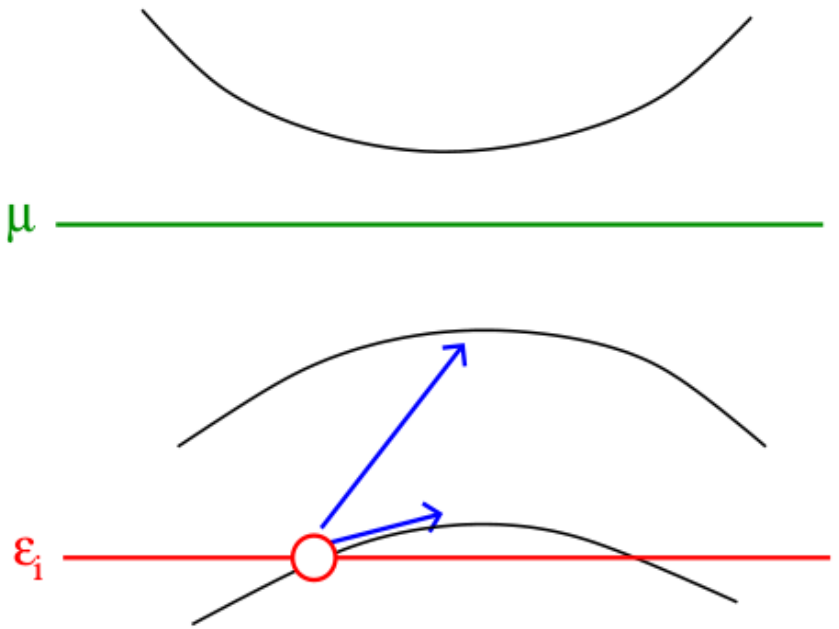
$$A(\omega) = |\mathrm{Im}\, G(\omega)| \;/\; \pi$$



Excitation lifetime

Hole self-energy:

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

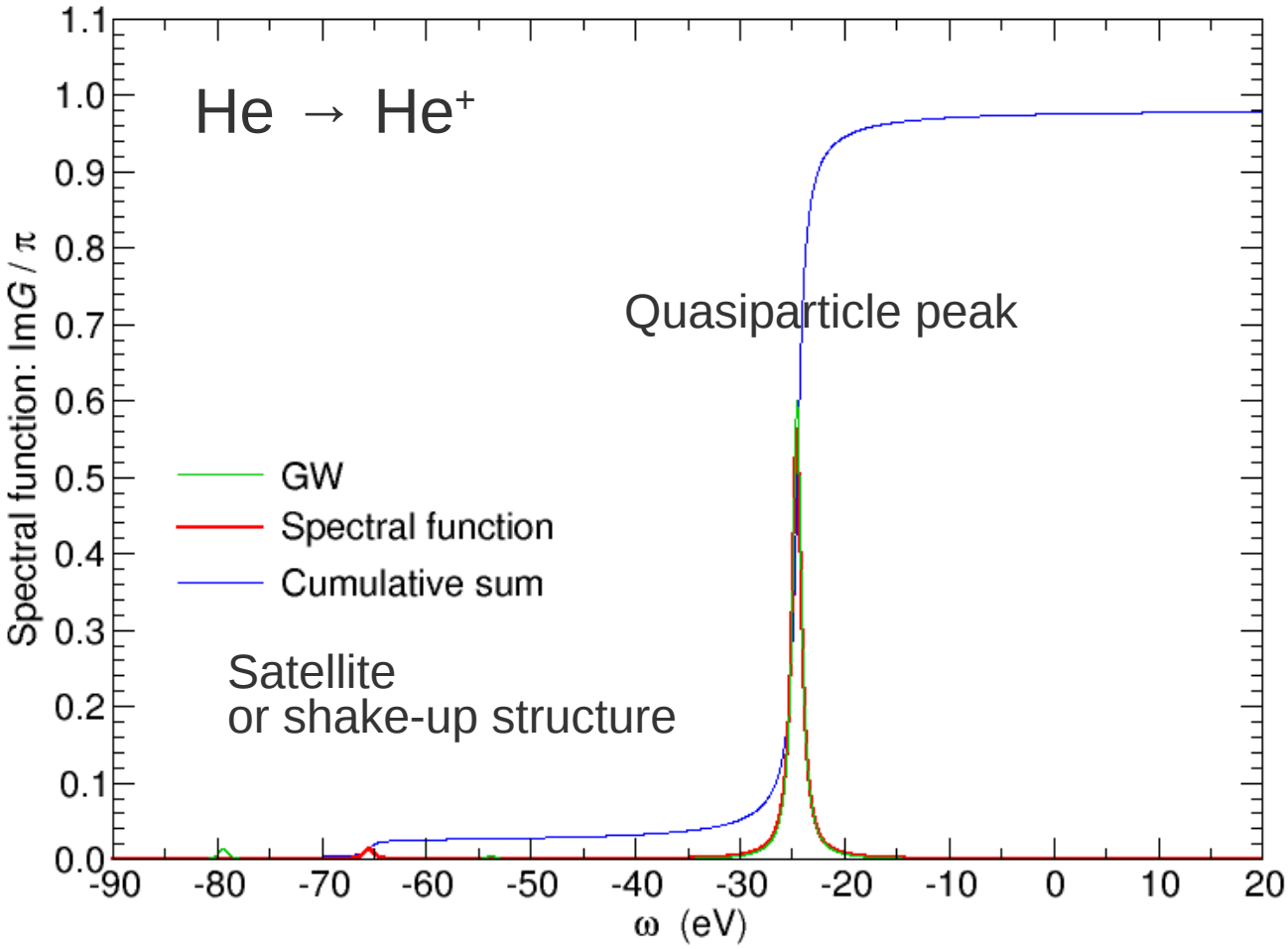


Exact realization of the Lehman decomposition

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

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

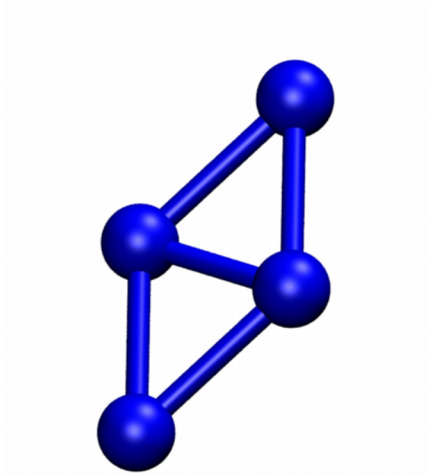
Obtained from FCI calculations



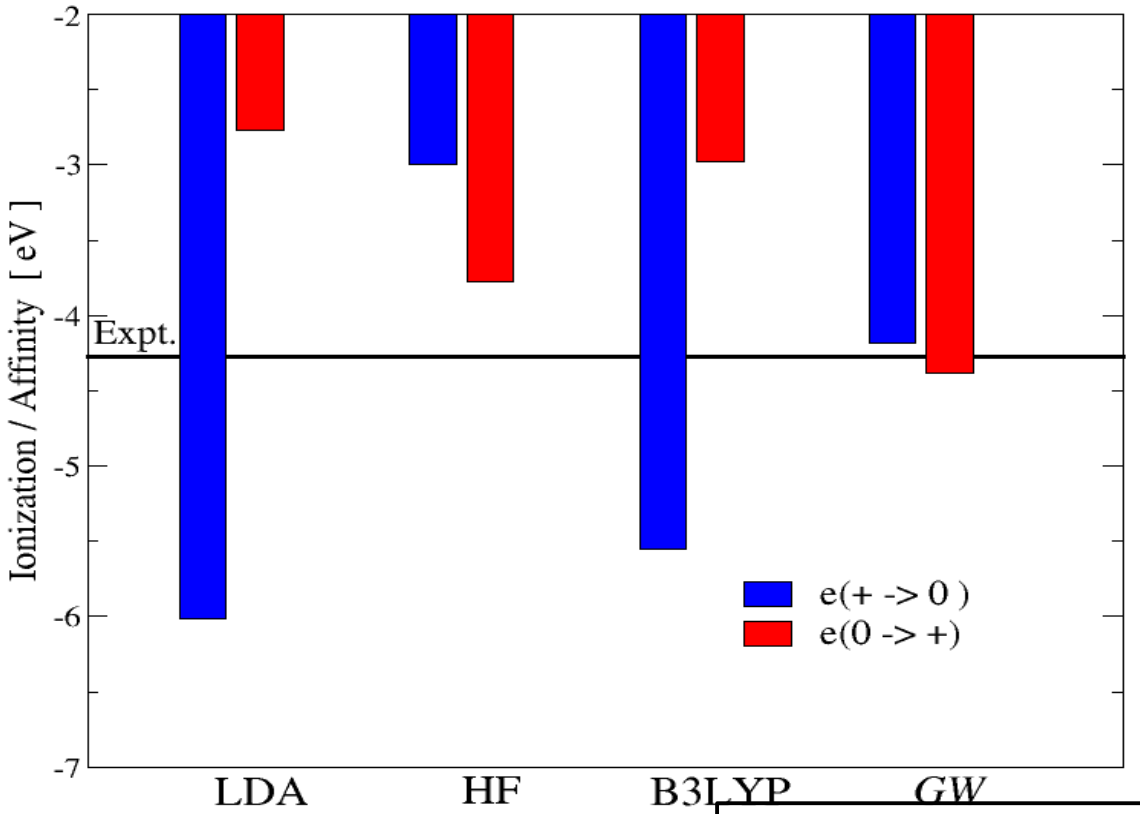
Clusters de sodium

$$Na_4^+ + e^- \Leftrightarrow Na_4$$

$$E_0(Na_4) - E_0(Na_4^+) = \begin{cases} \epsilon(\mathbf{HOMO}, \mathbf{Na_4}) \\ \epsilon(\mathbf{LUMO}, \mathbf{Na_4^+}) \end{cases}$$



Na_4^+/Na_4



Bruneval PRL (2009)

What is the best starting point for G_0W_0?

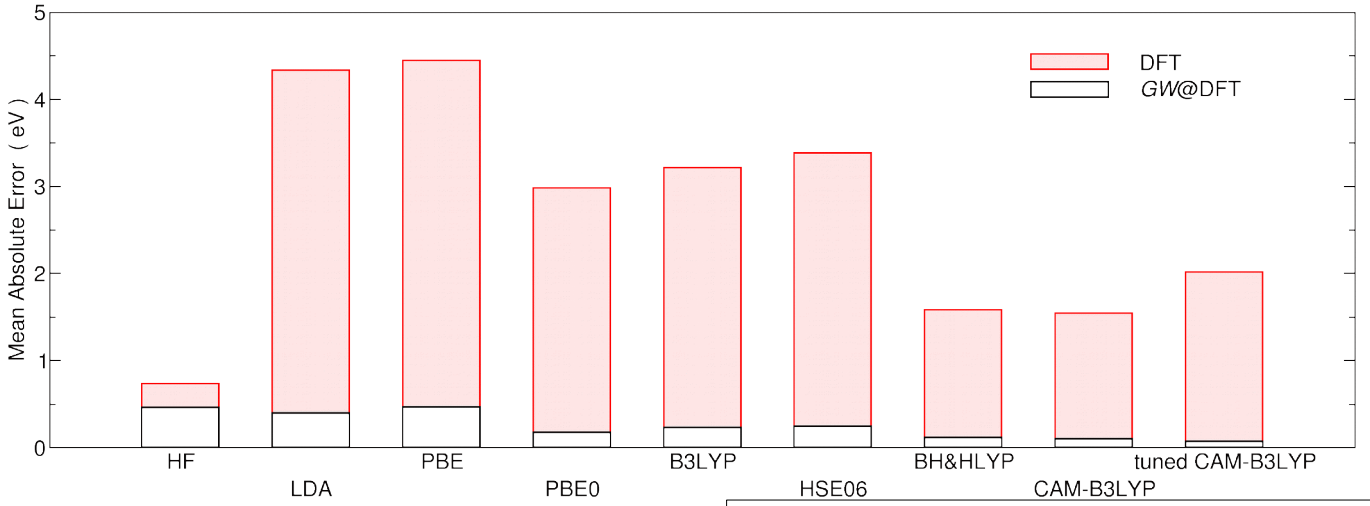
Ionization of small molecules

Journal of Chemical Theory and Computation — Article

Table 1. G_0W_0 HOMO Energy of the 34 Molecules Employing Different Starting Points with the cc-pVQZ Basis Set[a]

	GW@										
starting point	HF	LDA	PBE	PBE0	B3LYP	HSE06	BH&HLYP	CAM-B3LYP	tuned CAM-B3LYP	CCSD(T)	exp
LiH	−8.20	−7.24	−7.07	−7.66	−7.53	−7.47	−7.91	−8.03	−8.07	−7.94	
Li_2	−5.36	−5.13	−5.12	−5.29	−5.23	−5.19	−5.30	−5.32	−5.38	−5.17	
LiF	−11.62	−10.61	−10.37	−10.93	−10.82	−10.89	−11.29	−11.49	−11.45	−11.51	
Na_2	−4.98	−4.91	−4.89	−4.97	−4.96	−4.91	−4.97	−4.98	−5.01	−4.82	
NaCl	−9.36	−8.56	−8.43	−8.82	−8.77	−8.70	−9.06	−9.15	−9.22	−9.13	−9.80
CO	−14.97	−13.63	−13.55	−14.00	−13.92	−13.92	−14.36	−14.26	−14.11	−14.05	
CO_2	−14.38	−13.45	−13.32	−13.68	−13.57	−13.59	−13.91	−13.91	−13.82	−13.78	
CS	−13.08	−10.97	−10.93	−11.43	−11.31	−11.33	−11.79	−11.69	−11.55	−11.45	
C_2H_2	−11.65	−11.10	−11.08	−11.27	−11.23	−11.21	−11.40	−11.41	−11.41	−11.42	−11.49
C_2H_4	−10.85	−10.39	−10.37	−10.53	−10.52	−10.48	−10.65	−10.67	−10.66	−10.69	−10.68
CH_4	−14.86	−14.07	−14.03	−14.30	−14.27	−14.23	−14.52	−14.53	−14.48	−14.40	−14.40[44]
CH_3Cl	−11.74	−11.02	−10.98	−11.21	−11.18	−11.15	−11.41	−11.43	−11.41	−11.41	−11.29
CH_3OH	−11.69	−10.70	−10.64	−10.97	−10.89	−10.88	−11.20	−11.22	−11.17	−11.08	−10.96
CH_3SH	−9.81	−9.18	−9.17	−9.36	−9.35	−9.30	−9.53	−9.55	−9.53	−9.49	

Hybrids perform better, preferably with a large content of EXX ~ 50 %

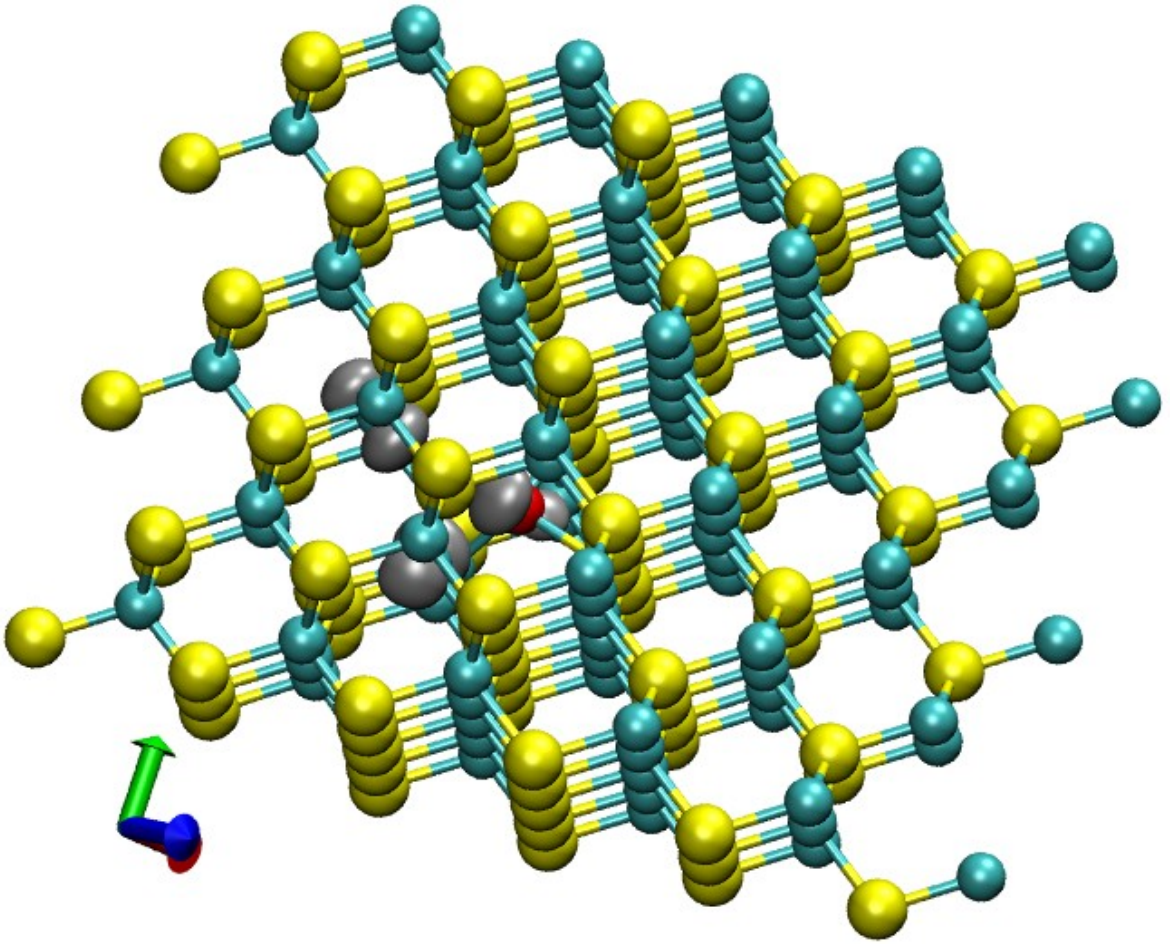


F. Bruneval & MAL Marques, JCTC (2013)

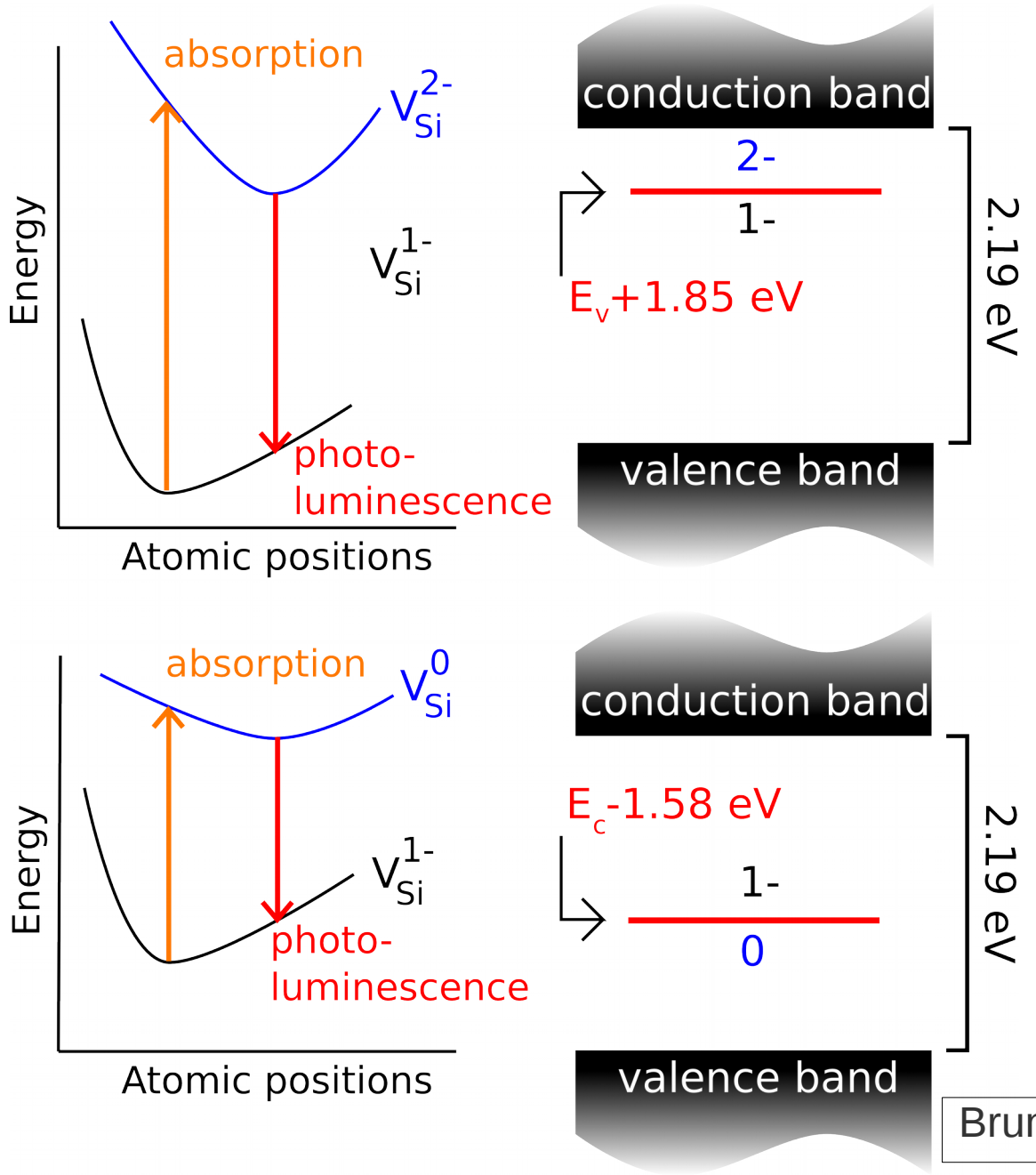
Defect calculation within GW approximation

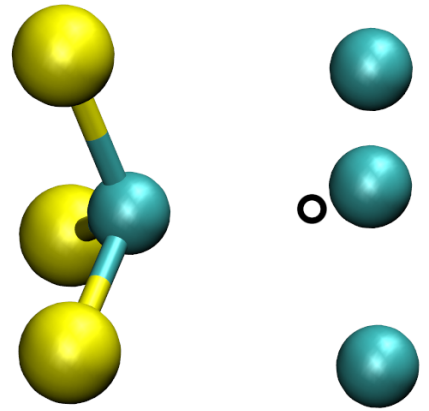
Up to 215 atoms

Cubic silicon carbide



Photoluminescence of V_{Si}

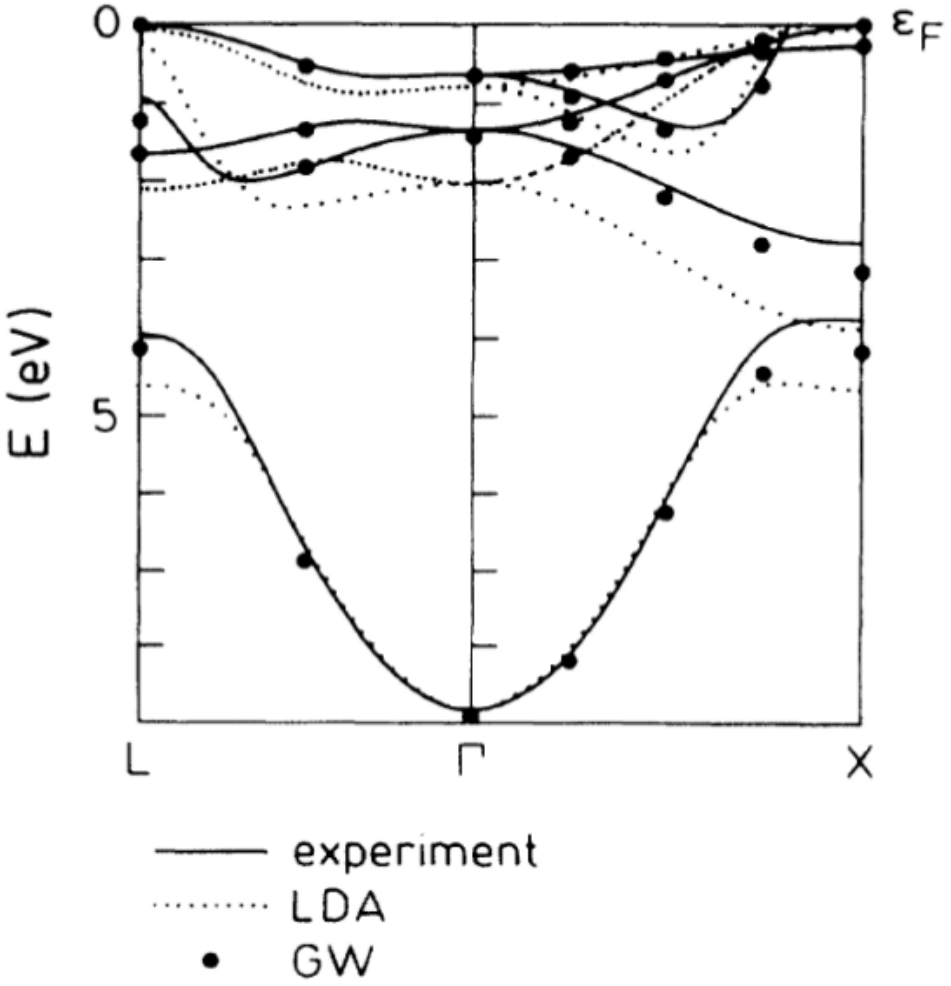




Bruneval and Roma PRB (2011)

3d metal band structure

Nickel

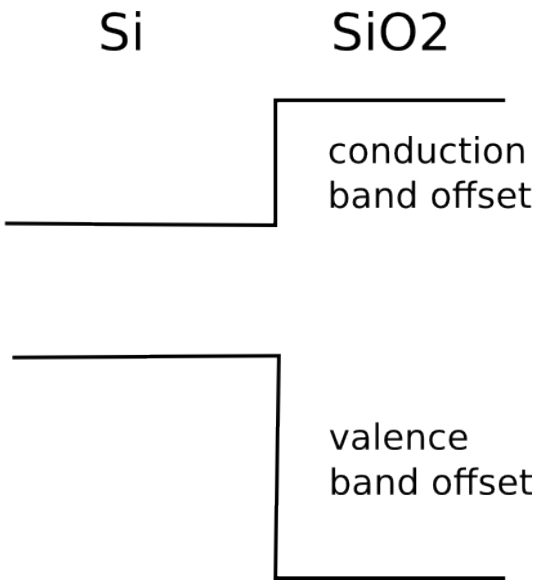


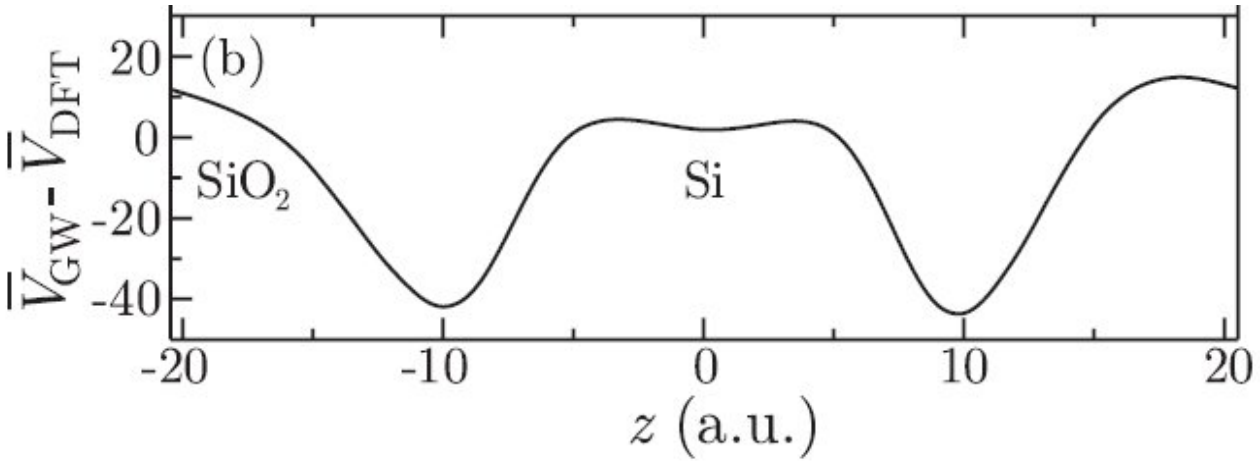
from F. Aryasetiawan, PRB **46** 13051 (1992).

Band Offset at the interface between two semiconductors

Very important for electronics!

Example: Si/SiO_2 interface for transistors





GW correction with respect to LDA

R. Shaltaf PRL (2008).

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

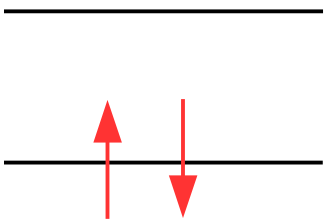
Szabo-Ostlung book chapter 3 teaches how to perform HF in this example:

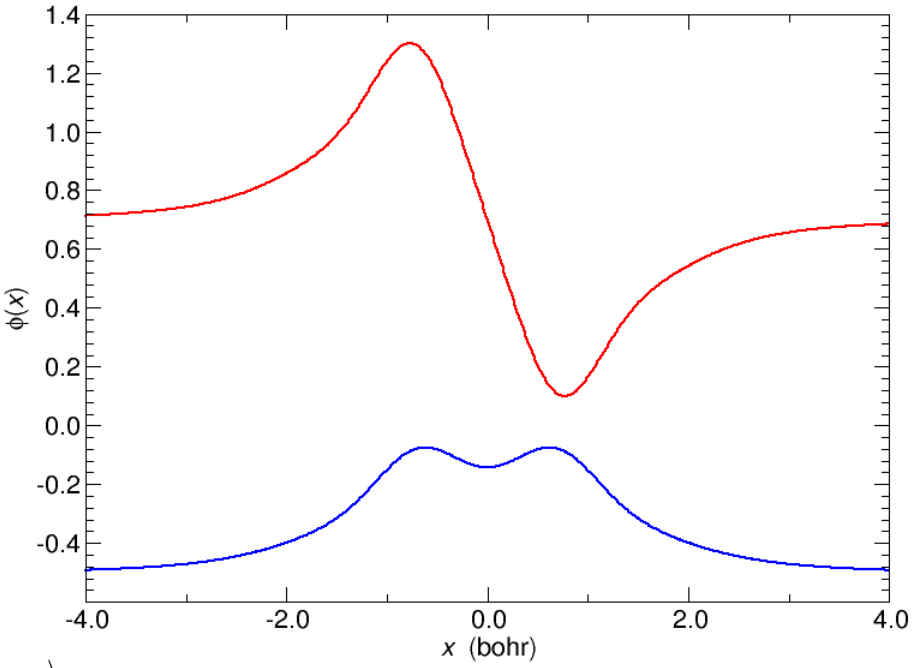
Basis: STO-3G r(H-H) = 1.4 bohr

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:

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

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

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

Atomic units

Exercice: H_2 in minimal basis: GW@HF

Find the location of the poles of W

Diagonalize the RPA equation

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

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

$v = (12|1/r|12) = 0.181$

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

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

Exercice: H_2 in minimal basis: GW@HF

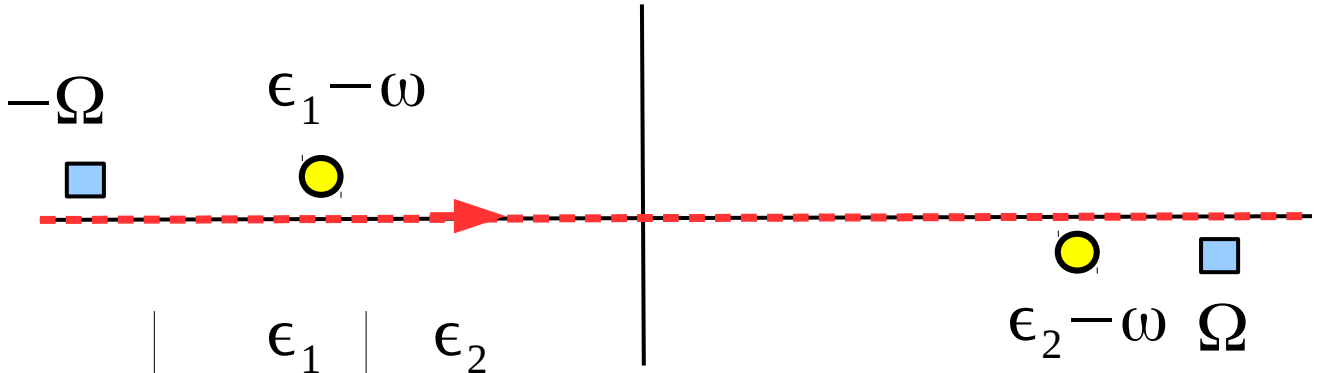
$$\Sigma_c(\omega) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega' G(\omega+\omega') W_p(\omega')$$

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

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

$$\Sigma_c(\omega) = \frac{i}{2\pi} \sum_{i\in\{1,2\}} \sum_{s\in\{1\to2,\,2\to1\}} \int_{-\infty}^{+\infty} d\omega' \frac{\alpha}{\omega+\omega'-\epsilon_i \pm i\eta} \times \frac{\beta}{\omega'-\Omega\pm i\eta}$$

Integration in the complex plane:



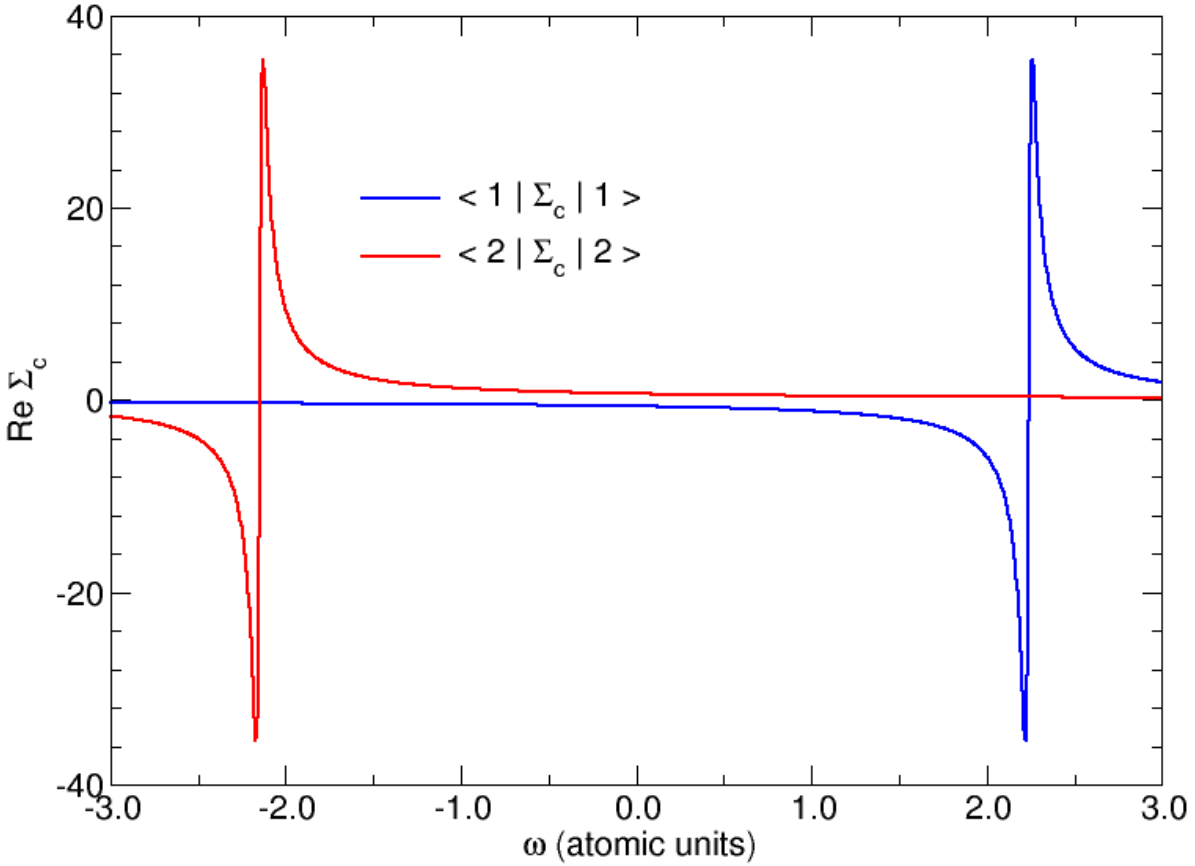
Pole table:

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

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



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

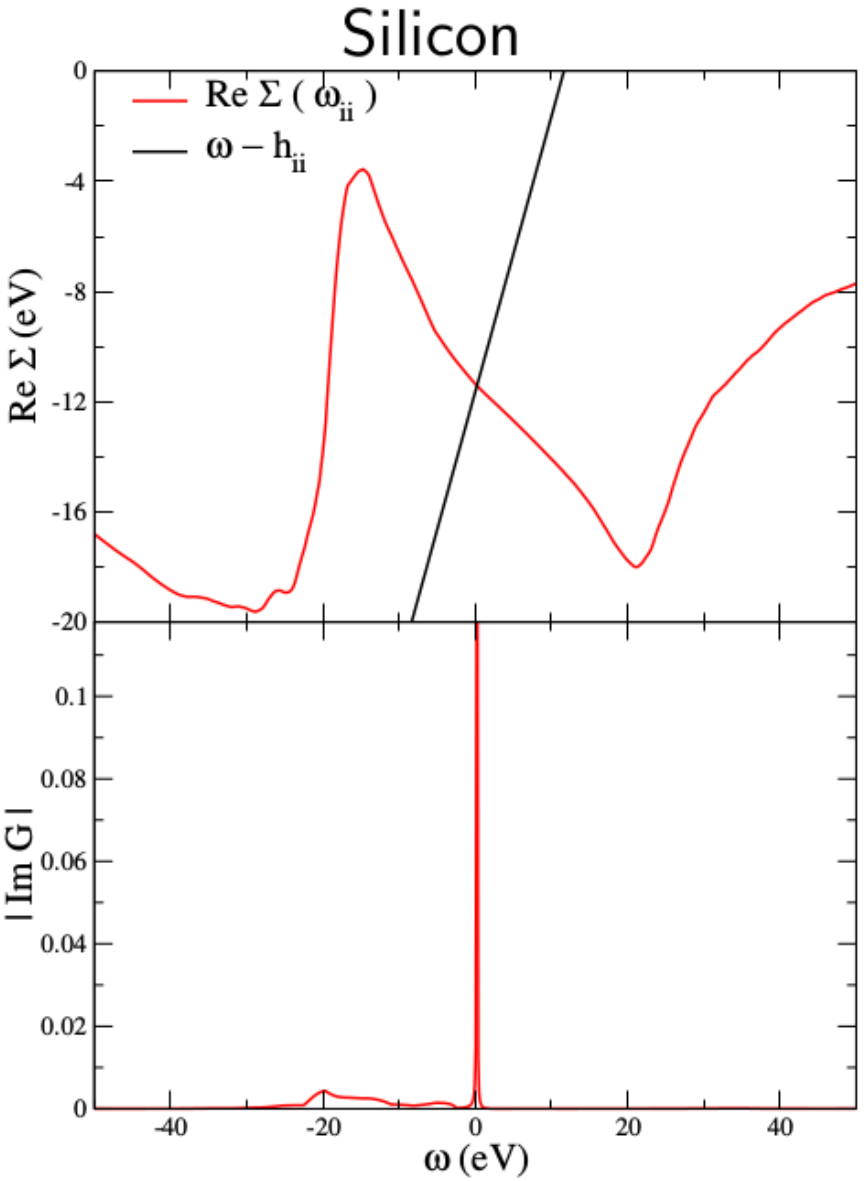
Jouvence, Quantum Materials 2018

Exercice: H_2 in minimal basis: GW@HF

Same conclusions hold for
a many-state case:

Bulk silicon

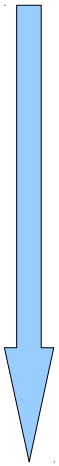
Plasmon frequency ~ 17 eV
Occupied states ~ -5 - 0 eV
Empty states ~ +2 - … eV



Exercise 1

Green's function in frequency domain

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



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

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

Exercise 2:

Fock exchange from Green's functions

$$\Sigma_x(1,2) = iG(1,2)v(1^+,2) \quad \Longrightarrow \quad \Sigma_x(\boldsymbol{r_1}, \boldsymbol{r_2}, \omega) = -\sum_{i\text{occ}} \frac{\phi_i(\boldsymbol{r_1})\phi_i^*(\boldsymbol{r_2})}{|\boldsymbol{r_1} - \boldsymbol{r_2}|}$$

Exercise 3: let's play with Dyson equations

1) The multiple faces of the Dyson equation

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

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

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

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

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

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

2) Combining the Dyson equations

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

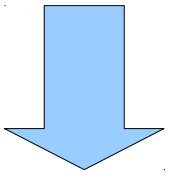
$$1 = \left[G_{\mathrm{KS}}^{-1} - \left(\Sigma - v_{xc}\right)\right] G$$

$$1 = \left[\omega - h_0 - \Sigma\right] G$$

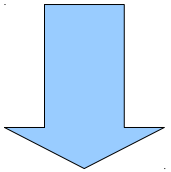
Exercise 4

Derive the standard Adler-Wiser formula (1963):

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



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

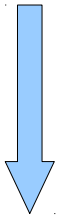


$$\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega) = \sum_{\substack{i\,\mathrm{occ}\\ j\,\mathrm{virt}}} \phi_i(\boldsymbol{r}_1)\phi_i^*(\boldsymbol{r}_2)\phi_j(\boldsymbol{r}_2)\phi_j^*(\boldsymbol{r}_1) \times\left[\frac{1}{\omega-(\epsilon_j-\epsilon_i)-i\eta}-\frac{1}{\omega-(\epsilon_i-\epsilon_j)+i\eta}\right]$$

Exercise 5

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

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



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

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

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

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).
Upward arrows are electrons, downward arrows are hole.

2. Diagrams should be connected.

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

4. Each intersection should conserve the particle numbers.

5. A valid diagram cannot be cut (by removing an arrow) into another lower order self-energy.