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

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I. Introduction: going beyond DFT

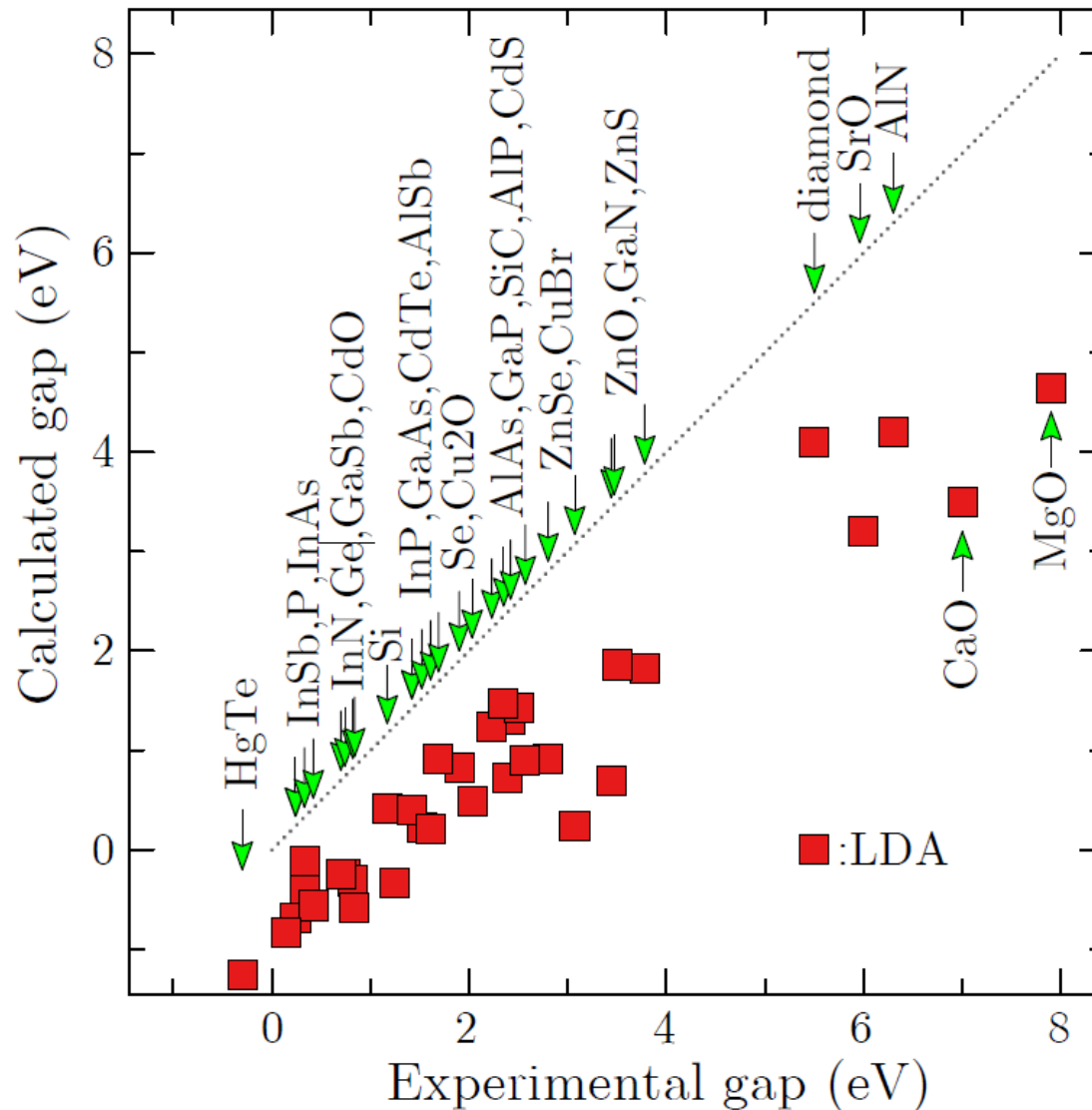
II. Introduction of the Green's function

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

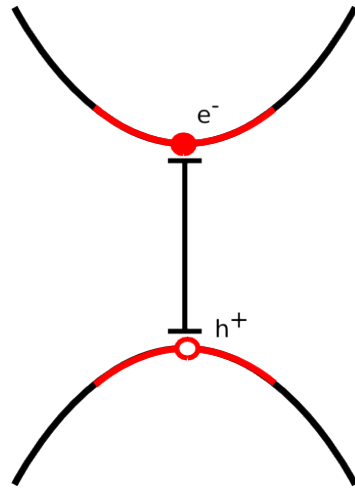


Band gap problem!

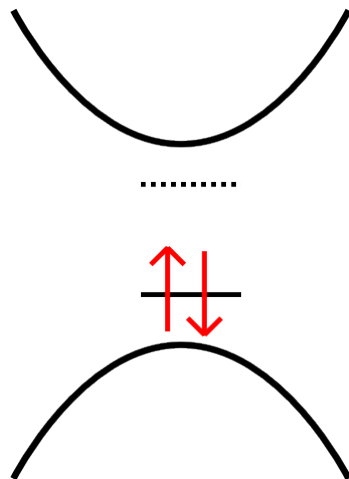


A pervasive problem

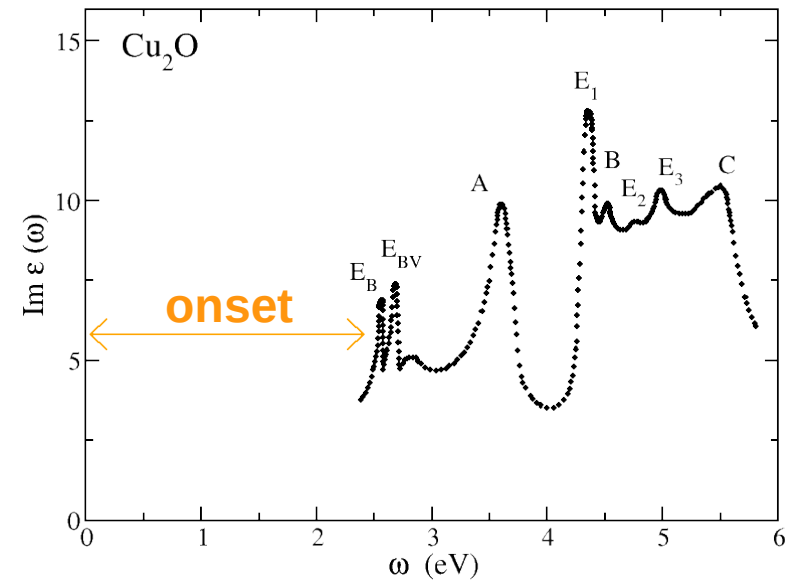
Effective masses
for transport in semiconductors



Defect formation energy,
dopant solubility



Optical absorption



Photoemission

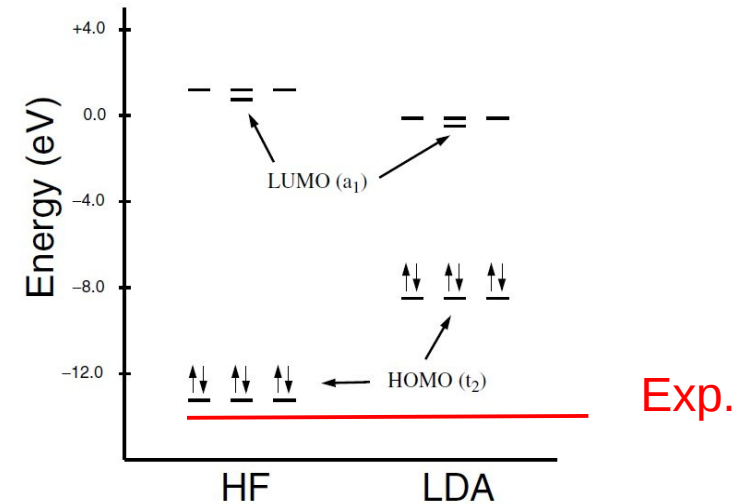


FIG. 1. Single-particle Hartree-Fock and local density approximation eigenvalue spectra (eV) for the SiH_4 molecule.

Gap re-normalization by a (metallic) substrate

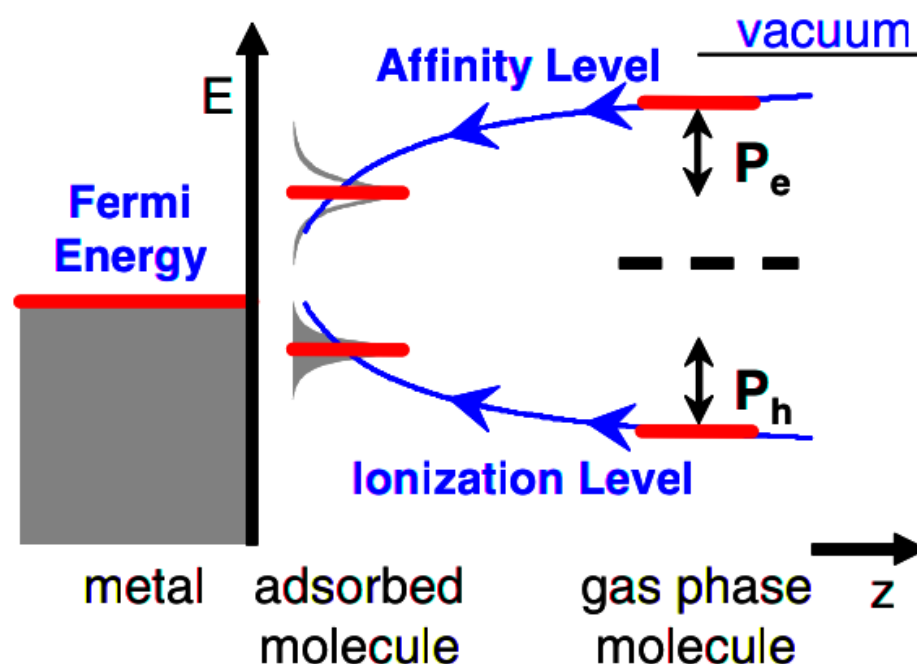


FIG. 1 (color online). Schematic energy level diagram indicating polarization shifts in the frontier energy levels (ionization and affinity) of a molecule upon adsorption on a metal surface.

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

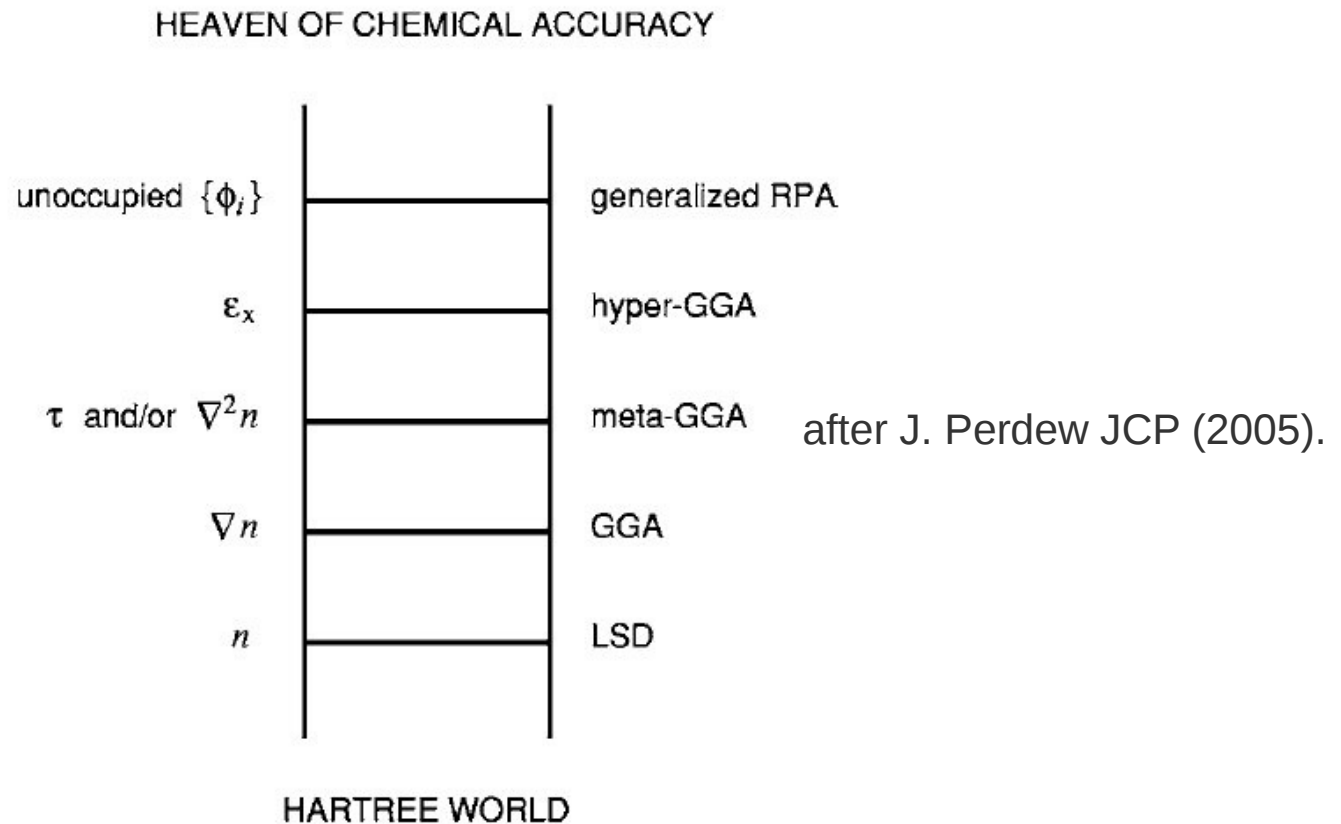


FIG. 1. Jacob's ladder of density functional approximations to the exchange-correlation energy.

Need to change the overall framework!

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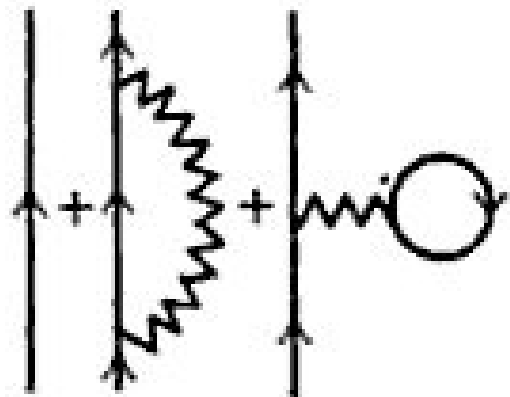
V. Applications

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

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


The diagram shows the expansion of the Green's function $G(\mathbf{r}t, \mathbf{r}'t')$ as a sum of three terms. The first term is a single vertical line with an upward arrow. The second term is a vertical line with an upward arrow, followed by a wavy interaction line (representing a Coulomb interaction) that connects to another vertical line with an upward arrow. The third term is a vertical line with an upward arrow, followed by a wavy interaction line that connects to a circle (representing a self-energy insertion), which then connects to a final vertical line with an upward arrow. Plus signs are placed between the first and second terms, and between the second and third terms.

The Green's function

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

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

- 1 $\Psi^\dagger(\mathbf{r} t)|N, 0\rangle$ is a (N+1) electron wavefunction not necessarily in the ground state
- 2 $\Psi^\dagger(\mathbf{r}' t')|N, 0\rangle$ is another (N+1) electron wavefunction

Let's compare the two of them!

Green's function definition

$$\langle N, 0 | \underbrace{\Psi(\mathbf{r}t)}_1 \underbrace{\Psi^\dagger(\mathbf{r}'t')}_2 | N, 0 \rangle$$

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

Mesures how an extra electron propagates from $(\mathbf{r}'t')$ to $(\mathbf{r}t)$.

Green's function definition

$$\underbrace{\langle N, 0 | \Psi^\dagger(\mathbf{r}' t')}_{\text{2}} \underbrace{\Psi(\mathbf{r} t) | N, 0 \rangle}_{\text{1}}$$
$$= i G^h(\mathbf{r}' t', \mathbf{r} t) \quad \text{for } t' > t$$

Mesures how a missing electron (= a hole) propagates from $(\mathbf{r} t)$ to $(\mathbf{r}' t')$.

Final expression for the Green's function

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

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

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

Closure relation

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

Lehman representation:

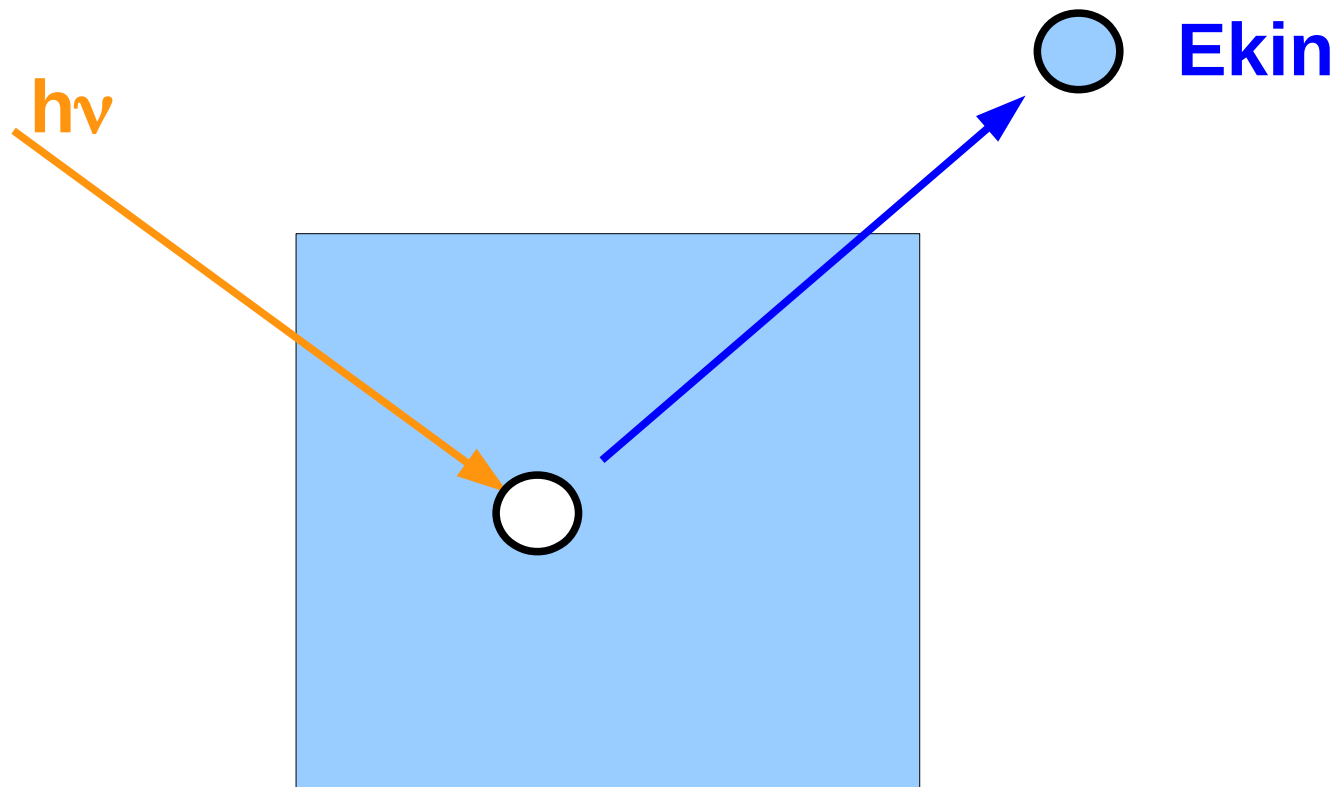
$$G(\mathbf{r}, \mathbf{r}', \omega) = \sum_i \frac{f_i(\mathbf{r}) f_i^*(\mathbf{r}')}{\omega - \epsilon_i \pm i\eta}$$

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

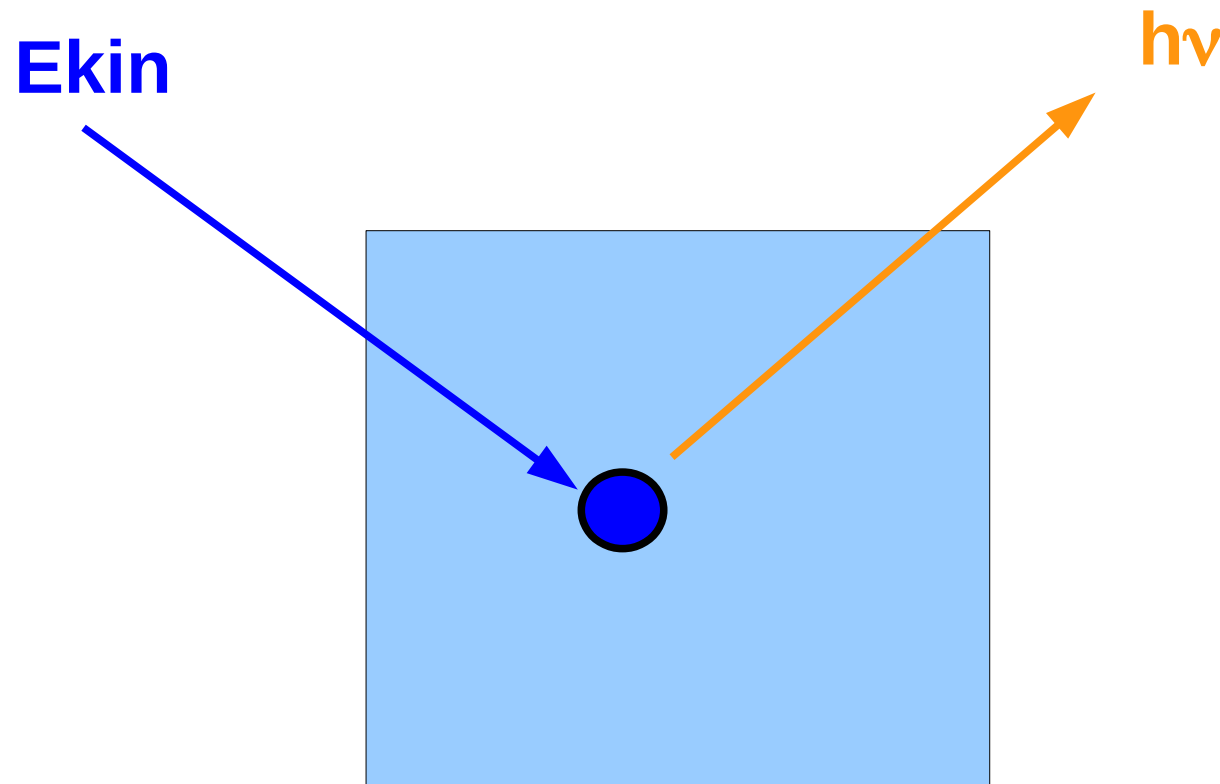
after

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

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:

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

Other properties of the Green's function

Get the electron density:

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

Galitskii-Migdal formula for the total energy:

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

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

$$\langle O \rangle = \lim_{t \rightarrow t'} \operatorname{Tr} [O G]$$

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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

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

In short:

$$[\omega - h_0] G_0 = 1 \quad \text{or} \quad G_0^{-1} = [\omega - h_0]$$

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

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

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

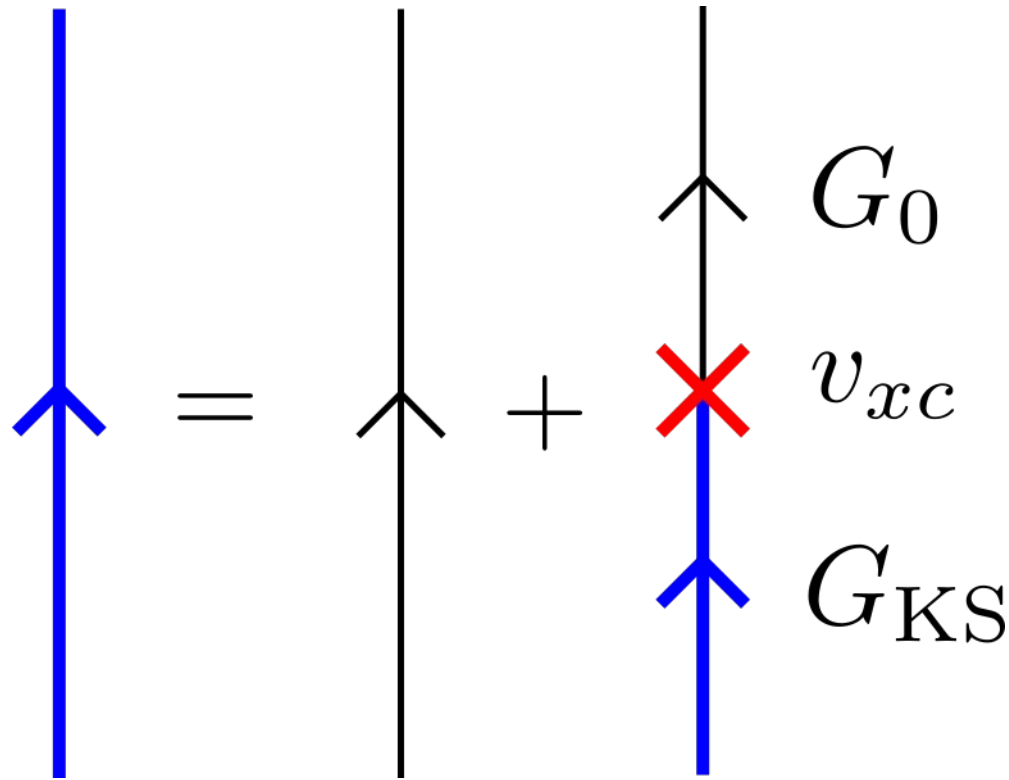
$$\hookrightarrow [G_0^{-1} - v_{\text{xc}}] G_{\text{KS}} = 1$$

$$\hookrightarrow G_{\text{KS}} = G_0 + G_0 v_{\text{xc}} G_{\text{KS}}$$

$$\hookrightarrow G_{\text{KS}} = G_0 + G_0 v_{\text{xc}} G_0 + G_0 v_{\text{xc}} G_0 v_{\text{xc}} G_0 + \dots$$

Exercise

A first contact with diagrams



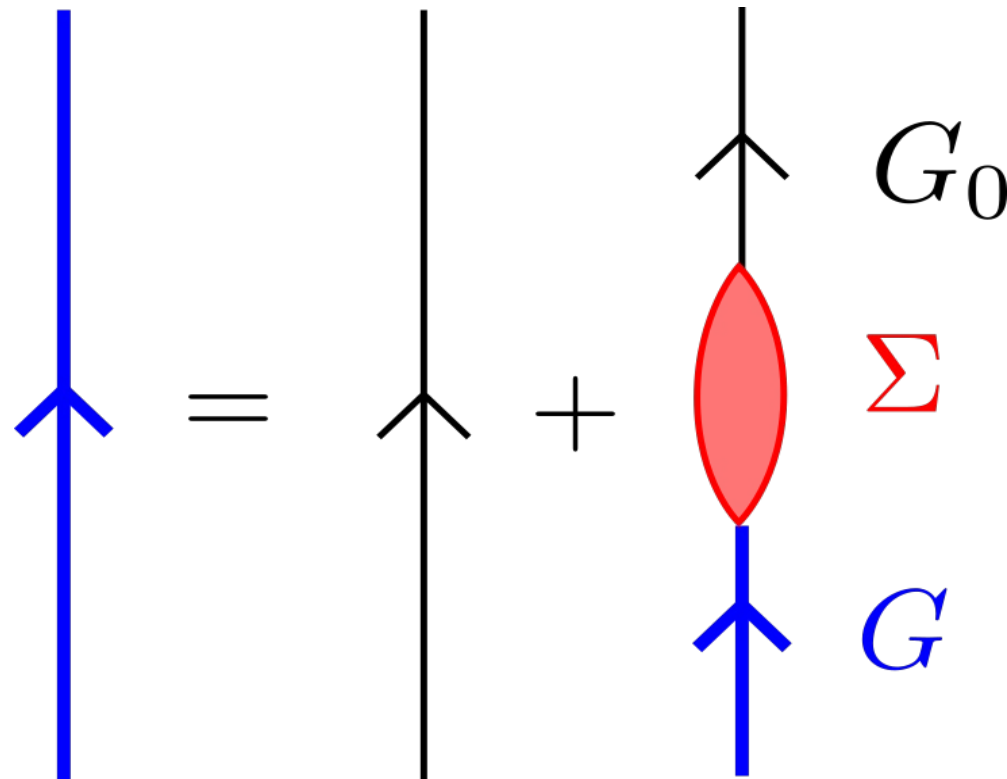
$$G_{\text{KS}}(1,2) = G_0(1,2) + \int d3 G_0(1,3) v_{xc}(3) G_{\text{KS}}(3,2)$$

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 needs G_3

G_3 needs G_4

G_4 needs 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):

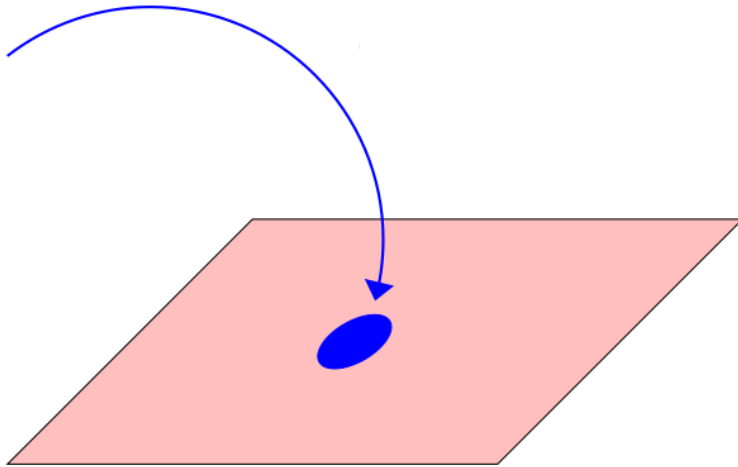
- Introduce the electrostatic response V to U $V(1) = U(1) - i \int d2 v(1,2) \delta G(2,2)$
- Calculate the variations of G with respect to V

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

1st order is GW

Shifting from U to V

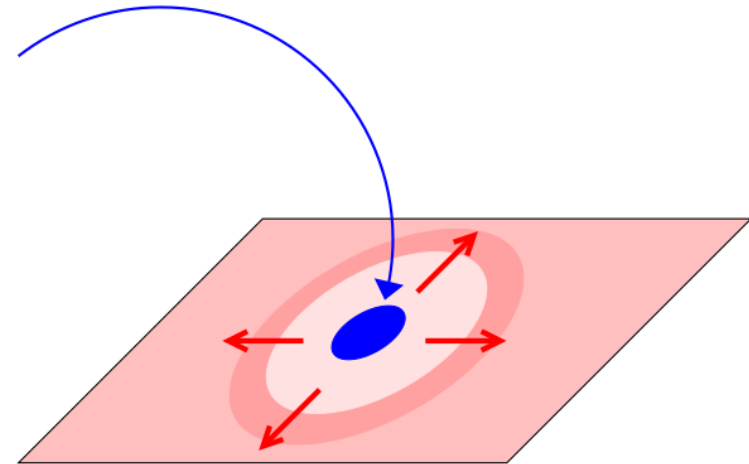
$$U(1) = \varepsilon \delta(\mathbf{r} - \mathbf{r}_1) \delta(t - t_1)$$



Everything is functional of U

$$G[U]$$

$$U(1) = \varepsilon \delta(\mathbf{r} - \mathbf{r}_1) \delta(t - t_1)$$



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

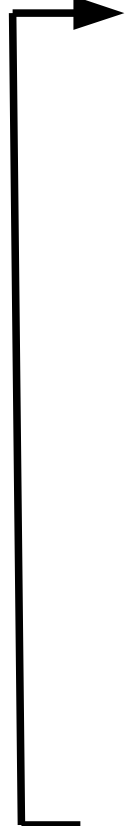
V also includes the electrostatic response

Everything is functional of V

$$G[V]$$

Hedin's coupled equations

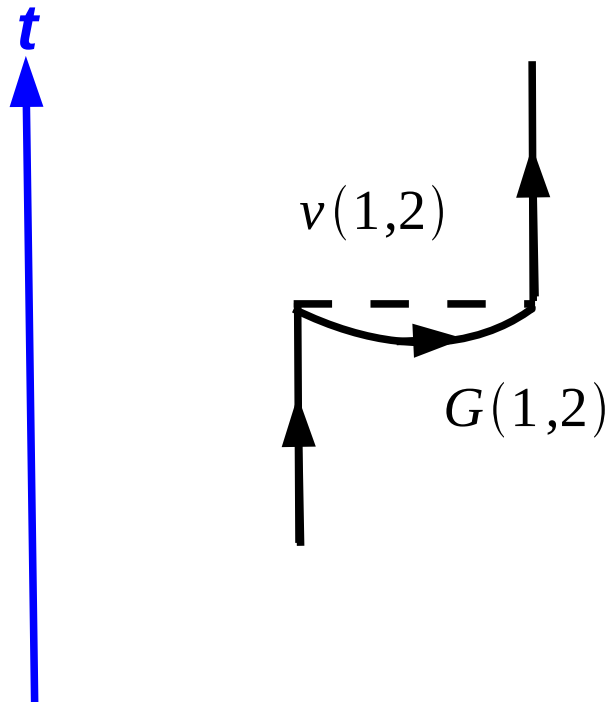
6 coupled equations: $1=(\mathbf{r}_1 t_1 \sigma_1)$ $2=(\mathbf{r}_2 t_2 \sigma_2)$



$G(1,2)=G_0(1,2)+\int d^3 4 G_0(1,3) \Sigma(3,4) G(4,2)$	Dyson equation
$\Sigma(1,2)=i \int d^3 4 G(1,3) W(1,4) \Gamma(4,2,3)$	self-energy
$\Gamma(1,2,3)=\delta(1,2) \delta(1,3)+\int d^4 567 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(5,7) \Gamma(6,7,3)$	vertex
$\chi_0(1,2)=-i \int d^3 4 G(1,3) G(4,1) \Gamma(3,4,2)$	polarizability
$\epsilon(1,2)=\delta(1,2)-\int d^3 v(1,3) \chi_0(3,2)$	dielectric matrix
$W(1,2)=\int d^3 \epsilon^{-1}(1,3) v(3,2)$	screened Coulomb interaction

Simplest approximation

$$\Sigma(1,2) = iG(1,2)v(1^+,2) \quad \longrightarrow \quad \text{Fock exchange}$$



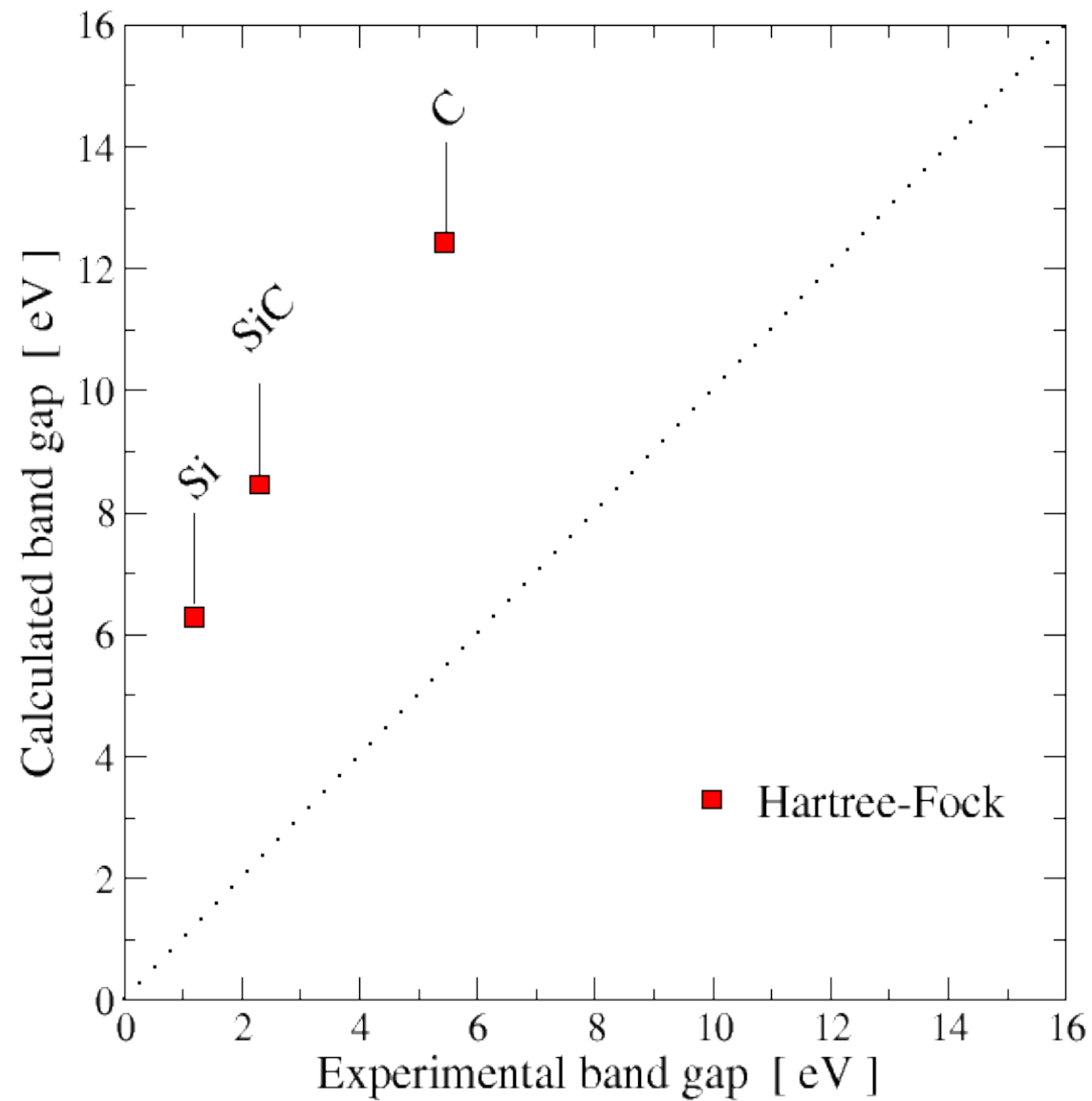
Dyson equation:

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

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

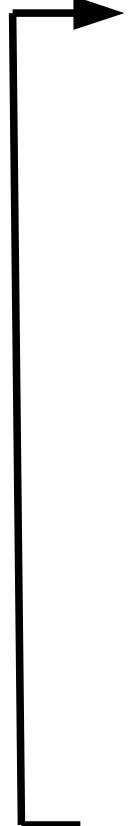
Not enough: Hartree-Fock is known to perform poorly for solids

Hartree-Fock approximation for band gaps



Hedin's coupled equations

6 coupled equations:


$$G(1,2) = G_0(1,2) + \int d^3 4 G_0(1,3) \Sigma(3,4) G(4,2) \quad \text{Dyson equation}$$
$$\Sigma(1,2) = i \int d^3 4 G(1,3) W(1,4) \Gamma(4,2,3) \quad \text{self-energy}$$
$$\Gamma(1,2,3) = \delta(1,2) \delta(1,3) + \int d^4 567 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(5,7) \Gamma(6,7,3)$$
$$\chi_0(1,2) = -i \int d^3 4 G(1,3) G(4,1) \Gamma(3,4,2)$$
$$\varepsilon(1,2) = \delta(1,2) - \int d^3 v(1,3) \chi_0(3,2)$$
$$W(1,2) = \int d^3 \varepsilon^{-1}(1,3) v(3,2) \quad \text{screened Coulomb interaction}$$

Hedin's coupled equations

6 coupled equations:

$$G(1,2) = G_0(1,2) + \int d^3x d^3y G_0(1,x) \Sigma(x,y) G(y,2)$$

Dyson equation

$$\Sigma(1,2) = i \int d^3x d^3y d^3z G(1,x) W(x,y) \Gamma(y,z,2)$$

self-energy

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int d^3x d^3y d^3z d^3w \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(5,7) \Gamma(6,7,3)$$

$$\chi_0(1,2) = -i \int d^3x d^3y G(1,x) G(x,y) \Gamma(y,2,1)$$

$$\varepsilon(1,2) = \delta(1,2) - \int d^3x v(1,x) \chi_0(x,2)$$

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

screened Coulomb interaction

Hedin's coupled equations

6 coupled equations:

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

Dyson equation

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

self-energy

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int d^4 567 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(5,7) \Gamma(6,7,3)$$

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

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

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

screened Coulomb interaction

Here comes the GW approximation

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

GW approximation

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

RPA approximation

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

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

Let us play with diagrams

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

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

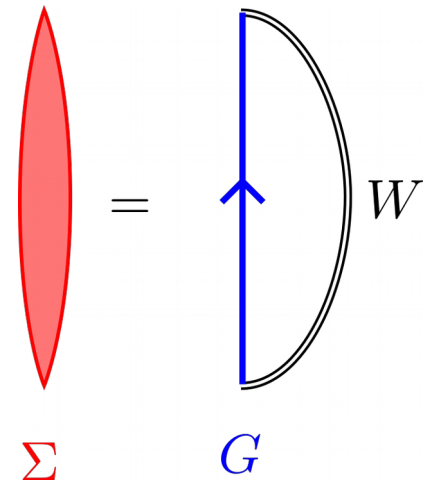
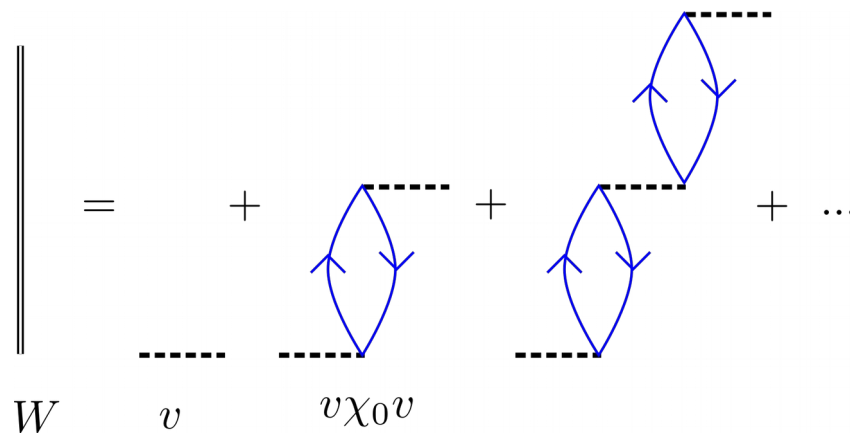
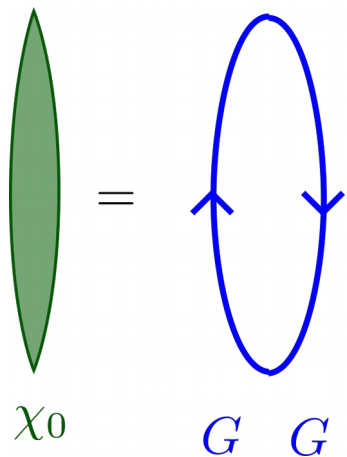
$$\varepsilon(1,2) = \delta(1,2) - \int d^3v \, v(1,3) \chi_0(3,2)$$

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

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

$$= v + v \chi_0 v + v \chi_0 v \chi_0 v + \dots$$

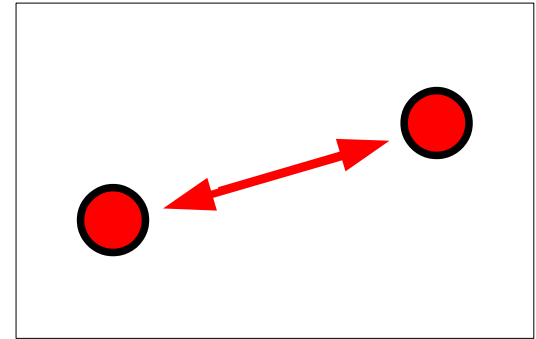
Infinite summation over bubble (or ring) diagrams



What is W?

Interaction between electrons in vacuum:

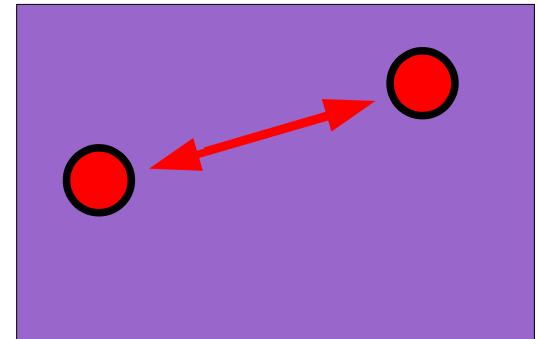
$$v(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$



Interaction between electrons in a homogeneous polarizable medium:

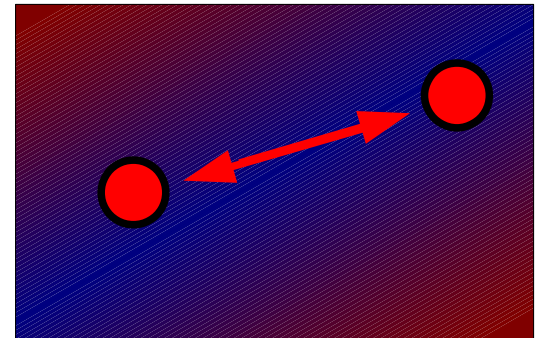
$$W(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$

Dielectric constant
of the medium



Dynamically screened interaction between electrons
in a general medium:

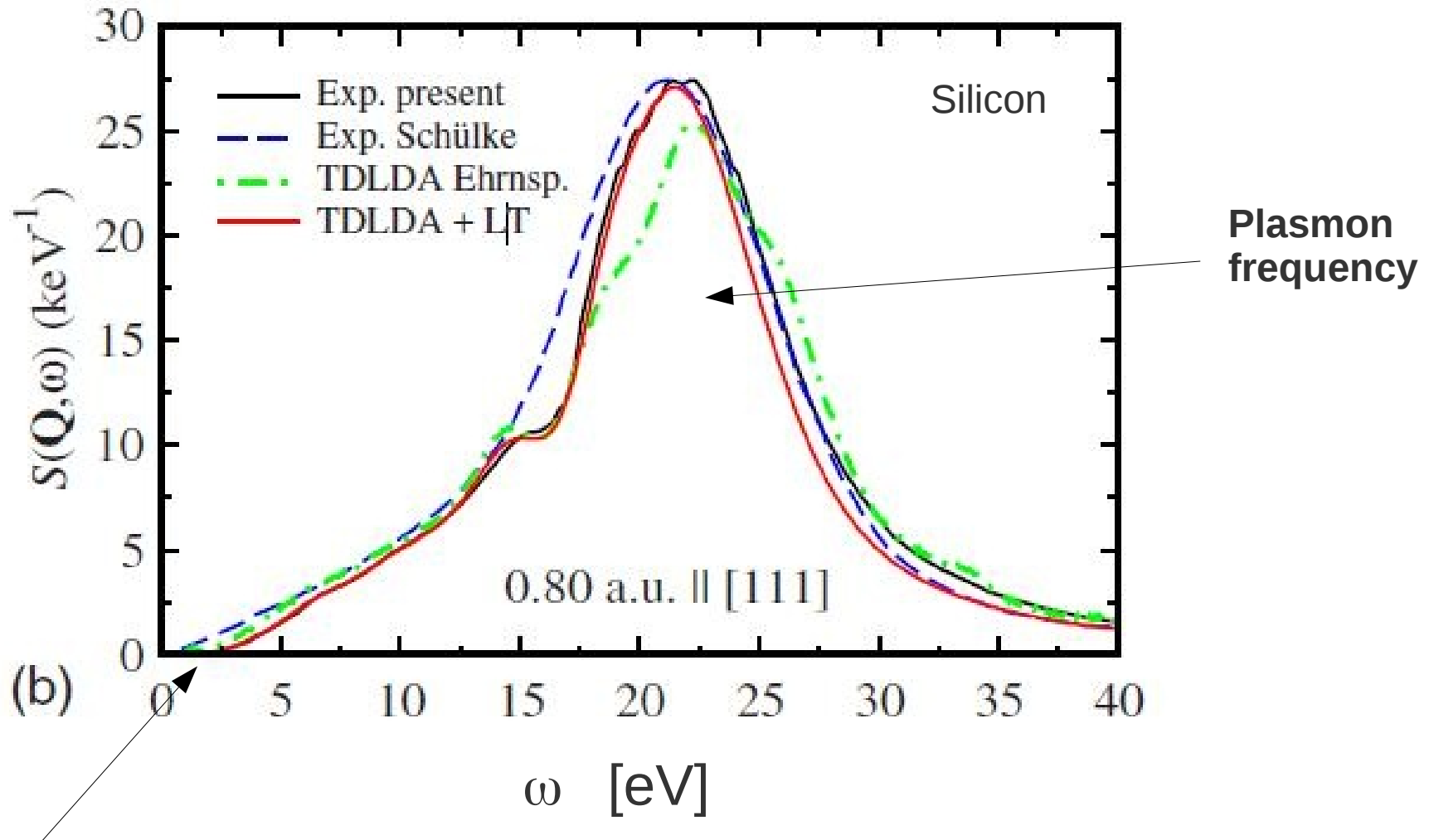
$$W(\mathbf{r}, \mathbf{r}', \omega) = \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r}'' \frac{\epsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega)}{|\mathbf{r}'' - \mathbf{r}'|}$$



W is frequency dependent

W can be measured directly by Inelastic X-ray Scattering

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



Zero below the band gap

H-C Weissker et al. PRB (2010)

Summary

GW viewed as a “super” Hartree-Fock

Hartree-Fock Approximation

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

= bare exchange

GW Approximation

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

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

Bare exchange

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

+ correlation

Non Hermitian
dynamic

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

Exercise

Summary: DFT vs GW

Electronic density

$$\rho(\mathbf{r})$$

Local and static



exchange-correlation potential

$$v_{xc}(\mathbf{r})$$

Approximations:

LDA, GGA, hybrids

Green's function

$$G(\mathbf{r}t, \mathbf{r}'t')$$

Non-local, dynamic
Depends onto empty states



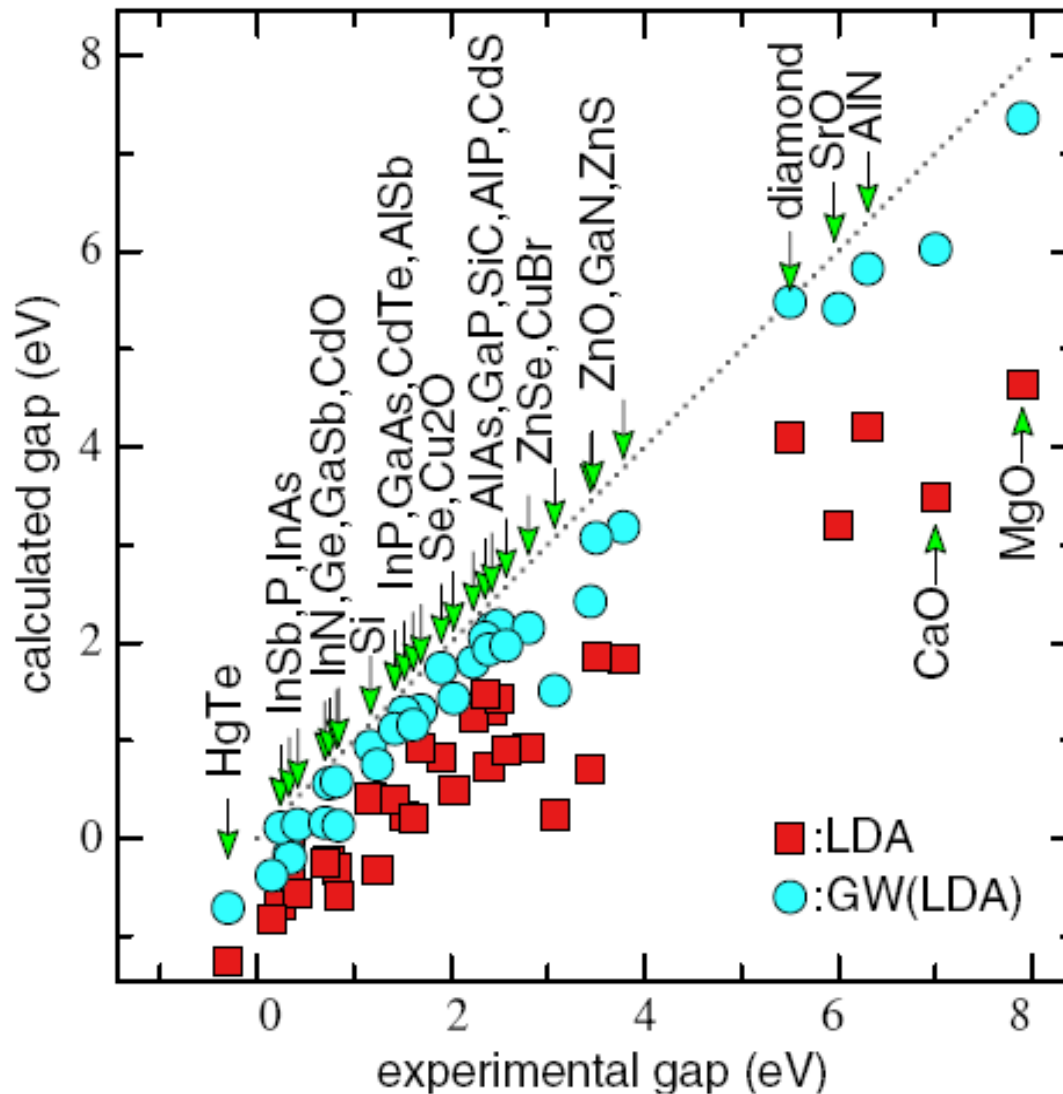
exchange-correlation operator
= self-energy

$$\Sigma_{xc}(\mathbf{r}t, \mathbf{r}'t')$$

GW approximation

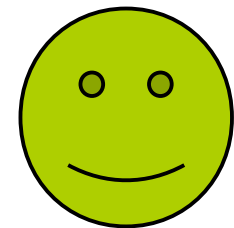
$$\Sigma_{GW}(\mathbf{r}t, \mathbf{r}'t') = iG(\mathbf{r}t, \mathbf{r}', t')W(\mathbf{r}t, \mathbf{r}'t')$$

GW approximation gets good band gap



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

No more a band gap problem !



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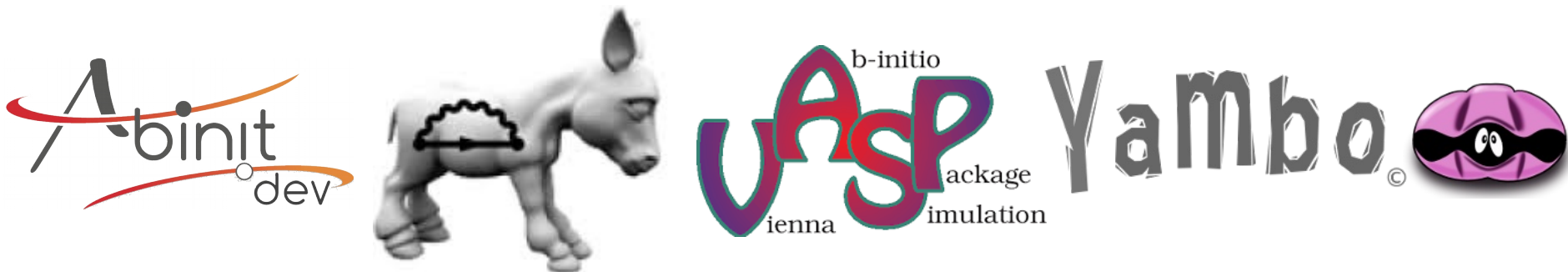
Historical recap of GW calculations

- 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

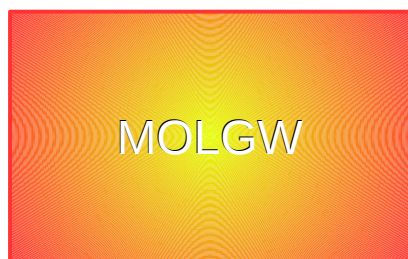
- For periodic solids: Abinit, BerkeleyGW, VASP, Yambo

based on plane-waves (with pseudo or PAW)



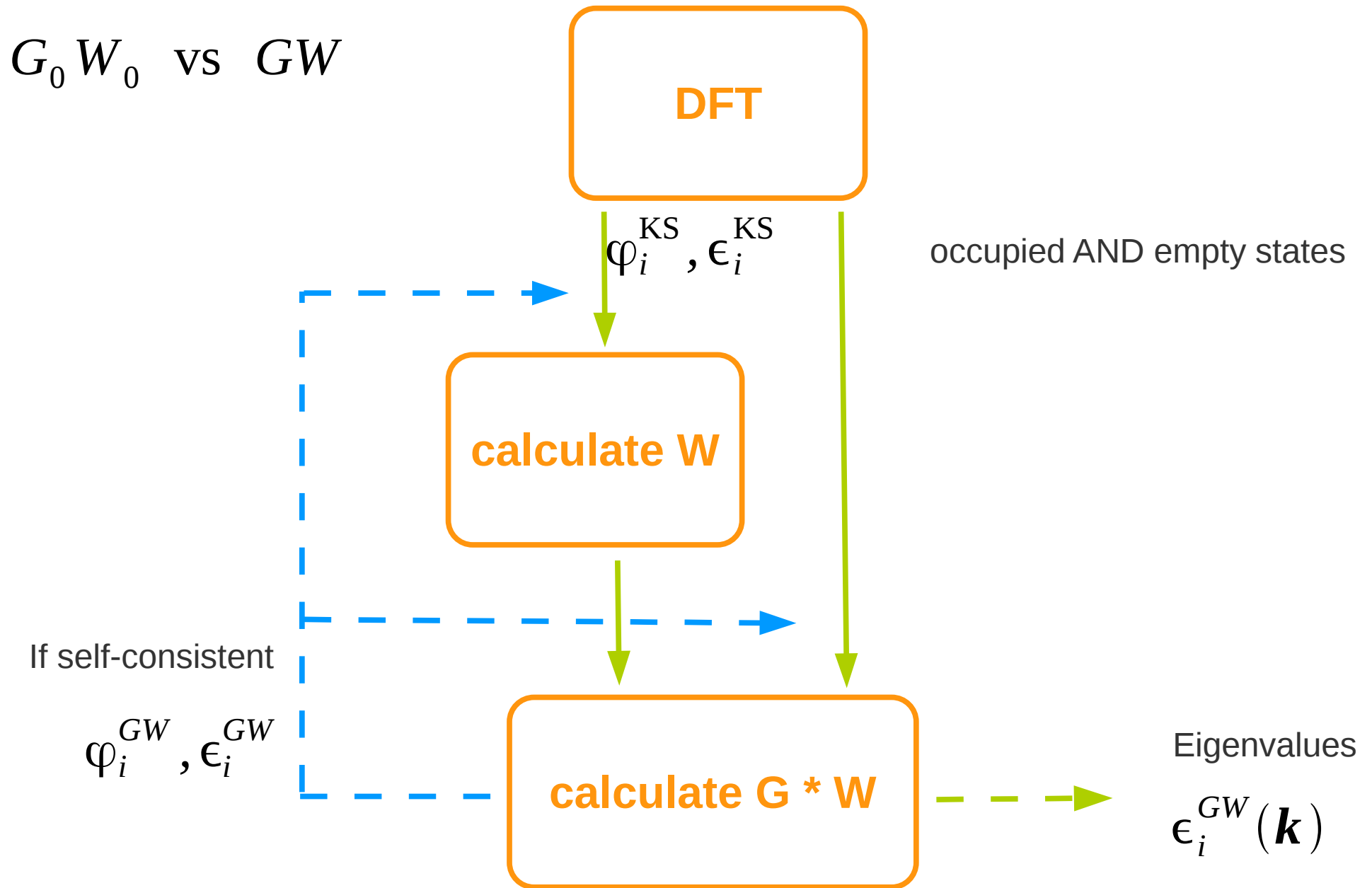
- For finite systems: MolGW, Fiesta, FHI-AIMS

based on localized orbitals (gaussians or slater or other)



What is common to all implementations

Flow chart of a typical GW calculation



How to get G ?

From Kohn-Sham DFT

Remember

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

which means

$$G^{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) = \sum_i \frac{\varphi_i^{\text{KS}}(\mathbf{r}) \varphi_i^{\text{KS}*}(\mathbf{r}')}{\omega - \epsilon_i^{\text{KS}} \pm i\eta}$$



Exercise



This expression will be used to get W and Σ

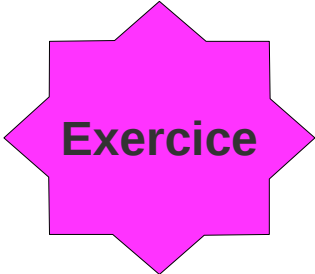
How to get W ?

From the RPA equation

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

which translates into

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



Exercise

This is the Alder-Wiser formula or the SOS formula

It involves empty states!

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

differs with implementations

GW obtained as a first-order perturbation

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

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

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

Approximation : $\varphi_i^{\text{GW}} \approx \varphi_i^{\text{KS}}$

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

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

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

Linearization of the energy dependance

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

Not yet known

Taylor expansion:

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

Final result:

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

where

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

Quasiparticle equation

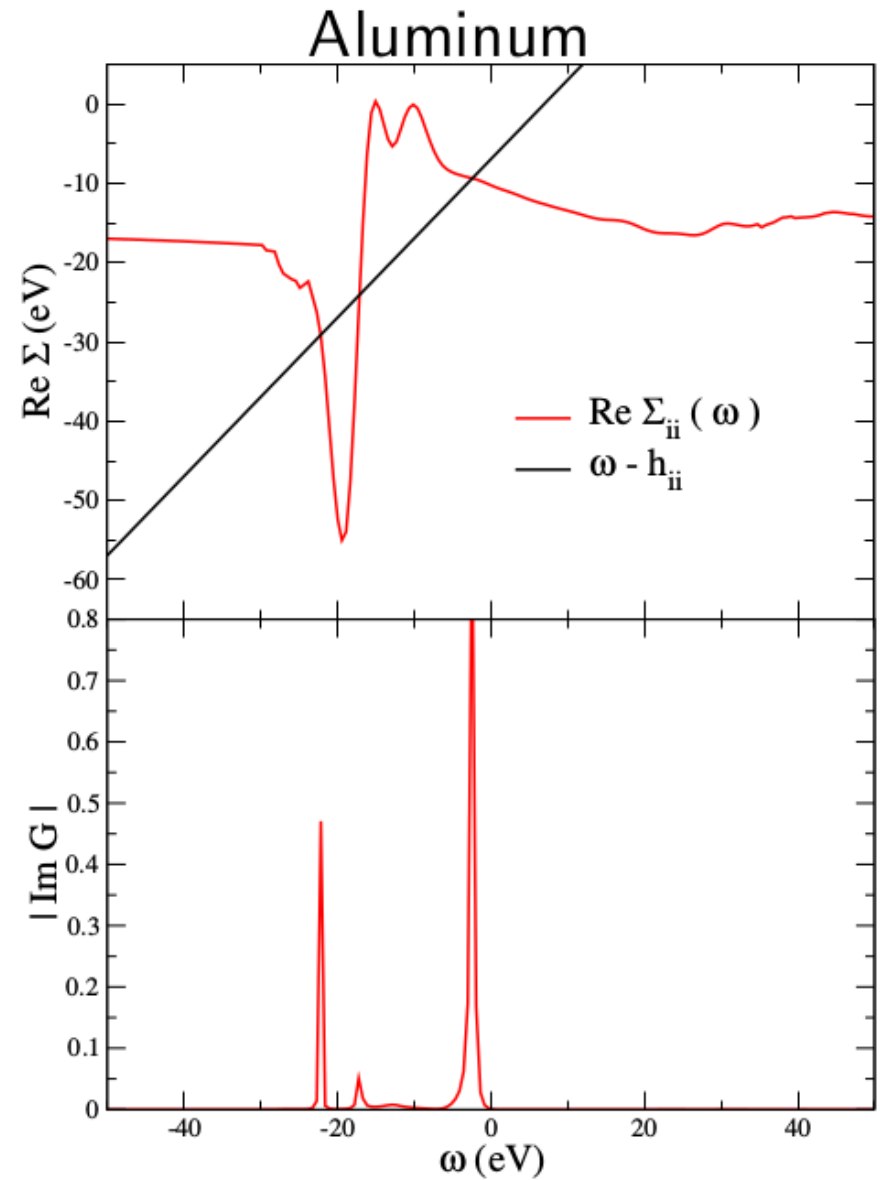
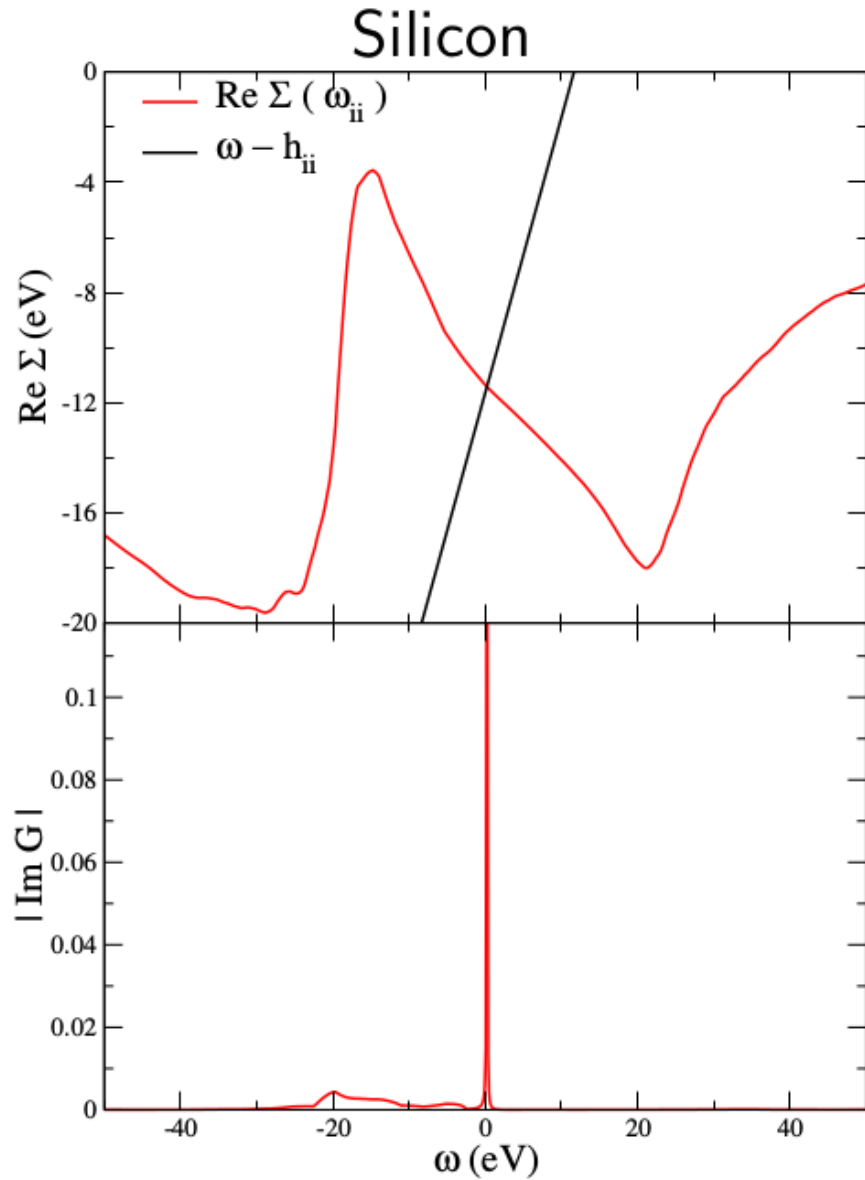
A typical ABINIT output for Silicon at Gamma point

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
 $E^{\text{GW}}_{\text{gap}}$ 3.212

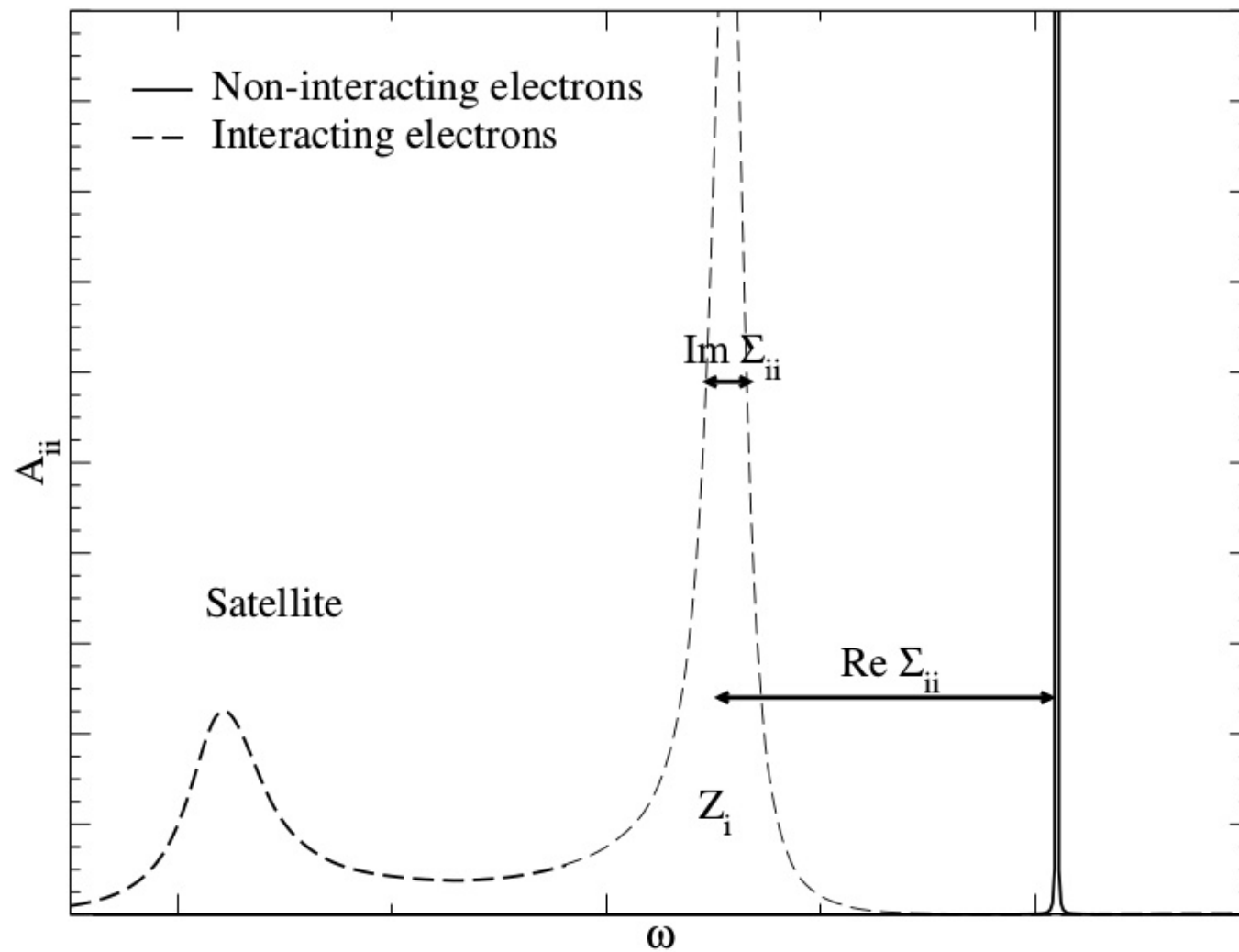
$$\epsilon_i^{\text{GW}} = \epsilon_i^{\text{LDA}} + Z_i \left\langle \varphi_i^{\text{LDA}} \left| \left[\sum_{xc} (\epsilon_i^{\text{LDA}}) - v_{xc}^{\text{LDA}} \right] \right| \varphi_i^{\text{LDA}} \right\rangle$$

Full quasiparticle solution



Spectral function

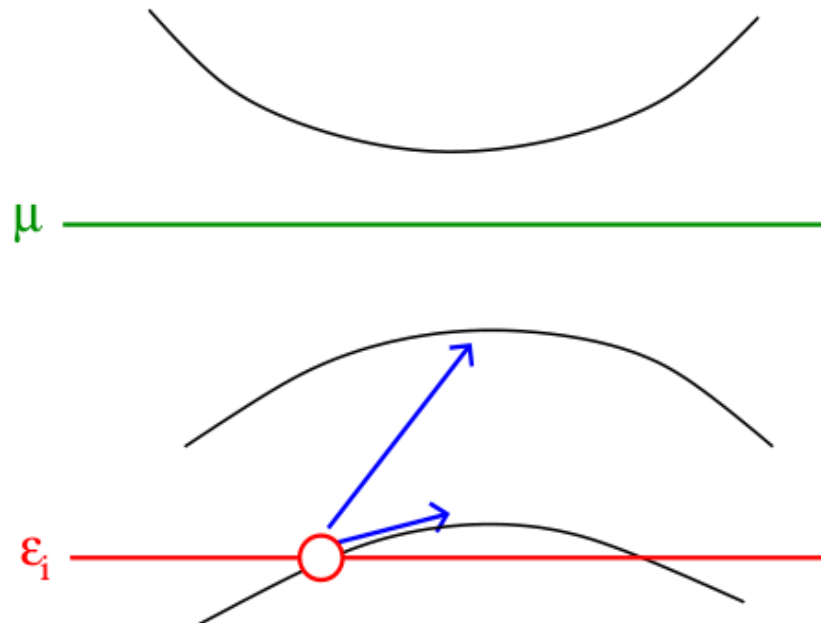
$$A(\omega) = |\text{Im} G(\omega)| / \pi$$



Excitation lifetime

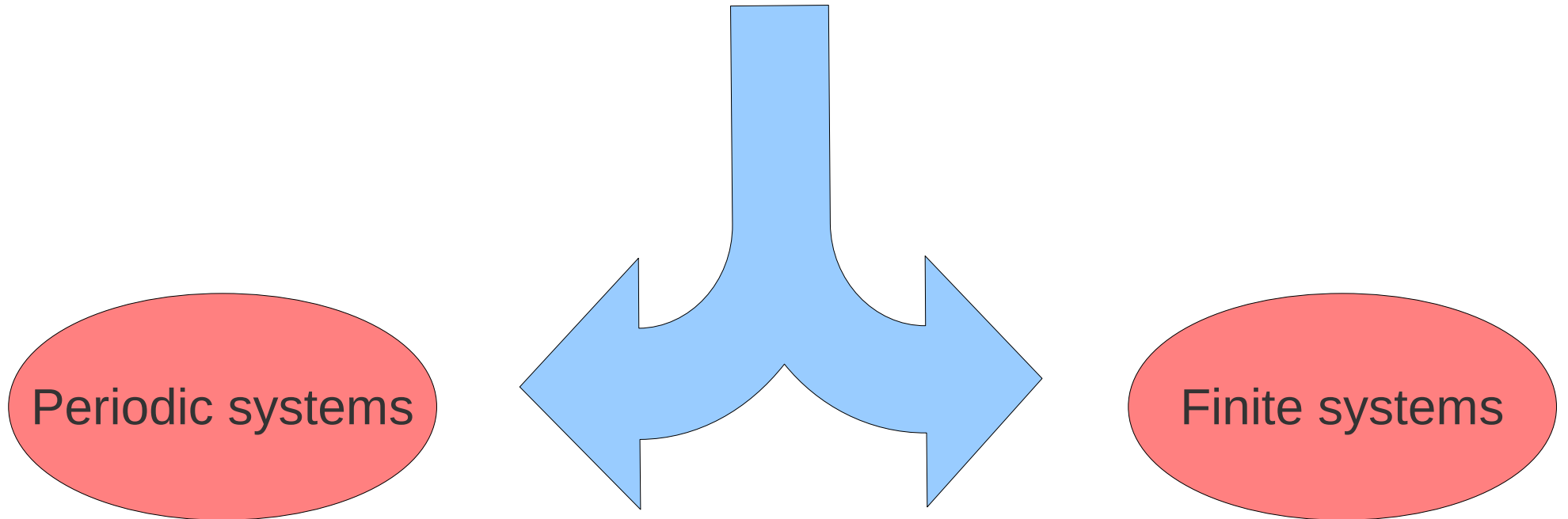
Hole self-energy:

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



When the paths split

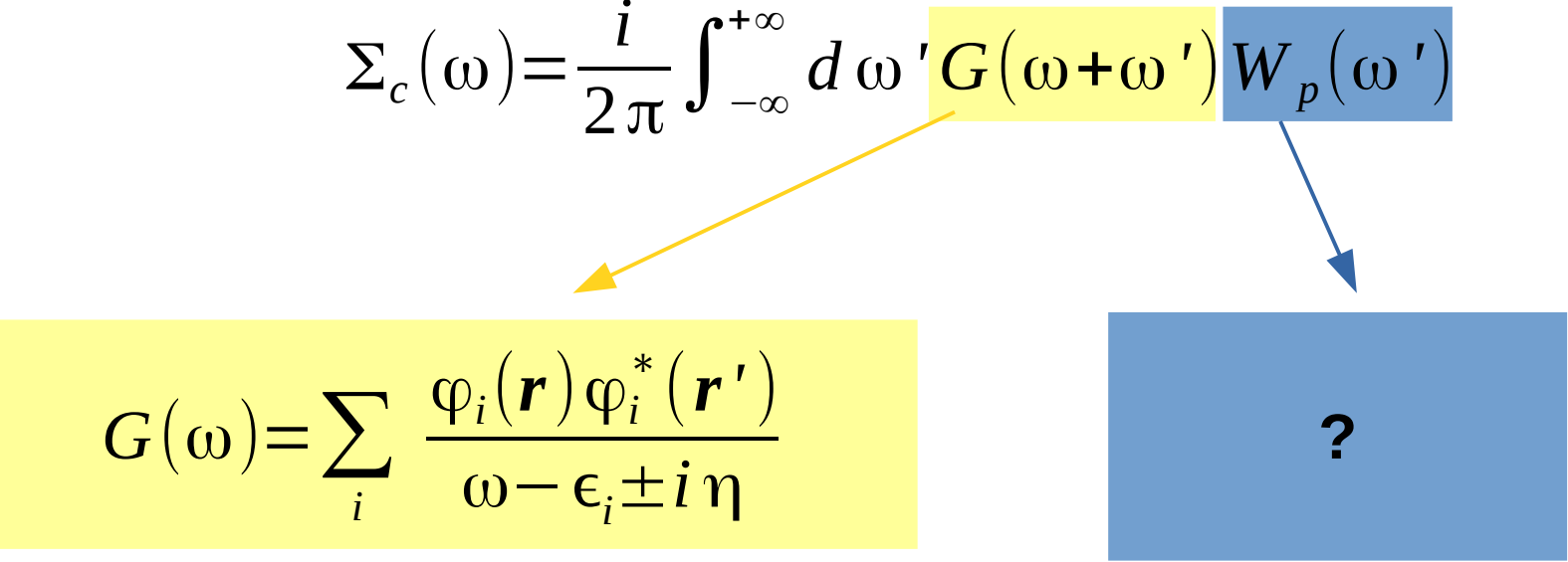
$$\Sigma(\mathbf{r}_1, \mathbf{r}_2, \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}_1, \mathbf{r}_2, \omega + \omega') W(\mathbf{r}_2, \mathbf{r}_1, \omega')$$



Self energy evaluation in GW

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

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


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

?

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

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}$$

1 vector of coefficients per $\mathbf{k}$ -point in the Brillouin zone

Then 2-point functions are

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

a matrix of coefficients per $\mathbf{q}$ -point in the BZ due to translational symmetry:

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

W in plane-waves and frequency space

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

$$(2) \quad \epsilon(1,2) = \delta(1,2) - \int d^3v(1,3) \chi_0(3,2)$$

$$(3) \quad W(1,2) = \int d^3\epsilon^{-1}(1,3) v(3,2)$$

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

$$(2) \quad \epsilon_{GG'}(\mathbf{q}, \omega) = \delta_{G,G'} - \sum_{G''} v_{GG''}(\mathbf{q}) \chi_{0G''G'}(\mathbf{q}, \omega) \quad \longleftarrow \quad v_{GG''}(\mathbf{q}) = \frac{4\pi}{|\mathbf{q} + \mathbf{G}|^2} \delta_{G,G''}$$

$$(3) \quad W_{GG'}(\mathbf{q}, \omega) = \epsilon_{GG'}^{-1}(\mathbf{q}, \omega) v_{G'}(\mathbf{q}) \quad \longleftarrow \quad \text{matrix inversion}$$

Analytic structure of $W(\omega)$

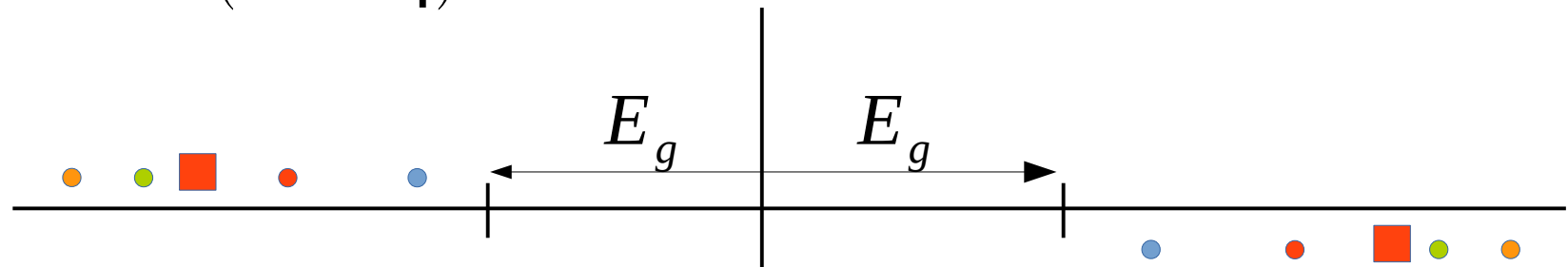
- Time ordered response function:

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

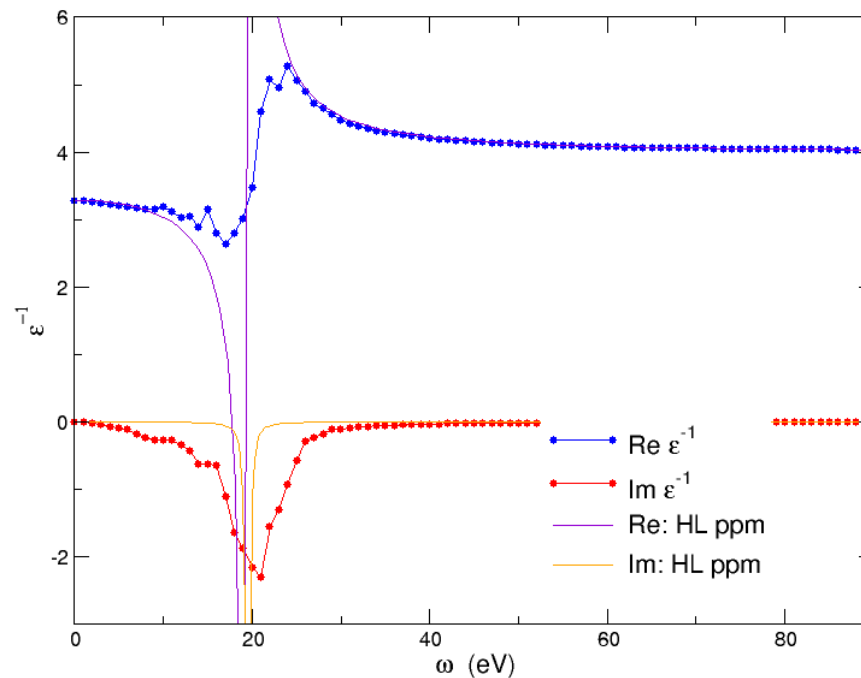
- Plasmon-pole model:

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

Complex plane:



Silicon:
For a given $\mathbf{q}+\mathbf{G}$:



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 $\int_0^{+\infty} \omega \operatorname{Im} \varepsilon^{-1}(\omega) d\omega = -\frac{\pi}{2} \omega_p^2$

- 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

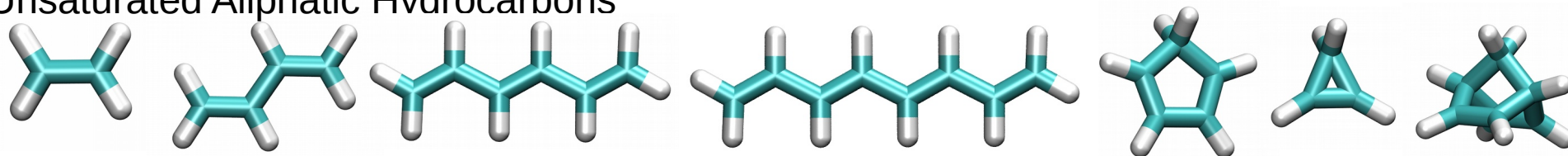
	HL	GN	Expt.
Γ_v	5.45	5.65	
Γ_c	8.71	8.87	
Direct Band gap	3.26	3.22	3.40 eV

Band gaps are almost the same

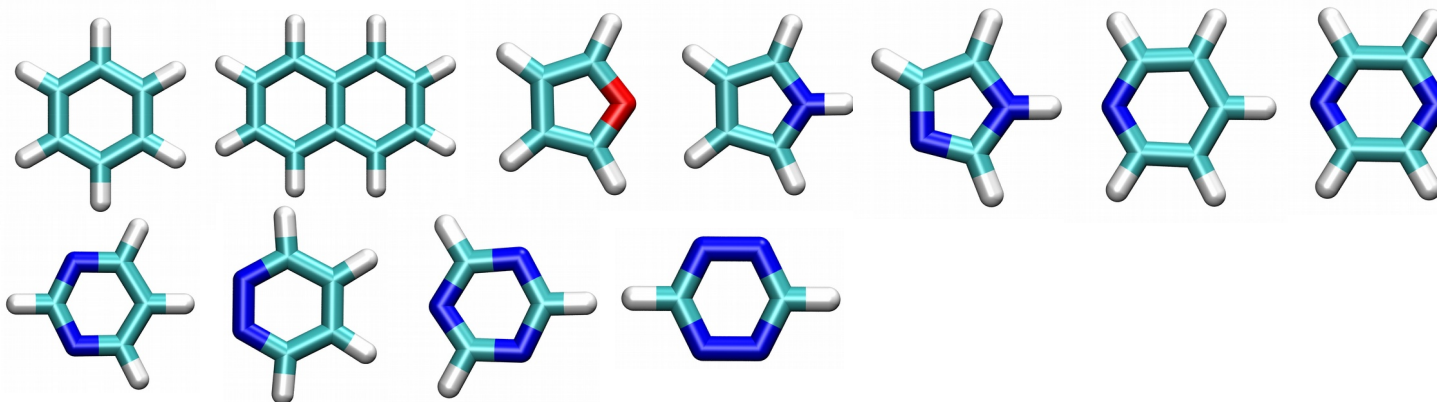
However, the absolute positioning of the bands is not (**0.2 eV difference!**)

Molecular systems

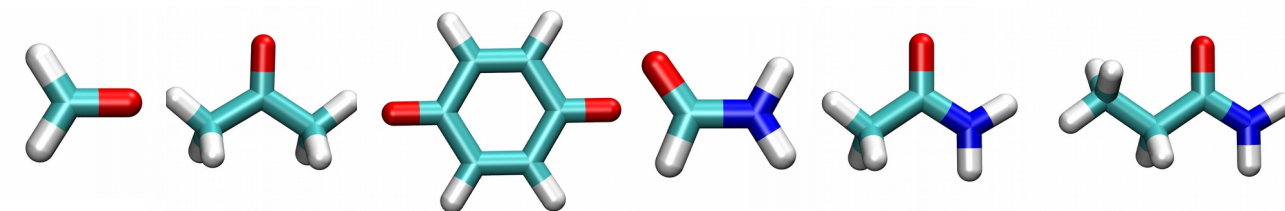
Unsaturated Aliphatic Hydrocarbons



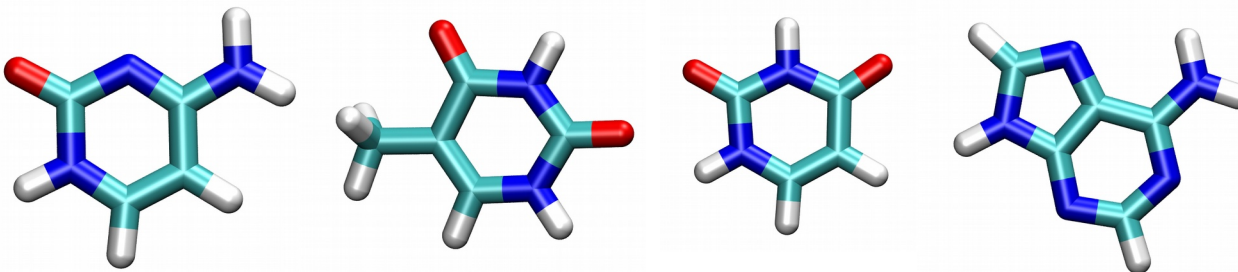
Aromatic Hydrocarbons and Heterocycles



Aldehydes, Ketones and Amides



Nucleobases



RPA in Linear Response

RPA screening equation:

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

In transition space:

$$\chi^{-1}(\omega) = \omega I + \underbrace{\begin{pmatrix} \epsilon_j - \epsilon_i & & \\ & \ddots & \\ & & \epsilon_l - \epsilon_k \end{pmatrix} - \begin{pmatrix} \langle i j | \frac{1}{r} | k l \rangle \end{pmatrix}}_{\text{Diagonalization instead of an inversion for each } \omega}$$

$|k l\rangle$
 $\langle i j|$

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:

$$\chi(\omega) = \chi_0(\omega) + \chi_0(\omega)(v + f_{xc})\chi(\omega) \quad \Leftrightarrow \quad \chi^{-1}(\omega) = \chi_0^{-1}(\omega) - v - f_{xc}$$

In transition space:

$$\chi^{-1}(\omega) = \omega I + \underbrace{\begin{pmatrix} \epsilon_j - \epsilon_i & & \\ & \ddots & \\ & & \epsilon_l - \epsilon_k \end{pmatrix} - \begin{pmatrix} (ij|\frac{1}{r}|kl) \end{pmatrix}}_{\text{Diagonalization instead of an inversion for each } \omega} - \begin{pmatrix} (ij|f_{xc}|kl) \end{pmatrix}$$

$\langle ij|$ $|kl\rangle$

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:

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

In transition space:

$$\chi^{-1}(\omega) = \omega I + \underbrace{\begin{pmatrix} \epsilon_j - \epsilon_i & & \\ & \ddots & \\ & & \ddots \end{pmatrix} - \begin{pmatrix} (ij|\frac{1}{r}|kl) \end{pmatrix}}_{\text{Diagonalization instead of an inversion for each } \omega} + \begin{pmatrix} (ij|W|kl) \end{pmatrix}$$

$\langle ij|$ $|kl\rangle$

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:

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


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

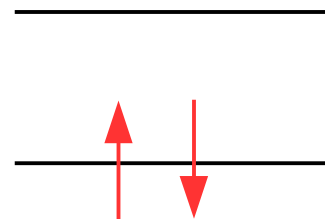

$$W_p(\omega) = \sum_s \frac{L_s(\mathbf{r}) R_s(\mathbf{r}')}{\omega - \Omega_s \pm i\eta}$$

Residue theorem yields the result straightforwardly.

H2 in minimal basis: GW@HF

$$\epsilon_{\text{HOMO}}^{\text{HF}} = -16.2 \text{ eV}$$

$$\epsilon_{\text{LUMO}}^{\text{HF}} = 19.4 \text{ eV}$$



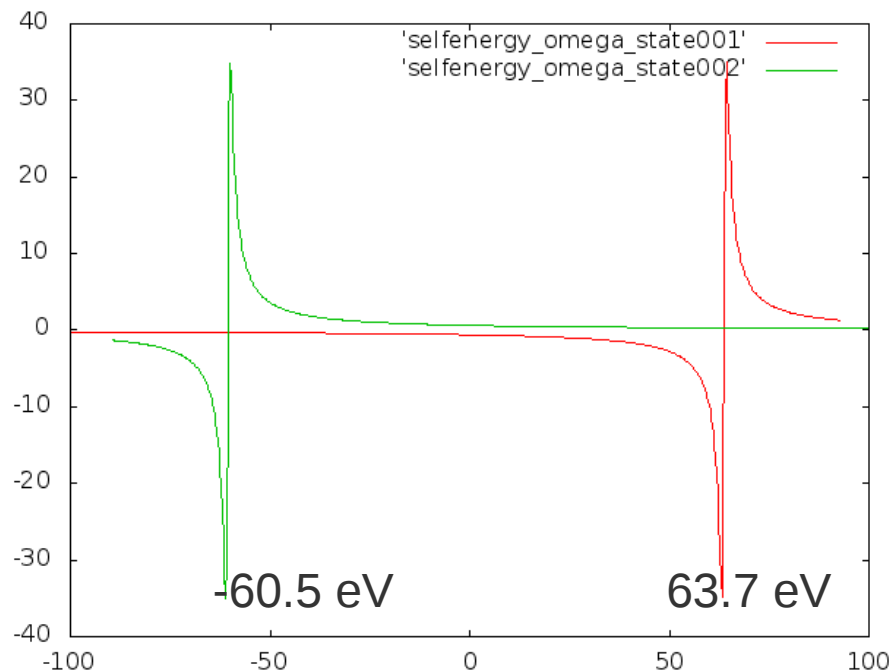
$$\Delta \epsilon = 35.6 \text{ eV}$$

Two transitions at

$$\Omega_+ = 44.3 \text{ eV}$$

$$\Omega_- = -44.3 \text{ eV}$$

Real part of
the self-energy:



$$\epsilon_{\text{HOMO}}^{\text{GW}} = -16.7 \text{ eV}$$

$$\epsilon_{\text{LUMO}}^{\text{GW}} = 19.9 \text{ eV}$$

I. Introduction: going beyond DFT

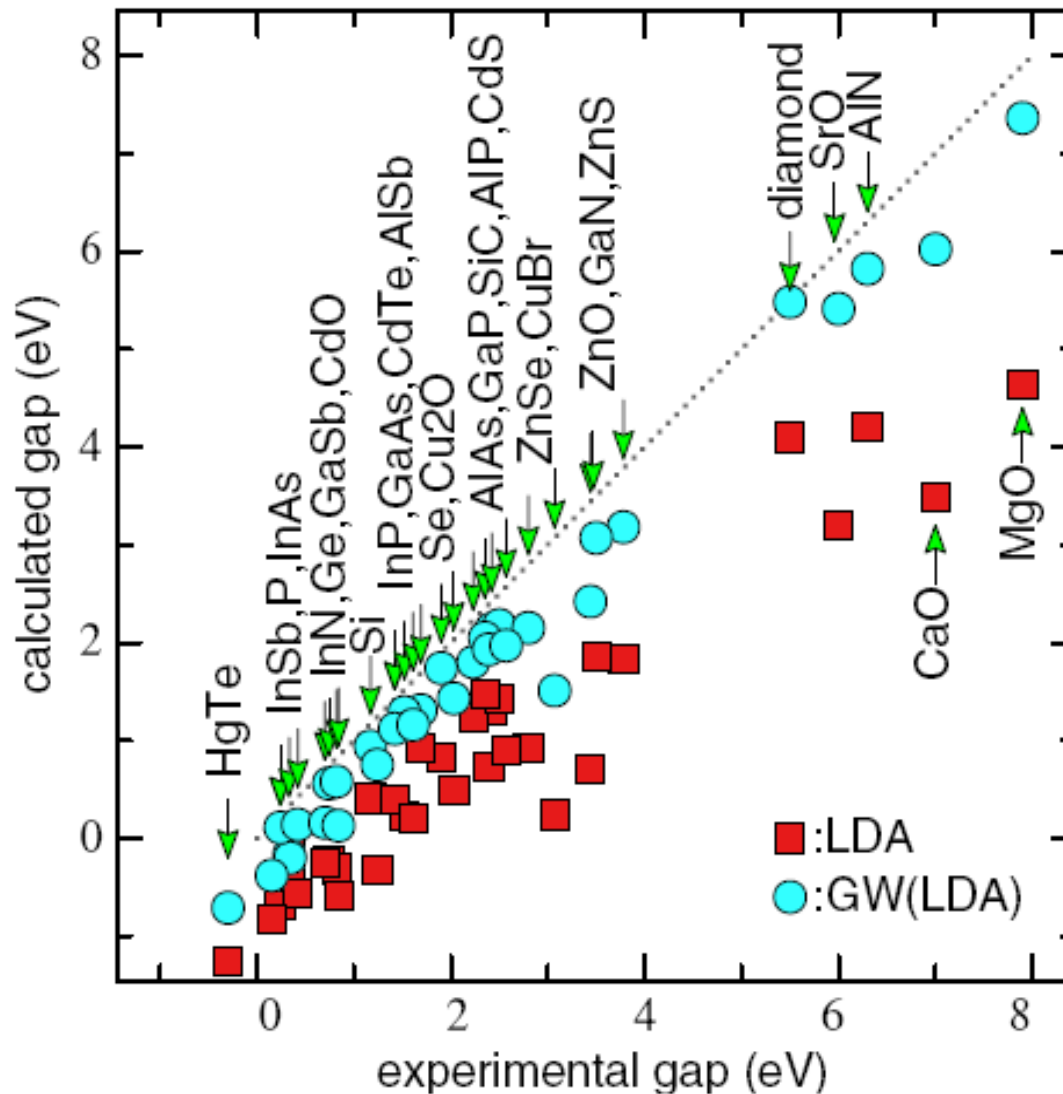
II. Introduction of the Green's function

III. Exact Hedin's equations and the GW approximation

IV. Calculating the GW self-energy in practice

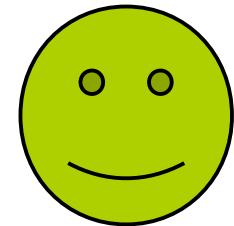
V. Applications

GW approximation gets good band gap

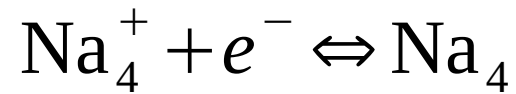


van Schilfgaarde *et al* PRL **96** 226402 (2008)

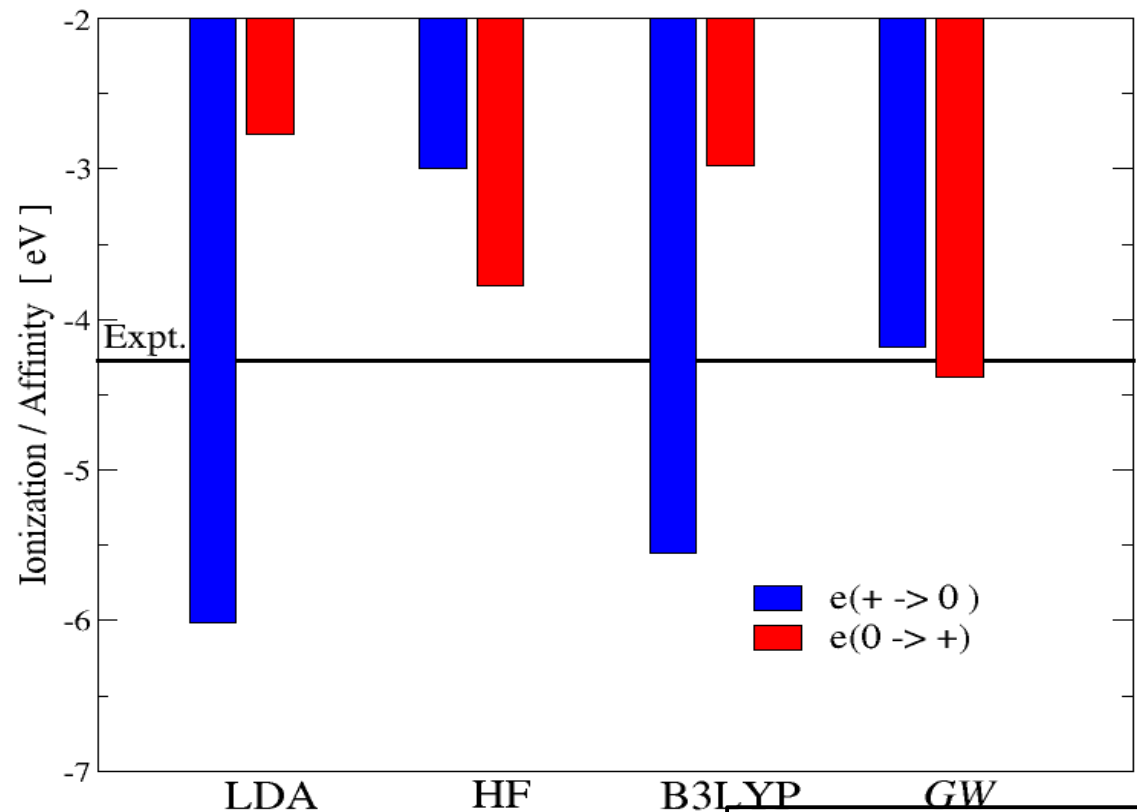
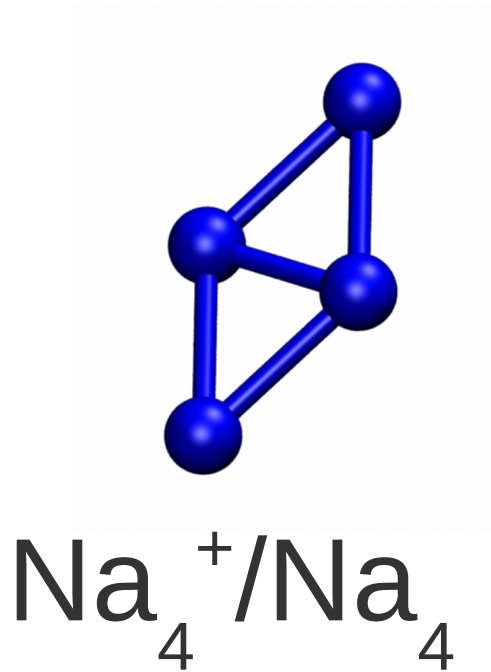
No more a band gap problem !



Clusters de sodium



$$E_0(\text{Na}_4) - E_0(\text{Na}_4^+) = \begin{cases} \epsilon(\text{HOMO}, \text{Na}_4) \\ \epsilon(\text{LUMO}, \text{Na}_4^+) \end{cases}$$



Bruneval PRL (2009)

What is the best starting point for G_0W_0 ?

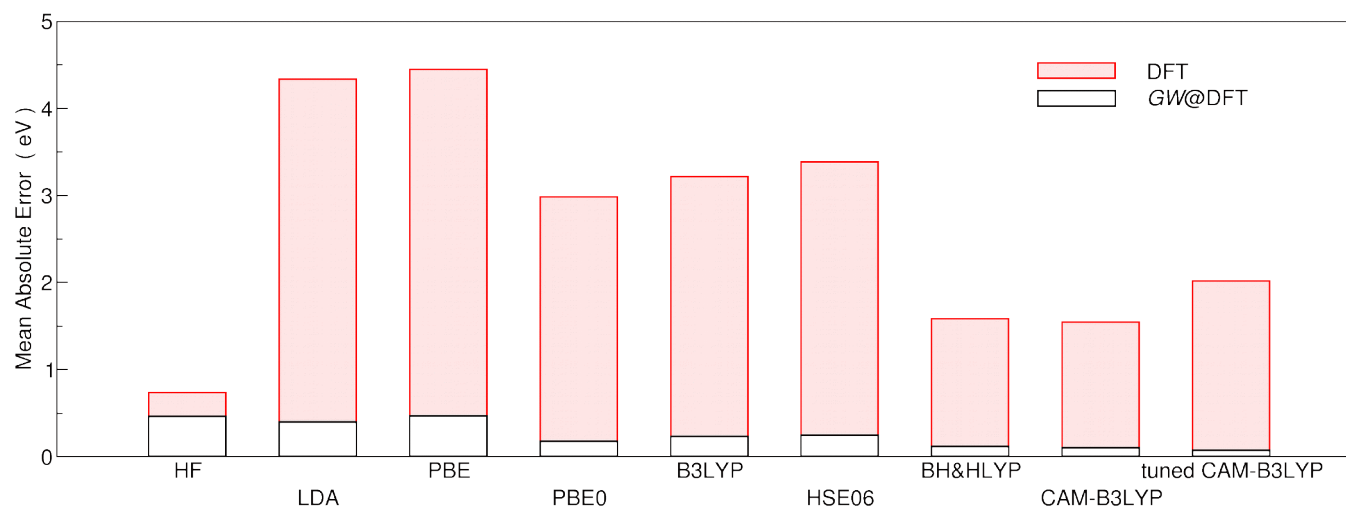
Ionization
of
small
molecules

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

starting point	GW@										exp
	HF	LDA	PBE	PBE0	B3LYP	HSE06	BH&HLYP	CAM-B3LYP	tuned CAM-B3LYP	CCSD(T)	
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 ₂ H ₂	-11.65	-11.10	-11.08	-11.27	-11.23	-11.21	-11.40	-11.41	-11.41	-11.42	-11.49
C ₂ H 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 ₃ Cl	-11.74	-11.02	-10.98	-11.21	-11.18	-11.15	-11.41	-11.43	-11.41	-11.41	-11.29
CH ₃ OH	-11.69	-10.70	-10.64	-10.97	-10.89	-10.88	-11.20	-11.22	-11.17	-11.08	-10.96
CH ₃ SH	-9.81	-9.18	-9.17	-9.36	-9.35	-9.30	-9.53	-9.55	-9.53	-9.49	



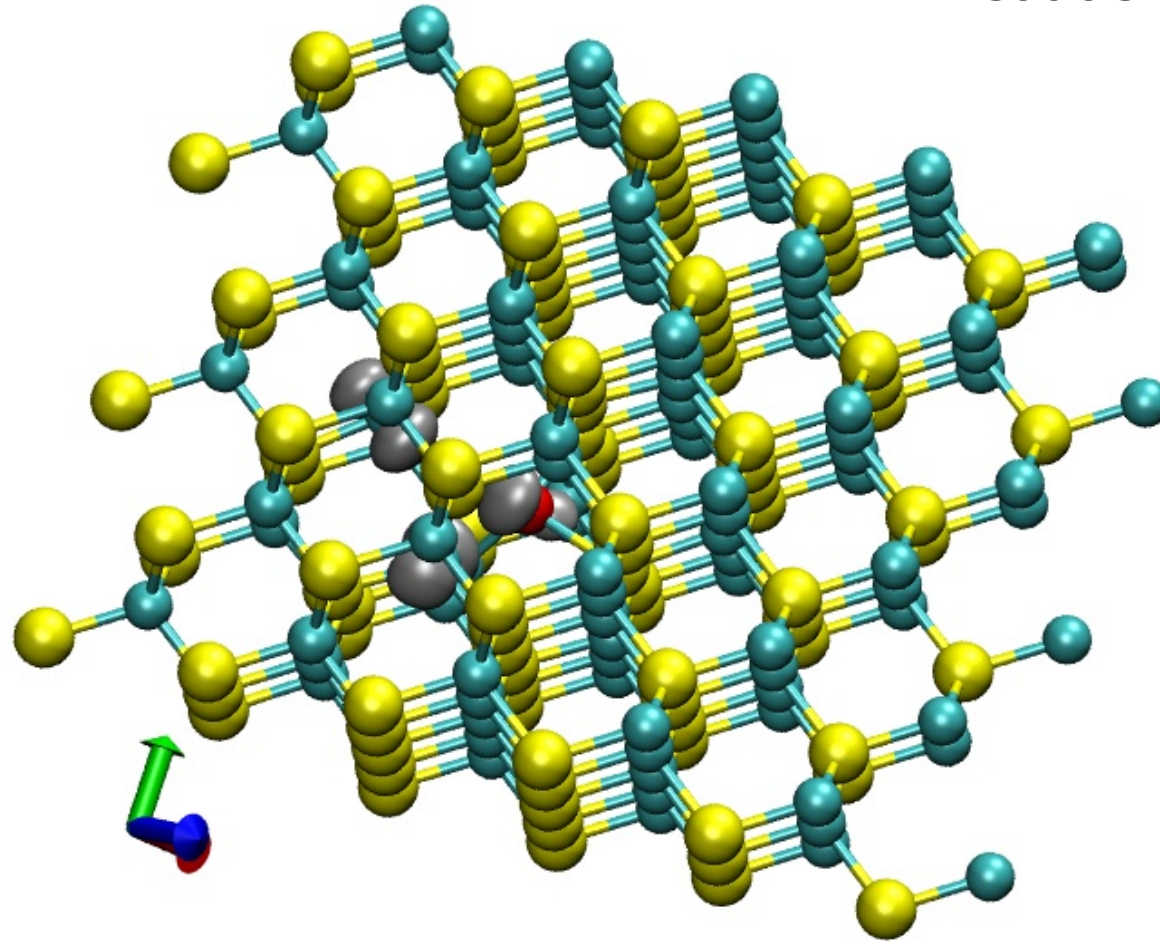
F. Bruneval & MAL Marques, JCTC (2013)

Aussois, ISTPC 2015

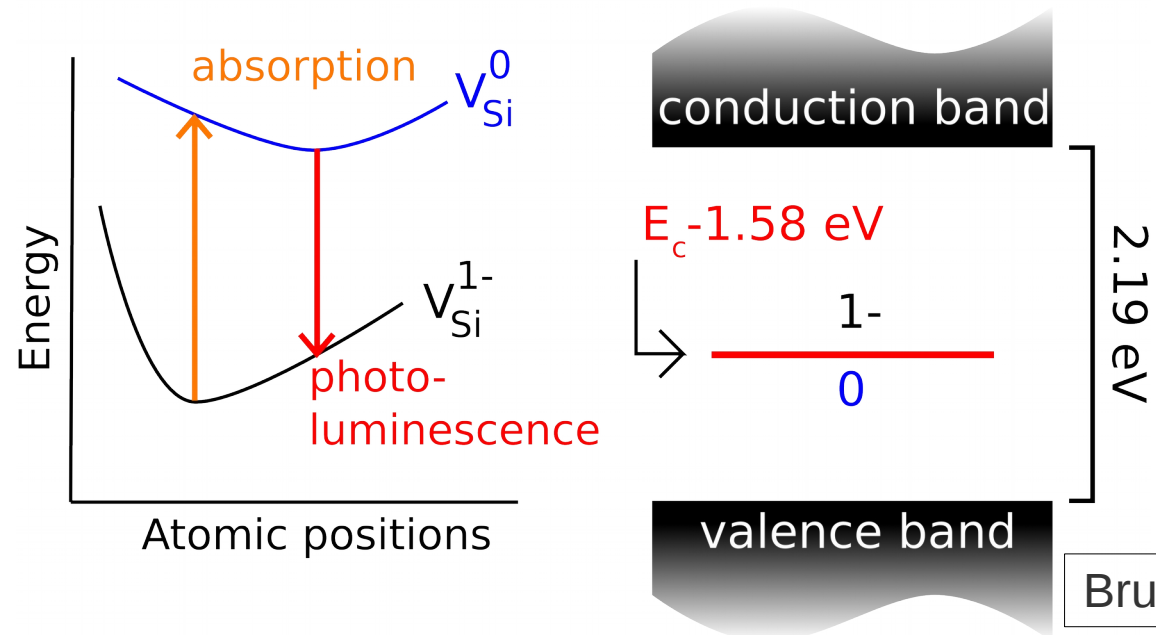
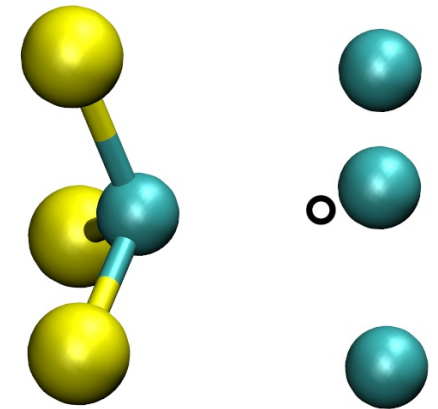
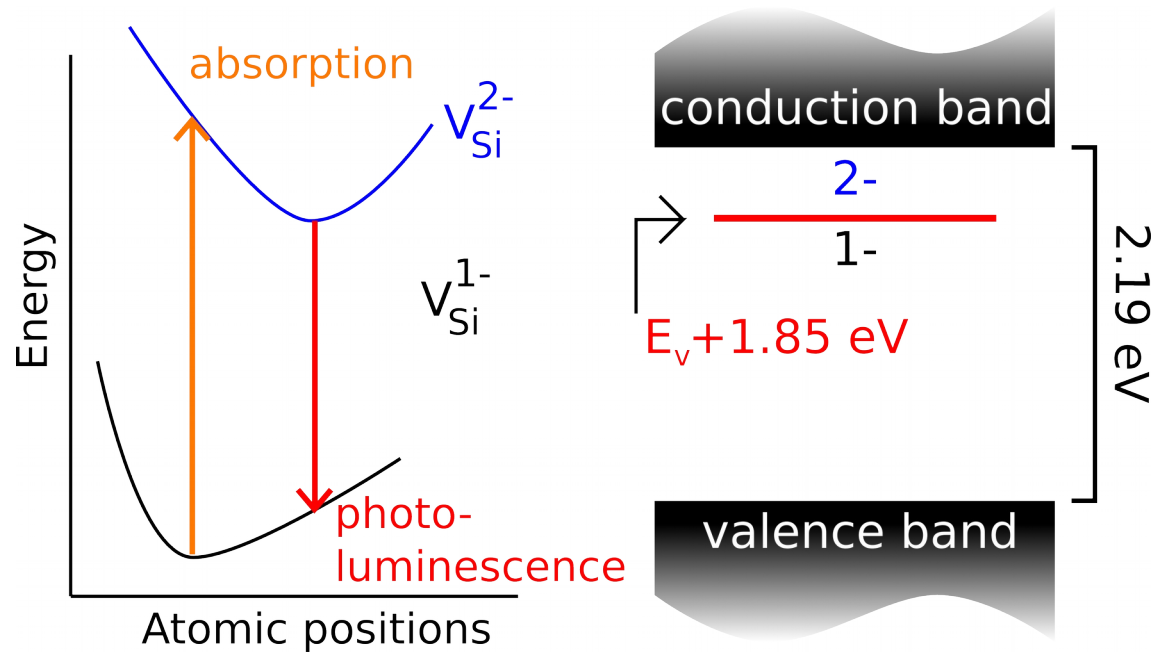
Defect calculation within GW approximation

Up to 215 atoms

Cubic silicon carbide



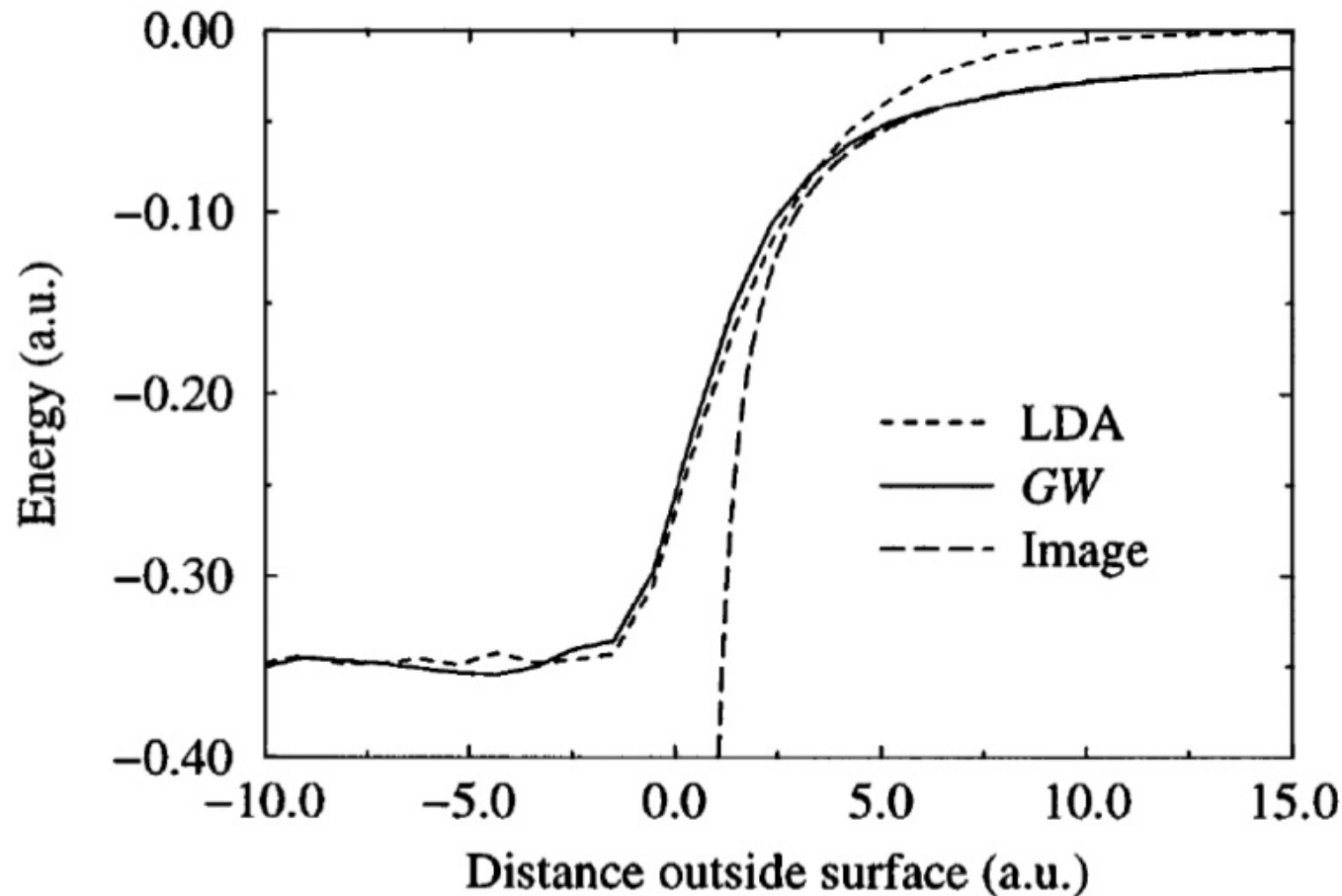
Photoluminescence of V_{Si}



Bruneval and Roma PRB (2011)

Correct long-range potential

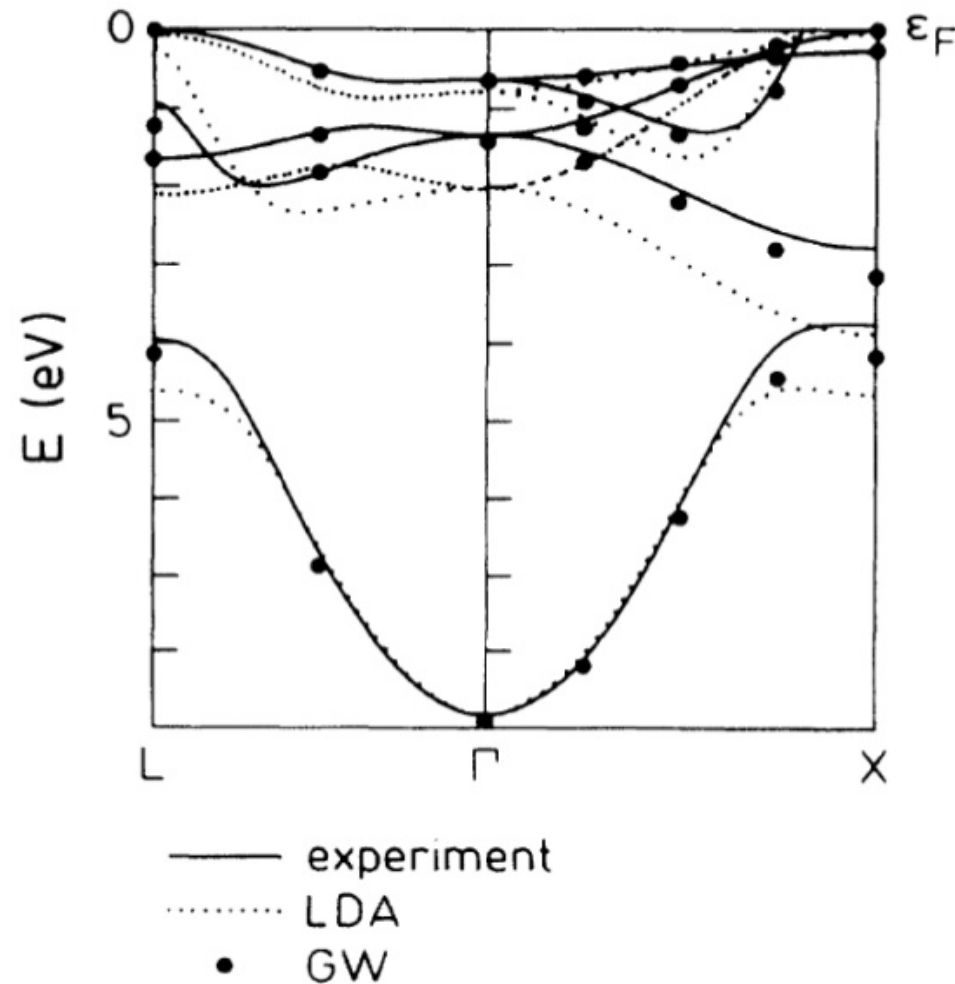
Al(111): potential



from I.D. White *et al*, PRL **80**, 4265 (1998).

3d metal band structure

Nickel

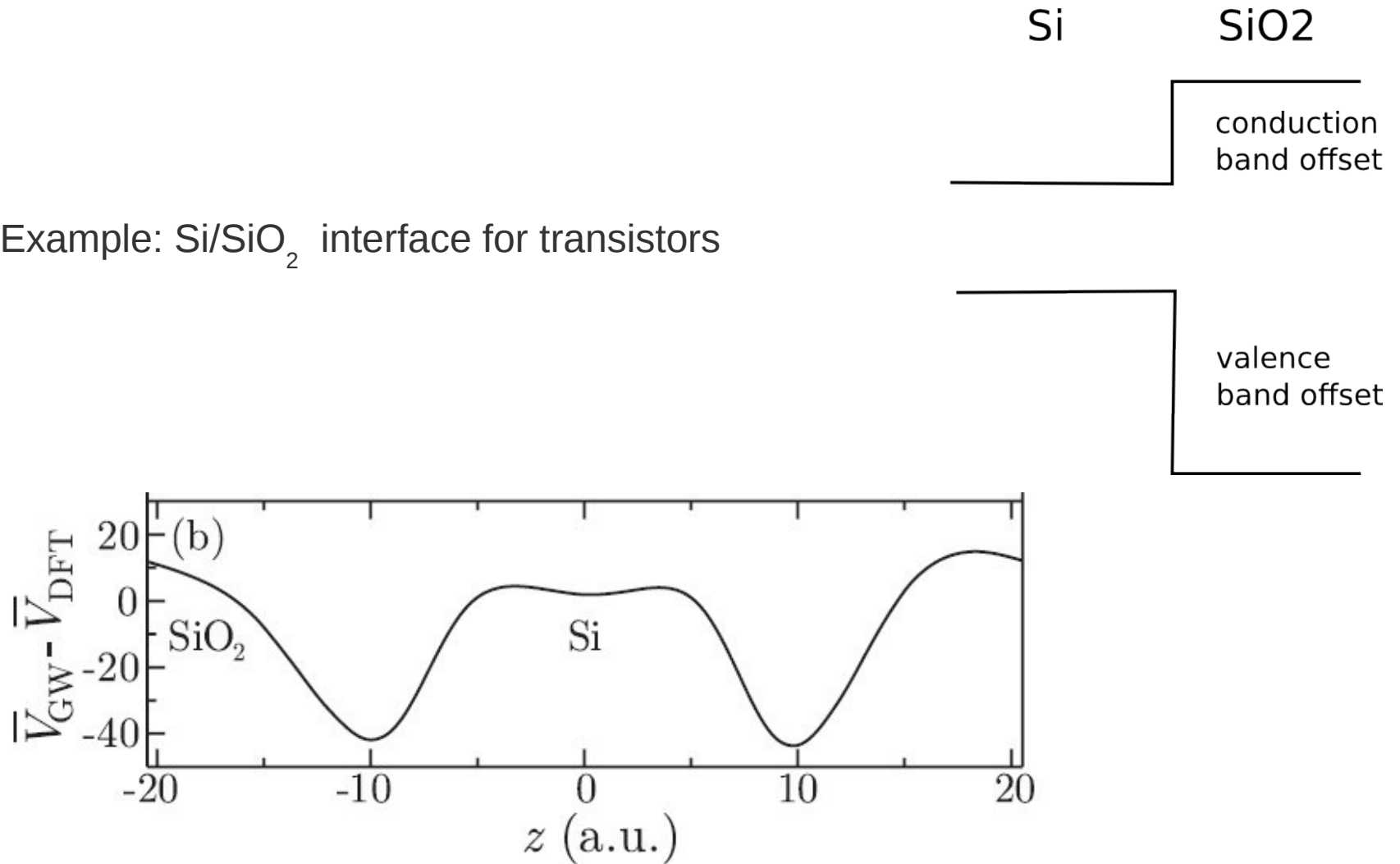


from F. Aryasetiawan, PRB **46** 13051 (1992).

Band Offset at the interface between two semiconductors

Very important for electronics!

Example: Si/SiO₂ 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. Lundqvist, 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

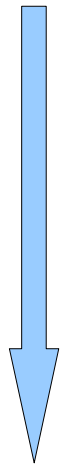
Codes:

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

Exercise 1

Green's function in frequency domain

$$iG(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \theta(t_1 - t_2) \sum_{i \text{ virt}} \varphi_i(\mathbf{r}_1) \varphi_i^*(\mathbf{r}_2) e^{-i\epsilon_i(t_1 - t_2)} \\ - \theta(t_2 - t_1) \sum_{i \text{ occ}} \varphi_i(\mathbf{r}_2) \varphi_i^*(\mathbf{r}_1) e^{-i\epsilon_i(t_2 - t_1)}$$



$$G(\mathbf{r}_1, \mathbf{r}_2, \omega) = \int d(t_1 - t_2) e^{i\omega(t_1 - t_2)} G(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2)$$

$$G(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_i \frac{\varphi_i(\mathbf{r}_1) \varphi_i^*(\mathbf{r}_2)}{\omega - \epsilon_i \pm i\eta}$$

Exercise 2:

Fock exchange from Green's functions

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

Exercise 3: let's play with Dyson equations

1) The multiple faces of the Dyson equation

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

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

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

$$\hookrightarrow G_{\text{KS}} = G_0 + G_0 v_{xc} G_{\text{KS}}$$

$$\hookrightarrow G_{\text{KS}} = G_0 + G_0 v_{xc} G_0 + G_0 v_{xc} G_0 v_{xc} G_0 + \dots$$

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

2) Combining the Dyson equations

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

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

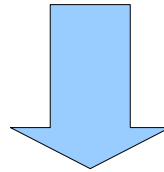
$$\hookrightarrow 1 = [G_{\text{KS}}^{-1} - (\Sigma - v_{xc})] G$$

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

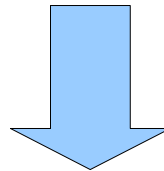
Exercise 4

Show the standard Adler-Wiser formula (1963):

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



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

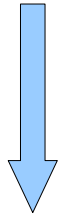


$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_{\substack{i \text{ occ} \\ j \text{ virt}}} \varphi_i(\mathbf{r}_1) \varphi_i^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_2) \varphi_j^*(\mathbf{r}_1) \\ \times \left[\frac{1}{\omega - (\epsilon_j - \epsilon_i) - i\eta} - \frac{1}{\omega - (\epsilon_i - \epsilon_j)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

Exercise 5

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

$$\Sigma(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) = i G(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) W(\mathbf{r}_2, \mathbf{r}_1, t_2 - t_1)$$



$$G(\mathbf{r}_1, \mathbf{r}_2, \omega) = \int dt_1 - dt_2 e^{i\omega(t_1 - t_2)} G(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$$

$$G(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) = \frac{1}{2\pi} \int d\omega e^{-i\omega(t_1 - t_2)} G(\mathbf{r}_1, \mathbf{r}_2, \omega)$$

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