

GW calculations with



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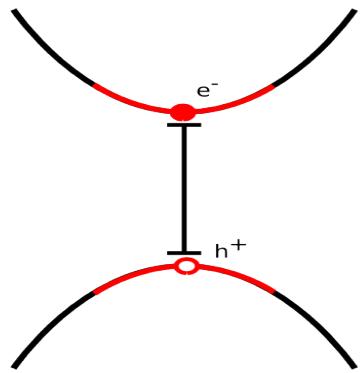
Outline

- I. Motivation: beyond DFT?
- II. Introducing the Green's function
- III. Exact Hedin's equations and the GW approximation
- IV. Calculating the GW self-energy in practice
- V. Applications

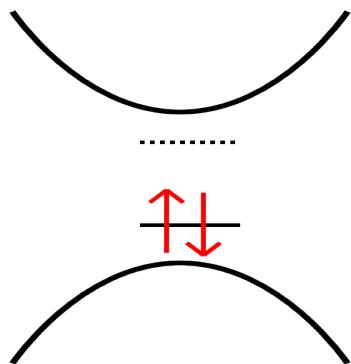


Band gaps in solid state physics

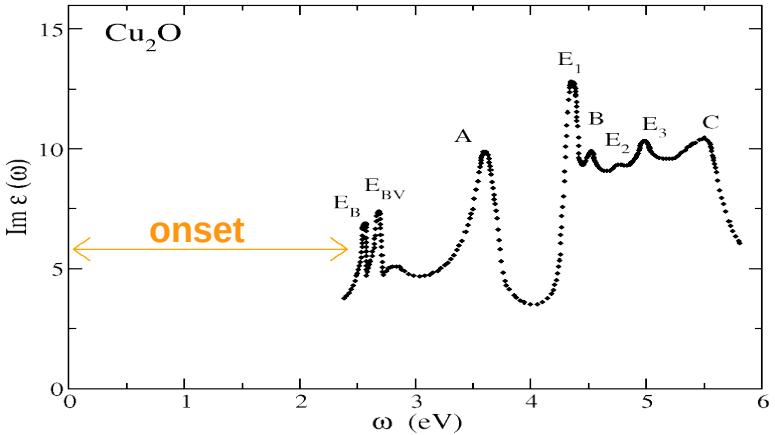
Effective masses
for transport in semiconductors



Defect formation energy,
dopant solubility



Optical absorption



Photoemission

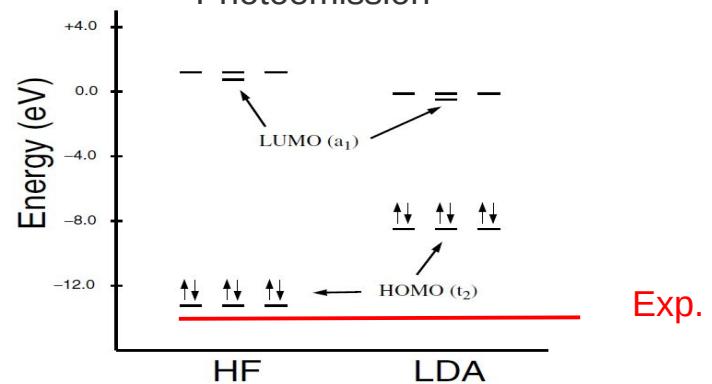
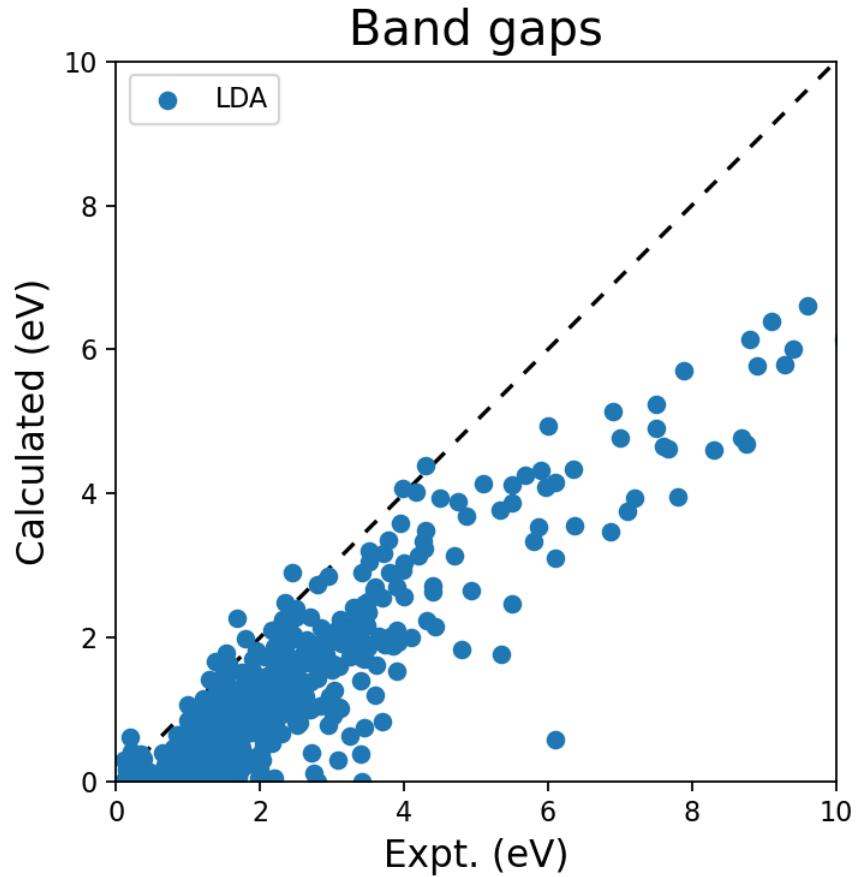


FIG. 1. Single-particle Hartree-Fock and local density approximation eigenvalue spectra (eV) for the SiH₄ molecule.





« Band gap problem » of DFT



Band gap problem!

data from Borlido *et al.* JCTC 2019





How to improve band gaps within DFT?

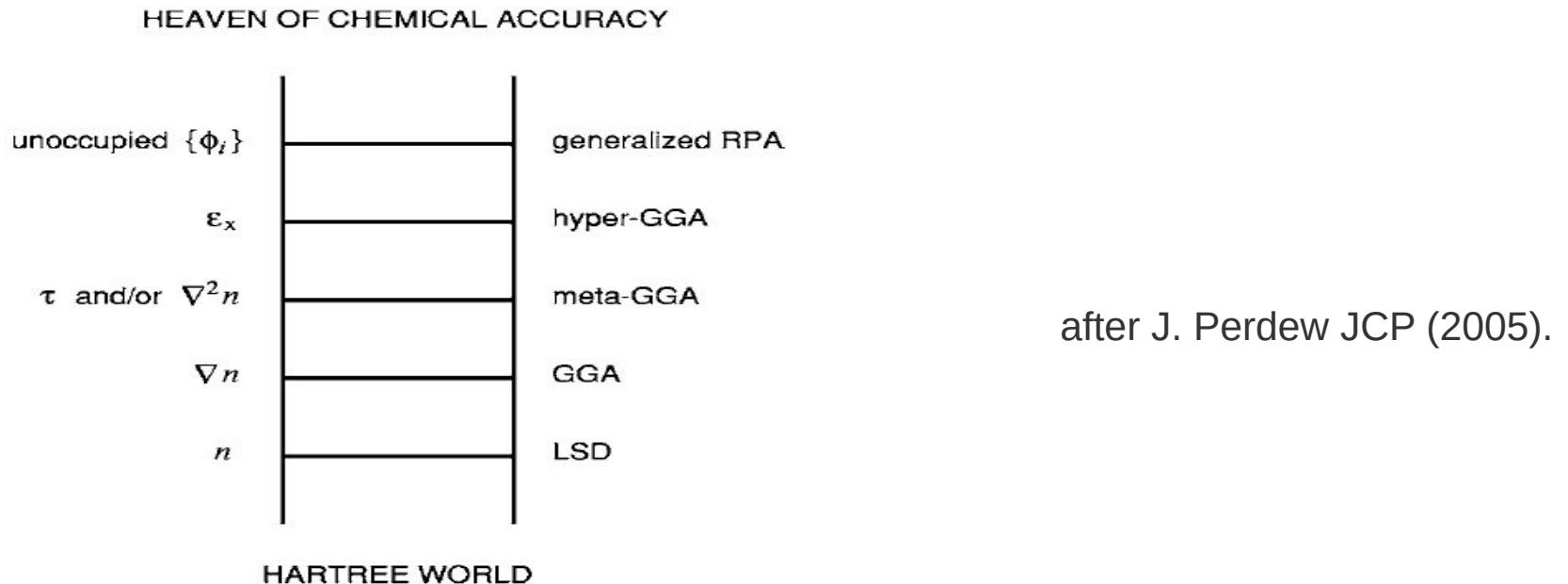
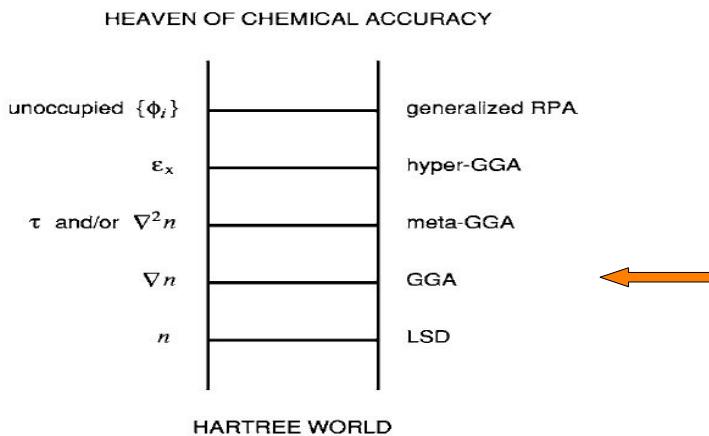
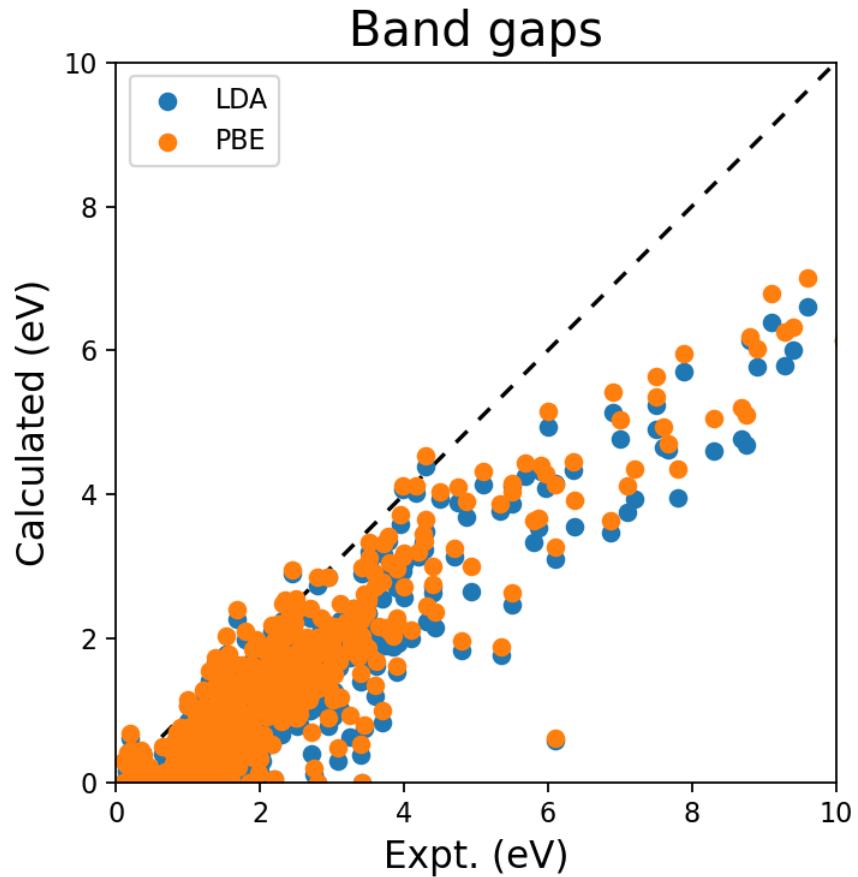


FIG. 1. Jacob's ladder of density functional approximations to the exchange-correlation energy.



« Band gap problem » of DFT

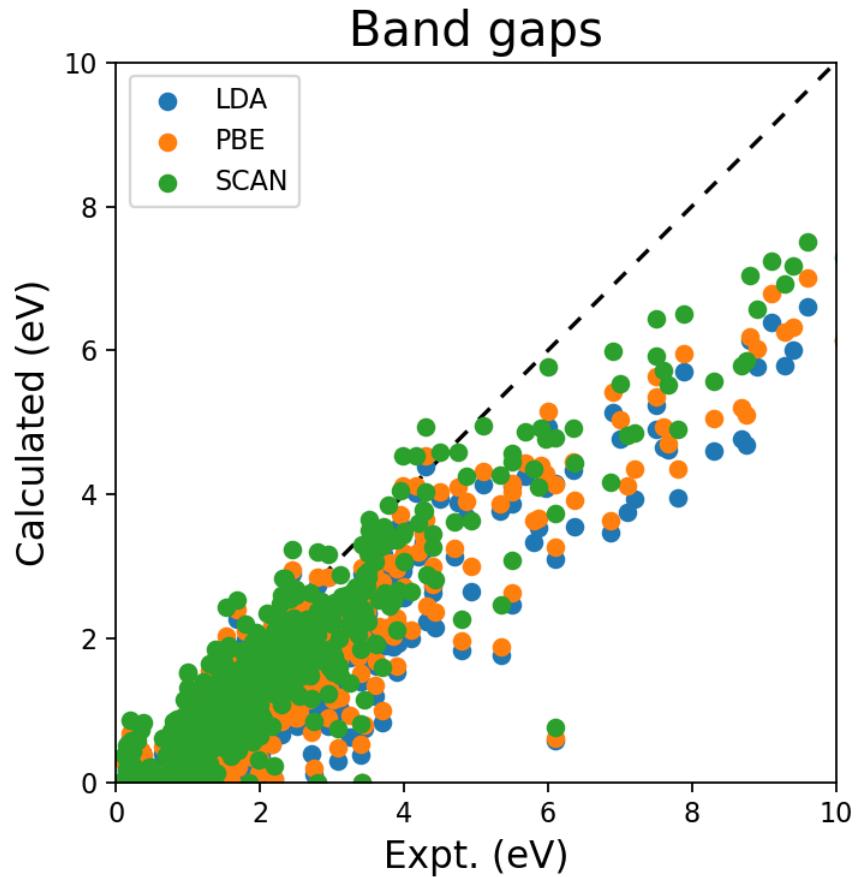


data from Borlido et al. JCTC 2019

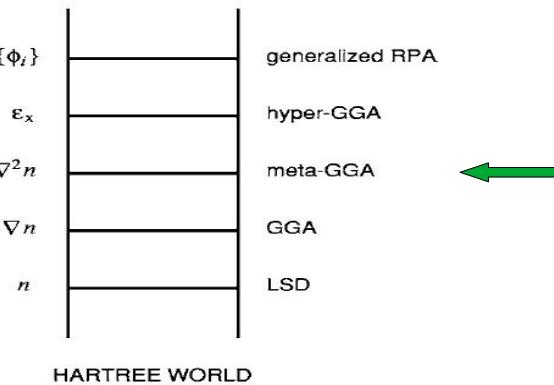




« Band gap problem » of DFT



AVEN OF CHEMICAL ACCURACY

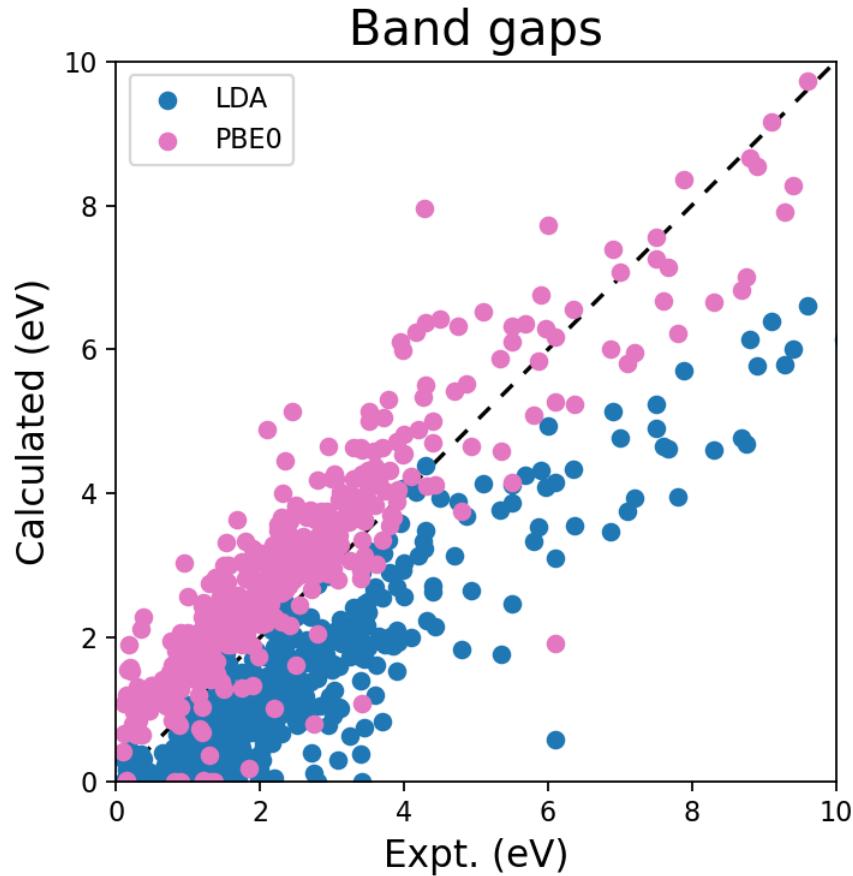


data from Borlido *et al.* JCTC 2019





Hybrid functionals mitigation



Non local exchange-correlation

$$\alpha \Sigma_x + (1 - \alpha) v_x^{\text{PBE}} + v_c^{\text{PBE}}$$

however with a parameter $\alpha = 0.25$

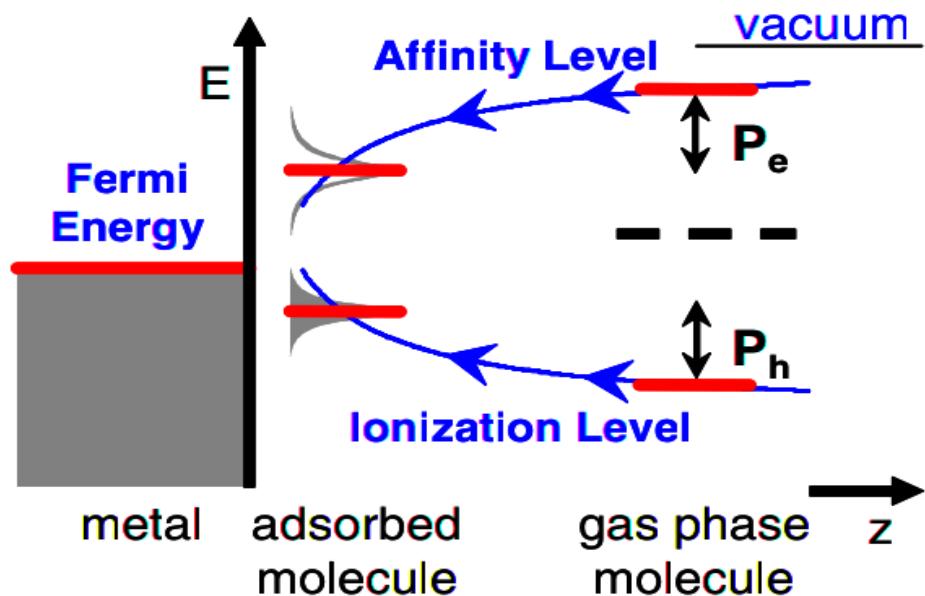
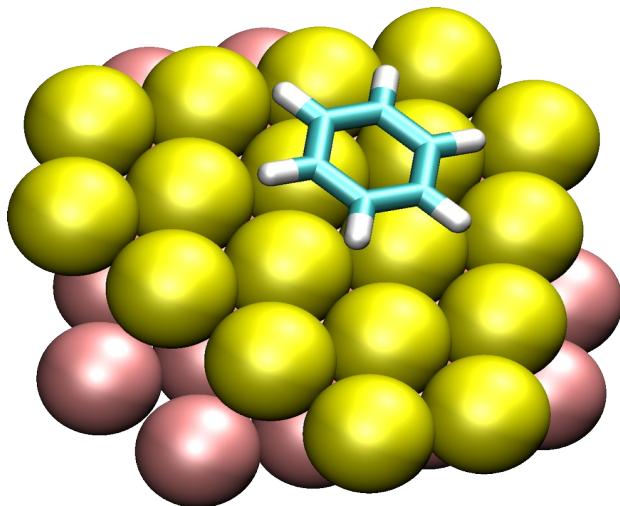
data from Borlido *et al.* JCTC 2019





Level renormalization in molecules

Benzene approaching a metallic surface



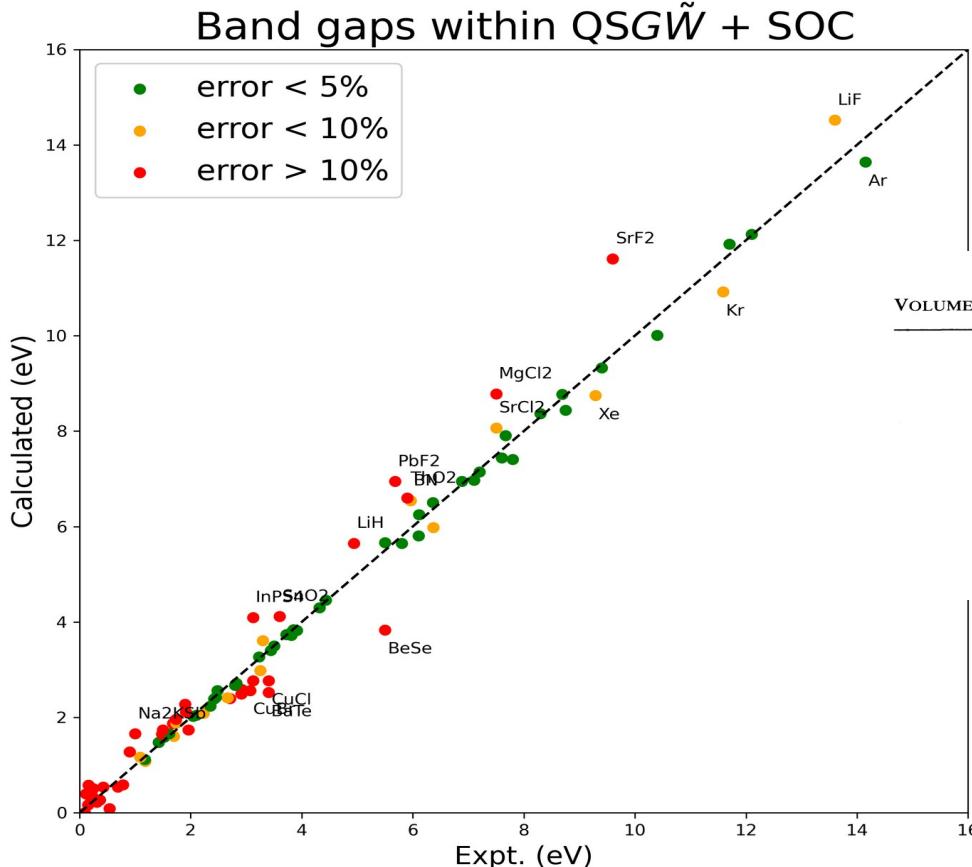
At the crossing point between physics and chemistry

No density-functional theory can treat this

Neaton, Hybertsen, Louie PRL (2006)



GW approximation for band gaps in solids



VOLUME 55, NUMBER 13

PHYSICAL REVIEW LETTERS

23 SEPTEMBER 1985

First-Principles Theory of Quasiparticles: Calculation of Band Gaps in Semiconductors and Insulators

Mark S. Hybertsen and Steven G. Louie

Department of Physics, University of California, Berkeley, California 94720
(Received 15 April 1985)

We present a first-principles theory for the quasiparticle energies of semiconductors and insulators. The full dielectric matrix is used to evaluate the nonlocal, energy-dependent electron self-energy operator. Both local-field effects and dynamical screening are found to be essential for understanding quasiparticle energies. Results for the band gaps, optical transitions, and band dispersions for silicon and diamond are in excellent agreement with existing experimental data.

GW yields excellent band gaps in solids

Grossman et al. arxiv (2025)



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Green's function theory = MBPT

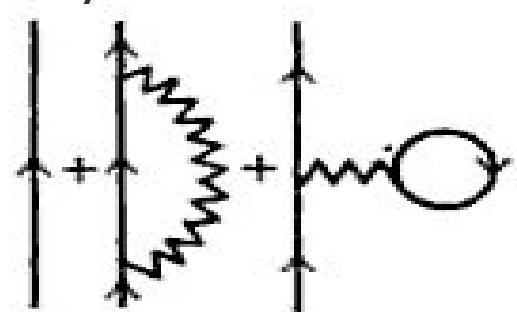
Historically older than the DFT (from the 40-50's)

Big shots: Feynman, Schwinger, Hubbard, Hedin, Lundqvist

Green's functions = particle propagator

Basic ingredient of a many-body theory

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





Building 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 → scalar product





Building the Green's function

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

1 2

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

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



Building the Green's function

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

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

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





Building the time-ordered 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

$$\begin{aligned} G(\mathbf{r} t, \mathbf{r}' t') &= G^>(\mathbf{r} t, \mathbf{r}' t') \theta(t - t') \\ &\quad + G^<(\mathbf{r} t, \mathbf{r}' t') \theta(t' - t) \end{aligned}$$

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



Lehman representation

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

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

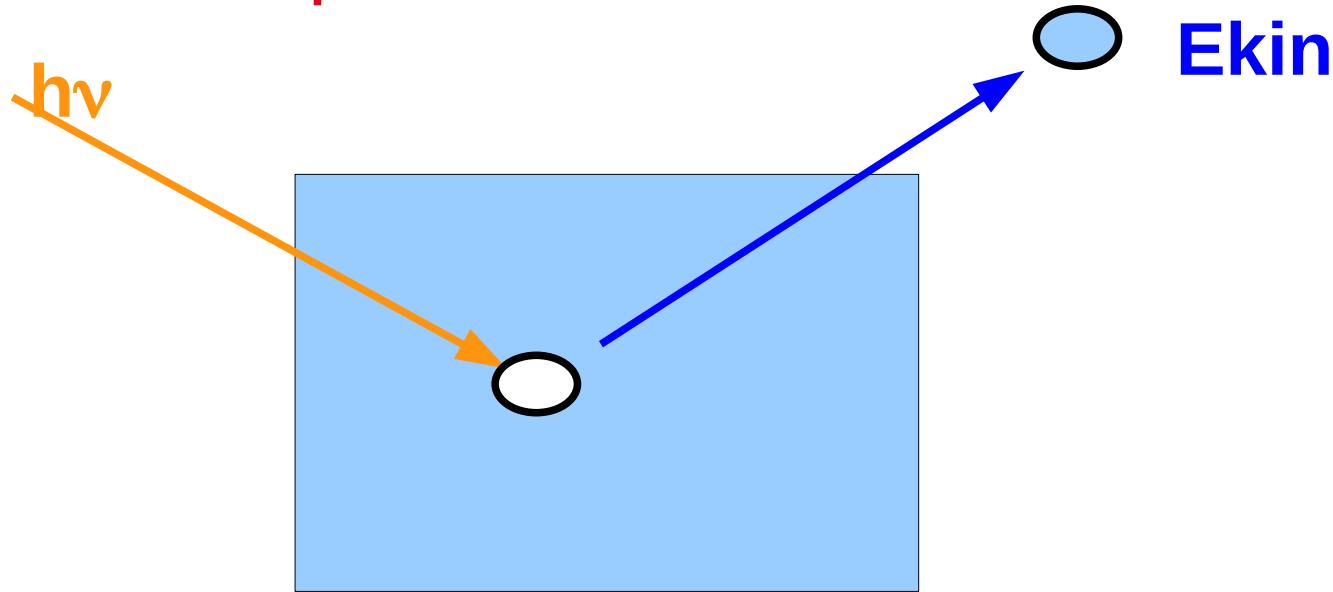
$$\epsilon_i = \begin{cases} E(N+1, i) - E(N, 0) \\ E(N, 0) - E(N-1, i) \end{cases}$$

Exact
excitation energies!





Direct link to photoemission



Energy conservation:

before

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

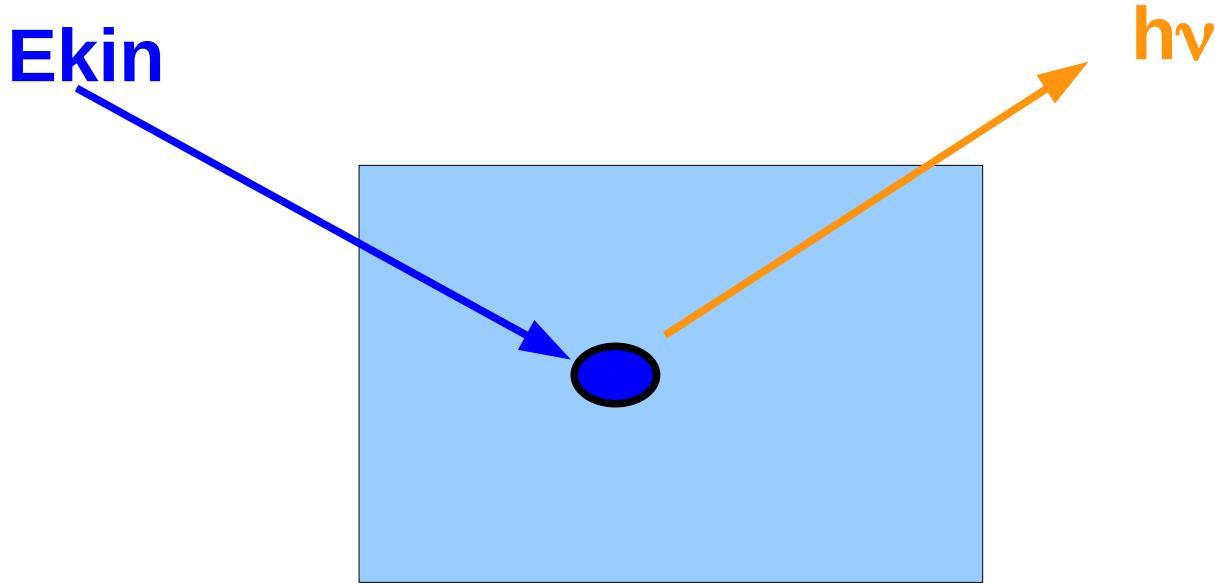
after

Quasiparticle energy:

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



And inverse photoemission



Energy conservation:

before

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

after

Quasiparticle energy:

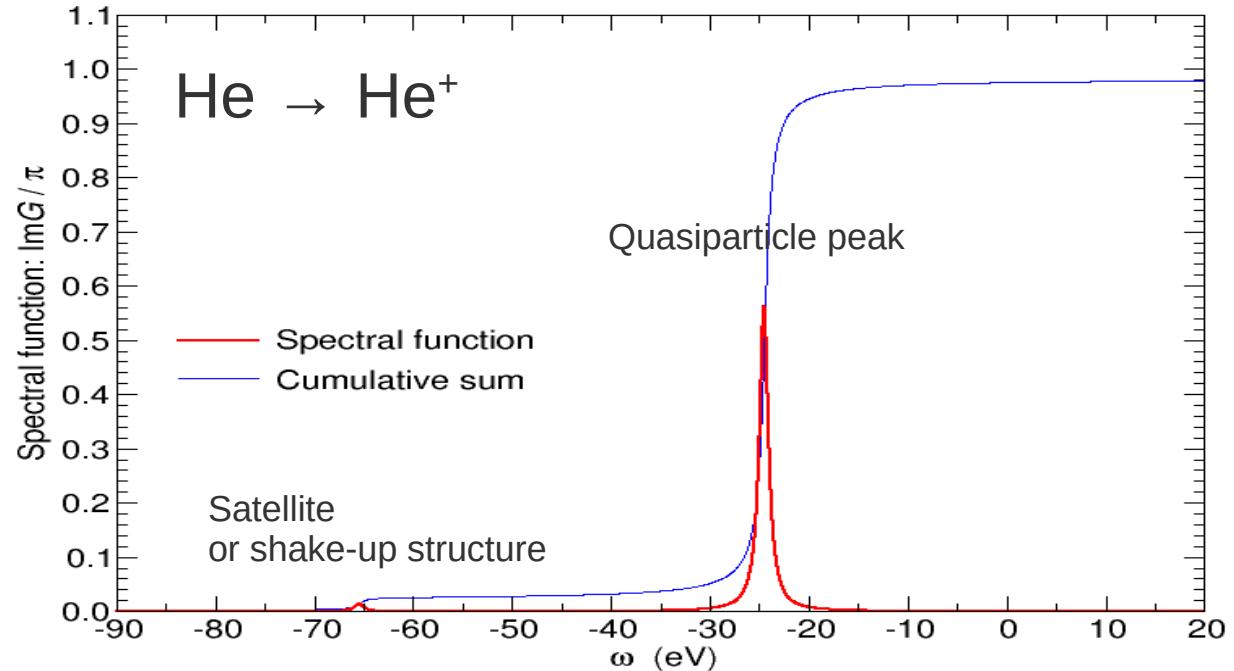
$$\epsilon_i = E(N+1,i) - E(N,0) = E_{kin} - h\nu$$

Exact realization of the Lehman decomposition

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

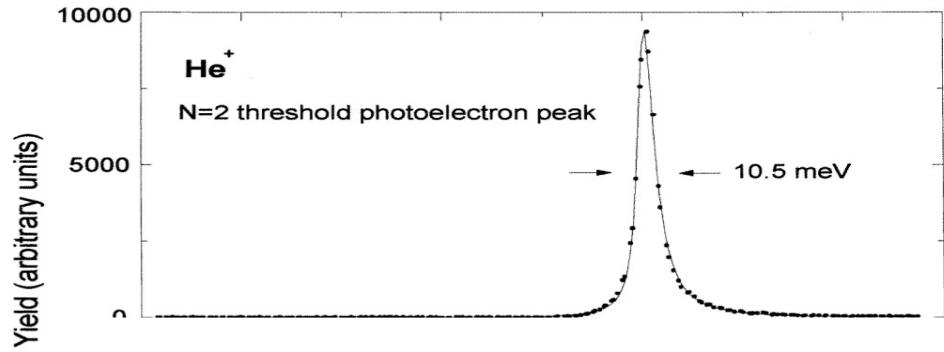
$N=2$
 $N-1=1$
 $m=1\ s$

Obtained from FCI calculations

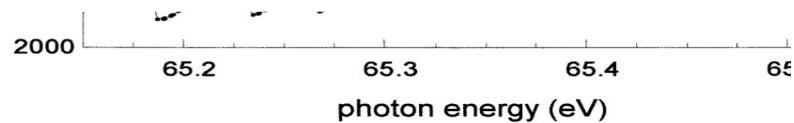




Are satellites something real?

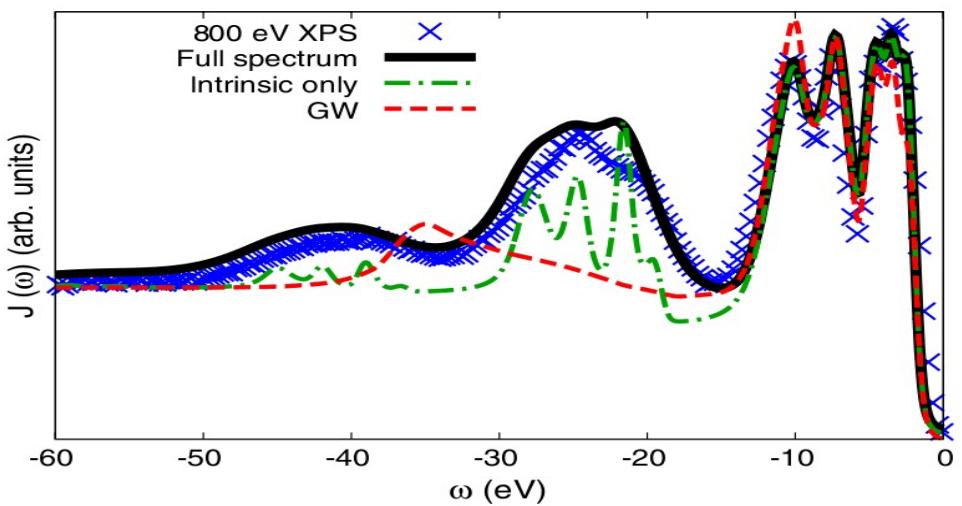


Helium gas
Thompson *et al.*
J. Phys. B: At. Mol. Opt. Phys. (1998)



Silicon crystal

Guzzo *et al.* PRL (2011)





Other data contained in 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:

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

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

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

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Dyson equation for the exact Green's function

Construct the operator that generates
the exact G
from the knowledge of the
non-interacting G_0

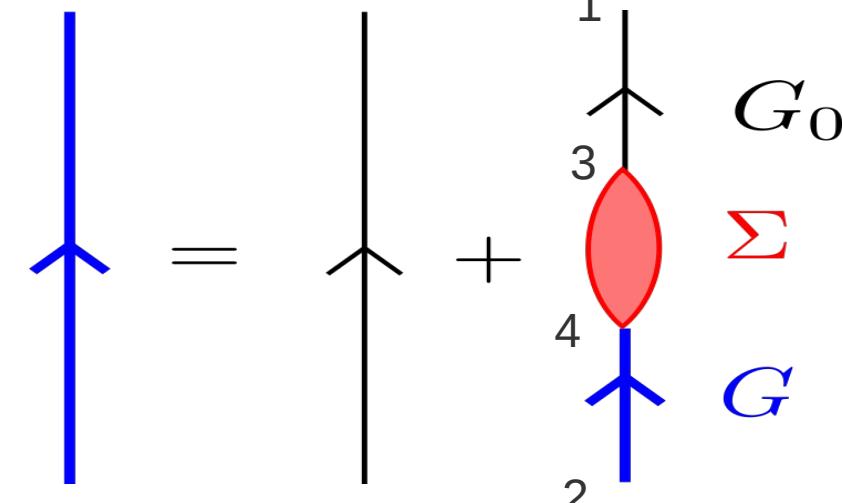
$$1 = \mathbf{r}_1 t_1 \sigma_1 \quad \int d3 G^{-1}(1, 2) G(2, 3) = \delta(1, 3)$$

$$\mathbf{G}^{-1}(1, 2) = G_0^{-1}(1, 2) - \Sigma(1, 2)$$

$$\mathbf{G}(1, 2) = G_0(1, 2) + \int d3d4 G_0(1, 3) \Sigma(3, 4) \mathbf{G}(4, 2)$$

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!



An infinite 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**

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

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

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

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

.....





Closed 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

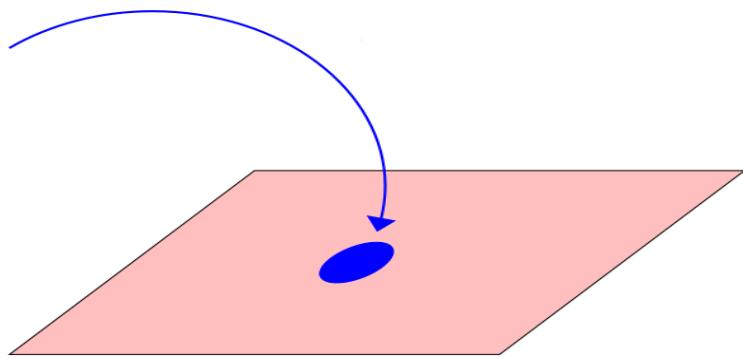
F. Bruneval, GW calculations with ABINIT





Everything is a functional of U or V

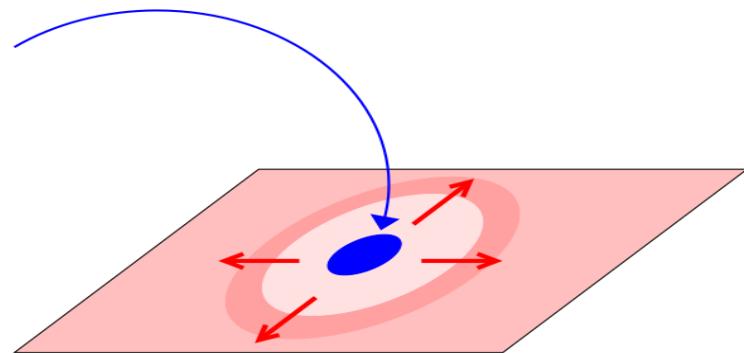
$$U(1) = \varepsilon \delta(\mathbf{r} - \mathbf{r}_1) \delta(t - t_1)$$



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 equations

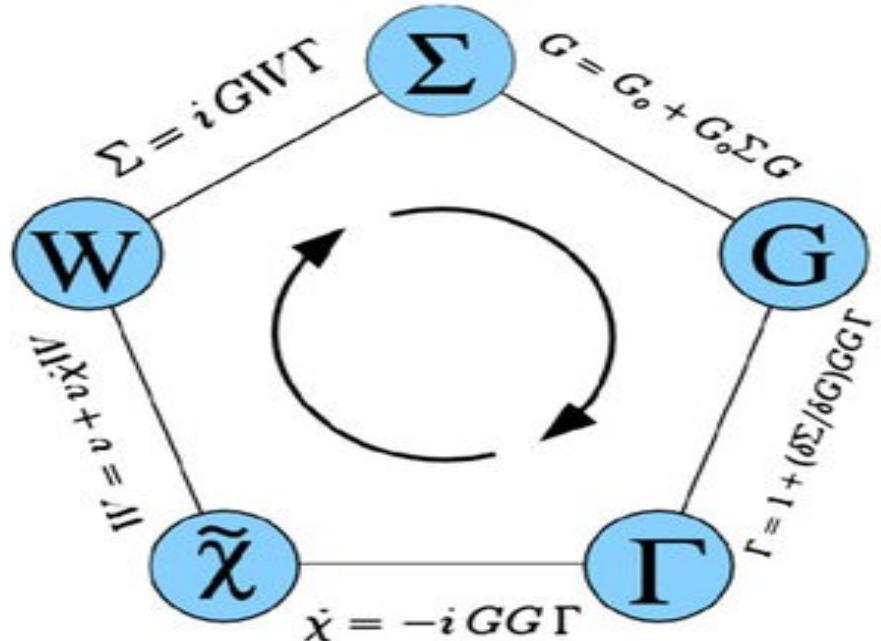
5 coupled equations:

$$1 = (\mathbf{r}_1 t_1 \sigma_1) \quad 2 = (\mathbf{r}_2 t_2 \sigma_2)$$

$$\begin{aligned} \rightarrow G(1,2) &= G_0(1,2) + \int d34 G_0(1,3) \Sigma(3,4) G(4,2) && \text{Dyson equation} \\ \Sigma(1,2) &= i \int d34 G(1,3) W(1,4) \Gamma(4,2,3) && \text{self-energy} \\ \Gamma(1,2,3) &= \delta(1,2) \delta(1,3) + \int d4567 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(5,7) \Gamma(6,7,3) && \text{vertex} \\ \widetilde{\chi}(1,2) &= -i \int d34 G(1,3) G(4,1) \Gamma(3,4,2) && \text{polarizability} \\ W(1,2) &= v(1,2) + \int d34 v(1,3) \widetilde{\chi}(3,4) W(4,2) && \text{screened Coulomb interaction} \end{aligned}$$

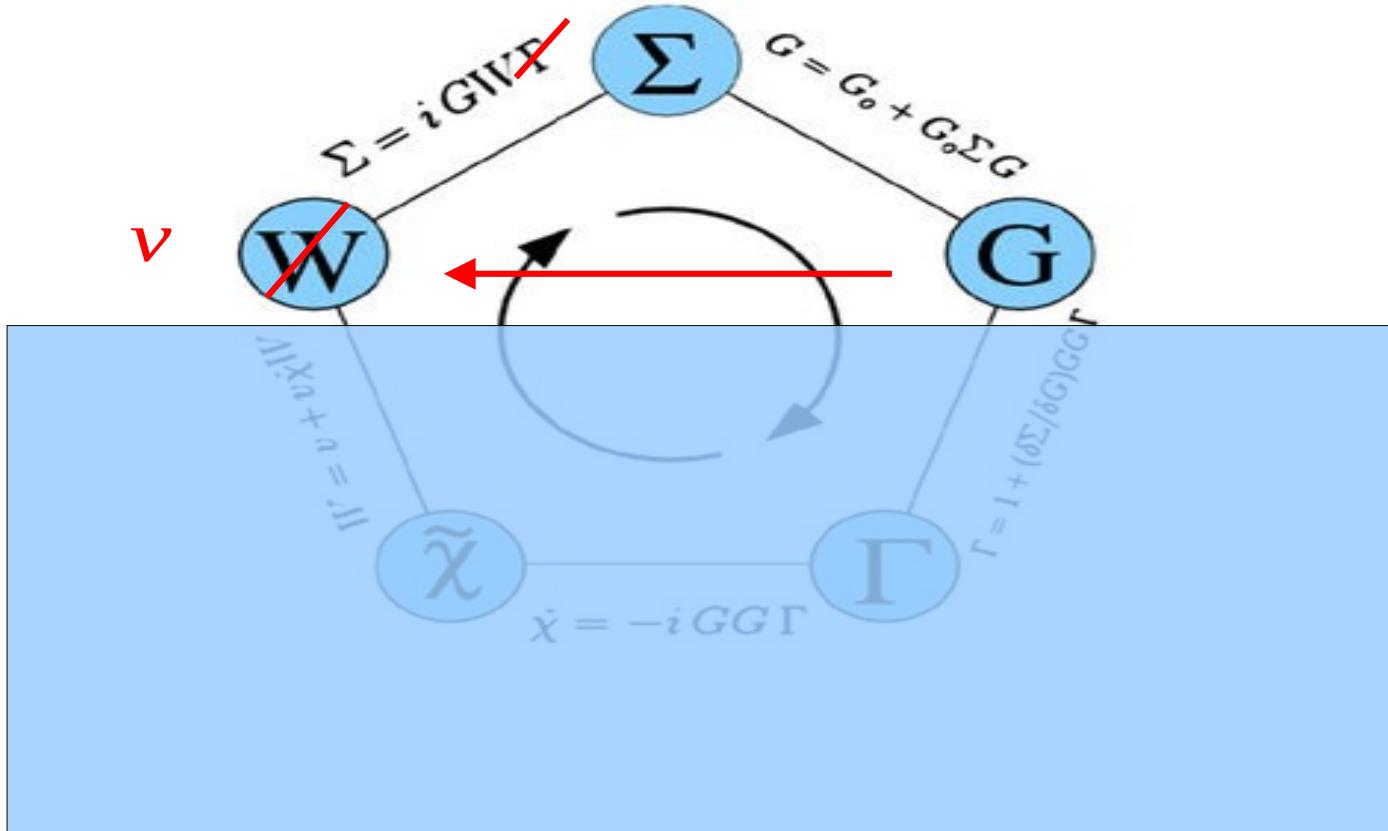


Hedin's pentagon





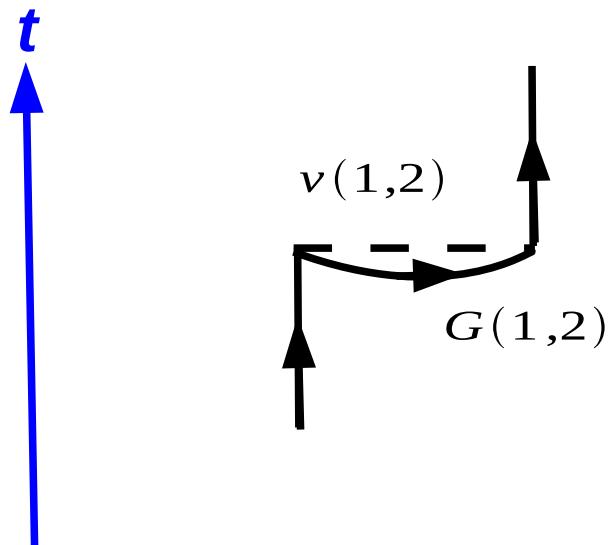
Hedin's pentagon short-circuited





Hartree-Fock approximation

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



Dyson equation:

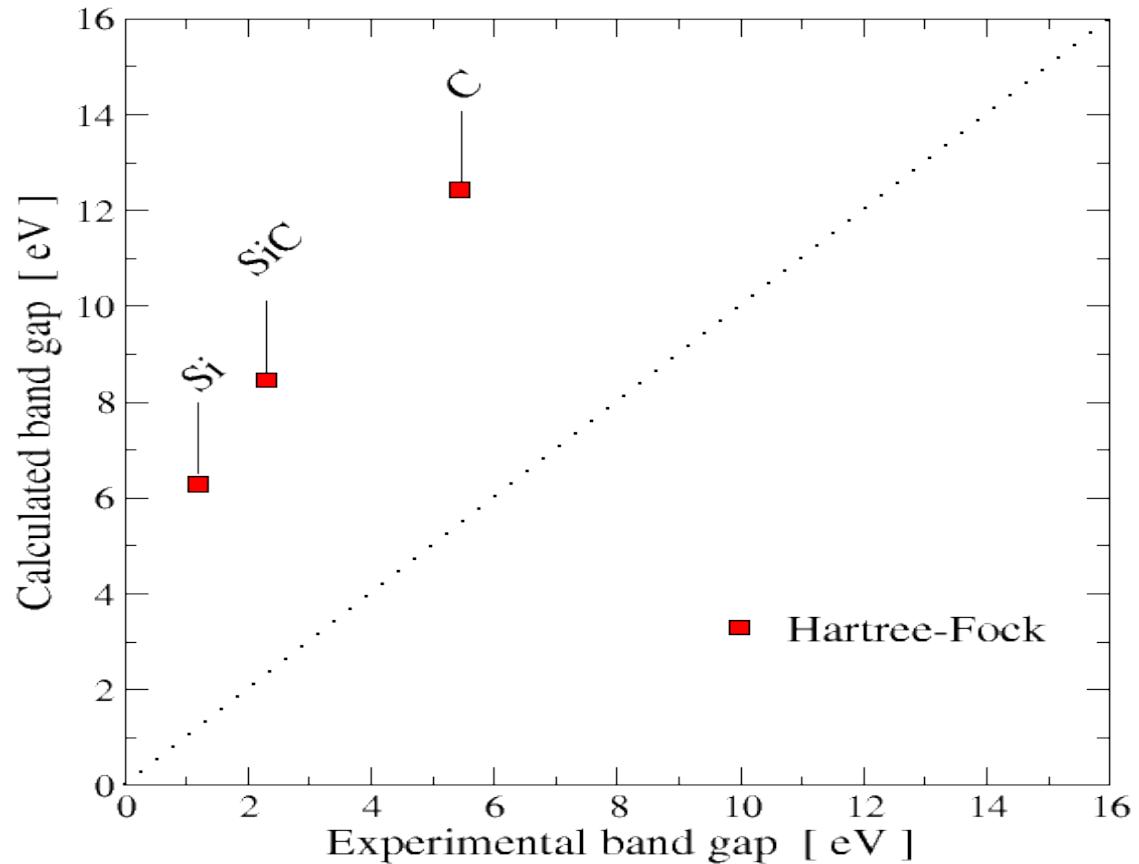
$$G = G_0 + G_0 \Sigma G$$

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





Hartree-Fock approximation in solids





Hedin's equations

5 coupled equations:

$$1 = (\mathbf{r}_1 t_1 \sigma_1) \quad 2 = (\mathbf{r}_2 t_2 \sigma_2)$$

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

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

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

polarizability

$$W(1,2) = v(1,2) + \int d34 v(1,3) \tilde{\chi}(3,4) W(4,2)$$

screened Coulomb interaction





Hedin's equations

5 coupled equations:

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Hedin's equations

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Dyson equation

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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

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

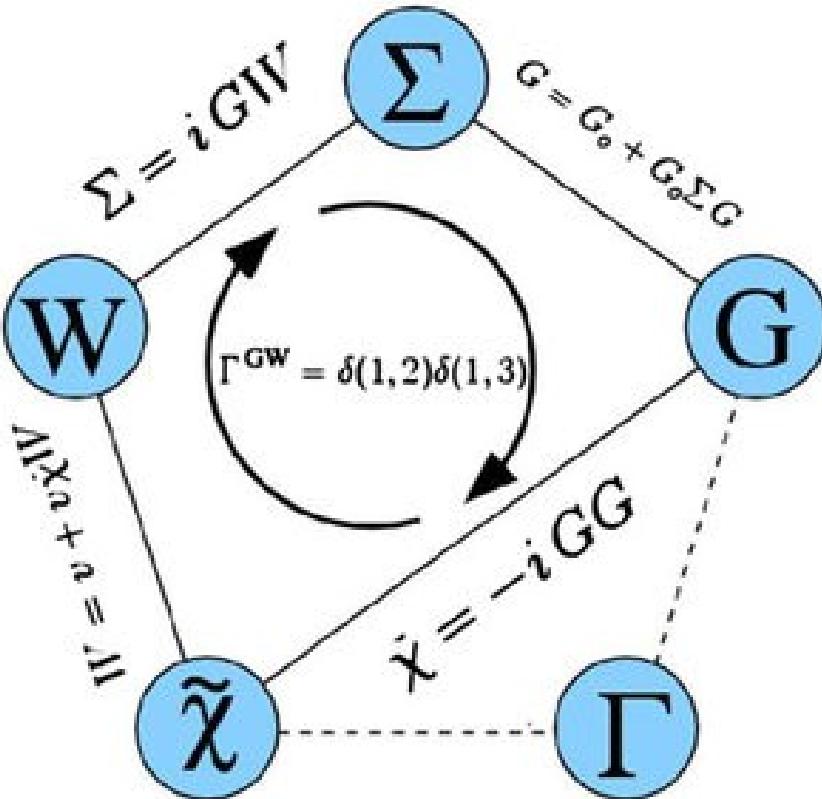
polarizability

$$W(1,2) = v(1,2) + \int d34 v(1,3) \tilde{\chi}(3,4) W(4,2)$$

screened Coulomb interaction



Hedin's pentagon is a quadri



short-cutting the vertex



And here comes the *GW* approximation

$$\Sigma(1,2) = iG(1,2)W(1,2)$$

GW approximation

$$\tilde{\chi}(1,2) = -iG(1,2)G(2,1)$$

RPA approximation

$$W(1,2) = v(1,2) + \int d34 v(1,3)\tilde{\chi}(3,4)W(4,2)$$

Dyson-like equation

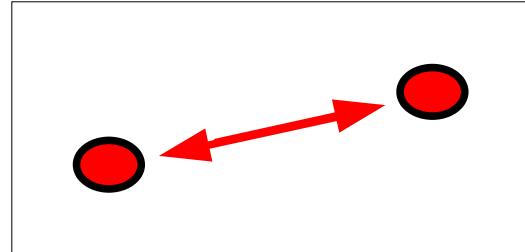




What is W ?

Interaction between electrons in vacuum:

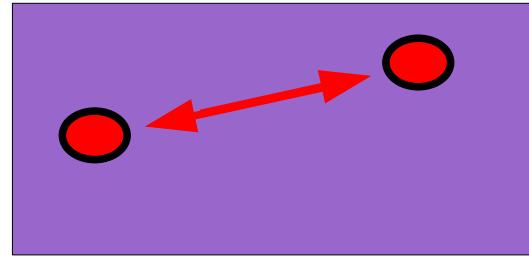
$$v(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$



Interaction between electrons in a homogeneous polarizable medium:

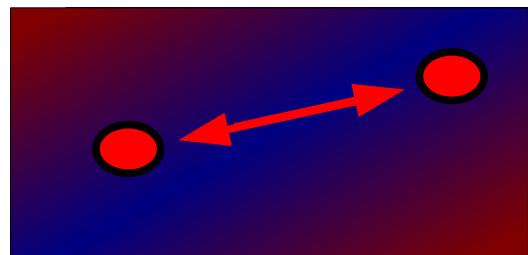
$$W(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$

Dielectric constant
of the medium



Dynamically screened interaction between electrons
in a general medium:

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





Summary





DFT versus Green's function theory

Electronic density

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



Green's function

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

Local and static

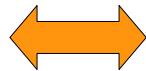


Non-local, dynamic
Depends onto empty states



exchange-correlation potential

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



exchange-correlation operator
= self-energy

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

Approximations:

LDA, GGA, hybrids

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 as a « boosted 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

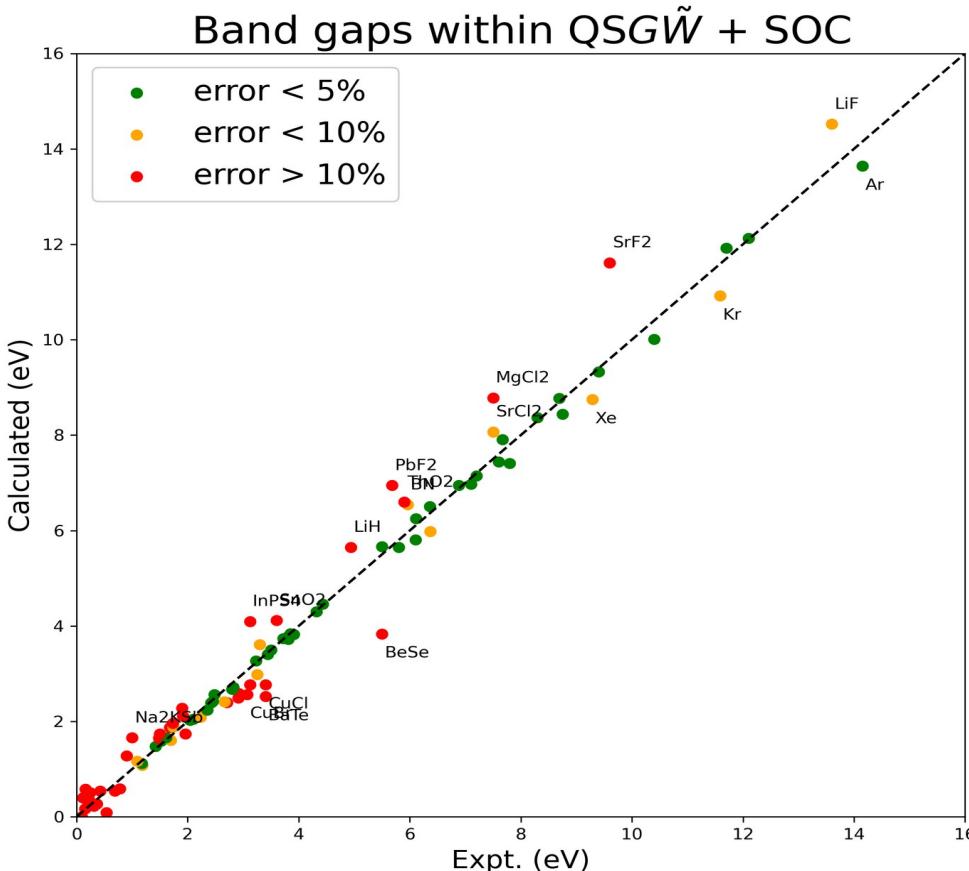
Non Hermitian
dynamic

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

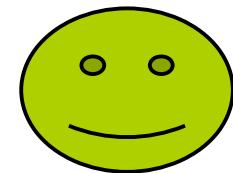




GW band gaps



No band gap problem anymore!



Grossman et al. arxiv (2025)



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GW formulas

$$\Sigma(1,2) = iG(1,2)W(1,2)$$

GW approximation

$$\tilde{\chi}(1,2) = -iG(1,2)G(2,1)$$

RPA approximation

$$W(1,2) = v(1,2) + \int d34 v(1,3) \tilde{\chi}(3,4) W(4,2)$$

Dyson-like equation





Historical recap of GW calculations in solids

- 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**

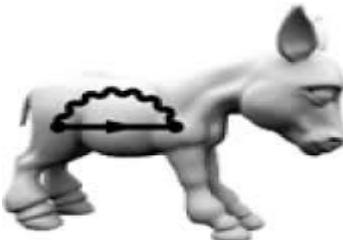




GW codes

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

based on plane-waves (with pseudo or PAW)



- For finite systems: MOLGW, Fiesta, FHI-AIMS, CP2K

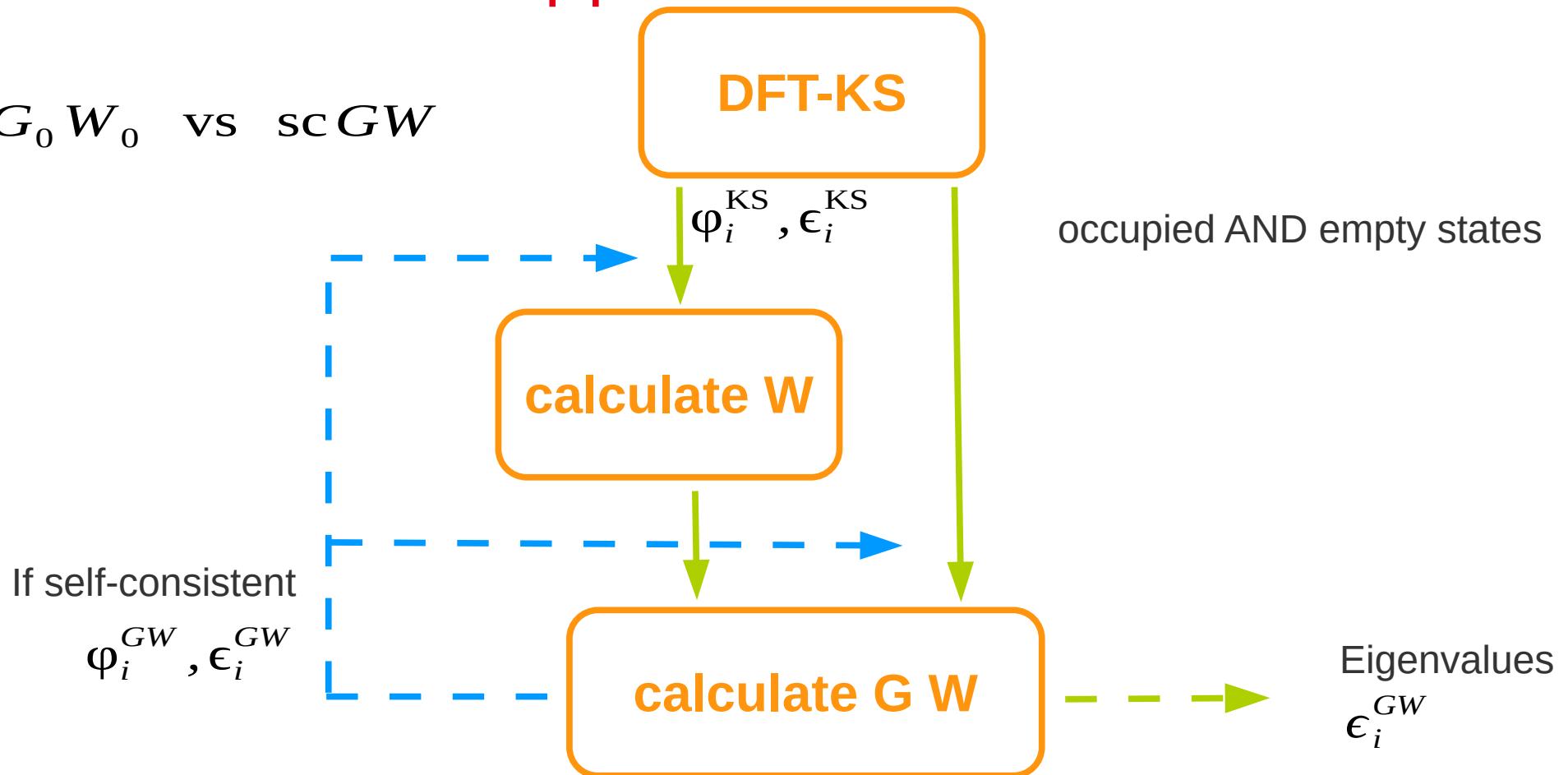
based on localized orbitals (Gaussians or Slater or other)





« one-shoot » GW approach

$G_0 W_0$ vs $sc\,GW$





First, get G_0

G_0 from Kohn-Sham DFT hamiltonian

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

Remember the Lehman representation of the exact G

$$G(\mathbf{r}, \mathbf{r}', \omega) = \sum_i \frac{f_i(\mathbf{r}) f_i^*(\mathbf{r}')}{\omega - \epsilon_i \pm i\eta} \quad f_i(\mathbf{r}) = \begin{cases} \langle N-1, i | \Psi(\mathbf{r}) | N, 0 \rangle, & \epsilon_i < \mu, \\ \langle N, 0 | \Psi(\mathbf{r}) | N+1, i \rangle, & \epsilon_i > \mu \end{cases}$$



This expression will be used in W and Σ



Second, get W_0

From the RPA equation

$$\tilde{\chi}(1, 2) = -iG_0(1, 2)G_0(2, 1) = \chi_0(1, 2)$$

Fourier transforming:

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \frac{i}{2\pi} \int d\omega' G_0(\mathbf{r}_1, \mathbf{r}_2, \omega + \omega')G_0(\mathbf{r}_2, \mathbf{r}_1, \omega')$$

Introducing G_0

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = -\frac{i}{2\pi} \int d\omega' \left(\sum_i \frac{\varphi_i(\mathbf{r}_1)\varphi_i^*(\mathbf{r}_2)}{\omega + \omega' - \epsilon_i \pm i\eta} \right) \cdot \left(\sum_j \frac{\varphi_j(\mathbf{r}_2)\varphi_j^*(\mathbf{r}_1)}{\omega' - \epsilon_j \pm i\eta} \right)$$

Then residue theorem:

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

This is the **Alder-Wiser formula** or the **SOS formula**.

It involves empty states!



Second, get W

$$W(\mathbf{r}_1, \mathbf{r}_2, \omega) = v(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3 v(\mathbf{r}_1, \mathbf{r}_3) \chi_0(\mathbf{r}_3, \mathbf{r}_4, \omega) W(\mathbf{r}_4, \mathbf{r}_2, \omega)$$

This is just an inversion.
We'll see later



Third, get Σ

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

This is “just” a convolution to calculate

In practice, we calculate matrix elements of Σ

$$\Sigma_{pq}(\omega) = \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_p^*(\mathbf{r}_1) \Sigma(\mathbf{r}_1, \mathbf{r}_2, \omega) \varphi_q(\mathbf{r}_2)$$



Diagonal approximation

Dyson equation:

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

And remember:

$$G^{KS \ -1}(\mathbf{r}, \mathbf{r}', \omega) = \sum_p \varphi_p^{KS}(\mathbf{r}) [\omega - \epsilon_i^{KS}] \varphi_p^{KS *}(\mathbf{r}')$$

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

$$G_{pq}^{KS \ -1}(\omega) = \delta_{pq} (\omega - \epsilon_p^{KS})$$

Approximation:

$$\langle p | \Sigma(\omega) - v_{xc} | q \rangle \approx \delta_{pq} \langle p | \Sigma(\omega) - v_{xc} | p \rangle$$

Hence G is **diagonal** in KS basis

$$G_{pq}^{-1}(\omega) \approx \delta_{pq} (\omega - \epsilon_p^{KS}) - \langle p | \Sigma(\omega) - v_{xc} | p \rangle$$



Quasiparticle energies

G is **diagonal** in KS basis

$$G_{pq}^{-1}(\omega) \approx \delta_{pq} \left(\omega - \epsilon_p^{\text{KS}} - \langle p | \Sigma(\omega) - v_{xc} | p \rangle \right)$$

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

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



Quasiparticle energies:

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

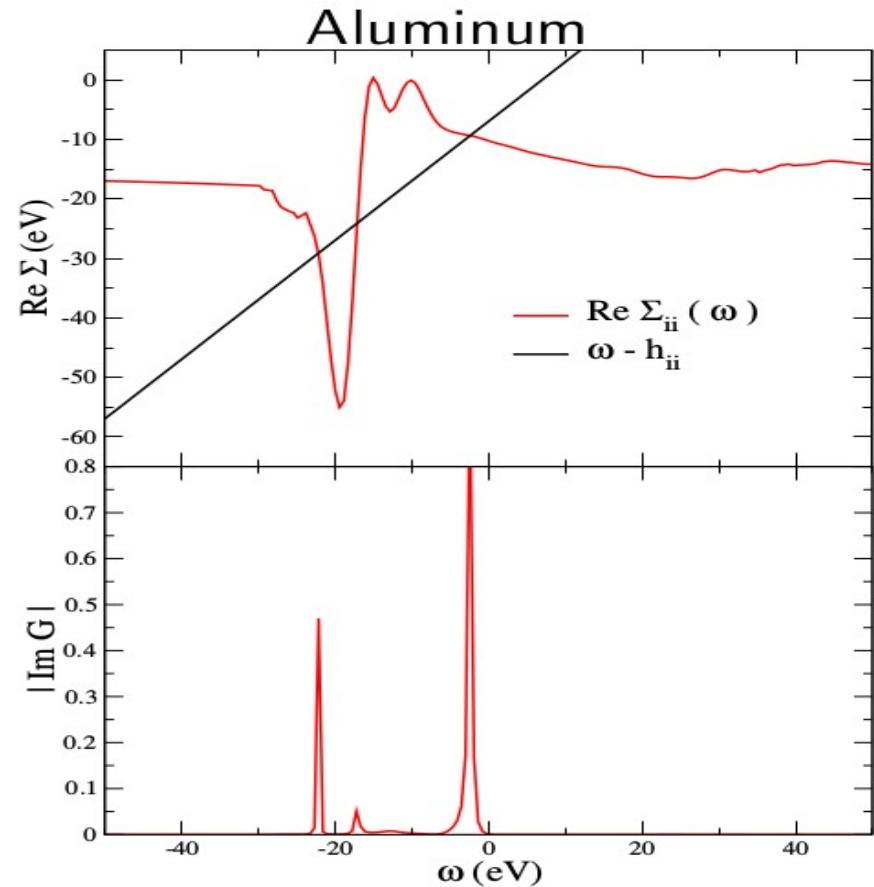
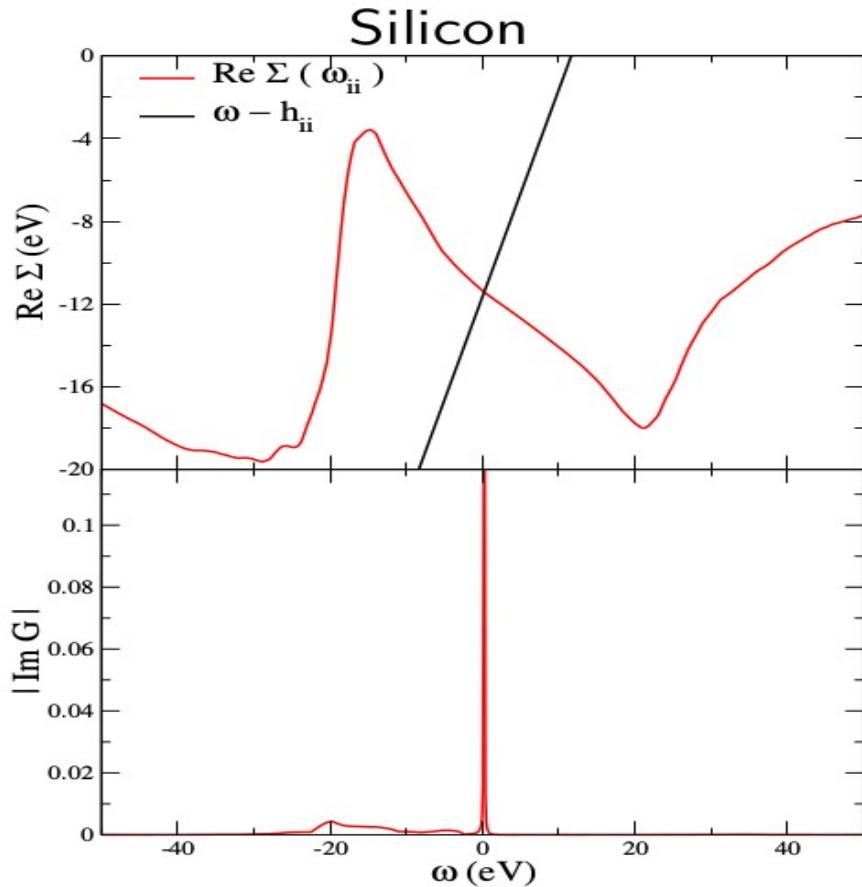
unknown variable on both sides of the equation





Graphical solution

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





Or linearization

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

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:

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

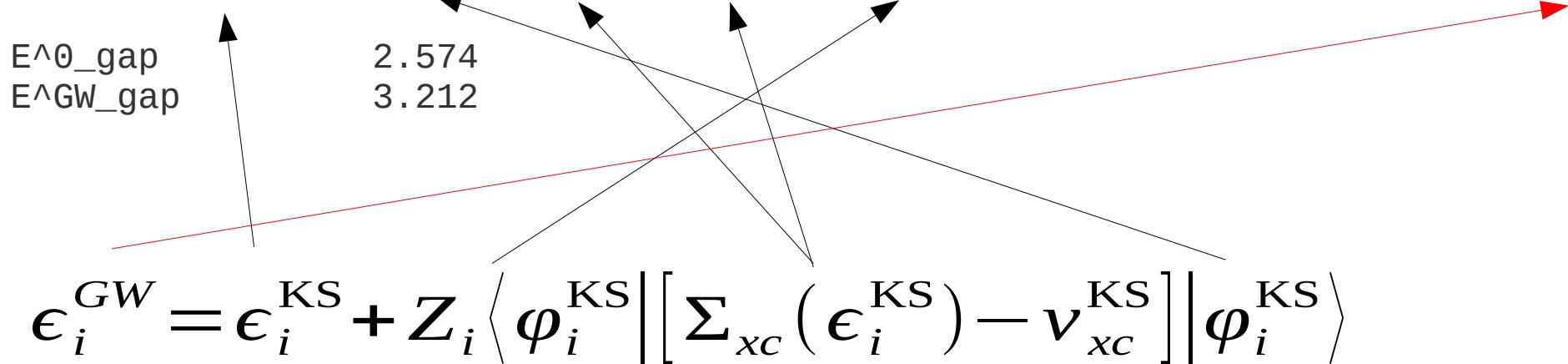
where $Z_i = 1 / \left(1 - \langle i | \frac{\partial \Sigma}{\partial \epsilon} | i \rangle \right)$





Typical ABINIT output: Silicon at Gamma point

k =	0.000	0.000	0.000						
Band	E ₀	<VxcDFT>	SigX	SigC(E ₀)	Z	dSigC/dE	Sig(E)	E-E ₀	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





What was left under the carpet...





Two-point (= non-local) functions with plane-waves

Remember 1-point functions are

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

1 vector of coefficients per 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 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

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

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

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

$$(1) \quad \chi_{0\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = \sum_{\mathbf{k}} \langle j\mathbf{k} - \mathbf{q} | e^{-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}_1} | i\mathbf{k} \rangle \langle i\mathbf{k} | e^{i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}_2} | j\mathbf{k} - \mathbf{q} \rangle$$

ecuteps i_{occ} j_{virt} nband

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

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

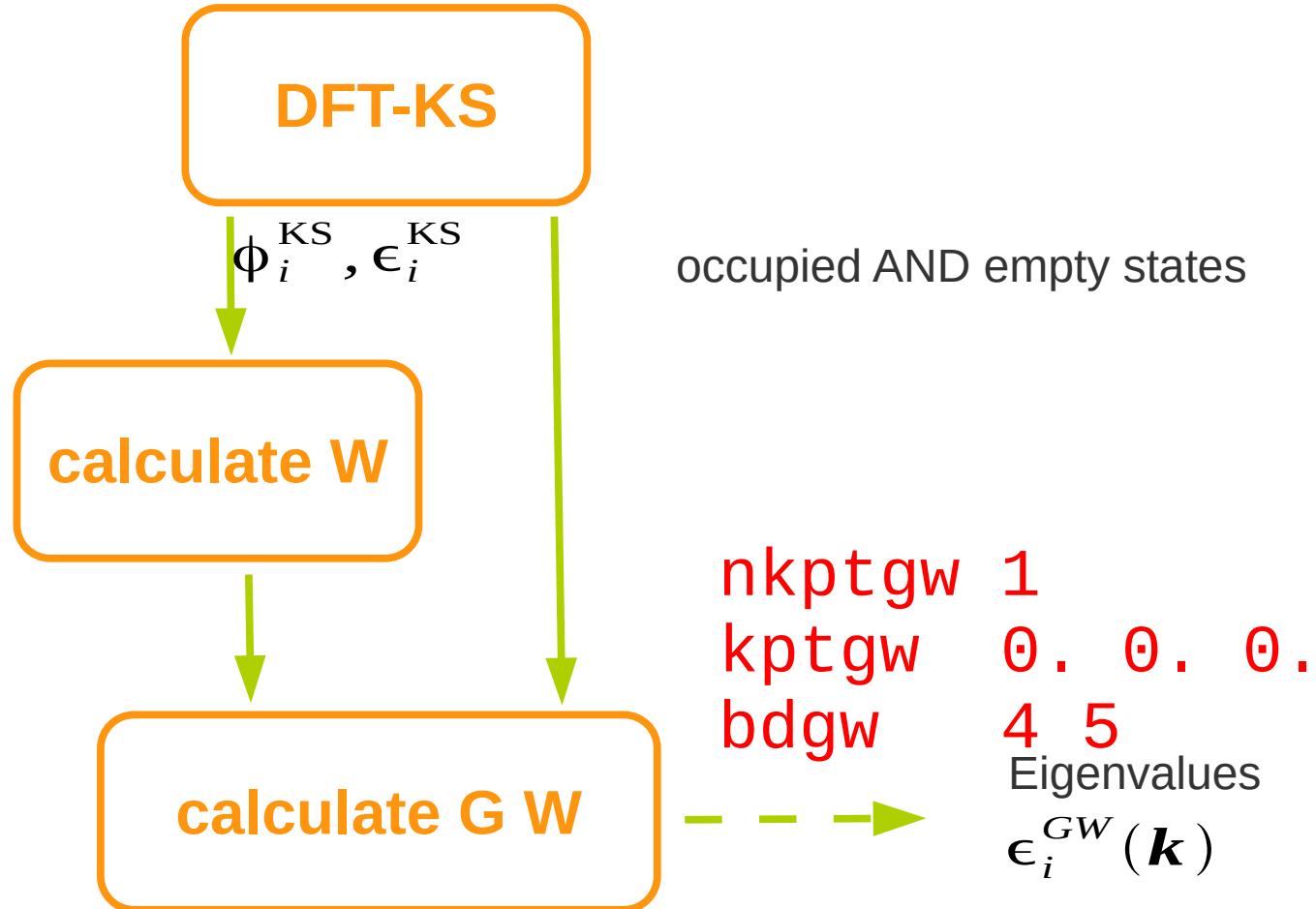
$$(3) \quad W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = \varepsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}, \mathbf{G}') v_{\mathbf{G}'}(\mathbf{q}) \quad \longleftarrow \quad \text{matrix inversion}$$



G_0W_0 calculation in ABINIT
ecut
nband1

optdriver 3
nband ≤ nband1
ecuteps

optdriver 4
nband ≤ nband1
ecutsigx = ecut





Frequency dependence in W causes headache

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

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



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



How to deal with the frequency dependence in W?

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



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

2 parameters need two constraints:

- Hybertsen-Louie (HL): $\varepsilon^{-1}(0)$ and f sum rule

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

Position of the pole

- 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!**)

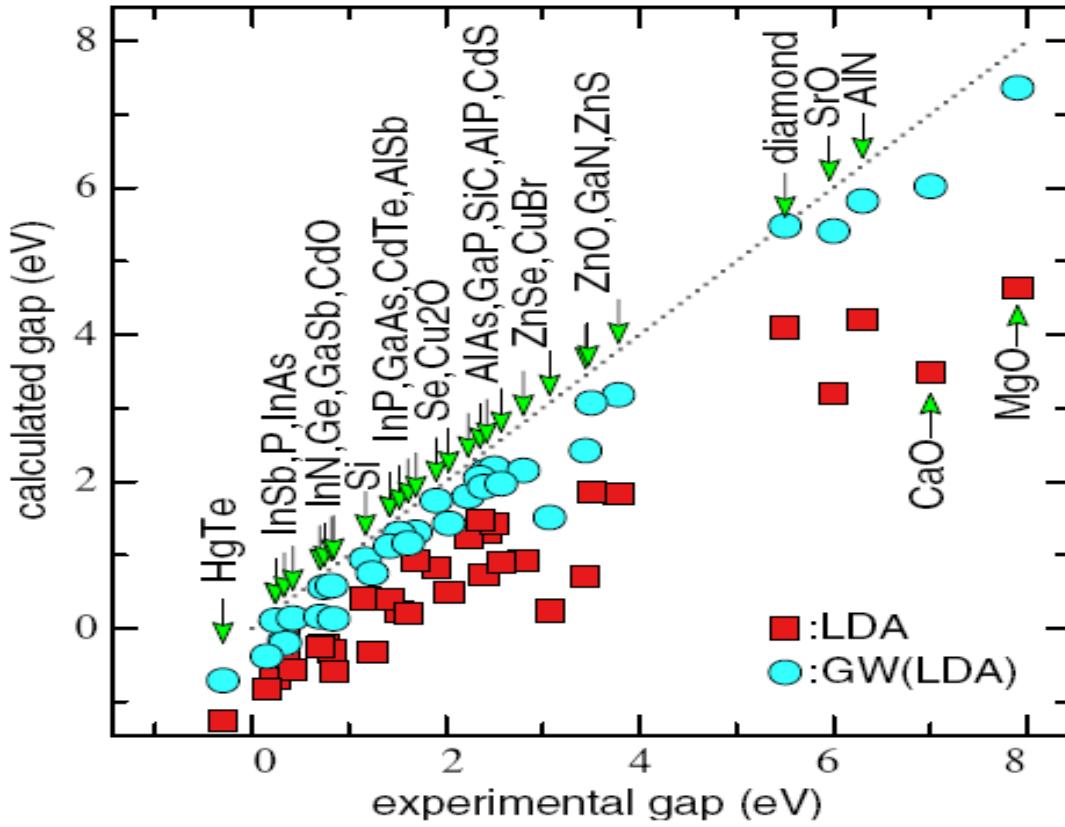


Outline

- I. Motivation: beyond DFT?
- II. Introducing the Green's function
- III. Exact Hedin's equations and the GW approximation
- IV. Calculating the GW self-energy in practice
- V. Applications



GW band gaps



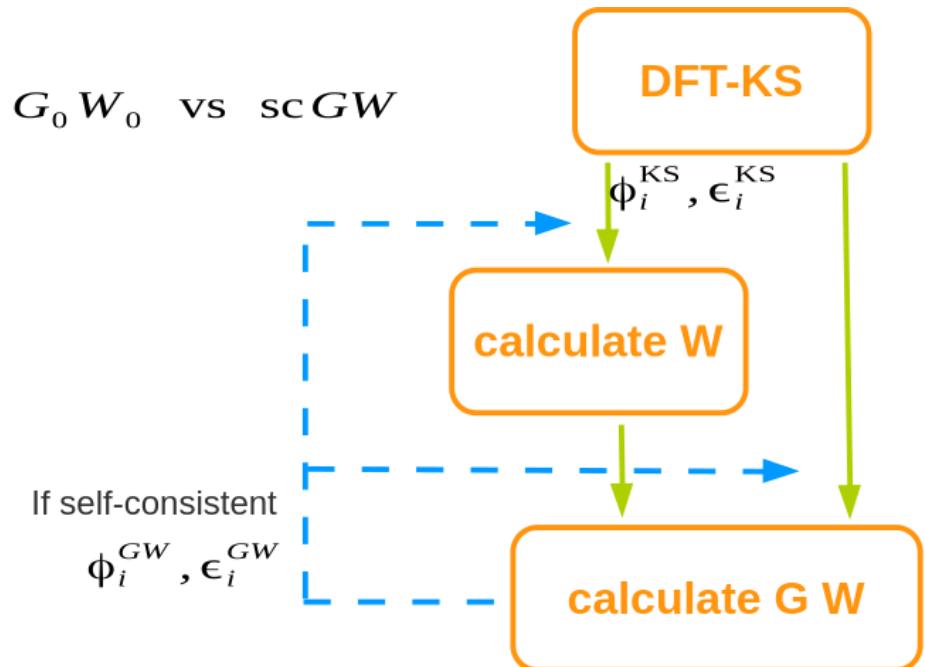
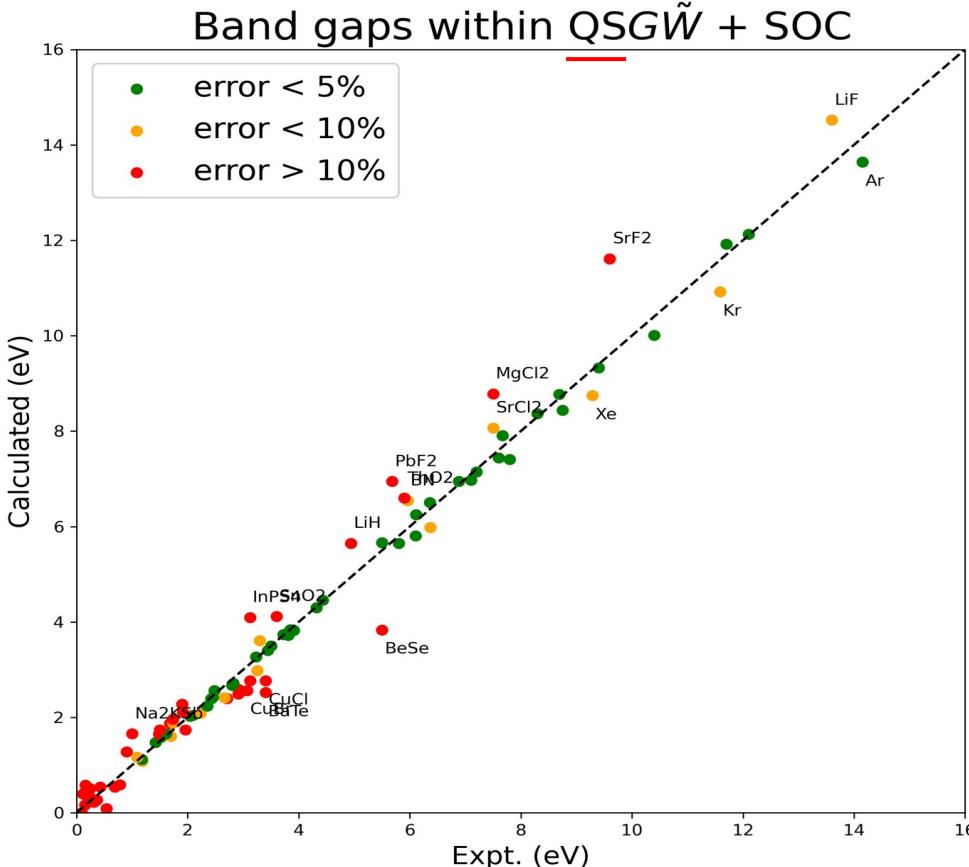
van Schilfgaarde et al PRL 96 226402 (2008)

No more a band gap problem !





QSGW band gaps



ABINIT is capable of QSGW

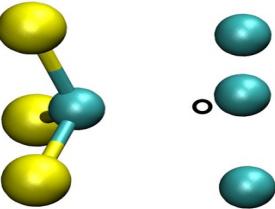
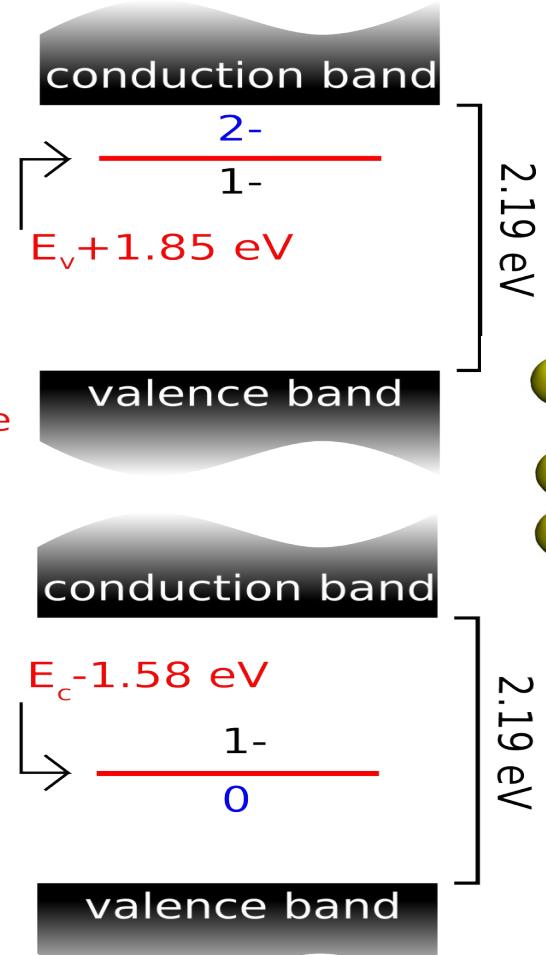
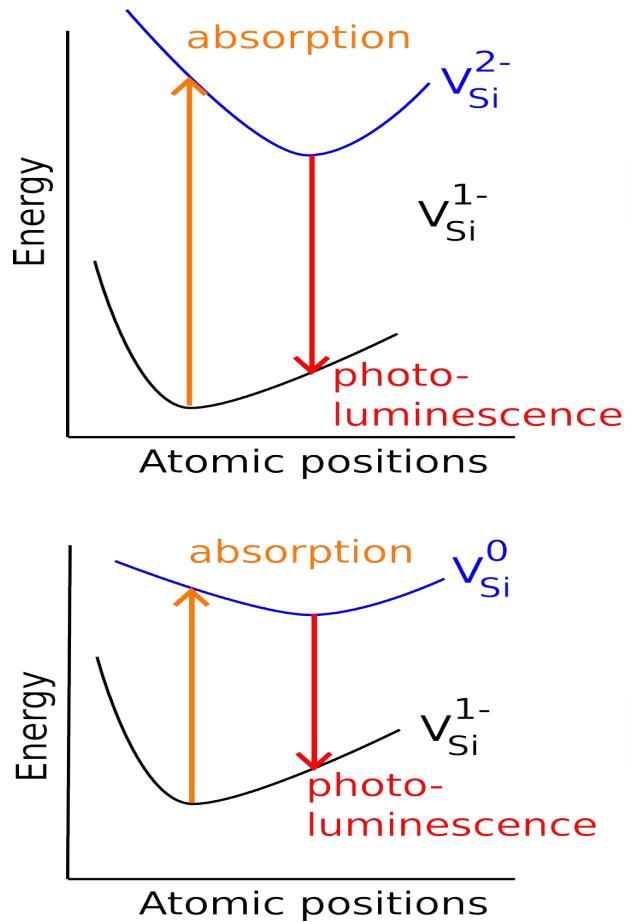
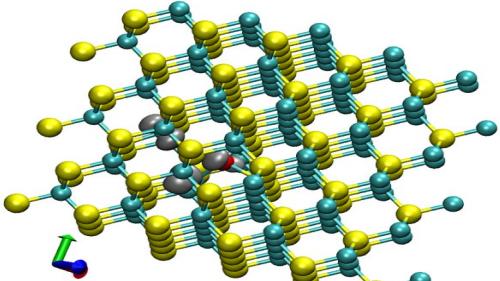
Grossman et al. arxiv (2025)





GW for defects?

215 atoms



Bruneval and Roma PRB (2011)



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:

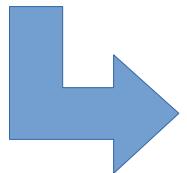
$$T = -\frac{1}{2} \sum_i f_i \iint d\mathbf{r} d\mathbf{r}' \varphi_i^*(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \nabla_{\mathbf{r}'}^2 \varphi_i^*(\mathbf{r}')$$

$$\gamma(\mathbf{r}, \mathbf{r}')$$

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

Surprising facts with density-matrices 1



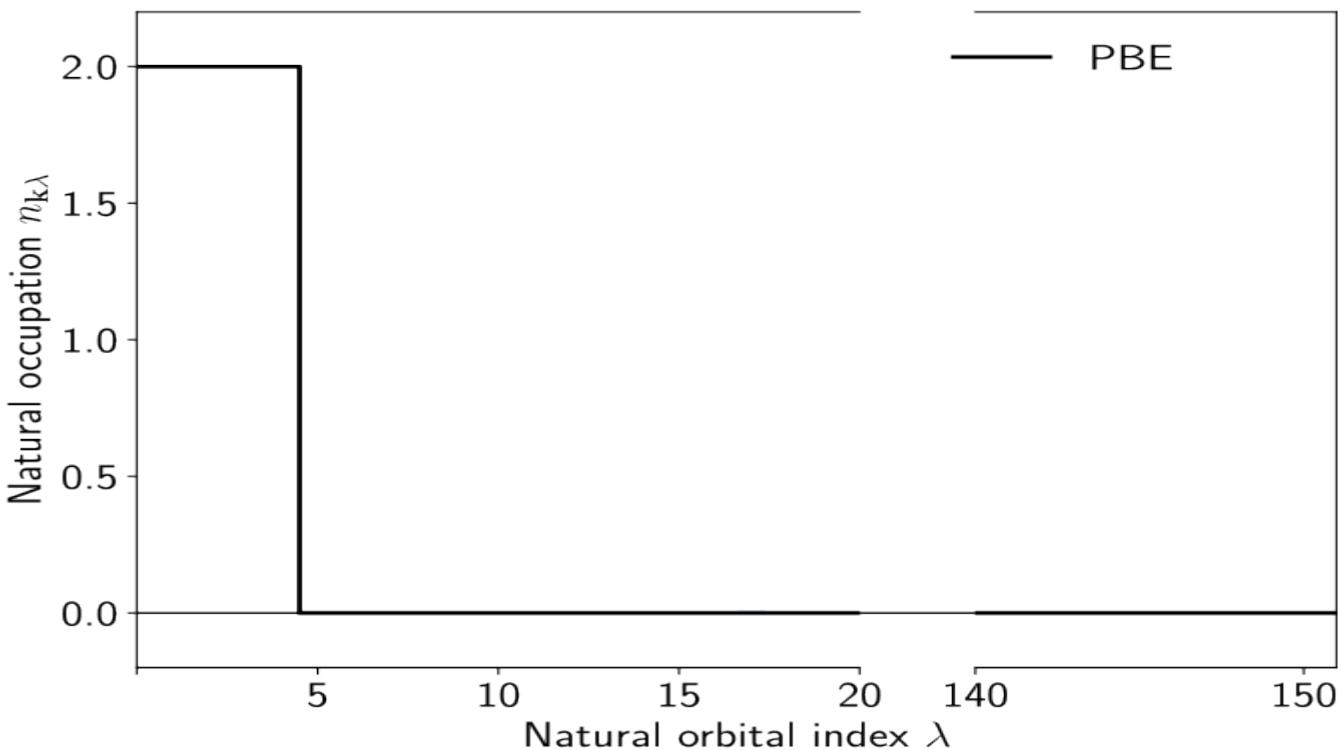
Diagonalization:

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

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



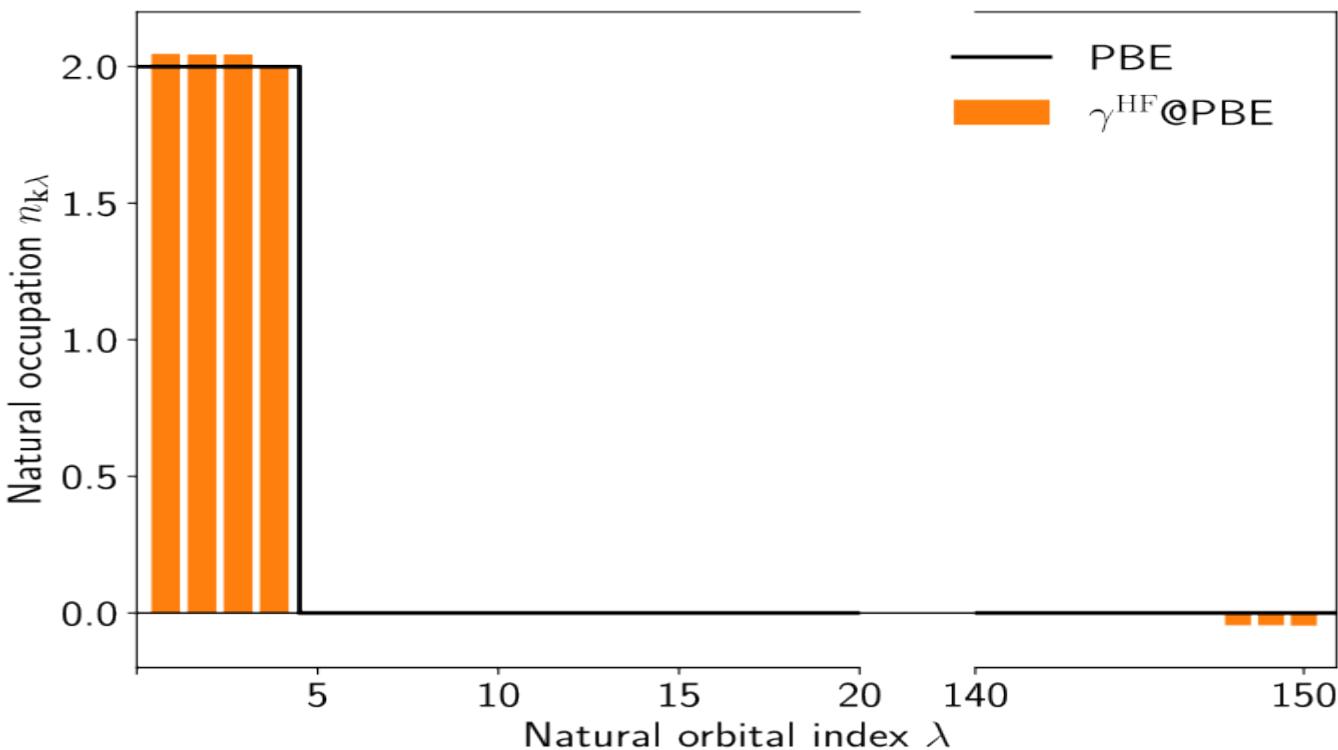
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Si



Surprising facts with density-matrices 1



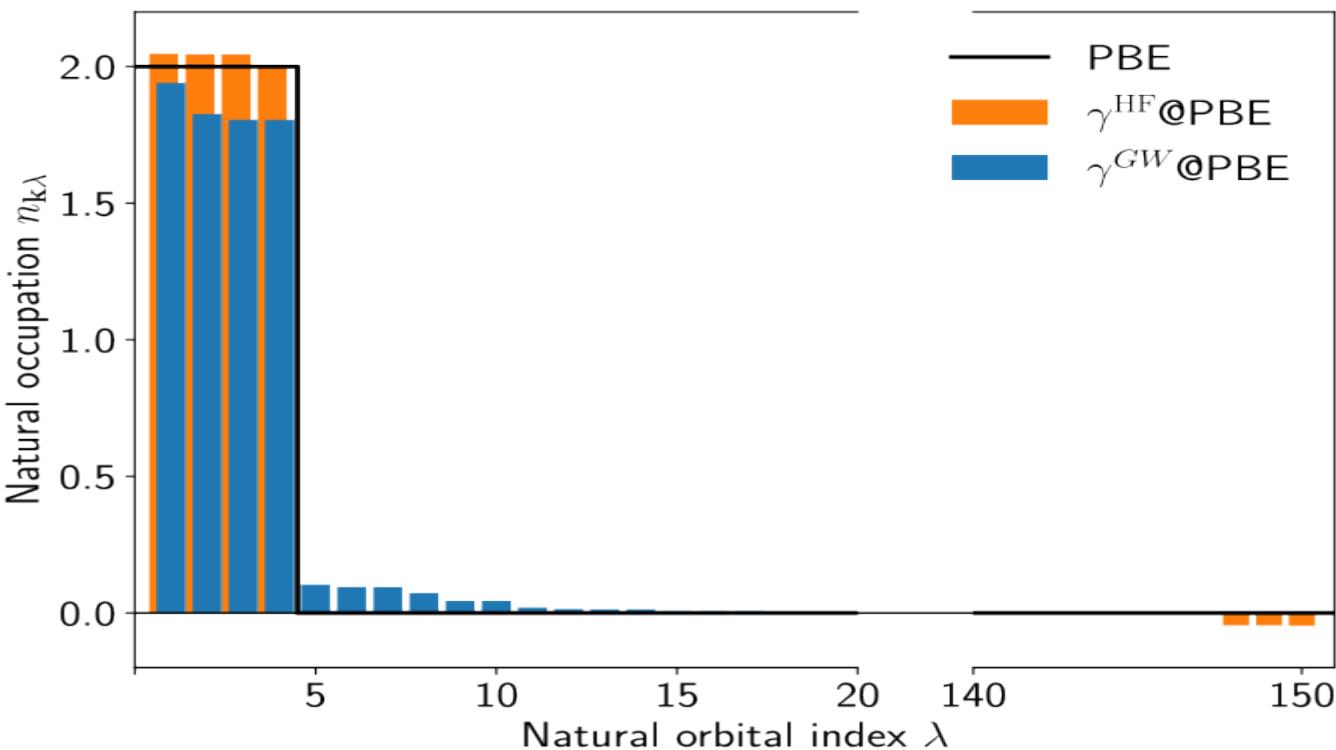
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Si



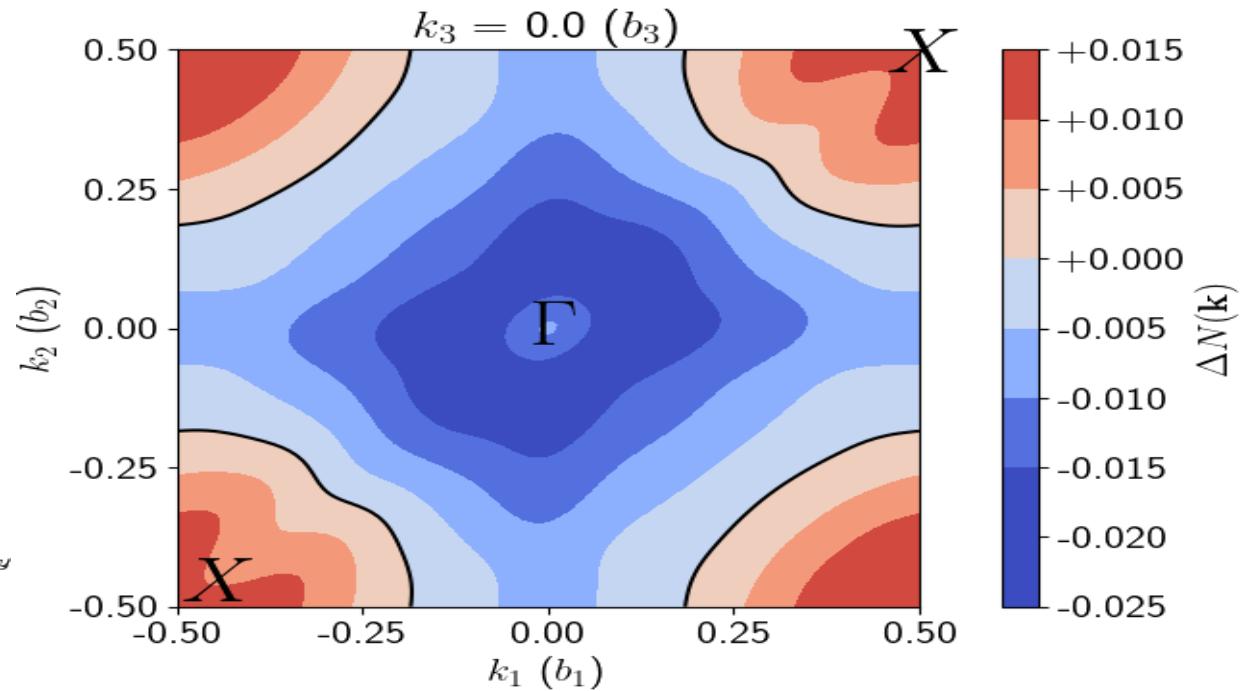
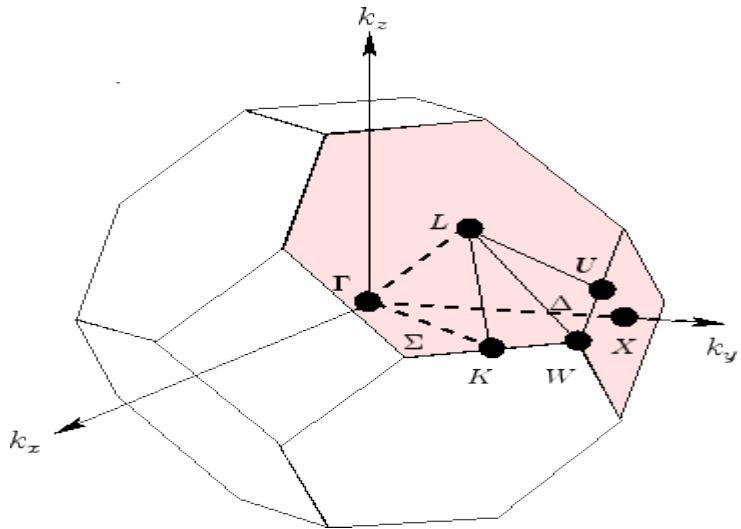
Surprising facts with density-matrices 2



Si

Electron count across the BZ

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

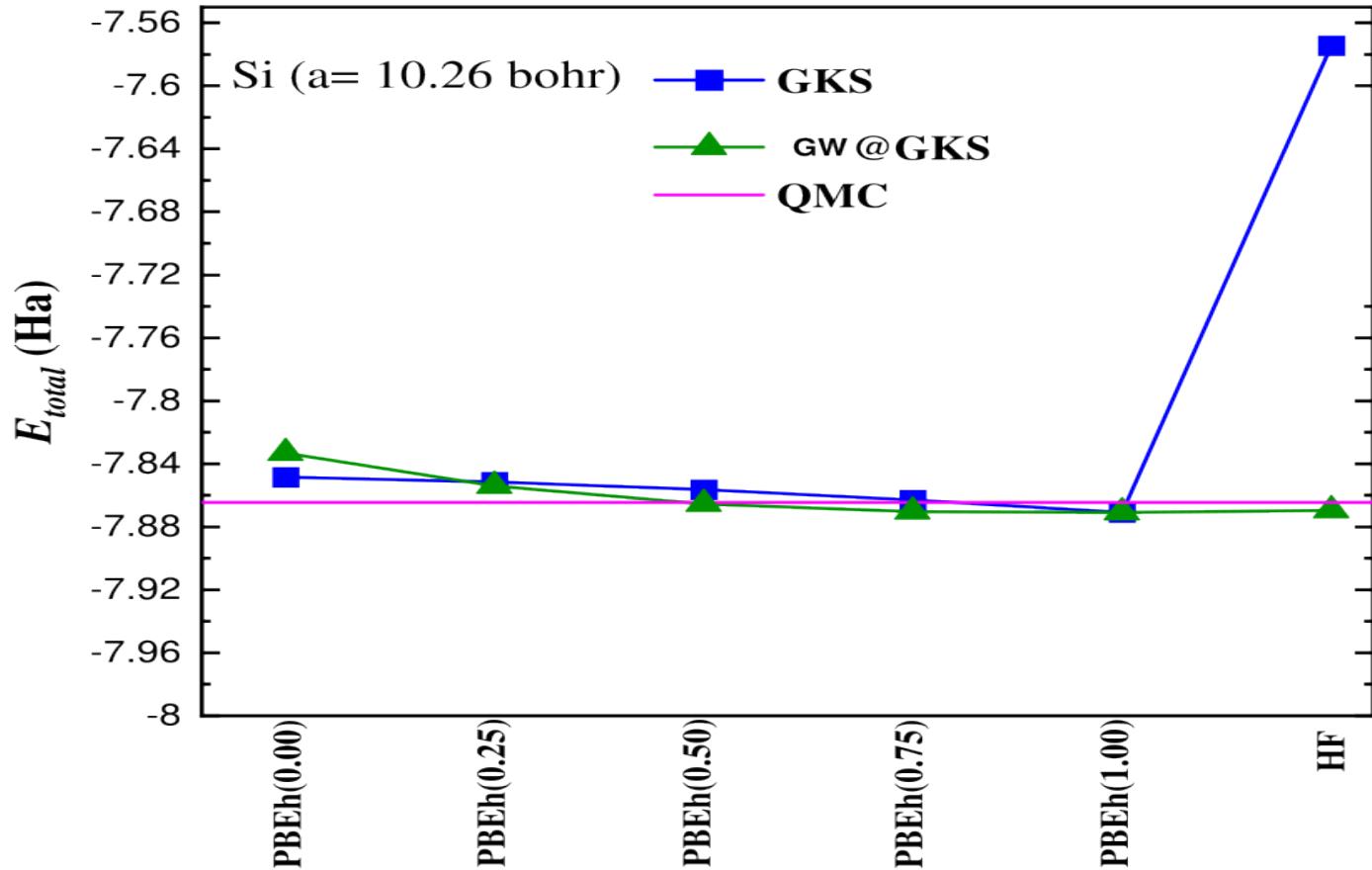


Varying number of electrons that sum up to the correct count!

Density matrix to estimate self-consistent GW energy



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





GWR = space-time approach

Traditional GW implementation scales as N^4 (quartic scaling)

See $\chi_{0\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = \sum_{\mathbf{k}} \langle j \mathbf{k} - \mathbf{q} | e^{-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}_1} | i \mathbf{k} \rangle \langle i \mathbf{k} | e^{i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}_2} | j \mathbf{k} - \mathbf{q} \rangle$

double plane-wave expansion double sum over states

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

But in real-space and time,

$$\tilde{\chi}(1, 2) = -iG_0(1, 2)G_0(2, 1) = \chi_0(1, 2)$$



GWR = space-time approach

VOLUME 74, NUMBER 10

PHYSICAL REVIEW LETTERS

6 MARCH 1995

Space-Time Method for *Ab Initio* Calculations of Self-Energies and Dielectric Response Functions of Solids

H. N. Rojas,* R. W. Godby, and R. J. Needs

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom

(Received 9 August 1994)

simple products

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, i\tau) = -iG_0(\mathbf{r}_1, \mathbf{r}_2, i\tau)G_0(\mathbf{r}_2, \mathbf{r}_1, -i\tau)$$

$$\Sigma(\mathbf{r}_1, \mathbf{r}_2, i\tau) = iG_0(\mathbf{r}_1, \mathbf{r}_2, i\tau)W(\mathbf{r}_1, \mathbf{r}_2, i\tau)$$

with

imaginary times

$$G_0(\mathbf{r}_1, \mathbf{r}_2, i\tau) = \begin{cases} i \sum_{n\mathbf{k}}^{\text{occ}} \varphi_{n\mathbf{k}}(\mathbf{r}_1) \varphi_{n\mathbf{k}}^*(\mathbf{r}_2) \exp(-\epsilon_{n\mathbf{k}}\tau), & \tau < 0 \\ -i \sum_{n\mathbf{k}}^{\text{unocc}} \varphi_{n\mathbf{k}}(\mathbf{r}_1) \varphi_{n\mathbf{k}}^*(\mathbf{r}_2) \exp(-\epsilon_{n\mathbf{k}}\tau), & \tau > 0 \end{cases}$$





GWR = space-time approach

Two subtleties:

1. Space variables

$$\chi_0(\mathbf{r}, \mathbf{R}, i\tau) = -iG_0(\mathbf{r}, \mathbf{R}, i\tau)G_0(\mathbf{R}, \mathbf{r}, -i\tau)$$

\mathbf{r} unitcell

\mathbf{R} solid (= N_k unitcell)

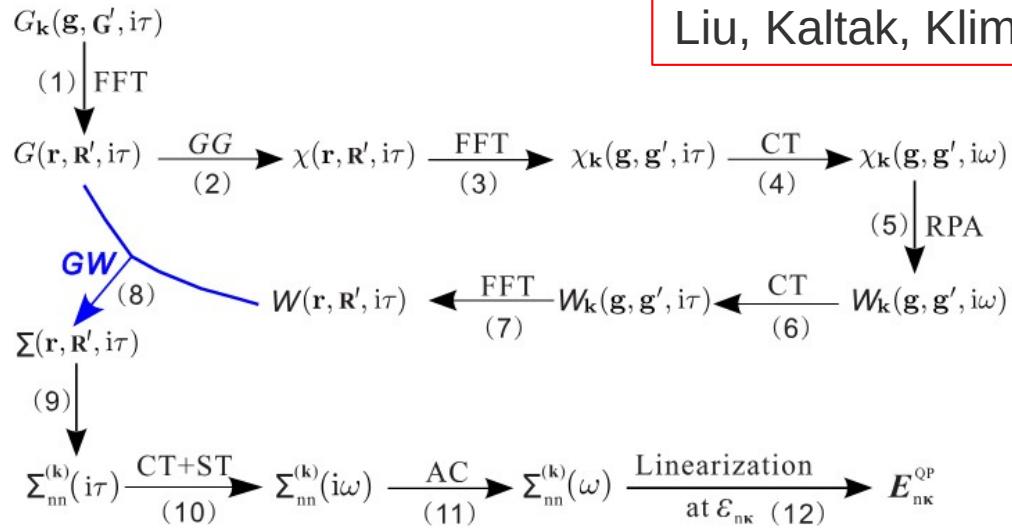
2. Back and forth imaginary time – imaginary freq Fourier transforms

Non-uniform grids: minmax technique



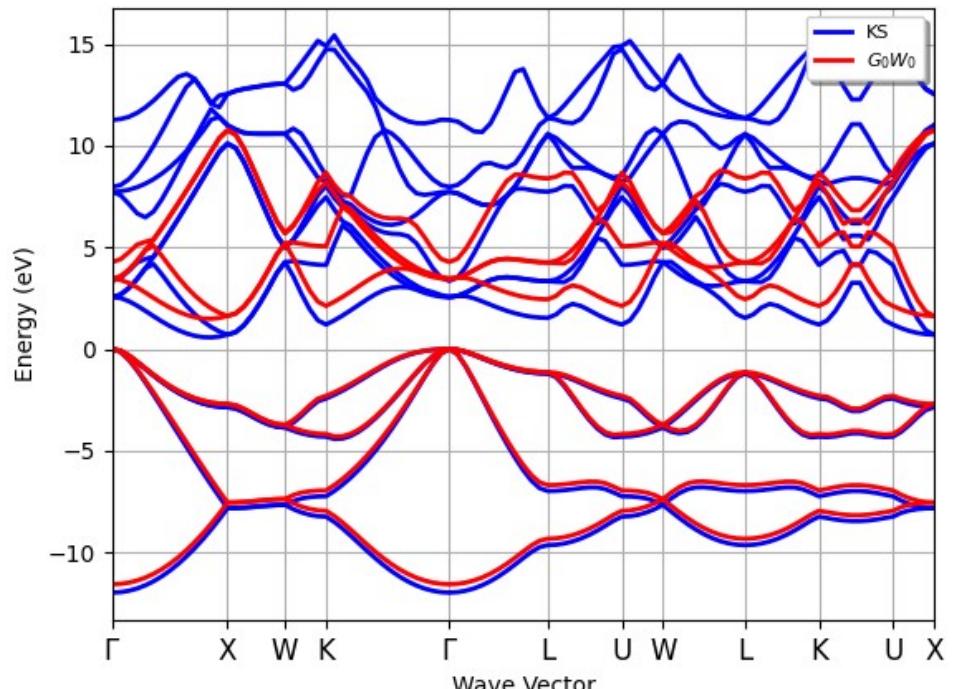


GWR = space-time approach



Liu, Kaltak, Klimes, PRB (2016)

Bulk silicon band structure
as obtained in
tutorial GWR1





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





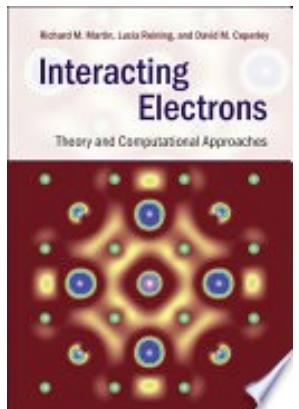
If you want to know more

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).
- L. Reining, “The GW approximation: content, successes and limitations”, <https://doi.org/10.1002/wcms.1344> (2017)
- R. Martin, L. Reining, D. Ceperley, “Interacting electrons” (2016)

Codes for solids:

- <https://www.yambo-code.eu/>
- <http://www.abinit.org>
- <http://www.vasp.org>
- <http://www.berkeleygw.org/>





Back-up slides



Satellites in GW?

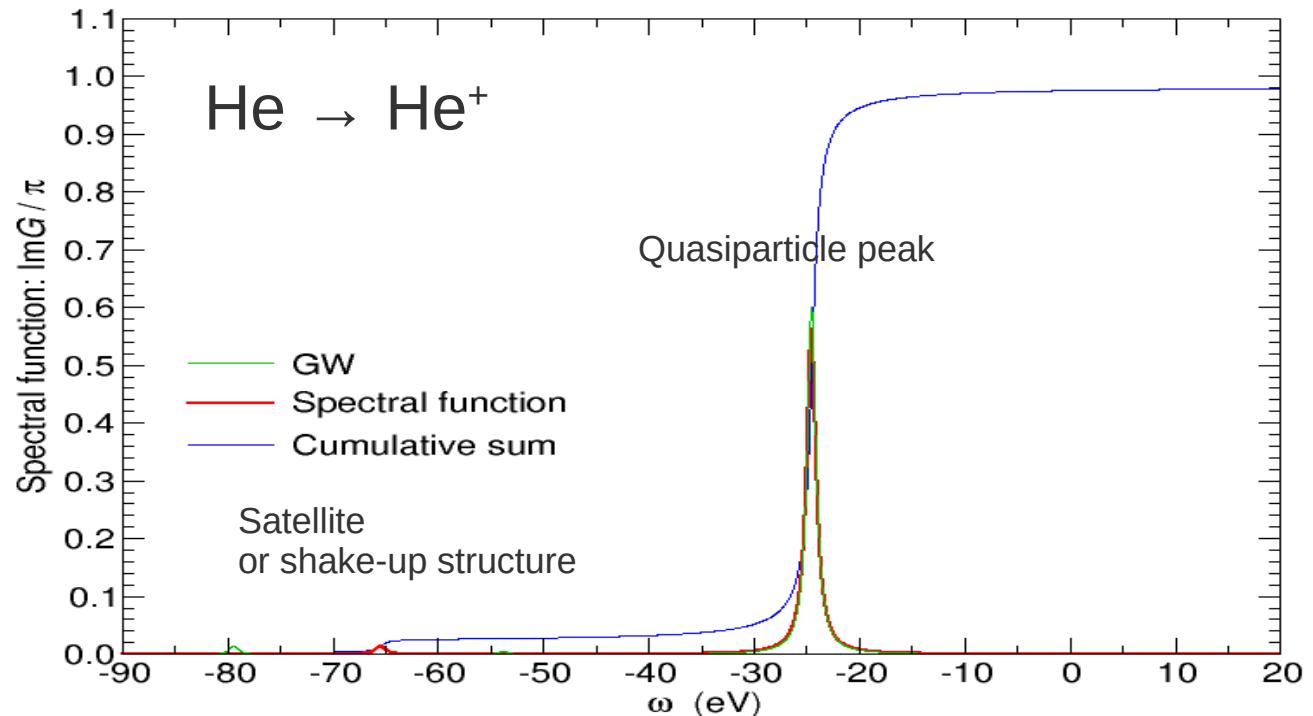
$$\langle m | G^h(\omega) | m \rangle = \sum_i \frac{\langle N0 | \hat{c}_m^+ | N-1i \rangle \langle N-1i | \hat{c}_m | N0 \rangle}{\omega - \epsilon_i - i\eta}$$

$$N=2$$

$$N-1=1$$

$$m=1\ s$$

Obtained from FCI calculations





GW for molecules?

Ionization potential of 100 small molecules

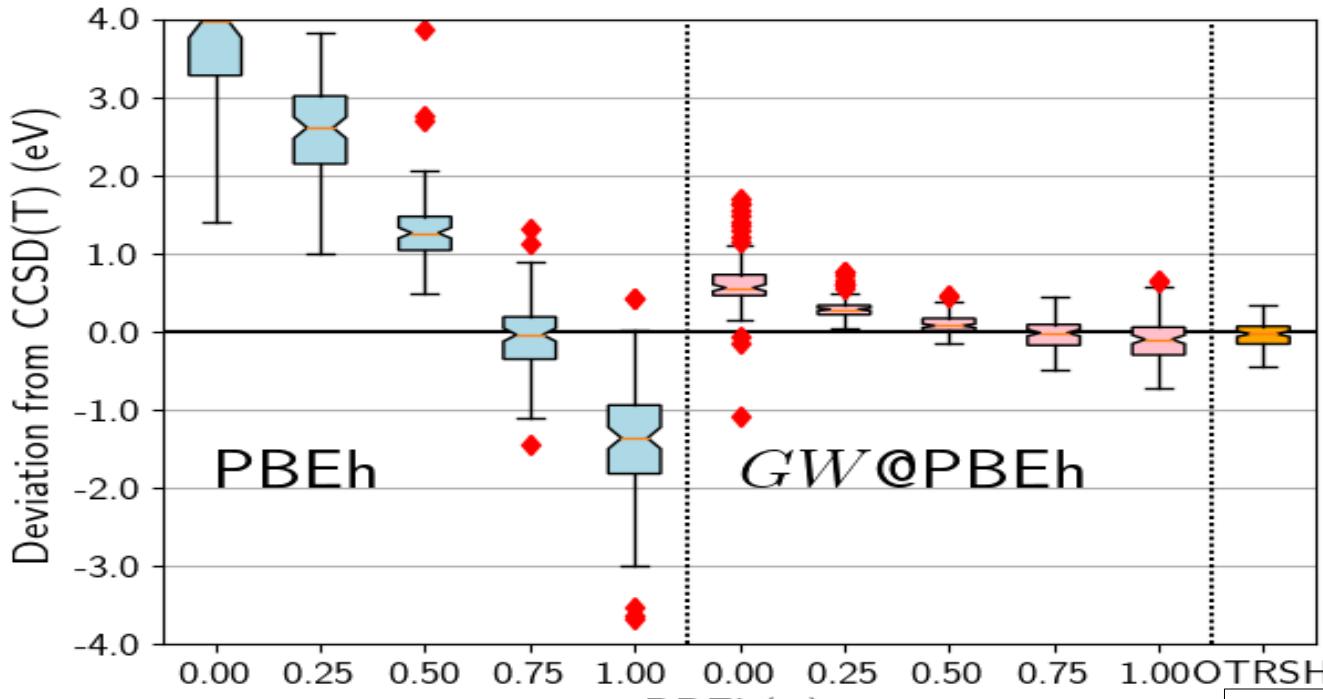
van Setten et al. JCTC (2015)

<https://gw100.wordpress.com/>

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

GW versus Coupled-cluster

$$E_{\text{CCSD(T)}}(\mathbf{X}^0) - E_{\text{CCSD(T)}}(\mathbf{X}^+)$$



$$v_{xc} = \alpha \sum_x + (1 - \alpha) v_x^{\text{PBE}} + v_c^{\text{PBE}}$$

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



Exercice: H₂ in minimal basis: GW@HF

Find the location of the poles of the self-energy

Szabo-Ostlung book chapter 3 teaches how

Basis: STO-3G $r(\text{H-H}) = 1.4 \text{ bohr}$

2 basis functions \rightarrow 2 eigenstates:

LUMO anti-bonding

HOMO bonding

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

In eigenvector basis:
Hamiltonian

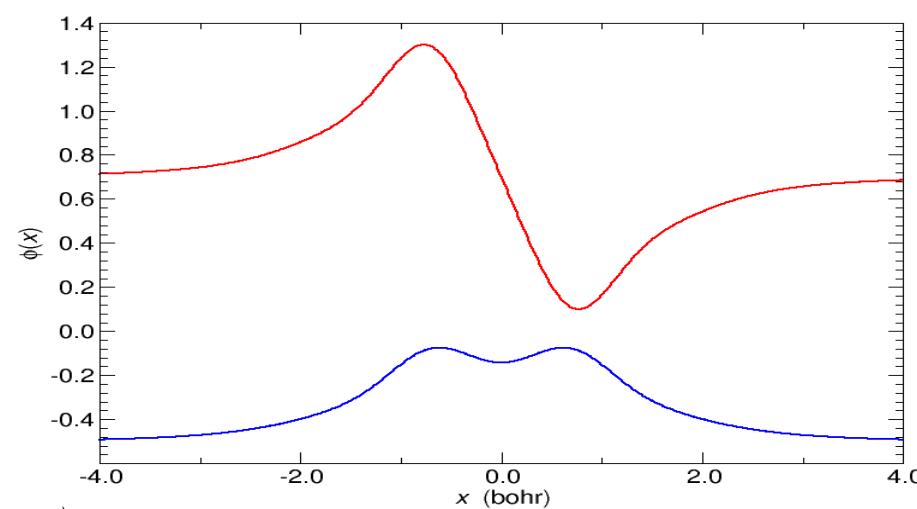
$$(11 | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | 11) = 0.675$$

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

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

Atomic units

F. Bruneval Coulomb interaction:



Bruyères-le-Châtel, Abinit school 2026

Exercice: H₂ in minimal basis: GW@HF

Find the location of the poles of W

Diagonalize the RPA equation

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

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

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

$$|12\rangle \quad |21\rangle$$

$$\begin{pmatrix} \langle 12 | & \langle 21 | \end{pmatrix} \begin{pmatrix} \frac{\omega - \Delta\epsilon}{2} & 0 \\ 0 & \frac{\omega + \Delta\epsilon}{-2} \end{pmatrix} - \begin{pmatrix} v & v \\ v & v \end{pmatrix}$$

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

Exercice: H₂ in minimal basis: GW@HF

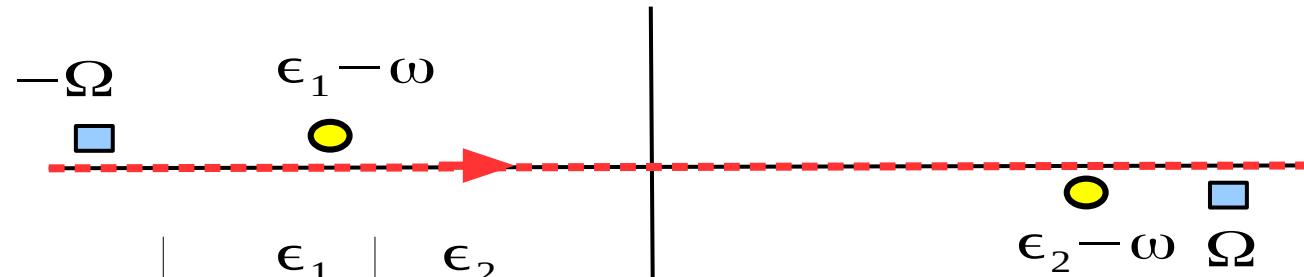
$$\Sigma_c(\omega) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega' G(\omega + \omega') W_p(\omega')$$

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

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

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

Integration in the complex plane:



Pole table:

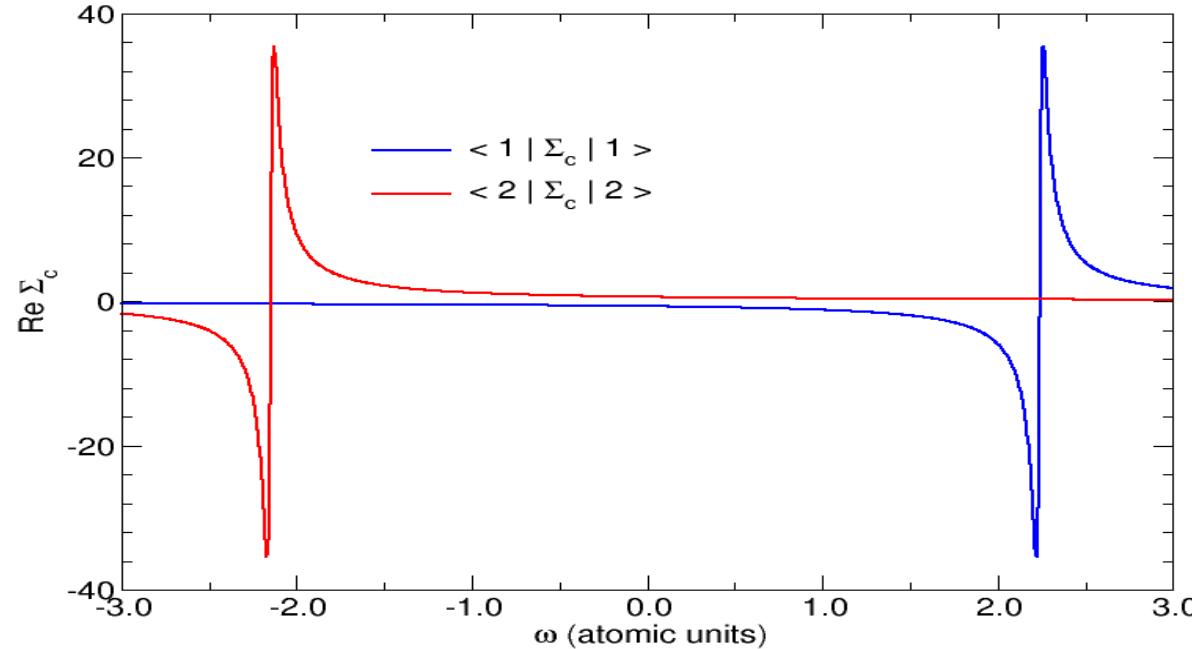
	ϵ_1	ϵ_2
$-\Omega$	X	$\epsilon_2 + \Omega$
Ω	$\epsilon_1 - \Omega$	X

Exercice: H₂ in minimal basis: GW@HF

$$\epsilon_2 + \Omega = 2.239$$

$$\epsilon_1 - \Omega = -2.147$$

Real part of
the self-energy
from MOLGW



$$\epsilon_{\text{HOMO}}^{GW} = -16.23 \text{ eV}$$

$$\epsilon_{\text{LUMO}}^{GW} = 18.74 \text{ eV}$$

Exercice: H₂ in minimal basis: GW@HF

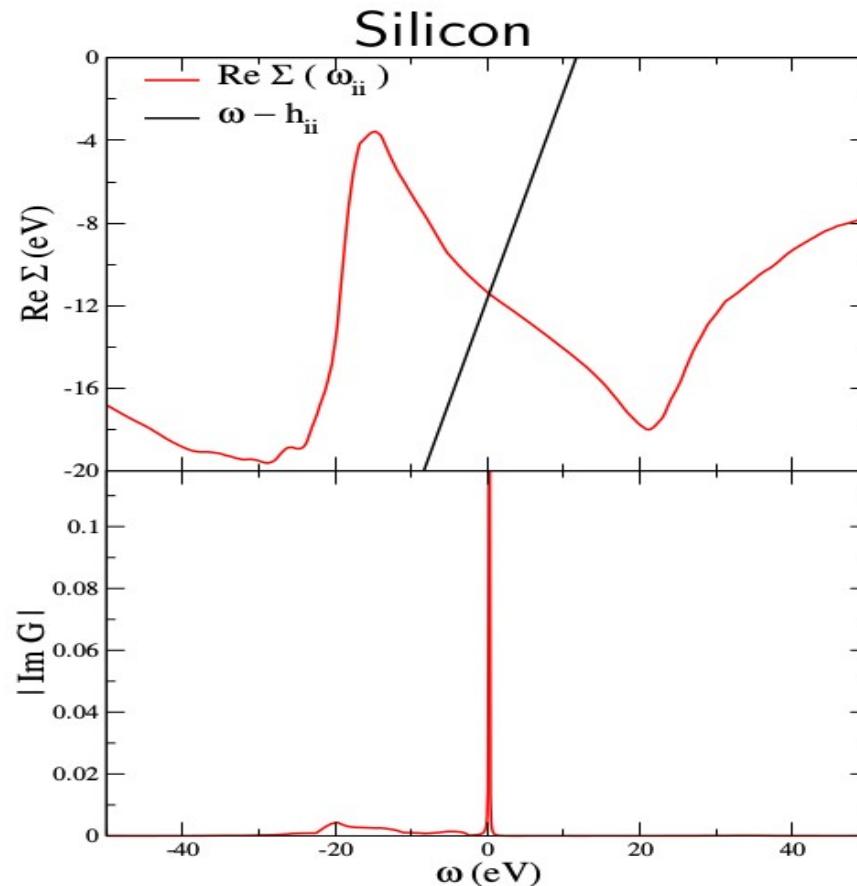
Same conclusions hold for
a many-state case:

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:

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

poles : a_i residues : A_i

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

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

Now with G

$$\lim_{z \rightarrow a} (z - a) G(z) = \lim_{z \rightarrow a} \frac{z - a}{z - \epsilon - \Sigma(z)}$$

$\frac{0}{0}$
undetermined

$$\begin{aligned} G(z) &= G_0^{-1}(z) - \Sigma(z) \\ &= z - \epsilon - \Sigma(z) \end{aligned}$$

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

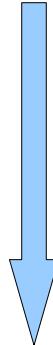
$$\begin{aligned} &= \lim_{z \rightarrow a} \frac{1}{1 - \Sigma(z)} = \frac{1}{1 - \Sigma(a)} \\ &= \Sigma(a) \end{aligned}$$

spectral weight

Exercise 1

Green's function in frequency domain

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


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

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

Exercise 2:

Fock exchange from Green's functions

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

Exercise 3: let's play with Dyson equations

1) The multiple faces of the Dyson equation

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

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

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

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

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

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

2) Combining the Dyson equations

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

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

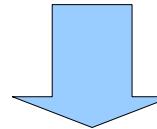
$$\hookrightarrow 1 = [G_{KS}^{-1} - (\Sigma - v_{xc})] G$$

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

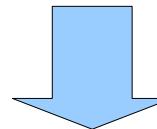
Exercise 4

Derive the standard Adler-Wiser formula (1963):

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



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



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

Exercice 4: solution (1/3)

Definitions:

$$G(\omega) = \int d\tau G(\tau) e^{i\omega\tau}$$

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

$$\int d\omega e^{i\omega\tau} = 2\pi \delta(\tau)$$

$$x(\tau) = -i G(\tau) G(-\tau)$$

Exercice 4: solution (2/3)

$$\begin{aligned}
 X(\omega) &= \int d\tau X(\tau) e^{i\omega\tau} = -\frac{i}{(2\pi)^2} \int d\tau \int d\omega_1 G(\omega_1) e^{-i\omega_1\tau} \int d\omega_2 G(\omega_2) e^{+i\omega_2\tau} e^{i\omega\tau} \\
 &= -\frac{i}{(2\pi)^2} \int d\omega_1 \left(\int d\omega_2 G(\omega_1) G(\omega_2) \right) \underbrace{\int d\tau e^{+i\tau(\omega + \omega_2 - \omega_1)}}_{\pi\delta(\omega + \omega_2 - \omega_1)} \\
 &= -\frac{i}{2\pi} \int d\omega_2 G(\omega + \omega_2) G(\omega_2) \\
 &= -\frac{i}{2\pi} \int d\omega_2 \sum_p \frac{\Phi_p(r) \Phi_p^*(r')}{\omega_p - \epsilon_p \pm iy} \times \sum_q \frac{\Phi_q(r) \Phi_q^*(r')}{\omega_q - \epsilon_q \pm iy}
 \end{aligned}$$

Exercice 4: solution (3/3)

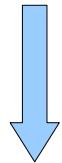
$$\begin{aligned}
 X(\omega) &= \int d\tau \chi(\tau) e^{i\omega\tau} = -\frac{i}{(2\pi)^2} \int d\tau \int d\omega_1 G(\omega_1) e^{-i\omega_1\tau} \int d\omega_2 G(\omega_2) e^{+i\omega_2\tau} e^{i\omega\tau} \\
 &= -\frac{i}{(2\pi)^2} \int d\omega_1 \int d\omega_2 G(\omega_1) G(\omega_2) \underbrace{\int d\tau e^{+i\tau(\omega + \omega_2 - \omega_1)}}_{2\pi \delta(\omega + \omega_2 - \omega_1)} \\
 &= -\frac{i}{2\pi} \int d\omega_2 G(\omega + \omega_2) G(\omega_2) \\
 &= -\frac{i}{2\pi} \int d\omega_2 \sum_p \frac{\Phi_p(r) \Phi_p^*(r')}{\omega - \epsilon_p \pm i\eta} \times \sum_q \frac{\Phi_q(r) \Phi_q^*(r')}{\omega_2 - \epsilon_q \pm i\eta} \\
 &= \sum_{ia} \frac{\Phi_i(r) \Phi_i^*(r') \Phi_a(r') \Phi_a^*(r)}{\epsilon_i - \epsilon_a - \omega + 2i\eta} \\
 &\quad + \sum_{ia} \frac{\Phi_a(r) \Phi_a^*(r') \Phi_i(r') \Phi_i^*(r)}{\epsilon_a + \epsilon_i - \epsilon_a + 2i\eta} \\
 &= \sum_{ia} \frac{\Phi \Phi \Phi \Phi}{\omega - (\epsilon_a - \epsilon_i) + 2i\eta} - \sum_{i0} \frac{\Phi \Phi \Phi \Phi}{\omega - (\epsilon_i - \epsilon_a) - 2i\eta}
 \end{aligned}$$

pole: $\omega_2 = \epsilon_p - \omega + i\eta$
 pole: $\epsilon_q + i\eta$
 pole: $\epsilon_i - \epsilon_a + i\eta$
 pole: $\epsilon_a - \epsilon_i + i\eta$

Exercise 5

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

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



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

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

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

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

3-rung ladder
SOX in Hartree
SOX in exchange

1 pair in SOX

PT2

SOX

GW_{TDHF}

1 interacting pair

2 interacting pairs etc.

GW

1 pair

3 pairs
4 pairs
etc.

2 pairs

$GW + SOSEX$

2 pairs in SOX
3 pairs in SOX
etc.

1 pair in H
1 pair in X

2 pairs in H2 pairs in X etc.

$GW + \gamma^{GW}$

Perturbation theory up to third order

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

$$A1 = - \sum \frac{(2V_{pkqj} - V_{pkjq})(2V_{jiab} - V_{jiba})V_{abki}}{(\epsilon_j + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_k + \epsilon_i - \epsilon_a - \epsilon_b)}$$

$$A2 = \sum \frac{(2V_{pcqb} - V_{pcbq})(2V_{jiab} - V_{jiba})V_{jica}}{(\epsilon_j + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_j + \epsilon_i - \epsilon_a - \epsilon_c)}$$

$$A3 = \sum \frac{(2V_{pcqj} - V_{pcjq})(2V_{jiab} - V_{jiba})V_{abci}}{(\epsilon_j + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_j - \epsilon_c)}$$

$$A4 = \sum \frac{(2V_{pjqc} - V_{pjcq})(2V_{jiab} - V_{jiba})V_{abci}}{(\epsilon_j + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_j - \epsilon_c)}$$

$$A5 = - \sum \frac{(2V_{pbqk} - V_{pbkq})(2V_{jiab} - V_{jiba})V_{ijka}}{(\epsilon_j + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_k - \epsilon_b)}$$

$$A6 = - \sum \frac{(2V_{pkqb} - V_{pkbq})(2V_{jiab} - V_{jiba})V_{ijka}}{(\epsilon_j + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_k - \epsilon_b)}$$

$$C1 = \sum \frac{(2V_{piab} - V_{piba})V_{abcd}V_{qicd}}{(\omega + \epsilon_i - \epsilon_a - \epsilon_b)(\omega + \epsilon_i - \epsilon_c - \epsilon_d)}$$

$$C2 = \sum \frac{(2V_{piab} - V_{piba})V_{abjk}V_{qijk}}{(\omega + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b)}$$

$$C3 = \sum \frac{(2V_{pijk} - V_{pijk})V_{abjk}V_{qfab}}{(\omega + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b)}$$

$$C4 = \sum \frac{(2V_{pajj} - V_{paji})V_{ijbc}V_{qabc}}{(\omega + \epsilon_a - \epsilon_i - \epsilon_j)(\epsilon_i + \epsilon_j - \epsilon_b - \epsilon_c)}$$

$$C5 = \sum \frac{(2V_{pabc} - V_{pacb})V_{ijbc}V_{qaij}}{(\omega + \epsilon_a - \epsilon_i - \epsilon_j)(\epsilon_i + \epsilon_j - \epsilon_b - \epsilon_c)}$$

$$C6 = - \sum \frac{(2V_{pakl} - V_{palk})V_{klkj}V_{qaij}}{(\omega + \epsilon_a - \epsilon_i - \epsilon_j)(\omega + \epsilon_a - \epsilon_k - \epsilon_l)}$$

$$D1 = \sum \left\{ \frac{V_{piab}[V_{ajic}(V_{qjcb} - 2V_{qjbc}) + V_{ajci}(V_{qjbc} - 2V_{qjcb})]}{(\omega + \epsilon_i - \epsilon_a - \epsilon_b)(\omega + \epsilon_j - \epsilon_b - \epsilon_c)} \right. \\ \left. + \frac{V_{piba}[V_{ajic}(4V_{qjbc} - 2V_{qjcb}) + V_{ajci}(V_{qjcb} - 2V_{qjbc})]}{(\omega + \epsilon_i - \epsilon_a - \epsilon_b)(\omega + \epsilon_j - \epsilon_b - \epsilon_c)} \right\}$$

$$D2 = \sum \left\{ \frac{V_{pica}[V_{abij}(4V_{qbcj} - 2V_{qbjc}) + V_{abji}(V_{qbjc} - 2V_{qbcj})]}{(\omega + \epsilon_i - \epsilon_a - \epsilon_c)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)} \right. \\ \left. + \frac{V_{piac}[V_{abij}(V_{qbjc} - 2V_{qbcj}) + V_{abji}(V_{qbcj} - 2V_{qbjc})]}{(\omega + \epsilon_i - \epsilon_a - \epsilon_c)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)} \right\}$$

$$D3 = \sum \left\{ \frac{V_{pcja}[V_{jicb}(V_{qiba} - 2V_{qiab}) + V_{jibc}(V_{qiab} - 2V_{qiba})]}{(\omega + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_j + \epsilon_i - \epsilon_b - \epsilon_c)} \right. \\ \left. + \frac{V_{pcaj}[V_{jicb}(4V_{qiab} - 2V_{qiba}) + V_{jibc}(V_{qiba} - 2V_{qiab})]}{(\omega + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_j + \epsilon_i - \epsilon_b - \epsilon_c)} \right\}$$

$$D4 = \sum \left\{ \frac{V_{pakj}[V_{jiab}(4V_{qikb} - 2V_{qikb}) + V_{jiba}(V_{qikb} - 2V_{qikb})]}{(\omega + \epsilon_a - \epsilon_j - \epsilon_k)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)} \right. \\ \left. + \frac{V_{pqjk}[V_{jiab}(V_{qikb} - 2V_{qikb}) + V_{jiba}(V_{qikb} - 2V_{qikb})]}{(\omega + \epsilon_a - \epsilon_j - \epsilon_k)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)} \right\}$$

$$D5 = \sum \left\{ \frac{V_{pibk}[V_{jiab}(V_{qajk} - 2V_{qakj}) + V_{jiba}(V_{qakj} - 2V_{qajk})]}{(\omega + \epsilon_a - \epsilon_j - \epsilon_k)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)} \right. \\ \left. + \frac{V_{pikb}[V_{jiab}(4V_{qakj} - 2V_{qajk}) + V_{jiba}(V_{qajk} - 2V_{qakj})]}{(\omega + \epsilon_a - \epsilon_j - \epsilon_k)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)} \right\}$$

$$D6 = - \sum \left\{ \frac{V_{paki}[V_{ibaj}(4V_{qbkj} - 2V_{qbjk}) + V_{ibja}(V_{qbjk} - 2V_{qbkj})]}{(\omega + \epsilon_a - \epsilon_i - \epsilon_k)(\omega + \epsilon_b - \epsilon_j - \epsilon_k)} \right. \\ \left. + \frac{V_{paik}[V_{ibaj}(V_{qbjk} - 2V_{qbkj}) + V_{ibja}(V_{qbkj} - 2V_{qbjk})]}{(\omega + \epsilon_a - \epsilon_i - \epsilon_k)(\omega + \epsilon_b - \epsilon_j - \epsilon_k)} \right\}$$

Exercice 6: effect of the other diagrams

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

