Introduction to the GW approximation

Common approximations & practical implementations

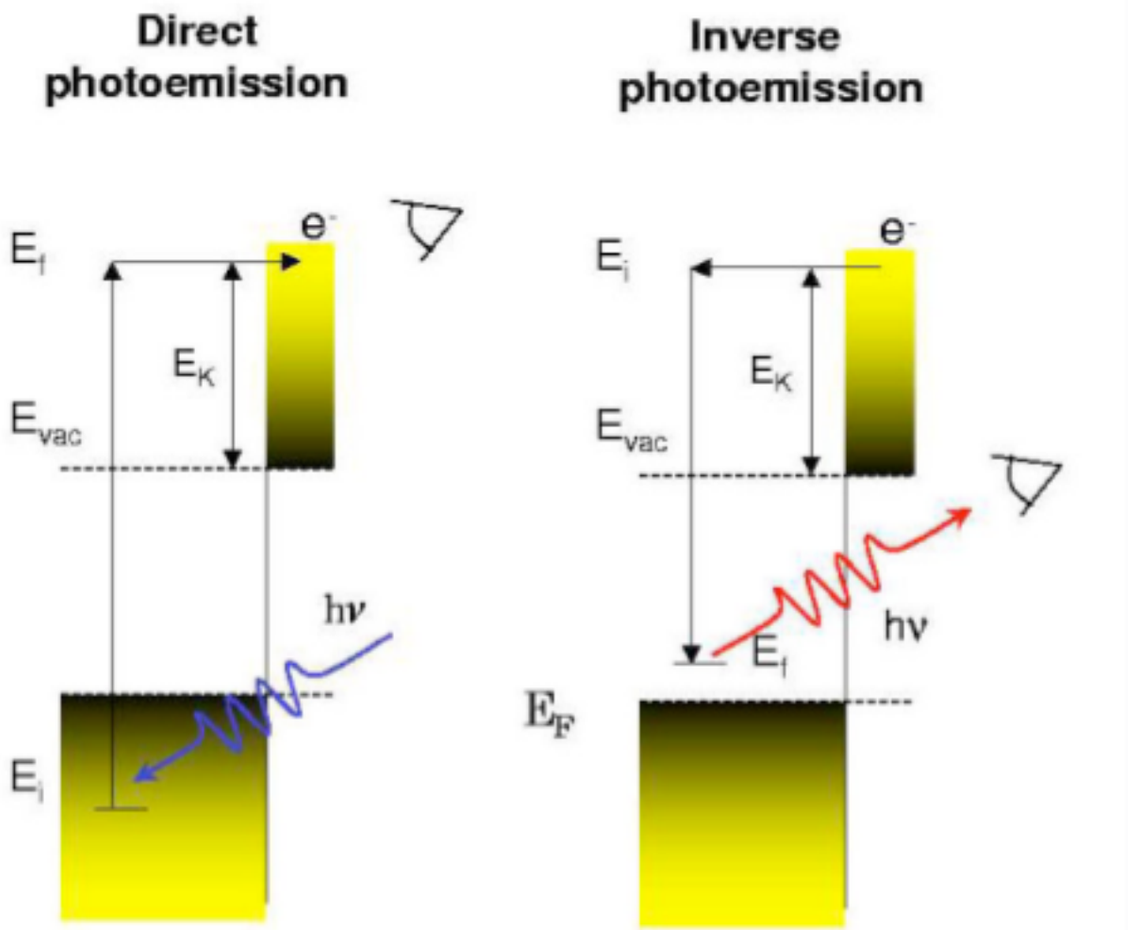
Daniele Varsano

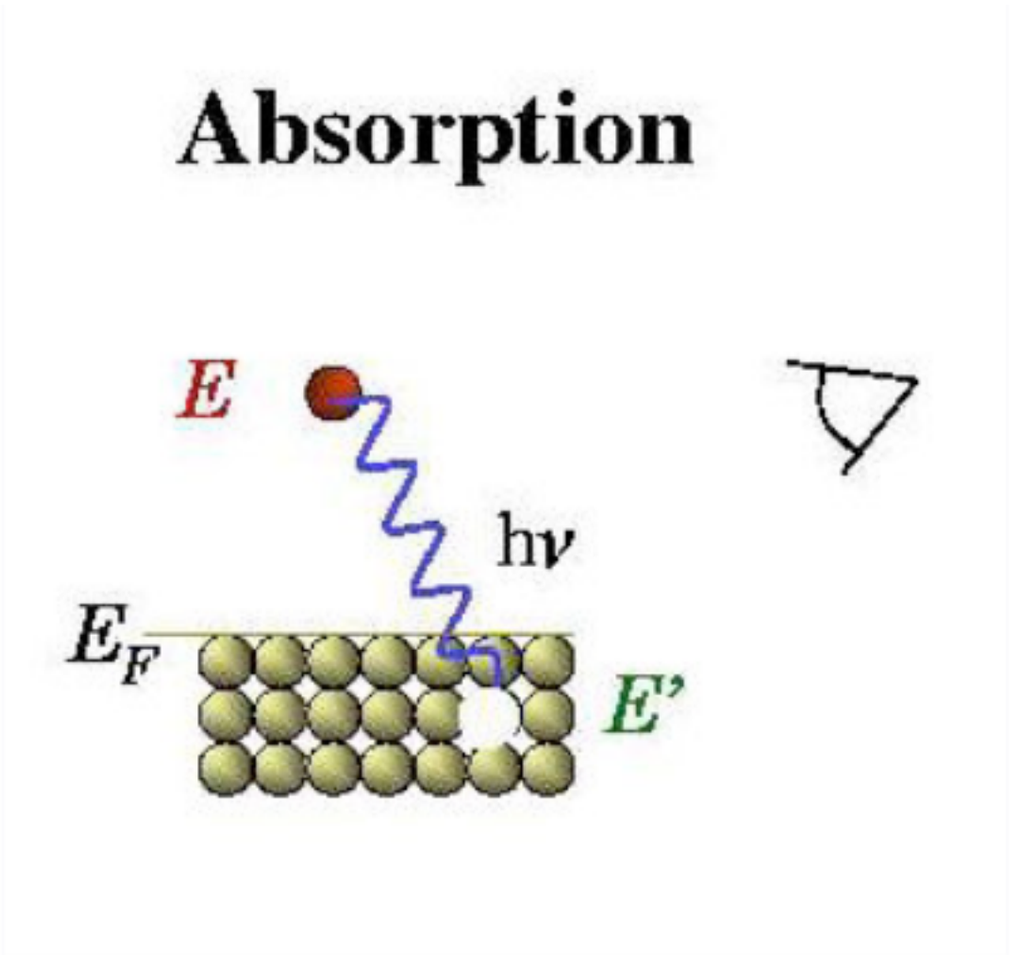
Institute of Nanoscience
National Research Council CNR,
Modena Italy

daniele.varsano@nano.cnr.it

the Yambo team

Charged and neutral excitations

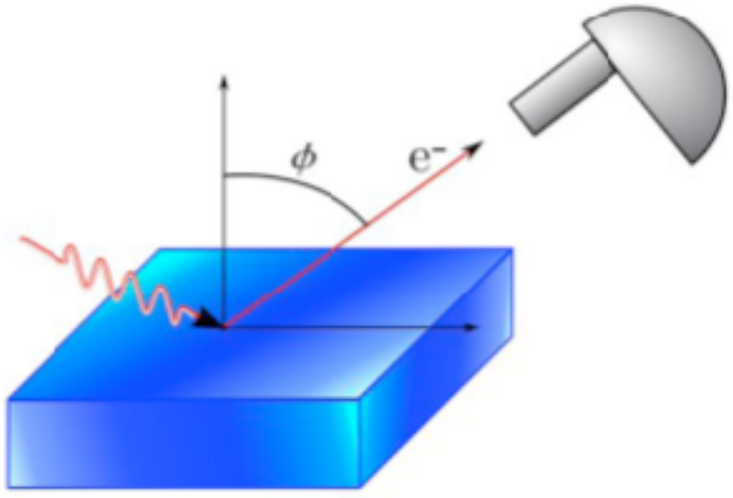




Charged excitations: photoemission and inverse photoemission

Neutral excitations: absorption

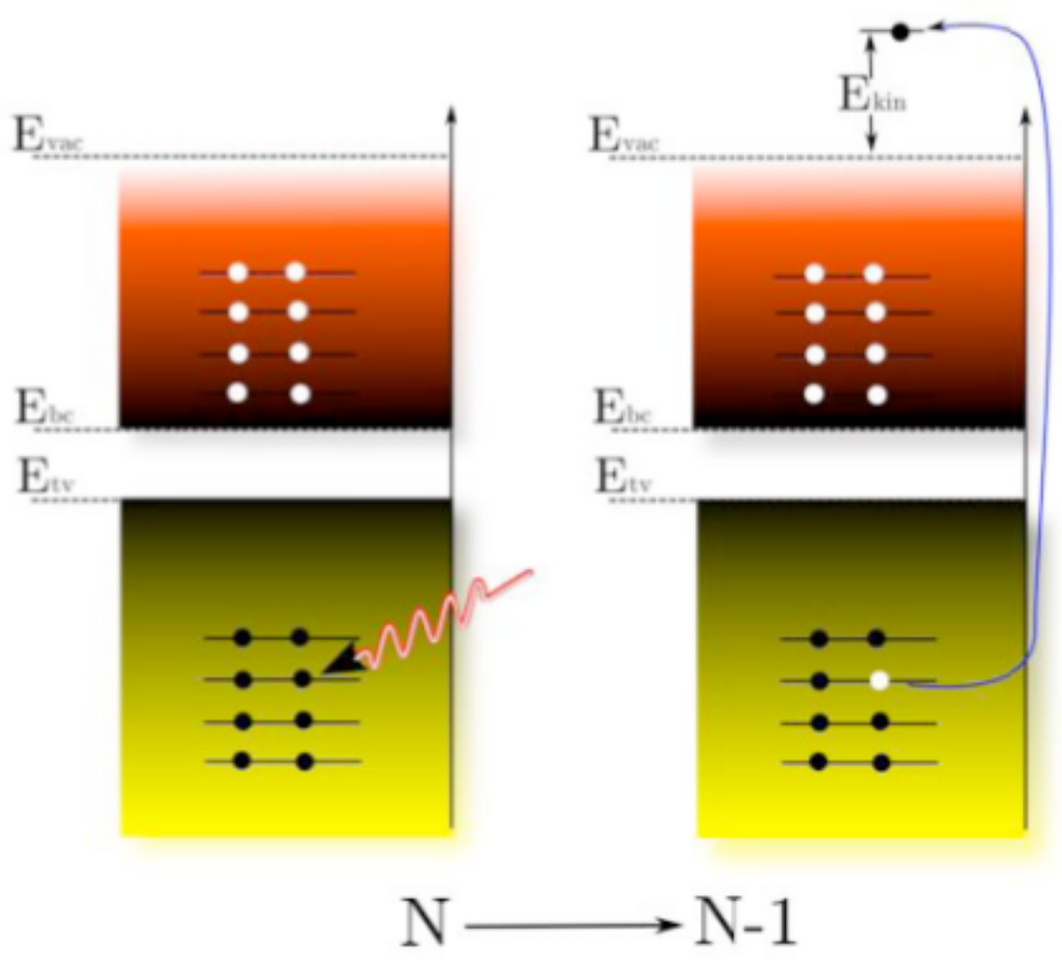
Direct photoemission



$$E(N)+h\nu = E(N-1)+[\Phi_w+E_{kin}]$$

$$E(N)-E(N-1) = [\Phi_w+E_{kin}]-h\nu$$

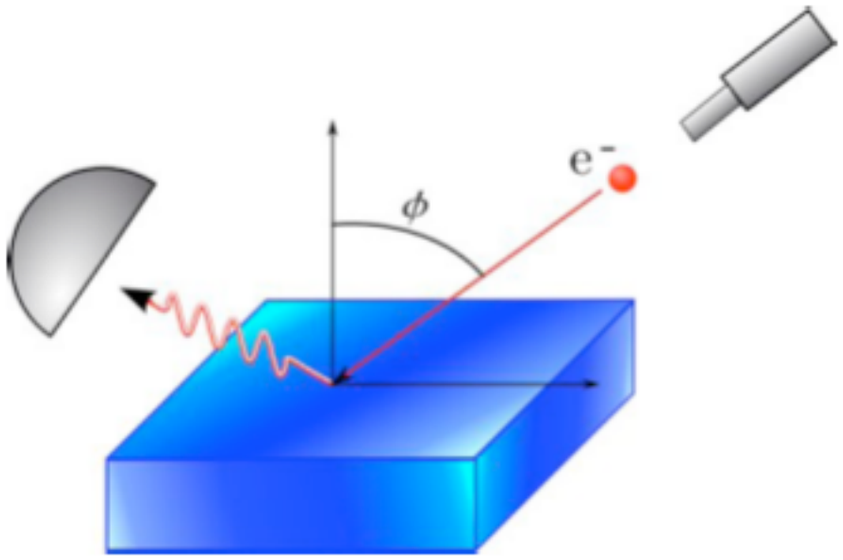
...plus momentum conservation ⇒ ARPES



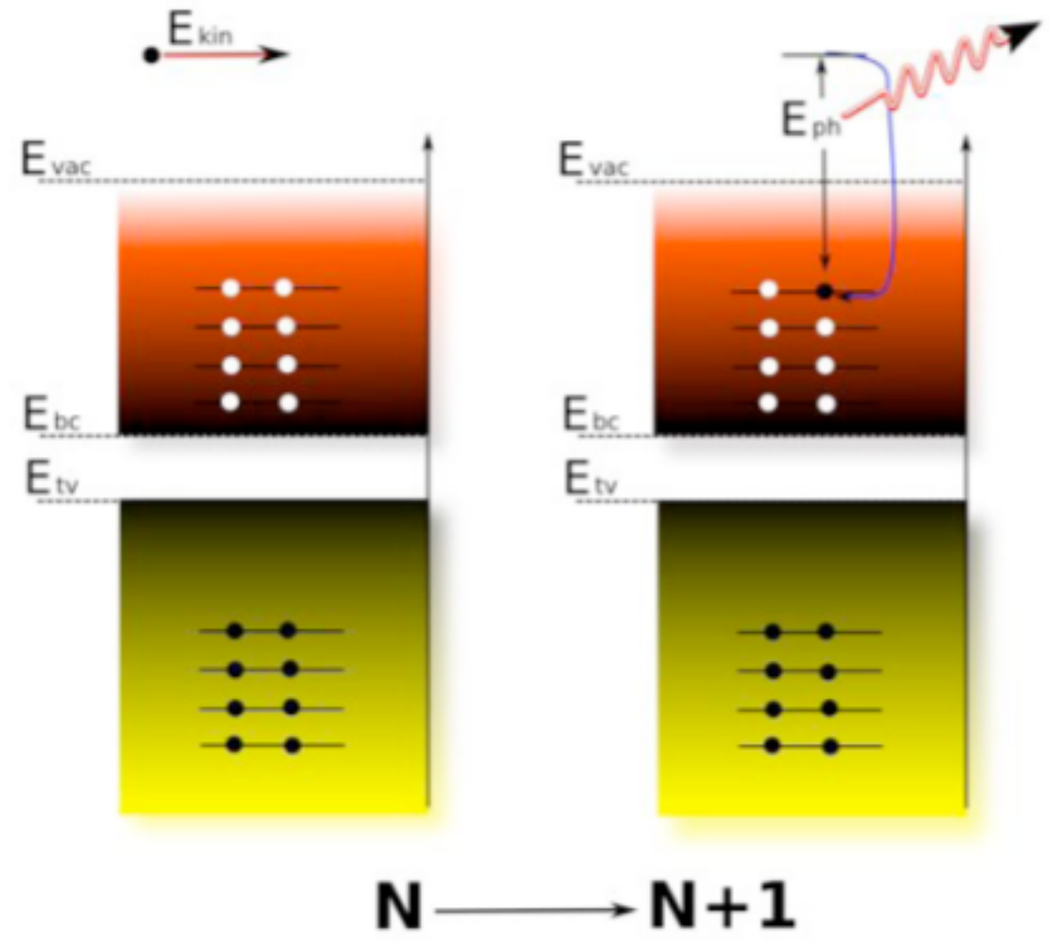
occupied states

Measure the density of occupied states

Inverse photoemission



electron in - photon out

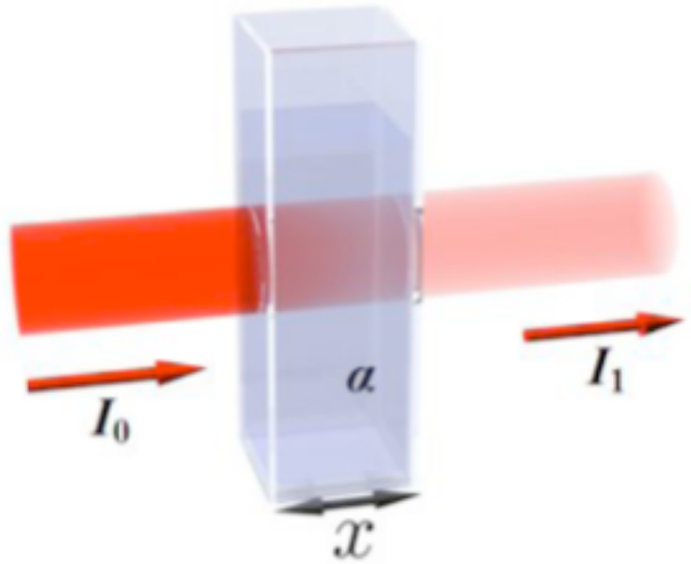


$$E(N+1) - E(N) = E_k + h\nu$$

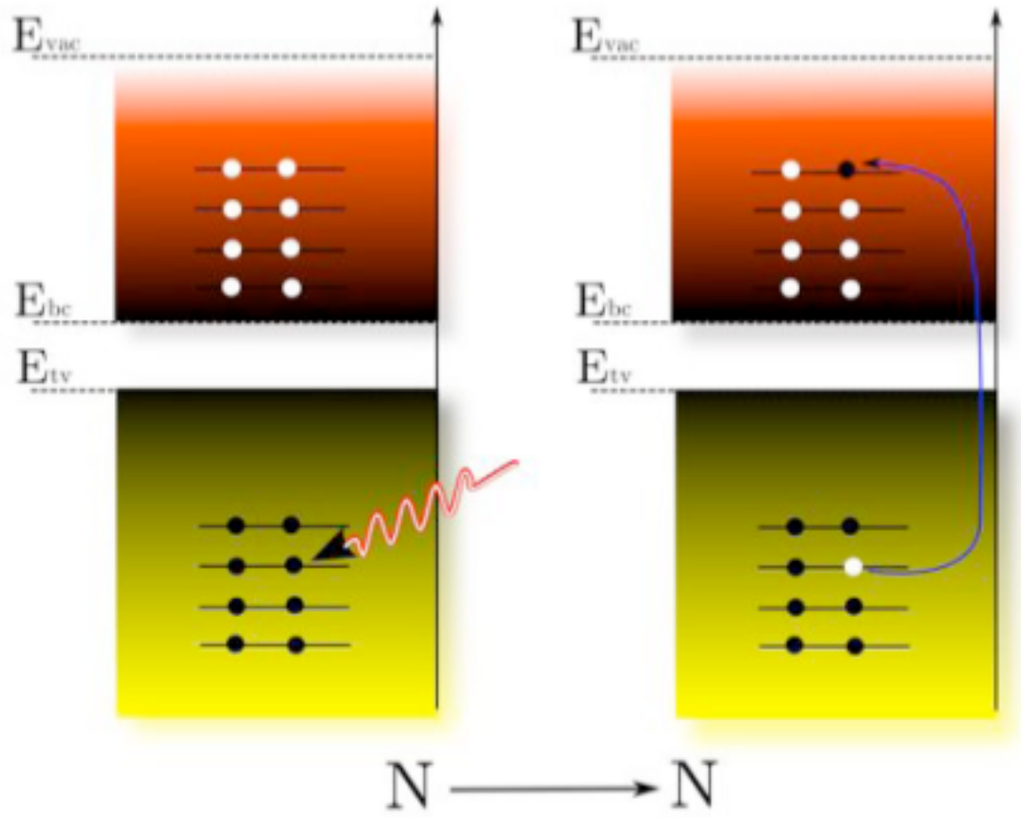
Measure the density of unoccupied states

empty states

Absorption



Beer-Lambert law: $I = I_0 e^{-\alpha x}$



$$\alpha \propto \mathrm{Im}\epsilon_M = \epsilon_2 \quad \Rightarrow \quad \text{extended system}$$

$$\sigma \propto \mathrm{Im}\epsilon_M = \epsilon_2 \quad \Rightarrow \quad \text{finite system}$$

Electron and hole are not decoupled, electrons feel the presence of the hole

Electronic structure calculations

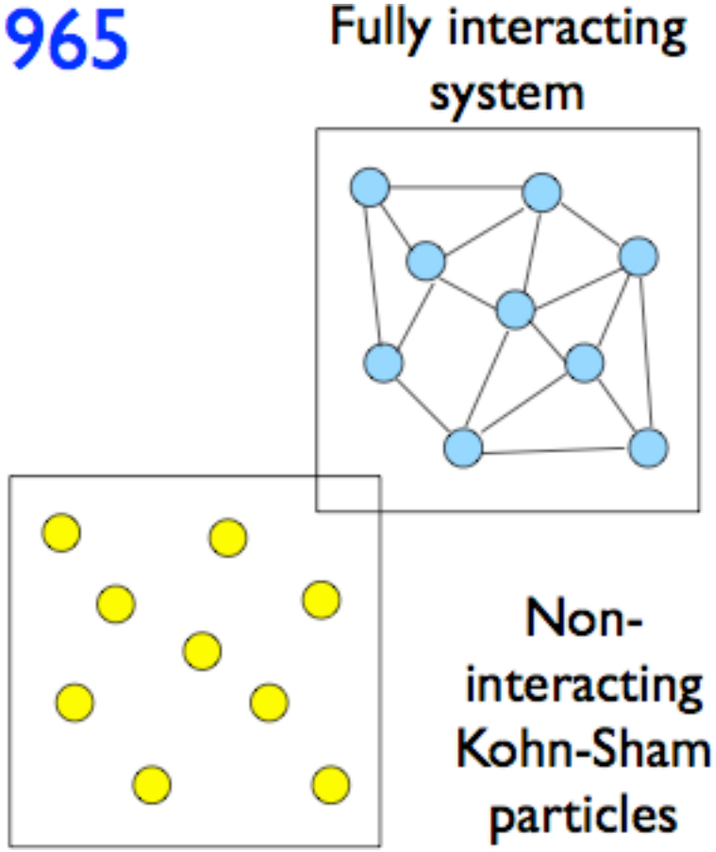
Kohn-Sham Equations 1965

$$\hat{h}_{KS}[n]|\psi_j>=\epsilon_j|\psi_j>$$

$$\hat{h}_{KS}[n]=-\frac{1}{2}\nabla^2+v_{ext}(\mathbf{r})+v_{Hartree}(\mathbf{r})+v_{xc}[n](\mathbf{r})$$

$$n(\mathbf{r})=\sum_j \theta(\mu-\epsilon_j)\psi_j^*(\mathbf{r})\psi_j(\mathbf{r})$$

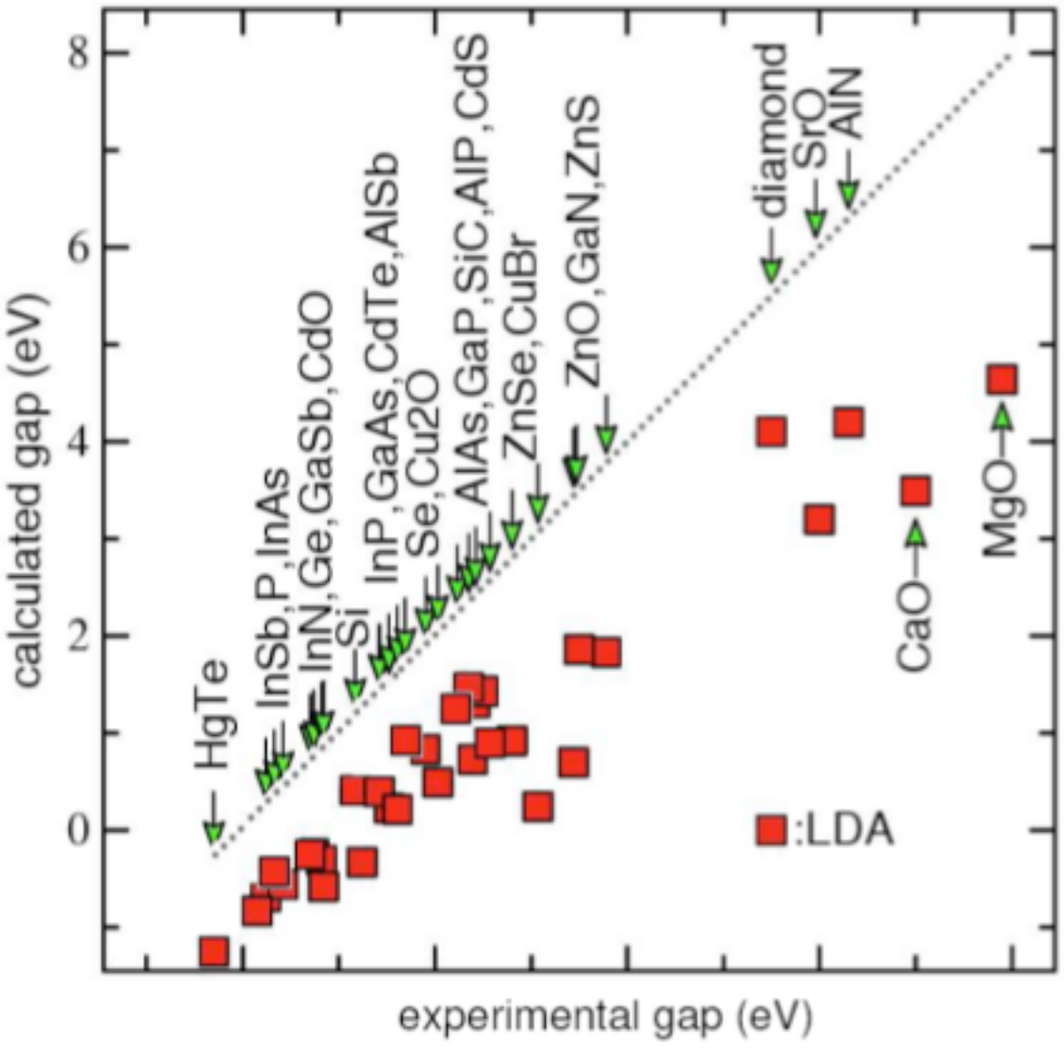
$$E_{GS}=\sum_j \theta(\mu-\epsilon_j)\epsilon_j - U[n] - \int d\mathbf{r} n(\mathbf{r}) v_{xc}[n](\mathbf{r}) + E_{xc}[n]$$



Moderate computational cost

Predict ground state geometries and electronic structures

Band Gap



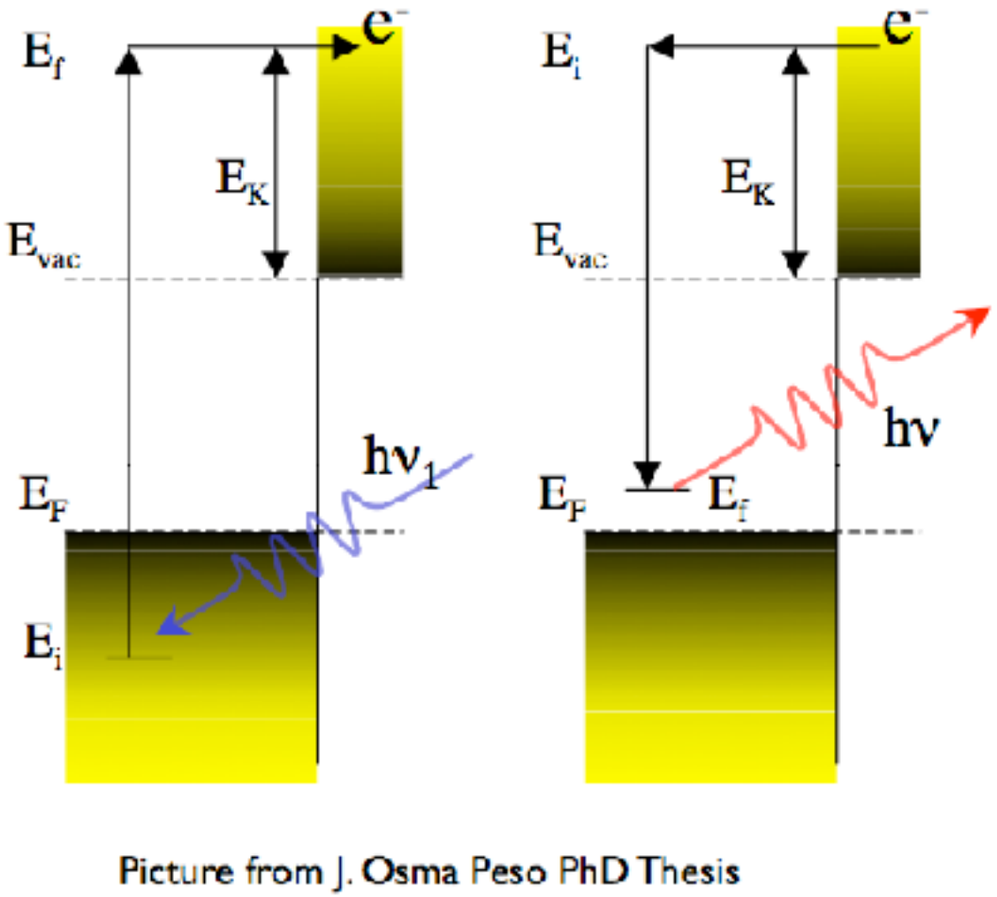
Si:
0.47 eV (LDA) vs 1.1 eV (expt)

GaAs:
0.30 eV (LDA) vs 1.4 eV (expt)

Adapted from M. van Schilfgaarde *et al.* PRL **96** (2006)

Huge discrepancy not due to the LDA

Band Gap: definition



Picture from J. Osma Peso PhD Thesis

Direct photoemission

$$\epsilon_i = E_{kin} - \hbar\omega$$

$$\epsilon_i = E_0^N - E_i^{N-1}$$

Total energy difference between the N-particle ground state and the (N-1) particle state that remains after the emission

Inverse photoemission

$$\epsilon_i = E_i^{N+1} - E_0^N$$

The ejection (removal) of an electron is always a many-body process

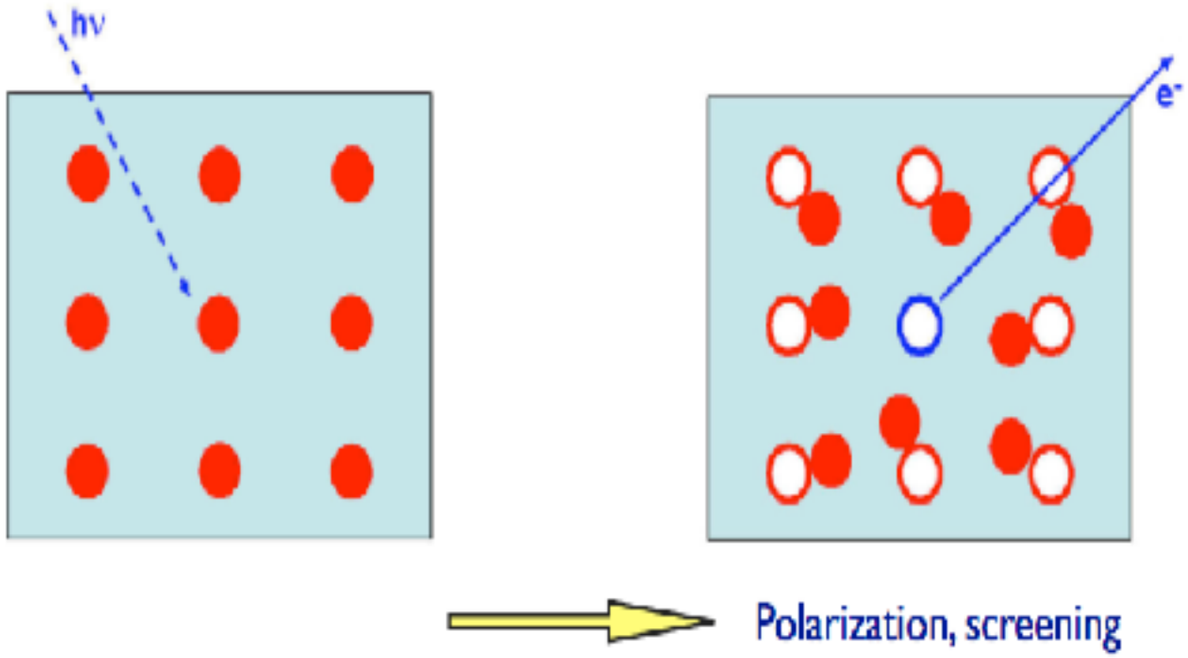
$$E_{gap} = (E_{N+1} - E_N) - (E_N - E_{N-1})$$

electron affinity — ionization potential

Quasiparticle

$$E_{gap} = (E_{N+1} - E_N) - (E_N - E_{N-1})$$

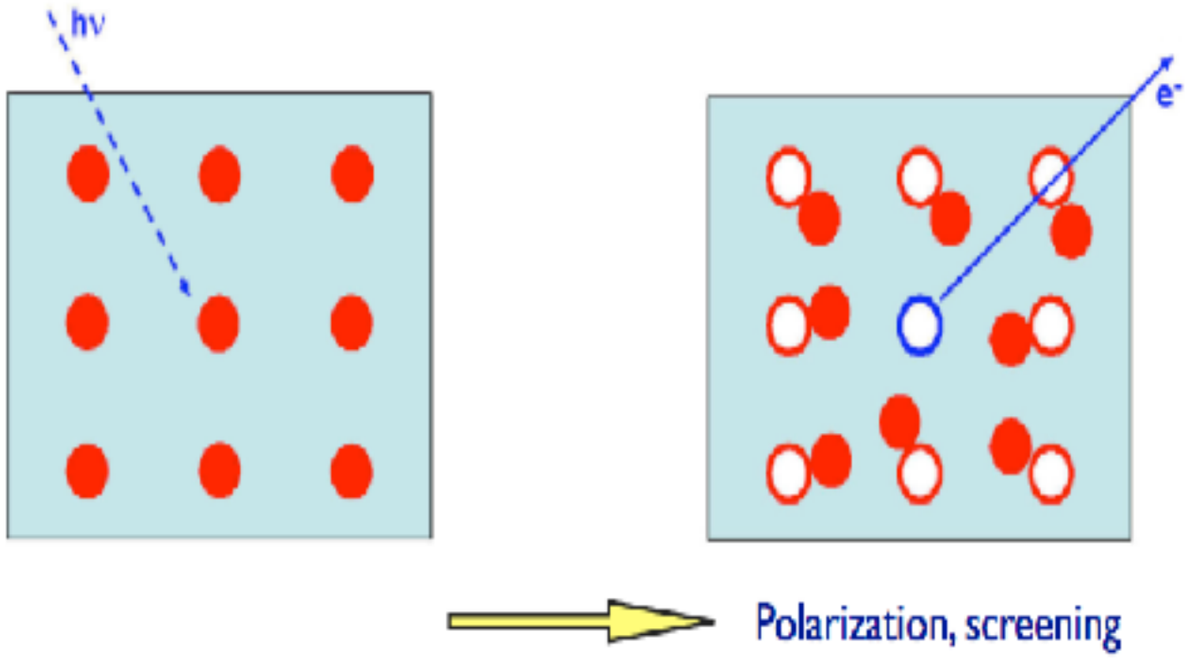
electron affinity ionization potential



Quasiparticle

$$E_{gap} = (E_{N+1} - E_N) - (E_N - E_{N-1})$$

electron affinity ionization potential



Electron injection

Repulsive Coulomb interaction creates a repulsive Coulomb hole around the the additional electrons

Direct photemission

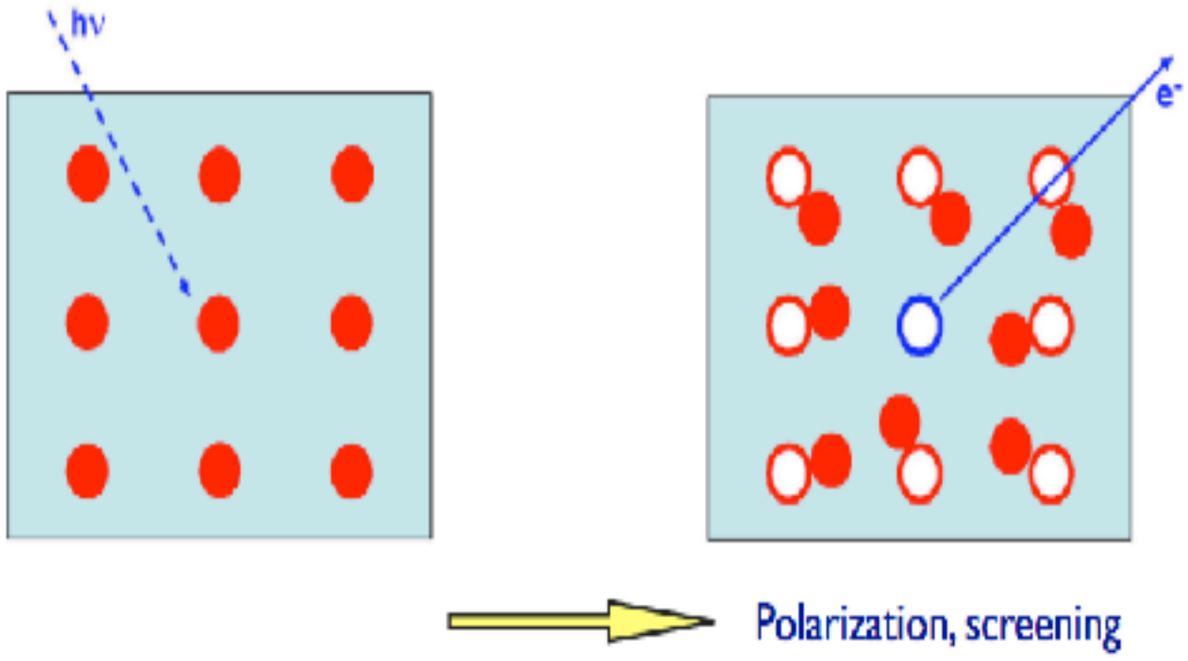
an electron leaves the system: also the Coulomb hole disappear

Relaxation - Screening - Correlation

Quasiparticle

$$E_{gap} = (E_{N+1} - E_N) - (E_N - E_{N-1})$$

electron affinity ionization potential



Electron injection

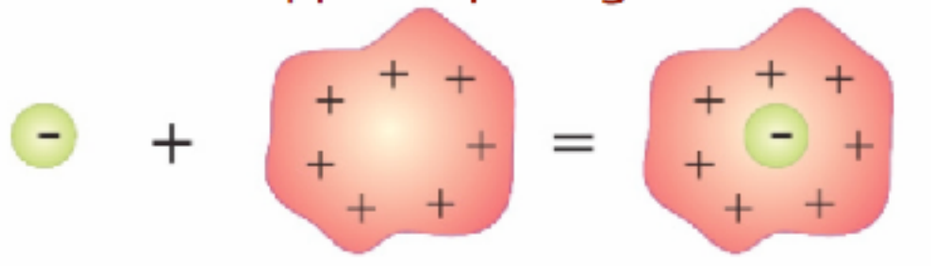
Repulsive Coulomb interaction creates a repulsive Coulomb hole around the the additional electrons

Direct photemission

an electron leaves the system: also the Coulomb hole disappear

Relaxation - Screening - Correlation

Relative to the ground- state N-electron system, the addition (removal) of an electron in indirect (direct) photoemission hence creates (annihilates) an ensemble consisting of the bare electron and its oppositely charges Coulomb hole.



Band Gap:

Can we calculate the QP gap directly using total energies from DFT-LDA?

Band Gap:

Can we calculate the QP gap directly using total energies from DFT-LDA?

$$E_G = \epsilon^N_{N+1} - \epsilon^N_N + \sum_i^{N+1} \Delta\epsilon^L_i + \sum_i^{N-1} \Delta\epsilon^H_i$$
$$- E_{\mathrm{Har}}[\Delta\rho^L] - E_{\mathrm{Har}}[\Delta\rho^H] + \int V^N_{\mathrm{Har}}(\mathbf{r})(\Delta\rho^H(\mathbf{r}) - \Delta\rho^L(\mathbf{r}))d\mathbf{r}$$
$$+ E_{\mathrm{XC}}[\rho^{N+1}] + E_{\mathrm{XC}}[\rho^{N-1}] - 2E_{\mathrm{XC}}[\rho^N]$$
$$- \int V^{N+1}_{\mathrm{XC}}(\mathbf{r})\rho^{N+1}(\mathbf{r})d\mathbf{r} - \int V^{N-1}_{\mathrm{XC}}(\mathbf{r})\rho^{N-1}(\mathbf{r})d\mathbf{r} + 2\int V^N_{\mathrm{XC}}(\mathbf{r})\rho^N(\mathbf{r})d\mathbf{r}$$

Kohn-Sham is NOT the QP gap

From: CE Patrick, Oxford 2011

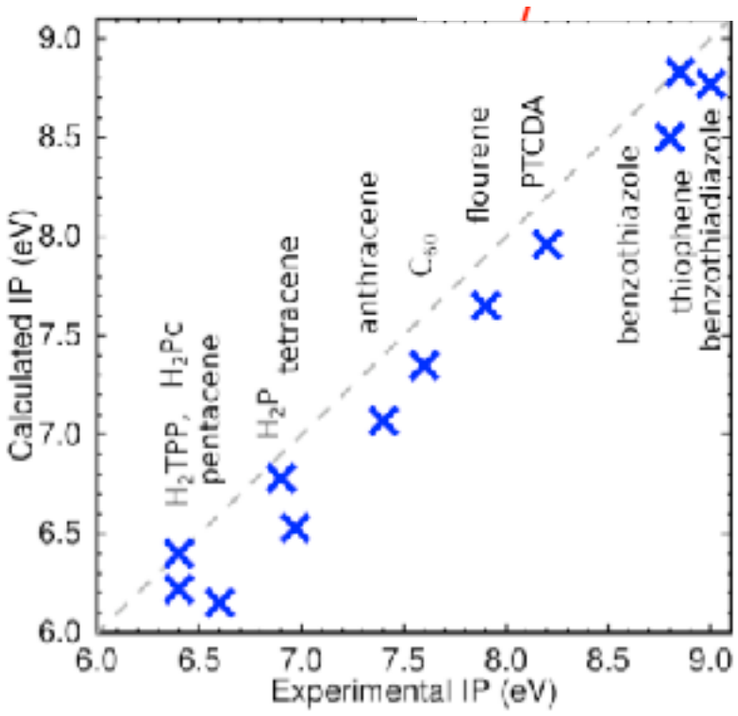
Band Gap:

Can we calculate the QP gap directly using total energies from DFT-LDA?

$$E_G = \epsilon^N_{N+1} - \epsilon^N_N + \sum_i^{N+1} \Delta\epsilon^L_i + \sum_i^{N-1} \Delta\epsilon^H_i$$
$$- E_{\rm Har}[\Delta\rho^L] - E_{\rm Har}[\Delta\rho^H] + \int V^N_{\rm Har}(\mathbf{r})(\Delta\rho^H(\mathbf{r}) - \Delta\rho^L(\mathbf{r}))d\mathbf{r}$$
$$+ E_{\rm XC}[\rho^{N+1}] + E_{\rm XC}[\rho^{N-1}] - 2E_{\rm XC}[\rho^N]$$
$$- \int V^{N+1}_{\rm XC}(\mathbf{r})\rho^{N+1}(\mathbf{r})d\mathbf{r} - \int V^{N-1}_{\rm XC}(\mathbf{r})\rho^{N-1}(\mathbf{r})d\mathbf{r} + 2\int V^N_{\rm XC}(\mathbf{r})\rho^N(\mathbf{r})d\mathbf{r}$$

From: CE Patrick, Oxford 2011

Kohn-Sham is NOT the QP gap



ΔSCF

reasonable results for molecules

C. E. Patrick and F. Giustino, PRL 109, 116801 (2012)]

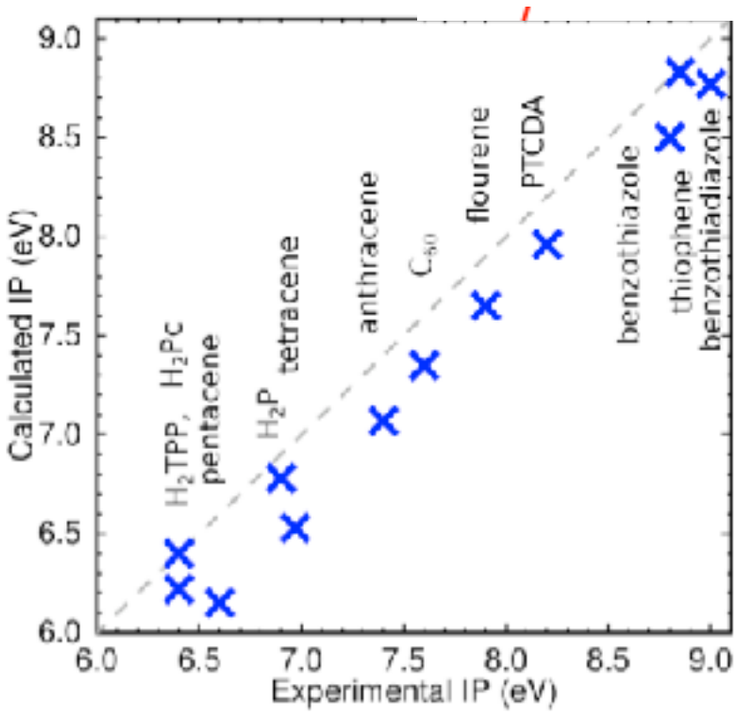
Band Gap:

Can we calculate the QP gap directly using total energies from DFT-LDA?

$$E_G = \epsilon^N_{N+1} - \epsilon^N_N + \sum_i^{N+1} \Delta\epsilon^L_i + \sum_i^{N-1} \Delta\epsilon^H_i$$
$$- E_{\rm Har}[\Delta\rho^L] - E_{\rm Har}[\Delta\rho^H] + \int V^N_{\rm Har}(\mathbf{r})(\Delta\rho^H(\mathbf{r}) - \Delta\rho^L(\mathbf{r}))d\mathbf{r}$$
$$+ E_{\rm XC}[\rho^{N+1}] + E_{\rm XC}[\rho^{N-1}] - 2E_{\rm XC}[\rho^N]$$
$$- \int V^{N+1}_{\rm XC}(\mathbf{r})\rho^{N+1}(\mathbf{r})d\mathbf{r} - \int V^{N-1}_{\rm XC}(\mathbf{r})\rho^{N-1}(\mathbf{r})d\mathbf{r} + 2\int V^N_{\rm XC}(\mathbf{r})\rho^N(\mathbf{r})d\mathbf{r}$$

From: CE Patrick, Oxford 2011

Kohn-Sham is NOT the QP gap

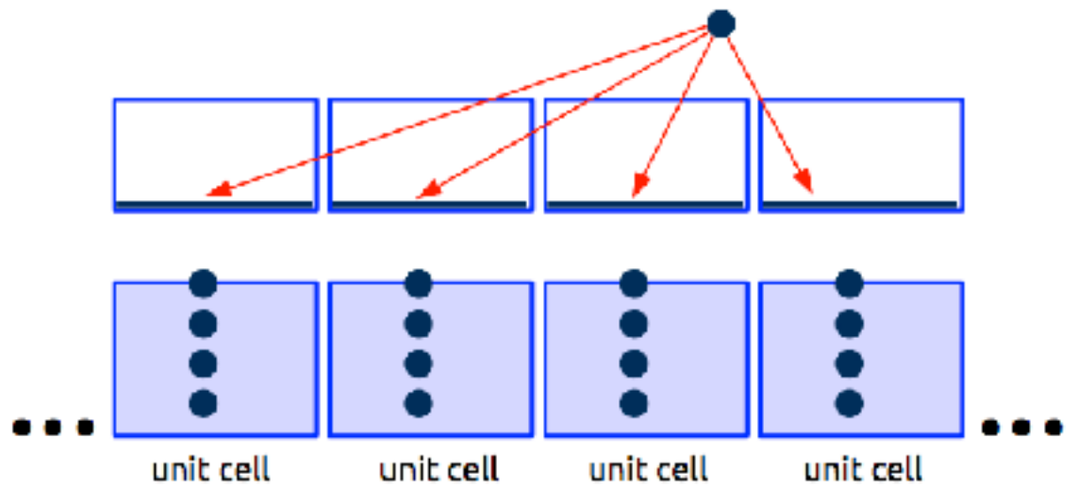


ΔSCF

reasonable results for molecules

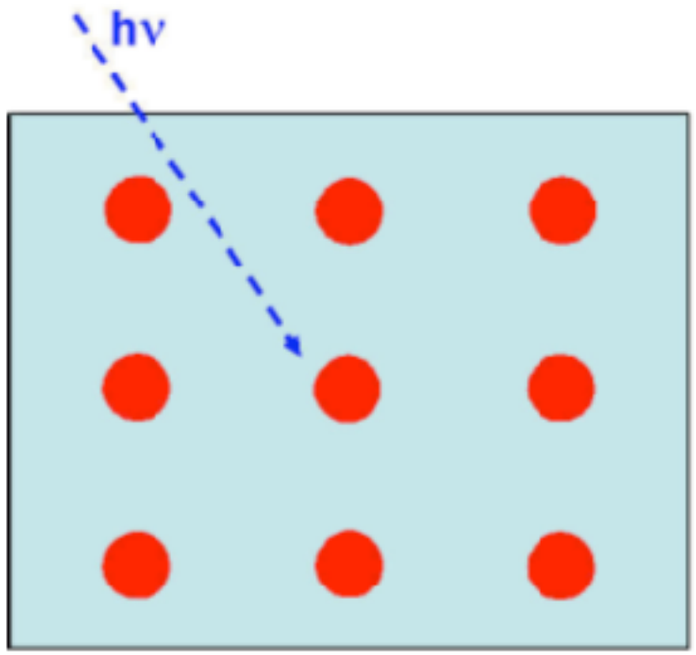
C. E. Patrick and F. Giustino, PRL 109, 116801 (2012)]

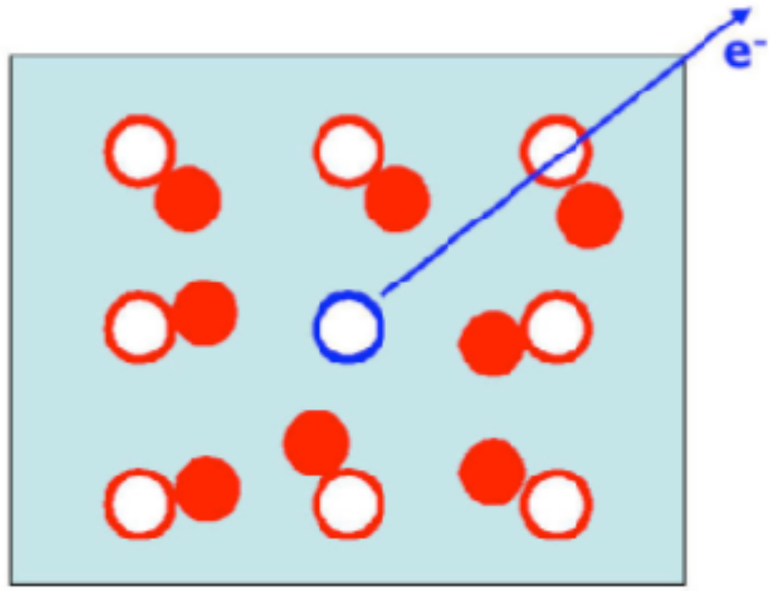
What about periodic solids ?



Infinitesimal extra charge per cell

Green function





Additional charge ⟶ Polarization, screening

Theoretical description involving the ejection or injection of electrons requires a framework that links the N-particle with the $(N \pm 1)$-particle system

Many Body Perturbation Theory

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

Green Function as a central variable

Contains the excitation energy ϵ_i

excitation lifetime

ground state density

expectation value one-particle operator Total Energy etc.

Green function

Definition and meaning of G

$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2)$$

probability amplitude for the propagation of an additional electron from (r_2,t_2) to (r_1,t_1) in a many body electron system with interacting H

$$\hat{H} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\hat{T}(\mathbf{r})\hat{\psi}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')V(\mathbf{r},\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})$$

$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2) =$$

Green function

Definition and meaning of G

$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2)$$

probability amplitude for the propagation of an additional electron from (r_2,t_2) to (r_1,t_1) in a many body electron system with interacting H

$$\hat{H} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\hat{T}(\mathbf{r})\hat{\psi}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')V(\mathbf{r},\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})$$

$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2) = \qquad |\Psi_0^N(t_2)\rangle$$

Green function

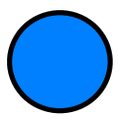
Definition and meaning of G

$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2)$$

probability amplitude for the propagation of an additional electron from (r_2,t_2) to (r_1,t_1) in a many body electron system with interacting H

$$\hat{H} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\hat{T}(\mathbf{r})\hat{\psi}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')V(\mathbf{r},\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})$$

(r_2,t_2)



$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2) = \qquad \hat{\psi}^\dagger(\mathbf{r_2})|\Psi_0^N(t_2)\rangle$$

Green function

Definition and meaning of G

$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2)$$

probability amplitude for the propagation of an additional electron from (r_2,t_2) to (r_1,t_1) in a many body electron system with interacting H

$$\hat{H} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\hat{T}(\mathbf{r})\hat{\psi}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')V(\mathbf{r},\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})$$

(r_2,t_2)

$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2) = \qquad U(t_1,t_2)\hat{\psi}^\dagger(\mathbf{r_2})|\Psi_0^N(t_2)\rangle$$

$$\hat{U}(t_1,t_2) = e^{\frac{-i}{\hbar}\hat{H}(t_1-t_2)} \qquad t_1 > t_2$$

Green function

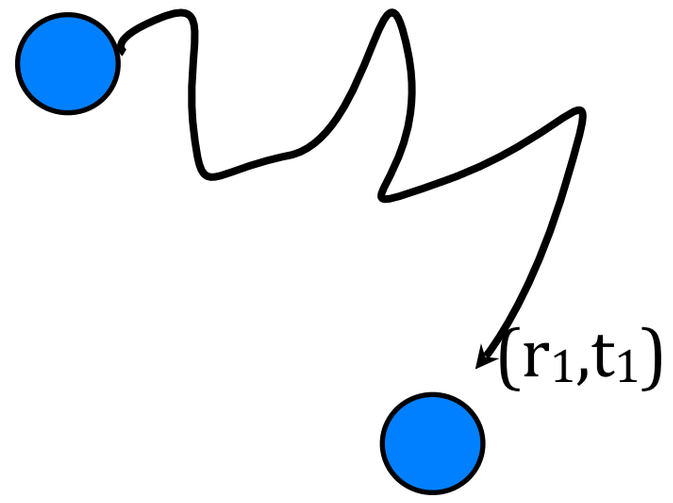
Definition and meaning of G

$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2)$$

probability amplitude for the propagation of an additional electron from (r_2,t_2) to (r_1,t_1) in a many body electron system with interacting H

$$\hat{H} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\hat{T}(\mathbf{r})\hat{\psi}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')V(\mathbf{r},\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})$$

(r_2,t_2)



$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2) = -\frac{i}{\hbar}\langle\Psi_0^N(t_1)|\ \hat{\psi}(\mathbf{r_1})\ U(t_1,t_2)\hat{\psi}^\dagger(\mathbf{r_2})|\Psi_0^N(t_2)\rangle$$

$$\hat{U}(t_1,t_2) = e^{\frac{-i}{\hbar}\hat{H}(t_1-t_2)} \qquad t_1 > t_2$$

Green function

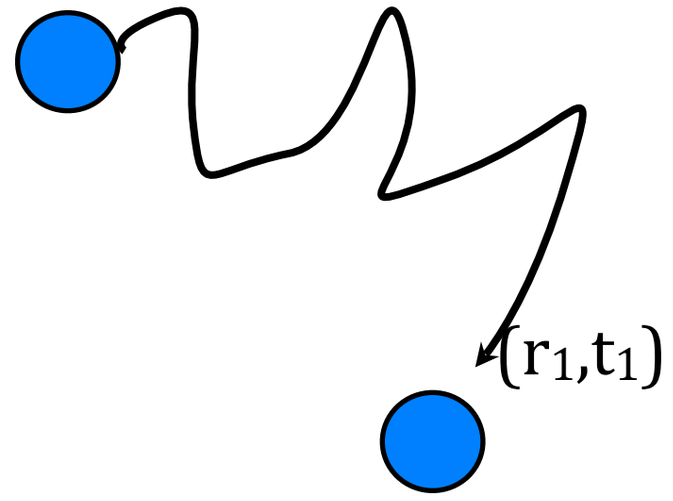
Definition and meaning of G

$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2)$$

probability amplitude for the propagation of an additional electron from (r_2,t_2) to (r_1,t_1) in a many body electron system with interacting H

$$\hat{H} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\hat{T}(\mathbf{r})\hat{\psi}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')V(\mathbf{r},\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})$$

(r_2,t_2)



$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2) = -\frac{i}{\hbar}\langle\Psi_0^N(t_1)|\ \hat{\psi}(\mathbf{r_1})\ U(t_1,t_2)\hat{\psi}^\dagger(\mathbf{r_2})|\Psi_0^N(t_2)\rangle$$

$$\hat{U}(t_1,t_2) = e^{\frac{-i}{\hbar}\hat{H}(t_1-t_2)} \qquad t_1 > t_2$$

$$G^e(\mathbf{r_1}t_1, \mathbf{r_2}t_2) = -\frac{i}{\hbar}\langle\Psi_0^N|\hat{\psi}(\mathbf{r_1},t_1)\hat{\psi}^\dagger(\mathbf{r_2},t_2)|\Psi_0^N\rangle\theta(t_1-t_2)$$

Green function

Similarly for an hole propagation

$$G^h(\mathbf{r_2}t_2,\mathbf{r_1}t_1) = -\frac{i}{\hbar}\langle\Psi_0^N|\hat{\psi}^\dagger(\mathbf{r_2},t_2)\hat{\psi}(\mathbf{r_1},t_1)|\Psi_0^N\rangle\theta(t_2-t_1)$$

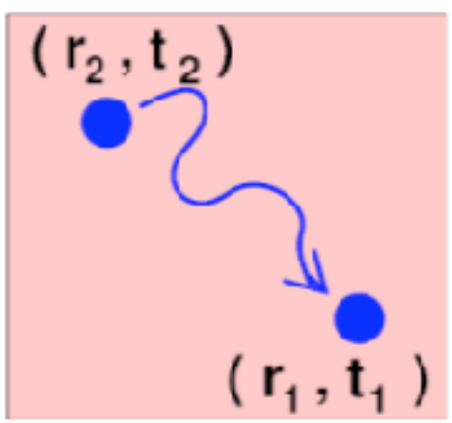
We define G as:

Time-ordered Green Function

$$G(\mathbf{r_1}t_1,\mathbf{r_2}t_2) = G^e(\mathbf{r_1}t_1,\mathbf{r_2}t_2) - G^h(\mathbf{r_2}t_2,\mathbf{r_1}t_1) = -\frac{i}{\hbar}\langle\Psi_0^N|\hat{T}[\hat{\psi}(r_1,t_1)\hat{\psi}^\dagger(r_2,t_2)]|\Psi_0^N\rangle$$

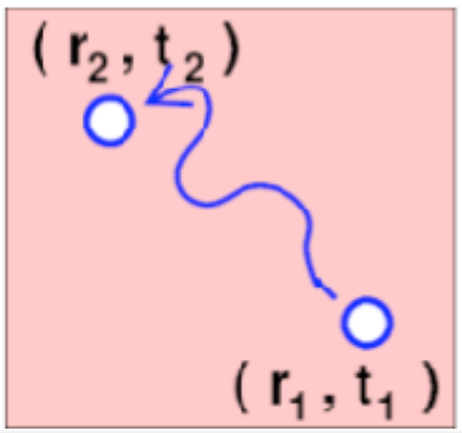
$t_1 > t_2$

$$\langle\Psi_0^N|\hat{\psi}(\mathbf{r_1},t_1)\hat{\psi}^\dagger(\mathbf{r_2},t_2)|\Psi_0^N\rangle$$



$t_1 < t_2$

$$-\langle\Psi_0^N|\hat{\psi}^\dagger(\mathbf{r_2},t_2)\hat{\psi}(\mathbf{r_1},t_1)|\Psi_0^N\rangle$$



Green function: Excitation spectrum

$$G(\mathbf{r_1}t_1,\mathbf{r_2}t_2) = -\frac{i}{\hbar}\langle\Psi_0^N|\hat{T}[\hat{\psi}(\mathbf{r_1}t_1)\hat{\psi}^\dagger(\mathbf{r_2}t_2)]|\Psi_0^N\rangle$$

$$G(\mathbf{r_1}t_1,\mathbf{r_2}t_2) = -i\langle\Psi_0^N|[\hat{\psi}(\mathbf{r_1})exp\Big[-i(H-E(N))(t_1-t_2)\Big]\hat{\psi}^\dagger(\mathbf{r_2})|\Psi_0^N\rangle\theta(t_1-t_2)$$
$$+i\langle\Psi_0^N|[\hat{\psi}^\dagger(\mathbf{r_2})exp\Big[-i(H-E(N))(t_1-t_2)\Big]\hat{\psi}(\mathbf{r_1})|\Psi_0^N\rangle\theta(t_2-t_1)$$

Insert a complete set of N+1 and N-1 particle states. $\sum_j |\Psi_j^{N\pm1}\rangle\langle\Psi_j^{N\pm1}| = 1$

$$G(\mathbf{r_1}t_1,\mathbf{r_2}t_2) = -i\sum_j f_j(\mathbf{r_1})f_j^*(\mathbf{r_2})e^{-i\epsilon_j(t_1-t_2)}\Big[\theta(t_1-t_2)\theta(\epsilon_j-\mu)-\theta(t_2-t_1)\theta(\mu-\epsilon_j\Big]$$

$$f_j(\mathbf{r_1}) = \begin{matrix}\langle\Psi_0^N|\hat{\psi}(\mathbf{r_1})|\Psi_j^{N+1}\rangle & \epsilon_j > \mu \\ \langle\Psi_j^{N-1}|\hat{\psi}(\mathbf{r_1})|\Psi_0^N\rangle & \epsilon_j < \mu\end{matrix} \qquad \epsilon_j = \begin{matrix}E(N+1,j)-E(N) & \epsilon_j > \mu \\ E(N)-E(N-1,j) & \epsilon_j < \mu\end{matrix}$$

Green function

$$G(\mathbf{r_1}t_1,\mathbf{r_2}t_2) = -i\sum_j f_j(\mathbf{r_1})f_j^*(\mathbf{r_2})e^{-i\epsilon_j(t_1-t_2)}\Big[\theta(t_1-t_2)\theta(\epsilon_j-\mu)-\theta(t_2-t_1)\theta(\mu-\epsilon_j\Big]$$

Fourier Transforming in frequency domain:

$$G(\mathbf{r_1},\mathbf{r_2},\omega) = \sum_j \frac{f_j(\mathbf{r_1})f_j^*(\mathbf{r_2})}{\omega-\epsilon_j+i\eta sgn(\epsilon_j-\mu)}$$

$$\epsilon_j = \begin{matrix} E(N+1,j)-E(N) \\ E(N)-E(N-1,j) \end{matrix}$$

$$f_j(\mathbf{r_1}) = \begin{matrix} \langle\Psi_0^N|\hat{\psi}(\mathbf{r_1})|\Psi_j^{N+1}\rangle & \epsilon_j > \mu \\ \langle\Psi_j^{N-1}|\hat{\psi}(\mathbf{r_1})|\Psi_0^N\rangle & \epsilon_j < \mu \end{matrix}$$

Green Function has poles at the true many-particle excitation energies

Self Energy

How to obtain G??

Self Energy

How to obtain G??

Perturbation theory starts from what is known to evaluate what is not known ...hoping that the difference is small

Let's say we know $G_0(\omega)$ that corresponds to the Hamiltonian H_0

(e.g. non interacting electrons)

$H = H_0 + H_1$, where the interaction is put in H_1

Self Energy

How to obtain G??

Perturbation theory starts from what is known to evaluate what is not known ...hoping that the difference is small

Let's say we know $G_0(\omega)$ that corresponds to the Hamiltonian H_0

(e.g. non interacting electrons)

$H = H_0 + H_1$, where the interaction is put in H_1

Everything that is unknown is put in

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

This is the definition of the Self Energy

Quasiparticle Equation

$$[\omega - \hat{H}_0]G(\omega) + i\int \Sigma(\omega)G(\omega) = 1$$

Let's suppose we know the Self Energy

and consider G_0 the Green function of a mean field system defined by

$$H_0 = -\frac{\nabla^2}{2m} + V_{ext} + \frac{e^2}{4\pi\epsilon_0}\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}'$$

single-particle Hamiltonian

Quasiparticle Equation

$$[\omega - \hat{H}_0]G(\omega) + i\int \Sigma(\omega)G(\omega) = 1$$

Let's suppose we know the Self Energy

and consider G_0 the Green function of a mean field system defined by

$$H_0 = -\frac{\nabla^2}{2m} + V_{ext} + \frac{e^2}{4\pi\epsilon_0}\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}'$$ single-particle Hamiltonian

Introducing the Lehmann representation for G

$$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

QP equation: looks similar to KS equation but:

Quasiparticle Equation

$$[\omega - \hat{H}_0]G(\omega) + i\int \Sigma(\omega)G(\omega) = 1$$

Let's suppose we know the Self Energy

and consider G_0 the Green function of a mean field system defined by

$$H_0 = -\frac{\nabla^2}{2m} + V_{ext} + \frac{e^2}{4\pi\epsilon_0}\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}'$$ single-particle Hamiltonian

Introducing the Lehmann representation for G

$$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

QP equation: looks similar to KS equation but:

$\sum$ contains many body effects (as V_{xc})

$\sum$ is not Hermitian, non-local, frequency dependent

Quasiparticle Equation

$$[\omega - \hat{H}_0]G(\omega) + i\int \Sigma(\omega)G(\omega) = 1$$

Let's suppose we know the Self Energy

and consider G_0 the Green function of a mean field system defined by

$$H_0 = -\frac{\nabla^2}{2m} + V_{ext} + \frac{e^2}{4\pi\epsilon_0}\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}'$$ single-particle Hamiltonian

Introducing the Lehmann representation for G

$$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

QP equation: looks similar to KS equation but:

Σ contains many body effects (as V_{xc})

Σ is not Hermitian, non-local, frequency dependent

V_{xc} part of the potential of a fictitious system

Σ potential felt by an added (removed) electron to (from) the system

Quasiparticle Equation

$$[\omega - \hat{H}_0]G(\omega) + i\int \Sigma(\omega)G(\omega) = 1$$

Let's suppose we know the Self Energy

and consider G_0 the Green function of a mean field system defined by

$$H_0 = -\frac{\nabla^2}{2m} + V_{ext} + \frac{e^2}{4\pi\epsilon_0}\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}'$$ single-particle Hamiltonian

Introducing the Lehmann representation for G

$$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

QP equation: looks similar to KS equation but:

Σ contains many body effects (as V_{xc})

Σ is not Hermitian, non-local, frequency dependent

V_{xc} part of the potential of a fictitious system

f_s not orthonormal

ϵ_s are complex

Σ potential felt by an added (removed) electron to (from) the system

GW Self Energy

QP equation describes the excitations of the Many-Body system

$$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

We have to know how is made the operator Σ

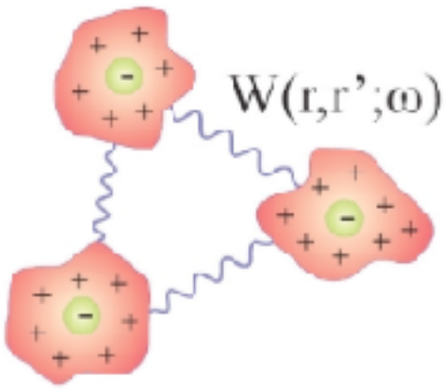
GW Self Energy

QP equation describes the excitations of the Many-Body system

$$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

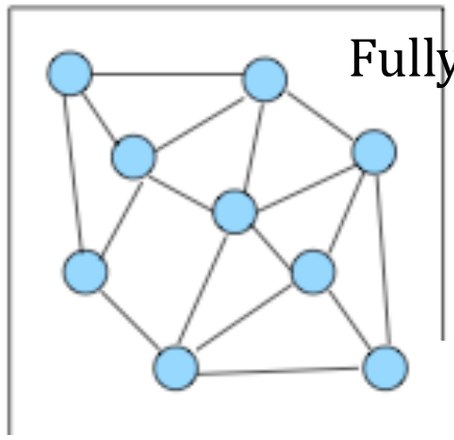
We have to know how is made the operator Σ

As a perturbation we do not consider the interaction V, but the screened Coulomb W that has reduced strength

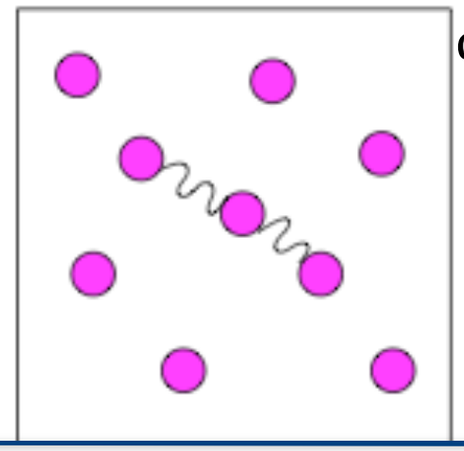


W = screened potential:
weaker than bare Coulomb interaction

$$W(r,r',\omega) = \int dr'' \frac{\epsilon^{-1}(r,r'',\omega)}{|r''-r'|}$$



Fully interacting electrons



Weakly interacting quasiparticle

Hedin's Equations

Set of integro-differential equation, whose self-consistent solution solves the many-electron problem

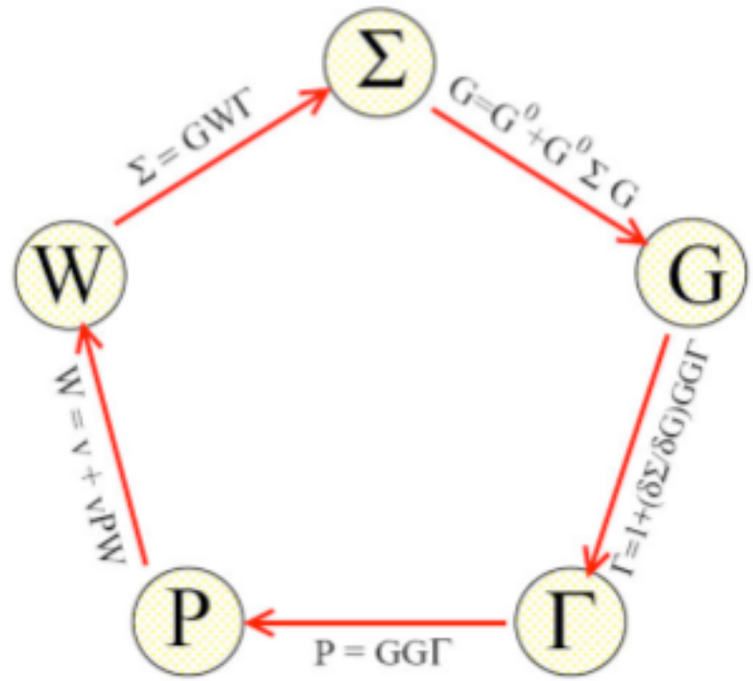
$$
\begin{aligned}
P(12) &= -i \int d(34) G(13) G(41^+) \Gamma(34,2) \\
W(12) &= V(12) + \int d(34) W(13) P(34) V(4,2) \\
\Sigma(12) &= i \int d(34) G(14) W(1^+3) \Gamma(42,3) \\
G(12) &= G^0(12) + \int d(34) G^0(13) \Sigma(34) G(42) \\
\Gamma(12,3) &= \delta(12)\delta(13) + \int d(4567) \frac{\partial \Sigma(12)}{\partial G(45)} G(46) G(75) \Gamma(67,3)
\end{aligned}
$$

L. Hedin, Phys Rev. 139, A 769 (1965)

How to obtain the Self energy: Iteration of Hedin's Equations and GW

They cannot be solved numerically as they contain functional derivatives, but they can be iterated to derive useful approximations

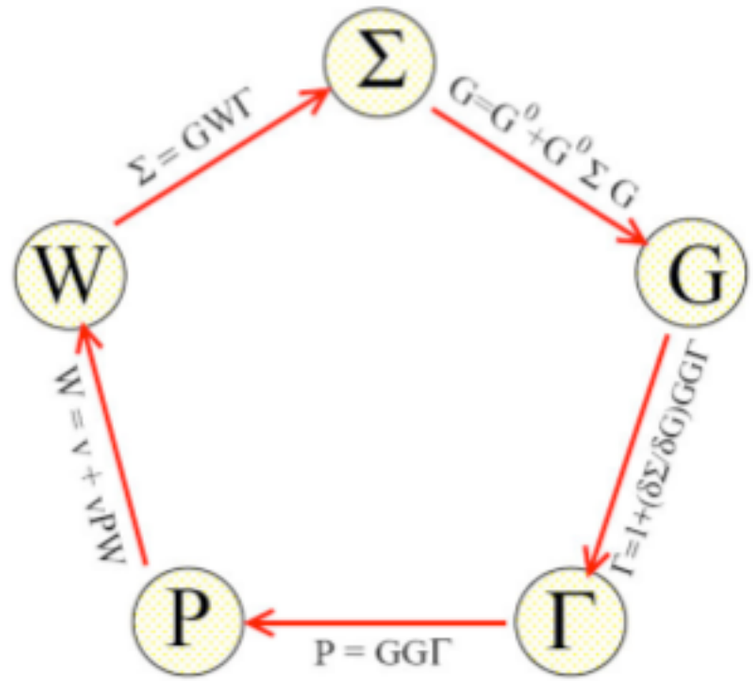
$$
\begin{aligned}
\Sigma &= iGW\Gamma \\
G &= G_0 + G_0\Sigma G \\
\Gamma &= 1 + \frac{\partial\Sigma}{\partial G}GG\Gamma \\
P &= -iGG\Gamma \\
W &= v + vPW
\end{aligned}
$$



How to obtain the Self energy: Iteration of Hedin's Equations and GW

They cannot be solved numerically as they contain functional derivatives, but they can be iterated to derive useful approximations

$$
\begin{aligned}
\Sigma &= iGW\Gamma \\
G &= G_0 + G_0\Sigma G \\
\Gamma &= 1 + \frac{\partial \Sigma}{\partial G} GG\Gamma \\
P &= -iGG\Gamma \\
W &= v + vPW
\end{aligned}
$$

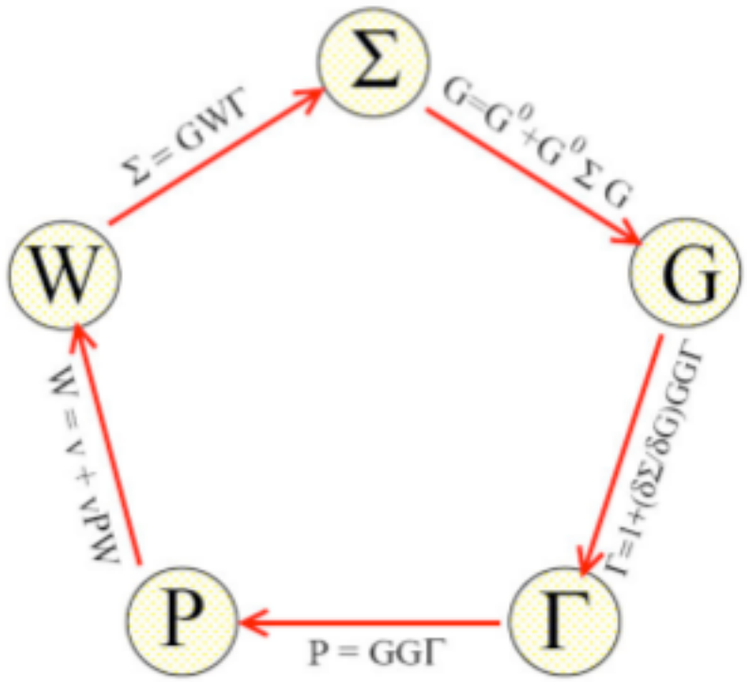


We start with $G = G_0$, $\Sigma = 0$

How to obtain the Self energy: Iteration of Hedin's Equations and GW

They cannot be solved numerically as they contain functional derivatives, but they can be iterated to derive useful approximations

$$
\begin{aligned}
\Sigma &= iGW\Gamma \\
G &= G_0 + G_0\Sigma G \\
\Gamma &= 1 \\
P &= -iGG\Gamma \\
W &= v + vPW
\end{aligned}
$$

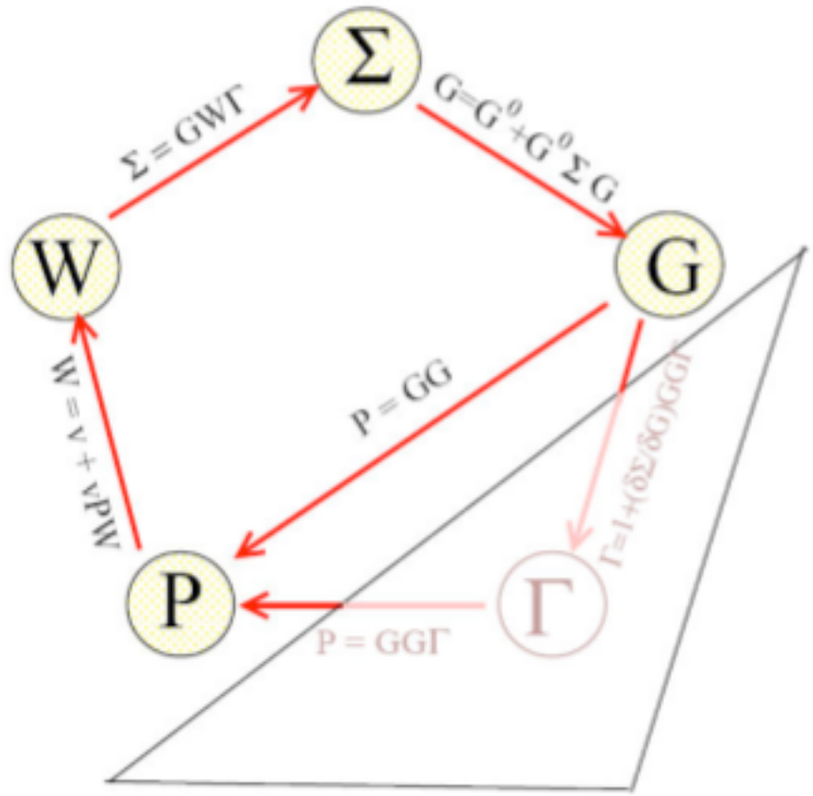


We start with $G = G_0$, $\Sigma = 0$

How to obtain the Self energy: Iteration of Hedin's Equations and GW

They cannot be solved numerically as they contain functional derivatives, but they can be iterated to derive useful approximations

$$\begin{aligned} \Sigma &= iGW \\ G &= G_0 + G_0 \Sigma G \\ \Gamma &= 1 \\ P &= -iGG \\ W &= v + vPW \end{aligned}$$

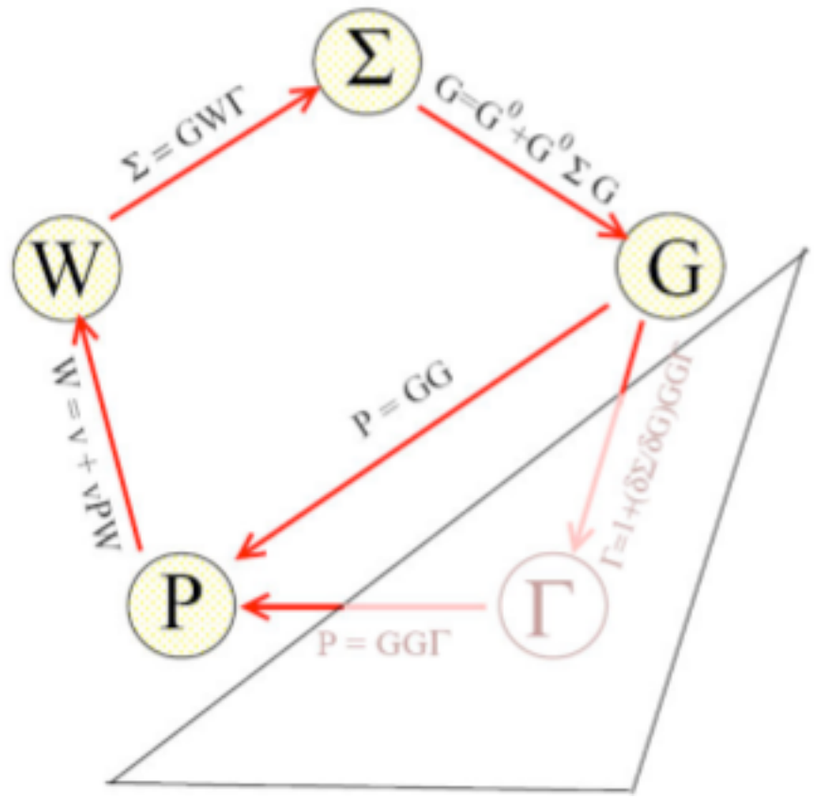


We start with $G = G_0$, $\Sigma = 0$

Iteration of Hedin's Equations and GW

They cannot be solved numerically as they contain functional derivatives, but they can be iterated to derive useful approximations

$$\Sigma = iGW$$
$$G = G_0 + G_0 \Sigma G$$
$$\Gamma = 1$$
$$P = -iGG$$
$$W = v + vPW$$



Remark:

The vertex Γ has been neglected ← **This is an approximation!!**

The equations can be solved self-consistently

Common approximation: $G = G_0$ ← **This is another approximation!!**

GW approximation in practice

Goal: $\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$

$$\Sigma = iGW$$

GW approximation in practice

Goal: $\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$

$\Sigma = iGW$

$G = G_0$ Green function of the non-interacting system

GW approximation in practice

Goal: $\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$

$\Sigma = iGW$

$G = G_0$ Green function of the non-interacting system

$$\Sigma^{GW}(\mathbf{r_1},\mathbf{r_2};\tau) = i\hbar G_0(\mathbf{r_1},\mathbf{r_2};\tau)W(\mathbf{r_1},\mathbf{r_2};\tau+\eta)$$

In Fourier space

$$\Sigma^{GW}(\mathbf{r_1},\mathbf{r_2};\omega) = \frac{i\hbar}{2\pi}\int_{-\infty}^{\infty} G_0(\mathbf{r_1},\mathbf{r_2};\omega+\omega')W(\mathbf{r_1},\mathbf{r_2};\omega')e^{i\omega'\eta}d\omega'$$

GW approximation in practice

Goal: $$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

$$\Sigma = iGW$$

$$G = G_0$$ Green function of the non-interacting system

$$\Sigma^{GW}(\mathbf{r_1},\mathbf{r_2};\tau) = i\hbar G_0(\mathbf{r_1},\mathbf{r_2};\tau)W(\mathbf{r_1},\mathbf{r_2};\tau+\eta)$$

In Fourier space

$$\Sigma^{GW}(\mathbf{r_1},\mathbf{r_2};\omega) = \frac{i\hbar}{2\pi}\int_{-\infty}^{\infty} G_0(\mathbf{r_1},\mathbf{r_2};\omega+\omega')W(\mathbf{r_1},\mathbf{r_2};\omega')e^{i\omega'\eta}d\omega'$$

Polarization and Screening

$$W = v + vPW$$

$$P(\mathbf{r_1},\mathbf{r_2};\tau) = -i\hbar G_0(\mathbf{r_1},\mathbf{r_2};\tau)G_0(\mathbf{r_2},\mathbf{r_1};-\tau)$$

GW approximation in practice

Goal: $\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$

$$\Sigma = iGW$$

$$P(\mathbf{r_1},\mathbf{r_2};\tau) = -i\hbar G_0(\mathbf{r_1},\mathbf{r_2};\tau)G_0(\mathbf{r_2},\mathbf{r_1};-\tau)$$

Starting point: solve an independent-particle calculation: e.g. LDA

$$H_0(\mathbf{r})\phi_j^0(\mathbf{r}) + V_{xc}(\mathbf{r})\phi_\mathbf{j}^\mathbf{0}(\mathbf{r}) = \epsilon_\mathbf{j}\phi_\mathbf{j}^\mathbf{0}(\mathbf{r})$$

By FT and using Lehmann representation

$$P(\mathbf{r_1},\mathbf{r_2};\omega) = \sum_i^{occ.}\sum_j^{unocc.} \phi_i^0(\mathbf{r})\phi_j^{0*}(\mathbf{r})\phi_i^{0*}(\mathbf{r}')\phi_j^0(\mathbf{r}') \times \left(\frac{1}{\hbar\omega + \epsilon_i^0 - \epsilon_j^0 + i\eta} - \frac{1}{\hbar\omega - \epsilon_i^0 + \epsilon_j^0 - i\eta}\right)$$

Polarization made of noninteracting electrons and holes

GW approximation in practice

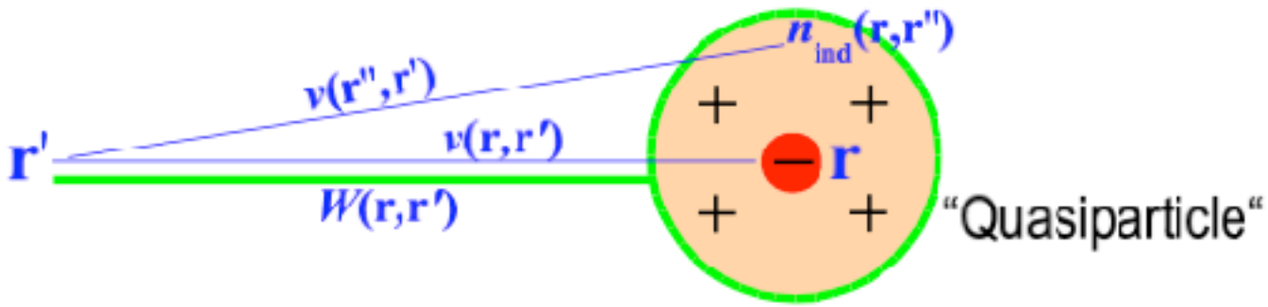
Goal: $$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

$$\Sigma = iGW$$

Screened potential

$$W(\mathbf{r_1},\mathbf{r_2};\omega) = \int \epsilon^{-1}(\mathbf{r_1},\mathbf{r}';\omega)v(\mathbf{r}',\mathbf{r_2})d\mathbf{r}' = v(\mathbf{r_1},\mathbf{r_2}) + \int n_{ind}(\mathbf{r_1},\mathbf{r}';\omega)v(\mathbf{r}',\mathbf{r_2})d\mathbf{r}'$$

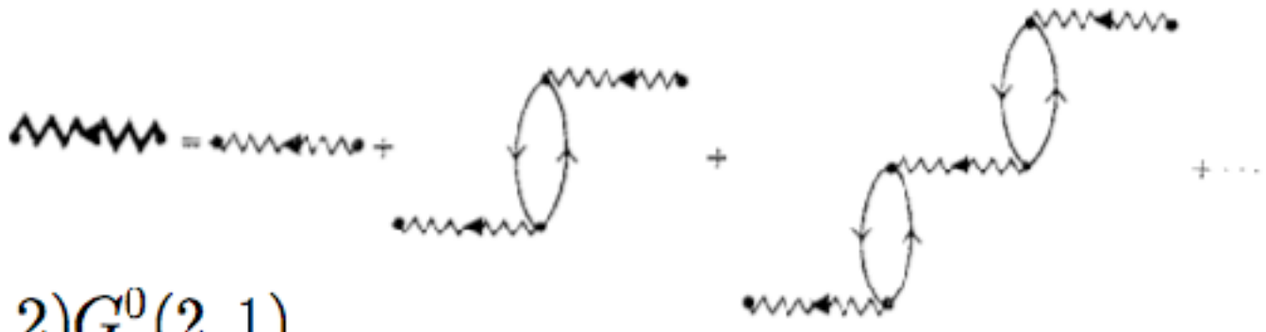
Classical (Hartree) interaction between additional charge and polarization charge



$$n_{ind}(\mathbf{r_1},\mathbf{r_2};\omega) = \int P^0(\mathbf{r_1},\mathbf{r}';\omega)V^{tot}(\mathbf{r}',\mathbf{r_2})d\mathbf{r}'$$

$$\epsilon(\mathbf{r_1},\mathbf{r_2};\omega) = \delta(\mathbf{r_1}-\mathbf{r_2}) - \int v(\mathbf{r_1}-\mathbf{r}')P^0(\mathbf{r}',\mathbf{r_2};\omega)d\mathbf{r}'$$

$$W = v + vPW$$



Using $P(1,2) = P^0(1,2) = G^0(1,2)G^0(2,1)$

Random Phase **Approximation** (RPA)

Evaluation of the Self-Energy

$$\Sigma^{GW} = G_0^{KS} W = G_0^{KS} V + G^{KS}(W - V) = \Sigma_x^{GW} + \Sigma_c^{GW}$$

Evaluation of the Self-Energy

$$\Sigma^{GW} = G_0^{KS} W = G_0^{KS} V + G^{KS}(W - V) = \Sigma_x^{GW} + \Sigma_c^{GW}$$

$$\Sigma_x^{GW}(\mathbf{r_1}, \mathbf{r_2}; \omega) = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} G_0^{KS}(\mathbf{r_1}, \mathbf{r_2}; \omega + \omega') v(\mathbf{r_1}, \mathbf{r_2}) e^{i\omega'\eta} d\omega'$$

can be integrated analytically

$$\langle \phi_i^{KS} | \Sigma_x^{GW} | \phi_i^{KS} \rangle = -\frac{e^2}{4\pi\epsilon_0} \sum_j^{occ.} \int \frac{\phi_i^{KS*}(\mathbf{r}) \phi_j^{KS}(\mathbf{r}) \phi_j^{KS*}(\mathbf{r}') \phi_i^{KS}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Hartree-Fock exchange term

Evaluation of the Self-Energy

$$\Sigma^{GW} = G_0^{KS} W = G_0^{KS} V + G^{KS}(W - V) = \Sigma_x^{GW} + \Sigma_c^{GW}$$

$$\Sigma_x^{GW}(\mathbf{r_1}, \mathbf{r_2}; \omega) = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} G_0^{KS}(\mathbf{r_1}, \mathbf{r_2}; \omega + \omega') v(\mathbf{r_1}, \mathbf{r_2}) e^{i\omega'\eta} d\omega'$$

can be integrated analytically

$$\langle \phi_i^{KS} | \Sigma_x^{GW} | \phi_i^{KS} \rangle = -\frac{e^2}{4\pi\epsilon_0} \sum_j^{occ.} \int \frac{\phi_i^{KS*}(\mathbf{r}) \phi_j^{KS}(\mathbf{r}) \phi_j^{KS*}(\mathbf{r}') \phi_i^{KS}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Hartree-Fock exchange term

$$\Sigma_c^{GW}(\mathbf{r_1}, \mathbf{r_2}; \omega) = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} G_0^{KS}(\mathbf{r_1}, \mathbf{r_2}; \omega + \omega') [W(\mathbf{r_1}, \mathbf{r_2}; \omega') - v(\mathbf{r_1}, \mathbf{r_2})] e^{i\omega'\eta} d\omega'$$

have to be computed numerically; most time consuming part

GW approximation in practice

Different implementations:

Reciprocal Space & Frequency Domain:

M. Hybertsen and S. Louie PRB 34, 5390 (1986)

Real Space and Real Time:

H.N. Rojas, R. W. Godby and R. J. Needs PRL 74, 1827 (1995)

Use of localized basis set:

H. Huebener, M. A. Perez-Osorio, P. Ordejon, and F. Giustino Eur. Phys. J. B 85, 321 (2012).
M. Rohlfing, P. Kruger, and J. Pollmann, Phys.Rev. B 52, 1905 (1995).
X. Blase, C. Attaccalite, and V. Olevano PRB 83, 115103 (2011)
F. Bruneval, T. Rangel, S.M. Hamed, M. Shao, C. Yang, and J.B. Neaton, Comput. Phys. Commun. **208**, 149 (2016)

Use of Wannier Function:

P. Umari, G. Stenuit and S. Baroni PRB 79, 201104(R) (2009)

Benchmarking codes: Reproducibility in G_0W_0 Calculations for Solids T. Rangel, M. Del Ben, D. Varsano et al. Computer Physics Communications 255 107242, (2020)

GW approximation in practice

Different implementations:

Reciprocal Space & Frequency Domain:
M. Hybertsen and S. Louie PRB 34, 5390 (1986)

Real Space and Real Time:
H.N. Rojas, R. W. Godby and R. J. Needs PRL 74, 1827 (1995)

Use of localized basis set:
H. Huebener, M. A. Perez-Osorio, P. Ordejon, and F. Giustino Eur. Phys. J. B 85, 321 (2012).
M. Rohlfing, P. Kruger, and J. Pollmann, Phys.Rev. B 52, 1905 (1995).
X. Blase, C. Attaccalite, and V. Olevano PRB 83, 115103 (2011)
F. Bruneval, T. Rangel, S.M. Hamed, M. Shao, C. Yang, and J.B. Neaton, Comput. Phys. Commun. **208**, 149 (2016)

Use of Wannier Function:
P. Umari, G. Stenuit and S. Baroni PRB 79, 201104(R) (2009)

Benchmarking codes: Reproducibility in G_0W_0 Calculations for Solids T. Rangel, M. Del Ben, D. Varsano et al. Computer Physics Communications 255 107242, (2020)

GW approximation in practice

Plane waves representation:

$$\langle n\mathbf{k}|\Sigma_x(\mathbf{r_1},\mathbf{r_2})|\mathbf{n'k'}\rangle = -\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{(2\pi)^3}\sum_{\mathbf{G}}\mathbf{v}(\mathbf{q}+\mathbf{G})\rho_{\mathbf{n},\mathbf{n_1}}(\mathbf{q},\mathbf{G})\rho^*_{\mathbf{n'n_1}}(\mathbf{q},\mathbf{G})\mathbf{f_{n_1k_1}}$$

$$\rho_{nn1}(\mathbf{q}+\mathbf{G}) = \langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n1\mathbf{k_1}\rangle$$

$$\langle n\mathbf{k}|\Sigma_c(\mathbf{r_1},\mathbf{r_2};\omega)|\mathbf{n'k'}\rangle = \frac{\mathbf{1}}{\mathbf{2}}\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{(2\pi)^3}\Big\{\sum_{\mathbf{GG'}}\mathbf{v}(\mathbf{q}+\mathbf{G})\rho_{\mathbf{n},\mathbf{n_1}}(\mathbf{q},\mathbf{G})\rho^*_{\mathbf{n'n_1}}(\mathbf{q},\mathbf{G'})\times$$

$$\times\int\frac{d\omega'}{2\pi}\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega')\Big[\frac{f_{n1(\mathbf{k}-\mathbf{q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k}-\mathbf{q})}-i\delta}+\frac{1-f_{n1(\mathbf{k}-\mathbf{q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k}-\mathbf{q})}+i\delta}\Big]\Big\}$$

What makes GW calculations even at G0W0 level rather “laborious”:

GW approximation in practice

Plane waves representation:

$$\langle n\mathbf{k}|\Sigma_x(\mathbf{r_1},\mathbf{r_2})|\mathbf{n'k'}\rangle = -\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{(2\pi)^3}\sum_{\mathbf{G}}\mathbf{v}(\mathbf{q}+\mathbf{G})\rho_{\mathbf{n},\mathbf{n_1}}(\mathbf{q},\mathbf{G})\rho^*_{\mathbf{n'n_1}}(\mathbf{q},\mathbf{G})\mathbf{f_{n_1k_1}}$$

$$\rho_{nn1}(\mathbf{q}+\mathbf{G}) = \langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n1\mathbf{k_1}\rangle$$

$$\langle n\mathbf{k}|\Sigma_c(\mathbf{r_1},\mathbf{r_2};\omega)|\mathbf{n'k'}\rangle = \frac{\mathbf{1}}{\mathbf{2}}\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{(2\pi)^3}\Big\{\sum_{\mathbf{GG'}}\mathbf{v}(\mathbf{q}+\mathbf{G})\rho_{\mathbf{n},\mathbf{n_1}}(\mathbf{q},\mathbf{G})\rho^*_{\mathbf{n'n_1}}(\mathbf{q},\mathbf{G'})\times$$

$$\times\int\frac{d\omega'}{2\pi}\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega')\Big[\frac{f_{n1(\mathbf{k}-\mathbf{q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k}-\mathbf{q})}-i\delta}+\frac{1-f_{n1(\mathbf{k}-\mathbf{q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k}-\mathbf{q})}+i\delta}\Big]\Big\}$$

What makes GW calculations even at G0W0 level rather “laborious”:

Careful is needed:

Integration over the Brillouin zone

GW approximation in practice

Plane waves representation:

$$\langle n\mathbf{k}|\Sigma_x(\mathbf{r_1},\mathbf{r_2})|\mathbf{n'k'}\rangle = -\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{(2\pi)^3}\sum_{\mathbf{G}}\mathbf{v}(\mathbf{q}+\mathbf{G})\rho_{\mathbf{n},\mathbf{n_1}}(\mathbf{q},\mathbf{G})\rho^*_{\mathbf{n'n_1}}(\mathbf{q},\mathbf{G})\mathbf{f_{n_1k_1}}$$

$$\rho_{nn1}(\mathbf{q}+\mathbf{G}) = \langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n1\mathbf{k_1}\rangle$$

$$\langle n\mathbf{k}|\Sigma_c(\mathbf{r_1},\mathbf{r_2};\omega)|\mathbf{n'k'}\rangle = \frac{1}{2}\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{(2\pi)^3}\Big\{\sum_{\mathbf{GG'}}\mathbf{v}(\mathbf{q}+\mathbf{G})\rho_{\mathbf{n},\mathbf{n_1}}(\mathbf{q},\mathbf{G})\rho^*_{\mathbf{n'n_1}}(\mathbf{q},\mathbf{G'})\times$$

$$\times\int\frac{d\omega'}{2\pi}\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega')\Big[\frac{f_{n1(\mathbf{k}-\mathbf{q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k}-\mathbf{q})}-i\delta}+\frac{1-f_{n1(\mathbf{k}-\mathbf{q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k}-\mathbf{q})}+i\delta}\Big]\Big\}$$

What makes GW calculations even at G0W0 level rather “laborious”:

Careful is needed:

Integration over the Brillouin zone

Sum over unoccupied states

GW approximation in practice

Plane waves representation:

$$\langle n\mathbf{k}|\Sigma_x(\mathbf{r_1},\mathbf{r_2})|\mathbf{n'k'}\rangle = -\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{(2\pi)^3}\sum_{\mathbf{G}}\mathbf{v}(\mathbf{q}+\mathbf{G})\rho_{\mathbf{n},\mathbf{n_1}}(\mathbf{q},\mathbf{G})\rho^*_{\mathbf{n'n_1}}(\mathbf{q},\mathbf{G})\mathbf{f_{n_1k_1}}$$

$$\rho_{nn1}(\mathbf{q}+\mathbf{G}) = \langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n1\mathbf{k_1}\rangle$$

$$\langle n\mathbf{k}|\Sigma_c(\mathbf{r_1},\mathbf{r_2};\omega)|\mathbf{n'k'}\rangle = \frac{1}{2}\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{(2\pi)^3}\Big\{\sum_{\mathbf{GG'}}\mathbf{v}(\mathbf{q}+\mathbf{G})\rho_{\mathbf{n},\mathbf{n_1}}(\mathbf{q},\mathbf{G})\rho^*_{\mathbf{n'n_1}}(\mathbf{q},\mathbf{G'})\times$$

$$\times\int\frac{d\omega'}{2\pi}\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega')\left[\frac{f_{n1(\mathbf{k}-\mathbf{q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k}-\mathbf{q})}-i\delta}+\frac{1-f_{n1(\mathbf{k}-\mathbf{q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k}-\mathbf{q})}+i\delta}\right]\Big\}$$

What makes GW calculations even at G0W0 level rather “laborious”:

Careful is needed:

Integration over the Brillouin zone

Sum over unoccupied states

Integration in energy domain

Exchange Self Energy

(7) Exchange self energy: `yambo -x`

$$\Sigma^x_{n\mathbf{k}} = \langle n\mathbf{k}|\Sigma^x(\mathbf{r}_1,\mathbf{r}_2)|n\mathbf{k}\rangle = -\sum_m \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G}} v(\mathbf{q}+\mathbf{G}) \left|\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G})\right|^2 f_{m(\mathbf{k}-\mathbf{q})}$$

See (6) — See (1)

occupied bands only

DFT k-grid
{q} = {k-k'}

G-vectors in the exchange
Number of RL vectors, or energy in Ry / mHa / etc
Tip: set to less than FFTGvecs

```
EXXRLvcs= 2487001   RL
```

```
%QPkrange
  1|  5| 20|  59|
  4|  8| 60|  80|
%
%QPerange (-V qp)
  1| 32| 0.0|-1.0|
%
```

nk, n'k' ranges where GW/Σ_x elements are calculated
first k-point | *last k-point* | *lower band* | *upper band*
This can be split over several lines for multiple groups
Tip: careful use of fewer k-points and bands reduces the calculation time; yambo will interpolate the rest
nk,nk' ranges (alternative method)
first k-point | *last k-point* | *lower energy* | *upper energy*

Correlation Self Energy

(8) Correlation part of self energy: `yambo -g n`

$$\Sigma^c_{n\mathbf{k}}(\omega) = \langle n\mathbf{k}|\Sigma^c|n\mathbf{k}\rangle = i\sum_m \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G},\mathbf{G}'} \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} \rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G})\rho^*_{nm}(\mathbf{k},\mathbf{q},\mathbf{G}') \times \int d\omega' G^0_{m\mathbf{k}-\mathbf{q}}(\omega-\omega')\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega')$$

```
% GbndRnge
  1| 50|
%
```

Bands used in the GW summation
QP energies usually shows slow convergence
Tip: If you are interested in gaps, energy differences converge faster

```
NGsBlkXp= 100   RL
```
Response block size
See (9)

```
%QPkrange
  1|  5| 20|  59|
  4|  8| 60|  80|
%
%QPerange (-V qp)
  1| 32| 0.0|-1.0|
%
```

nk, n'k' ranges where GW/Σ_c elements are calculated
first k-point | last k-point | lower band | upper band
This can be split over several lines for multiple groups
Tip: careful use of fewer k-points and bands reduces the calculation time; yambo will interpolate the rest

GW approximation in practice: Plasmon-Pole approximation

$$\langle n\mathbf{k}|\Sigma_c(\mathbf{r_1},\mathbf{r_2};\omega)|\mathbf{n'k'}\rangle = \frac{\mathbf{1}}{\mathbf{2}}\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{\mathbf{(2\pi)^3}}\Big\{\sum_{\mathbf{GG'}}\mathbf{v(q+G)}\rho_{\mathbf{n,n_1}}(\mathbf{q,G})\rho^{*}_{\mathbf{n'n_1}}(\mathbf{q,G'})\times$$

$$\times\int\frac{d\omega'}{2\pi}\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega')\Big[\frac{f_{n1(\mathbf{k-q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k-q})}-i\delta}+\frac{1-f_{n1(\mathbf{k-q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k-q})}+i\delta}\Big]\Big\}$$

GW approximation in practice: Plasmon-Pole approximation

$$\langle n\mathbf{k}|\Sigma_c(\mathbf{r_1},\mathbf{r_2};\omega)|\mathbf{n'k'}\rangle = \frac{\mathbf{1}}{\mathbf{2}}\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{(\mathbf{2\pi})^{\mathbf{3}}}\Big\{\sum_{\mathbf{GG'}}\mathbf{v(q+G)}\rho_{\mathbf{n,n_1}}(\mathbf{q,G})\rho^{*}_{\mathbf{n'n_1}}(\mathbf{q,G'})\times$$

$$\times\int\frac{d\omega'}{2\pi}\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega')\Big[\frac{f_{n1(\mathbf{k-q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k-q})}-i\delta}+\frac{1-f_{n1(\mathbf{k-q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k-q})}+i\delta}\Big]\Big\}$$

$-\Im\{\epsilon^{-1}\}$ Electron Energy Loss spectrum

All components exhibit a peak, otherwise the amplitude is small

Model Dielectric function: Plasmon-Pole approximation

GW approximation in practice: Plasmon-Pole approximation

$$\langle n\mathbf{k}|\Sigma_c(\mathbf{r_1},\mathbf{r_2};\omega)|\mathbf{n'k'}\rangle = \frac{\mathbf{1}}{\mathbf{2}}\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{\mathbf{(2\pi)^3}}\Big\{\sum_{\mathbf{GG'}}\mathbf{v(q+G)}\rho_{\mathbf{n,n_1}}(\mathbf{q},\mathbf{G})\rho^{*}_{\mathbf{n'n_1}}(\mathbf{q},\mathbf{G'})\times$$

$$\times\int\frac{d\omega'}{2\pi}\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega')\Big[\frac{f_{n1(\mathbf{k-q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k-q})}-i\delta}+\frac{1-f_{n1(\mathbf{k-q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k-q})}+i\delta}\Big]\Big\}$$

$-\Im\{\epsilon^{-1}\}$ Electron Energy Loss spectrum

All components exhibit a peak, otherwise the amplitude is small

Model Dielectric function: Plasmon-Pole approximation

$$\Im\epsilon^{-1}_{GG'}(q,\omega) = A_{GG'}(q)\{\delta[\omega-\tilde{\omega}_{GG'}(q)]-\delta[\omega+\tilde{\omega}_{GG'}(q)]\}$$

$$\Re\epsilon^{-1}_{GG'}(q,\omega) = \delta_{GG'}+\frac{\Omega_{GG'}(q)}{\omega-\tilde{\omega}_{GG'}(q)}$$

The energy integral is now analytic

GW approximation in practice: Plasmon-Pole approximation

$$\langle n\mathbf{k}|\Sigma_c(\mathbf{r_1},\mathbf{r_2};\omega)|\mathbf{n'k'}\rangle = \frac{\mathbf{1}}{\mathbf{2}}\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{\mathbf{(2\pi)^3}}\Big\{\sum_{\mathbf{GG'}}\mathbf{v(q+G)}\rho_{\mathbf{n,n_1}}(\mathbf{q},\mathbf{G})\rho^{*}_{\mathbf{n'n_1}}(\mathbf{q},\mathbf{G'})\times$$

$$\times\int\frac{d\omega'}{2\pi}\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega')\Big[\frac{f_{n1(\mathbf{k-q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k-q})}-i\delta}+\frac{1-f_{n1(\mathbf{k-q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k-q})}+i\delta}\Big]\Big\}$$

$-\Im\{\epsilon^{-1}\}$ Electron Energy Loss spectrum

All components exhibit a peak, otherwise the amplitude is small

Model Dielectric function: Plasmon-Pole approximation

$$\Im\epsilon^{-1}_{GG'}(q,\omega) = A_{GG'}(q)\{\delta[\omega-\tilde{\omega}_{GG'}(q)]-\delta[\omega+\tilde{\omega}_{GG'}(q)]\}$$

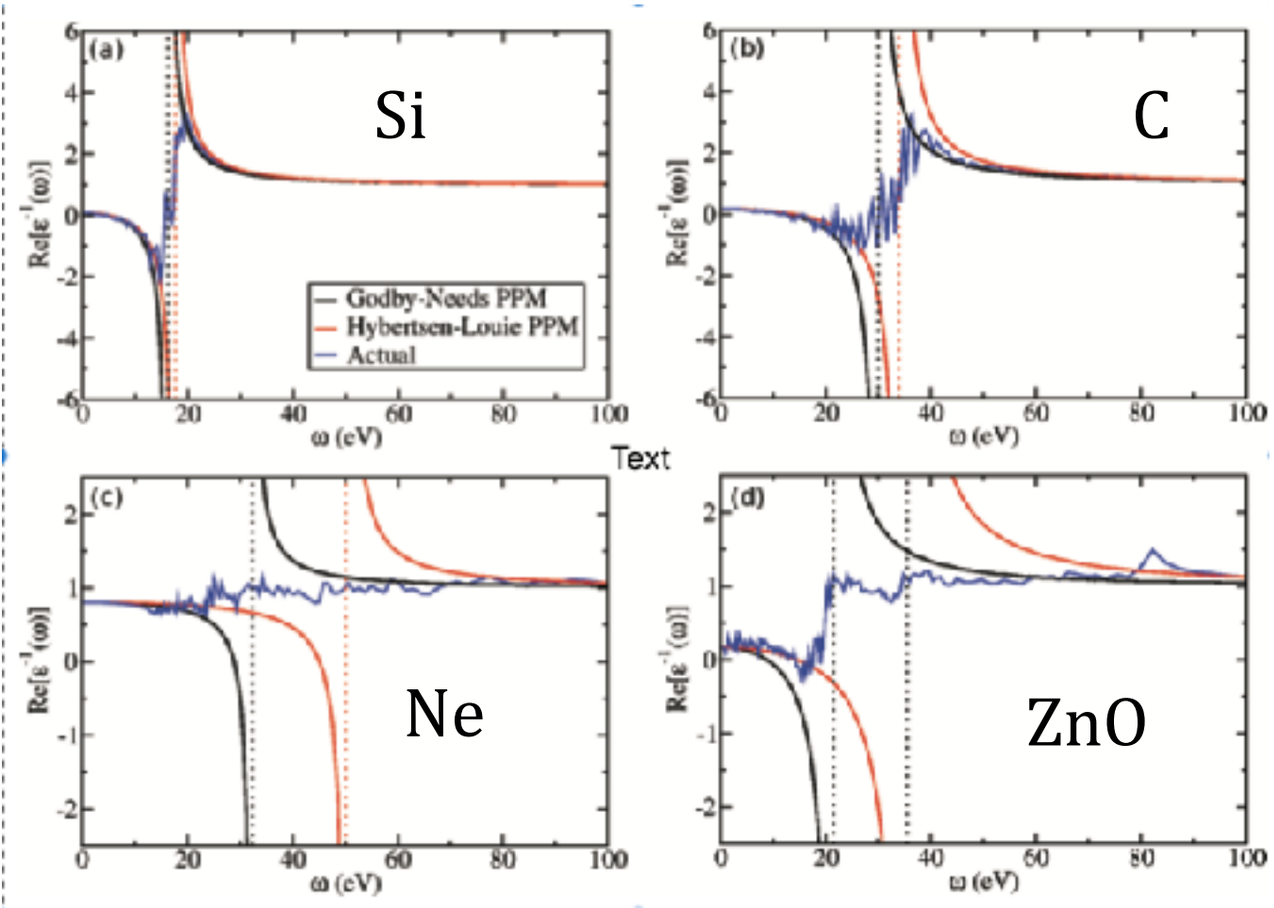
$$\Re\epsilon^{-1}_{GG'}(q,\omega) = \delta_{GG'}+\frac{\Omega_{GG'}(q)}{\omega-\tilde{\omega}_{GG'}(q)}$$

The energy integral is now analytic

Different recipes to evaluate poles and residues

M. Hybertsen and S. Louie PRB **34,** 5390 1986
R. W. Godby and R. J. Needs, PRL. **62,** 1169 (1989).
G. E. Engel and B. Farid, PRB **47,** 15931 (1993).

GW approximation in practice: Plasmon-Pole approximation



Text

	GN	HL	vdLH	EF	Numerical	Expt.
Si	1.20	1.25	1.23	1.26	1.21	1.24
C	6.10	6.25	6.25	6.29	6.15	6.11
Ge	0.68	0.72	0.70	0.71	0.69	0.85
Ne	19.65	20.99	20.51	19.99	19.41	21.50
AlN	5.55	5.73	5.71	5.74	5.59	6.29
GaN	3.51	3.61	3.62	3.66	3.54	3.44
GaAs	1.13	1.15	1.14	1.16	1.13	1.59
MgO	7.13	7.61	7.46	7.39	7.13	7.85
ZnO	2.27	2.80	2.30	2.37	2.17	3.53

PPA become questionable when $\epsilon^{-1}_{GG'}$ differs from single-pole

Ex: interfaces, d electrons in copper: A. Marini, G. Onida, R. Del Sole PRL 88, 01643 (2002)

Real part along real axis

P. Larson, M. Dvorak, and Z. Wu Phys Rev. B **88**, 125205 (2013)

ZnO case M. Stankovki et al. Phys Rev. B **84**, 241201 (2011)

Full integration is needed: alternative methods; e.g:
Frequency dependence in GW made simple using a multi-pole approximation D. A. Leon, C. Cardoso, T. Chiarotti, D. Varsano, E. Molinari, and A. Ferretti Phys. Rev. B 104, 115157 (2021)

The plasmon pole approximation

(9) Plasmon Pole approximation (PPA): `yambo -p p`

Components of the Dielectric matrix approximated has a single pole functions:

$$\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) \sim \delta_{\mathbf{G},\mathbf{G}'} + \mathbf{R}_{\mathbf{G},\mathbf{G}'}(\mathbf{q})[(\omega - \mathbf{\Omega}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) + i0^+)^{-1} - (\omega + \Omega_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) - i0^+)^{-1}]$$

Residuals $R_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$ and energies $\Omega_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$ are found by imposing the PPA to reproduce the exact ϵ^{-1} function at ω = 0 and ω = iE_{PPA} with E_{PPA} being a suitable user-defined parameter.

$$R_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = -\frac{\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega=\mathbf{0})\Omega_{\mathbf{G},\mathbf{G}'}}{\mathbf{2}}$$

$$\Omega_{\mathbf{G},\mathbf{G}'} = E_{PPA}\sqrt{\frac{\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega=\mathbf{E_{PPA}})}{\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega=\mathbf{0}) - \epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega=\mathbf{E_{PPA}})}}$$

The QP energies should not depend too much on the choice of imaginary plasmon frequency. **Tip:** Choose a value higher in energy than the plasmon peak (EELS spectrum)

```
% BndsRnXp
 1 | 100 |
```
Bands used (empty & filled)
Range from 1 to nbnd
Reduce range to lower memory.

NGsBlkXp= 100 RL
Response block size

PPAPntXp= 27.21138 eV
PPA imaginary energy

GW approximation in practice

Goal: $\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$ $\Sigma = iGW$

Once we know $\Sigma^{GW} = G^0W^0$

GW approximation in practice

Goal: $\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$ $\Sigma = iGW$

Once we know $\Sigma^{GW} = G^0W^0$

$f_i^{QP}(\mathbf{r}) \approx \phi_i^{KS}(\mathbf{r})$

This is another approximation, very frequently used and not always valid!

GW approximation in practice

Goal: $\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$ $\Sigma = iGW$

Once we know $\Sigma^{GW} = G^0W^0$

$f_i^{QP}(\mathbf{r}) \approx \phi_i^{KS}(\mathbf{r})$ **This is another approximation, very frequently used and not always valid!**

(8a) Dyson Solver: `yambo -g n/s`

$$E_{nk}^{QP} = \epsilon_{nk} + \langle\psi_{nk}|\Sigma(E_{nk}^{QP}) - V_{xc}|\psi_{nk}\rangle$$

DysSolver= "n" First order expansion around KS eigenvalue

$$E_{nk}^{QP} = \epsilon_{nk} + Z_{nk}\langle\psi_{nk}|\Sigma(\epsilon_{nk}) - V_{xc}|\psi_{nk}\rangle$$

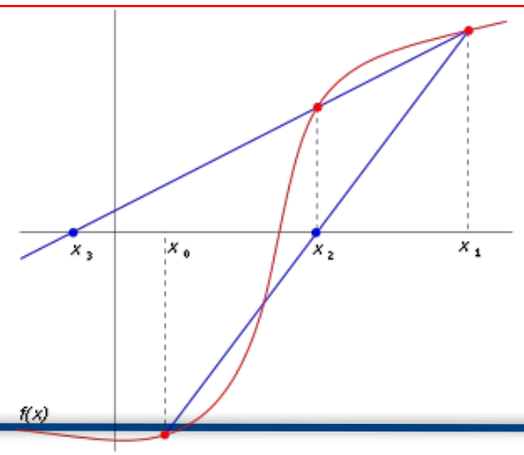
$$Z_{nk} = \left[1 - \frac{d\Sigma_{nk}(\omega)}{d\omega}\Big|_{\omega=\epsilon_{nk}}\right]^{-1}$$

dScStep= 0.10000 eV # [GW] Energy step to evaluate Z

DysSolver= "s" Secant iterative method

https://en.wikipedia.org/wiki/Secant_method

$$x_n = x_{n-1} - f(x_{n-1})\frac{x_{n-1} - x_{n-2}}{f(x_{n-1}) - f(x_{n-2})} = \frac{x_{n-2}f(x_{n-1}) - x_{n-1}f(x_{n-2})}{f(x_{n-1}) - f(x_{n-2})}$$



Accelerating convergence wrt number of bands

$$< n\mathbf{k}|\Sigma_c(\epsilon_{\mathbf{k},n})|n\mathbf{k} >= \frac{1}{2\pi N_k \Omega}\int d\omega' \sum_{n_1 \leqslant N_b}\sum_{\mathbf{qGG'}} [W_{\mathbf{GG'}}(\mathbf{q},\omega') - \delta_{\mathbf{GG'}} v(\mathbf{q}+\mathbf{G})]$$

$$\times \frac{\rho_{nn_1}(\mathbf{q}+\mathbf{G})\rho^*_{nn_1}(\mathbf{q}+\mathbf{G'})}{\omega' - \epsilon_{\mathbf{k}-\mathbf{q},n} + \epsilon_{\mathbf{k},n_1} \pm i\eta}$$

$$\rho_{nn_1}(\mathbf{q}+\mathbf{G}) =< \mathbf{k}-\mathbf{q}, n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\mathbf{k}, n_1 >$$

Extrapolar correction:

$$\Delta_{k,n} = \frac{1}{2\pi N_k \Omega}\int d\omega' \sum_{\mathbf{qGG'}} \frac{[W_{\mathbf{GG'}}(\mathbf{q},\omega') - \delta_{\mathbf{GG'}} v(\mathbf{q}+\mathbf{G})]}{\omega' - \bar{\epsilon}_\Sigma + \epsilon_{\mathbf{k}n} + i\eta}$$

$$\times[< \mathbf{k}, n|e^{i(\mathbf{G}-\mathbf{G'})}|\mathbf{k}, n > - \sum_{n_1 \leqslant N_b} \rho_{nn_1}(\mathbf{q}+\mathbf{G})\rho^*_{nn_1}(\mathbf{q}+\mathbf{G'})]$$

F. Bruneval and X. Gonze PRB **78**, 085125 2008

Accelerating convergence wrt number of bands

$$< n\mathbf{k}|\Sigma_c(\epsilon_{\mathbf{k},n})|n\mathbf{k} >= \frac{1}{2\pi N_k \Omega}\int d\omega' \sum_{n_1 \leqslant N_b}\sum_{\mathbf{qGG'}} [W_{\mathbf{GG'}}(\mathbf{q},\omega') - \delta_{\mathbf{GG'}} v(\mathbf{q}+\mathbf{G})]$$

$$\times \frac{\rho_{nn_1}(\mathbf{q}+\mathbf{G})\rho^*_{nn_1}(\mathbf{q}+\mathbf{G'})}{\omega' - \epsilon_{\mathbf{k}-\mathbf{q},n} + \epsilon_{\mathbf{k},n_1} \pm i\eta}$$

$$\rho_{nn_1}(\mathbf{q}+\mathbf{G}) =< \mathbf{k}-\mathbf{q}, n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\mathbf{k}, n_1 >$$

Extrapolar approximation: assume all the stats above Nb have the same “average” high energy: $\bar{\epsilon}_\Sigma$

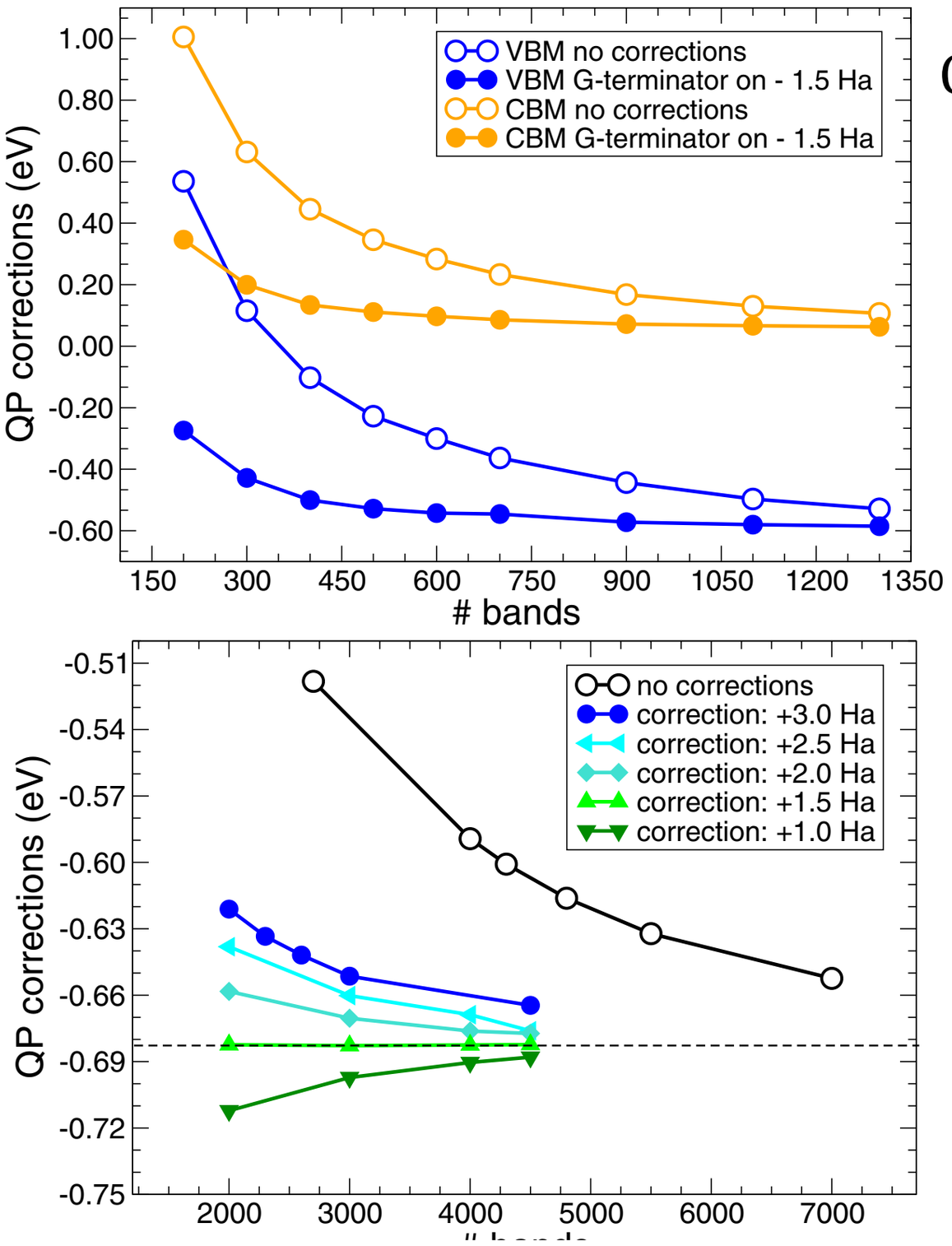
Extrapolar correction:

$$\Delta_{k,n} = \frac{1}{2\pi N_k \Omega}\int d\omega' \sum_{\mathbf{qGG'}} \frac{[W_{\mathbf{GG'}}(\mathbf{q},\omega') - \delta_{\mathbf{GG'}} v(\mathbf{q}+\mathbf{G})]}{\omega' - \bar{\epsilon}_\Sigma + \epsilon_{\mathbf{k}n} + i\eta}$$

$$\times[< \mathbf{k}, n|e^{i(\mathbf{G}-\mathbf{G'})}|\mathbf{k}, n > - \sum_{n_1 \leqslant N_b} \rho_{nn_1}(\mathbf{q}+\mathbf{G})\rho^*_{nn_1}(\mathbf{q}+\mathbf{G'})]$$

F. Bruneval and X. Gonze PRB **78**, 085125 2008

Accelerating convergence wrt number of bands



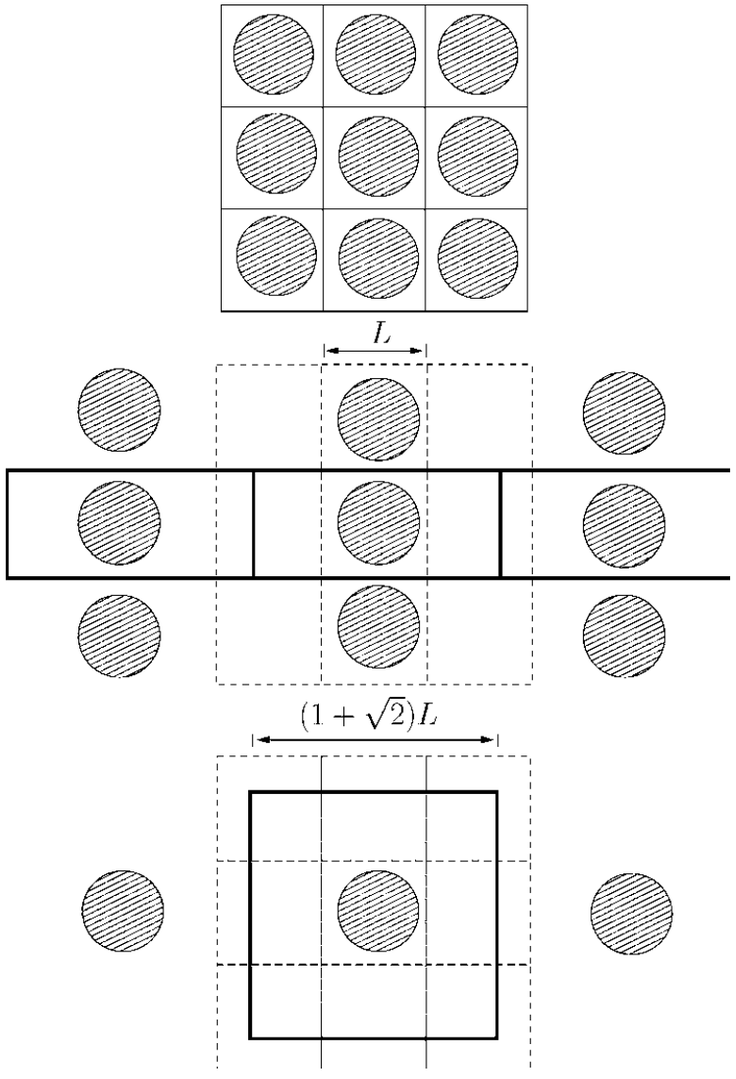
CBM and VBM GW correction for bulk silicon

VBM GW correction for TiO2 Nanowire (108 occupied bands)

D. Sangalli et al. J. Phys.: Condens. Matter **31** (2019) 325902

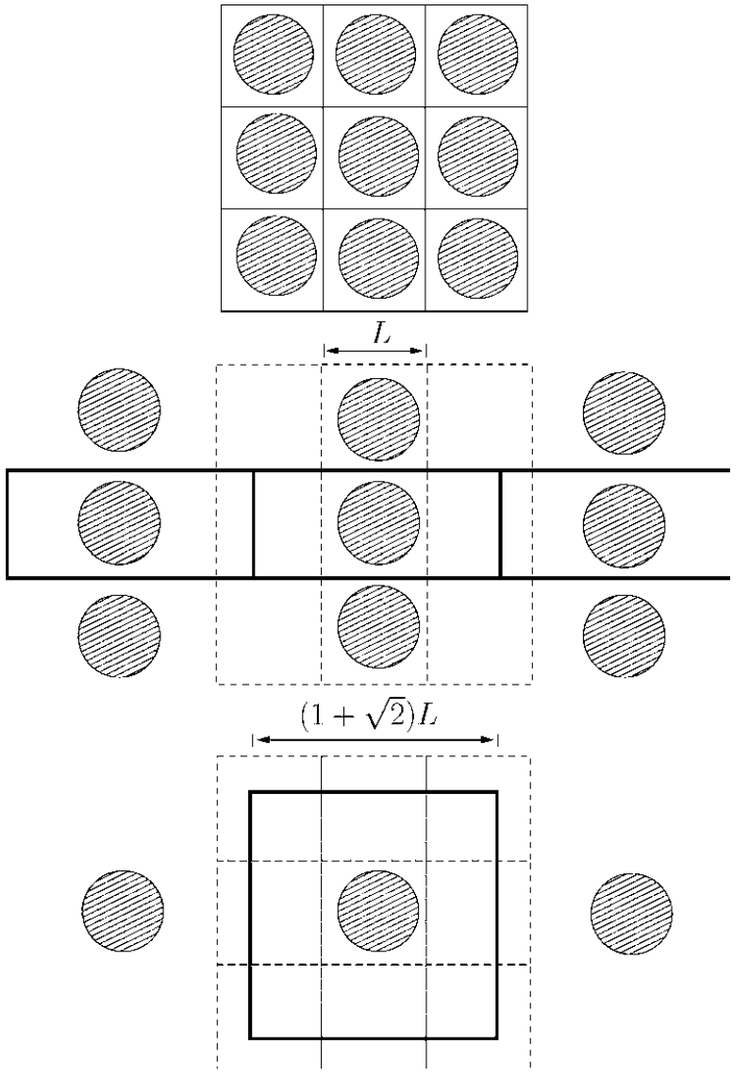
Non periodic 3D systems: nanostructures

Avoiding spurious replica interactions in non periodic directions



Non periodic 3D systems: nanostructures

Avoiding spurious replica interactions in non periodic directions



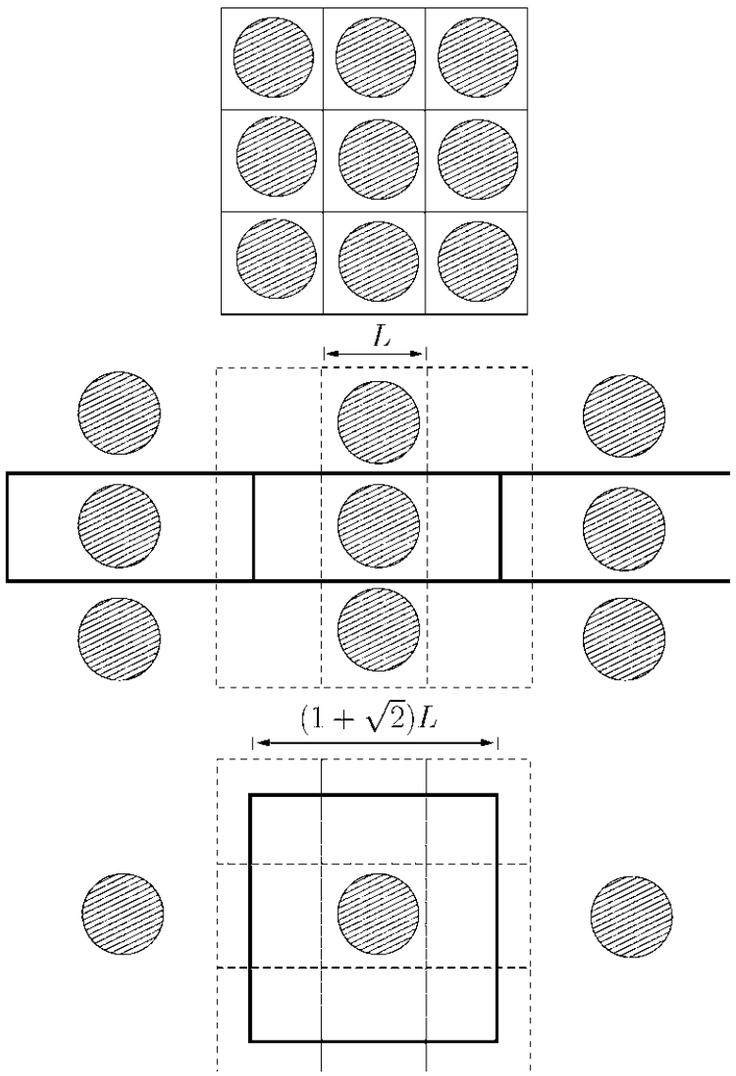
Coulomb cutoff technique for supercell calculations

$$\tilde{V}_c(r) = \begin{cases} 1/r & \text{if } r \in \mathcal{D} \\ 0 & \text{if } r \notin \mathcal{D} \end{cases}$$

Different geometries according to the dimensionality

Non periodic 3D systems: nanostructures

Avoiding spurious replica interactions in non periodic directions



Coulomb cutoff technique for supercell calculations

$$\tilde{V}_c(r) = \begin{cases} 1/r & \text{if } r \in \mathcal{D} \\ 0 & \text{if } r \notin \mathcal{D} \end{cases}$$

Different geometries according to the dimensionality

$$\tilde{V}_c(G) = \frac{4\pi}{G^2}[1 - cos(GR)]$$ Sphere 0D

$$\tilde{V}_c(\mathbf{q}, G) = \frac{4\pi}{|\mathbf{q_z} + \mathbf{G}|^2}[1 + G_\perp R J_1(G_\perp R)K_0(|G_z|R) - |G_z|RJ_0(G_\perp R)K_1(|G_z|R)]$$ Cylinder 1D

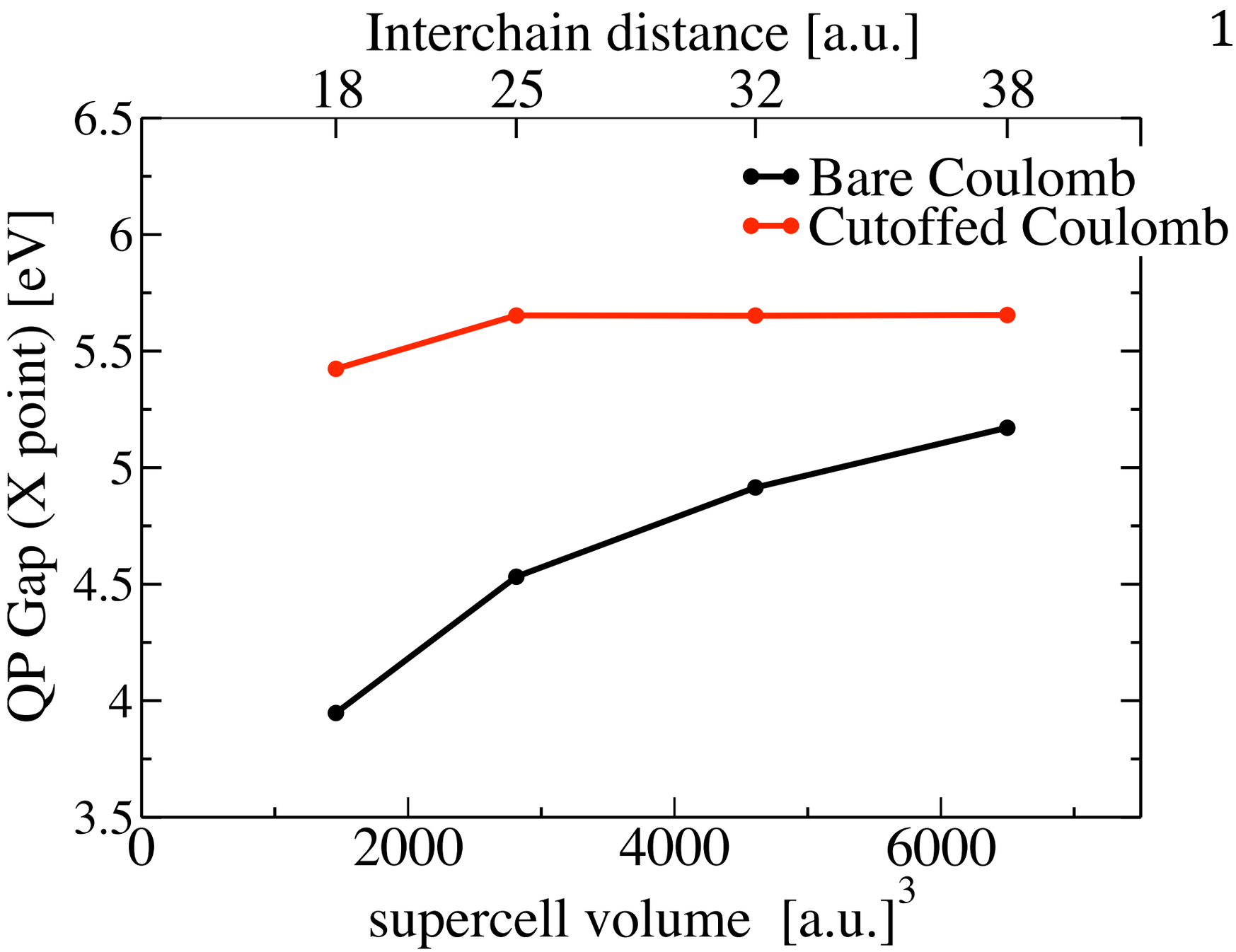
$$\tilde{V}_c(\mathbf{q}, G) = \frac{4\pi}{|\mathbf{q}_\parallel + \mathbf{G}|^2}[1 - e^{-|\mathbf{q}_\parallel + \mathbf{G}_\parallel|L/2} cos(G_z L/2)]$$ WS 2D

C. A. Rozzi, D. Varsano, A. Marini, A. Rubio and E.K.U Gross. Physical Review B 73, 205119 (2006).

S. Ismail-Beigi Physical Review B 73, 233103 (2006).

Non periodic 3D systems: nanostructures

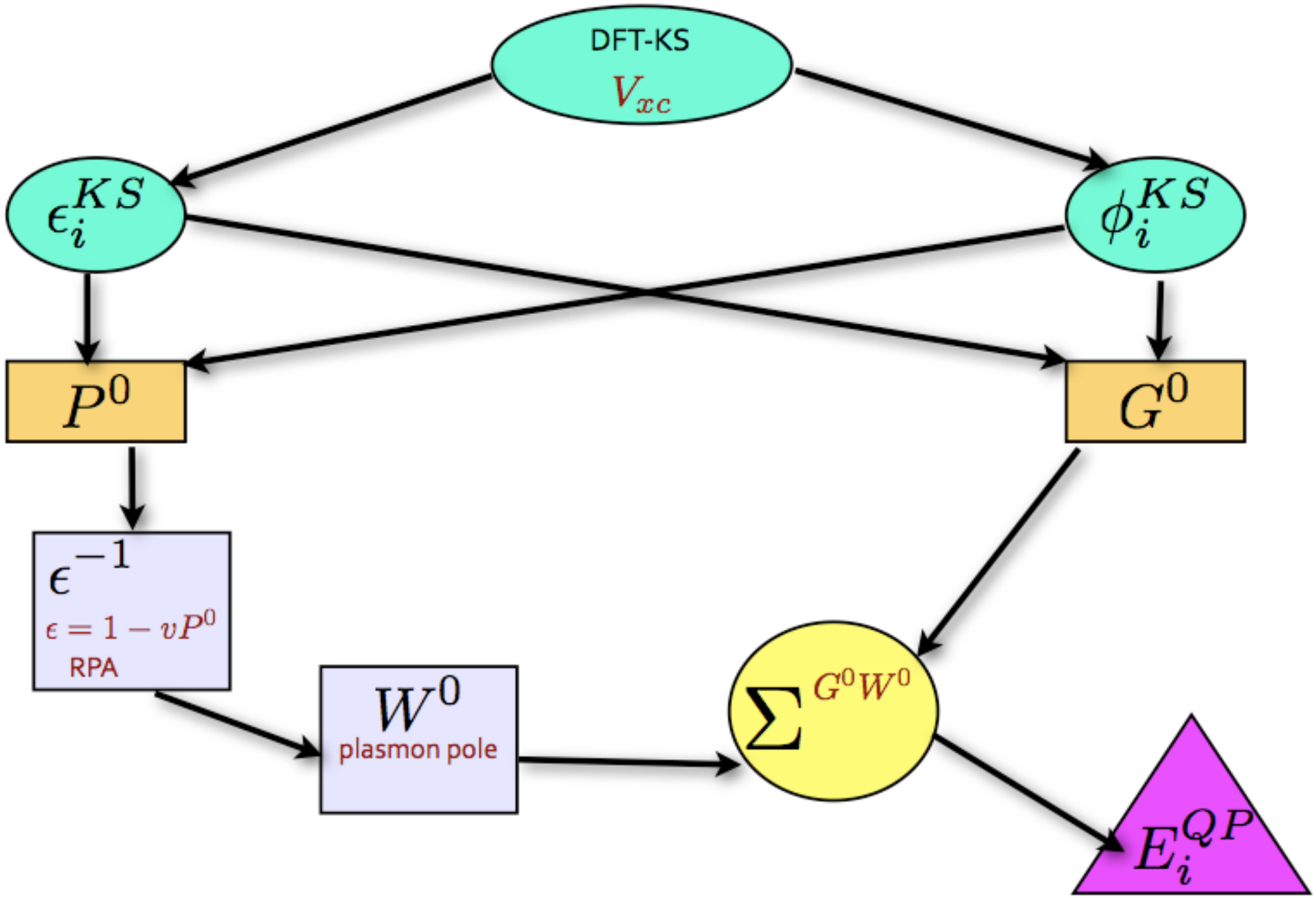
1D system: atomic chain



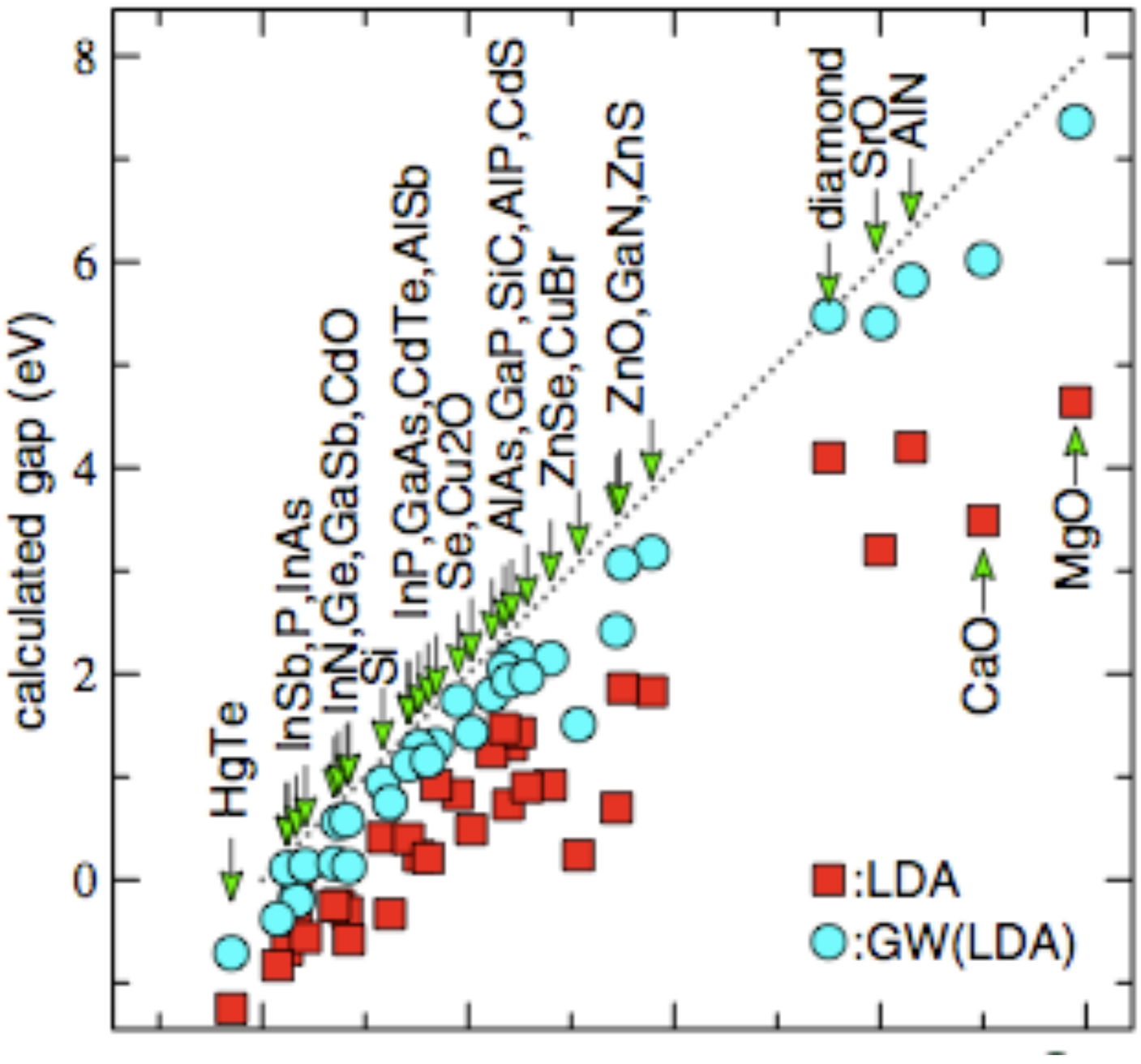
C. A. Rozzi, D. Varsano, A. Marini, A. Rubio and E.K.U Gross. Physical Review B 73, 205119 (2006).

GW approximation in practice

Summary: G^0W^0



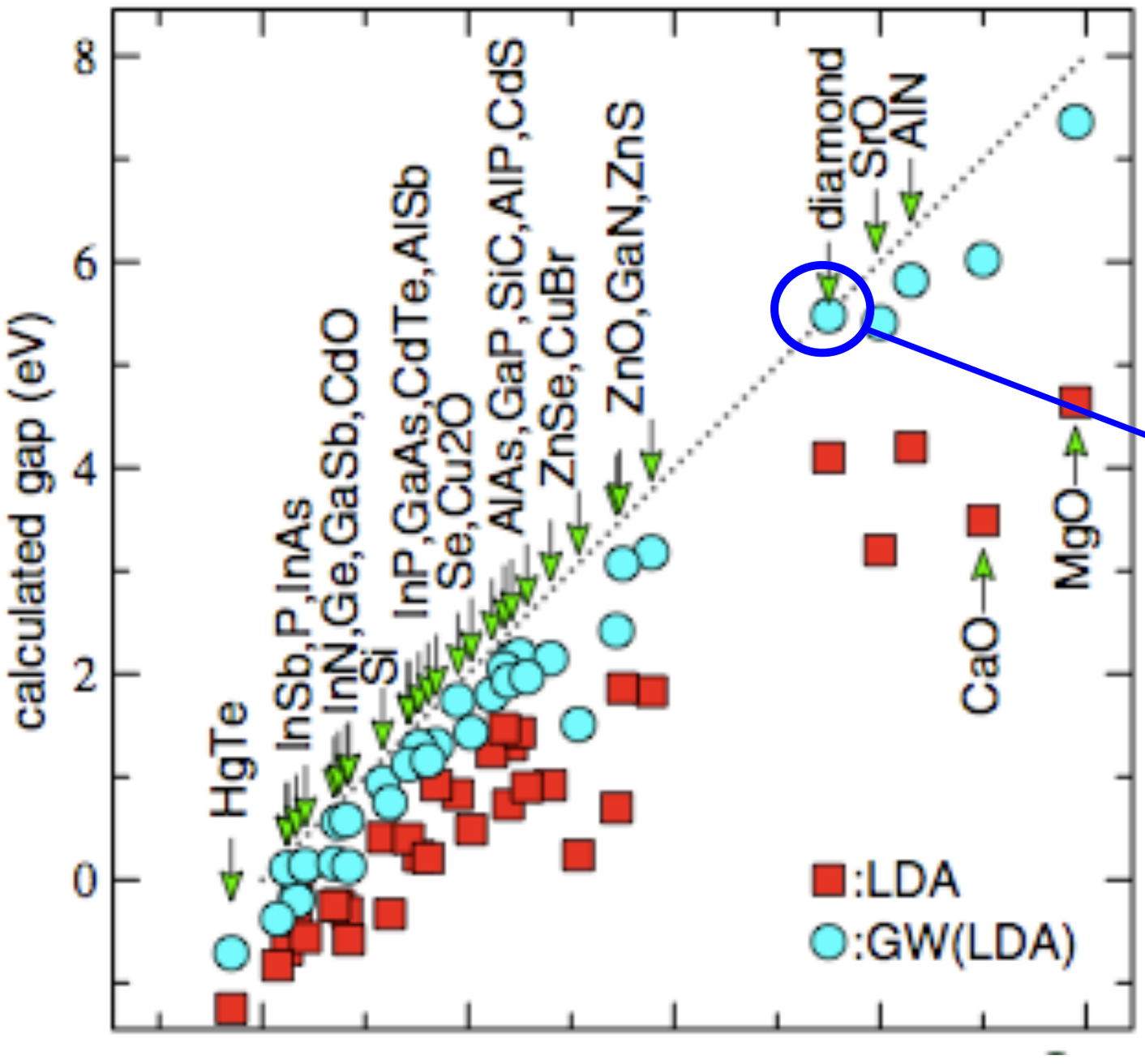
Some GW results: semiconductor band gaps



GW band gaps: huge improvement wrt the LDA

M. van Schilfgaarde, Takao Kotani, and S. Faleev PRL **96,** 226402 (2006)

Some GW results: semiconductor band gaps

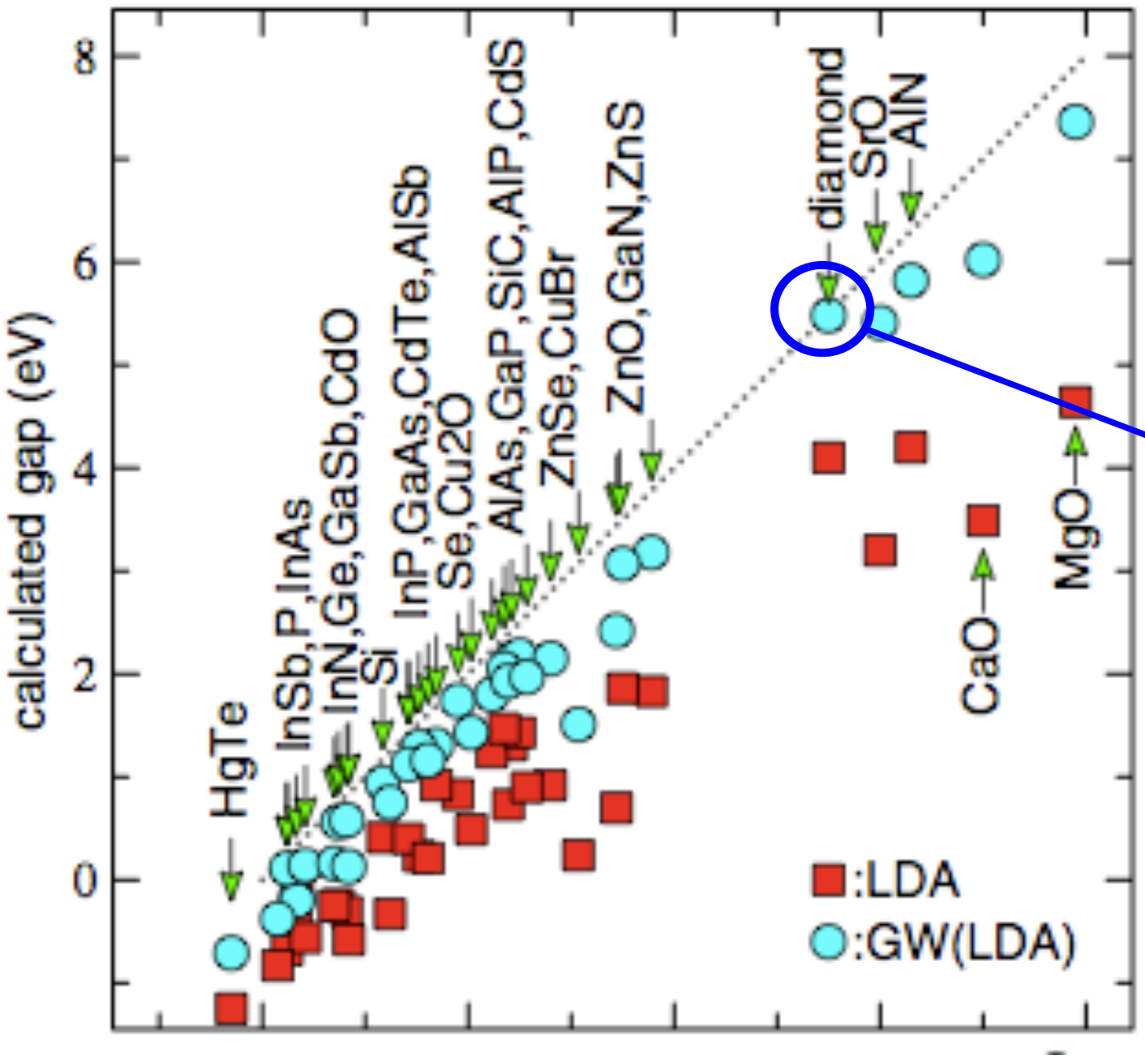


GW band gaps: huge improvement wrt the LDA

Very good agreement with the experiment!!

M. van Schilfgaarde, Takao Kotani, and S. Faleev PRL **96,** 226402 (2006)

Some GW results: semiconductor band gaps



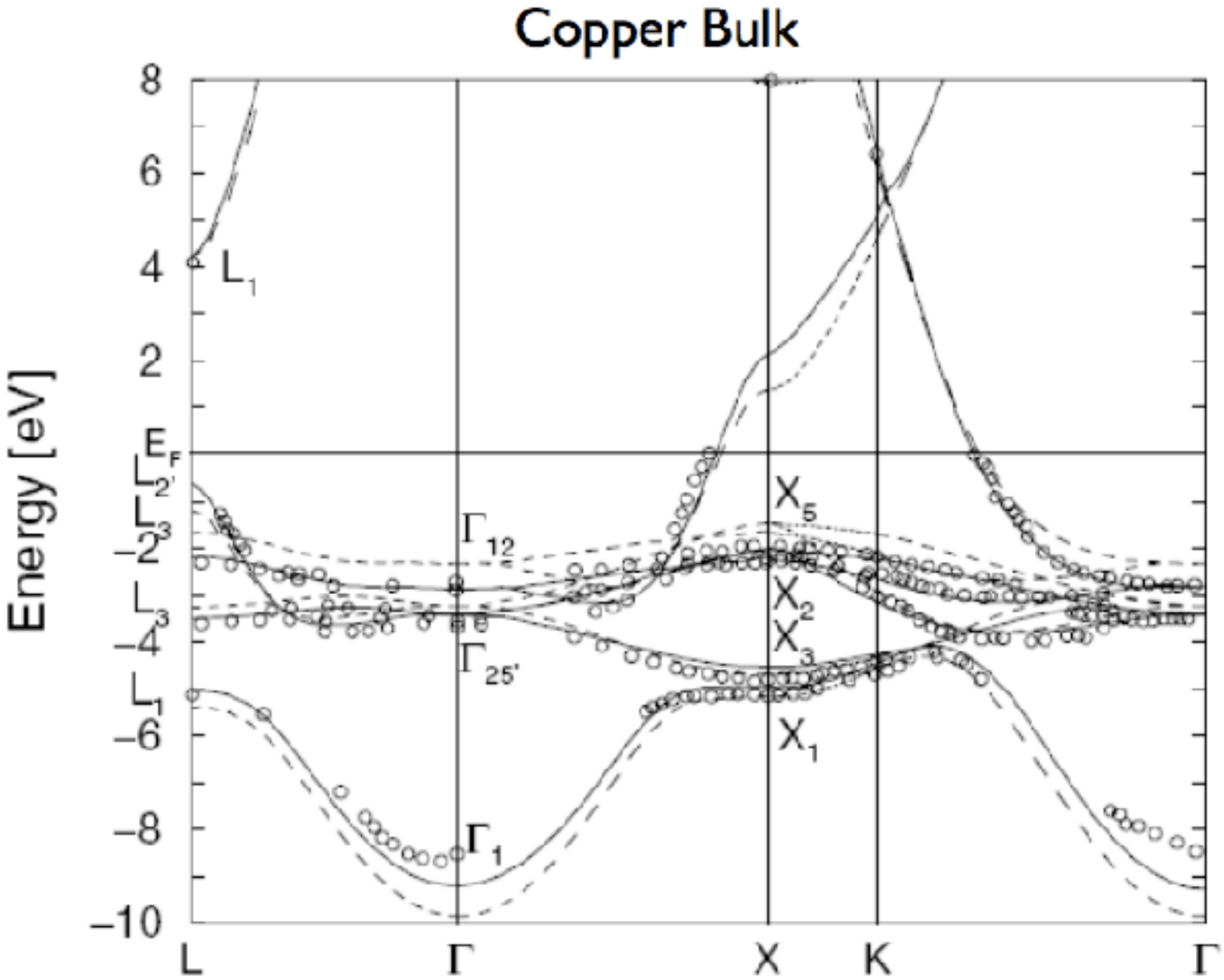
GW band gaps: huge improvement wrt the LDA

Very good agreement with the experiment!!

But for a wrong reason!!!!

M. van Schilfgaarde, Takao Kotani, and S. Faleev PRL **96,** 226402 (2006)

Some GW results: metal band structure



Breakdown of Plasmon Pole approximation

exchange effect between 3d and 3s and 3p core orbitals are crucial

A. Marini et. al. Phys. Rev. Lett. 88 (2002)

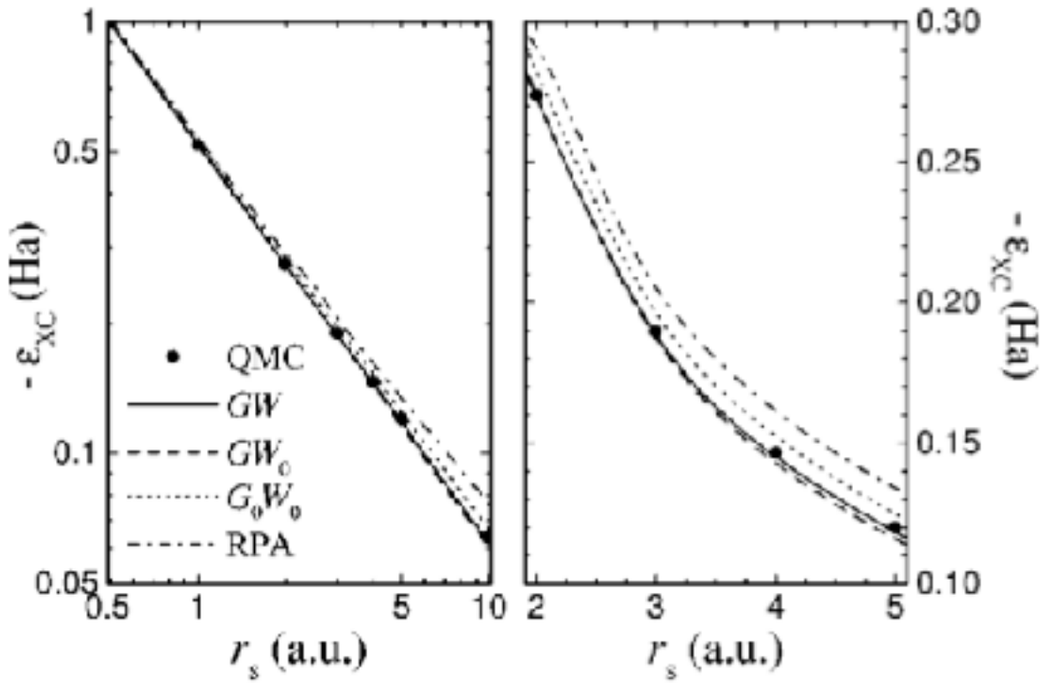
Energies and potential by GW

Green Function gives access to Total Energy (Galitskii and Migdal 1958)

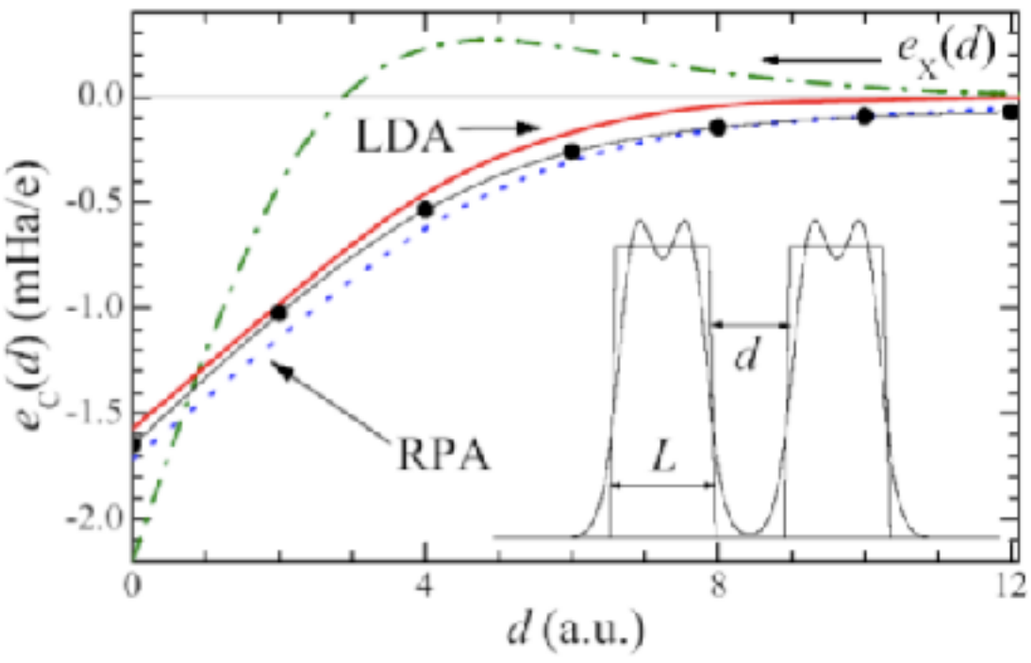
$$E = \langle \hat{T} + \hat{V} \rangle = \langle \hat{H} \rangle = -\frac{i}{2} \int d\mathbf{r} \lim_{\eta \to 0} \lim_{\mathbf{r_2} \to \mathbf{r_1}} \left[i\hbar \frac{\partial}{\partial t} - \frac{\hbar^2 \nabla^2}{2m} \right] G(\mathbf{r_1} t_1, \mathbf{r_2} t_1 + \eta)$$

Ground state properties

3DEG



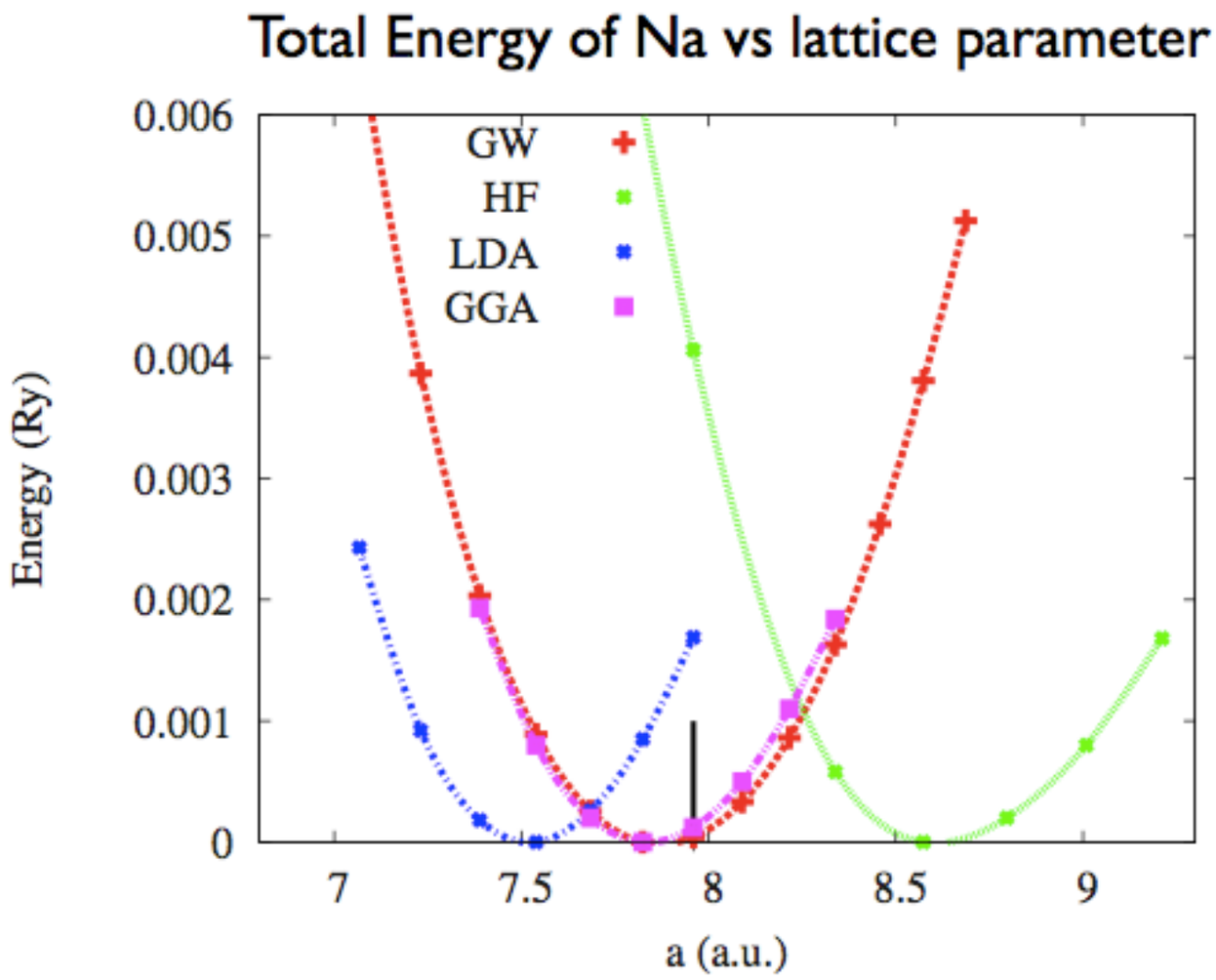
Quasi 2DEG



Capture VdW behaviour $\frac{1}{d^2}$ behaviour at large distance

P. Garcia Gonzalez and R.W. Godby , Phys. Rev. Lett. 88 (2002); Phys. Rev. B, 63 (2001)

Energies by GW



Kutepov et al. PRB 80, 041103 (2009)

Bulk Silicon band Gap

Bulk Silicon Band Gap (eV)	
Experiment	1.17
LDA	0.46
HF	6.27
G^0W^0	1.14
scGW	1.55

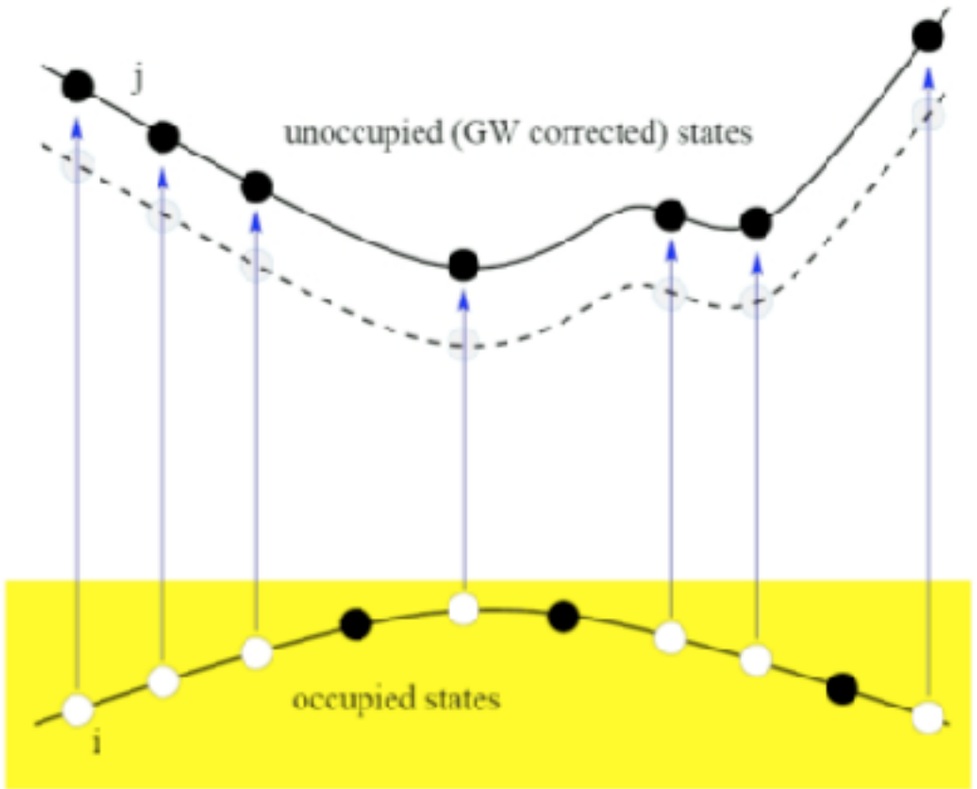
Good energy ...comparable with GGA

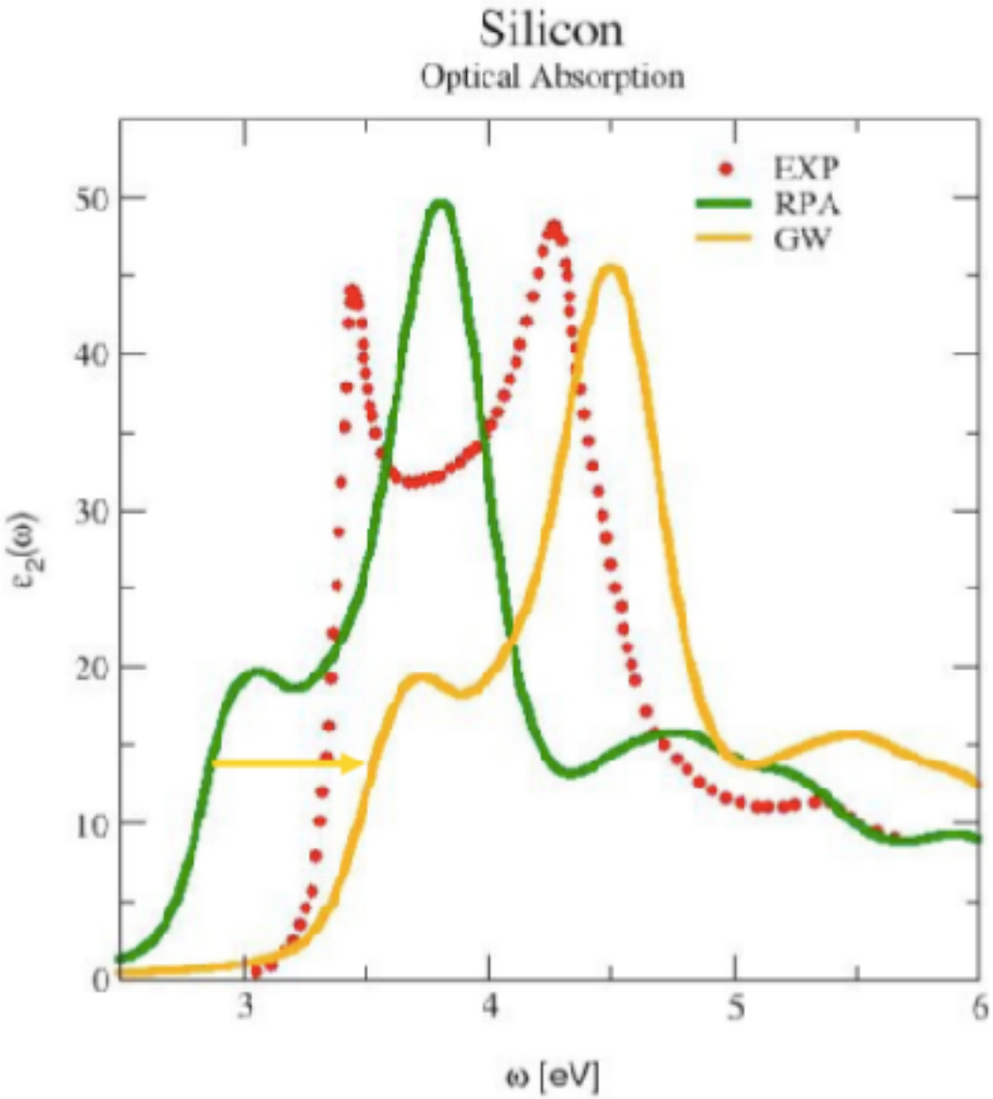
...but one-electron spectra are worse

Optical absorption?

Independent transitions:

$$\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle\varphi_j|\mathbf{e}\cdot\mathbf{v}|\varphi_i\rangle|^2 \delta(E_j - E_i - \omega)$$

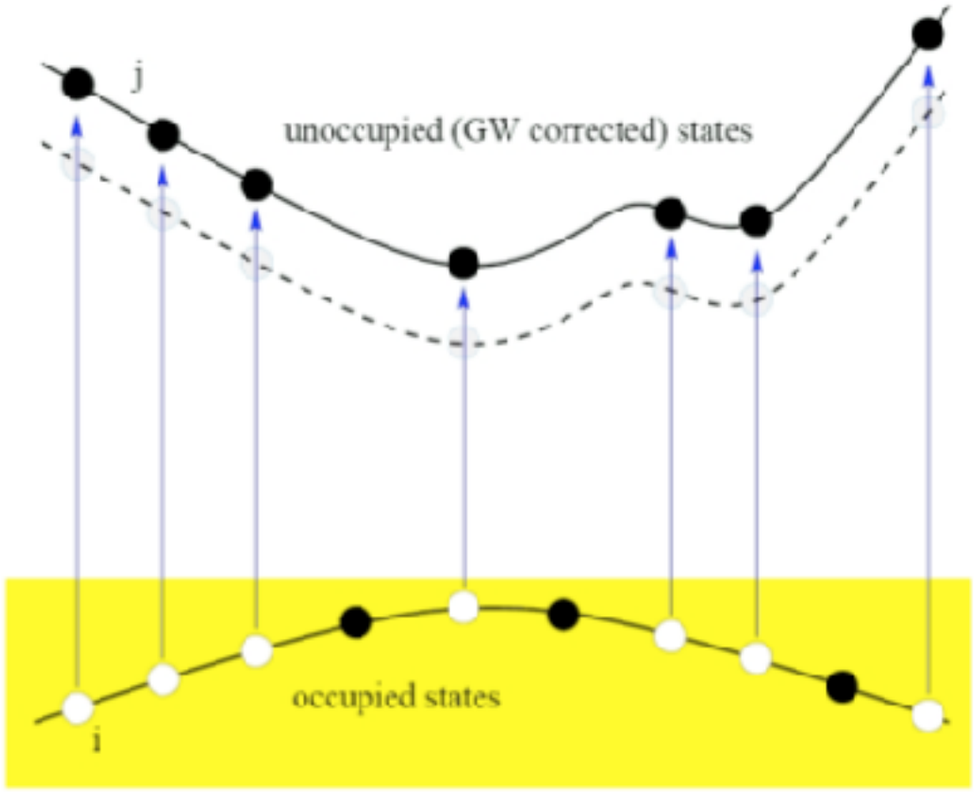


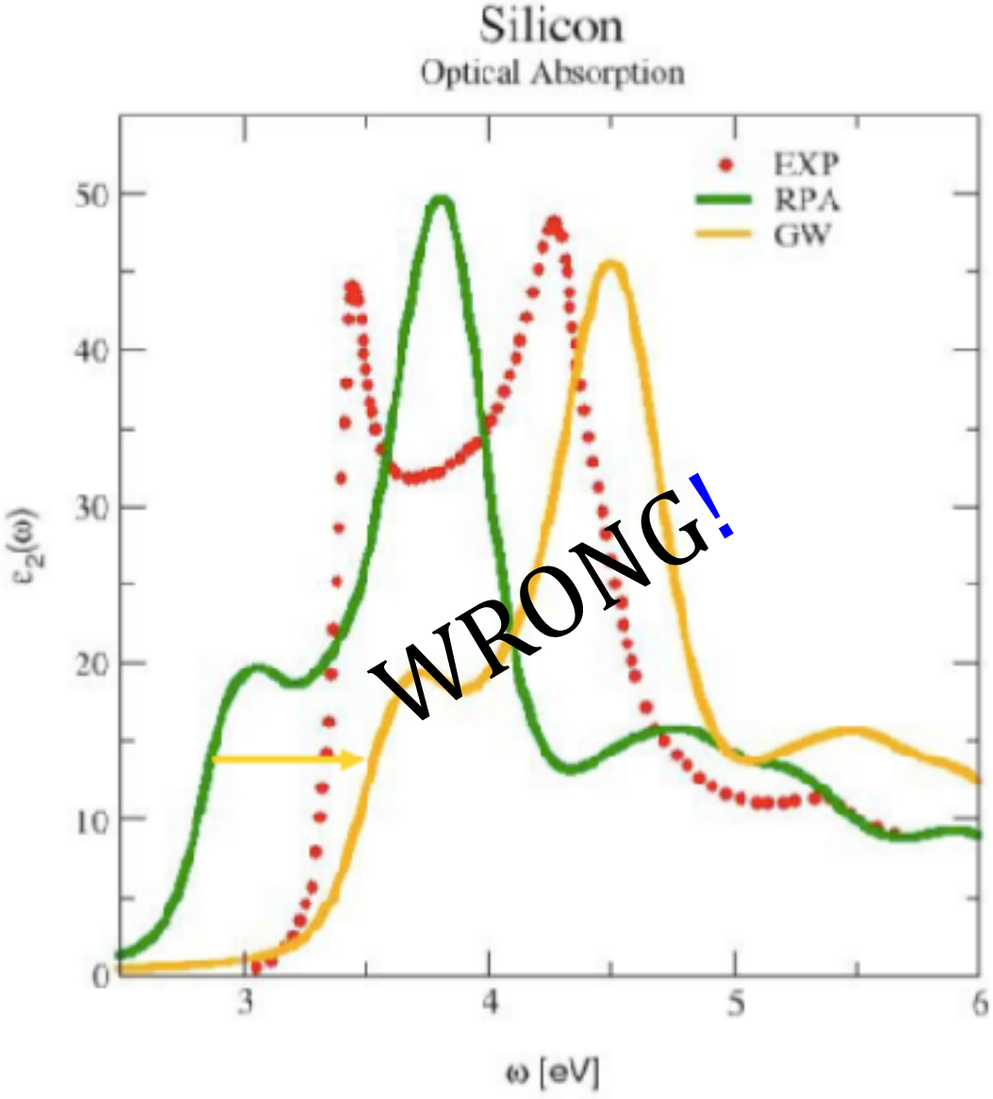


Optical absorption?

Independent transitions:

$$\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle\varphi_j|\mathbf{e}\cdot\mathbf{v}|\varphi_i\rangle|^2 \delta(E_j - E_i - \omega)$$





Something important is missing!!!

Conclusive remarks: GW many virtues!!!

Conclusive remarks: GW many virtues!!!

GW: parameter-free method which provides in most of the case accurate results (QP energies, but also total energies, lifetimes)

Conclusive remarks: GW many virtues!!!

GW: parameter-free method which provides in most of the case accurate results (QP energies, but also total energies, lifetimes)

GW: Starting point for absorption spectroscopy - excitonic effects: Bethe-Salpeter

Conclusive remarks: GW many virtues!!!

GW: parameter-free method which provides in most of the case accurate results (QP energies, but also total energies, lifetimes)

GW: Starting point for absorption spectroscopy - excitonic effects: Bethe-Salpeter

G^0W^0 today is feasible for medium size systems: algorithms suitable for HPC computation (also hybrids architectures, GPU cards).

If your results do not match the experiments:

If your results do not match the experiments:

Before asking to the forum what I'm doing wrong…

If your results do not match the experiments:

Before asking to the forum what I'm doing wrong…

Check carefully your convergence parameter (the boring part…)

If your results do not match the experiments:

Before asking to the forum what I'm doing wrong…

Check carefully your convergence parameter (the boring part…)

Even at G^0W^0 level, several convergence parameter and approximations have to be carefully checked:

If your results do not match the experiments:

Before asking to the forum what I'm doing wrong…

Check carefully your convergence parameter (the boring part…)

Even at G^0W^0 level, several convergence parameter and approximations have to be carefully checked:

Integration over Bz

If your results do not match the experiments:

Before asking to the forum what I'm doing wrong…

Check carefully your convergence parameter (the boring part…)

Even at G^0W^0 level, several convergence parameter and approximations have to be carefully checked:

Integration over Bz

k-points samplings

If your results do not match the experiments:

Before asking to the forum what I'm doing wrong…

Check carefully your convergence parameter (the boring part…)

Even at G^0W^0 level, several convergence parameter and approximations have to be carefully checked:

Integration over Bz

k-points samplings

sum over unoccupied states

If your results do not match the experiments:

Before asking to the forum what I'm doing wrong…

Check carefully your convergence parameter (the boring part…)

Even at G^0W^0 level, several convergence parameter and approximations have to be carefully checked:

Integration over Bz

k-points samplings

sum over unoccupied states

plane wave cutoffs

If your results do not match the experiments:

Before asking to the forum what I'm doing wrong…

Check carefully your convergence parameter (the boring part…)

Even at G^0W^0 level, several convergence parameter and approximations have to be carefully checked:

Integration over Bz

k-points samplings

sum over unoccupied states

plane wave cutoffs

Plasmon-pole approximation validity

If your results do not match the experiments:

Before asking to the forum what I'm doing wrong…

Check carefully your convergence parameter (the boring part…)

Even at G^0W^0 level, several convergence parameter and approximations have to be carefully checked:

Integration over Bz

k-points samplings

sum over unoccupied states

convergence of the screening

plane wave cutoffs

Plasmon-pole approximation validity

If your results do not match the experiments:

Before asking to the forum what I'm doing wrong…

Check carefully your convergence parameter (the boring part…)

Even at G^0W^0 level, several convergence parameter and approximations have to be carefully checked:

Integration over Bz

k-points samplings

sum over unoccupied states

convergence of the screening

plane wave cutoffs

Plasmon-pole approximation validity

psuedopotentials

Even if you converged everything in a pedantic way:

Do not forget:

Even if you converged everything in a pedantic way:

Do not forget:

GW: it is an approximation for the self energy: Vertex effects missing

Even if you converged everything in a pedantic way:

Do not forget:

GW: it is an approximation for the self energy: Vertex effects missing

GW: Many approximations enters in a practical calculations:

Even if you converged everything in a pedantic way:

Do not forget:

GW: it is an approximation for the self energy: Vertex effects missing

GW: Many approximations enters in a practical calculations:

- in it's widespread G^0W^0 flavor it is not self-consistent: strong **dependence on the DFT starting point** (specially true for molecules. Start from hybrid DFT?)

- Even in partial self consistent flavour usually **QP wave function assumed to be the same as the initial KS wave function**

- Screening treated at **RPA** level

- Frequency dependence of the screening usually approximated with a **PP model**

Even if you converged everything in a pedantic way:

Do not forget:

GW: it is an approximation for the self energy: Vertex effects missing

GW: Many approximations enters in a practical calculations:

- in it's widespread G^0W^0 flavor it is not self-consistent: strong **dependence on the DFT starting point** (specially true for molecules. Start from hybrid DFT?)

- Even in partial self consistent flavour usually **QP wave function assumed to be the same as the initial KS wave function**

- Screening treated at **RPA** level

- Frequency dependence of the screening usually approximated with a **PP model**

GW successful in the interpretation of spectroscopical properties of many systems but calculations need careful checks and relies on different approximations that can fail.

References

Seminal papers:

L. Hedin Phys. Rev. A 139, A796 (1965)
L. Hedin, S. Lundqvist . in Solid State Physics, 23, 1–181 (1970)

Reviews:

Aryasetiawan F., Gunnarsson O. The *GW* method. Rep. Prog. Phys. 61:237 (1998)

Aulbur W. G., Jönsson L., Wilkins J. W. in Solid State Physics, Vol. 54, 1–218 (2000)

D. Golze, M. Dvorak, and P. Rinke Front Chem. 2019; 7: 377.

Reining, L, WIREs Comput Mol Sci, 8: e1344. (2018)

Yambo code implementation:

A. Marini, C. Hogan, M. Gruning and D. Varsano Comp. Phys. Comm. 180, 1293 (2009)

D. Sangalli et al. J. Phys.: Condens. Matter 31 (2019) 325902

Acknowledgments

Website: www.yambo-code.eu
Forum: www.yambo-code.eu/forum

Yambo developers team

Thank you for your attention

Website: www.max-centre.eu

MaX CoE @max_center2

MaX Centre for Materials at the exascale

Contact: daniele.varsano@nano.cnr.it