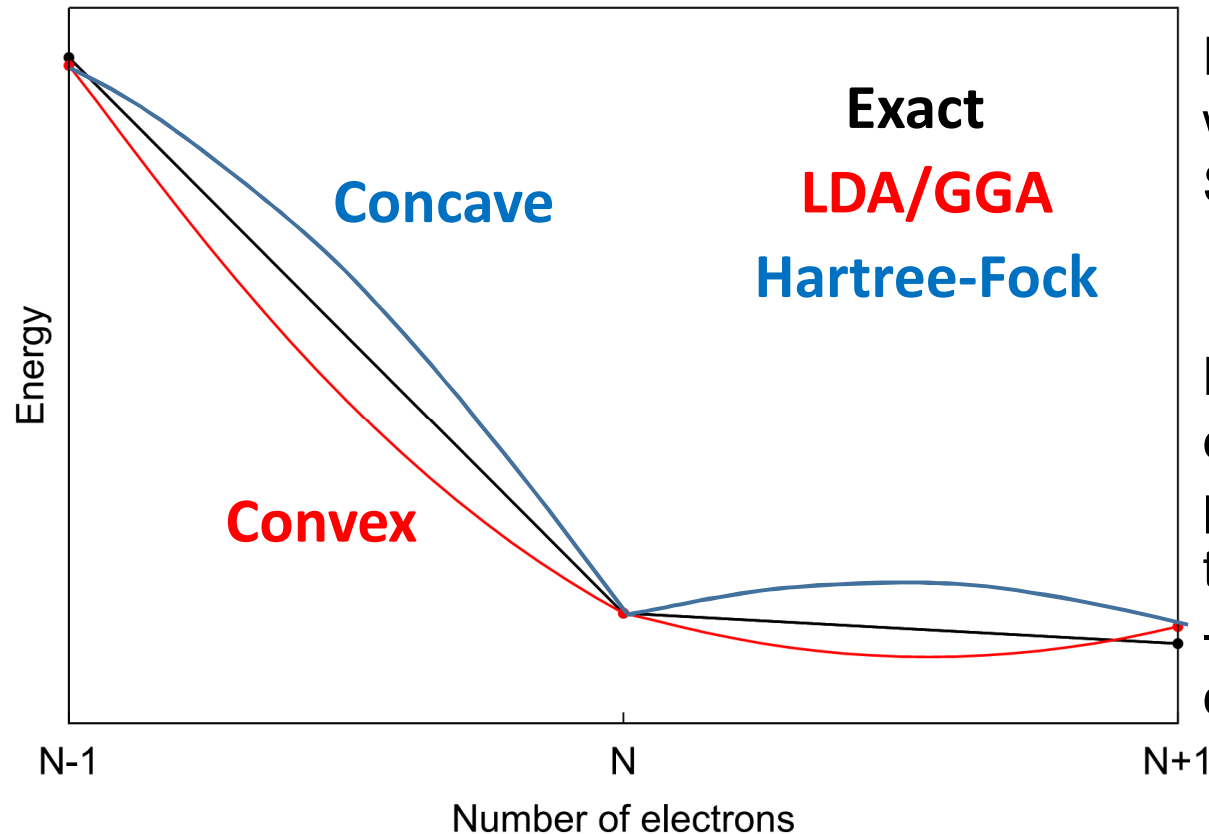


Advanced Materials Modeling

*Center for Energy Science and Technology (CEST)
Skolkovo Institute of Science and Technology
Moscow, Russia*

Approximate functionals

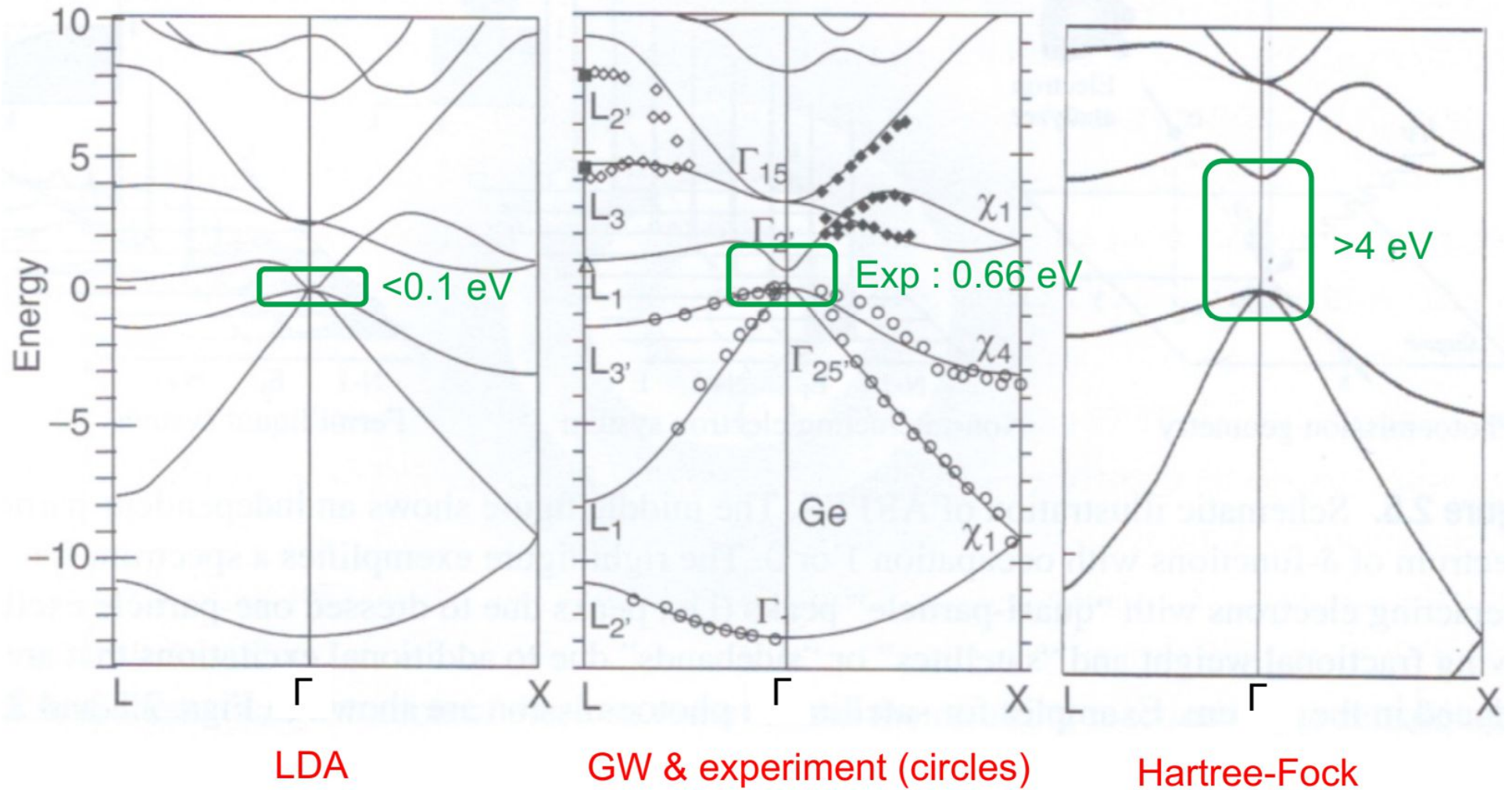
□ Dependence $E(N)$ for an approximate functional:



Hartree-Fock is a functional within generalized Kohn-Sham scheme: $E = E[\{\psi\}]$

More “DFT-like”: Optimized effective potentials (local potentials that approximate the non-local HF exchange) - numerically complex and computationally expensive

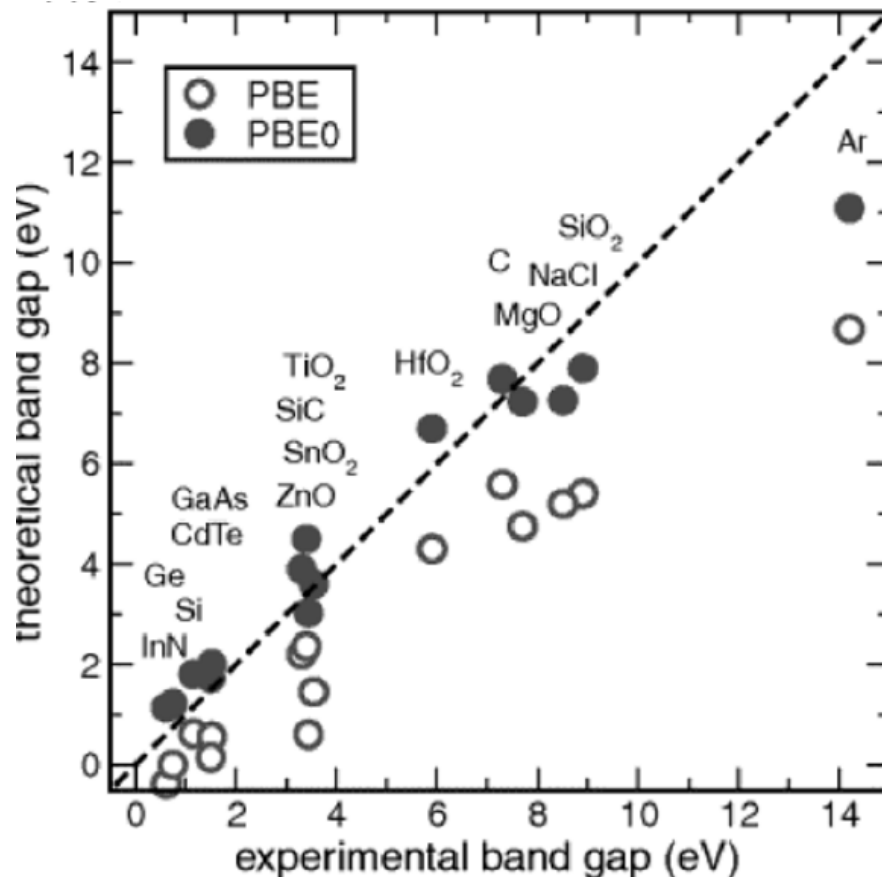
Germanium band structure



Hybrid functionals

□ Hybrid functionals

$$E^{PBE0} = 0.25E_X^{HF}(\{\psi^{KS}\}) + 0.75E_X^{PBE} + E_C^{PBE}$$



From: “Advanced Calculations for Defects in Materials: Electronic Structure Methods”, Alkauskas, Deák, Neugebauer, Pasquarello, Van de Walle (eds.), Willey-VCH (2011)

Band gap problem

❑ Observable gap:

$$E_{gap}^{obs} = (E(M+1) - E(M)) - (E(M) - E(M-1))$$

❑ Kohn-Sham gap:

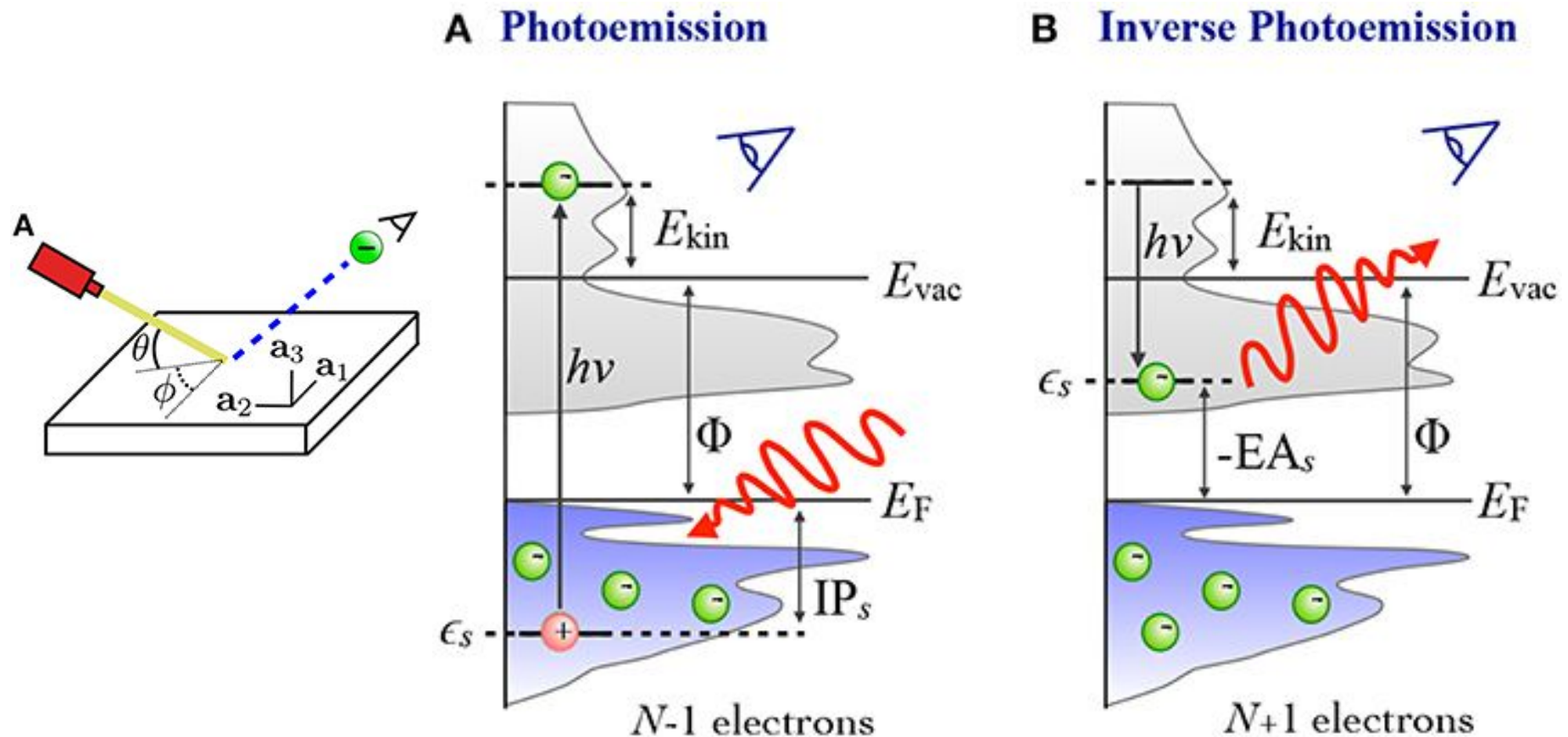
$$E_{gap}^{KS} = \epsilon_{LUMO}^M - \epsilon_{HOMO}^M$$

Are they the same?

No!

Hybrid functionals - partial remedy (parameters!)

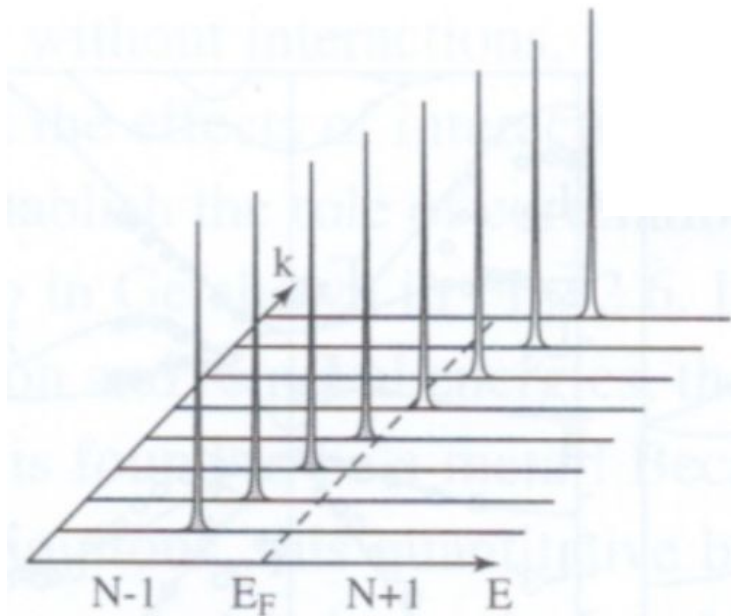
Charged excitations: Photoelectron spectroscopy



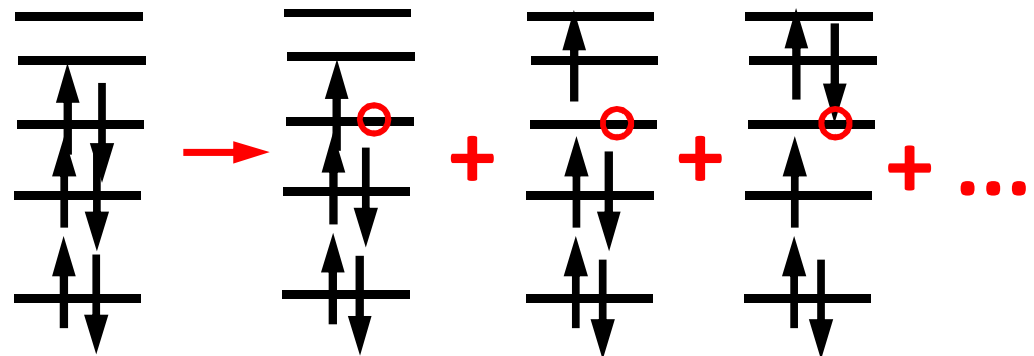
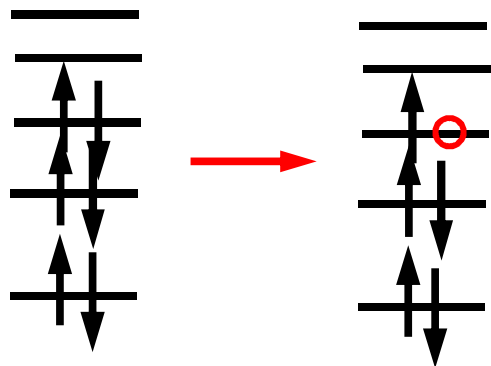
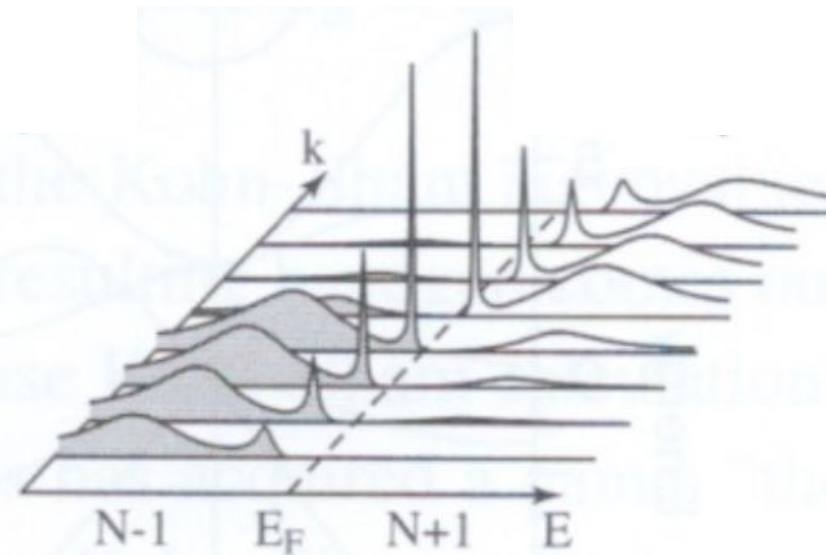
$$\epsilon_s = \begin{cases} E(N) - E(N-1, s), & \epsilon_s < \epsilon_{Fermi} \\ E(N+1, s) - E(N), & \epsilon_s > \epsilon_{Fermi} \end{cases}$$

Many-body effects

(Effective) non-interacting electrons (HF, DFT, hybrid)



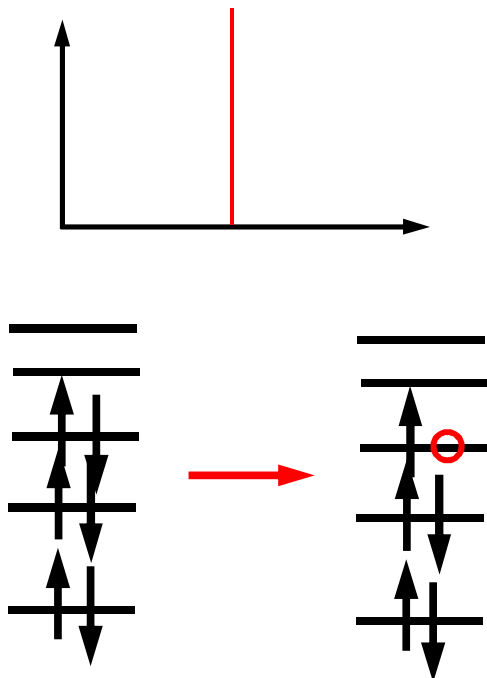
Many-body



Many-body effects

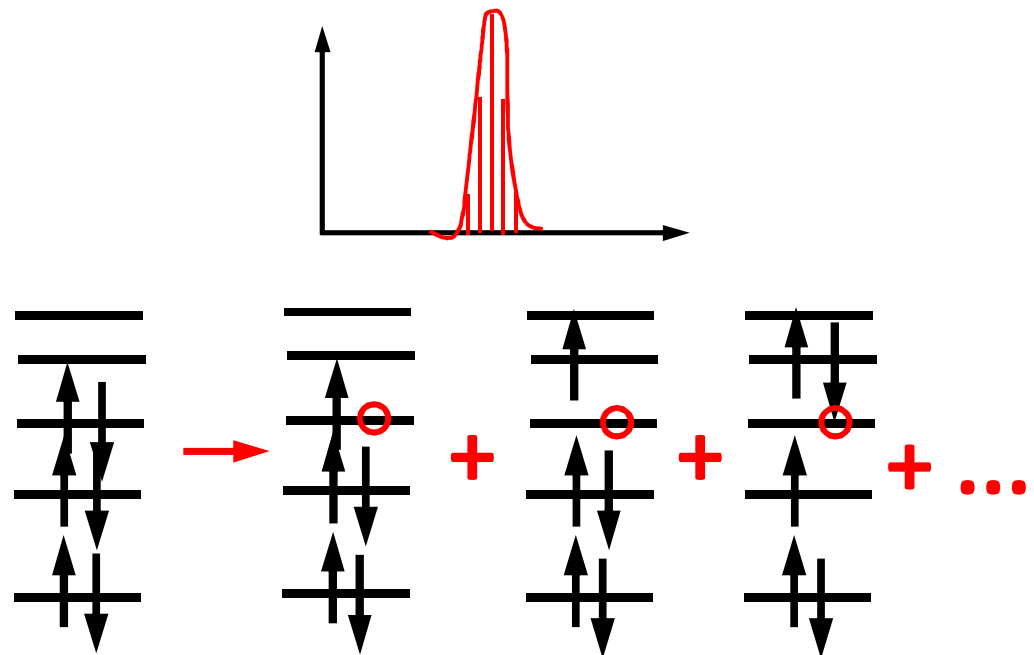
(Effectively) non-interacting
electrons (HF, DFT, hybrid)

One final configuration \rightarrow
zero spectral line width \rightarrow
infinite lifetime of holes and
electrons (stationary states)

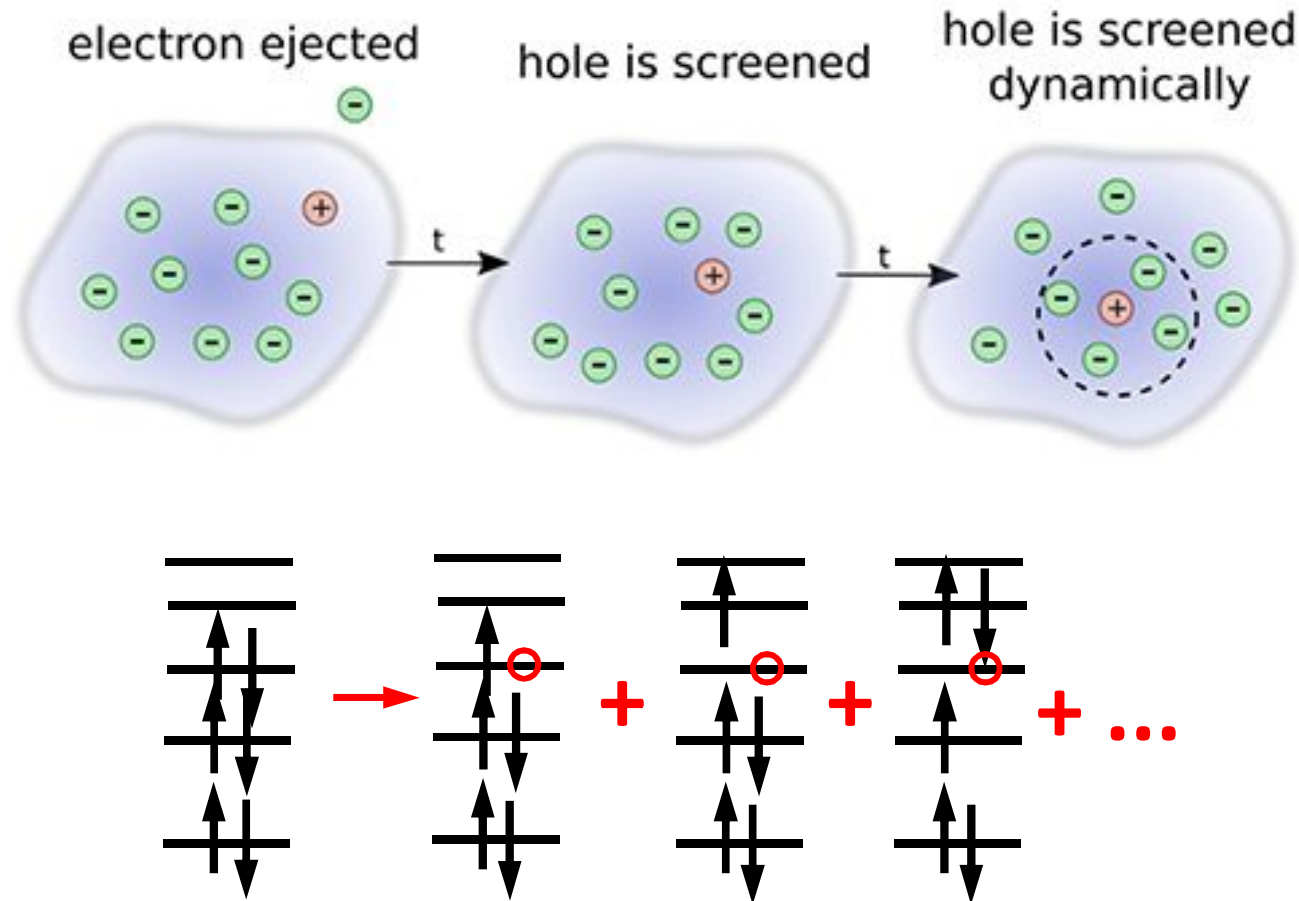


Many-body

Manifold of near-degenerate
configurations \rightarrow finite
spectral line width \rightarrow finite
lifetime of holes and
electrons (metastable states)

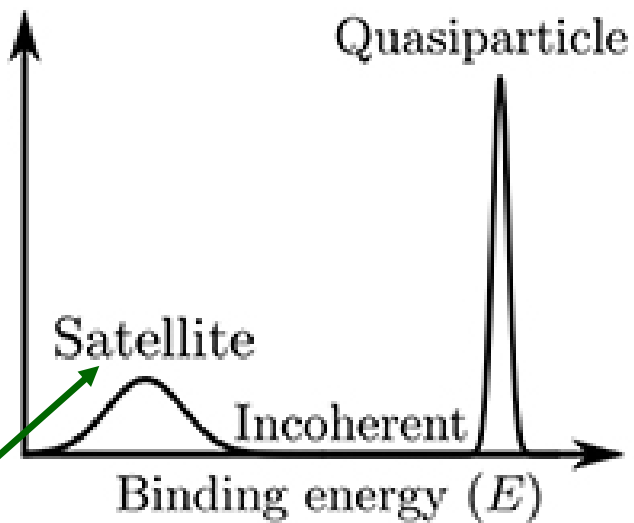
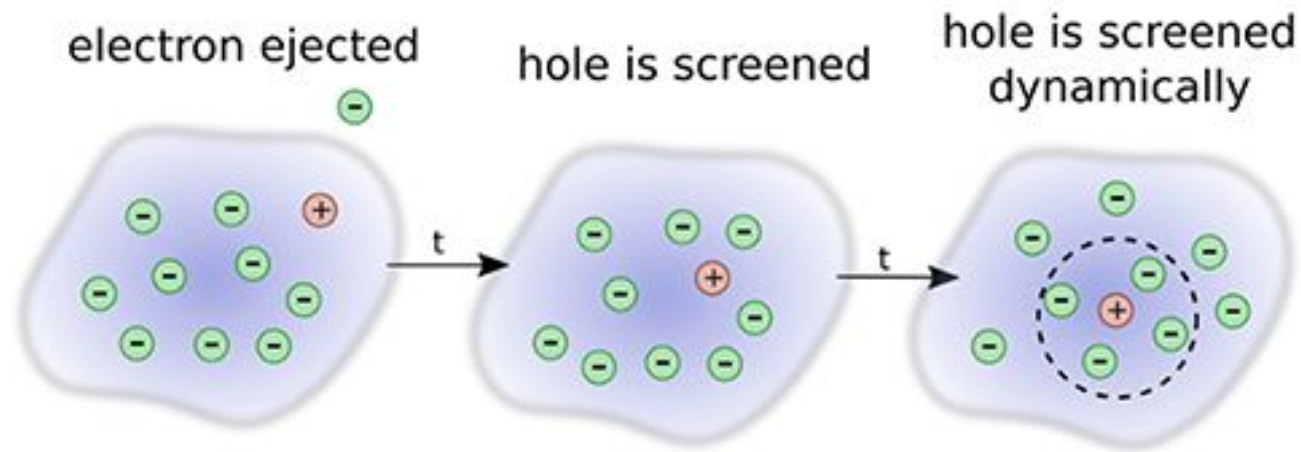


Quasiparticles



Screening - certain group of excitations up to infinite order (each short-lived (virtual), but overall significant effect)

Quasiparticles



collective excitations (plasmons, magnons)

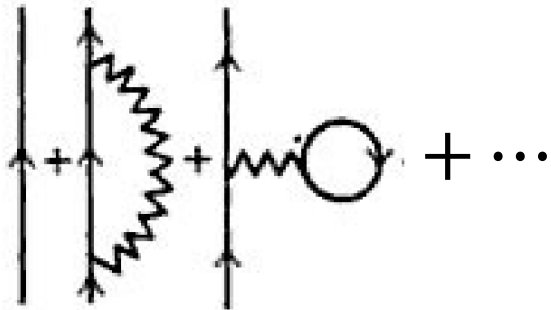
Many-body perturbation theory

Historically older than DFT (1950s-60s)

Developed by Feynman, Schwinger, Hubbard, Hedin, Lundqvist

Can be formulated in different ways, one of which - via a dynamic quantity called Green's function

Green's function - propagator:

$$G(\mathbf{r}t, \mathbf{r}'t') = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} + \dots$$


The diagram shows the expansion of the Green's function $G(\mathbf{r}t, \mathbf{r}'t')$ as a sum of Feynman diagrams. The first diagram is a single vertical line with an upward arrow. The second diagram consists of a vertical line with an upward arrow, followed by a plus sign, then a loop formed by two vertical lines with upward arrows connected by two wavy lines, followed by another plus sign. The third diagram consists of a vertical line with an upward arrow, followed by a plus sign, then a wavy line connected to a circle with an arrow pointing into it, followed by another plus sign and an ellipsis. This represents the Dyson equation for the Green's function.

The Green's function

Exact ground-state wave function of N -electron system: $|N, 0\rangle$

Creation and annihilation operators (Heisenberg picture):

$$\hat{\psi}^+(\mathbf{r}, t), \hat{\psi}(\mathbf{r}, t)$$

$\hat{\psi}^+(\mathbf{r}, t)|N, 0\rangle$ - $(N+1)$ -electron wave function, not necessarily in the ground state

$\hat{\psi}(\mathbf{r}, t)|N, 0\rangle$ - $(N-1)$ -electron wave function, not necessarily in the ground state

$$G^e(\mathbf{r}t, \mathbf{r}'t') = -i\langle N, 0|\hat{\psi}(\mathbf{r}, t)\hat{\psi}^+(\mathbf{r}', t')|N, 0\rangle, t > t'$$

- probability amplitude to find electron at (\mathbf{r}, t) after introducing it at (\mathbf{r}', t')

The Green's function

Exact ground-state wave function of N -electron system: $|N, 0\rangle$

Creation and annihilation operators (Heisenberg picture):

$$\hat{\psi}^+(\mathbf{r}, t), \hat{\psi}(\mathbf{r}, t)$$

$$G^e(\mathbf{r}t, \mathbf{r}'t') = -i\langle N, 0 | \hat{\psi}(\mathbf{r}, t) \hat{\psi}^+(\mathbf{r}', t') | N, 0 \rangle, t > t'$$

- probability amplitude to find *electron* at (\mathbf{r}, t) after introducing it at (\mathbf{r}', t')

$$G^h(\mathbf{r}'t', \mathbf{r}t) = -i\langle N, 0 | \hat{\psi}^+(\mathbf{r}', t') \hat{\psi}(\mathbf{r}, t) | N, 0 \rangle, t' > t$$

- probability amplitude to find *hole* at (\mathbf{r}', t') after introducing it at (\mathbf{r}, t)

The Green's function

$$G^e(\mathbf{r}t, \mathbf{r}'t') = -i\langle N, 0 | \hat{\psi}(\mathbf{r}, t) \hat{\psi}^+(\mathbf{r}', t') | N, 0 \rangle, t > t'$$

- probability amplitude to find *electron* at (\mathbf{r}, t) after introducing it at (\mathbf{r}', t')

$$G^h(\mathbf{r}'t', \mathbf{r}t) = -i\langle N, 0 | \hat{\psi}^+(\mathbf{r}', t') \hat{\psi}(\mathbf{r}, t) | N, 0 \rangle, t' > t$$

- probability amplitude to find *hole* at (\mathbf{r}', t') after introducing it at (\mathbf{r}, t)

Total Green's function:

$$G(\mathbf{r}'t', \mathbf{r}t) = -i\langle N, 0 | \hat{T}[\hat{\psi}(\mathbf{r}, t) \hat{\psi}^+(\mathbf{r}', t')] | N, 0 \rangle$$

with \hat{T} - time-ordering operator

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

The Green's function - connection to spectroscopy

Charged excitations - dynamical process

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

closure relation: $\sum_{M,i} |M, i\rangle \langle M, i| = \hat{1}$



sum over all many-body eigenstates of systems with all possible charges M (but only $M=N\pm 1$ contribute)



+Fourier transform
over time ($\Delta t \rightarrow \omega$)

Lehman representation:

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

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

The Green's function - connection to properties

Galitskii-Migdal formula for total energy:

$$E_{total} = \frac{1}{\pi} \int_{-\infty}^{\mu} d\omega \text{Tr}[(\omega - \hat{h}_0) \text{Im}G(\omega)]$$

μ ← Fermi energy (electronic chemical potential)

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

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

The Green's function - equations

$$i \frac{\partial}{\partial t} \hat{\psi}(\mathbf{r}, t) = [\hat{\psi}(\mathbf{r}, t), \hat{H}] \quad \text{equation of motion for any operator}$$

Writing the Hamiltonian as a function of the field operators and using the commutation relation between them

$$i \frac{\partial}{\partial t} \hat{\psi}(\mathbf{r}, t) = \left[\hat{h}^0 + \int d^3 r' \frac{\hat{\psi}^\dagger(\mathbf{r}'', t) \hat{\psi}(\mathbf{r}'', t)}{|\mathbf{r} - \mathbf{r}''|} \right] \hat{\psi}(\mathbf{r}, t)$$



$$\left(i \frac{\partial}{\partial t} - \hat{h}^0 \right) G(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') + \int d^3 r'' \frac{G_2(\mathbf{r}t, \mathbf{r}''t, \mathbf{r}''t, \mathbf{r}'t')}{|\mathbf{r} - \mathbf{r}''|}$$

With the two-particle Green's function:

$$G_2(\mathbf{r}t, \mathbf{r}''t, \mathbf{r}''t, \mathbf{r}'t') = -i \left\langle N, 0 \left| \hat{\psi}^\dagger(\mathbf{r}'', t) \hat{\psi}(\mathbf{r}'', t) \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right| N, 0 \right\rangle$$

The Green's function - equations

$$\left(i \frac{\partial}{\partial t} - \hat{h}^0\right) G(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \\ + \int d^3r'' \frac{G_2(\mathbf{r}t, \mathbf{r}''t, \mathbf{r}''t, \mathbf{r}'t')}{|\mathbf{r} - \mathbf{r}''|}$$

→ need two-particle Green's function to find one-particle, three-particle for two-particle, ... - **intractable**

Idea: introduce a new function - *self-energy*:

$$\int d^3r'' \frac{G_2(\mathbf{r}t, \mathbf{r}''t, \mathbf{r}''t, \mathbf{r}'t')}{|\mathbf{r} - \mathbf{r}''|} = \int dt'' \int d^3r'' \bar{\Sigma}(\mathbf{r}t, \mathbf{r}''t'') G(\mathbf{r}''t'', \mathbf{r}'t')$$

The largest contribution (Hartree potential) is separated out:

$$\Sigma(\mathbf{r}t, \mathbf{r}''t'') = \bar{\Sigma}(\mathbf{r}t, \mathbf{r}''t'') - v_H(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}'')\delta(t - t'')$$

The Green's function - equations

$$\left(i \frac{\partial}{\partial t} - \hat{h}^0\right) G(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \\ + \int d^3r'' \frac{G_2(\mathbf{r}t, \mathbf{r}''t, \mathbf{r}''t', \mathbf{r}'t')}{|\mathbf{r} - \mathbf{r}''|}$$

The largest contribution (Hartree potential) is separated out:

$$\Sigma(\mathbf{r}t, \mathbf{r}''t'') = \bar{\Sigma}(\mathbf{r}t, \mathbf{r}''t'') - v_H(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}'')\delta(t - t'')$$



$$\left(i \frac{\partial}{\partial t} - \hat{h}^0(\mathbf{r}) - v_H(\mathbf{r})\right) G(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') + \\ \int dt'' \int d^3r'' \Sigma(\mathbf{r}t, \mathbf{r}''t'') G(\mathbf{r}''t'', \mathbf{r}'t')$$

The Green's function - equations

Let us denote $rt, r't', \dots$ as $1, 2, \dots$

Introducing *non-interacting* Green's function $G_0(1,2)$:

$$\left(i \frac{\partial}{\partial t} - \hat{h}^0(1) - v_H(1) \right) G_0(1,2) = \delta(1-2)$$

we obtain equation for *interacting* Green's function:

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

 **Dyson equation**

$$G(1,2) = G_0(1,2) + \int d(3,4) G_0(1,3) \Sigma(3,4) G_0(4,2) + \\ + \int d(3,4,5,6) G_0(1,3) \Sigma(3,4) G_0(4,5) \Sigma(5,6) G_0(6,2) + \dots$$

Dyson series: particle propagates and is sometimes scattered by Σ

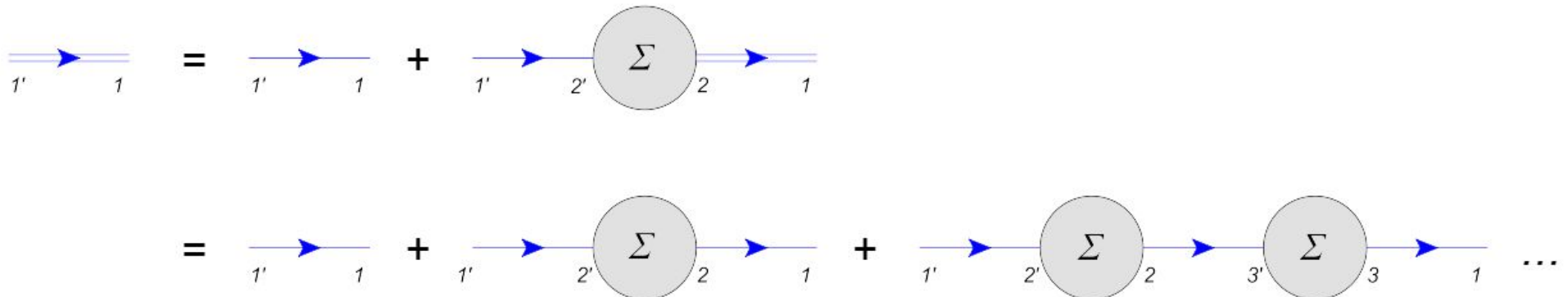
The Green's function - diagrams

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

↑
Dyson equation

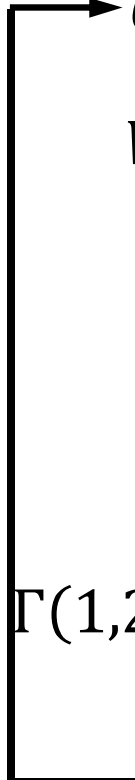
$$G(1,2) = G_0(1,2) + \int d(3,4) G_0(1,3) \Sigma(3,4) G_0(4,2) + \\ + \int d(3,4,5,6) G_0(1,3) \Sigma(3,4) G_0(4,5) \Sigma(5,6) G_0(6,2) + \dots$$

Dyson series: particle propagates and is sometimes scattered by Σ



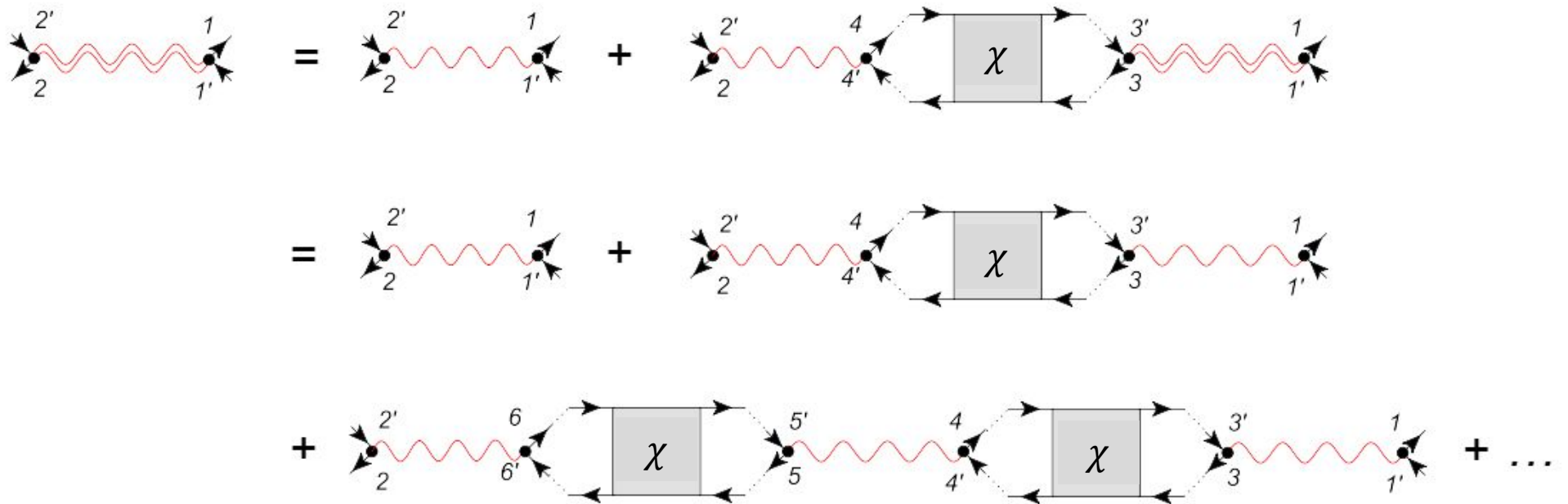
Hedin's equations

In 1965, Hedin expanded the Green's function and the self-energy in terms of the *screened* instead of the bare Coulomb interaction:


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

Hedin's equations - diagrams

$$W(1,2) = v(1,2) + \int d(3,4) v(1,3) \chi(3,4) W(4,2)$$



Hedin's equations - approximations

The simplest approximation:

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

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

Hedin's equations - approximations

The simplest approximation:

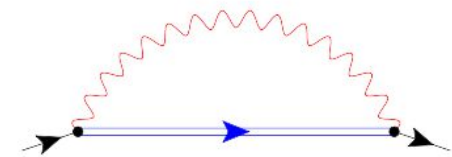
$$\Sigma(1,2) = iG(1,2)v(1,2) = \frac{\langle N, 0 | \hat{T} [\hat{\psi}(\mathbf{r}, t) \hat{\psi}^+(\mathbf{r}', t')] | N, 0 \rangle}{|\mathbf{r} - \mathbf{r}'|}$$

$$\sum_{M,i} |M, i\rangle \langle M, i| = \hat{1}$$



$$\Sigma(1,2) \sim \sum_i \frac{\psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- Fock exchange!



self-consistency

$$\text{Diagram 1} = \text{Diagram 2} + \text{Diagram 3}$$

Diagram 1: A horizontal blue line with an arrow pointing right, labeled 1' at the start and 1 at the end.

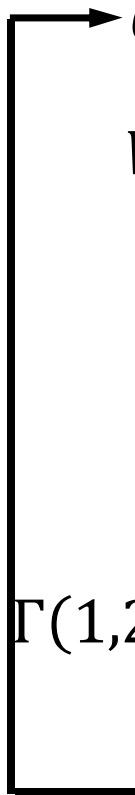
Diagram 2: A horizontal blue line with an arrow pointing right, labeled 1' at the start and 1 at the end.

Diagram 3: A horizontal blue line with an arrow pointing right, labeled 1' at the start and 2' at the end, followed by a grey circle labeled Σ , then a horizontal blue line with an arrow pointing right, labeled 2 at the start and 1 at the end.

$$= \text{Diagram 2} + \text{Diagram 3} + \text{Diagram 4} + \dots$$

Diagram 4: A horizontal blue line with an arrow pointing right, labeled 1' at the start and 2' at the end, followed by a grey circle labeled Σ , then a horizontal blue line with an arrow pointing right, labeled 2 at the start and 3' at the end, followed by another grey circle labeled Σ , then a horizontal blue line with an arrow pointing right, labeled 3 at the start and 1 at the end.

Hedin's equations - approximations



$$G(1,2) = G_0(1,2) + \int d(3,4) G_0(1,3) \Sigma(3,4) G(4,2) \quad \text{Dyson equation}$$

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

$$\varepsilon(1,2) = \delta(1,2) - \int d(3) v(1,3) \chi(3,2) \quad \text{dielectric matrix}$$

$$\chi(1,2) = -i \int d(3,4) G(1,3) G(4,1) \Gamma(3,4,2) \quad \text{polarizability}$$
~~$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int d(4,5,6,7) \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(7,5) \Gamma(6,7,3) \quad \text{vertex}$$~~

$$\Sigma(1,2) = i \int d(3,4) G(1,4) W(1,3) \Gamma(4,2,3) \quad \text{self-energy}$$

Hedin's equations - approximations

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

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

Hedin's equations - approximations

$$\Sigma(1,2) = iG(1,2)W(1,2) \quad \text{GW approximation}$$

$$\chi(1,2) = -iG(1,2)G(2,1) \quad \text{random-phase approximation (RPA)}$$

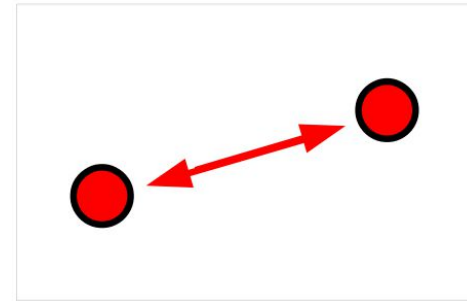
$$W(1,2) = \int d(3) \varepsilon^{-1}(1,3) v(3,2)$$

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

Screened Coulomb interaction W

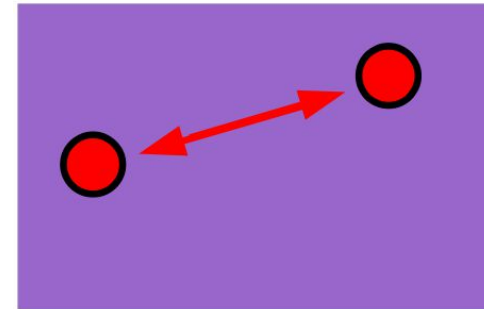
Bare Coulomb interaction (in vacuum):

$$v(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$



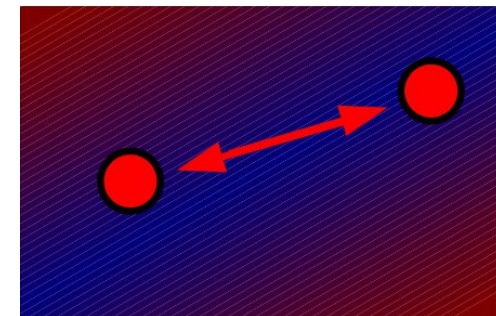
Screened Coulomb interaction (in homogeneous polarizable medium):

$$W(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\epsilon |\mathbf{r}_1 - \mathbf{r}_2|}$$



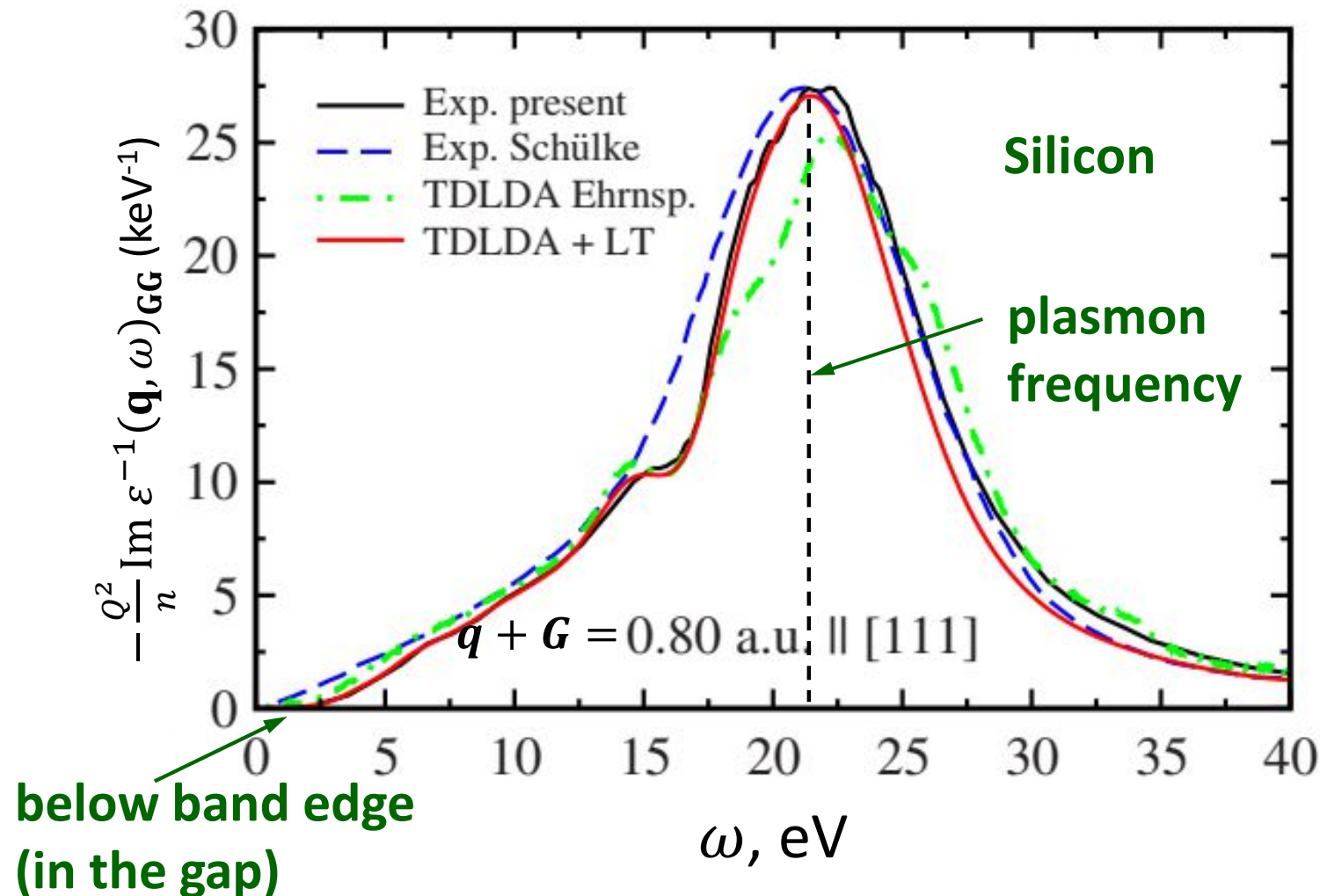
Dynamically screened interaction in a general medium:

$$W(\mathbf{r}_1, \mathbf{r}_2, \omega) = \int d^3r_3 \frac{\epsilon^{-1}(\mathbf{r}_1, \mathbf{r}_3, \omega)}{|\mathbf{r}_3 - \mathbf{r}_2|}$$



Screened Coulomb interaction W

$W(\epsilon^{-1})$ is frequency-dependent, can be measured experimentally:

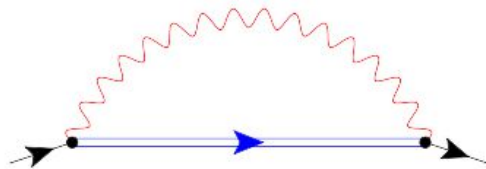


GW as an advanced Hartree-Fock approximation

Hartree-Fock approximation

$$\Sigma(\mathbf{r}_1, \mathbf{r}_2) = i \int d\omega G(\mathbf{r}_1, \mathbf{r}_2, \omega) v(\mathbf{r}_1, \mathbf{r}_2)$$

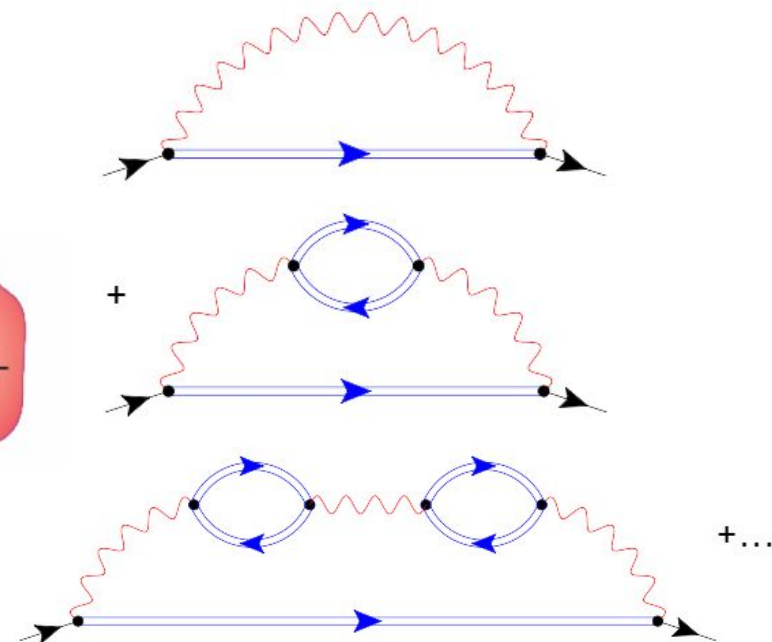
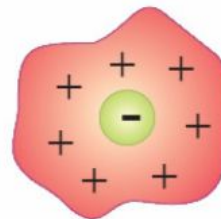
- bare exchange



GW approximation

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

- HF exchange plus correlation



GW is a screened version of HF

From DFT to *GW*

Dyson's equation for $G \rightarrow$ effective quasiparticle equation
(using Lehmann's representation):

$$\hat{h}_0 \psi_i^{GW}(\mathbf{r}) + \int d^3 r' \tilde{\Sigma}(\mathbf{r}, \mathbf{r}', \epsilon_i^{GW}) |\psi_i^{GW}\rangle = \epsilon_i^{GW} |\psi_i^{GW}\rangle$$

where

$$\tilde{\Sigma}(\mathbf{r}, \mathbf{r}', \epsilon_i^{GW}) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}', \epsilon_i^{GW} + \omega') W(\mathbf{r}, \mathbf{r}', \omega')$$

From DFT to GW

Lehman's representation: $G(\mathbf{r}', \mathbf{r}, \omega) = \sum_i \frac{\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}')}{\omega - \epsilon_i \pm i\eta}$

$\psi_i(\mathbf{r}), \epsilon_i$ - complicated many-body objects

For effectively independent electrons (Kohn-Sham DFT):

$$G_0(\mathbf{r}', \mathbf{r}, \omega) = \sum_i \frac{\psi_i^{KS*}(\mathbf{r})\psi_i^{KS}(\mathbf{r}')}{\omega - \epsilon_i^{KS} \pm i\eta} \quad \text{-this could be a good guess for } G$$

GW equations: $[\hat{h}_0 + \tilde{\Sigma}(\epsilon_i^{GW})]|\psi_i^{GW}\rangle = \epsilon_i^{GW}|\psi_i^{GW}\rangle$

KS equations: $[\hat{h}_0 + v_{XC}^{KS}]|\psi_i^{KS}\rangle = \epsilon_i^{KS}|\psi_i^{KS}\rangle$

Approximation: $\psi_i^{GW} = \psi_i^{KS}$

From DFT to GW

$$G_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_i \frac{\psi_i^{KS*}(\mathbf{r}') \psi_i^{KS}(\mathbf{r})}{\omega - \epsilon_i^{KS} \pm i\eta}$$

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

$$\varepsilon(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r}, \mathbf{r}') - \int d^3r'' \frac{\chi_0(\mathbf{r}'', \mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}''|}$$

$$W_0(\mathbf{r}, \mathbf{r}', \omega) = \int d^3r'' \frac{\varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega)}{|\mathbf{r}'' - \mathbf{r}'|}$$

$$\tilde{\Sigma}(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' G_0(\mathbf{r}, \mathbf{r}', \omega + \omega') W_0(\mathbf{r}, \mathbf{r}', \omega')$$

From DFT to *GW*

The quasiparticle energies:

$$\epsilon_i^{GW} = \epsilon_i^{KS} + \langle \psi_i^{KS} | [\tilde{\Sigma}(\epsilon_i^{GW}) - v_{XC}^{KS}] | \psi_i^{KS} \rangle$$

SCF cycle for $\epsilon_i^{GW} \rightarrow$ quasiparticle self-consistent *GW* (ev*GW*₀)

One-shot *GW* (*G*₀*W*₀):

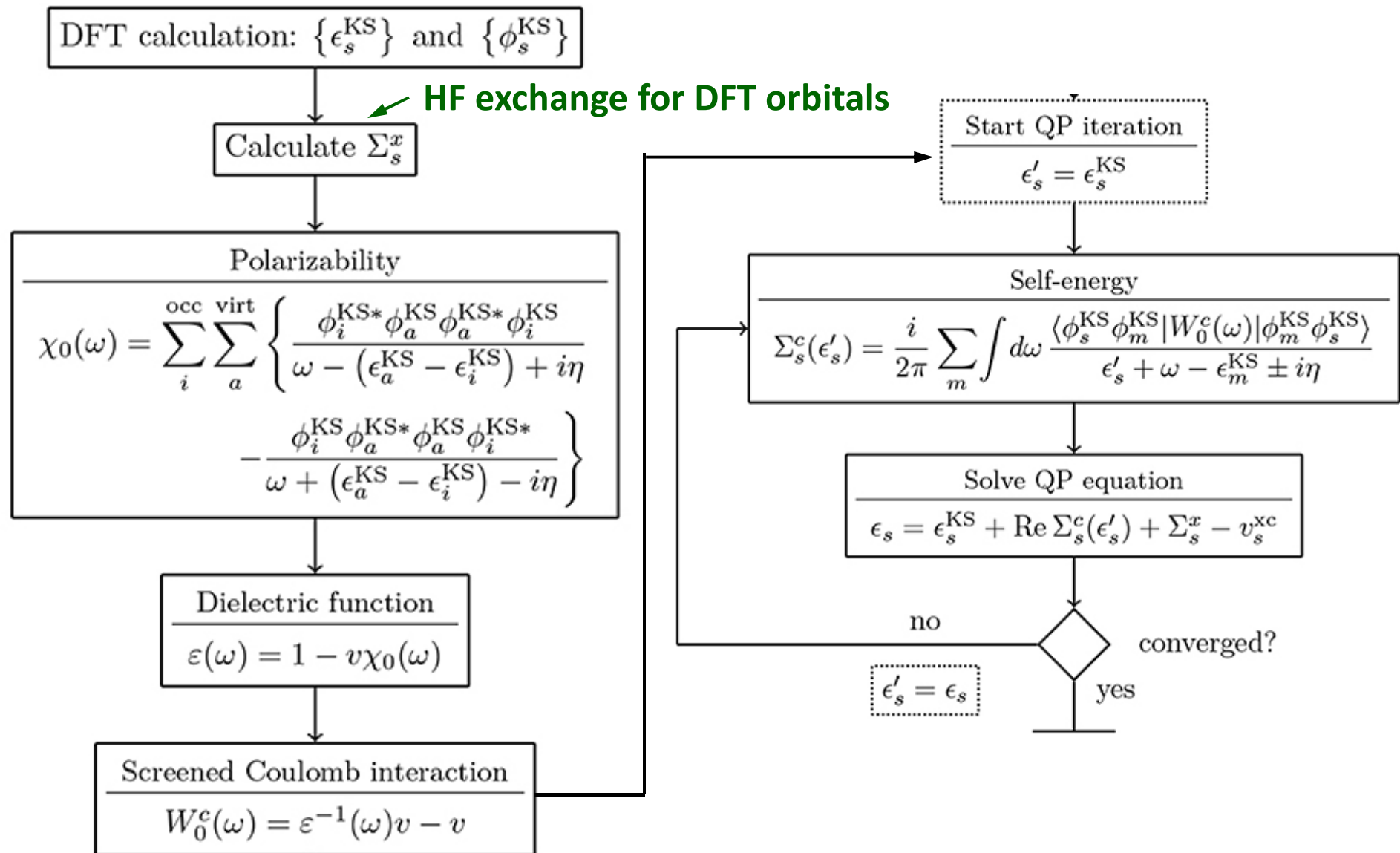
$$\tilde{\Sigma}(\epsilon_i^{GW}) \approx \tilde{\Sigma}(\epsilon_i^{KS}) + (\epsilon_i^{GW} - \epsilon_i^{KS}) \frac{\partial \tilde{\Sigma}}{\partial \epsilon_i}$$



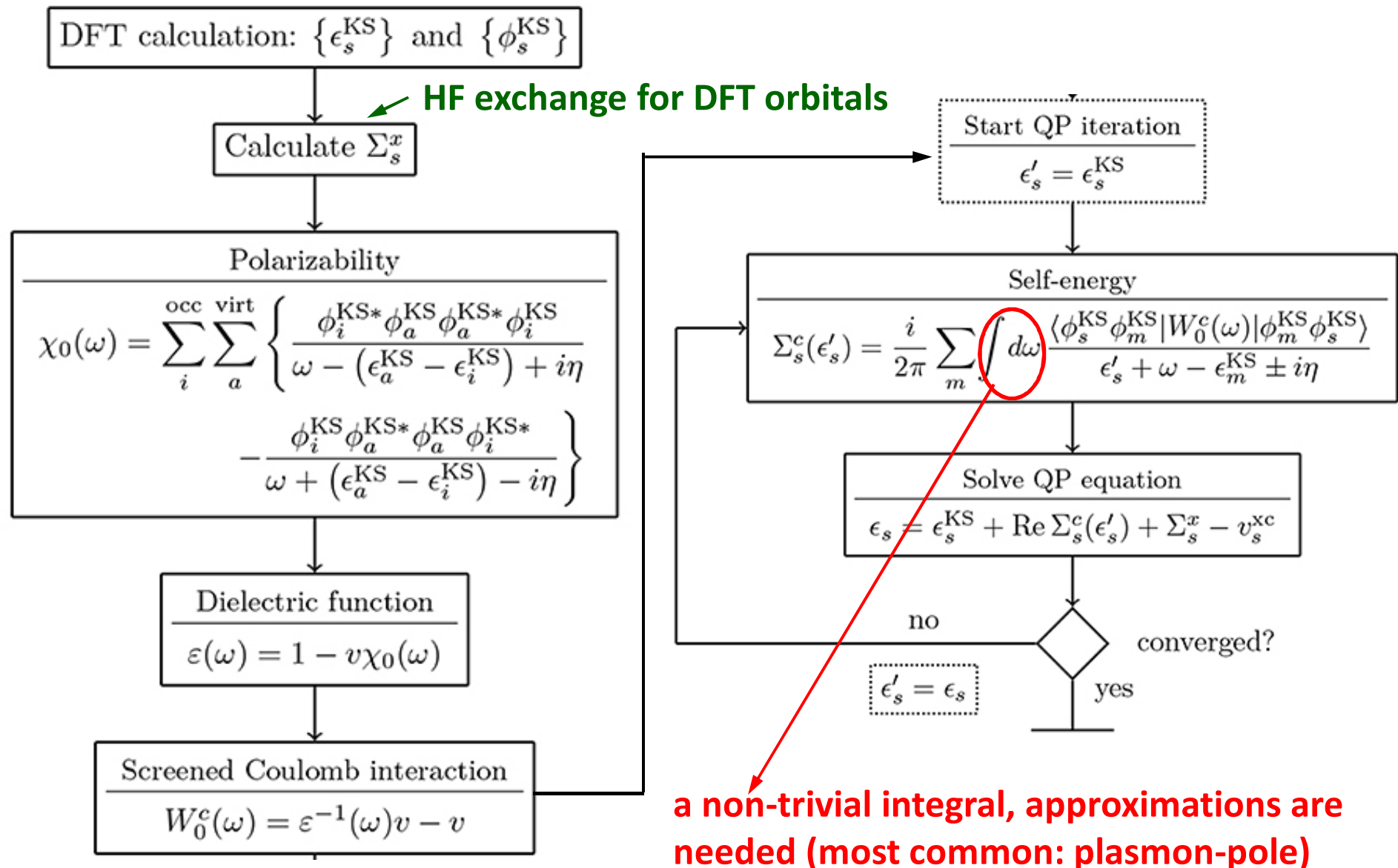
$$\epsilon_i^{GW} = \epsilon_i^{KS} + \frac{1}{1 - \frac{\partial \tilde{\Sigma}(\epsilon_i^{KS})}{\partial \epsilon_i}} \langle \psi_i^{KS} | [\tilde{\Sigma}(\epsilon_i^{KS}) - v_{XC}^{KS}] | \psi_i^{KS} \rangle$$

Fully self-consistent *GW*: SCF cycle for ϵ_i^{GW} and ψ_i^{GW}

From DFT to GW

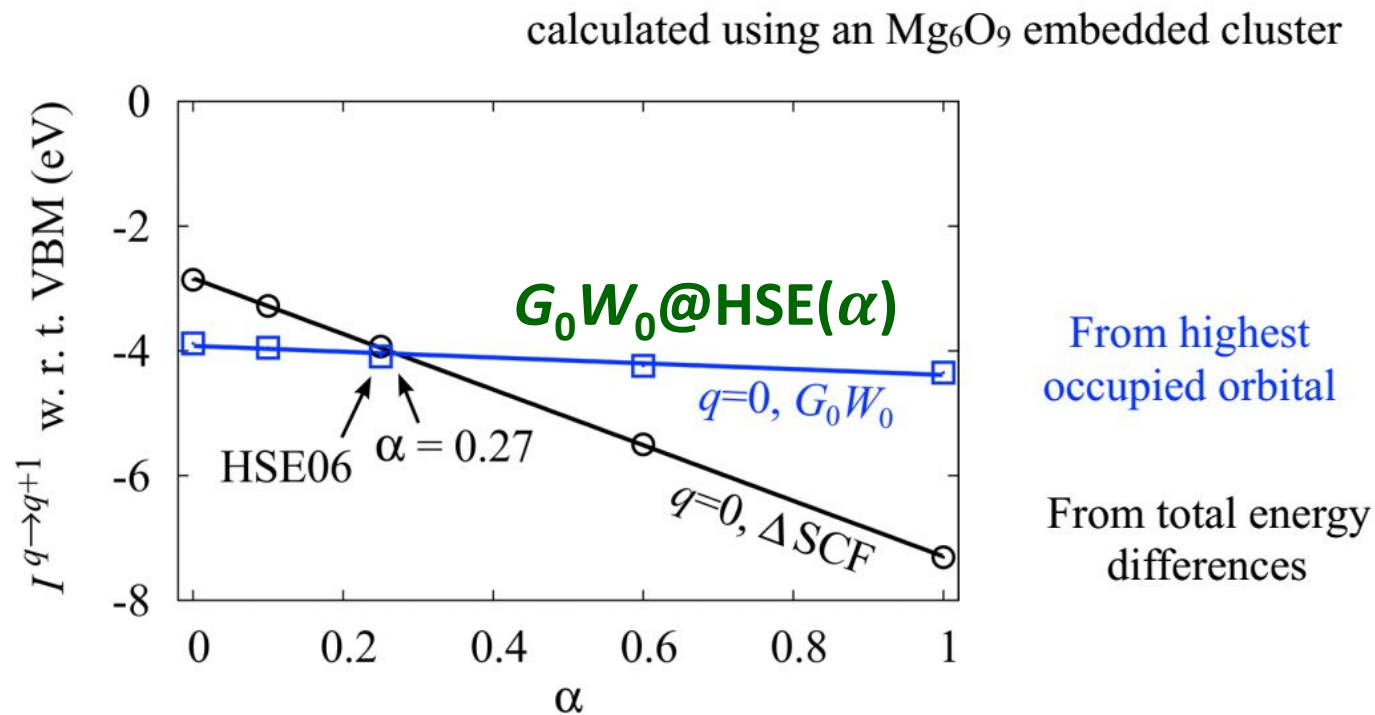


From DFT to GW



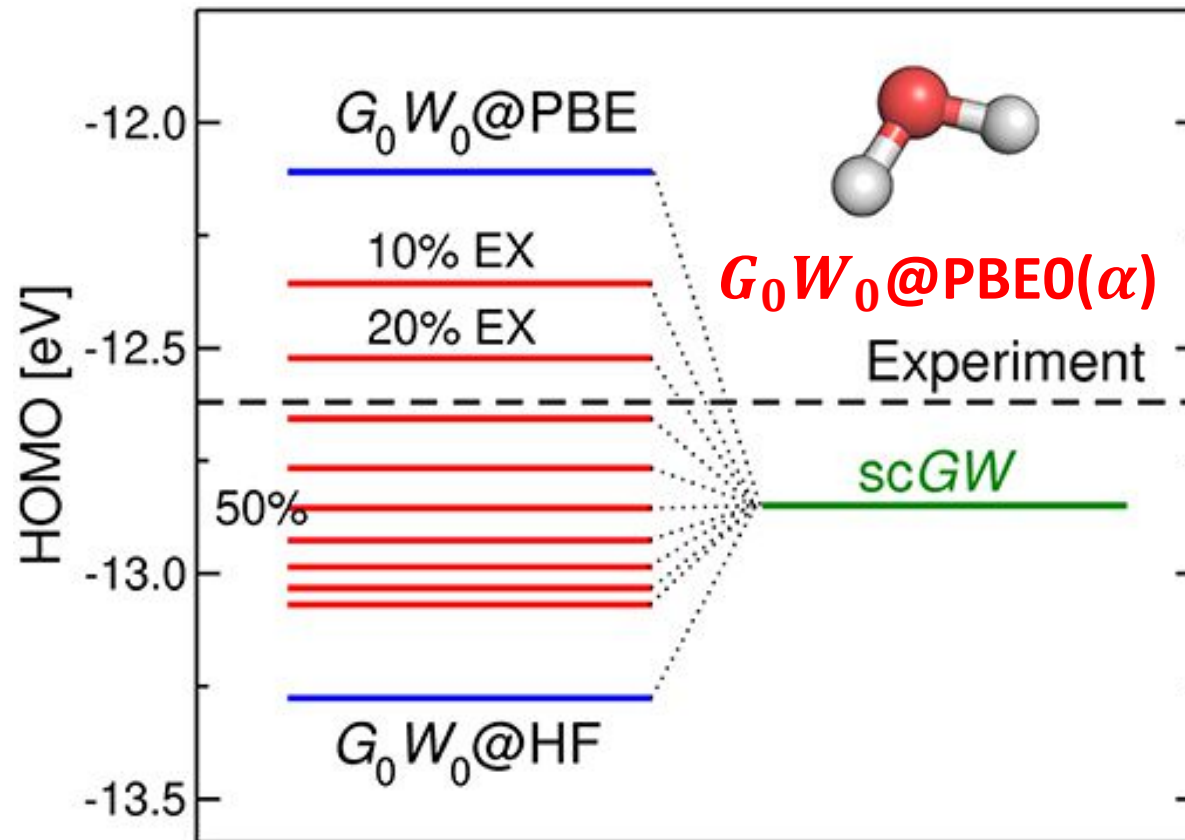
GW: starting-point dependence

Non-self-consistency \rightarrow dependence on starting KS band structure

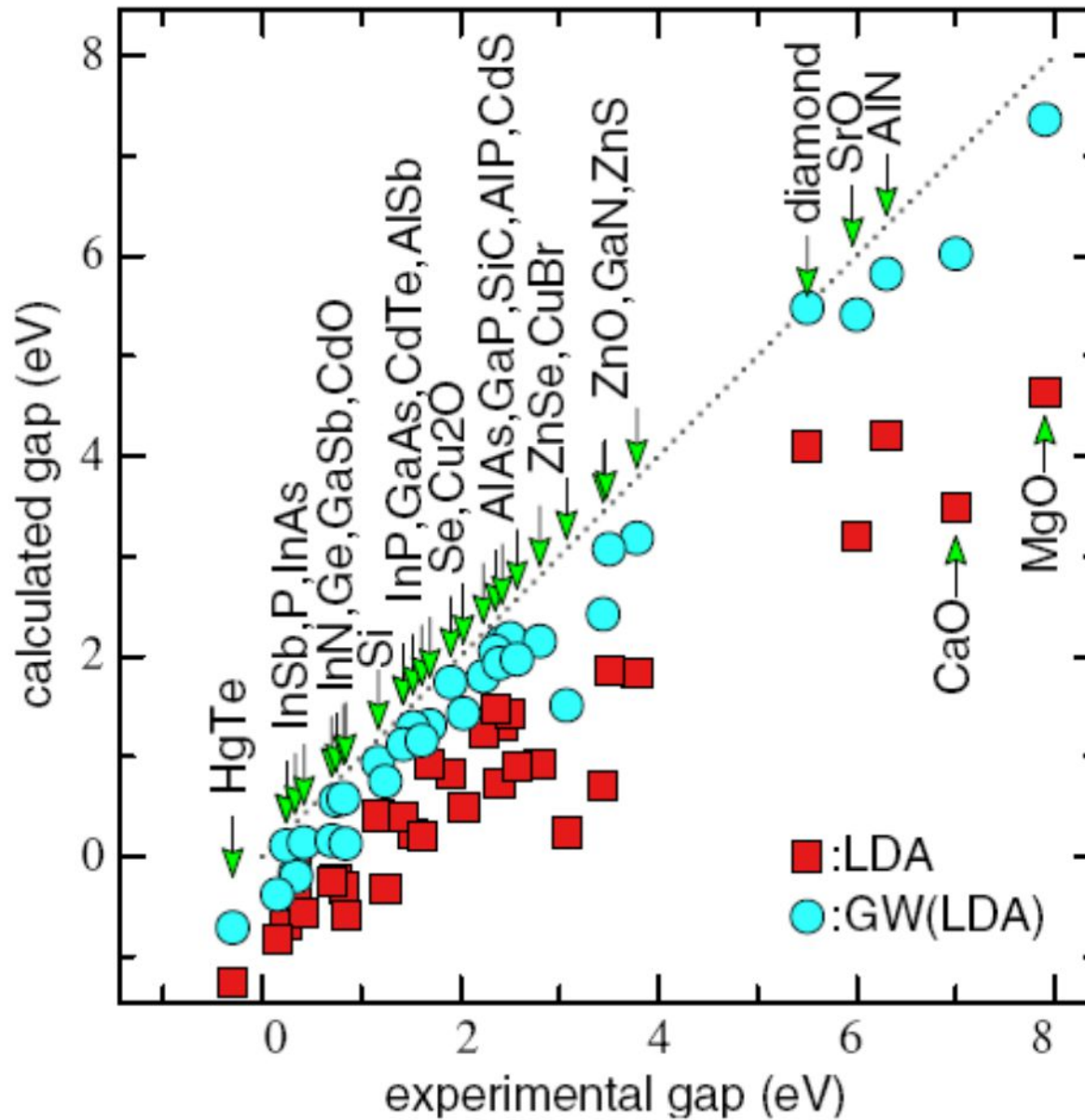


GW: starting-point dependence

Non-self-consistency \rightarrow dependence on starting KS band structure

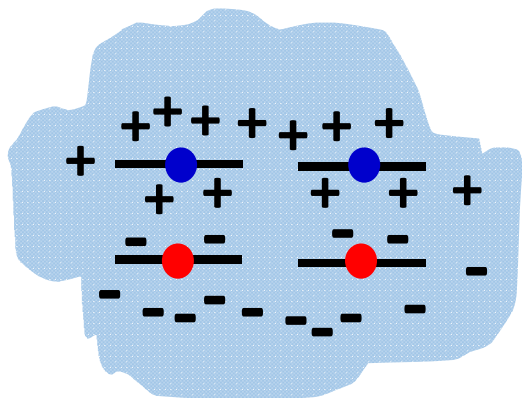


GW: accurate band structure

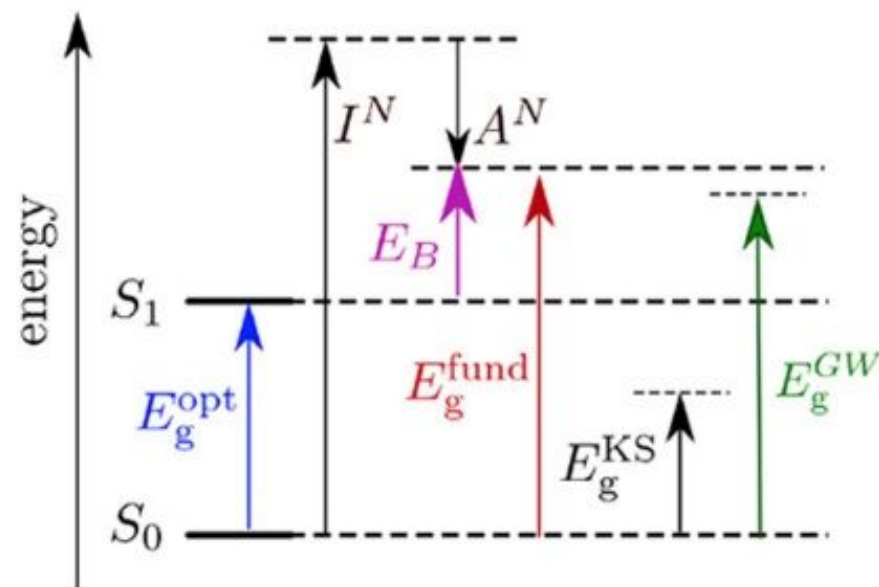
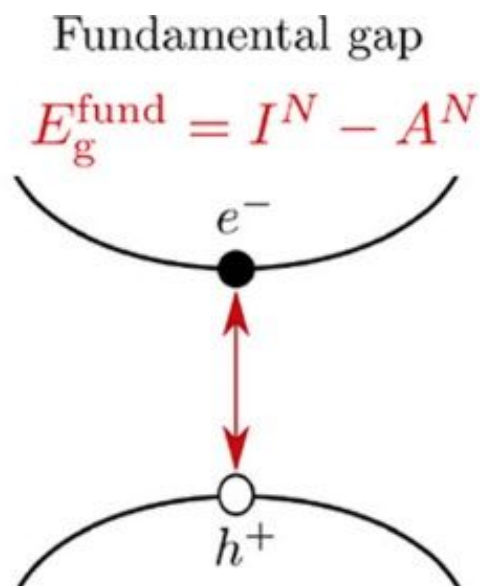
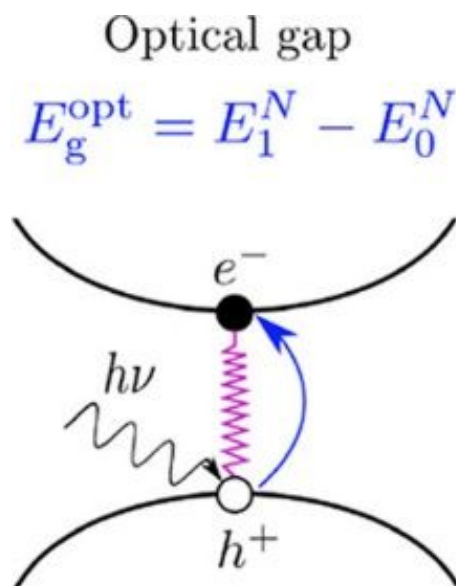


after van Schilfgaarde *et al* PRL **96** 226402 (2008)

Neutral excitations: Bethe-Salpeter equation



Excited electron and hole interact with each other. Bethe and Salpeter: Take into account screening!



Neutral excitations: Bethe-Salpeter equation

Dyson's equation for one-particle Green's function:

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



Dyson's equation for two-particle correlation function

($L(1, 2; 1', 2') = -G_2(1, 2, 1', 2') + G(1, 1')G(2, 2')$):

$$L(1,2; 1', 2') = L_0(1,2; 1', 2') + \int d(3,4,5,6) L_0(1,4; 1', 3) \Xi(3,5; 4,6) L(6,2; 5,2')$$

With $L_0(1,2; 1', 2') = G(1,2')G(2,1')$ - the non-interacting 4-point susceptibility, and *BSE kernel*

$$i\Xi(3,5; 4,6) = v(3,6)\delta(3,4)\delta(5,6) + i \frac{\delta\Sigma(3,4)}{\delta G(6,5)}$$

also appeared in GW in the vertex equation (higher-order screening effects)

Neutral excitations: Bethe-Salpeter equation

Bethe-Salpeter equation:

$$L(1,2; 1', 2') = L_0(1,2; 1', 2') + \int d(3,4,5,6) L_0(1,4; 1', 3) \Xi(3,5; 4,6) L(6,2; 5,2')$$

$$i\Xi(3,5; 4,6) = v(3,6)\delta(3,4)\delta(5,6) + i \frac{\delta\Sigma(3,4)}{\delta G(6,5)} \quad \text{BSE kernel}$$



Time-dependent DFT equation (TD-DFT):

$$\chi(1,2) = \chi_0(1,2) + \int d(3,4) \chi_0(1, 3) \Xi^{\text{DFT}}(3,4) \chi(4,2)$$

$$i\Xi^{\text{DFT}}(3,4) = v(3,4) + i \frac{\delta V_{\text{XC}}(3)}{\delta n(4)} \quad \text{TD-DFT kernel}$$

Neutral excitations: Bethe-Salpeter equation

$$L(1,2; 1', 2') = L_0(1,2; 1', 2') + \int d(3,4,5,6) L_0(1,4; 1', 3) \mathbf{E}(3,5; 4,6) L(6,2; 5,2')$$

$$i\mathbf{E}(3,5; 4,6) = v(3,6)\delta(3,4)\delta(5,6) + i \frac{\delta\Sigma(3,4)}{\delta G(6,5)} \quad \text{BSE kernel}$$

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

$$i\mathbf{E}(3,5; 4,6) \approx v(3,6)\delta(3,4)\delta(5,6) - W(3,4)\delta(3,6)\delta(4,5)$$

where $\frac{\delta W}{\delta G}$ is neglected (higher orders in W)

Neutral excitations: Bethe-Salpeter equation

$$L(1,2; 1', 2') = L_0(1,2; 1', 2') + \int d(3,4,5,6) L_0(1,4; 1', 3) \mathbf{E}(3,5; 4,6) L(6,2; 5,2')$$

$$i\mathbf{E}(3,5; 4,6) \approx v(3,6)\delta(3,4)\delta(5,6) - W(3,4)\delta(3,6)\delta(4,5)$$

Taking static limit $W(\omega \rightarrow 0)$ and expressing equation for $L(1, 2; 1', 2')$ in the basis of products $\psi_i^{KS}(\mathbf{r}_h)\psi_a^{KS}(\mathbf{r}_e)$:

$$\begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix} \begin{pmatrix} X^m \\ Y^m \end{pmatrix} = \Omega_m \begin{pmatrix} X^m \\ Y^m \end{pmatrix}$$

(similar to Casida TD-DFT equations)

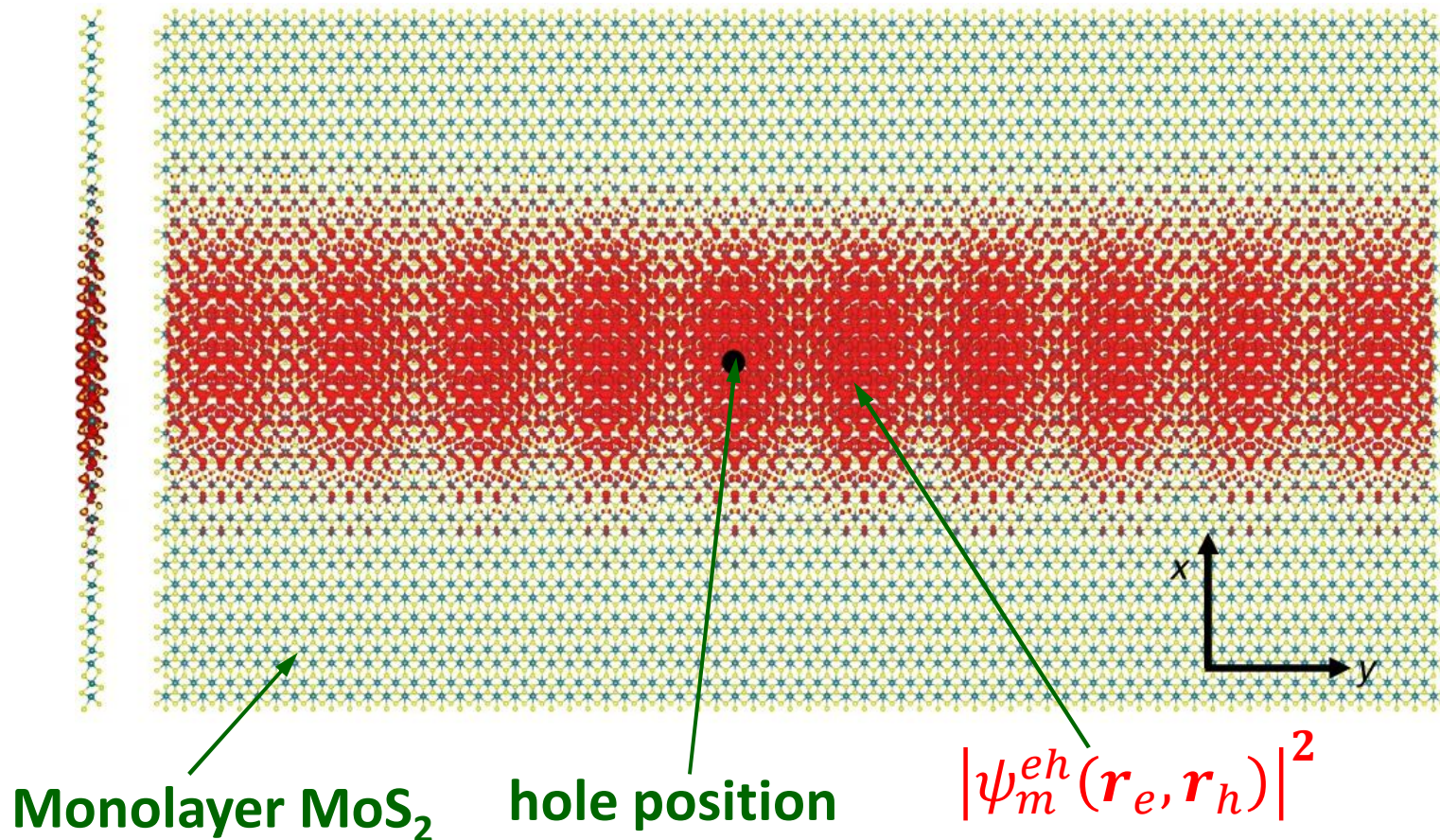
Electron-hole eigenstates:

$$\psi_m^{eh}(\mathbf{r}_e, \mathbf{r}_h) = \sum_{ia} X_{ia}^m \psi_i^{KS}(\mathbf{r}_h) \psi_a^{KS}(\mathbf{r}_e) + Y_{ia}^m \psi_i^{KS}(\mathbf{r}_e) \psi_a^{KS}(\mathbf{r}_h)$$

Neutral excitations: Bethe-Salpeter equation

Electron-hole eigenstates:

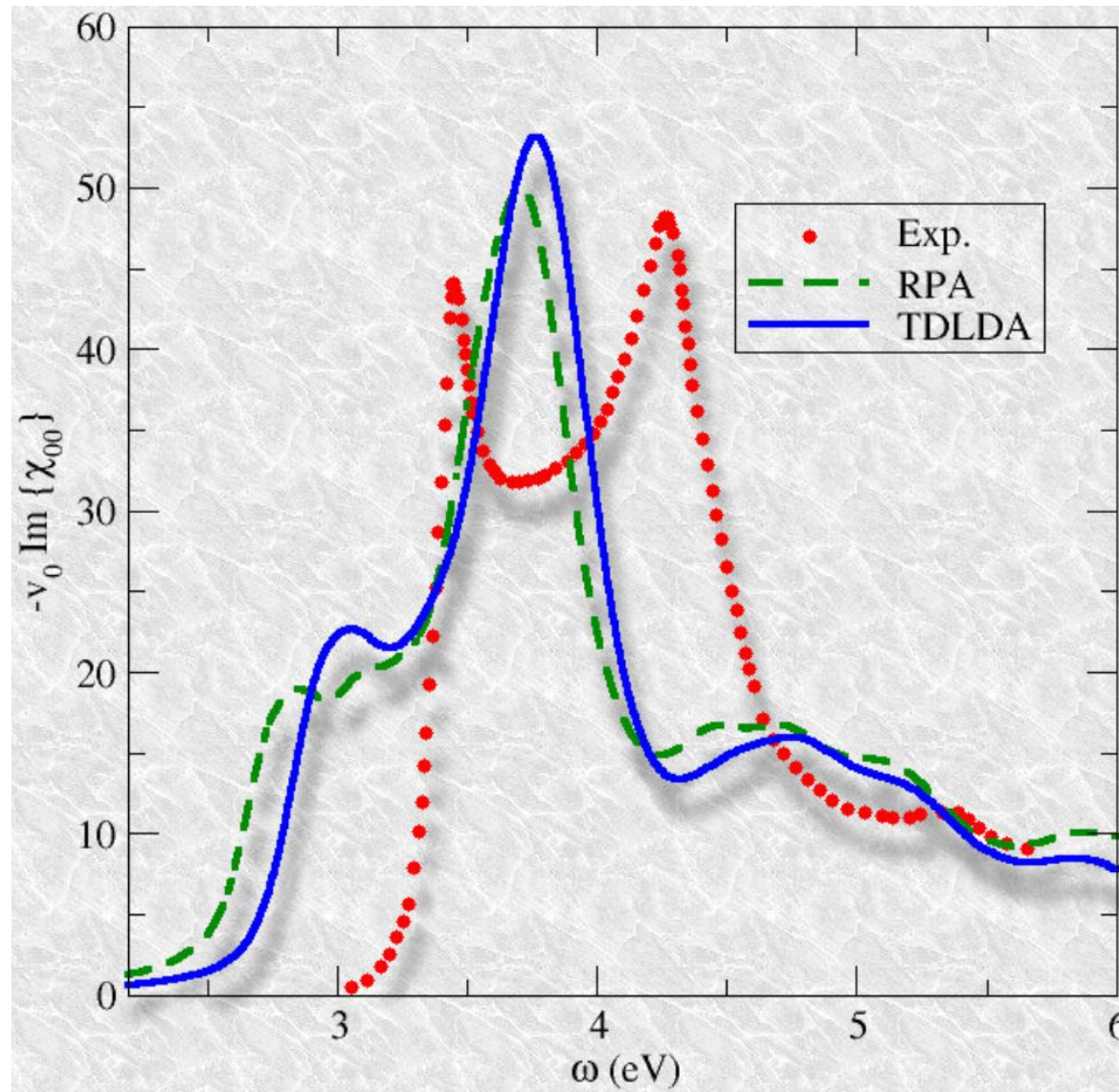
$$\psi_m^{eh}(\mathbf{r}_e, \mathbf{r}_h) = \sum_{ia} X_{ia}^m \psi_i^{KS}(\mathbf{r}_h) \psi_a^{KS}(\mathbf{r}_e) + Y_{ia}^m \psi_i^{KS}(\mathbf{r}_e) \psi_a^{KS}(\mathbf{r}_h)$$



Varsano *et al.*, Nature Nanotech. **15**, 367 (2020)

Neutral excitations: Bethe-Salpeter equation

Optical absorption spectrum of Si:



Neutral excitations: Bethe-Salpeter equation

Optical absorption spectrum of Si:

