Advanced Materials Modeling

Center for Energy Science and Technology (CEST)
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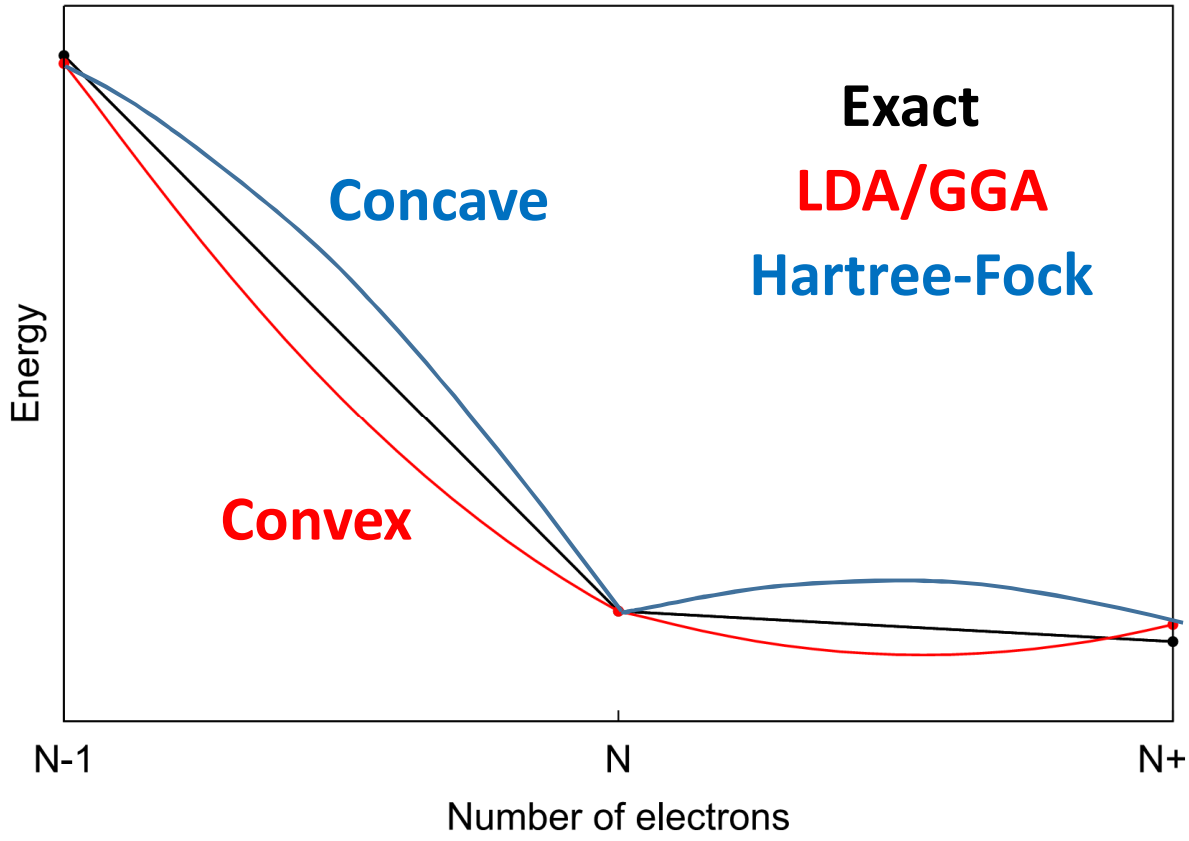
Approximate functionals

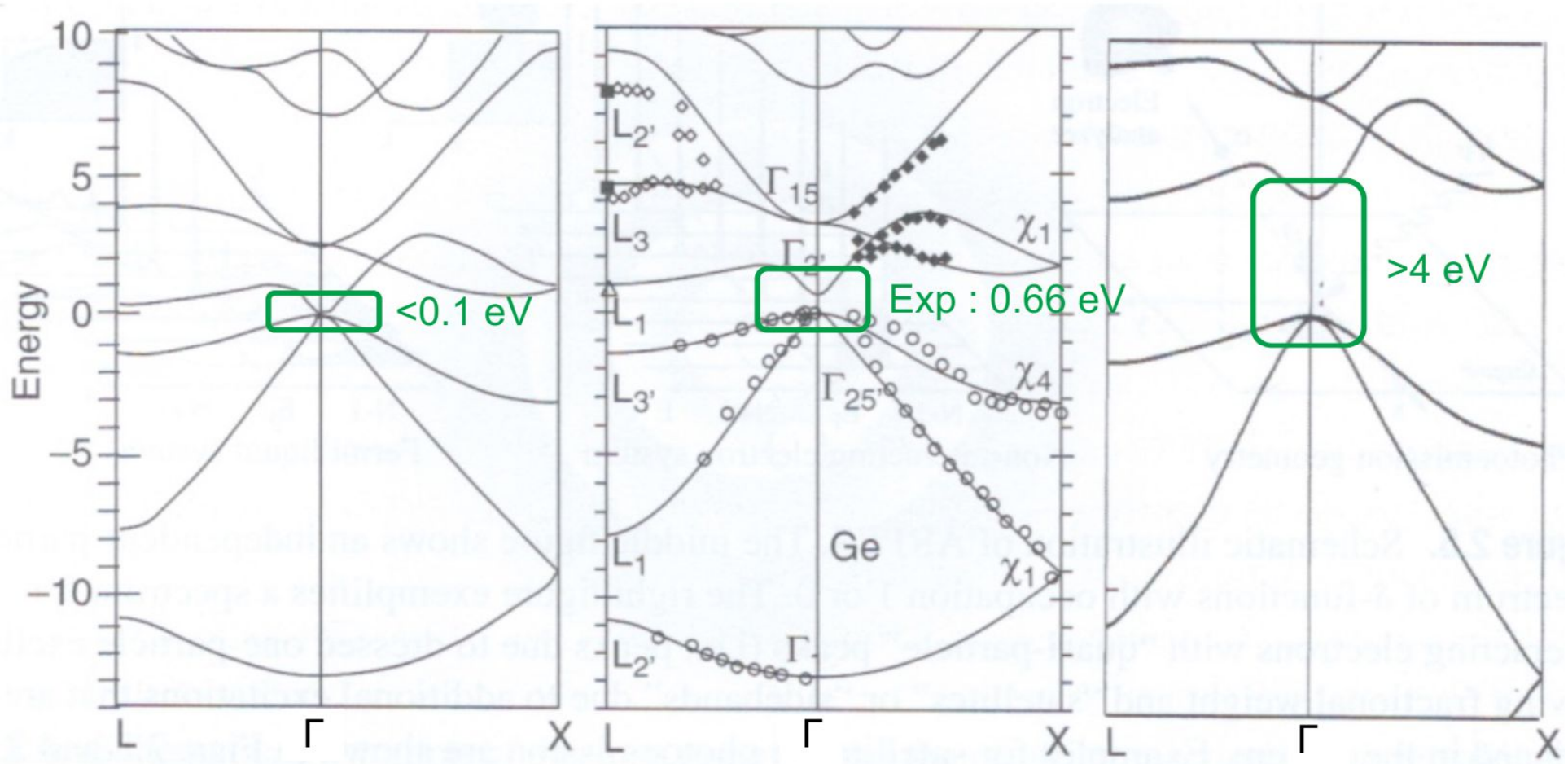
- **Dependence $E(N)$ for an approximate functional:**



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



LDA

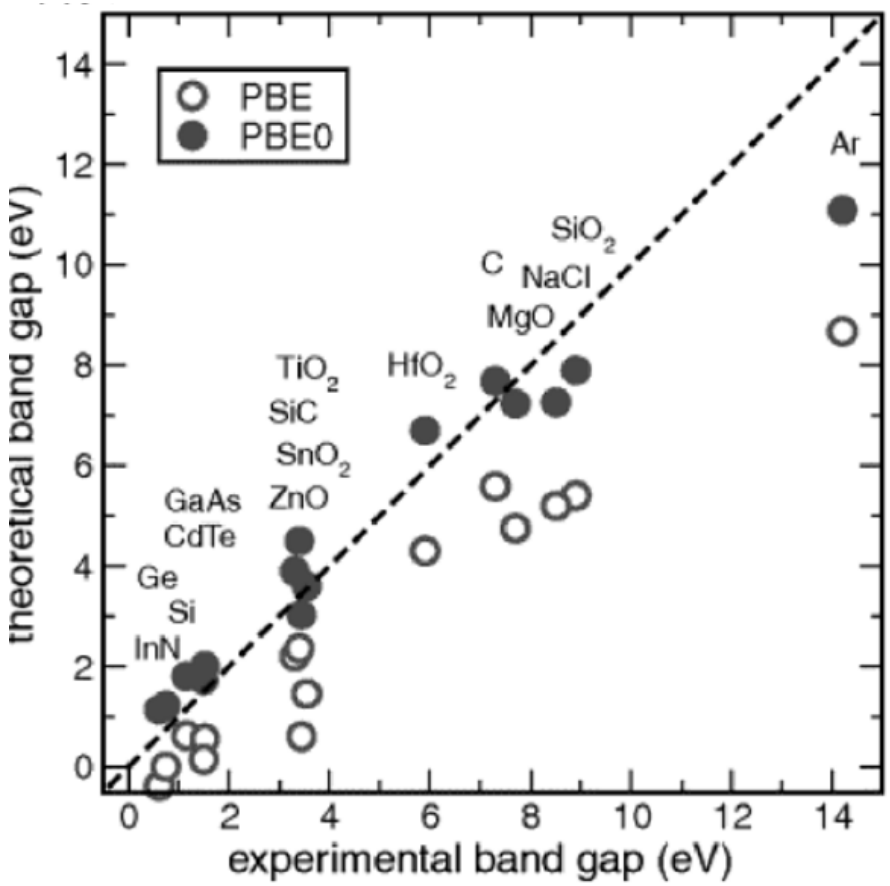
GW & experiment (circles)

Hartree-Fock

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:**

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

- **Kohn-Sham gap:**

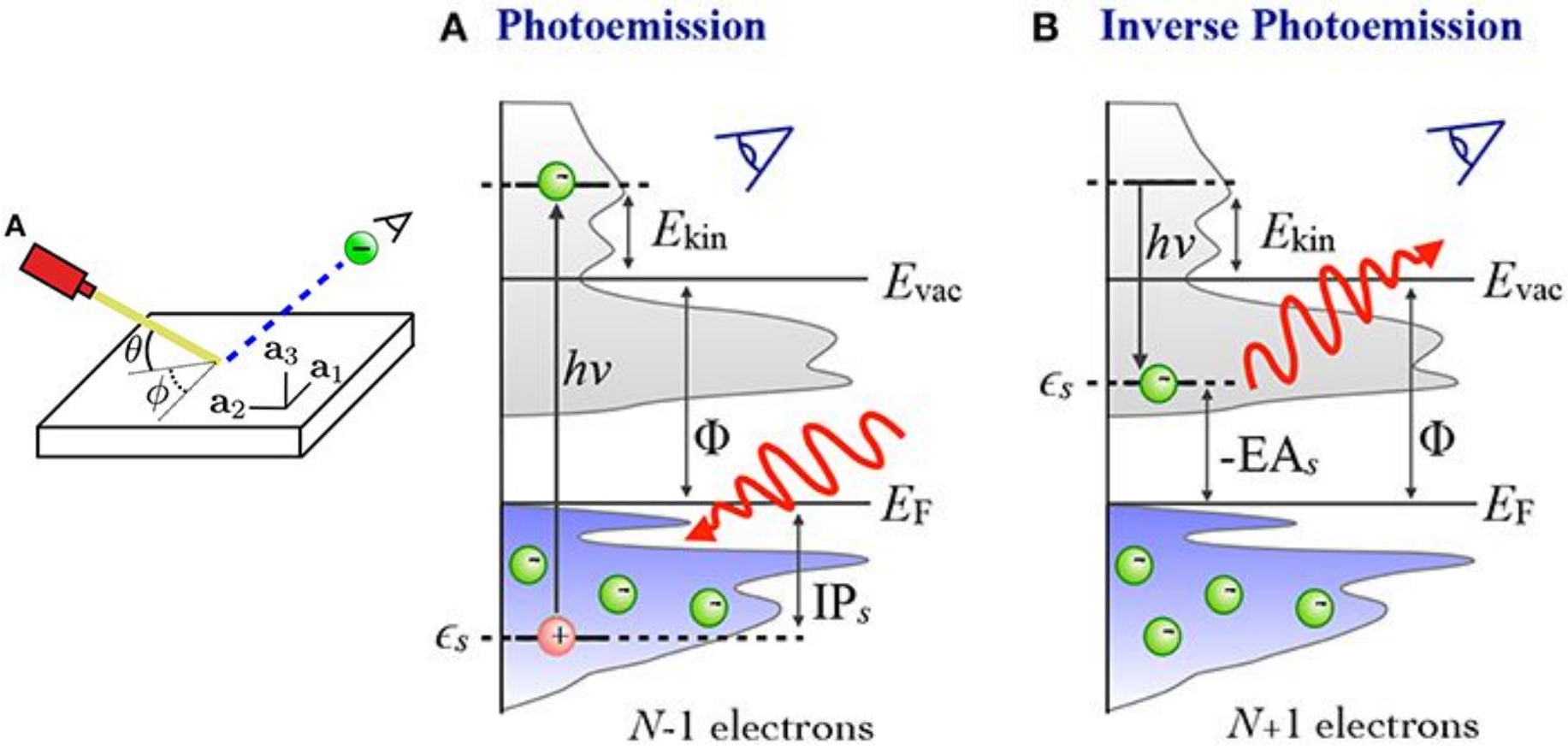
$$E_{gap}^{KS} = \varepsilon_{LUMO}^{M} - \varepsilon_{HOMO}^{M}$$

Are they the same?

No!

Hybrid functionals - partial remedy (parameters!)

Charged excitations: Photoelectron spectroscopy

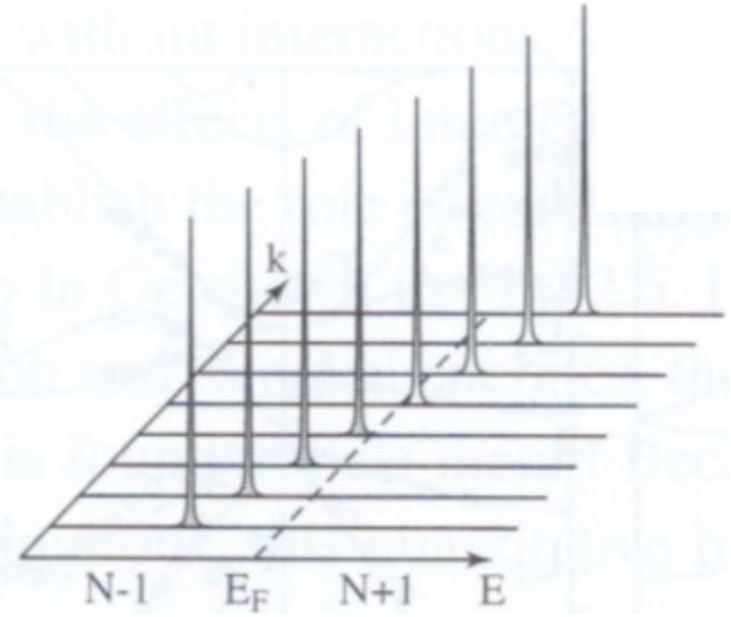


$$\epsilon_s = \begin{cases} E(N) - E(N-1,s), \epsilon_s < \epsilon_{Fermi} \\ E(N+1,s) - E(N), \epsilon_s > \epsilon_{Fermi} \end{cases}$$

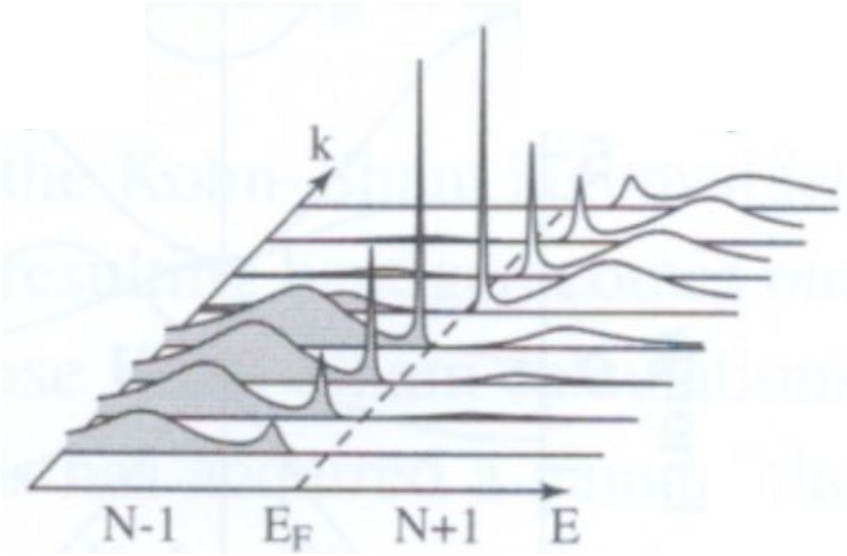
Golze, Dvorak, and Rinke, Front. Chem. 7, 377 (2019)

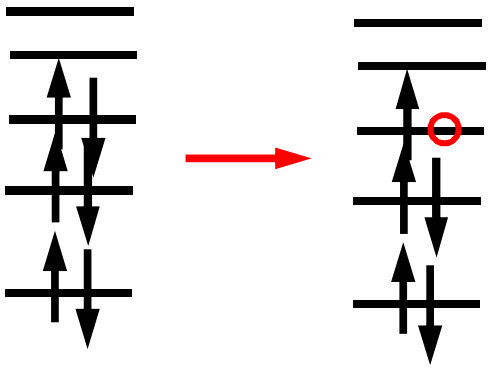
Many-body effects

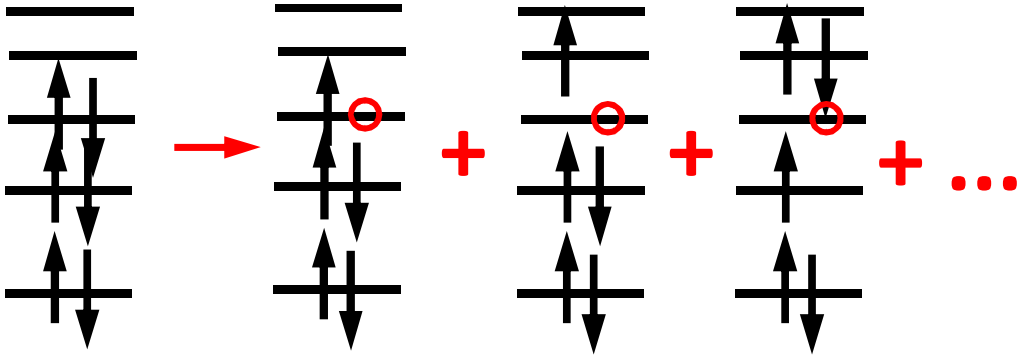
(Effective) non-interacting electrons (HF, DFT, hybrid)



Many-body



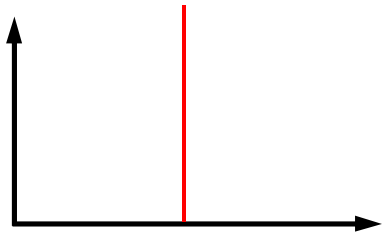


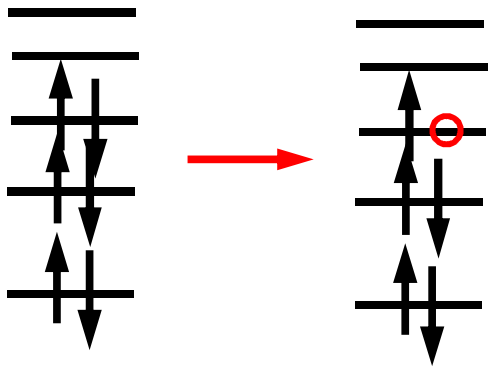


Many-body effects

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

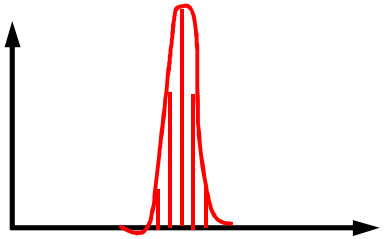
One final configuration → zero spectral line width → infinite lifetime of holes and electrons (stationary states)

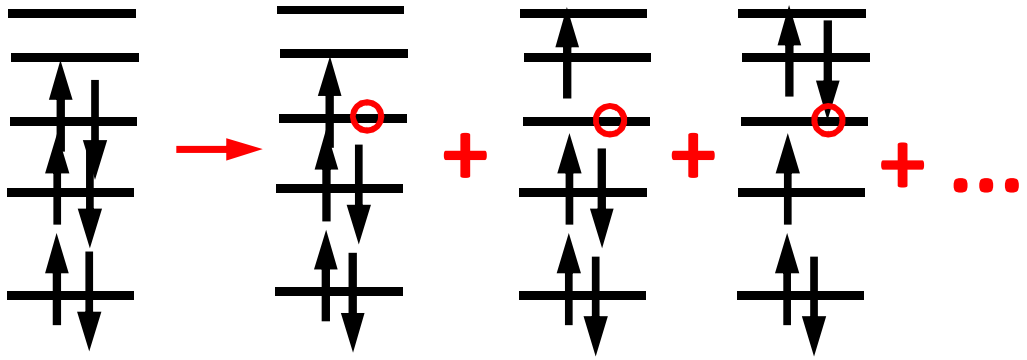




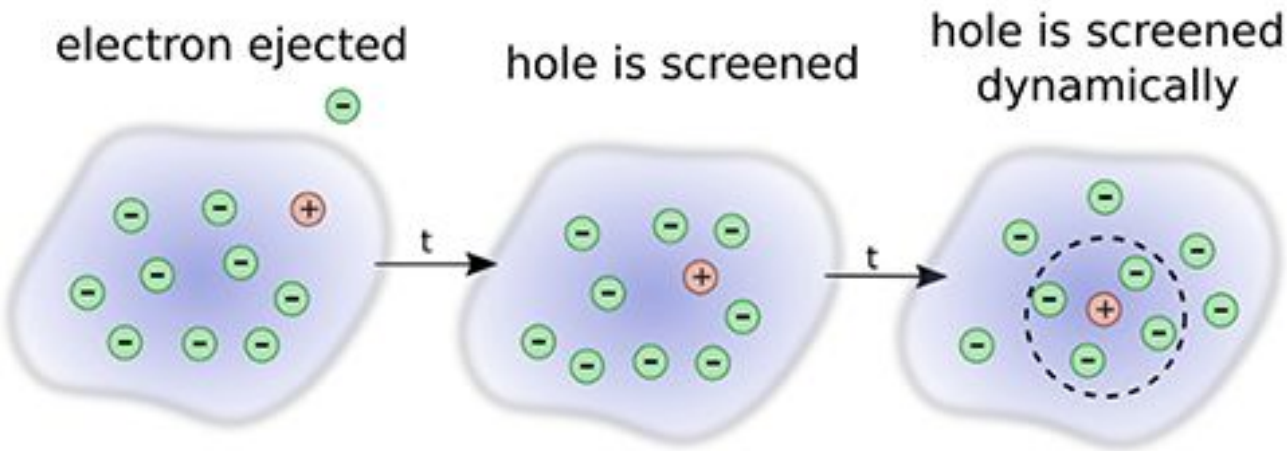
Many-body

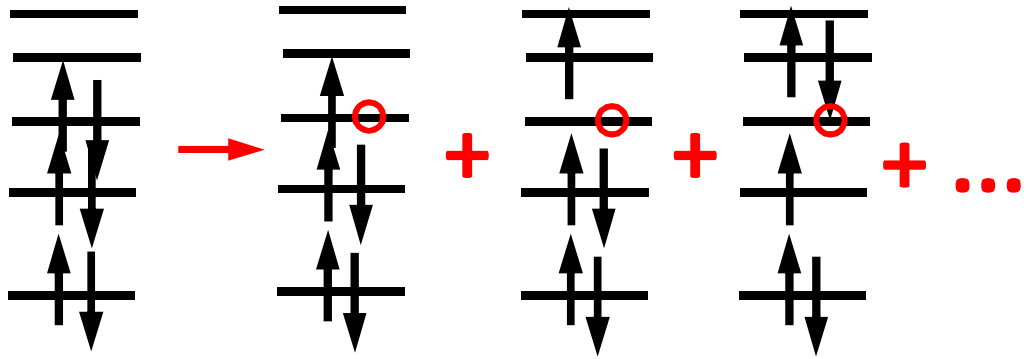
Manifold of near-degenerate configurations → finite spectral line width → finite lifetime of holes and electrons (metastable states)





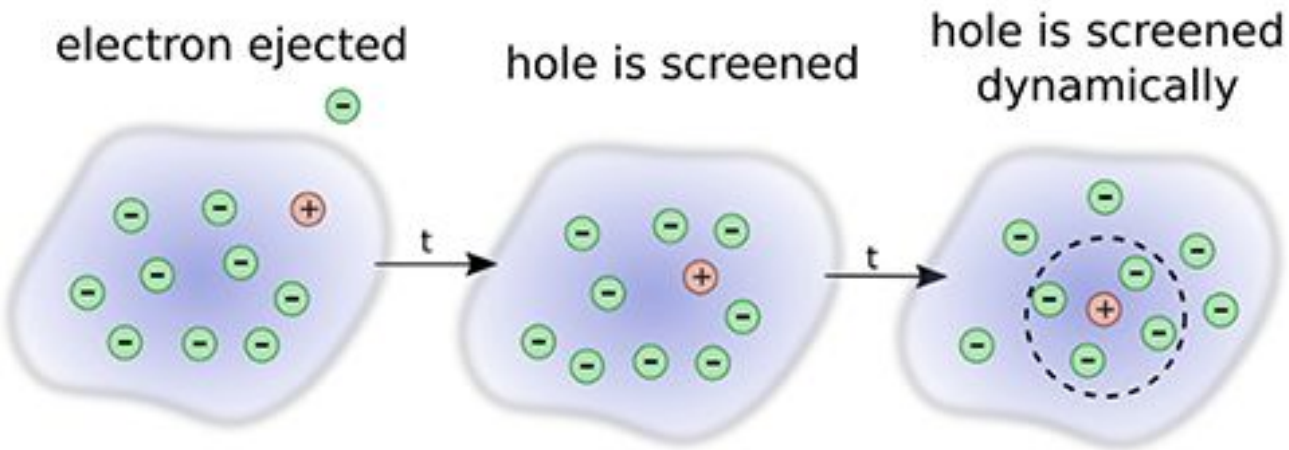
Quasiparticles

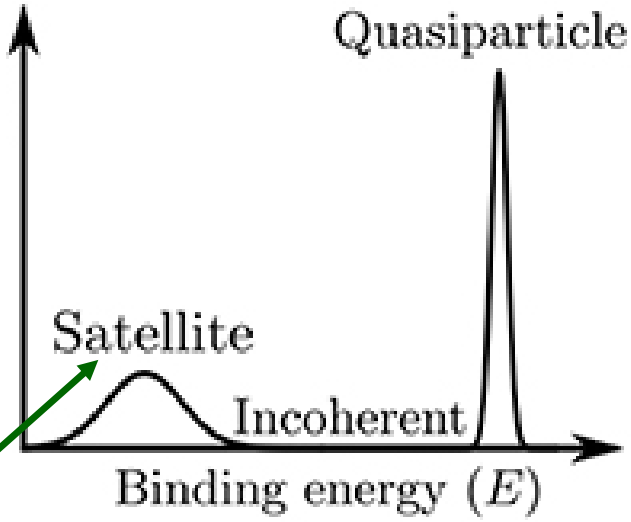




Screening - certain group of excitations up to infinite order (each short-lived (virtual), but overall significant effect)

Quasiparticles





collective excitations (plasmons, magnons)

Many-body perturbation theory

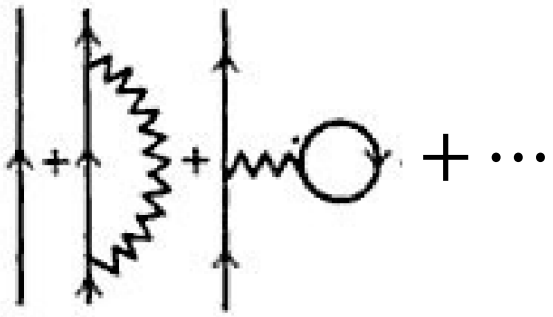
Historically older than DFT (1950s-60s)

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:

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



$+ \cdots$

The Green's function

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

Creation and annihilation operators (Heisenberg picture):

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

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

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

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

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

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

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

The Green's function

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

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

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

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

Total Green's function:

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

with $\hat{T}$ - time-ordering operator

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

The Green's function - connection to spectroscopy

Charged excitations - dynamical process

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

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±1 contribute)

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

Lehman representation:

$$G(\boldsymbol{r}', \boldsymbol{r}, \omega) = \sum_i \frac{\psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r}')}{\omega - \epsilon_i \pm i\eta} \qquad \epsilon_i = \begin{cases} E(N) - E(N-1,i) \\ E(N+1,i) - E(N) \end{cases}$$

exact excitation energies

The Green's function - connection to properties

Galitskii-Migdal formula for total energy:

Fermi energy (electronic chemical potential)

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

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

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

The Green's function - equations

$$i\frac{\partial}{\partial t}\hat{\psi}(\boldsymbol{r},t) = [\hat{\psi}(\boldsymbol{r},t), \hat{H}]$$

equation of motion for any operator

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

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

With the two-particle Green's function:

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

The Green's function - equations

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

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

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

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

The largest contribution (Hartree potential) is separated out:

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

The Green's function - equations

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

The Green's function - equations

Let us denote $\boldsymbol{rt, r't'}$, ... as 1, 2, ...

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

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

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

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

Dyson series: particle propagates and is sometimes scattered by Σ

The Green's function - diagrams

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

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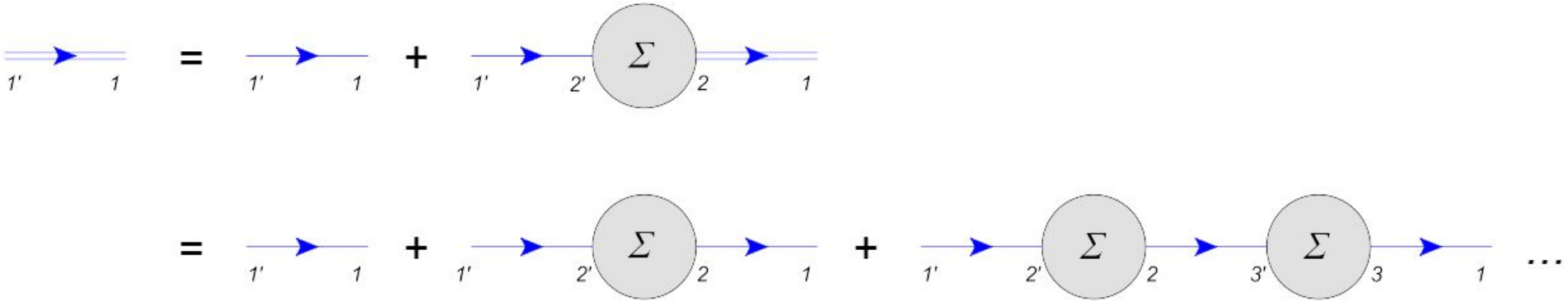
Dyson series: particle propagates and is sometimes scattered by Σ



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:

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

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

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

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

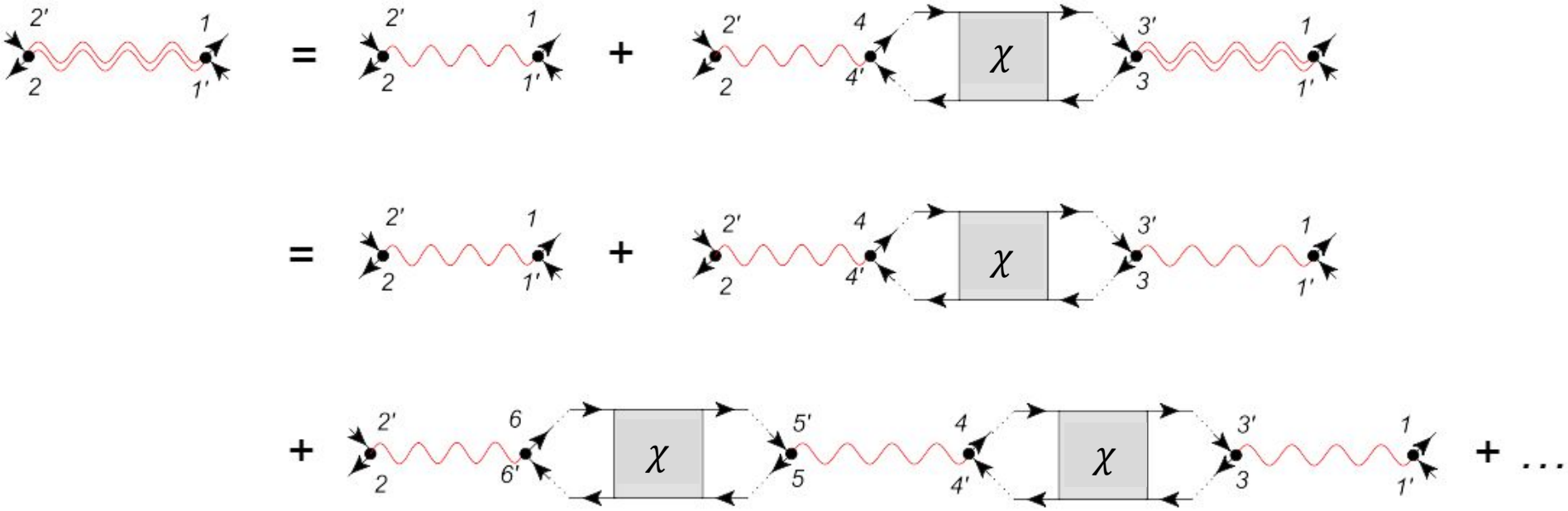
$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int d(4,5,6,7) \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(7,5) \Gamma(6,7,3)$$ **vertex**

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

Golze, Dvorak, and Rinke, Front. Chem. 7, 377 (2019)

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:

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

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

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

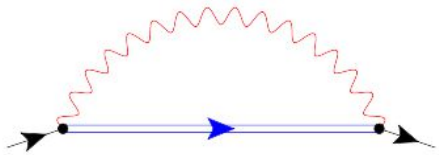
$$\Sigma(1,2) = iG(1,2)v(1,2)$$

Hedin's equations - approximations

The simplest approximation:

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

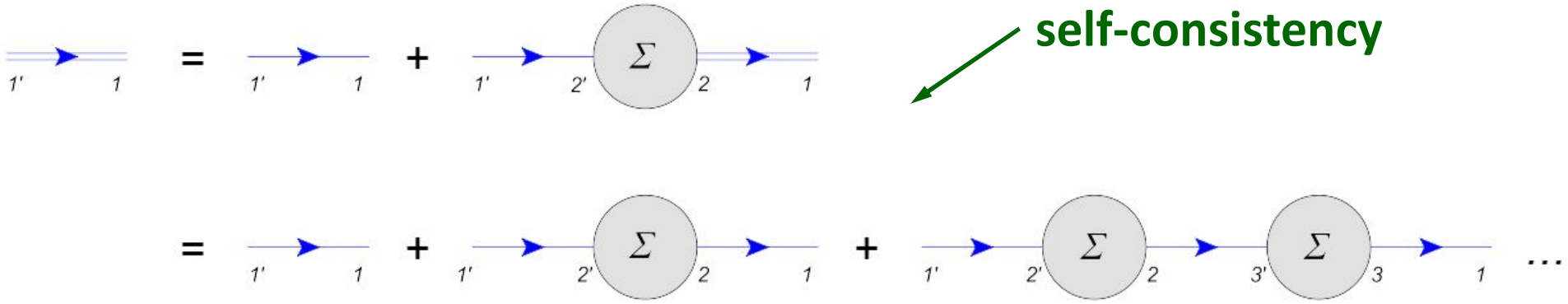
$$\sum_{M,i}|M,i\rangle\langle M,i| = \hat{1}$$



$$\Sigma(1,2) \sim \sum_{i} \frac{\psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

- Fock exchange!

self-consistency



Hedin's equations - approximations

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

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

Hedin's equations - approximations

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

$$\chi(1,2) = -iG(1,2)G(2,1)$$ **random-phase approximation (RPA)**

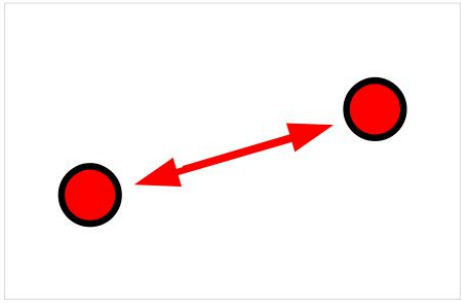
$$W(1,2) = \int d(3)\varepsilon^{-1}(1,3)v(3,2)$$

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

Screened Coulomb interaction *W*

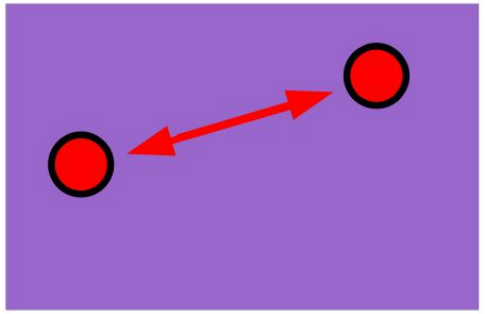
Bare Coulomb interaction (in vacuum):

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



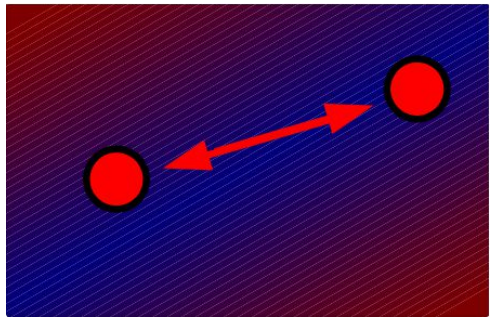
Screened Coulomb interaction (in homogeneous polarizable medium):

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



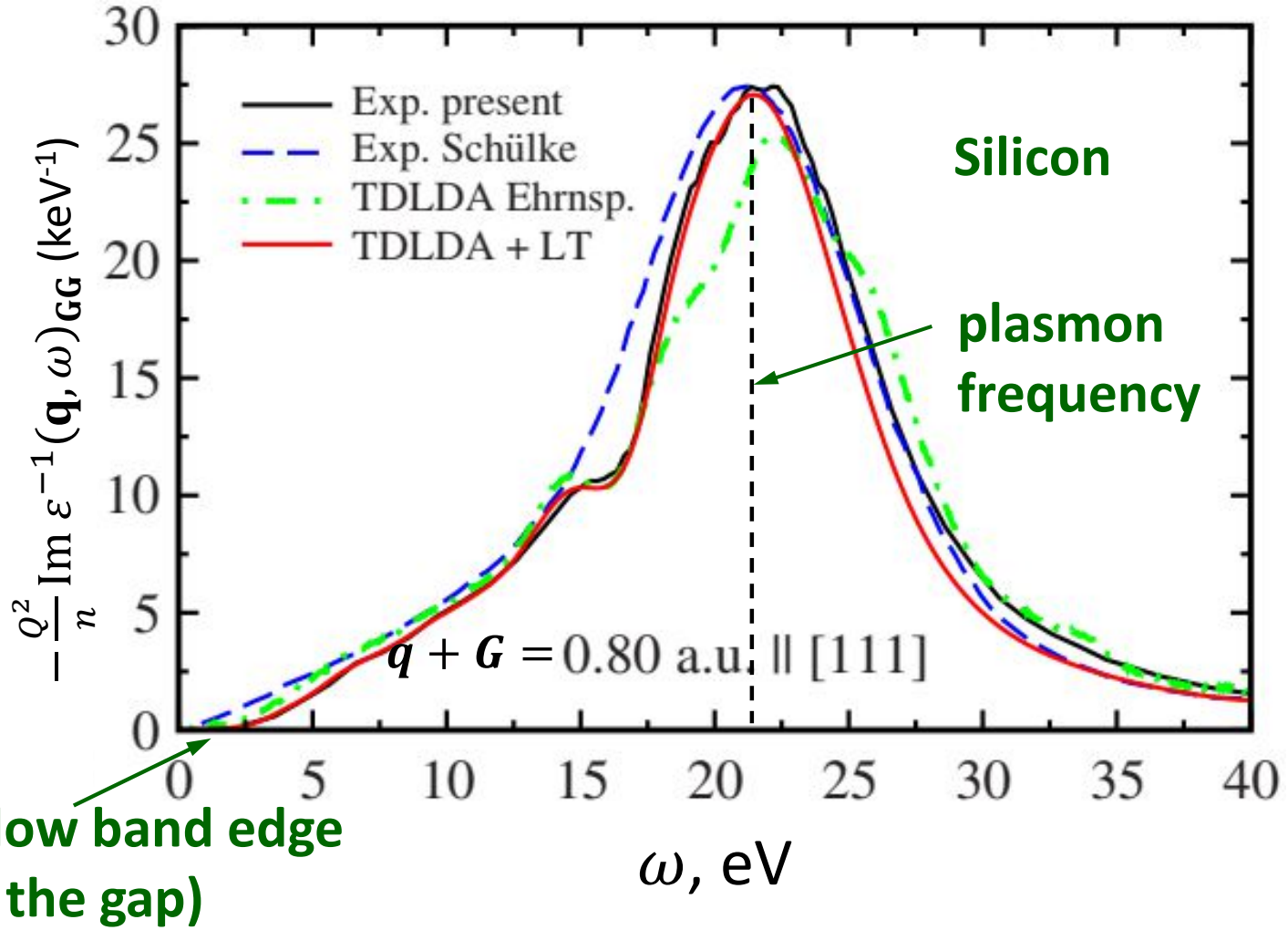
Dynamically screened interaction in a general medium:

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



Screened Coulomb interaction *W*

W **(ε^{-1}) is frequency-dependent, can be measured experimentally:**



below band edge (in the gap)

Weissker *et al.*, Phys. Rev. B 81, 085104 (2010)

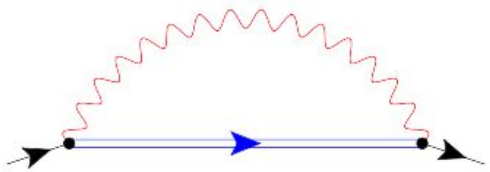
GW as an advanced Hartree-Fock approximation

Hartree-Fock approximation

$$\Sigma(\boldsymbol{r}_1, \boldsymbol{r}_2) =$$

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

- bare exchange

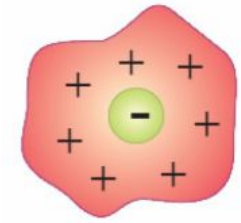


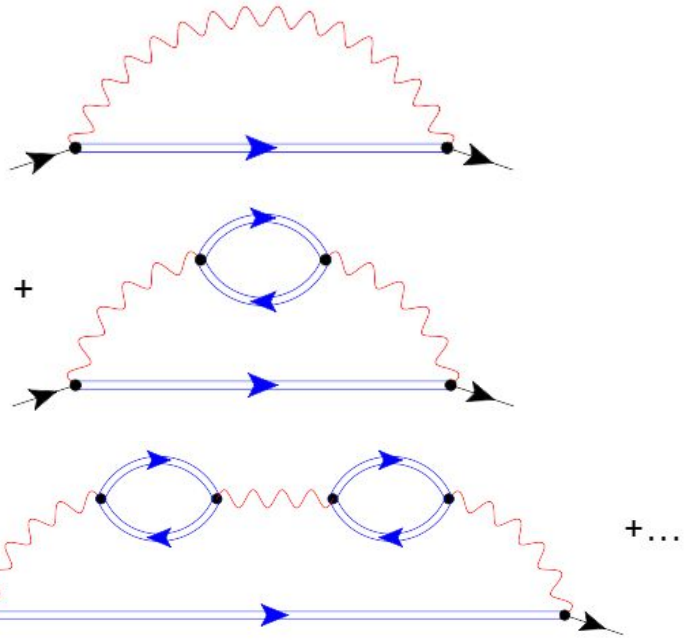
GW approximation

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

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

- HF exchange plus correlation





***GW* is a screened version of HF**

From DFT to *GW*

Dyson's equation for *G* → effective quasiparticle equation:

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

where

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

From DFT to *GW*

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

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

For effectively independent electrons (Kohn-Sham DFT):

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

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

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

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

From DFT to *GW*

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

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

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

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

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

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 ϵ_i^{GW} → quasiparticle self-consistent *GW* (ev*GW*$_0$)

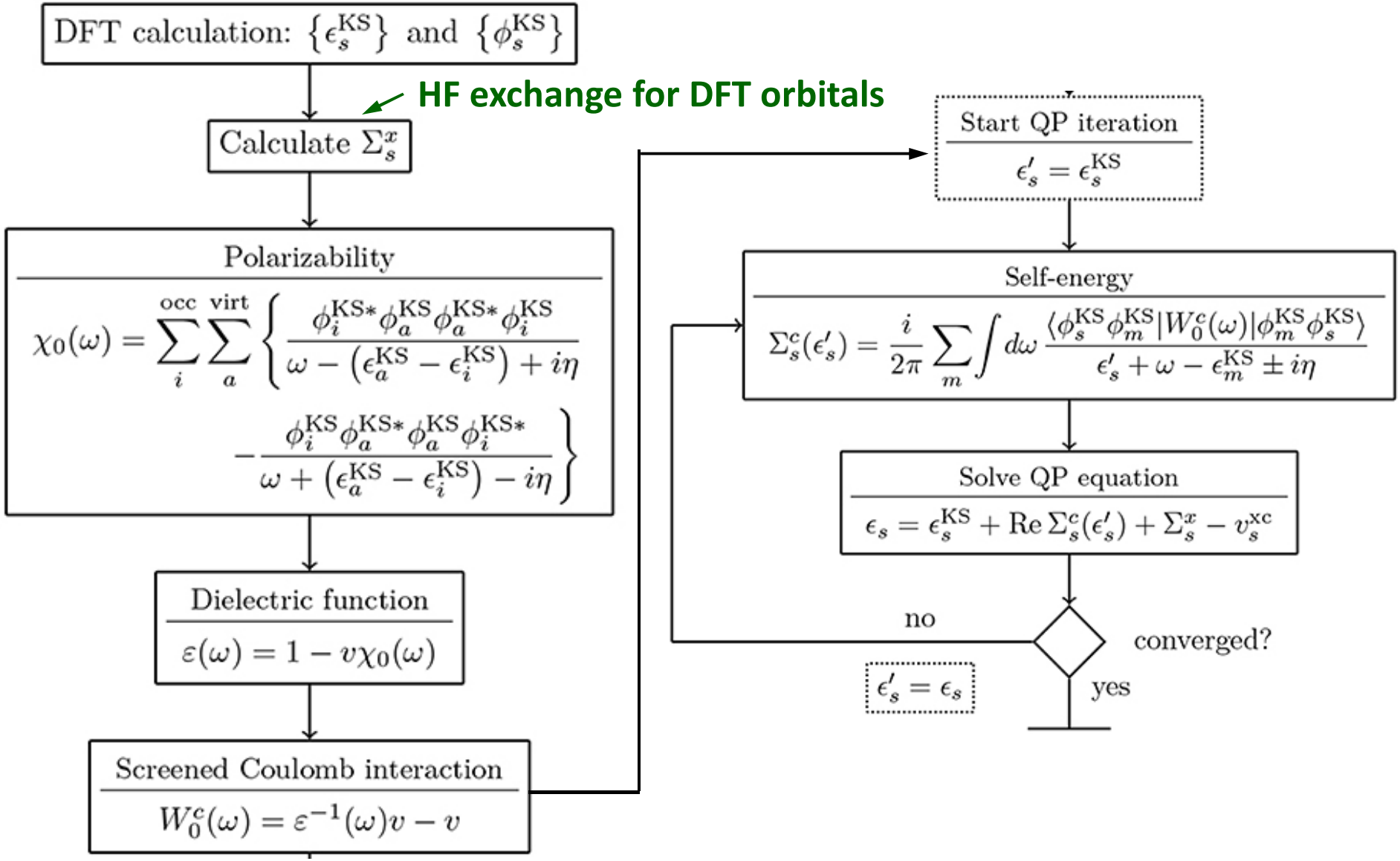
One-shot *GW* (*G*$_0$*W*$_0$):

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

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

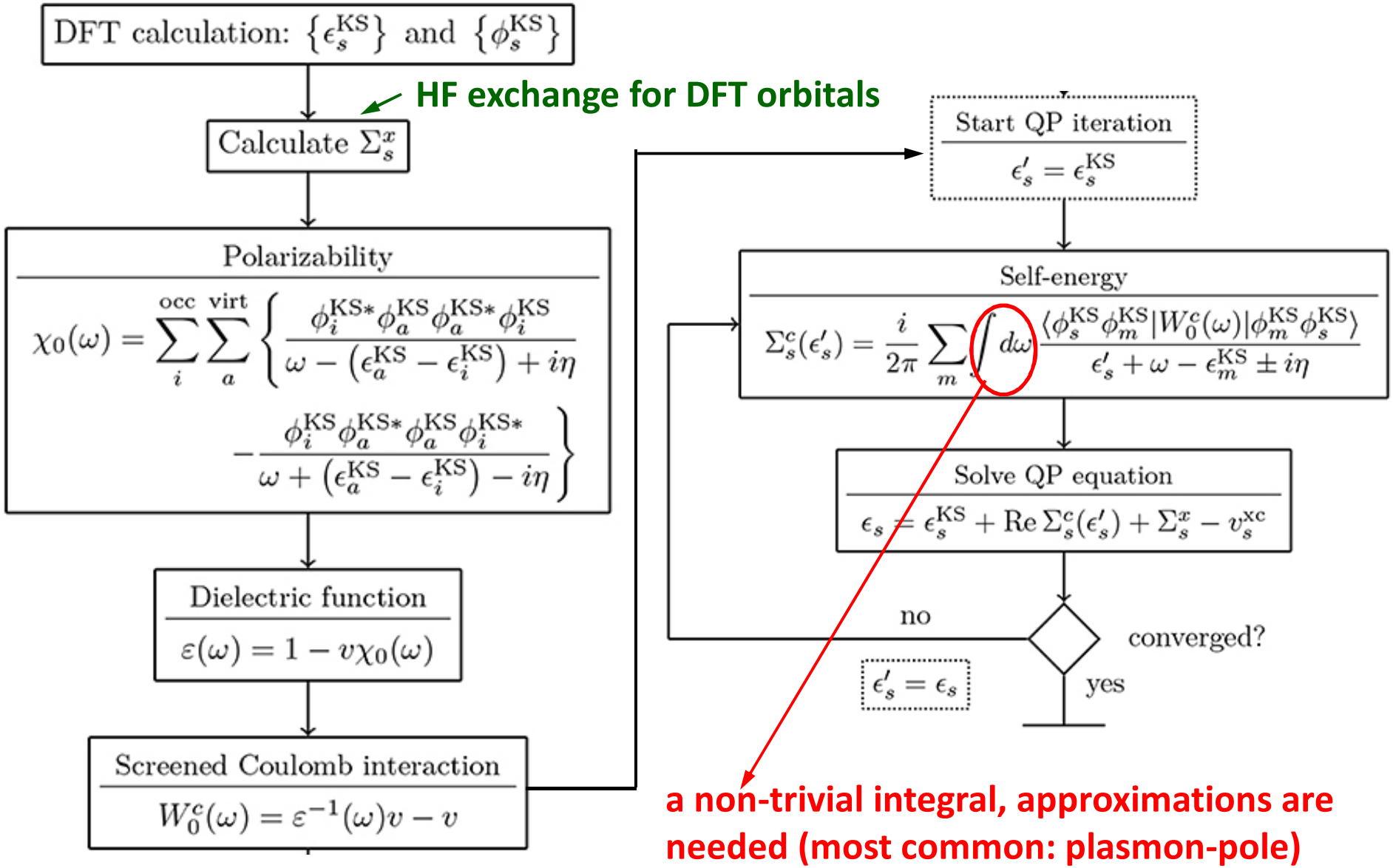
Fully self-consistent *GW*: SCF cycle for ϵ_i^{GW} and ψ_i^{GW}

From DFT to *GW*



Golze, Dvorak, and Rinke, Front. Chem. 7, 377 (2019)

From DFT to *GW*

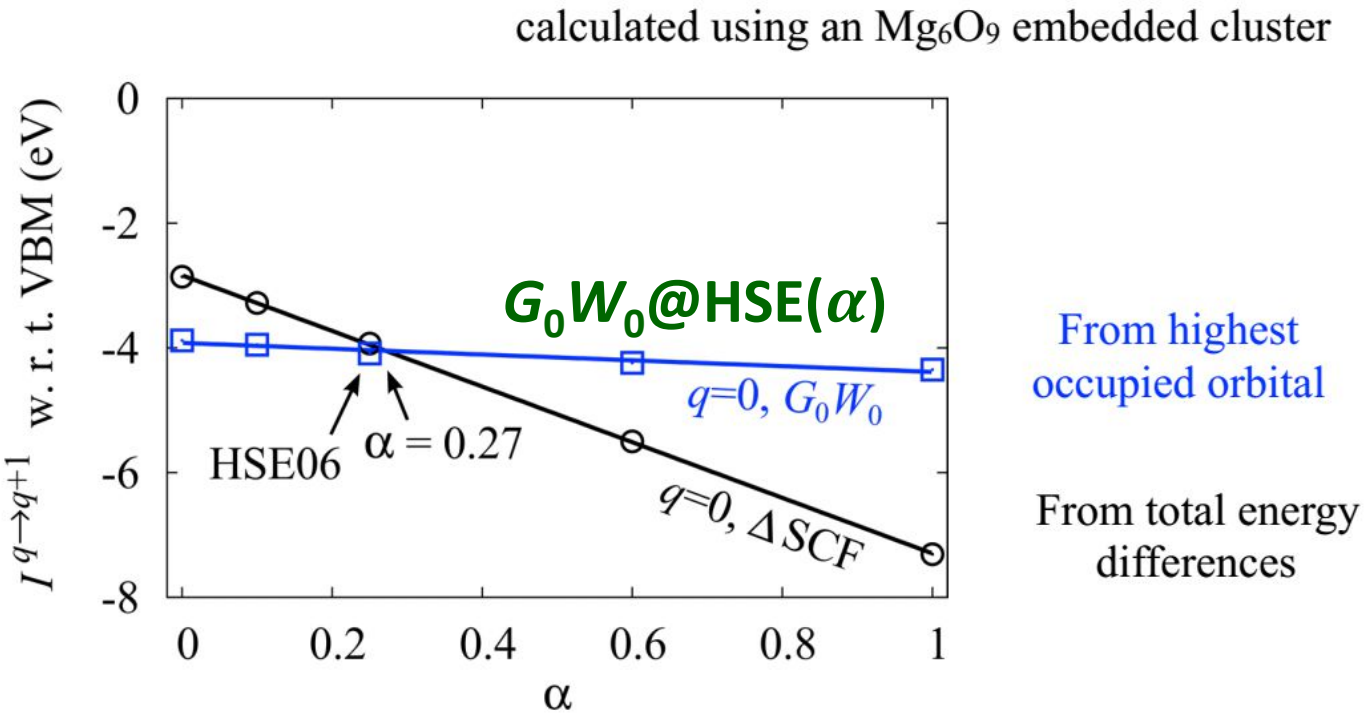


a non-trivial integral, approximations are needed (most common: plasmon-pole)

Golze, Dvorak, and Rinke, Front. Chem. 7, 377 (2019)

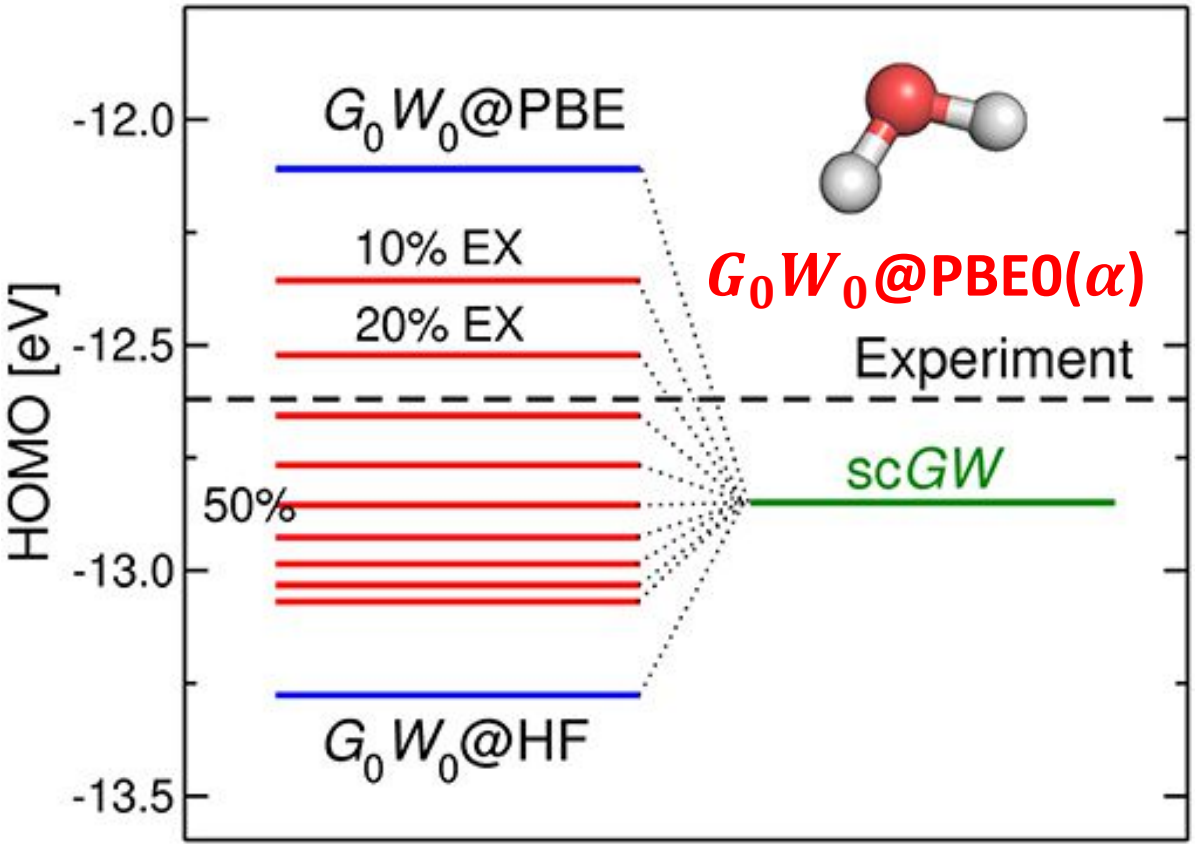
GW: starting-point dependence

Non-self-consistency → dependence on starting KS band structure



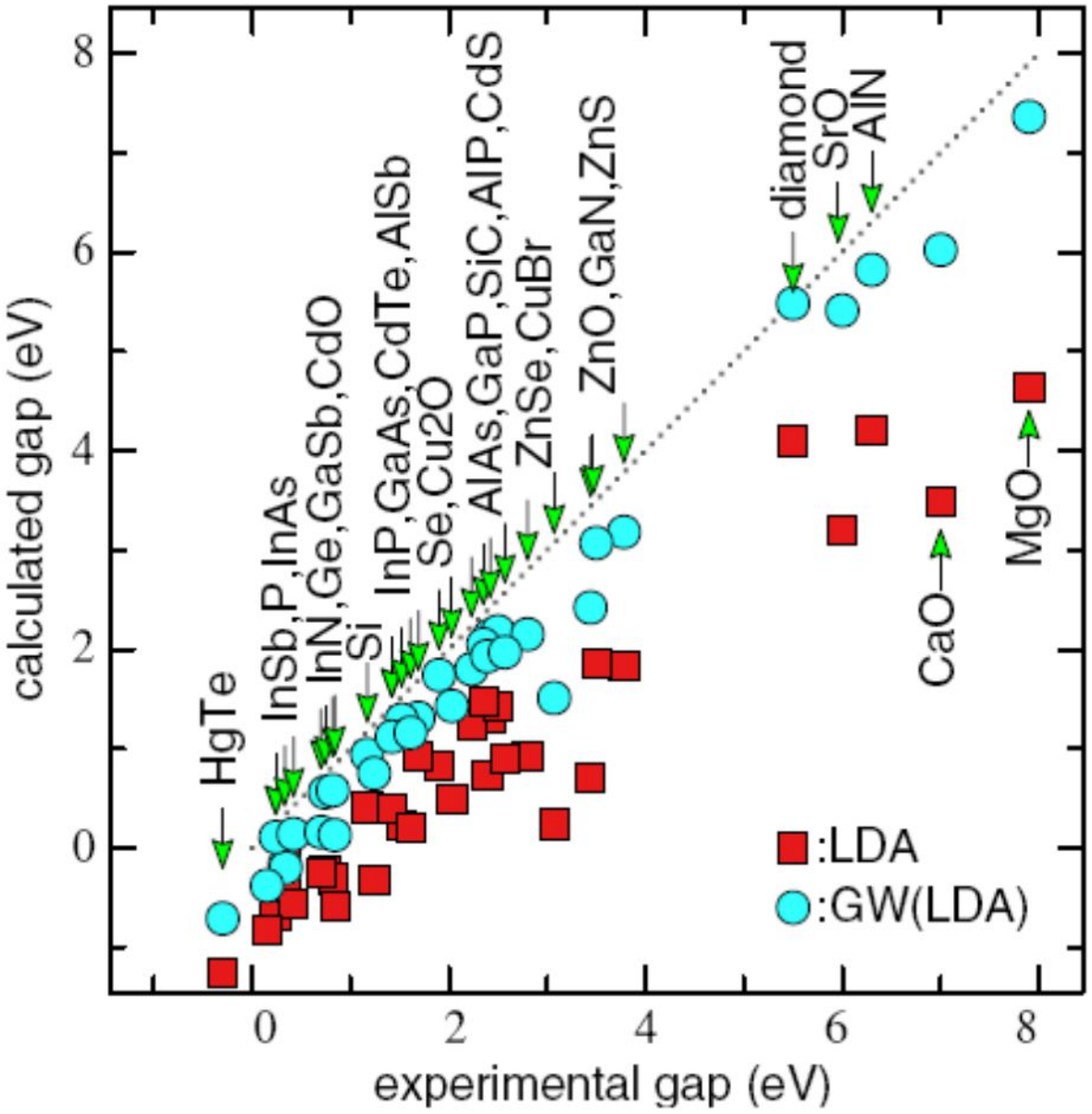
GW: starting-point dependence

Non-self-consistency → dependence on starting KS band structure



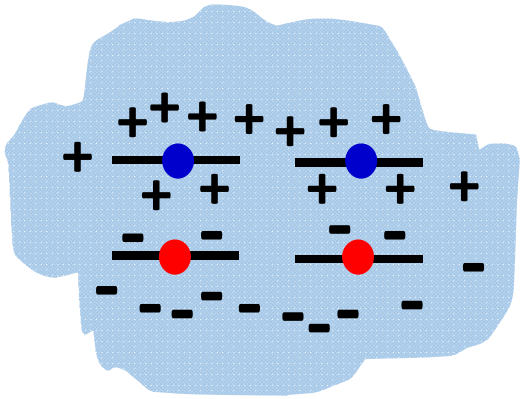
Golze, Dvorak, and Rinke, Front. Chem. 7, 377 (2019)

GW: accurate band structure

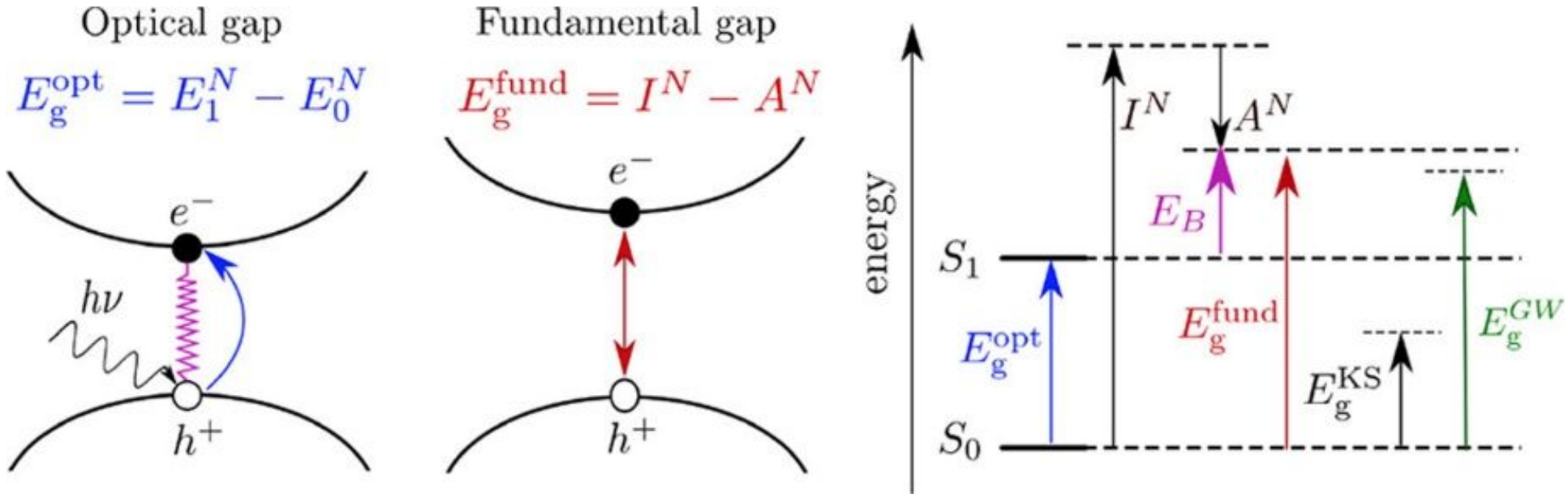


after van Schilfgaarde *et al* PRL **96** 226402 (2008)

Neutral excitations: Bethe-Salpeter equation



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



Blase *et al.*, J. Phys. Chem. Lett. **11**, 7371 (2020)

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 ($\boldsymbol{L(1,2;1',2') = -G_2(1,2,1',2') + G(1,1')G(2,2')}$):

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

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:

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

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

Time-dependent DFT equation (TD-DFT):

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

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

Neutral excitations: Bethe-Salpeter equation

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

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

BSE kernel

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

$$i\Xi(3,5;4,6) \approx v(3,6)\delta(3,4)\delta(5,6) - W(3,4)\delta(3,6)\delta(4,5)$$

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

Neutral excitations: Bethe-Salpeter equation

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

$$i\Xi(3,5;4,6) \approx v(3,6)\delta(3,4)\delta(5,6) - W(3,4)\delta(3,6)\delta(4,5)$$

Taking static limit $W(\omega \to 0)$:

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

(similar to Casida TD-DFT equations)

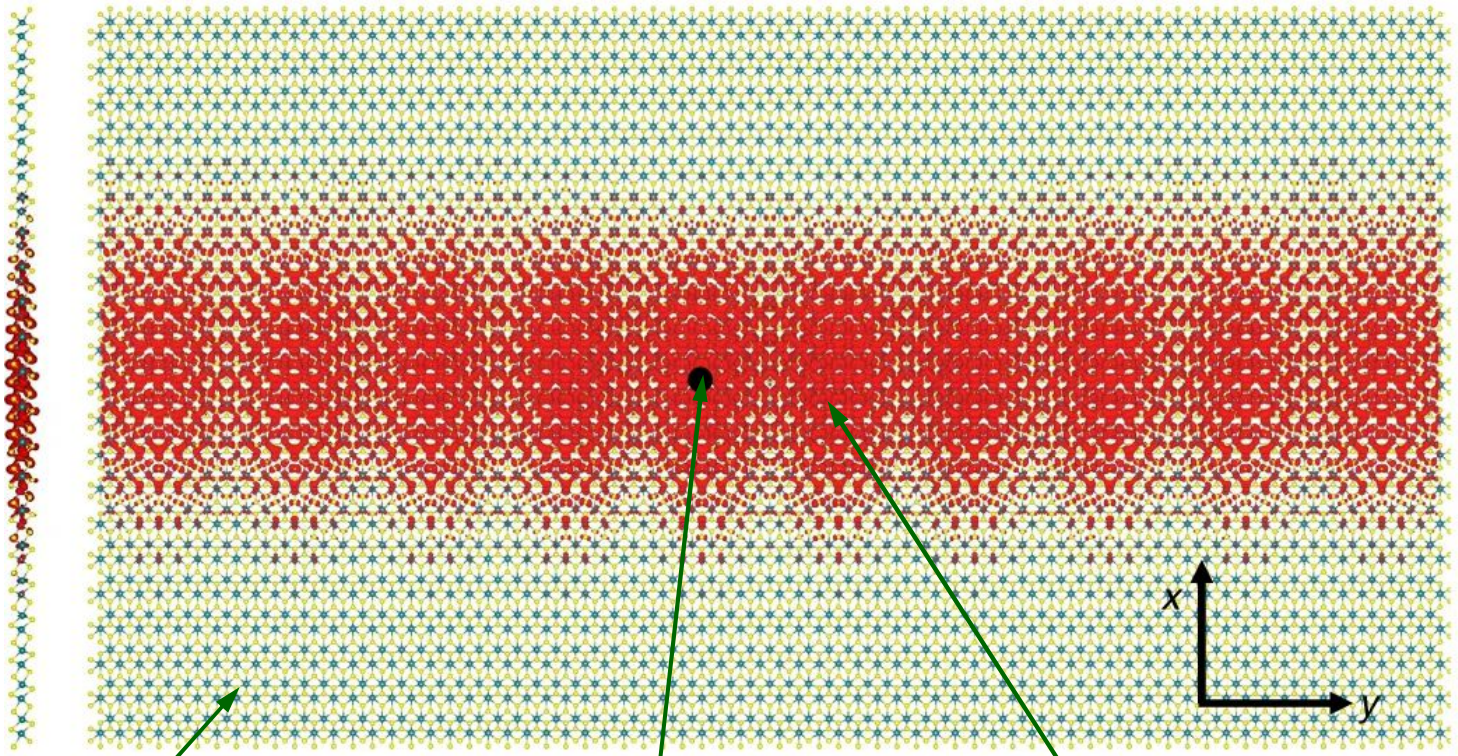
Electron-hole eigenstates:

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

Neutral excitations: Bethe-Salpeter equation

Electron-hole eigenstates:

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

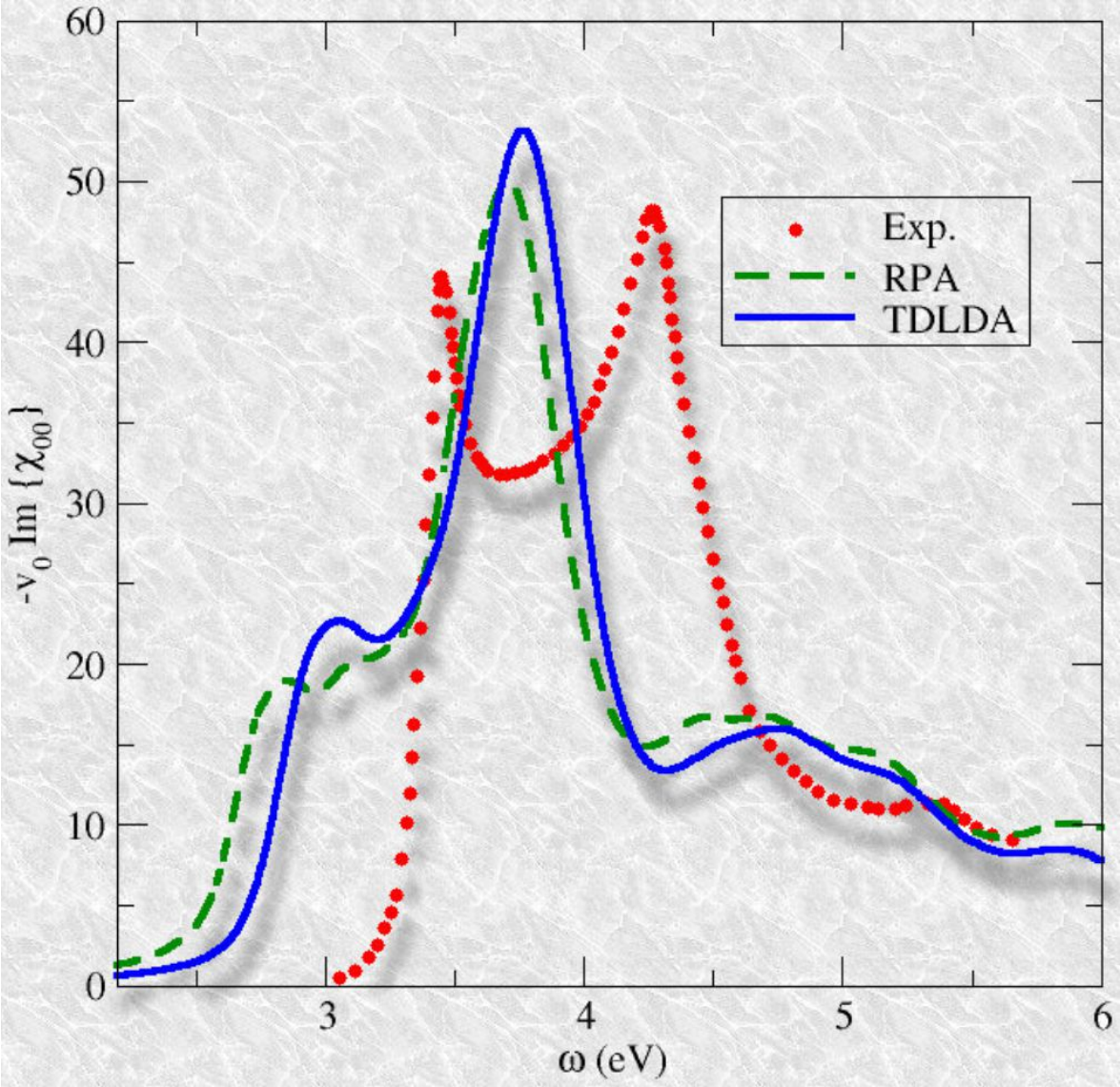


Monolayer MoS_2 **hole position** $\left|\psi_m^{eh}(\boldsymbol{r}_e, \boldsymbol{r}_h)\right|^2$

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

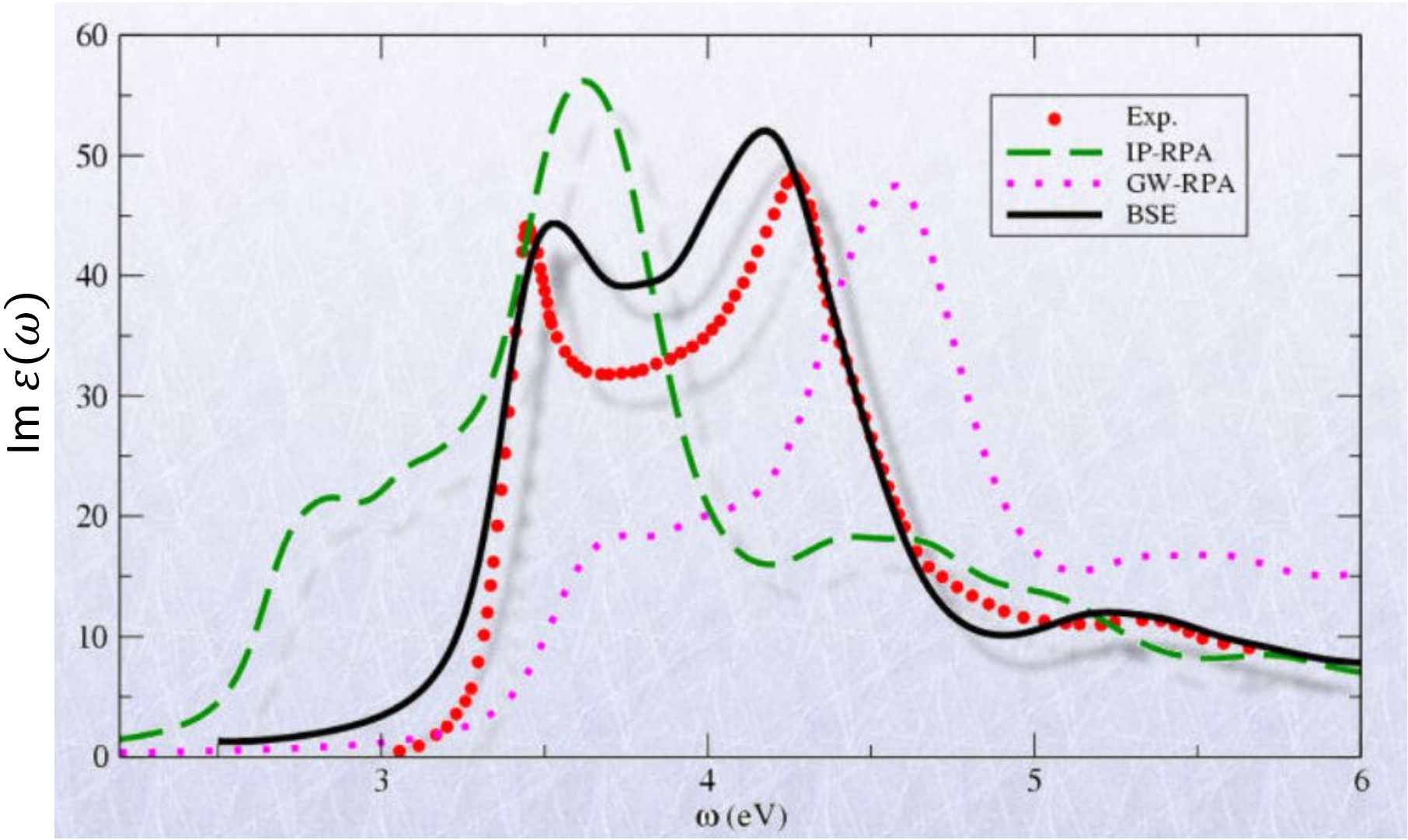
Neutral excitations: Bethe-Salpeter equation

Optical absorption spectrum of Si:



Neutral excitations: Bethe-Salpeter equation

Optical absorption spectrum of Si:



Onida, Reining, Rubio, Rev. Modern Phys. **74**, 601 (2002)