DRIVING THE EXASCALE TRANSITION

SAPIENZA UNIVERSITÀ DI ROMA

the Yambo team

MORE-TEM

Introduction to the GW approximation:

common approximations & pratical implementations

A. Guandalini

ENCCS/MaX workshop

15/03/2024

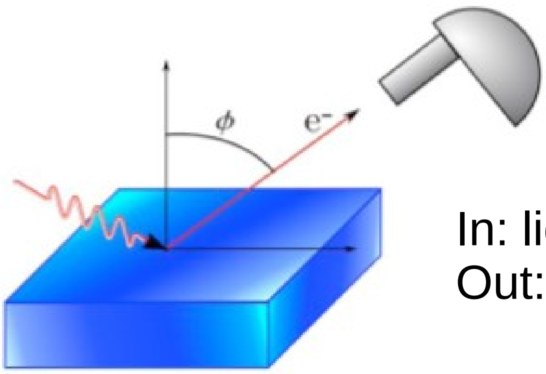
Outline

- Physics of excited states;
- from many-body perturbation theory to the GW approximation;
- GW in practice;
- recent advancement.

Physics of excited states

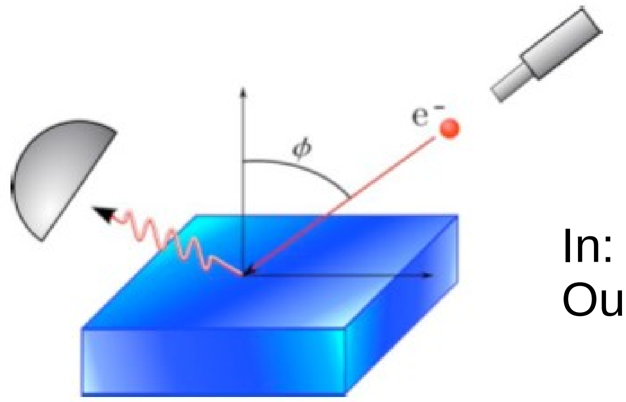
Excited state spectroscopy

Direct photoemission



In: light
Out: electrons

Inverse photoemission

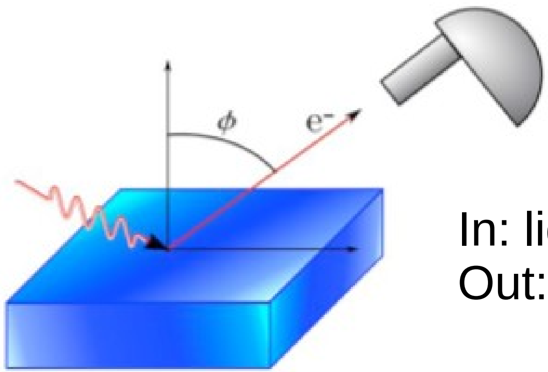


In: electrons
Out: light

[1] Sketch from Nano Lett. 23, 24, 11835–11841 (2023)

Excited state spectroscopy

Direct photoemission



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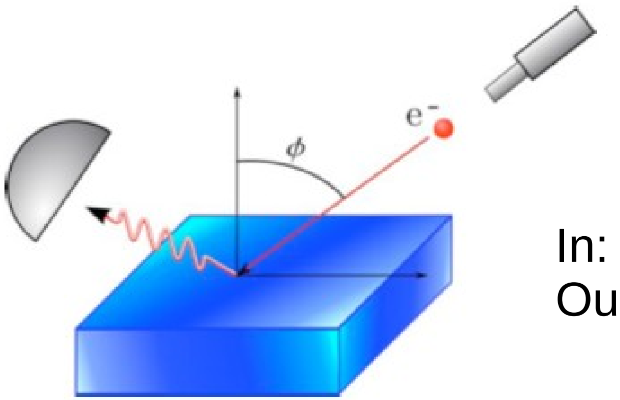
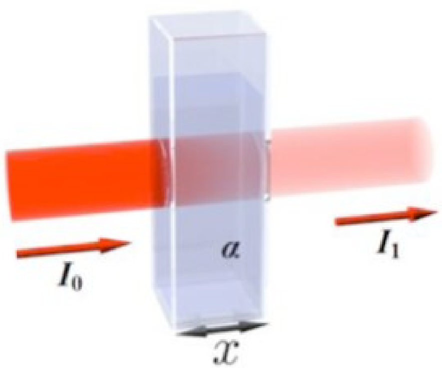


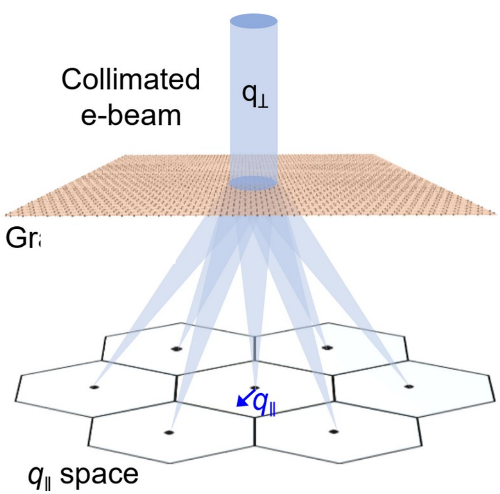
In: electrons
Out: light

Optical absorption



In: light
Out: light

Electron energy loss[1]



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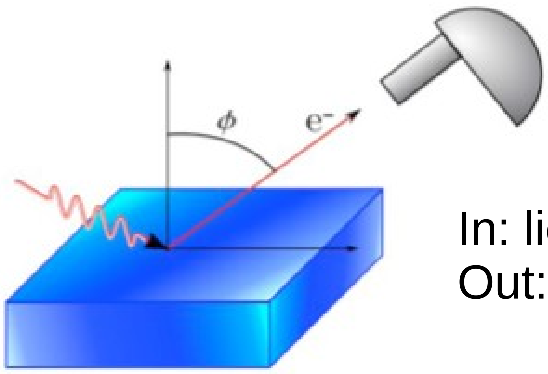
Excited state spectroscopy

Direct photoemission

Inverse photoemission

Charged excitations



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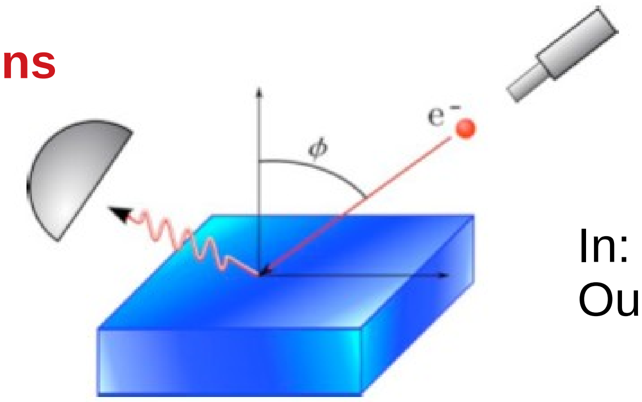
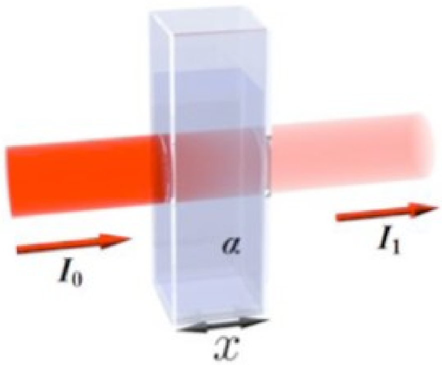


In: electrons
Out: light

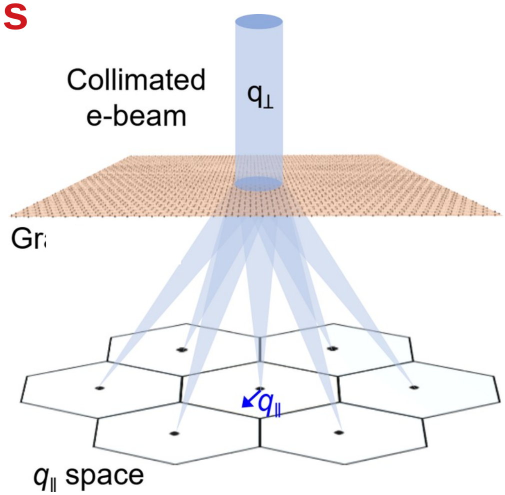
Optical absorption

Electron energy loss[1]

Neutral excitations



In: light
Out: light



In: electrons
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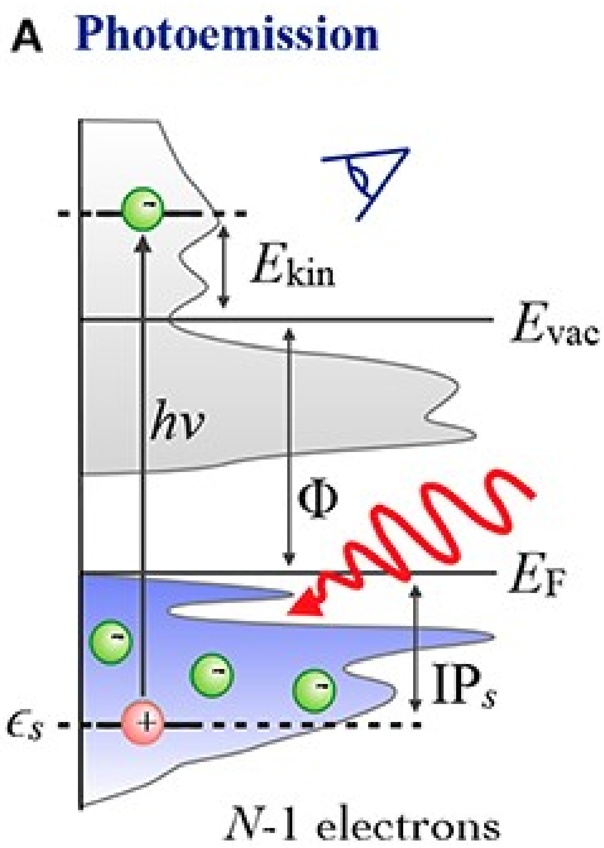
Direct (inverse) photoemission spectroscopy[1]

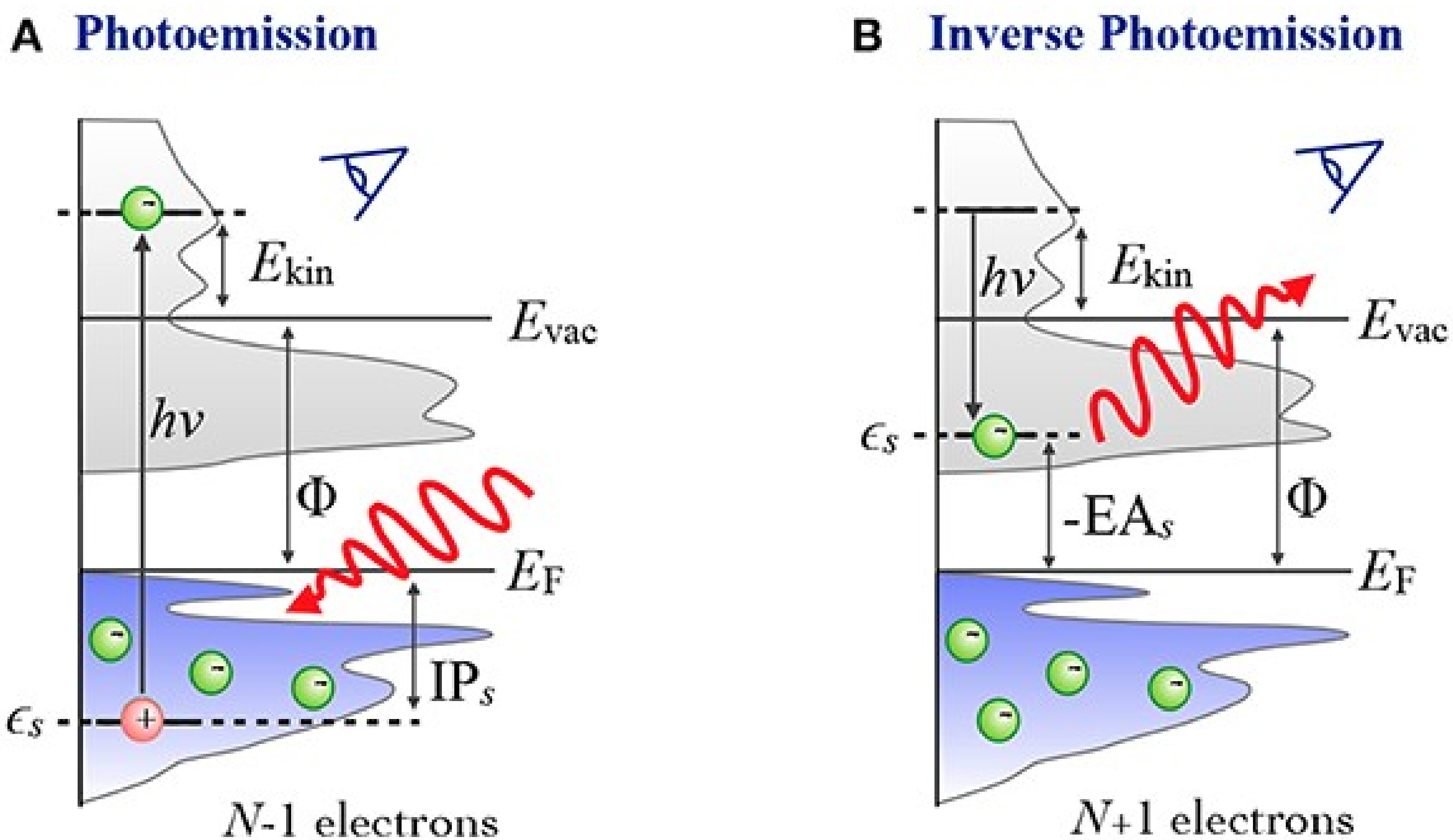


$$E(N) + \hbar\omega = E(N-1) + [\phi_W + E_{\mathrm{kin}}]$$

$$E(N) - E(N-1) = [\phi_W + E_{\mathrm{kin}}] - \hbar\omega$$

[1] Sketch from Front. Chem. 7:377 (2019)

Direct (inverse) photoemission spectroscopy[1]



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$$E(N+1) - E(N) = E_k + \hbar\omega$$

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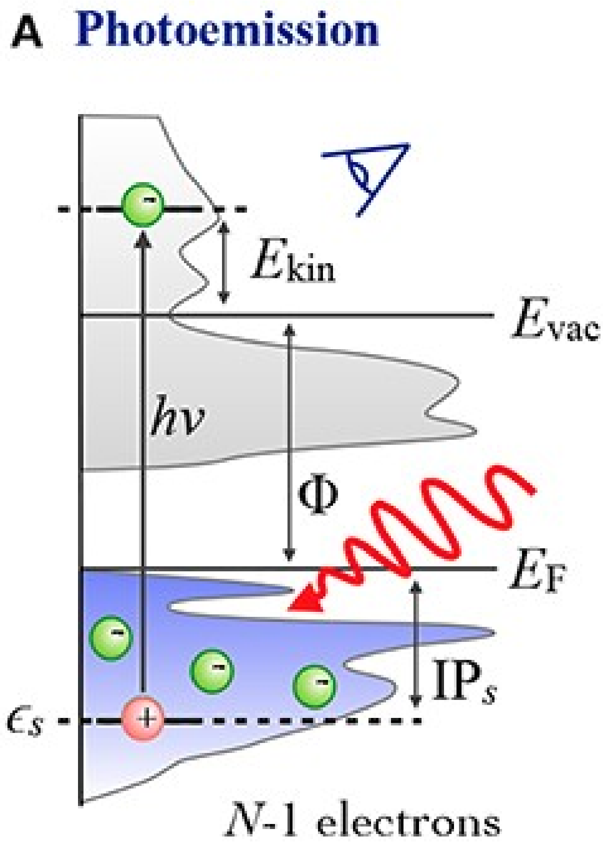
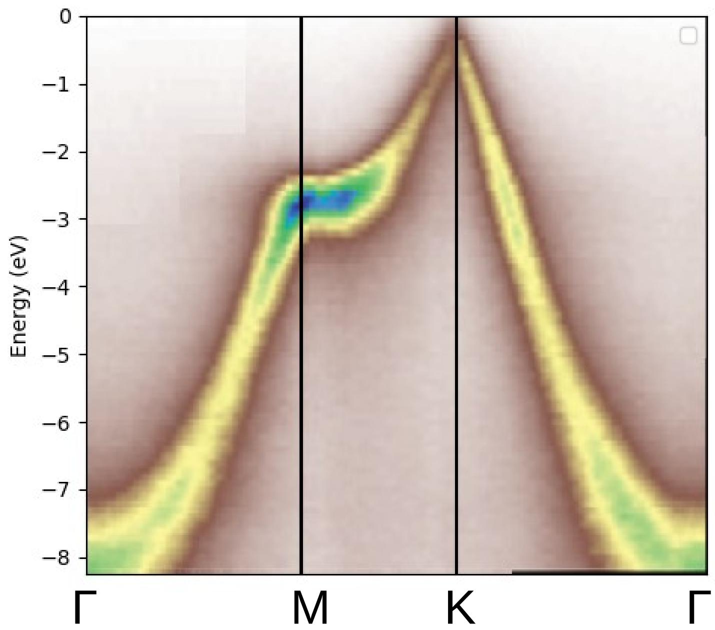
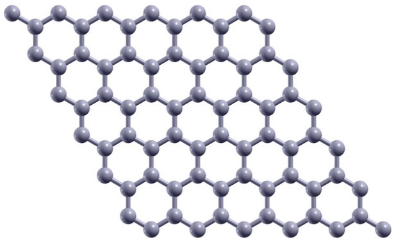
Direct (inverse) photoemission spectroscopy[1]



Angle-resolved photoemission spectroscopy (ARPES) [2]



Graphene



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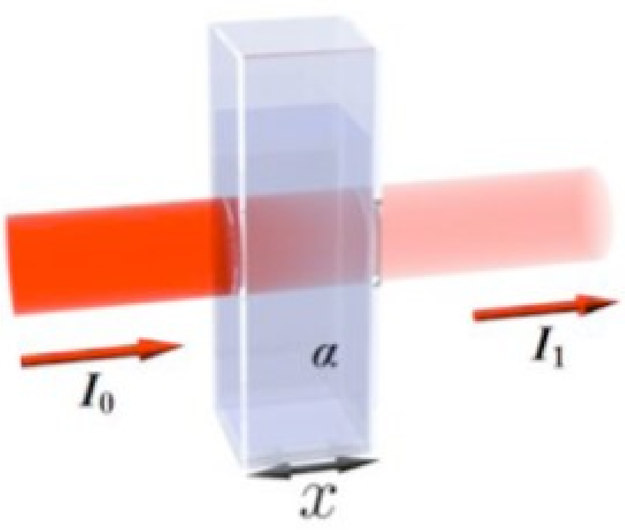
[1] Sketch from Front. Chem. 7:377 (2019); [2] K. R. Knox et al. Phys. Rev. B 84, 115401 (2011)

Optical absorption



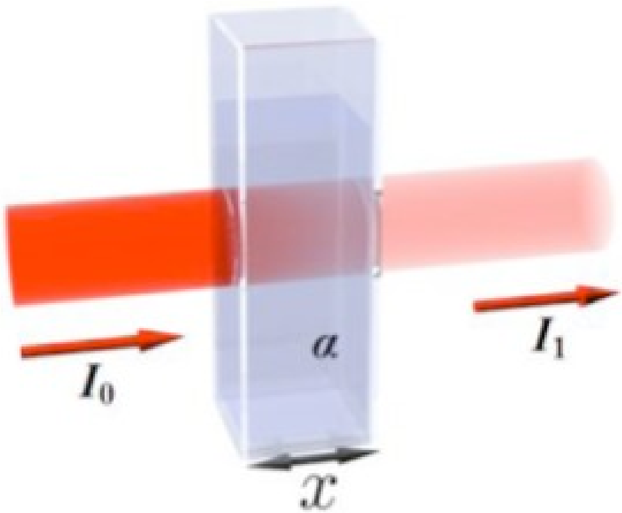
Beer-Lambert law: $I = I_0 e^{-\alpha x}$

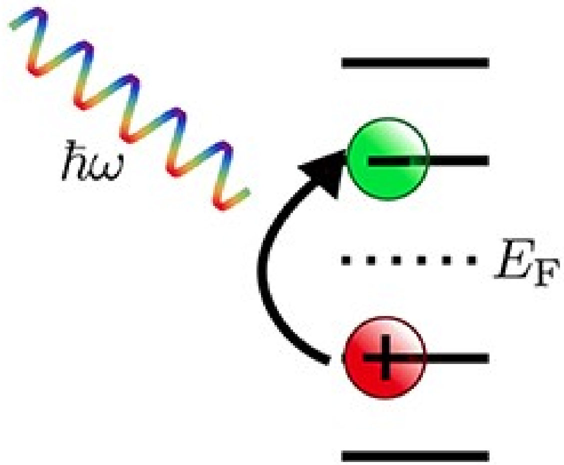
$$\alpha(\omega) \propto \mathrm{Im}[\epsilon_{\mathrm{M}}(\omega)]$$

No change in electron number

[1] Phys. Rev. Lett. 81, 2312 (1998)

Optical absorption





electrons and
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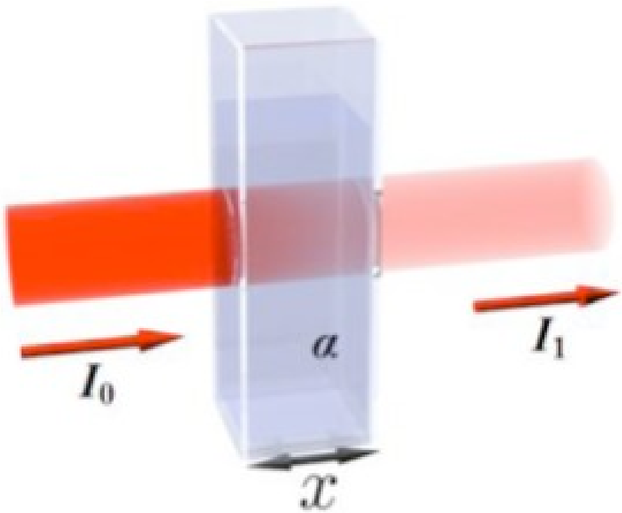

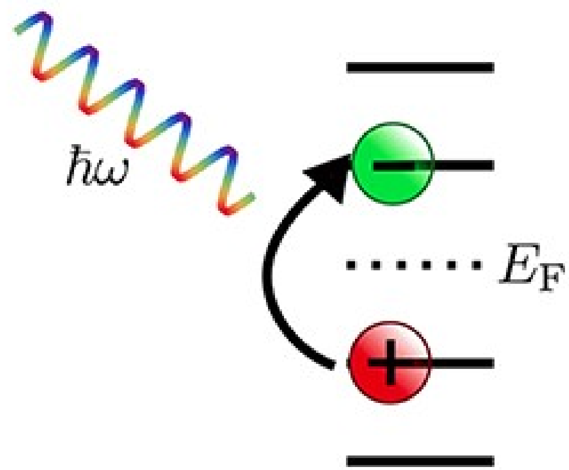

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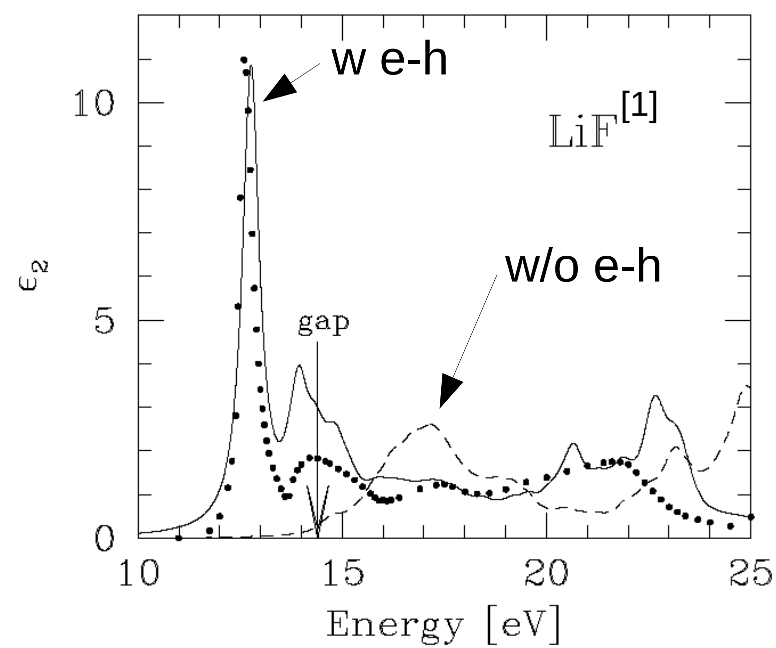

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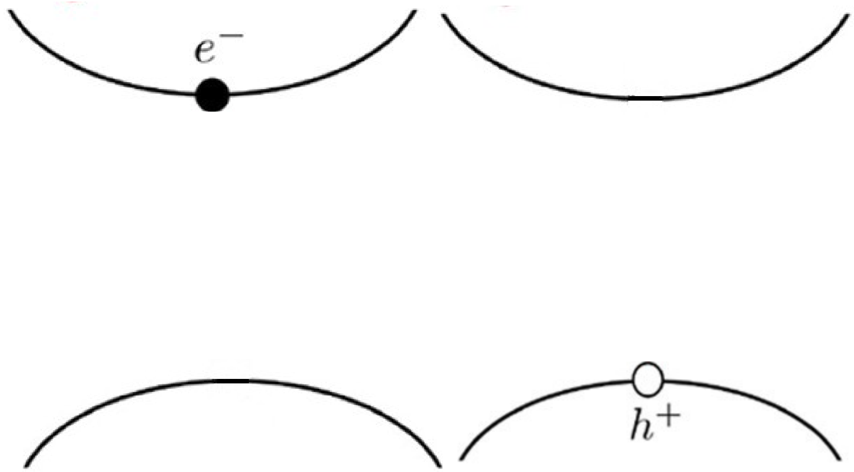
Charged and neutral excitations

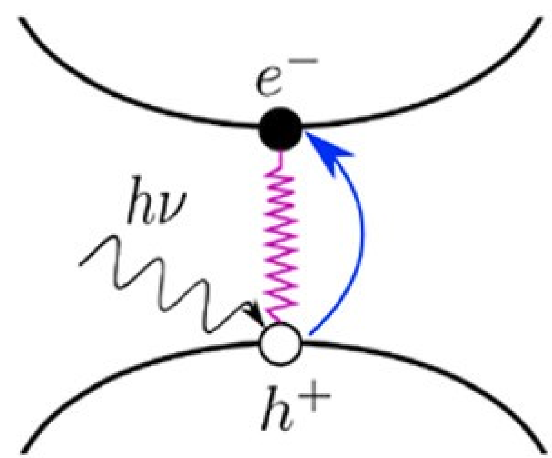
Fundamental gap

$$E_{\mathrm{g}}^{\mathrm{fund}} = E_0(N+1) - E_0(N-1)$$



Optical gap

$$E_{\mathrm{g}}^{\mathrm{opt}} = E_1(N) - E_0(N)$$



[1] Figure from J. Phys. Chem. Lett. 11, 17, 7371–7382 (2020)

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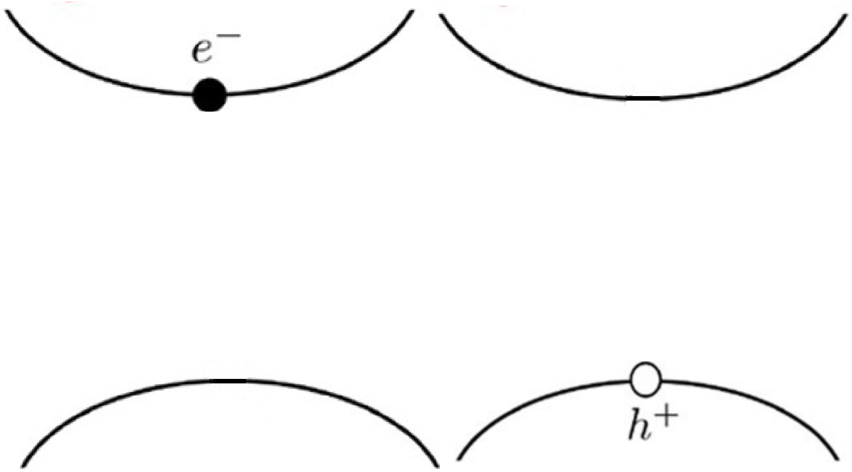

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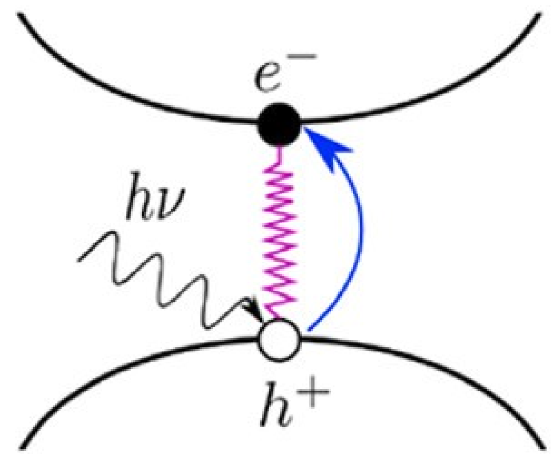
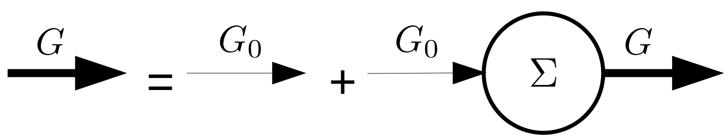
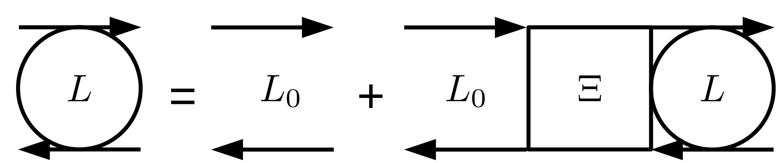


GW approximation



$$\epsilon^{\mathrm{QP}}_{n\mathbf{k}} \approx \varepsilon^0_{n\mathbf{k}} + Z_{n\mathbf{k}} \left\langle \psi^0_{n\mathbf{k}} \middle| \Sigma(\varepsilon^0_{n\mathbf{k}})0 \middle| \psi^0_{n\mathbf{k}} \right\rangle$$

Bethe-Salpeter equation



$$\mathrm{L}^{vc\mathbf{k}}_{v'c'\mathbf{k}'}(\mathbf{Q},\omega) = L^{vc\mathbf{k}}_{0v'c'\mathbf{k}'}(\mathbf{Q},\omega)$$
$$+\mathrm{L}^{\overline{vc\mathbf{k}}}_{0v'c'\mathbf{k}'}(\omega)\,\Xi^{\overline{\overline{vc}}\mathbf{k}}_{0\overline{vc}\mathbf{k}}(\mathbf{Q})\,L^{vc\mathbf{k}}_{\overline{\overline{vc}}}(\mathbf{Q},\omega)$$

[1] Figure from J. Phys. Chem. Lett. 11, 17, 7371–7382 (2020)

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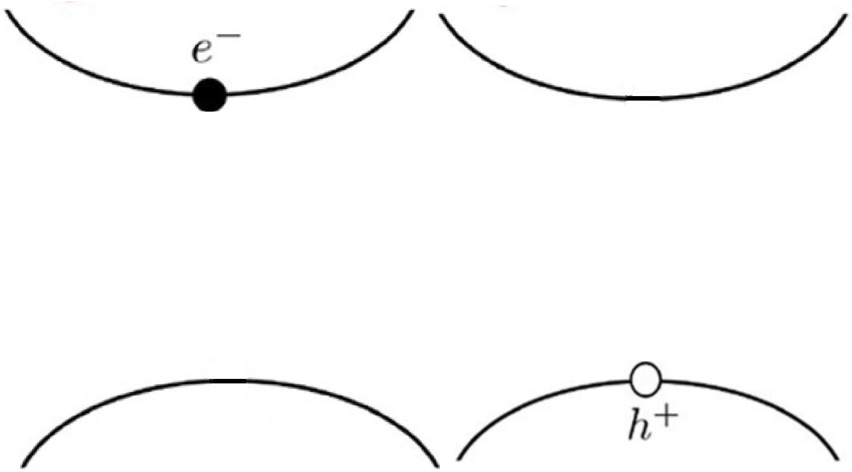

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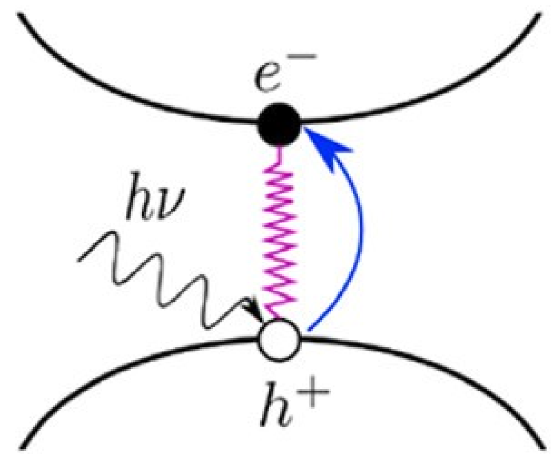

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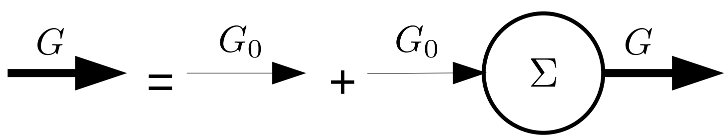

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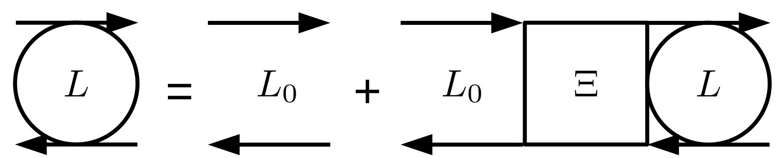

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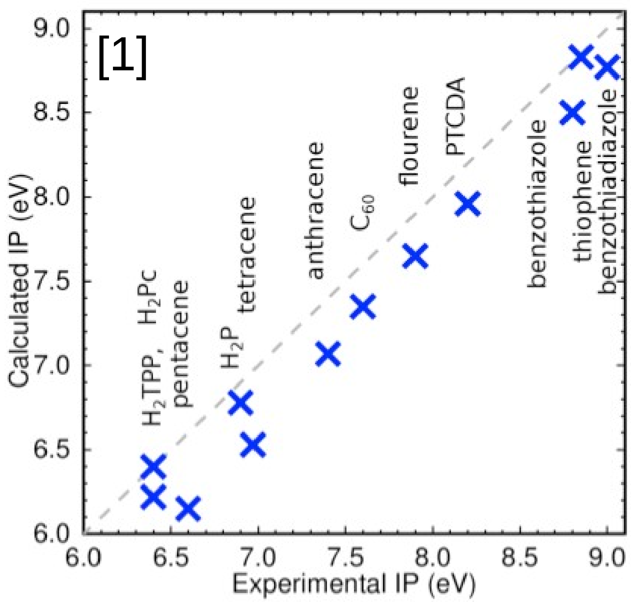
The band gap problem of DFT



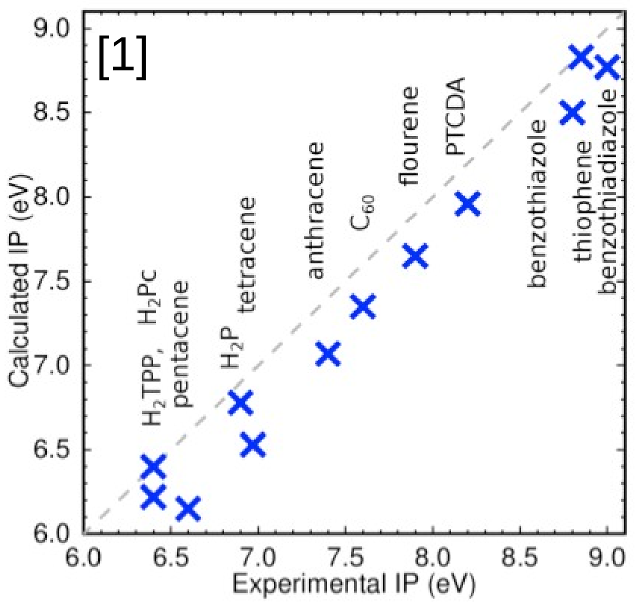
Finite sized systems (ΔSCF):

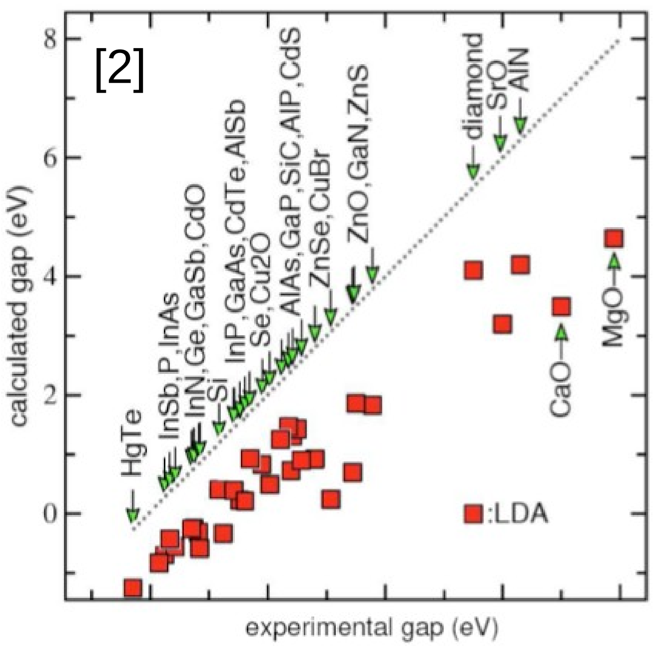
$$E_\mathrm{g} = E_0^\mathrm{DFT}(N+1) - 2E_0^\mathrm{DFT}(N) + E_0^\mathrm{DFT}(N-1)$$

with semi-local functionals: reasonable approximation for molecules

[1] Phys. Rev. Lett. 109, 116801 (2012);

The band gap problem of DFT





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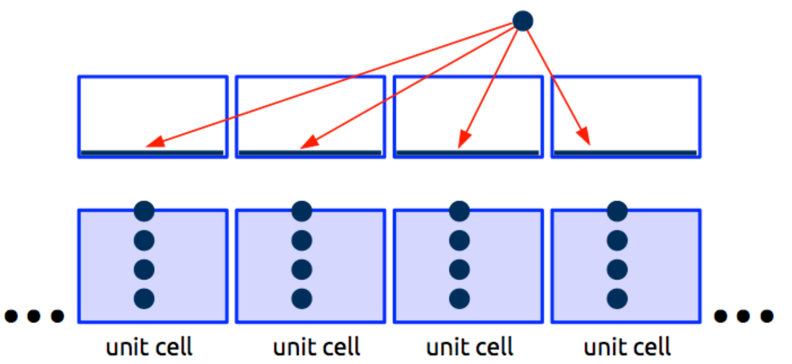
Add an electron to a solid

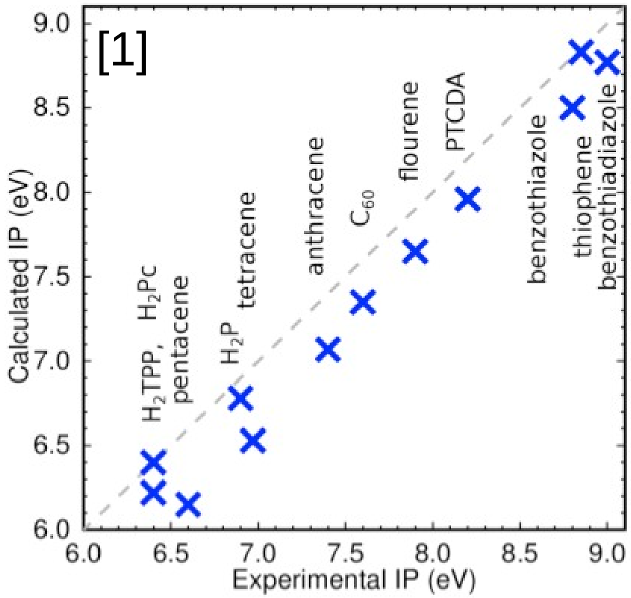


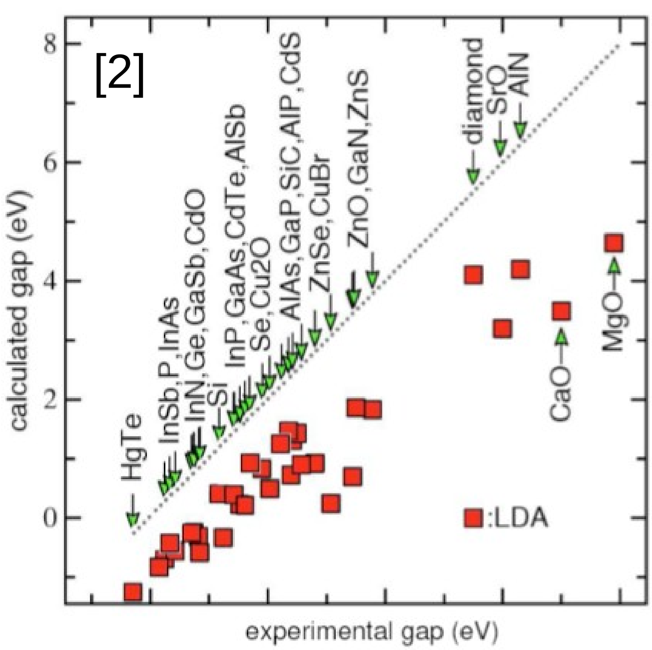
infinitesimal charge per cell → $E_{\mathrm{g}} \approx E_{\mathrm{KS}}$

the KS gap does not reproduce the band gap

[1] Phys. Rev. Lett. 109, 116801 (2012); [2] Adapted from Phys. Rev. Lett. 96, 226402 (2006)

The band gap problem of DFT





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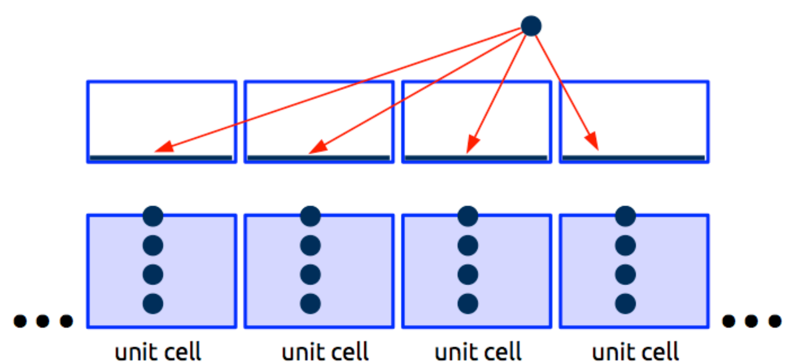
with semi-local functionals: reasonable

N.B. there are advanced functionals that reproduce the gap, but this is a different field of research

Add an electron to a solid



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From many-body perturbation theory to the GW approximation

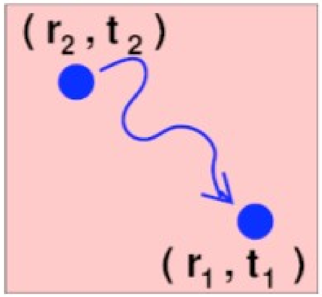
One-particle Green function

One-particle Green function definition

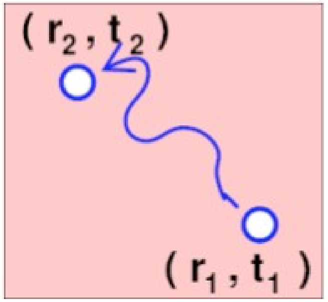
$$G(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) = -i \left\langle \Psi_0^N \middle| \hat{T}[\hat{\psi}(\mathbf{r}_1, t_1)\hat{\psi}^\dagger(\mathbf{r}_2, t_2)] \middle| \Psi_0^N \right\rangle$$

Probability amplitude for the propagation of an additional electron from (r_2,t_2) to (r_1,t_1) or an additional hole from (r_1,t_1) to (r_2,t_2).

electron



hole



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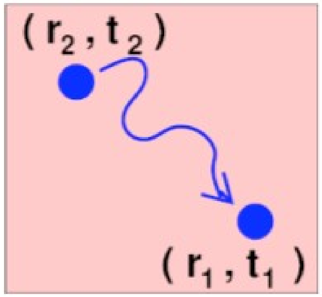

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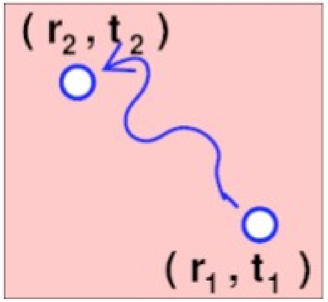
Lehmann representation:

hole



$$G(\mathbf{r}_1, \mathbf{r}_2, \omega) = \lim_{\eta \to 0^+} \sum_j \frac{f_j(\mathbf{r}_1) f_j^*(\mathbf{r}_2)}{\omega - \epsilon_j + i\eta \mathrm{sgn}(\epsilon_\mathrm{j} - \mu)}$$

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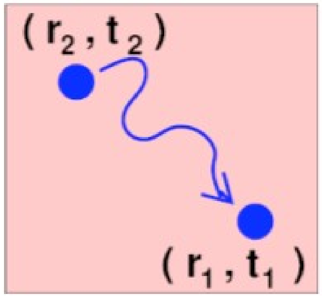

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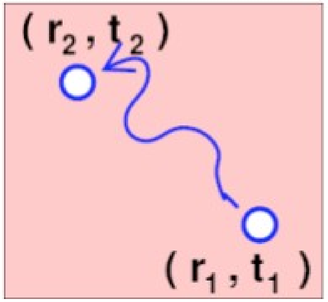

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Physics included in G:

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

$$\epsilon_j = \begin{cases} E(N+1, j) - E(N) & \epsilon_j > \mu \\ E(N) - E(N-1, j) & \epsilon_j < \mu \end{cases}$$

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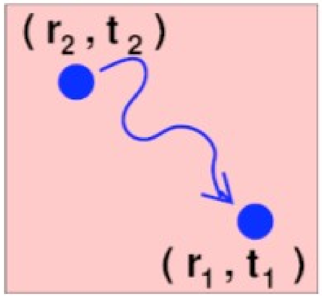

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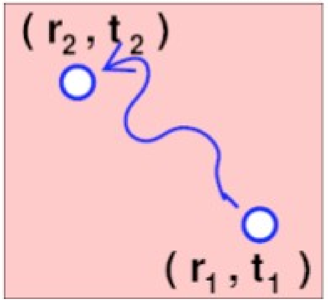

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Physics included in G:

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

Goal: find the poles of the one particle Green function.

Many-body perturbation theory

We split the Hamiltonian into bare and interaction:

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

$$\hat{H}_0 = \hat{H}_{\mathrm{KS}} \qquad \hat{H}_1 = \frac{1}{2}\int dr \int dr' \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')\hat{V}(\mathbf{r},\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r}) - \int dr \hat{\psi}^\dagger(\mathbf{r})\hat{v}_{\mathrm{Hxc}}(\mathbf{r})\hat{\psi}(\mathbf{r})$$

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then use many-body perturbation theory with infinite resummation, Feynman diagrams etc.

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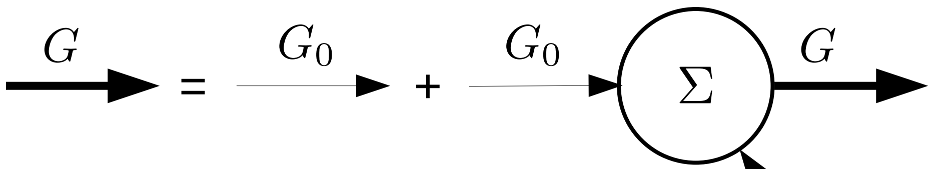
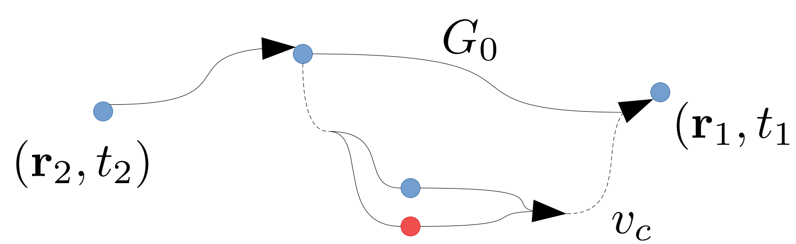
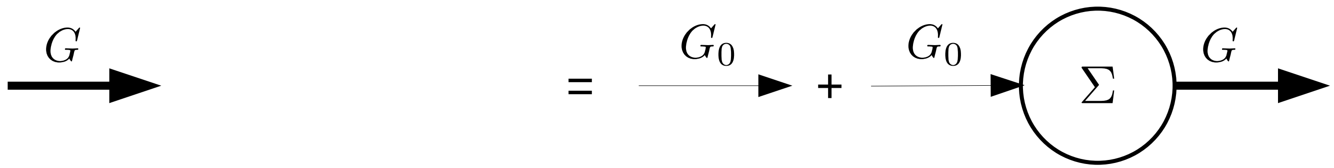
Dyson equation for the interacting G

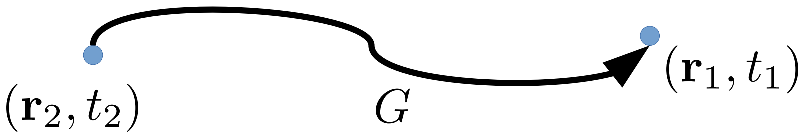


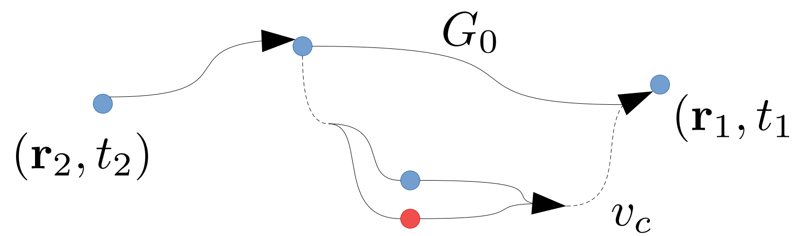


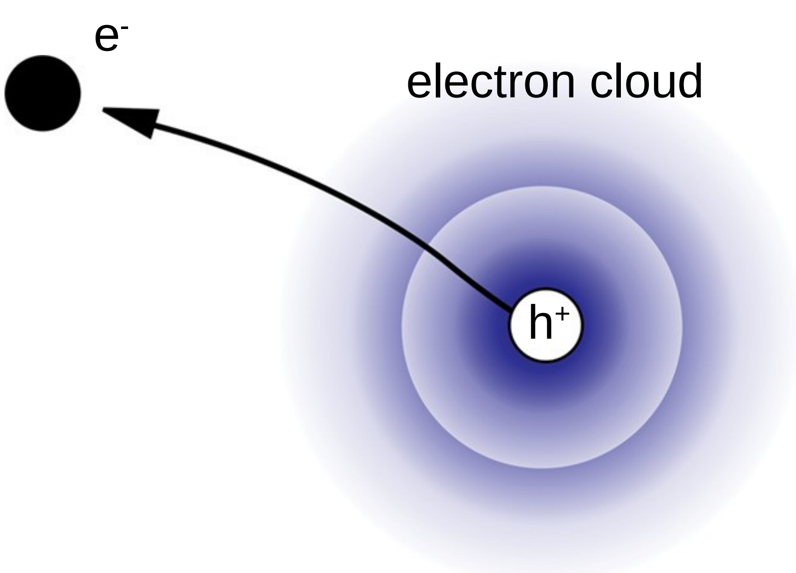
self-energy: incorporates scattering events within the solid

The quasi-particle concept









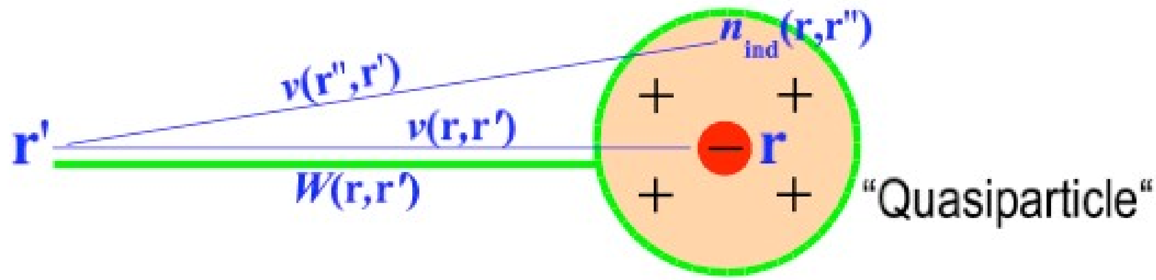
Poles of G are treated as quasi-particles: collective modes which behave qualitatively as a single-particle excitation

[1] Figures form WIREs Comput Mol Sci, 8: e1344 (2018)

Screened interaction W

$$W(\mathbf{r},\mathbf{r}',\omega) = \int d\mathbf{r}_1 \epsilon^{-1}(\mathbf{r},\mathbf{r}_1,\omega) v(\mathbf{r}_1 - \mathbf{r}') = v(\mathbf{r}-\mathbf{r}') + \int d\mathbf{r}_1 n_{\mathrm{ind}}(\mathbf{r},\mathbf{r}_1,\omega) v(\mathbf{r}_1 - \mathbf{r}')$$

Classical (Hartree) interaction between additional charge and polarization charge



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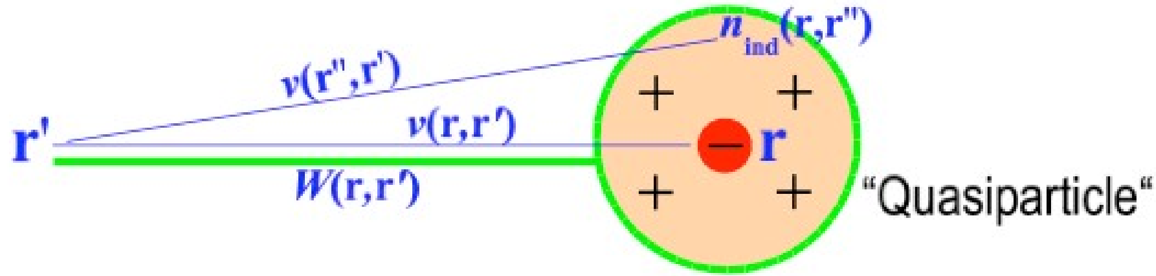
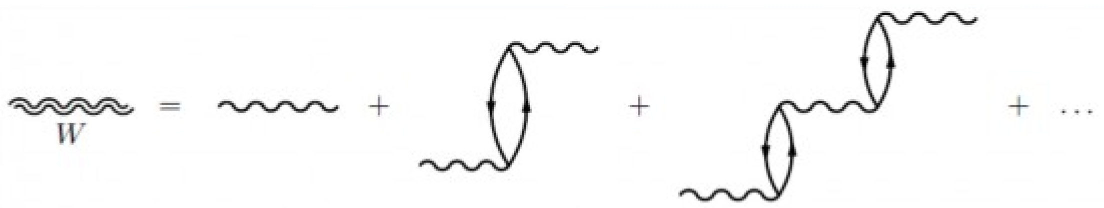


$$n_{\mathrm{ind}}(\mathbf{r},\mathbf{r}',\omega) = \int d\mathbf{r}_1 P^0(\mathbf{r},\mathbf{r}_1,\omega) V^{\mathrm{tot}}(\mathbf{r}_1 - \mathbf{r}')$$

$$\epsilon(\mathbf{r},\mathbf{r}',\omega) = \delta(\mathbf{r}-\mathbf{r}') - \int d\mathbf{r}_1 v(\mathbf{r}-\mathbf{r}_1) P^0(\mathbf{r}_1,\mathbf{r}',\omega)$$

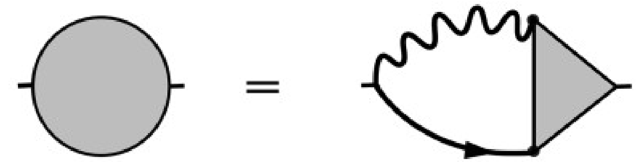
$$W = v + vPW$$



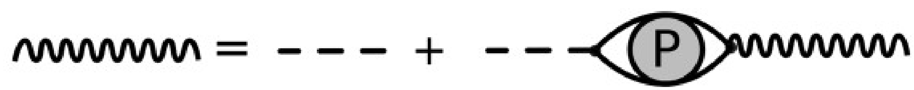
$$P(1,2) \approx P^0(1,2) = G^0(1,2)G^0(2,1)$$ random phase approximation (RPA)

Hedin’s equations

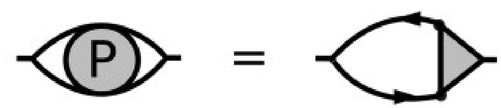
1) $\Sigma(1,2) = iG(1,\bar{4})W(1^+,\bar{3})\Gamma(\bar{4},2;\bar{3})$



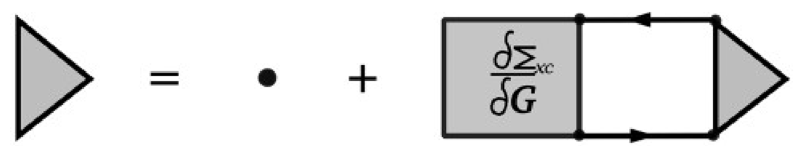
2) $W(1,2) = v_c(1,2) + v_c(1,\bar{3})P(\bar{3},\bar{4})W(\bar{4},2)$



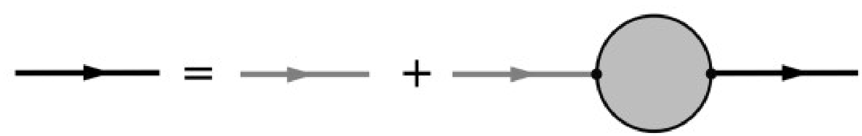
3) $P(1,2) = -iG(1,\bar{3})G(\bar{4},1)\Gamma(\bar{3},\bar{4};2)$



4) $$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \frac{\delta\Sigma(1,2)}{\delta G(\bar{4},\bar{5})}G(\bar{4},\bar{6})G(\bar{7},\bar{5})\Gamma(\bar{6},\bar{7};3)$$



5) $G(1,2) = G_0(1,2) + G_0(1,\bar{3})\Sigma(\bar{3},\bar{4})G(\bar{4},2)$



The GW approximation

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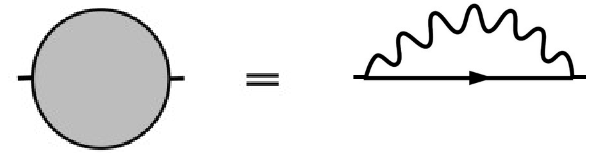

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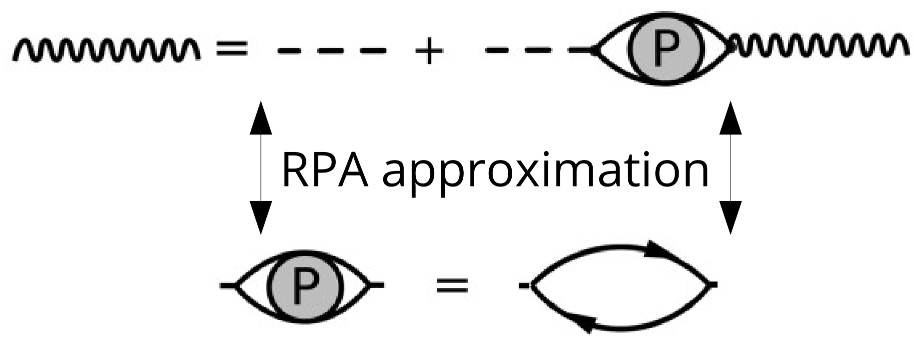

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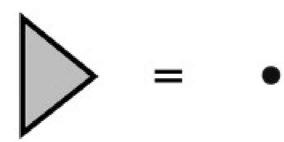
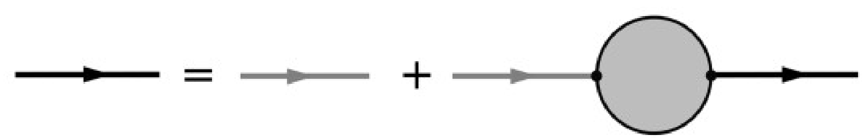


5) $G(1,2) = G_0(1,2) + G_0(1,\bar{3})\Sigma(\bar{3},\bar{4})G(\bar{4},2)$



The G_0W_0 approximation

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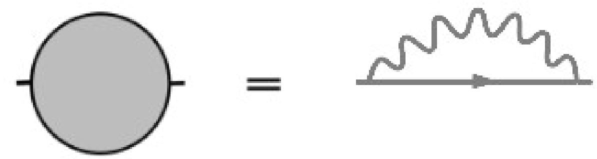

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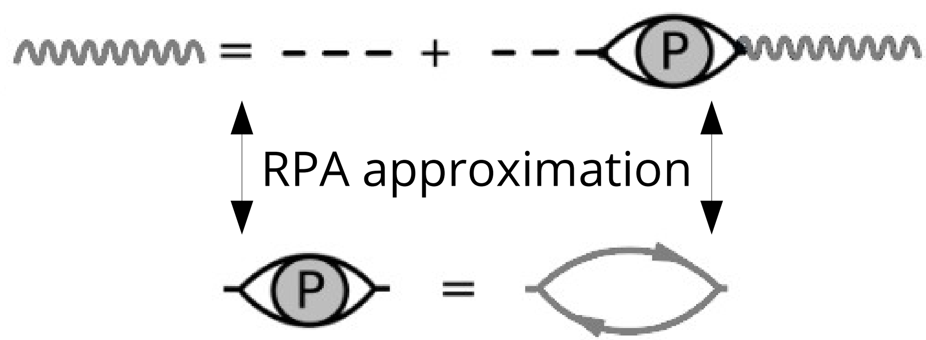

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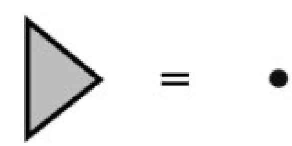

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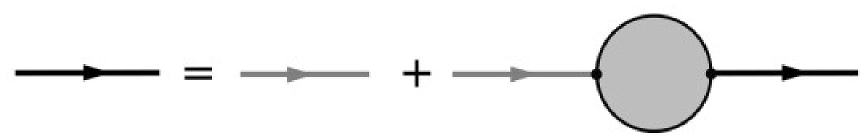

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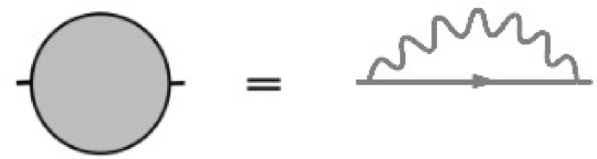

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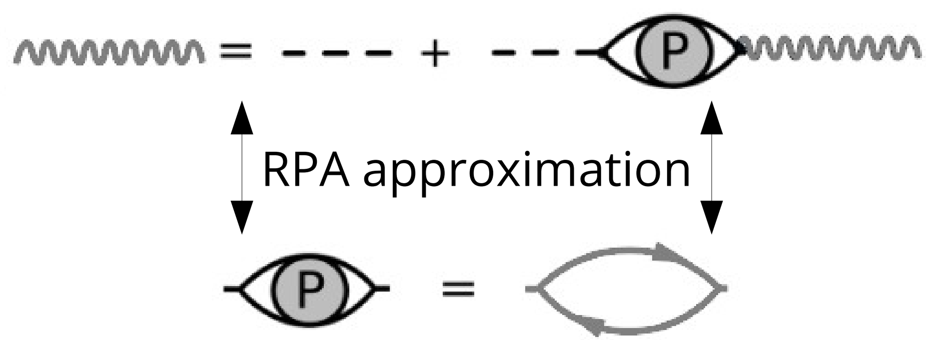

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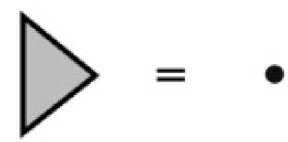

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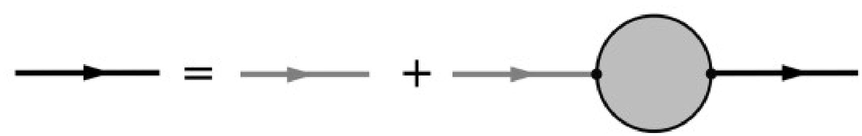
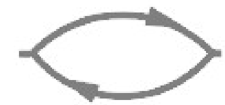
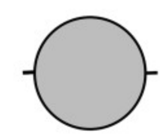


GW in practice

Basis set representation

	Plane waves $\{\varphi_{\mathbf{G}}(\mathbf{r})\}$	KS states $\{\psi_i^{KS}(\mathbf{r})\}$	
$\chi^0(1,2)$	$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$	$\chi^0_{ij}(\omega)$	
$v_c(1-2)$	$v_c(\mathbf{q}+\mathbf{G})$	$v^{kl}_{c,ij}$	
$W(1,2)$	$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$	$W^{kl}_{ij}(\omega)$	
$G_0(1,2)$	$G_{0,\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$	$G_{0,i}(\omega)\delta_{ij}$	
$\Sigma(1,2)$	$\Sigma_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$	$\Sigma_{ij}(\omega)$	

Matrix elements to change base: $\rho_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}) = \langle\psi_{n\mathbf{k}}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\psi_{m\mathbf{k}-\mathbf{q}}\rangle$

Convergence parameters: E_{cut},N_{bnds}. Interconnected!

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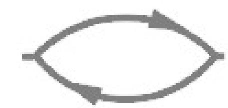
$\chi^0(1,2)$	$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$		
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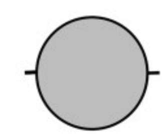
$\Sigma(1,2)$		$\Sigma_{ij}(\omega)$	

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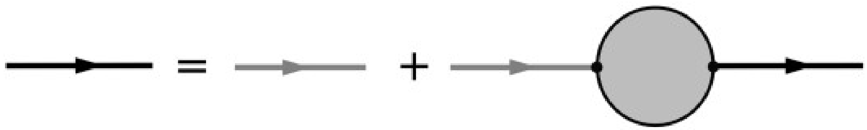
Solution of the Dyson equation of G



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

- Non-linear eigenvalue problem:

$$\hat{H}^{\mathrm{KS}} f_{n\mathbf{k}}^{\mathrm{QP}}(\mathbf{r}) + \int d\mathbf{r}' \left[\Sigma(\mathbf{r},\mathbf{r}',\varepsilon_{n\mathbf{k}}^{\mathrm{QP}}) - \delta(\mathbf{r}-\mathbf{r}')v_{xc}(\mathbf{r})\right] f_{n\mathbf{k}}^{\mathrm{QP}}(\mathbf{r}') = \varepsilon_{n\mathbf{k}}^{\mathrm{QP}} f_{n\mathbf{k}}^{\mathrm{QP}}(\mathbf{r})$$

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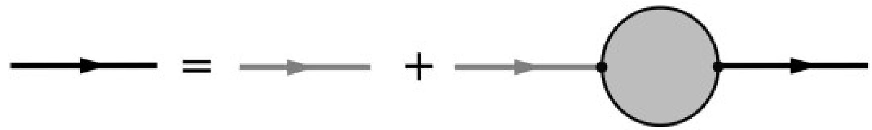

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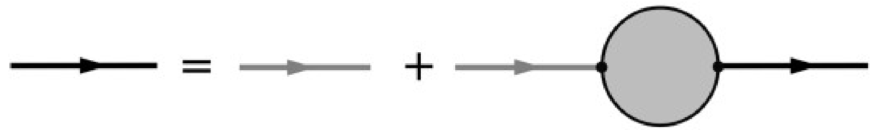
- Orbital approximation: $f_{n\mathbf{k}}^{\mathrm{QP}}(\mathbf{r}) \approx \psi_{n\mathbf{k}}^{\mathrm{KS}}(\mathbf{r})$

$$\varepsilon_{n\mathbf{k}}^{\mathrm{QP}} = \varepsilon_{n\mathbf{k}}^{\mathrm{KS}} + \langle \psi_{n\mathbf{k}} | \Sigma(\varepsilon_{n\mathbf{k}}^{\mathrm{QP}}) - v_{xc} | \psi_{n\mathbf{k}} \rangle$$

Solution of the Dyson equation of G



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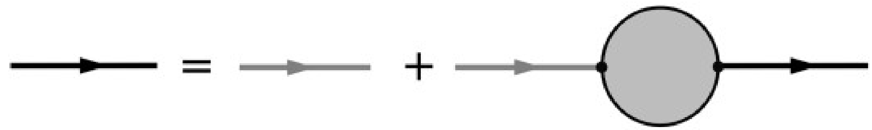
- Newton method:

$$\varepsilon_{n\mathbf{k}}^{\mathrm{QP}} \approx \varepsilon_{n\mathbf{k}}^{\mathrm{KS}} + Z_{n\mathbf{k}}\langle\psi_{n\mathbf{k}}|\Sigma(\varepsilon_{n\mathbf{k}}^{\mathrm{KS}}) - v_{xc}|\psi_{n\mathbf{k}}\rangle \qquad Z_{n\mathbf{k}} = \left[1 - \left.\frac{d\Sigma(\omega)}{d\omega}\right|_{\omega=\varepsilon_{n\mathbf{k}}^{\mathrm{KS}}}\right]^{-1}$$

Solution of the Dyson equation of G



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

- Hamiltonian formulation:

$$\hat{H}^{\mathrm{KS}} f^{\mathrm{QP}}_{n\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}' \left[\Sigma(\mathbf{r},\mathbf{r}',\varepsilon^{\mathrm{QP}}_{n\mathbf{k}}) - \delta(\mathbf{r}-\mathbf{r}')v_{xc}(\mathbf{r})\right] f^{\mathrm{QP}}_{n\mathbf{k}}(\mathbf{r}') = \varepsilon^{\mathrm{QP}}_{n\mathbf{k}} f^{\mathrm{QP}}_{n\mathbf{k}}(\mathbf{r})$$

- Quasiparticle approximation: $f^{\mathrm{QP}}_{n\mathbf{k}}(\mathbf{r}) \approx \psi^{\mathrm{KS}}_{n\mathbf{k}}(\mathbf{r})$

$$\varepsilon^{\mathrm{QP}}_{n\mathbf{k}} = \varepsilon^{\mathrm{KS}}_{n\mathbf{k}} + \langle\psi_{n\mathbf{k}}|\Sigma(\varepsilon^{\mathrm{QP}}_{n\mathbf{k}}) - v_{xc}|\psi_{n\mathbf{k}}\rangle$$

finite differences
Δω = 0.1 eV

- Newton method:

$$\varepsilon^{\mathrm{QP}}_{n\mathbf{k}} \approx \varepsilon^{\mathrm{KS}}_{n\mathbf{k}} + Z_{n\mathbf{k}}\langle\psi_{n\mathbf{k}}|\Sigma(\varepsilon^{\mathrm{KS}}_{n\mathbf{k}}) - v_{xc}|\psi_{n\mathbf{k}}\rangle$$

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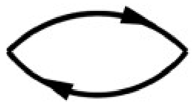
Screened interaction W

- Irreducible polarizability:

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = 2\sum_{cv}\int \frac{d\mathbf{k}}{(2\pi)^3}\left[\frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega+\varepsilon_{v\mathbf{k}-\mathbf{q}}-\varepsilon_{c\mathbf{k}}+i\eta} - \frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega+\varepsilon_{v\mathbf{k}-\mathbf{q}}-\varepsilon_{c\mathbf{k}}-i\eta}\right]$$



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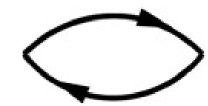
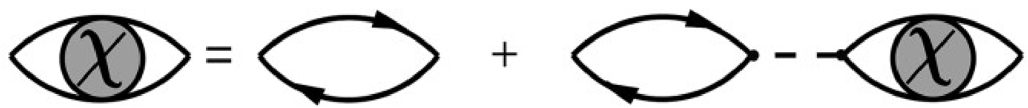


- Dyson equation for the polarizability (G space):

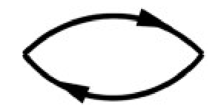


$$\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = [\delta_{\mathbf{G}\mathbf{G}''} + v(\mathbf{q}+\mathbf{G}'')\chi^0_{\mathbf{G}\mathbf{G}''}(\mathbf{q},\omega)]^{-1}\chi^0_{\mathbf{G}''\mathbf{G}'}(\mathbf{q},\omega)$$

Screened interaction W

- Irreducible polarizability:

$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = 2\sum_{cv}\int \frac{d\mathbf{k}}{(2\pi)^3}\left[\frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G'})}{\omega+\varepsilon_{v\mathbf{k-q}}-\varepsilon_{c\mathbf{k}}+i\eta} - \frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G'})}{\omega+\varepsilon_{v\mathbf{k-q}}-\varepsilon_{c\mathbf{k}}-i\eta}\right]$$



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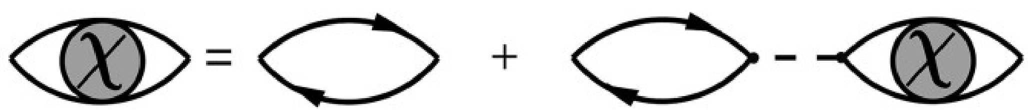


$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = [\delta_{\mathbf{GG''}} + v(\mathbf{q}+\mathbf{G''})\chi^0_{\mathbf{GG''}}(\mathbf{q},\omega)]^{-1}\chi^0_{\mathbf{G''G'}}(\mathbf{q},\omega)$$

- Response function

$$\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega) = \delta_{\mathbf{GG'}} + v(\mathbf{q}+\mathbf{G})\chi_{\mathbf{GG'}}(\mathbf{q},\omega)$$

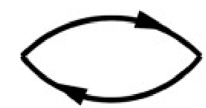
- Screened interaction

$$W_{\mathbf{GG'}}(\mathbf{q},\omega) = \epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega)v(\mathbf{q}+\mathbf{G'})$$

Screened interaction W

- Irreducible polarizability:

$$\chi^0_{\mathbf{GG}'}(\mathbf{q},\omega) = 2\sum_{cv}\int \frac{d\mathbf{k}}{(2\pi)^3}\left[\frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega+\varepsilon_{v\mathbf{k}-\mathbf{q}}-\varepsilon_{c\mathbf{k}}+i\eta} - \frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega+\varepsilon_{v\mathbf{k}-\mathbf{q}}-\varepsilon_{c\mathbf{k}}-i\eta}\right]$$



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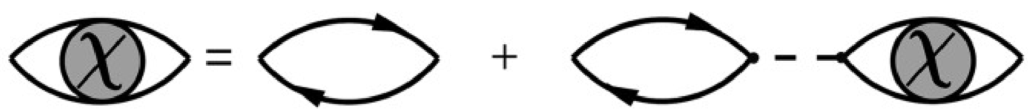


$$\chi_{\mathbf{GG}'}(\mathbf{q},\omega) = [\delta_{\mathbf{GG}''} + v(\mathbf{q}+\mathbf{G}'')\chi^0_{\mathbf{GG}''}(\mathbf{q},\omega)]^{-1}\chi^0_{\mathbf{G}''\mathbf{G}'}(\mathbf{q},\omega)$$

- Response function

$$\epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega) = \delta_{\mathbf{GG}'} + v(\mathbf{q}+\mathbf{G})\chi_{\mathbf{GG}'}(\mathbf{q},\omega)$$

- Screened interaction

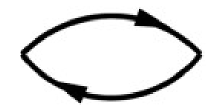
$$W_{\mathbf{GG}'}(\mathbf{q},\omega) = \epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega)v(\mathbf{q}+\mathbf{G}')$$

This is often the most time consuming part of the computation

Screened interaction W

- Irreducible polarizability:

$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = 2\sum_{cv}\int \frac{d\mathbf{k}}{(2\pi)^3}\left[\frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G'})}{\omega+\varepsilon_{v\mathbf{k-q}}-\varepsilon_{c\mathbf{k}}+i\eta} - \frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G'})}{\omega+\varepsilon_{v\mathbf{k-q}}-\varepsilon_{c\mathbf{k}}-i\eta}\right]$$



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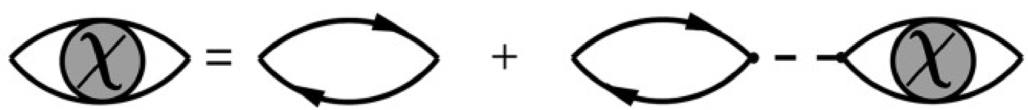

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- Response function

$$\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega) = \delta_{\mathbf{GG'}} + v(\mathbf{q}+\mathbf{G})\chi_{\mathbf{GG'}}(\mathbf{q},\omega)$$

- Screened interaction

$$W_{\mathbf{GG'}}(\mathbf{q},\omega) = \epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega)v(\mathbf{q}+\mathbf{G'})$$

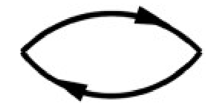
Convergence with respect to the number of planewaves

Convergence with respect to the number of bands

Screened interaction W

- Irreducible polarizability:

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = 2\sum_{cv} \boxed{\int \frac{d\mathbf{k}}{(2\pi)^3}} \left[\frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega + \varepsilon_{v\mathbf{k}-\mathbf{q}} - \varepsilon_{c\mathbf{k}} + i\eta} - \frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega + \varepsilon_{v\mathbf{k}-\mathbf{q}} - \varepsilon_{c\mathbf{k}} - i\eta} \right]$$



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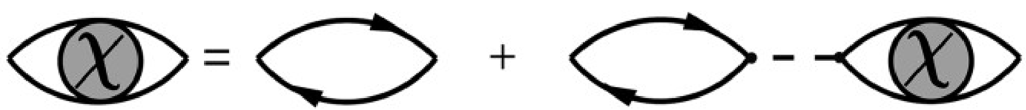


$$\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = [\delta_{\mathbf{G}\mathbf{G}''} + v(\mathbf{q}+\mathbf{G}'')\chi^0_{\mathbf{G}\mathbf{G}''}(\mathbf{q},\omega)]^{-1}\chi^0_{\mathbf{G}''\mathbf{G}'}(\mathbf{q},\omega)$$

- Response function

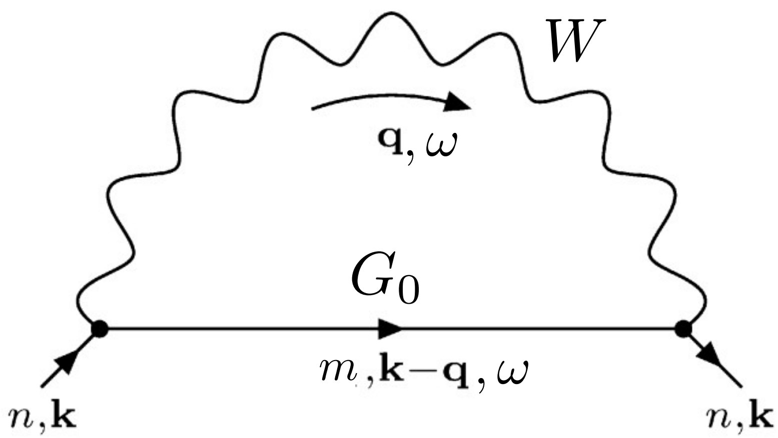
$$\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \delta_{\mathbf{G}\mathbf{G}'} + v(\mathbf{q}+\mathbf{G})\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$$

Convergence with respect to the BZ sampling

- Screened interaction

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)v(\mathbf{q}+\mathbf{G}')$$

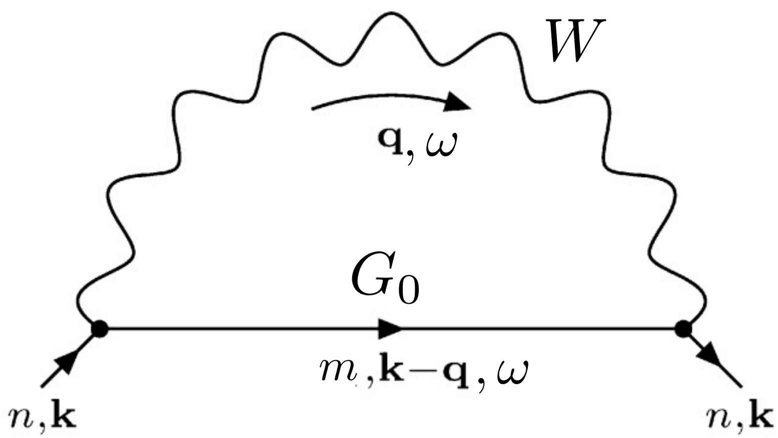
GW Self-energy



$$\Sigma_{n\mathbf{k}}(\omega) = \int d\omega' \int \frac{d\mathbf{q}}{(2\pi)^3} \sum_m G_0^{m\mathbf{k}-\mathbf{q}}(\omega - \omega') W_{mm\mathbf{k}-\mathbf{q}}^{nn\mathbf{k}}(\omega')$$

- $G_0^{m\mathbf{k}}(\omega) = \dfrac{f_{n\mathbf{k}}}{\omega - \varepsilon_{m\mathbf{k}} - i\eta} + \dfrac{1 - f_{n\mathbf{k}}}{\omega + \varepsilon_{m\mathbf{k}} + i\eta}$
- $W_{mm\mathbf{k}-\mathbf{q}}^{nn\mathbf{k}}(\omega) = \sum_{\mathbf{G}\mathbf{G}'} \rho_{nm}^*(\mathbf{q}, \mathbf{G}) W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) \rho_{nm}(\mathbf{q}, \mathbf{G}')$

GW Self-energy



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- $W = v + W^c$
- $\Sigma_{n\mathbf{k}}^x(\omega) = \int d\omega' \int \frac{d\mathbf{q}}{(2\pi)^3} \sum_m G_0^{m\mathbf{k}-\mathbf{q}}(\omega - \omega') v_{mm\mathbf{k}-\mathbf{q}}^{nn\mathbf{k}}$
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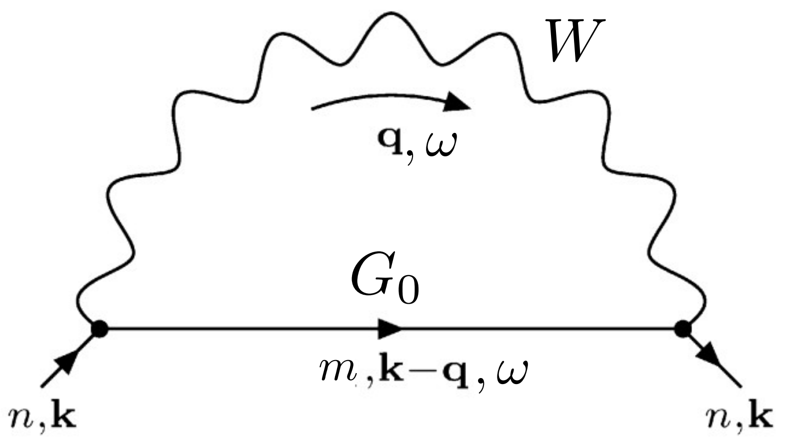
GW Self-energy



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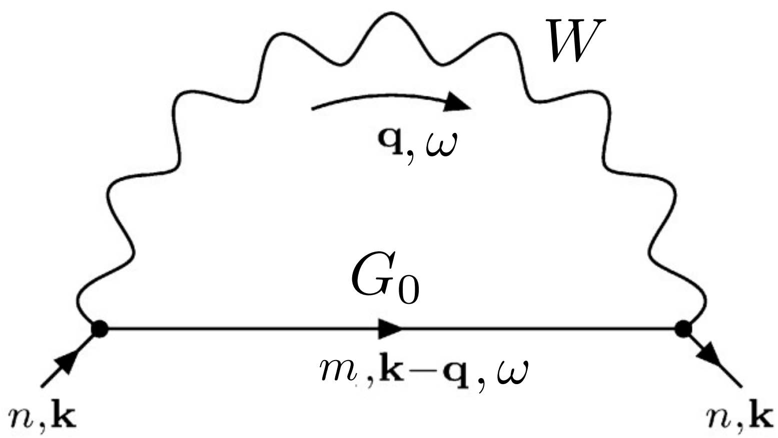
- $\Sigma_{n\mathbf{k}}^c(\omega) = \int d\omega' \int \frac{d\mathbf{q}}{(2\pi)^3} \sum_m G_0^{m\mathbf{k}-\mathbf{q}}(\omega - \omega') W_{mm\mathbf{k}-\mathbf{q}}^{c\ nn\mathbf{k}}(\omega')$
- Plasmon pole approximation → analytic integration over ω'

GW Self-energy



$$\Sigma_{n\mathbf{k}}(\omega) = \Sigma^x_{n\mathbf{k}} + \Sigma^c_{n\mathbf{k}}(\omega)$$

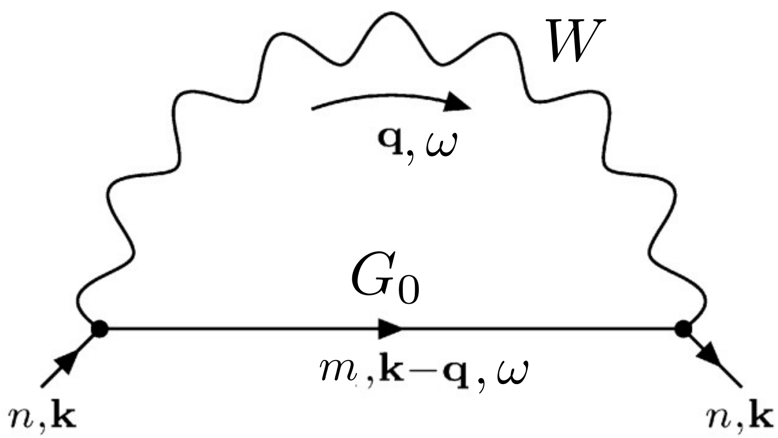
- $\Sigma^x_{n\mathbf{k}} = -\sum_m^{\text{occ.}} \int_{\text{BZ}} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G}} v(\mathbf{q}+\mathbf{G}) |\rho_{nm\mathbf{k}}(\mathbf{q},\mathbf{G})|^2$

Plasmon residue

- $\Sigma^c_{n\mathbf{k}}(\omega) = \lim_{\eta\to 0} \sum_m \int_{\text{BZ}} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G}\mathbf{G}'} \frac{\rho_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}) R_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) \rho^*_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega + [\Omega_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) + i\eta] sgn(\mu - \varepsilon^{\text{KS}}_{m\mathbf{k}-\mathbf{q}}) - \varepsilon^{\text{KS}}_{m\mathbf{k}-\mathbf{q}}}$

Plasmon pole

GW Self-energy



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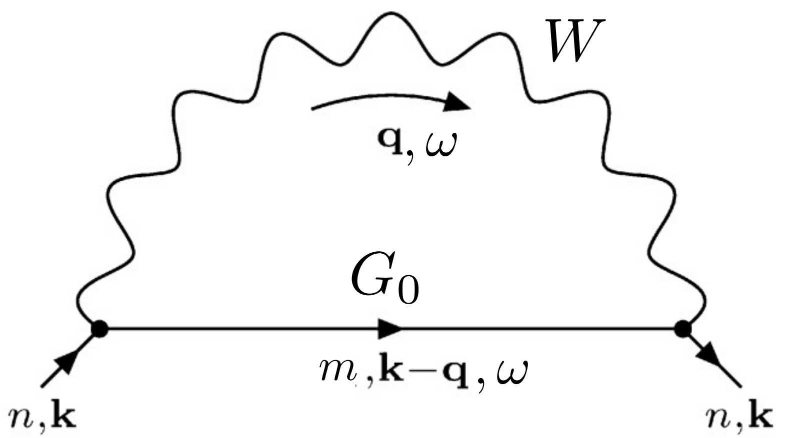
Convergence with respect to the number of planewaves

Convergence with respect to the number of bands

GW Self-energy



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Convergence with respect to the BZ sampling

The G_0W_0 method in one slide

DFT: $\{\varepsilon_{m\mathbf{k}}\}, \{\psi_{m\mathbf{k}}(\mathbf{r})\}$ $\longrightarrow$ $G_0^{m\mathbf{k}}(\omega) = \frac{\delta_{mv}}{\omega - \varepsilon_{m\mathbf{k}} - i\eta} + \frac{\delta_{mc}}{\omega - \varepsilon_{m\mathbf{k}} + i\eta}$

$$\chi^0_{\mathbf{GG}'}(\mathbf{q},\omega) = 2\sum_{cv}\int \frac{d\mathbf{k}}{(2\pi)^3}\left[\frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega + \varepsilon_{m\mathbf{k}-\mathbf{q}} - \varepsilon_{n\mathbf{k}} + i\eta} - \frac{\rho_{cv\mathbf{k}}(\mathbf{q},\mathbf{G})\rho^*_{cv\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega + \varepsilon_{m\mathbf{k}-\mathbf{q}} - \varepsilon_{n\mathbf{k}} - i\eta}\right]$$

$$\chi_{\mathbf{GG}'}(\mathbf{q},\omega) = [\delta_{\mathbf{GG}''} + v(\mathbf{q}+\mathbf{G}'')\chi^0_{\mathbf{GG}''}(\mathbf{q},\omega)]^{-1}\chi^0_{\mathbf{G}''\mathbf{G}'}(\mathbf{q},\omega)$$

$$\epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega) = \delta_{\mathbf{GG}'} + v(\mathbf{q}+\mathbf{G})\chi_{\mathbf{GG}'}(\mathbf{q},\omega)$$

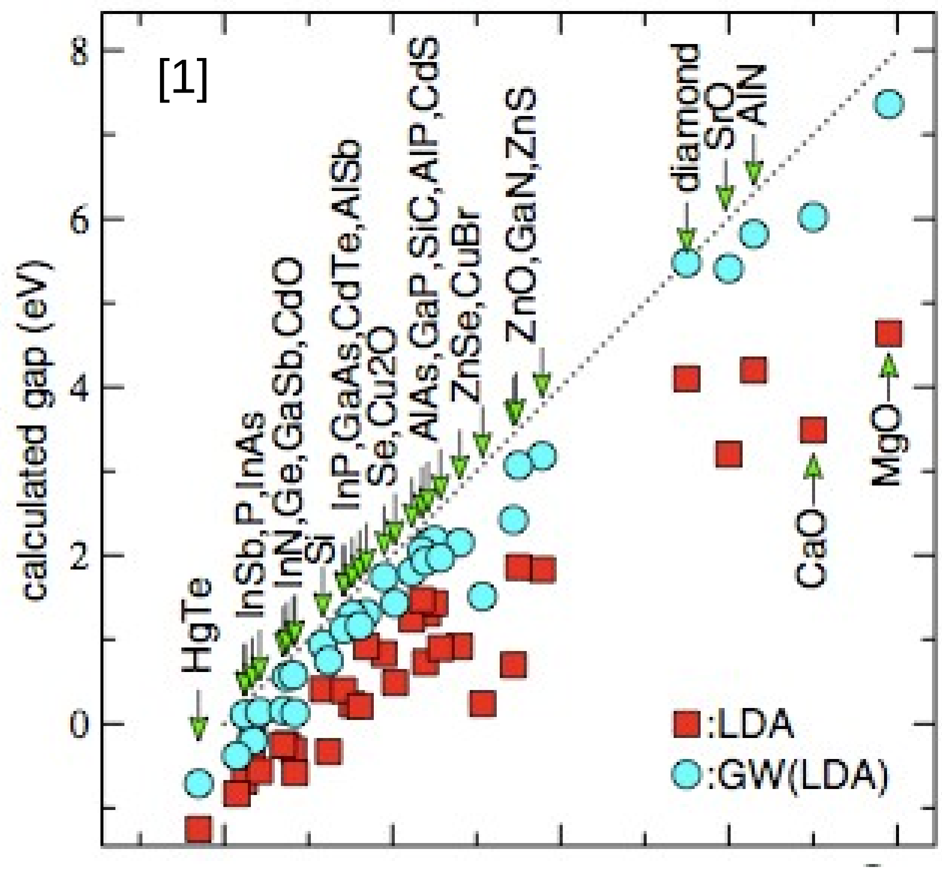
$$W_{\mathbf{GG}'}(\mathbf{q},\omega) = \epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega)v(\mathbf{q}+\mathbf{G}')$$

$$\Sigma^x_{n\mathbf{k}} = -\sum_m^{\text{occ.}}\int_{\text{BZ}} \frac{d\mathbf{q}}{(2\pi)^3}\sum_{\mathbf{G}} v(\mathbf{q}+\mathbf{G})|\rho_{nm\mathbf{k}}(\mathbf{q},\mathbf{G})|^2 f_{m\mathbf{k}-\mathbf{q}}$$

$$\Sigma^c_{n\mathbf{k}}(\omega) = \lim_{\eta\to 0}\sum_m\int_{\text{BZ}}\frac{d\mathbf{q}}{(2\pi)^3}\sum_{\mathbf{GG}'}\frac{\rho_{nm\mathbf{k}}(\mathbf{q},\mathbf{G})R_{\mathbf{GG}'}(\mathbf{q})\rho^*_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega + [\Omega_{\mathbf{GG}'}(\mathbf{q}) + i\eta]sgn(\mu - \varepsilon^{\text{KS}}_{m\mathbf{k}-\mathbf{q}}) - \varepsilon^{\text{KS}}_{m\mathbf{k}-\mathbf{q}}}$$

$$\varepsilon^{\text{QP}}_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}} + Z_{n\mathbf{k}}\left[\Sigma_{n\mathbf{k}}(\varepsilon_{n\mathbf{k}}) - \langle n\mathbf{k}|v_{xc}|n\mathbf{k}\rangle\right]$$

Accuracy of GW calculations



GW band gaps: huge improvement wrt the LDA

[1] Phys. Rev. Lett. 96, 226402 (2006)

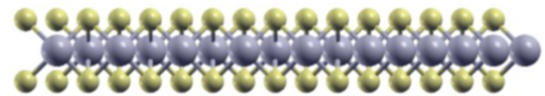
Recent advances

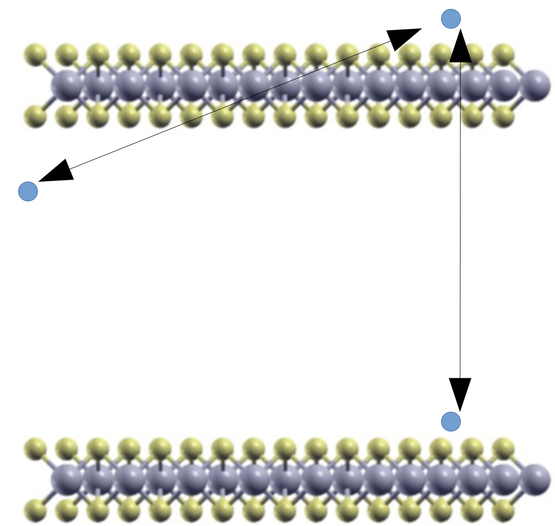
GW in 2D materials: Coulomb cutoff

Bare Coulomb interaction

Real space: $v(|\mathbf{r}_1 - \mathbf{r}_2|) = \dfrac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$

Fourier space: $v(\mathbf{q}+\mathbf{G}) = \dfrac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}$





[1] Ismail-Beigi. Phys. Rev. B. **73**, 233103 (2006)   [2] Rozzi et al. Phys. Rev. B 73, 205119 (2006)

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Fourier space: $v(\mathbf{q} + \mathbf{G}) = \dfrac{4\pi}{|\mathbf{q} + \mathbf{G}|^2}$

<u>Truncated</u> Coulomb interaction[1][2]

Heaviside theta

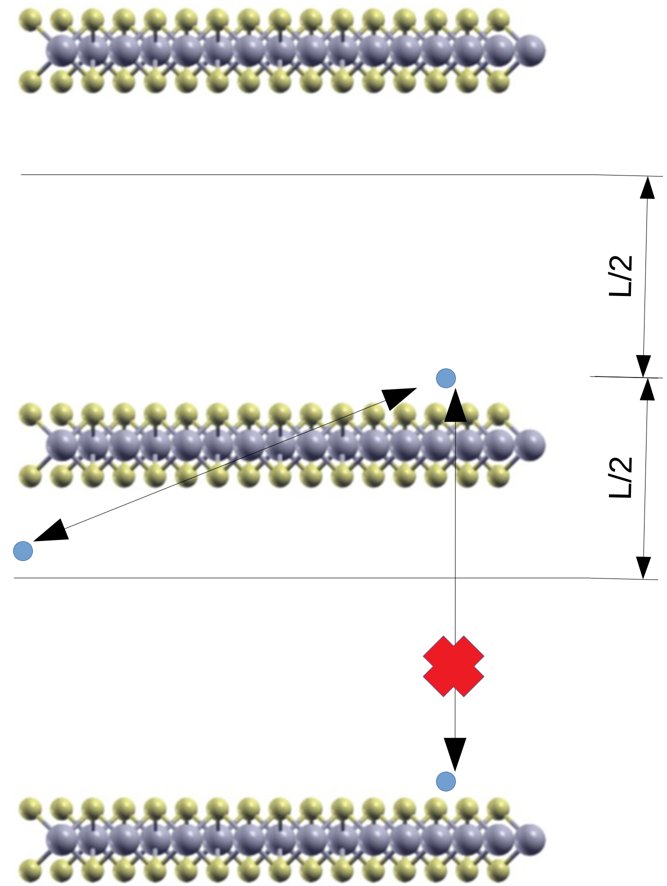
Real space:

$$v^{\mathrm{slab}}(|\mathbf{r}_1 - \mathbf{r}_2|) = \frac{\Theta(L/2 - |z_1 - z_2|)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Fourier space:

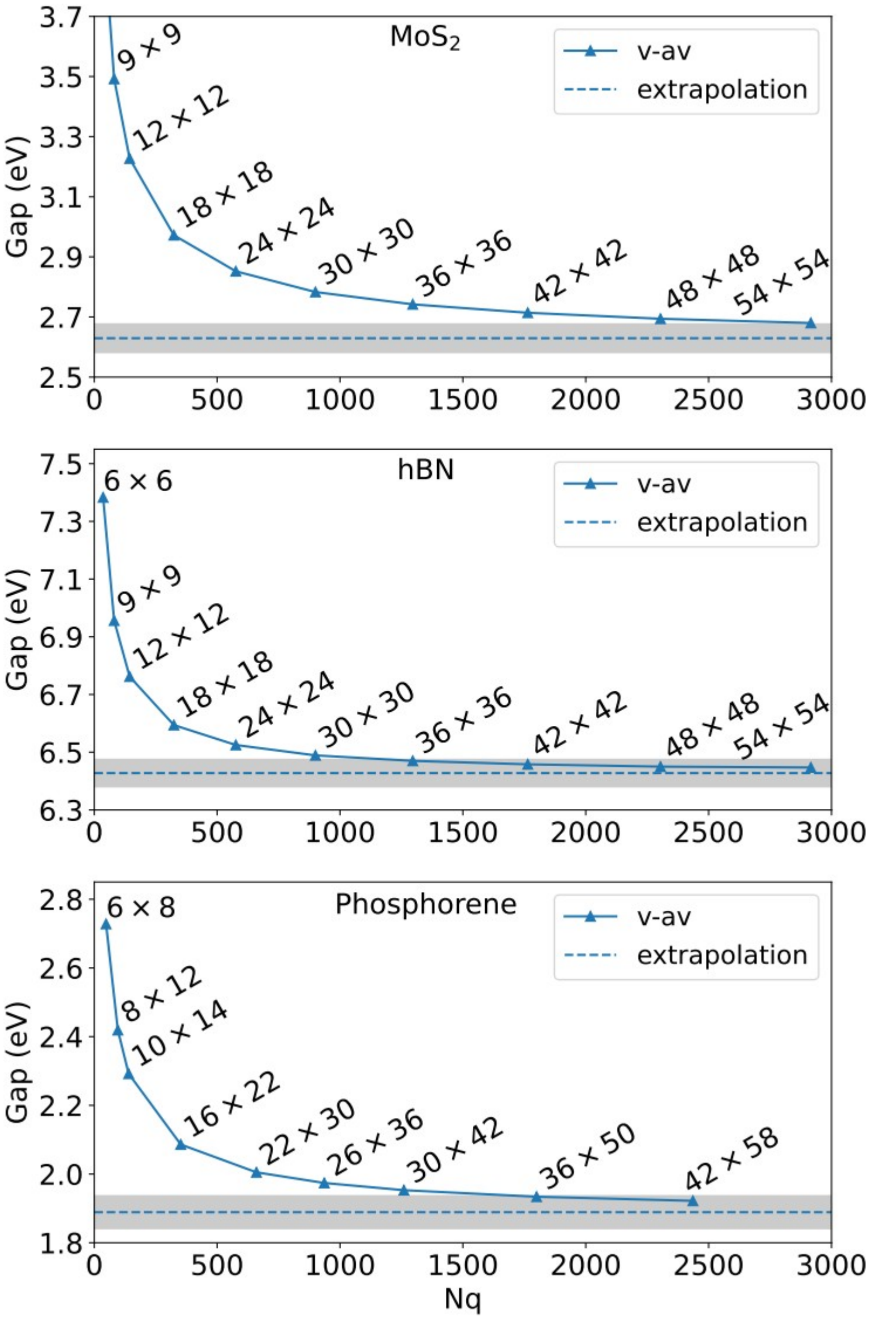
$$v^{\mathrm{slab}}(\mathbf{q} + \mathbf{G}) = \frac{4\pi}{|\mathbf{q} + \mathbf{G}|^2}\left[1 - e^{\mathbf{q}_\parallel + \mathbf{G}_\parallel L/2}\cos(\mathbf{G}_\perp L/2)\right]$$

$$v^{\mathrm{slab}}(|\mathbf{q}| \to 0) = \frac{2\pi}{|\mathbf{q}|}$$



[1] Ismail-Beigi. Phys. Rev. B. **73**, 233103 (2006) [2] Rozzi et al. Phys. Rev. B 73, 205119 (2006)

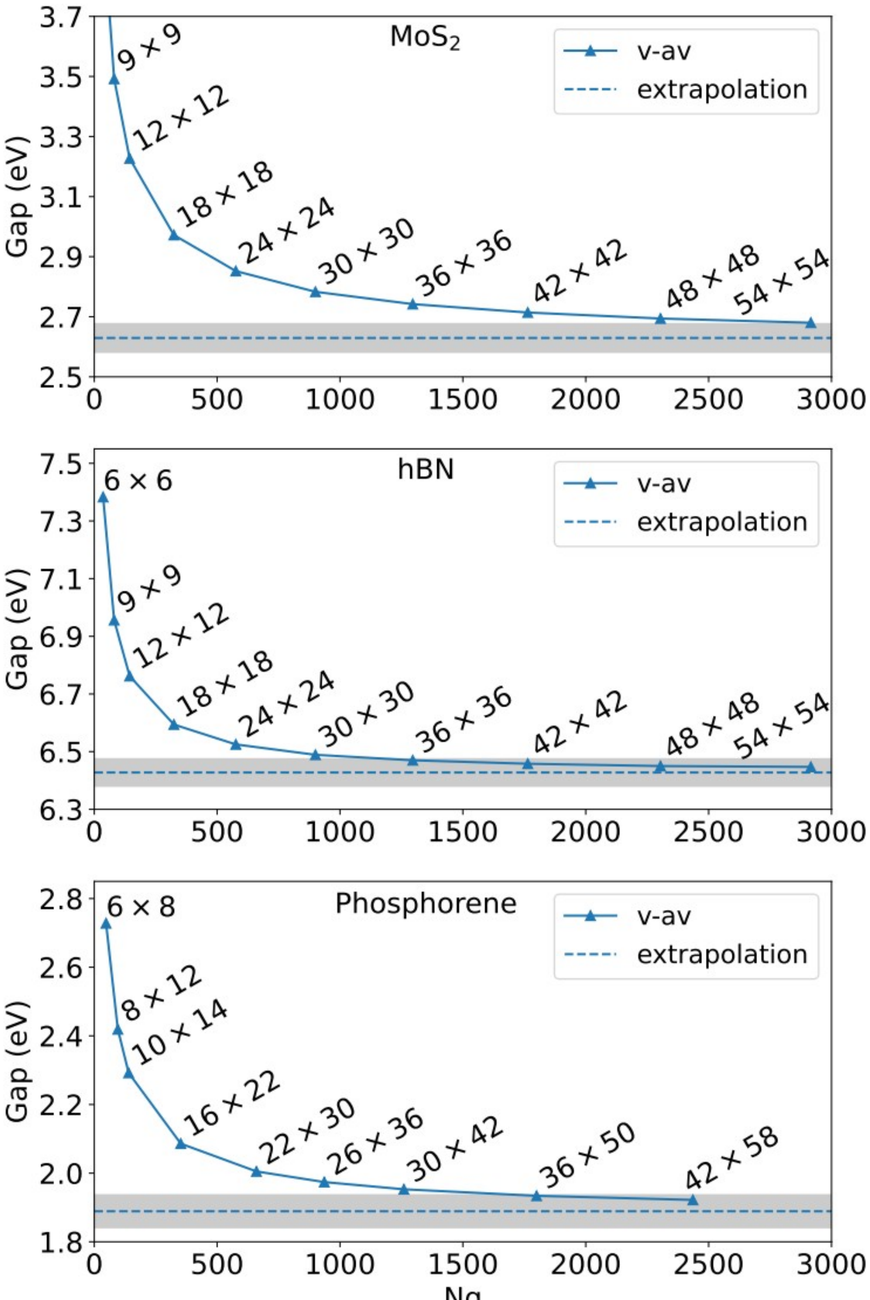
GW in 2D materials: convergence acceleration[1]

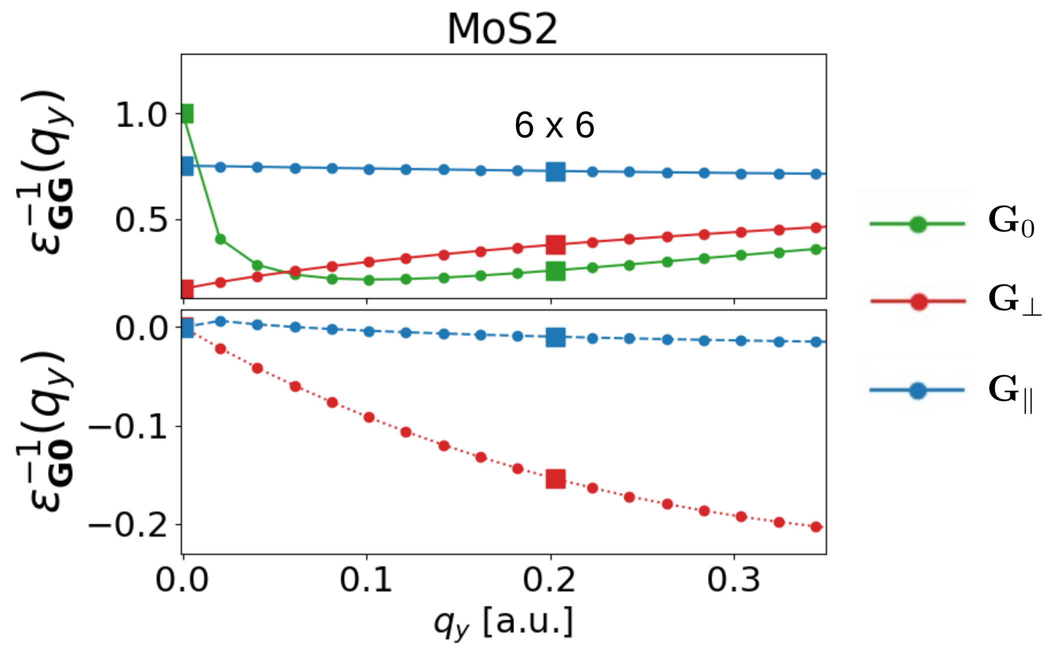


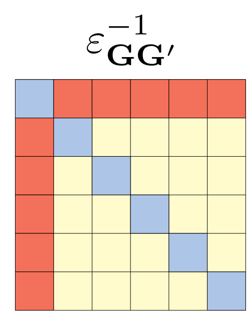
[1] npj Comput. Mat. Vol. 9, 44 (2023)

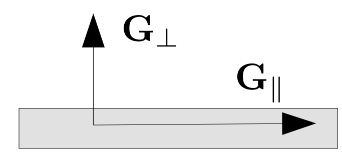
Metti tutte le referenze

GW in 2D materials: convergence acceleration[1]







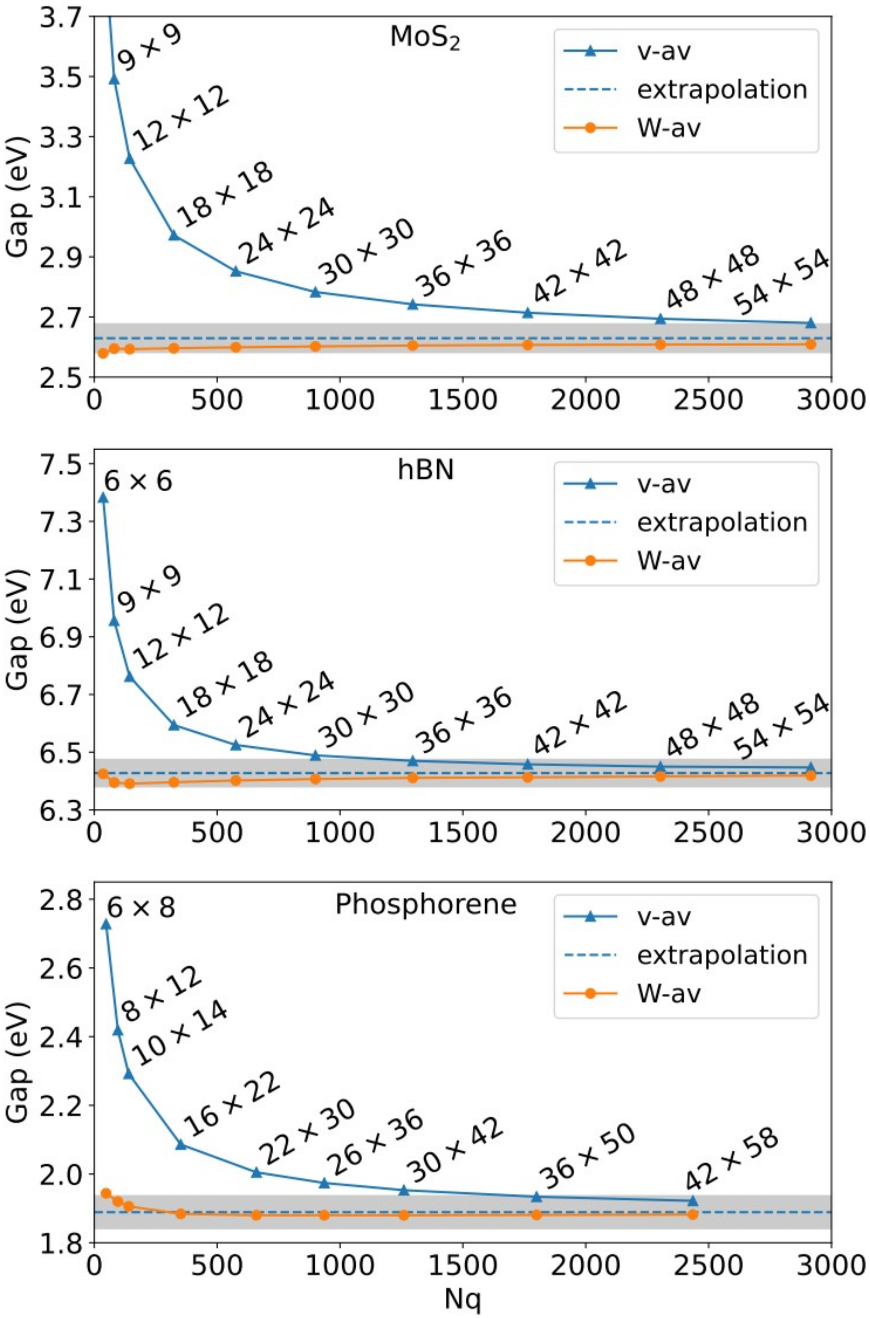


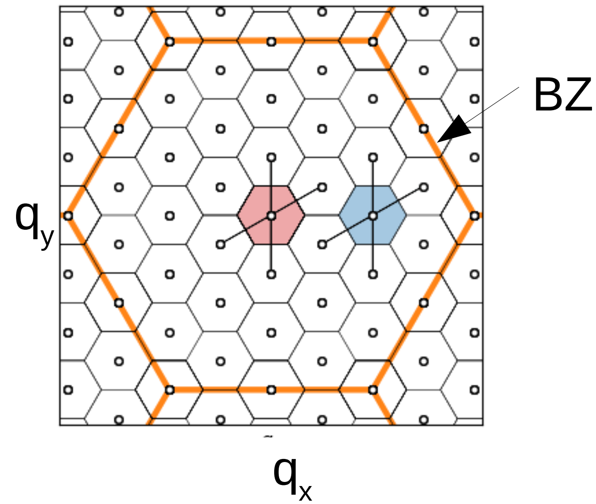
2D material

$$\Sigma^{c}_{n\mathbf{k}}(\omega) \approx \sum_{\mathbf{q},\mathbf{G},\mathbf{G'}} f^{c}_{n\mathbf{k}}(\mathbf{q},\mathbf{G},\mathbf{G'},\omega)\overline{W}^{c}_{\mathbf{GG'}}(\mathbf{q})$$

[1] Guandalini et al., npj Comput. Mat. Vol. 9, 44 (2023)

GW in 2D materials: convergence acceleration[1]

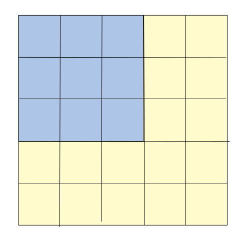




W-average method [3]:

- $\Sigma^{c}_{n\mathbf{k}}(\omega) \approx \sum_{\mathbf{q},\mathbf{G},\mathbf{G}'} f^{c}_{n\mathbf{k}}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega)\overline{W}^{c}_{\mathbf{G}\mathbf{G}'}(\mathbf{q})$
- $\overline{W}^{c}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) \equiv \frac{1}{D_\Gamma}\int_{D_\Gamma} \frac{d\mathbf{q}'}{(2\pi)^3} W^{c}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}+\mathbf{q}')$
- Interpolation + Monte Carlo integrals
- Correction applied up to a given $|G^{lim}|^2$.

$W^{c}_{\mathbf{G}\mathbf{G}'}$



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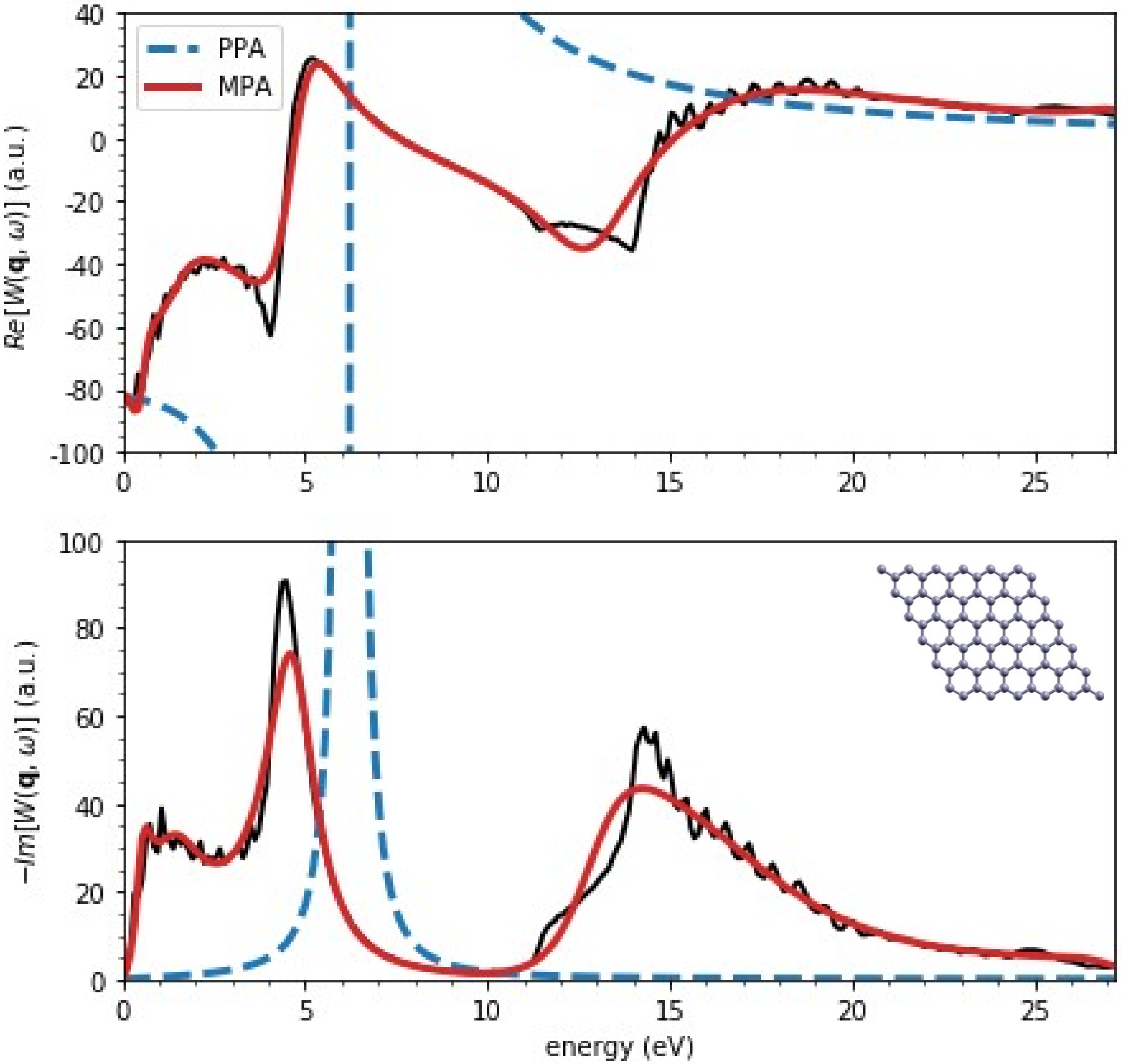
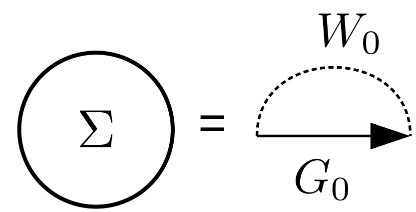
Beyond the plasmon-pole approximation[1]



$$W_0^{\mathrm{PPA}}(\omega) = \frac{2R\Omega}{\omega^2 - \Omega^2}$$

$$W_0^{\mathrm{MPA}}(\omega) = \sum_{n}^{n_p} \frac{2R_n\Omega_n}{\omega^2 - \Omega_n^2}$$

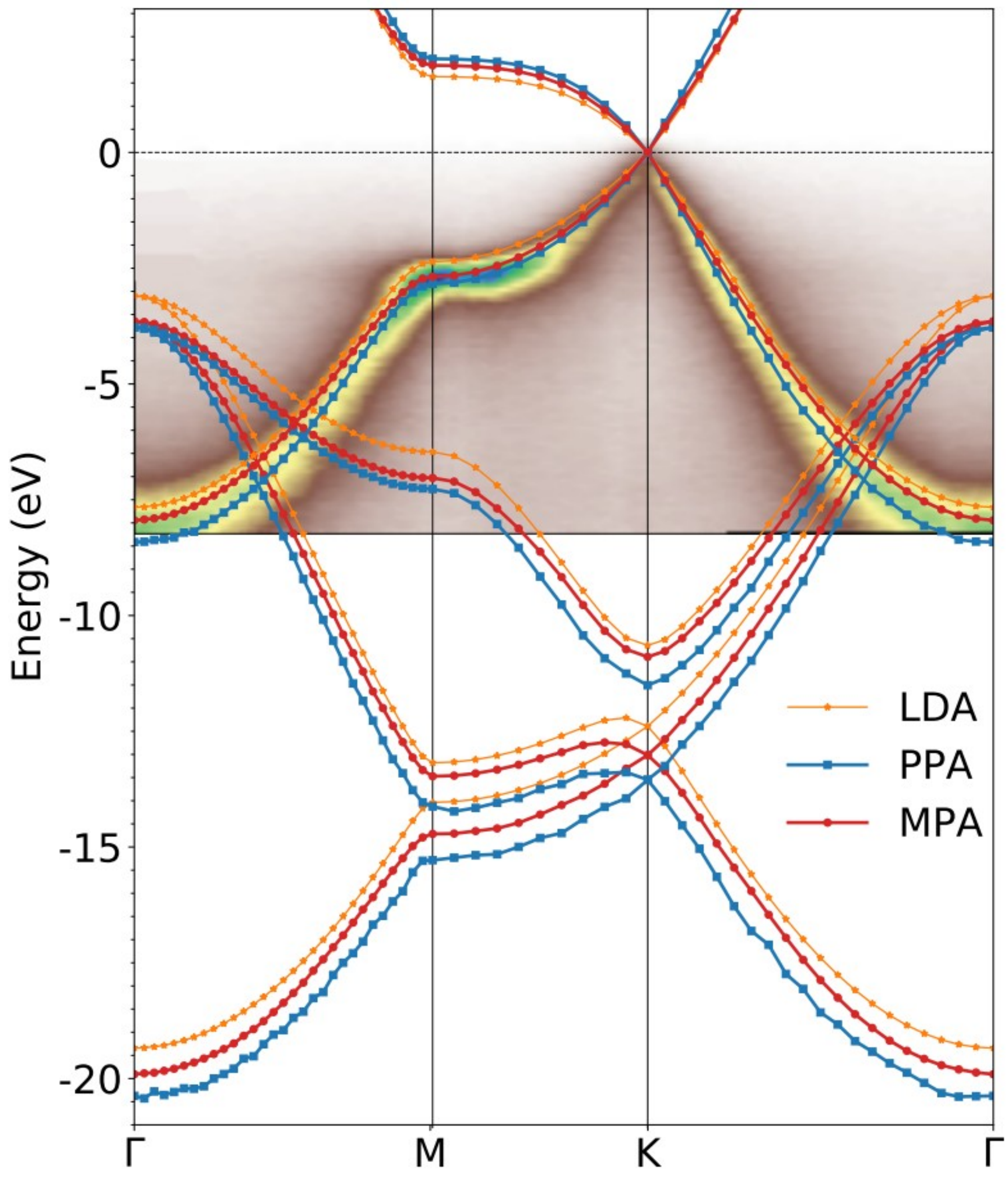


$$\Sigma_{n\mathbf{k}}(\omega) = \int d\omega' G_0(\omega - \omega')W_0(\omega')$$

- PPA reproduces static and high-frequency limits of the real part.
- MPA reproduces all the features.

[1] D. A. Leon et al. Phys. Rev. B 104, 115157 (2021)

Example: band structure of freestanding graphene[1]



- GW increase Fermi velocity and gaps in accordance with ARPES[1];
- DFT underestimate quasi-particle energies;
- G_0W_0 with MPA differs fro deeper states.
- Both W-av and MPA are needed to accurately describe GW bands in graphene.

[1] A. Guandalini, D.A. Leon et al. Phys. Rev. B 109, 075120 (2024)

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- Recent advancements:
  - W-av method to integrate W over the BZ
  - Multi-pole approximation to describe $W(\omega)$

References

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- Recent advancements:

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  - A. Guandalini et al. npj Comput. Mat. Vol. 9, 44 (2023)
  - A. Guandalini, D.A. Leon et al. Phys. Rev. B 109, 075120 (2024)