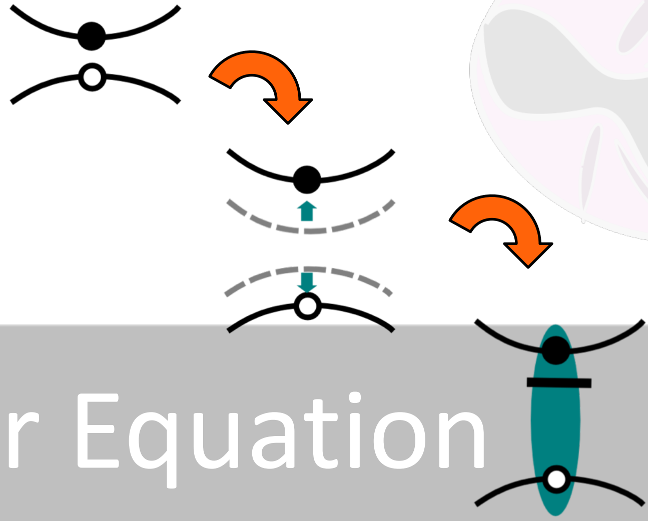

Bethe-Salpeter Equation

Time-dependent approach

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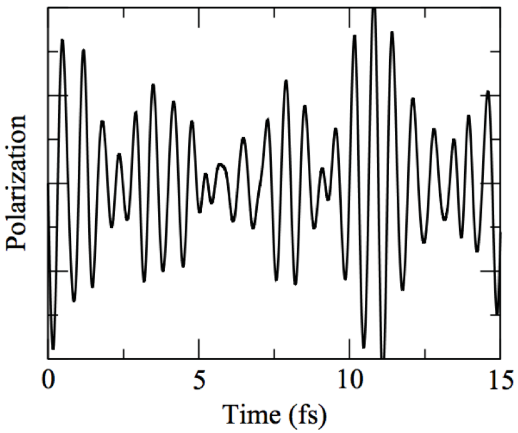
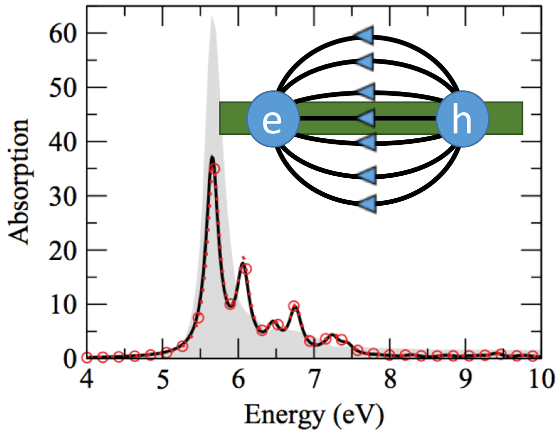


Fourier transform

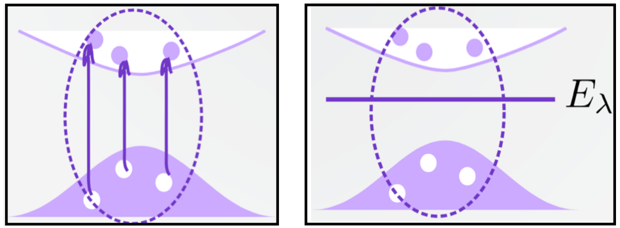


Beyond the independent-particle picture

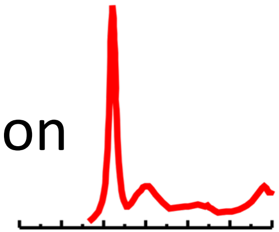
The equation of motion of the response function

$$\mathrm{i}\frac{\partial}{\partial t}\rho(t) = \ldots$$

The electron-hole interaction

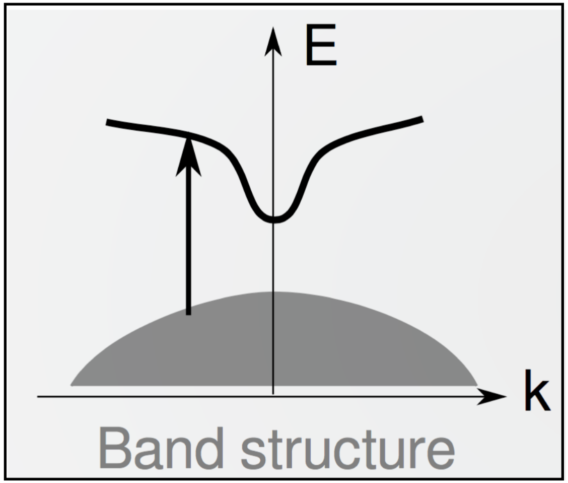


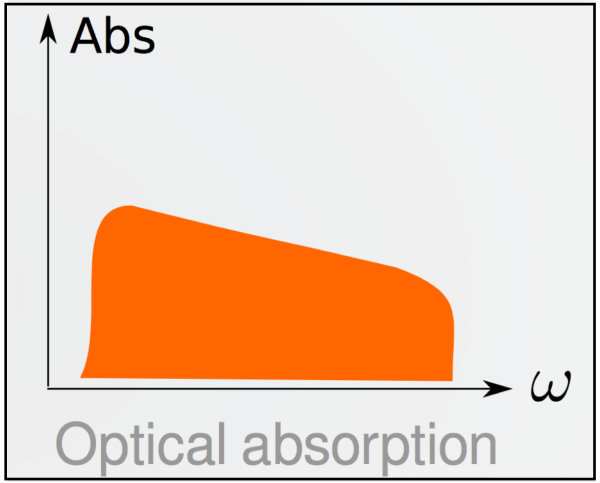
The Bethe-Salpeter equation



Going beyond the independent-particle picture

Knowledge of the electronic system
=> Description of its excitations
=> Predictive theoretical spectroscopy





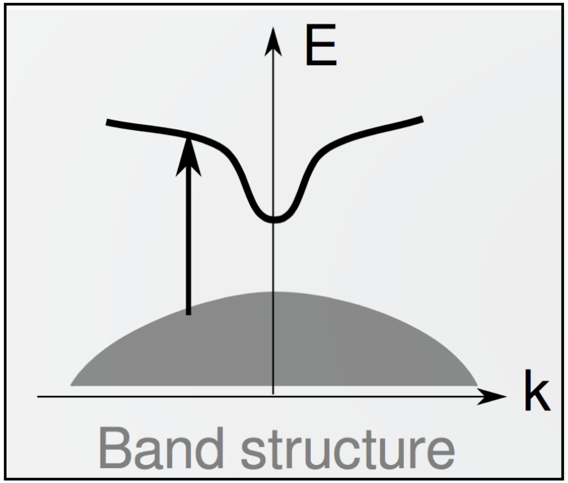
Going beyond the independent-particle picture

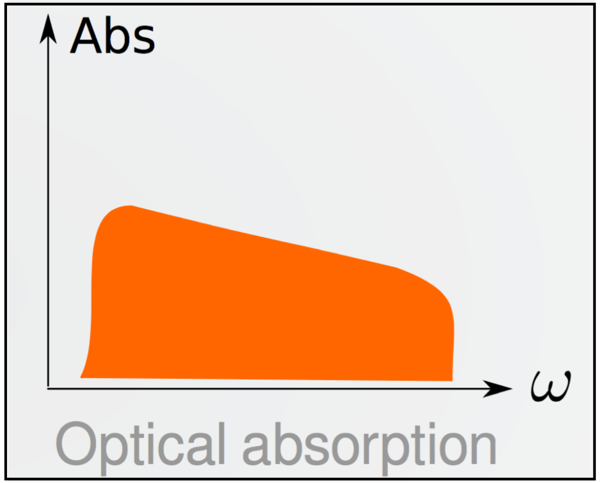
From Fermi's golden rule we know that:

$$\mathrm{Abs}(\omega) \propto \sum_{cvk} D^2_{cvk}\ \delta(\omega - [E_{ck} - E_{vk}])$$

Optical strength

Electronic transitions





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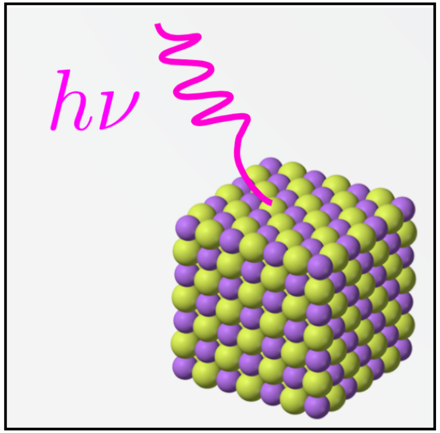
Lithium fluoride



Let's do a DFT+GW calculation:

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Going beyond the independent-particle picture

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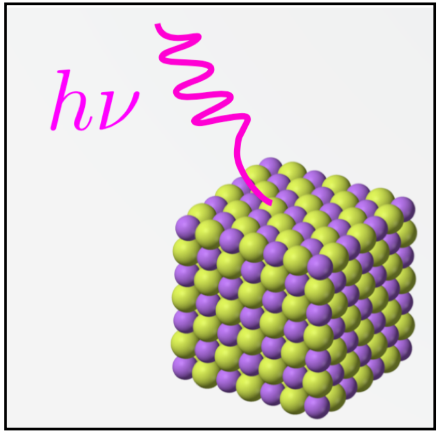
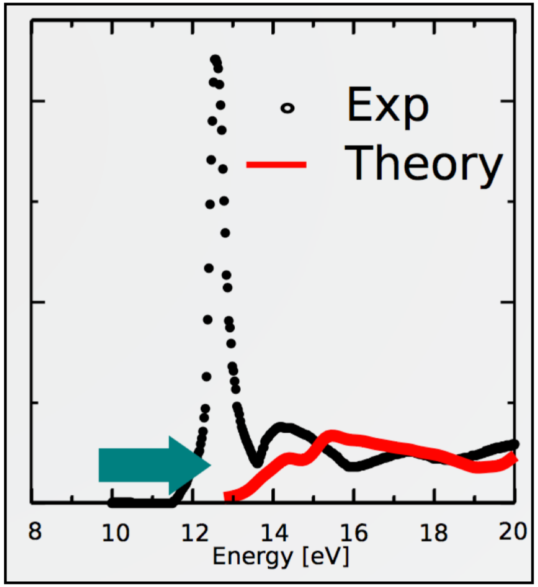


Let's do a DFT+GW calculation:

Completely wrong! Presence of **below band gap** excitations!



Going beyond the independent-particle picture

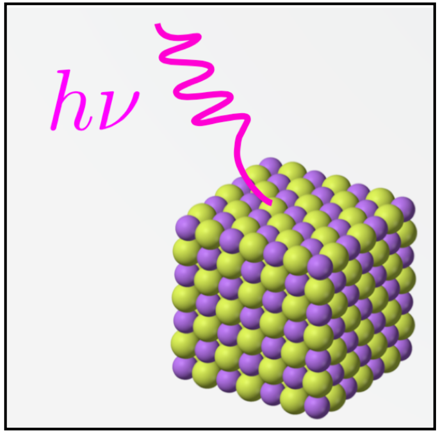
We need to account for the **electron-hole interaction**

$$\mathrm{Abs}(\omega) \propto \sum_{\lambda} \left| \sum_{cvk} A_{\lambda}^{cvk} \, D_{cvk} \right|^2 \delta(\omega - E_{\lambda})$$

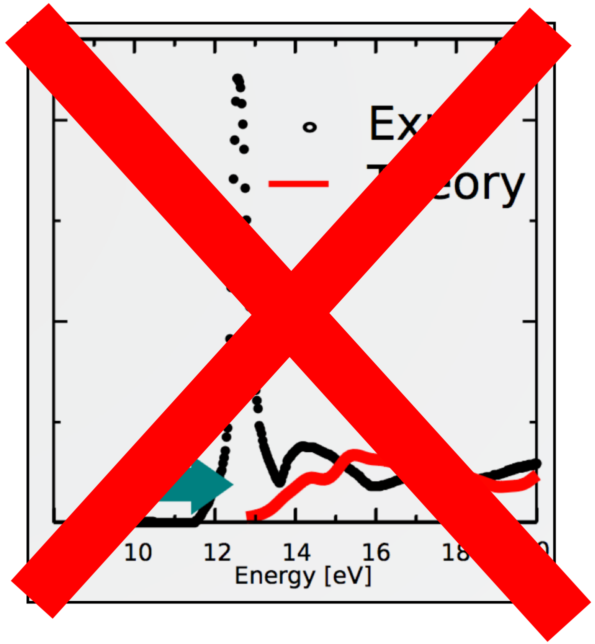
Optical strength

Exciton energies

Lithium fluoride



New quantities are **solutions of the BSE**!



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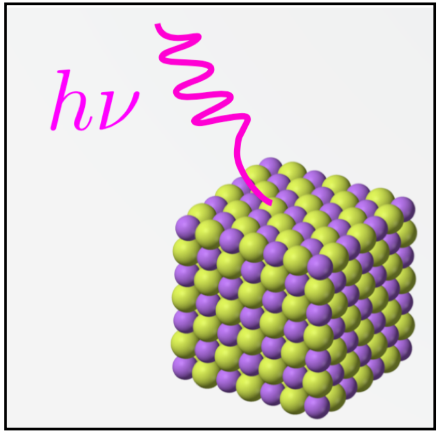

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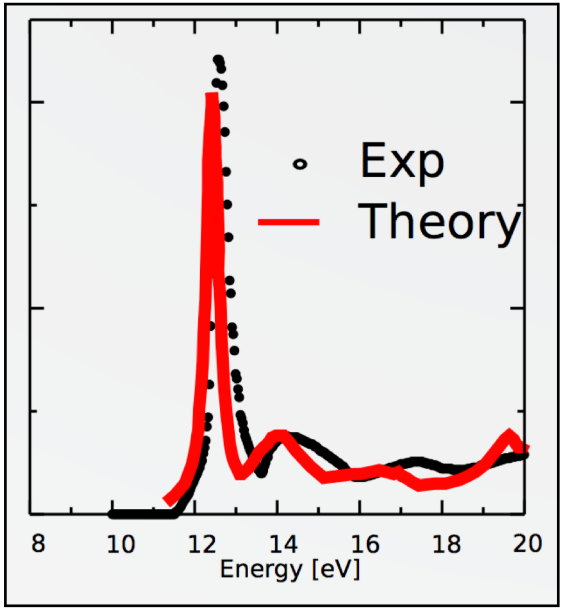
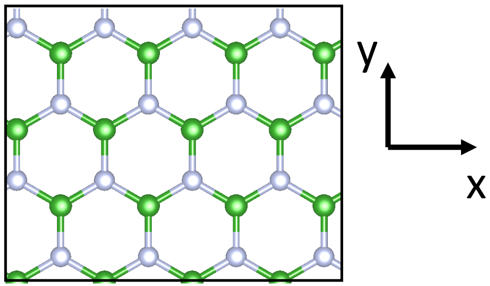
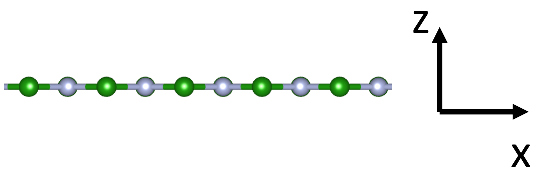


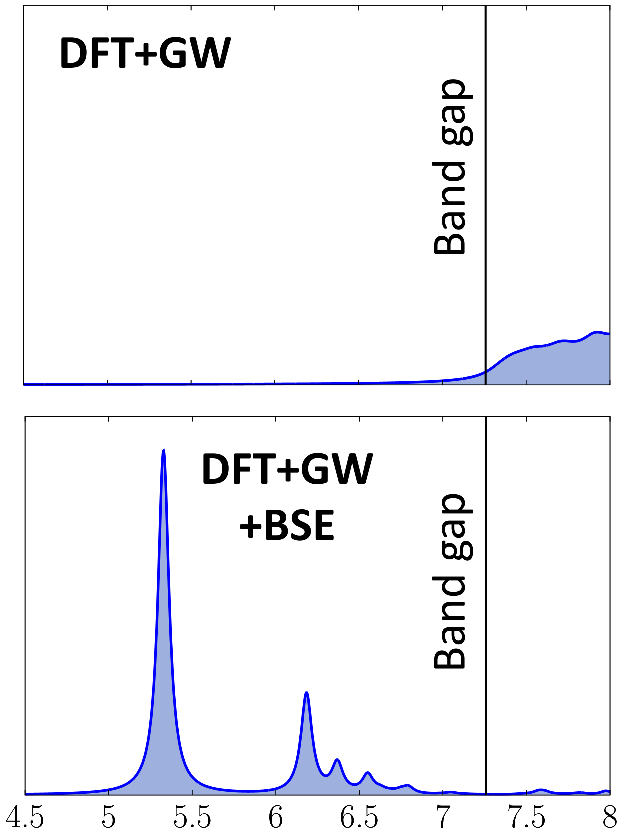
Going beyond the independent-particle picture

Especially relevant to **layered/2D materials**

Hexagonal boron nitride







Going beyond the independent-particle picture

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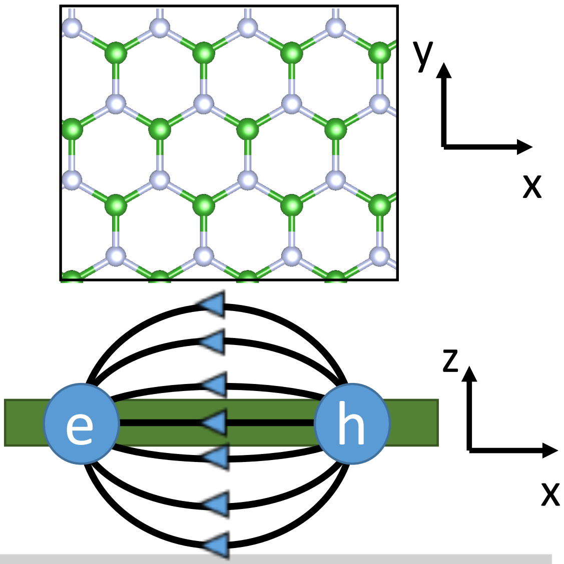
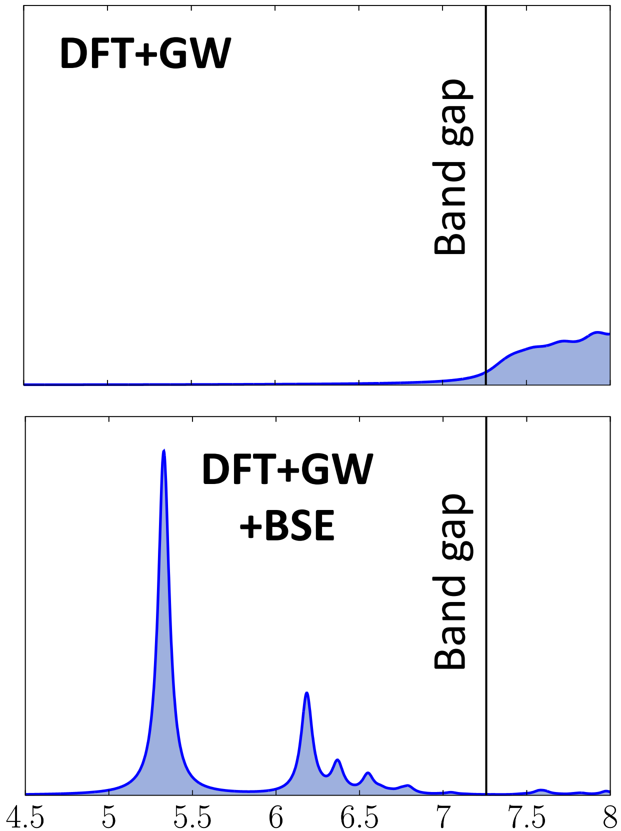


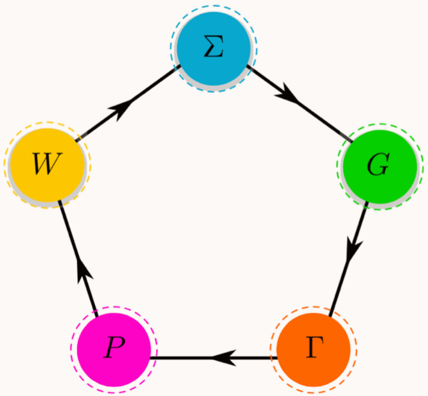


How can we derive the BSE?

Non-equilibrium dynamics of the response function

$$\chi(12) = \frac{\delta\rho(1)}{\delta V_{\text{ext}}(2)} \rightarrow \mathrm{i}\frac{\partial\chi(12)}{\partial t} = \ldots$$

Iteration of Hedin's equations that contain the response function



$$\chi(12) = \frac{\delta\rho(1)}{\delta V_{\text{ext}}(2)} \rightarrow$$

$$^{4}L(1234) = \frac{\delta G(12)}{\delta V_{\text{ext}(34)}}$$

G. Strinati, Riv. Nuovo Cim. 11, 12 (1988)

Generalization of the response function to 4-point…

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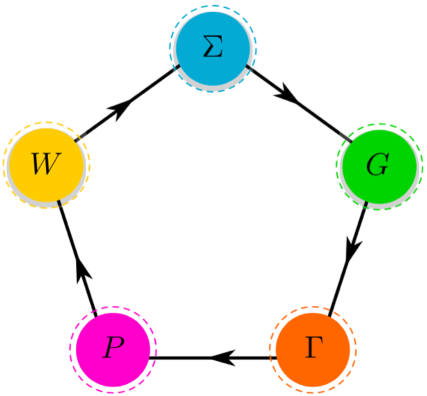

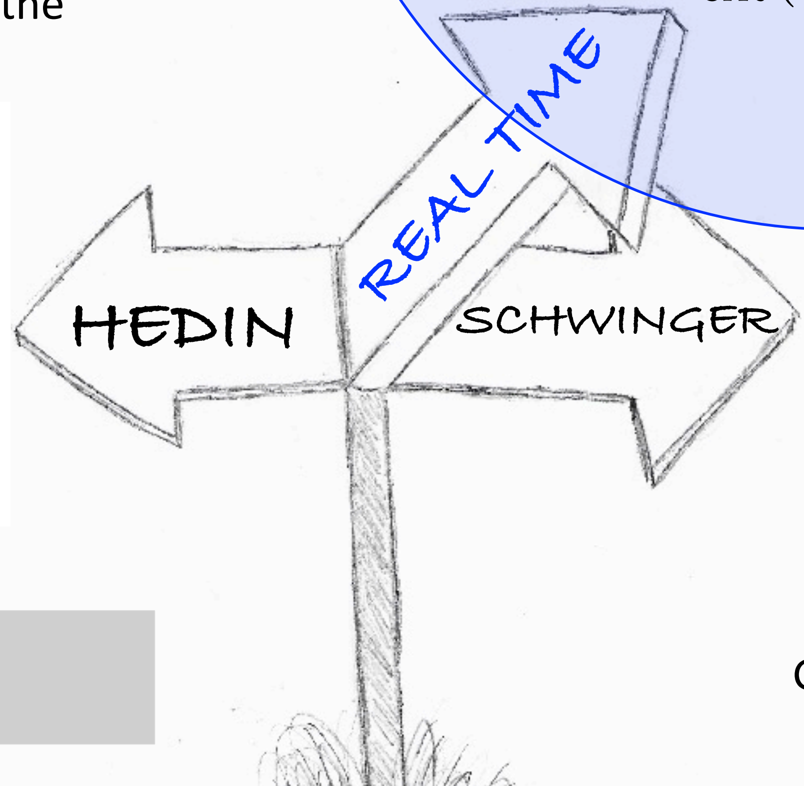

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Generalization of the response function to 4-point…

Choosing a description for the electronic system

Single-particle Hamiltonian from Hartree-Fock

$$\hat{H}^0 = \hat{T}_e + V_{e-N} + \hat{V}^H[\rho^0] + \hat{\Sigma}^x[\rho^0]$$

We may also build the Hamiltonian from DFT (Kohn-Sham), DFT + G_0W_0, etc.

Choosing a description for the electronic system

Single-particle Hamiltonian from Hartree-Fock

$$\hat{H}^0 = \hat{T}_e + V_{e-N} + \hat{V}^H[\rho^0] + \hat{\Sigma}^x[\rho^0]$$

$\hat{H}^0 \left| n \right\rangle = E_n \left| n \right\rangle$ Single-particle energies

$\langle \mathbf{r} | n \rangle = \varphi_n(\mathbf{r})$ Bloch function

Choosing a description for the electronic system

Single-particle Hamiltonian from Hartree-Fock

$$\hat{H}^0 = \hat{T}_e + V_{e-N} + \hat{V}^H[\rho^0] + \hat{\Sigma}^x[\rho^0]$$

Equilibrium particle density

$$\hat{\rho}^0(\mathbf{r}) = \sum_n |\varphi_n(\mathbf{r})|^2 \hat{c}_n^\dagger \hat{c}_n$$

$$\rho^0(\mathbf{r}) = \langle \hat{\rho}^0(\mathbf{r}) \rangle = \sum_n |\varphi_n(\mathbf{r})|^2 f_n$$

State occupations
[at zero T and for semiconductors either 0 or 1]

Time-dependent Hamiltonian and density matrix

Full Hamiltonian

$$\hat{H}(t) = \hat{H}^0 + U(t) + \Delta\hat{V}^H[\rho(t)] + \Delta\hat{\Sigma}^x[\rho(t)]$$

External field

Time-dependent Hamiltonian and density matrix

Full Hamiltonian

$$\hat{H}(t) = \hat{H}^0 + U(t) + \Delta\hat{V}^H[\rho(t)] + \Delta\hat{\Sigma}^x[\rho(t)]$$

$$\Delta\hat{V}^H[\rho(t)] = \hat{V}^H[\rho(t)] - \hat{V}^H[\rho^0]$$

$$\Delta\hat{\Sigma}^x[\rho(t)] = \hat{\Sigma}^x[\rho(t)] - \hat{\Sigma}^x[\rho^0]$$

If the density changes, its functionals also change

the Yambo team

Time-dependent Hamiltonian and density matrix

Full Hamiltonian

$$\hat{H}(t) = \hat{H}^0 + U(t) + \Delta\hat{V}^H[\rho(t)] + \Delta\hat{\Sigma}^x[\rho(t)]$$

Density matrix out of equilibrium

$$\hat{\rho}(\mathbf{r},t) = -\mathrm{i}\lim_{t'\to t}\hat{G}(\mathbf{r},t,t') = \sum_{n_1 n_2}\varphi_{n_1}(\mathbf{r})\varphi^*_{n_2}(\mathbf{r})\hat{\rho}_{n_2 n_1}(t)$$

$$\hat{\rho}_{n_2 n_1}(t) = \hat{c}^\dagger_{n_2}(t)\hat{c}_{n_1}(t)$$

Linear response function

As we have seen in a previous lecture (Kubo / Linear response):

$$\chi(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta\rho(\mathbf{r}t)}{\delta U(\mathbf{r}'t')}\bigg|_{U=0}$$

Linear response function

As we have seen in a previous lecture (Kubo / Linear response):

$$\chi(\mathbf{r}t,\mathbf{r}'t') = \left.\frac{\delta\rho(\mathbf{r}t)}{\delta U(\mathbf{r}'t')}\right|_{U=0}$$

with

$$\chi(\mathbf{r}t,\mathbf{r}'t') = \sum_{\substack{n_1 n_2\\ n_3 n_4}} \varphi_{n_1}(\mathbf{r})\varphi^*_{n_2}(\mathbf{r})\varphi^*_{n_3}(\mathbf{r}')\varphi_{n_4}(\mathbf{r}')\chi^R_{\substack{n_1 n_2\\ n_3 n_4}}(t,t')$$

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And then

$$\chi_{\substack{n_1 n_2\\ n_3 n_4}}(t,t') = \left.\frac{\delta\rho_{n_1 n_2}(t)}{\delta U_{n_3 n_4}(t')}\right|_{U=0}$$

We need to find the equation of motion for the response function!

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Equation of motion

For the density matrix (for more info attend Real Time lecture):

$$\mathrm{i}\frac{\partial}{\partial t}\rho_{n_1 n_2}(t) = \left[\hat{H}(t), \hat{\rho}(t)\right]_{n_1 n_2}$$

Equation of motion

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$$\mathrm{i}\frac{\partial}{\partial t}\rho_{n_1 n_2}(t) = \left[\hat{H}(t), \hat{\rho}(t)\right]_{n_1 n_2}$$

For the response function (taking the functional derivative of the above):

$$\mathrm{i}\frac{\partial}{\partial t}\chi^{n_1 n_2}_{n_3 n_4}(t,t') = \frac{\delta}{\delta U_{n_3 n_4}(t')}\left[\hat{H}(t), \hat{\rho}(t)\right]_{n_1 n_2}$$

The solution of this equation will yield the BSE!

Taking care of the two-particle kernel

Rewriting the density functionals

$$\Delta V^{H}_{n_1 n_2}[\rho(t)]$$

Taking care of the two-particle kernel

Rewriting the density functionals

$$\Delta V^{H}_{n_1 n_2}[\rho(t)] = \sum_{m_1 m_2} \int \mathrm{d}\bar{\bar{t}}\; \frac{\delta V^{H}_{n_1 n_2}[\rho(t)]}{\delta U_{m_1 m_2}(\bar{\bar{t}})}\; \delta U_{m_1 m_2}(\bar{\bar{t}})$$

Taking care of the two-particle kernel

Rewriting the density functionals

$$
\Delta V^{H}_{n_1 n_2}[\rho(t)] = \sum_{m_1 m_2} \int \mathrm{d}\bar{\bar{t}}\; \frac{\delta V^{H}_{n_1 n_2}[\rho(t)]}{\delta U_{m_1 m_2}(\bar{\bar{t}})}\; \delta U_{m_1 m_2}(\bar{\bar{t}})
$$

$$
= \sum_{\substack{m_1 m_2 \\ m_2 m_4}} \int \mathrm{d}\bar{\bar{t}}\mathrm{d}\bar{t}\; \frac{\delta V^{H}_{n_1 n_2}[\rho(t)]}{\delta \rho_{m_3 m_4}(\bar{t})} \frac{\delta \rho_{m_3 m_4}[\rho(\bar{t})]}{\delta U_{m_1 m_2}(\bar{\bar{t}})}\; \delta U_{m_1 m_2}(\bar{\bar{t}})
$$

χ

Taking care of the two-particle kernel

Rewriting the density functionals

$$\Delta V^{H}_{n_1 n_2}[\rho(t)] = \sum_{m_1 m_2} \int \mathrm{d}\bar{\bar{t}}\, \frac{\delta V^{H}_{n_1 n_2}[\rho(t)]}{\delta U_{m_1 m_2}(\bar{\bar{t}})}\, \delta U_{m_1 m_2}(\bar{\bar{t}})$$

$$= \sum_{\substack{m_1 m_2 \\ m_2 m_4}} \int \mathrm{d}\bar{\bar{t}}\mathrm{d}\bar{t}\, \frac{\delta V^{H}_{n_1 n_2}[\rho(t)]}{\delta \rho_{m_3 m_4}(\bar{t})} \frac{\delta \rho_{m_3 m_4}[\rho(\bar{t})]}{\delta U_{m_1 m_2}(\bar{\bar{t}})}\, \delta U_{m_1 m_2}(\bar{\bar{t}})$$

χ

By doing the same for $\Delta\Sigma^{x}$ we obtain:

Taking care of the two-particle kernel

Rewriting the density functionals

$$\Delta V^{H}_{n_1 n_2}[\rho(t)] + \Delta \Sigma^{x}_{n_1 n_2}[\rho(t)] =$$

$$= \sum_{\substack{m_1 m_2 \\ m_2 m_4}} \int \mathrm{d}\bar{\bar{t}}\,\mathrm{d}\bar{t} \left[\frac{\delta V^{H}_{n_1 n_2}[\rho(t)]}{\delta \rho_{m_3 m_4}(\bar{t})} + \frac{\delta \Sigma^{x}_{n_1 n_2}[\rho(t)]}{\delta \rho_{m_3 m_4}(\bar{t})} \right] \chi^{m_3 m_4}_{m_1 m_2}(\bar{t}, \bar{\bar{t}})\, \delta U_{m_1 m_2}(\bar{\bar{t}})$$

Two-particle "kernel"

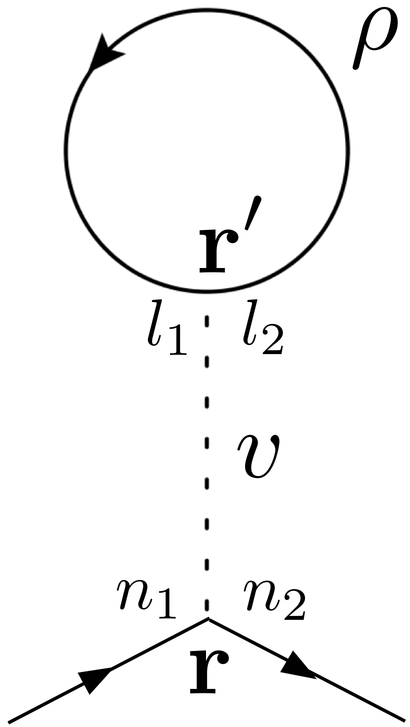
In order to proceed we will write down explicitly $V^{H}_{n_1 n_2}$ and $\Sigma^{x}_{n_1 n_2}$ and then compute the derivatives

Time-dependent Hartree

$$V^H_{n_1 n_2}(t) = \langle i | \int \mathrm{d}^3 r' \, \frac{\rho(\mathbf{r}' t)}{|\mathbf{r} - \mathbf{r}'|} \, | j \rangle =$$

$$= \int \mathrm{d}^3 r \, \mathrm{d}^3 r' \; \varphi^*_{n_1}(\mathbf{r}) \frac{\rho(\mathbf{r}' t)}{|\mathbf{r} - \mathbf{r}'|} \varphi_{n_2}(\mathbf{r})$$

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



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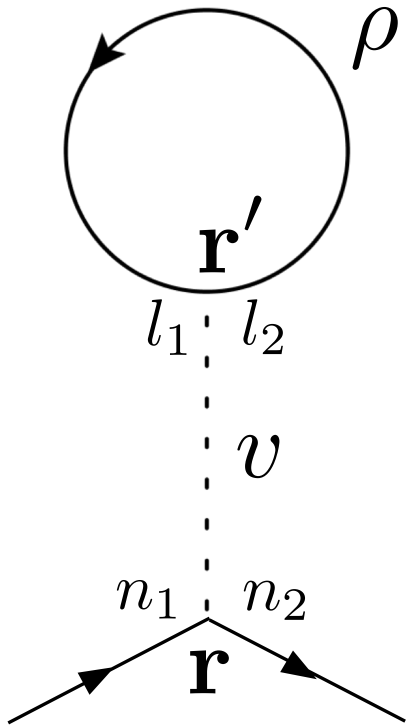
We insert the expansion of the time-dependent density

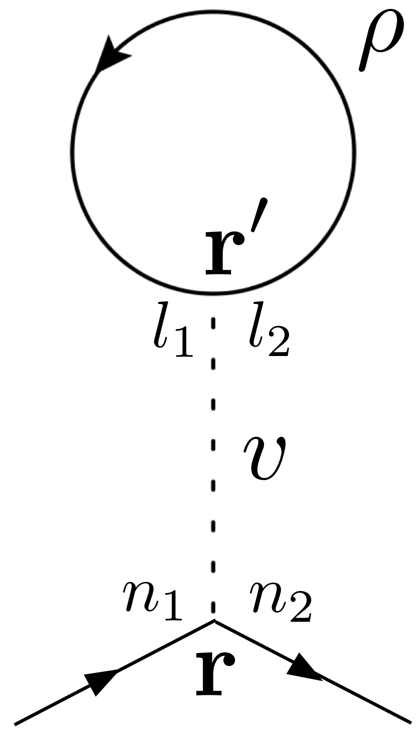
$$v(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$$



Time-dependent Hartree

$$V^H_{n_1 n_2}(t) = 2 \sum_{l_1 l_2} \rho_{l_1 l_2}(t) \int \mathrm{d}^3 r \, \mathrm{d}^3 r' \; \varphi^*_{n_1}(\mathbf{r}) \varphi^*_{l_1}(\mathbf{r}') \varphi_{l_2}(\mathbf{r}') \varphi_{n_2}(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

$$\equiv 2 \sum_{l_1 l_2} \rho_{l_1 l_2}(t) \, V_{\substack{n_1 n_2 \\ l_1 l_2}}$$



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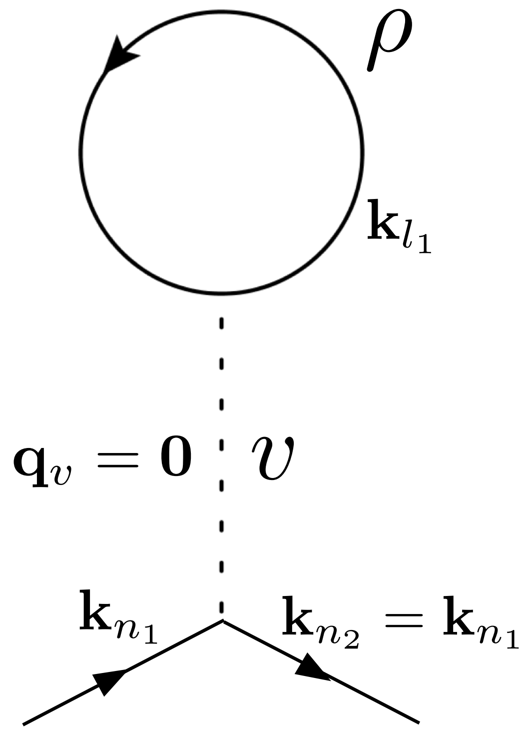
$$\equiv 2\sum_{l_1 l_2} \rho_{l_1 l_2}(t)\, V_{\substack{n_1 n_2 \\ l_1 l_2}}$$



Momentum conservation implies that V^H does not carry an internal momentum

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Time-dependent Hartree

$$V^{H}_{n_1 n_2}(t) = 2 \sum_{l_1 l_2} \rho_{l_1 l_2}(t) \; \left[V^{q_v=0}\right]_{\substack{n_1 n_2 \\ l_1 l_2}}$$

Time-dependent Hartree

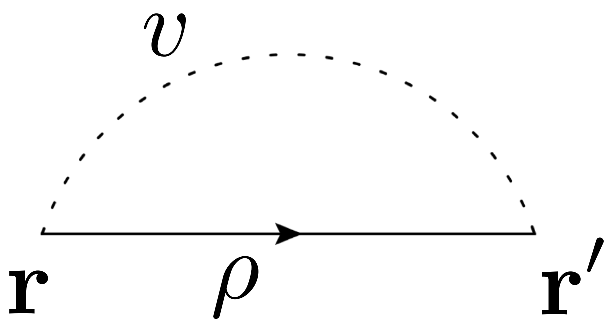
$$V^H_{n_1 n_2}(t) = 2\sum_{l_1 l_2} \rho_{l_1 l_2}(t)\ \left[V^{q_v=0}\right]_{\substack{n_1 n_2 \\ l_1 l_2}}$$

$$\frac{\delta V^H_{n_1 n_2}(t)}{\delta \rho_{m_3 m_4}(\bar{t})} = 2\left[V^{q_v=0}\right]_{\substack{n_1 n_2 \\ m_3 m_4}} \delta(t-\bar{t})$$

Exchange (and correlation) self-energy

Time-dependent exchange

$$\Sigma^x(\mathbf{r}t, \mathbf{r}'t) = \mathrm{i}G^0(\mathbf{r}t, \mathbf{r}'t)v(\mathbf{r}, \mathbf{r}')$$
$$= -\rho(\mathbf{r}\mathbf{r}', t)v(\mathbf{r}, \mathbf{r}')$$



Exchange (and correlation) self-energy

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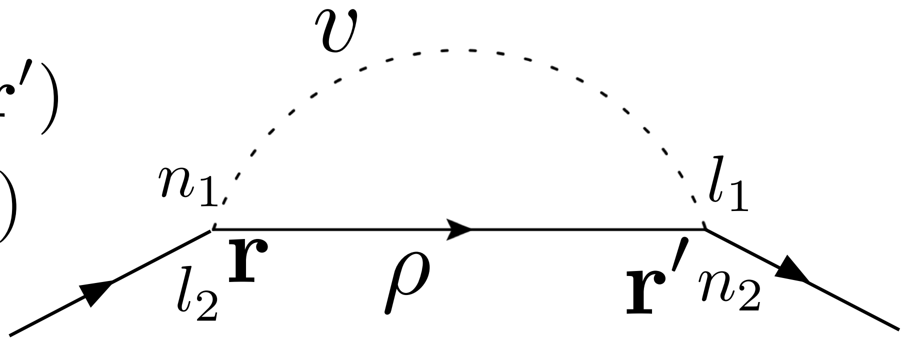


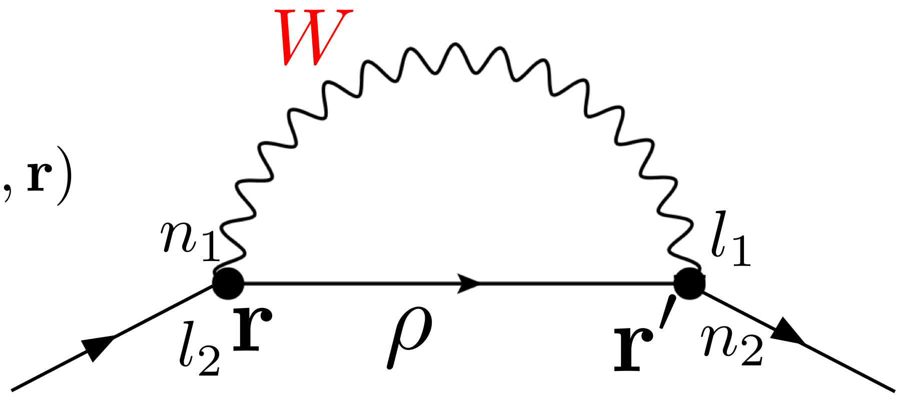
$$\Sigma^x_{n_1 n_2}(t) = -\sum_{l_1 l_2} \rho_{l_1 l_2}(t) \int \mathrm{d}^3 r\, \mathrm{d}^3 r' \; \varphi^*_{l_1}(\mathbf{r}')\varphi_{l_2}(\mathbf{r})\varphi^*_{n_1}(\mathbf{r})\varphi_{n_2}(\mathbf{r}')v(\mathbf{r},\mathbf{r}')$$

ISSUE: the **unscreened** Coulomb interaction overbinds electron and holes, giving wrong optical spectra.

Exchange (and correlation) self-energy

Time-dependent SEX

$$W(\mathbf{r},\mathbf{r}') = \int \mathrm{d}^3r'' \varepsilon^{-1}_{RPA}(\mathbf{r},\mathbf{r}'')v(\mathbf{r}'',\mathbf{r})$$



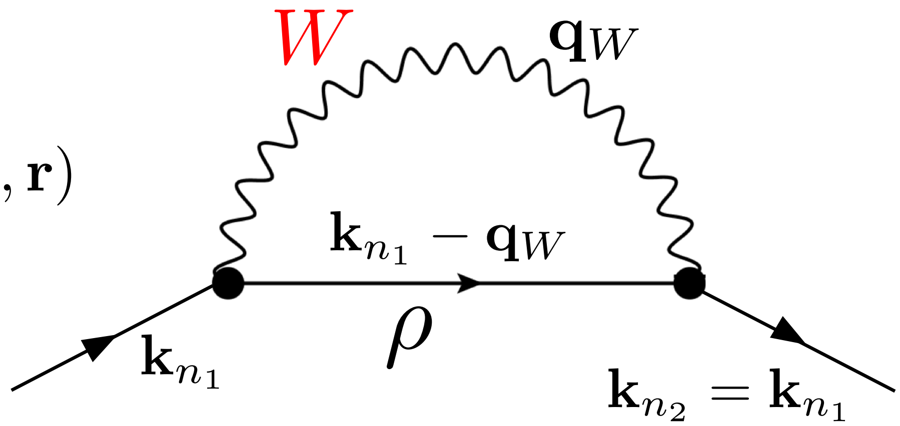
SOLUTION: we replace the Fock term with the statically screened exchange (SEX)

$$\Sigma^{\mathrm{SEX}}_{n_1 n_2}(t) = -\sum_{l_1 l_2} \rho_{l_1 l_2}(t) \int \mathrm{d}^3r\, \mathrm{d}^3r'\; \varphi^*_{l_1}(\mathbf{r}')\varphi_{l_2}(\mathbf{r})\varphi^*_{n_1}(\mathbf{r})\varphi_{n_2}(\mathbf{r}')W(\mathbf{r},\mathbf{r}')$$

Exchange (and correlation) self-energy

Time-dependent SEX

$$W(\mathbf{r},\mathbf{r}') = \int \mathrm{d}^3r'' \varepsilon^{-1}_{RPA}(\mathbf{r},\mathbf{r}'')v(\mathbf{r}'',\mathbf{r})$$



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Exchange (and correlation) self-energy

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$$\Sigma^{\mathrm{SEX}}_{n_1 n_2}(t) = -\sum_{l_1 l_2} \rho_{l_1 l_2}(t) W_{\substack{n_1 l_2 \\ l_1 n_2}}$$

Exchange (and correlation) self-energy

Time-dependent SEX

$$\Sigma^{\mathrm{SEX}}_{n_1 n_2}(t) = -\sum_{l_1 l_2} \rho_{l_1 l_2}(t) W_{\substack{n_1 l_2 \\ l_1 n_2}}$$

$$\frac{\delta \Sigma^{\mathrm{SEX}}_{n_1 n_2}(t)}{\delta \rho_{m_3 m_4}(\bar{t})} = -W_{\substack{n_1 m_2 \\ m_1 n_2}} \, \delta(t - \bar{t}) \quad \longrightarrow \quad \frac{\delta W}{\delta \rho}$$

NEGLECTED!
(Higher order in the interaction)

Solving the equation of motion

$$
\begin{aligned}
\mathrm{i}\frac{\partial}{\partial t}\chi_{\substack{n_1n_2\\n_3n_4}}(t,t') &= \frac{\delta}{\delta U_{n_3n_4}(t')}\left[\hat{H}^0(t),\hat{\rho}(t)\right]_{n_1n_2} \qquad \text{(A)}\\
&+ \frac{\delta}{\delta U_{n_3n_4}(t')}\left[\hat{U}(t),\hat{\rho}(t)\right]_{n_1n_2} \qquad \text{(B)}\\
&+ \frac{\delta}{\delta U_{n_3n_4}(t')}\left[-\sum_{\substack{m_1m_2\\m_3m_4}}\int \mathrm{d}\bar{\bar{t}}\left(\hat{W}-2\hat{V}\right)\chi^R_{\substack{m_3m_4\\m_1m_2}}\delta U_{m_1m_2}(\bar{\bar{t}}),\hat{\rho}(t)\right]_{n_1n_2} \qquad \text{(C)}
\end{aligned}
$$

Solving the equation of motion

Computing the commutators…

A

$$\left[\hat{H}^0, \hat{\rho}(t)\right]_{n_1 n_2} = \langle n_1 | \hat{H}^0 \hat{\rho}(t) | n_2 \rangle - \langle n_1 | \hat{\rho}(t) \hat{H}^0 | n_2 \rangle$$

$$= (E_{n_1} - E_{n_2}) \rho_{n_1 n_2}(t)$$

Solving the equation of motion

Computing the commutators…

A

$$\left[\hat{H}^0, \hat{\rho}(t)\right]_{n_1 n_2} = \langle n_1| \hat{H}^0 \hat{\rho}(t) |n_2\rangle - \langle n_1| \hat{\rho}(t) \hat{H}^0 |n_2\rangle$$

$$= (E_{n_1} - E_{n_2})\rho_{n_1 n_2}(t)$$

B

$$\left[\hat{U}(t), \hat{\rho}(t)\right]_{n_1 n_2} = \left[\hat{U}(t), \hat{\rho}^0\right]_{n_1 n_2}$$

→ We stay at 1^{st} order in U

$$= (f_{n_2} - f_{n_1})U_{n_1 n_2}(t)$$

Solving the equation of motion

Computing the commutators…

A

$$\left[\hat{H}^0, \hat{\rho}(t)\right]_{n_1 n_2} = \langle n_1| \hat{H}^0 \hat{\rho}(t) |n_2\rangle - \langle n_1| \hat{\rho}(t) \hat{H}^0 |n_2\rangle$$
$$= (E_{n_1} - E_{n_2})\rho_{n_1 n_2}(t)$$

C

Analogous to B

Solving the equation of motion

Computing the derivative…

$$\mathrm{i}\frac{\partial}{\partial t}\chi_{n_3 n_4}^{n_1 n_2}(t-t') = (E_{n_1} - E_{n_2})\chi_{n_3 n_4}^{n_1 n_2}(t-t') + \mathrm{i}(f_{n_2} - f_{n_1})\left[-\mathrm{i}\delta_{n_1 n_3}\delta_{n_2 n_4} + \sum_{m_3 m_4} K_{\;m_3 m_4}^{\;n_1 n_2}\chi_{n_3 n_4}^{m_3 m_4}(t-t')\right]$$

Solving the equation of motion

Computing the derivative…

$$\mathrm{i}\frac{\partial}{\partial t}\chi^{n_1 n_2}_{n_3 n_4}(t-t') = (E_{n_1}-E_{n_2})\chi^{n_1 n_2}_{n_3 n_4}(t-t') + \mathrm{i}(f_{n_2}-f_{n_1})\left[-\mathrm{i}\delta_{n_1 n_3}\delta_{n_2 n_4} + \sum_{m_3 m_4} K^{\;n_1 n_2}_{\;m_3 m_4}\,\chi^{m_3 m_4}_{n_3 n_4}(t-t')\right]$$

e-h pair created at time *t* and recombined ad time *t'*

$$\chi(t,t') = \chi(t-t')$$

Solving the equation of motion

Computing the derivative…

$$
\mathrm{i}\frac{\partial}{\partial t}\chi^{n_1 n_2}_{n_3 n_4}(t-t') = (E_{n_1} - E_{n_2})\chi^{n_1 n_2}_{n_3 n_4}(t-t') + \mathrm{i}(f_{n_2} - f_{n_1})\left[-\mathrm{i}\delta_{n_1 n_3}\delta_{n_2 n_4} + \sum_{m_3 m_4} K^{\,n_1 n_2}_{\,m_3 m_4}\chi^{m_3 m_4}_{n_3 n_4}(t-t')\right]
$$

e-h pair created at time *t* and recombined ad time *t'*

$$
\chi(t,t') = \chi(t-t')
$$

Electron-hole interaction kernel

$$
-\mathrm{i}K^{\,n_1 n_2}_{\,m_3 m_4} = W^{n_1 m_4}_{m_3 n_2} - 2\left[V^{q_v=0}\right]^{n_1 n_2}_{m_3 m_4}
$$

Solving the equation of motion

Computing the derivative…

$$
\mathrm{i}\frac{\partial}{\partial t}\chi^{n_1 n_2}_{n_3 n_4}(t-t') = (E_{n_1} - E_{n_2})\chi^{n_1 n_2}_{n_3 n_4}(t-t') + \mathrm{i}(f_{n_2} - f_{n_1})\left[-\mathrm{i}\delta_{n_1 n_3}\delta_{n_2 n_4} + \sum_{m_3 m_4} K^{\ n_1 n_2}_{\ m_3 m_4}\chi^{m_3 m_4}_{n_3 n_4}(t-t')\right]
$$

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$$

Electron-hole attractive interaction (binding term)

Repulsive contribution

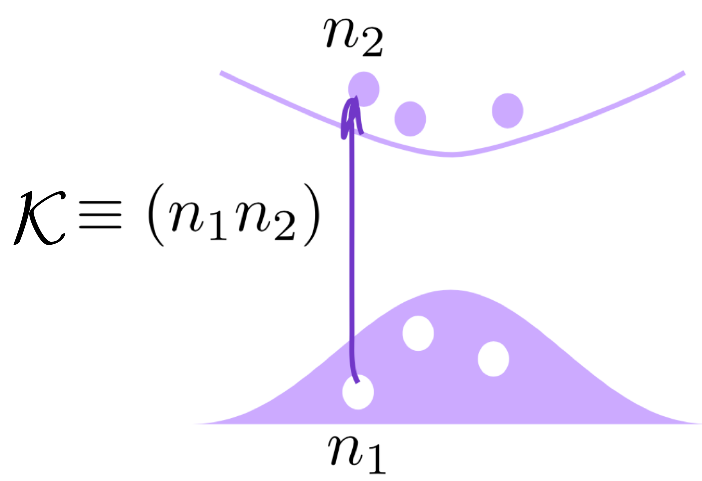
Solving the equation of motion

Switching to the transition basis…

A basis of electron-hole transitions

$$\langle \mathbf{r} | n_1 n_2 \rangle = \varphi^*_{n_1}(\mathbf{r})\varphi_{n_2}(\mathbf{r})$$

$$|n_1 n_2\rangle = |\mathcal{K}\rangle$$



Solving the equation of motion

Switching to the transition basis…

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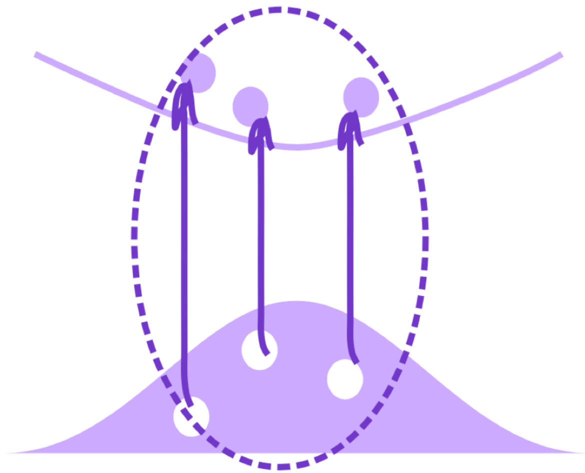

$$\mathrm{i} \frac{\partial}{\partial t} \chi_{\mathcal{K}\mathcal{K}'}(t-t') = \Delta E_{\mathcal{K}} \; \chi_{\mathcal{K}\mathcal{K}'}(t-t') + \mathrm{i} f_{\mathcal{K}} \left[-\mathrm{i}\delta_{\mathcal{K}\mathcal{K}'} + \sum_{\overline{\mathcal{K}}} K_{\mathcal{K}\overline{\mathcal{K}}} \; \chi_{\overline{\mathcal{K}}\mathcal{K}'}(t-t') \right]$$

Solving the equation of motion

Taking the Fourier transform…

$$(\omega - \Delta E_{\mathcal{K}})\ \chi_{\mathcal{K}\mathcal{K}'}(\omega) = \mathrm{i} f_{\mathcal{K}} \left[-\mathrm{i}\delta_{\mathcal{K}\mathcal{K}'} + \sum_{\overline{\mathcal{K}}} K_{\mathcal{K}\overline{\mathcal{K}}}\ \chi_{\overline{\mathcal{K}}\mathcal{K}'}(\omega) \right]$$

Solving the equation of motion

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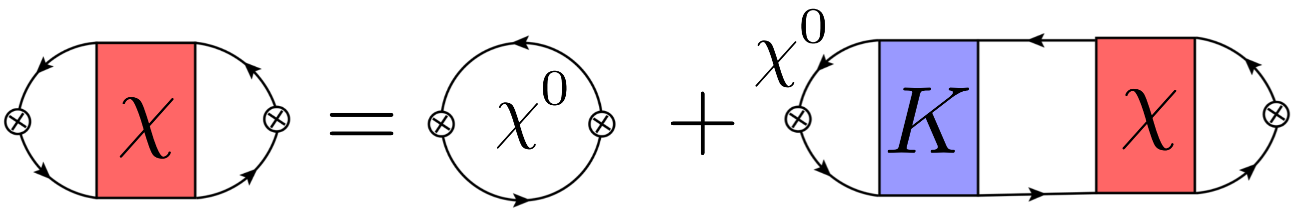
If K=0, we obtain the independent-particle response.
It is diagonal in the transition basis!

$$\chi^{0}_{\mathcal{K}}(\omega) = \frac{f_{\mathcal{K}}}{\omega - \Delta E_{\mathcal{K}}}$$

Bethe-Salpeter equation

(As Dyson-like equation)

$$\chi_{\mathcal{K}\mathcal{K}'}(\omega) = \chi^0_{\mathcal{K}}(\omega) + \chi^0_{\mathcal{K}}(\omega)\sum_{\overline{\mathcal{K}}} K_{\mathcal{K}\overline{\mathcal{K}}}\ \chi_{\overline{\mathcal{K}}\mathcal{K}'}(\omega)$$



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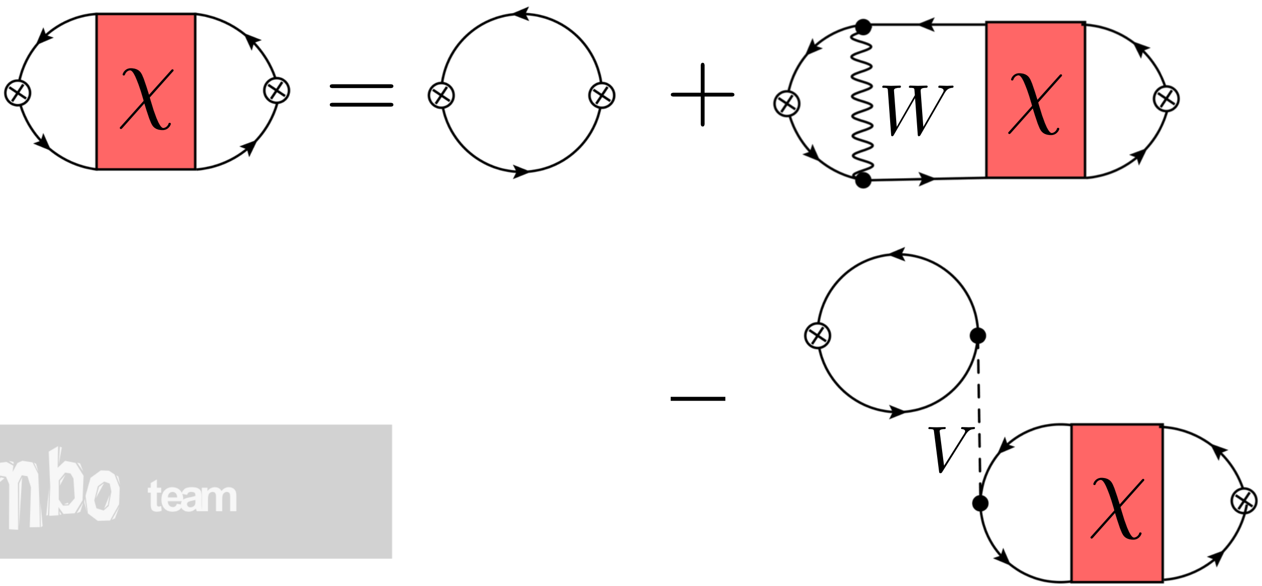

Inversion of the BSE

We isolate the response function on the left hand side

$$\sum_{\overline{\mathcal{K}}} \left[(\omega - \Delta E_{\mathcal{K}})\delta_{\mathcal{K}\overline{\mathcal{K}}} - \mathrm{i} f_{\mathcal{K}} K_{\mathcal{K}\overline{\mathcal{K}}} \right] \chi_{\overline{\mathcal{K}}\mathcal{K}'}(\omega) = f_{\mathcal{K}} \delta_{\mathcal{K}\mathcal{K}'}$$

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… and recognize a **two-particle Hamiltonian**

$$\sum_{\overline{\mathcal{K}}} \left[\omega\delta_{\mathcal{K}\overline{\mathcal{K}}} - (\Delta E_{\mathcal{K}}\delta_{\mathcal{K}\overline{\mathcal{K}}} + \mathrm{i} f_{\mathcal{K}} K_{\mathcal{K}\overline{\mathcal{K}}})\right] \chi_{\overline{\mathcal{K}}\mathcal{K}'}(\omega) = f_{\mathcal{K}'}$$

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$$\sum_{\overline{\mathcal{K}}} \left[\omega\delta_{\mathcal{K}\overline{\mathcal{K}}} - H^{2p}_{\mathcal{K}\overline{\mathcal{K}}} \right] \chi_{\overline{\mathcal{K}}\mathcal{K}'}(\omega) = f_{\mathcal{K}'}$$

Inversion of the BSE

In matrix form we have

$$\left[\mathbb{1}\omega - \hat{H^{2p}}\right] \cdot \hat{\chi} = \vec{f}$$

And after performing matrix inversion

$$\hat{\chi} = \left[\mathbb{1}\omega - \hat{H}^{2p}\right]^{-1} \cdot \vec{f}$$

This indeed looks like a two-particle propagator

Inversion of the BSE

If we diagonalize the excitonic Hamiltonian

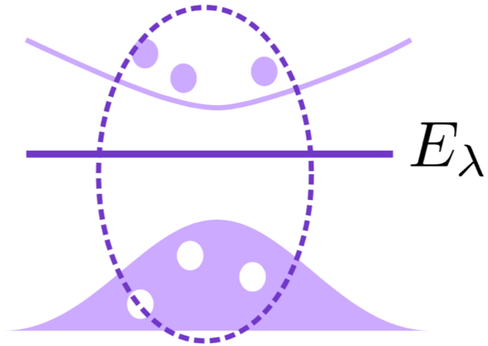
$$\hat{H}^{2p}\left|\lambda\right\rangle = E_\lambda \left|\lambda\right\rangle$$

Excitonic basis

Exciton energies

$$\langle \mathcal{K} | \lambda \rangle = A_\lambda^{\mathcal{K}}$$

Exciton coefficients



Then the equation for the response function can be finally written in terms of the **excitonic basis**

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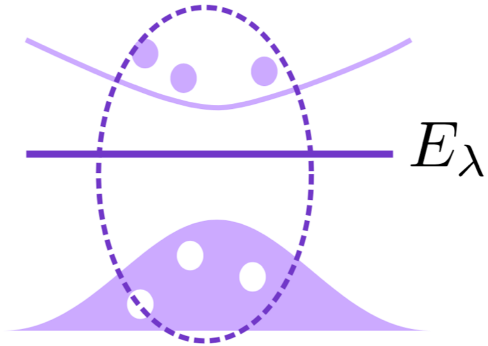

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$$\hat{\chi} = \left[\mathbb{1}\omega - \hat{H}^{2p}\right]^{-1} \cdot \vec{f}$$

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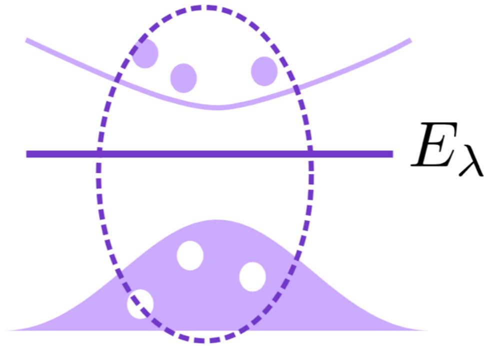

Then the equation for the response function can be finally written in terms of the **excitonic basis**

$$\hat{\chi} = \sum_\lambda \frac{\left|\lambda\right\rangle \left\langle\lambda\right|}{\omega - E_\lambda} \cdot \vec{f}$$

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$$\hat{H}^{2p}\,|\lambda\rangle = E_\lambda\,|\lambda\rangle$$

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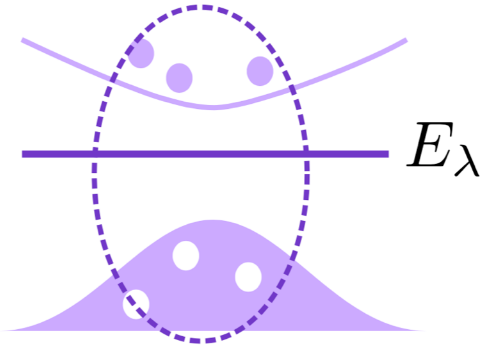

Then the equation for the response function can be finally written in terms of the **excitonic basis**

$$\chi_{\mathcal{K}\mathcal{K}'}(\omega) = \left[\frac{\delta\rho}{\delta U}\right]_{\mathcal{K}\mathcal{K}'}(\omega) = \sum_\lambda \frac{A_\lambda^{\mathcal{K}}\left(A_\lambda^{\mathcal{K}'}\right)^*}{\omega - E_\lambda}$$

[v->c transitions]

Excitonic Hamiltonian

In the end, the problem of the **correlated propagation of particles and holes**, i.e., the **spectroscopy of neutral excitations**, can be reduced to the diagonalization of an effective two-particle Hamiltonian

$$H^{2p}_{\mathcal{K}\mathcal{K}'} = \Delta E_{\mathcal{K}} \delta_{\mathcal{K}\mathcal{K}'} + \mathrm{i} f_{\mathcal{K}} K_{\mathcal{K}\mathcal{K}'}$$

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Screened interaction and mixing of electronic transitions:

$$K_{\mathcal{K}\mathcal{K}'} = \mathrm{i}\left[W_{\mathcal{K}\mathcal{K}'} - 2V_{\mathcal{K}\mathcal{K}'}\right]$$

Excitonic Hamiltonian

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Ingredients:

Quasiparticle energies (**DFT + GW**)	Single-particle wave functions (**DFT**)	Static electronic screening (**DFT + RPA**)
E_n	$\varphi_n(\mathbf{r})$	$\varepsilon^{-1}_{\mathrm{RPA}}$

Take-home message

- **Independent-particle picture fails** to reproduce key spectral features due to lack of **electron-hole interaction**
- The **electron-hole interaction** can be accounted for in the **dynamics of the excited** electronic **system**
- **The equation of motion for the response function** reduces to the diagonalization of an **effective two-particle Hamiltonian** in the basis of electronic transitions
- This yields the **optical absorption** in the **excitonic picture**

References

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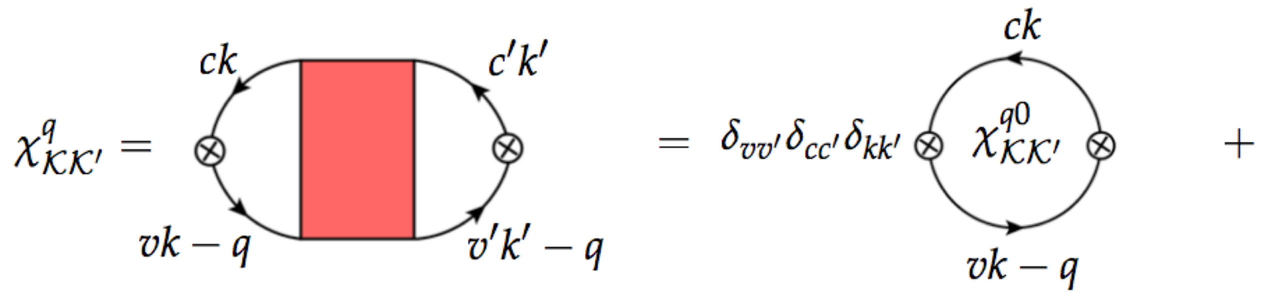
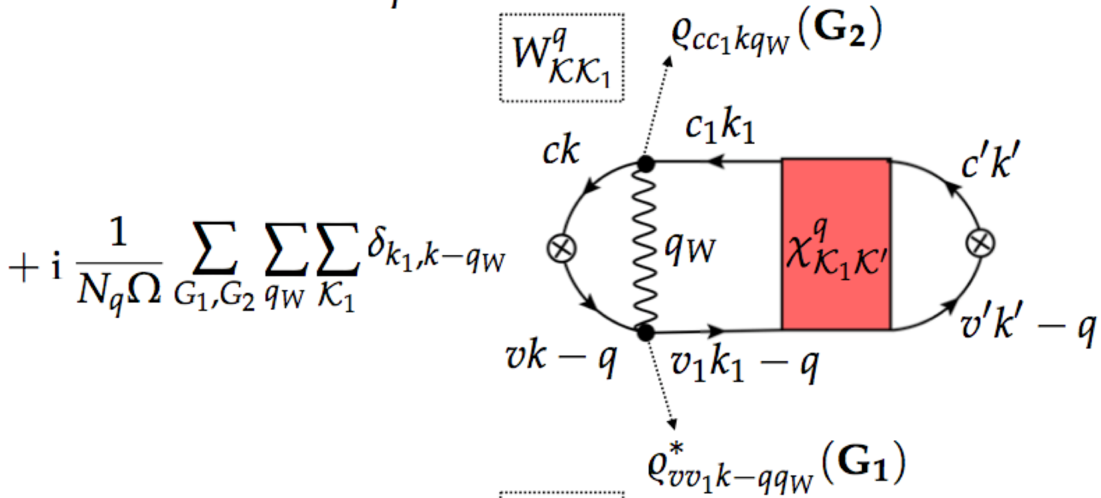
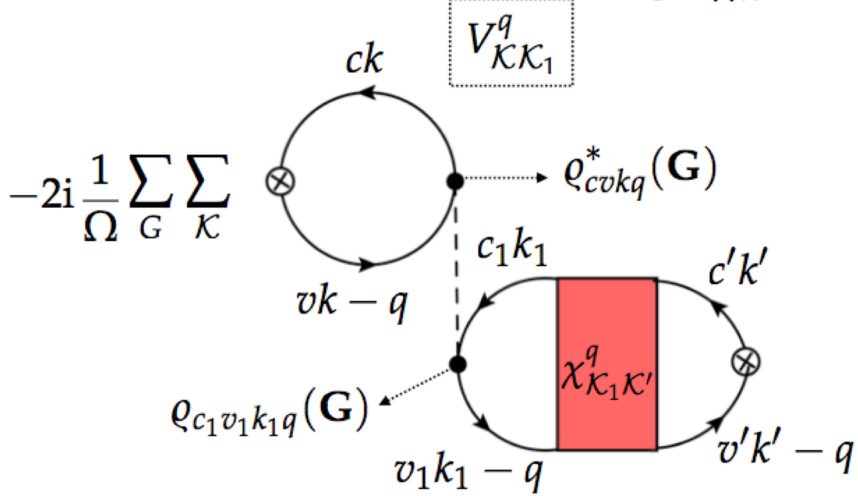
- Attaccalite, Grüning & Marini, PRB 84, 245110 (2011)
- Perfetto, Sangalli, Marini & Stefanucci, PRB 92, 205304, (2015)







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