Bethe-Salpeter Equation
Time-dependent approach

Fourier transform
Beyond the independent-particle picture

The equation of motion of the response function

\[ i \frac{\partial}{\partial t} \rho(t) = ... \]

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:

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

Electronic transitions

Optical strength

Band structure

Optical absorption
Going beyond the independent-particle picture

From Fermi’s golden rule we know that:

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

Lithium fluoride

Let’s do a DFT+GW calculation:
Going beyond the independent-particle picture

From Fermi’s golden rule we know that:

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

Electronic transitions

Lithium fluoride

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

\[ \text{Abs}(\omega) \propto \sum_{\lambda} \left| \sum_{cvk} A_{\lambda}^{cvk} D_{cvk} \right|^2 \delta(\omega - E_{\lambda}) \]

Lithium fluoride

New quantities are solutions of the BSE!
Going beyond the independent-particle picture

We need to account for the electron-hole interaction

\[
\text{Abs}(\omega) \propto \sum_\lambda \left| \sum_{cvk} A_{\lambda}^{cvk} D_{cvk} \right|^2 \delta(\omega - E_\lambda)
\]

Lithium fluoride

New quantities are solutions of the BSE!

\[ \text{Exp} \quad \text{Theory} \]

Energy [eV]
Going beyond the independent-particle picture

Especially relevant to layered/2D materials

Hexagonal boron nitride

Band gap

DFT+GW

Band gap

DFT+GW +BSE

4.5 5 5.5 6 6.5 7 7.5 8

4.5 5 5.5 6 6.5 7 7.5 8
Going beyond the independent-particle picture

Especially relevant to layered/2D materials

Hexagonal boron nitride

Band gap

DFT+GW

+ BSE

Band gap
How can we derive the BSE?

Non-equilibrium dynamics of the response function

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


Generalization of the response function to 4-point...
How can we derive the BSE?

Iteration of Hedin’s equations that contain the response function

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

Non-equilibrium dynamics of the response function

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

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


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 + G₀W₀, etc.
Choosing a description for the electronic system

Single-particle Hamiltonian from Hartree-Fock

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

\[ \hat{H}^0 |n\rangle = E_n |n\rangle \quad \text{Single-particle energies} \]

\[ \langle r | n \rangle = \varphi_n(r) \quad \text{Bloch function} \]
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

\[ \hat{\rho}^0 (\mathbf{r}) = \sum_n |\varphi_n (\mathbf{r})|^2 \hat{c}^\dagger_n \hat{c}_n \]

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

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
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

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

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

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

\[ \chi(r_t, r'_t') = \frac{\delta \rho(r_t)}{\delta U(r'_t')} \Bigg|_{U=0} \]
Linear response function

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

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

with

$$\chi(rt, r't') = \sum_{n_1 n_2 n_3 n_4} \varphi_{n_1}(r) \varphi_{n_2}^*(r) \varphi_{n_3}^*(r') \varphi_{n_4}(r') \chi_{n_1 n_2}^{R_{n_3 n_4}}(t, t')$$
Linear response function

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

$$\chi(r_t, r'_t') = \frac{\delta \rho(r_t)}{\delta U(r'_t')} \bigg|_{U=0}$$

with

$$\chi(r_t, r'_t') = \sum_{n_1 n_2 \atop n_3 n_4} \varphi_{n_1}(r) \varphi^*_{n_2}(r) \varphi^*_{n_3}(r') \varphi_{n_4}(r') \chi_{n_1 n_2}^{R_{n_3 n_4}}(t, t')$$

And then

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

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

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

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

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

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

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

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

The solution of this equation will yield the BSE!
Taking care of the two-particle kernel

Rewriting the density functionals

\[ \Delta V_{n_1 n_2}^H [\rho(t)] \]
Taking care of the two-particle kernel

Rewriting the density functionals

$$\Delta V_{n_1 n_2}^H[\rho(t)] = \sum_{m_1 m_2} \int d\tilde{t} \frac{\delta V_{n_1 n_2}^H[\rho(t)]}{\delta U_{m_1 m_2}(\tilde{t})} \delta U_{m_1 m_2}(\tilde{t})$$
Taking care of the two-particle kernel

Rewriting the density functionals

\[
\Delta V_{n_1n_2}^H[\rho(t)] = \sum_{m_1 m_2} \int d\bar{t} \delta V_{n_1n_2}^H[\rho(t)] \frac{\delta U_{m_1 m_2}(\bar{t})}{\delta U_{m_1 m_2}(t)} \delta U_{m_1 m_2}(\bar{t})
\]

\[
= \sum_{m_1 m_2 m_2 m_4} \int d\bar{t} d\bar{t} \delta V_{n_1n_2}^H[\rho(t)] \frac{\delta \rho_{m_3 m_4}[\rho(t)]}{\delta \rho_{m_3 m_4}(\bar{t})} \frac{\delta U_{m_1 m_2}(\bar{t})}{\delta U_{m_1 m_2}(\bar{t})} \delta U_{m_1 m_2}(\bar{t})
\]

\[\chi\]
Taking care of the two-particle kernel

Rewriting the density functionals

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

\[ = \sum_{m_1 m_2 \atop m_2 m_4} \int d\bar{t} d\bar{\tau} \frac{\delta V^H_{n_1 n_2}[\rho(t)]}{\delta \rho_{m_3 m_4}(\bar{\tau})} \frac{\delta \rho_{m_3 m_4}[\rho(\bar{\tau})]}{\delta U_{m_1 m_2}(\bar{t})} \delta U_{m_1 m_2}(\bar{t}) \]

By doing the same for \( \Delta \Sigma^x \) we obtain:
Taking care of the two-particle kernel

Rewriting the density functionals

\[ \Delta V_{n_1 n_2}^H [\rho(t)] + \Delta \Sigma_{n_1 n_2}^x [\rho(t)] = \]

\[ = \sum_{m_1 m_2} \int dt \int dt' \left[ \frac{\delta V_{n_1 n_2}^H [\rho(t)]}{\delta \rho_{m_3 m_4}(t)} + \frac{\delta \Sigma_{n_1 n_2}^x [\rho(t)]}{\delta \rho_{m_3 m_4}(t)} \right] \chi_{m_3 m_4}^{(t, t')}(t, \bar{t}) \delta U_{m_1 m_2}(\bar{t}) \]

Two-particle “kernel”

In order to proceed we will write down explicitly \( V_{n_1 n_2}^H \) and \( \Sigma_{n_1 n_2}^x \) and then compute the derivatives
Time-dependent Hartree

\[ V_{n_1 n_2}^H(t) = \langle i | \int \frac{\rho(r')}{|r - r'|} \, d^3r' | j \rangle = \]
\[ = \int d^3r \, d^3r' \, \varphi_{n_1}^*(r) \frac{\rho(r')}{|r - r'|} \varphi_{n_2}(r) \]

\[ v(r, r') = \frac{1}{|r - r'|} \]
We insert the expansion of the time-dependent density

\[ V_{n_1 n_2}^H(t) = \langle i | \int d^3 r' \frac{\rho(r')}{|r - r'|} | j \rangle = \]

\[ = \int d^3 r \, d^3 r' \, \varphi^*_n(r) \frac{\rho(r')}{|r - r'|} \varphi_n(r) \]

We insert the expansion of the time-dependent density

\[ v(r, r') = \frac{1}{|r - r'|} \]
Time-dependent Hartree

\[ V_{n_1n_2}^H(t) = 2 \sum_{l_1l_2} \rho_{l_1l_2}(t) \int d^3r \, d^3r' \, \varphi_{n_1}^*(r)\varphi_{l_1}^*(r')\varphi_{l_2}(r')\varphi_{n_2}(r) \frac{1}{|r - r'|} \]

\[ \equiv 2 \sum_{l_1l_2} \rho_{l_1l_2}(t) \, V_{n_1n_2}^{l_1l_2} \]

\[ \rho \]

\[ r' \]

\[ l_1 \quad l_2 \]

\[ \varphi_{n_1} \quad \varphi_{l_1} \quad \varphi_{l_2} \quad \varphi_{n_2} \]

\[ n_1 \quad n_2 \]

\[ r \]
Time-dependent Hartree

\[ V_{n_1n_2}^H(t) = 2 \sum_{l_1l_2} \rho_{l_1l_2}(t) \int d^3r \, d^3r' \, \varphi_{l_1}^*(r) \varphi_{l_2}^*(r') \varphi_{l_2}(r') \varphi_{l_1}(r) \frac{1}{|r - r'|} \]

\[ \equiv 2 \sum_{l_1l_2} \rho_{l_1l_2}(t) V_{n_1n_2}^{l_1l_2} \]

Momentum conservation implies that \( V^H \) does not carry an internal momentum
Time-dependent Hartree

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

\[ V_{n_1n_2}(t) = 2 \sum_{l_1l_2} \rho_{l_1l_2}(t) [V_{qv=0}]_{n_1n_2}^{l_1l_2} \]

\[ \frac{\delta V_{n_1n_2}(t)}{\delta \rho_{m_3m_4}(t)} = 2 [V_{qv=0}]_{n_1n_2}^{m_3m_4} \delta(t - \bar{t}) \]
Exchange (and correlation) self-energy

Time-dependent exchange

\[ \Sigma^x(\mathbf{r}_t, \mathbf{r}'_t) = iG^0(\mathbf{r}_t, \mathbf{r}'_t)\nu(\mathbf{r}, \mathbf{r}') \]
\[ = -\rho(\mathbf{r}\mathbf{r}', t)\nu(\mathbf{r}, \mathbf{r}') \]
Exchange (and correlation) self-energy

Time-dependent exchange

\[
\sum^x (r_t, r'_t) = iG^0 (r_t, r'_t) v(r, r') = -\rho(rr', t) v(r, r')
\]

\[
\sum^x_{n_1 n_2} (t) = -\sum_{l_1 l_2} \rho_{l_1 l_2} (t) \int d^3r \, d^3r' \, \varphi^*_l (r') \varphi_{l_2} (r) \varphi^*_n (r) \varphi_{n_2} (r') v(r, r')
\]

**ISSUE:** the unscreened Coulomb interaction overbinds electron and holes, giving wrong optical spectra.
Exchange (and correlation) self-energy

Time-dependent SEX

\[ W(r, r') = \int d^3r'' \varepsilon_{RPA}^{-1}(r, r'') v(r'', r) \]

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

\[ \Sigma_{n_1n_2}^{\text{SEX}}(t) = - \sum_{l_1l_2} \rho_{l_1l_2}(t) \int d^3r d^3r' \ \varphi_{l_1}^*(r') \varphi_{l_2}(r) \varphi_{n_1}^*(r) \varphi_{n_2}(r') W(r, r') \]
Exchange (and correlation) self-energy

**Time-dependent SEX**

\[ W(r, r') = \int d^3r'' \varepsilon_{RPA}^{-1}(r, r'') \nu(r'', r) \]

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

\[ \Sigma_{n_1n_2}^{\text{SEX}}(t) = - \sum_{l_1l_2} \rho_{l_1l_2}(t) \int d^3r \, d^3r' \, \phi_{l_1}^*(r') \phi_{l_2}(r) \phi_{n_1}^*(r) \phi_{n_2}(r') W(r, r') \]
Exchange (and correlation) self-energy

Time-dependent SEX

\[
\sum_{n_1n_2}^{SEX}(t) = - \sum_{l_1l_2} \rho_{l_1l_2}(t) W_{n_1l_2}^{n_1l_2}
\]
Exchange (and correlation) self-energy

Time-dependent SEX

\[
\sum_{n_1 n_2} \text{SEX} (t) = - \sum_{l_1 l_2} \rho_{l_1 l_2} (t) W_{n_1 l_2}^{l_1 l_2}
\]

\[
\frac{\delta \sum_{n_1 n_2} \text{SEX} (t)}{\delta \rho_{m_3 m_4} (t)} = - W_{n_1 m_2}^{m_1 n_2} \delta(t - \bar{t})
\]

\[
\frac{\delta W}{\delta \rho}
\]

NEGLECTED!
(Higher order in the interaction)
Solving the equation of motion

\[ i \frac{\partial}{\partial t} \chi_{n_1n_2}^{n_3n_4}(t,t') = \frac{\delta}{\delta U_{n_3n_4}(t')} \left[ \hat{H}^0(t), \hat{\rho}(t) \right]_{n_1n_2} \]

\[ + \frac{\delta}{\delta U_{n_3n_4}(t')} \left[ \hat{U}(t), \hat{\rho}(t) \right]_{n_1n_2} \]

\[ + \frac{\delta}{\delta U_{n_3n_4}(t')} \left[ - \sum_{m_1m_2} \int d\tilde{t} \left( \hat{W} - 2\hat{V} \right) \chi_{m_3m_4}^{R_{m_1m_2}} \delta U_{m_1m_2}(\tilde{t}), \hat{\rho}(t) \right]_{n_1n_2} \]
Solving the equation of motion

Computing the commutators...

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

Computing the commutators...

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

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

We stay at 1st order in $U$
Solving the equation of motion

Computing the commutators...

\[
\left[ \hat{H}^0, \hat{\rho}(t) \right]_{n_1n_2} = \langle n_1 | \hat{H}^0 \hat{\rho}(t) | n_2 \rangle - \langle n_1 | \hat{\rho}(t) \hat{H}^0 | n_2 \rangle \\
= (E_{n_1} - E_{n_2}) \rho_{n_1n_2}(t)
\]

Analogous to B
Solving the equation of motion

Computing the derivative...

\[ i \frac{\partial}{\partial t} \chi_{n_1 n_2}^{n_3 n_4}(t - t') = (E_{n_1} - E_{n_2}) \chi_{n_1 n_2}^{n_3 n_4}(t - t') \]

\[ + i (f_{n_2} - f_{n_1}) \left[ -i \delta_{n_1 n_3} \delta_{n_2 n_4} + \sum_{m_3 m_4} K_{n_1 n_2}^{m_3 m_4} \chi_{m_3 m_4}^{n_3 n_4}(t - t') \right] \]
Solving the equation of motion

Computing the derivative...

\[ i \frac{\partial}{\partial t} \chi_{n_3n_4}^{n_1n_2}(t - t') = (E_{n_1} - E_{n_2}) \chi_{n_3n_4}^{n_1n_2}(t - t') + i(f_{n_2} - f_{n_1}) \left[ -i \delta_{n_1n_3} \delta_{n_2n_4} + \sum_{m_3m_4} K_{n_1n_2}^{m_3m_4} \chi_{n_3n_4}^{m_3m_4}(t - t') \right] \]

e-h pair created at time \( t \) and recombined at time \( t' \)

\[ \chi(t, t') = \chi(t - t') \]
Solving the equation of motion

Computing the derivative...

\[ \frac{i}{\partial t} \chi_{n_1 n_2}^{n_3 n_4}(t - t') = (E_{n_1} - E_{n_2}) \chi_{n_1 n_2}^{n_3 n_4}(t - t') \]

\[ + i(f_{n_2} - f_{n_1}) \left[ -i \delta_{n_1 n_3} \delta_{n_2 n_4} + \sum_{m_3 m_4} K_{n_1 n_2}^{m_3 m_4} \chi_{m_3 m_4}^{n_3 n_4}(t - t') \right] \]

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

\[ \chi(t, t') = \chi(t - t') \]

**Electron-hole interaction kernel**

\[ -i K_{n_1 n_2}^{m_3 m_4} = W_{n_1 m_4}^{m_3 n_2} - 2 [V_{q_v=0}^{\text{m_3 m_4}}]_{n_1 n_2} \]
Solving the equation of motion

Computing the derivative...

\[ i \frac{\partial}{\partial t} \chi_{n_1 n_2}^{n_3 n_4} (t - t') = (E_{n_1} - E_{n_2}) \chi_{n_1 n_2}^{n_3 n_4} (t - t') \]

\[ + i(f_{n_2} - f_{n_1}) \left[ -i \delta_{n_1 n_3} \delta_{n_2 n_4} + \sum_{m_3 m_4} \left( K \chi_{m_1 m_2}^{m_3 m_4} (t - t') \right) \right] \]

e-h pair created at time \( t \) and recombined at time \( t' \)

\[ \chi(t, t') = \chi(t - t') \]

Electron-hole interaction kernel

\[ -iK \chi_{n_1 n_2}^{m_3 m_4} = W_{n_1 m_4}^{m_3 n_2} - 2 \left[ V^{q_v=0} \right]_{n_1 n_2}^{m_3 m_4} \]

Electron-hole attractive interaction (binding term)
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...

A basis of electron-hole transitions

\[ \langle r | n_1 n_2 \rangle = \varphi_{n_1}^*(r) \varphi_{n_2}(r) \]
\[ |n_1 n_2\rangle = |\mathcal{K}\rangle \]

\[ i \frac{\partial}{\partial t} \chi_{\mathcal{KK}'}(t - t') = \Delta E_{\mathcal{K}} \chi_{\mathcal{KK}'}(t - t') \]

\[ + i f_{\mathcal{K}} \left[ -i \delta_{\mathcal{KK}'} + \sum_{\mathcal{KK}'} K_{\mathcal{KK}'} \chi_{\mathcal{KK}'}(t - t') \right] \]
Solving the equation of motion

Taking the Fourier transform...

\[(\omega - \Delta E_K) \chi_{KK'}(\omega) = i f_K \left[ -i \delta_{KK'} + \sum_{\overline{K}} K_{K\overline{K}} \chi_{\overline{K}KK'}(\omega) \right] \]
Solving the equation of motion

Taking the Fourier transform...

\[
(\omega - \Delta E_K) \chi_{\mathcal{K} \mathcal{K}'}(\omega) = i f_K \left[ -i\delta_{\mathcal{K} \mathcal{K}'} + \sum_{\overline{\mathcal{K}}} K_{\mathcal{K} \overline{\mathcal{K}}} \chi_{\overline{\mathcal{K}} \mathcal{K}'}(\omega) \right]
\]

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

\[
\chi^0_{\mathcal{K}}(\omega) = \frac{f_K}{\omega - \Delta E_K}
\]
Bethe-Salpeter equation
(As Dyson-like equation)

\[
\chi_{\kappa\kappa'}(\omega) = \chi^0_{\kappa}(\omega) + \chi^0_{\kappa}(\omega) \sum_{\overline{\kappa}} K_{\kappa\overline{\kappa}} \chi_{\overline{\kappa}\kappa'}(\omega)
\]
Bethe-Salpeter equation

(As Dyson-like equation)

\[
\chi_{KK'}(\omega) = \chi^0_{KK}(\omega) + \chi^0_{KK}(\omega) \sum_{\overline{KK}} K_{KK'} \chi_{\overline{KK}'}(\omega)
\]
Inversion of the BSE

We isolate the response function on the left hand side

\[ \sum_{\overline{K}} \left[ (\omega - \Delta E_K) \delta_{KK'} - i f \delta_{KK'} \right] \chi_{\overline{KK}'}(\omega) = f \delta_{KK'} \]
Inversion of the BSE

We isolate the response function on the left hand side

\[ \sum_{\bar{\mathcal{K}}} [(\omega - \Delta E_{\mathcal{K}})\delta_{\mathcal{K}\bar{\mathcal{K}}} - i f_{\mathcal{K}} K_{\mathcal{K}\bar{\mathcal{K}}}] \chi_{\bar{\mathcal{K}}\mathcal{K}',(\omega) = f_{\mathcal{K}} \delta_{\mathcal{K}\mathcal{K}'}\]

... and recognize a two-particle Hamiltonian

\[ \sum_{\bar{\mathcal{K}}} [\omega \delta_{\mathcal{K}\bar{\mathcal{K}}} - (\Delta E_{\mathcal{K}} \delta_{\mathcal{K}\bar{\mathcal{K}}} + i f_{\mathcal{K}} K_{\mathcal{K}\bar{\mathcal{K}}})] \chi_{\bar{\mathcal{K}}\mathcal{K}',(\omega) = f_{\mathcal{K}'}\]
Inversion of the BSE

We isolate the response function on the left hand side

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

... and recognize a two-particle Hamiltonian

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

\[
\sum_{\overline{K}} \left[ \omega \delta_{KK} - H^{2p}_{KK} \right] \chi_{KK'}(\omega) = f_{K'}
\]
Inversion of the BSE

In matrix form we have

\[
\begin{bmatrix}
1\omega - \hat{H}^{2p}
\end{bmatrix} \cdot \hat{\chi} = \vec{f}
\]

And after performing matrix inversion

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

This indeed looks like a two-particle propagator
Inversion of the BSE

If we diagonalize the excitonic Hamiltonian

\[ \hat{H}^{2p} |\lambda\rangle = E_\lambda |\lambda\rangle \]

Excitonic basis

Exciton energies

Then the equation for the response function can be finally written in terms of the \textit{excitonic basis}.
Inversion of the BSE

If we diagonalize the excitonic Hamiltonian

\[
\hat{H}^{2p} |\lambda\rangle = E_{\lambda} |\lambda\rangle
\]

\[
\langle \mathcal{K}|\lambda\rangle = A^\mathcal{K}_\lambda
\]

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

\[
\hat{\chi} = \left[1 - \hat{H}^{2p} \omega \right]^{-1} \cdot \vec{f}
\]
Inversion of the BSE

If we diagonalize the excitonic Hamiltonian

\[ \hat{H}^{2p} |\lambda\rangle = E_\lambda |\lambda\rangle \]

Excitonic basis

\[ \langle K | \lambda \rangle = A^K_\lambda \]

Exciton energies

Exciton coefficients

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

\[ \hat{\chi} = \sum_\lambda \frac{|\lambda\rangle \langle \lambda|}{\omega - E_\lambda} \cdot \vec{f} \]
Inversion of the BSE

If we diagonalize the excitonic Hamiltonian

\[ \hat{H}^{2p} |\lambda\rangle = E_\lambda |\lambda\rangle \]

Excitonic basis

\[ \langle \mathcal{K} |\lambda\rangle = A^K_\lambda \]

Exciton energies

Then the equation for the response function can be finally written in terms of the \textbf{excitonic basis}

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

[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

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

\[ H_{KK'}^{2p} = \Delta E_K \delta_{KK'} + i f_K K_{KK'} \]

Screened interaction and mixing of electronic transitions:

\[ K_{KK'} = i [W_{KK'} - 2V_{KK'}] \]
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

$$H_{KK'}^{2p} = \Delta E_K \delta_{KK'} + i f_K K_{KK'}$$

Ingredients:

- Quasiparticle energies (DFT + GW): $E_n$
- Single-particle wave functions (DFT): $\varphi_n(r)$
- Static electronic screening (DFT + RPA): $\varepsilon_{\text{RPA}}^{-1}$
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

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