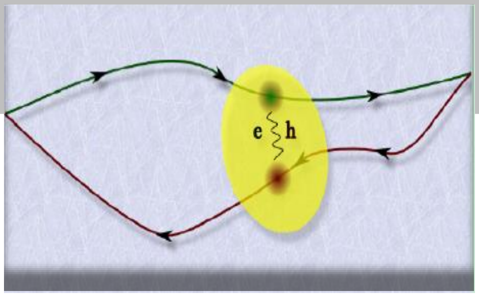
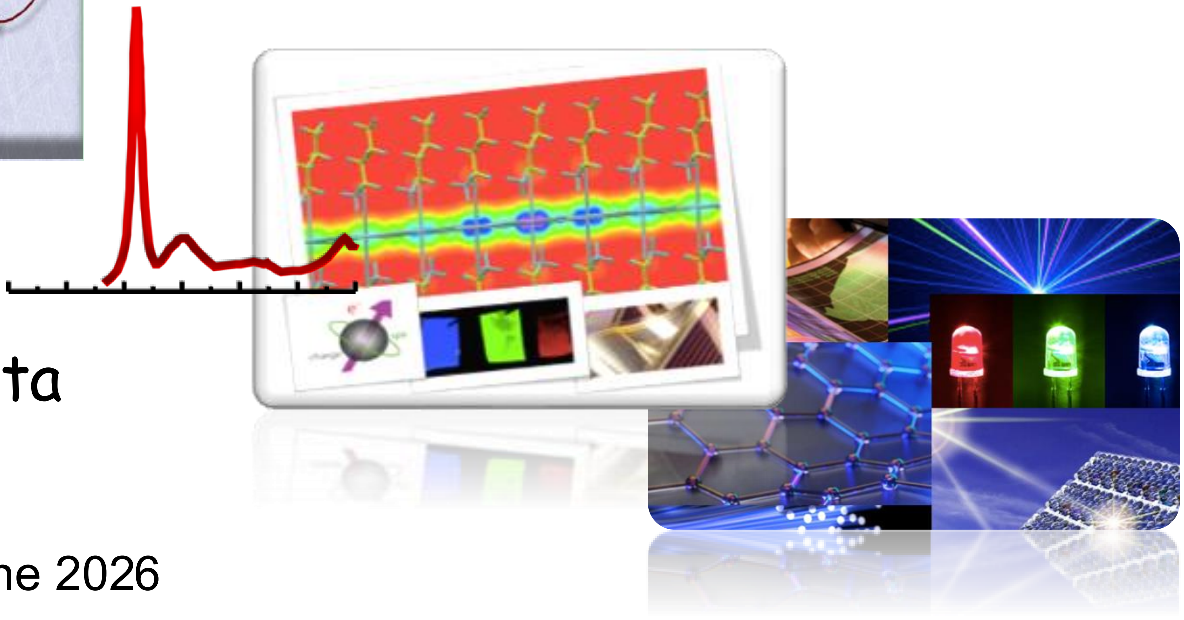
Joint ICTP MARVEL College

Bethe-Salpeter Equation: theory and Applications



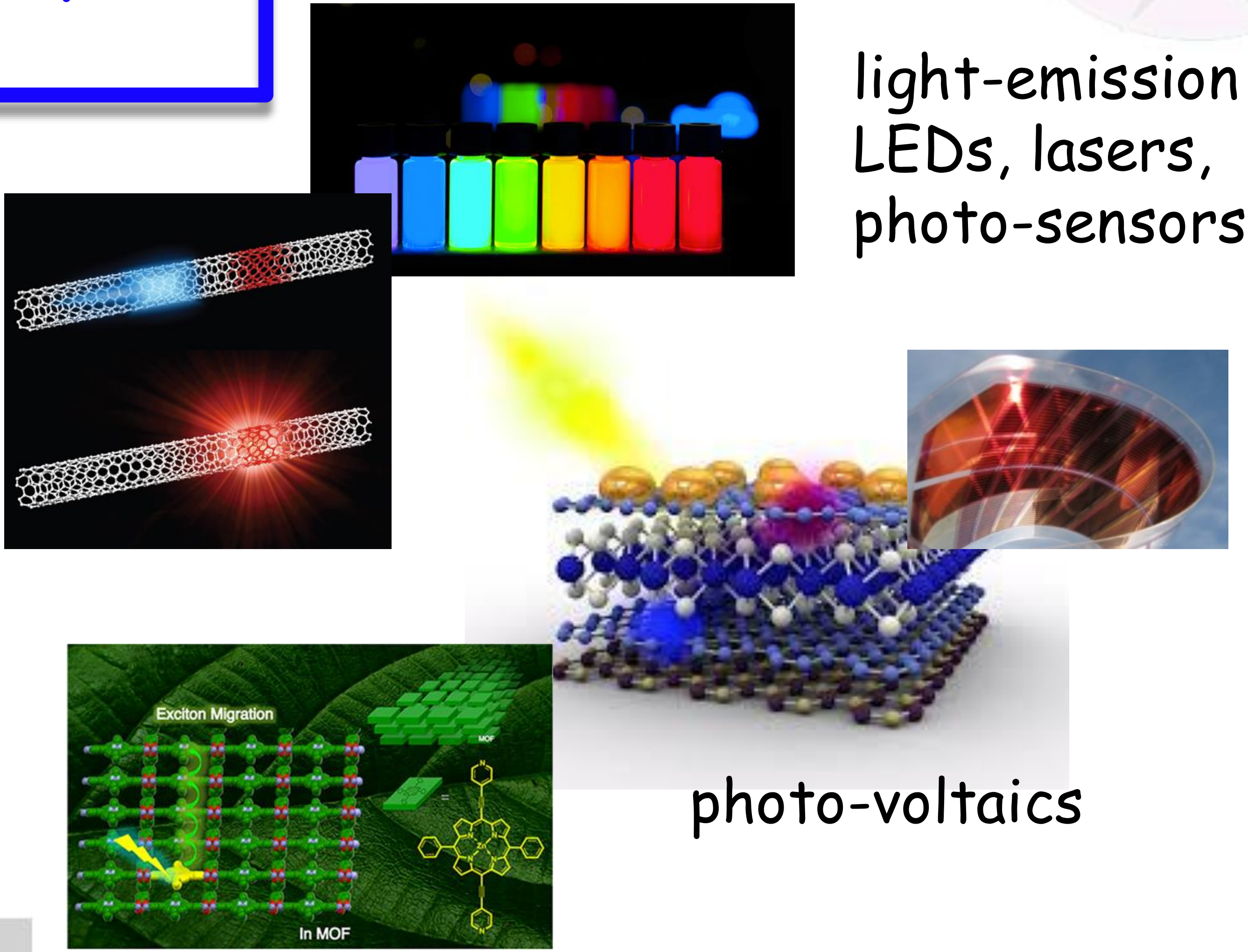


Maurizia Palummo
INFN, Dipartimento di Fisica
Università di Roma Tor Vergata

2-12 June 2026

Motivations

- ✓ **Calculate & Reproduce**
- ✓ **Understand & explain**
- ✓ **Predict**



light-emission
LEDs, lasers,
photo-sensors

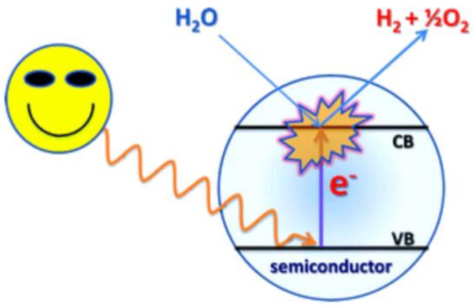


photo-catalysis

photo-voltaics

photo-chemistry

OUTLINE

What we have learned so far

(Main missing physical ingredients)

the Bethe-Salpeter Equation (BSE) : physical concepts & derivation

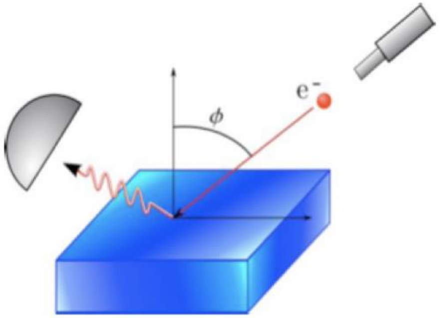
the BSE & spin

Applications

CHARGED EXCITATIONS ≠ NEUTRAL EXCITATIONS

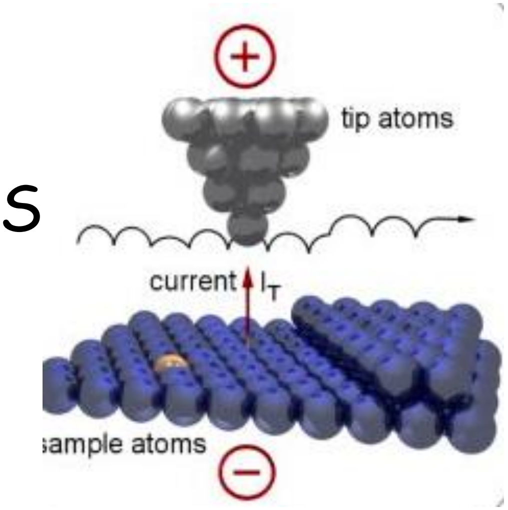
$$E^*_{N+1} - E_N, E_N - E^*_{N-1}$$

$$E^*_N - E_N$$

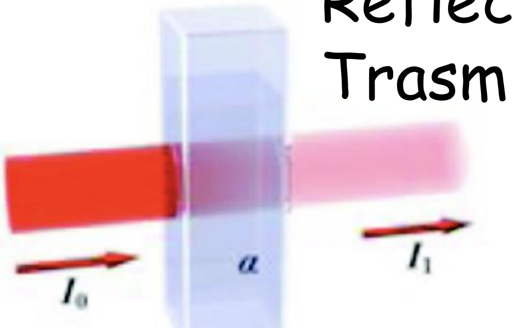


PES,IPES

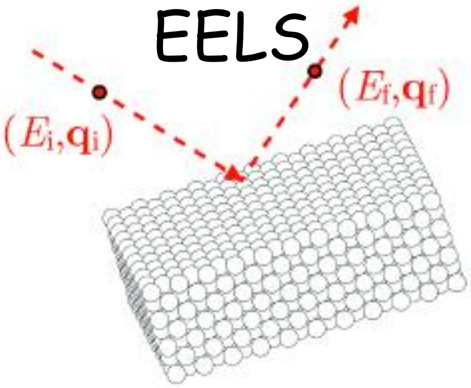
STS



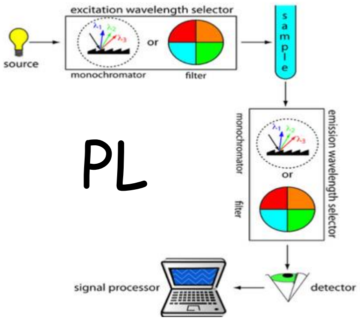
Absorption,
Reflection,
Trasmission



EELS



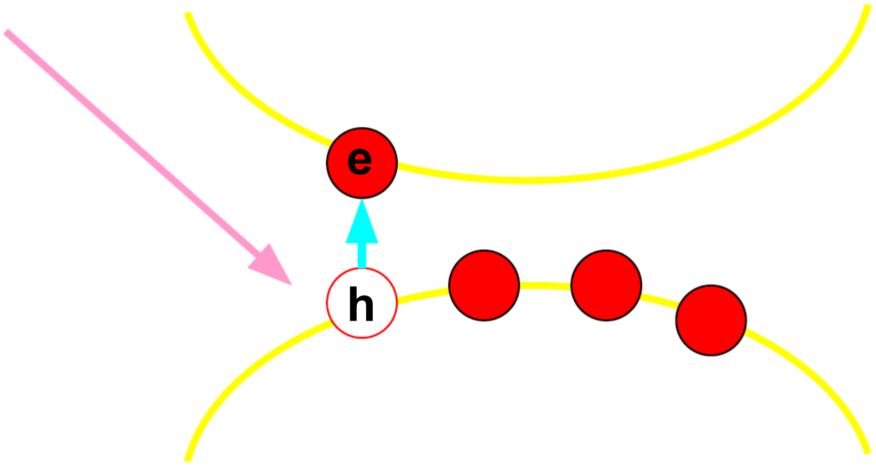
PL

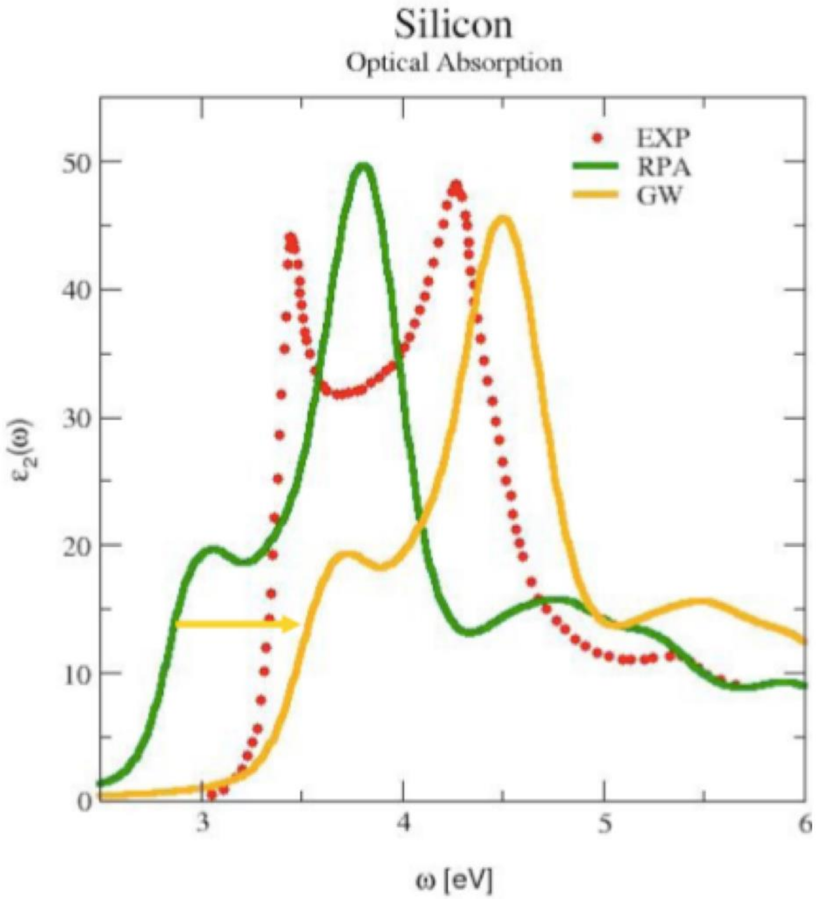


Independent electronic transitions

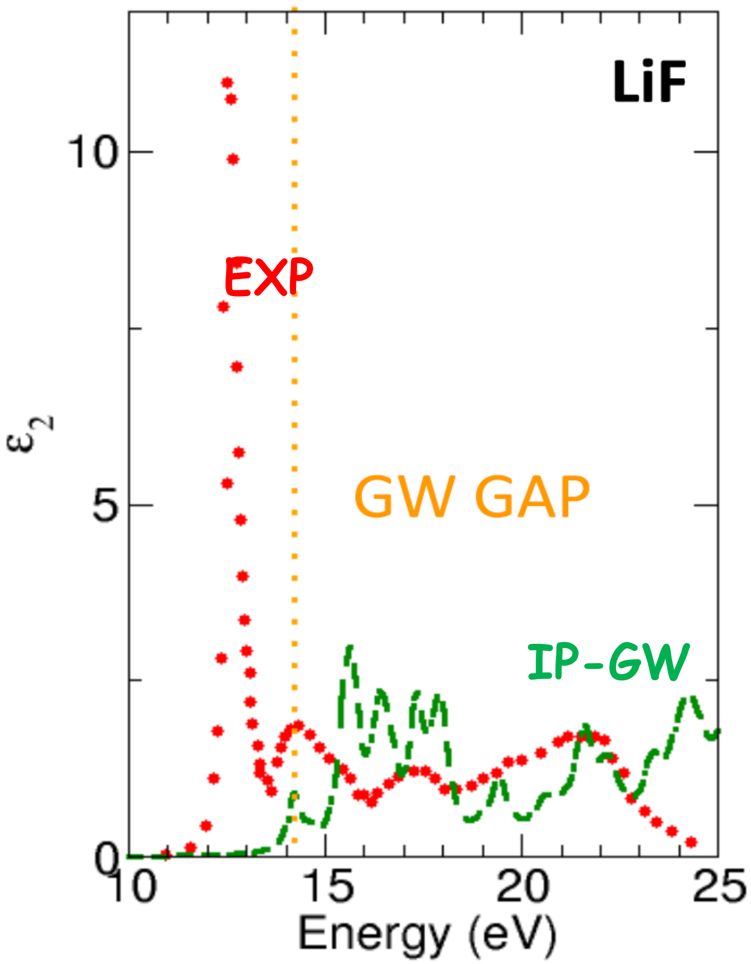
In the linear response regime:

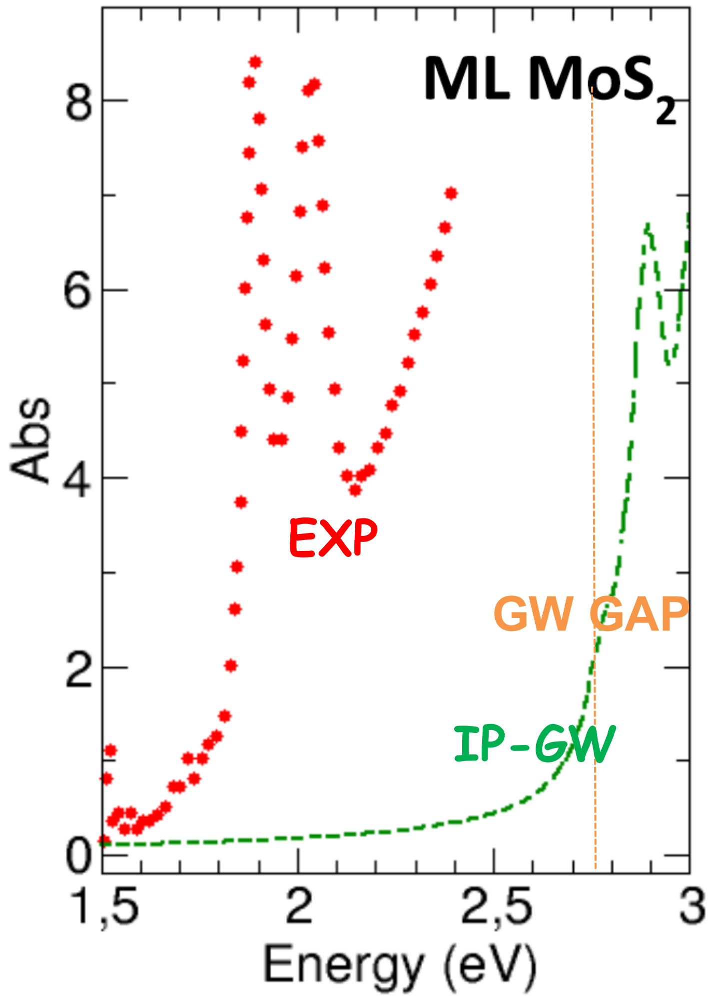
$$Abs \propto \sum_{cv} |<c|\hat{\epsilon}\cdot\vec{D}|v>|^2\delta(\hbar\omega-(E_c-E_v))$$



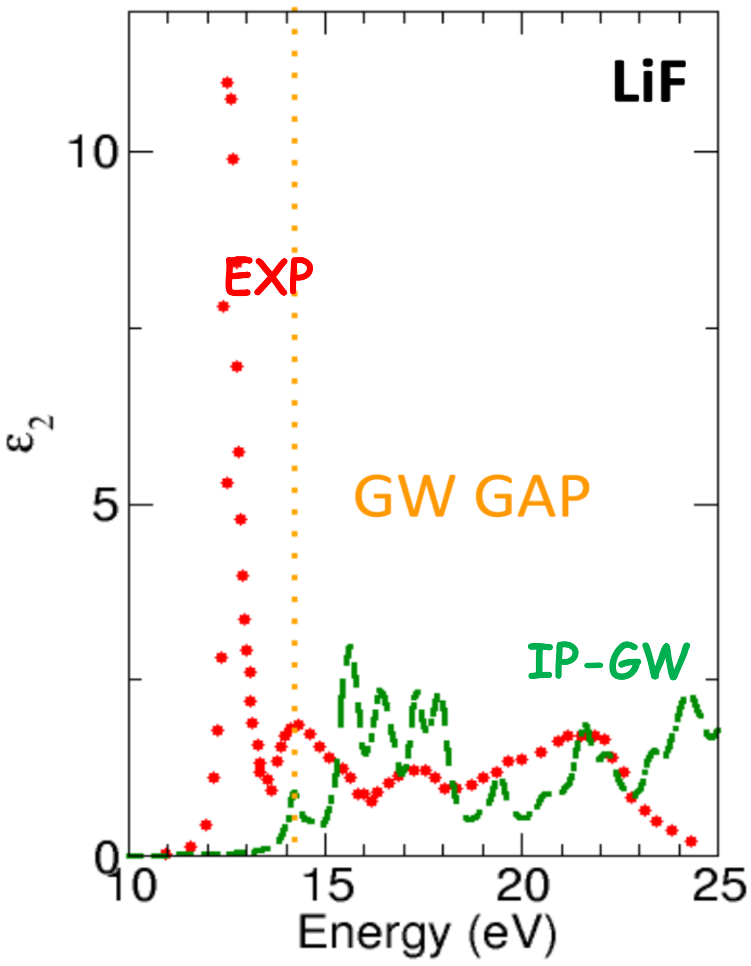


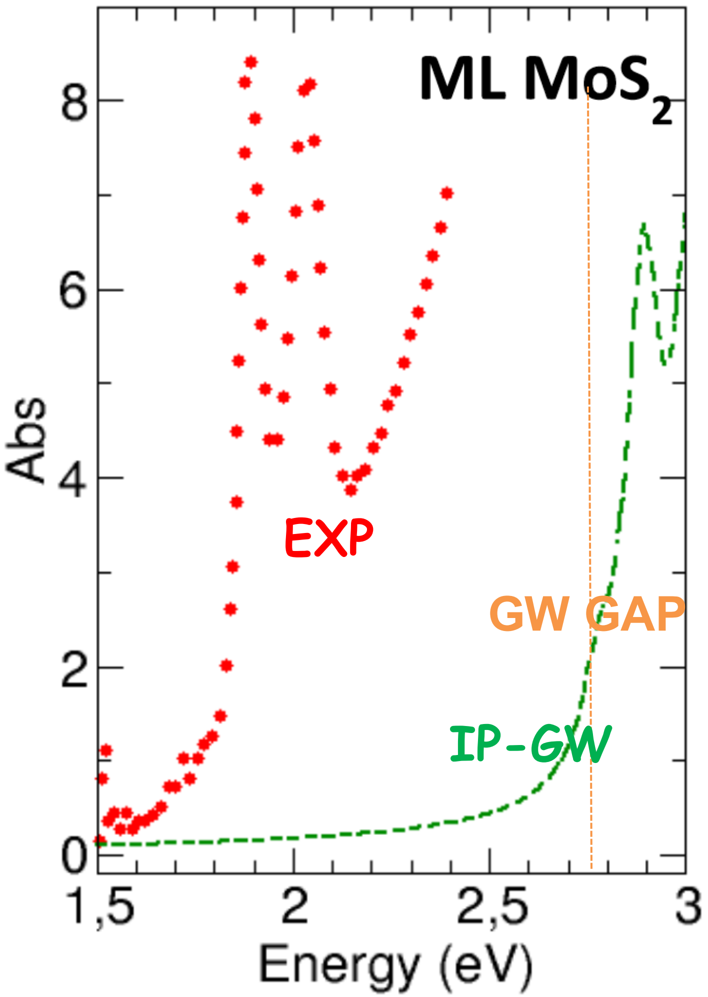
Not enough both at DFT or GW level


LiF
EXP
GW GAP
IP-GW
ε_2
10
5
0
10
15
20
25
Energy (eV)

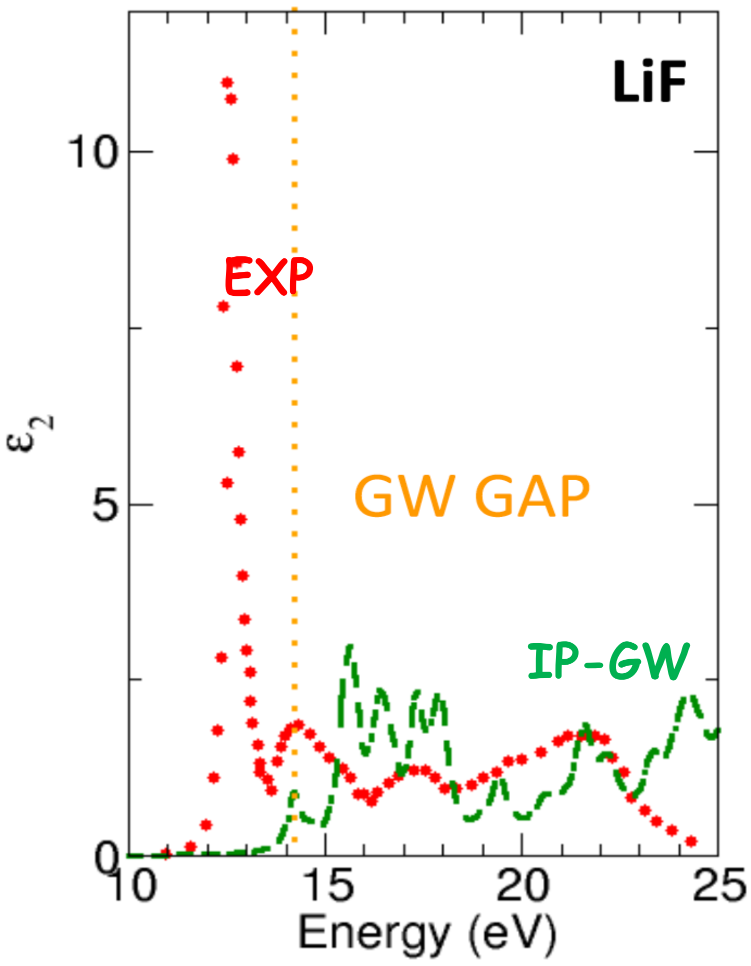

ML MoS$_2$
EXP
GW GAP
IP-GW
Abs
8
6
4
2
0
1,5
2
2,5
3
Energy (eV)

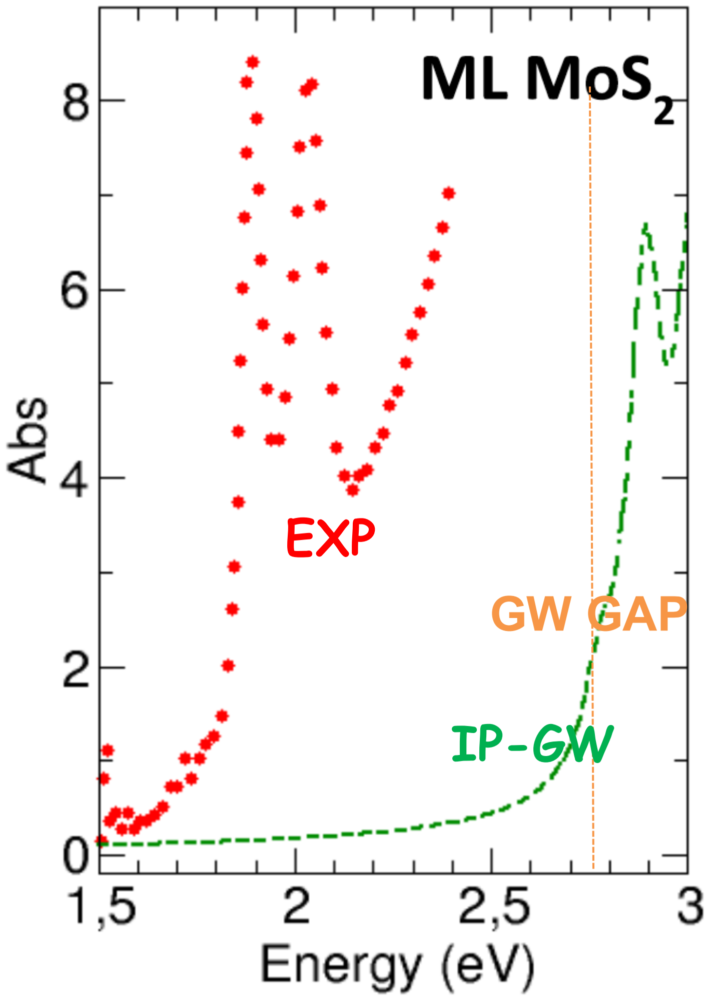
Very bad agreement for insulating or low-dimensional materials





Very bad agreement for insulating or low-dimensional materials



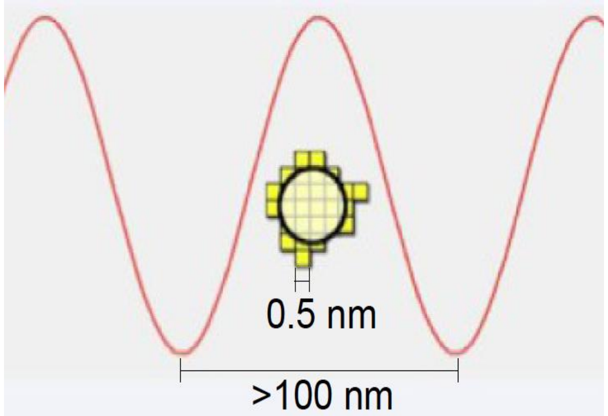


Which are the missing physical ingredients?

Local Fields Effects (LFE) : The contributions to the macroscopic dielectric function ε_M due to rapid oscillations of the induced potential produced by an external slowly varying potential

H. Ehrenreich, in the Optical Properties of Solids, Varenna Course XXXIV 1966
D. L. Johnson, Physical Review B 12, 3428 (1975)
S. L. Adler, Physical Review 126,413 (1962)

Local Fields Effects (LFE) : The contributions to the macroscopic dielectric function ε_M due to rapid oscillations of the induced potential produced by an external slowly varying potential

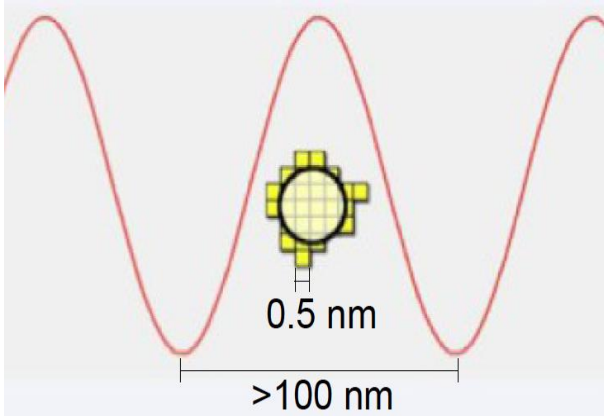


$$\epsilon_M = \frac{<< V_{ext} >>}{<< V_{tot} >>} = \frac{<< V_{ext} >>}{<< \epsilon^{-1} V_{ext} >>}$$

$$= \frac{V_{ext}}{<< \epsilon^{-1} >> \; V_{ext}} = \frac{1}{<< \epsilon^{-1} >>}$$

H. Ehrenreich, in the Optical Properties of Solids, Varenna Course XXXIV 1966
D. L. Johnson, Physical Review B 12, 3428 (1975)
S. L. Adler, Physical Review 126,413 (1962)

Local Fields Effects (LFE) : The contributions to the macroscopic dielectric function ε_M due to rapid oscillations of the induced potential produced by an external slowly varying potential



$$\epsilon_M = \frac{<< V_{ext} >>}{<< V_{tot} >>} = \frac{<< V_{ext} >>}{<< \epsilon^{-1} V_{ext} >>}$$

$$= \frac{V_{ext}}{<< \epsilon^{-1} >> \; V_{ext}} = \frac{1}{<< \epsilon^{-1} >>}$$

Microscopic/Macroscopic connection

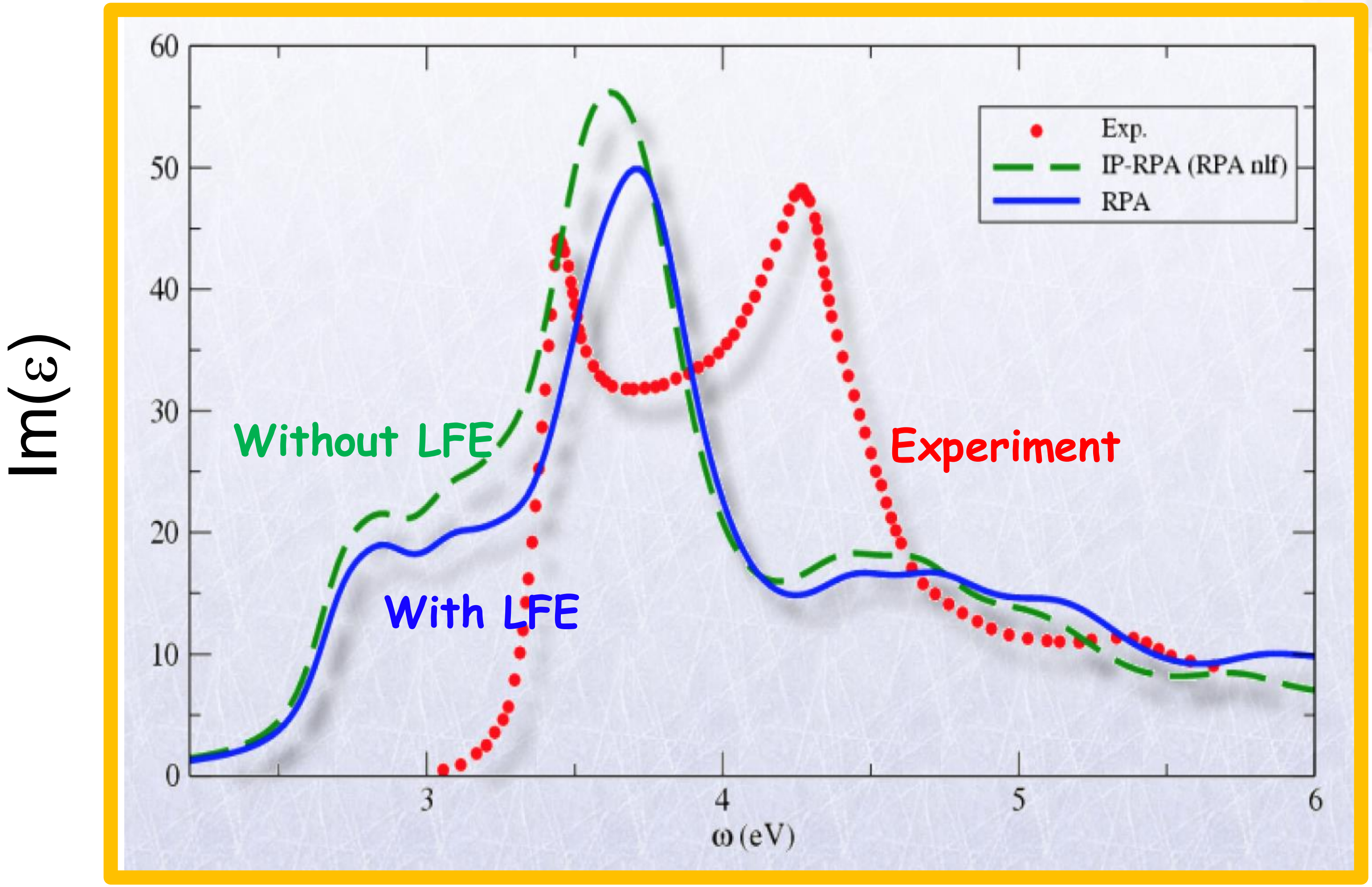
In reciprocal space (periodic systems) :

$$\boxed{\epsilon_M(\mathbf{q},\omega) = \frac{1}{\epsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)}}$$

H. Ehrenreich, in the Optical Properties of Solids, Varenna Course XXXIV 1966
D. L. Johnson, Physical Review B 12, 3428 (1975)
S. L. Adler, Physical Review 126,413 (1962)

Local field Effects

(bulk silicon)



The inclusion of LFE is not enough

Alternative formulations of LFE

$$\epsilon_M(\omega) = \lim_{q\to 0} \frac{1}{\epsilon^{-1}_{00}(q,\omega)}$$

$$Abs \propto \Im[\epsilon_M]$$

$$EELS \propto -\Im[\epsilon_M^{-1}] = -\Im[1 + v_0\chi_{00}]$$

Alternative formulations of LFE

$$\epsilon_M(\omega) = \lim_{q \to 0} \frac{1}{\epsilon^{-1}_{00}(q,\omega)}$$

$$Abs \propto \Im[\epsilon_M]$$

$$EELS \propto -\Im[\epsilon^{-1}_M] = -\Im[1 + v_0 \chi_{00}]$$

Irreducible polarizability

$$\chi = P + P[v_{G=0} + v_{G\neq 0}]\chi$$

reducible polarizability

Alternative formulations of LFE

$$\epsilon_M(\omega) = \lim_{q \to 0} \frac{1}{\epsilon^{-1}_{00}(q,\omega)}$$

$$Abs \propto \Im[\epsilon_M]$$

$$EELS \propto -\Im[\epsilon_M^{-1}] = -\Im[1 + v_0 \chi_{00}]$$

Irreducible polarizability

$$\chi = P + P[v_{G=0} + v_{G \neq 0}]\chi$$

reducible polarizability

Introducing a modified polarizability $$\bar{P} = P + P\bar{v}\bar{P}$$

(see i.e Onida, Reining, Rubio RMP 2002)

Alternative formulations of LFE

$$\epsilon_M(\omega) = \lim_{q\to 0} \frac{1}{\epsilon^{-1}_{00}(q,\omega)}$$

$$Abs \propto \Im[\epsilon_M]$$

$$EELS \propto -\Im[\epsilon^{-1}_M] = -\Im[1 + v_0\chi_{00}]$$

Irreducible polarizability

$$\chi = P + P[v_{G=0} + v_{G\neq 0}]\chi$$

reducible polarizability

$$\bar{v} = \begin{cases} 0 & G = 0 \\ \frac{4\pi}{|q+G|^2} & G \neq 0 \end{cases}$$

Coulomb term without long-range part

Introducing a modified polarizability $\bar{P} = P + P\bar{v}\bar{P}$

(see i.e Onida, Reining, Rubio RMP 2002)

Alternative formulations of LFE

$$\epsilon_M(\omega) = \lim_{q\to 0} \frac{1}{\epsilon^{-1}_{00}(q,\omega)}$$

$$Abs \propto \Im[\epsilon_M]$$

$$EELS \propto -\Im[\epsilon_M^{-1}] = -\Im[1 + v_0\chi_{00}]$$

Irreducible polarizability

$$\chi = P + P[v_{G=0} + v_{G\neq 0}]\chi$$

reducible polarizability

$$\bar{v} = \begin{cases} 0 & G = 0 \\ \frac{4\pi}{|q+G|^2} & G \neq 0 \end{cases}$$

Coulomb term without long-range part

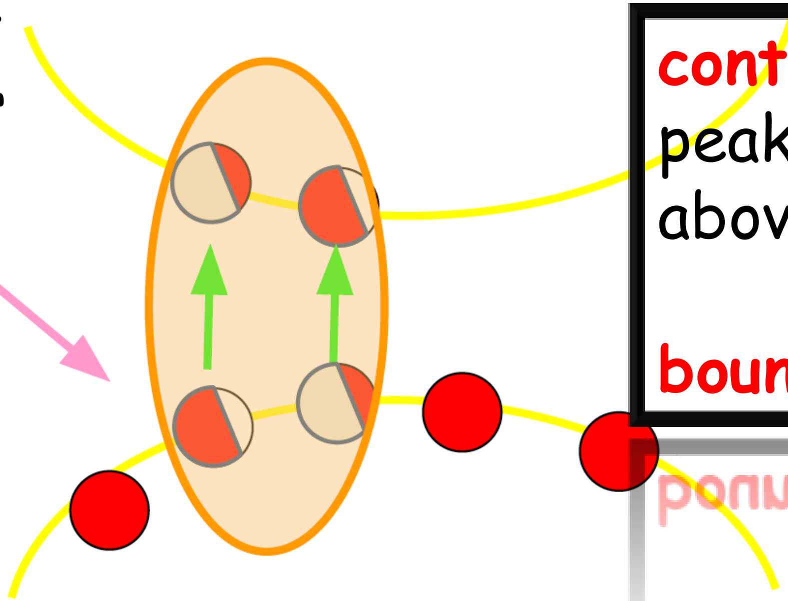
Introducing a modified polarizability $\bar{P} = P + P\bar{v}\bar{P}$

$$\epsilon_M(\omega) = 1 - \lim_{q\to 0} v(\mathbf{q})_0 \bar{P}_{00}(\mathbf{q},\omega)$$

(see i.e Onida, Reining, Rubio RMP 2002)

Electron-hole interaction

electrons and holes
are not indipendent
but feel each other

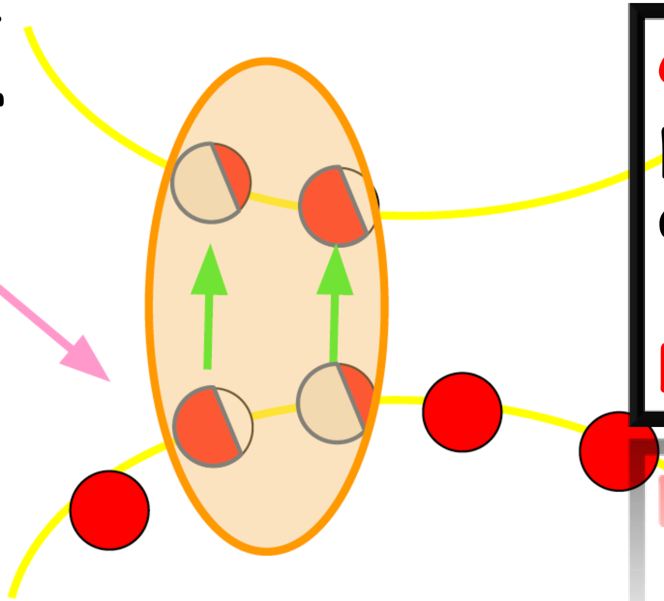


continuum excitons
peaks renormalization
above the electronic gap

bound excitons below it

Electron-hole interaction

electrons and holes
are not indipendent
but feel each other



continuum excitons
peaks renormalization
above the electronic gap

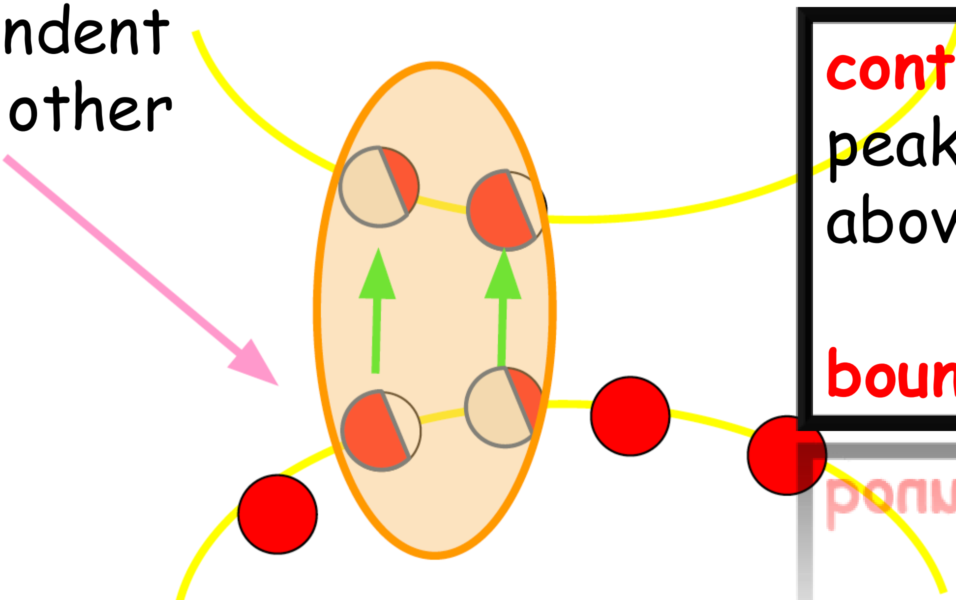
bound excitons below it

BSE

$$Abs(\omega) \propto \sum_{\lambda} |\hat{\epsilon} \cdot \vec{D}_{\lambda}|^2 \delta(\hbar\omega - E^{exc}_{\lambda})$$

Electron-hole interaction

electrons and holes
are not indipendent
but feel each other



continuum excitons
peaks renormalization
above the electronic gap

bound excitons below it

BSE

$$Abs(\omega) \propto \sum_{\lambda} |\hat{\epsilon} \cdot \vec{D}_{\lambda}|^2 \delta(\hbar\omega - E_{\lambda}^{exc})$$

Excitonic dipoles

$$\vec{D}_{\lambda} = \sum_{cv} < c|\vec{r}|v > A_{\lambda}^{cv}$$

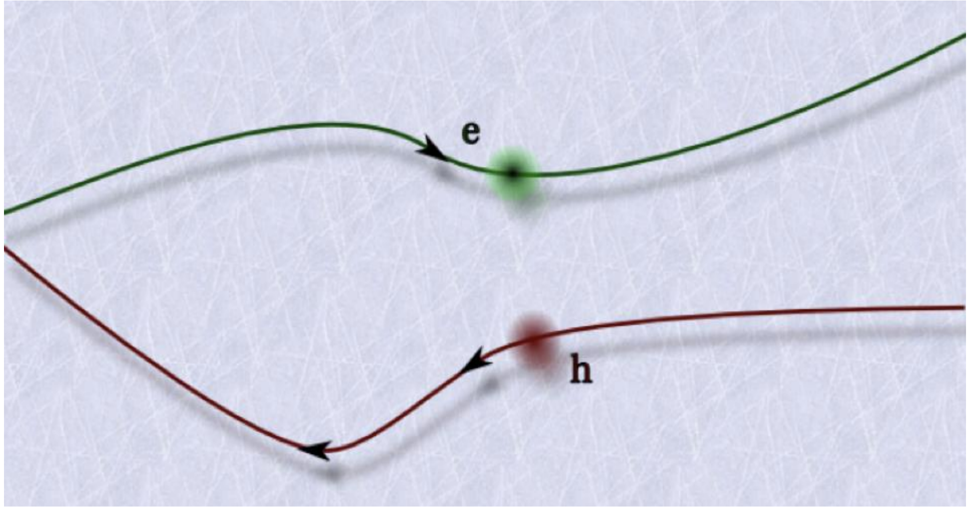
$$H^{exc}_{(vc),(v'c')} A_{\lambda}^{vc} = E_{\lambda}^{exc} A_{\lambda}^{vc}$$

Excitonic hamiltonian

Excitonic eigenvectors

Excitonic eigenvalues

Key quantity : Polarizability/response function



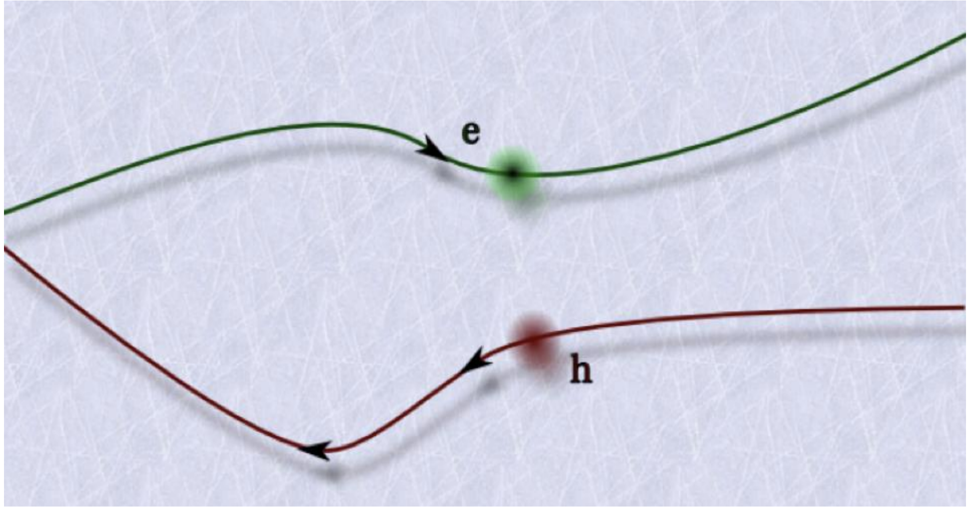
At the IP level

$$P(12) = -iG(12)G(21) = P_0(12)$$

$$1 \equiv \mathbf{r}_1, \sigma_1, t_1 \ldots$$

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

Key quantity : Polarizability/response function



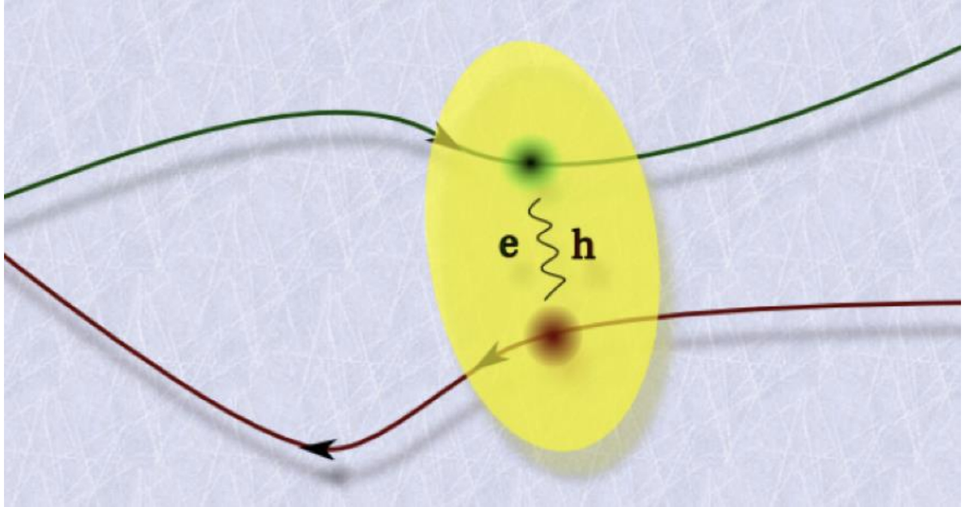
At the IP level

$$P(12) = -iG(12)G(21) = P_0(12)$$

$$1 \equiv \mathbf{r}_1, \sigma_1, t_1 \ldots$$

Beyond it

$$P(12) = -iG(13)G(42)\Gamma(342)$$



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

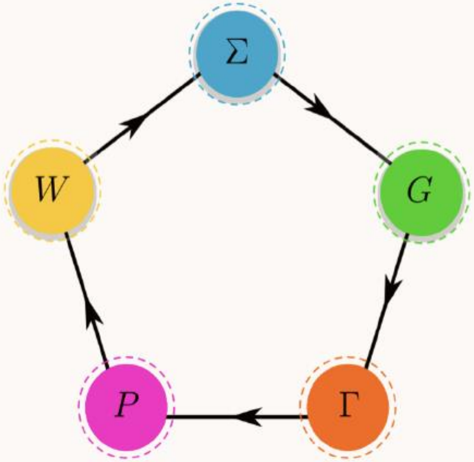
BSE: the derivations

See Lecture online on yambo webpage

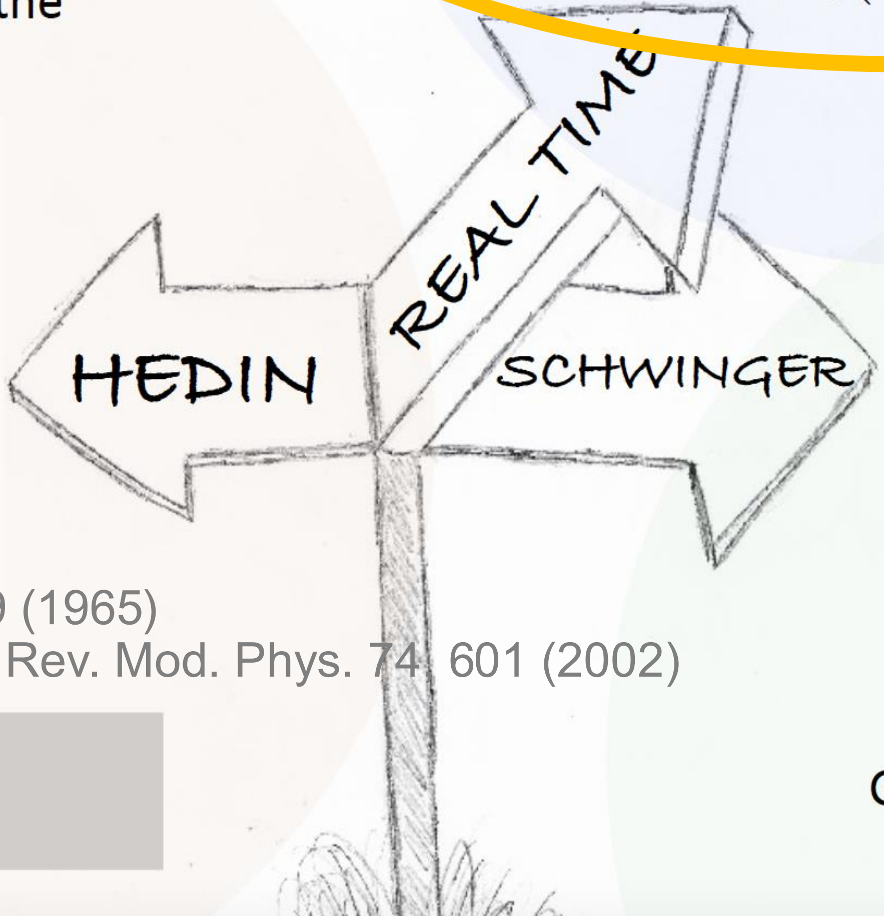
Non-equilibrium dynamics of the response function

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

Iteration of Hedin's equations that contain the response function



L.Hedin Phys Rev 139 (1965)
Onida Reining, Rubio Rev. Mod. Phys. 74, 601 (2002)



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

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

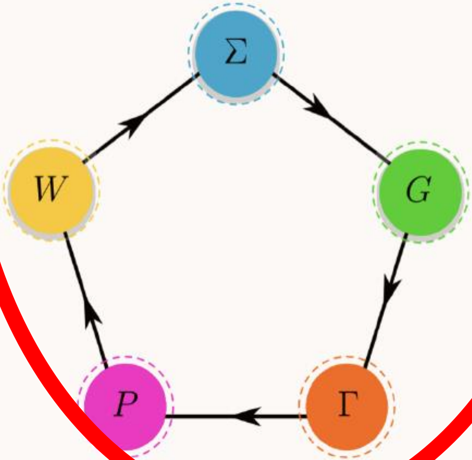
G. Strinati, Riv. Nuovo Cim. 11, 12 (1988)

Generalization of the response function to 4-point…

BSE: the derivations

Route 1

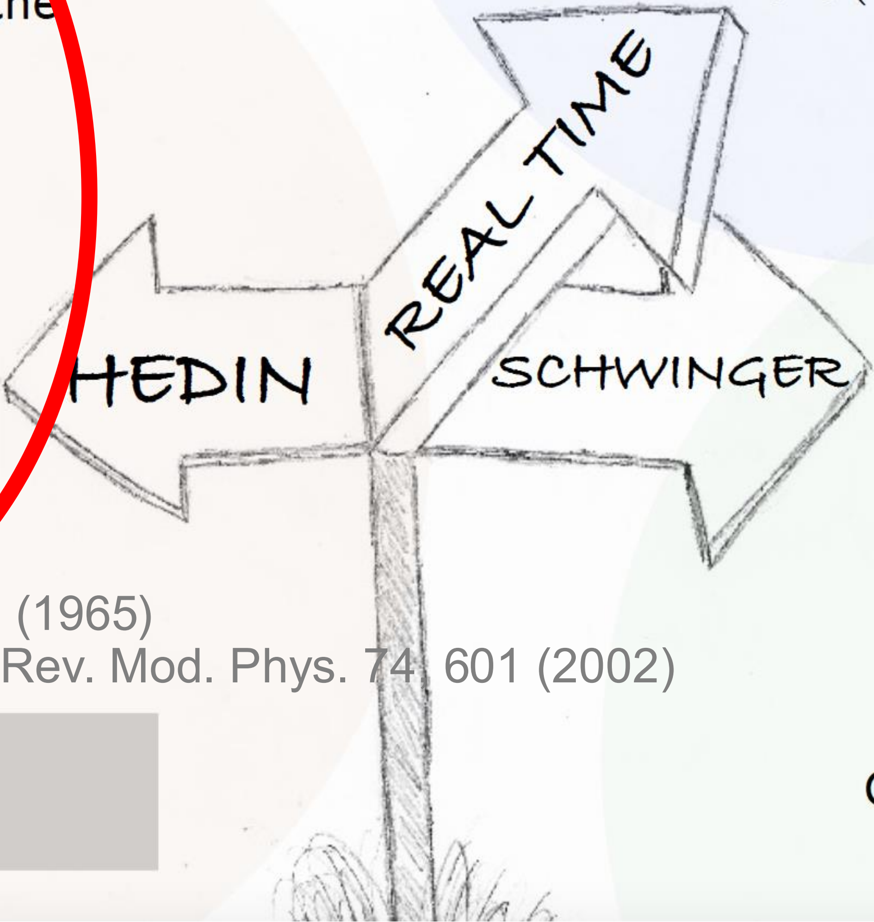
Iteration of Hedin's equations that contain the response function



L.Hedin Phys Rev 139 (1965)
Onida Reining, Rubio Rev. Mod. Phys. 74, 601 (2002)

Non-equilibrium dynamics of the response function

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



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

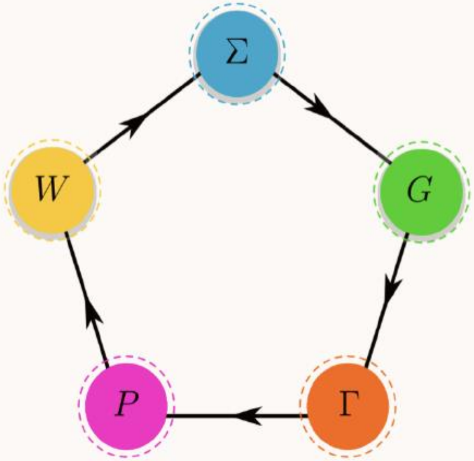
$$^4L(1234) = \frac{\delta G(12)}{\delta V_{\rm ext(34)}}$$

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

Generalization of the response function to 4-point…

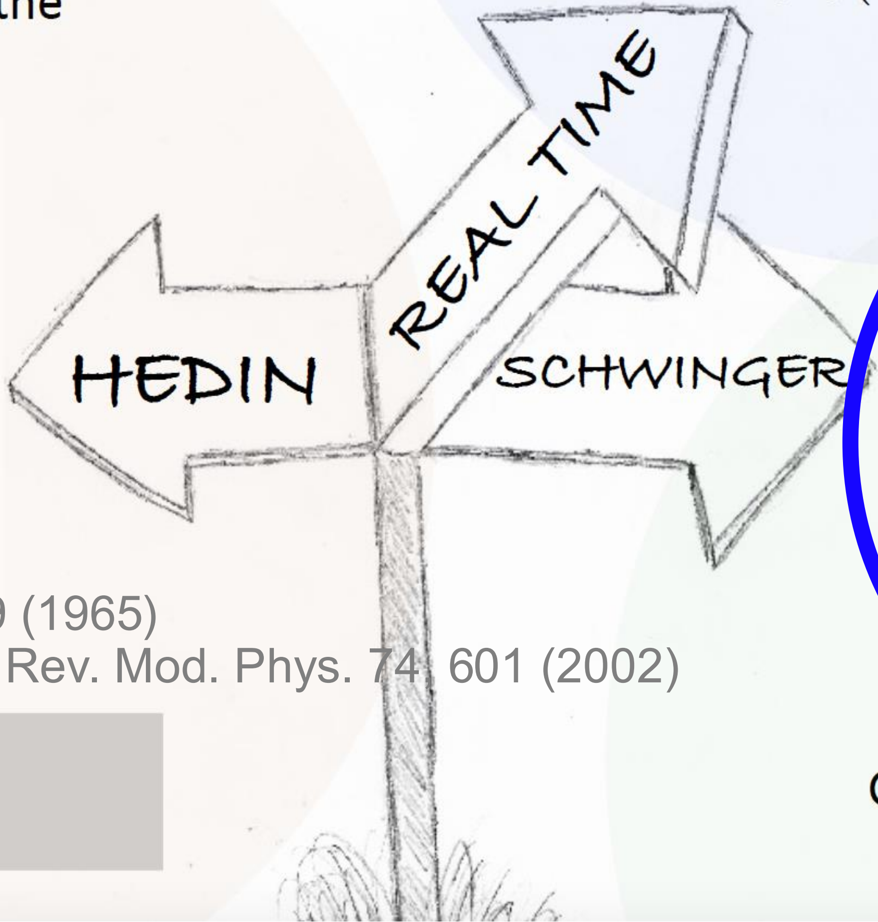
BSE: the derivations

Iteration of Hedin's equations that contain the response function



L.Hedin Phys Rev 139 (1965)

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



Non-equilibrium dynamics of the response function

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

Route 2

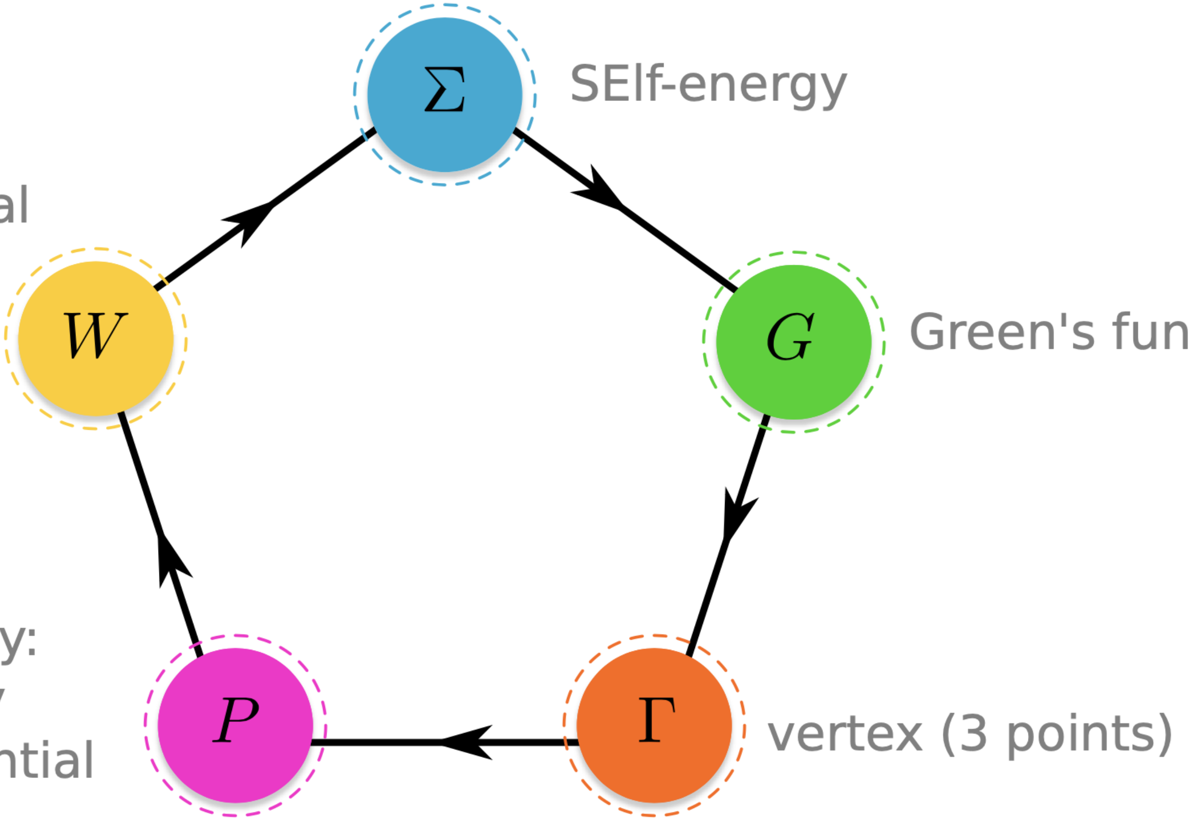
$$\chi(12) = \frac{\delta\rho(1)}{\delta V_{\mathrm{ext}}(2)} \rightarrow$$

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

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

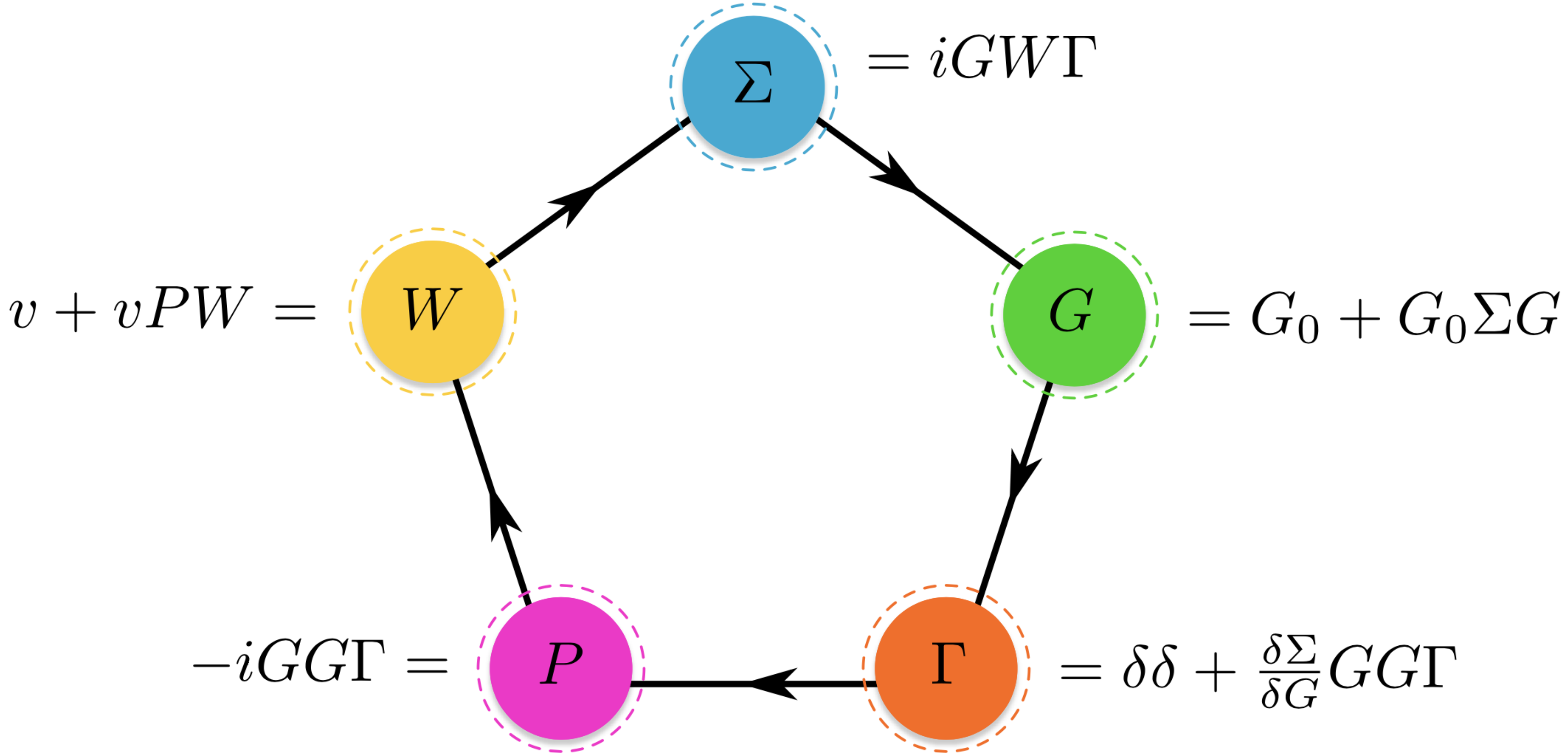
Generalization of the response function to 4-point...

BSE - Route 1



Hedin's Pentagon
set of integro-differential equations

BSE - Route 1



$$\Sigma = iGW\Gamma$$

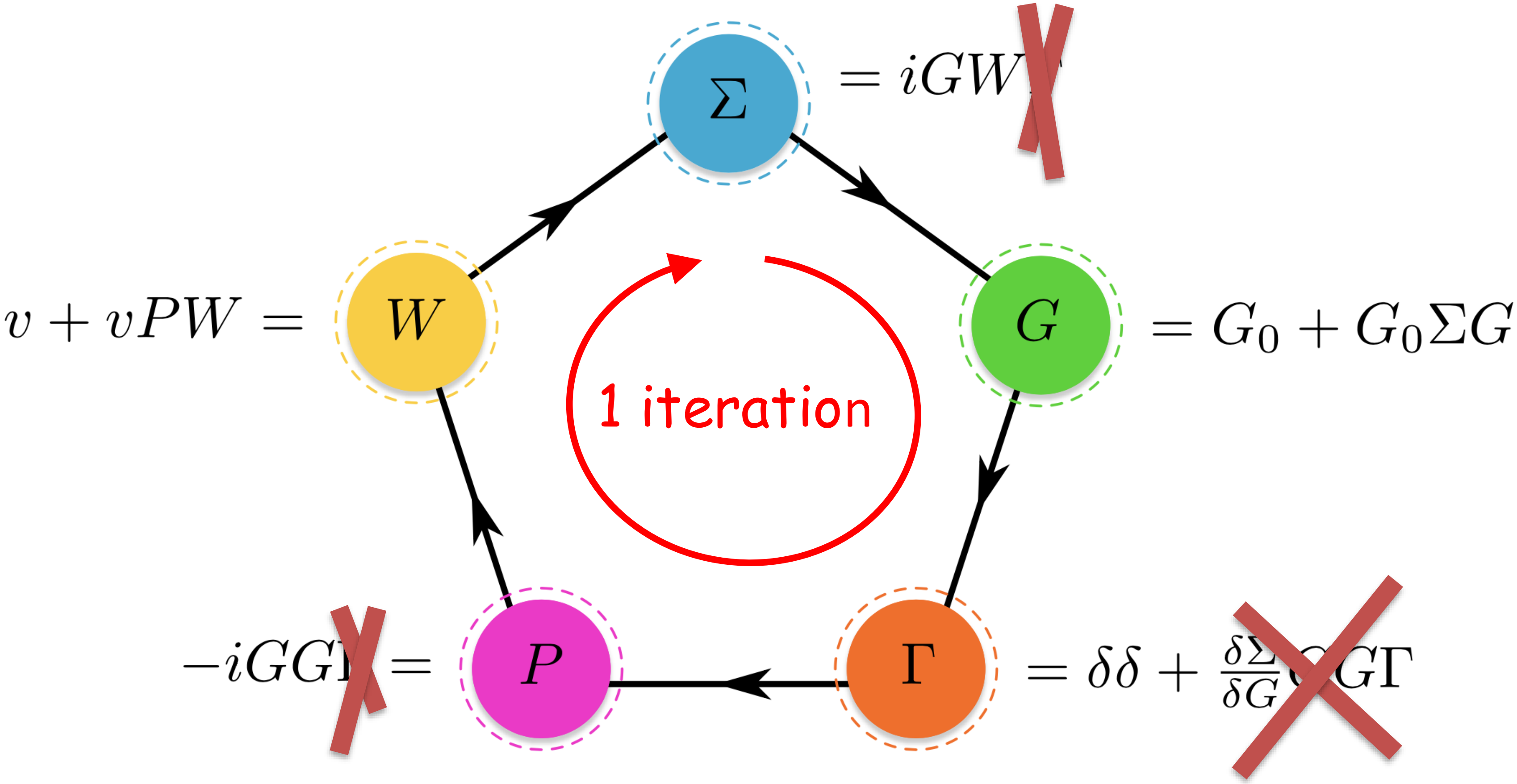
$$G = G_0 + G_0\Sigma G$$

$$\Gamma = \delta\delta + \frac{\delta\Sigma}{\delta G}GG\Gamma$$

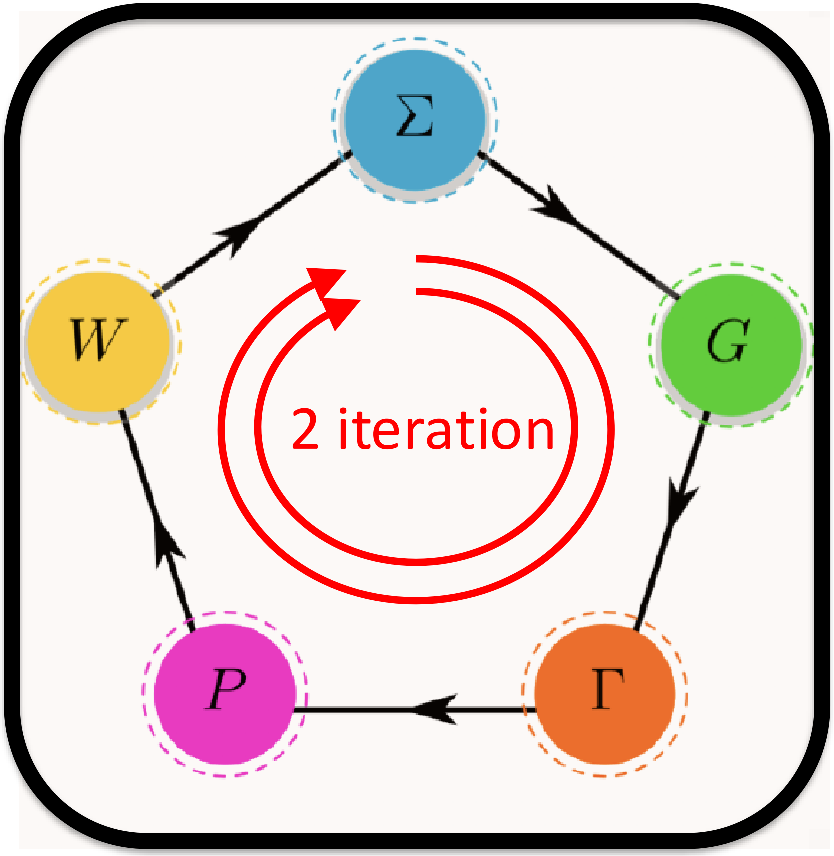
$$-iGG\Gamma = P$$

$$v + vPW = W$$

BSE - Route 1


$\Sigma = iGW\cancel{\Gamma}$
$G = G_0 + G_0\Sigma G$
$\Gamma = \delta\delta + \cancel{\frac{\delta\Sigma}{\delta G}GG\Gamma}$
$-iGG\cancel{\Gamma} = P$
$v + vPW = W$
1 iteration

BSE - Route 1



From $\Sigma = iGW$

The vertex equation is:

$$\Gamma = \delta\delta + \frac{\delta\Sigma}{\delta G} GG\Gamma$$

Using:

$$\frac{\delta\Sigma}{\delta G} = iW + iG\cancel{\frac{\delta W}{\delta G}} \simeq iW$$

The equation for the vertex becomes :

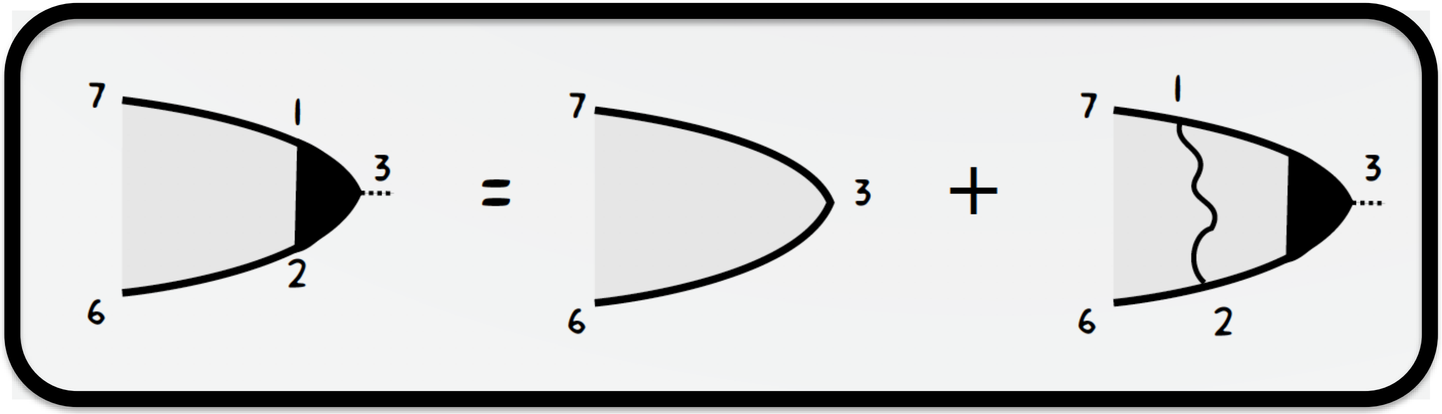
$$\boxed{\Gamma = \delta\delta + iWGG\Gamma}$$

BSE - Route 1

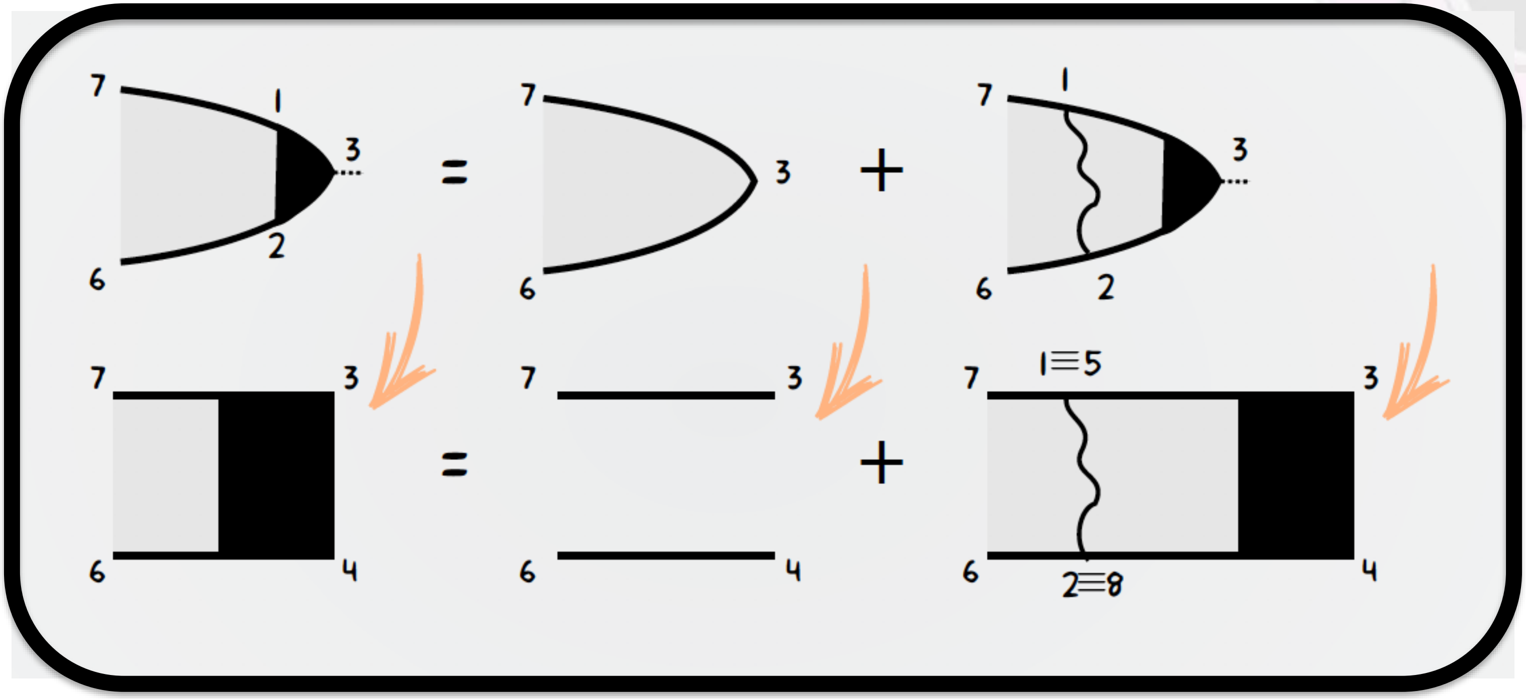
From the vertex equation to a 3-point irreducible polarizability

Multiplying the 3-point vertex by –iGG and integrating over (12):

$${}^3\tilde{P}(763) = -iG(73)G(36)+i\int d(12)W(1^+2)G(71)G(26)\,{}^3\tilde{P}(123)$$



BSE - Route 1



$${}^4\tilde{P}(7634) = {}^4P_0(7634) - \int d(1258)\,{}^4P_0(7612)\,{}^4W(1258)\,{}^4\tilde{P}(5834)$$

$${}^4P_0(7634) = -iG_0(73)G_0(64)$$

$${}^4W(1258) = W(1^+2)\delta(15)\delta(28)$$

Dyson-like equation
for the 4-point irreducible polarizability

BSE - Route 1

Combining this equation for the irreducible polarizability:

$${}^4\tilde{P} = {}^4P_0 + {}^4P_0(-W)\,{}^4\tilde{P}$$

and the equation that connects the irreducible to the reducible polarizability

$${}^4\bar{P} = {}^4\tilde{P} + {}^4\tilde{P}\bar{v}\,{}^4\bar{P}$$

BSE - Route 1

Combining this equation for the irreducible polarizability:

$${}^4\tilde{P} = {}^4P_0 + {}^4P_0(-W)\,{}^4\tilde{P}$$

and the equation that connects the irreducible to the reducible polarizability

$${}^4\bar{P} = {}^4\tilde{P} + {}^4\tilde{P}\,\bar{v}\,{}^4\bar{P}$$

A Dyson-like equation for the modified (reducible) 4-point polarizability can be obtained:

$$\boxed{{}^4\bar{P} = {}^4P_0 + {}^4P_0(\bar{v} - W)\bar{P} = {}^4P_0 + {}^4P_0 K \bar{P}}$$

Excitonic kernel

BSE - Route 1

Combining this equation for the irreducible polarizability:

$${}^4\tilde{P} = {}^4P_0 + {}^4P_0(-W){}^4\tilde{P}$$

and the equation that connects the irreducible to the reducible polarizability

$${}^4\bar{P} = {}^4\tilde{P} + {}^4\tilde{P}\bar{v}\,{}^4\bar{P}$$

A Dyson-like equation for the modified (reducible) 4-point polarizability can be obtained:

Free e-h propagation

$$\boxed{{}^4\bar{P} = {}^4P_0 + {}^4P_0(\bar{v} - W)\bar{P} = {}^4P_0 + {}^4P_0 K\bar{P}}$$

BSE - Route 1

Combining this equation for the irreducible polarizability:

$$ {}^4\tilde{P} = {}^4P_0 + {}^4P_0(-W)\,{}^4\tilde{P} $$

and the equation that connects the irreducible to the reducible polarizability

$$ {}^4\bar{P} = {}^4\tilde{P} + {}^4\tilde{P}\bar{v}\,{}^4\bar{P} $$

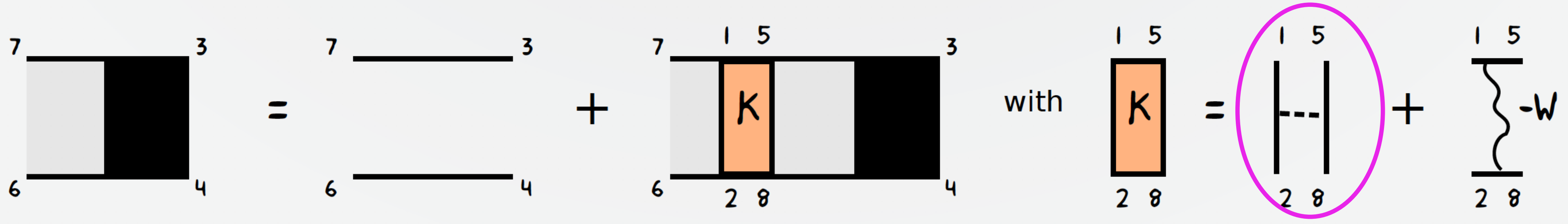
A Dyson-like equation for the modified (reducible) 4-point polarizability can be obtained:

Free e-h propagation

$$ \boxed{ {}^4\bar{P} = {}^4P_0 + {}^4P_0(\bar{v} - W)\bar{P} = {}^4P_0 + {}^4P_0 K \bar{P} } $$

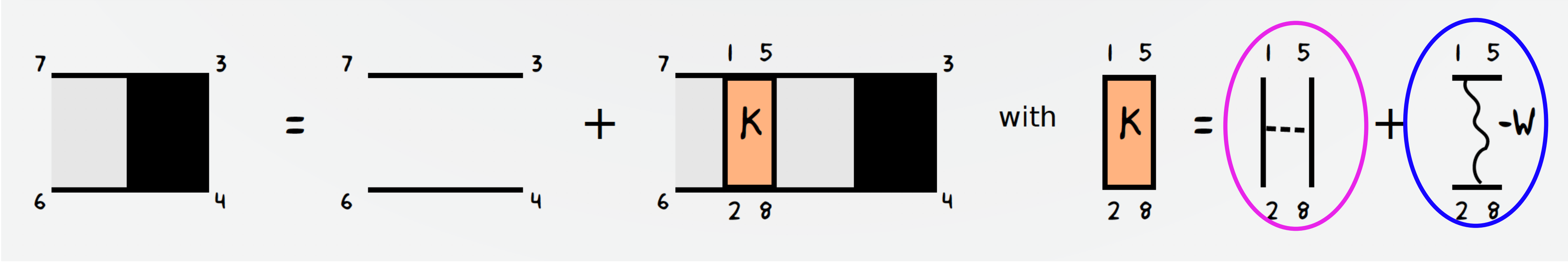
Excitonic kernel

$$ {}^4\bar{P} = {}^4P_0 + {}^4P_0(\bar{v} - W)\bar{P} = {}^4P_0 + {}^4P_0 K \bar{P} $$



e-h exchange interaction (repulsive) responsible for LF effects

$$ {}^4\bar{P} = {}^4P_0 + {}^4P_0(\bar{v} - W)\bar{P} = {}^4P_0 + {}^4P_0 K \bar{P} $$

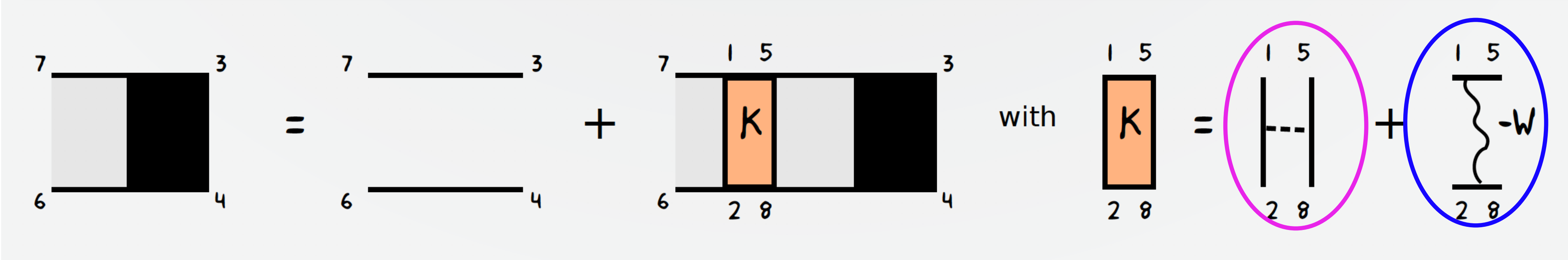


e-h exchange interaction (repulsive) responsible for LF effects

e-h direct interaction (attractive)

the Yambo team

$$^4\bar{P} = {}^4P_0 + {}^4P_0(\bar{v} - W)\bar{P} = {}^4P_0 + {}^4P_0 K\bar{P}$$

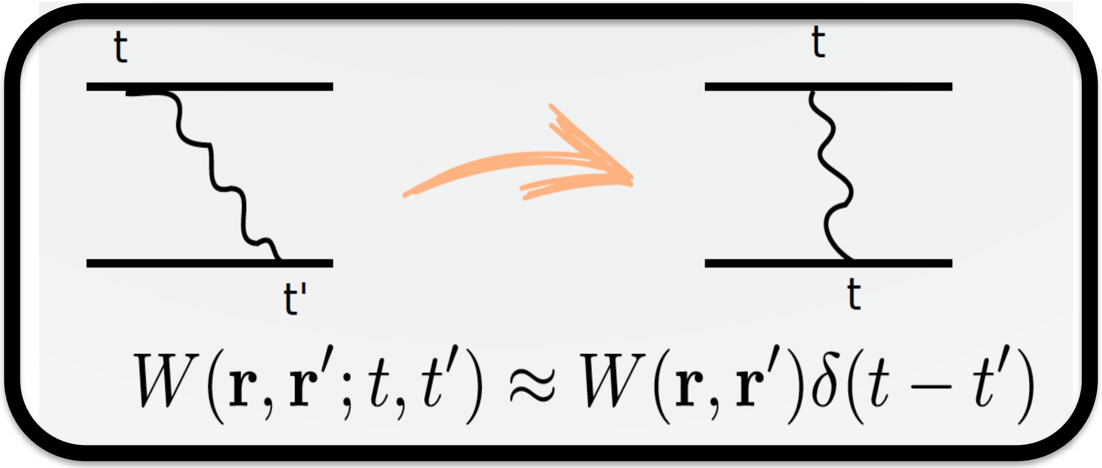


e-h exchange interaction (repulsive) responsible for LF effects

e-h direct interaction (attractive)

Common approximations

- In P_o G is calculated from GoWo
- We neglect how the screening changes with G
- W is W_o RPA **static**



$$W(\mathbf{r},\mathbf{r}';t,t') \approx W(\mathbf{r},\mathbf{r}')\delta(t-t')$$

Beyond SBSE G. Strinati PRL 49, 1519 (1982); PRB 29, 5718 (1984), A. Marini R. Del Sole Phys Rev Lett.91 17 (2003)

BSE - Route 2

$$\chi(1,2) = \frac{\delta\rho(1)}{\delta V_{ext}(2)} \qquad \rho(1) = -iG(1,1^{+})$$

Notation: 1^{+} means $r_1 t_1 + \eta$ with $\eta \to 0$

We can introduce a 4-point correlation function:

$$L(1,2,3,4) = \frac{\delta G(1,2)}{\delta V_{ext}(3,4)}$$

$$\Downarrow$$

$$\boxed{\chi(1,2) = -iL(1,1,2,2)}$$

So now we must look for an equation for L

BSE - Route 2

$$\delta\,(G\,G^{-1}) = 0 \qquad \frac{\delta G}{\delta V_{ext}} = -G \cdot \frac{\delta G^{-1}}{\delta V_{ext}} \cdot G$$

$$L(1,2,3,4) = \frac{\delta G(1,2)}{\delta V_{ext}(3,4)} = -G(1,5)\frac{\delta G^{-1}(5,6)}{\delta V_{ext}(3,4)}G(6,2)$$

BSE - Route 2

$$L(1,2,3,4) = \frac{\delta G(1,2)}{\delta V_{ext}(3,4)} = -G(1,5)\frac{\delta G^{-1}(5,6)}{\delta V_{ext}(3,4)}G(6,2)$$

$$\boxed{G^{-1}(5,6) = G_0^{-1}(5,6) - V_{ext}(5,6) - \Sigma(5,6)}$$

Hartree $\mathrm{V_H} + \tilde{\Sigma}$ Exchange-correlation

BSE - Route 2

$$L(1,2,3,4) = \frac{\delta G(1,2)}{\delta V_{ext}(3,4)} = -G(1,5)\frac{\delta G^{-1}(5,6)}{\delta V_{ext}(3,4)}G(6,2)$$

$$= -G(1,5)\frac{\delta[G_0^{-1}(5,6) - V_{ext}(5,6) - \Sigma(5,6)]}{\delta V_{ext}(3,4)}G(6,2)$$

BSE - Route 2

$$L(1,2,3,4) = \frac{\delta G(1,2)}{\delta V_{ext}(3,4)} = -G(1,5)\frac{\delta G^{-1}(5,6)}{\delta V_{ext}(3,4)}G(6,2)$$

$$= -G(1,5)\frac{\delta[\cancel{G_0^{-1}(5,6)} - V_{ext}(5,6) - \Sigma(5,6)]}{\delta V_{ext}(3,4)}G(6,2)$$

$$\delta(5,3)\delta(6,4)$$

BSE - Route 2

$$L(1,2,3,4) = \frac{\delta G(1,2)}{\delta V_{ext}(3,4)} = -G(1,5)\frac{\delta G^{-1}(5,6)}{\delta V_{ext}(3,4)}G(6,2)$$

L_0

$$= G(1,3)G(4,2) + G(1,5)G(6,2)\frac{\delta \Sigma(5,6)}{\delta V_{ext}(3,4)}$$

BSE - Route 2

$$L(1,2,3,4) = \frac{\delta G(1,2)}{\delta V_{ext}(3,4)} = -G(1,5)\frac{\delta G^{-1}(5,6)}{\delta V_{ext}(3,4)}G(6,2)$$

L_0

$$= G(1,3)G(4,2) + G(1,5)G(6,2)\frac{\delta\Sigma(5,6)}{\delta V_{ext}(3,4)}$$

$$\boxed{\frac{\delta\Sigma(5,6)}{\delta V_{ext}(3,4)} = \frac{\delta\Sigma(5,6)}{\delta G(7,8)}\frac{\delta G(7,8)}{\delta V_{ext}(3,4)} = \Xi(5,6,7,8)L(7834)}$$

BSE - Route 2

$$\Xi(5,6,7,8) = \frac{\delta\Sigma(5,6)}{\delta G(7,8)}$$

$$= \boxed{\frac{\delta V_H(5)\delta(5,6)}{\delta G(7,8)}} + \frac{\delta\tilde{\Sigma}(5,6)}{\delta G(7,8)}$$

$$\boxed{\frac{\delta V_H(5)\delta(5,6)}{\delta G(7,8)} = -iv(5,7)\delta(5,6)\delta(7,8)}$$

BSE - Route 2

$$\Xi(5,6,7,8) = \frac{\delta\Sigma(5,6)}{\delta G(7,8)}$$

$$= \frac{\delta V_H(5)\delta(5,6)}{\delta G(7,8)} + \frac{\delta\tilde{\Sigma}(5,6)}{\delta G(7,8)}$$

$$\boxed{\frac{\delta V_H(5)\delta(5,6)}{\delta G(7,8)} = -iv(5,7)\delta(5,6)\delta(7,8)}$$

$$\boxed{\frac{\delta\tilde{\Sigma}(5,6)}{\delta G(7,8)} \sim i\frac{\delta[G(5,6)W(5,6)]}{\delta G(7,8)} \sim iW(5,6)\delta(57)\delta(6,8)}$$

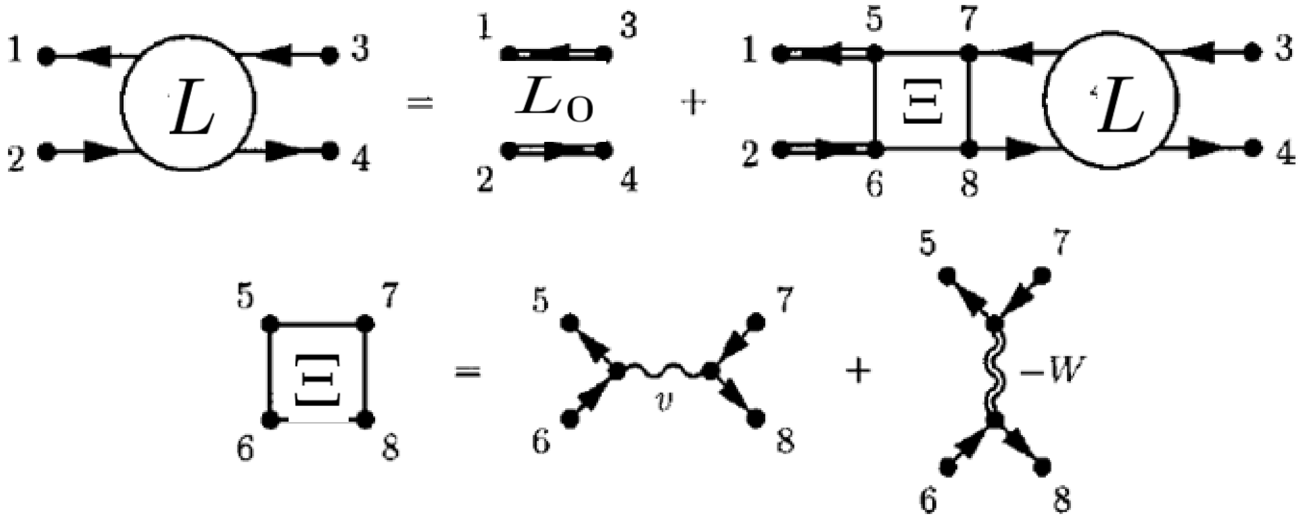
the Yambo team

BSE - Route 2

Independent electron-hole propagator $L_0(1234) = G(13)G(42)$

Two Particle correlation function $L(1234) = G_2(1234) - G(13)G(42)$

$$\boxed{L(1234) = L_0(1234) + L_0(1256)\Xi(5678)L(7834)}$$



How do we solve the BSE?

Assuming that only a small set of single-particle transitions contribute to the relevant spectral features, it is convenient to move to **"transition space"**.

The transition-space matrix element of a generic 4-point function is computed as:

$$
\begin{aligned}
A_{tt'} &= A_{(n_1,n_2)(n_3,n_4)} \\
&= \int dr_1 dr_2 dr_3 dr_4 A(1,2,3,4)\phi_{n_1}(r_1)\phi^*_{n_2}(r_2)\phi^*_{n_3}(r_3)\phi_{n_4}(r_4)
\end{aligned}
$$

This will allow to rewrite the BSE as an
effective two particle excitonic Hamiltonian

Excitonic Hamiltonian

In transitions space we have:

$$\bar{P}_{(n_1n_2)(n_3n_4)}(\omega) = (\hat{I}\omega - H^{exc})^{-1}_{(n_1n_2)(n_3n_4)}(f_{n_3} - f_{n_4})$$

Where:

$$\boxed{H^{exc}_{(n_1,n_2)(n_3,n_4)} = (\epsilon^{qp}_{n1} - \epsilon^{qp}_{n2})\delta_{n_1,n_3}\delta_{n_2,n_4} + (f_{n_1} - f_{n_2})(\bar{v} - W)_{(n_1,n_2)(n_3,n_4)}}$$

Excitonic Hamiltonian

In transitions space we have :

$$\bar{P}_{(n_1 n_2)(n_3 n_4)}(\omega) = (\hat{I}\omega - H^{exc})^{-1}_{(n_1 n_2)(n_3 n_4)}(f_{n_3} - f_{n_4})$$

Where:

$$\boxed{H^{exc}_{(n_1,n_2)(n_3,n_4)} = (\epsilon^{qp}_{n1} - \epsilon^{qp}_{n2})\delta_{n_1,n_3}\delta_{n_2,n_4} + (f_{n_1} - f_{n_2})(\bar{v} - W)_{(n_1,n_2)(n_3,n_4)}}$$

$$n_1 n_2 \;\; n_3 n_4 \rightarrow \quad \downarrow$$

$$\begin{array}{c|c}
 & \begin{array}{cccc} \{v'c'\} & \{c'v'\} & \{v'\bar{v}'\} & \{c'\bar{c}'\} \end{array} \\
\begin{array}{c} \{vc\} \\ \{cv\} \\ \{v\bar{v}\} \\ \{c\bar{c}\} \end{array} &
\begin{pmatrix}
H^{exc}_{(vc),(v'c')} & K_{(vc),(c'v')} & K_{(vc),(v'\bar{v}')} & K_{(vc),(c'\bar{c}')} \\
-K_{(cv),(v'c')} & -H^{exc}_{(cv),(v'c')} & -K_{(cv),(v'\bar{v}')} & -K_{(cv),(c'\bar{c}')} \\
0 & 0 & (\epsilon_{\bar{v}} - \epsilon_v)\delta_{v,v'}\delta_{\bar{v},\bar{v}'} & 0 \\
0 & 0 & 0 & (\epsilon_{\bar{c}} - \epsilon_c)\delta_{c,c'}\delta_{\bar{c},\bar{c}'}
\end{pmatrix}
\end{array}$$

For extended systems

$n = n,\mathbf{k}$

Excitonic Hamiltonian

In transitions space we have :

$$\bar{P}_{(n_1 n_2)(n_3 n_4)}(\omega) = (\hat{I}\omega - H^{exc})^{-1}_{(n_1 n_2)(n_3 n_4)}(f_{n_3} - f_{n_4})$$

Where:

$$\boxed{H^{exc}_{(n_1,n_2)(n_3,n_4)} = (\epsilon^{qp}_{n1} - \epsilon^{qp}_{n2})\delta_{n_1,n_3}\delta_{n_2,n_4} + (f_{n_1} - f_{n_2})(\bar{v} - W)_{(n_1,n_2)(n_3,n_4)}}$$

$$\begin{array}{c|cccc}
n_1 n_2 \;\; n_3 n_4 \rightarrow & \{v'c'\} & \{c'v'\} & \{v'\bar{v}'\} & \{c'\bar{c}'\} \\
\downarrow & & & & \\
\{vc\} & H^{exc}_{(vc),(v'c')} & K_{(vc),(c'v')} & \xcancel{K_{(vc),(v'\bar{v}')}} & \xcancel{K_{(vc),(c'\bar{c}')}} \\
\{cv\} & -K_{(cv),(v'c')} & -H^{exc}_{(cv),(v'c')} & \xcancel{-K_{(cv),(v'\bar{v}')}} & \xcancel{-K_{(cv),(c'\bar{c}')}} \\
\{v\bar{v}\} & 0 & 0 & \xcancel{(\epsilon_{\bar{v}} - \epsilon_v)\delta_{v,v'}\delta_{\bar{v},\bar{v}'}} & \xcancel{0} \\
\{c\bar{c}\} & 0 & 0 & \xcancel{0} & \xcancel{(\epsilon_{\bar{c}} - \epsilon_c)\delta_{c,c'}\delta_{\bar{c},\bar{c}'}}
\end{array}$$

Only terms between occupied and unoccupied pairs contribute to the dielectric function

Excitonic Hamiltonian

Resonant

$$\begin{pmatrix} H^{exc,res}_{(vc),(v'c')} & K_{(vc),(c'v')} \\ -[K_{(vc),(c'v')}]^{*} & -[H^{exc,res}_{(v,c),(v'c')}]^{*} \end{pmatrix}$$

Anti-Resonant

In a compact notation :

$$\begin{pmatrix} R & C \\ -C^{*} & -R^{*} \end{pmatrix}$$

R is hermitian
C is symmetric

Excitonic Hamiltonian

Resonant

coupling

$$\begin{pmatrix} H^{exc,res}_{(vc),(v'c')} & K_{(vc),(c'v')} \\ -[K_{(vc),(c'v')}]^* & -[H^{exc,res}_{(v,c),(v'c')}]^* \end{pmatrix}$$

Anti-Resonant

In a compact notation :

$$\begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix}$$

R is hermitian
C is symmetric

Excitonic Hamiltonian

$$\begin{pmatrix} H^{exc,res}_{(vc),(v'c')} & \xcancel{K_{(vc),(c'v')}} \\ -[\xcancel{K_{(vc),(c'v')}}]^* & -[H^{exc,res}_{(v,c),(v'c')}]^* \end{pmatrix}$$

Tamm-Dancoff Approximation (TDA)

In most cases, it works fine. All the times there is a sharp distinction between excitonic and plasmonic excitations. Valid if the coupling terms are small !!

Resonant Excitonic Hamiltonian

$$\begin{pmatrix} H^{exc,res}_{(vc),(v'c')} & \cancel{K_{(vc),(c'v')}} \\ \cancel{-[K_{(vc),(c'v')}]^*} & \cancel{-[H^{exc,res}_{(v,c),(v'c')}]^*} \end{pmatrix}$$

Good approximation to calculate
the optical spectra of extended systems

What about spin?

What about spin?

Collinear
non spin-polarized
$s^2 s_z$

Collinear
spin-polarized
s_z

What about spin?

Collinear
non spin-polarized
$S^2 S_z$

Collinear
spin-polarized
S_z

Non collinear
$\xcancel{S^2 S_z}$

What about spin?

Collinear
non spin-polarized
$s^2 s_z$

Collinear
spin-polarized
s_z

Non collinear
$\xcancel{s^2 s_z}$

$$\begin{pmatrix}\phi_{n\uparrow}(\mathbf{r})\\ 0\end{pmatrix} \quad \text{or} \quad \begin{pmatrix}0\\ \phi_{n\downarrow}(\mathbf{r})\end{pmatrix}$$

$$\begin{pmatrix}\phi_{n\uparrow}(\mathbf{r})\\ \phi_{n\downarrow}(\mathbf{r})\end{pmatrix}$$

SPINOR

What about spin?

Collinear
non spin-polarized
$S^2 S_z$

Collinear
spin-polarized
S_z

Non collinear
$\xcancel{S^2 S_z}$

$$\begin{pmatrix} \phi_{n\uparrow}(\mathbf{r}) \\ 0 \end{pmatrix} \text{ or } \begin{pmatrix} 0 \\ \phi_{n\downarrow}(\mathbf{r}) \end{pmatrix}$$

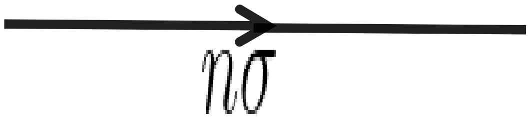
$$\begin{pmatrix} \phi_{n\uparrow}(\mathbf{r}) \\ \phi_{n\downarrow}(\mathbf{r}) \end{pmatrix}$$

SPINOR

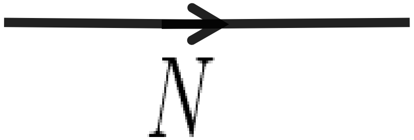
$$\phi_{n\uparrow}(\mathbf{r}) = \phi_{n\downarrow}(\mathbf{r})$$
$$\epsilon_{n\uparrow} = \epsilon_{n\downarrow}$$

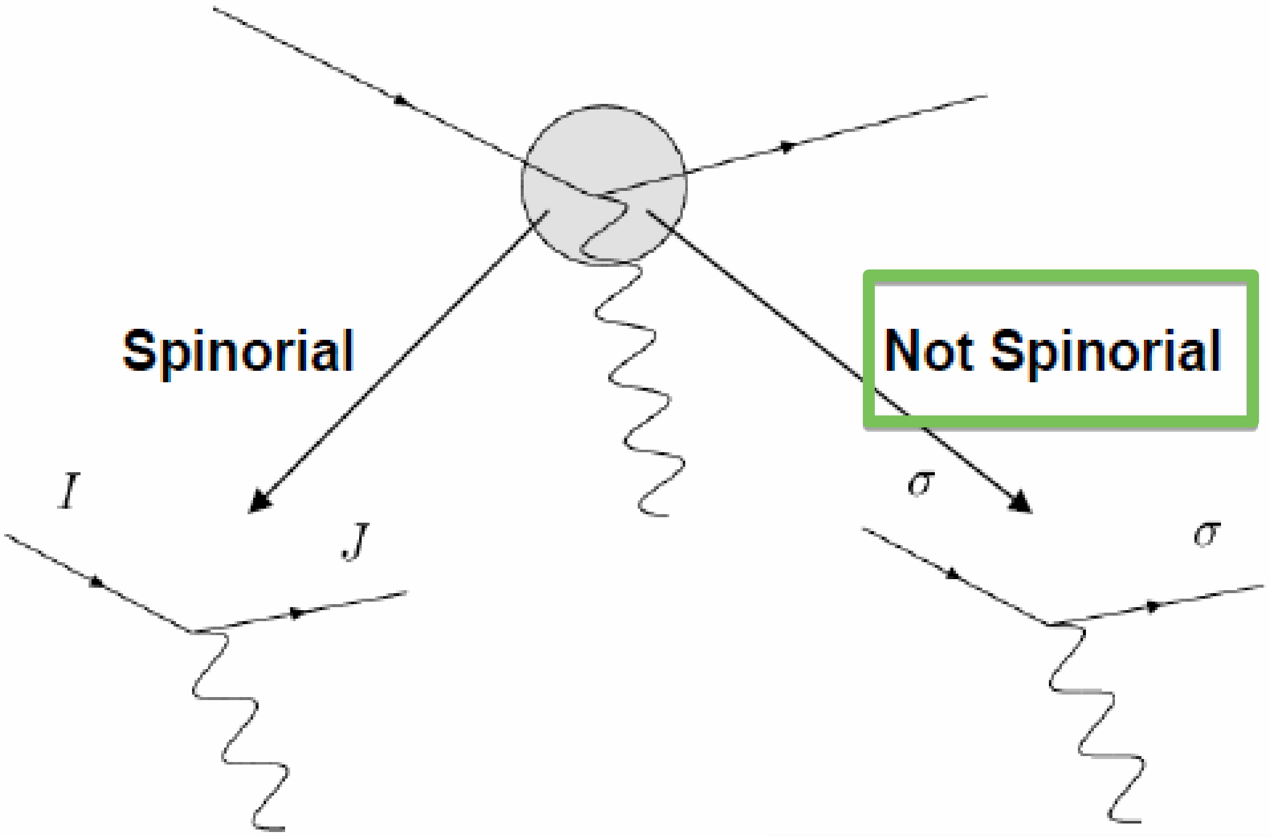
$$\phi_{n\uparrow}(\mathbf{r}) \neq \phi_{n\downarrow}(\mathbf{r})$$
$$\epsilon_{n\uparrow} \neq \epsilon_{n\downarrow}$$

$$\vec{\phi}_N(\mathbf{r})$$
$$\epsilon_N$$



$\sigma = \uparrow, \downarrow \quad n = n, k$



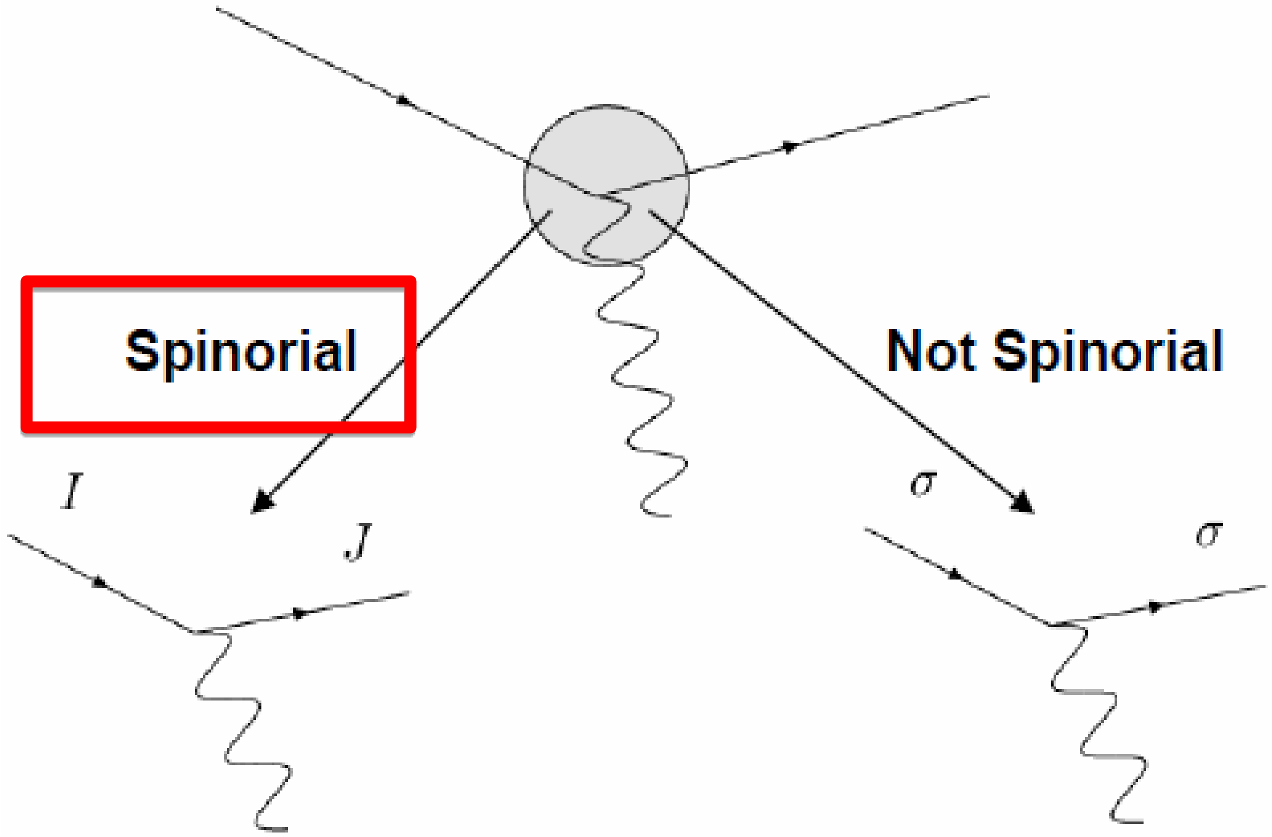


Spinorial

Not Spinorial

$$\sum_{\sigma} \int d^3r\, \phi^*_{I\sigma}(r)\phi_{J\sigma}(r)$$

$$\boxed{\int d^3r\, \phi^*_{\sigma}(r)\phi_{\sigma}(r)}$$



Spinorial

Not Spinorial

$$\boxed{\sum_{\sigma} \int d^3r\, \phi^*_{I\sigma}(r)\phi_{J\sigma}(r)}$$

$$\int d^3r\, \phi^*_{\sigma}(r)\phi_{\sigma}(r)$$

Collinear case

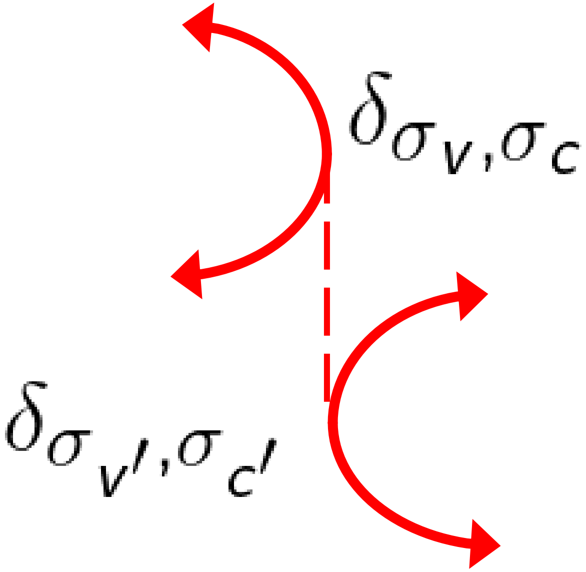
$$H^{exc}_{(v\sigma_v c\sigma_c),(v'\sigma_{v'}c'\sigma_{c'})} =$$

$$(H^{diag} + K^{x} + K^{c})_{(v\sigma_v c\sigma_c),(v'\sigma_{v'}c'\sigma_{c'})}$$

Diagonal part

$$H^{diag}_{(v\sigma_v c\sigma_c),(v'\sigma_{v'}c'\sigma_{c'})} = (\epsilon^{qp}_{c\sigma_c} - \epsilon^{qp}_{v\sigma_v})\delta_{v,v'}\delta_{c,c'}\delta_{\sigma_c,\sigma'_c}\delta_{\sigma_v,\sigma'_v}$$

Collinear case



Exchange

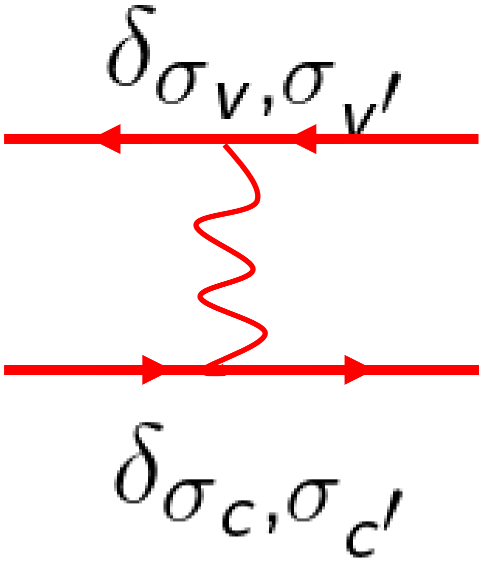
$$K^{x}_{(v\sigma_v c\sigma_c),(v'\sigma_{v'}c'\sigma_{c'})} = \bar{v}_{(v\sigma_v c\sigma_c),(v'\sigma_{v'}c'\sigma_{c'})}\delta_{\sigma_c,\sigma_v}\delta_{\sigma_{c'},\sigma_{v'}}$$

$$= \int d^3r d^3r' \phi^*_{c\sigma}(r)\phi_{v\sigma}(r)\bar{v}(r-r')\phi_{c'\sigma'}(r')\phi^*_{v'\sigma'}(r')$$

where

$$\sigma = \sigma_v, \sigma_c,$$
$$\sigma' = \sigma_{v'}, \sigma_{c'}$$

Collinear case



Correlation

$$K^{c}_{(v\sigma_v c\sigma_c),(v'\sigma_{v'}c'\sigma_{c'})} = -W_{(v\sigma_v c\sigma_c),(v'\sigma_{v'}c'\sigma_{c'})}\delta_{\sigma_c,\sigma_{c'}}\delta_{\sigma_v,\sigma_{v'}}$$

$$= \int d^3r d^3r' \phi^*_{c\sigma}(r)\phi^*_{c'\sigma}(r) W(r-r')\phi_{v\sigma'}(r')\phi^*_{v'\sigma'}(r')$$

with $\sigma = \sigma_c, \sigma_{c'}$
$\sigma' = \sigma_v, \sigma_{v'}$

Excitonic kernel in G-space

Exchange term

$$K^{x}_{vc\mathbf{k},v'c'\mathbf{k}'} = \bar{V}_{vc\mathbf{k},v'c'\mathbf{k}'} = \frac{1}{\Omega}\sum_{\mathbf{G}\neq 0} v(\mathbf{G})\langle c\mathbf{k}|e^{i\mathbf{G}\mathbf{r}}|v\mathbf{k}\rangle\langle v'\mathbf{k}'|e^{-i\mathbf{G}'\mathbf{r}}|c'\mathbf{k}'\rangle$$

Single sum over G

Correlation or direct term

$$K^{c}_{vc\mathbf{k},v'c'\mathbf{k}'} = W_{vc\mathbf{k},v'c'\mathbf{k}'} = \frac{1}{\Omega}\sum_{\mathbf{G},\mathbf{G}'} v(\mathbf{q}+\mathbf{G})\boxed{\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q})}\langle c\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}|c'\mathbf{k}'\rangle\langle v'\mathbf{k}'|e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}}|v\mathbf{k}\rangle\delta_{\mathbf{q}\mathbf{k}-\mathbf{k}'}$$

Double sum
over G and G'

Static Dielectric
matrix: most time
consuming part of
the calculation!

BSE & spin

Collinear non spin-polarized case

$$\begin{array}{cc}
 & \begin{array}{cccc} (v'\uparrow c'\uparrow) & (v'\uparrow c'\downarrow) & (v'\downarrow c'\uparrow) & (v'\downarrow c'\downarrow) \end{array} \\
\begin{array}{c} (v\uparrow c\uparrow) \\ (v\uparrow c\downarrow) \\ (v\downarrow c\uparrow) \\ (v\downarrow c\downarrow) \end{array} &
\begin{pmatrix}
H^{diag}+K^{c}+K^{x} & 0 & 0 & K^{x} \\
0 & H^{diag}+K^{c} & 0 & 0 \\
0 & 0 & H^{diag}+K^{c} & 0 \\
K^{x} & 0 & 0 & H^{diag}+K^{c}+K^{x}
\end{pmatrix}
\end{array}$$

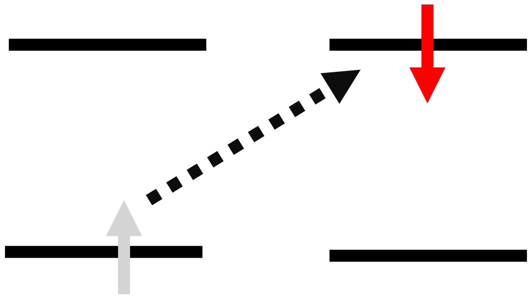
$$\phi_{n\uparrow}(\mathbf{r}) = \phi_{n\downarrow}(\mathbf{r})$$
$$\epsilon_{n\uparrow} = \epsilon_{n\downarrow}$$

BSE & spin

Collinear non spin-polarized case

$$\begin{array}{c|cccc}
 & (v'\uparrow c'\uparrow) & (v'\uparrow c'\downarrow) & (v'\downarrow c'\uparrow) & (v'\downarrow c'\downarrow) \\
\hline
(v\uparrow c\uparrow) & H^{diag}+K^{c}+K^{x} & 0 & 0 & K^{x} \\
(v\uparrow c\downarrow) & 0 & \boxed{H^{diag}+K^{c}} & 0 & 0 \\
(v\downarrow c\uparrow) & 0 & 0 & H^{diag}+K^{c} & 0 \\
(v\downarrow c\downarrow) & K^{x} & 0 & 0 & H^{diag}+K^{c}+K^{x}
\end{array}$$

$$\phi_{n\uparrow}(\mathbf{r}) = \phi_{n\downarrow}(\mathbf{r})$$
$$\epsilon_{n\uparrow} = \epsilon_{n\downarrow}$$

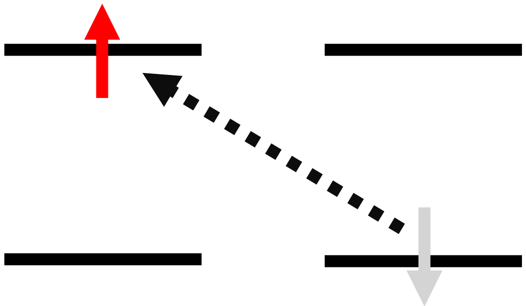


BSE & spin

Collinear non spin-polarized case

$$\begin{array}{c|cccc}
 & (v'\uparrow c'\uparrow) & (v'\uparrow c'\downarrow) & (v'\downarrow c'\uparrow) & (v'\downarrow c'\downarrow) \\
\hline
(v\uparrow c\uparrow) & H^{diag}+K^c+K^x & 0 & 0 & K^x \\
(v\uparrow c\downarrow) & 0 & H^{diag}+K^c & 0 & 0 \\
(v\downarrow c\uparrow) & 0 & 0 & \boxed{H^{diag}+K^c} & 0 \\
(v\downarrow c\downarrow) & K^x & 0 & 0 & H^{diag}+K^c+K^x
\end{array}$$

$$\boxed{\begin{array}{c} \phi_{n\uparrow}(\mathbf{r}) = \phi_{n\downarrow}(\mathbf{r}) \\ \epsilon_{n\uparrow} = \epsilon_{n\downarrow} \end{array}}$$

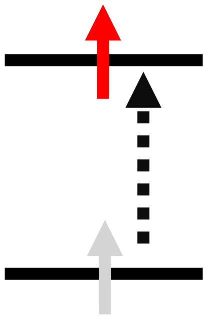


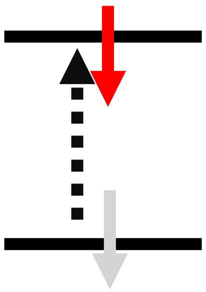
BSE & spin

Collinear non spin-polarized case

$$\begin{array}{c|cccc} & (v'\uparrow c'\uparrow) & (v'\uparrow c'\downarrow) & (v'\downarrow c'\uparrow) & (v'\downarrow c'\downarrow) \\ \hline (v\uparrow c\uparrow) & H^{diag}+K^{c}+K^{x} & 0 & 0 & K^{x} \\ (v\uparrow c\downarrow) & 0 & H^{diag}+K^{c} & 0 & 0 \\ (v\downarrow c\uparrow) & 0 & 0 & H^{diag}+K^{c} & 0 \\ (v\downarrow c\downarrow) & K^{x} & 0 & 0 & H^{diag}+K^{c}+K^{x} \end{array}$$

$$\phi_{n\uparrow}(\mathbf{r}) = \phi_{n\downarrow}(\mathbf{r})$$
$$\epsilon_{n\uparrow} = \epsilon_{n\downarrow}$$





The only transitions which contribute to optical absorption within the dipole approximation (spin-selection rule)

BSE & spin

Collinear non spin-polarized case

Since also S^2 is conserved → Rotate in the basis of singlet and triplet exciton states

$$Singlet = \frac{(v\uparrow c\uparrow + v\downarrow c\downarrow)}{\sqrt{2}}$$

$$Triplet = \begin{cases} \frac{(v\uparrow c\uparrow - v\downarrow c\downarrow)}{\sqrt{2}} \\ v\uparrow c\downarrow \\ v\downarrow c\uparrow \end{cases}$$

electron and hole have **antiparallel spins**

e and h have **parallel spins**

$$\begin{pmatrix} \boxed{H^{diag} + 2K^x + K^c} & 0 & 0 & 0 \\ 0 & H^{diag} + K^c & 0 & 0 \\ 0 & 0 & H^{diag} + K^c & 0 \\ 0 & 0 & 0 & H^{diag} + K^c \end{pmatrix}$$

Triplets are always lower in energy than singlets

BSE & spin

Collinear spin-polarized case

$$\begin{array}{c|cccc}
 & (v'\uparrow c'\uparrow) & (v'\uparrow c'\downarrow) & (v'\downarrow c'\uparrow) & (v'\downarrow c'\downarrow) \\
\hline
(v\uparrow c\uparrow) & H^{\text{diag}}_{\uparrow\uparrow}+K^{x}_{\uparrow\uparrow}+K^{c}_{\uparrow\uparrow} & 0 & 0 & K^{x}_{\uparrow\downarrow} \\
(v\uparrow c\downarrow) & 0 & H^{\text{diag}}_{\uparrow\downarrow}+K^{c}_{\uparrow\downarrow} & 0 & 0 \\
(v\downarrow c\uparrow) & 0 & 0 & H^{\text{diag}}_{\downarrow\uparrow}+K^{c}_{\downarrow\uparrow} & 0 \\
(v\downarrow c\downarrow) & K^{x}_{\downarrow\uparrow} & 0 & 0 & H^{\text{diag}}_{\downarrow\downarrow}+K^{x}_{\downarrow\downarrow}+K^{c}_{\downarrow\downarrow}
\end{array}$$

n=n,k

$$\phi_{n\uparrow}(\mathbf{r}) \neq \phi_{n\downarrow}(\mathbf{r})$$
$$\epsilon_{n\uparrow} \neq \epsilon_{n\downarrow}$$

$$\Delta S_z = 1$$

*2*N MATRIX Cannot be further blocked …*

Spin-flip excitons, dark

the Yambo team

BSE & spin

Collinear spin-polarized case

$$\begin{array}{c|cccc} & (v'\uparrow c'\uparrow) & (v'\uparrow c'\downarrow) & (v'\downarrow c'\uparrow) & (v'\downarrow c'\downarrow) \\ \hline (v\uparrow c\uparrow) & H^{\mathrm{diag}}_{\uparrow\uparrow}+K^{x}_{\uparrow\uparrow}+K^{c}_{\uparrow\uparrow} & 0 & 0 & K^{x}_{\uparrow\downarrow} \\ (v\uparrow c\downarrow) & 0 & H^{\mathrm{diag}}_{\uparrow\downarrow}+K^{c}_{\uparrow\downarrow} & 0 & 0 \\ (v\downarrow c\uparrow) & 0 & 0 & H^{\mathrm{diag}}_{\downarrow\uparrow}+K^{c}_{\downarrow\uparrow} & 0 \\ (v\downarrow c\downarrow) & K^{x}_{\downarrow\uparrow} & 0 & 0 & H^{\mathrm{diag}}_{\downarrow\downarrow}+K^{x}_{\downarrow\downarrow}+K^{c}_{\downarrow\downarrow} \end{array}$$

n=n,k

$$\phi_{n\uparrow}(\mathbf{r}) \neq \phi_{n\downarrow}(\mathbf{r})$$
$$\epsilon_{n\uparrow} \neq \epsilon_{n\downarrow}$$

$$\Delta S_z = 0$$

*2*N MATRIX Cannot be further blocked …*

Spin-conserving excitons , bright

BSE & spin

(non collinear case -SOC)

$$H^{exc}_{(vc),(v'c')} = (\epsilon^{qp}_{c} - \epsilon^{qp}_{v})\delta_{c,c'}\delta_{v,v'}$$
$$+K^{x}_{(vc),(v'c')} + K^{c}_{(vc),(v'c')}$$

4*N X 4*N matrix

Matrix cannot be blocked
… mixing with spin-flip transitions

BSE & spin

(non collinear case - SOC)

$$K^{c}_{(vc),(v'c')} =$$

$$\int d^3r d^3r' \sum_{\sigma} \phi^*_{c\sigma}(r)\phi_{c'\sigma}(r) W(r-r') \sum_{\sigma'} \phi_{v\sigma'}(r')\phi^*_{v'\sigma'}(r')$$

BSE & spin

(non collinear case - SOC)

$$K^{c}_{(vc),(v'c')} =$$

$$\int d^3r d^3r' \boxed{\sum_{\sigma}} \phi^*_{c\sigma}(r)\phi_{c'\sigma}(r) W(r-r') \boxed{\sum_{\sigma'}} \phi_{v\sigma'}(r')\phi^*_{v'\sigma'}(r')$$

the Yambo team

BSE & spin

(non collinear case)

$$K^{x}_{(vc),(v'c')} =$$

$$\int d^3r d^3r' \sum_{\sigma} \phi^*_{c\sigma}(r)\phi_{v\sigma}(r)v(r-r') \sum_{\sigma'} \phi_{c'\sigma'}(r)\phi^*_{v'\sigma'}(r')$$

BSE solvers

$$\boxed{\epsilon_M \Leftrightarrow \bar{P} \Leftrightarrow (\hat{I}\omega - H^{exc})^{-1}_{(n_1 n_2)(n_3 n_4)}}$$

BSE solvers

$$\boxed{\epsilon_M \Leftrightarrow \bar{P} \Leftrightarrow \left(\hat{I}\omega - H^{exc}\right)^{-1}_{(n_1 n_2)(n_3 n_4)}}$$

Inversion

Lapack/scalapack
Libraries

Recursive approach
Lanczos/Haydock
Very efficient
good MPI scalability

Only spectrum

BSE solvers

$$\boxed{\epsilon_M \Leftrightarrow \bar{P} \Leftrightarrow (\hat{I}\omega - H^{exc})^{-1}_{(n_1n_2)(n_3n_4)}}$$

Diagonalization

$$\boxed{\sum_{\lambda,\lambda'} \frac{A^{n_1n_2}_{\lambda} S^{-1}_{\lambda,\lambda'} A^{*n_3n_4}_{\lambda'}}{\omega - E^{exc}_{\lambda}}}$$

with $S_{\lambda,\lambda'} = \sum_{n_1n_2,n_3n_4} A^{*n_1n_2}_{\lambda} A^{n_3n_4}_{\lambda'}$

- **Lapack/scalapack** libraries
  All Eigenvectors/eigenvalues

- **Slepc/Petsc** libraries (for large-scale sparse eigenvalue problems)
  Only a limited number eigev/vect

Inversion

Lapack/scalapack
Libraries

Recursive approach
Lanczos/Haydock
Very efficient
good MPI scalability

Only spectrum

BSE solvers: diagonalization

Considering the full excitonic hamiltonian:

$$\epsilon_M(\omega) = 1 - 4\pi \cdot lim_{q\to 0}\frac{1}{q^2}\sum_{\lambda,\lambda'}\sum_{n_1 n_2} < n_1|e^{-i\mathbf{q}\cdot\mathbf{r}}|n_2 > \frac{A_\lambda^{n_1 n_2}}{E_\lambda^{exc}-\omega-i\eta}\times$$

$$S^{-1}_{\lambda,\lambda'}\sum_{n_3 n_4} < n_4|e^{i\mathbf{q}\cdot\mathbf{r}'}|n_3 > A^{*n_3 n_4}_{\lambda'}(f_{n_4}-f_{n_3})$$

BSE solvers: diagonalization

Considering the full excitonic hamiltonian:

$$\epsilon_M(\omega) = 1 - 4\pi \cdot lim_{q\to 0}\frac{1}{q^2}\sum_{\lambda,\lambda'}\sum_{n_1 n_2} < n_1|e^{-i\mathbf{q}\cdot\mathbf{r}}|n_2 > \frac{A_\lambda^{n_1 n_2}}{E_\lambda^{exc}-\omega-i\eta}\times$$

$$S^{-1}_{\lambda,\lambda'}\sum_{n_3 n_4} < n_4|e^{i\mathbf{q}\cdot\mathbf{r}'}|n_3 > A_{\lambda'}^{*n_3 n_4}(f_{n_4}-f_{n_3})$$

Considering only the resonant excitonic hamiltonian:

$$\Im[\epsilon_M(\omega)] = lim_{q\to 0}\frac{4\pi}{q^2}\sum_{\lambda}|\sum_{vc} < c|e^{i\mathbf{q}\cdot\mathbf{r}}|v > A_\lambda^{vc}|^2\delta(E_\lambda^{exc}-\omega)$$

BSE solvers: diagonalization

Considering the full excitonic hamiltonian:

$$\epsilon_M(\omega) = 1 - 4\pi \cdot lim_{q\to 0}\frac{1}{q^2}\sum_{\lambda,\lambda'}\sum_{n_1 n_2} < n_1|e^{-i\mathbf{q}\cdot\mathbf{r}}|n_2 > \frac{A_\lambda^{n_1 n_2}}{E_\lambda^{exc} - \omega - i\eta}\times$$

$$S^{-1}_{\lambda,\lambda'}\sum_{n_3 n_4} < n_4|e^{i\mathbf{q}\cdot\mathbf{r}'}|n_3 > A_{\lambda'}^{*n_3 n_4}(f_{n_4} - f_{n_3})$$

Considering only the resonant excitonic hamiltonian:

$$\Im[\epsilon_M(\omega)] = 4\pi^2\sum_{\lambda}|\hat{D}_\lambda|^2\delta(E_\lambda^{exc} - \omega)$$

using

$$\mathcal{D}_\lambda = \sum_{vc} < c|\hat{e}\cdot\mathbf{r}|v > A_\lambda^{vc} =< \lambda|\hat{e}\cdot\mathbf{r}|0 >$$

BSE solvers: iterative inversion

$$\Im\left[\epsilon_M(\omega)\right] = 4\pi^2 \sum_{\lambda} |\hat{D}_\lambda|^2 \delta(E_\lambda^{exc} - \omega)$$

$$= 4\pi^2 lim_{q\to 0} \sum_{\lambda} | < \lambda|\hat{\mathbf{e}} \cdot \frac{e^{-i\mathbf{q}\cdot\mathbf{r}}}{q}|0 > |^2 \delta(E_\lambda^{exc} - \hbar\omega)$$

$$= 4\pi^2 lim_{q\to 0} \sum_{\lambda} < 0|\hat{\mathbf{e}} \cdot \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{q}|\lambda >< \lambda|\hat{\mathbf{e}} \cdot \frac{e^{-i\mathbf{q}\cdot\mathbf{r}}}{q}|0 > \delta(E_\lambda^{exc} - \hbar\omega)$$

$$\boxed{= \Im\left\{-4\pi\, lim_{q\to 0} < 0|\hat{\mathbf{e}} \cdot \frac{e^{-i\mathbf{q}\cdot\mathbf{r}}}{q} \frac{1}{\hbar\omega - H^{exc} + i\eta} \boxed{\hat{\mathbf{e}} \cdot \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{q}|0 >}\right\}}$$

The Haydock/Lanczos approach

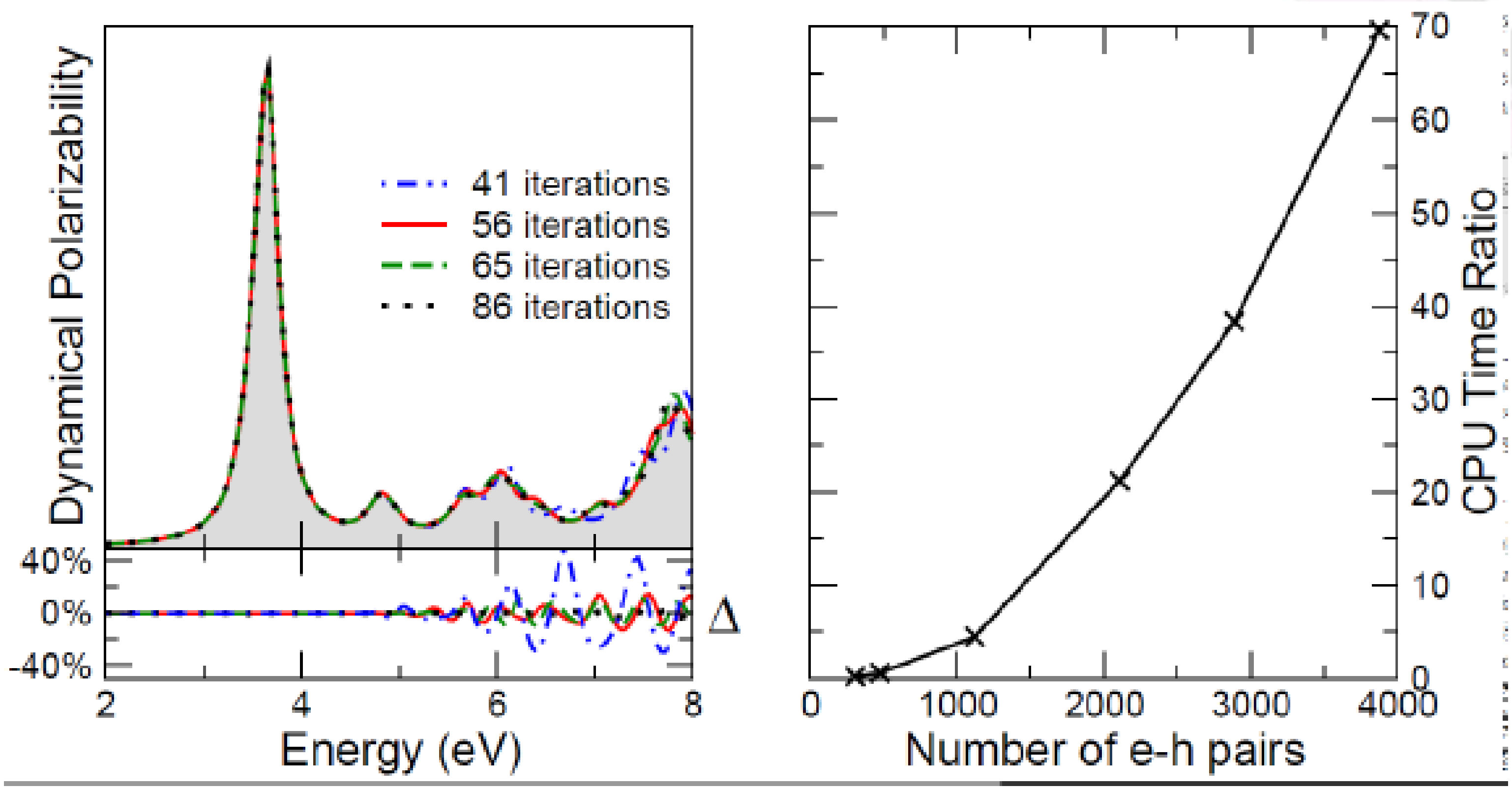
$$I(z) = \Im\left[< 0|\hat{O}^\dagger \frac{1}{(z-\hat{H}+i\eta)}\boxed{\hat{O}|0 >}\right] = \Im\left[< P|\frac{1}{(z-\hat{H}+i\eta)}|P >\right]$$

$$\boxed{|P\rangle} = |1\rangle \qquad a_i = \langle i|H|i\rangle \qquad b_i = |H|i\rangle - a_i|i\rangle - b_{i-1}|i-1\rangle|$$

$$|i+1\rangle = \frac{H|i\rangle - a_i|i\rangle - b_{i-1}|i-1\rangle}{b_i};$$

$$I(z) = \Im\left(\frac{1}{z - a_1 - \frac{b_1^2}{z-a_2-\frac{b_2^2}{z-a_3+\ldots}}}\right)$$

The Haydock/Lanczos approach



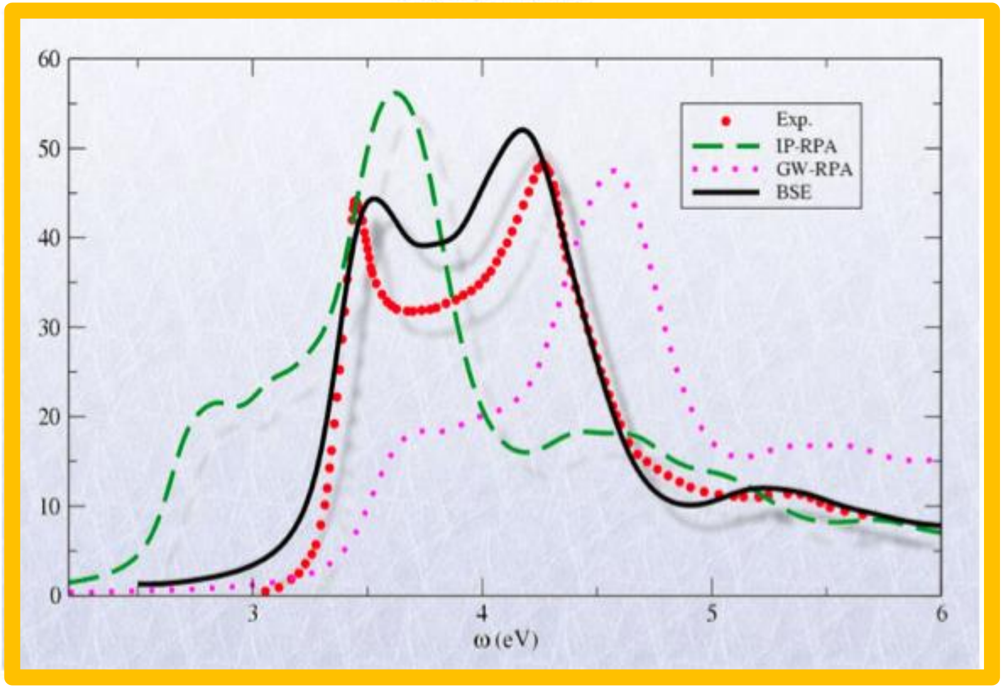
Number of iterations ~100-200 almost independent from matrix size - Easy to MPI parallelization

Method generalized also to non hermitian matrices

Gruning et al Nanoletters 6, 257 (2010)

SOME APPLICATIONS

Continuum & bound excitons


Bulk silicon

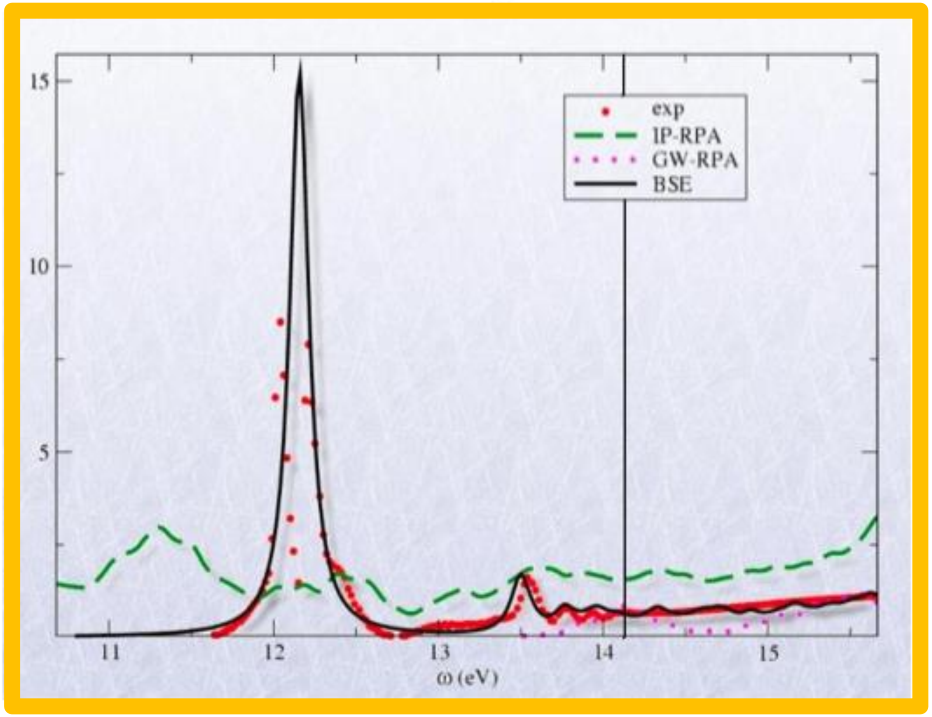
G. Onida, L. Reining, and A. Rubio, RMP **74** (2002).

covalent bond
small gap
Large dielectric screening

$$E_\lambda^{exc} \simeq E_c^{QP} - E_v^{QP}$$

weak bond
wide gap
Low dielectric screening
Large e-h attraction -W

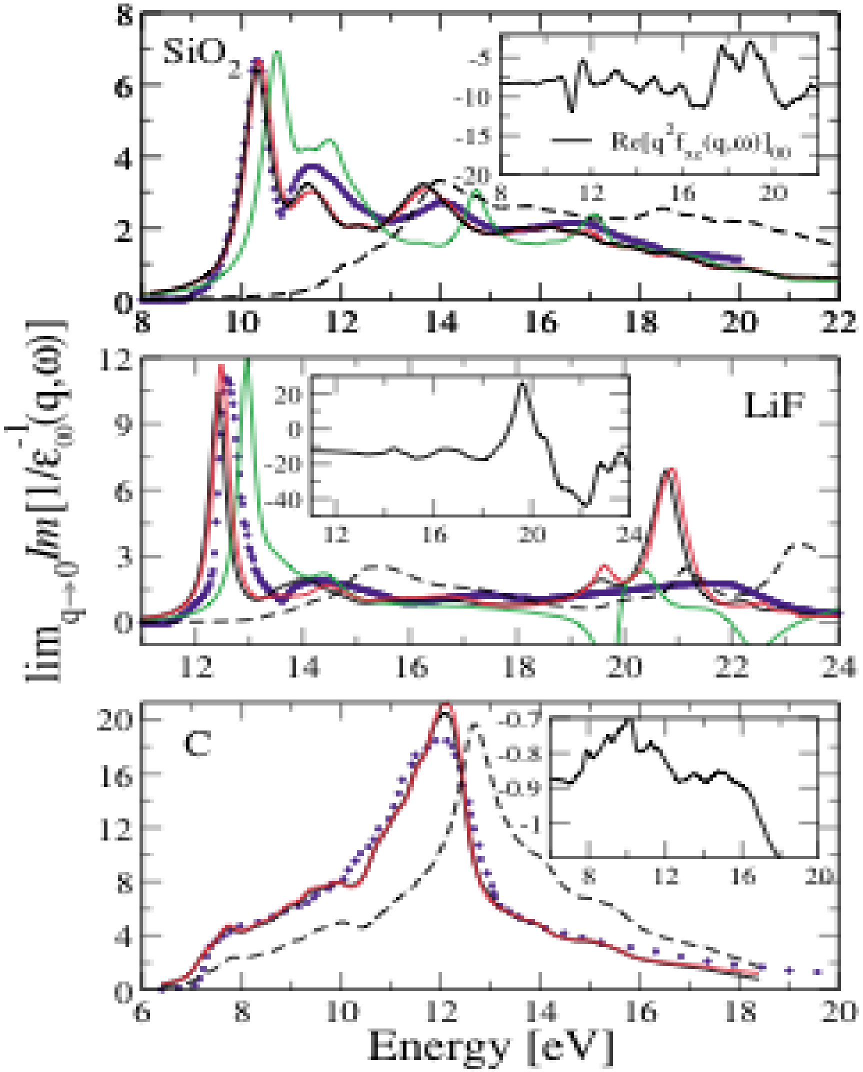
$$E_\lambda^{exc} << E_c^{QP} - E_v^{QP}$$


Solid argon

F. Sottile, M. Marsili, V. Olevano, and L. Reining, PRB **76** (2007).

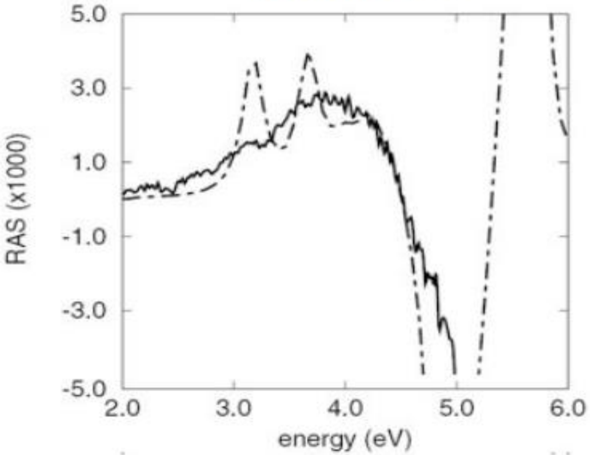
Bulks - surfaces – liquids

Bulk Materials



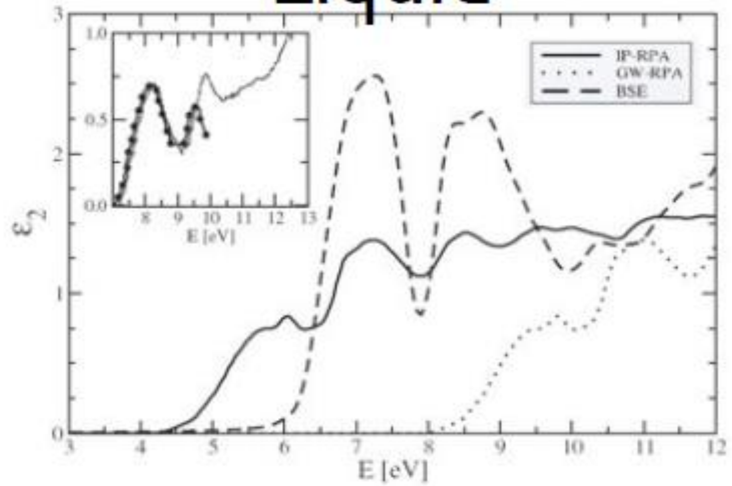
A. Marini et al. PRL 91 256402 (2003)

Surface



Diamond(100)(2x1)
M. Palummo, *et al.*, PRL **94** (2005).

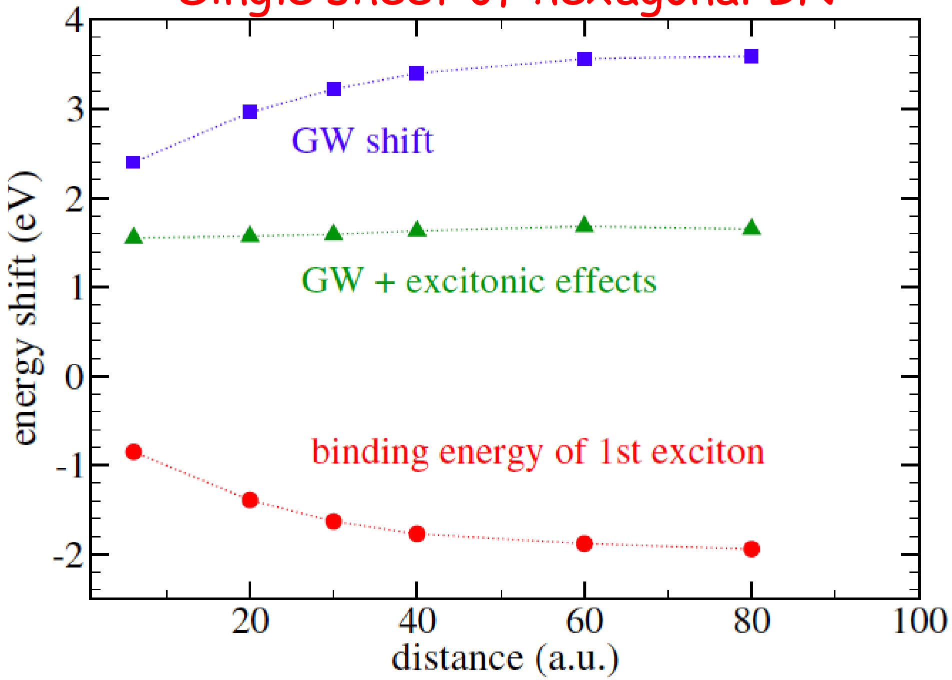
Liquid

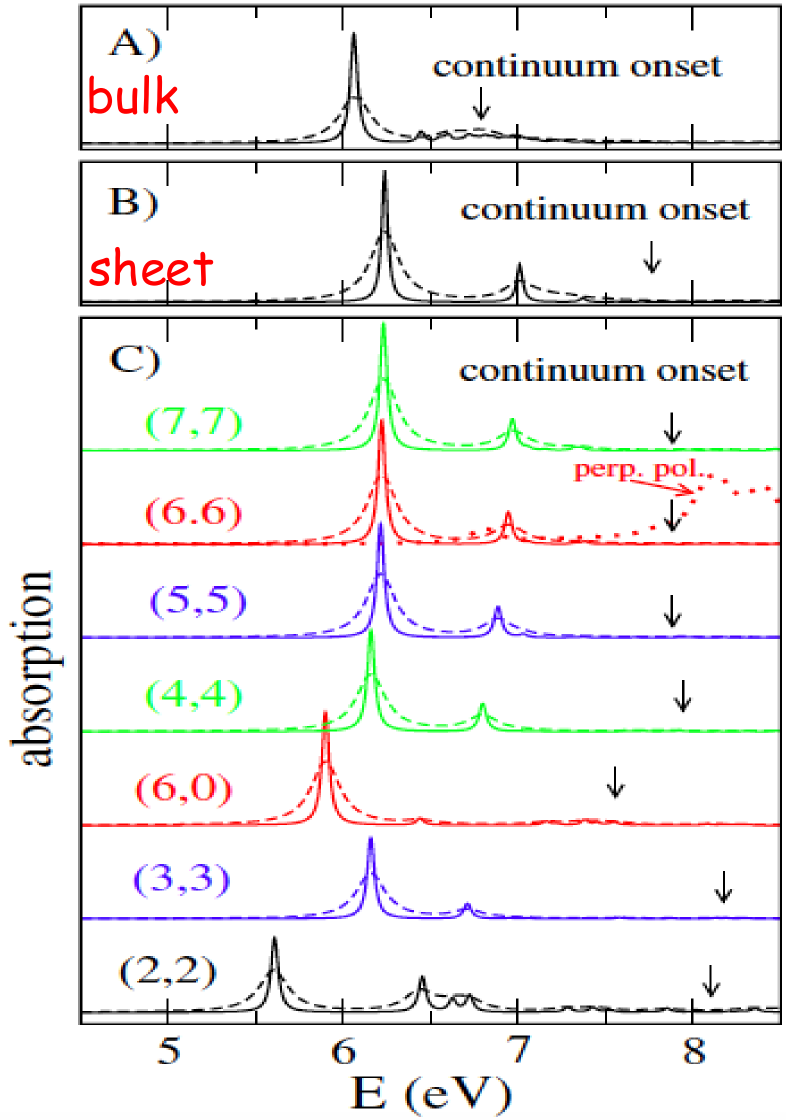


Liquid water
V. Garbuio, *et al.*, PRL **97** (2006).

1D-materials : BN nanotubes

Low-dimensionality & small screening
Large quasi-particle corrections
+ Strongly bound excitons


Single sheet of hexagonal BN


GW + Bethe Salpeter

Need to converge the vacuum size

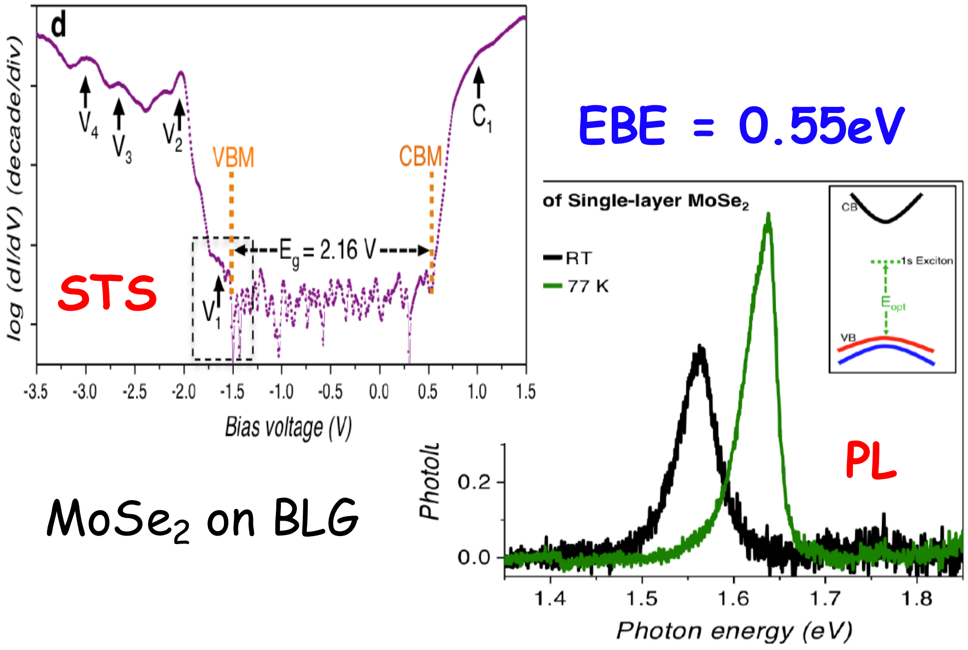
L. Wirtz, A. Marini, A. Rubio PRL 96, 126104 (2006)

2D-materials

- ✓ screening strongly reduced
- ✓ large quantum confinement

- ✓ Electronic gap >> optical gap
- ✓ Strongly bound excitons

EBE = 0.55eV



STS

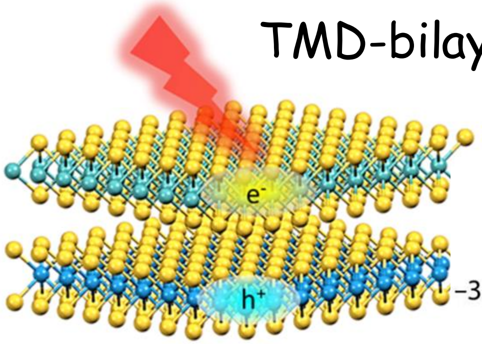
PL

MoSe$_2$ on BLG

Ugeda et al. Nature Mat 2014. (2014)

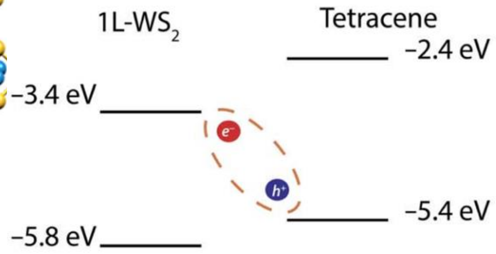
Interlayer/Charge-transfer excitons

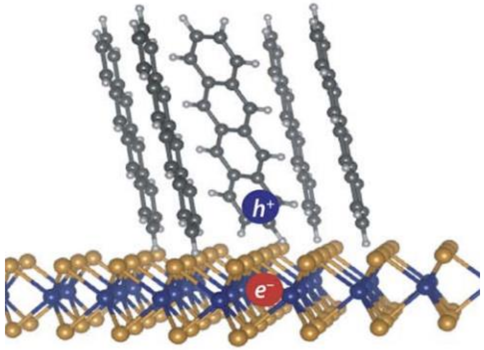
TMD-bilayer



X Hong et al
Nat. Nan 2014

Type II interface



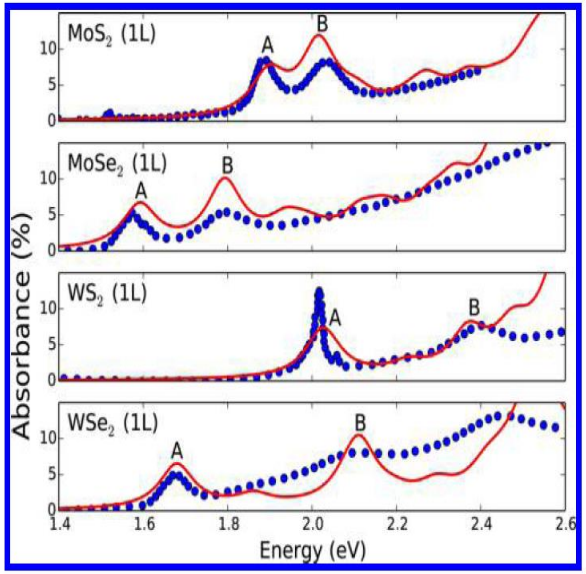


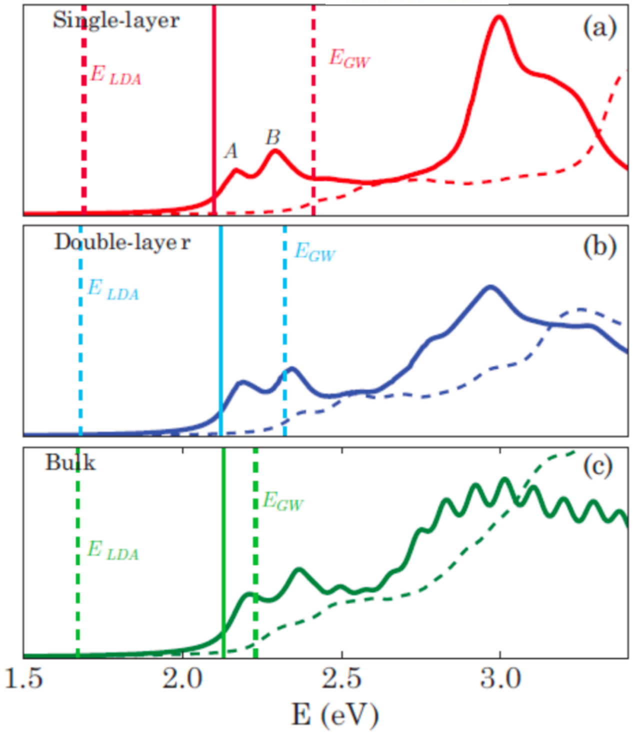
T.Zhou et al Science Advance 2018

WS2/tetracene

2D-materials

M.Palummo et al NL 2015

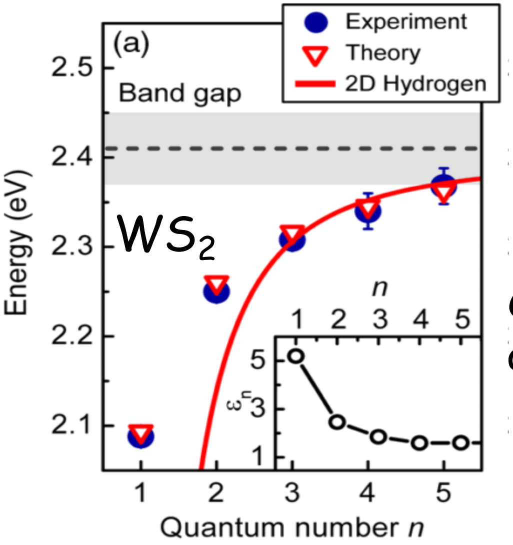




Molina-Sànchez et al. PRB (2013)

MoS$_2$

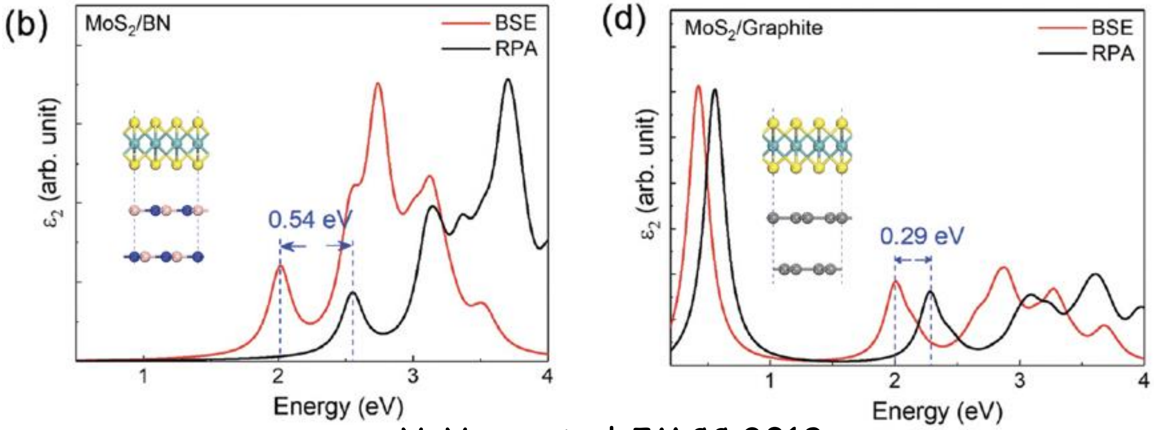
A.Molinas Sanchez et al. PRB2013



WS$_2$

Chernikov et al PRL2014

Optical versus electronic gap (role of



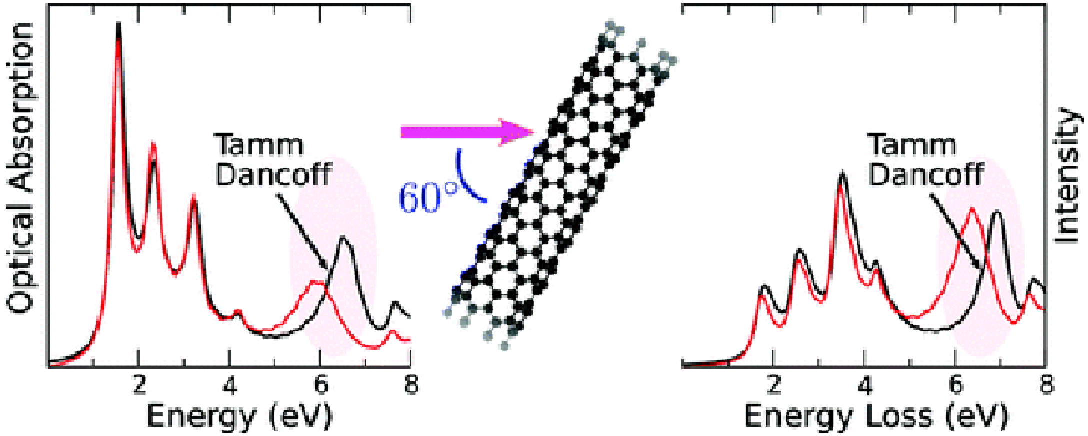
Y. Yang et al JMCC 2019

Beyond Tamm-Dancoff approximation

$$H = \left(\begin{array}{c|cc} & |eh\rangle & |he\rangle \\ \hline \langle eh| & R & C \\ \langle he| & -C^* & -R^* \end{array}\right)$$

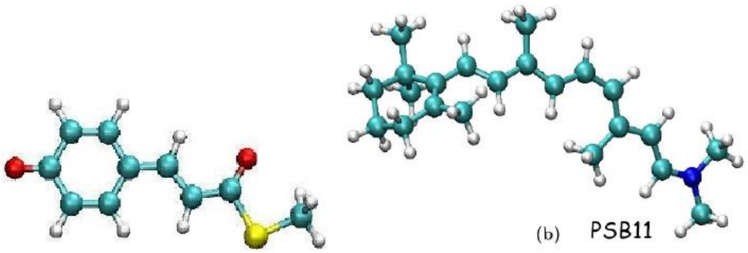
Mixed excitonic-plasmonic excitations in nanostructures

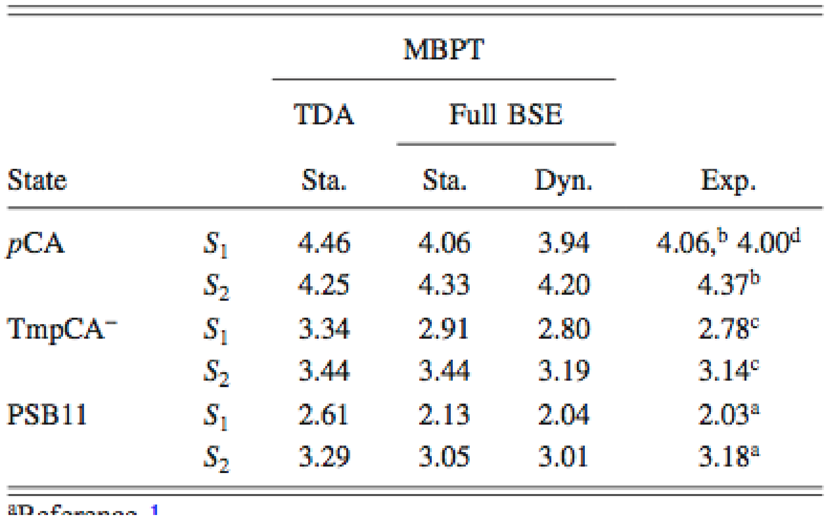
(M. Gruning et alNanoletters, **6**, 257(2010))



Excited states of biological chromophores

(Y. Ma et al J. Chem. Theory Comput., **6**, 257–265 (2010))



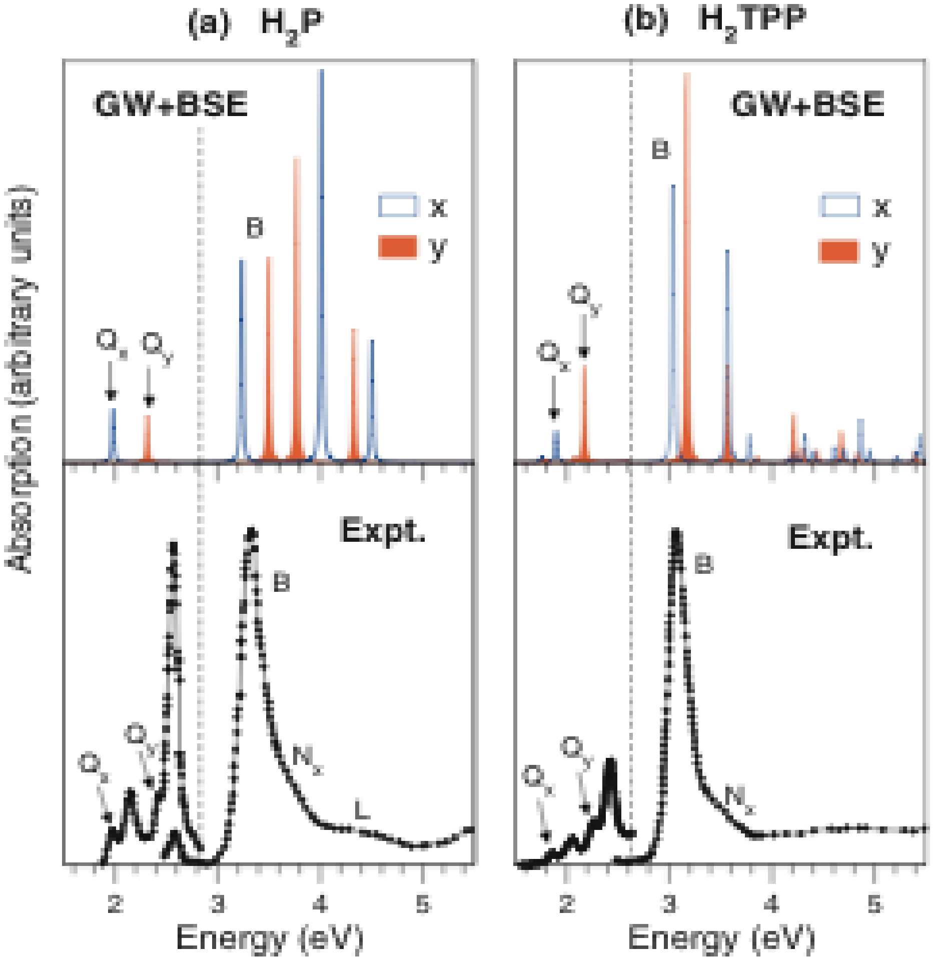


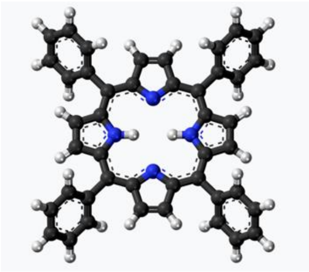
		MBPT			
		TDA	Full BSE		
State		Sta.	Sta.	Dyn.	Exp.
*p*CA	S_1	4.46	4.06	3.94	4.06,^{b} 4.00^d
	S_2	4.25	4.33	4.20	4.37^b
TmpCA$^-$	S_1	3.34	2.91	2.80	2.78^c
	S_2	3.44	3.44	3.19	3.14^c
PSB11	S_1	2.61	2.13	2.04	2.03^a
	S_2	3.29	3.05	3.01	3.18^a

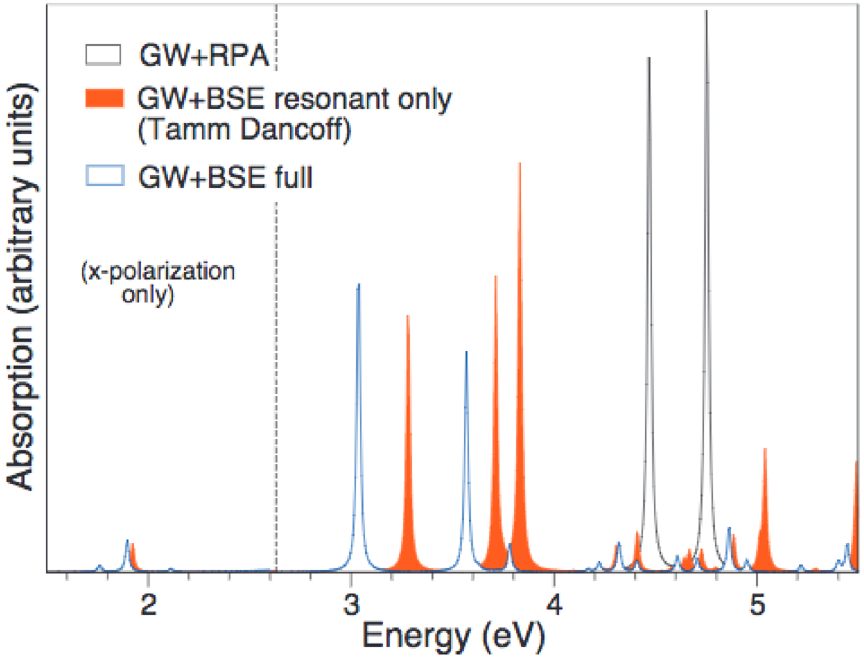
^{a}Reference 1

Beyond Tamm-Dancoff approximation

Free-base porphyrins molecules





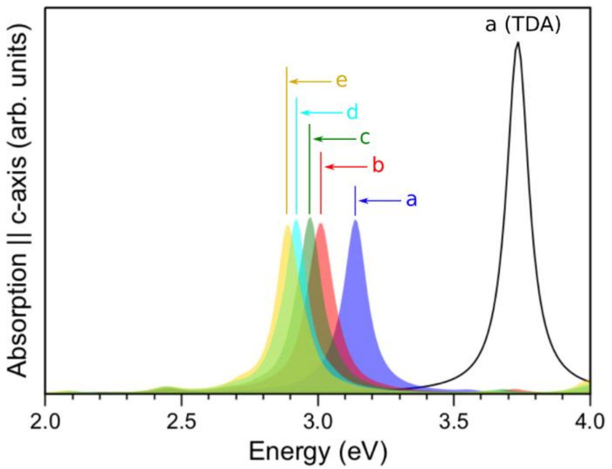


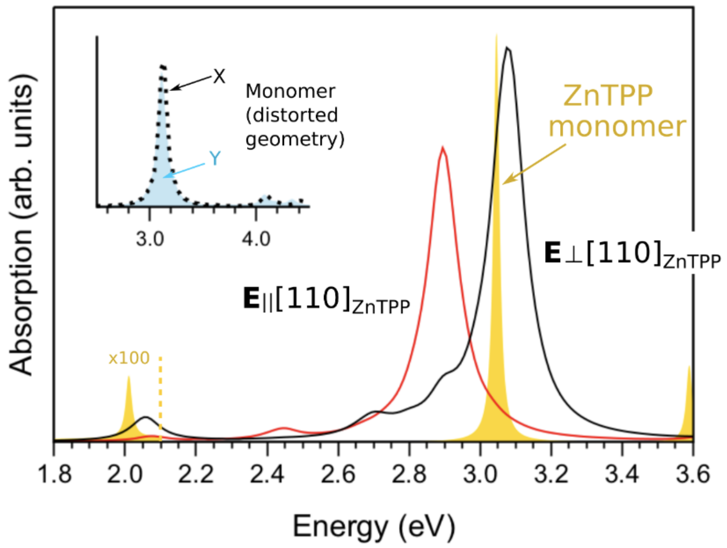
M. Palummo , C.Hogan et al.
JCP 131 84102 (2009)

Beyond Tamm-Dancoff approximation

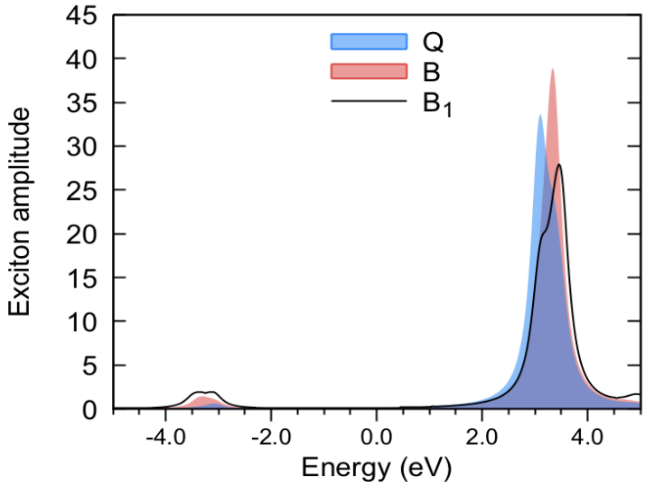
Zn-based porphyrine crystal

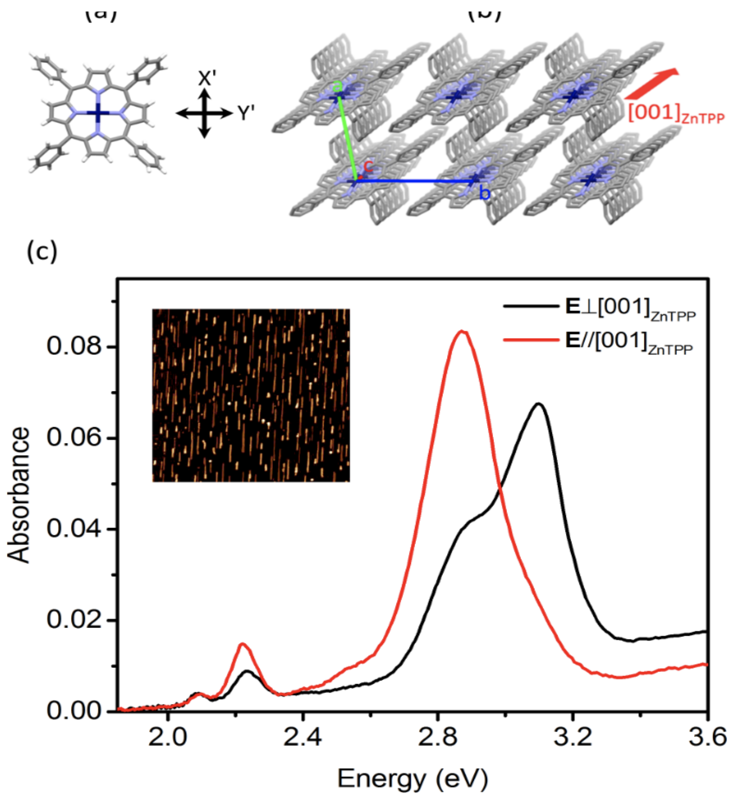
increasing single-particle transitions





BSE

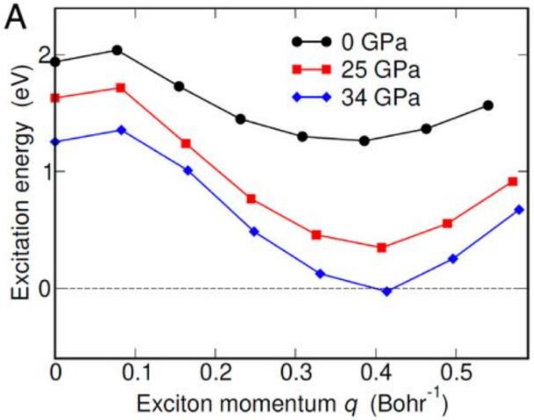




EXP

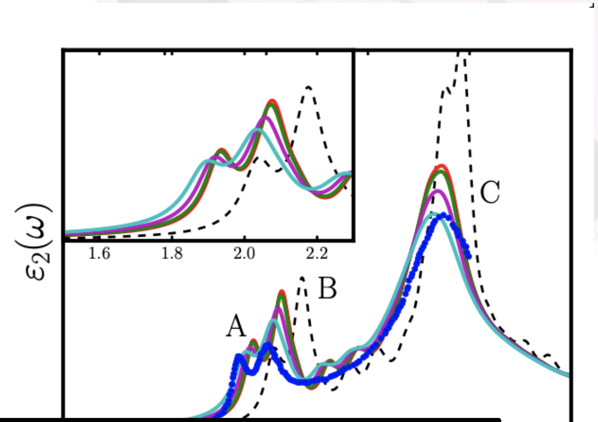
M. Palummo , et al
JPCL 2021

Finite-momentum BSE



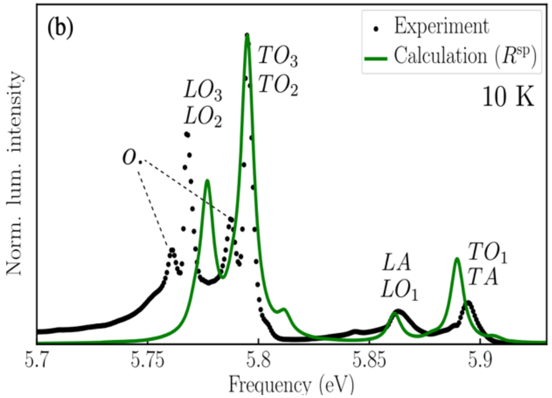
F.Fossard et al PRB 96 2017
S.Ataei et al PNAS 118,13 2021

Finite-temperature BSE



A.Marini PRL 101, 106405 (2008)
E Cannuccia, A Marini PRL 107 (25), 255501
A.Molinas-Sanchez PRB 93, 155435 2016

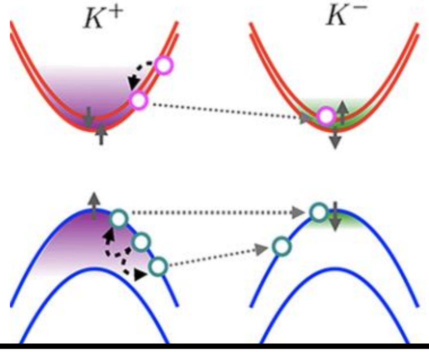
Phonon-assisted PL spectra

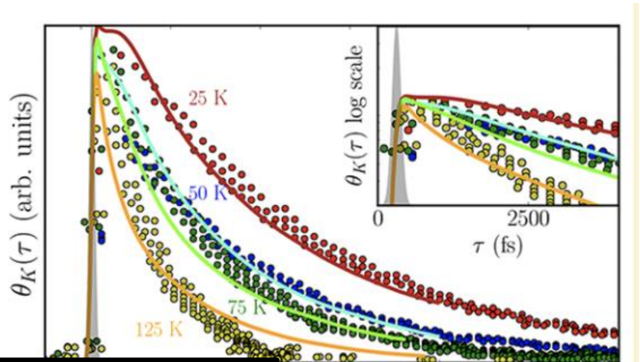


E.Cannuccia et al PRB2019
F.Paleari et al PRL2019
HY Chen et al PRL2020
Y.Chan et al NL2023

Real-time BSE

Ultrafast carrier dynamics/
transient absorption spectra/





C.Attaccalite et al PRB 84 2011
D.Sangalli et al PRB 93 2016
AM Sanchez et al Nano Letters 2017

References

- derivation of the equation (bound state of deuteron)
  - E. E. Salpeter and H. A. Bethe, PR **84**, 1232 (1951).
- BSE for exciton calculations
  - L.J. Sham and T.M. Rice, PR **144**, 708 (1966).
  - W. Hanke and L. J. Sham, PRL **43**, 387 (1979).
- first *ab initio* calculation
  - G. Onida, L. Reining, R. W. Godby, R. Del Sole, and W. Andreoni, PRL **75**, 818 (1995).
- first *ab initio* calculations in extended systems
  - S. Albrecht, L. Reining, R. Del Sole, and G. Onida, PRL **80**, 4510 (1998).
  - L. X. Benedict, E. L. Shirley, and R. B. Bohn, PRL **80**, 4514 (1998).
  - M. Rohlfing and S. G. Louie, PRL **81**, 2312 (1998).

Reviews:
Giovanni Onida, Lucia Reining, and Angel Rubio. Rev. Mod. Phys. **74**, 601 2002
Giovanni Bussi Phys. Scr. 2004 141, X.Blase at al. JPCL 2020, 11, 17, 7371–7382
SPIN M. Marsili et al PRB 2021 arXiv:2103.02266

Thank you for your attention

Look at www.yambo-code.eu

the Yambo team

1. Many-body perturbation theory calculations using the yambo code
   Journal of Physics: Condensed Matter 31, 325902 (2019)
2. Yambo: an ab initio tool for excited state calculations
   Comp. Phys. Comm. 144, 180 (2009)

Credits to Margherita Marsili & Myrta Gruning for some slides adapted

Bethe-Salpeter calculation step by step

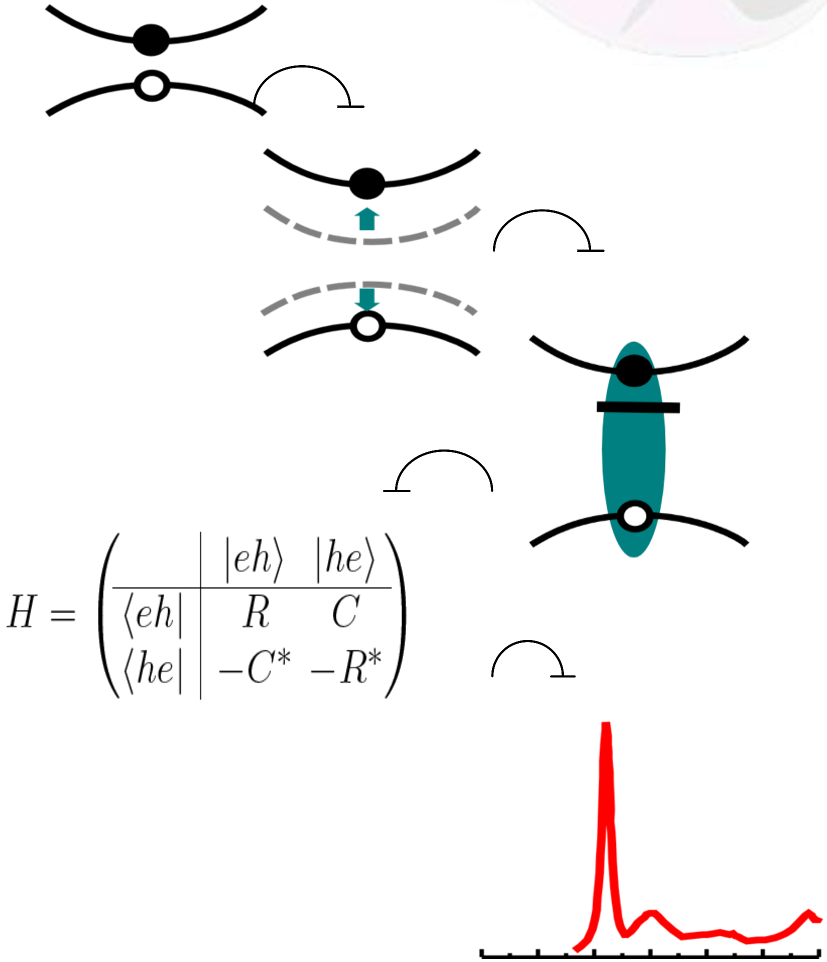
DFT calculation (here from pw.x)

Calculation of QP corrections

Calculation of the screening W

Calculation of the BS matrix

Solution of the BS equation



$$H = \left(\begin{array}{c|cc} & |eh\rangle & |he\rangle \\ \hline \langle eh| & R & C \\ \langle he| & -C^* & -R^* \end{array}\right)$$

BSE in the eh-space

$$H = \left(\begin{array}{c|cc} & |eh\rangle & |he\rangle \\ \hline \langle eh| & R & C \\ \langle he| & -C^{*} & -R^{*} \end{array}\right)$$

[BSK] runlevel: yambo -o b

main variables:

```
optics                    # [R OPT] Optics
bse                     # [R BSE] Bethe Salpeter Equation.
BSEmod= ”retarded"    # [BSE] resonant/retarded/coupling
BSKmod= ”SEX"        # [BSE] IP/Hartree/HF/ALDA/SEX
% BLongDir
 1.000000 | 0.000000 | 0.000000 |   # [BSS] [cc] Electric Field
%
% BSEBands
  1 |  8 |   # [BSK] Bands range   that enters in the BSE matrix
```

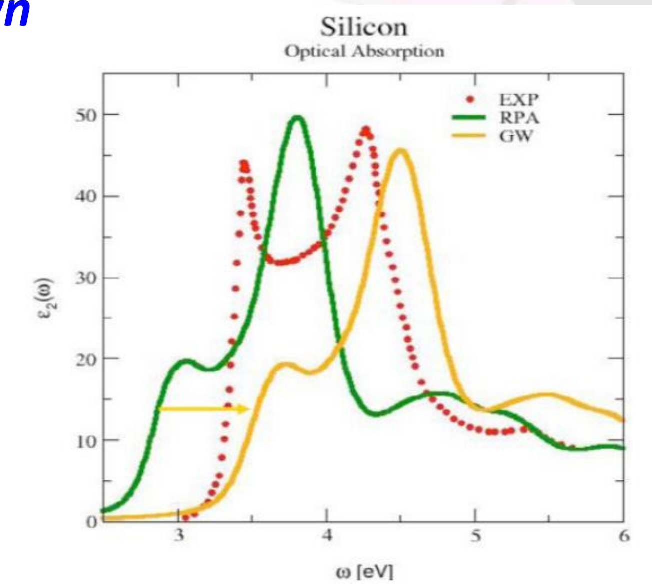
the Yambo team

The QP transitions energies (in the diagonal terms of H_{exc})

1. *You can compute the quasi-particle corrections as shown in the GW tutorial*

```
[Xd] runlevel: yambo -g n/s
```

and import them later when you compute the optical spectrum



```
KfnQPdb= "E< ndb.QP"  # [EXTQP BSK BSS] Database
```

2. *Or you can take it from the literature and insert the right parameters (scissor + streaching) in the input file later when you compute the spectrum*

```
% KfnQP_E
 0.80000 | 1.000000 | 1.000000 | #[EXTQP BSK BSS] E parameter (c/v) eV|adim|adim
%
```

Calculation of the static screening:

$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = 2\sum_{nn'}\int_{BZ}\frac{d\mathbf{k}}{(2\pi)^3}\rho^*_{n'n\mathbf{k}}(\mathbf{q},\mathbf{G})\,\rho_{n'n\mathbf{k}}(\mathbf{q},\mathbf{G'})\,f_{n\mathbf{k}-\mathbf{q}}(1-f_{n'\mathbf{k}})\times \left[\frac{1}{\omega+\varepsilon_{n\mathbf{k}-\mathbf{q}}-\varepsilon_{n'\mathbf{k}}+i0^+}-\frac{1}{\omega+\varepsilon_{n'\mathbf{k}}-\varepsilon_{n\mathbf{k}-\mathbf{q}}-i0^+}\right].$$

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

Random-Phase-Approximation

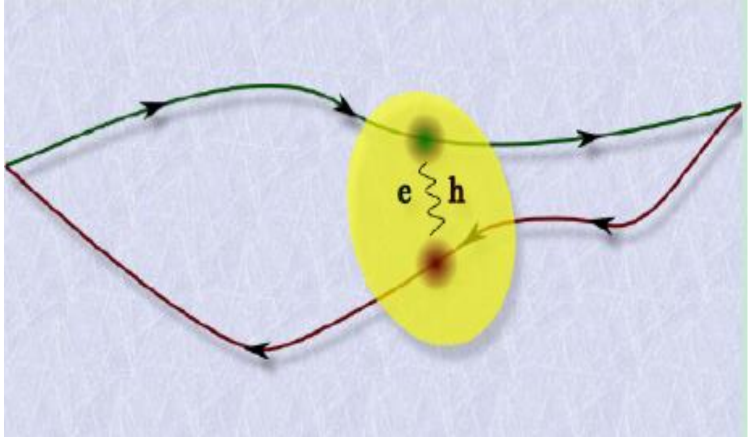
$$\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega) = \delta_{\mathbf{GG'}} + v(\mathbf{q}+\mathbf{G})\,\chi_{\mathbf{GG'}}(\mathbf{q},\omega).$$

Static : $\omega = 0$

[Xs] runlevel: yambo -b:

This is needed to construct the BSE kernel

```
em1s                      # [R Xs] Static Inverse Dielectric Matrix
Chimod= "hartree"   # [X] IP/Hartree/ALDA/LRC/BSfxc
% BndsRnXs
  1 |  8     |                 # [Xs] Polarization function bands
%
NGsBlkXs= 1     RL    # [Xs] Response block size
% LongDrXs
 1.000000 | 0.000000 | 0.000000 |       # [Xs] [cc] Electric Field
%
```



Or take the screening from the dynamical screening:

[Xd] runlevel: yambo -d / yambo -p p

Maybe you previously calculated the dynamical dielectric, so you have the ndb.em1d or the ndb.pp database, and you can use the static part reading them ...

Calculation of the BS matrix:

$$W_{\substack{nn'\mathbf{k}\\ ss'\mathbf{k}_1}} = \frac{1}{\Omega N_q}\sum_{\mathbf{G}\mathbf{G}'}\rho_{ns}\left(\mathbf{k},\mathbf{q}=\mathbf{k}-\mathbf{k}_1,\mathbf{G}\right)\rho^*_{n's'}\left(\mathbf{k}_1,\mathbf{q}=\mathbf{k}-\mathbf{k}_1,\mathbf{G}'\right)\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}v\left(\mathbf{q}+\mathbf{G}'\right),$$

$$\bar{V}_{\substack{nn'\mathbf{k}\\ ss'\mathbf{k}_1}} = \frac{1}{\Omega N_q}\sum_{\mathbf{G}\neq 0}\rho_{nn'}\left(\mathbf{k},\mathbf{q}=0,\mathbf{G}\right)\rho^*_{ss'}\left(\mathbf{k}_1,\mathbf{q}=0,\mathbf{G}\right)v\left(\mathbf{G}\right).$$

$$H_{\substack{nn'\mathbf{k}\\ mm'\mathbf{k}'}} = \left(\varepsilon_{n\mathbf{k}}-\varepsilon_{n'\mathbf{k}}\right)\delta_{nm}\delta_{n'm'}\delta_{\mathbf{k}\mathbf{k}'} + \left(f_{n'\mathbf{k}}-f_{n\mathbf{k}}\right)\left[2\bar{V}_{\substack{nn'\mathbf{k}\\ mm'\mathbf{k}'}} - W_{\substack{nn'\mathbf{k}\\ mm'\mathbf{k}'}}\right].$$

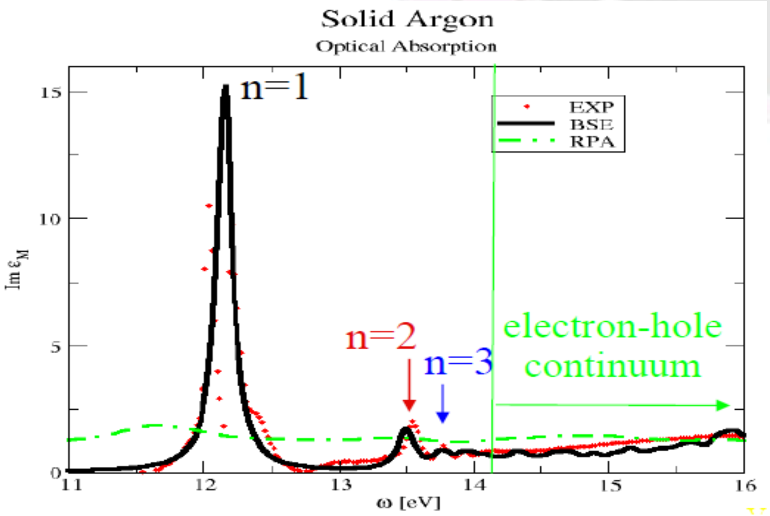
[BSK] runlevel: yambo -o b -k sex,

main variables:

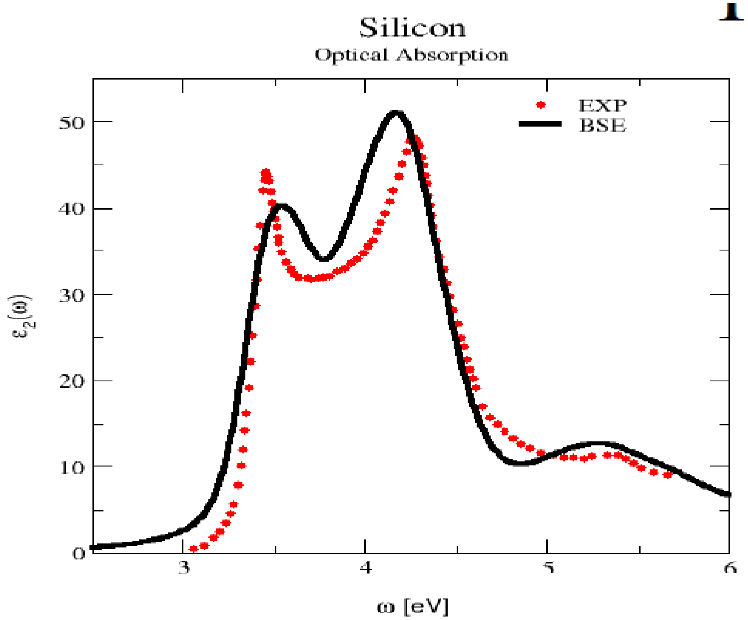
```
KfnQPdb= "none"          # [EXTQP BSK BSS] Database
BSEmod= ”retarded"        # [BSE] resonant/retarted/coupling
BSKmod= "SEX"           # [BSE] IP/Hartree/HF/ALDA/SEX
BSENGexx= 2085    RL  # [BSK] Exchange components
BSENGBlk= 500      RL   # [BSK] Screened interaction block size
#WehCpl           # [BSK] eh interaction included also in coupling
```

Solve the eh matrix for BSE: main variables

$$H = \left(\begin{array}{c|cc} & |eh\rangle & |he\rangle \\ \hline \langle eh| & R & C \\ \langle he| & -C^{*} & -R^{*} \end{array}\right)$$



[BSS] runlevel , yambo -y <opt>, main variables:



you can use the diagonalization solver or the Haydock solver

(or also the inversion solver)

Solve the eh matrix : diagonalization

Standard diagonalization:

$$H = \left(\begin{array}{c|cc} & |eh\rangle & |he\rangle \\ \hline \langle eh| & R & C \\ \langle he| & -C^* & -R^* \end{array}\right) \longrightarrow \begin{array}{l} \text{eigenstates } |\lambda\rangle \\ \text{eigenvalues } E_\lambda \\ \text{eigenvectors } A^\lambda_{n'n\mathbf{k}} = \langle n'n\mathbf{k}|\lambda\rangle \end{array}$$

[BSS] runlevel , yambo -y d

```
Bss # [R BSS] Bethe Salpeter Equation solver
BSSmod= "d"   # [BSS]
        (h)aydock/(d)iagonalization/(i)nversion`
```

```
% BEnRange
  0.00000 | 10.00000 | eV   # [BSS] Energy range
%
% BDmRange
  0.10000 |  0.10000 | eV  # [BSS] Damping range
%
BEnSteps= 100       # [BSS] Energy steps
```

Then the dielectric function:

$$\epsilon_M(\omega) \equiv 1 - \lim_{\mathbf{q}\to 0} \frac{8\pi}{|\mathbf{q}|^2 \Omega N_q} \sum_{nn'\mathbf{k}} \sum_{mm'\mathbf{k}'} \rho^*_{n'n\mathbf{k}}(\mathbf{q},\mathbf{G})\, \rho_{m'm\mathbf{k}'}(\mathbf{q},\mathbf{G}') \sum_\lambda \frac{A^\lambda_{n'n\mathbf{k}} \left(A^\lambda_{m'm\mathbf{k}'}\right)^*}{\omega - E_\lambda},$$

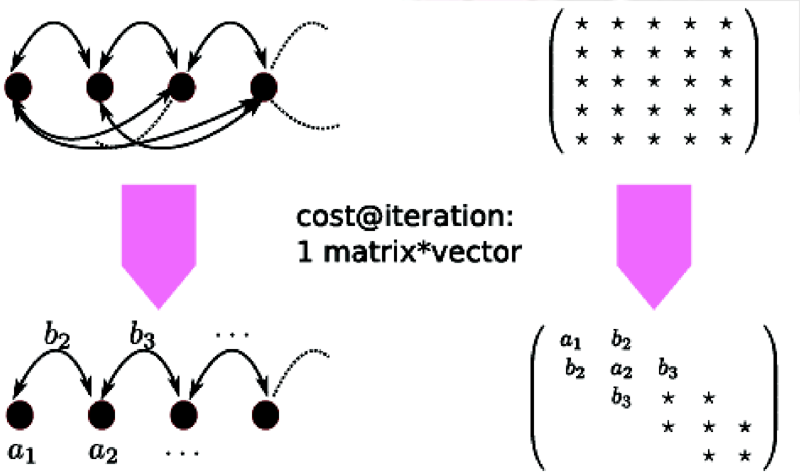
Solve the eh matrix: Lanczos-Haydock method

Lanczos-Haydock method:

[BSS] runlevel , yambo -y h

```
bss                # [R BSS] Bethe Salpeter Equation solver
BSSmod= "h"    # [BSS]
(h)aydock/(d)iagonalization/(i)nversion`
BSHayTrs= -0.02000      # [BSS] [o/o] Haydock treshold.
Strict(>0)/Average(<0)


 % BEnRange
   0.00000 | 10.00000 | eV    # [BSS] Energy range
 %
 % BDmRange
   0.10000 |  0.10000 | eV    # [BSS] Damping range
 %
 BEnSteps= 100              # [BSS] Energy steps
```



cost@iteration:
1 matrix*vector

This allows to rewrite
the dielectric function as:

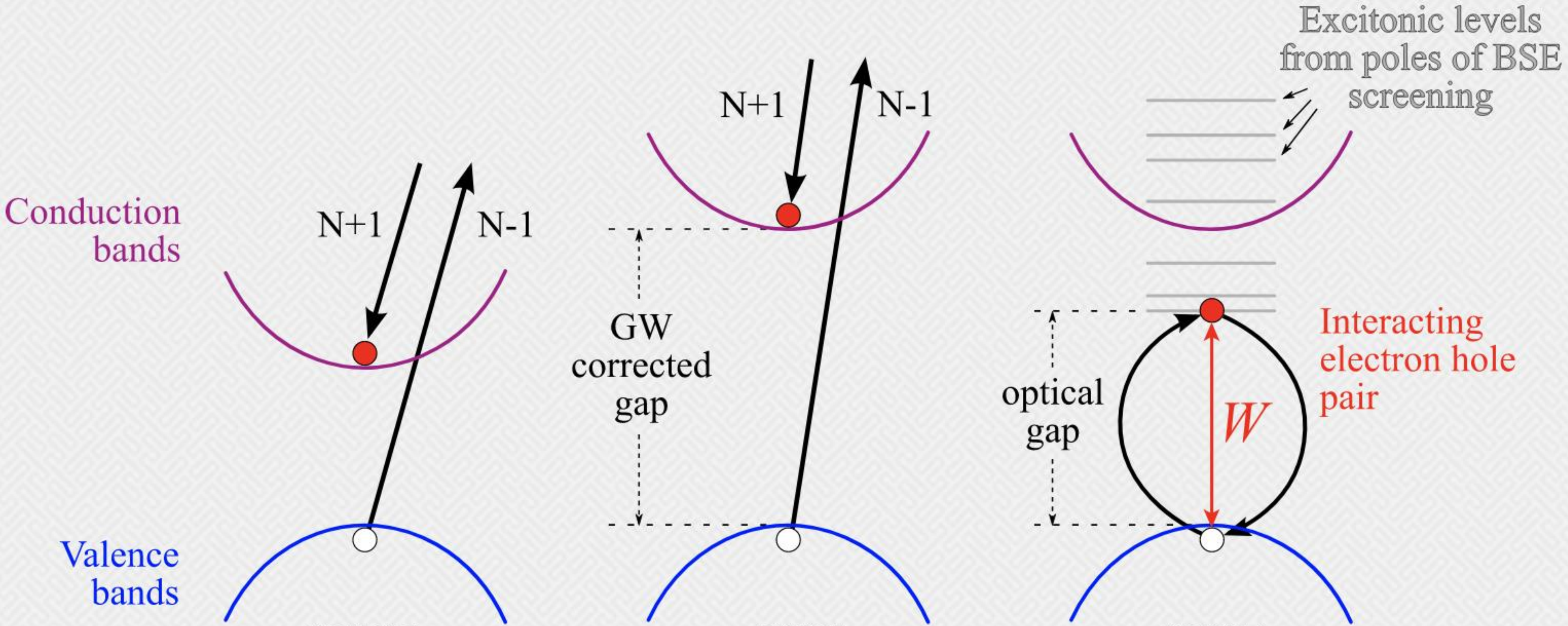
$$\epsilon(\omega) \rightarrow \langle P|(\omega - H)^{-1}|P\rangle = \cfrac{1}{(\omega - a_1) - \cfrac{b_2^2}{(\omega - a_2) - \cfrac{b_3^2}{\dots}}}$$

$$|P\rangle = \lim_{\mathbf{q}\to 0} \frac{1}{|\mathbf{q}|} |vc\mathbf{k}\rangle \langle v\mathbf{k}-\mathbf{q}|e^{-i\mathbf{q}\cdot\mathbf{r}}|c\mathbf{k}\rangle$$

Thank you again …for your attention

the Yambo team

1. Many-body perturbation theory calculations using the yambo code
   Journal of Physics: Condensed Matter 31, 325902 (2019)
2. Yambo: an ab initio tool for excited state calculations
   Comp. Phys. Comm. 144, 180 (2009)



DFT

Neutral excitations as a combination of single.

- ✗ **Wrong band structure**
- ✗ **Noninteracting electron-hole pair**

GW

Neutral excitations as a combination of single.

- ✓ **GW corrected band structure**
- ✗ **Noninteracting electron-hole pair**

BSE

Real two-body propagator and many-body problem.

- ✓ **GW corrected band structure**
- ✓ **Interacting electron-hole pair**

The response functions jungle: a short summary

From linear response

$$\epsilon^{-1} = 1 + v\chi$$

$$\boxed{\chi = \frac{\delta\rho}{\delta V_{ext}}}$$

irreducible

$$\chi = \tilde{\chi} + \tilde{\chi} v \chi$$

$$\bar{\chi} = \tilde{\chi} + \tilde{\chi} \bar{v} \bar{\chi}$$

reducible

$$\boxed{\begin{aligned} \epsilon_M &= (<< 1 + v\chi >>)^{-1} \\ \epsilon_M &= << 1 - v\bar{\chi} >> \end{aligned}}$$

$$\Re\left[\chi(\omega)\right] = \Re\left[\chi(-\omega)\right]$$

$$\Im\left[\chi(\omega)\right] = -\Im\left[\chi(-\omega)\right]$$

From MBPT

$$\epsilon = 1 - v\tilde{P}$$

irreducible
from Hedin eq.

$$P = \tilde{P} + \tilde{P} v P$$

$$\bar{P} = \tilde{P} + \tilde{P} \bar{v} \bar{P}$$

reducible

$$\boxed{\begin{aligned} \epsilon_M &= (<< 1 + vP >>)^{-1} \\ \epsilon_M &= << 1 - v\bar{P} >> \end{aligned}}$$

$$P(\omega) = P(-\omega)$$

the Yambo team

$$\Re\left\{\chi(\omega)\right\} = \Re\left\{P(\omega)\right\}$$

$$\Im\left\{\chi(\omega)\right\} = sign(\omega)\Im\left\{P(\omega)\right\}$$

Mathematical derivation of BSE in transition space

$$L^0(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},\mathbf{r_4};\omega) = \sum_{ij}(f_j - f_i)\frac{\phi_j(\mathbf{r_1})\phi_i^*(\mathbf{r_2})\phi_i(\mathbf{r_3})\phi_j^*(\mathbf{r_4})}{\omega - (E_i - E_j)}$$

The free e-h propagator becomes

$$L^0_{(n_1 n_2)(n_3 n_4)} = i\frac{f_{n1} - f_{n2}}{\omega - (E_{n2} - E_{n1})}\delta_{n_1 n_3}\delta_{n_2 n_4}$$

Using a more compact notation: $(n_1 n_2) \rightarrow t$

$$L^0_{tt'} = i\frac{f_t}{\omega - \Delta E_t}\delta_{tt'}$$

L_0 is diagonal in t-space

Effective 2-particle Hamiltonian

We rewrite the BSE in transition space as:

$$\bar{L}_{tt'} = L^{0}_{tt'} + iL^{0}_{tt''}\bar{\Xi}_{t''t'''}\bar{L}_{t'''t'}$$

$$(n_1 n_2) \to t$$

We will show that this equivalent to

$$\bar{\chi}_{tt'} = -i\bar{L}_{tt'} = [\hat{I}\omega - H^{exc}]^{-1}_{tt'} f_{t'}$$

where H^{exc} is the two-particle excitonic Hamiltonian

$$H^{exc}_{tt'} = \Delta E_{t}\ \delta_{tt'} + f_t \Xi_{tt'}$$

Effective 2-particle Hamiltonian

$$\bar{L}_{tt'} = L^0_{tt'} + iL^0_{tt''}\bar{\Xi}_{t''t'''}\bar{L}_{t'''t'}$$

is equivalent to

$$\bar{\chi}_{tt'} = -i\bar{L}_{tt'} = [\hat{I}\omega - H^{exc}]^{-1}_{tt'} f_{t'}$$

PROOF:

$$\bar{L}_{tt'} = (1 - iL^0\Xi)^{-1}_{tt''} L^0_{t''t'} = (L^{0\,-1} - i\Xi)^{-1}_{tt'}$$

Effective 2-particle Hamiltonian

$$\bar{L}_{tt'} = L^0_{tt'} + iL^0_{tt''}\bar{\Xi}_{t''t'''}\bar{L}_{t'''t'}$$

is equivalent to

$$\bar{\chi}_{tt'} = -i\bar{L}_{tt'} = [\hat{I}\omega - H^{exc}]^{-1}_{tt'} f_{t'}$$

PROOF:

$$\bar{L}_{tt'} = (1 - iL^0\Xi)^{-1}_{tt''} L^0_{t''t'} = (L^{0\,-1} - i\Xi)^{-1}_{tt'}$$

$$(L^{0\,-1} - i\Xi)_{tt'} = -i\tfrac{\omega - \Delta E_t}{f_t}\delta_{tt'} + i\Xi_{tt'} =$$

$$= \tfrac{i}{f_t}[-\omega\delta_{tt'} + \Delta E_t\delta_{tt'} + f_t\Xi_{tt'}]$$

Effective 2-particle Hamiltonian

$$\bar{L}_{tt'} = L^{0}_{tt'} + iL^{0}_{tt''}\bar{\Xi}_{t''t'''}\bar{L}_{t'''t'}$$

is equivalent to

$$\bar{\chi}_{tt'} = -i\bar{L}_{tt'} = [\hat{I}\omega - H^{exc}]^{-1}_{tt'} f_{t'}$$

PROOF:

$$\bar{L}_{tt'} = (L^{0\,-1} - i\Xi)^{-1}_{tt'}$$

$$(L^{0\,-1} - i\Xi)_{tt'} = \frac{i}{f_t}[-\omega\delta_{tt'} + \underbrace{\Delta E_t\delta_{tt'} + f_t\Xi_{tt'}}_{H^{exc}}]$$