

# Introduction to the Bethe-Salpeter equation for excitons

Matteo Gatti

*European Theoretical Spectroscopy Facility (ETSF)*  
*LSI - Ecole Polytechnique & Synchrotron SOLEIL - France*  
[matteo.gatti@polytechnique.fr](mailto:matteo.gatti@polytechnique.fr) - <http://etsf.polytechnique.fr>

ISTPC 2022



# Acknowledgements



Palaiseau theoretical spectroscopy group



Pierluigi Cudazzo Jaakko Koskelo

# References



G. Strinati

Rivista del Nuovo Cimento **11**, (12)1 (1988).



M. Rohlfing and S. G. Louie

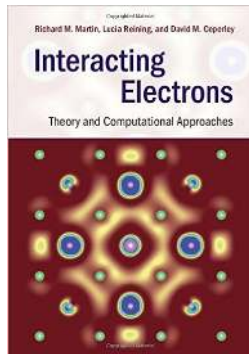
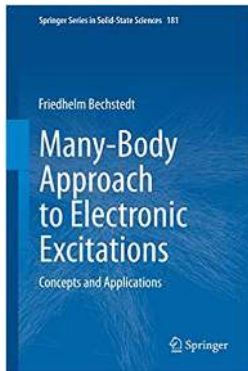
Phys. Rev. B **62**, 4927 (2000).



G. Onida, L. Reining, and A. Rubio

Rev. Mod. Phys. **74**, 601 (2002).

# Books



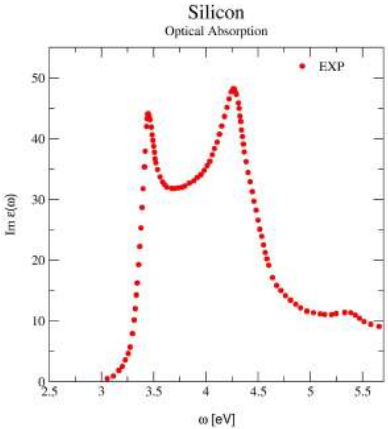
# Outline

- 1 Motivations
- 2 The Bethe-Salpeter equation: basic theory and approximations
- 3 Solution of the Bethe-Salpeter equation in practice
- 4 Prototypical results: success and limitations
- 5 Wannier, Frenkel and charge transfer excitons
- 6 Connection with TDDFT

# Outline

- 1 Motivations
- 2 The Bethe-Salpeter equation: basic theory and approximations
- 3 Solution of the Bethe-Salpeter equation in practice
- 4 Prototypical results: success and limitations
- 5 Wannier, Frenkel and charge transfer excitons
- 6 Connection with TDDFT

# Motivation



Exp. at 30 K from: P. Lautenschlager *et al.*, Phys. Rev. B **36**, 4821 (1987).

**Theoretical spectroscopy**

- Calculate and reproduce
- Understand and explain
- Predict

$\alpha(\omega) \propto \text{Im}\epsilon(\mathbf{q} \rightarrow 0, \omega)$  (extended systems) absorption coefficient  
 $\sigma(\omega) \propto \text{Im}\epsilon(\mathbf{q} \rightarrow 0, \omega)$  (finite systems) photoabsorption cross section

## Theoretical Spectroscopy

- Which kind of spectra?
- Which kind of tools?

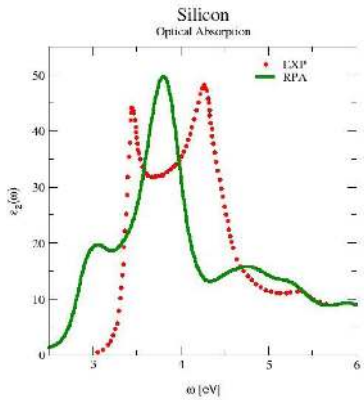
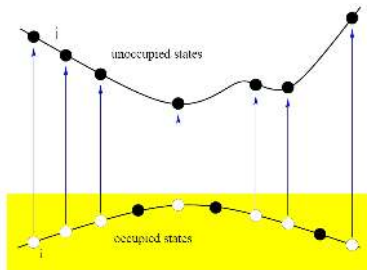




# Independent particles: Kohn-Sham

Independent transitions:

$$\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle \varphi_j | \mathbf{e} \cdot \mathbf{v} | \varphi_i \rangle|^2 \delta(\epsilon_j - \epsilon_i - \omega)$$



What is wrong?

What is missing?

# GW corrections

## Standard perturbative $G_0W_0$

$$H_0(\mathbf{r})\varphi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r})$$

$$H_0(\mathbf{r})\phi_i(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \omega = E_i) \phi_i(\mathbf{r}') = E_i \phi_i(\mathbf{r})$$

First-order perturbative corrections with  $\Sigma = iGW$ :

$$E_i - \epsilon_i = \langle \varphi_i | \Sigma - V_{xc} | \varphi_i \rangle$$

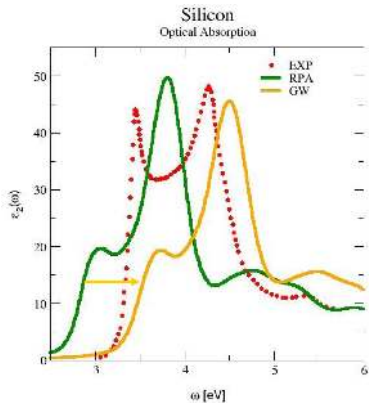
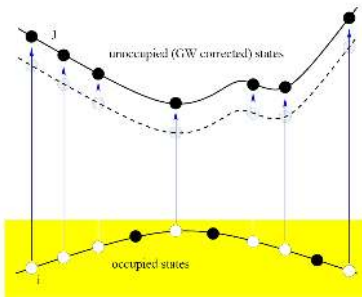
Hybersten and Louie, PRB **34** (1986);

Godby, Schlüter and Sham, PRB **37** (1988)

# Independent (quasi)particles: GW

Independent transitions:

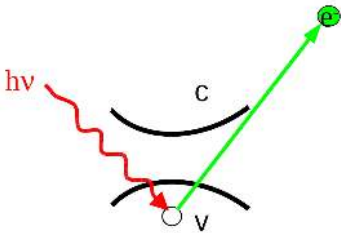
$$\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle \varphi_j | \mathbf{e} \cdot \mathbf{v} | \varphi_i \rangle|^2 \delta(E_j - E_i - \omega)$$



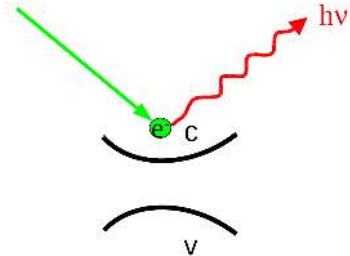
What is wrong?  
What is missing?

# GW bandstructure: photoemission

Direct Photoemission

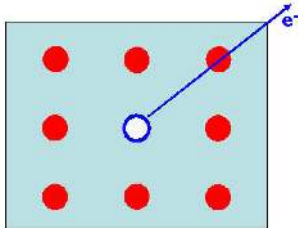
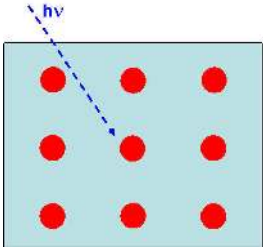


Inverse Photoemission

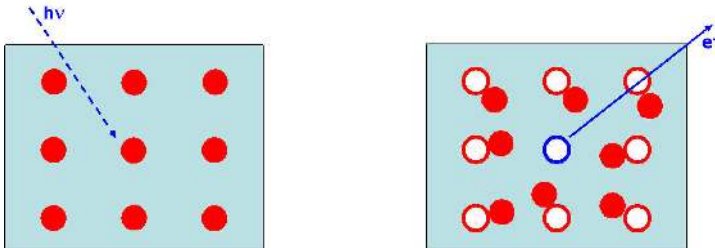


One-particle excitations  $\rightarrow$  poles of one-particle Green's function  $G$

# GW bandstructure: photoemission



# GW bandstructure: photoemission



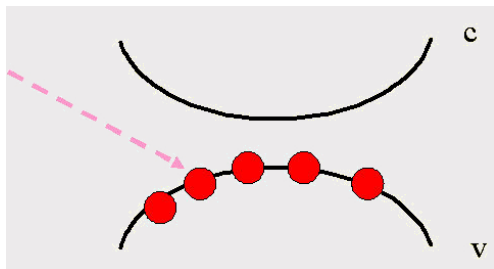
additional charge → reaction: polarization, screening

## GW approximation

- 1 polarization made of noninteracting electron-hole pairs (RPA)
- 2 classical (Hartree) interaction between additional charge and polarization charge



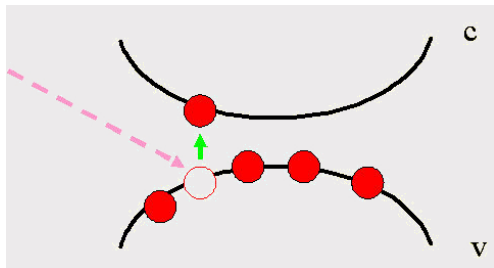
# Absorption



Two-particle excitations  $\rightarrow$  poles of two-particle Green's function

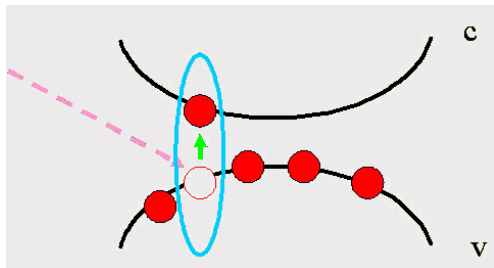
Excitonic effects = electron - hole interaction

# Absorption



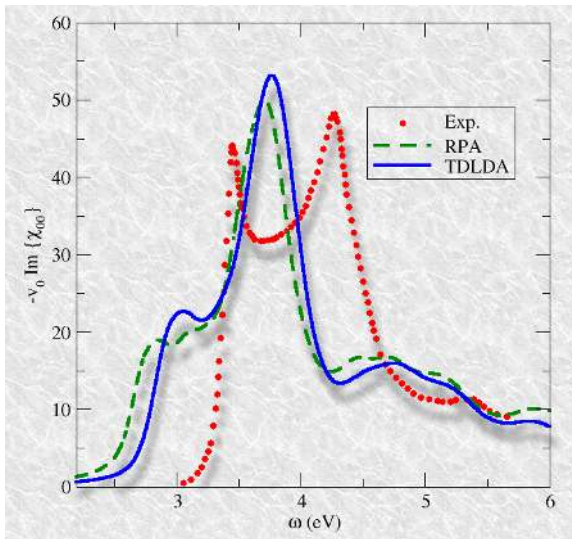
Two-particle excitations  $\rightarrow$  poles of two-particle Green's function  
Excitonic effects = electron - hole interaction

# Absorption



Two-particle excitations  $\rightarrow$  poles of two-particle Green's function  
Excitonic effects = electron - hole interaction

# Why do we have to study more than TDDFT?



Bulk silicon: absorption

# TDDFT vs. MBPT: different worlds, same physics

## TDDFT

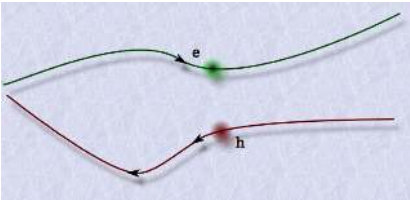
- based on the density: a many-body theory of a collective variable
- moves density around
- response function  $\chi$ : neutral excitations
- is efficient (simple)

## MBPT

- based on Green's functions
- moves (quasi)particles around
- one-particle  $G$ : electron addition and removal - GW  
two-particle  $L$ : electron-hole excitation - BSE
- is intuitive (easy)

# Two-particle correlation function $L$

$$L_0(1234) = -iG(13)G(42)$$

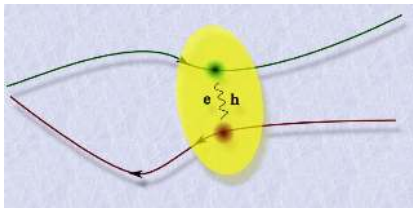


Independent particles

Notation: index 1 stands for space,time (and spin)

# Two-particle correlation function $L$

$$L(1234)$$



Interacting particles (excitonic effects)

Notation: index 1 stands for space,time (and spin)

# Outline

- 1 Motivations
- 2 The Bethe-Salpeter equation: basic theory and approximations**
- 3 Solution of the Bethe-Salpeter equation in practice
- 4 Prototypical results: success and limitations
- 5 Wannier, Frenkel and charge transfer excitons
- 6 Connection with TDDFT



# TDDFT vs. MBPT

## TDDFT

- Key variable: density  $\rho(1)$

## MBPT

- Key variable: Green's function  $G(12)$



# TDDFT vs. MBPT

## TDDFT

- Key variable: density  $\rho(1)$
- Linear response:

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

- Dyson equation:

$$\chi(12) = \chi^0(12) + \int d34 \chi^0(13) [v(34) + f_{xc}(34)] \chi(42)$$

with  $f_{xc}(34) = \delta V_{xc}(3)/\delta\rho(4)$

## MBPT

- Key variable: Green's function  $G(12)$
- Linear response:

$$L(1234) = -i \frac{\delta G(12)}{\delta V_{ext}(34)}$$

- Dyson equation = Bethe-Salpeter equation:

$$L(1234) = L_0(1234) + \int d5678 L_0(1256) \left[ v(57) \delta(56) \delta(78) + i \frac{\delta \Sigma(56)}{\delta G(78)} \right] L(7834)$$

# TDDFT - MBPT connection

The connection

$$-iG(11^+) = \rho(1) \quad \Rightarrow \quad L(11^+22^+) = \chi(12)$$

Notation:  $1^+$  means  $r_1 t_1 + \eta$  with  $\eta \rightarrow 0$

# Reminder: Dyson equation

## Dyson equation

$$G(12) = G_H(12) + \int d34 G_H(13) [\Sigma(34) + V_{ext}(34)] G(42)$$

where  $G_H$  is the Hartree Green's function:

$$G_H(\omega) = (\omega - H_0)^{-1} \Rightarrow G_H^{-1}(\omega) = (\omega - H_0)$$

where  $H_0$  is the Hartree Hamiltonian =  $T + V_H$

From now on: integration over repeated variables is understood

# Reminder: Dyson equation

## Dyson equation

$$G(12) = G_H(12) + \int d34 G_H(13) [\Sigma(34) + V_{ext}(34)] G(42)$$

where  $G_H$  is the Hartree Green's function:

$$G_H(\omega) = (\omega - H_0)^{-1} \Rightarrow G_H^{-1}(\omega) = (\omega - H_0)$$

where  $H_0$  is the Hartree Hamiltonian =  $T + V_H$

From now on: integration over repeated variables is understood

## Exercise

$$G^{-1}(12) = G_H^{-1}(12) - \Sigma(12) - V_{ext}(12)$$

# The Bethe-Salpeter equation

## Exercise

Formal derivation

$$L(1234) = -i \frac{\delta G(12)}{\delta V_{ext}(34)}$$

# The Bethe-Salpeter equation

## Exercise

Formal derivation

$$L(1234) = -i \frac{\delta G(12)}{\delta V_{ext}(34)} = +i G(15) \frac{\delta G^{-1}(56)}{\delta V_{ext}(34)} G(62)$$



# The Bethe-Salpeter equation

## Exercise

### Formal derivation

$$\begin{aligned}
 L(1234) &= -i \frac{\delta G(12)}{\delta V_{ext}(34)} = +iG(15) \frac{\delta G^{-1}(56)}{\delta V_{ext}(34)} G(62) \\
 &= +iG(15) \frac{\delta [G_H^{-1}(56) - V_{ext}(56) - \Sigma(56)]}{\delta V_{ext}(34)} G(62)
 \end{aligned}$$

# The Bethe-Salpeter equation

## Exercise

Formal derivation

$$\begin{aligned}
 L(1234) &= -i \frac{\delta G(12)}{\delta V_{ext}(34)} = +iG(15) \frac{\delta G^{-1}(56)}{\delta V_{ext}(34)} G(62) \\
 &= +iG(15) \frac{\delta [G_H^{-1}(56) - V_{ext}(56) - \Sigma(56)]}{\delta V_{ext}(34)} G(62) \\
 &= -iG(13)G(42) + iG(15)G(62) \left[ \frac{\delta V_H(5)\delta(56)}{\delta V_{ext}(34)} - \frac{\delta \Sigma(56)}{\delta V_{ext}(34)} \right]
 \end{aligned}$$

# The Bethe-Salpeter equation

## Exercise

Formal derivation

$$\begin{aligned}
 L(1234) &= -i \frac{\delta G(12)}{\delta V_{ext}(34)} = +iG(15) \frac{\delta G^{-1}(56)}{\delta V_{ext}(34)} G(62) \\
 &= +iG(15) \frac{\delta[G_H^{-1}(56) - V_{ext}(56) - \Sigma(56)]}{\delta V_{ext}(34)} G(62) \\
 &= -iG(13)G(42) + iG(15)G(62) \left[ \frac{\delta V_H(5)\delta(56)}{\delta V_{ext}(34)} - \frac{\delta \Sigma(56)}{\delta V_{ext}(34)} \right] \\
 &= -iG(13)G(42) + iG(15)G(62) \left[ \frac{\delta V_H(5)\delta(56)}{\delta G(78)} - \frac{\delta \Sigma(56)}{\delta G(78)} \right] \frac{\delta G(78)}{\delta V_{ext}(34)}
 \end{aligned}$$

# The Bethe-Salpeter equation

## Exercise

### Formal derivation

$$\begin{aligned}
 L(1234) &= -i \frac{\delta G(12)}{\delta V_{ext}(34)} = +iG(15) \frac{\delta G^{-1}(56)}{\delta V_{ext}(34)} G(62) \\
 &= +iG(15) \frac{\delta [G_H^{-1}(56) - V_{ext}(56) - \Sigma(56)]}{\delta V_{ext}(34)} G(62) \\
 &= -iG(13)G(42) + iG(15)G(62) \left[ \frac{\delta V_H(5)\delta(56)}{\delta V_{ext}(34)} - \frac{\delta \Sigma(56)}{\delta V_{ext}(34)} \right] \\
 &= -iG(13)G(42) + iG(15)G(62) \left[ \frac{\delta V_H(5)\delta(56)}{\delta G(78)} - \frac{\delta \Sigma(56)}{\delta G(78)} \right] \frac{\delta G(78)}{\delta V_{ext}(34)}
 \end{aligned}$$

$$L(1234) = L_0(1234) + L_0(1256) \left[ v(57)\delta(56)\delta(78) + i \frac{\delta \Sigma(56)}{\delta G(78)} \right] L(7834)$$

# The Bethe-Salpeter equation in the GW approximation

## Approximations

$$L = L_0 + L_0 \left( v + i \frac{\delta \Sigma}{\delta G} \right) L$$

# The Bethe-Salpeter equation in the GW approximation

## Approximations

$$L = L_0 + L_0 \left( v + i \frac{\delta \Sigma}{\delta G} \right) L$$

Approximation:

$$\Sigma \approx iGW$$

# The Bethe-Salpeter equation in the GW approximation

## Approximations

$$L = L_0 + L_0 \left( v - \frac{\delta(GW)}{\delta G} \right) L$$

Approximation:

$$\Sigma \approx iGW \qquad \frac{\delta(GW)}{\delta G} = W + G \frac{\delta W}{\delta G} \approx W$$

# The Bethe-Salpeter equation in the GW approximation

## Approximations

We finally obtain:

$$L = L_0 + L_0(v - W)L$$



# Static BSE

## Further approximation: Cancellations between

- 1 Quasiparticle approximation to  $G$  in  $L_0(1234) = -iG(13)G(42)$   
⇒ Only GW quasiparticle energies  $E_i$  at the place of Kohn-Sham eigenvalues  $\epsilon_i$
- 2 Static approximation to  $W$

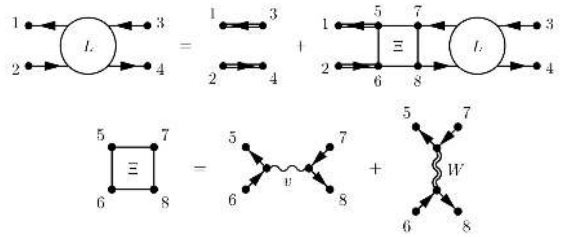
$$W(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) \Rightarrow W(\mathbf{r}_1, \mathbf{r}_2, \omega = 0)\delta(t_1 - t_2)$$

F. Bechstedt *et al.* Phys. Rev. Lett. **78** (1997).  
P. Cudazzo and L. Reining, Phys. Rev. Research **2** (2020)

# The Bethe-Salpeter equation in the GW approximation

## The Bethe-Salpeter equation in the GW approximation

$$L(1234) = L_0(1234) + L_0(1256)[v(57)\delta(56)\delta(78) - W(56)\delta(57)\delta(68)]L(7834)$$



- $v$  = repulsive e-h exchange interaction (dipole-dipole type)
- $W$  = attractive e-h direct interaction (monopole-monopole type)

# Outline

- 1 Motivations
- 2 The Bethe-Salpeter equation: basic theory and approximations
- 3 Solution of the Bethe-Salpeter equation in practice**
- 4 Prototypical results: success and limitations
- 5 Wannier, Frenkel and charge transfer excitons
- 6 Connection with TDDFT

## Absorption

$$\text{Abs}(\omega) = \lim_{\mathbf{q} \rightarrow 0} \text{Im} \epsilon_M(\mathbf{q}, \omega)$$

$$\text{Abs}(\omega) = - \lim_{\mathbf{q} \rightarrow 0} \text{Im} [v_{\mathbf{G}=0}(\mathbf{q}) \bar{\chi}_{\mathbf{G}=0, \mathbf{G}'=0}(\mathbf{q}, \omega)]$$

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

Absorption  $\rightarrow$  response to  $V_{\text{ext}} + V_{\text{ind}}^{\text{macro}}$

## EELS

$$\text{EELS}(\omega) = - \lim_{\mathbf{q} \rightarrow 0} \text{Im} [1/\epsilon_M(\mathbf{q}, \omega)]$$

$$\text{EELS}(\omega) = - \lim_{\mathbf{q} \rightarrow 0} \text{Im} [v_{\mathbf{G}=0}(\mathbf{q}) \chi_{\mathbf{G}=0, \mathbf{G}'=0}(\mathbf{q}, \omega)]$$

$$\chi = P + P(v_0 + \bar{v})\chi$$

EELS  $\rightarrow$  response to  $V_{\text{ext}}$

# Micro-macro connection

## Microscopic-Macroscopic connection: local fields

$$\epsilon_M(\mathbf{q}, \omega) = 1 - v_{\mathbf{G}=0}(\mathbf{q}) \bar{\chi}_{\mathbf{G}=0, \mathbf{G}'=0}(\mathbf{q}, \omega)$$

$$\bar{\chi}_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega) = P_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega) + P_{\mathbf{G}, \mathbf{G}_1}(\mathbf{q}, \omega) \bar{v}_{\mathbf{G}_1}(\mathbf{q}) \bar{\chi}_{\mathbf{G}_1, \mathbf{G}'}(\mathbf{q}, \omega)$$

$$\bar{v}_{\mathbf{G}}(\mathbf{q}) = \begin{cases} 0 & \text{for } \mathbf{G} = 0 \\ v_{\mathbf{G}}(\mathbf{q}) & \text{for } \mathbf{G} \neq 0 \end{cases}$$

Hanke, Adv. Phys. **27** (1978).

# Micro-macro connection

## Microscopic-Macroscopic connection: local fields

$$\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = P_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) + P_{\mathbf{G},\mathbf{G}_1}(\mathbf{q},\omega)v_{\mathbf{G}_1}(\mathbf{q})\chi_{\mathbf{G}_1,\mathbf{G}'}(\mathbf{q},\omega)$$

$$\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q},\omega) = \delta_{\mathbf{G},\mathbf{G}'} + v_{\mathbf{G}}(\mathbf{q})\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$$

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

Adler, Phys. Rev. **126** (1962); Wiser, Phys. Rev. **129** (1963).

# Solving BSE

$$L(1234) = L_0(1234) + L_0(1256)[v(57)\delta(56)\delta(78) - W(56)\delta(57)\delta(68)]L(7834)$$

# Solving BSE

$$\bar{L}(1234) = L_0(1234) + L_0(1256)[\bar{v}(57)\delta(56)\delta(78) - W(56)\delta(57)\delta(68)]\bar{L}(7834)$$



# Solving BSE

$$\bar{L}(1234) = L_0(1234) + L_0(1256)[\bar{v}(57)\delta(56)\delta(78) - W(56)\delta(57)\delta(68)]\bar{L}(7834)$$

## Static $W$

Simplification:

$$W(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) \Rightarrow W(\mathbf{r}_1, \mathbf{r}_2)\delta(t_1 - t_2)$$

$$\bar{L}(1234) \Rightarrow \bar{L}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, t - t') \Rightarrow \bar{L}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega)$$

# Solving BSE

## Dielectric function

$$\bar{L}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4\omega) = L_0(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4\omega) + \int d\mathbf{r}_5d\mathbf{r}_6d\mathbf{r}_7d\mathbf{r}_8 L_0(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_5\mathbf{r}_6\omega) \times \\ \times [\bar{v}(\mathbf{r}_5\mathbf{r}_7)\delta(\mathbf{r}_5\mathbf{r}_6)\delta(\mathbf{r}_7\mathbf{r}_8) - W(\mathbf{r}_5\mathbf{r}_6)\delta(\mathbf{r}_5\mathbf{r}_7)\delta(\mathbf{r}_6\mathbf{r}_8)]\bar{L}(\mathbf{r}_7\mathbf{r}_8\mathbf{r}_3\mathbf{r}_4\omega)$$

$$\epsilon_M(\omega) = 1 - \lim_{\mathbf{q} \rightarrow 0} \left[ v_{\mathbf{G}=0}(\mathbf{q}) \int d\mathbf{r}d\mathbf{r}' e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')} \bar{L}(\mathbf{r}, \mathbf{r}, \mathbf{r}', \mathbf{r}', \omega) \right]$$

# Solving BSE

$$\begin{aligned} \bar{L}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4\omega) &= L_0(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4\omega) + \int d\mathbf{r}_5 d\mathbf{r}_6 d\mathbf{r}_7 d\mathbf{r}_8 L_0(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_5\mathbf{r}_6\omega) \times \\ &\times [\bar{v}(\mathbf{r}_5\mathbf{r}_7)\delta(\mathbf{r}_5\mathbf{r}_6)\delta(\mathbf{r}_7\mathbf{r}_8) - W(\mathbf{r}_5\mathbf{r}_6)\delta(\mathbf{r}_5\mathbf{r}_7)\delta(\mathbf{r}_6\mathbf{r}_8)] \bar{L}(\mathbf{r}_7\mathbf{r}_8\mathbf{r}_3\mathbf{r}_4\omega) \end{aligned}$$

How to solve it?

# Solving BSE

$$\bar{L}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4\omega) = L_0(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4\omega) + \int d\mathbf{r}_5d\mathbf{r}_6d\mathbf{r}_7d\mathbf{r}_8 L_0(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_5\mathbf{r}_6\omega) \times$$

$$\times [\bar{v}(\mathbf{r}_5\mathbf{r}_7)\delta(\mathbf{r}_5\mathbf{r}_6)\delta(\mathbf{r}_7\mathbf{r}_8) - W(\mathbf{r}_5\mathbf{r}_6)\delta(\mathbf{r}_5\mathbf{r}_7)\delta(\mathbf{r}_6\mathbf{r}_8)]\bar{L}(\mathbf{r}_7\mathbf{r}_8\mathbf{r}_3\mathbf{r}_4\omega)$$

How to solve it?

Transition space

$$\bar{L}_{(n_1n_2)(n_3n_4)}(\omega) = \langle \phi_{n_1}^*(\mathbf{r}_1)\phi_{n_2}(\mathbf{r}_2) | \bar{L}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4\omega) | \phi_{n_3}^*(\mathbf{r}_3)\phi_{n_4}(\mathbf{r}_4) \rangle = \langle\langle \bar{L} \rangle\rangle$$

## Exercise

$$L_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) = \sum_{ij} (f_j - f_i) \frac{\phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \phi_i(\mathbf{r}_3) \phi_j^*(\mathbf{r}_4)}{\omega - (E_i - E_j)}$$

Calculate:

$$\langle\langle L_0 \rangle\rangle = \frac{f_{n_1} - f_{n_2}}{\omega - (E_{n_2} - E_{n_1})} \delta_{n_1 n_3} \delta_{n_2 n_4}$$

# Solving BSE

## BSE in transition space

We consider only resonant optical transitions for a nonmetallic system:  $(n_1 n_2) = (v \mathbf{k} c \mathbf{k}) \Rightarrow (vc)$

$$\bar{L} = L_0 + L_0(\bar{v} - W)\bar{L}$$

$$\bar{L} = [1 - L_0(\bar{v} - W)]^{-1} L_0$$

$$\bar{L} = [L_0^{-1} - (\bar{v} - W)]^{-1}$$

$$\bar{L}_{(vc)(v'c')}(\omega) = [(E_c - E_v - \omega)\delta_{vv'}\delta_{cc'} + (f_v - f_c)\langle\langle \bar{v} - W \rangle\rangle]^{-1}(f_{c'} - f_{v'})$$

# Solving BSE

$$\bar{L}_{(vc)(v'c')}(\omega) = [(E_c - E_v - \omega)\delta_{vv'}\delta_{cc'} + (f_v - f_c)\langle\langle \bar{v} - W \rangle\rangle]^{-1}(f_{c'} - f_{v'})$$

# Solving BSE

$$\bar{L}_{(vc)(v'c')}(\omega) = [(E_c - E_v - \omega)\delta_{vv'}\delta_{cc'} + (f_v - f_c)\langle\langle\bar{v} - W\rangle\rangle]^{-1}(f_{c'} - f_{v'})$$

$$\bar{L} \rightarrow [H_{exc} - \omega I]^{-1}$$

$$H_{exc}^{(vc)(v'c')} = (E_c - E_v)\delta_{vv'}\delta_{cc'} + (f_v - f_c)\langle vc|\bar{v} - W|v'c'\rangle$$



# Solving BSE

## Excitonic hamiltonian

$$H_{exc}^{(vc)(v'c')} = (E_c - E_v)\delta_{vv'}\delta_{cc'} + (f_v - f_c)\langle vc|\bar{v} - W|v'c'\rangle$$

## Spectral representation of a hermitian operator

$$[H_{exc} - \omega I]^{-1} = \sum_{\lambda} \frac{|A_{\lambda}\rangle\langle A_{\lambda}|}{E_{\lambda} - \omega}$$

$$H_{exc}A_{\lambda} = E_{\lambda}A_{\lambda}$$

$$\bar{L}_{(vc)(v'c')}(\omega) = \sum_{\lambda} \frac{A_{\lambda}^{(vc)} A_{\lambda}^{*(v'c')}}{E_{\lambda} - \omega} (f_{c'} - f_{v'})$$

# Absorption spectra in BSE

## Excitonic hamiltonian

$$H_{exc}A_\lambda = E_\lambda A_\lambda$$

$$H_{exc}^{(vc)(v'c')} = (E_c - E_v)\delta_{vv'}\delta_{cc'} + (f_v - f_c)\langle vc|\bar{v} - W|v'c'\rangle$$

## Matrix elements

$$\langle vc|\bar{v}|v'c'\rangle = 2 \int dr_1 \int dr_2 \phi_v(r_1)\phi_c^*(r_1)\bar{v}(r_1, r_2)\phi_{v'}^*(r_2)\phi_{c'}(r_2)$$

$$\langle vc| - W|v'c'\rangle = - \int dr_1 \int dr_2 \phi_v(r_1)\phi_{v'}^*(r_1)W(r_1, r_2)\phi_c^*(r_2)\phi_{c'}(r_2)$$

## Absorption spectrum

$$Abs(\omega) \propto \sum_\lambda \left| \sum_{vc} A_\lambda^{(vc)} \langle v|D|c\rangle \right|^2 \delta(E_\lambda - \omega)$$

# Absorption spectra in BSE

## Independent (quasi)particles

$$Abs(\omega) \propto \sum_{vc} |\langle v|D|c \rangle|^2 \delta(E_c - E_v - \omega)$$

## Excitonic effects

$$[H_{el} + H_{hole} + H_{el-hole}]A_\lambda = E_\lambda A_\lambda$$

$$Abs(\omega) \propto \sum_\lambda \left| \sum_{vc} A_\lambda^{(vc)} \langle v|D|c \rangle \right|^2 \delta(E_\lambda - \omega)$$

- mixing of transitions:  $|\langle v|D|c \rangle|^2 \rightarrow \left| \sum_{vc} A_\lambda^{(vc)} \langle v|D|c \rangle \right|^2$
- modification of excitation energies:  $E_c - E_v \rightarrow E_\lambda$

# BSE calculations

## A three-step method

### 1 LDA calculation

⇒ Kohn-Sham wavefunctions  $\varphi_i$

### 2 GW calculation

⇒ GW energies  $E_i$  and screened Coulomb interaction  $W$

### 3 BSE calculation

solution of  $H_{exc} A_\lambda = E_\lambda A_\lambda$  with:

$$H_{exc}^{(vc)(v'c')} = (E_c - E_v)\delta_{vv'}\delta_{cc'} + (f_v - f_c)\langle vc|\bar{v} - W|v'c'\rangle$$

⇒ excitonic eigenstates  $A_\lambda, E_\lambda$

⇒ spectra  $\epsilon_M(\omega)$

# Screening the Coulomb interaction

## Bethe-Salpeter equation: GW approximation

$$L(1234) = L_0(1234) + L_0(1256)[v(57)\delta(56)\delta(78) - W(56)\delta(57)\delta(68)]L(7834)$$

# Screening the Coulomb interaction

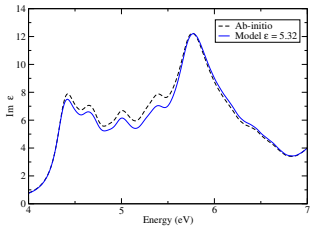
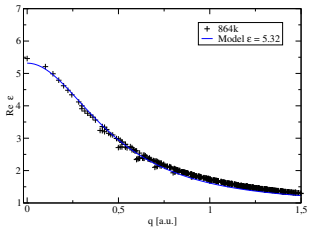
## Bethe-Salpeter equation: Hartree-Fock approximation

$$L(1234) = L_0(1234) + L_0(1256)[v(57)\delta(56)\delta(78) - v(56)\delta(57)\delta(68)]L(7834)$$

$W = \epsilon^{-1}v$

GW with no screening is Hartree-Fock  
 BSE with no screening is time-dependent Hartree-Fock

# Screening the Coulomb interaction



Silver chloride, A. Lorin *et al.*, PRB 104 (2021)

## Model dielectric function

$$\epsilon(q) = 1 + \frac{1}{\frac{1}{\epsilon(q=0)-1} + \alpha \left(\frac{q}{q_{TF}}\right)^2 + \frac{q^4}{4\omega_p}}$$

G. Cappellini *et al.*, PRB 47 (1993).

Note the similarities with TDDFT hybrids (with local range separation)

# Adiabatic TDDFT vs. BSE

## Bethe-Salpeter equation

- Non-local self-energy:  $V_{ext}(1) + V_H(1) + \Sigma(1, 2)$
- Four-point Dyson equation:  

$$L(1234) = L_0(1234) + L_0(1256) \left[ v(57)\delta(56)\delta(78) + i \frac{\delta\Sigma(56)}{\delta G(78)} \right] L(7834)$$
- Matrix elements (excitonic hamiltonian):

$$\langle vc|v|v'c' \rangle = 2 \int dr_1 dr_2 \phi_v(r_1) \phi_c^*(r_1) v(r_1, r_2) \phi_{v'}^*(r_2) \phi_{c'}(r_2)$$

$$\langle vc| - W|v'c' \rangle = - \int dr_1 dr_2 \phi_v(r_1) \phi_{v'}^*(r_1) W(r_1, r_2) \phi_c^*(r_2) \phi_{c'}(r_2)$$

## Adiabatic TDDFT

- Local Kohn-Sham potential:  $V_{ext}(1) + V_H(1) + V_{xc}(1)$
- Two-point Dyson equation:  $\chi(12) = \chi^0(12) + \chi^0(13)[v(34) + f_{xc}(34)]\chi(42)$
- Matrix elements (Casida equation):

$$\langle vc|v|v'c' \rangle = 2 \int dr_1 dr_2 \phi_v(r_1) \phi_c^*(r_1) v(r_1, r_2) \phi_{v'}^*(r_2) \phi_{c'}(r_2)$$

$$\langle vc|f_{xc}|v'c' \rangle = 2 \int dr_1 dr_2 \phi_v(r_1) \phi_c^*(r_1) f_{xc}(r_1, r_2) \phi_{v'}^*(r_2) \phi_{c'}(r_2)$$

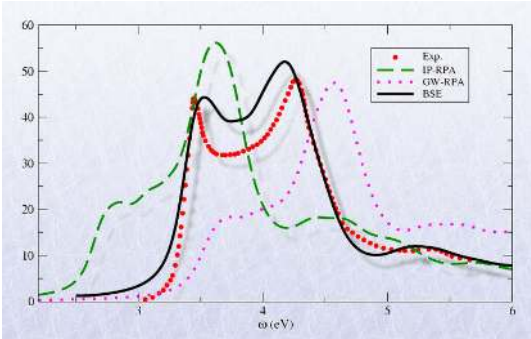


# Outline

- 1 Motivations
- 2 The Bethe-Salpeter equation: basic theory and approximations
- 3 Solution of the Bethe-Salpeter equation in practice
- 4 Prototypical results: success and limitations**
- 5 Wannier, Frenkel and charge transfer excitons
- 6 Connection with TDDFT

# Continuum excitons

Bulk silicon

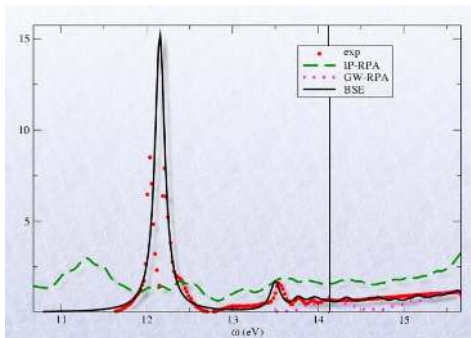


G. Onida, L. Reining, and A. Rubio, RMP **74** (2002).

# Bound excitons

$$\text{Binding energy} = E_{GW}^{gap} - E_{\lambda}$$

Solid argon

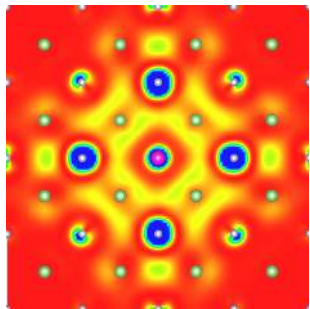
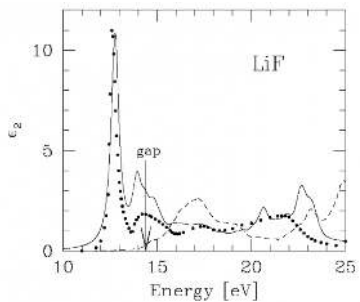


F. Sottile *et al.* PRB **76** (2007).

# Exciton analysis

Exciton amplitude: 
$$\Psi_{\lambda}(\mathbf{r}_h, \mathbf{r}_e) = \sum_{vc} A_{\lambda}^{(vc)} \phi_v^*(\mathbf{r}_h) \phi_c(\mathbf{r}_e)$$

Lithium Fluoride: fix  $\bar{\mathbf{r}}_h$  and plot  $|\Psi_{\lambda}(\bar{\mathbf{r}}_h, \mathbf{r}_e)|^2$

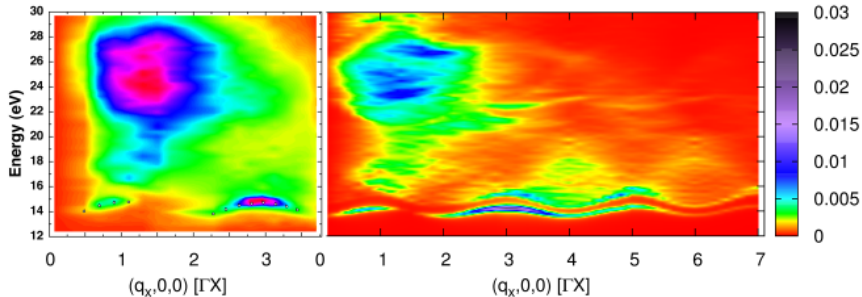


# Exciton dispersion: IXS

## Lithium Fluoride

Experiment

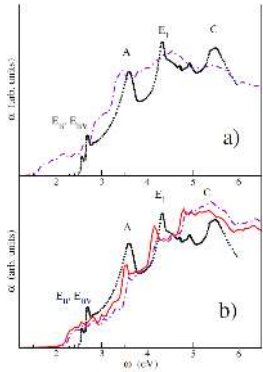
Theory



P. Abbamonte *et al.*, PNAS **105** (2008); M. Gatti and F. Sottile, PRB **88** (2013).

# Self-consistency in the BSE

Difference between  $G_0W_0$  and QSGW ingredients in the BSE:  $\text{Cu}_2\text{O}$



F. Bruneval *et al.*, PRL **97** (2006)

# Finite systems: atoms and molecules

## Molecular systems

Calculations of vertical excitation energies  $E_\lambda$  from full BSE matrix

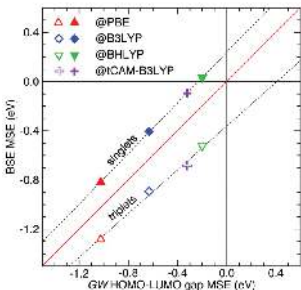
$$\begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix} \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix} = E_\lambda \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix}$$

- Benchmarks of singlet/triplet energies with respect to accurate quantum chemical methods
- Assessment of quality of ingredients (different levels of self-consistency)
- Charge-transfer excitations  $E_{CT}(R) = EA - IP - 1/R$

Reviewed in: X. Blase, I. Duchemin, D. Jacquemin, Chem. Soc. Rev. **47** (2018)

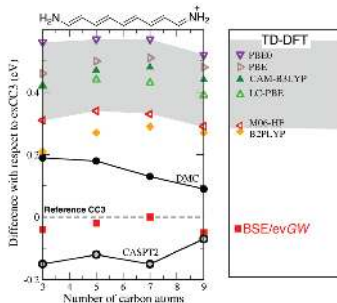
# Finite systems: atoms and molecules

Mean-signed errors for Thiel's set



F. Bruneval *et al.*  
 J. Chem. Phys. **142** (2015).

Errors for streptocyanine chains

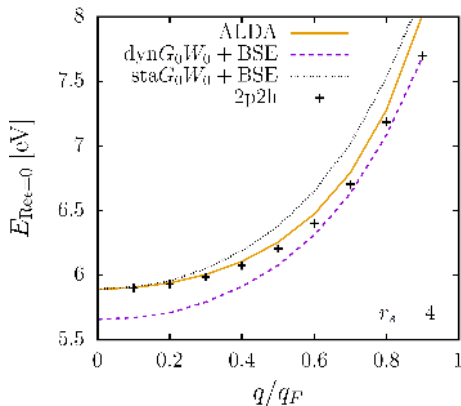


P. Boulanger *et al.*  
 J. Chem. Theory Comput. **10** (2014)



# Problem of consistency

## Plasmon dispersion in HEG



Jaakko Koskelo, unpublished (2019).

# Missing dynamical effects

## Beyond static BSE

- Correction to excitation energies and spectra

G. Strinati, PRL **49** (1982) and PRB **29** (1984); M. Rohlfing and S. G. Louie, PRB **62** (2000); A. Marini and R. Del Sole, PRL **91** (2003); Y. Ma, M. Rohlfing, and C. Molteni, PRB **80** (2009); S. Gao *et al.*, Nanolett. **16** (2016); P. F. Loos and X. Blase, J. Chem. Phys. **153** (2020)

# Missing dynamical effects

## Beyond static BSE

- Correction to excitation energies and spectra

G. Strinati, PRL **49** (1982) and PRB **29** (1984); M. Rohlfing and S. G. Louie, PRB **62** (2000); A. Marini and R. Del Sole, PRL **91** (2003); Y. Ma, M. Rohlfing, and C. Molteni, PRB **80** (2009); S. Gao *et al.*, Nanolett. **16** (2016); P. F. Loos and X. Blase, J. Chem. Phys. **153** (2020)

- Multiple excitations in molecules (and also solids: *dd* excitations and double plasmons)

P. Romaniello *et al.*, J. Chem. Phys. **130** (2009); D. Sangalli *et al.*, J. Chem. Phys. **134** (2011); E. Rebolini and J. Toulouse, J. Chem. Phys. **144** (2016); V. Olevano, J. Toulouse, and P. Schuck, J. Chem. Phys. **150** (2019).

# Missing dynamical effects

## Beyond static BSE

- Correction to excitation energies and spectra

G. Strinati, PRL **49** (1982) and PRB **29** (1984); M. Rohlfing and S. G. Louie, PRB **62** (2000); A. Marini and R. Del Sole, PRL **91** (2003); Y. Ma, M. Rohlfing, and C. Molteni, PRB **80** (2009); S. Gao *et al.*, Nanolett. **16** (2016); P. F. Loos and X. Blase, J. Chem. Phys. **153** (2020)

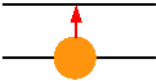
- Multiple excitations in molecules (and also solids: *dd* excitations and double plasmons)

P. Romaniello *et al.*, J. Chem. Phys. **130** (2009); D. Sangalli *et al.*, J. Chem. Phys. **134** (2011); E. Rebolini and J. Toulouse, J. Chem. Phys. **144** (2016); V. Olevano, J. Toulouse, and P. Schuck, J. Chem. Phys. **150** (2019).

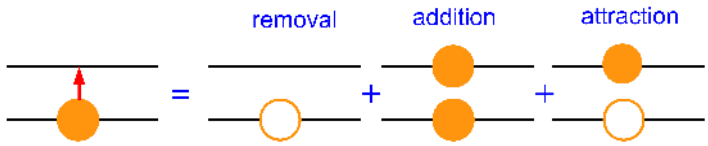
- Exciton self-energy and cumulant expansion (coupling with bosons)

P. Cudazzo and L. Reining, Phys. Rev. Research **2** (2020)

# One electron limit: A detour?



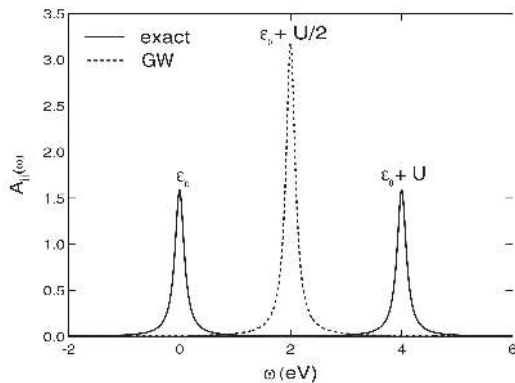
# One electron limit: A detour?



Perfect cancellation

# One electron limit: A detour?

Atomic limit of Hubbard dimer with one spin-up electron:  
addition of one spin-down electron



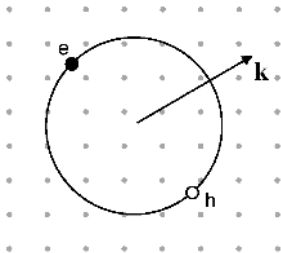
# Outline

- 1 Motivations
- 2 The Bethe-Salpeter equation: basic theory and approximations
- 3 Solution of the Bethe-Salpeter equation in practice
- 4 Prototypical results: success and limitations
- 5 Wannier, Frenkel and charge transfer excitons**
- 6 Connection with TDDFT



# Wannier and Frenkel excitons

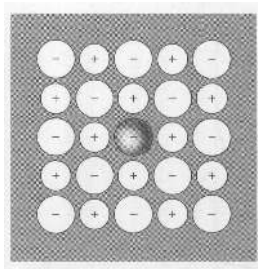
## Wannier exciton



weakly bound: delocalised  
over many lattice sites

*semiconductors*

## Frenkel exciton



tightly bound: localised  
on few sites

*wide gap insulators*

# The Wannier model

## Bethe-Salpeter equation

$$H_{exc} A_\lambda = E_\lambda A_\lambda$$

$$H_{exc}^{(vc)(v'c')} = (E_c - E_v) \delta_{vv'} \delta_{cc'} + \langle\langle \bar{v} - W \rangle\rangle$$

## Wannier model

- two parabolic bands

$$E_c - E_v = E_g + \frac{k^2}{2\mu} \rightarrow -\frac{\nabla^2}{2\mu}$$

- no local fields ( $\bar{v} = 0$ ) and effective screened  $W$

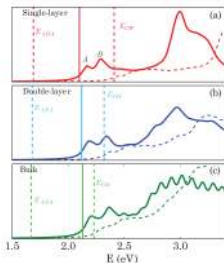
$$W(\mathbf{r}, \mathbf{r}') = \frac{1}{\epsilon |\mathbf{r} - \mathbf{r}'|}$$

- solution = Rydberg series for effective H atom

$$E_\lambda = E_g - \frac{R_{eff}}{\lambda^2} \quad \text{with} \quad R_{eff} = \frac{\mu}{2\epsilon^2}$$

# Two dimensions

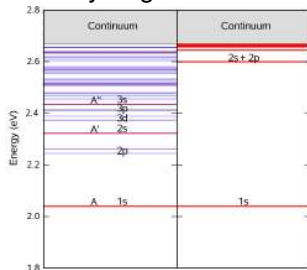
## Larger binding energy



MoS<sub>2</sub> absorption spectrum

A. Molina Sanchez *et al.*, PRB **88** (2013).

## Non-hydrogenic series



Exciton energies

E.g. A. Chernikov *et al.*, PRL **113** (2014).

## Macroscopic interaction in 2D

$$W(r) = \frac{1}{4\alpha_{2D}} \left[ H_0 \left( \frac{r}{r_0} \right) - Y_0 \left( \frac{r}{r_0} \right) \right]$$

$r_0 = 2\pi\alpha_{2D}$  and  $H_0, Y_0$  Struve and Bessel functions 2nd kind

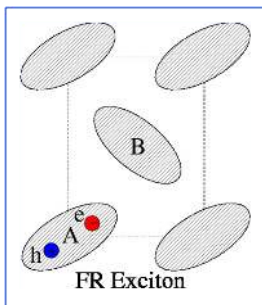
L.V. Keldysh, JETP Lett. **29** (1979); P. Cudazzo, I.V. Tokatly, A. Rubio, PRB **84** (2011).

# Frenkel and charge transfer excitons

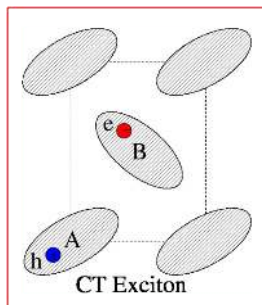
When electrons are localised  
(wavefunctions with small overlap)

$$\hat{H}_{ex} = \begin{pmatrix} \hat{H}^{FR} & \hat{H}^{hopping} \\ \hat{H}^{hopping} & \hat{H}^{CT} \end{pmatrix}$$

Frenkel exciton



Charge transfer exciton

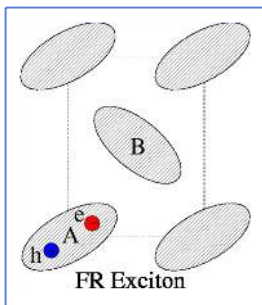


# Frenkel and charge transfer excitons

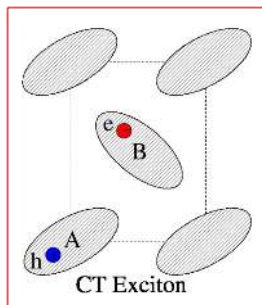
When electrons are localised  
(wavefunctions with small overlap)

$$\hat{H}_{ex} = \begin{pmatrix} \hat{H}^{FR} & \hat{H}^{hoping} \\ \hat{H}^{hoping} & \hat{H}^{CT} \end{pmatrix}$$

Frenkel exciton



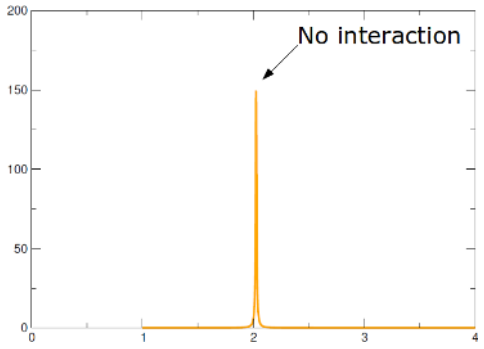
Charge transfer exciton



# Frenkel and charge transfer excitons

$$E_{FR}^{\pm} = \Delta\epsilon$$

$$E_{CT}^{\pm} = \Delta\epsilon$$

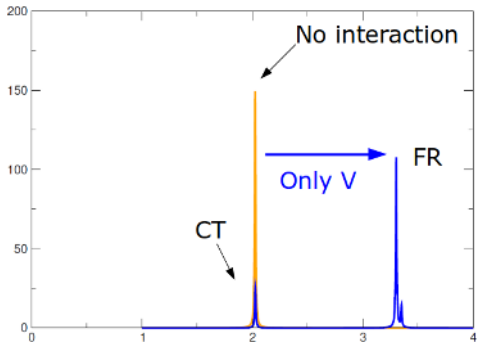


Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).

# Frenkel and charge transfer excitons

$$E_{FR}^{\pm} = \Delta\epsilon + I \pm J$$

$$E_{CT}^{\pm} = \Delta\epsilon$$



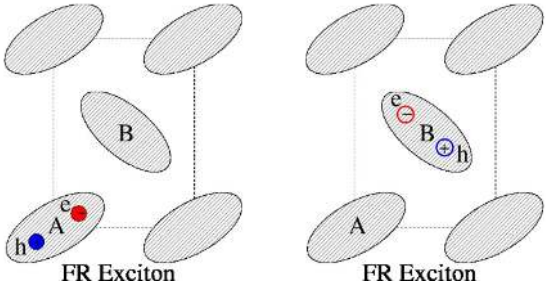
Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).

# Frenkel and charge transfer excitons

$$E_{FR}^{\pm} = \Delta\epsilon + I \pm J$$

$$E_{CT}^{\pm} = \Delta\epsilon$$

## Frenkel exciton & Davydov splitting



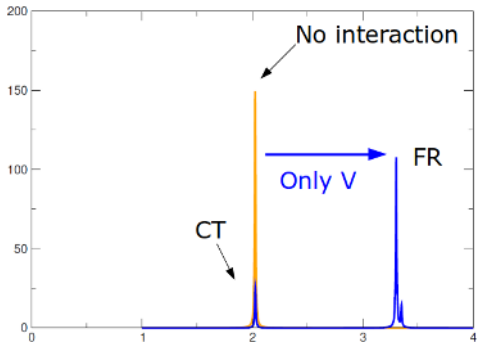
Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).



# Frenkel and charge transfer excitons

$$E_{FR}^{\pm} = \Delta\epsilon + I \pm J$$

$$E_{CT}^{\pm} = \Delta\epsilon$$

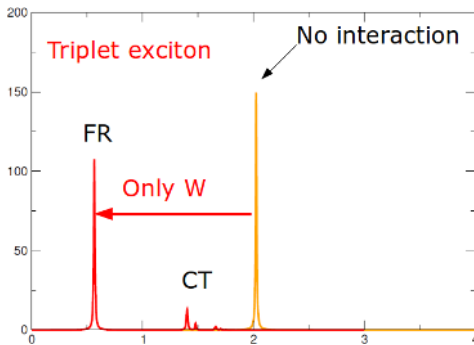


Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).

# Frenkel and charge transfer excitons

$$E_{FR}^{\pm} = \Delta\epsilon - W$$

$$E_{CT}^{\pm} = \Delta\epsilon - \tilde{W}$$

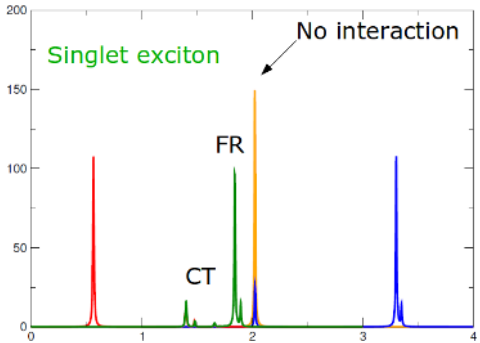


Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).

# Frenkel and charge transfer excitons

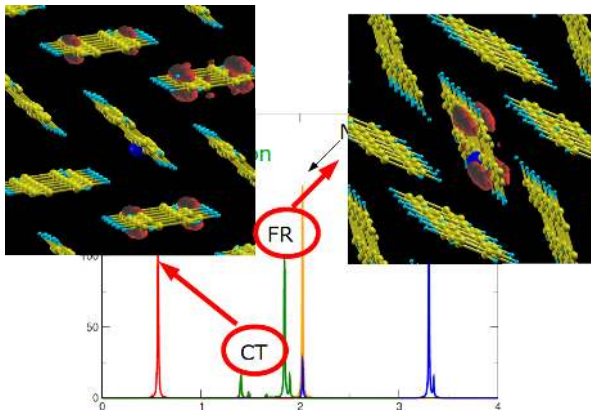
$$E_{FR}^{\pm} = \Delta\epsilon + I \pm J - W$$

$$E_{CT}^{\pm} = \Delta\epsilon - \tilde{W}$$



Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).

# Frenkel and charge transfer excitons



Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).

# Wannier and Frenkel excitons: dispersion

## Exciton dispersion

$E_\lambda(\mathbf{q})$  = Exciton dispersion: exciton energy as a function of the momentum carried by the electron-hole pair

## Wannier and Frenkel models

- Wannier exciton

$$E_\lambda(\mathbf{q}) = E_\lambda(\mathbf{q} = 0) + \frac{q^2}{2(m_e^* + m_h^*)}$$

Free propagation: band structure effect (singlet=triplet)

- Frenkel exciton

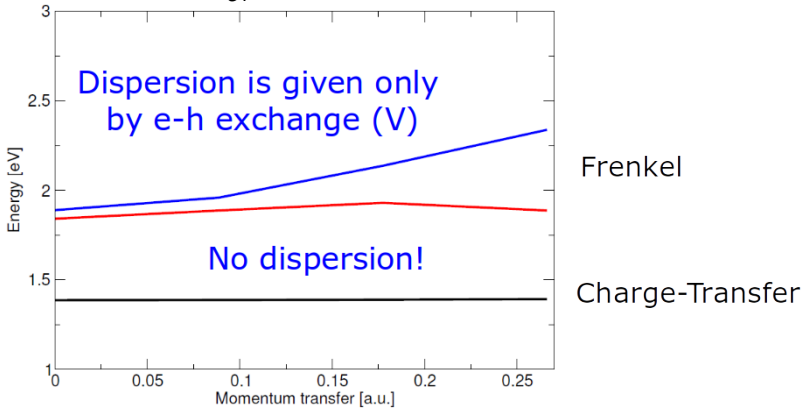
$$E_\lambda(\mathbf{q}) = E_\lambda^{ii} + \sum_j e^{i\mathbf{q}(\mathbf{R}_j - \mathbf{R}_i)} E_\lambda^{jj}$$

Dipole-dipole interaction: Destroy electron-hole pair at site  $i$  and create at site  $j$

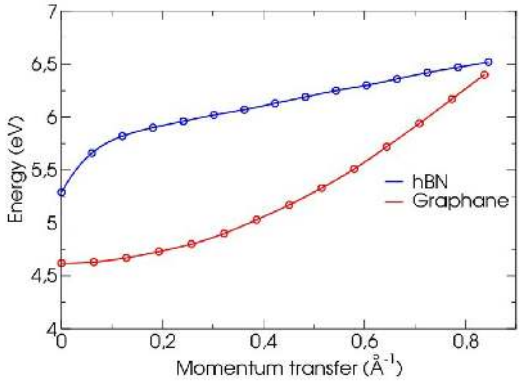
# Exciton dispersion: Frenkel and charge transfer

$$E_{FR}^{\pm}(\mathbf{q}) = \Delta\epsilon + I(\mathbf{q}) \pm J(\mathbf{q}) - W$$

$$E_{CT}^{\pm}(\mathbf{q}) = \Delta\epsilon - \tilde{W}$$



# Exciton dispersion: two dimensions



P. Cudazzo *et al.* PRL **116** (2016)

# Outline

- 1 Motivations
- 2 The Bethe-Salpeter equation: basic theory and approximations
- 3 Solution of the Bethe-Salpeter equation in practice
- 4 Prototypical results: success and limitations
- 5 Wannier, Frenkel and charge transfer excitons
- 6 Connection with TDDFT**



# MBPT vs. TDDFT: different electrons

## MBPT

$$L = L_0 + L_0(\mathbf{v} + \Xi)L$$

## TDDFT

$$\chi = \chi_0 + \chi_0(\mathbf{v} + \mathbf{f}_{xc})\chi$$

# MBPT vs. TDDFT: different electrons

## MBPT

$L = L_0 \Rightarrow$  GW energies

## TDDFT

$\chi = \chi_0 \Rightarrow$  Kohn-Sham energies

## Observation

- $f_{xc}$  has 2 tasks:
- bandgap opening ( $\rightarrow$  GW)
  - excitonic effects ( $\rightarrow$  BSE)

# $f_{xc}$ kernel

## Definitions

$$P = \chi_0 + \chi_0 f_{xc} P : \text{irreducible polarizability } P$$
$$\chi = P + P v \chi : \text{reducible polarizability } \chi$$

# $f_{xc}$ kernel

## Definitions

$P = \chi_0 + \chi_0 f_{xc} P$  : irreducible polarizability  $P$

$\chi = P + P v \chi$  : reducible polarizability  $\chi$

$$f_{xc} = f_{xc}^{(1)} + f_{xc}^{(2)}$$

$f_{xc}^{(1)} \Rightarrow$  bandgap opening       $f_{xc}^{(2)} \Rightarrow$  excitonic effects

$$P_0 = \chi_0 + \chi_0 f_{xc}^{(1)} P_0 \quad P = P_0 + P_0 f_{xc}^{(2)} P$$

$\chi_0 \Rightarrow$  Kohn-Sham energies       $P_0 \Rightarrow$  GW energies

# MBPT vs. TDDFT: different maths

## MBPT

$$L = L_0 + L_0(v + \Xi)L$$

## TDDFT

$$\chi = P_0 + P_0(v + f_{xc}^{(2)})\chi$$

## Observation

- BSE is a 4-point equation
- TDDFT is a 2-point equation

# MBPT vs. TDDFT: different maths

## MBPT

$$L = L_0 + L_0(v + \Xi)L$$

## TDDFT

$$\chi = P_0 + P_0(v + f_{xc}^{(2)})\chi$$

## Observation

- BSE is a 4-point equation  $\Rightarrow$  unavoidable
- TDDFT is a 2-point equation  $\Rightarrow$  can be rewritten as 4-point eq.

# TDDFT: 4-point formulation

## Definition

$$\chi = P_0 + P_0(v + f_{xc}^{(2)})\chi$$

⇓

$${}^4\chi = L_0 + L_0(v + F_{xc}){}^4\chi$$

$${}^4\chi(1122) = \chi(12) \quad L_0(1122) = P_0(12)$$

Hamiltonian (Casida) formulation:

$$H_{TDDFT}^{(vc)(v'c')} = (E_c - E_v)\delta_{vv'}\delta_{cc'} + (f_v - f_c)[\langle\langle v \rangle\rangle + \langle\langle f_{xc} \rangle\rangle]$$

# MBPT & TDDFT

## MBPT

$$L = L_0 + L_0(v + \Xi)L$$

## TDDFT

$${}^4\chi = L_0 + L_0(v + F_{xc}){}^4\chi$$

## Combination

$$L = {}^4\chi + {}^4\chi(\Xi - F_{xc})L$$



# $f_{xc}$ kernel

What is the  $f_{xc}$  kernel of TDDFT?

It is the 2-point kernel  $f_{xc}^{(2)}$ :

$$F_{xc}(1234) = f_{xc}^{(2)}(13)\delta(12)\delta(34)$$

that yields equal 2-point polarizabilities:

$${}^4\chi(1122) = \chi(12) = L(1122)$$

# $f_{xc}$ kernel

## Exact $f_{xc}$

$$L(1234) = {}^4\chi(1234) + {}^4\chi(1256)[\Xi(5678) - f_{xc}^{(2)}(57)\delta(56)\delta(78)]L(7834)$$

# $f_{xc}$ kernel

## Exact $f_{xc}$

$$L(1234) = {}^4\chi(1234) + {}^4\chi(1256)[\Xi(5678) - f_{xc}^{(2)}(57)\delta(56)\delta(78)]L(7834)$$

$$L(1122) = {}^4\chi(1122) + {}^4\chi(1156)[\Xi(5678) - f_{xc}^{(2)}(57)\delta(56)\delta(78)]L(7822)$$

$f_{xc}$  kernelExact  $f_{xc}$ 

$$L(1234) = {}^4\chi(1234) + {}^4\chi(1256)[\Xi(5678) - f_{xc}^{(2)}(57)\delta(56)\delta(78)]L(7834)$$

$$L(1122) = {}^4\chi(1122) + {}^4\chi(1156)[\Xi(5678) - f_{xc}^{(2)}(57)\delta(56)\delta(78)]L(7822)$$

Since  $L(1122) = {}^4\chi(1122) = \chi(12)$ :

$$0 = {}^4\chi(1156)[\Xi(5678) - f_{xc}^{(2)}(57)\delta(56)\delta(78)]L(7822)$$

... solve for  $f_{xc}^{(2)}$

# $f_{xc}$ kernel

Exact  $f_{xc}$

$$f_{xc}^{(2)}(34) = \chi^{-1}(31)^4 \chi(1156) \Xi(5678) L(7822) \chi^{-1}(24)$$

# The Nanoquanta kernel

## Approximations

- 1 usual BSE implementation:  $\Xi(1234) = -W(12)\delta(13)\delta(24)$
- 2 first-order linearizations:  
 $\chi(12) = P_0(12)$  and  $L(1233) = \chi(1233) = -iG(13)G(32)$

## Nanoquanta $f_{xc}$

$$f_{xc}^{(2)}(34) = P_0^{-1}(31)G(15)G(61)W(56)G(52)G(26)P_0^{-1}(24)$$

# The Nanoquanta kernel

## Approximations

- 1 usual BSE implementation:  $\Xi(1234) = -W(12)\delta(13)\delta(24)$
- 2 first-order linearizations:  
 $\chi(12) = P_0(12)$  and  $L(1233) = \chi(1233) = -iG(13)G(32)$

## Nanoquanta $f_{xc}$

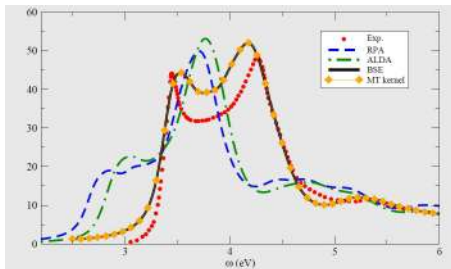
$$f_{xc}^{(2)}(34) = P_0^{-1}(31)G(15)G(61)W(56)G(52)G(26)P_0^{-1}(24)$$

## Observations

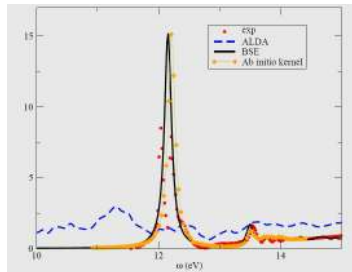
- $f_{xc}$  is "ultranonlocal"
- $f_{xc}$  is frequency dependent ("memory") – but  $W$  is static...

# The Nanoquanta kernel

## Bulk Silicon



## Solid Argon

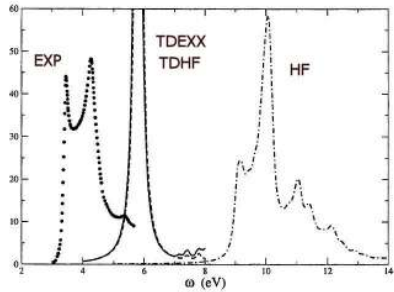


Reviewed in S. Botti *et al.* Rep. Prog. Phys. **70** (2007).



# TDEXX

### Bulk Silicon



TDEXX misses long-range screening

F. Bruneval, F. Sottile, V. Olevano, and L. Reining, JCP **124** (2006).

# Many thanks!

