

Introduction to the Bethe-Salpeter equation for excitons

Matteo Gatti and you all present

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

RASESMA 2023 - TU Kenya - Nairobi



References



[G. Strinati](#)

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



[M. Rohlfing and S. G. Louie](#)

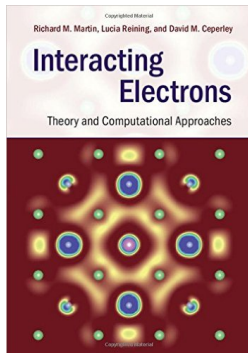
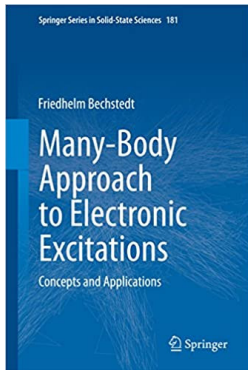
Phys. Rev. B **62**, 4927 (2000).



[G. Onida, L. Reining, and A. Rubio](#)

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

Books



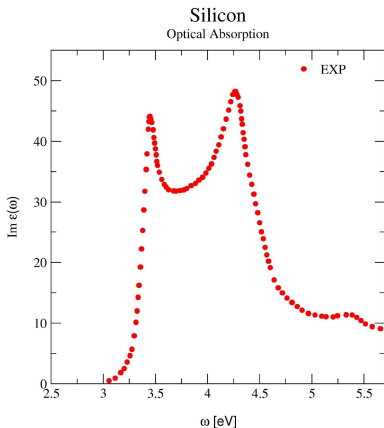
Outline

- 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

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

Theoretical Spectroscopy

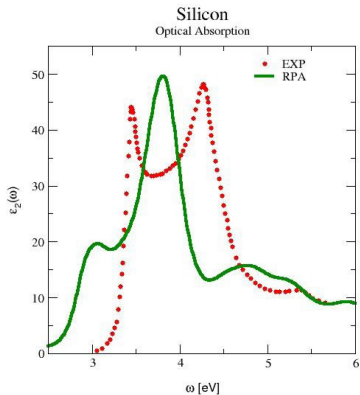
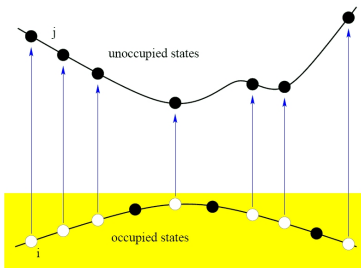
- Which kind of spectra?
- Which kind of tools?



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 $\Sigma = iGW$:

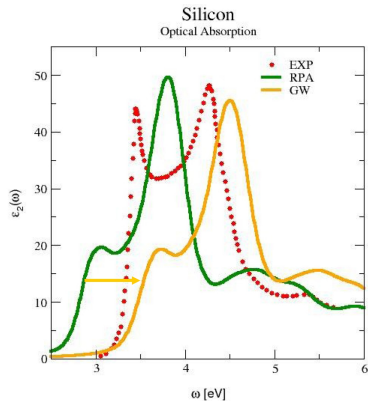
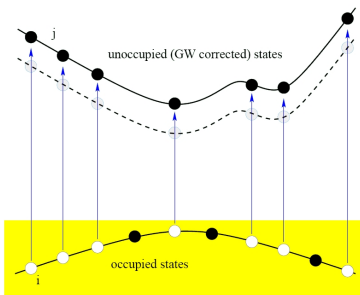
$$E_i - \epsilon_i = \langle \varphi_i | \Sigma - V_{xc} | \varphi_i \rangle$$

Hybersten and Louie, PRB **34** (1986);
 Godby, Schlüter and Sham, PRB **37** (1988)

Independent (quasi)particles: GW

Independent transitions:

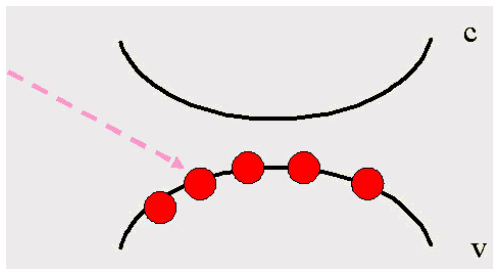
$$\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle \varphi_j | \mathbf{e} \cdot \mathbf{v} | \varphi_i \rangle|^2 \delta(E_j - E_i - \omega)$$



What is wrong?

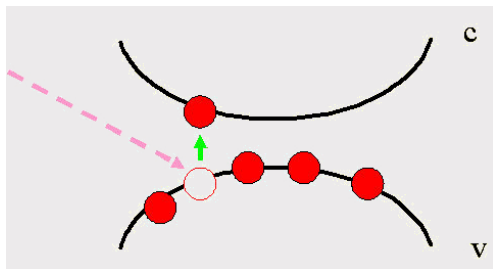
What is missing?

Absorption



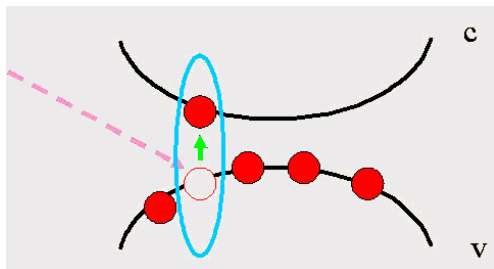
Two-particle excitations $\rightarrow$ poles of two-particle Green's function
 Excitonic effects = electron - hole interaction

Absorption



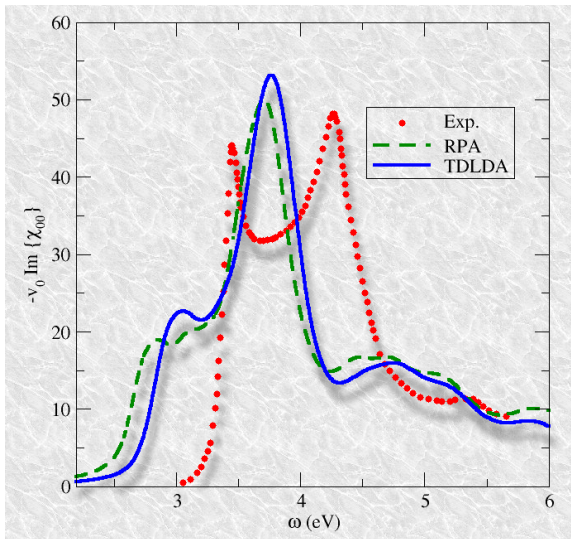
Two-particle excitations $\rightarrow$ poles of two-particle Green's function
 Excitonic effects = electron - hole interaction

Absorption



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

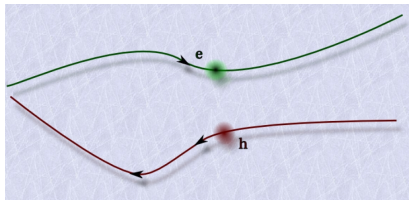
Why do we have to study more than TDDFT?



Bulk silicon: absorption

Two-particle correlation function L

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

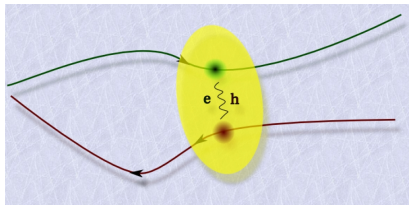


Independent particles

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:

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

MBPT

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

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

TDDFT vs. MBPT

TDDFT

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

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

- Dyson equation:

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

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

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

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

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

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

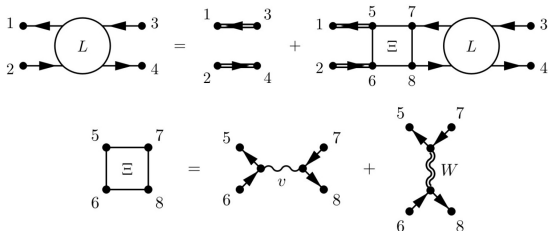
F. Bechstedt *et al.* Phys. Rev. Lett. **78** (1997).

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_{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

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

How to solve it?

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: $(n_1 n_2) = (v \mathbf{k} c \mathbf{k}) \Rightarrow (vc)$

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

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

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

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

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

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

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

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

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 φ_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_λ, E_λ

⇒ 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

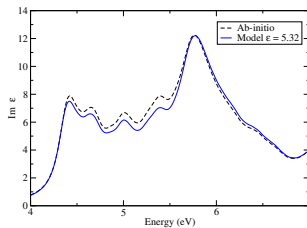
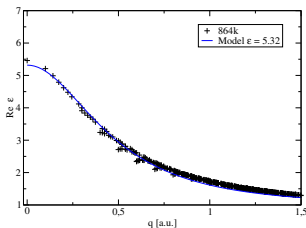
$$L(1234) = L_0(1234) + L_0(1256)[v(57)\delta(56)\delta(78) - v(56)\delta(57)\delta(68)]L(7834)$$

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

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

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

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):

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

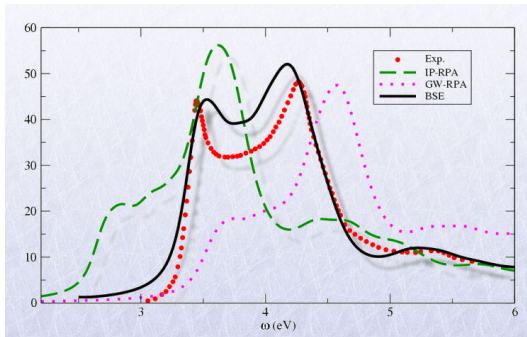
$$\langle vc | f_{xc} | v' c' \rangle = 2 \int dr_1 dr_2 \phi_v(r_1) \phi_c^*(r_1) f_{xc}(r_1, r_2) \phi_{v'}^*(r_2) \phi_{c'}(r_2)$$

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

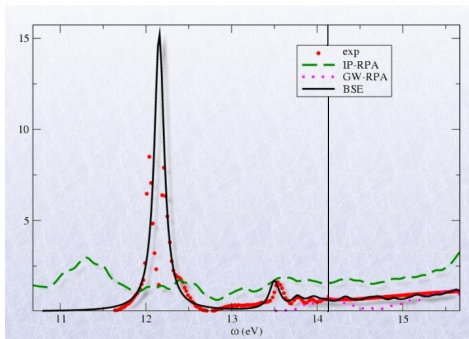


G. Onida, L. Reining, and A. Rubio, RMP **74** (2002).

Bound excitons

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

Solid argon

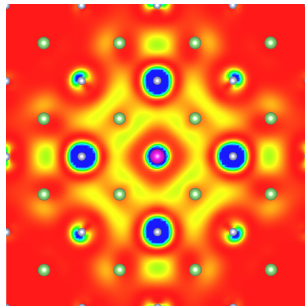
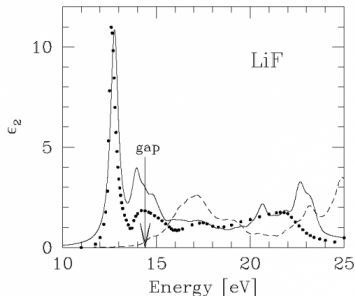


F. Sottile *et al.* PRB **76** (2007).

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 $|\Psi_{\lambda}(\bar{\mathbf{r}}_h, \mathbf{r}_e)|^2$

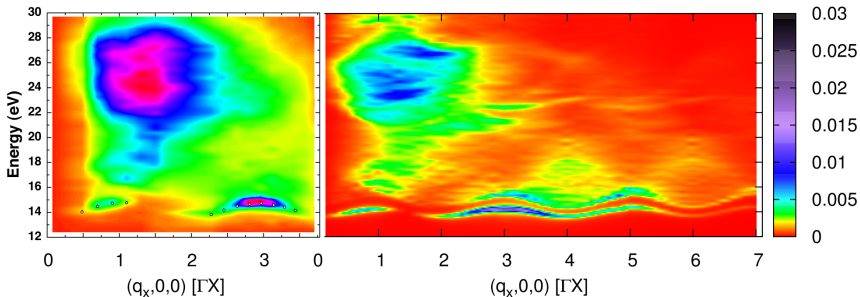


Exciton dispersion: IXS

Lithium Fluoride

Experiment

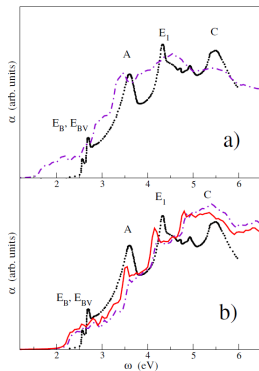
Theory



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: Cu_2O



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

Finite systems: atoms and molecules

Molecular systems

Calculations of vertical excitation energies E_λ from full BSE matrix

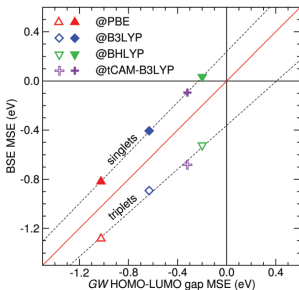
$$\begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix} \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix} = E_\lambda \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix}$$

- 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

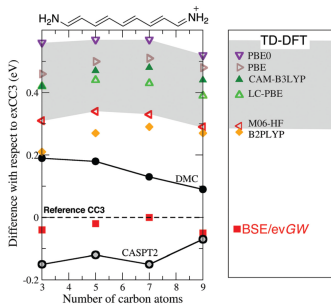
Mean-signed errors for Thiel's set



F. Bruneval *et al.*

J. Chem. Phys. **142** (2015).

Errors for streptocyanine chains

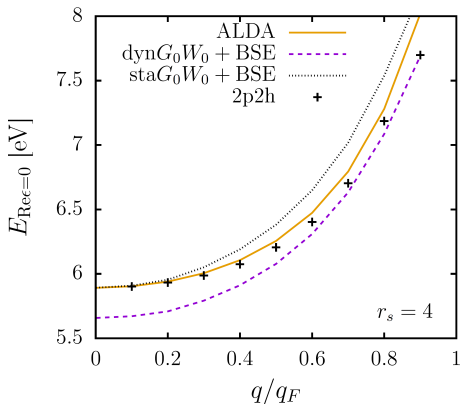


P. Boulanger *et al.*

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)

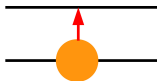
P. Romaniello *et al.*, J. Chem. Phys. **130** (2009); D. Sangalli *et al.*, J. Chem. Phys. **134** (2011); E. Rebolini and J. Toulouse, J. Chem. Phys. **144** (2016); V. Olevano, J. Toulouse, and P. Schuck, J. Chem. Phys. **150** (2019).

Missing dynamical effects

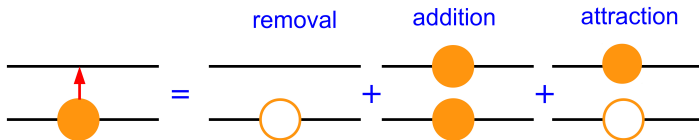
Beyond static BSE

- 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?



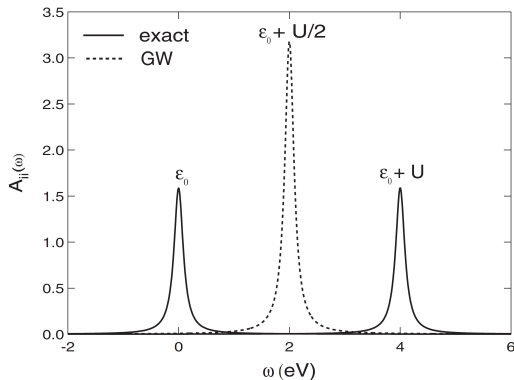
One electron limit: A detour?



Perfect cancellation

One electron limit: A detour?

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

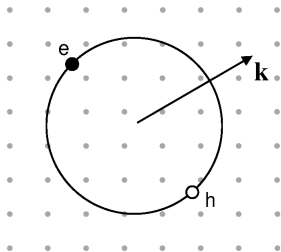


Outline

- 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

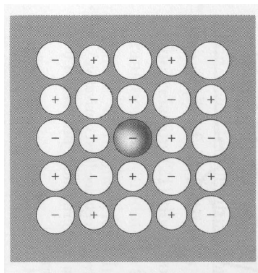
Wannier exciton



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

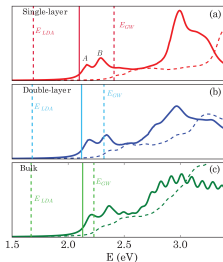
$$W(\mathbf{r}, \mathbf{r}') = \frac{1}{\epsilon|\mathbf{r} - \mathbf{r}'|}$$

- 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

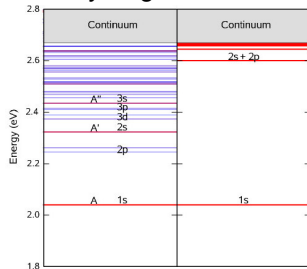
Larger binding energy



MoS₂ absorption spectrum

A. Molina Sanchez *et al.*, PRB **88** (2013). E.g. A. Chernikov *et al.*, PRL **113** (2014).

Non-hydrogenic series



Exciton energies

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

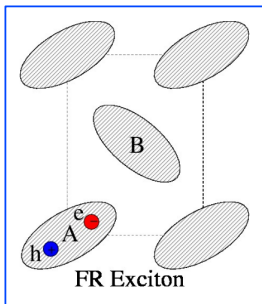
L.V. Keldysh, JETP Lett. **29** (1979); P. Cudazzo, I.V. Tokatly, A. Rubio, PRB **84** (2011).

Frenkel and charge transfer excitons

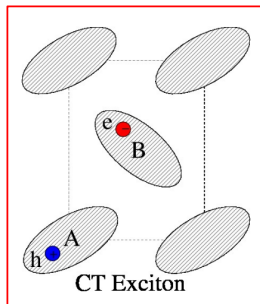
When electrons are localised
(wavefunctions with small overlap)

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

Frenkel exciton



Charge transfer exciton

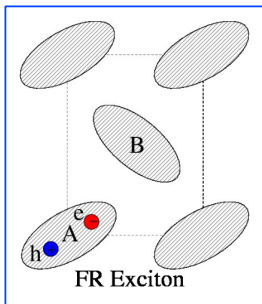


Frenkel and charge transfer excitons

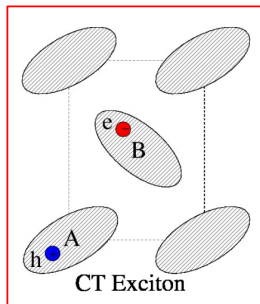
When electrons are localised
(wavefunctions with small overlap)

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

Frenkel exciton



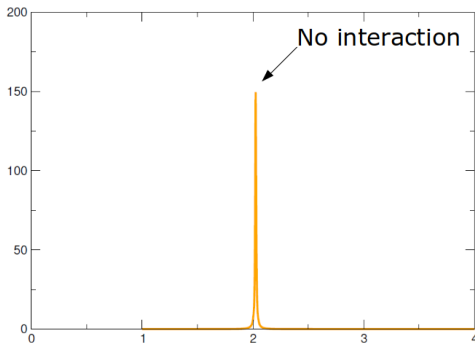
Charge transfer exciton



Frenkel and charge transfer excitons

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

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

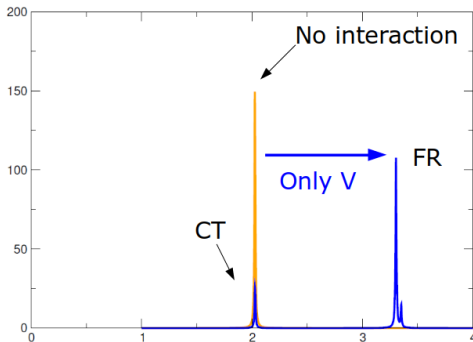


Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).

Frenkel and charge transfer excitons

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

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



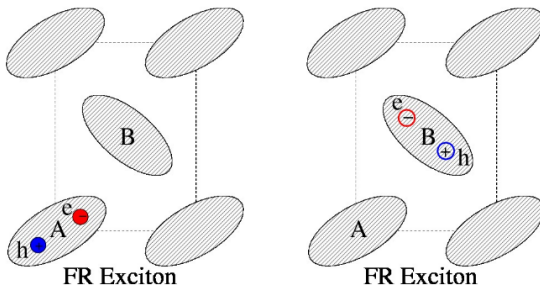
Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).

Frenkel and charge transfer excitons

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

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

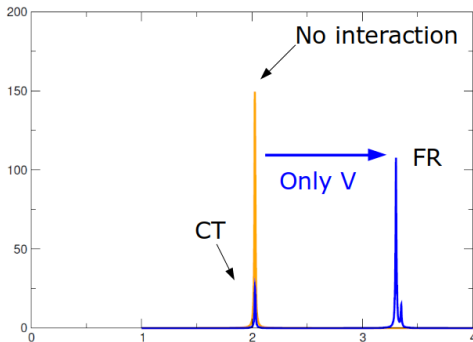
Frenkel exciton & Davydov splitting



Frenkel and charge transfer excitons

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

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

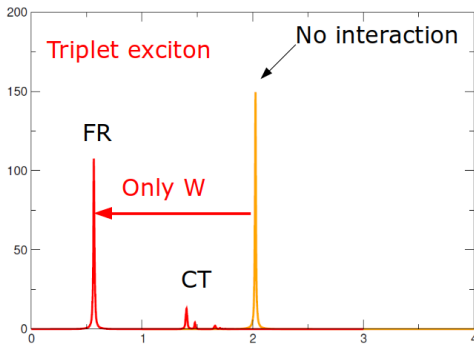


Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).

Frenkel and charge transfer excitons

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

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

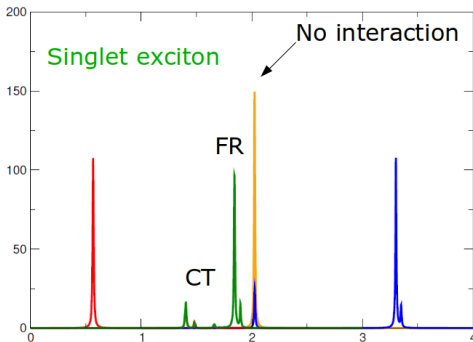


Reviewed in P. Cudazzo *et al.* J. Phys.: Condens. Matter **27** (2015).

Frenkel and charge transfer excitons

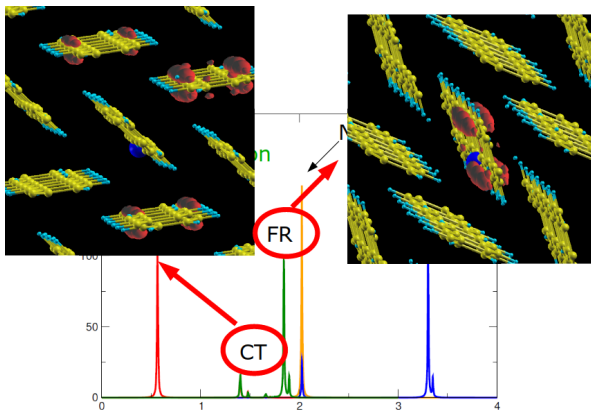
$$E_{FR}^{\pm} = \Delta\epsilon + I \pm J - W$$

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



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

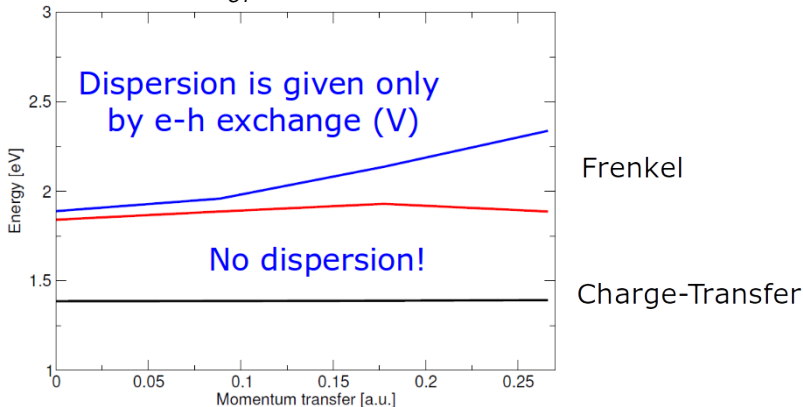
$$E_\lambda(\mathbf{q}) = E_\lambda^{ii} + \sum_j e^{i\mathbf{q}(\mathbf{R}_j - \mathbf{R}_i)} E_\lambda^{jj}$$

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

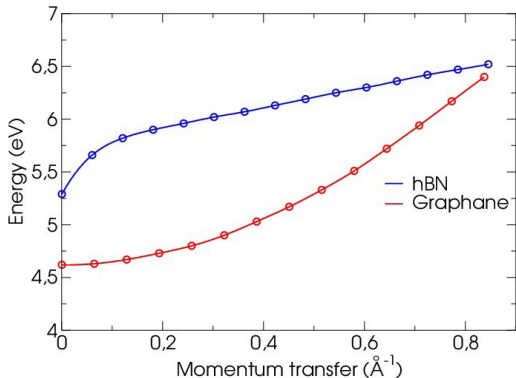
Exciton dispersion: Frenkel and charge transfer

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

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



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

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

TDDFT

$$\chi = \chi_0 + \chi_0(\nu + f_{xc})\chi$$

MBPT vs. TDDFT: different electrons

MBPT

$$L = L_0 \quad \Rightarrow \quad \text{GW energies}$$

TDDFT

$$\chi = \chi_0 \quad \Rightarrow \quad \text{Kohn-Sham energies}$$

Observation

f_{xc} has 2 tasks:

- bandgap opening ($\rightarrow$ GW)
- excitonic effects ($\rightarrow$ BSE)

f_{xc} kernel

Definitions

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

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

f_{xc} kernel

Definitions

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

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

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

$f_{xc}^{(1)} \Rightarrow$ 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

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

$$\Downarrow$$

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

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

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

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

TDDFT

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

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} kernel

Exact f_{xc}

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

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

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}

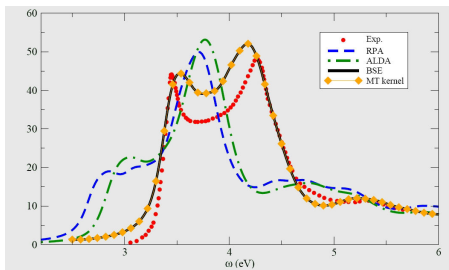
$$f_{xc}^{(2)}(34) = P_0^{-1}(31)G(15)G(61)W(56)G(52)G(26)P_0^{-1}(24)$$

Observations

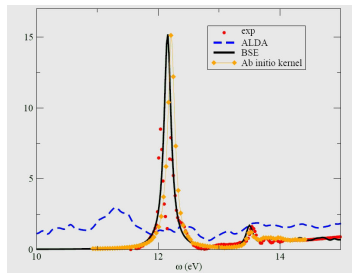
- f_{xc} is "ultranonlocal"
- f_{xc} is frequency dependent ("memory") – but W is static...

The Nanoquanta kernel

Bulk Silicon



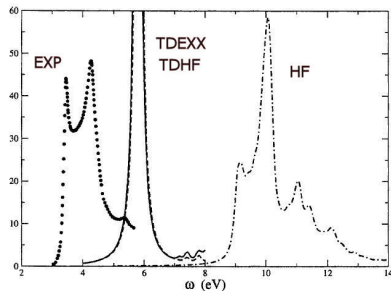
Solid Argon



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!

