Introduction to the Bethe-Salpeter equation

Matteo Gatti

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

ISTPC 2017 - Aussois

Outline

1. Motivations
2. The Bethe-Salpeter: basic theory
3. The Bethe-Salpeter in practice
4. Prototypical results

References

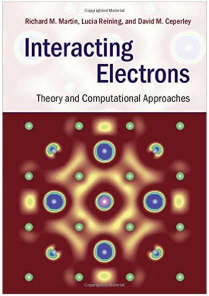
G. Strinati
Rivista del Nuovo Cimento **11**, (12)1 (1988).

M. Rohlfing and S. G. Louie
Phys. Rev. B **62**, 4927 (2000).

Giovanni Onida, Lucia Reining, and Angel Rubio
Rev. Mod. Phys. **74**, 601 (2002).

References

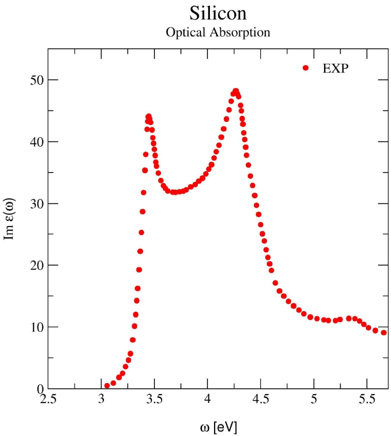
Richard M. Martin, Lucia Reining, David M. Ceperley
Interacting electrons: theory and computational approaches
(Cambridge University Press, 2016)



Outline

1. Motivations
2. The Bethe-Salpeter: basic theory
3. The Bethe-Salpeter in practice
4. Prototypical results

Motivation



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

Theoretical spectroscopy

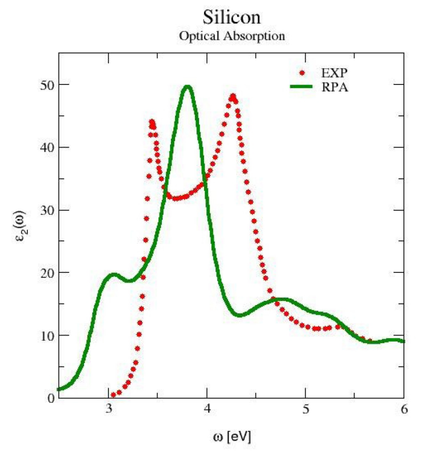
- Calculate and reproduce
- Understand and explain
- Predict

Theoretical Spectroscopy

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

Why do we have to study more than (TD)DFT?

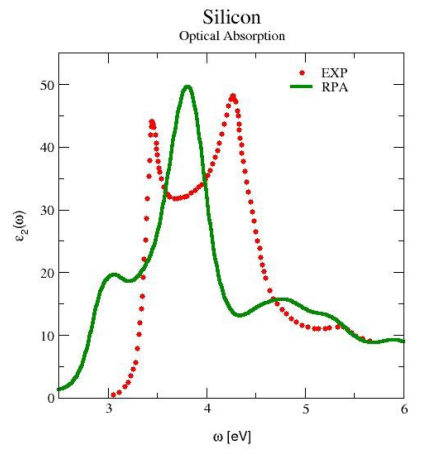
Absorption spectrum of bulk silicon in DFT



How can we understand this?

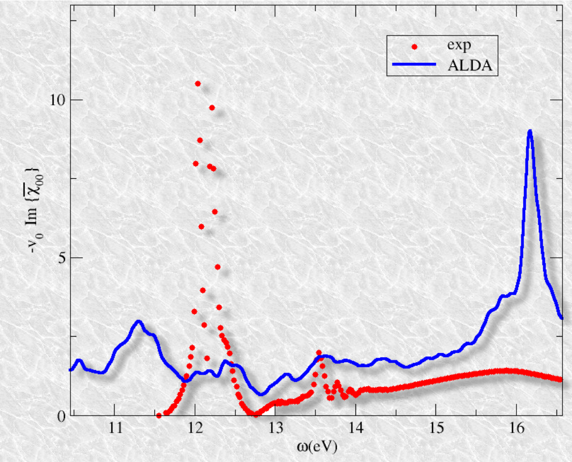
Why do we have to study more than (TD)DFT?

Absorption spectrum of bulk silicon in DFT



Spectroscopy is exciting!

Why do we have to study more than (TD)DFT?



Solid argon: absorption

MBPT vs. TDDFT: different worlds, same physics

MBPT

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

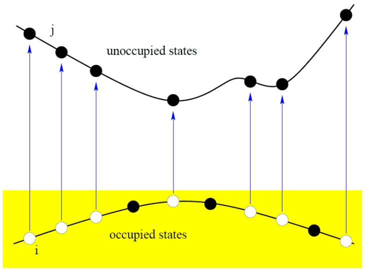
TDDFT

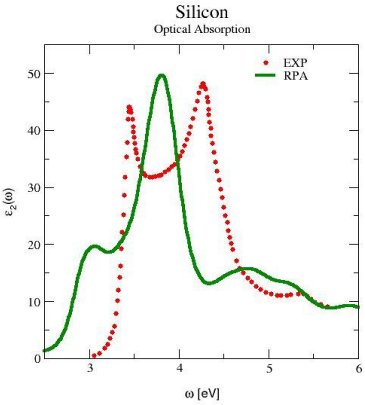
- based on the density
- response function χ: neutral excitations
- moves density around
- is efficient (simple)

Independent particles: Kohn-Sham

Independent transitions:

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





GW corrections

Standard perturbative G_0W_0

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

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

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

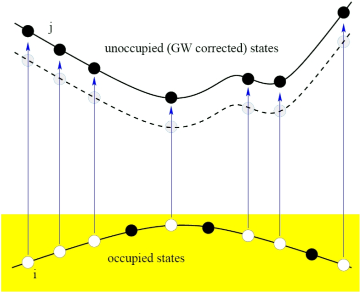
$$E_i - \epsilon_i = \langle\varphi_i|\Sigma - V_{xc}|\varphi_i\rangle$$

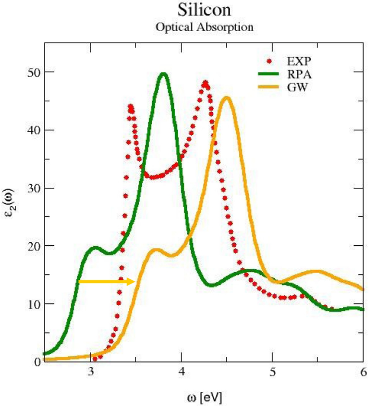
Hybersten and Louie, PRB **34** (1986);
Godby, Schlüter and Sham, PRB **37** (1988)

Independent (quasi)particles: GW

Independent transitions:

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



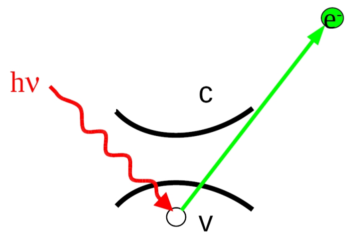


What is wrong?

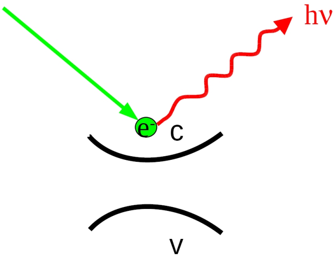
What is missing?

Photoemission: one-particle Green's function

Direct Photoemission



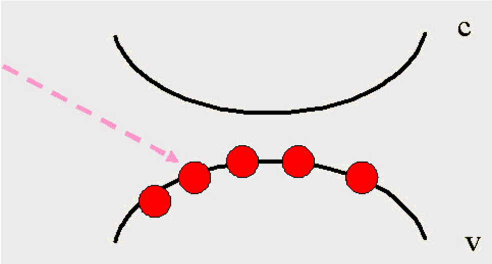
Inverse Photoemission



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

GW approximation

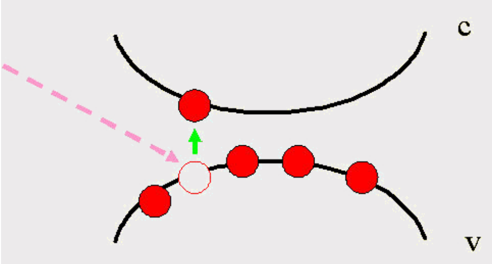
Absorption: two-particle Green's function



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

Excitonic effects = electron - hole interaction

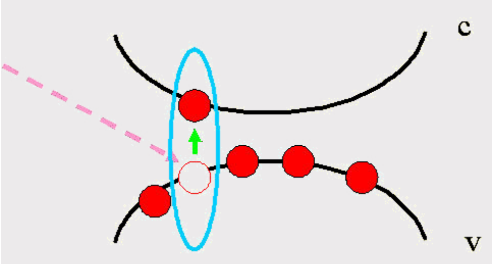
Absorption: two-particle Green's function



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

Excitonic effects = electron - hole interaction

Absorption: two-particle Green's function



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

Excitonic effects = electron - hole interaction

Outline

1. Motivations
2. The Bethe-Salpeter: basic theory
3. The Bethe-Salpeter in practice
4. Prototypical results

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:

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

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:

$$L(1234) = L_0(1234) + \int d5678L_0(1256)\left[v(57)\delta(56)\delta(78) + i\frac{\delta\Sigma(56)}{\delta G(78)}\right]L(7834)$$

TDDFT - MBPT connection

The connection

$$-iG(11) = \rho(1) \quad \Rightarrow \quad L(1122) = \chi(12)$$

Reminder: Dyson equation

Dyson equation

$$G(12) = G_0(12) + \int d34 G_0(13)[\Sigma(34) + V_{ext}(34)]G(42)$$

where G_0 is the Hartree Green's function:

$$G_0(\omega) = (\omega - H_0)^{-1} \Rightarrow G_0^{-1}(\omega) = (\omega - H_0)$$

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

From now on: integration over repeated variables is understood

Reminder: Dyson equation

Dyson equation

$$G(12) = G_0(12) + \int d34 G_0(13)[\Sigma(34) + V_{ext}(34)]G(42)$$

where G_0 is the Hartree Green's function:

$$G_0(\omega) = (\omega - H_0)^{-1} \Rightarrow G_0^{-1}(\omega) = (\omega - H_0)$$

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

From now on: integration over repeated variables is understood

Exercise

$$G^{-1}(12) = G_0^{-1}(12) - \Sigma(12) - V_{ext}(12)$$

The Bethe-Salpeter equation

Exercise

Formal derivation

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

$$= +iG(15)\frac{\delta[G_0^{-1}(56) - V_{ext}(56) - \Sigma(56)]}{\delta V_{ext}(34)}G(62)$$

$$= -iG(13)G(42) + iG(15)G(62)\left[\frac{\delta V_H(5)\delta(56)}{\delta V_{ext}(34)} - \frac{\delta\Sigma(56)}{\delta V_{ext}(34)}\right]$$

$$= -iG(13)G(42) + iG(15)G(62)\left[\frac{\delta V_H(5)\delta(56)}{\delta G(78)} - \frac{\delta\Sigma(56)}{\delta G(78)}\right]\frac{\delta G(78)}{\delta V_{ext}(34)}$$

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

The Bethe-Salpeter equation

Approximations

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

The Bethe-Salpeter equation

Approximations

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

Approximation:

$\Sigma \approx iGW$

The Bethe-Salpeter equation

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

Approximations

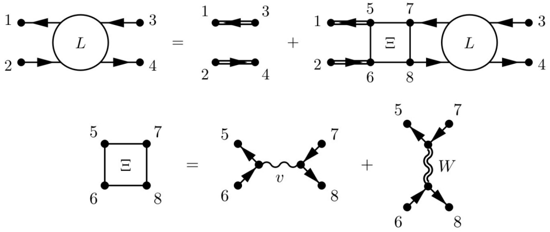
Final result:

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

The Bethe-Salpeter equation

Bethe-Salpeter equation

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



Time-dependent Hartree-Fock

Bethe-Salpeter equation

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

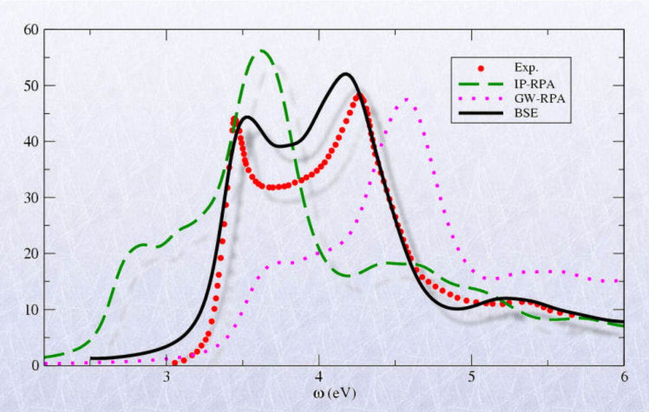
Time-dependent Hartree-Fock

Bethe-Salpeter equation

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

Absorption spectra in BSE

Bulk silicon



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

Outline

1 Motivations

2 The Bethe-Salpeter: basic theory

3 The Bethe-Salpeter in practice

4 Prototypical results

Absorption

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

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

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

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

EELS

$$\mathrm{Eels}(\omega) = -\lim_{\mathbf{q}\to 0} \mathrm{Im}[1/\epsilon_M(\mathbf{q},\omega)]$$

$$\mathrm{Eels}(\omega) = -\lim_{\mathbf{q}\to 0} \mathrm{Im}\left[v_{\mathbf{G}=0}(\mathbf{q})\chi_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)\right]$$

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

Eels $\rightarrow$ response to V_{ext}

Solving BSE

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

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

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

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

Solving BSE

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

How to solve it?

Solving BSE

$$\bar{L}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4\omega) = L_0(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\mathbf{r}_4\omega) + \int d\mathbf{r}_5 d\mathbf{r}_6 d\mathbf{r}_7 d\mathbf{r}_8\, L_0(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_5\mathbf{r}_6\omega)\times$$

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

How to solve it?

Transition space

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

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

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

Solving BSE

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

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

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

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

Independent (quasi)particles

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

Excitonic effects

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

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

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

BSE calculations

A three-step method

1. LDA calculation
   $\Rightarrow$ Kohn-Sham wavefunctions φ_i
2. GW calculation
   $\Rightarrow$ GW energies E_i and screened Coulomb interaction W
3. BSE calculation

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

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

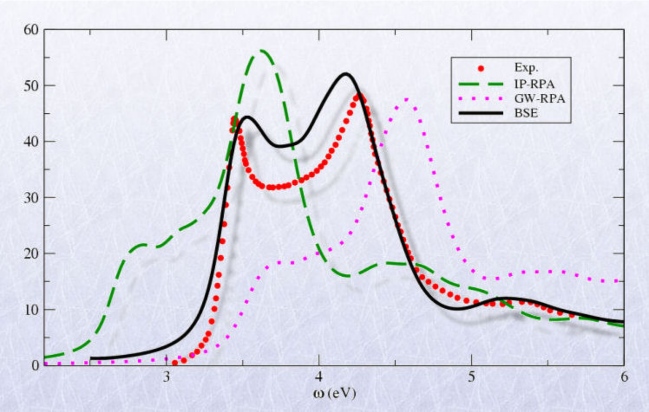
   $\Rightarrow$ excitonic eigenstates A_λ, E_λ
   $\Rightarrow$ spectra $\epsilon_M(\omega)$

Outline

1. Motivations
2. The Bethe-Salpeter: basic theory
3. The Bethe-Salpeter in practice
4. Prototypical results

Continuum excitons

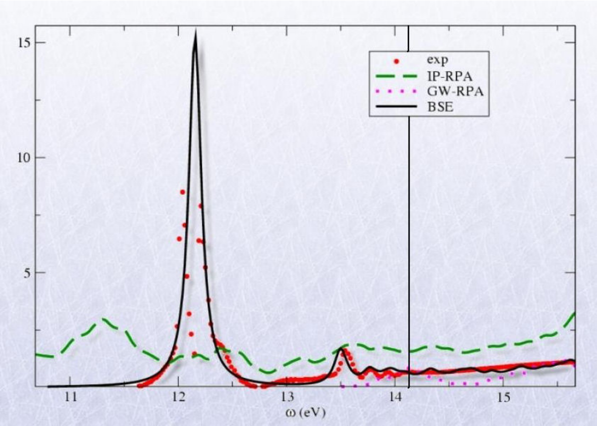
Bulk silicon



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

Bound excitons

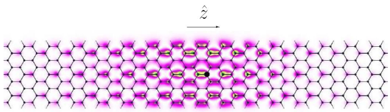
Solid argon



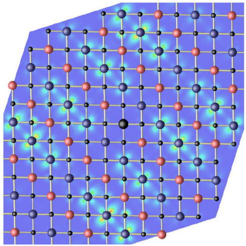
F. Sottile, M. Marsili, V. Olevano, and L. Reining, PRB **76** (2007).

Exciton analysis

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



Graphene nanoribbon



Manganese Oxide

D. Prezzi, *et al.*, PRB **77** (2008).

C. Rödl, *et al.*, PRB **77** (2008).

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

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

- 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

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

Many thanks!

Slow Science®

Acknowledgements

- Fabien Bruneval
- Valerio Olevano
- Lucia Reining
- Francesco Sottile