Introduction to Green's functions

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ETSF Users' Meeting and Training Day

Ecole Polytechnique - 22 October 2010

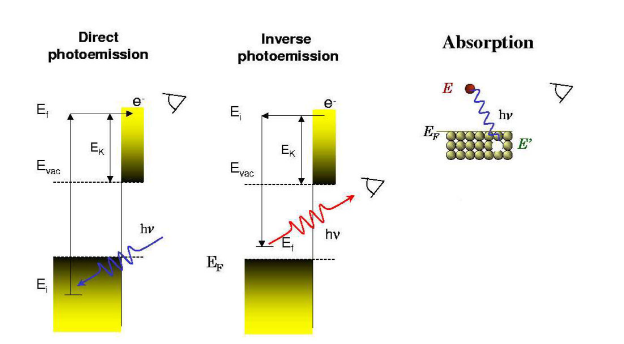
European Theoretical Spectroscopy Facility

Outline

Outline

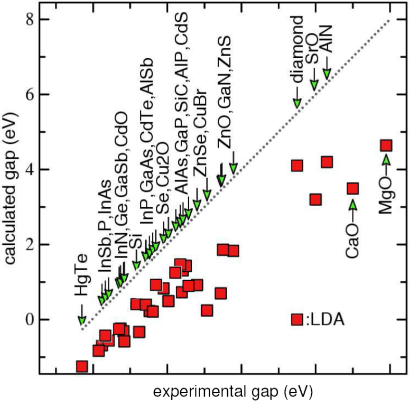
Electronic Spectroscopy

Here only two categories:



1. charged excitations: photoemission and inverse photoemission
2. neutral excitations: absorption and electron energy loss

Why do we have to study more than DFT?



adapted from M. van Schilfgaarde *et al.*, PRL **96** (2006).

MBPT vs. TDDFT: different worlds, same physics

(TD)DFT

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

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)

Table of characters

- Density: local in space and time
  $\rho(\mathbf{r}_1, t_1)$
- Density matrix: non-local in space
  $\gamma(\mathbf{r}_1, \mathbf{r}_2, t)$
- One-particle Green's function: non-local in space and time:
  $G(\mathbf{r}_1, \mathbf{r}_2, t_1, t_2)$

- $G(1,2) \equiv G(\mathbf{r}_1, \mathbf{r}_2, t_1, t_2)$
- $G(\mathbf{r}_1, \mathbf{r}_2, t_1, t_2) = G(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) \Rightarrow G(\mathbf{r}_1, \mathbf{r}_2, \omega)$
- $\rho(\mathbf{r}_1, t_1) = -iG(\mathbf{r}_1, \mathbf{r}_1, t_1, t_1^+)$

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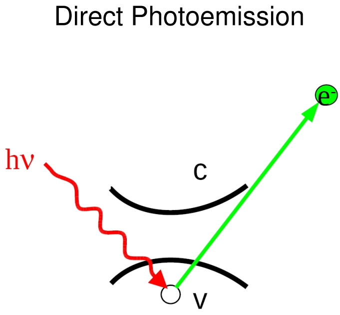
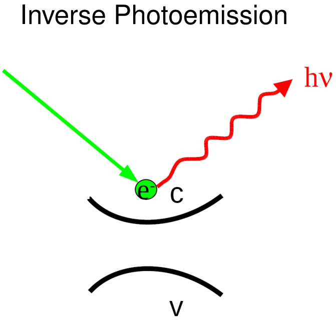
Outline

Photoemission





One-particle Green's function

The one-particle Green's function G

Definition and meaning of G:

$$iG(\mathbf{r_1}, t_1; \mathbf{r_2}, t_2) = \langle N | T\left[\psi(\mathbf{r_1}, t_1)\psi^{\dagger}(\mathbf{r_2}, t_2)\right] | N \rangle$$

$$\text{for} \quad t_1 > t_2 \Rightarrow iG(\mathbf{r_1}, t_1; \mathbf{r_2}, t_2) = \langle N | \psi(\mathbf{r_1}, t_1)\psi^{\dagger}(\mathbf{r_2}, t_2) | N \rangle \tag{1}$$

$$\text{for} \quad t_1 < t_2 \Rightarrow iG(\mathbf{r_1}, t_1; \mathbf{r_2}, t_2) = -\langle N | \psi^{\dagger}(\mathbf{r_2}, t_2)\psi(\mathbf{r_1}, t_1) | N \rangle \tag{2}$$

One-particle Green's function

The one-particle Green's function G

Definition and meaning of G:

$$iG(\mathbf{r_1}, t_1; \mathbf{r_2}, t_2) = \langle N| T \left[\psi(\mathbf{r_1}, t_1)\psi^\dagger(\mathbf{r_2}, t_2)\right] |N\rangle$$

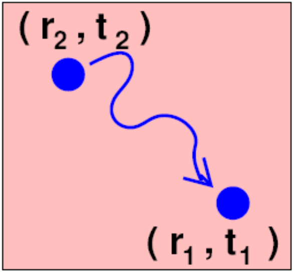
$$\text{for} \quad t_1 > t_2 \Rightarrow iG(\mathbf{r_1}, t_1; \mathbf{r_2}, t_2) = \langle N|\psi(\mathbf{r_1}, t_1)\psi^\dagger(\mathbf{r_2}, t_2)|N\rangle \qquad (1)$$

$$\text{for} \quad t_1 < t_2 \Rightarrow iG(\mathbf{r_1}, t_1; \mathbf{r_2}, t_2) = -\langle N|\psi^\dagger(\mathbf{r_2}, t_2)\psi(\mathbf{r_1}, t_1)|N\rangle \qquad (2)$$

One-particle Green's function

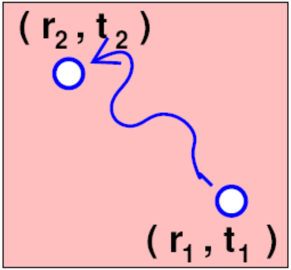
$t_1 > t_2$

$\langle N|\psi(\mathbf{r_1}, t_1)\psi^\dagger(\mathbf{r_2}, t_2)|N\rangle$



$t_1 < t_2$

$-\langle N|\psi^\dagger(\mathbf{r_2}, t_2)\psi(\mathbf{r_1}, t_1)|N\rangle$



One-particle Green's function

What is G ?

Definition and meaning of G:

$$G(\mathbf{r_1}, t_1; \mathbf{r_2}, t_2) = -i < N| T \left[\psi(\mathbf{r_1}, t_1) \psi^\dagger(\mathbf{r_2}, t_2) \right] |N >$$

Insert a complete set of $N+1$ or $N-1$-particle states. This yields

$$\begin{aligned} G(\mathbf{r_1}, t_1; \mathbf{r_2}, t_2) = & -i \sum_j f_j(\mathbf{r_1}) f_j^*(\mathbf{r_2}) e^{-i\varepsilon_j(t_1 - t_2)} \times \\ & \times [\theta(t_1 - t_2)\theta(\varepsilon_j - \mu) - \theta(t_2 - t_1)\Theta(\mu - \varepsilon_j)]; \end{aligned}$$

where:

$$\varepsilon_j = \begin{array}{ll} E(N+1, j) - E(N), & \varepsilon_j > \mu \\ E(N) - E(N-1, j), & \varepsilon_j < \mu \end{array}$$

$$f_j(\mathbf{r_1}) = \begin{array}{ll} \langle N | \psi(\mathbf{r_1}) | N+1, j \rangle, & \varepsilon_j > \mu \\ \langle N-1, j | \psi(\mathbf{r_1}) | N \rangle, & \varepsilon_j < \mu \end{array}$$

One-particle Green's function

What is G? - Fourier transform

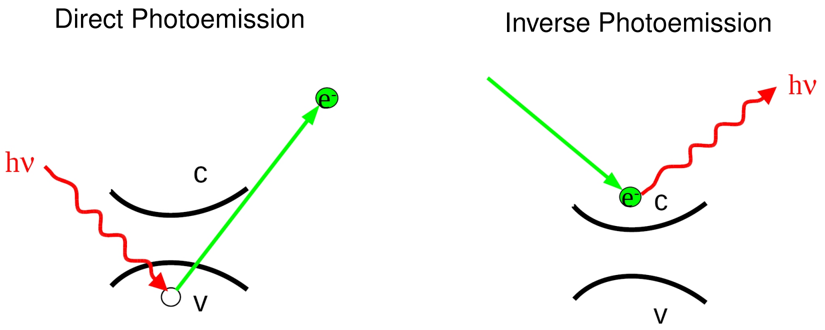
Fourier Transform:

$$G(\mathbf{x},\mathbf{x}',\omega)=\sum_j \frac{f_j(\mathbf{x})f_j^*(\mathbf{x}')}{\omega-\varepsilon_j+i\eta sgn(\varepsilon_j-\mu)}.$$

Spectral function:

$$A(\mathbf{x},\mathbf{x}';\omega)=\frac{1}{\pi}\mid \mathrm{Im}G(\mathbf{x},\mathbf{x}';\omega)\mid=\sum_j f_j(\mathbf{x})f_j^*(\mathbf{x}')\delta(\omega-\varepsilon_j).$$

Photoemission



One-particle excitations → poles of one-particle Green's function G

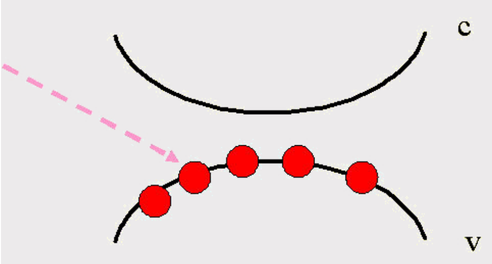
One-particle Green's function

One-particle Green's function

From one-particle G we can obtain:

- one-particle excitation spectra
- ground-state expectation value of any one-particle operator: e.g. density ρ or density matrix γ:
  $\rho(\mathbf{r}, t) = -iG(\mathbf{r}, \mathbf{r}, t, t^{+}) \qquad \gamma(\mathbf{r}, \mathbf{r}', t) = -iG(\mathbf{r}, \mathbf{r}', t, t^{+})$
- ground-state total energy

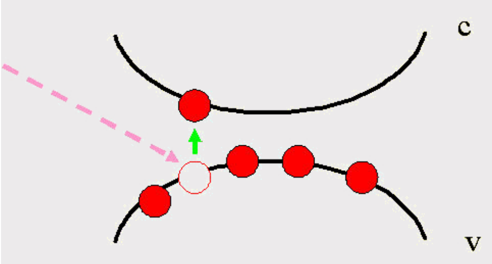
Absorption



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

Excitonic effects = electron - hole interaction

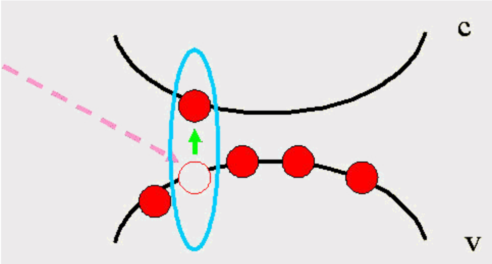
Absorption



Two-particle excitations → poles of two-particle Green's function L

Excitonic effects = electron - hole interaction

Absorption



Two-particle excitations → poles of two-particle Green's function L

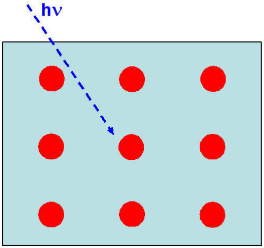
Excitonic effects = electron - hole interaction

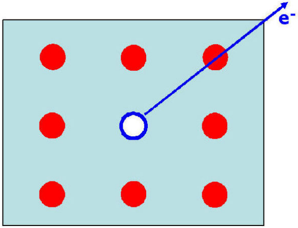
Table of characters

- $G(1,2)$: one-particle Green's function (2 points)
- $L(1,2,3,4)$: two-particle Green's function (4 points)

Outline

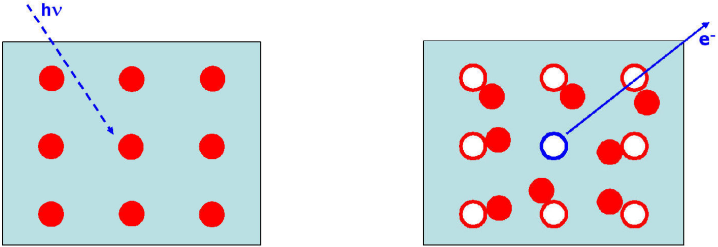
GW bandstructure: photoemission





additional charge →

GW bandstructure: photoemission



additional charge → reaction: polarization, screening

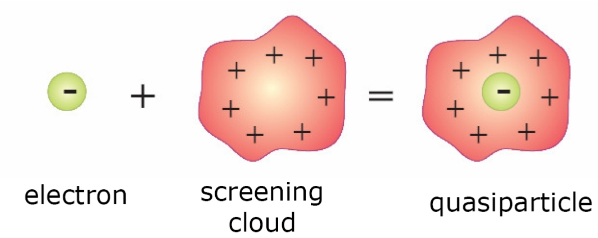
GW approximation

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

L. Hedin, Phys. Rev. **139** (1965)

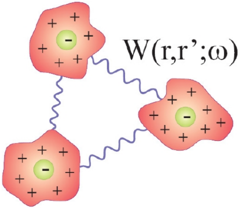
GW and Hartree-Fock

Quasiparticle



GW and Hartree-Fock

Screened potential W



W = screened potential:
weaker than bare Coulomb interaction

$$W(r,r',\omega) = \int dr'' \frac{\varepsilon^{-1}(r,r'',\omega)}{|r''-r'|}$$

GW and Hartree-Fock

Hartree-Fock

$$\Sigma(12) = iG(12)v(1^+2)$$

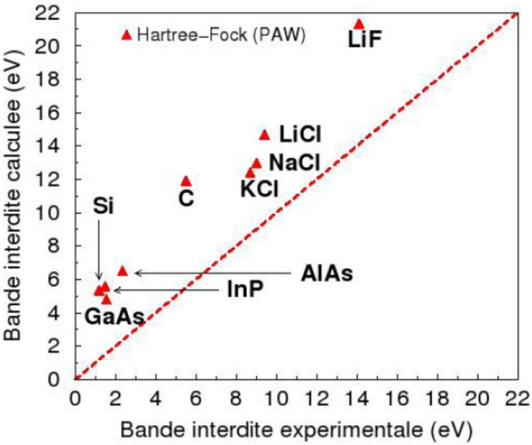
- v infinite range in space
- v is static
- Σ is nonlocal, hermitian, static

GW

$$\Sigma(12) = iG(12)W(1^+2)$$

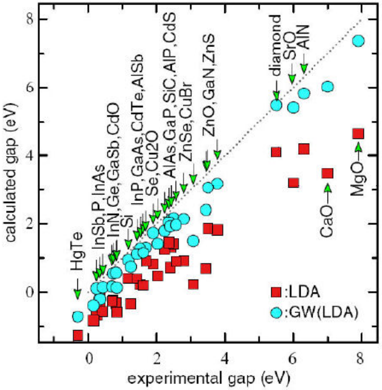
- W is short ranged
- W is dynamical
- Σ is nonlocal, complex, dynamical

GW and Hartree-Fock



from Brice Arnaud

GW and Hartree-Fock



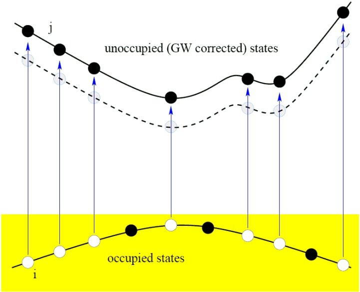
M. van Schilfgaarde *et al.*, PRL **96** (2006).

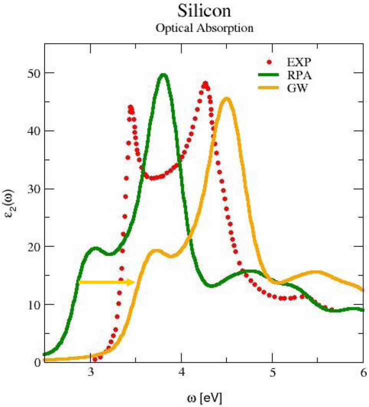
Outline

Independent (quasi)particles: GW

Independent transitions:

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

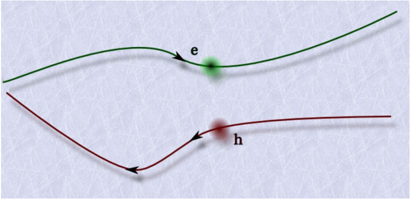




What is wrong?

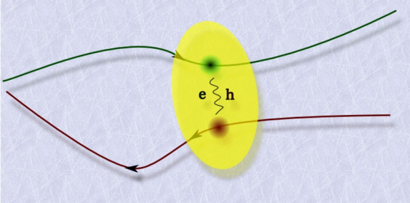
What is missing?

Beyond RPA



Independent particles (RPA)

Beyond RPA



Interacting particles (excitonic effects)

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: the Bethe-Salpeter equation

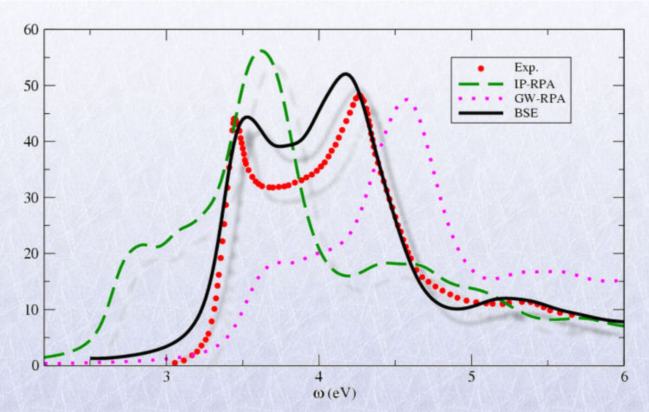
$$[H_{el} + H_{hole} + H_{el-hole}]A_\lambda = E_\lambda A_\lambda$$

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

- 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: $E_c - E_v \to E_\lambda$

Absorption spectra in BSE

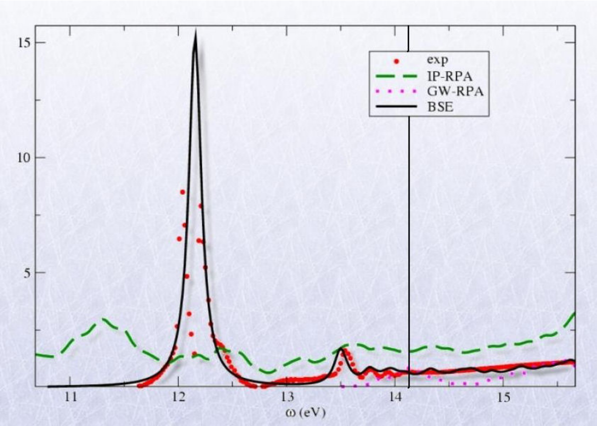
Bulk silicon



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

Bound excitons

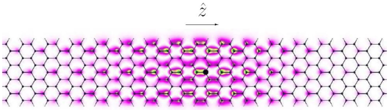
Solid argon



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

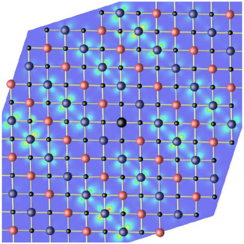
Exciton analysis

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

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



Manganese Oxide

C. Rödl, *et al.*, PRB **77** (2008).

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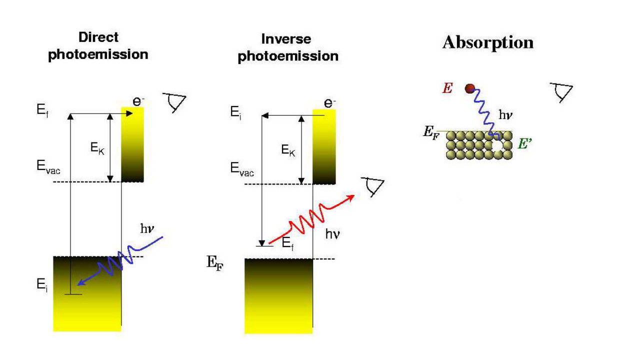

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