# Optical Excitations and Linear Response Theory

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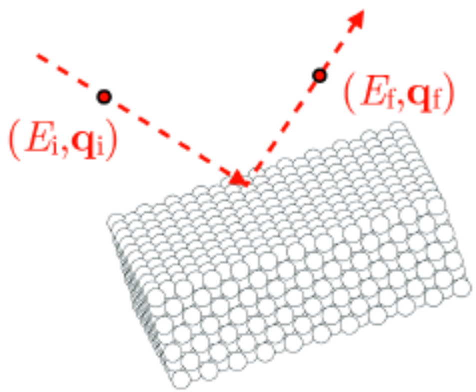

The Kubo Formula

Micro-Macro connection

Diagrams, Schwinger and...density matrix

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# Experimental Motivations

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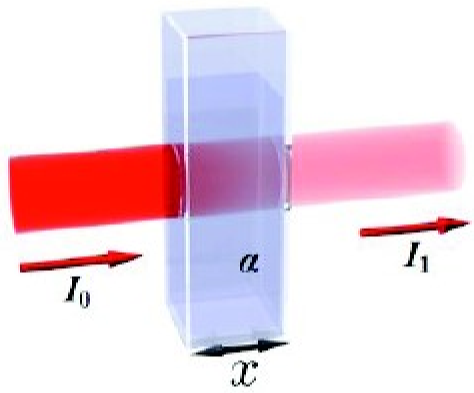
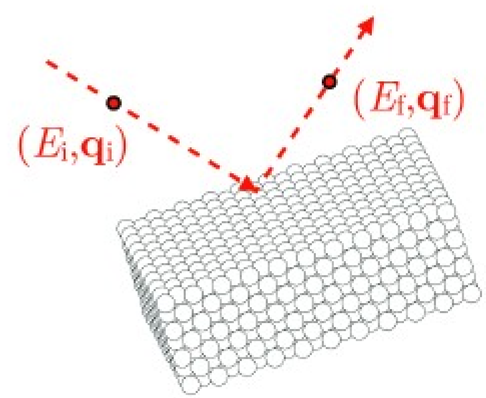
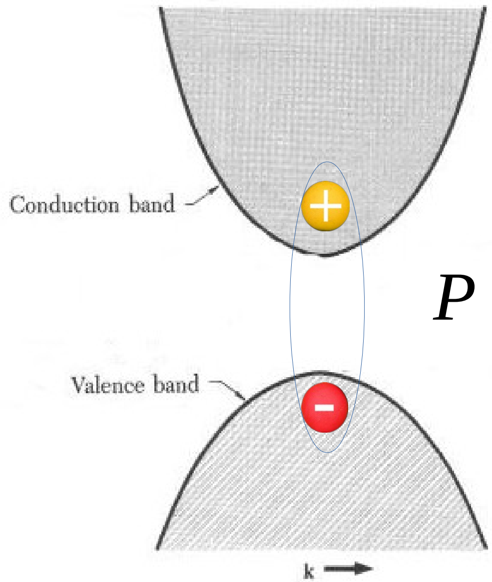



**Transmission**
**Beer-Lambert Law $I=I_0 e^{-\alpha x}$**




**Scattering of electrons or X-Ray**

# Linear (and beyond) Response




**Linear Optics:**

- Weak perturbations

$$P(t)=\chi^1 E(t)+\chi^2 E^2(t)+\ldots$$

polarization. Especially in the linear regime, there are no populations of electrons, holes or excitons at all—that is, the system is unexcited—and a probe beam merely tests the transition possibilities of the system. If you see resonances, as in the case of the pronounced peaks in the linear absorption spectra, this implies that for these frequencies the light–matter coupling is particularly strong. Clearly, in the linear case this cannot have any relation to the possible existence of exciton populations.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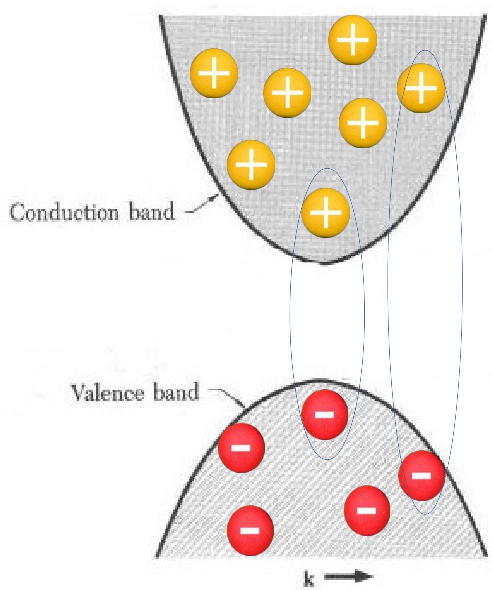
Semiconductor excitons in new light, Nat Mater. 5, 523 (2006)



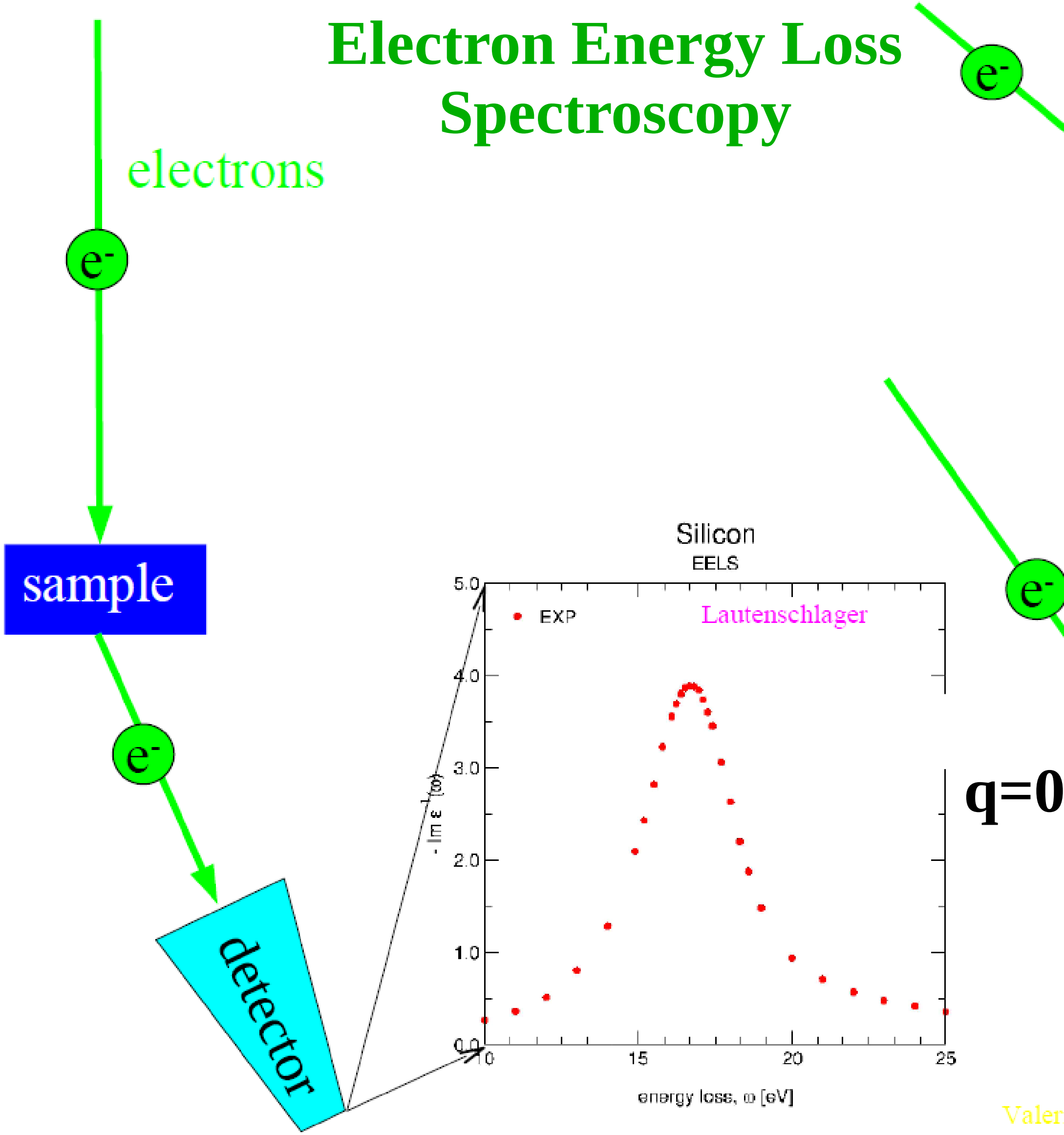

**Non-perturbative phenomena:**

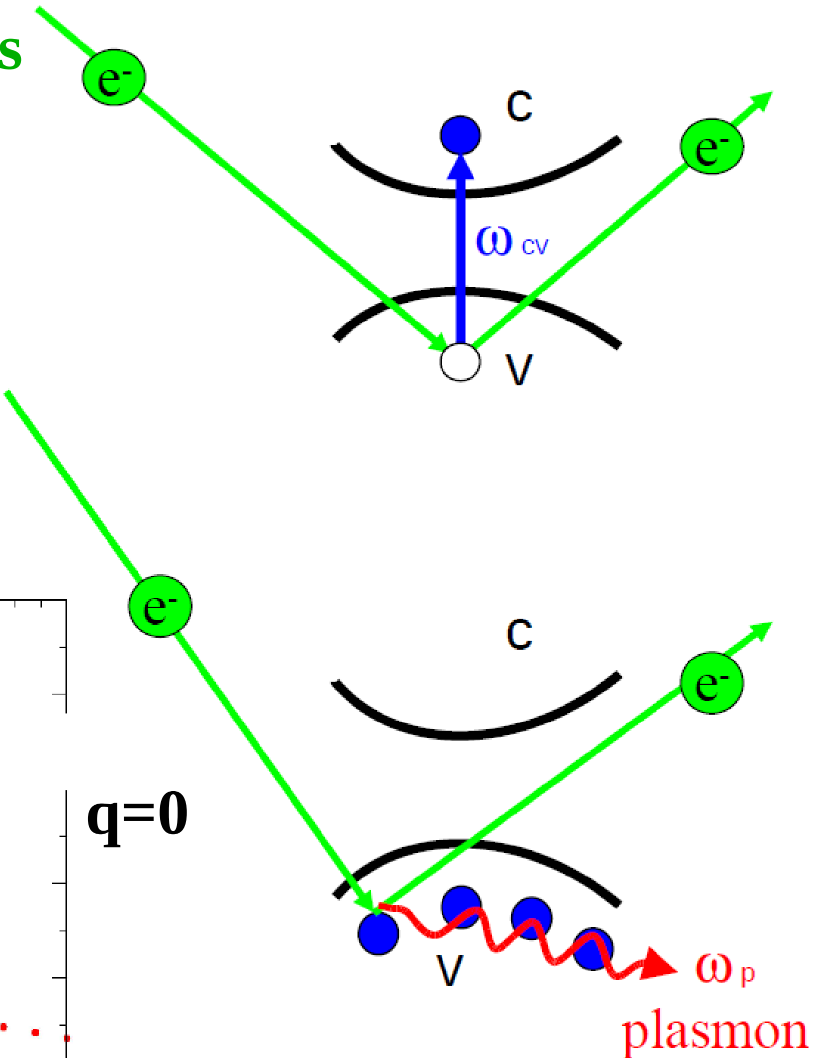
- Arbitrary Strong perturbations
- High carriers density

$$P(t)=\chi^1[E]E(t)+\chi^2[E]E^2(t)+\ldots$$

# EELS, IXSS and absorption

## Electron Energy Loss Spectroscopy

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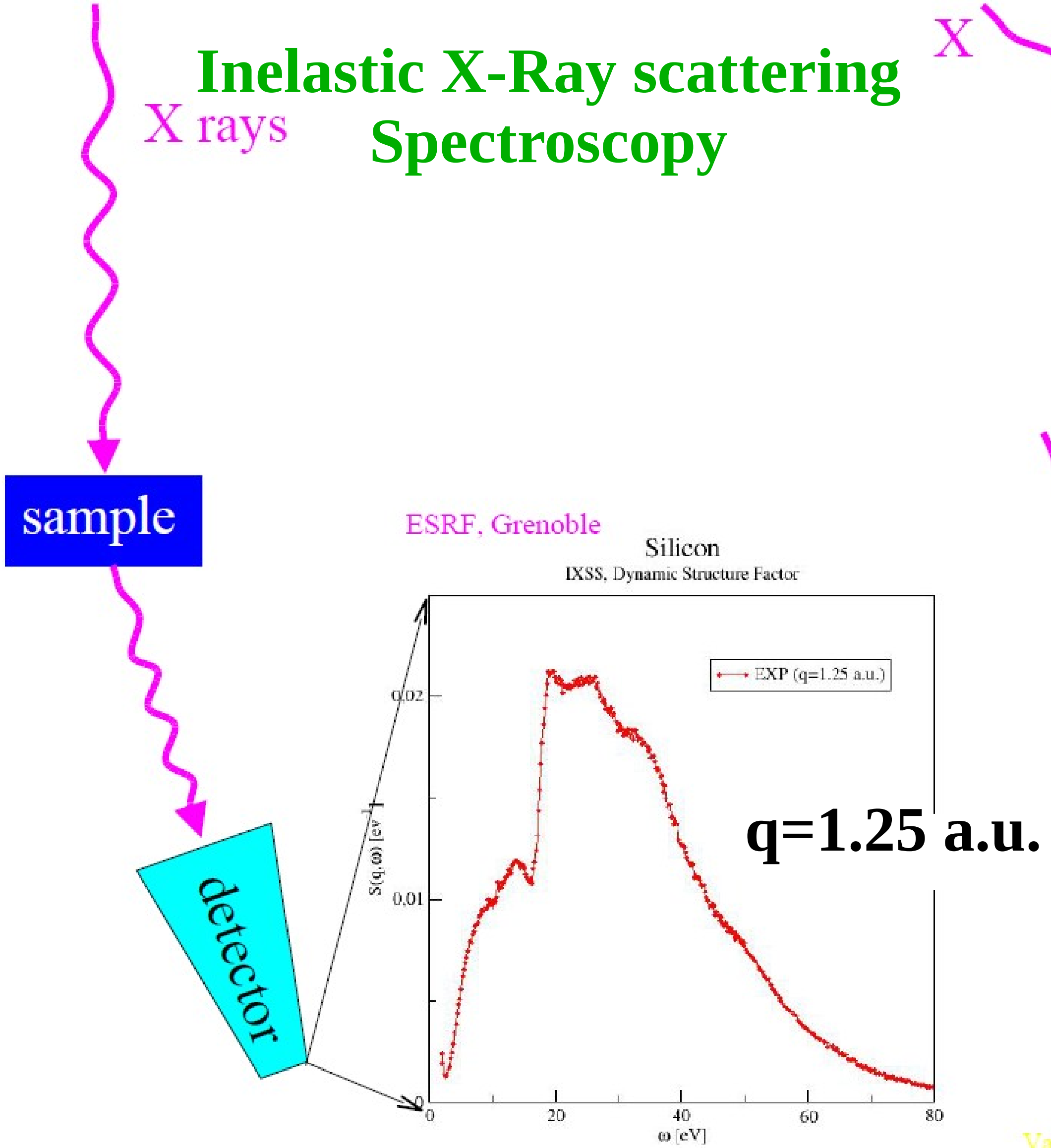
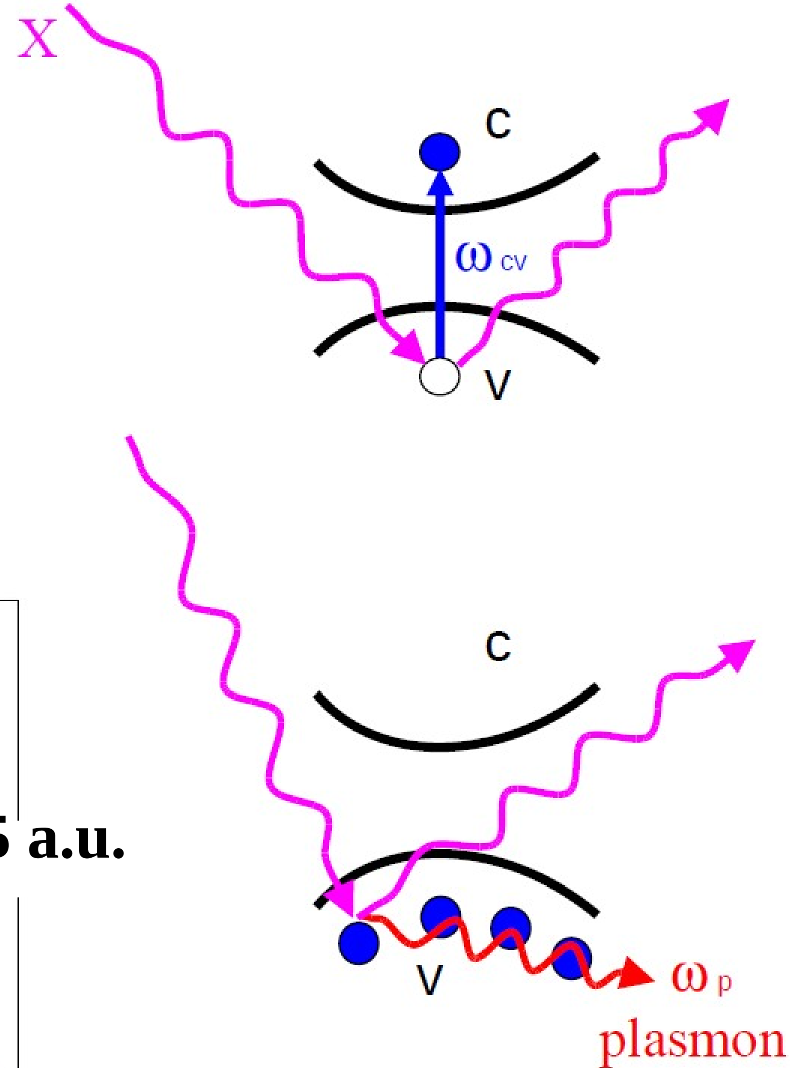
# EELS, IXSS and absorption

## Inelastic X-Ray scattering Spectroscopy

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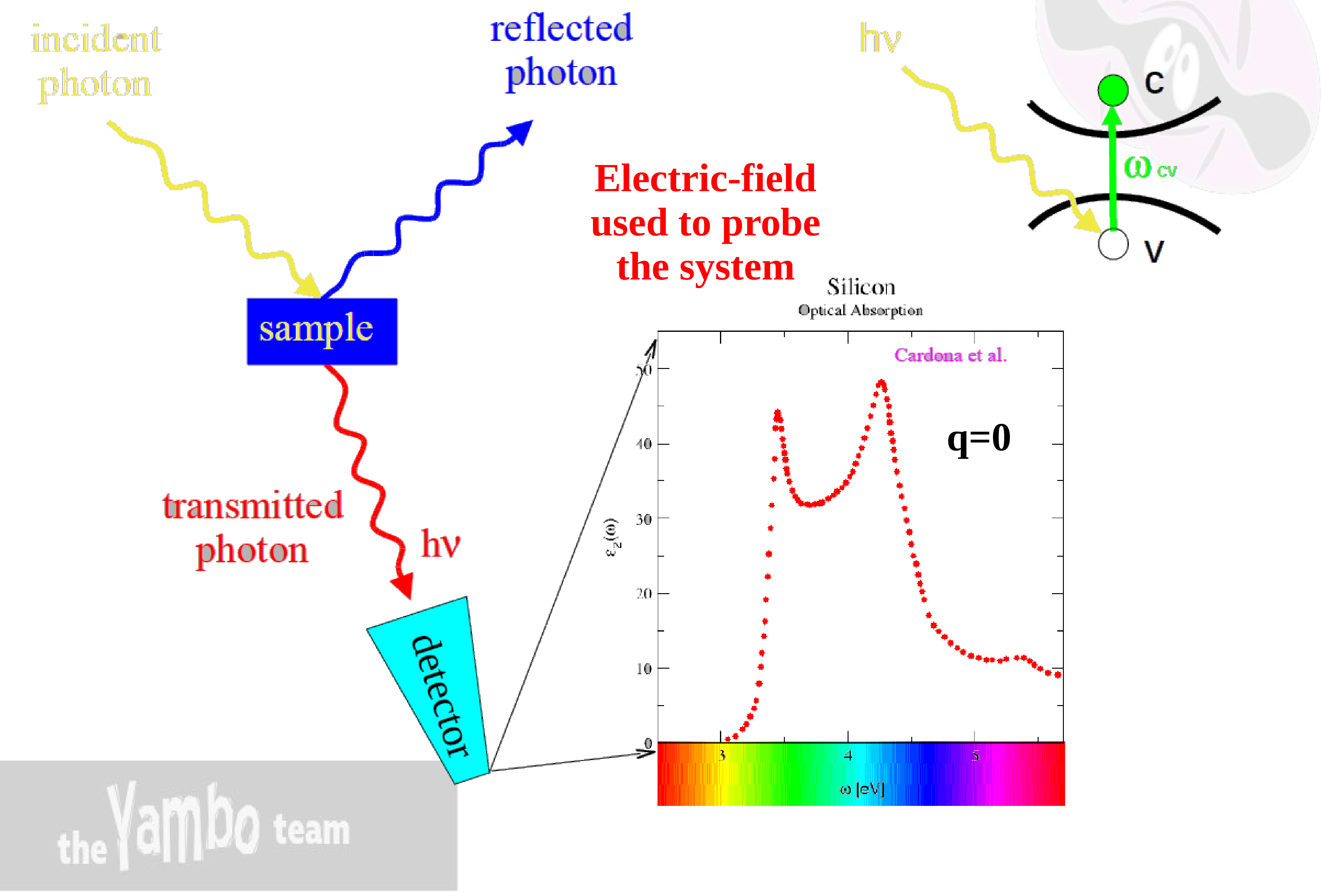
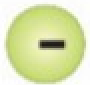
# EELS, IXSS and absorption

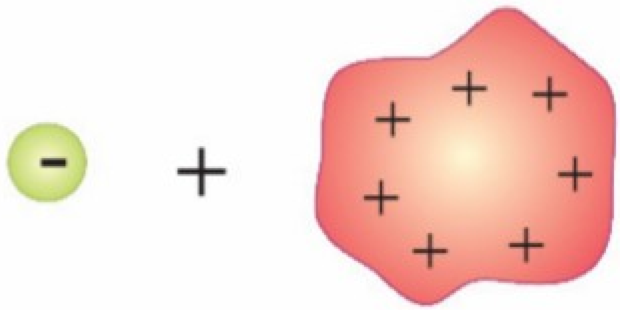


# The Kubo Formula

# The "dielectric way" to the MB problem

$\delta\rho(\vec{r})$ 

$$\phi^{ext}(\vec{r}) = \int d\vec{r}\,'\,|\vec{r}-\vec{r}\,'|^{-1}\,\delta\rho(\vec{r})$$



# The Kubo Formula

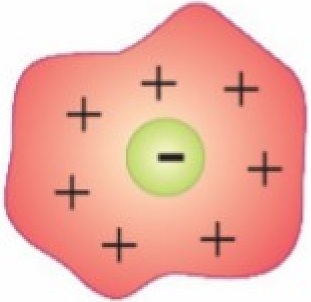
$$H_{tot} = H + H^{ext}(t) = H + \sum_i \phi^{ext}(\mathbf{r}_i, t) = H + \int d\mathbf{r}\, \rho(\mathbf{r})\, \phi^{ext}(\mathbf{r}, t)$$

The external potential “induces” a (time-dependent) density perturbation

$$\rho^{ind}(t) = \langle \Phi(t) | \hat{\rho} | \Phi(t) \rangle - \langle \Phi | \hat{\rho} | \Phi \rangle$$

$$|\Phi(t)\rangle = |\Phi_0\rangle + \int_{-\infty}^{t} dt'\, H_I^{ext}(t') |\Phi(t)\rangle \approx |\Phi_0\rangle + \int_{-\infty}^{t} dt'\, H_I^{ext}(t') |\Phi_0\rangle$$

$$\rho^{ind}(r, t) = \int_{-\infty}^{t} dt' \int dr'\, \chi_{\rho\rho}(rr', t - t')\, \phi^{ext}(t')$$



With the causal response function

$$\chi_{\rho\rho}(\mathbf{r}\mathbf{r}', t) \equiv -i \langle [\rho_I(\mathbf{r}, t), \rho_I(\mathbf{r}')] \rangle = -i \langle [\delta\rho_I(\mathbf{r}, t), \delta\rho_I(\mathbf{r}')] \rangle$$

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# Maxwell...

[H. Ehrenreich, *The Optical Porperties of Solids*, Academic, New York (1965); L.P. Kadanoff and C. Martin, Phys. Rev. **84**, 1232 (1951)]

$$\rho^{ind}(\mathbf{r},t) = \int_{-\infty}^{t} dt' \int_{-\infty}^{\infty} d\mathbf{r}'\, \chi_{\rho\rho}(\mathbf{r}\mathbf{r}', t-t')\, \phi^{ext}(\mathbf{r}', t')$$

$$\nabla \cdot \mathbf{E}^{tot}(\mathbf{r},t) = 4\pi \left[\rho^{ind}(\mathbf{r},t) + \rho^{ext}(\mathbf{r},t)\right]$$

$$\mathbf{E}^{tot}(\mathbf{r},\omega) = \int d\mathbf{r}'\, \epsilon^{-1}(\mathbf{r}\mathbf{r}',\omega)\, \mathbf{E}^{ext}(\mathbf{r}',\omega)$$

$$\epsilon^{-1}(rr',t) = \delta(r-r') + \int dt\, v(r-t)\chi_{\rho\rho}(tr',t)$$

$$\mathbf{E}^{tot}(\mathbf{q},\omega) = \epsilon_M^{-1}(\mathbf{q},\omega)\, \mathbf{E}^{ext}(\mathbf{q},\omega)$$

$$\epsilon_M^{-1}(\mathbf{q},\omega) \equiv \langle\langle \epsilon^{-1}(\mathbf{r}\mathbf{r}', \mathbf{q}\omega)\rangle\rangle_0$$

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# Response and Green's Functions

$$\chi_{\rho\rho}(\mathbf{r}\mathbf{r}',t) \equiv -i\langle[\rho_I(\mathbf{r},t),\rho_I(\mathbf{r}')]\rangle = -i\langle[\delta\rho_I(\mathbf{r},t),\delta\rho_I(\mathbf{r}')]\rangle$$

**Diagrams**

$$\rho^{ind}(r,t)=\int_{-\infty}^{t} dt'\int dr'\chi_{\rho\rho}(rr',t-t')\phi^{ext}(t')$$

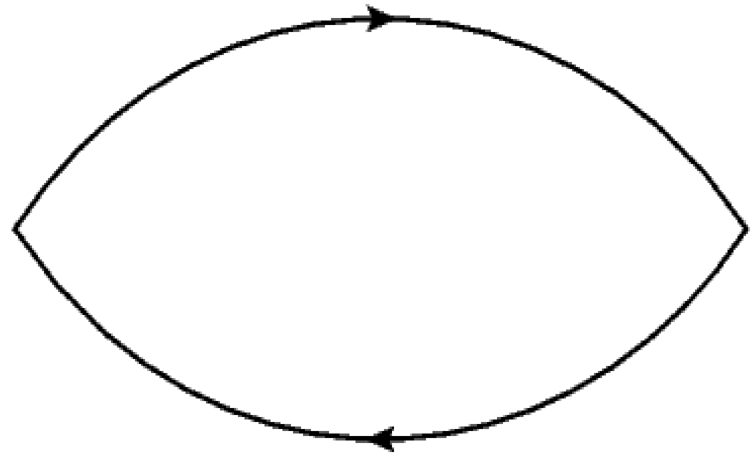
$$\chi_{\rho\rho}(t-t')\equiv\frac{\delta\rho^{ind}(t)}{\delta\phi^{ext}(t')}$$

**Schwinger**
**(Hedin's Pentagon)**

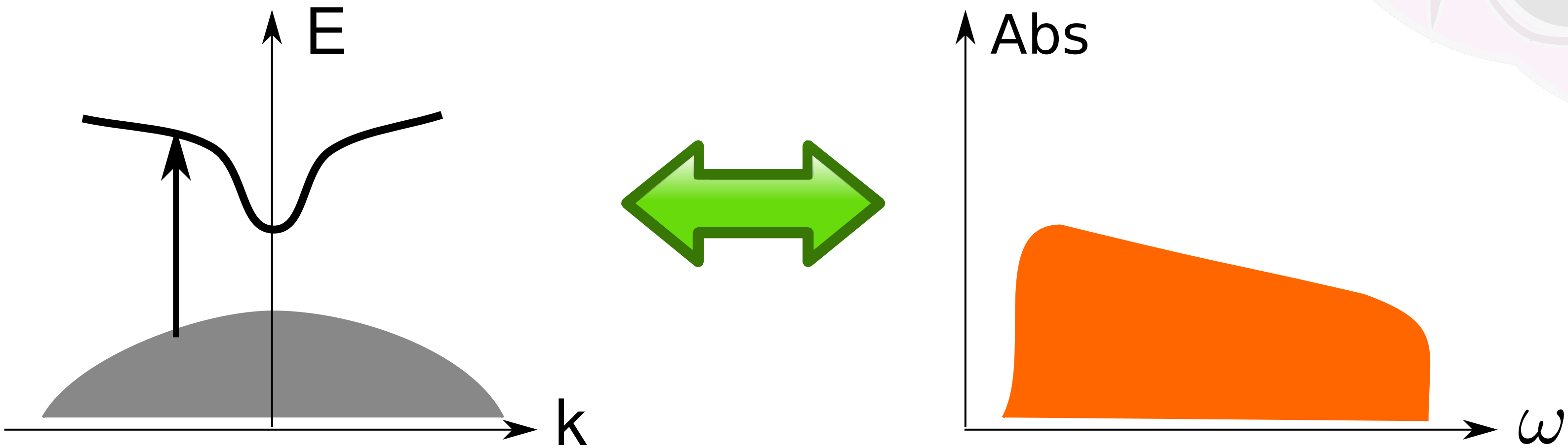
$$\partial_t\chi_{\rho\rho}(t-t')\equiv\frac{\partial_t\delta\rho^{ind}(t)}{\delta\phi^{ext}(t')}$$

**Density matrix formulation**

$$\chi_{\rho\rho}(t-t') \overset{?}{\approx}$$



# Can we get optical excitations directly from the electronic structure?




Band structure

Optical absorption

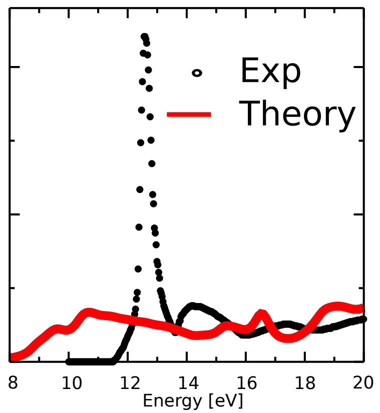
From Fermi-Golden rule + approximation $E_N^{\mathrm{fin}} - E_N^0 = E_{c\mathbf{k}} - E_{v\mathbf{k}}$

$$\mathrm{Abs}(\omega) \propto \sum_{v,c} \int_{\mathrm{BZ}} d\mathbf{k} |\langle v\mathbf{k}|\hat{D}|c\mathbf{k}\rangle|^2 \delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega)$$

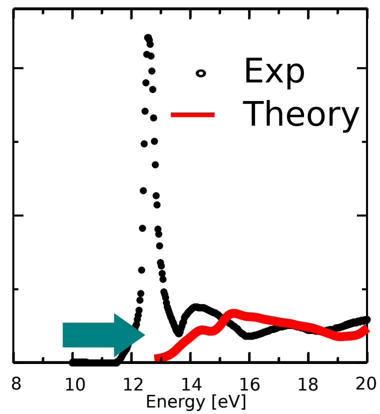
# Does this approach give reasonable results?

## Test against optical absorption in bulk LiF:

with Kohn-Sham band-structure



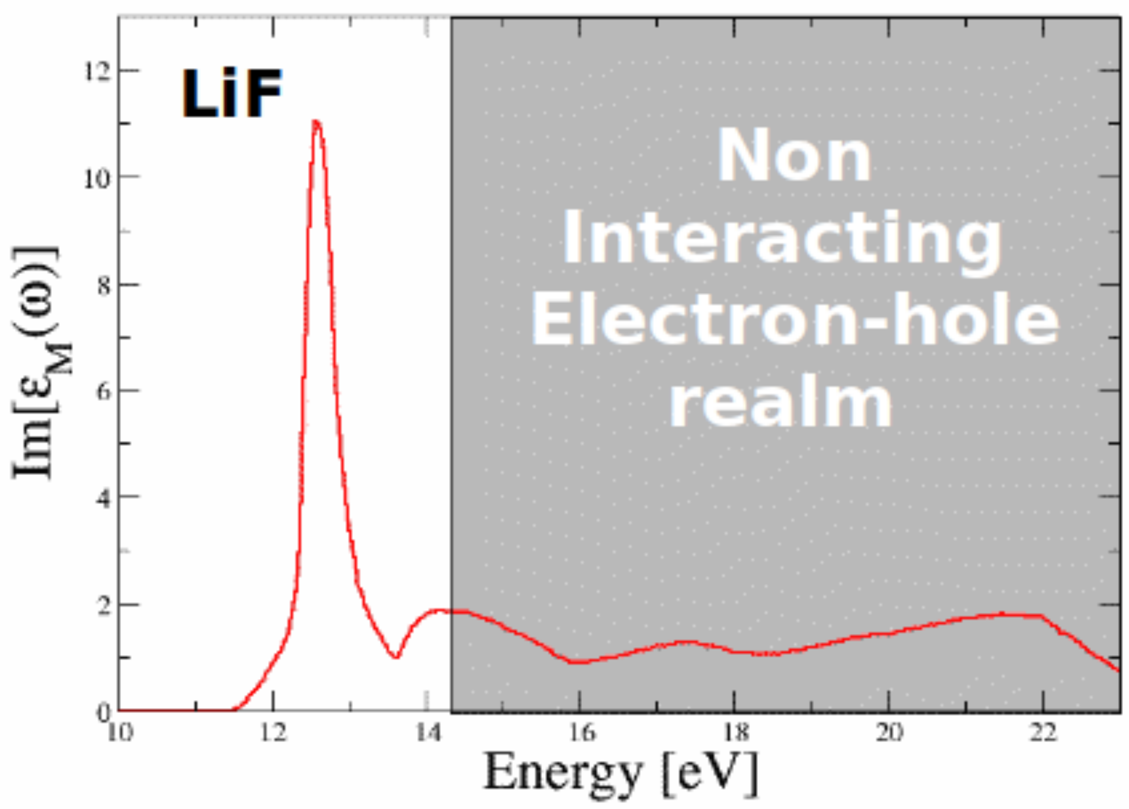

with quasiparticle band-structure



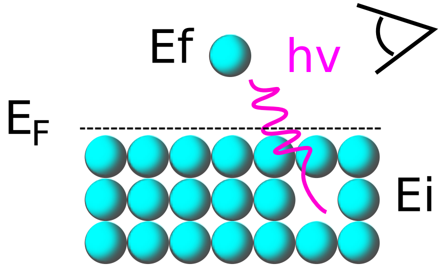

Fermi-Golden rule + approximation $E_N^{\mathrm{fin}} - E_N^0 = E_{c\mathbf{k}} - E_{v\mathbf{k}}$

$$\mathrm{Abs}(\omega) \propto \sum_{v,c} \int_{\mathrm{BZ}} d\mathbf{k} |\langle v\mathbf{k}|\hat{D}|c\mathbf{k}\rangle|^2 \delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega)$$

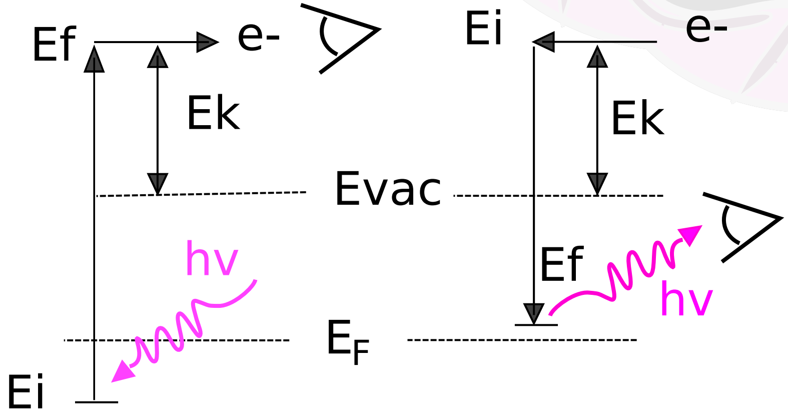
# Excitonic states in the single-particle energy forbidden region



# What physical effect is missing?




$\neq$




OPTICAL ABSORPTION $\neq$ SUM OF INVERSE/DIRECT PHOTOEMISSION PROCESSES

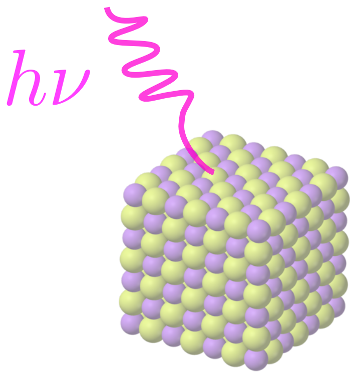
OPTICAL EXCITATION ENERGY $\neq$ DIFFERENCE OF QUASIPARTICLE ENERGIES

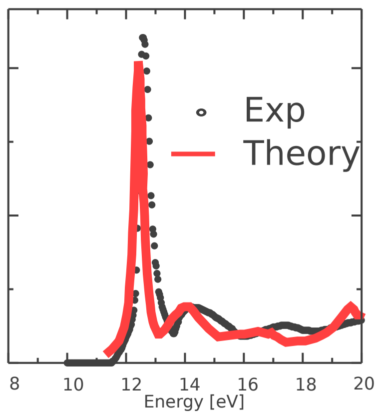
# Missing physics is electron-hole interaction: coupling among transitions

$$E_N^{\mathrm{fin}} - E_N^0 = E_\lambda \neq E_{c\mathbf{k}} - E_{v\mathbf{k}}$$

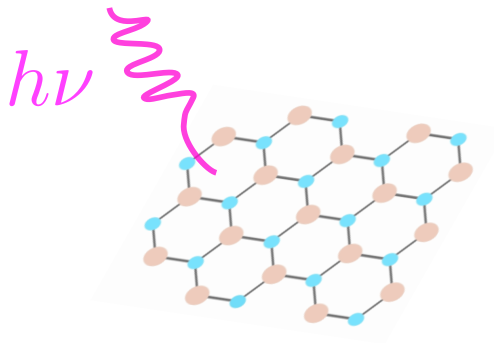
$$\mathrm{Abs}(\omega) \propto \sum_\lambda \sum_{v,c} \int_{\mathrm{BZ}} d\mathbf{k}\, |A_\lambda^{cv\mathbf{k}} \langle v\mathbf{k}|\hat{D}|c\mathbf{k}\rangle|^2 \delta(E_\lambda - \hbar\omega)$$

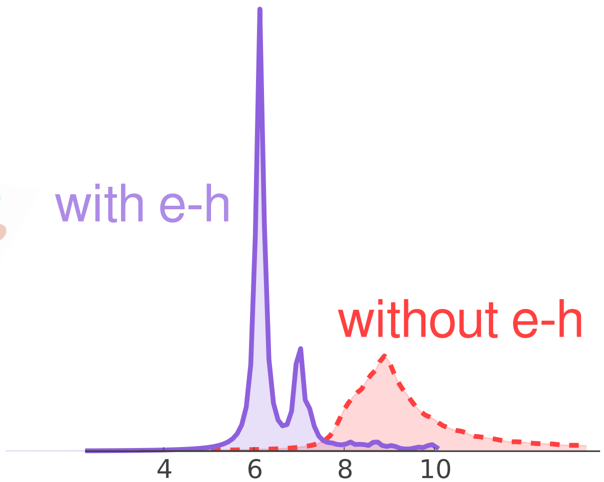
back to LiF optical spectrum




same effects in 2D materials



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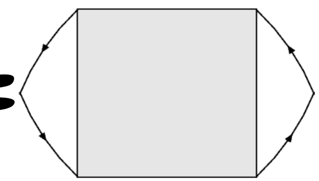
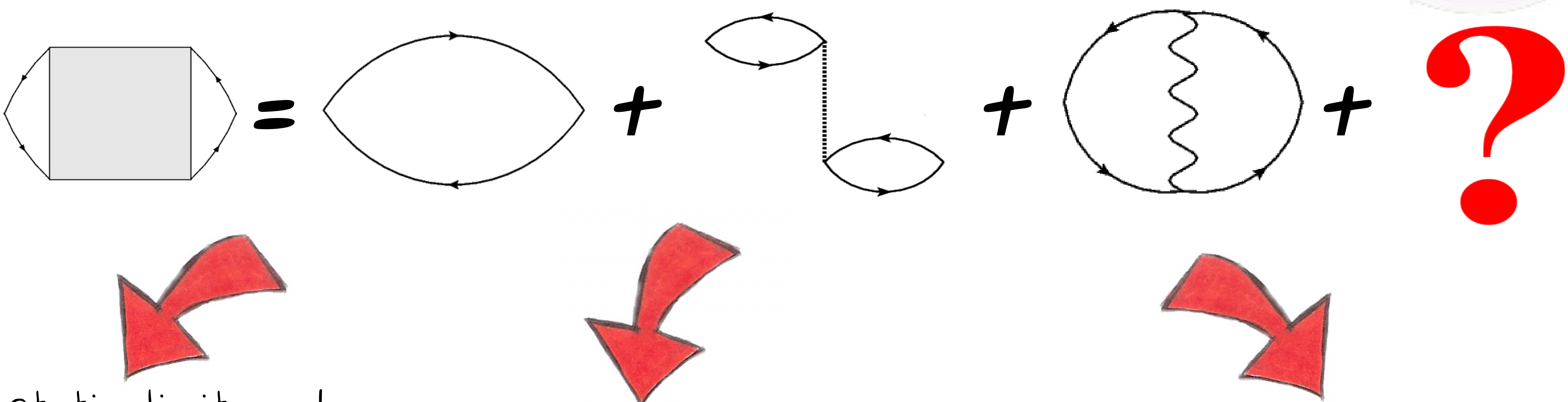
# The Bethe-Salpeter Equation: an (over)simplified introduction

# The Diagrammatic Approach

$$\chi(1,2) \equiv \frac{\delta\rho(1)}{\delta(V_{ext}(2)+V_H(2))} =$$





Static limit and
Dynamics effects
cancellation(?)

Conserving?

Partial Summation

# The Schwinger Approach

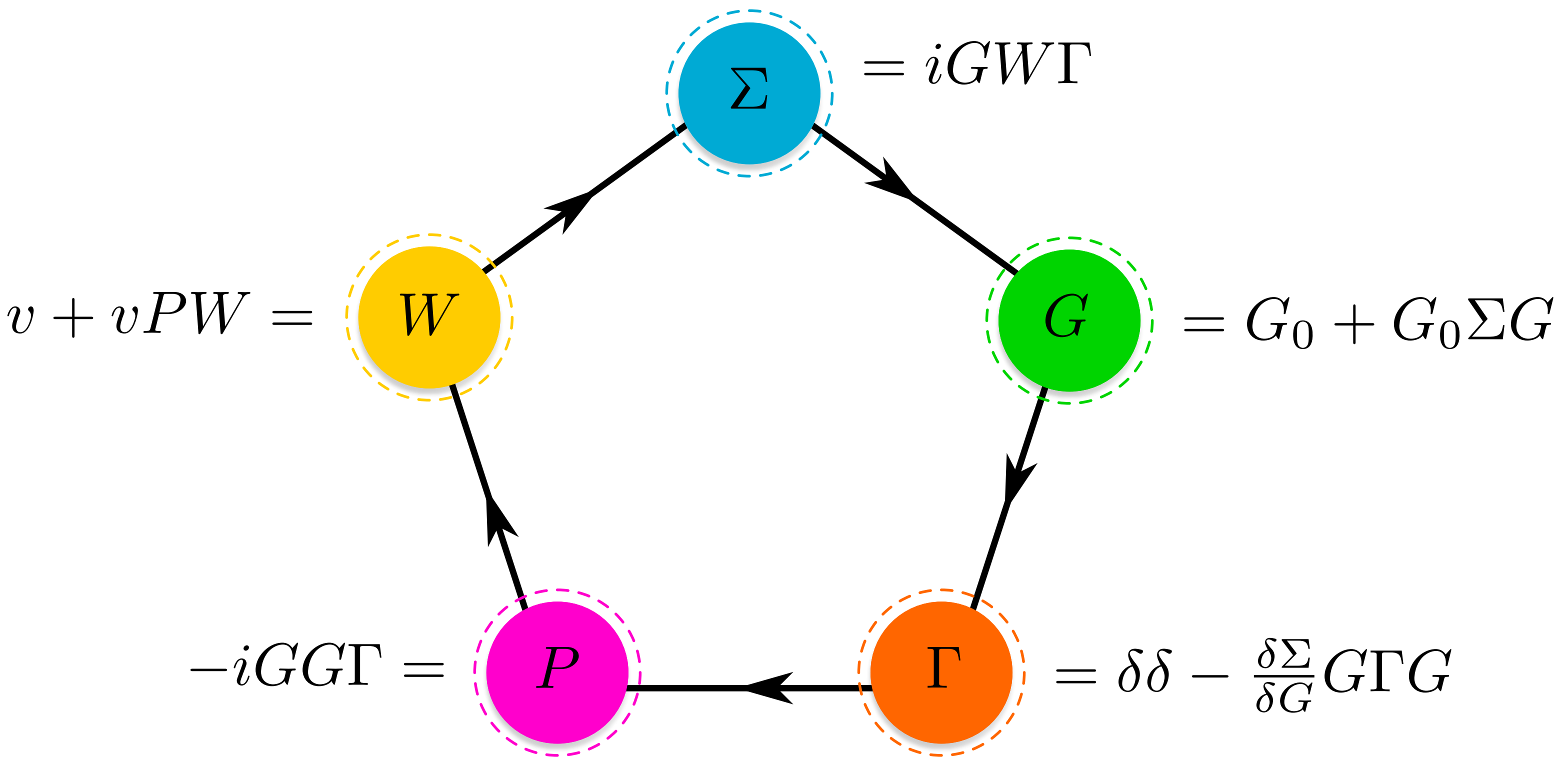
$$\chi(1,2) \equiv \frac{\delta \rho(1)}{\delta(V(2))} = i \frac{\delta G(1,1^{+})}{\delta(V(2))}$$

Chain-rule

$$\chi(1,2) = i \iint d3\, d4\, G(1,3) \frac{\delta G^{-1}(3,1)}{\delta(V(2))} G(4,1) = i \iint d3\, d4\, G(1,3)\, \Gamma(3,4;2)\, G(4,1)$$

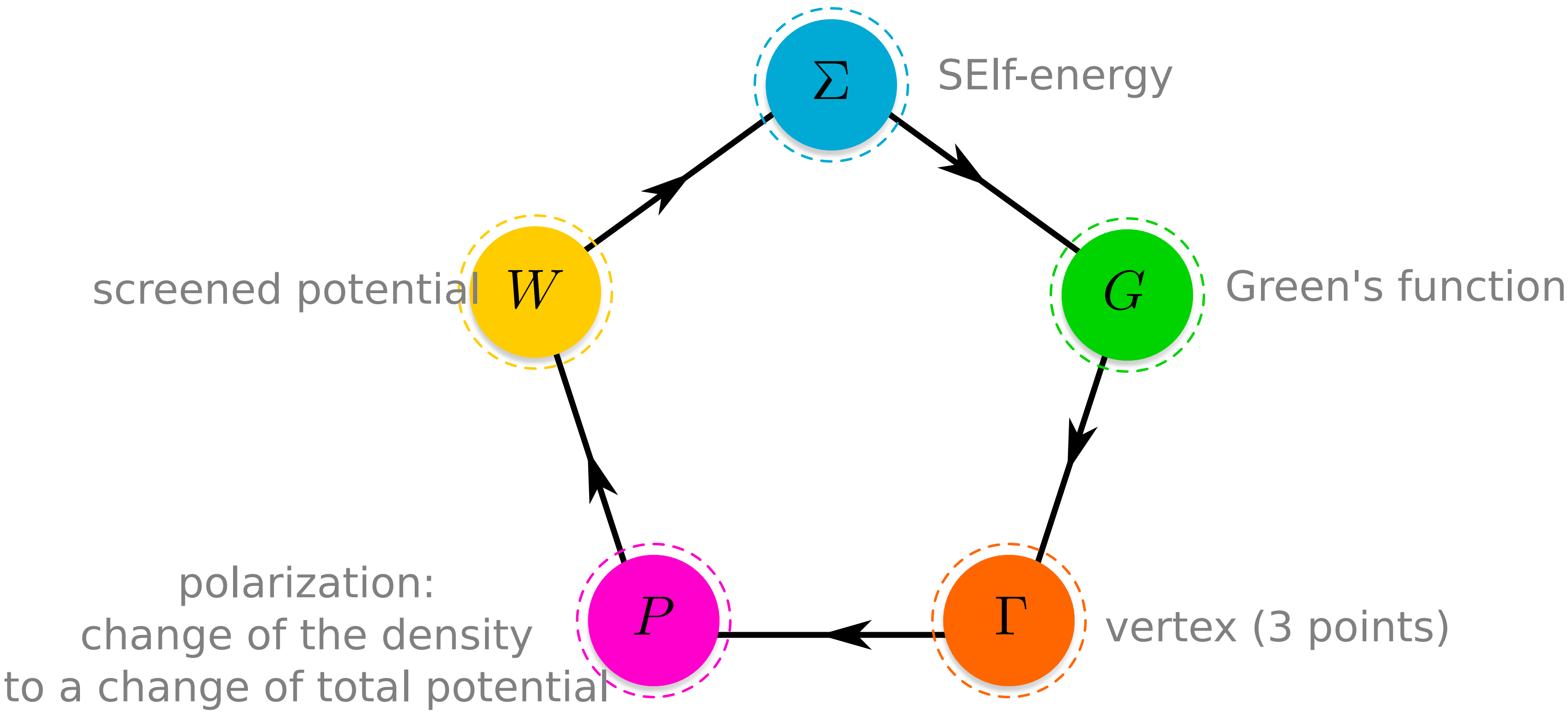
# Carrying on with Schwinger functional derivative method eventually obtain Hedin equations

can be iterated analytically:

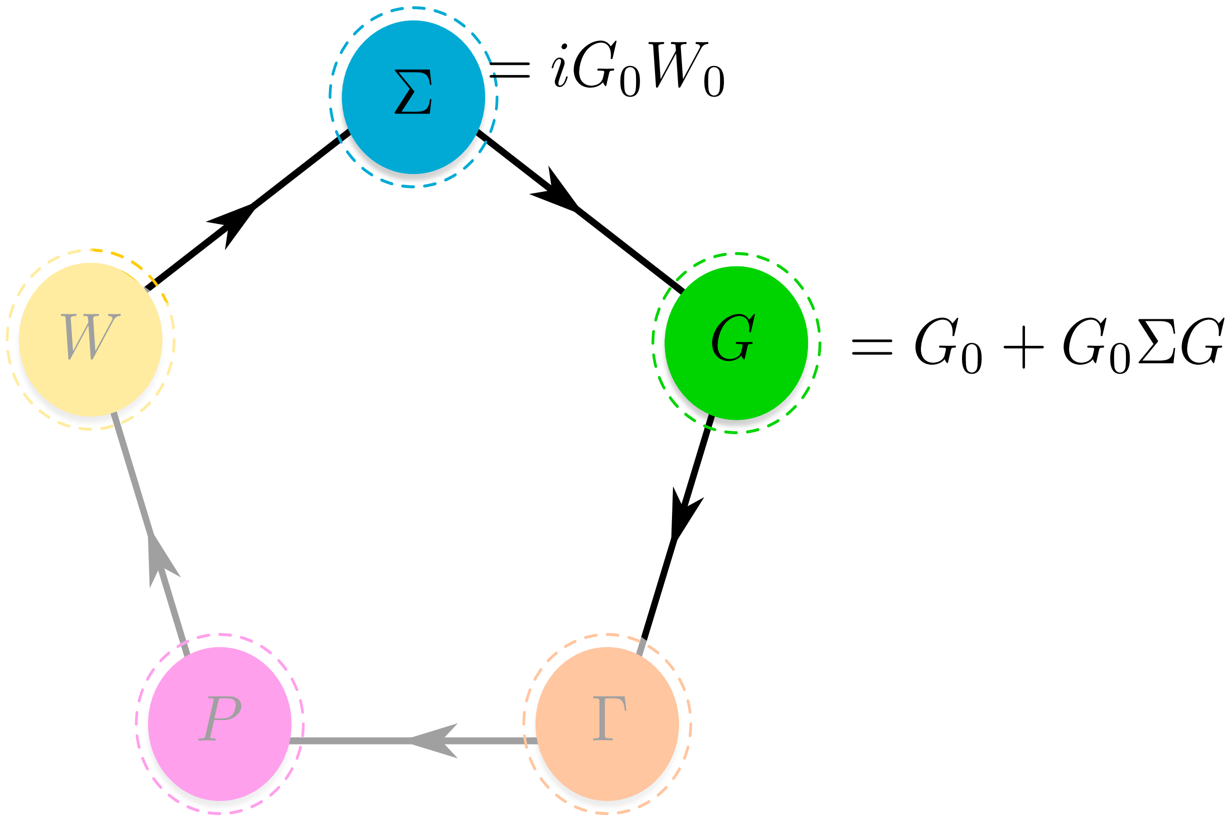


# Carrying on with Schwinger functional derivative method eventually obtain Hedin equations

set of coupled integro-differential equation for:



# GW approximation for the self-energy can be obtained rigorously from Hedin's equations



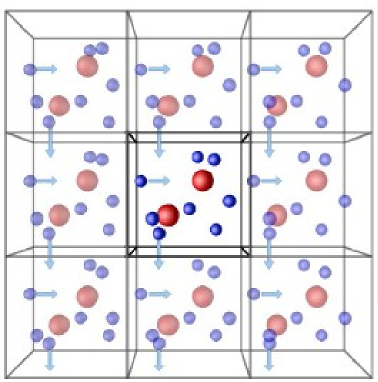
# The micro-Macro connection

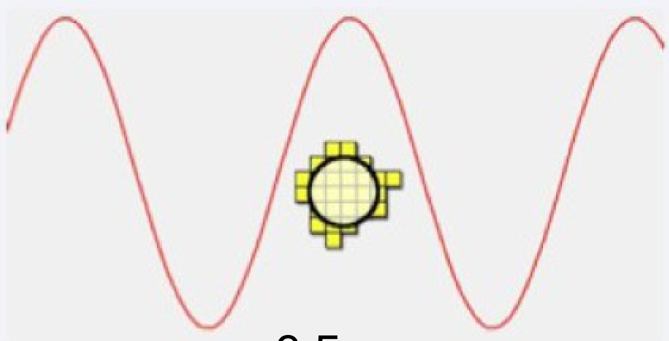
# Micro-macro connection

$$\epsilon^{-1} V^{ext} = V^{tot} \qquad \langle \epsilon^{-1} V^{ext} \rangle = \langle V^{tot} \rangle$$

At long wavelength, external fields are slowly varying over the unit cell:

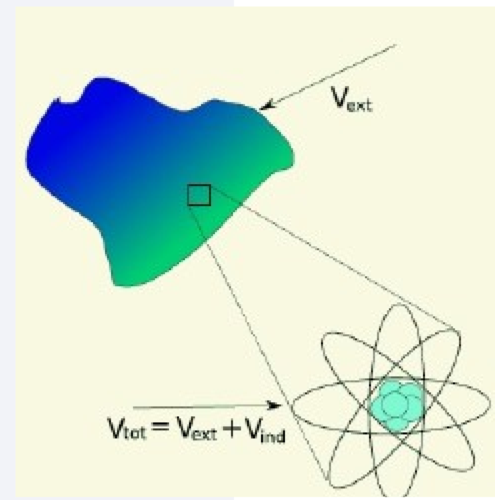
- dimension of the unit cell for silicon: 0.5 nm
- visible radiation 400 nm < $\lambda$ < 800 nm





0.5 nm

>100 nm




$$\langle \epsilon^{-1} \rangle V^{ext} = \langle V^{tot} \rangle$$

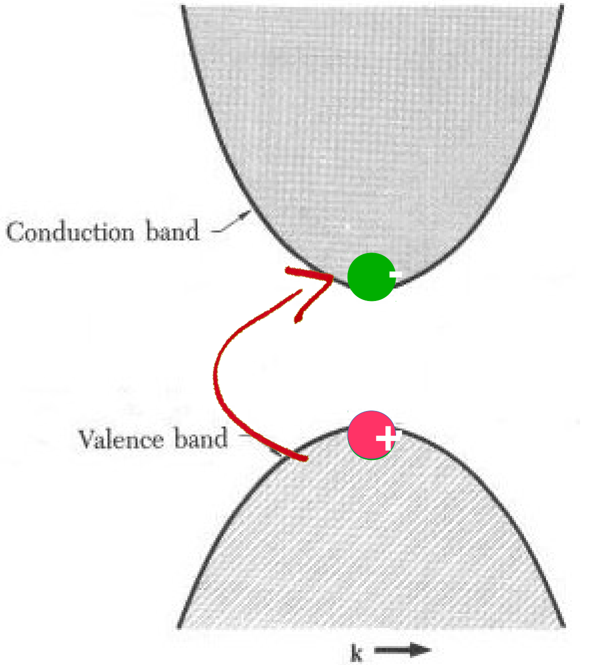
$$\epsilon_M^{-1} V^{ext} = V_M^{tot} \qquad \epsilon_M^{-1} = \langle 1 + v\chi \rangle$$

# The microscopic response function

$$\epsilon_M^{-1} = \langle 1 + v\chi \rangle$$

$$\chi = \frac{\rho_{ind}}{V_{ext}} \xrightarrow{\textbf{approximation}} \chi_0 = \frac{\rho_{ind}^{IP}}{V_{ext}}$$

$$\chi_0(r, r', \omega) = \sum_{ij} \frac{\psi_j(r)\psi_i^*(r)\psi_i(r')\psi_j^*(r')}{\omega - \Delta\epsilon_{ij} + i\eta}$$




$$\chi = \frac{\delta\rho_{ind}}{\delta V_{ext}} = \frac{\delta\rho_{ind}}{\delta V_{tot}} \frac{\delta V_{tot}}{\delta V_{ext}} \sim \frac{\delta\rho_{ind}^{IP}}{\delta V_{tot}} \frac{\delta V_{tot}}{\delta V_{ext}}$$

$$\chi = \chi^0 + \chi^0 v \chi$$

Random Phase Approximation

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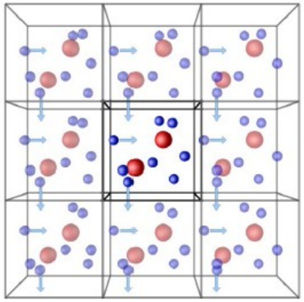
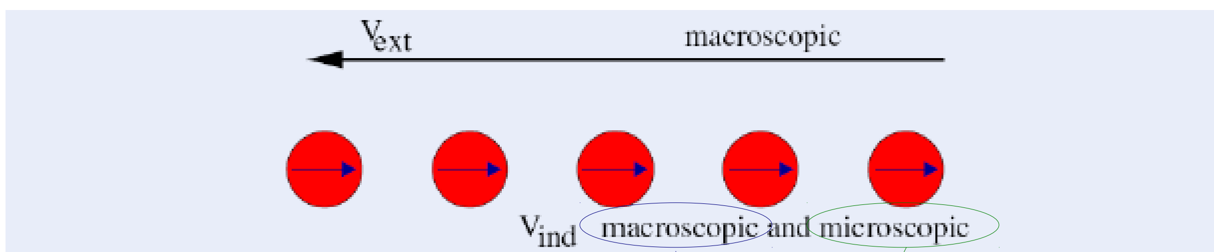


# Reciprocal space

$$\chi(r+R, r'+R', t-t') \rightarrow \chi_{G,G'}(\boldsymbol{q},\omega)$$

$$\langle \epsilon_M^{-1}(\boldsymbol{q},\omega)\rangle = 1 + v_{G=0}\chi_{G=0,G'=0}(\boldsymbol{q},\omega)$$

$$\langle \chi(\boldsymbol{q},\omega)\rangle = \chi_{G=0,G'=0}(\boldsymbol{q},\omega)$$




The classical macroscopic induced field

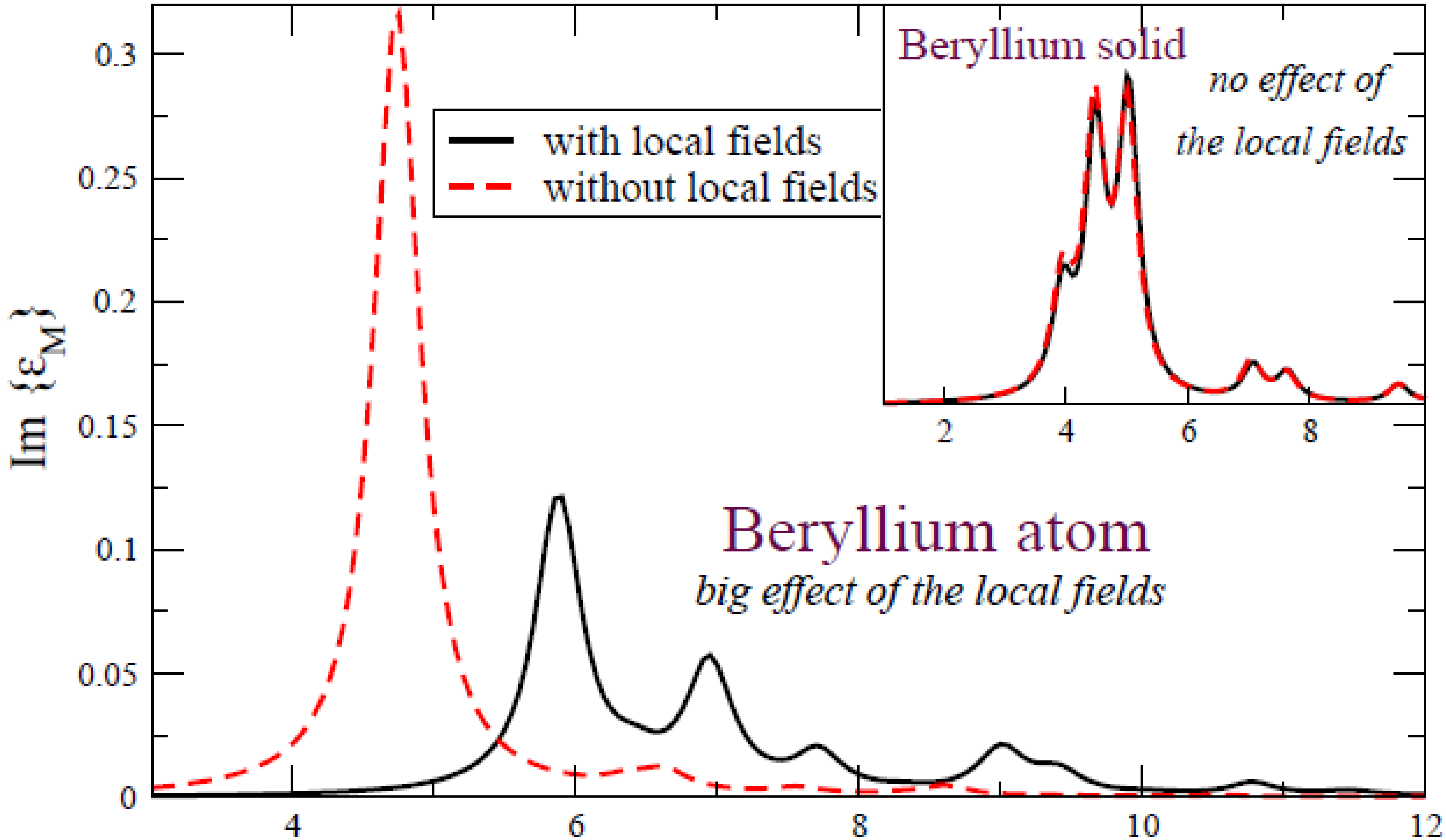
Full quantum part
"DFT version"

$$\chi(\boldsymbol{q},\omega) = \chi^0(\boldsymbol{q},\omega) + \chi^0(\boldsymbol{q},\omega)(v_{G=0} + v_{G>0})\chi(\boldsymbol{q},\omega)$$

The microscopic classical field.

# The local fields effect

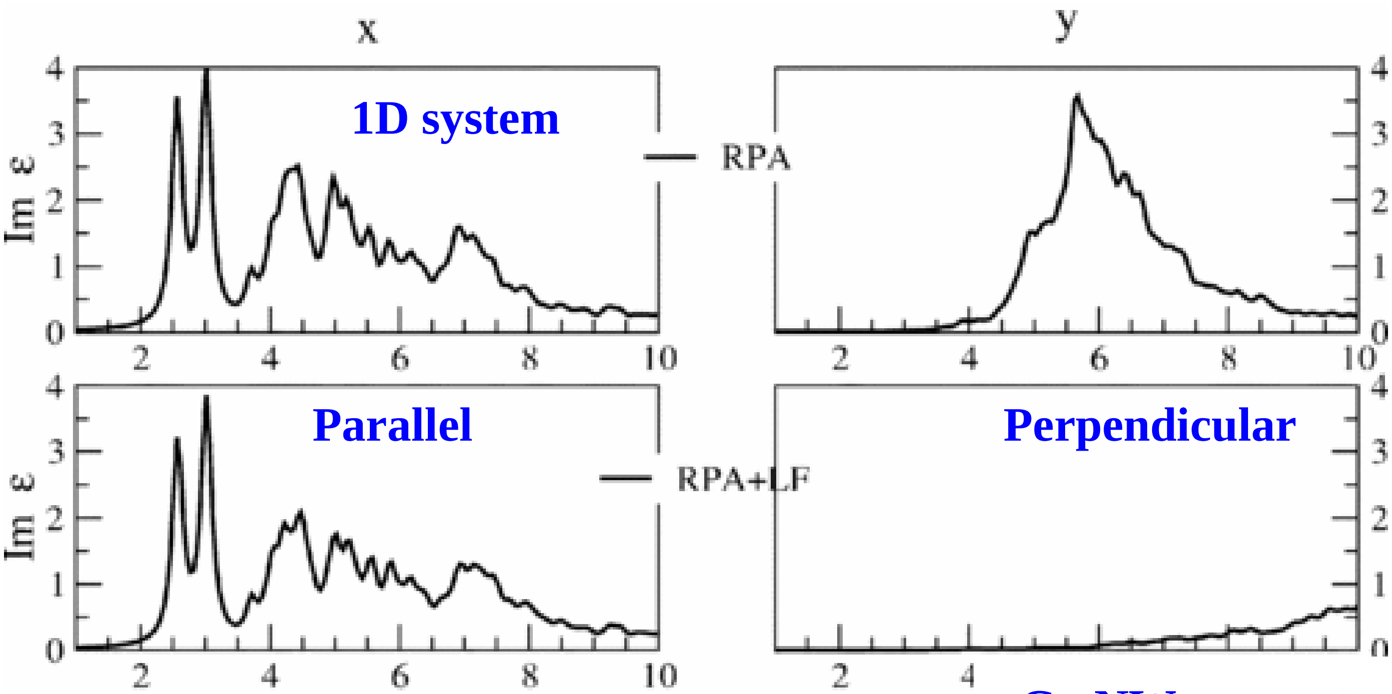
$$\chi(\boldsymbol{q},\omega)=\chi^0(\boldsymbol{q},\omega)+\chi^0(\boldsymbol{q},\omega)(v_{G=0}+v_{G>0})\chi(\boldsymbol{q},\omega)$$




**The effects is <u>usually:</u>**
**- small in solids**
**- important in isolated systems**

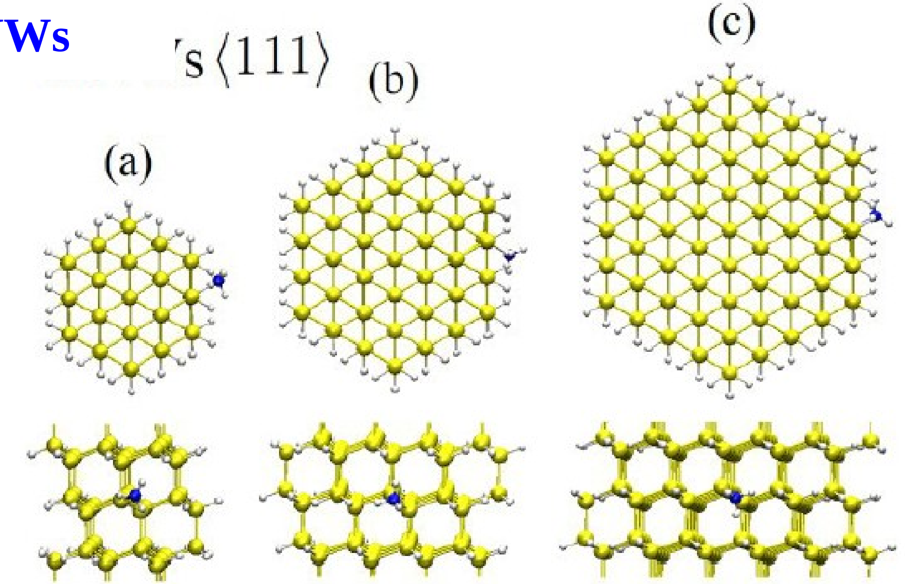
# The local fields effect

$$\chi(\boldsymbol{q},\omega)=\chi^0(\boldsymbol{q},\omega)+\chi^0(\boldsymbol{q},\omega)(v_{G=0}+v_{G>0})\chi(\boldsymbol{q},\omega)$$



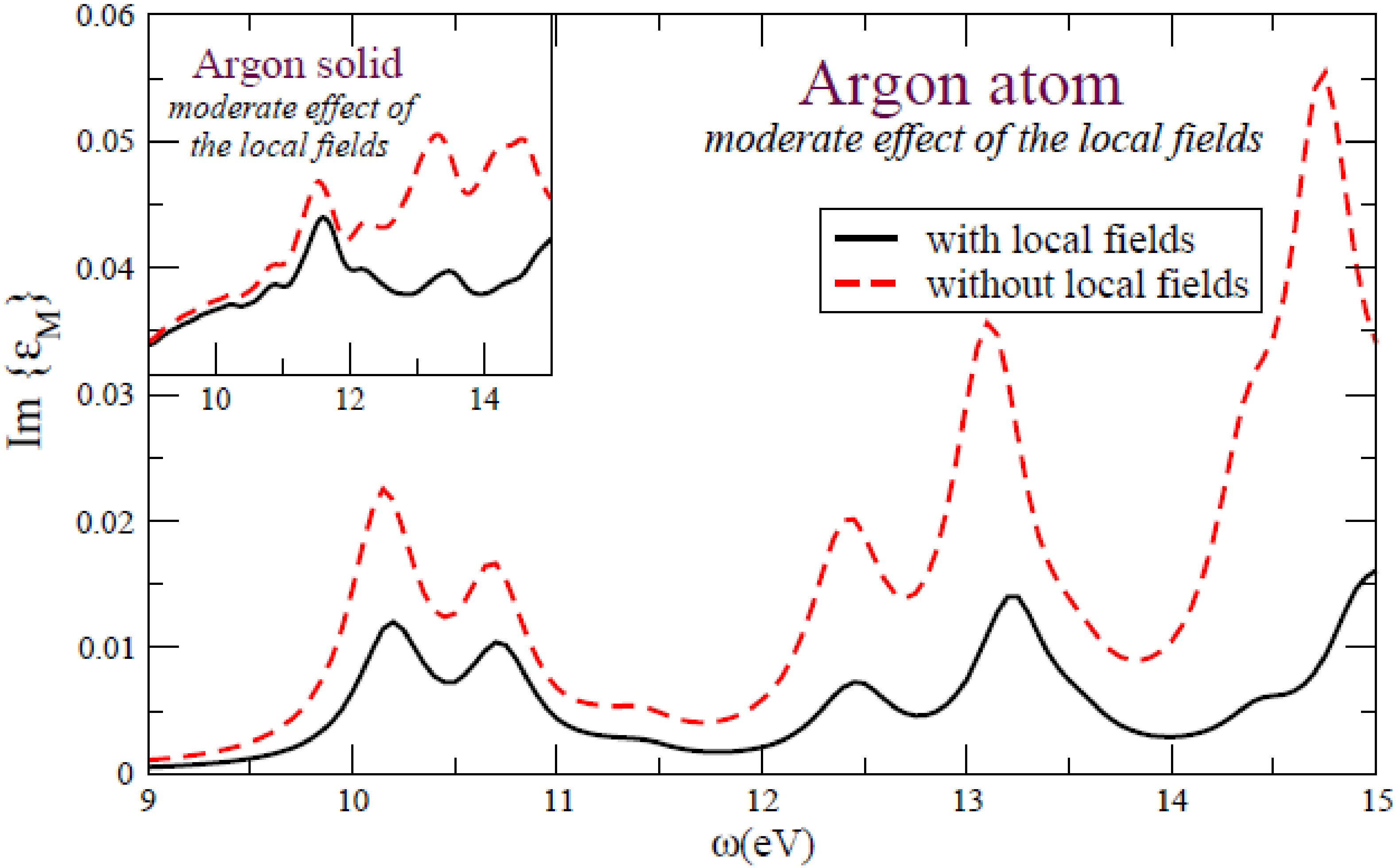

Phys. Rev. B 72, 153310 (2005)

**Ge-NWs**



# The local fields effect

$$\chi(\boldsymbol{q},\omega)=\chi^0(\boldsymbol{q},\omega)+\chi^0(\boldsymbol{q},\omega)(v_{G=0}+v_{G>0})\chi(\boldsymbol{q},\omega)$$

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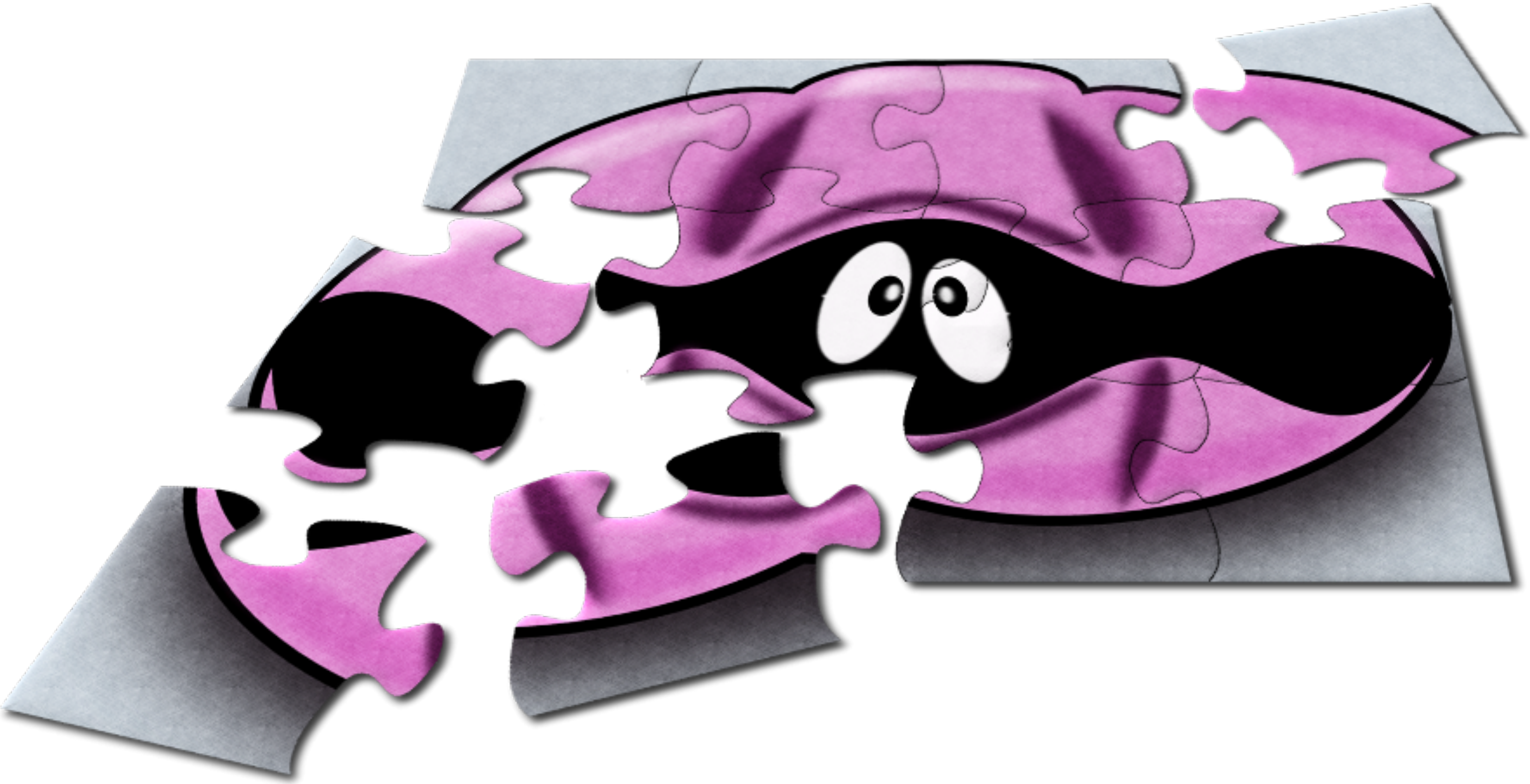

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1. Many-body perturbation theory calculations using the yambo code
   Journal of Physics: Condensed Matter 31, 325902 (2019)
2. Yambo: an ab initio tool for excited state calculations
   Comp. Phys. Comm. 144, 180 (2009)