Advanced Materials Modeling Beyond DFT 2 : GW + Optic

+ Experiments : total energy, band gap, spectroscopies ?

+ Charged excitations and Green's function G

+ GW approximation (incl. self-consistency and miscellaneous tricks)

+ Optical characteristics of materials

+ Time-dependent perturbation theory and Adler-Wiser formula

+ Local fields from TD-DFT

+ Bethe-Salpeter equation

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# A basic reference on first-principles simulations of interacting electrons
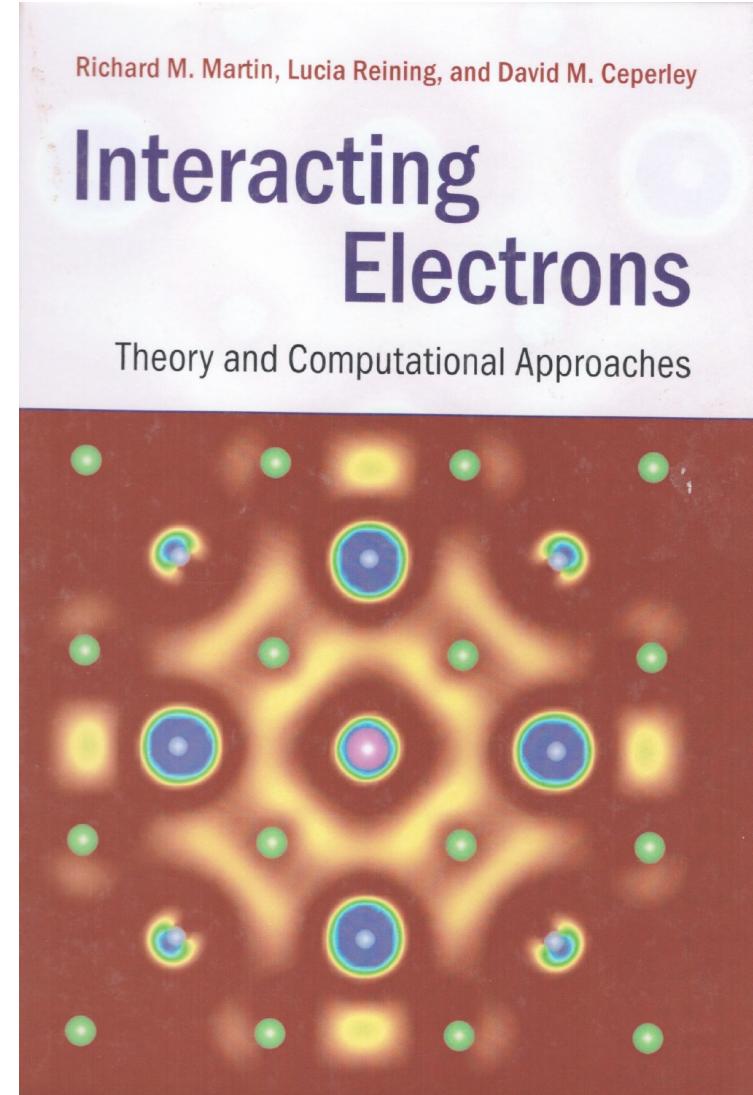
Richard M. Martin, L. Reining & D.M. Ceperley

Cambridge University Press, 2016

Interacting electrons:

Theory and computational approaches

(ISBN: 978-0-521-87150-1)

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Many-body physics

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Systems with n electrons and N nuclei

- Born-Oppenheimer approximation.
- Nuclei are treated as distinct particles, without spin. Internal structure is neglected. Only charge, mass and (classical) position taken into account.

Wavefunction :

$$\Psi_e(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, ..., \mathbf{r}_n, \sigma_n; \mathbf{R}_1, \mathbf{R}_2, ... \mathbf{R}_N)$$ + antisymmetry for electron exchange

Electronic Hamiltonian, in atomic units (without spin-orbit) :

$$\hat{T}_e = \sum_{i=1}^{n} -\frac{\nabla_{r_i}^2}{2} \qquad \hat{V}_{eN} = \sum_{A}^{N} \sum_{i}^{n} \frac{-Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \qquad \hat{V}_{ee} = \sum_{\substack{(i,j) \\ i<j}}^{(n,n)} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{H}_e = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee}$$

$$\boxed{\hat{H}_e \left| \Psi_e \right\rangle = E_e \left| \Psi_e \right\rangle}$$

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Simplified notations

(1) Arguments of wavefunction :

$$\Psi_e(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2;...;\mathbf{r}_n,\sigma_n) \implies \Psi_e(1,2,...,n)$$

"1" becomes a symbol to denote $\mathbf{r}_1,\sigma_1$

(2) Define also $\quad r_{ij} \triangleq |\mathbf{r}_i - \mathbf{r}_j| \qquad \hat{V}_{ee} = \sum_{\substack{(i,j)\\i<j}}^{(n,n)} \frac{1}{r_{ij}}$

and "one-particle" part of Hamitonian

$$\hat{V}_{eN} = \sum_A^N \sum_i^n \frac{-Z_A}{r_{iA}} = \sum_i^n \hat{V}_N(\mathbf{r}_i) \qquad\qquad \hat{h}^N(i) \triangleq -\frac{\nabla^2_{r_i}}{2} + \hat{V}_N(\mathbf{r}_i)$$

Hamitonian becomes :

$$\left(\sum_i^n \hat{h}^N(i) + \sum_{\substack{(i,j)\\i<j}}^{(n,n)} \frac{1}{r_{ij}} \right) \Psi_e(1,2,...,n) = E_e \Psi_e(1,2,...,n)$$

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Separation of variables

$$\left(\sum_{i}^{n} \hat{h}^{N}(i) + \boxed{\sum_{\substack{(i,j)\\i<j}}^{(n,n)} \frac{1}{r_{ij}}} \right) \Psi_{e}(1,2,...,n) = E_{e} \Psi_{e}(1,2,...,n)$$

+ antisymmetry for electron exchange

Interelectronic coupling does not
allow to separate electronic coordinates

Mean-field approximation (like DFT)

$$\sum_{\substack{(i,j)\\i<j}}^{(n,n)} \frac{1}{r_{ij}} \quad \text{replaced by} \quad \sum_{i} \hat{V}_{Hxc}(i) \qquad \hat{h}_{MF}^{N}(i) = \hat{h}^{N}(i) + \hat{V}_{Hxc}(i)$$

$$\left(\sum_{i}^{n} \hat{h}_{MF}^{N}(i) \right) \Psi_{MF,e}(1,2,...,n) = E_{MF} \Psi_{MF,e}(1,2,...,n)$$

+ antisymmetry for electron exchange
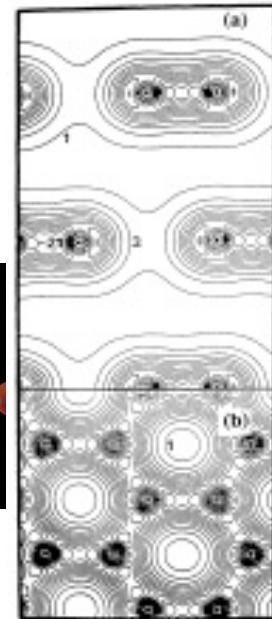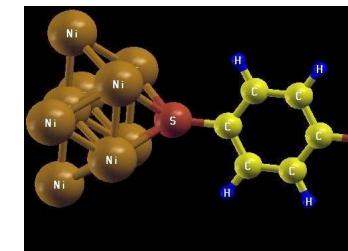
gives solutions as
Slater determinants of 1-particle wavefunctions
mean-field energy=sum of 1-particle eigenenergies,
must be corrected to give electronic energy (avoid double-counting)

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Experiments:
total energy,
band gap,
spectroscopies ?

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Properties from first-principles

Computation of ...
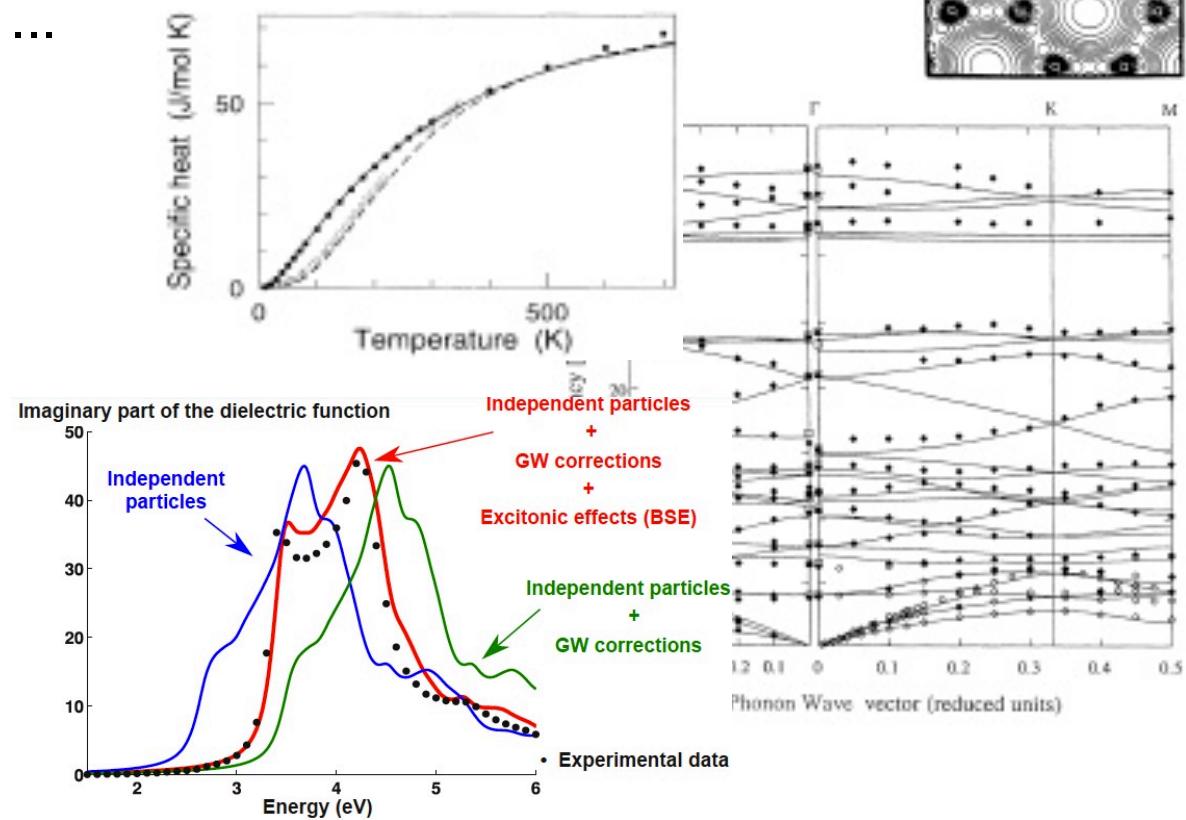
interatomic distances, angles, **total energies**
electronic charge densities, electronic energies

A basis for the computation of ...

chemical reactions
electronic transport
vibrational properties
thermal capacity
dielectric behaviour
optical response
superconductivity
surface properties
spectroscopic responses
...

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Density Functional Perturbation Theory

Many physical properties = derivatives of **total energy**

(or suitable thermodynamic potential) with respect to perturbations.

Consider :

- atomic displacements (phonons)
- dilatation/contraction of primitive cell
- homogeneous external field   (electric field, magnetic field ...)

Derivatives of total energy (electronic part + nuclei-nuclei interaction) :

1st order derivatives : forces, stresses, dipole moment ...

2nd order derivatives : dynamical matrix, elastic constants, dielectric susceptibility

atomic polar tensors or Born effective charge tensors

piezoelectricity, internal strains ...

3rd order derivatives : non-linear dielectric susceptibility, Raman susceptibilities

electro-optic effect, phonon - phonon interaction, Grüneisen parameters, ...

Further properties obtained by integration over phononic degrees of freedom :

entropy, thermal expansion, phonon-limited thermal conductivity ...

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The DFT bandgap problem (I)

- DFT is a ground state theory

  => no direct interpretation of Kohn-Sham eigenenergies ε_i in

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|}\,d\mathbf{r}_1 + V_{xc}(\mathbf{r}) \right)\psi_i(\mathbf{r}) = \varepsilon_i\,\psi_i(\mathbf{r})$$

- However $\{\varepsilon_i\}$ are similar to "quasi-particle" band structure :
  LDA / GGA results for valence bands are rather accurate ...
  but NOT for the band gap $$E_g^{KS} = \varepsilon_c - \varepsilon_v$$

- The band gap can alternatively be obtained from total energy differences

$$E_g = \{E(N+1) - E(N)\} - \{E(N) - E(N-1)\}$$ [correct expression !]

  (where $E(N)$ is the total energy of the N - electron system)

Difference between ionisation potential and electronic affinity

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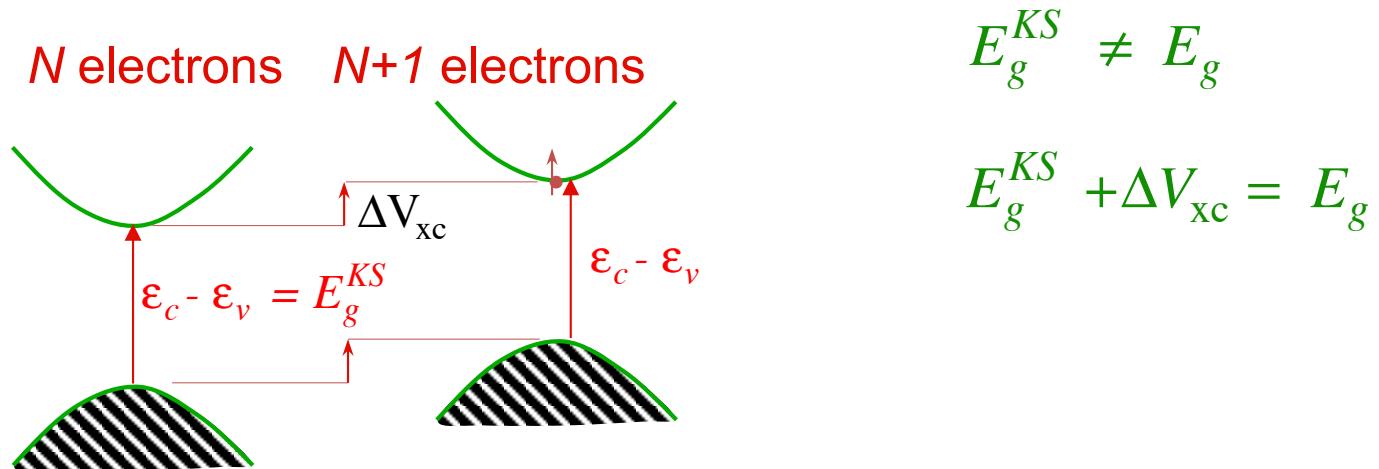
The DFT bandgap problem (II)

- For LDA & GGA, *XC* potential is continuous functional of electron number

$$\varepsilon_i = \frac{\partial E}{\partial f_i} \qquad \textit{[Janak's theorem]}$$
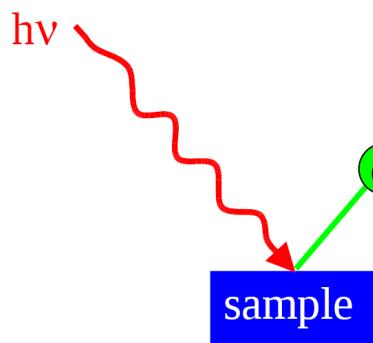
$$\Rightarrow \quad E_g^{KS} = \varepsilon_c - \varepsilon_v \underset{N \to \infty}{=} E_g = E(N+1) + E(N-1) - 2E(N)$$

- *XC* potential : discontinuous with particle number at gap energy

N electrons   *N+1* electrons

ΔV_{xc}

$\varepsilon_c - \varepsilon_v = E_g^{KS}$

$\varepsilon_c - \varepsilon_v$

$$E_g^{KS} \neq E_g$$

$$E_g^{KS} + \Delta V_{xc} = E_g$$
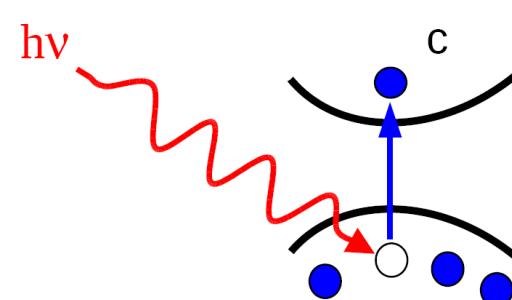
- Band gap : adding / removing an electron = charged electronic excitations
NOT transferring an electron from valence to conduction

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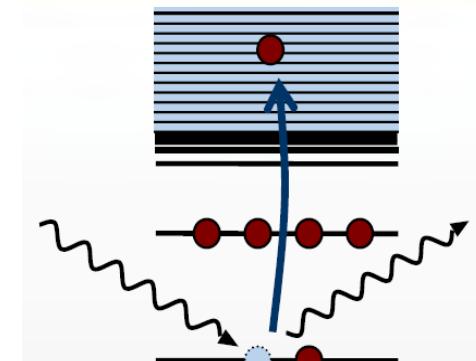
Spectroscopies : photons & electrons

hν

e⁻

sample
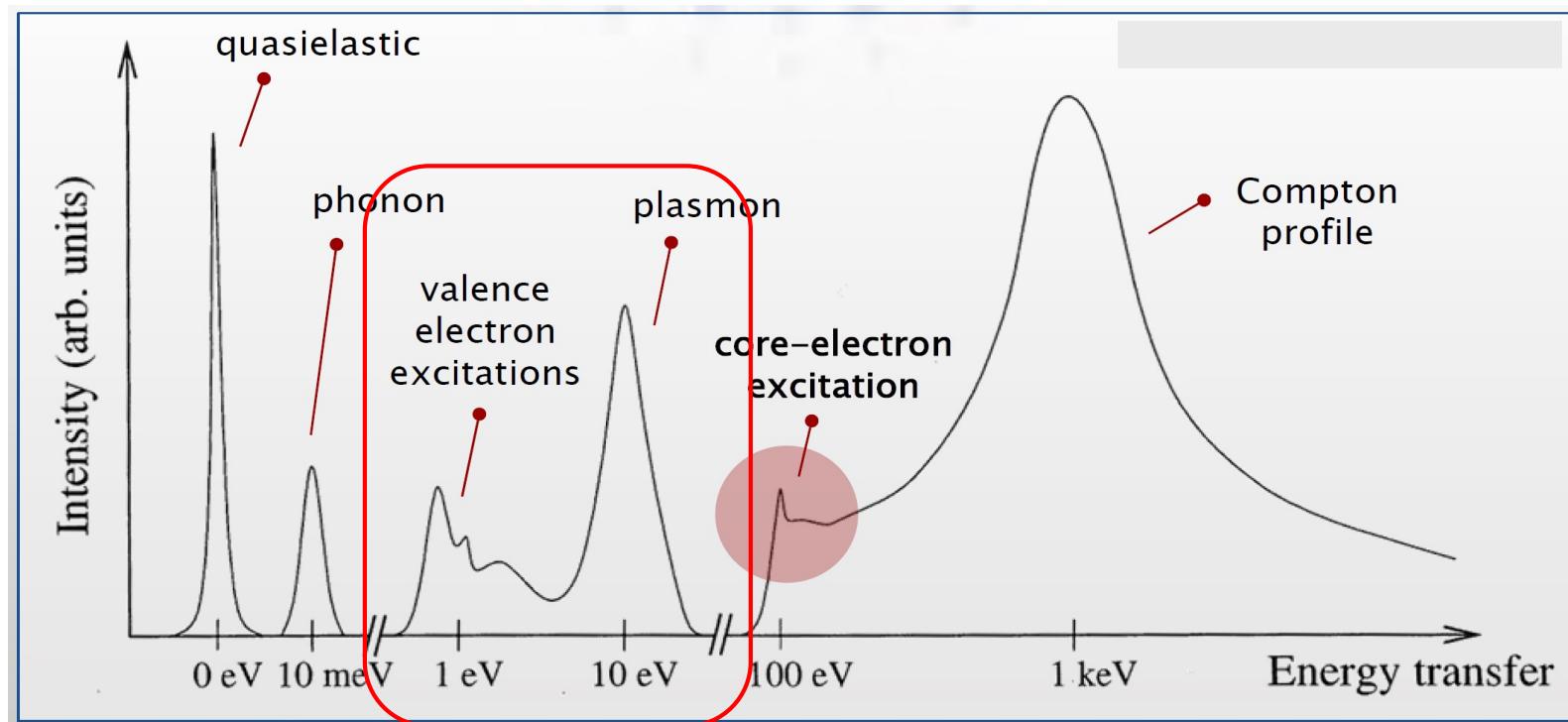
direct photoemission

hν

c

v
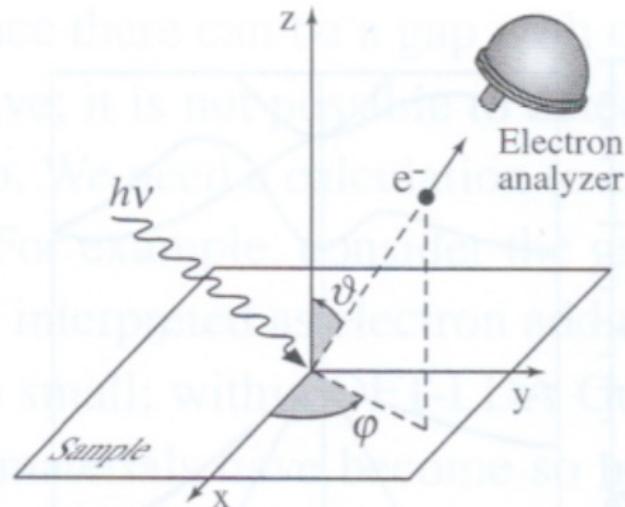
absorption

light scattering

quasielastic

phonon   plasmon   Compton profile

valence electron excitations

core–electron excitation

Intensity (arb. units)

0 eV   10 meV   1 eV   10 eV   100 eV   1 keV   Energy transfer

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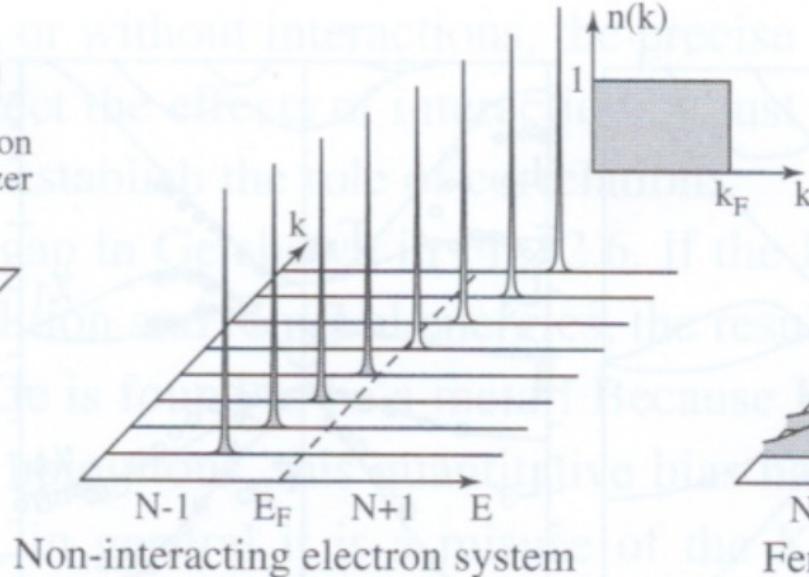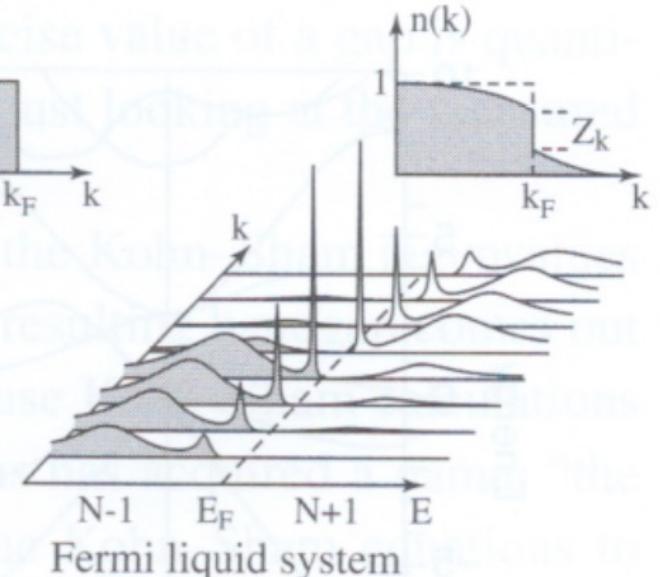
Photoemission experiment

Photoemission geometry
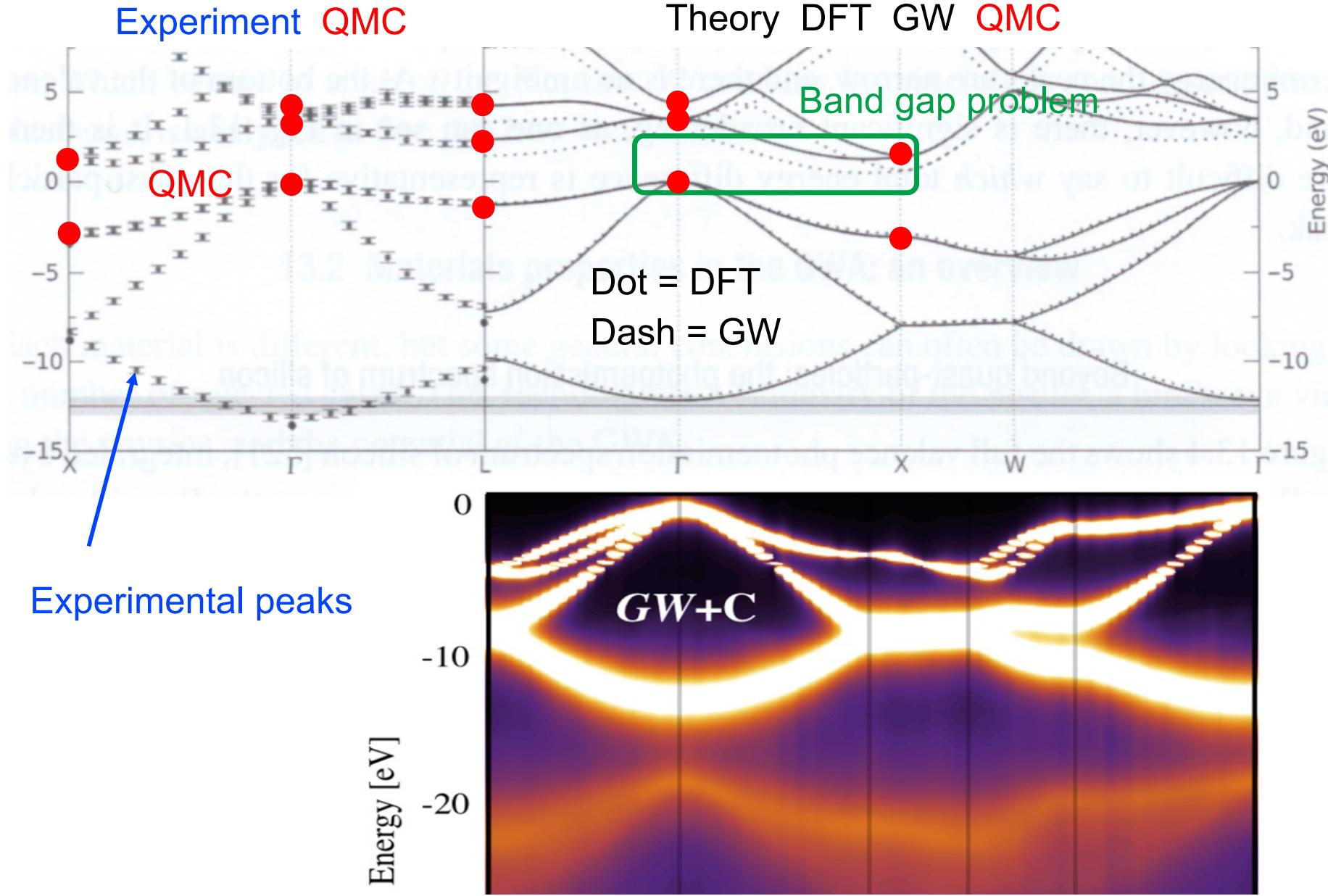
Non-interacting electron system
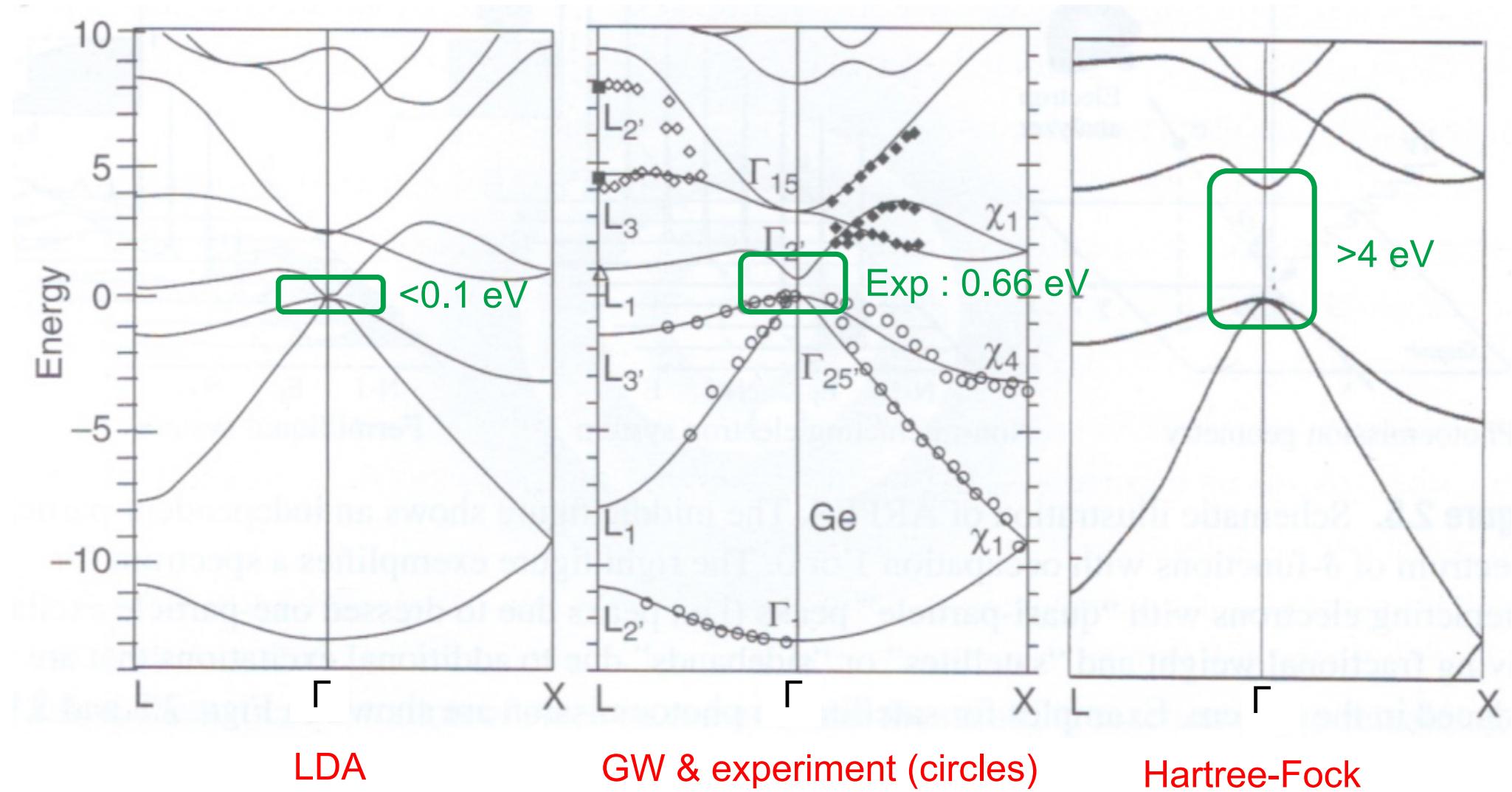
Fermi liquid system

Similar for inverse photoemission …

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Silicon band structure

Experiment QMC   Theory DFT GW QMC

QMC

Band gap problem

Dot = DFT
Dash = GW

Experimental peaks

GW+C

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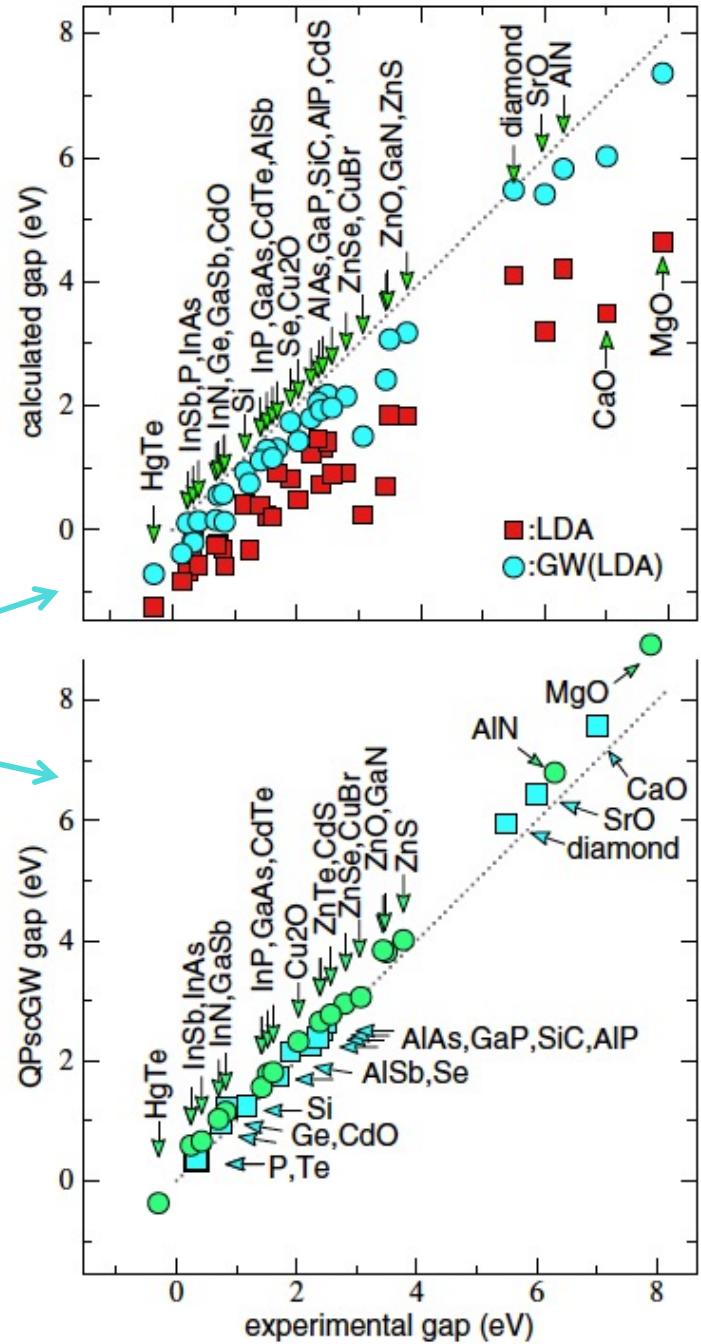
Germanium band structure

<0.1 eV

Exp : 0.66 eV

>4 eV

LDA   GW & experiment (circles)   Hartree-Fock

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GW approximation

- Heavier than DFT/LDA
  (e.g. CPU time x100...x1000)

- Start from DFT calculation,
  then can be one-shot (GW@LDA)
  or self-consistent (SCGW)

- SCGW "Gold standard"
  (within 0.1...0.3eV),
  but GW@LDA is often fine

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Charged excitations and Green's function

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Back to undergrad Quantum Mechanics

Starting point : Time-Dependent Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

e.g. for 1 particle

$$i\hbar\frac{\partial\psi}{\partial t}\bigg|_{(\mathbf{r},t)} = -\frac{\hbar^2}{2m}\vec{\nabla}^2\psi\bigg|_{(\mathbf{r},t)} + V(\mathbf{r},t)\psi(\mathbf{r},t)$$

If Hamiltonian does not depend on time,

$$\hat{H} = \sum_{i=1,n} -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_i} + V(\mathbf{r}_1,...,\mathbf{r}_n)$$

then separation of variables $\quad \psi(\mathbf{r}_1,...\mathbf{r}_n,t) = \varphi(\mathbf{r}_1,...\mathbf{r}_n).f(t)$

$$\Rightarrow \quad i\hbar\frac{\partial f}{\partial t} = Ef \qquad = \varphi(\mathbf{r}_1,...\mathbf{r}_n).e^{-i\frac{Et}{\hbar}}$$

Energy : linked to phase acquired upon propagation.

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The 1-particle Green's function

Exact ground state wavefunction for *N* electrons $\left| N,0 \right\rangle$

Creation, annihilation operators $\psi^{+}(\mathbf{r},t), \psi(\mathbf{r},t)$

$\psi^{+}(\mathbf{r},t)\left| N,0 \right\rangle$ is a (N+1) electron wavefunction, not necessarily in the ground-state (neither in a pure excited state)

$\psi^{+}(\mathbf{r}',t')\left| N,0 \right\rangle$ is another (N+1) electron wavefunction

Let's compare them !

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The 1-particle Green's function

$$iG^e(\mathbf{r}t,\mathbf{r}'t') = \langle N,0|\psi(\mathbf{r},t)\psi^+(\mathbf{r}',t')|N,0\rangle \quad \text{for} \quad t > t'$$

Measures how an extra electron propagates from $\mathbf{r}'t'$ to $\mathbf{r}t$

$$iG^h(\mathbf{r}'t',\mathbf{r}t) = \langle N,0|\psi^+(\mathbf{r}',t')\psi(\mathbf{r},t)|N,0\rangle \quad \text{for} \quad t' > t$$

Measures how an extra hole propagates from $\mathbf{r}t$ to $\mathbf{r}'t'$

$$G(\mathbf{r}t,\mathbf{r}'t') = G^e(\mathbf{r}t,\mathbf{r}'t') - G^h(\mathbf{r}'t',\mathbf{r}t)$$

Compact expression that describes propagation of either an extra electron or an extra hole, depending on time-ordering

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Lehmann representation

$$iG^e(\mathbf{r}t, \mathbf{r}'t') = \langle N,0 | \psi(\mathbf{r},t) \quad \psi^+(\mathbf{r}',t') | N,0 \rangle$$

Closure relation based on
   complete set of eigenvectors
   with eigenenergies $E(N \pm 1, i)$

$$\sum_{M,i} | M,i \rangle \langle M,i |$$

$$iG^h(\mathbf{r}'t', \mathbf{r}t) = \langle N,0 | \psi^+(\mathbf{r}',t') \quad \psi(\mathbf{r},t) | N,0 \rangle$$

Then, Fourier transform,
$$G(\mathbf{r},\mathbf{r}';\omega) = \sum_i \frac{f_i(\mathbf{r})f_i^*(\mathbf{r}')}{\omega - \varepsilon_i \pm i\eta}$$

where
$$\varepsilon_i = \begin{cases} E(N+1,i) - E(N,0) \\ E(N,0) - E(N-1,i) \end{cases}$$

are exact excitation energies (affinities or ionisation) !

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GW approximation to the electronic band structure

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Many-body perturbation theory

Historically older than DFT (from the 40-50's) !
Big names : Feynman, Schwinger, Hubbard, Hedin, Lundqvist
Heavy formalism ! Not amenable to 1-hour presentation …
Diagrammatic representation of perturbative terms
Based on Green's functions = propagators
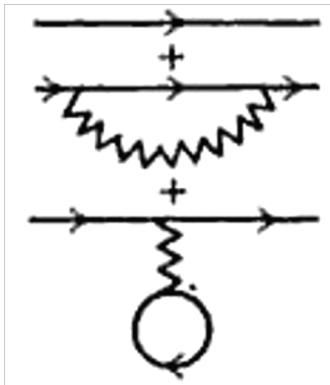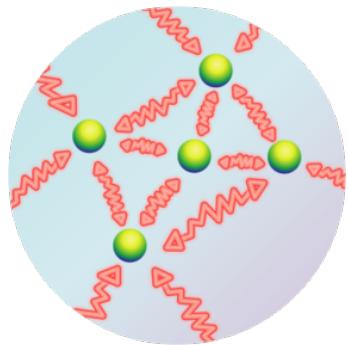
1-particle

$$G(\mathbf{r},t;\mathbf{r}',t')$$
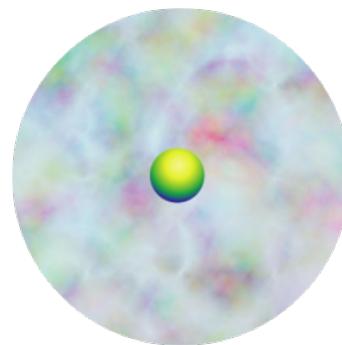
Propagation without Coulomb interactions
+
Propagation with polarization of medium
+
Propagation with mean-field electrostatic
                    interaction with other electrons
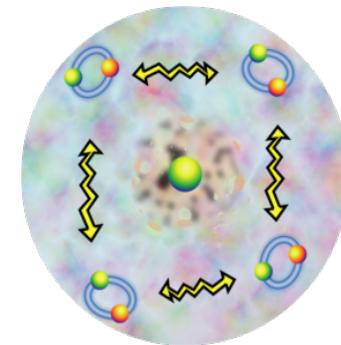
GW approximation

Wavefunctions   DFT   GW

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\psi_i(\mathbf{r}) = \varepsilon_i^{KS}\psi_i(\mathbf{r}) \qquad \text{DFT}$$

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_i(\mathbf{r}) + \int \boxed{\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_i^{QP})}\psi_i(\mathbf{r}')d\mathbf{r}' = \varepsilon_i^{QP}\psi_i(\mathbf{r})$$

$$\boxed{\Sigma(\mathbf{r},\mathbf{r}';\omega)} = \lim_{\delta\to 0+}\frac{i}{2\pi}\int d\omega' e^{i\omega'\delta}\ \boxed{G}(\mathbf{r},\mathbf{r}';\omega+\omega')\ \boxed{W}(\mathbf{r},\mathbf{r}';\omega') \qquad \text{GW}$$

Self energy   Green's function   Screened interaction

AMM lecture Beyond DFT 2

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Screened interaction and susceptibility

Computation of the susceptibility (for screening of Coulomb)

Adler-Wiser expression, see later

$$\chi_0(\mathbf{r},\mathbf{r}';\omega) = -\sum_{\substack{n \\ occ}} \sum_{\substack{m \\ unocc}}^{\infty} \left(\frac{\varphi_n^*(\mathbf{r})\varphi_m(\mathbf{r})\varphi_m^*(\mathbf{r}')\varphi_n(\mathbf{r}')}{\varepsilon_m - \varepsilon_n - \omega - i\delta} + \frac{\varphi_n(\mathbf{r})\varphi_m^*(\mathbf{r})\varphi_m(\mathbf{r}')\varphi_n^*(\mathbf{r}')}{\varepsilon_m - \varepsilon_n + \omega + i\delta} \right)$$

Approximation : from independent-particle approximation
Usually starting from KS eigenenergies and eigenfunction

Double sum over a large number of independent « transitions »
Seven-dimensional objects (in black)
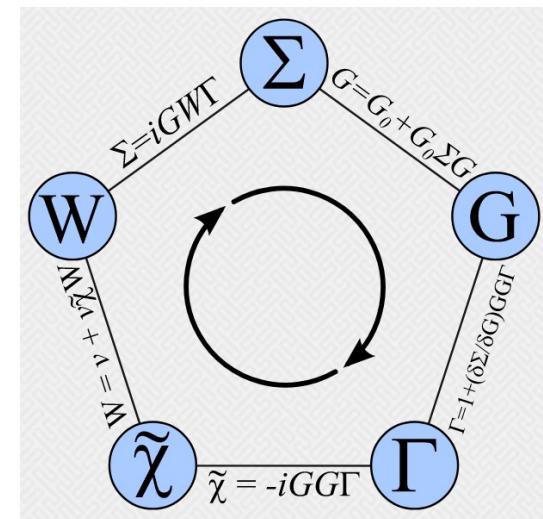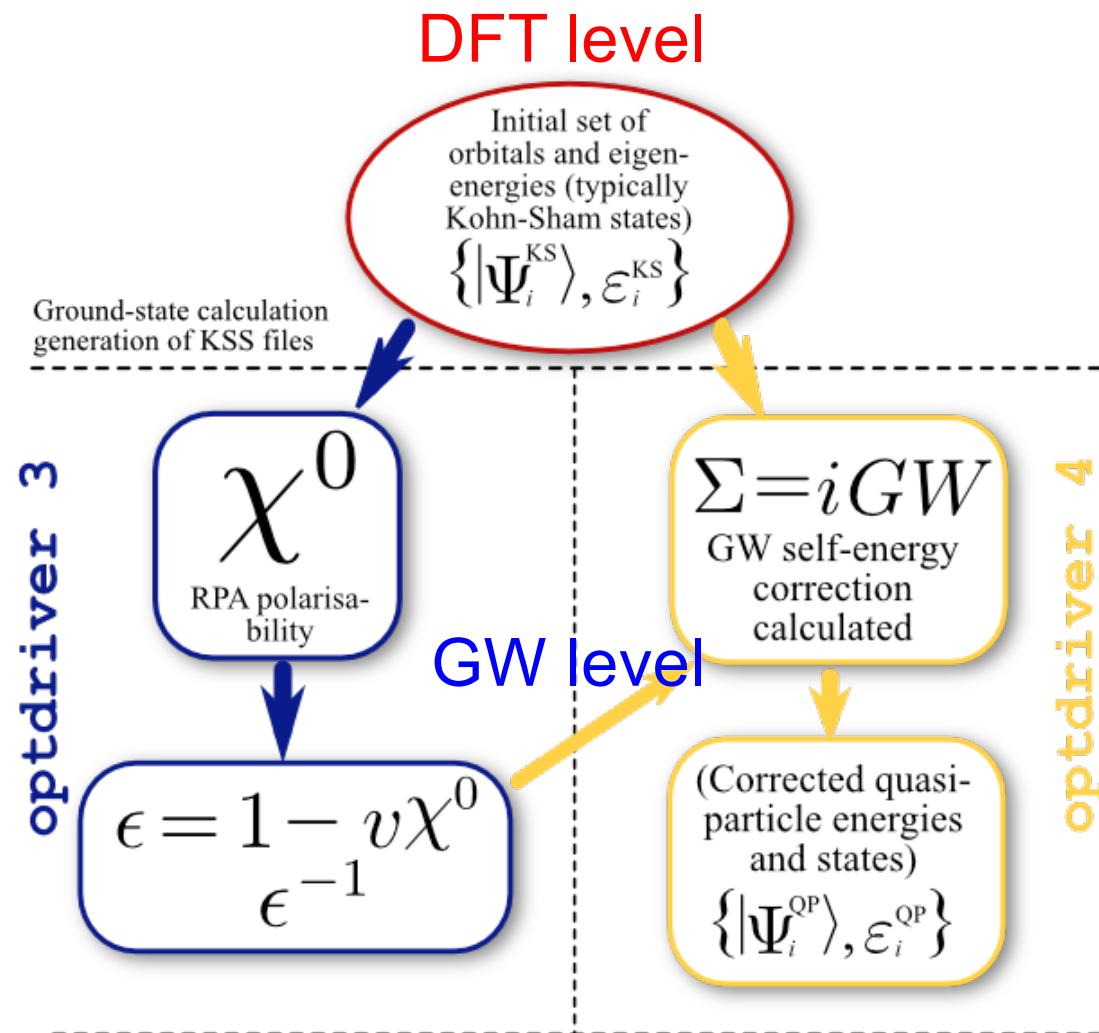
$$\varepsilon(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}') - \int V_C(\mathbf{r}-\mathbf{r}'')\chi_0(\mathbf{r}'',\mathbf{r}';\omega)d\mathbf{r}''$$ Dielectric function

$$W(\mathbf{r},\mathbf{r}';\omega) = \int \varepsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)V_C(\mathbf{r}''-\mathbf{r})d\mathbf{r}''$$ Screened interaction
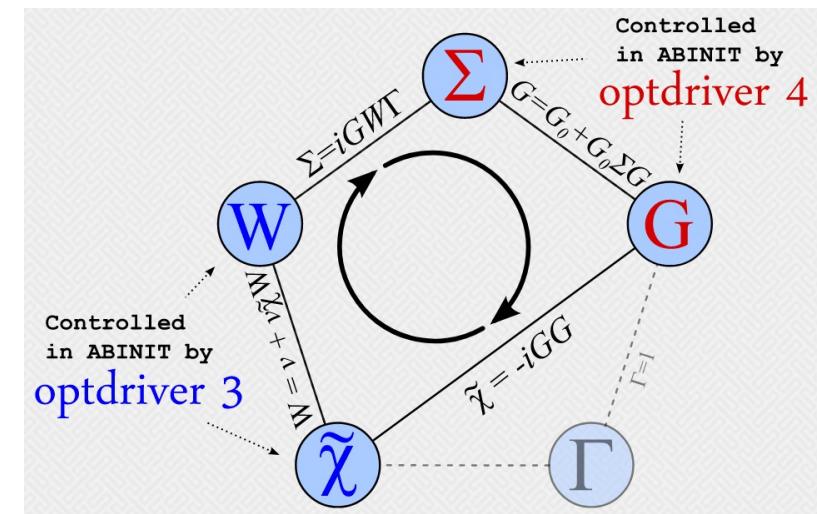
$$G(\mathbf{r},\mathbf{r}';\omega) = \sum_n \frac{\varphi_n(\mathbf{r})\varphi_n^*(\mathbf{r}')}{\omega - \varepsilon_n}$$ Usually starting from KS eigenenergies and eigenfunction

Independent-particle Green's function

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Self-consistent GW

DFT level

Initial set of orbitals and eigen-energies (typically Kohn-Sham states)
$$\{|\Psi_i^{KS}\rangle, \varepsilon_i^{KS}\}$$

Ground-state calculation generation of KSS files

optdriver 3

χ^0

RPA polarisability

GW level

$\epsilon = 1 - v\chi^0$
ϵ^{-1}

$\Sigma = iGW$

GW self-energy correction calculated

optdriver 4

(Corrected quasi-particle energies and states)
$$\{|\Psi_i^{QP}\rangle, \varepsilon_i^{QP}\}$$

$\Sigma = iGW\Gamma$ Σ $G = G_0 + G_0\Sigma G$ G

$W = v + v\tilde{\chi}W$ W $\Gamma = 1 + (\delta\Sigma/\delta G)GG\Gamma$ Γ

$\tilde{\chi}$ $\tilde{\chi} = -iGG\Gamma$
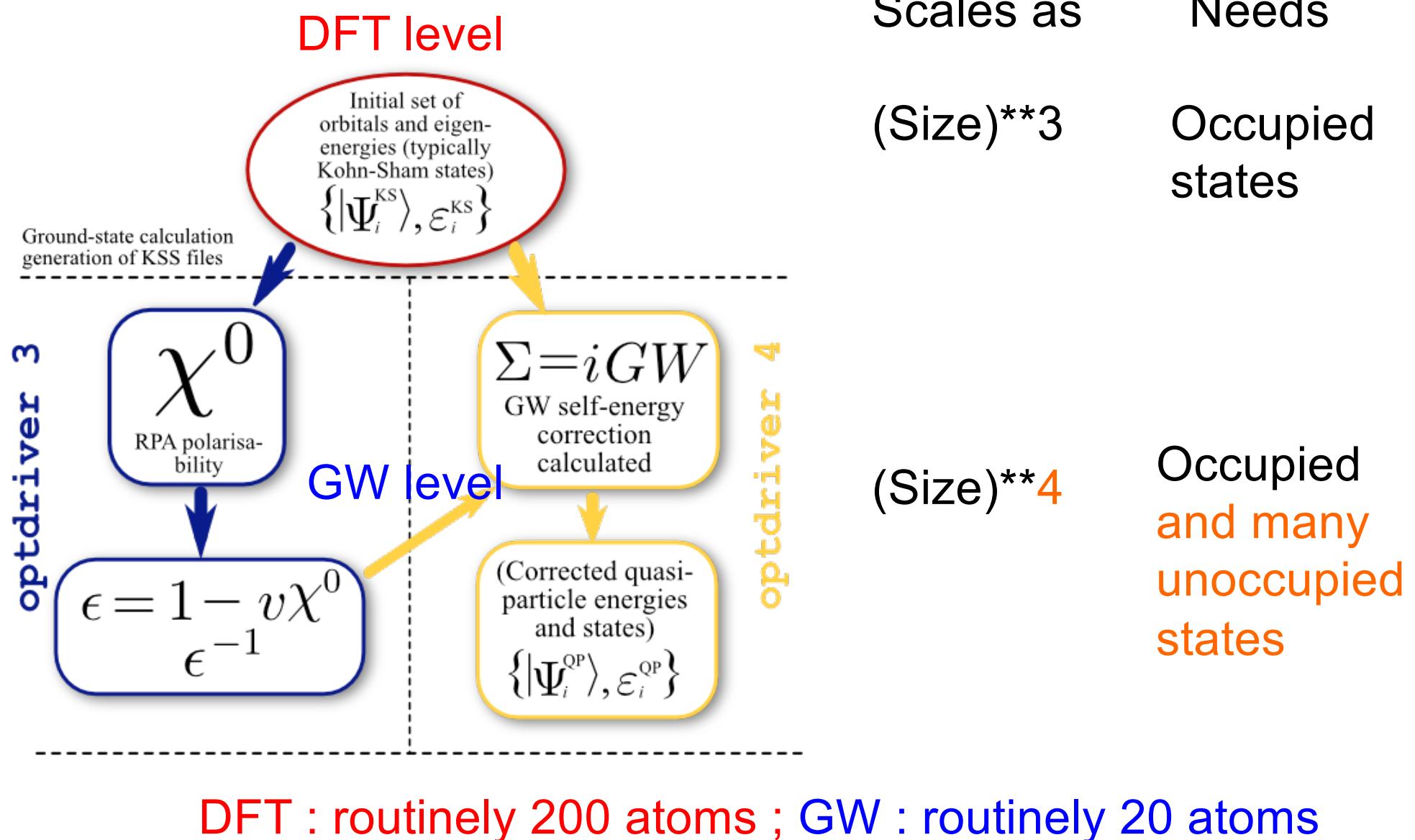
Neglect of Γ
(vertex corrections)

Controlled in ABINIT by
optdriver 4

Controlled in ABINIT by
optdriver 3

$\Sigma = iGW\Gamma$ Σ $G = G_0 + G_0\Sigma G$ G

$W = v + v\tilde{\chi}W$ W

$\tilde{\chi} = -iGG$ $\tilde{\chi}$ $\Gamma = 1$ Γ

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GW computational bottlenecks

Scales as   Needs

DFT level

Ground-state calculation generation of KSS files

optdriver 3

optdriver 4

GW level

(Size)**3   Occupied
                   states

(Size)**4   Occupied
                   and many
                   unoccupied
                   states

DFT : routinely 200 atoms ; GW : routinely 20 atoms

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Avoiding full self-consistency

$G_0 W_0$: DFT => G_0, W_0 => Σ => compute eigenenergies STOP

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) \right)\psi_i(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\varepsilon_i^{QP})\psi_i(\mathbf{r}')d\mathbf{r}' = \varepsilon_i^{QP}\psi_i(\mathbf{r})$$

GW_0 : DFT => G_0, W_0 => Σ => eigenenergies+eigenfunctions
then iterate on $G => \Sigma$ => compute eigenenergies

$$G(\mathbf{r},\mathbf{r}';\omega) = \sum_n \frac{\varphi_n(\mathbf{r})\varphi_n^*(\mathbf{r}')}{\omega - \varepsilon_n}$$

$e\text{-}GW$: DFT => G_0, W_0 => Σ => compute eigenenergies
then update energies in $G, W => \Sigma$ => compute eigenenergies

$$\chi_0(\mathbf{r},\mathbf{r}';\omega) = -\sum_{\substack{n \\ occ}}\sum_{\substack{m \\ unocc}}^{\infty}\left(\frac{\varphi_n^*(\mathbf{r})\varphi_m(\mathbf{r})\varphi_m^*(\mathbf{r}')\varphi_n(\mathbf{r}')}{\varepsilon_m - \varepsilon_n - \omega - i\delta} + \frac{\varphi_n(\mathbf{r})\varphi_m^*(\mathbf{r})\varphi_m(\mathbf{r}')\varphi_n^*(\mathbf{r}')}{\varepsilon_m - \varepsilon_n + \omega + i\delta} \right)$$

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Plasmon-pole models to decrease CPU time

$$\chi_0(\mathbf{r},\mathbf{r}';\omega) = -\sum_{\substack{n \\ occ}} \sum_{\substack{m \\ unocc}}^{\infty} \left(\frac{\varphi_n^*(\mathbf{r})\varphi_m(\mathbf{r})\varphi_m^*(\mathbf{r}')\varphi_n(\mathbf{r}')}{\varepsilon_m - \varepsilon_n - \omega - i\delta} + \frac{\varphi_n(\mathbf{r})\varphi_m^*(\mathbf{r})\varphi_m(\mathbf{r}')\varphi_n^*(\mathbf{r}')}{\varepsilon_m - \varepsilon_n + \omega + i\delta} \right)$$

Scales as   (Size)**4

Sparing evaluations at many frequencies ?
Plasmon-pole models (PPM) allows one to deduce
frequency dependence from either static susceptibility only,
or static and dynamic susceptibility at only one frequency.
$\Rightarrow$ one order of magnitude speed-up.

Most often : Godby-Needs plasmon pole

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Linearized quasi-particle equation

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_i^{KS}(\mathbf{r}) + V_{xc}(\mathbf{r})\psi_i^{KS}(\mathbf{r}) = \varepsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$$

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_i^{QP}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\varepsilon_i^{QP})\psi_i^{QP}(\mathbf{r}')d\mathbf{r}' = \varepsilon_i^{QP}\psi_i^{QP}(\mathbf{r})$$

Self-energy $\Sigma(\vec{r},\vec{r}';\varepsilon_i^{QP})$ depends on ε_i^{QP} ?!

Rewrite quasi-particle equation :

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right)\psi_i^{QP}(\vec{r}) + \int\left(\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_i^{QP}) - V_{xc}(\mathbf{r})\right)\psi_i^{QP}(\mathbf{r}')d\mathbf{r}' = \varepsilon_i^{QP}\psi_i^{QP}(\mathbf{r})$$

Treat difference between self-energy and V_{xc} as perturbation
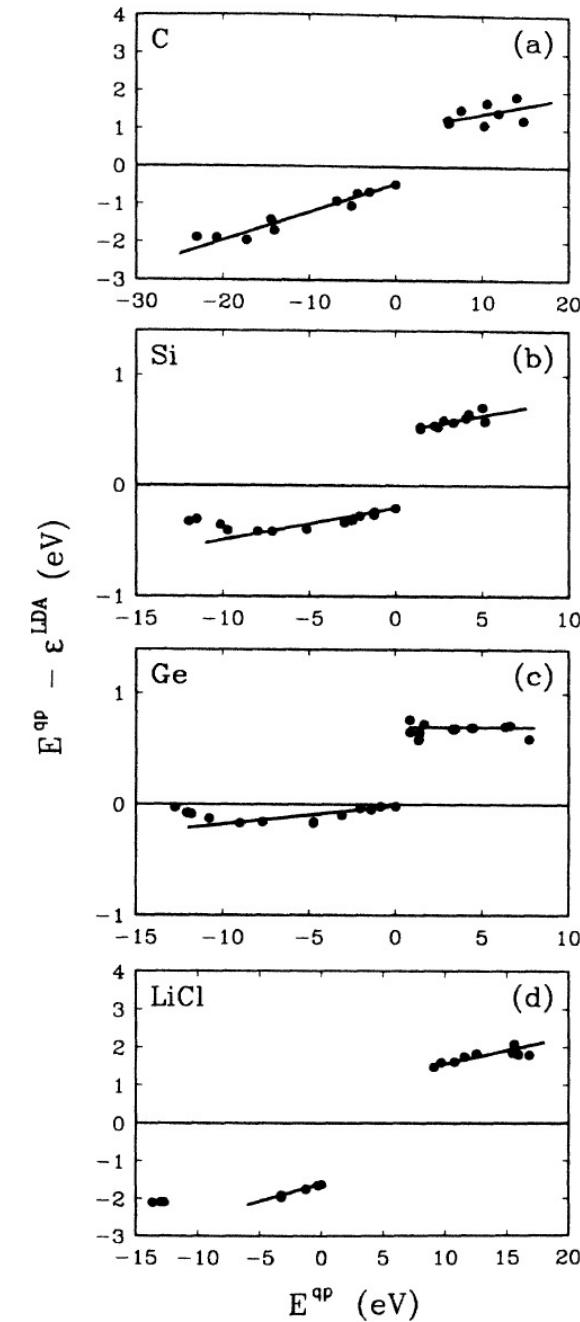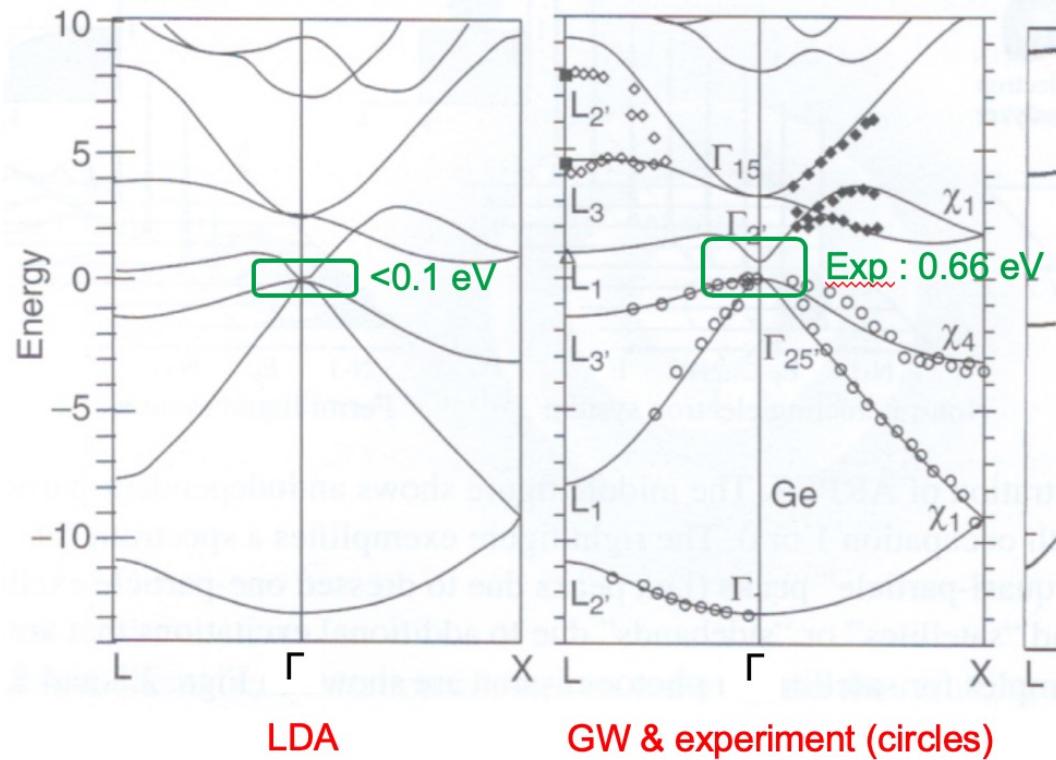
$$\varepsilon_i^{QP} = \varepsilon_i^{KS} + \left\langle \psi_i^{KS}\middle|\Sigma(\varepsilon_i^{QP}) - V_{xc}\middle|\psi_i^{KS}\right\rangle$$

Moreover
$$\Sigma(\varepsilon_i^{QP}) = \Sigma(\varepsilon_i^{KS}) + (\varepsilon_i^{QP} - \varepsilon_i^{KS})\left.\frac{\partial\Sigma}{\partial\varepsilon}\right|_{\varepsilon_i^{KS}}$$

Thus
$$\boxed{\varepsilon_i^{QP} = \varepsilon_i^{KS} + Z_i\left\langle\psi_i^{KS}\middle|\Sigma(\varepsilon_i^{KS}) - V_{xc}\middle|\psi_i^{KS}\right\rangle}$$

with $\quad Z_i^{-1} = 1 - \left\langle\psi_i^{KS}\middle|\left.\frac{\partial\Sigma}{\partial\varepsilon}\right|_{\varepsilon_i^{KS}}\middle|\psi_i^{KS}\right\rangle$

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Band gap correction : a scissor ?
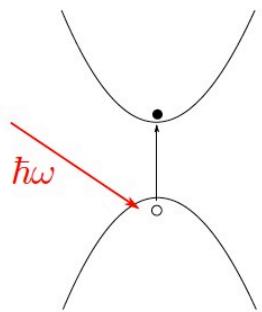
LDA   GW & experiment (circles)

<0.1 eV   Exp : 0.66 eV

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Optical characteristics of materials

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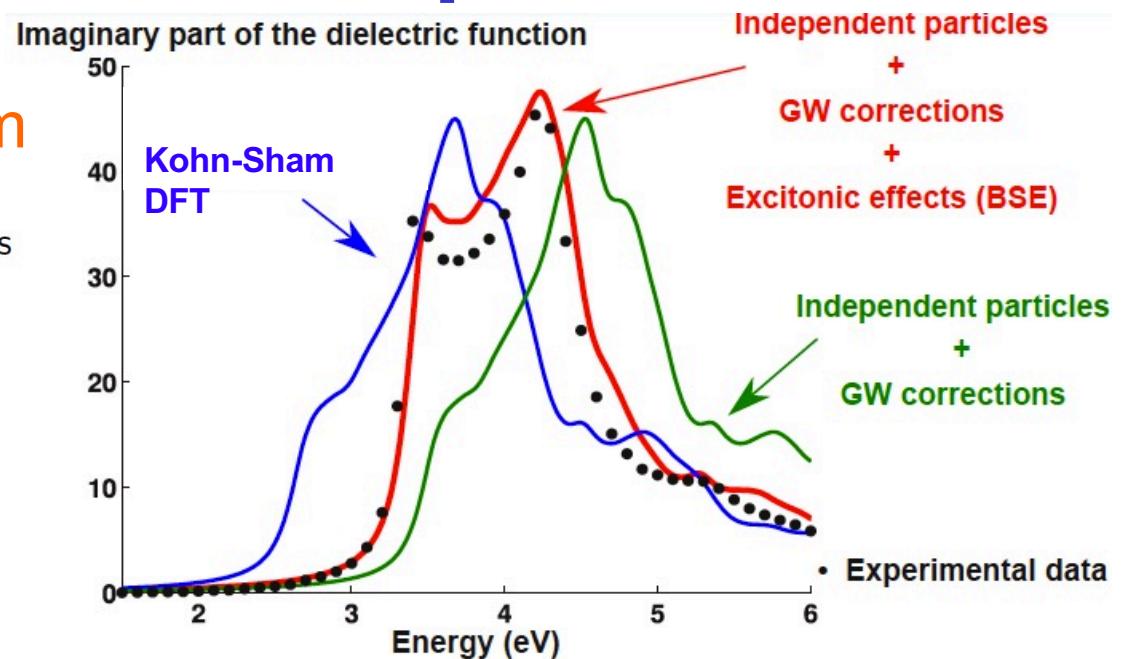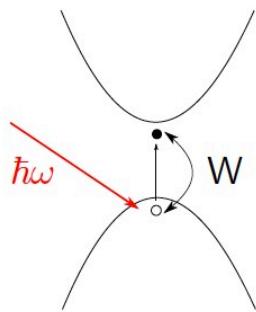
Optical response : absorption

Silicon absorption spectrum

Independent electrons   Interacting electrons
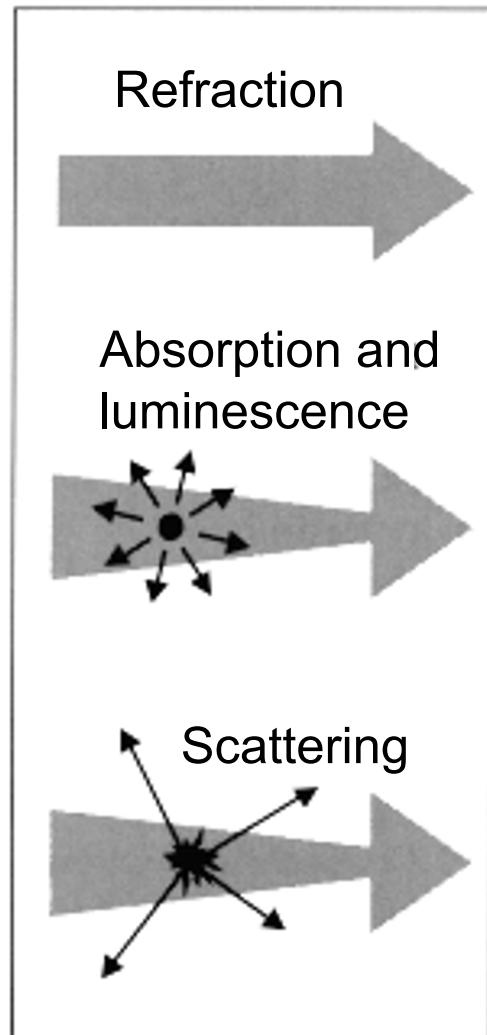
$\hbar\omega$ $\hbar\omega$ W

Imaginary part of the dielectric function

Independent particles + GW corrections + Excitonic effects (BSE)

Kohn-Sham DFT

Independent particles + GW corrections

· Experimental data

Energy (eV)

Beyond DFT, with Many-Body Perturbation Theory ... need :
- band gap correction (GW) [still independent particle IPA]
- excitonic corrections (Bethe-Salpeter Equation - BSE)

Optical spectrum, relation with the dielectric function

$$\operatorname{Im} \varepsilon(\omega) = 1 + 4\pi \operatorname{Im} \chi(\omega)$$

Neutral electronic excitations

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Optical processes inside materials

Refraction

Absorption and luminescence

Scattering

Refraction causes reduction in wave velocity

Absorption causes attenuation.

Luminescence can accompany absorption if excited state re-emit by spontaneous emission (different frequency !)

Scattering causes redirection of light.

Diminishing width of the arrow for absorption and scattering represents attenuation of the beam.

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Maxwell equations

Macroscopic fields, in the presence of matter (gas, liquid, solid)
Four basic vector fields (space-time functions) :

$\mathbf{E}$ electric field

$\mathbf{H}$ magnetic field

$\mathbf{D}$ displacement field

$\mathbf{B}$ magnetic flux density

+ Charge density ρ and current density $\mathbf{j}$

$$\nabla \cdot \mathbf{D} = \rho$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{H} = \mathbf{j} + \frac{\partial \mathbf{D}}{\partial t}$$

(SI units)

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Constitutive equations

Mawxell equations completed by « constitutive equations » :
define displacement and magnetic flux density fields, as well as
charge density and current, from the electric and magnetic fields.

Exemple :   (isotropic media, linear regime, low frequencies - max 100MHz)

Electric and magnetic susceptibilities χ and χ_M (adim.)

$$\mathbf{P} = \varepsilon_0 \chi \, \mathbf{E}$$

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$$

$$\mathbf{D} = \varepsilon_0 \varepsilon_r \mathbf{E}$$

$$\varepsilon_r = 1 + \chi$$

$$\mathbf{M} = \chi_M \mathbf{H}$$

$$\mathbf{B} = \mu_0 \, (\mathbf{H} + \mathbf{M})$$

$$\mathbf{B} = \mu_0 \, \mu_r \mathbf{H}$$

$$\mu_r = 1 + \chi_M$$

(Relative) dielectric constant ε_r (Relative) magnetic permeability $\boldsymbol{\mu}_r$

(Note : susceptibilities vanish in vacuum)

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Wave equation in vacuum

Maxwell's equations in vacuum $\quad \mu_{\mathrm{r}} = \varepsilon_r = 1$
Or in a medium with no free charges or currents
(no absorption of energy, no decay)

$$\nabla \times \mathbf{E} = -\,\mu_0\mu_r\,\frac{\partial \mathbf{H}}{\partial t} \qquad\qquad \nabla \times \mathbf{H} = \varepsilon_0\varepsilon_r\frac{\partial \mathbf{E}}{\partial t}$$

$$\nabla \times (\nabla \times \mathbf{E}) = -\,\mu_0\mu_r\varepsilon_0\varepsilon_r\frac{\partial^2 \mathbf{E}}{\partial t^2}$$

We know $\qquad \nabla \times (\nabla \times \mathbf{E}) = \nabla(\nabla.\mathbf{E}) - \nabla^2 \mathbf{E}$

No charge means $\qquad \nabla . \mathbf{E} = \dfrac{\rho}{\varepsilon_{\mathrm{r}}\varepsilon_0} = 0$

Wave equation : $\qquad \boxed{\nabla^2 \mathbf{E} = \mu_0\mu_r\varepsilon_0\varepsilon_r\dfrac{\partial^2 \mathbf{E}}{\partial t^2}}$

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Electromagnetic waves

$$\nabla^2 \mathbf{E} = \mu_0 \mu_r \varepsilon_0 \varepsilon_r \frac{\partial^2 \mathbf{E}}{\partial t^2}$$

Solution : plane waves $\quad \mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i(\mathbf{kr} - \omega t)} + (c.c.)$

and arbitrary linear combinations (for different $\mathbf{k}$ values)

$\mathbf{k}$ wavevector $\qquad \omega$ angular frequency $\qquad \lambda$ wavelength

$$k = \frac{2\pi}{\lambda} = \frac{\omega}{\upsilon} \qquad \upsilon \text{ velocity of the waves} \qquad \frac{1}{\upsilon^2} = \mu_0 \mu_r \varepsilon_0 \varepsilon_r$$

$$\upsilon = \frac{1}{\sqrt{\varepsilon_r \mu_r}} c \qquad n = \frac{c}{\upsilon} = \sqrt{\varepsilon_r \mu_r} \qquad \text{index of refraction}$$

$$c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} = 2.998 \times 10^8 \text{ms}^{-1} \qquad \varepsilon_0 = 8.8541878... \times 10^{-12} \text{Fm}^{-1}$$

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Complex index of refraction

Now, examine a real material, with currents (still isotropic, for convenience).

Start again from Maxwell's Eqs. with the rotational and
time derivative

$$\nabla \times \mathbf{E} = - \frac{\partial \mathbf{B}}{\partial t} \qquad \nabla \times \mathbf{H} = \mathbf{j} + \frac{\partial \mathbf{D}}{\partial t}$$

Constitutive equations :
$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E} \qquad \mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \qquad \mathbf{B} = \mu_0 \mu_r \mathbf{H}$$

Moreover, include Ohm's law (conductivity) :
current induced by an electric field

$$\boxed{\mathbf{j} = \sigma \mathbf{E}}$$

$$\nabla^2 \mathbf{E} = \sigma \mu_0 \mu_r \frac{\partial \mathbf{E}}{\partial t} + \mu_0 \mu_r \varepsilon_0 \varepsilon_r \frac{\partial^2 \mathbf{E}}{\partial t^2}$$

Plane waves (with complex **k**) are still solutions :

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 e^{i(\mathbf{k}\mathbf{r} - \omega t)} + (c.c.) \qquad k^2 = i\sigma\mu_0\mu_r\omega + \mu_0\mu_r\varepsilon_0\varepsilon_r\omega^2$$

$$k = \tilde{n}\frac{\omega}{c} \qquad \boxed{\tilde{n}^2 = \mu_r\varepsilon_r + i\frac{\mu_r\sigma}{\varepsilon_0\omega}} \qquad \tilde{n} \quad \text{complex index of refraction}$$

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Complex index of refraction (II)

Define $\quad \tilde{n} = n + i\kappa$ $\qquad n \quad$ normal refractive index

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \kappa \quad$ extinction coefficient

$$k = \tilde{n}\frac{\omega}{c} = (n + i\kappa)\frac{\omega}{c}$$

$$E(z,t) = E_0\, e^{i(kz-\omega t)} + \left(E_0\right)^* e^{-i(k^*z-\omega t)}$$

$$E(z,t) = E_0 e^{i(\omega\tilde{n}z/c - \omega t)} + E_0^* e^{-i(\omega\tilde{n}^*z/c - \omega t)} = \boxed{e^{-\kappa\omega z/c}} \left(E_0 e^{i(\omega n z/c - \omega t)} + E_0^* e^{-i(\omega n z/c - \omega t)}\right)$$

(Exponential decrease) times (propagating wave)

absorption   refraction

One expects $\;\kappa\;$ and $\;n\;$ to be positive numbers

Microscopic wave equation

Hypothesis :   focusing on response to electric field
magnetic field response is negligible,

Wave equation for electric field becomes

$$\nabla \times \left(\nabla \times \mathbf{E}(\mathbf{r},t) \right) = -\frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2}(\mathbf{r},t) - \mu_0 \frac{\partial \mathbf{j}}{\partial t}(\mathbf{r},t) - \mu_0 \frac{\partial^2 \mathbf{P}}{\partial t^2}(\mathbf{r},t)$$

Then, analysis of relationship between electric field,
and induced current and polarisation fields, in the linear regime

If $\mathbf{E}_1(\mathbf{r},t)$ $\Longrightarrow$ $\mathbf{j}_1(\mathbf{r}',t'),\mathbf{P}_1(\mathbf{r}',t')$

and $\mathbf{E}_2(\mathbf{r},t)$ $\Longrightarrow$ $\mathbf{j}_2(\mathbf{r}',t'),\mathbf{P}_2(\mathbf{r}',t')$

Then $\lambda_1\mathbf{E}_1(\mathbf{r},t) + \lambda_2\mathbf{E}_2(\mathbf{r},t)$ $\Longrightarrow$ $\lambda_1\mathbf{j}_1(\mathbf{r}',t') + \lambda_2\mathbf{j}_2(\mathbf{r}',t')$

$\lambda_1\mathbf{P}_1(\mathbf{r}',t') + \lambda_2\mathbf{P}_2(\mathbf{r}',t')$

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Polarizability and conductivity

- Hypothesis of linear-response regime :

$$P_\beta(\mathbf{r},t) = \iint \sum_\gamma \boxed{\alpha_{\beta\gamma}(\mathbf{r},t;\mathbf{r}',t')} E_\gamma(\mathbf{r}',t') d\mathbf{r}' dt' \qquad \textcolor{red}{\text{polarizability}}$$

$$j_\beta(\mathbf{r},t) = \iint \sum_\gamma \boxed{\sigma_{\beta\gamma}(\mathbf{r},t;\mathbf{r}',t')} E_\gamma(\mathbf{r}',t') d\mathbf{r}' dt' \qquad \textcolor{red}{\text{conductivity}}$$

- Causal response
- Invariance with respect to time translation :

  dependence only with respect to t-t' ; can be Fourier-transformed => frequency

- Is the response local ?   As first approximation :

  Yes, if the field is slowly varying compared to atomic details

  = Neglect of « local fields » ; polarizability = bulk characteristics

$$\boxed{P_\beta(\omega) = \sum_\gamma \alpha_{\beta\gamma}(\omega) E_\gamma(\omega)} \qquad \text{(the same for the conductivity)}$$

$$\left(\nabla \times (\nabla \times \mathbf{E}(\omega))\right)_\beta = \frac{\omega^2}{c^2} \sum_\gamma \boxed{\varepsilon_{\beta\gamma}(\omega)} E_\gamma(\omega) \qquad \textcolor{red}{\text{Wave equation}}$$

$$\boxed{\varepsilon_{\beta\gamma}(\omega)} = 1 + \frac{\alpha_{\beta\gamma}(\omega)}{\varepsilon_0} + i\frac{\sigma_{\beta\gamma}(\omega)}{\varepsilon_0 \omega} \qquad \textcolor{green}{\textbf{Complex macroscopic dielectric tensor,}}$$
$$\textcolor{green}{\textbf{function of frequency => absorption and velocity}}$$

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Wrap-up and an example (SiO$_2$-glass)

$$\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$$

n normal refractive index

κ extinction coefficient

$$\boxed{\tilde{n}^2(\omega) = \varepsilon(\omega)}$$
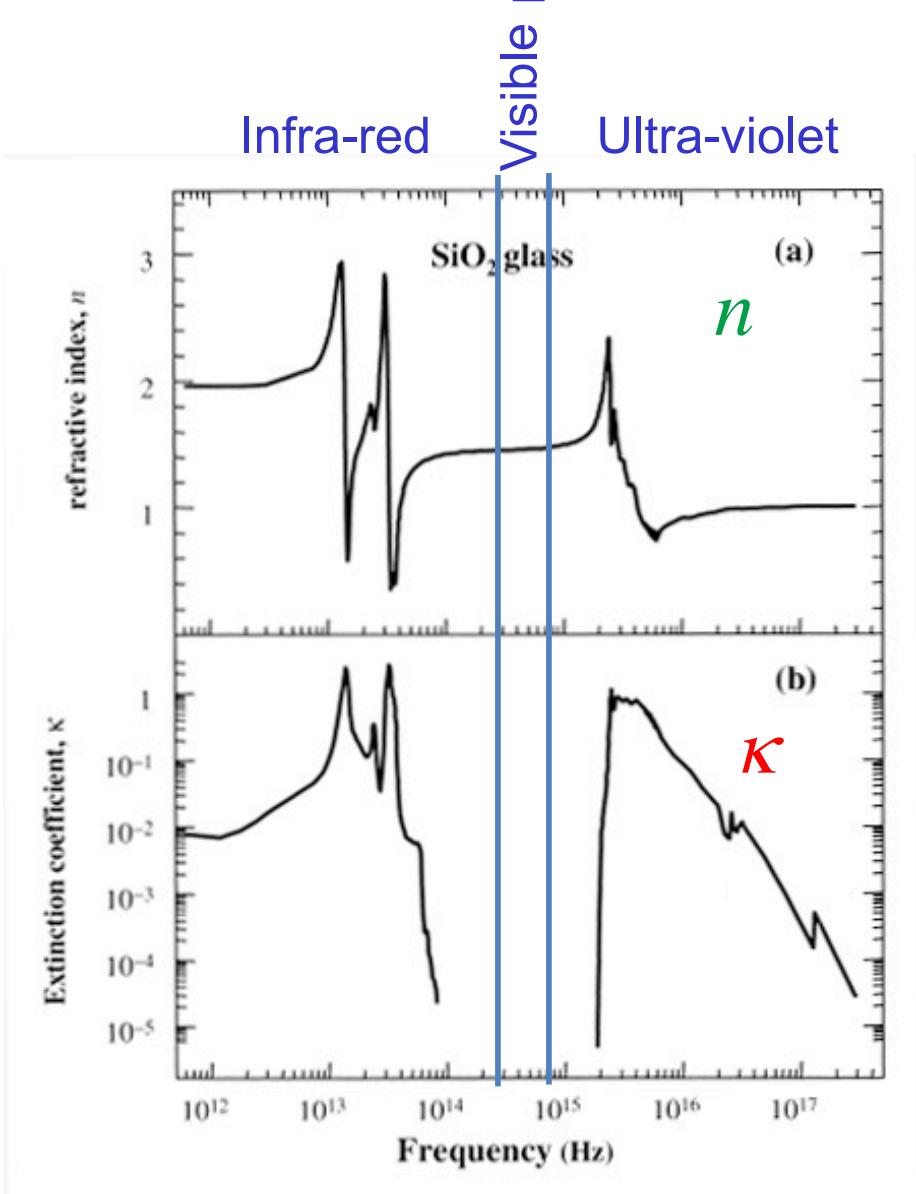
$$E(z,t) = e^{-\kappa\omega z/c}(E_0 e^{i(\omega n z/c - \omega t)} + E_0^* e^{-i(\omega n z/c - \omega t)})$$

Absorption   Refraction

Relationship between

$n(\omega)$ and $\kappa(\omega)$?

How to compute them ?

Kramers-Kronig relations
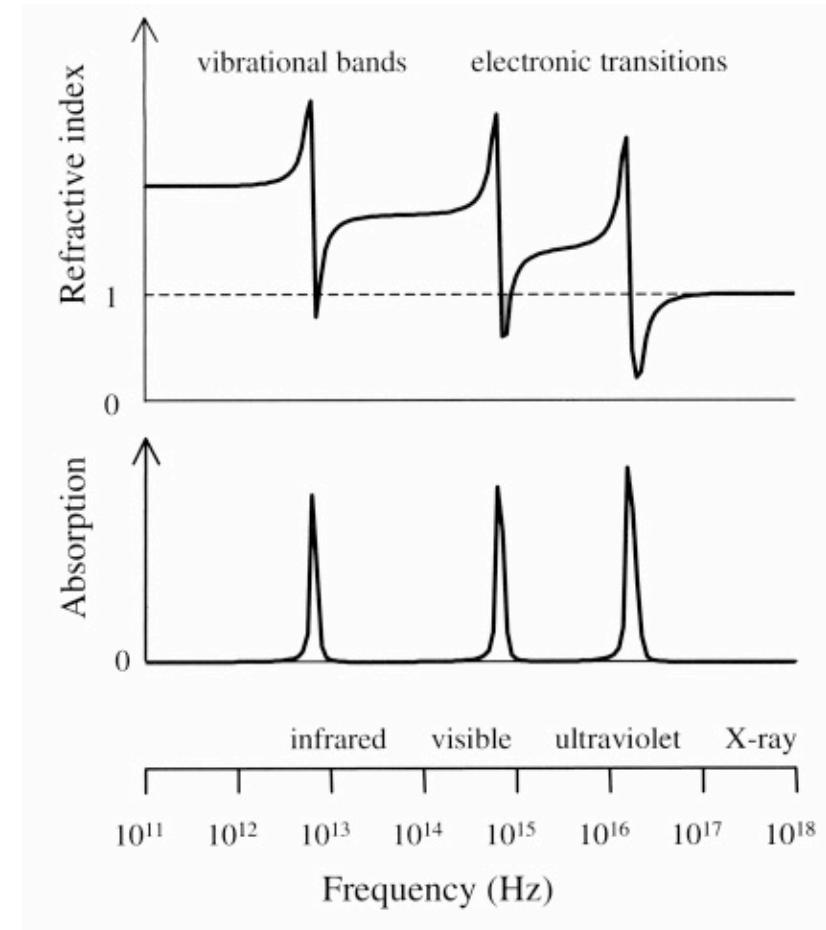
$$\mathfrak{R}\varepsilon(\omega') - 1 = \frac{2}{\pi} P \int_0^{+\infty} \frac{\mathfrak{I}\varepsilon(\omega)\omega}{\omega^2 - \omega'^2} d\omega \qquad \mathfrak{I}\varepsilon(\omega') = -\frac{2\omega'}{\pi} P \int_0^{+\infty} \frac{\mathfrak{R}\varepsilon(\omega)}{\omega^2 - \omega'^2} d\omega \ .$$

Come from causality

Relationship between real and imaginary
part of dielectric function :
knowing one gives the other.

Allows to check validity of results or to
compute the other if one accurately known

Typical behaviour :
Absorptions at a series of frequencies,
    delta functions centered on ω_i
Refractive index behaves like $1/(\omega - \omega_i)$

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Time-dependent perturbation theory
and
Adler-Wiser formula

Time-dependent perturbation

Time-dependent Schrödinger equation :

$$\hat{H}(t)\big|\psi(t)\big\rangle = \mathrm{i}\hbar\,\frac{\partial\big|\psi(t)\big\rangle}{\partial t}$$

Hamiltonian : static part and a perturbation

$$\boxed{\hat{H}(t) = \hat{H}^{(0)} + \Delta\hat{H}(t)} \quad \text{with} \quad \hat{H}^{(0)} = -\frac{\hbar^2\vec{\nabla}^2}{2m} + V(\mathbf{r})$$

Unperturbed (static) reference state :

$$\big|\psi_n^{(0)}(t)\big\rangle = \big|\phi_n^{(0)}\big\rangle\,\mathrm{e}^{-\mathrm{i}\omega_n t} \quad \text{with} \quad E_n = \hbar\omega_n$$

$$\hat{H}^{(0)}\big|\phi_n^{(0)}\big\rangle = E_n^{(0)}\big|\phi_n^{(0)}\big\rangle$$

We consider only time-space "separable" perturbations :

$$\Delta\hat{H}(t) = \Delta\hat{H}.f(t) \qquad\qquad f(t) \text{ is monochromatic (one frequency)}$$

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Wavefunction changes

If monochromatic, causal, perturbation :

$$\Delta \hat{H}(t) = \lambda \left(\hat{H}^+ e^{-i\omega t} e^{\delta^+ t} + (\text{h.c.}) \right) \quad \text{with} \quad \delta^+ > 0, \ \delta^+ \to 0$$

$$\hat{H}^- \text{ is the hermitian conjugate of } \hat{H}^+$$

Perturbation treatment :

$$\left| \psi_n(t) \right\rangle = \left| \phi_n^{(0)} \right\rangle e^{-i\omega_n t} + \lambda \left(\left| \phi_n^+ \right\rangle e^{-i(\omega_n + \omega)t} e^{\delta^+ t} + \left| \phi_n^- \right\rangle e^{-i(\omega_n - \omega)t} e^{\delta^+ t} \right) + O(\lambda^2)$$

Use of the TD Schrödinger equation, and identification of terms of same order in λ and same temporal behaviour :

$$\left[\hat{H}^{(0)} - \hbar(\omega_n^{(0)} + \omega + i\delta^+) \right] \left| \phi_n^+ \right\rangle = -\hat{H}^+ \left| \phi_n^{(0)} \right\rangle$$

$$\left[\hat{H}^{(0)} - \hbar(\omega_n^{(0)} - \omega + i\delta^+) \right] \left| \phi_n^- \right\rangle = -\hat{H}^- \left| \phi_n^{(0)} \right\rangle$$

Expansion as a sum over eigenstates of the unperturbed, static, Hamiltonian

$$\left| \phi_n^+ \right\rangle = \sum_m c_{nm}^+ \left| \phi_m^{(0)} \right\rangle \qquad\qquad \left| \phi_n^- \right\rangle = \sum_m c_{nm}^- \left| \phi_m^{(0)} \right\rangle$$

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Coefficients in the static basis

$$\left[\hat{H}^{(0)} - \hbar(\omega_n^{(0)} + \omega + i\delta^+) \right] \sum_m c_{nm}^+ \left| \phi_m^{(0)} \right\rangle = -\hat{H}^+ \left| \phi_n^{(0)} \right\rangle$$

$$\Rightarrow \sum_m c_{nm}^+ \left[\hbar\omega_m^{(0)} - \hbar(\omega_n^{(0)} + \omega + i\delta^+) \right] \left| \phi_m^{(0)} \right\rangle = -\hat{H}^+ \left| \phi_n^{(0)} \right\rangle$$

Introduce the transition frequency $\quad \omega_{mn} = \omega_m^{(0)} - \omega_n^{(0)}$

$$\Rightarrow \sum_m c_{nm}^+ \left[\hbar\omega_{mn} - \hbar\omega - i\hbar\delta^+ \right] \left| \phi_m^{(0)} \right\rangle = -\hat{H}^+ \left| \phi_n^{(0)} \right\rangle$$

and isolate the contribution of eigenstate m by premultiplying, and use of orthonormality condition :

$$\Rightarrow c_{nm}^+ \left[\hbar\omega_{mn} - \hbar\omega - i\hbar\delta^+ \right] = -\left\langle \phi_m^{(0)} \right| \hat{H}^+ \left| \phi_n^{(0)} \right\rangle$$

$$\boxed{c_{nm}^+ = \frac{-\left\langle \phi_m^{(0)} \right| \hat{H}^+ \left| \phi_n^{(0)} \right\rangle}{\hbar\omega_{mn} - \hbar\omega - i\hbar\delta^+}}$$

For the negative frequency contribution : $\quad \boxed{c_{nm}^- = \frac{-\left\langle \phi_m^{(0)} \right| \hat{H}^- \left| \phi_n^{(0)} \right\rangle}{\hbar\omega_{mn} + \hbar\omega - i\hbar\delta^+}}$

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Wrap-up and density change

$$\left|\psi_n(t)\right\rangle = \left|\phi_n^{(0)}\right\rangle e^{-i\omega_n t} + \lambda\left(\left|\phi_n^+\right\rangle e^{-i(\omega_n^{(0)}+\omega)t} e^{\delta^+ t} + \left|\phi_n^-\right\rangle e^{-i(\omega_n^{(0)}-\omega)t} e^{\delta^+ t}\right) + O(\lambda^2)$$

$$\left|\phi_n^+\right\rangle = \sum_m c_{nm}^+ \left|\phi_m^{(0)}\right\rangle \qquad \left|\phi_n^-\right\rangle = \sum_m c_{nm}^- \left|\phi_m^{(0)}\right\rangle$$

$$c_{nm}^+ = \frac{-\left\langle\phi_m^{(0)}\left|\hat{H}^+\right|\phi_n^{(0)}\right\rangle}{\hbar\omega_{mn} - \hbar\omega - i\hbar\delta^+} \qquad c_{nm}^- = \frac{-\left\langle\phi_m^{(0)}\left|\hat{H}^-\right|\phi_n^{(0)}\right\rangle}{\hbar\omega_{mn} + \hbar\omega - i\hbar\delta^+}$$

Analysis of electronic density (consider non-spin-polarized system, occupation numbers f allowed to vary between 0 and 1) :

$$n(\mathbf{r},t) = \sum_{j\sigma\,occ} f_{j\sigma}\psi_{j\sigma}^*(\mathbf{r},t)\psi_{j\sigma}(\mathbf{r},t)$$

Perturbation expansion of the electronic density :

$$n(\mathbf{r},t) = n^{(0)}(\mathbf{r}) + \lambda\left(n^+(\mathbf{r})e^{-i\omega t}e^{\delta^+ t} + (c.c.)\right) + O(\lambda^2)$$

$$n^+(\mathbf{r}) = \sum_{j\sigma} f_{j\sigma}\left(\phi_{j\sigma}^{(0)*}(\mathbf{r})\phi_{j\sigma}^+(\mathbf{r}) + \phi_{j\sigma}^{-*}(\mathbf{r})\phi_{j\sigma}^{(0)}(\mathbf{r})\right) \quad \text{and} \quad n^-(\mathbf{r}) = \left(n^+(\mathbf{r})\right)^*$$

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Adler-Wiser formula

Response of a system of independent electrons
with a time-varying local potential of well-defined frequency
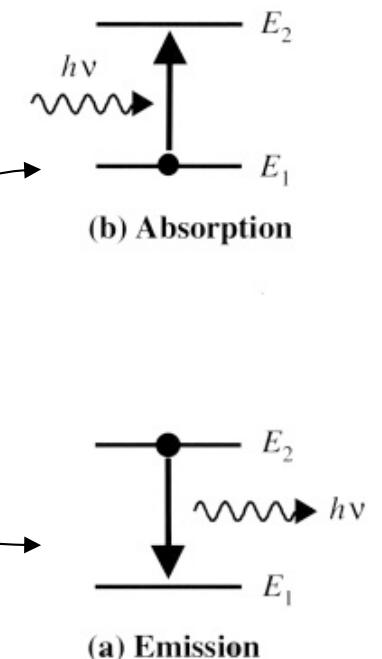
$$n^{(1)}(\mathbf{r},\omega) = \int \chi_0(\mathbf{r},\mathbf{r}';\omega) V^{(1)}(\mathbf{r}',\omega) \, d\mathbf{r}'$$

$$\chi_0(\mathbf{r},\mathbf{r}';\omega) = \sum_\sigma \sum_n \sum_m (f_{m\sigma} - f_{n\sigma}) \frac{\varphi_{n\sigma}^*(\mathbf{r})\varphi_{m\sigma}(\mathbf{r})\varphi_{m\sigma}^*(\mathbf{r}')\varphi_{n\sigma}(\mathbf{r}')}{(\varepsilon_{m\sigma} - \varepsilon_{n\sigma}) - \omega - i\delta^+}$$

- Contributions from each pair of levels of different occupation
- Fulfills the causality principle
- Real part symmetric in frequency,
   imaginary part anti-symmetric in frequency

$$\lim_{\substack{\delta^+ \to 0 \\ \delta^+ > 0}} \frac{1}{\omega_{mn} - \omega - i\delta^+} = \frac{1}{\omega_{mn} - \omega} + i\pi\delta(\omega_{mn} - \omega)$$

$$\lim_{\substack{\delta^+ \to 0 \\ \delta^+ > 0}} \frac{1}{\omega_{mn} + \omega + i\delta^+} = \frac{1}{\omega_{mn} + \omega} - i\pi\delta(\omega_{mn} + \omega)$$

(b) Absorption

(a) Emission

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Adler-Wiser in periodic case

For the absorption in semiconductors, result of quantum mechanical calculations :

$$\Im\left(\varepsilon_{\alpha\beta}(\omega)\right) = \frac{4\pi^2 e^2 \hbar^2}{3m^2\omega^2} \sum_{s=\pm1} s \sum_{\sigma} \frac{1}{(2\pi)^3}$$

$$\boxed{\int_{BZ} \sum_{n\,occ} \sum_{m\,unocc} \delta\left(\varepsilon_{m\mathbf{k}\sigma} - \varepsilon_{n\mathbf{k}\sigma} - s\hbar\omega\right) \langle u_{n\mathbf{k}\sigma}|\hat{p}_\alpha|u_{m\mathbf{k}\sigma}\rangle \langle u_{m\mathbf{k}\sigma}|\hat{p}_\beta|u_{n\mathbf{k}\sigma}\rangle\, d\mathbf{k}}$$

where :

- u functions are periodic part of Bloch functions
- s sum gives resonant and anti-resonant contributions
- at each $\mathbf{k}$ point, contribution from each pair of occupied and unoccupied state, with strict conservation of total energy   « Sum-over-states »
- tensorial character of the dielectric function appears inside the two matrix elements of the momentum operator (a vector quantity)

$\langle u_{n\mathbf{k}\sigma}|\hat{p}_\alpha|u_{m\mathbf{k}\sigma}\rangle$ actually computed from $\langle u_{n\mathbf{k}\sigma}|\frac{\partial}{\partial k_\alpha}|u_{m\mathbf{k}\sigma}\rangle$ (see DFPT lecture)

Real part computed from Kramers-Kronig formula :

$$\Re\left(\varepsilon_{\alpha\beta}(\omega')\right) = 1 + \frac{2}{\pi} P \int_0^{+\infty} \frac{\Im\left(\varepsilon_{\alpha\beta}(\omega)\right)\omega}{\omega^2 - \omega'^2}\, d\omega$$

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Metals : Drude contribution

For the absorption in metals, lacking intraband contribution, also present in the homogeneous electron gas, even in the classical treatment (proposed by Drude)

Classical propagation of a particle in a homogeneous medium and viscous forces (=loss of energy due to collisions)

$$m_0 \frac{d^2 x}{dt^2} + m_0 \gamma \frac{dx}{dt} = -eE(t) = -eE_0 e^{-i\omega t} .$$

$$x(t) = \frac{eE(t)}{m_0(\omega^2 + i\gamma\omega)} .$$

N particles per unit volume to create a polarization

$$D = \varepsilon_r \varepsilon_0 E = \varepsilon_0 E + P = \varepsilon_0 E - \frac{Ne^2 E}{m_0(\omega^2 + i\gamma\omega)} .$$

$$\varepsilon_r(\omega) = 1 - \frac{Ne^2}{\varepsilon_0 m_0} \frac{1}{(\omega^2 + i\gamma\omega)} .$$
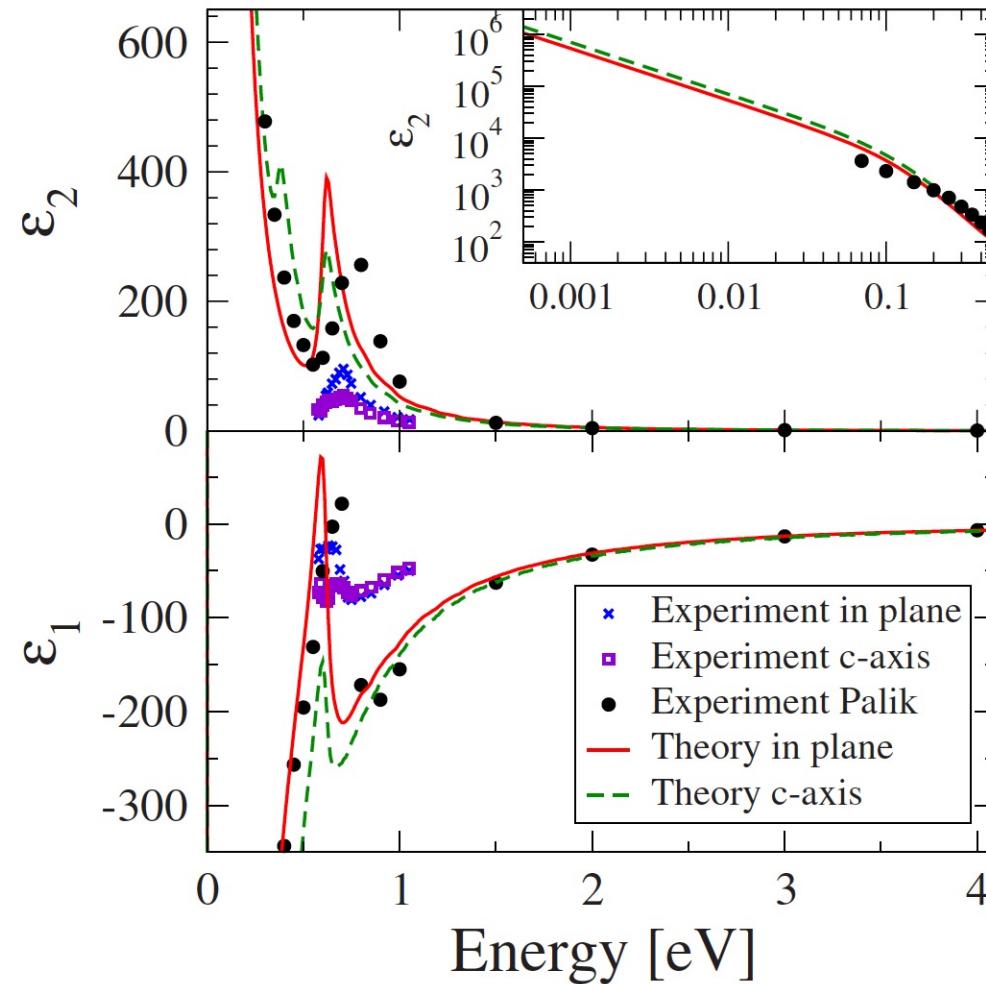
So-called "plasma frequency" : $\omega_p = \left(\frac{Ne^2}{\varepsilon_0 m_0} \right)^{\frac{1}{2}} .$

$$\boxed{\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{(\omega^2 + i\gamma\omega)} .}$$

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Magnesium dielectric function

Imaginary part

Real part

Cazzaniga et al, Phys. Rev. B82, 035104 (2010)

AMM lecture Beyond DFT 2

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Missing electron-electron interaction

« Sum-over-states » (SOS) formula :

$$\Im\left(\varepsilon_{\alpha\beta}(\omega)\right) = \frac{4\pi^2 e^2 \hbar^2}{3m^2\omega^2} \sum_{s=\pm 1} s \sum_{\sigma} \frac{1}{(2\pi)^3} \boxed{\int_{BZ} \sum_{n\,\text{occ}} \sum_{m\,\text{unocc}} \delta\left(\varepsilon_{m\mathbf{k}\sigma} - \varepsilon_{n\mathbf{k}\sigma} - s\hbar\omega\right)} \langle u_{n\mathbf{k}\sigma}|\hat{p}_\alpha|u_{m\mathbf{k}\sigma}\rangle\langle u_{m\mathbf{k}\sigma}|\hat{p}_\beta|u_{n\mathbf{k}\sigma}\rangle d\mathbf{k}$$

Wavefunctions and eigenenergies from a fixed potential (effective)
Might be :   DFT (any XC approximation)
                 GW
=> Determine the absorption edge, linked with the joint density of state
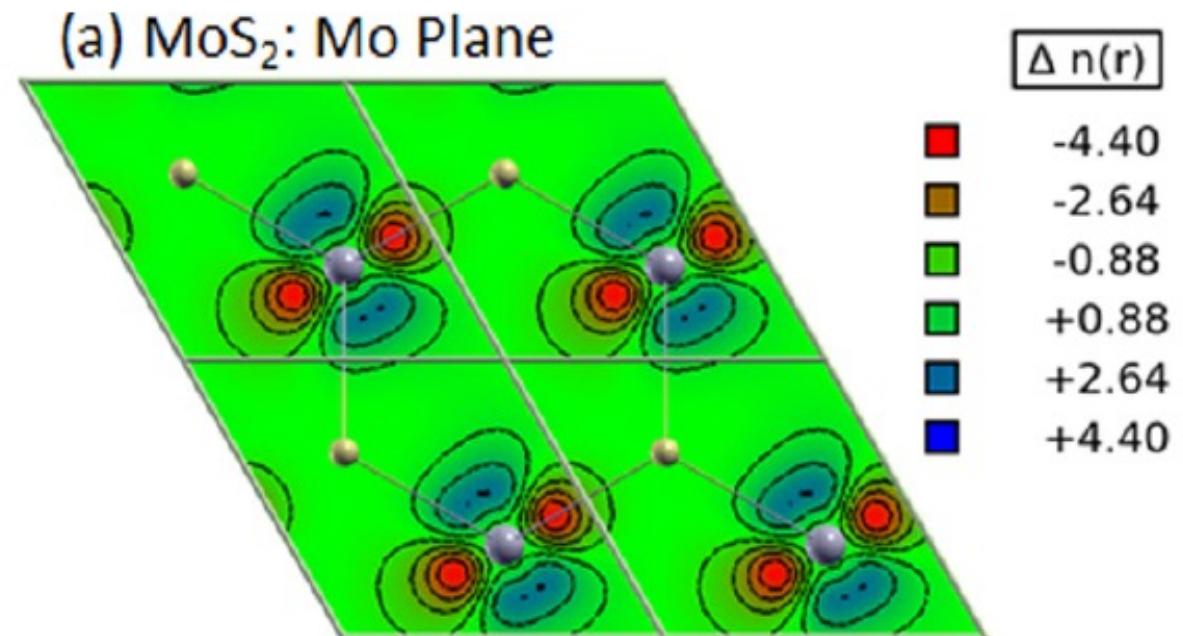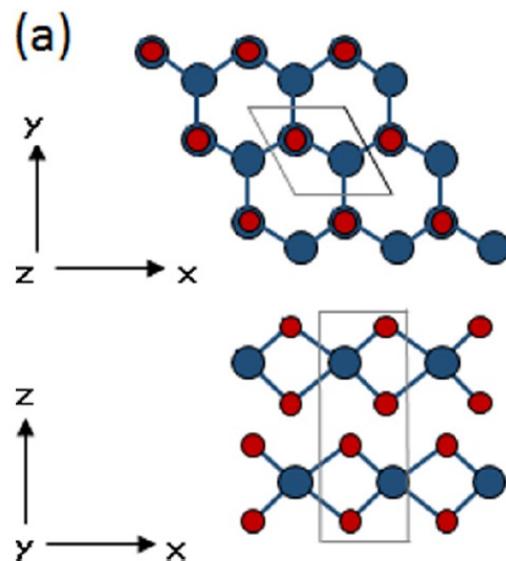
Missing two effects due to electron-electron interaction
    - Local field effects (homogeneous electric field creates
        a local modification of density, that creates a change of potential,
        that creates an absorption of energy)
        NO change of absorption edge, only changes of intensities
    - Excitonic effects = creation of a bound electron-hole pair
        Change absorption edge, decrease the energy to absorb a photon

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Local fields
from TD-DFT

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Local change of electronic density

(a)

(a) MoS$_2$: Mo Plane

Δ n(r)
■ -4.40
■ -2.64
■ -0.88
■ +0.88
■ +2.64
■ +4.40

Electric field in the x (horizontal) direction

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Density-functional theory TD linear response: treatment of local fields

System in its ground-state
Apply small TD perturbation characterized by some frequency.
Watch density change.
Linear regime : associated Fourier components
related by frequency-dependent susceptibility
or density-density response function

$$n^{(1)}(\mathbf{r},\omega) = \int \chi(\mathbf{r},\mathbf{r}';\omega) V_{ext}^{(1)}(\mathbf{r}',\omega) d\mathbf{r}'$$

This susceptibility can be computed within TD-DFT,
for a given choice of TD-XC functional

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TD Hartree and XC kernels

Change of external potential induces change of density, that induces change of Hartree and XC potential.
For Hartree potential :

$$V_H^{(1)}(\mathbf{r},\omega) = \int \frac{1}{|\mathbf{r}\text{-}\mathbf{r}'|} n^{(1)}(\mathbf{r}',\omega) d\mathbf{r}'$$

Supposing TD XC functional known:
explicit expression for the change, in term of TD XC kernel

$$V_{XC}^{(1)}(\mathbf{r},\omega) = \int K_{XC}(\mathbf{r},\mathbf{r}',\omega) n^{(1)}(\mathbf{r}',\omega) d\mathbf{r}'$$

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XC kernels : local / adiabatic approximation

Combining local approximation and adiabatic approximation, TD XC kernel is simple:

- independent of frequency (local in time),
- local in space,
- determined by a local XC energy density,
  function of local unperturbed density.

$$K_{XC}(\mathbf{r},\mathbf{r}',\omega) = \left.\frac{d^2 e_{XC}}{dn}\right|_{n^{(0)}(\mathbf{r})} \delta(\mathbf{r}\text{-}\mathbf{r}')$$

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The independent-particle susceptibility

TD external, Hartree, and XC changes of potential combine to give total change of Kohn-Sham potential seen by independent electrons :

$$V_{KS}^{(1)}(\mathbf{r},\omega) = V_{ext}^{(1)}(\mathbf{r},\omega) + V_H^{(1)}(\mathbf{r},\omega) + V_{XC}^{(1)}(\mathbf{r},\omega)$$

Change of density due to this potential
from independent-particle susceptibility $\chi_0(\mathbf{r},\mathbf{r}';\omega)$

$$n^{(1)}(\mathbf{r},\omega) = \int \chi_0(\mathbf{r},\mathbf{r}';\omega) V_{KS}^{(1)}(\mathbf{r}',\omega) d\mathbf{r}'$$

Adler and Wiser expression

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Dyson equation for susceptibility (I)

Combine these equations or their inverse (assuming they can be inverted)

$$V_{KS}^{(1)}(\mathbf{r},\omega) = V_{ext}^{(1)}(\mathbf{r},\omega) + V_H^{(1)}(\mathbf{r},\omega) + V_{XC}^{(1)}(\mathbf{r},\omega)$$

$$V_{KS}^{(1)}(\mathbf{r}',\omega) = \int \chi_0^{-1}(\mathbf{r},\mathbf{r}';\omega) n^{(1)}(\mathbf{r},\omega) d\mathbf{r}'$$

$$V_{ext}^{(1)}(\mathbf{r}',\omega) = \int \chi^{-1}(\mathbf{r},\mathbf{r}';\omega) n^{(1)}(\mathbf{r},\omega) d\mathbf{r}'$$

$$V_H^{(1)}(\mathbf{r},\omega) = \int \frac{1}{|\mathbf{r}\text{-}\mathbf{r}'|} n^{(1)}(\mathbf{r}',\omega) d\mathbf{r}'$$

$$V_{XC}^{(1)}(\mathbf{r},\omega) = \int K_{XC}(\mathbf{r},\mathbf{r}',\omega) n^{(1)}(\mathbf{r}',\omega) d\mathbf{r}'$$

Valid for all perturbations, thus :

$$\chi_0^{-1}(\mathbf{r},\mathbf{r}';\omega) = \chi^{-1}(\mathbf{r},\mathbf{r}';\omega) + \frac{1}{|\mathbf{r}\text{-}\mathbf{r}'|} + K_{XC}(\mathbf{r},\mathbf{r}',\omega)$$

$$\boxed{\chi^{-1}(\mathbf{r},\mathbf{r}';\omega) = \chi_0^{-1}(\mathbf{r},\mathbf{r}';\omega) - \frac{1}{|\mathbf{r}\text{-}\mathbf{r}'|} - K_{XC}(\mathbf{r},\mathbf{r}',\omega)}$$

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Dyson equation for susceptibility (II)

Exact formula for the inverse of the susceptibility

$$\chi^{-1}(\mathbf{r},\mathbf{r}';\omega) = \chi_0^{-1}(\mathbf{r},\mathbf{r}';\omega) - \frac{1}{|\mathbf{r}\text{-}\mathbf{r}'|} - K_{XC}(\mathbf{r},\mathbf{r}',\omega)$$

Exact XC kernel,
to be approximated

$$\chi_0(\mathbf{r},\mathbf{r}';\omega) = \sum_\sigma \sum_n \sum_m \left(f_{m\sigma} - f_{n\sigma}\right) \frac{\varphi_{n\sigma}^*(\mathbf{r})\varphi_{m\sigma}(\mathbf{r})\varphi_{m\sigma}^*(\mathbf{r}')\varphi_{n\sigma}(\mathbf{r}')}{\left(\varepsilon_{m\sigma} - \varepsilon_{n\sigma}\right) - \omega - i\delta^+}$$
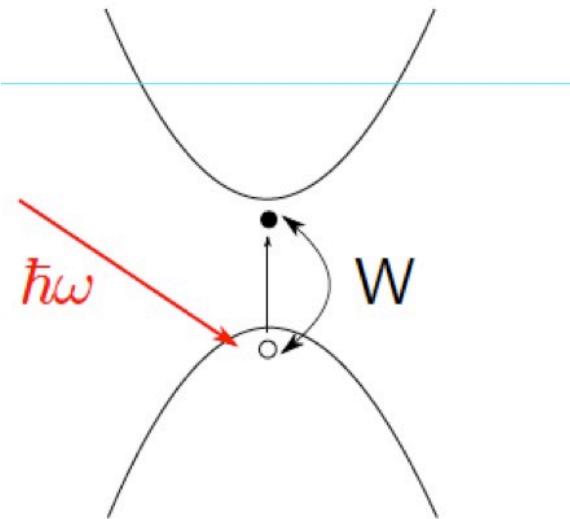
This is an exact expression for the independent-particle susceptibility, if the exact KS eigenenergies and eigenfunctions (occ/unocc) are known. In practice these must be approximated.

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Bethe-Salpeter equation

Dielectric response of interacting particles : Excitons

Exciton = bound electron-hole pair

Interacting electrons

2-particles

$$G_2(\mathbf{r}_1,t_1;\mathbf{r}_2,t_2;\mathbf{r}_3,t_3;\mathbf{r}_4,t_4)$$

Bethe-Salpeter

GW

Exchange

Screened Coulomb

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Bethe-Salpeter equation

$$H^{eff} \phi^\lambda = E_\lambda \phi^\lambda$$
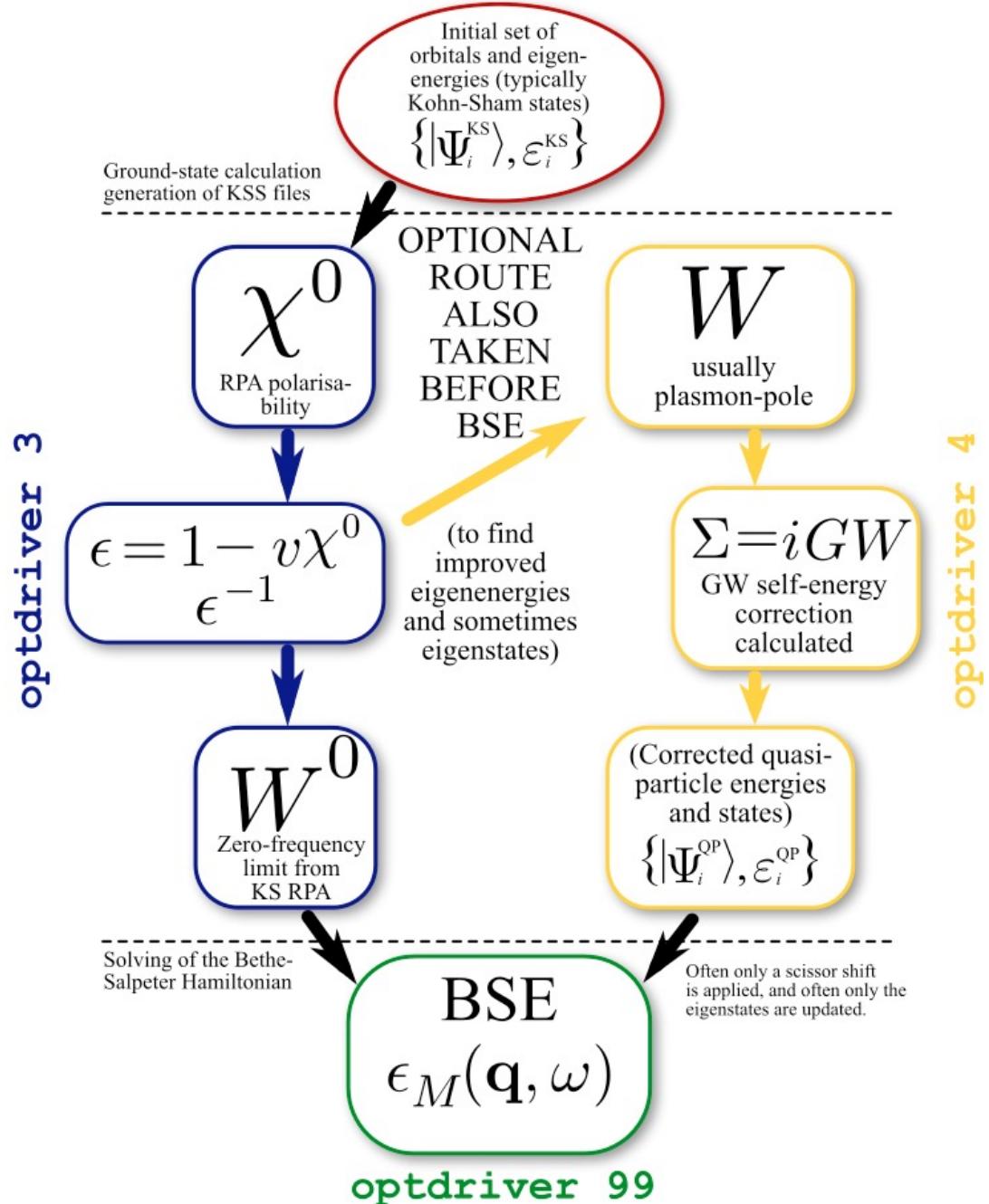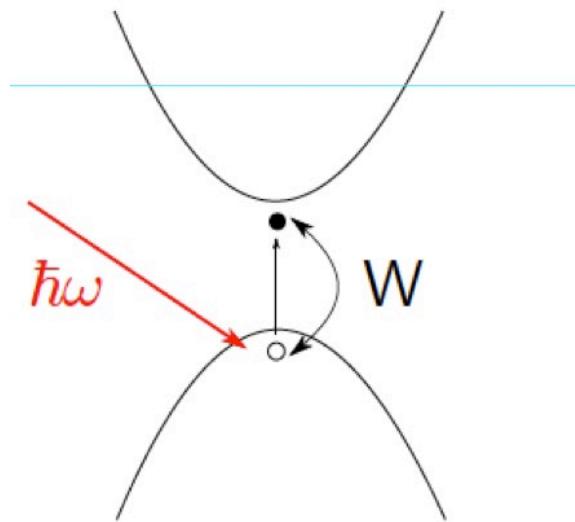
$$H^{eff}_{(vc\mathbf{k},v'c'\mathbf{k}')} = \underbrace{(E_{c\mathbf{k}} - E_{v\mathbf{k}})\mathbf{I}}_{\substack{\text{Transition} \\ \text{energies} \\ \Delta E_{cv}(\mathbf{k})}} + \underbrace{\bar{v}_{(vc\mathbf{k},v'c'\mathbf{k}')}}_{\substack{\text{Exchange} \\ \text{term}}} - \underbrace{W_{(vc\mathbf{k},v'c'\mathbf{k}')}}_{\substack{\text{Screened Coulomb} \\ \text{interaction}}}$$

$$\varepsilon(\omega) = 1 + 4\pi\chi(\omega) = 1 - \lim_{\mathbf{q}\to 0} v(\mathbf{q}) \underbrace{\left\langle P(\mathbf{q}) \left| (H^{eff} - I\omega)^{-1} \right| P(\mathbf{q}) \right\rangle}_{\text{Computed using iterative technique}}$$

$$P(\mathbf{q})_{n_1 n_2} = \left\langle n_1 \left| e^{iqr} \right| n_2 \right\rangle$$
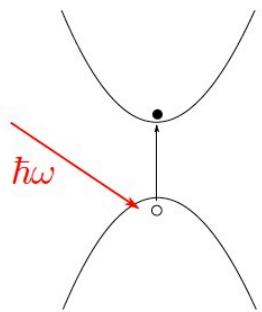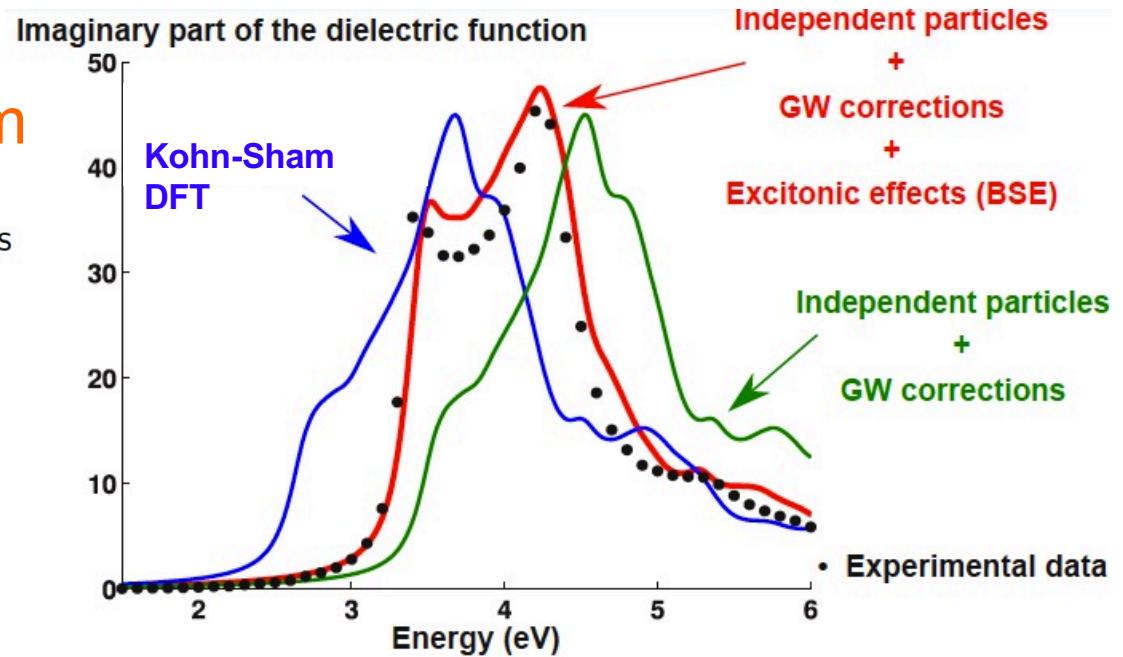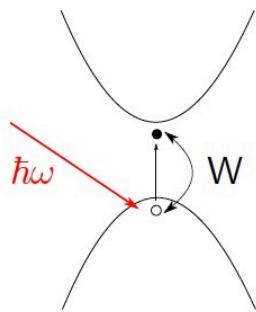
AMM lecture Beyond DFT 2

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GW + BSE

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Optical response : absorption

Silicon absorption spectrum

Beyond DFT, with Many-Body Perturbation Theory ... need :
- band gap correction (GW) [still independent particle IPA]
- excitonic corrections (Bethe-Salpeter Equation - BSE)

Optical spectrum, relation with the dielectric function

$$\mathrm{Im}\,\varepsilon(\omega) = 1 + 4\pi\,\mathrm{Im}\,\chi(\omega)$$ Neutral electronic excitations

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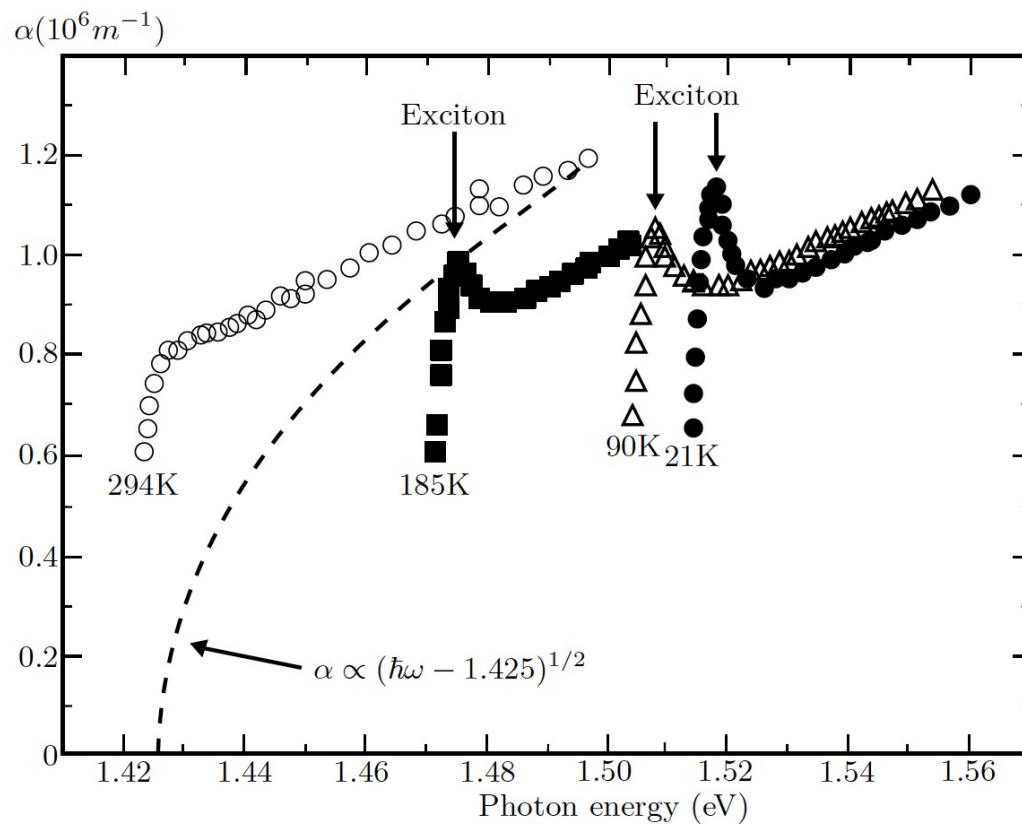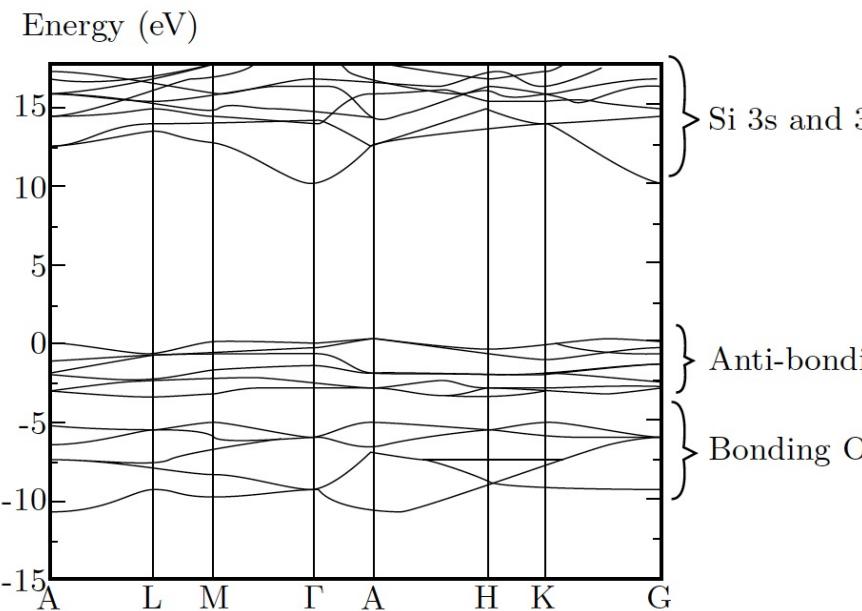
Experimental signature of excitons

Absorption of GaAs between 21 K and 294 K. The dashed line is an attempt to fit the absorption edge using a square root function, with a value of E_g equal to 1.425 eV, which is appropriate for GaAs at 294 K.

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SiO₂ band structure and dielectric function

Energy (eV)

15

10

5

0 — Anti-bonding O 2p

-5 — Bonding O 2p

-10

-15

A   L   M   Γ   A   H   K   G

Si 3s and 3p
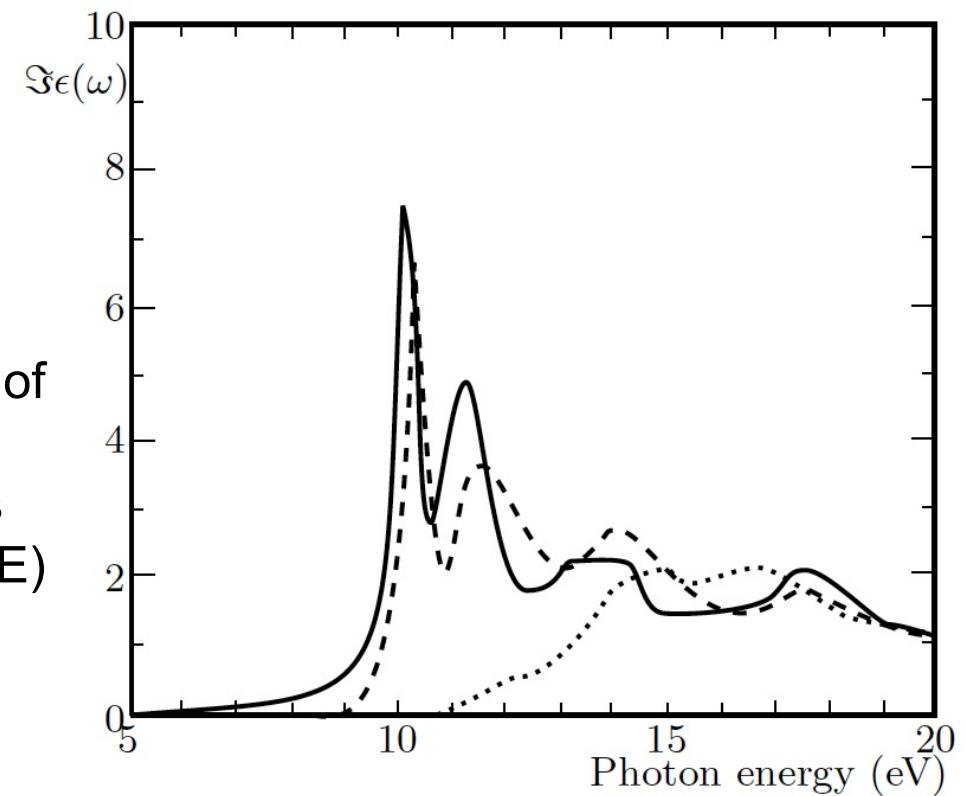
Band structure
of alpha-quartz

Imaginary part of dielectric function of
alpha-quartz.
Dotted line : theory without excitons
Solid line : theory with excitons (BSE)
Dashed line : experiment.

$\Im\epsilon(\omega)$

10

8

6

4

2

0

5   10   15   20

Photon energy (eV)

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SiO$_2$ refractive index and extinction coefficient

Vibrational excitations

Infra-red

Visible

Ultra-violet

n

κ

Electronic excitations

SiO$_2$ glass (a)

refractive index, n

Extinction coefficient, κ

(b)

Frequency (Hz)

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