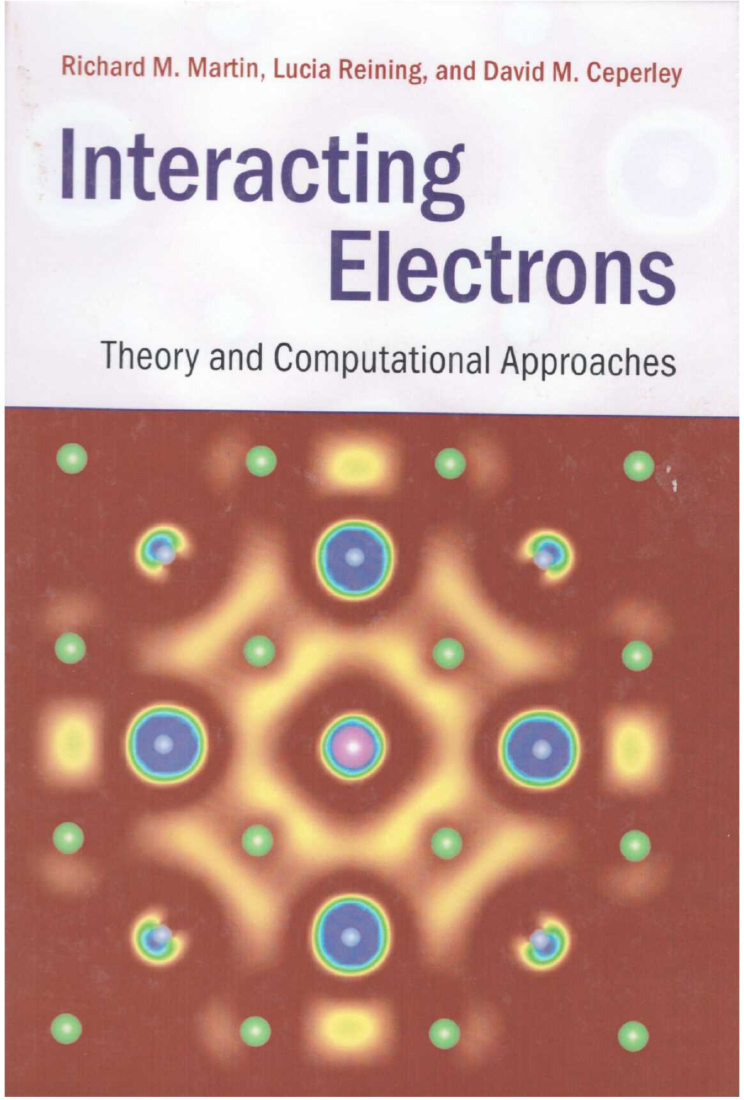
Advanced Materials Modeling
Lecture of 23 april

- + 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

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)

Many-body physics

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 :

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

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

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

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

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

Skoltech

Simplified notations

(1) Arguments of wavefunction :

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

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

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

and "one-particle" part of Hamitonian

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

Hamitonian becomes :

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

Separation of variables

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

+ antisymmetry for electron exchange

Interelectronic coupling does not
allow to separate electronic coordinates

Mean-field approximation (like DFT)

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

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

+ antisymmetry for electron exchange

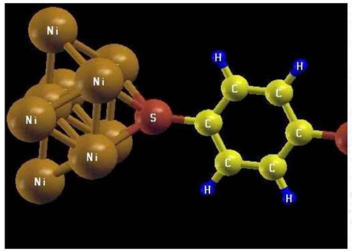
gives solutions as
Slater determinants of 1-particle wavefunctions
mean-field energy=sum of 1-particle eigenenergies,
must be corrected to give electronic energy (avoid double-counting)

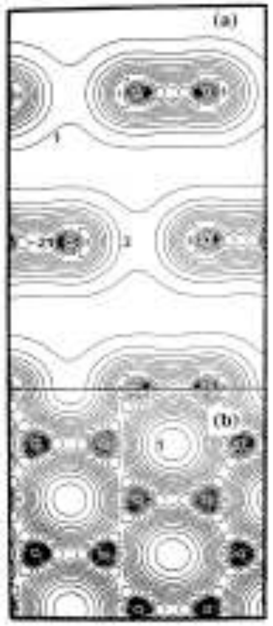
Experiments:
total energy,
band gap,
spectroscopies ?

Properties from first-principles

Computation of ...

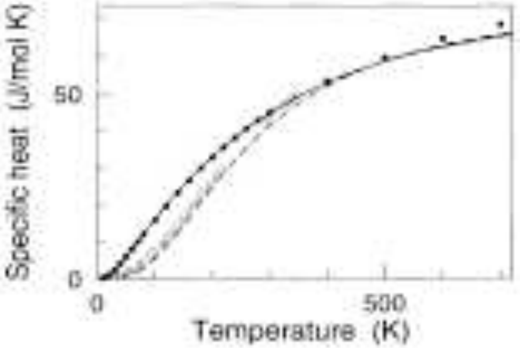
- interatomic distances, angles, **total energies**
- electronic charge densities, electronic energies

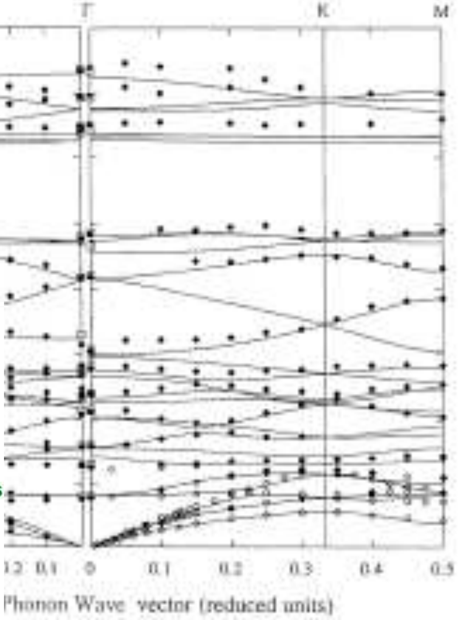


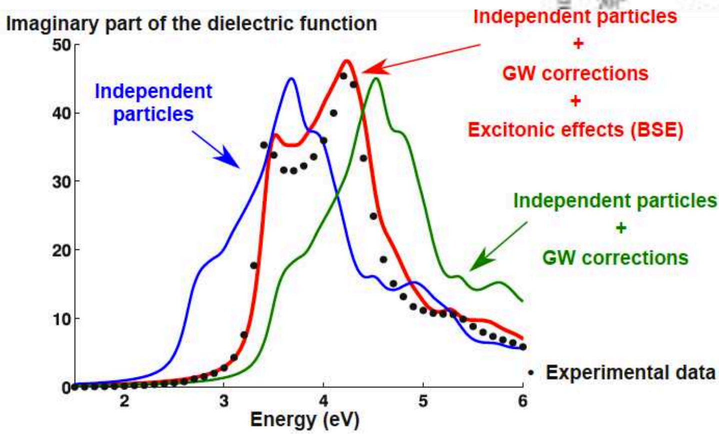


A basis for the computation of ...

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







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 ...

The DFT bandgap problem (I)

- DFT is a ground state theory
  =>no direct interpretation of Kohn-Sham eigenenergies ε_i in

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

- However { ε_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

$$E_g = \{E(N+1) - E(N)\} - \{E(N) - E(N\text{-}1)\}$$

[correct expression !]

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

Difference between ionisation potential and electronic affinity

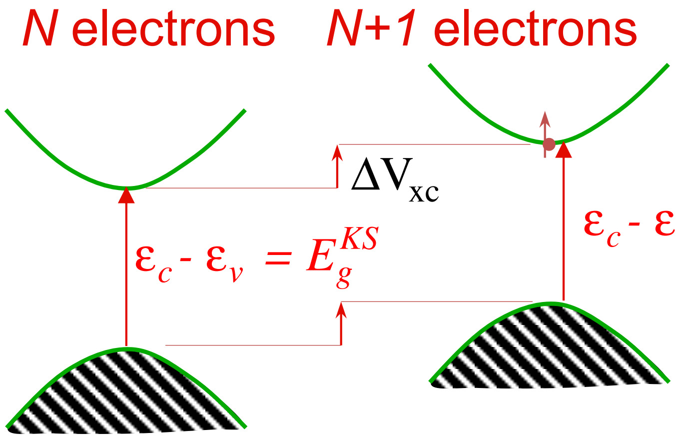
The DFT bandgap problem (II)

- 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



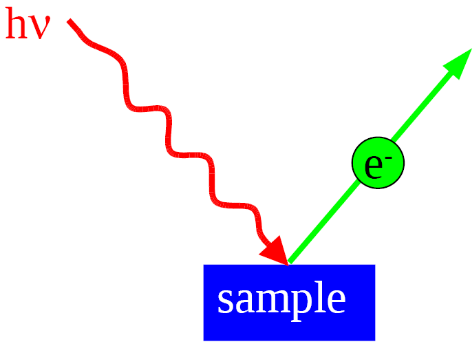
$$E_g^{KS} \neq E_g$$

$$E_g^{KS} + \Delta V_{xc} = E_g$$

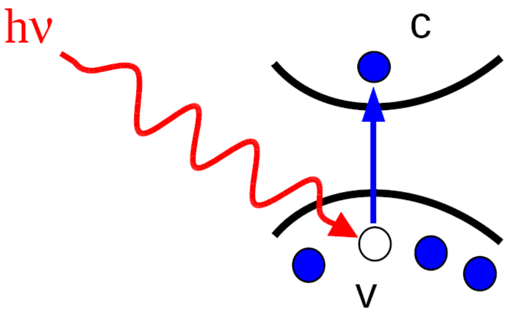
- Band gap : adding / removing an electron = charged electronic excitations

NOT transferring an electron from valence to conduction

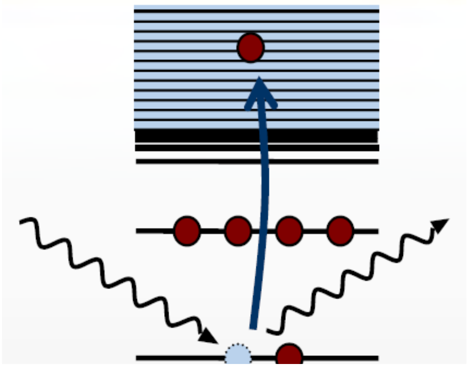
Spectroscopies : photons & electrons



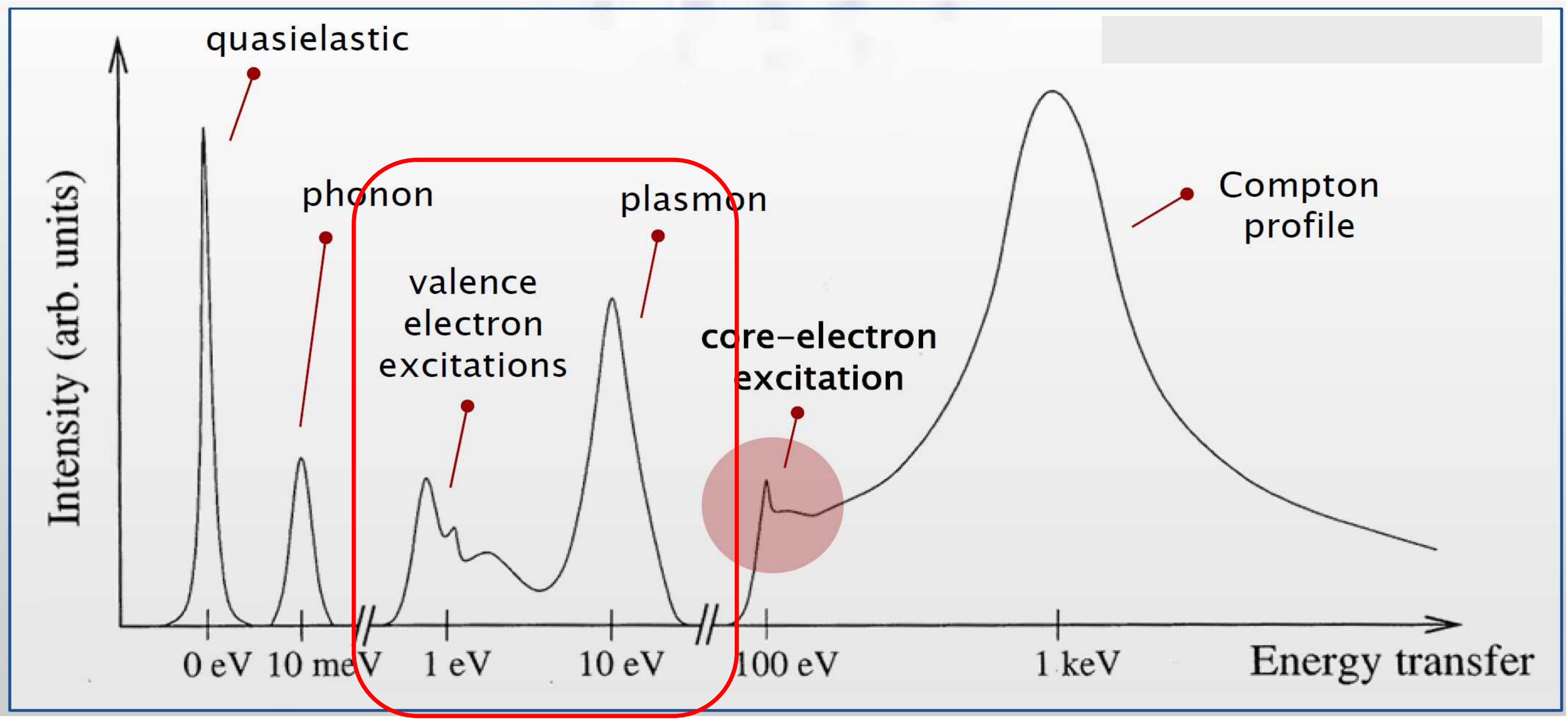
direct photoemission



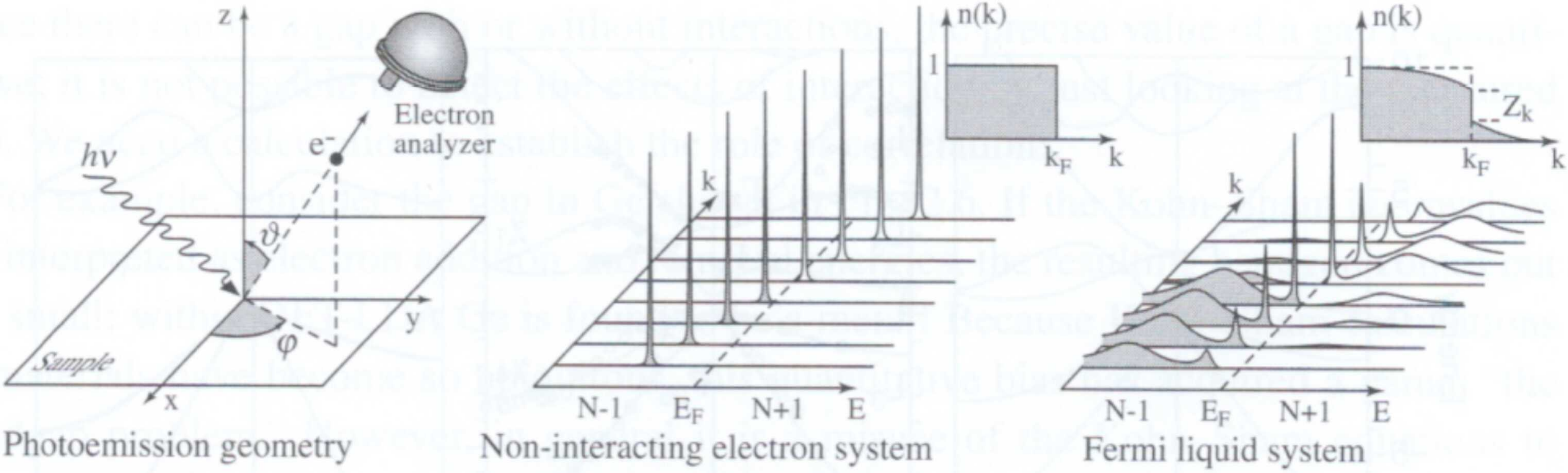
absorption



light scattering



Photoemission experiment



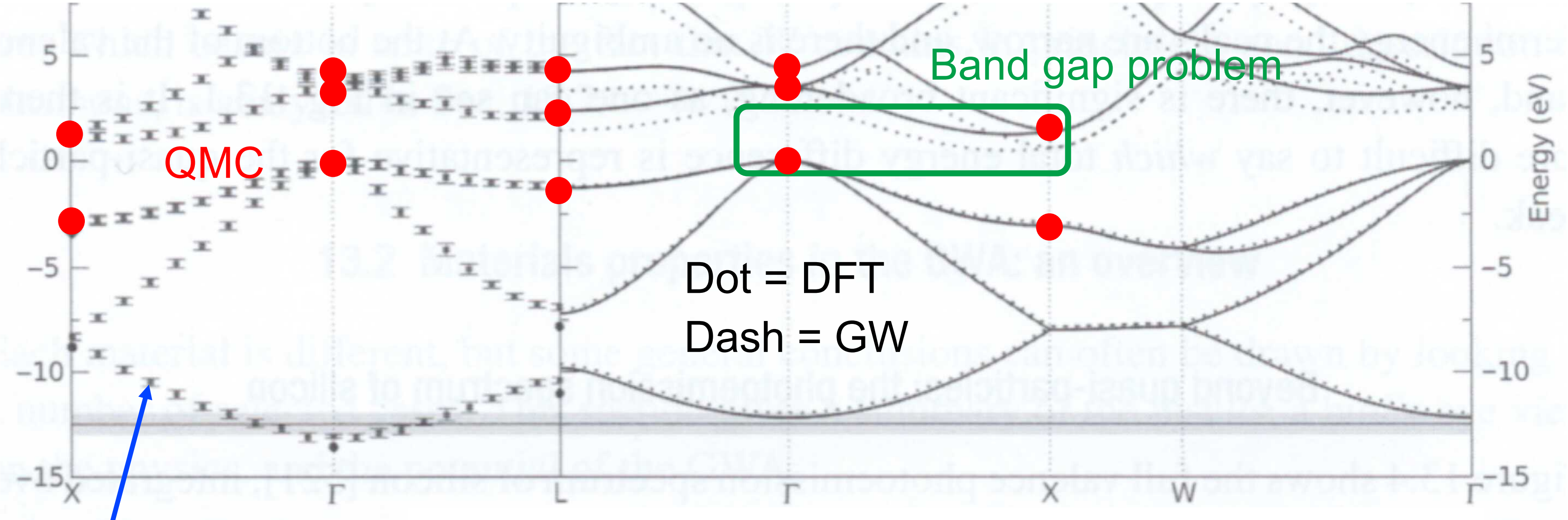
Photoemission geometry   Non-interacting electron system   Fermi liquid system

Similar for inverse photoemission …

Silicon band structure

Experiment QMC

Theory DFT GW QMC



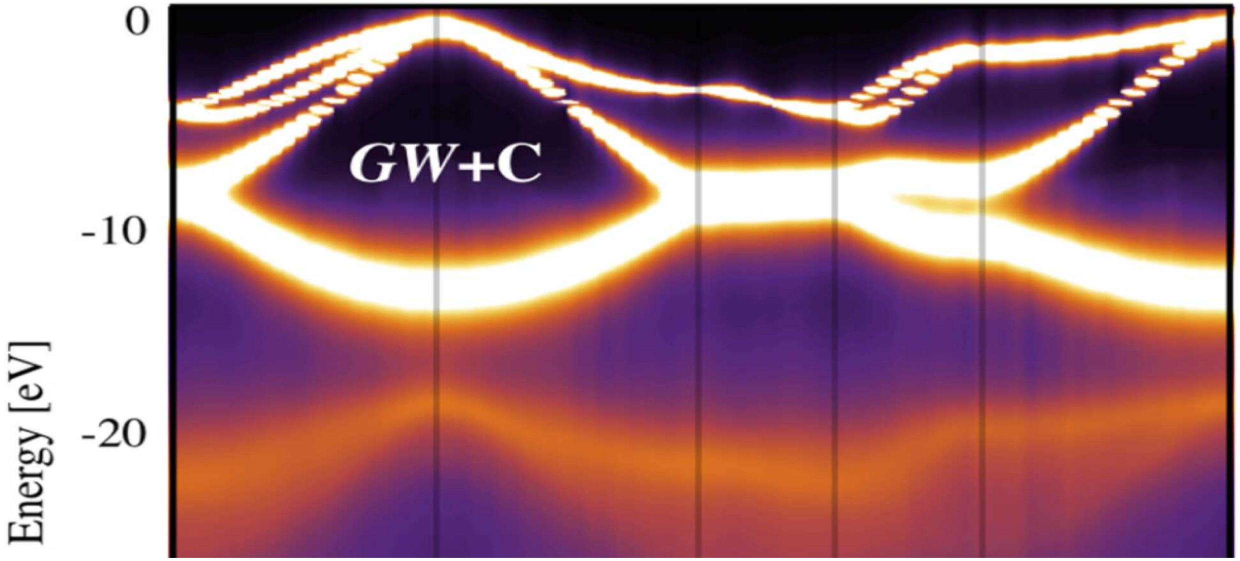
QMC

Band gap problem

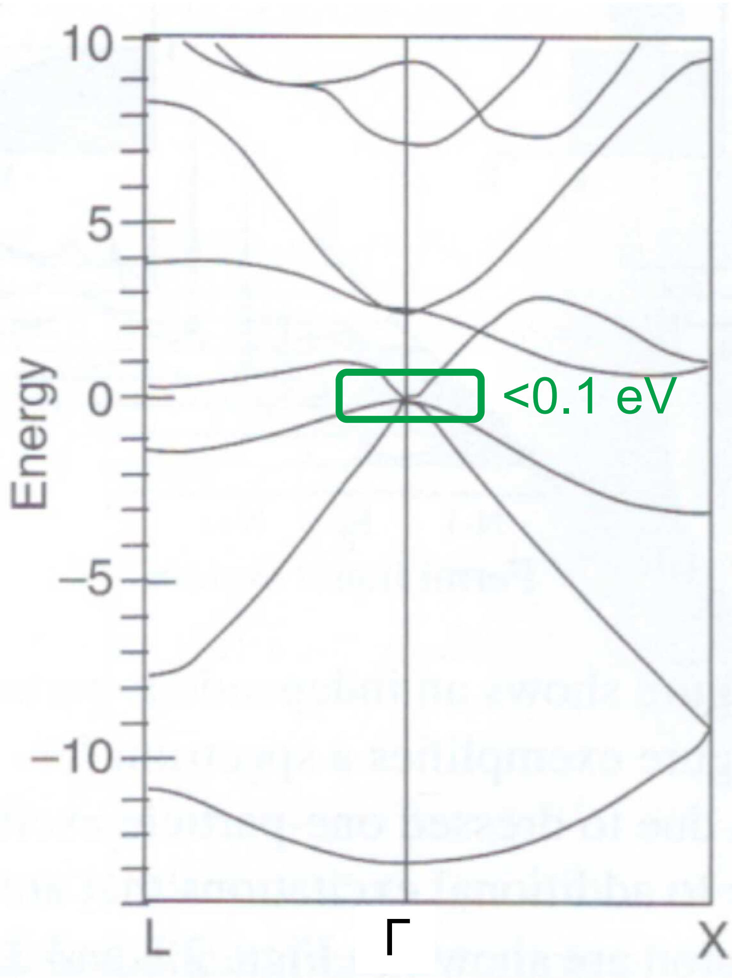
Dot = DFT

Dash = GW

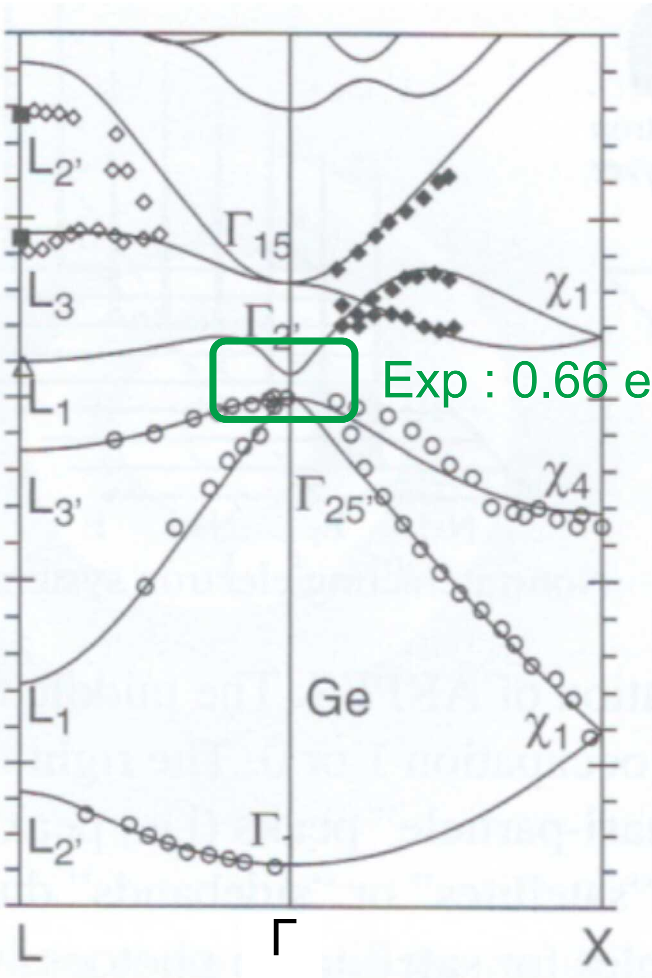
Experimental peaks



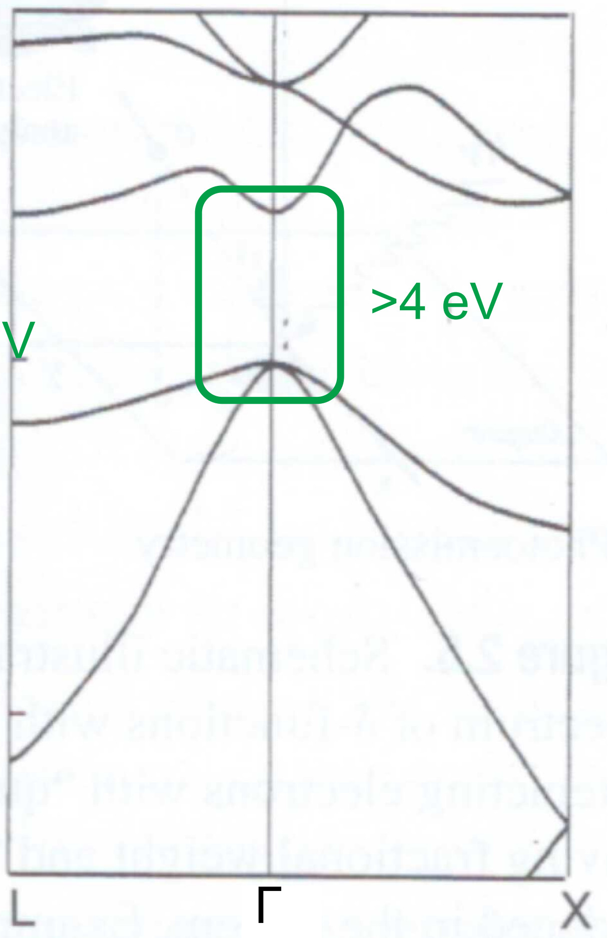
Germanium band structure



LDA



GW & experiment (circles)



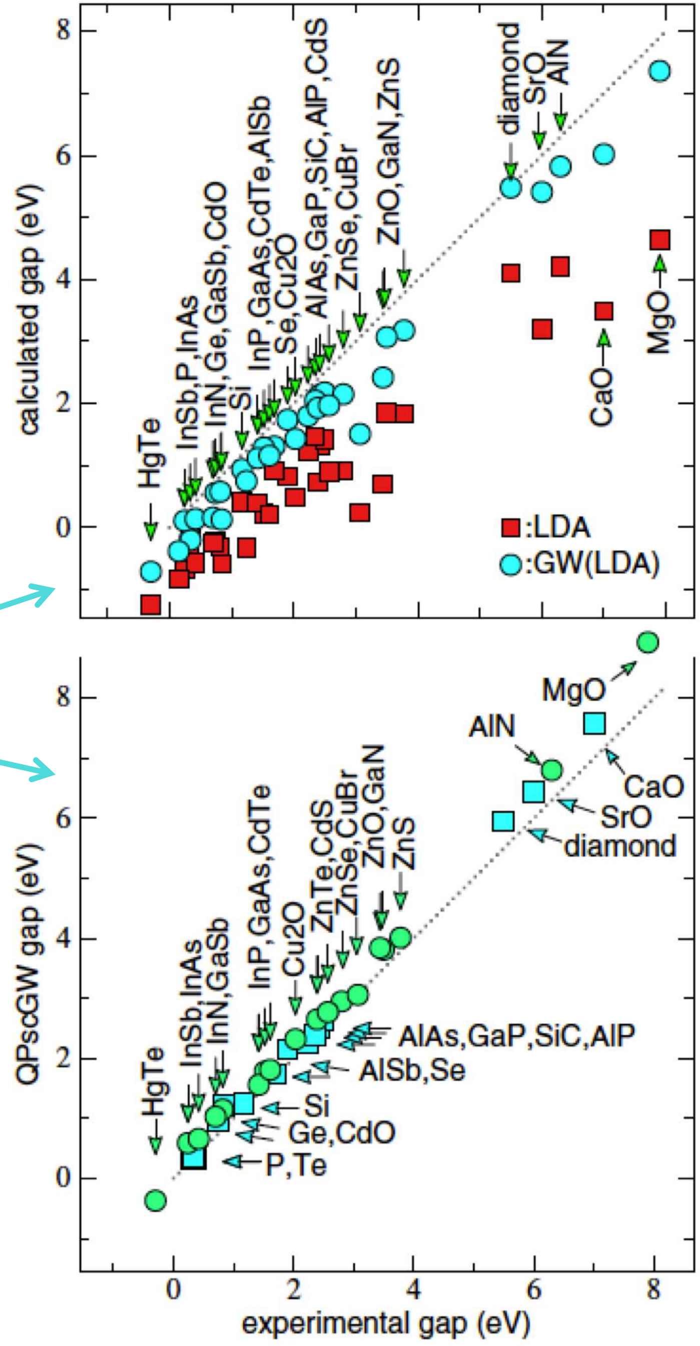
Hartree-Fock

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



Charged excitations and Green's function

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

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

If Hamiltonian does not depend on time,

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

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

$$\Rightarrow \quad i\hbar\frac{\partial f}{\partial t} = \quad Ef$$

$$= \varphi(\mathbf{r}_1,\dots\mathbf{r}_n).\boxed{e^{-i\frac{Et}{\hbar}}}$$

Energy : linked to phase acquired upon propagation.

The 1-particle Green’s function

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

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

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

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

Let’s compare them !

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 $\mathbf{r}'t'$

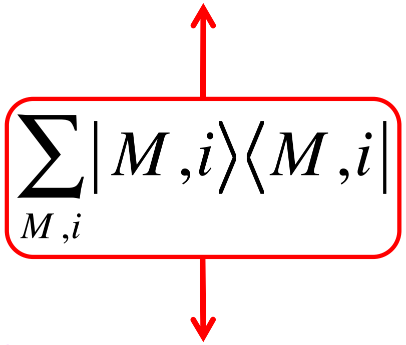
$$G(\mathbf{r}t,\mathbf{r}'t') = G^e(\mathbf{r}t,\mathbf{r}'t') - G^h(\mathbf{r}'t',\mathbf{r}t)$$

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

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 $E(N \pm 1,i)$



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

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

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) !

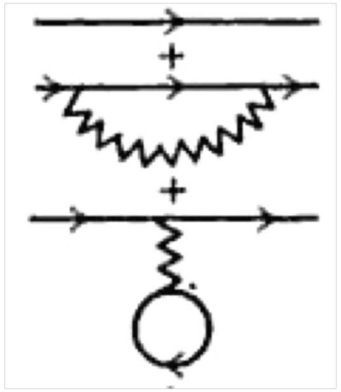
GW approximation to the electronic band structure

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

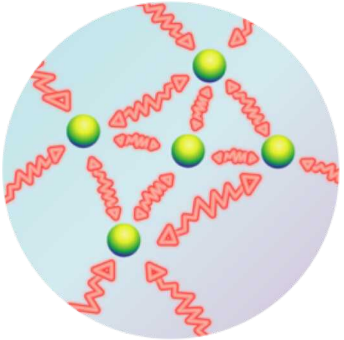
1-particle

$G(\mathbf{r},t;\mathbf{r}',t')$

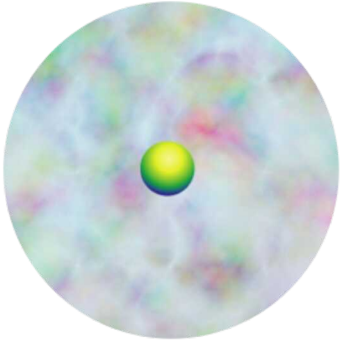


Propagation without Coulomb interactions
+
Propagation with polarization of medium
+
Propagation with mean-field electrostatic interaction with other electrons

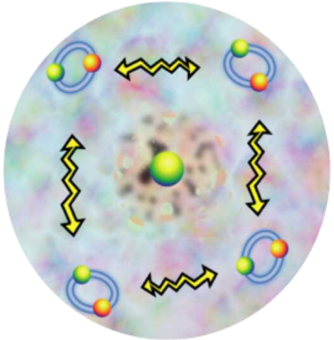
GW approximation



Wavefunctions



DFT



GW

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

DFT

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

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

GW

Self energy

Green's function

Screened interaction

Screened interaction and susceptibility

Computation of the susceptibility (for screening of Coulomb)

Adler-Wiser expression, see later

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

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

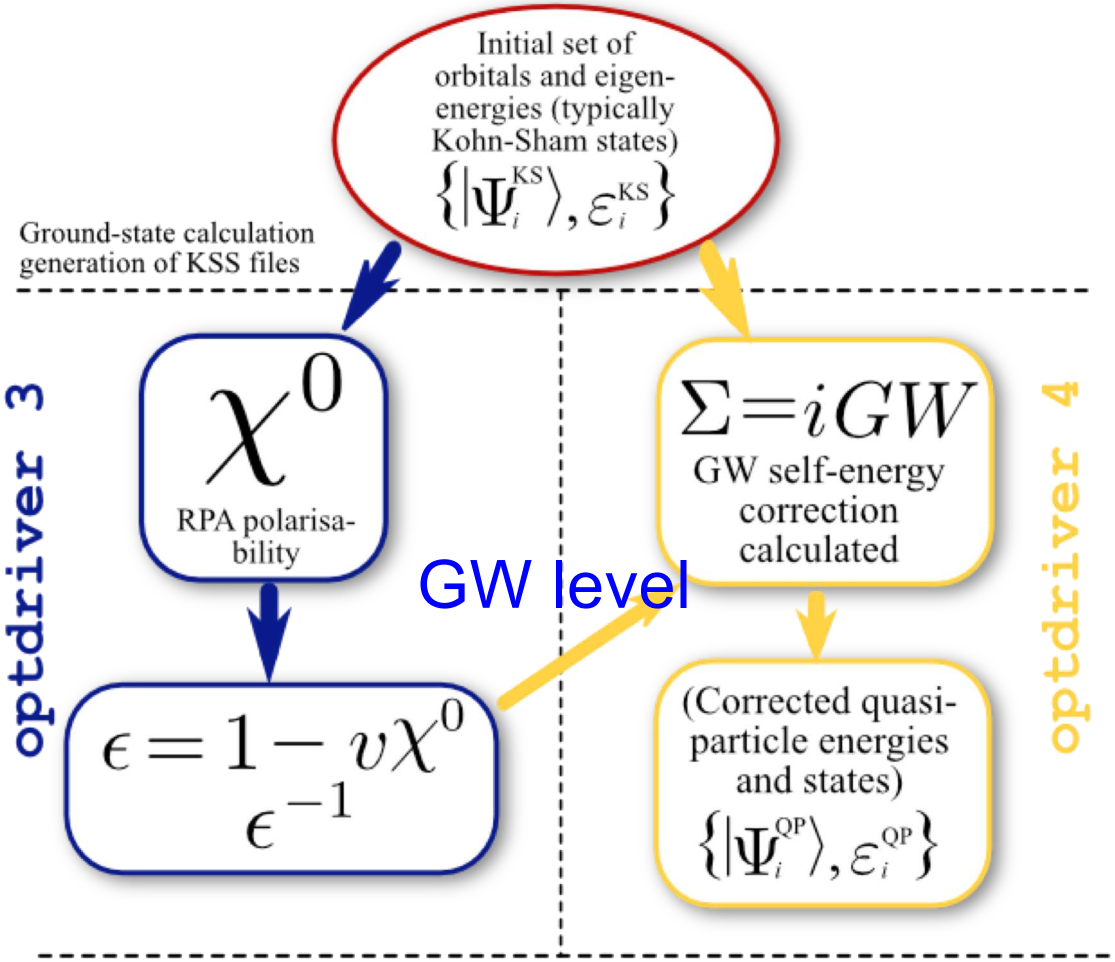
$$G(\mathbf{r},\mathbf{r}';\omega)=\sum_n\frac{\varphi_n(\mathbf{r})\varphi_n^*(\mathbf{r}')}{\omega-\varepsilon_n}$$

Usually starting from
KS eigenenergies and eigenfunction

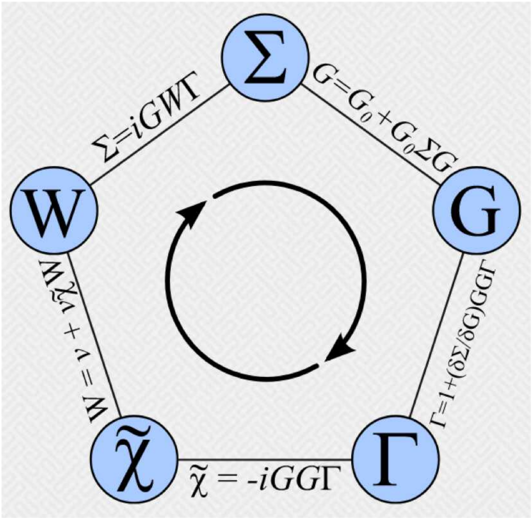
Independent-particle Green’s function

Self-consistent GW

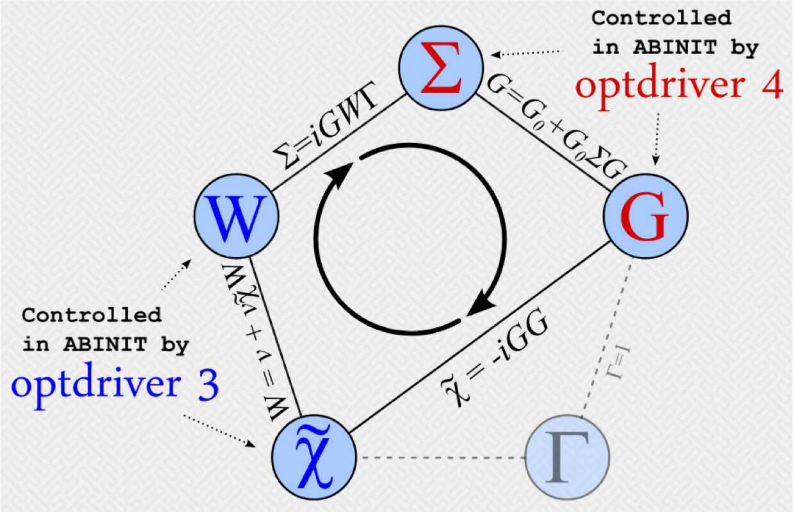
DFT level



GW level

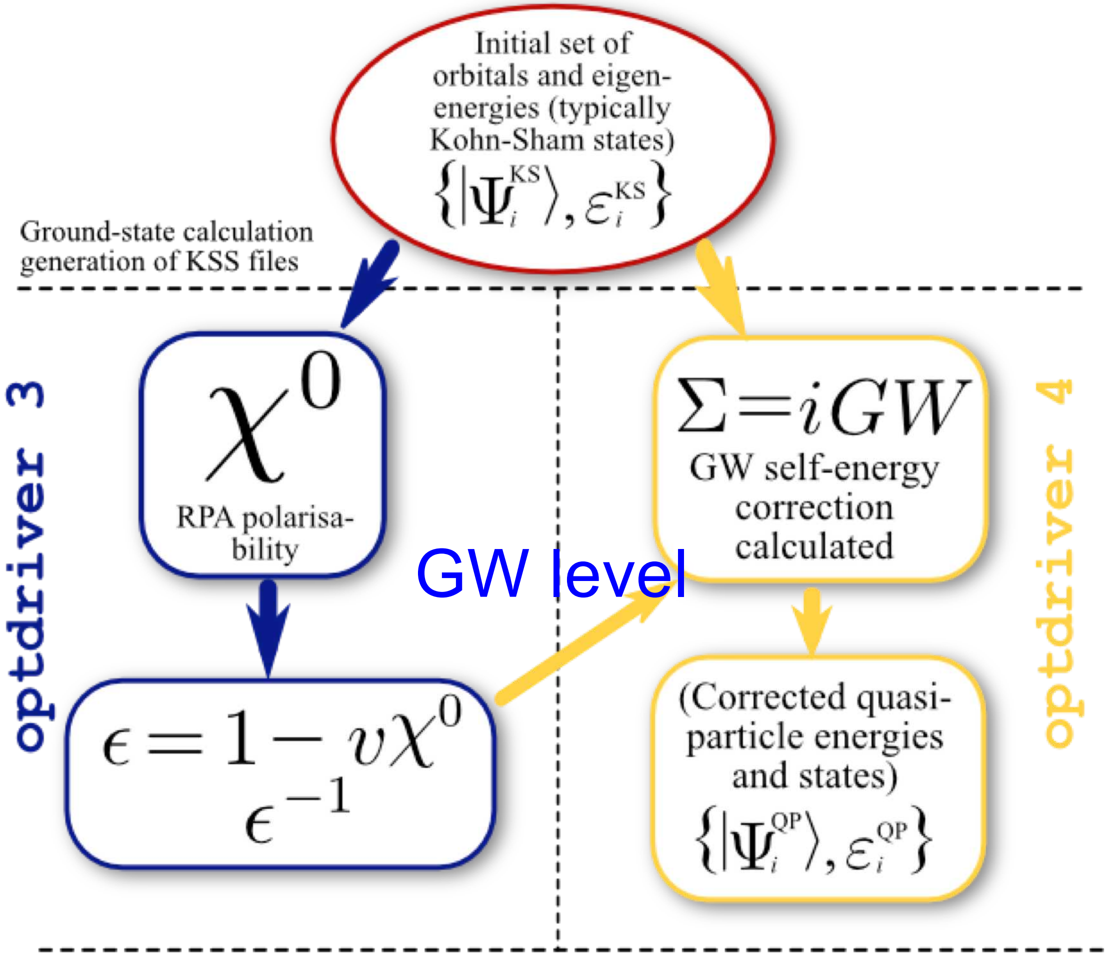


Neglect of Γ
(vertex corrections)



GW computational bottlenecks

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

$\epsilon = 1 - v\chi^0$

ϵ^{-1}

GW level

optdriver 4

$\Sigma = iGW$ GW self-energy correction calculated

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

Scales as	Needs
(Size)**3	Occupied states
(Size)**4	Occupied and many unoccupied states

DFT : routinely 200 atoms ; GW : routinely 20 atoms

Avoiding full self-consistency

G_0W_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 => Σ => 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 => Σ => compute eigenenergies

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

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

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

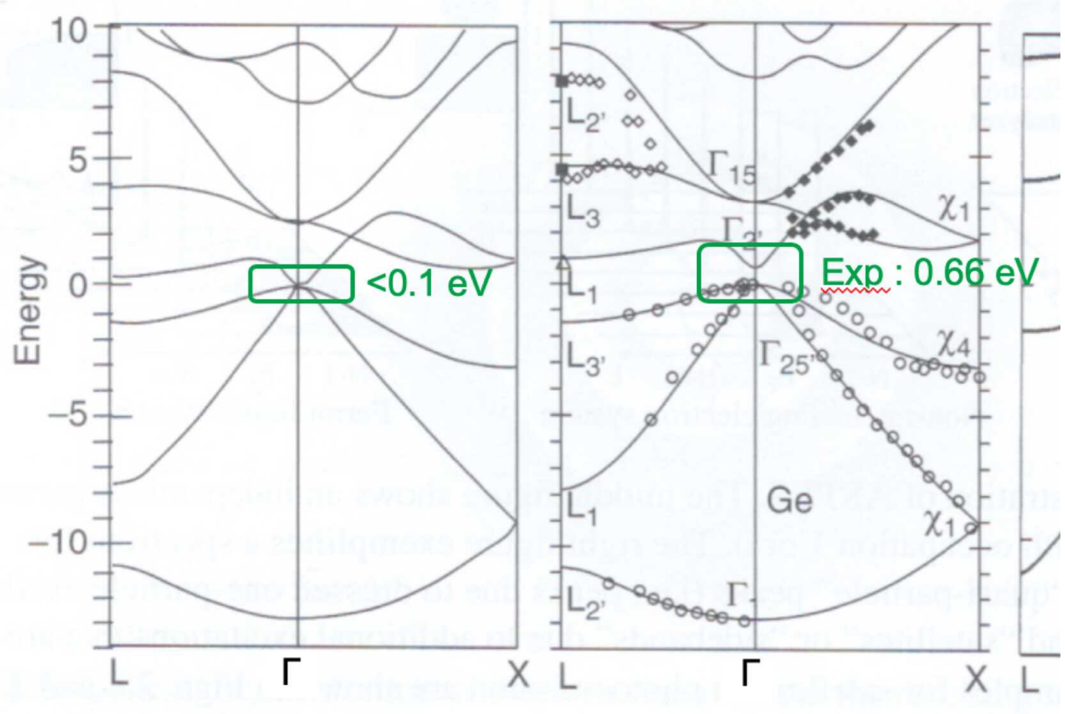
$$\varepsilon_i^{QP} = \varepsilon_i^{KS} + \left\langle \psi_i^{KS} \middle| \Sigma(\varepsilon_i^{QP}) - V_{xc} \middle| \psi_i^{KS} \right\rangle$$

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

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

Band gap correction : a scissor ?

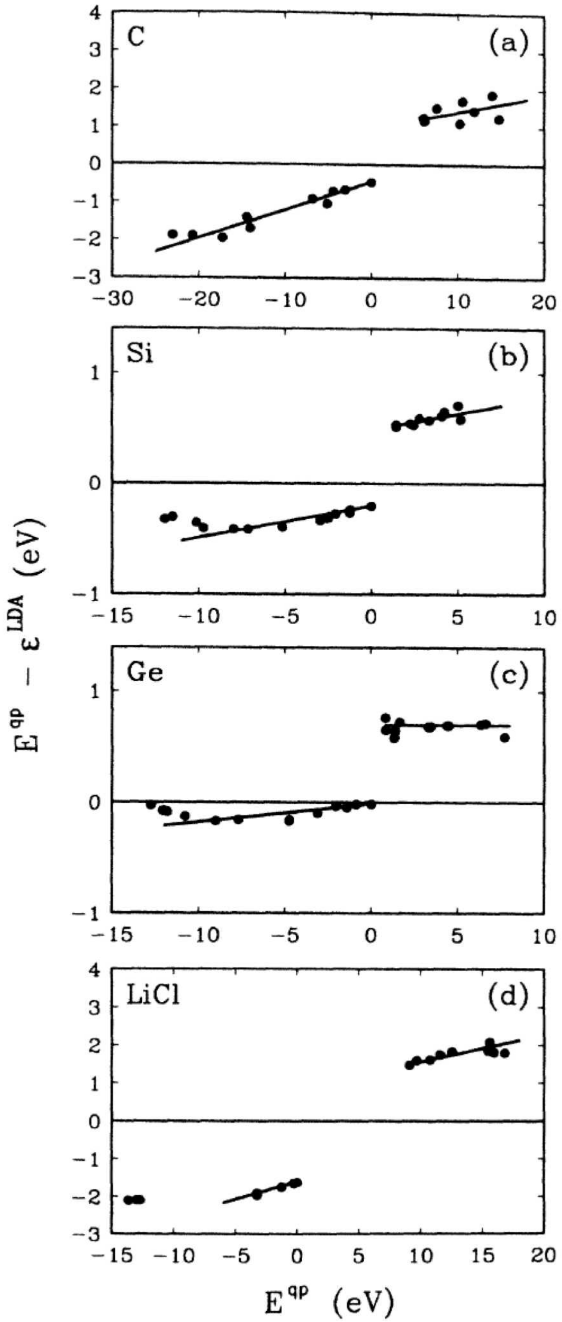


<0.1 eV

Exp : 0.66 eV

LDA

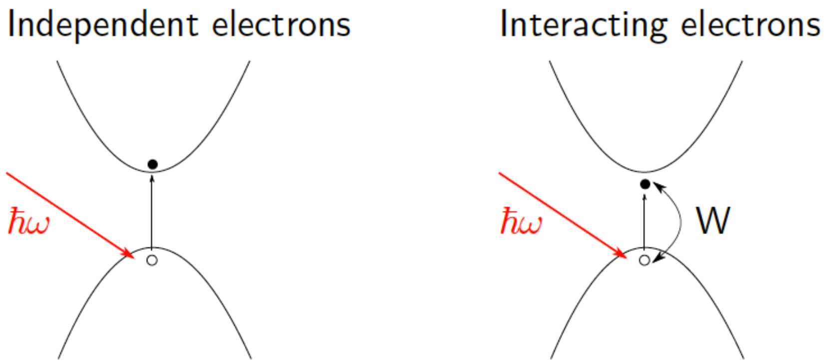
GW & experiment (circles)

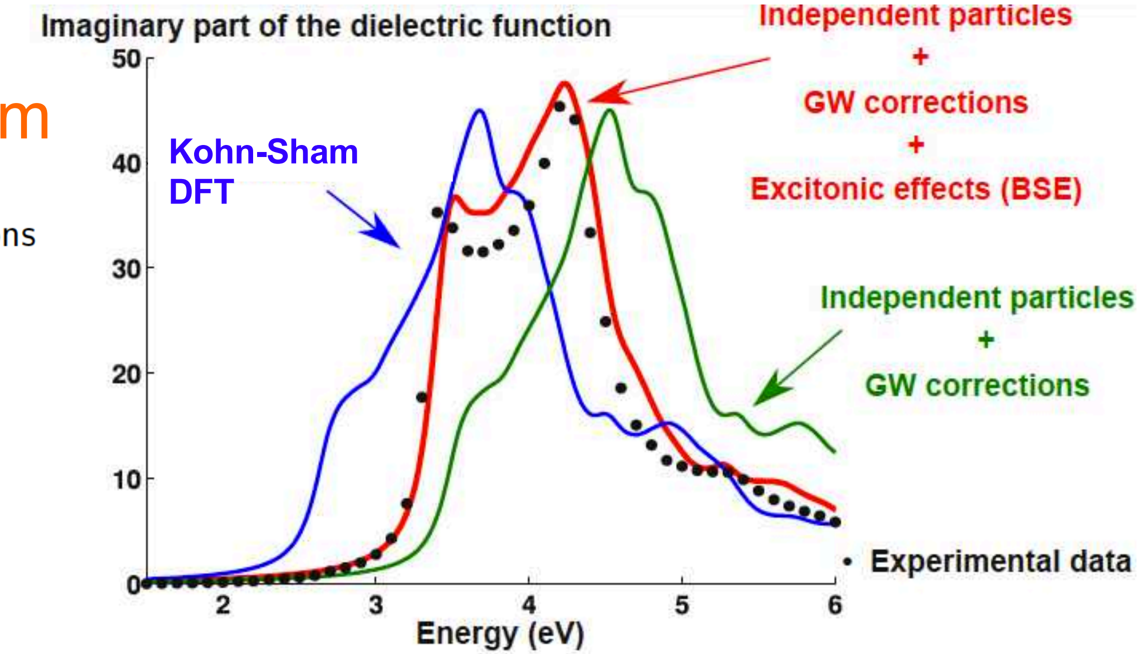


Optical characteristics of materials

Optical response : absorption

Silicon absorption spectrum





Beyond DFT, with Many-Body Perturbation Theory ... need :

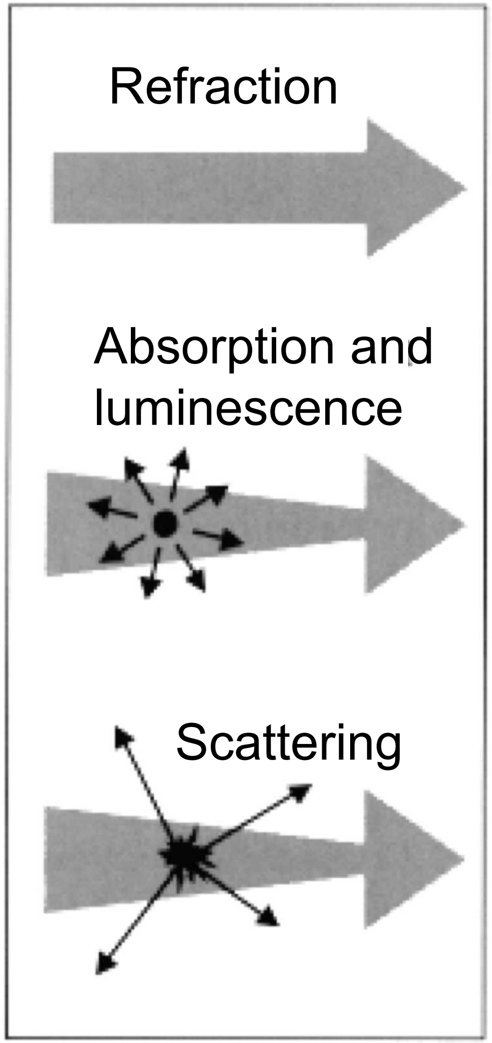
- band gap correction (GW) [still independent particle IPA]
- excitonic corrections (Bethe-Salpeter Equation - BSE)

Optical spectrum, relation with the dielectric function

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

Neutral electronic excitations

Optical processes inside materials



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.

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 $\mathbf{j}$

$$
\begin{aligned}
\nabla \,.\, \mathbf{D} &= \rho \\
\nabla \,.\, \mathbf{B} &= 0 \\
\nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\
\nabla \times \mathbf{H} &= \mathbf{j} + \frac{\partial \mathbf{D}}{\partial t}
\end{aligned}
$$

(SI units)

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.)

$$\mathbf{P} = \varepsilon_0 \chi \, \mathbf{E} \qquad \mathbf{M} = \chi_M \mathbf{H}$$

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \qquad \mathbf{B} = \mu_0 \, (\mathbf{H} + \mathbf{M})$$

$$\mathbf{D} = \varepsilon_0 \varepsilon_r \mathbf{E} \qquad \mathbf{B} = \mu_0 \, \mu_r \mathbf{H}$$

$$\varepsilon_{\mathrm{r}} = 1 + \chi \qquad \mu_{\mathrm{r}} = 1 + \chi_M$$

(Relative) dielectric constant ε_{r} (Relative) magnetic permeability μ_{r}

(Note : susceptibilities vanish in vacuum)

Wave equation in vacuum

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

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

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

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

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

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

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 $\mathbf{E}\,(\mathbf{r},\mathrm{t}) = \mathbf{E}_0 \mathrm{e}^{i(\mathbf{kr}-\omega t)} + (\mathrm{c.c.})$

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

$\mathbf{k}$ wavevector ω angular frequency λ wavelength

$$k = \frac{2\pi}{\lambda} = \frac{\omega}{\upsilon}$$

υ velocity of the waves $\frac{1}{\upsilon^2} = \mu_0\mu_\mathrm{r}\varepsilon_0\varepsilon_\mathrm{r}$

$$\upsilon = \frac{1}{\sqrt{\varepsilon_r\mu_r}}c$$

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

$$\boxed{c = \frac{1}{\sqrt{\mu_0\varepsilon_0}} = 2.998 \times 10^8\mathrm{ms}^{-1}}$$

$$\boxed{\varepsilon_0 = 8.8541878\ldots \times 10^{-12}\mathrm{Fm}^{-1}}$$

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 $\mathbf{k}$) are still solutions :

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

$$k = \tilde{n}\frac{\omega}{c} \qquad \boxed{\tilde{n}^2 = \mu_r \varepsilon_r + i\,\frac{\mu_r \sigma}{\varepsilon_0 \omega}}$$

$\tilde{n}$ complex index of refraction

Complex index of refraction (II)

Define $\tilde{n} = n + i\kappa$

n normal refractive index

κ extinction coefficient

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

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

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

(Exponential decrease) times (propagating wave)

absorption refraction

One expects κ 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

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

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

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

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

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

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

Polarizability and conductivity

- Hypothesis of linear-response regime :

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

polarizability

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

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

$$\boxed{P_\beta(\omega) = \sum_\gamma \alpha_{\beta\gamma}(\omega) E_\gamma(\omega)}$$

(the same for the conductivity)

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

Wave equation

$$\boxed{\varepsilon_{\beta\gamma}(\omega)} = 1 + \frac{\alpha_{\beta\gamma}(\omega)}{\varepsilon_0} + i\frac{\sigma_{\beta\gamma}(\omega)}{\varepsilon_0 \omega}$$

Complex macroscopic dielectric tensor, function of frequency => absorption and velocity

Wrap-up and an example (SiO_2-glass)

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

n normal refractive index

κ extinction coefficient

$$\boxed{\tilde{n}^2(\omega) = \varepsilon(\omega)}$$

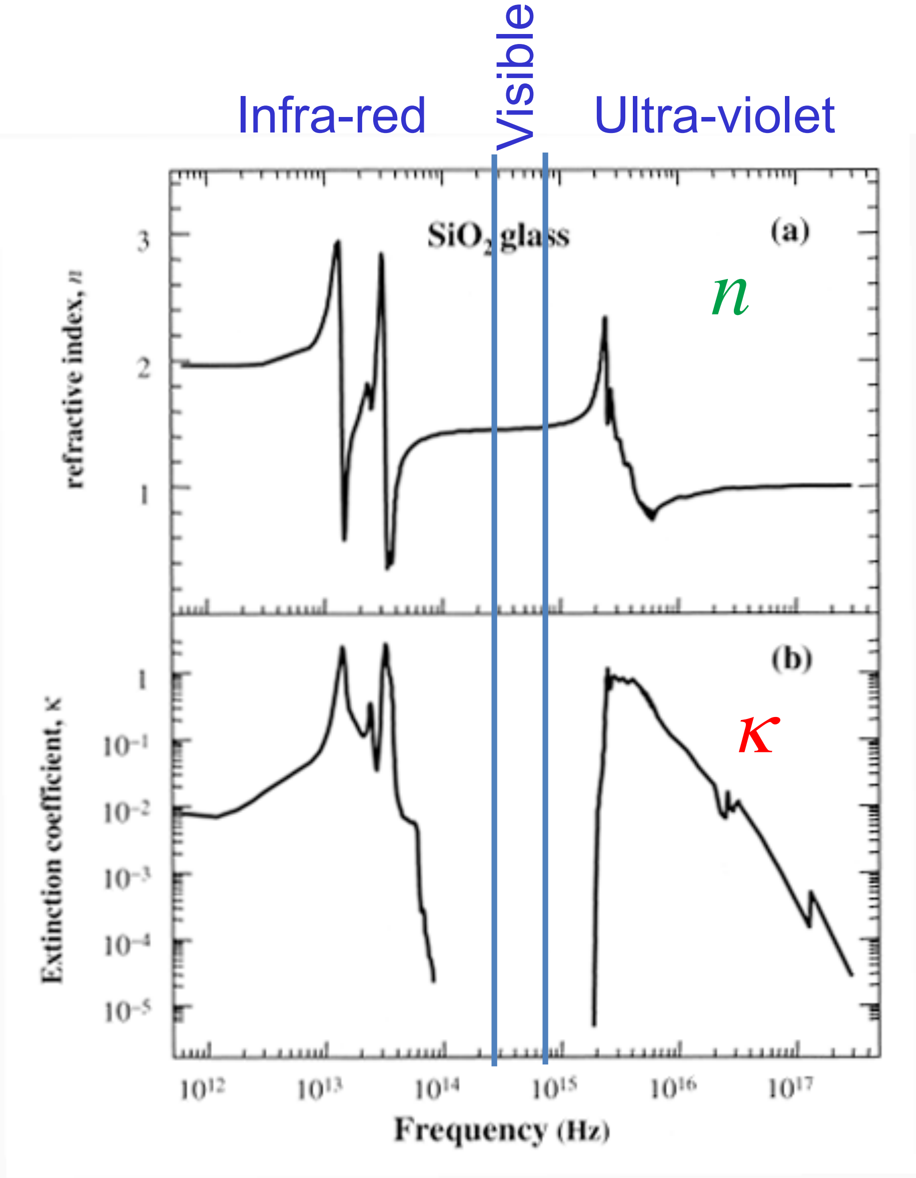
$$E(z,t) = \mathrm{e}^{-\kappa\omega z/c}(E_0\mathrm{e}^{i(\omega nz/c-\omega t)} + E_0^*\mathrm{e}^{-i(\omega nz/c-\omega t)})$$

Absorption Refraction

Relationship between

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

How to compute them ?



Kramers-Kronig relations

$$\Re\varepsilon(\omega')-1 = \frac{2}{\pi} P\int_0^{+\infty} \frac{\Im\varepsilon(\omega)\omega}{\omega^2-\omega'^2}\, d\omega$$

$$\Im\varepsilon(\omega') = -\frac{2\omega'}{\pi} P\int_0^{+\infty} \frac{\Re\varepsilon(\omega)}{\omega^2-\omega'^2}\, d\omega\ .$$

Come from causality

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

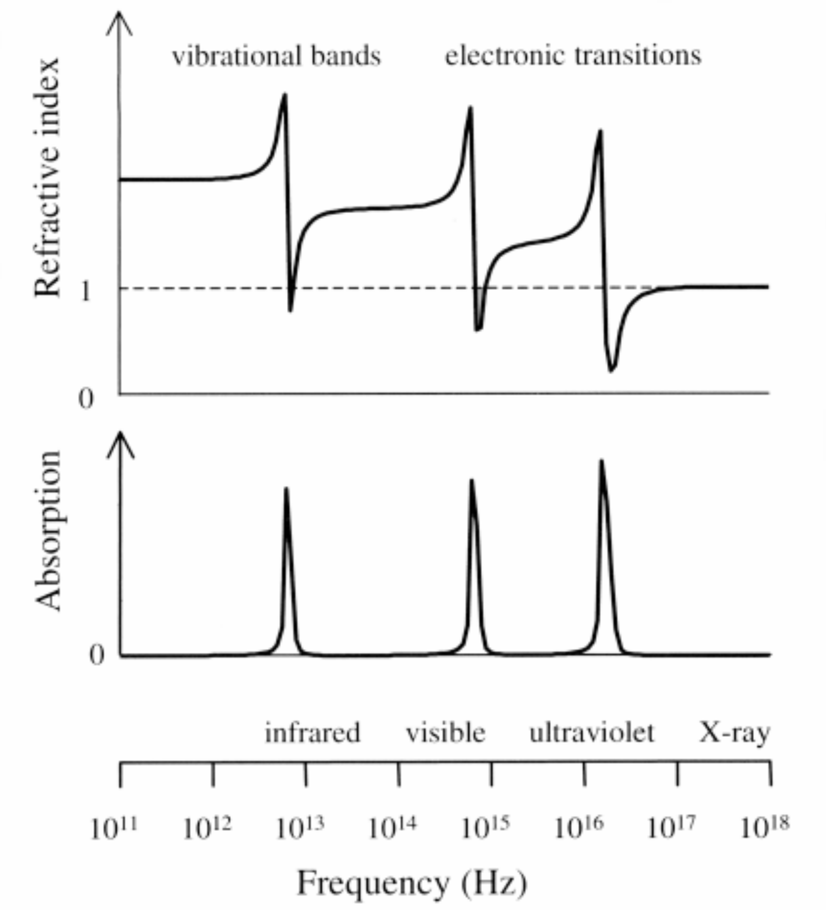
Allows to check validity of results or to compute the other if one accurately known

Typical behaviour :

Absorptions at a series of frequencies,

delta functions centered on ω_i

Refractive index behaves like $1/(\omega - \omega_i)$



Time-dependent perturbation theory and Adler-Wiser formula

Time-dependent perturbation

Time-dependent Schrödinger equation :

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

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 :

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

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

We consider only time-space "separable" perturbations :

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

Wavefunction changes

If monochromatic, causal, perturbation :

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

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

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

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

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 $\omega_{mn} = \omega_m^{(0)} - \omega_n^{(0)}$

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

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

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

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

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

Wrap-up and density change

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

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

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

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 :

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

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

Adler-Wiser formula

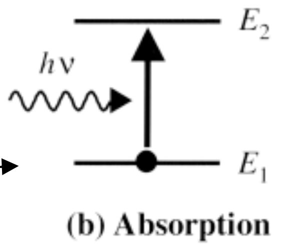
Response of a system of independent electrons
with a time-varying local potential of well-defined frequency

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

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

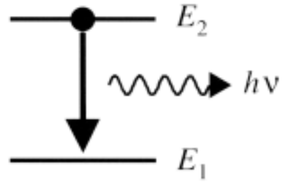
- Contributions from each pair of levels of different occupation
- Fulfills the causality principle
- Real part symmetric in frequency,
  imaginary part anti-symmetric in frequency

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



(b) Absorption

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



(a) Emission

Adler-Wiser in periodic case

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

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

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

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)

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

Real part computed from Kramers-Kronig formula :

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

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)

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

N particles per unit volume to create a polarization

$$D = \varepsilon_\mathrm{r}\varepsilon_0 E = \varepsilon_0 E + P = \varepsilon_0 E - \frac{Ne^2 E}{m_0(\omega^2 + i\gamma\omega)}. \qquad \varepsilon_\mathrm{r}(\omega) = 1 - \frac{Ne^2}{\varepsilon_0 m_0} \frac{1}{(\omega^2 + i\gamma\omega)}.$$

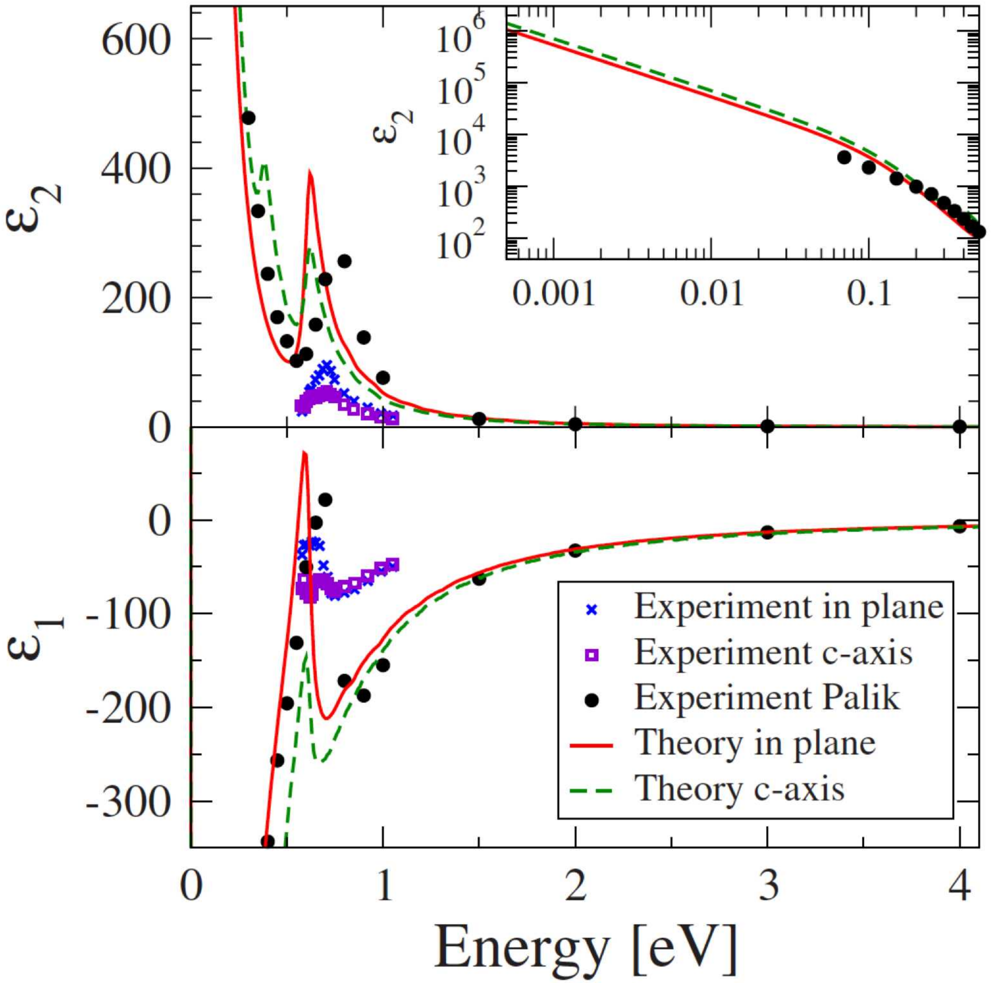
So-called "plasma frequency" : $\omega_\mathrm{p} = \left(\frac{Ne^2}{\varepsilon_0 m_0} \right)^{\frac{1}{2}}.$

$$\boxed{\varepsilon_\mathrm{r}(\omega) = 1 - \frac{\omega_\mathrm{p}^2}{(\omega^2 + i\gamma\omega)}.}$$

Magnesium dielectric function

Imaginary part

Real part



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

Missing electron-electron interaction

« Sum-over-states » (SOS) formula :

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

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

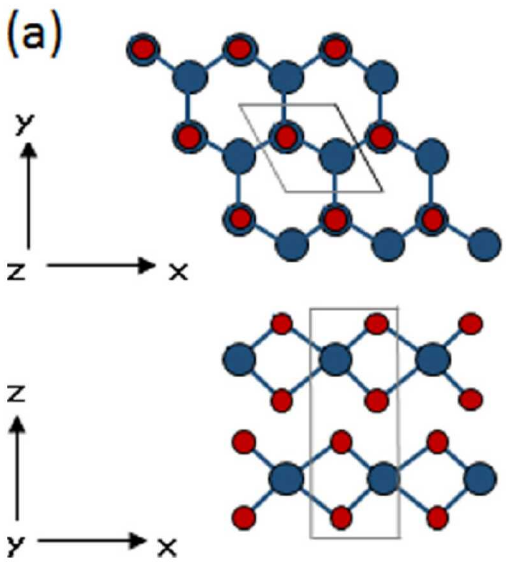
Wavefunctions and eigenenergies from a fixed potential (effective)
Might be : DFT (any XC approximation)
GW
=> Determine the absorption edge, linked with the joint density of state

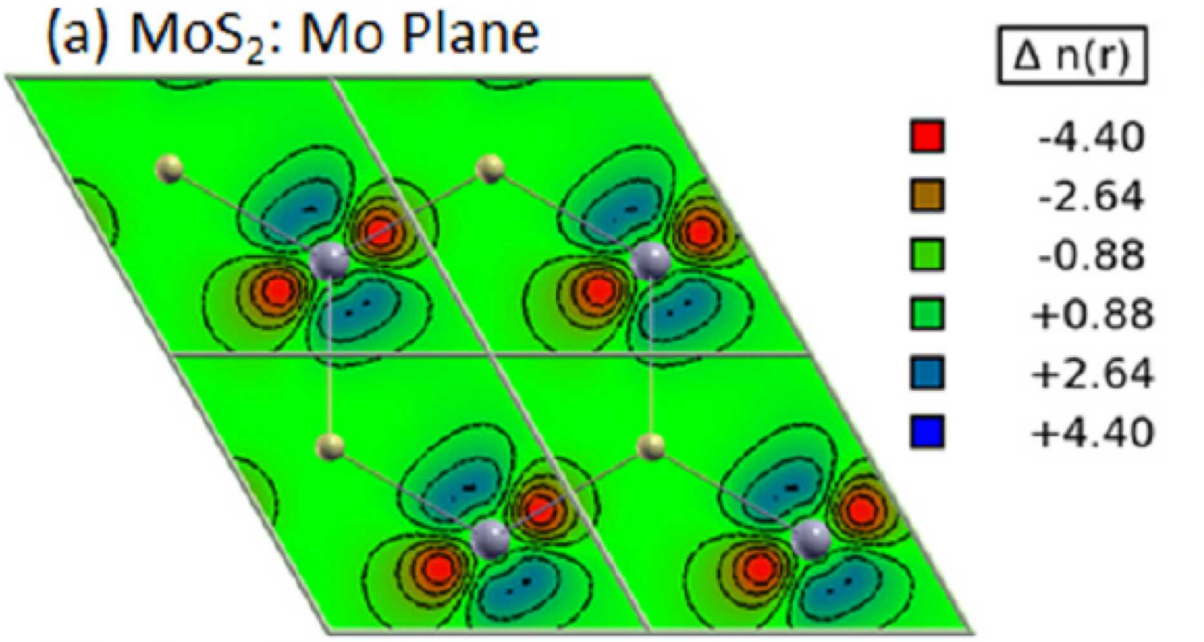
Missing two effects due to electron-electron interaction

- 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

Local fields from TD-DFT

Local change of electronic density





Electric field in the x (horizontal) direction

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

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

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

TD Hartree and XC kernels

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

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

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

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

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.

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

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

Dyson equation for susceptibility (I)

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

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

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

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

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

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

Valid for all perturbations, thus :

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

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

Dyson equation for susceptibility (II)

Exact formula for the inverse of the susceptibility

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

Exact XC kernel,
to be approximated

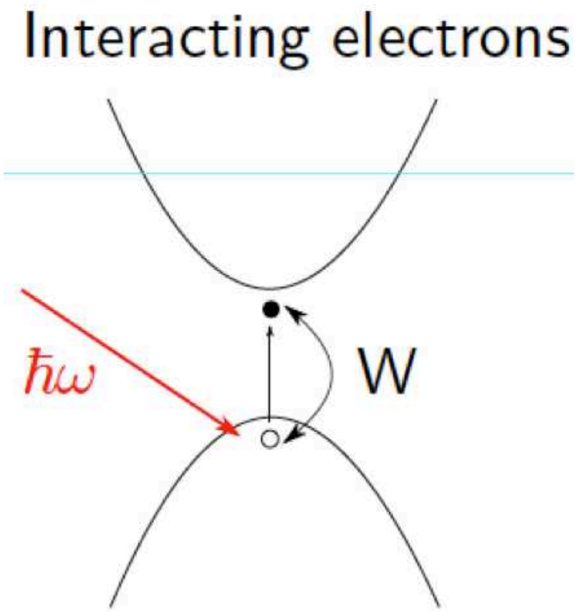
$$\chi_0(\mathbf{r},\mathbf{r}';\omega) = \sum_{\sigma}\sum_{n}\sum_{m}\left(f_{m\sigma} - f_{n\sigma}\right)\frac{\varphi^*_{n\sigma}(\mathbf{r})\varphi_{m\sigma}(\mathbf{r})\varphi^*_{m\sigma}(\mathbf{r}')\varphi_{n\sigma}(\mathbf{r}')}{\left(\varepsilon_{m\sigma} - \varepsilon_{n\sigma}\right) - \omega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

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.

Bethe-Salpeter equation

Dielectric response of interacting particles : Excitons

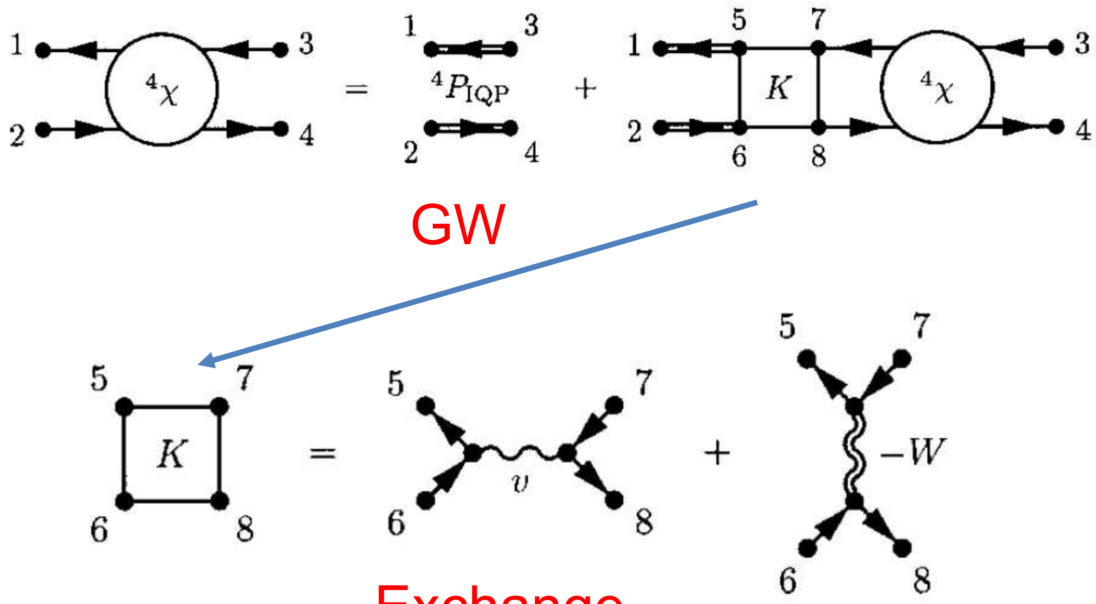
Exciton = bound electron-hole pair



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

Bethe-Salpeter equation

$$H^{eff}\phi^{\lambda} = E_{\lambda}\phi^{\lambda}$$

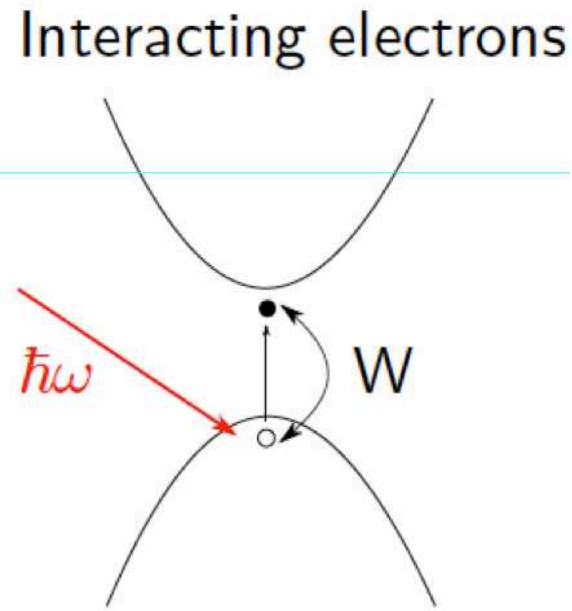
$$H^{eff}_{(vc\mathbf{k},v'c'\mathbf{k}')} = \underbrace{(E_{c\mathbf{k}} - E_{v\mathbf{k}})}_{\substack{\text{Transition}\\ \text{energies}\\ \Delta E_{cv}(\mathbf{k})}}\mathbf{I} + \underbrace{\bar{v}_{(vc\mathbf{k},v'c'\mathbf{k}')}}_{\substack{\text{Exchange}\\ \text{term}}} - \underbrace{W_{(vc\mathbf{k},v'c'\mathbf{k}')}}_{\substack{\text{Screened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

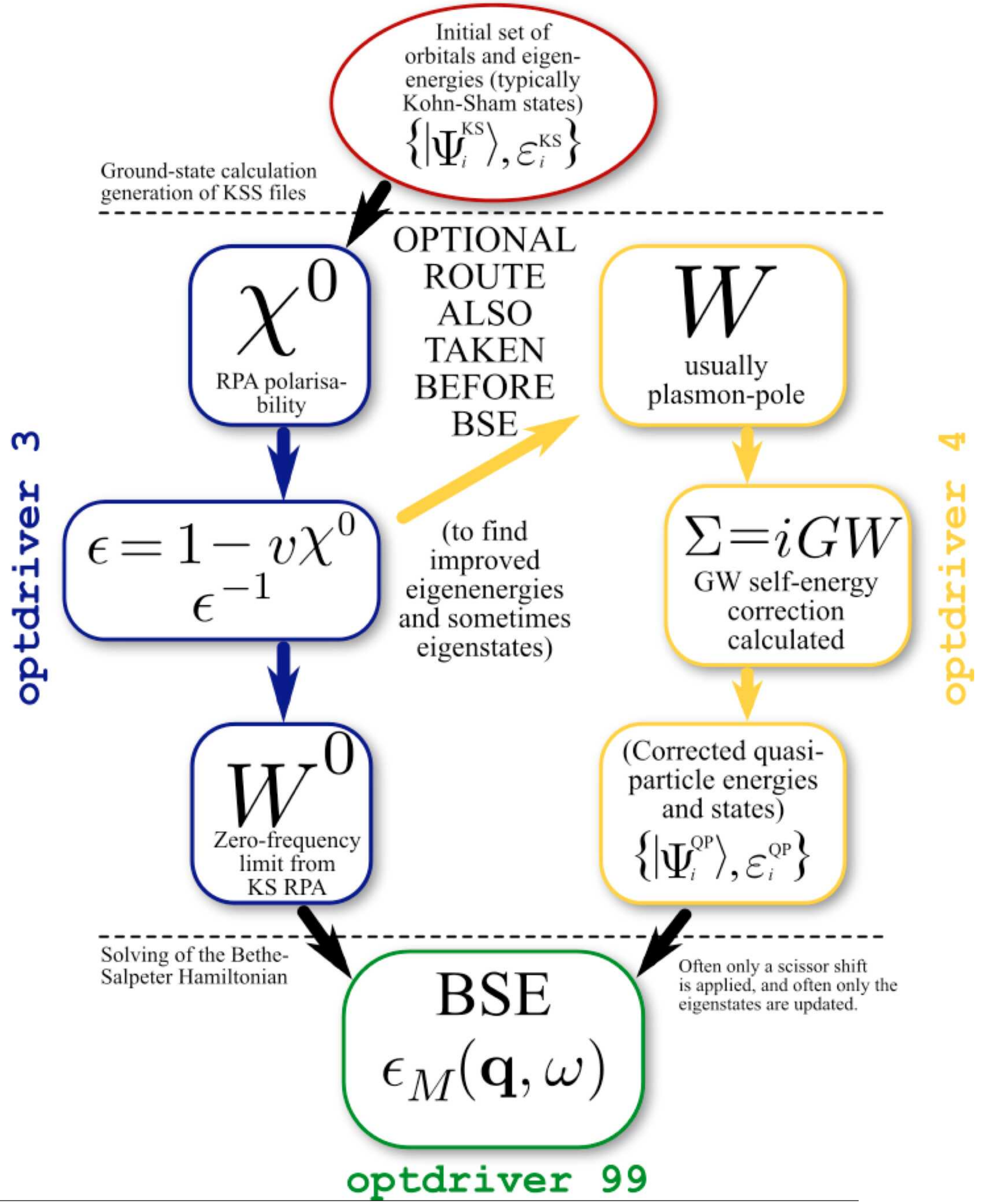
$$\varepsilon(\omega) = 1 + 4\pi\chi(\omega) = 1 - \lim_{\mathbf{q}\to 0} v(\mathbf{q}) \underbrace{\left\langle P(\mathbf{q}) \middle| (H^{eff} - I\omega)^{-1} \middle| P(\mathbf{q}) \right\rangle}_{\text{Computed using iterative technique}}$$

$$P(\mathbf{q})_{n_1 n_2} = \left\langle n_1 \middle| e^{iqr} \middle| n_2 \right\rangle$$

Skoltech

GW + BSE





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

χ^0
RPA polarisa-bility

$\epsilon = 1 - v\chi^0$
ϵ^{-1}

W^0
Zero-frequency limit from KS RPA

OPTIONAL ROUTE ALSO TAKEN BEFORE BSE

(to find improved eigenenergies and sometimes eigenstates)

W
usually plasmon-pole

$\Sigma = iGW$
GW self-energy correction calculated

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

`optdriver 3`

`optdriver 4`

Solving of the Bethe-Salpeter Hamiltonian

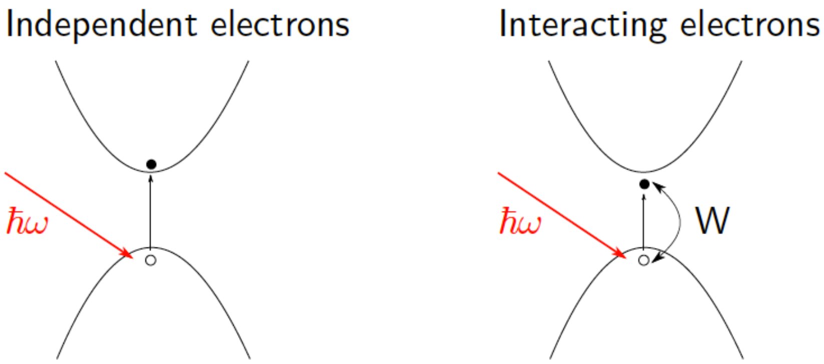
BSE
$\epsilon_M(\mathbf{q}, \omega)$

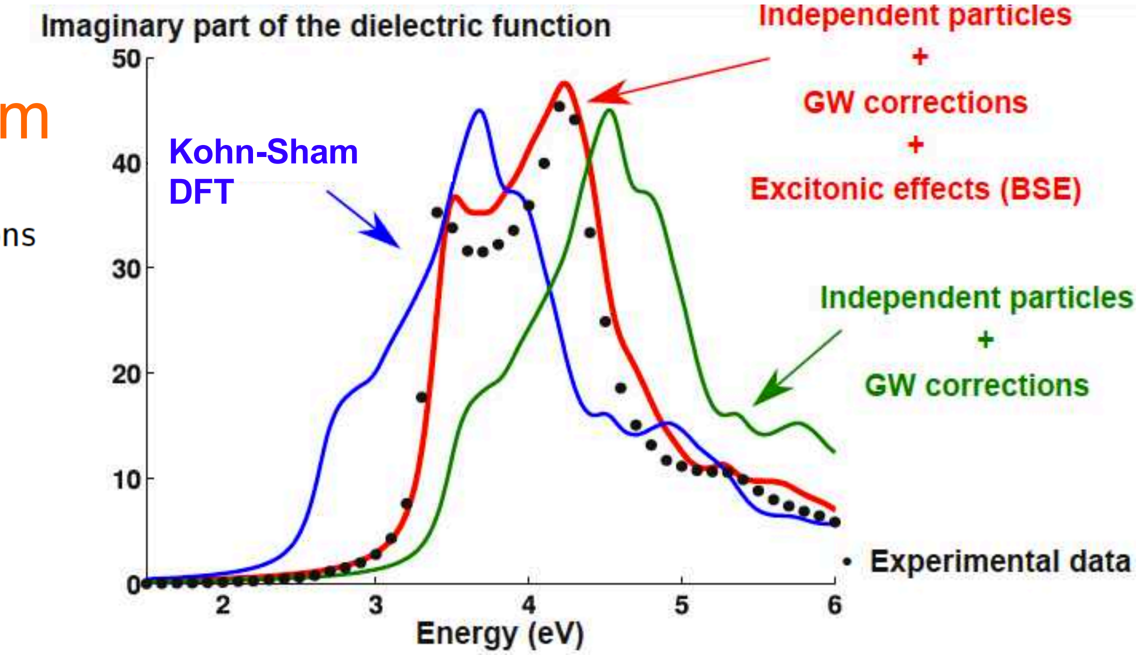
Often only a scissor shift is applied, and often only the eigenstates are updated.

`optdriver 99`

Optical response : absorption

Silicon absorption spectrum





Beyond DFT, with Many-Body Perturbation Theory ... need :

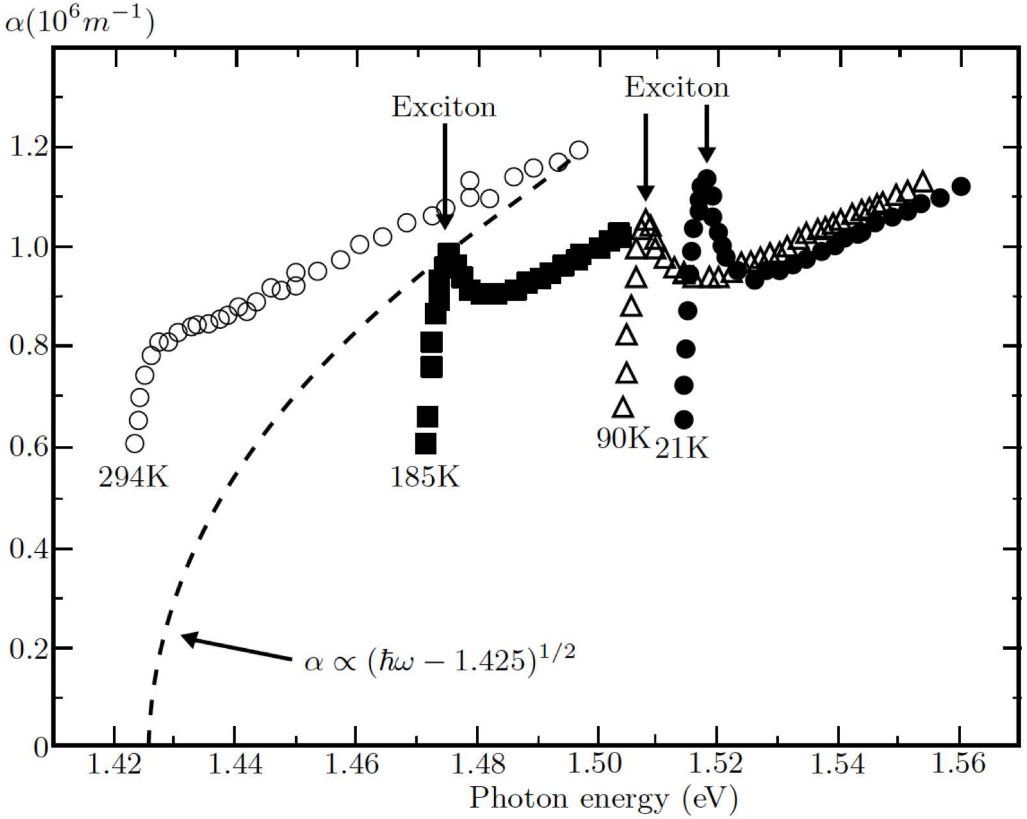
- band gap correction (GW) [still independent particle IPA]
- excitonic corrections (Bethe-Salpeter Equation - BSE)

Optical spectrum, relation with the dielectric function

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

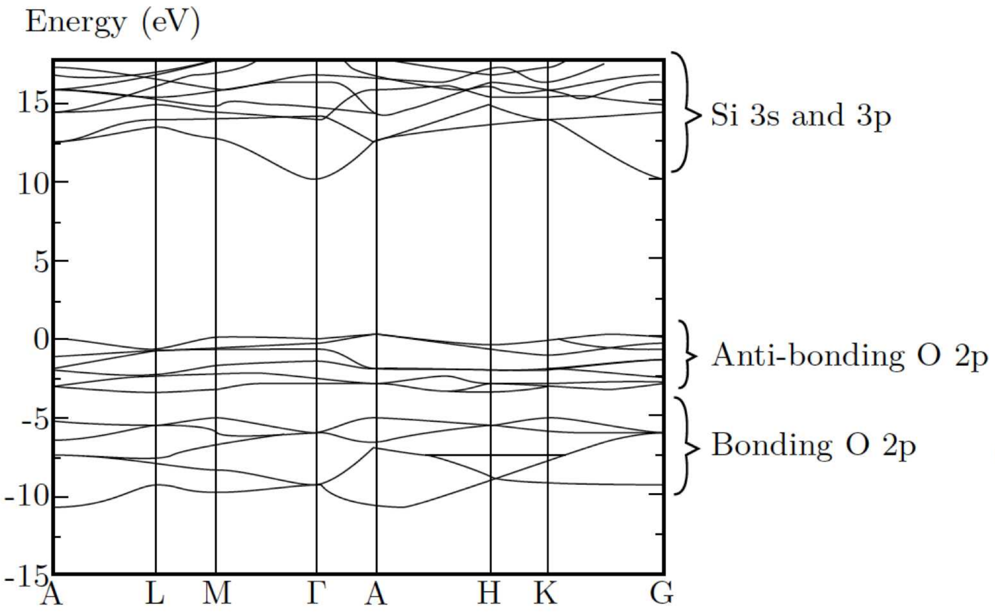
Neutral electronic excitations

Experimental signature of excitons

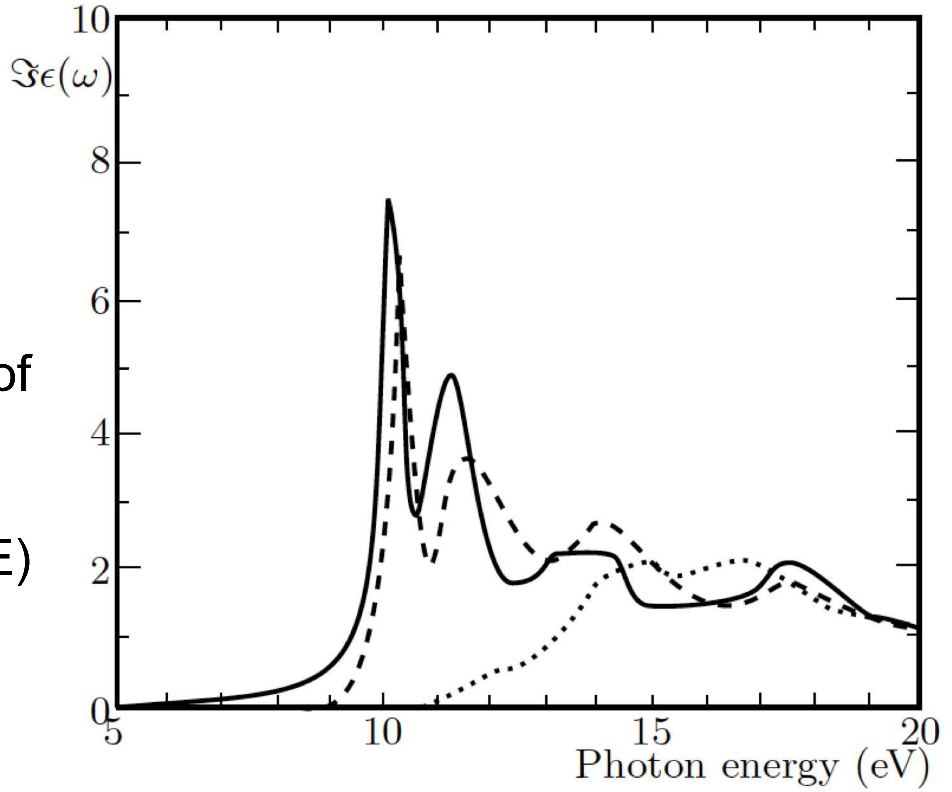


Absorption of GaAs between 21 K and 294 K. The dashed line is an attempt to fit the absorption edge using a square root function, with a value of E_g equal to 1.425 eV, which is appropriate for GaAs at 294 K.

SiO_2 band structure and dielectric function

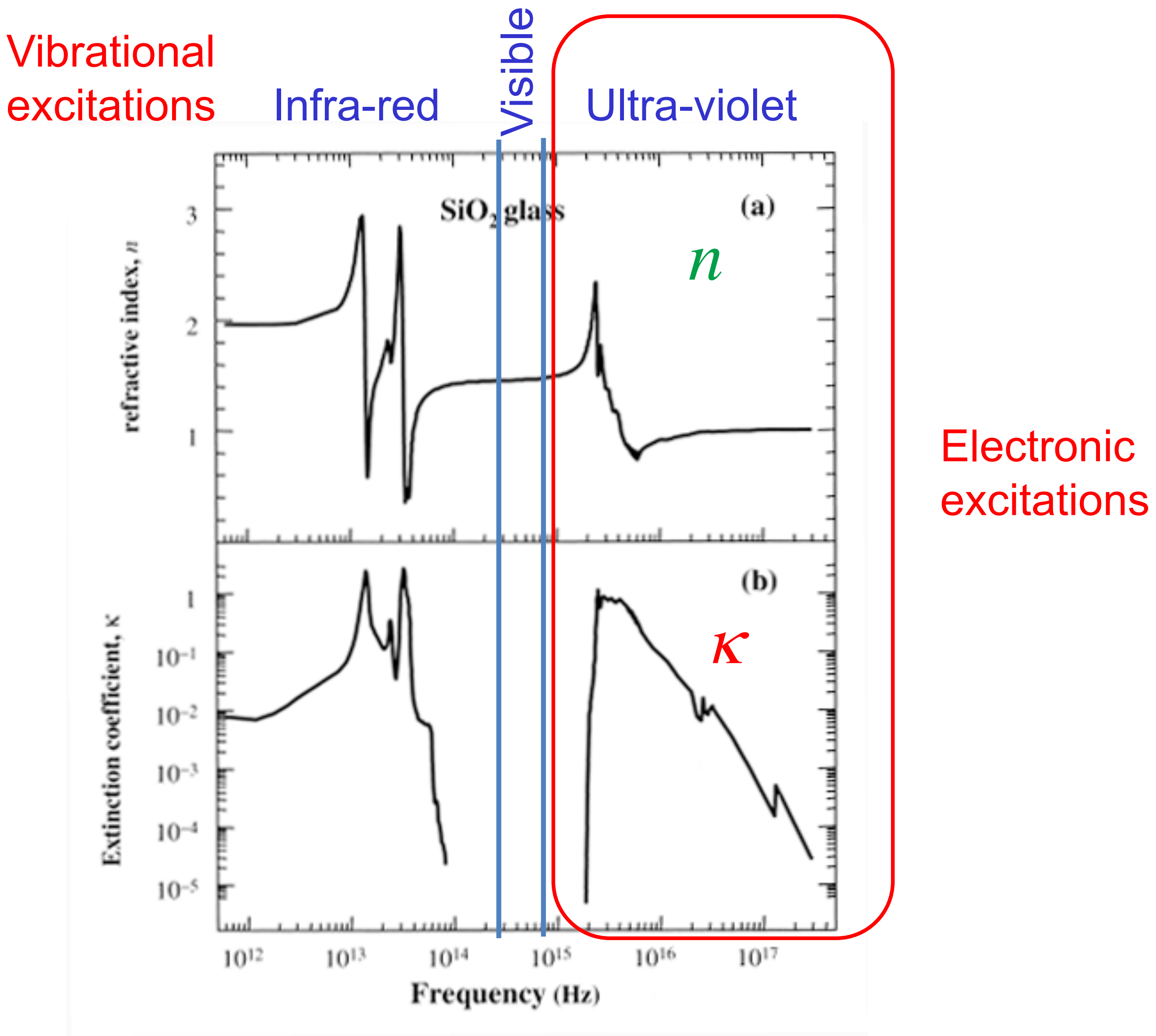


Band structure
of alpha-quartz



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

SiO_2 refractive index and extinction coefficient



Vibrational excitations

Infra-red

Visible

Ultra-violet

n

κ

Electronic excitations