MBPT and TDDFT
Theory and Tools for
Electronic-Optical Properties
Calculations in Material Science

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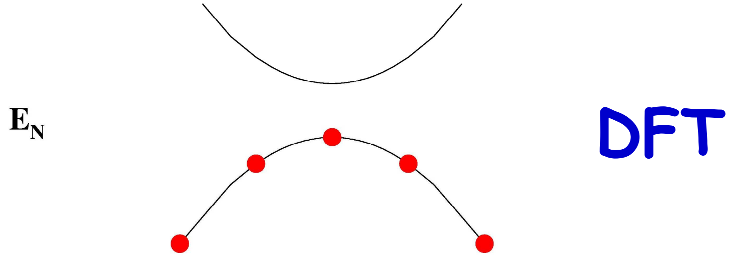
Outline of the Lectures

- Many Body Problem
- DFT elements; examples
- DFT drawbacks
- excited properties:

  electronic and optical spectroscopies. elements of theory
- Many Body Perturbation Theory: GW
- codes, examples of GW calculations
- **Many Body Perturbation Theory: BSE**
- **codes, examples of BSE calculations**
- Time Dependent DFT
- codes, examples of TDDFT calculations
- state of the art, open problems

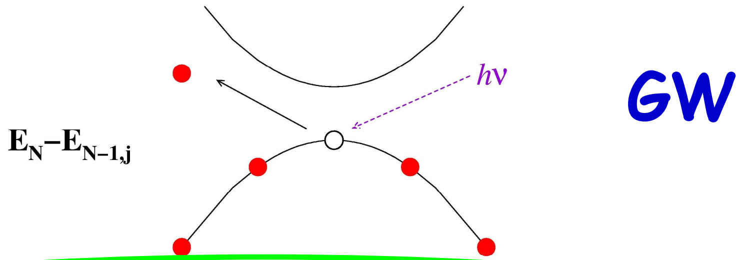
Computational cost

Ground State properties (Total energy):



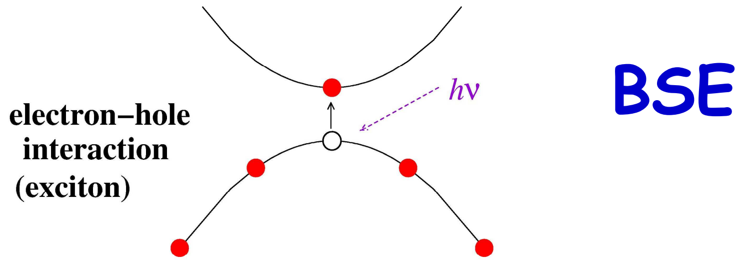
$$(-\frac{1}{2}\nabla^2 + V^{ext} + V^H + V_{xc})\phi_j^{KS}(\vec{r}) = \varepsilon_j^{KS}\phi_j^{KS}(\vec{r})$$

1 particle excitations (photoemission)



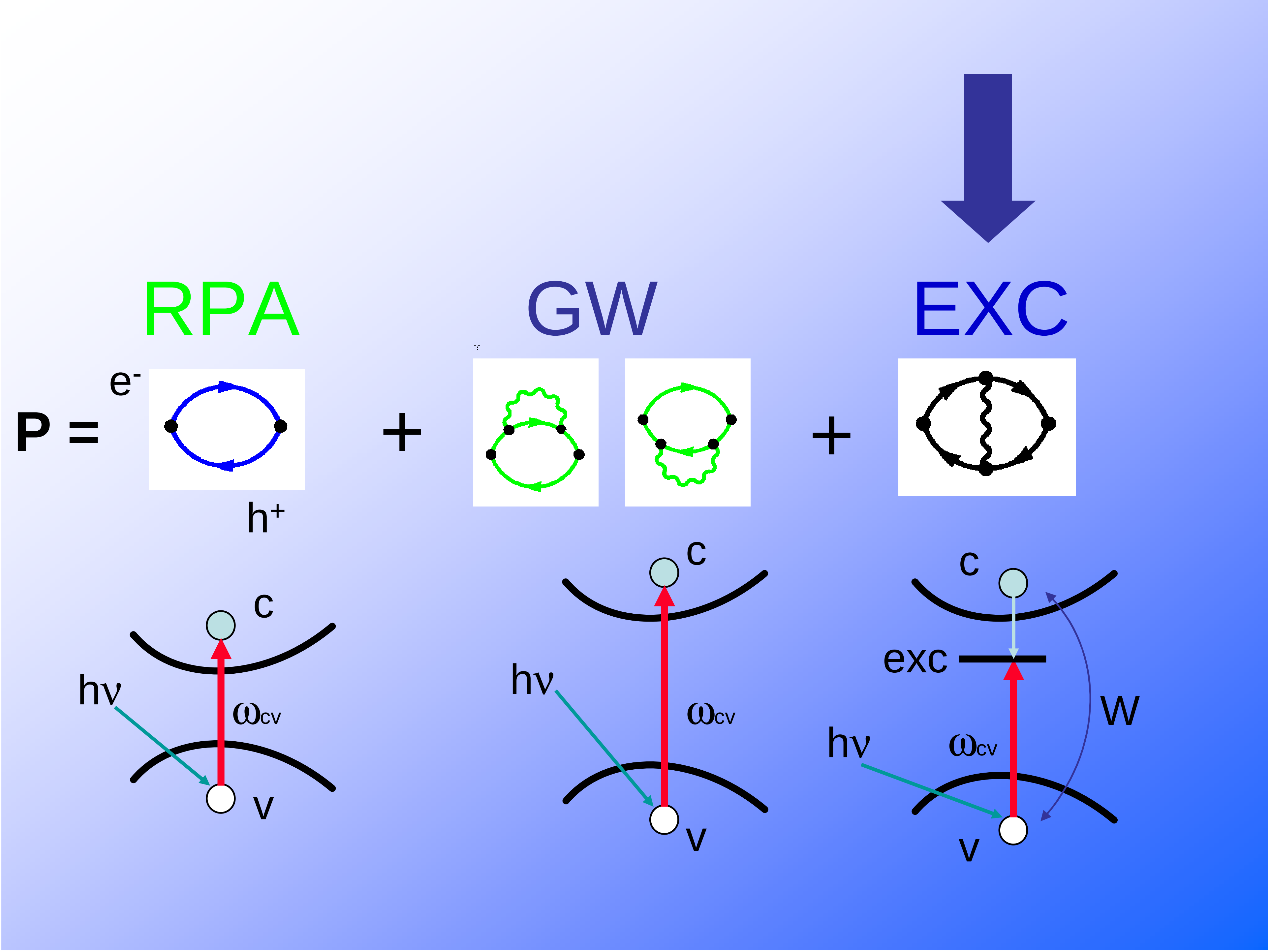
$$(-\frac{1}{2}\nabla^2 + V^{ext} + V^H)\Psi_j^{QP}(\vec{r}) + \int \Sigma(\vec{r},\vec{r'},\varepsilon_j^{QP})\Psi_j^{QP}(\vec{r'})d\vec{r'} = \varepsilon_j^{QP}\Psi_j^{QP}(\vec{r})$$

2 particle excitations (absorption)



excitonic effects

e^{-}-h^{+} interaction in optical spectra: response function beyond RPA


RPA
GW
EXC
P =
e-
h+
+
+
c
v
hν
ωcv
c
v
hν
ωcv
c
exc
v
hν
ωcv
W

Hedin's Equations

many body effects → quasi-particle

$$\Sigma(12)=i\int G(13)\Gamma(324)W(41)d(34),$$

$$W(12)=v(12)+\int v(13)P(34)W(42)d(34),$$

$$P(12)=-i\int G(13)G(41)\Gamma(342)d(34),$$

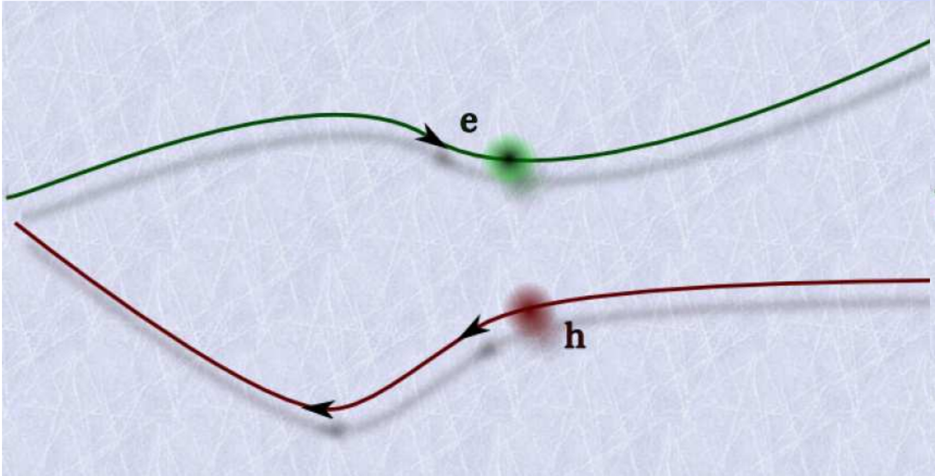
$$\Gamma(123)=\delta(12)\delta(13)$$

$$+\int \frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(673)d(4567),$$

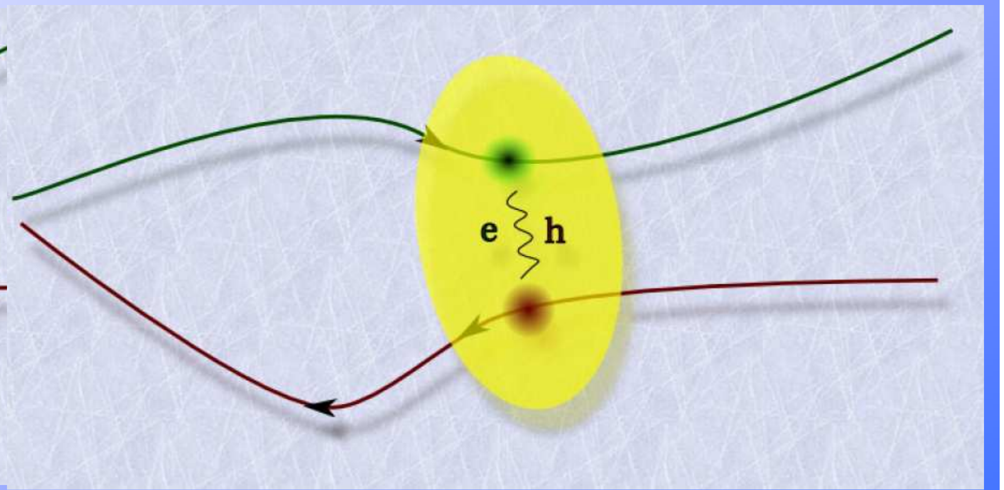
$$G(12)=G_0(12)+\int G_0(13)\,\Sigma(34)\,G(34)\,d(34)$$

two-particle excitations →
poles of two-particle Green's function L
Excitonic effects = electron - hole interaction

$P(12) = -iG(12)G(21) = P_0(12)$
Independent particles (RPA)



$P(12) = -iG(13)G(42)\Gamma(342)$
Interacting particles (excitonic effects)



Two-Particle Effects: Bethe-Salpeter Equation

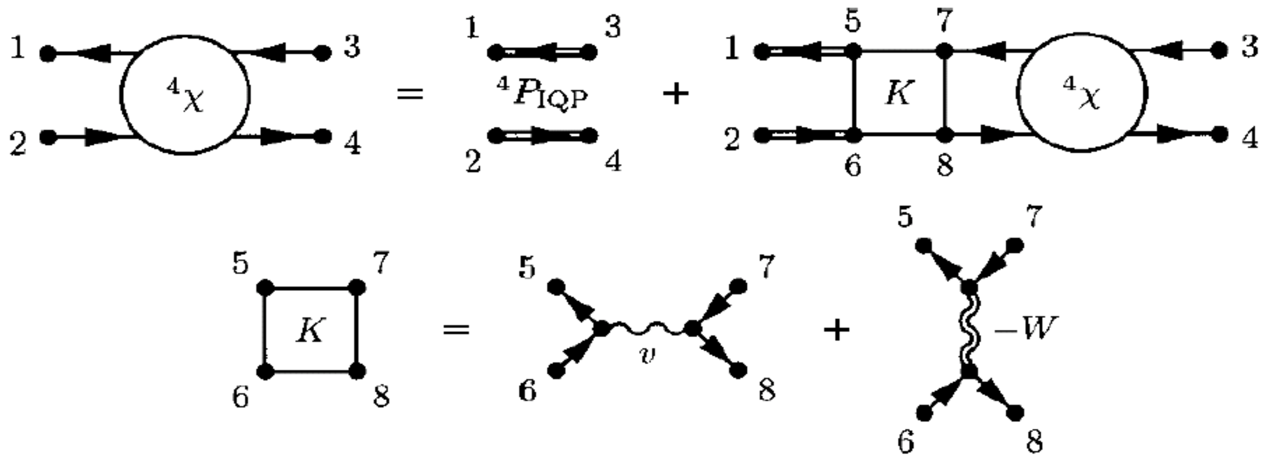
neutral excitations
Dyson equation for polarizability L, for the two-particle Green function

$$\Sigma = iGW \qquad \delta\Sigma / \delta G = iW$$

$$\Gamma(123) = \delta(12)\,\delta(13) + iW(1^+2)\int d(67)\,G(16)\,G(72)\,\Gamma(673)$$

$$^3P(312) \equiv -i\int d(67)\,G(16)\,G(72)\,\Gamma(673)$$

$$^3P(345) = -iG(43)\,G(35) + i\int d(12)\,G(41)\,G(25)\,W(1^+2)\;{}^3P(312)$$



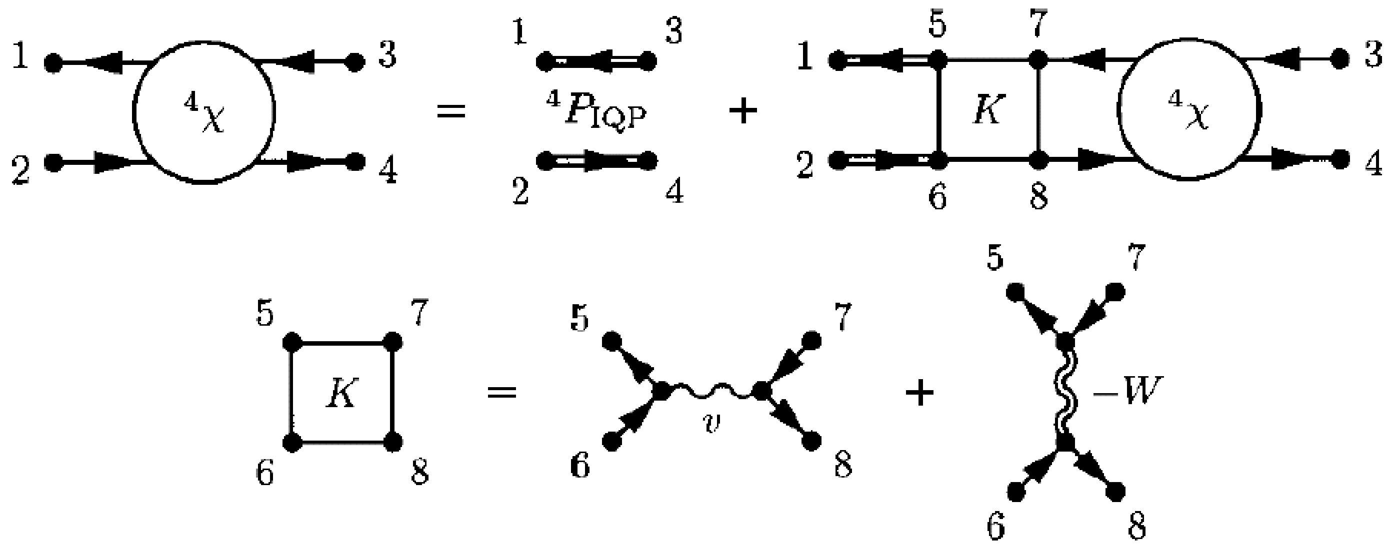
$$ {}^4\bar{P} = {}^4P_{IQP} + {}^4P_{IQP} K \, {}^4\bar{P} $$

e$^-$-h$^+$ screened attraction

$$ K(1234) = \delta(12)\,\delta(34)\,\bar{v}(13) - \delta(13)\,\delta(24)\,W(12) $$

$$ {}^4\chi = {}^4P_{IQP} + {}^4P_{IQP} K \, {}^4\chi $$

e$^-$-h$^+$ exchange



The BSE Equation

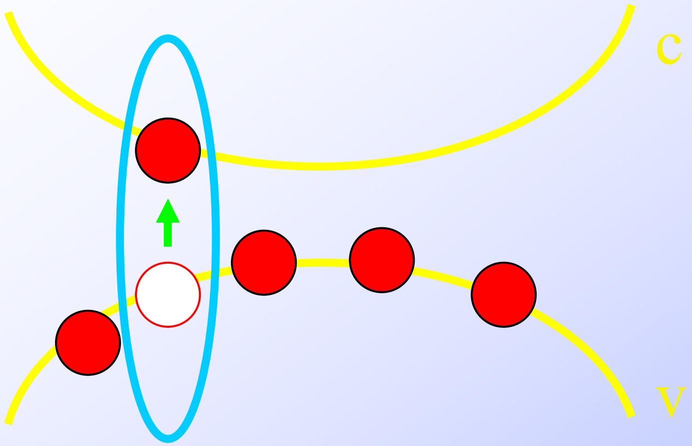
$$\boxed{\overline{P} = P_{IQP} + P_{IQP}\ \Xi\,\overline{P}}$$

$$\overline{P}(\omega) = \left(1 - P_{IQP}\Xi\right)^{-1}\ P_{IQP}(\omega)$$

the interaction kernel is :

$$\Xi = \overline{v} - W$$

$$\Xi(x_1, x_1'; x_2, x_2') = \frac{\delta\left(V_H(x_1) + \Sigma(x_2, x_2')\right)}{\delta G(x_1, x_1')}$$



electron-hole interaction

excitonic effects

$$(H_{el} + H_{hole} + H_{el\text{-}hole})\, A_\lambda = E_\lambda\, A_\lambda$$

$$Abs(\omega) \sim \Sigma_\lambda | \Sigma_{vc} \langle v|D|c\rangle A_\lambda^{vc}|^2\, \delta\, (E_\lambda - \omega)$$

-> mixing of transitions

-> modification of excitation energies

- ground state calculation, in order to find the KS eigenvalues and wavefunctions

Approximations: use of pseudo-potentials and LDA for the exchange-correlation potential

- calculation of dielectric function is performed, with independent-particle polarizability

Approximations: dielectric matrix calculated within the RPA

- standard GWA to find quasi-particle energies

Approximations: GWA, Plasmon-pole model

- screening W, independent-quasi-particle polarizability for 2 particles

static limit for W; LDA wavefunctions

- BSE calculation using polarizability and Kernel

Approximations: only the resonant part of the excitonic Hamiltonian is considered.

convergence problem

cutoff (number of plane waves)
bands (empty states, fundamental in epsilon1 and screening)
k-points (depending on the complexity of the band structure, ex of simple semiconductors, metals, TiO_2)
vacuum: more and more important from RPA to GW to BSE, because of the long range nature of screening

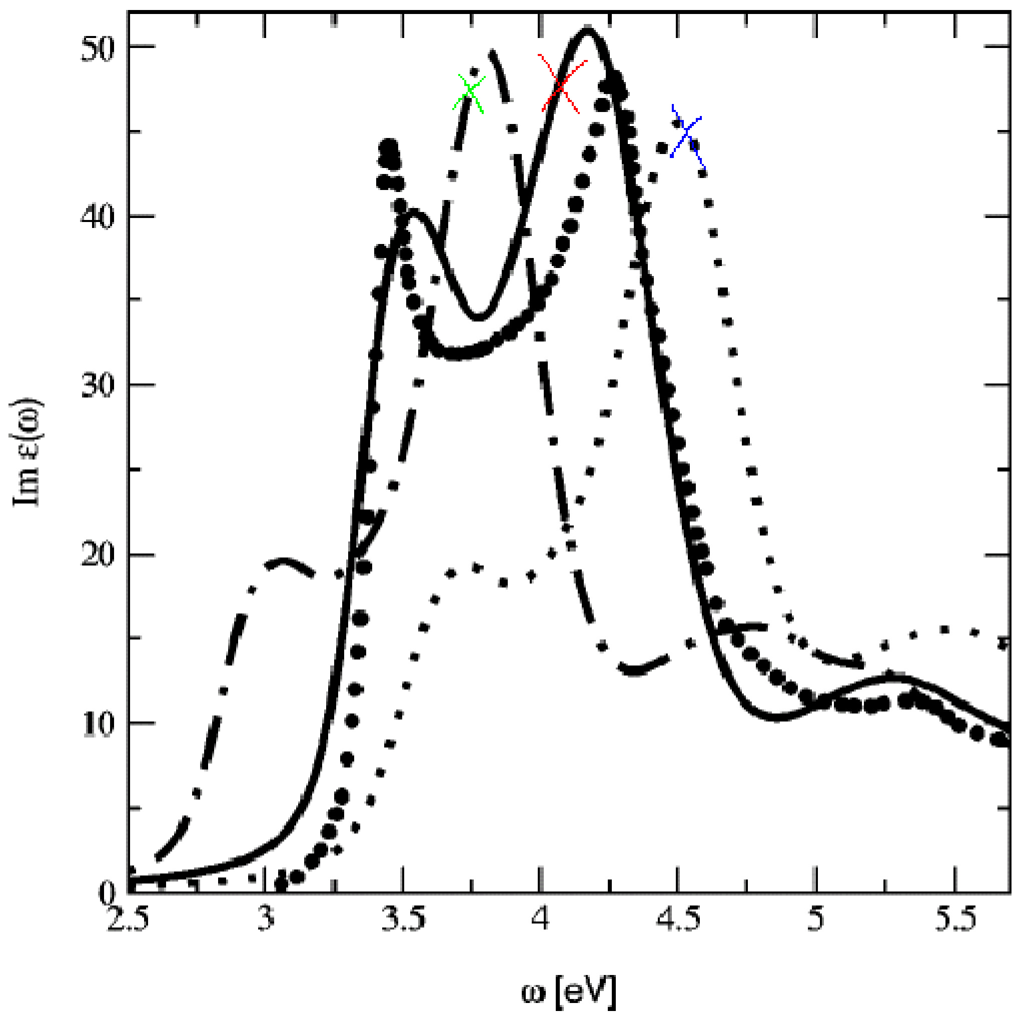
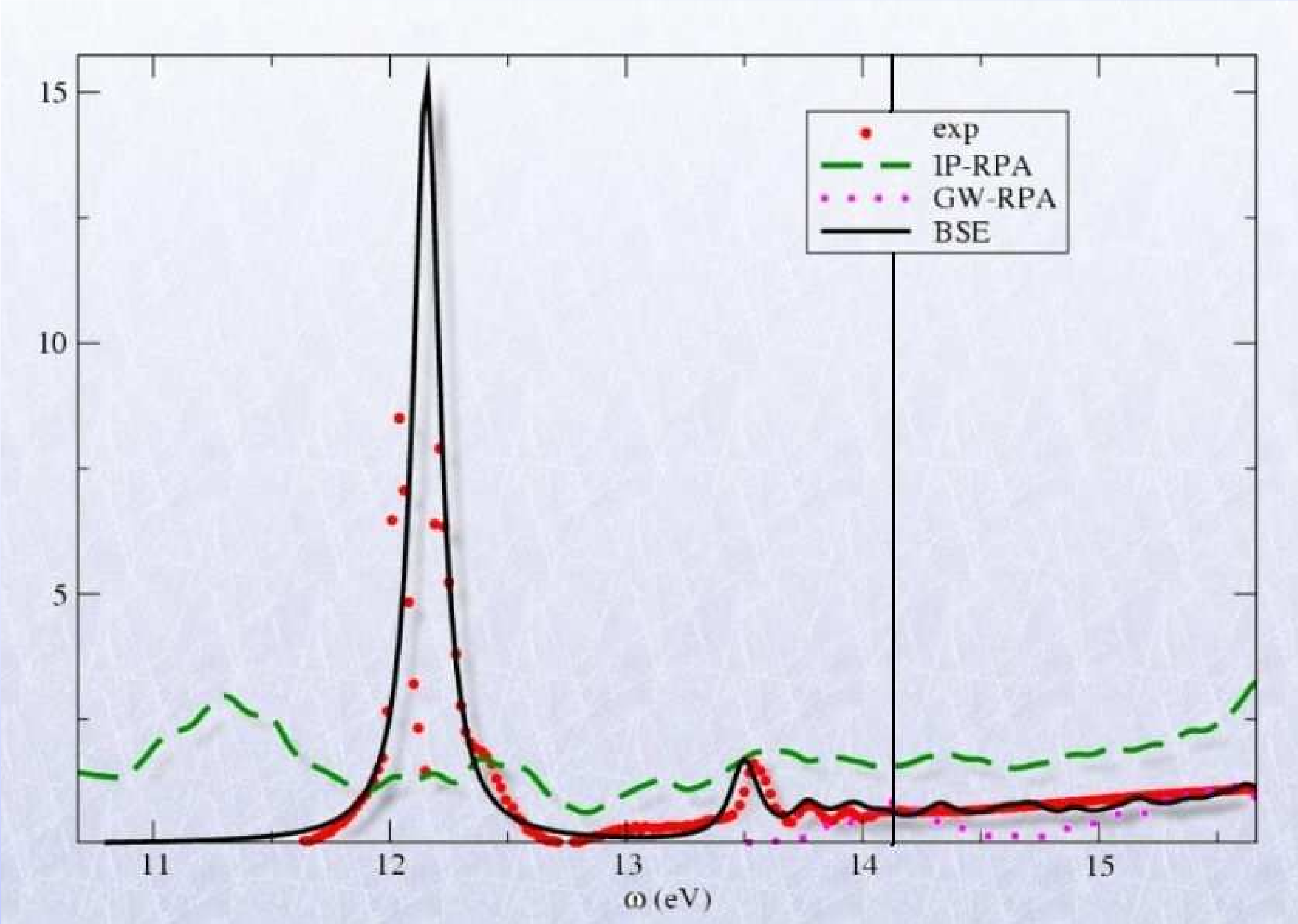
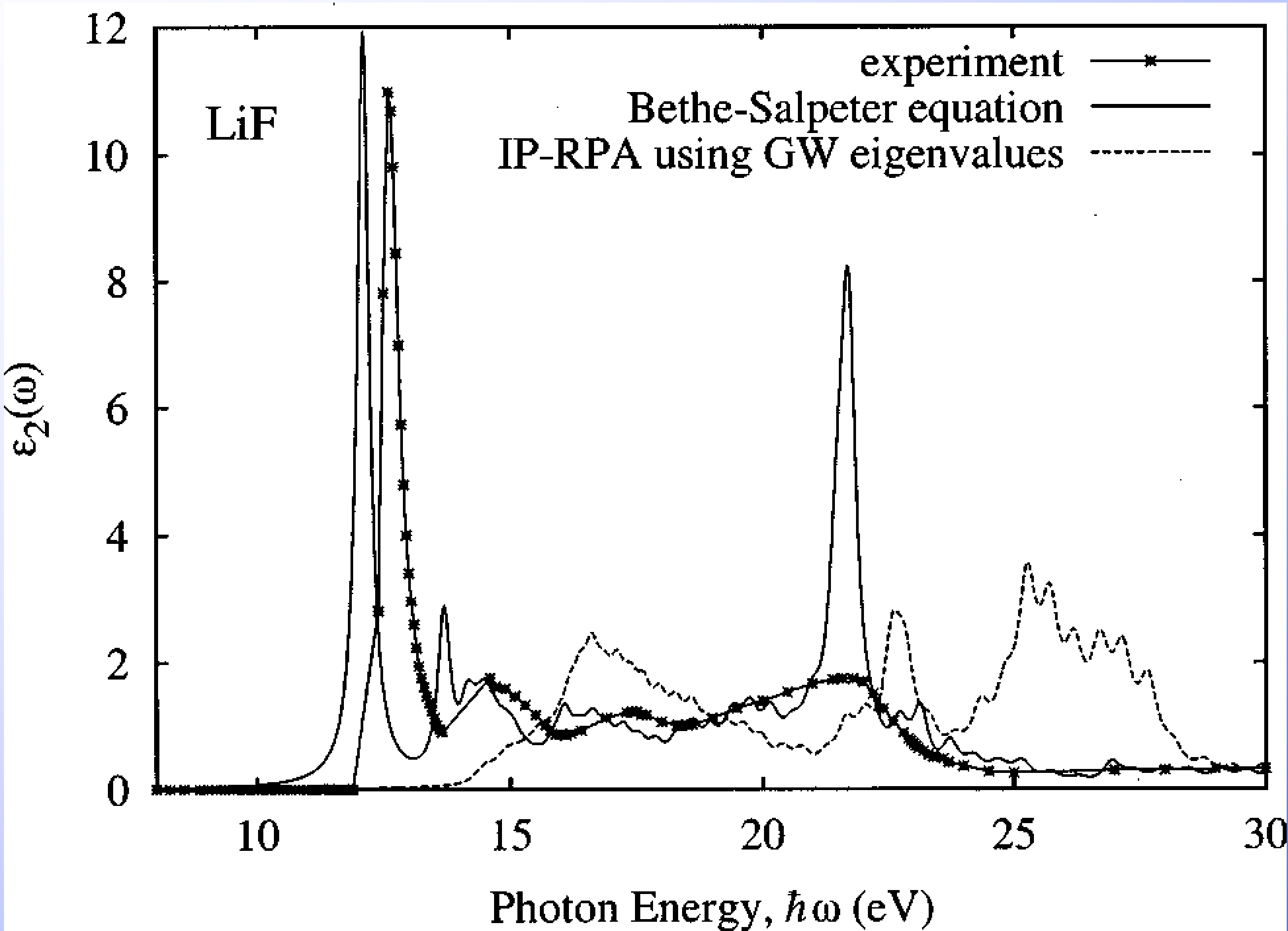


FIG. 5. Silicon absorption spectrum [Im(ε_M)]: ●, experiment (Lautenschlager *et al.*, 1987); dash-dotted curve, RPA, including local field effects; dotted curve, *GW*-RPA; solid curve, Bethe-Salpeter equation.



solid argon



12
10
8
6
4
2
0
$\varepsilon_2(\omega)$
LiF
experiment
Bethe-Salpeter equation
IP-RPA using GW eigenvalues
10
15
20
25
30
Photon Energy, $\hbar\omega$ (eV)

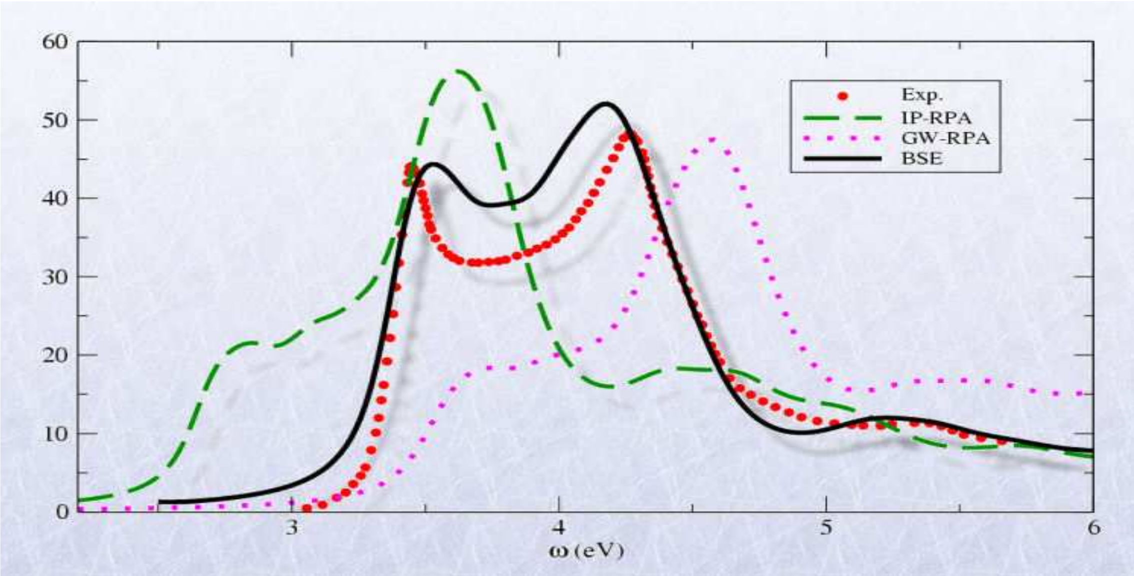
```
lchiodo@corvo:~/RUNS_YAMBO/TUT_Si$ /opt/yambo/bin/yambo -H

Tool: yambo 3.2.1 rev.477
 Description: A shiny pot of fun and happiness [C.D.Hogan]

 -h                :Short Help
 -H                :Long Help
 -J <opt>          :Job string identifier
 -V <opt>          :Input file verbosity
                    opt=RL,kpt,sc,qp,io,gen,resp
 -F <opt>          :Input file
 -I <opt>          :Core I/O directory
 -O <opt>          :Additional I/O directory
 -C <opt>          :Communications I/O directory
 -N                :Skip MPI initialization
 -D                :DataBases properties
 -S                :DataBases fragmentation
 -i                :Initialization
 -o <opt>          :Optics [opt=(c)hi/(b)se/(t)dhf]
 -t <opt>          :The TDDFTs [opt=(a)LDA/(b)SE/(l)RC]
 -c                :Coulomb interaction
 -x                :Hartree-Fock Self-energy and local XC
 -d                :Dynamical Inverse Dielectric Matrix
 -b                :Static Inverse Dielectric Matrix
 -p <opt>          :GW approximations [opt=(p)PA/c(HOSEX)]
 -g <opt>          :Dyson Equation solver
                    opt=n(ewton)/s(ecant)/g(reen)
 -l                :GoWo Quasiparticle lifetimes
 -y <opt>          :BSE solver [opt=h/d/i/t]
 -a                :ACFDT Total Energy
```

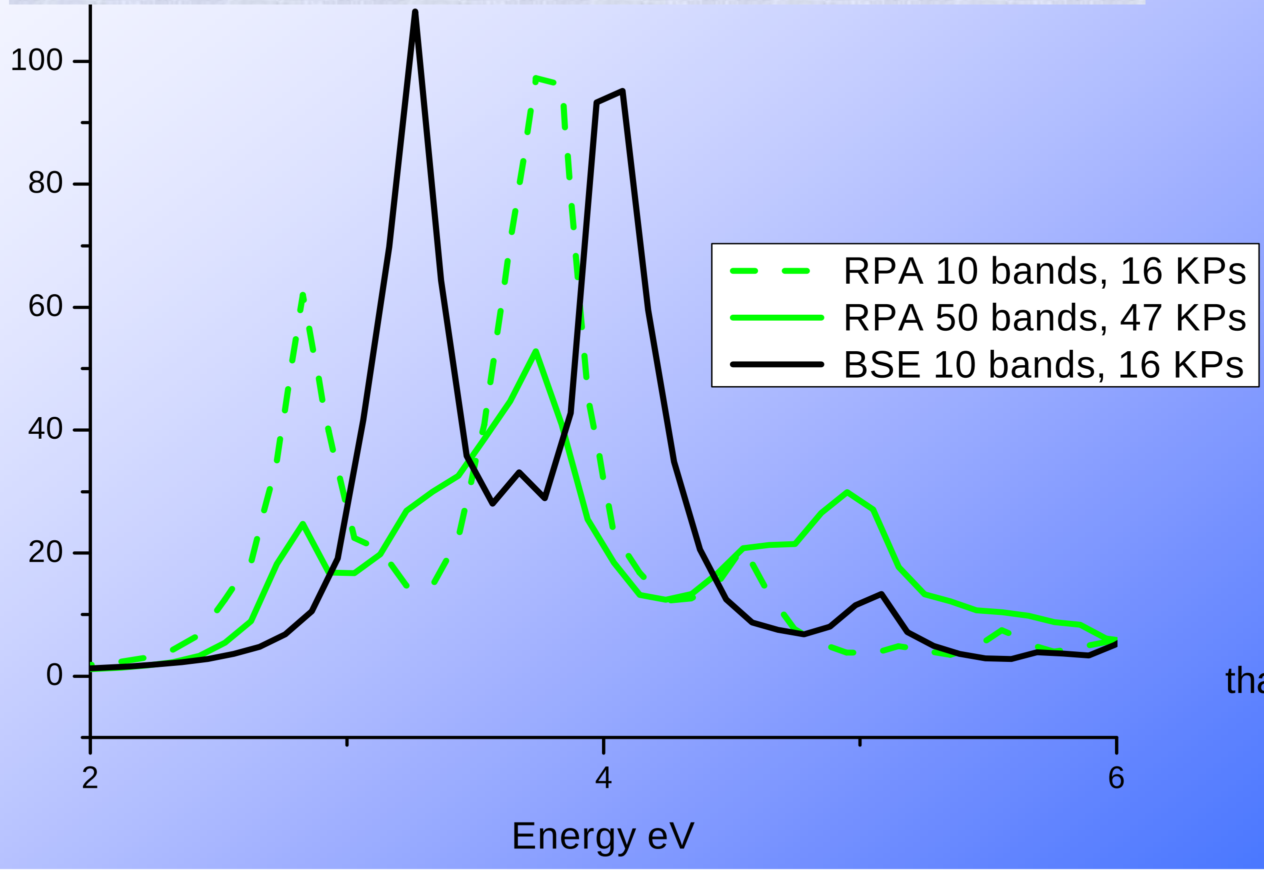
yambo –b

yambo -y h -o b -V 4

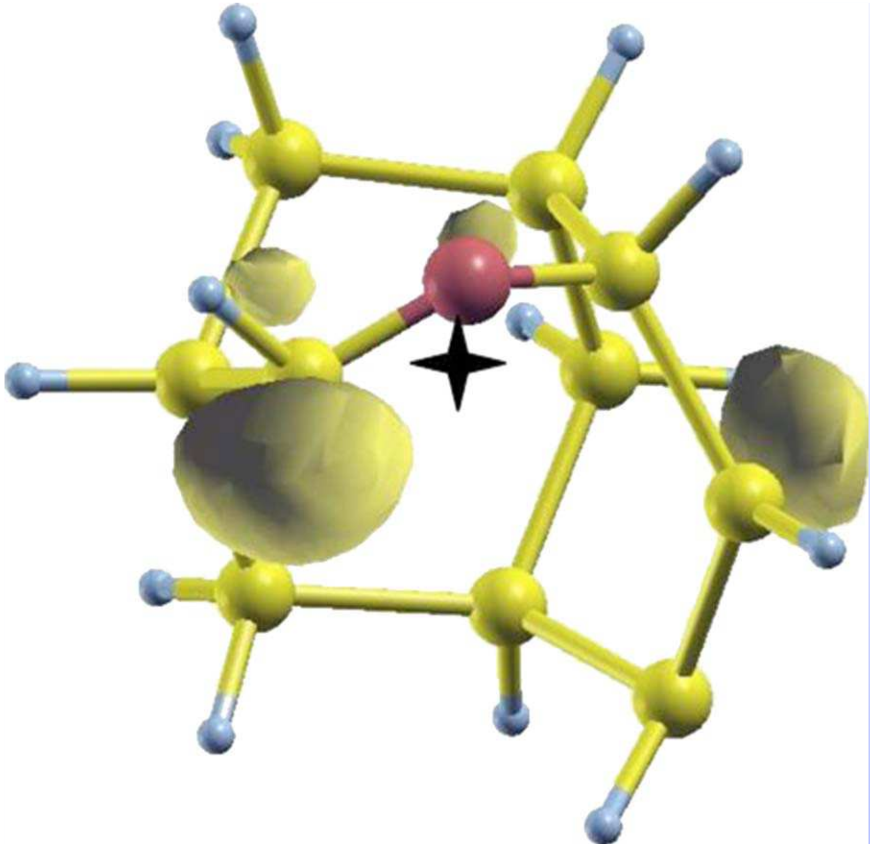
```
#                Version 3.2.1 Revision 477
#                 http://www.yambo-code.org
#
optics                            # [R OPT] Optics
chi                               # [R CHI] Dyson equation for Chi.
FFTGvecs= 229           RL        # [FFT] Plane-waves
% QpntsRXd
  1 | 1 |                        # [Xd] Transferred momenta
%
% BndsRnXd
  1 | 10 |                        # [Xd] Polarization function bands
%
NGsBlkXd= 1             RL        # [Xd] Response block size
% EnRngeXd
  0.00000 | 10.00000 | eV         # [Xd] Energy range
%
% DmRngeXd
  0.10000 |  0.10000 | eV         # [Xd] Damping range
%
ETStpsXd= 100                     # [Xd] Total Energy steps
% LongDrXd
 1.000000 | 0.000000 | 0.000000 |      # [Xd] [cc] Electric Field
```

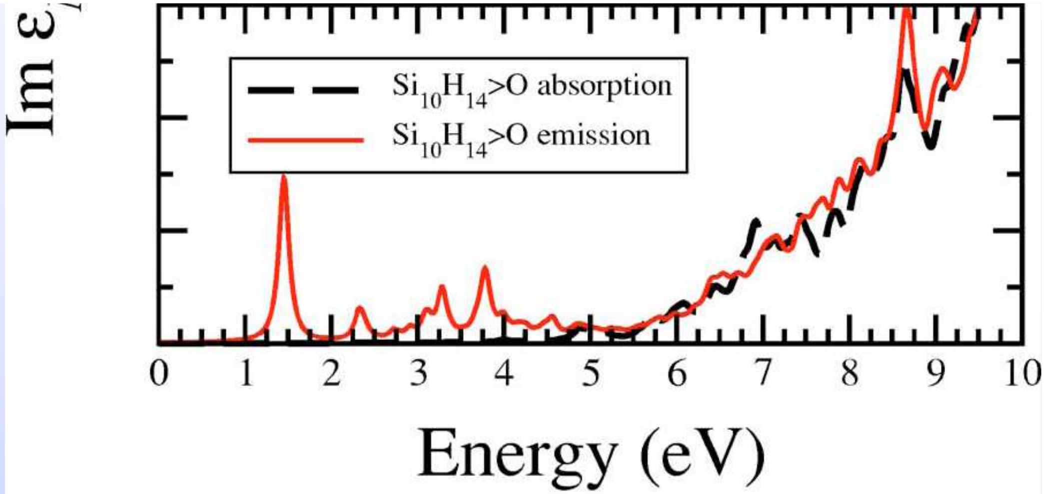
```
FFTGvecs= 229           RL    # [FFT] Plane-waves
 | % QpntsRXd
 |  1 | 1 |                    # [Xd] Transferred momenta
 | %
 | % BndsRnXd
 |    1 |  50 |                # [Xd] Polarization function bands
 | %
 | NGsBlkXd= 113          RL    # [Xd] Response block size
 | % EnRngeXd
 |   0.00000 | 10.00000 | eV    # [Xd] Energy range
 | %
 | % DmRngeXd
 |   0.10000 |  0.10000 | eV    # [Xd] Damping range
 | %
 | ETStpsXd= 100                # [Xd] Total Energy steps
```

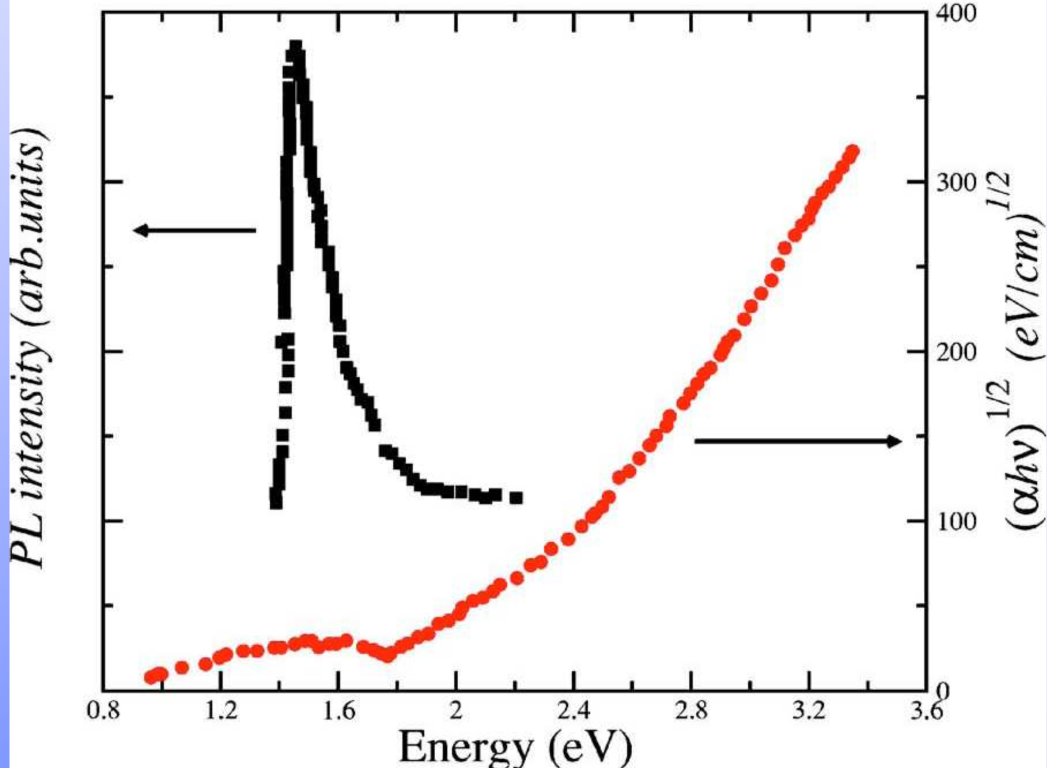




thanks to M. Bertocchi for Si data







E. Luppi, et al., PRB **75**, 033303 (2007)