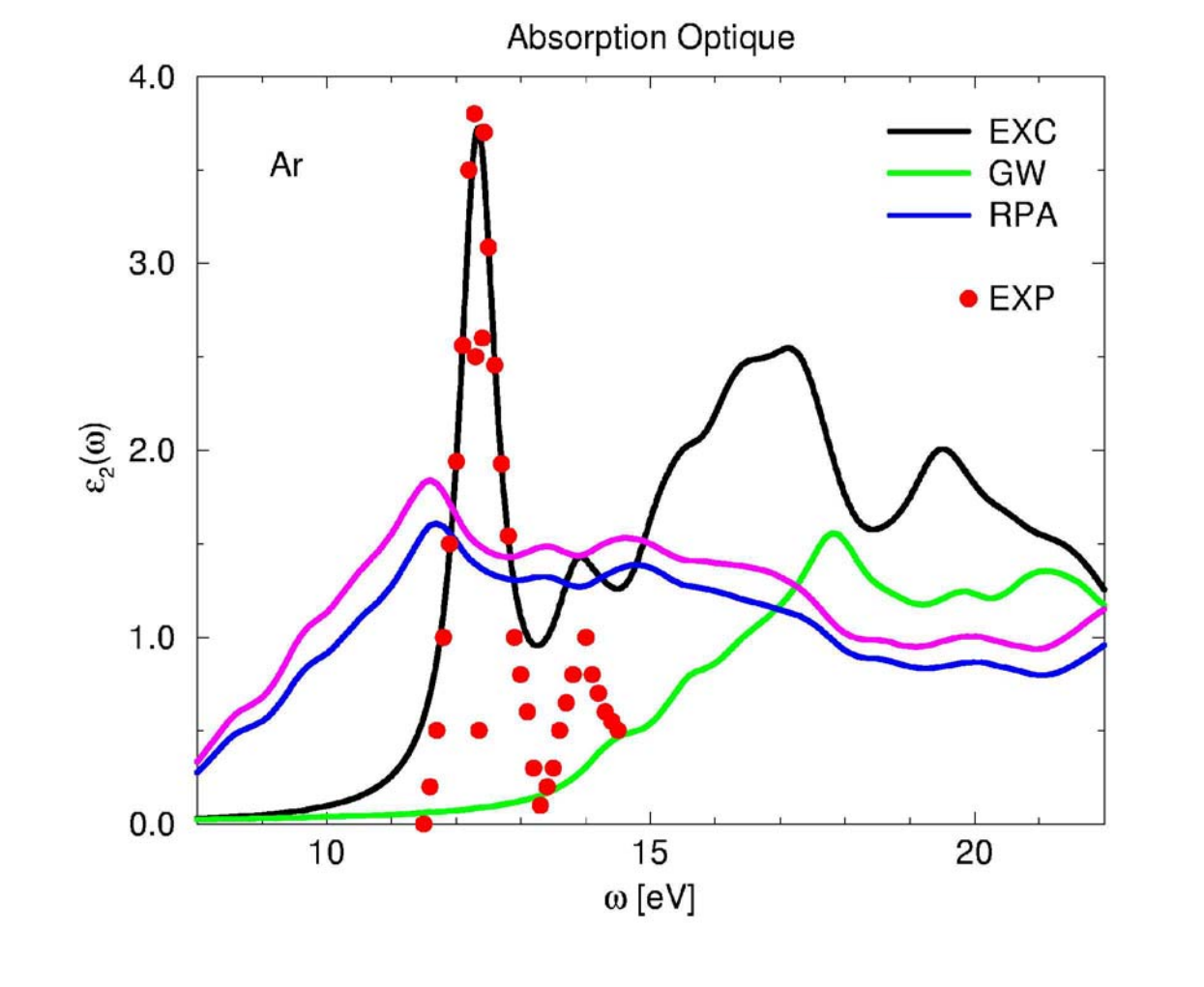
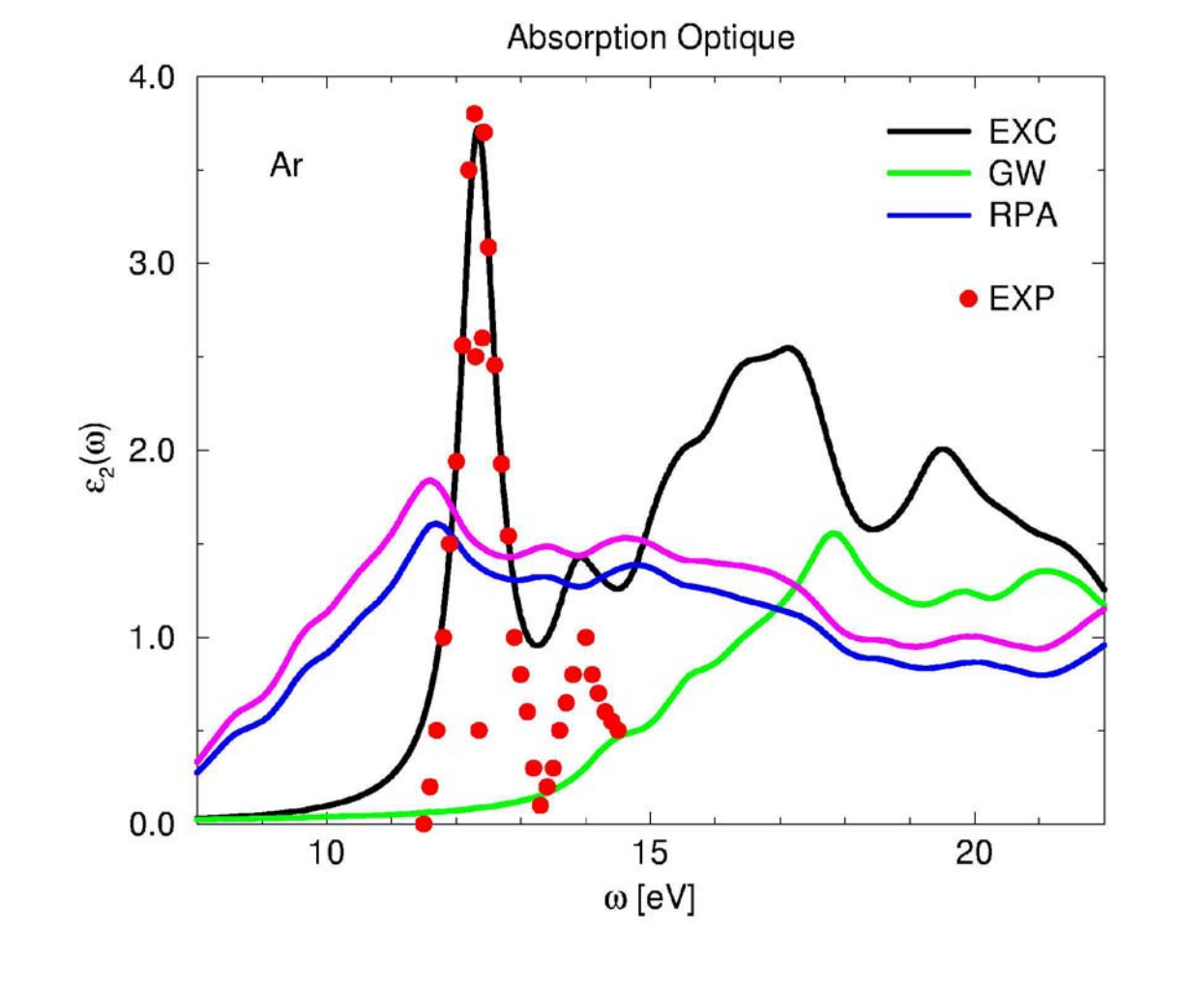
Why loose your time to calculate -iGG ???



Why loose your time to calculate -iGG ???



V. Olevano et al., 2000

Exchange and correlation effects described in **MBPT and TDDFT**

European Theoretical Spectroscopy Facility
http://www.etsf.edu

Exchange and correlation……

1) Back to the 1-particle G, Hedin's equations

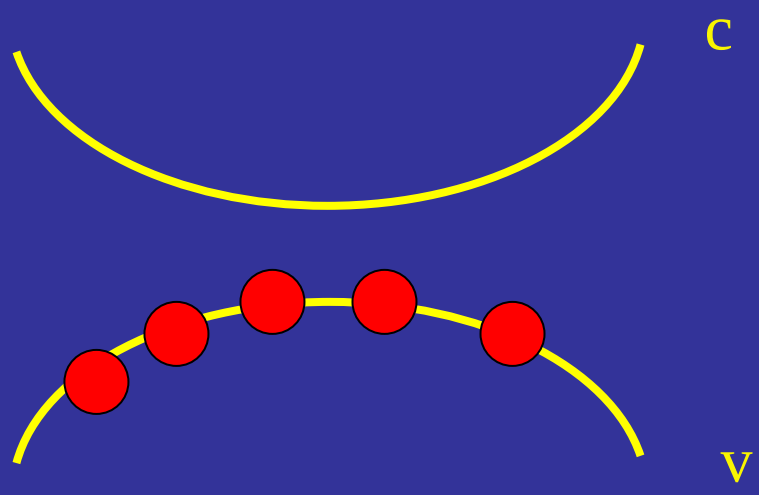
2) Vertex corrections in the polarizability
   a) Iteration of Hedin's equation: the BSE
   b) GW approximation – THE BSE
   c) The Bethe Salpeter equation in practice

3) Results

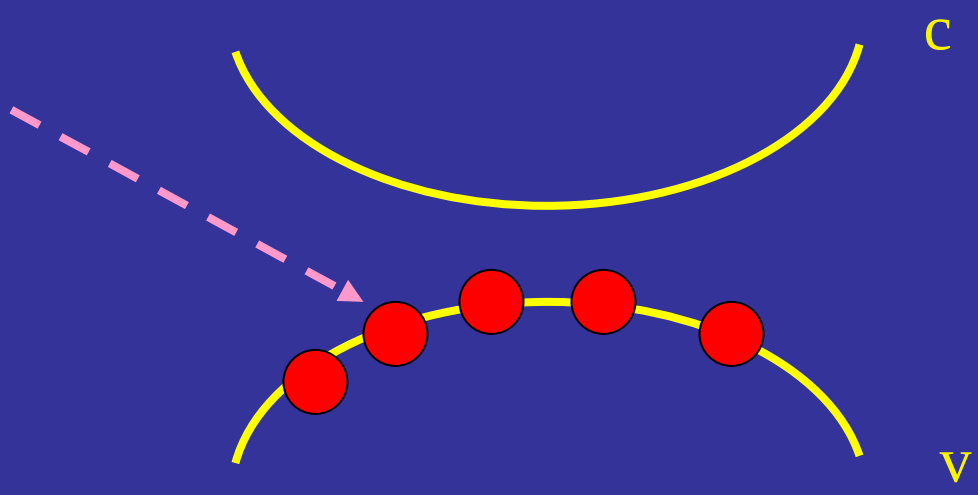
4) TDDFT and BSE
   a) the Kohn-Sham and the quasiparticle worlds
   b) TDDFT from MBPT
   c) MBPT from TDDFT

5) Outlook

MBPT: What is “an electron”?



What is “an electron”?



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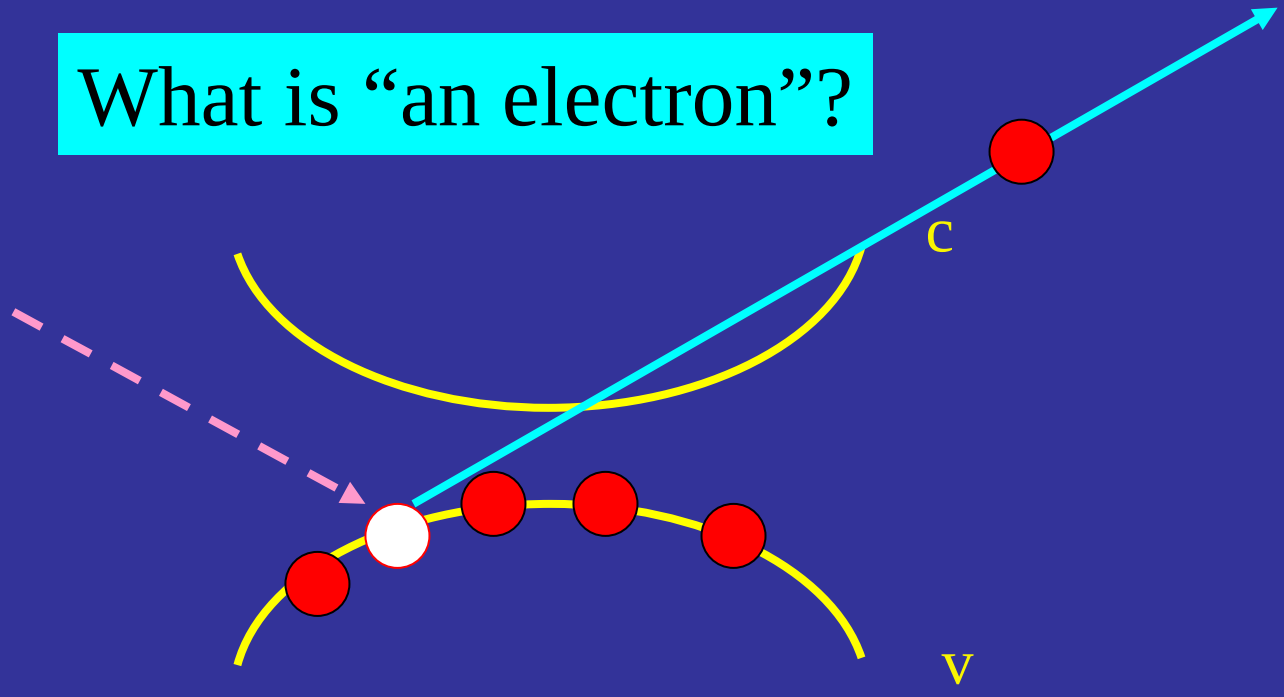
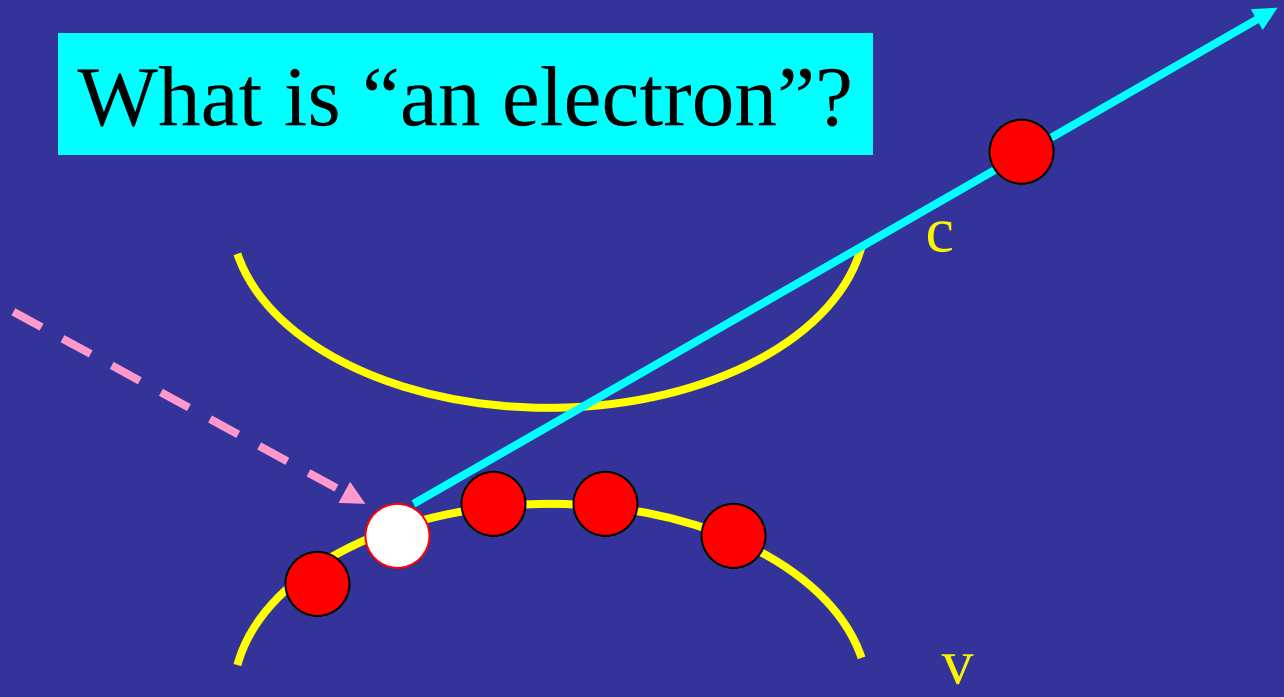


What is “an electron”?



Hole - (N-1) electrons

Koopmans theorem

(e.g. Hartee Fock)

$$(-\nabla^2/2 + V_{ext} + V_H + V_{xc}\,)\,|n\rangle = E_n\,|n\rangle$$

$$(-\nabla^2/2 + V_{ext} + V_H + \Sigma_x\,|n\rangle = E_n\,|n\rangle$$

$V_{xc}(r)$ versus $\Sigma_x(r,r')$

Exchange

Relaxation - dynamical correlations

$$(-\nabla^2/2 + V_{ext} + V_H + \Sigma_x)\,|n\rangle = E_n\,|n\rangle$$

$$(-\nabla^2/2 + V_{ext} + V_H + \Sigma(E_n))\,|n\rangle = E_n\,|n\rangle$$

$\Sigma_x(r,r')$ versus $\Sigma(r,r',E_n)$

Hartree : $\rho(r)$

Hartree - Fock : $\rho(r,r')$

Beyond : $\rho(r,r',t,t')$

One-particle Green's function:

$$G(x,x',t,t') = -i\langle N|\, T[\psi(xt)\, \psi^{+}(x't')]\, |N\rangle$$

If $|N\rangle$ = 1 Slater determinant:

for $t<t'$

$$G(x,x',t,t') \rightarrow i\Sigma_{m\ occ}\varphi_m(x)\varphi_m(x')\, e^{-i\varepsilon_m(t-t')}$$

"time dependent density matrix"

Poles of G are one-QP-excitation energies

How to get G?

$\partial/\partial t\ G = \ldots\ldots\ldots$

……leads to $G^{(2)}$ (4 field operators)

Introduce potential Σ..... $(G^{-1} = G_H^{-1} - \Sigma)$

…….to be defined implicitly

Perturbation $\delta V_{ext} \rightarrow \Sigma = - iGv(\delta G^{-1}/\delta V_{ext})$

How to get G?

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Introduce potential Σ..... $(G^{-1} = G_H^{-1} - \Sigma)$

…….to be defined implicitly

Perturbation δV_{ext} → $\Sigma = -\, iGv(\delta G^{-1}/\delta V_{ext})$

Hedin's equations

$$\Sigma = i \int GW\Gamma$$

$$W = v + \int v\, P\, W$$

$$P = - i \int GG\Gamma$$

$$\Gamma = 1 + \int \delta\Sigma/\delta G\; GG\Gamma$$

$$(G^{-1} = G_H^{-1} - \Sigma)$$

L. Hedin, 1965

$$\Sigma = i \int G W \Gamma$$

$$W = v + \int v\, P\, W$$

$$P = - i \int G G \Gamma$$

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$$\Gamma = 1$$

$$\Sigma = i \int G W \Gamma$$

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$$(G^{-1} = G_H^{-1} - \Sigma)$$

$$\Gamma = 1$$

$$\Sigma = i \int G W \Gamma = i\, GW$$

$$W = v + \int v\, P\, W$$

$$P = -\, i \int G G \Gamma = -iGG$$

$$\Gamma = 1 + \int \delta\Sigma/\delta G\; GG\Gamma$$

$$(G^{-1} = G_H^{-1} - \Sigma)$$

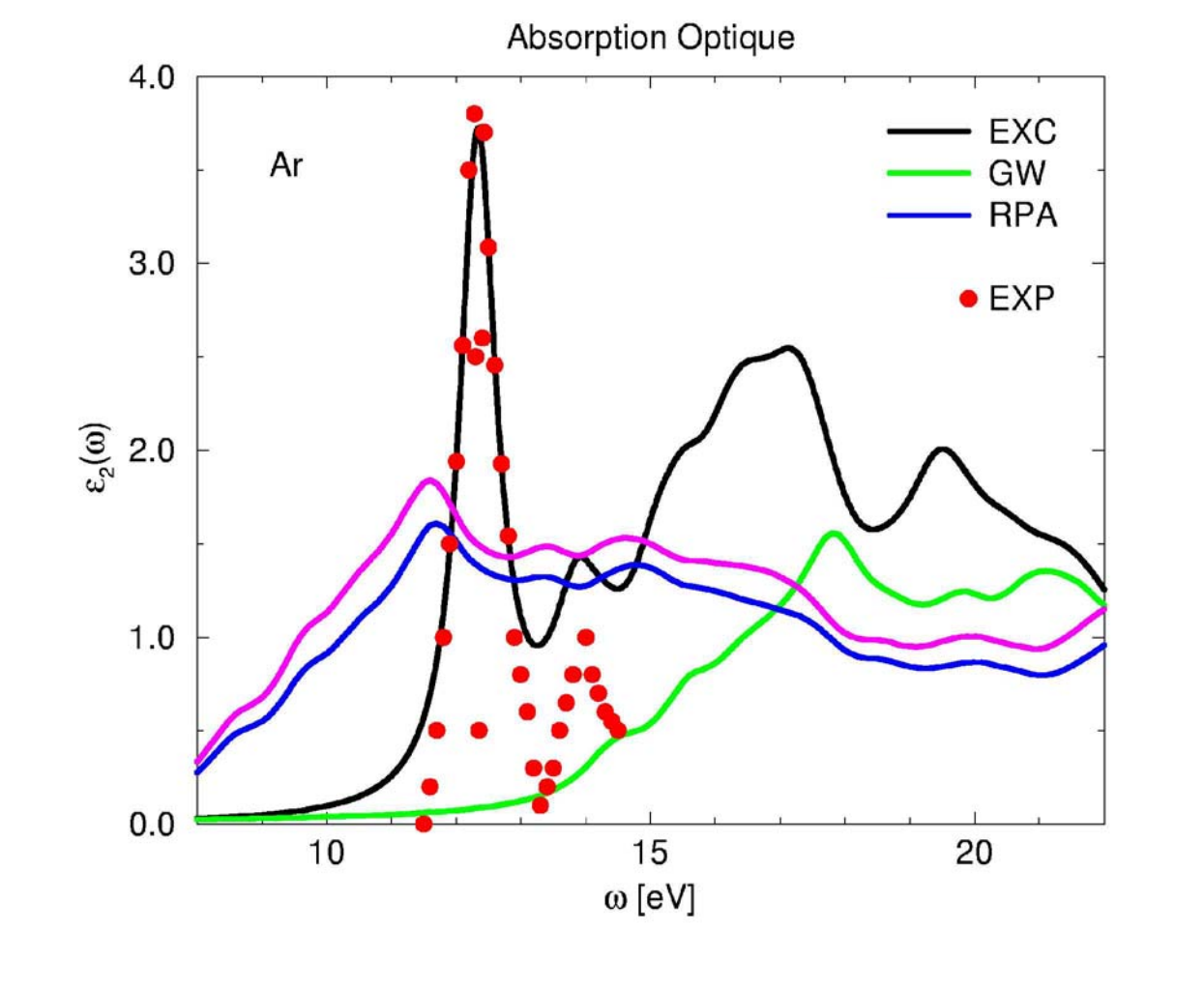
$$\Gamma = 1$$

GW Approximation, Hedin 1965

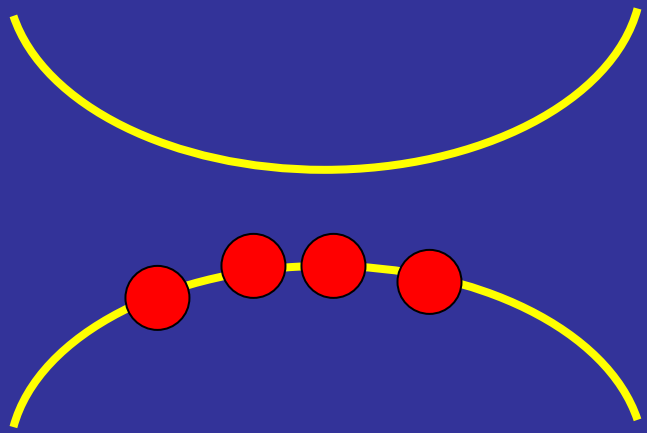
E_c-E_v (minimum, eV)

	DFT-KS	Σ=iGW	Exp.
Silicon	0.55	1.19	1.17
Diamond	4.26	5.64	5.48
MgO	5.3	7.8	7.83

But sometimes Absorption is VERY bad



What is an absorption spectrum?



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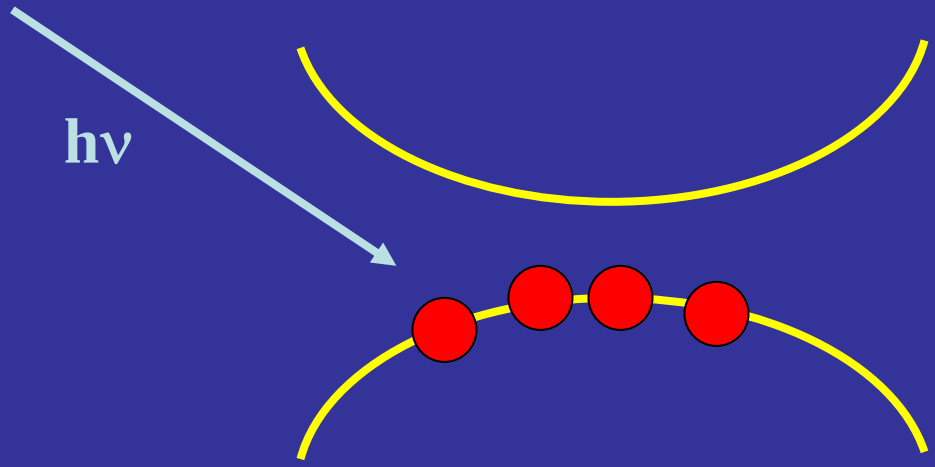

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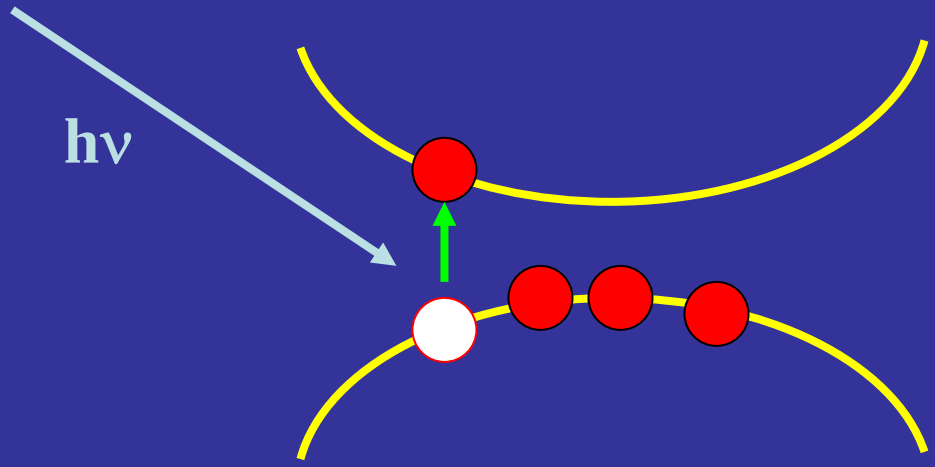
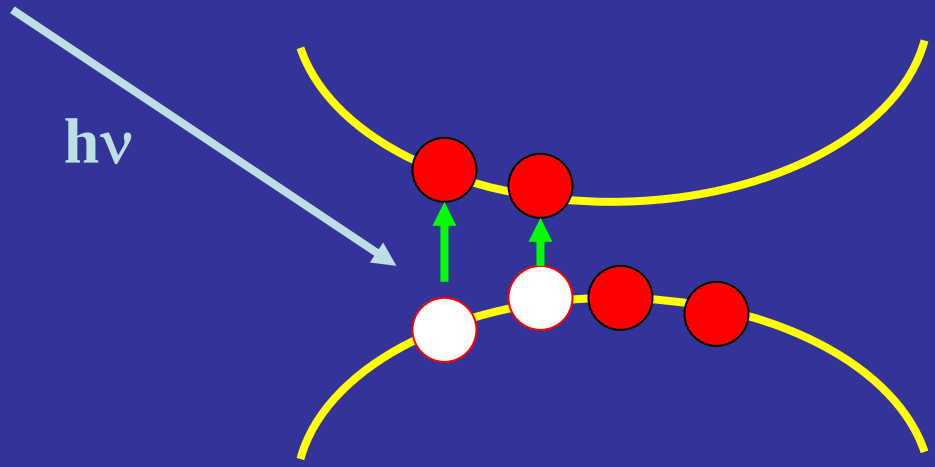


What is a spectrum?



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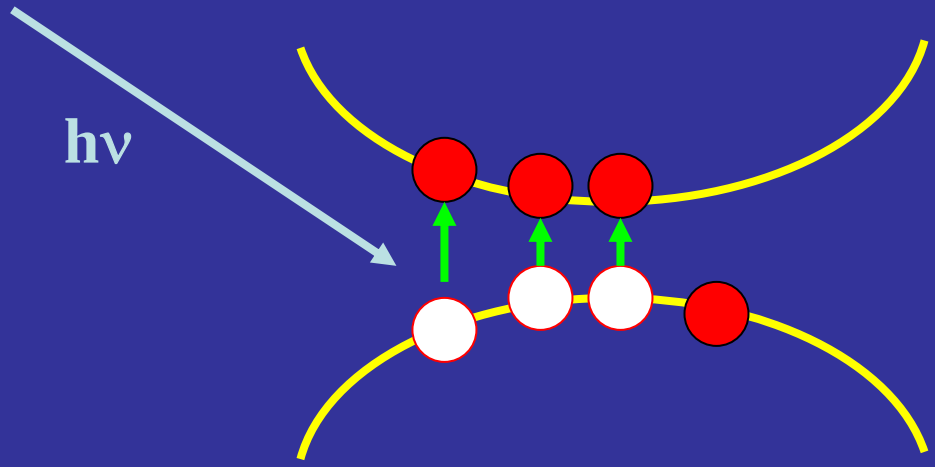

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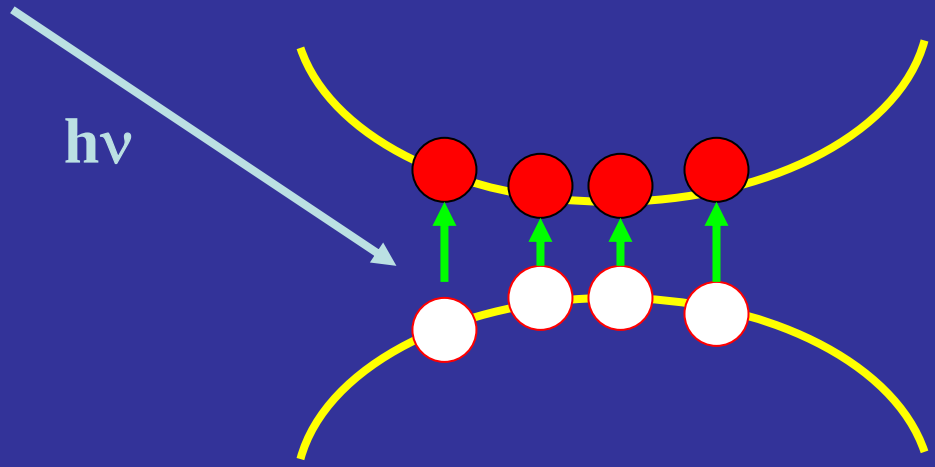
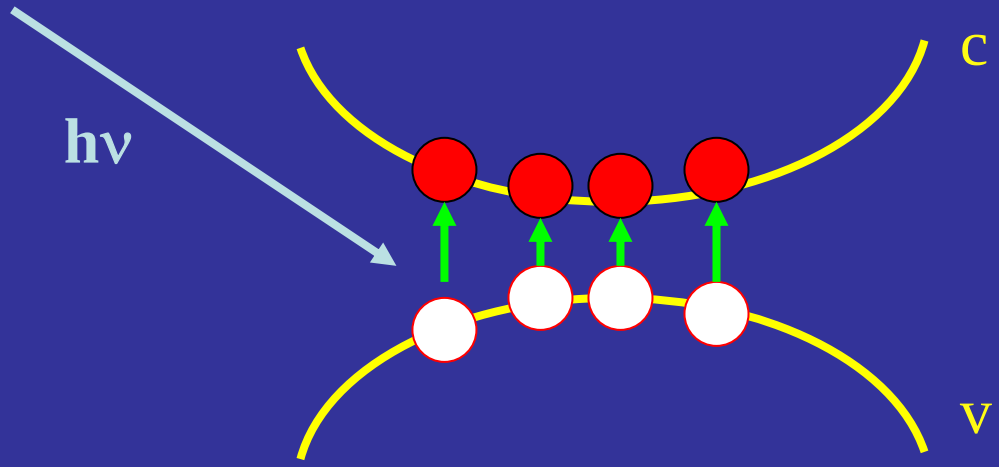


Independent electrons and transitions



$$Im[\chi_0] \sim \Sigma_{vc} |\langle v|D|c\rangle|^2 \, \delta (E_c - E_v - \omega)$$

P = -iGG

$$\Sigma = i \int G W \Gamma = i\, GW$$

$$W = v + \int v\, P\, W$$

$$P = -\, i \int G G \Gamma = -iGG$$

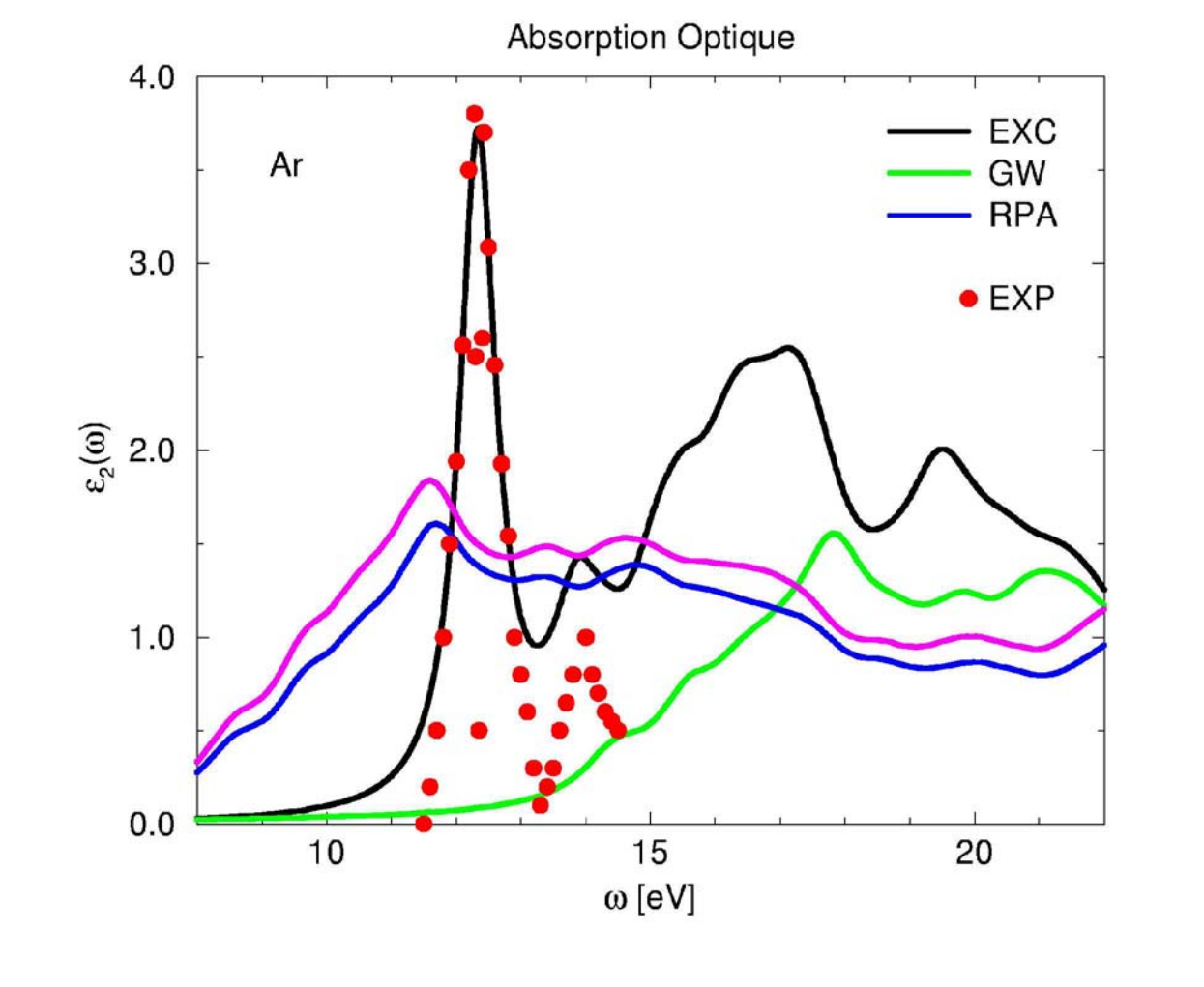
$$\Gamma = 1 + \int \delta\Sigma/\delta G\; GG\Gamma$$

$$(G^{-1} = G_H^{-1} - \Sigma)$$

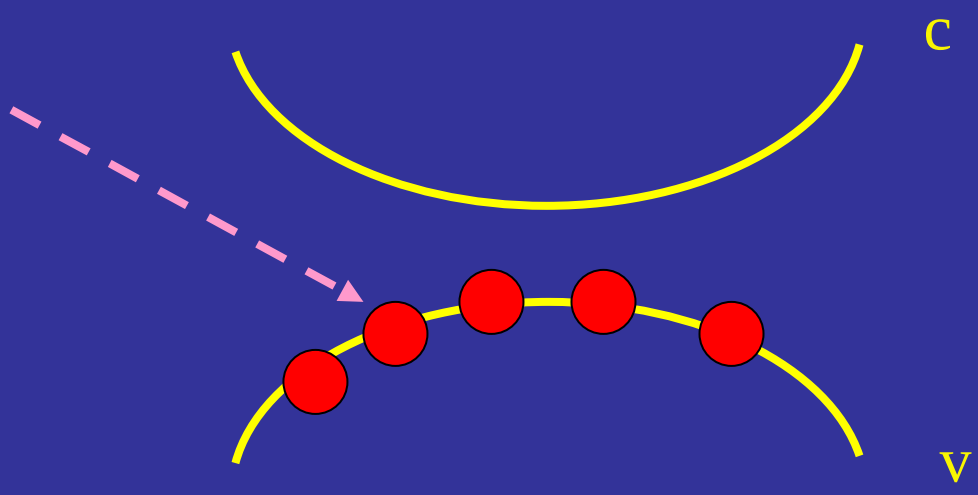
$$\Gamma = 1$$

GW Approximation, Hedin 1965

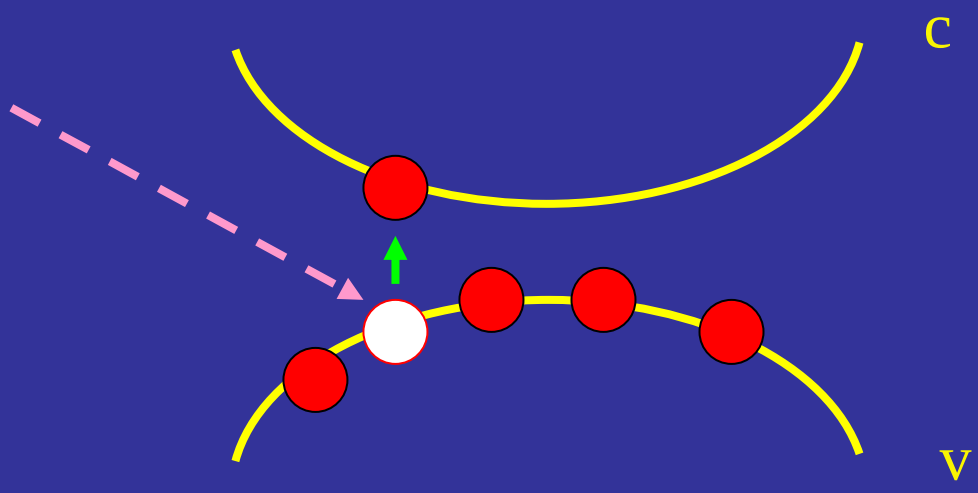
But sometimes Absorption is VERY bad



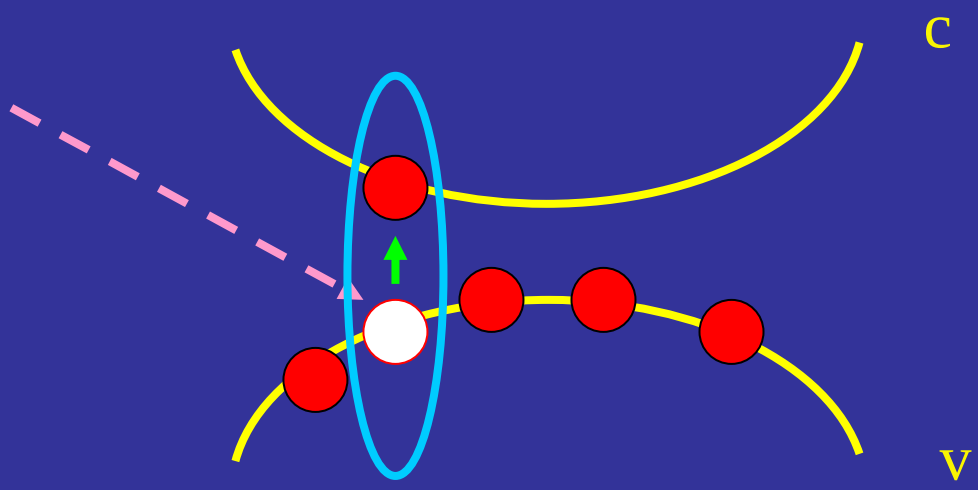
Absorption ?



Absorption ?



Absorption ?

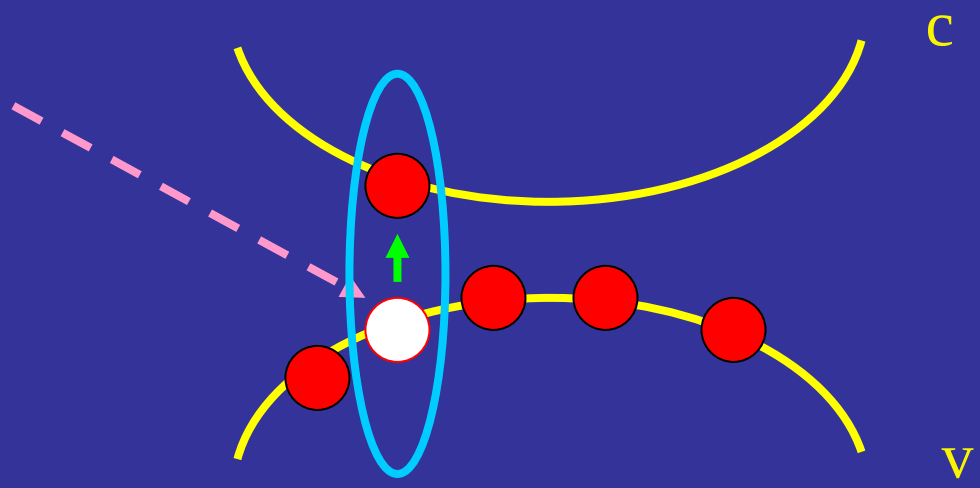


Electron-hole interaction

Excitonic effects

Bethe-Salpeter Equation

Absorption ?



Variation of potential

Electron-hole interaction

Excitonic effects

Bethe-Salpeter Equation

$\Gamma = 1$

$\Sigma = i \int G W \cancel{\Gamma}$

$W = v + \int v\, P\, W$

$P = - i \int G G \cancel{\Gamma}$ **RPA form**

$\Gamma = 1 + \int \delta\Sigma/\delta G\; GG\Gamma$

$\Gamma = 1$

$\Sigma = i \int G W \Gamma$

$W = v + \int v\, P\, W$

$P = - i \int G G \Gamma$

$$\Gamma = 1 + \int \delta\Sigma/\delta G\; GG\Gamma$$

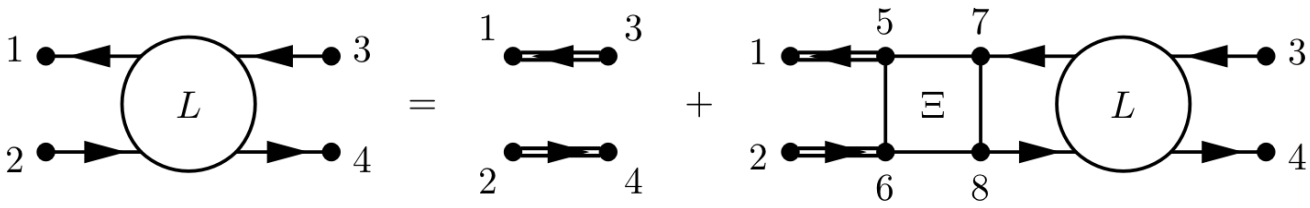
$$-i \int GG\Gamma = - i\, GG - i \int GG \int \delta\Sigma/\delta G\; GG\Gamma$$

$P = P_0 + P_0\, \delta\Sigma/\delta G\; iP$ **Bethe Salpeter**

$\Sigma = i\, GW$

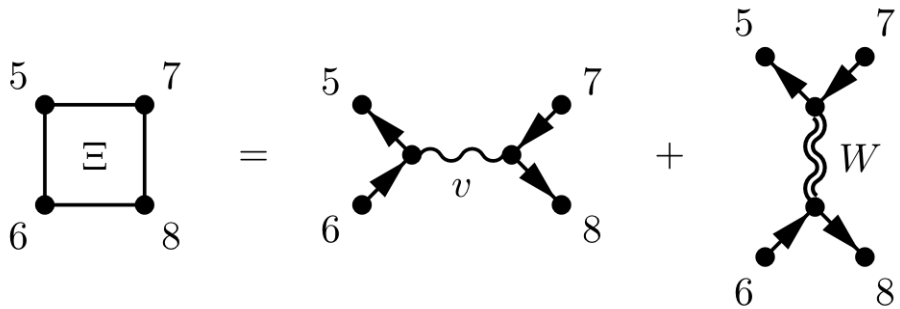
$P \cong P_0 - P_0\, W\, P$ $\qquad$ $\chi = P_0 + P_0\, (v-W)\, \chi$

Bethe-Salpeter Equation



$$L = L^{(0)} + L^{(0)} \Xi L$$

Bethe-Salpeter Equation



$$\Xi = \delta\Sigma / \delta G \cong v_c - W$$

Ξ = BSE Kernel

Σ = Self-Energy

Coulombian (Local Fields)

W =Screened Interaction (e-h interaction, Excitonic Effects)

$$\chi = \chi_0 + \chi_0 (v\text{-}W)\, \chi$$

$$\langle vc|\, \chi\, |v'c'\rangle = \langle vc|\, \chi_0 \ldots\ldots\ldots\ldots$$

$$\chi_{vc}^{\,v'c'} = [[1 - \chi_0(v\text{-}W)]^{-1}]_{vc}^{\,v''c''}[\chi_0]_{v''c''}^{\,v'c'}$$

$$\chi_{vc}^{\,v'c'} = [(E_c\text{-}E_v) + (v\text{-}W)]^{-1}{}_{vc}^{\,v'c'}$$

$$H^{-1} = \Sigma_\lambda\, A_\lambda A_\lambda^{*}/(E_\lambda\text{-}\omega) \qquad H\, A_\lambda = E_\lambda\, A_\lambda$$

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

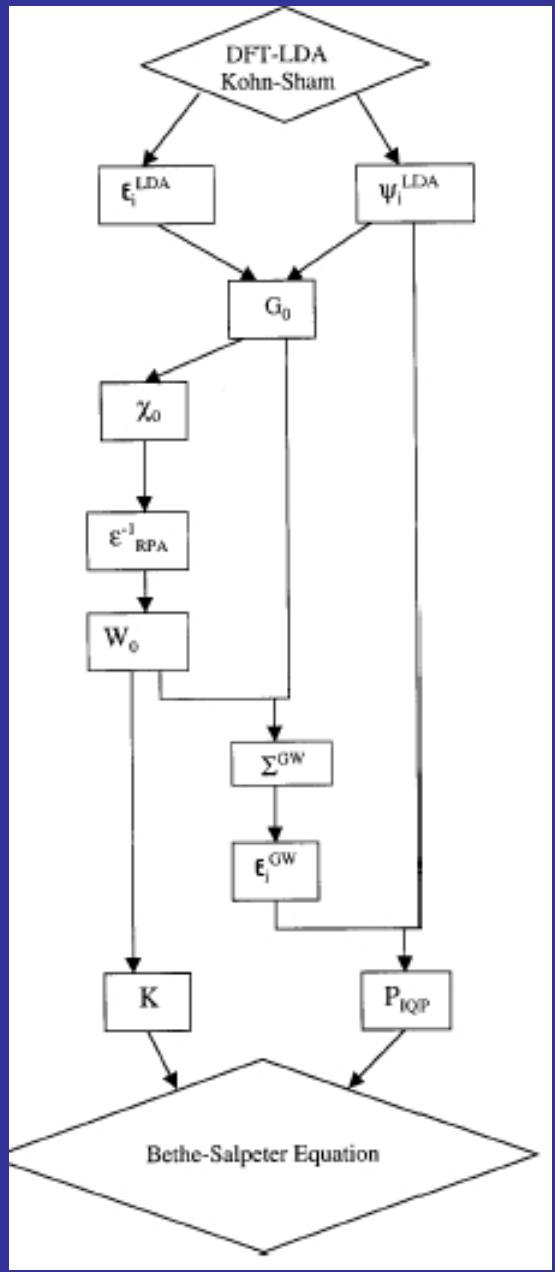
Variation of potential

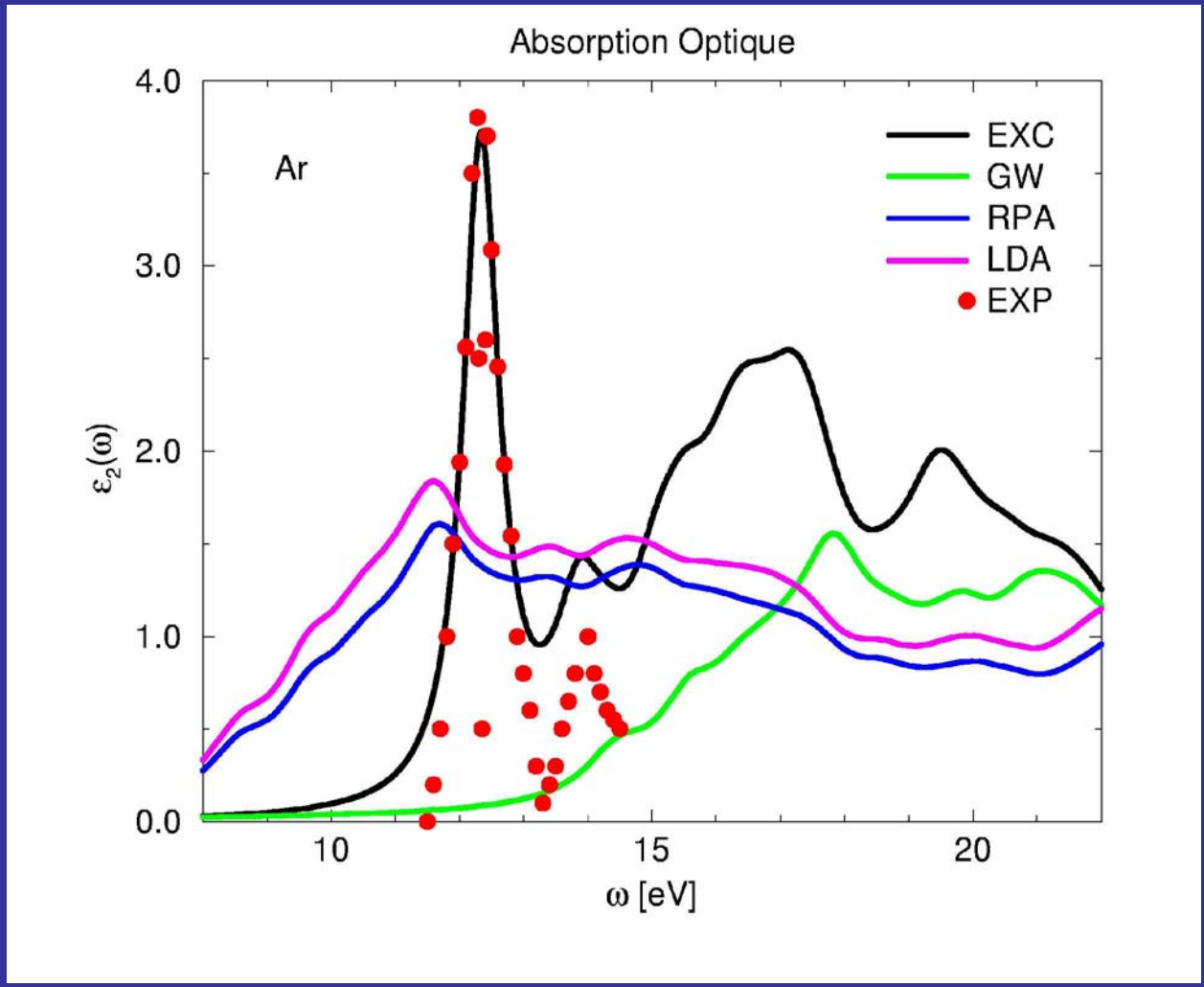
$$Im[\varepsilon] \sim \Sigma_{vc} |\langle v|D|c\rangle|^2 \qquad \delta (E_c - E_v - \omega)$$

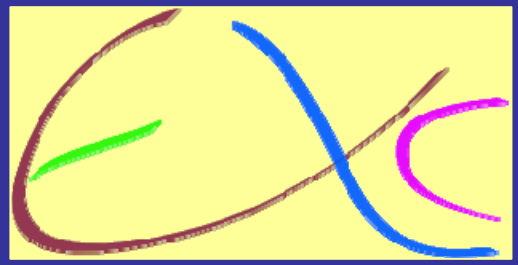
$$Im[\varepsilon] \sim \Sigma_\lambda | \Sigma_{vc} \langle v|D|c\rangle A_\lambda^{vc}|^2 \delta (E_\lambda - \omega)$$

->Mixing of transitions

->Modification of excitation energies

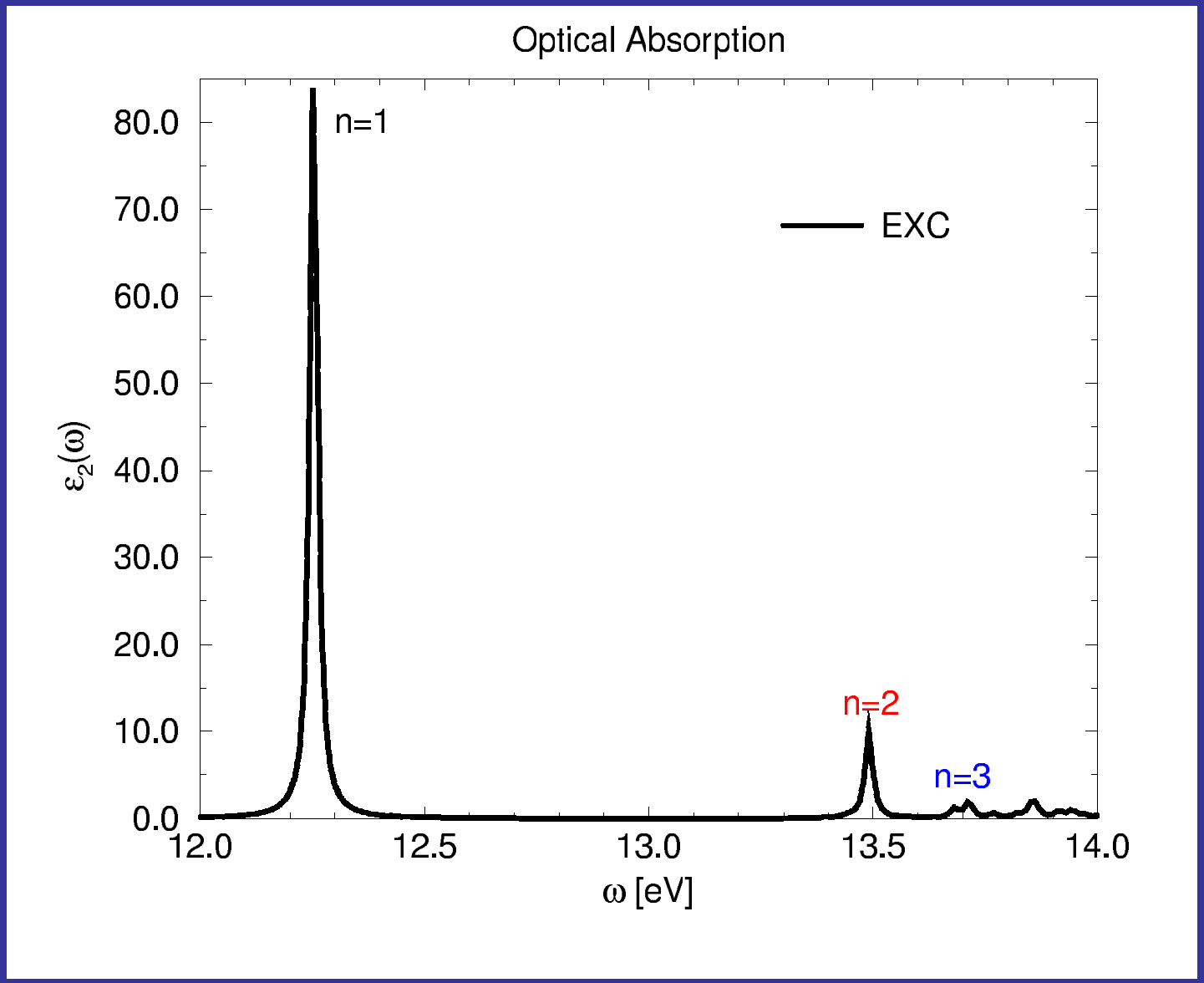

DFT-LDA
Kohn-Sham
ϵ_i^{LDA}
ψ_i^{LDA}
G_0
χ_0
ε^{-1}_{RPA}
W_0
Σ^{GW}
ϵ_i^{GW}
K
P_{IQP}
Bethe-Salpeter Equation

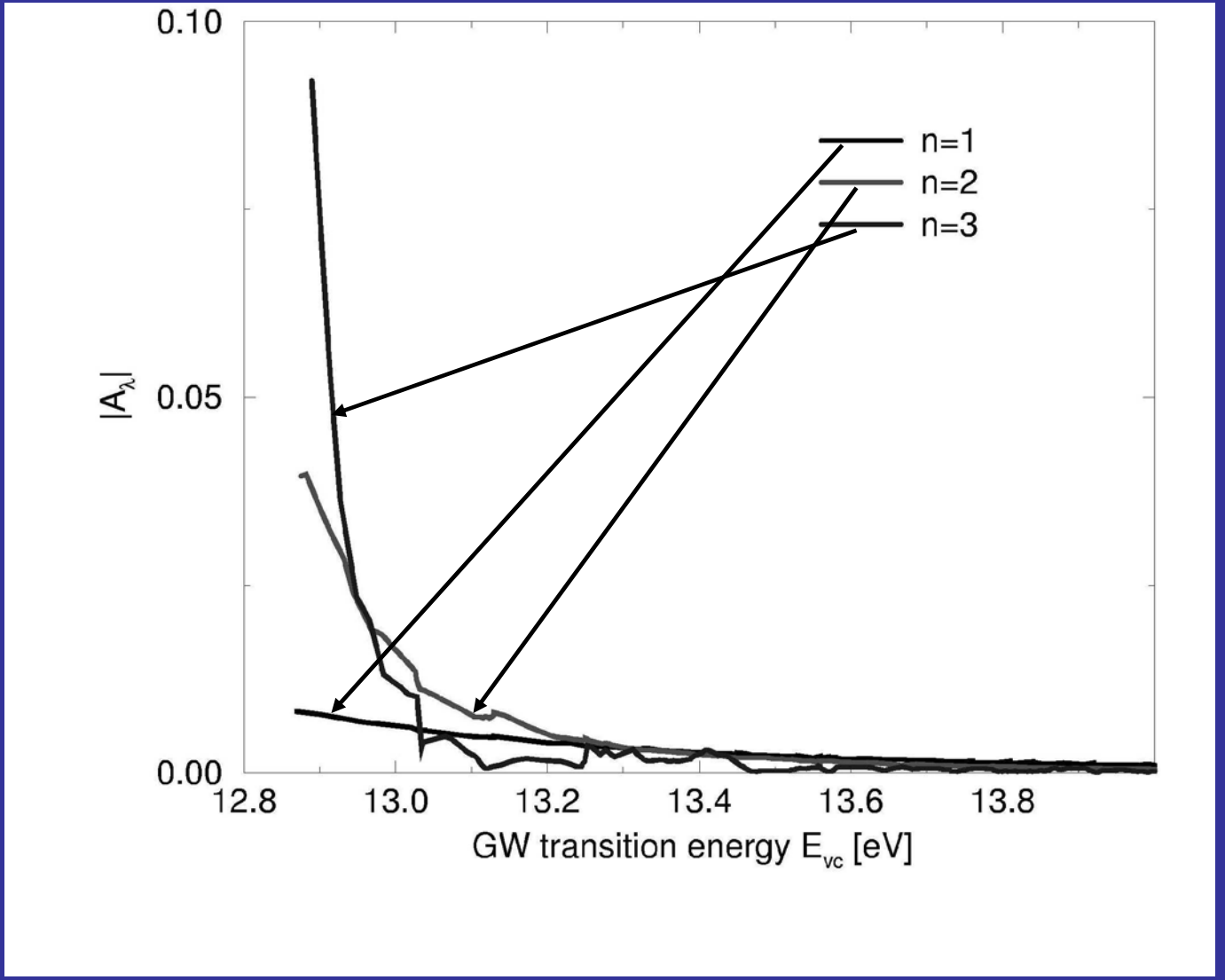




V. Olevano et al., 2000

http://www.bethe-salpeter.org


Optical Absorption
n=1
EXC
n=2
n=3
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
ε2(ω)
12.0
12.5
13.0
13.5
14.0
ω [eV]


0.10
0.05
0.00
$|A_\lambda|$
n=1
n=2
n=3
12.8
13.0
13.2
13.4
13.6
13.8
GW transition energy E_{vc} [eV]

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

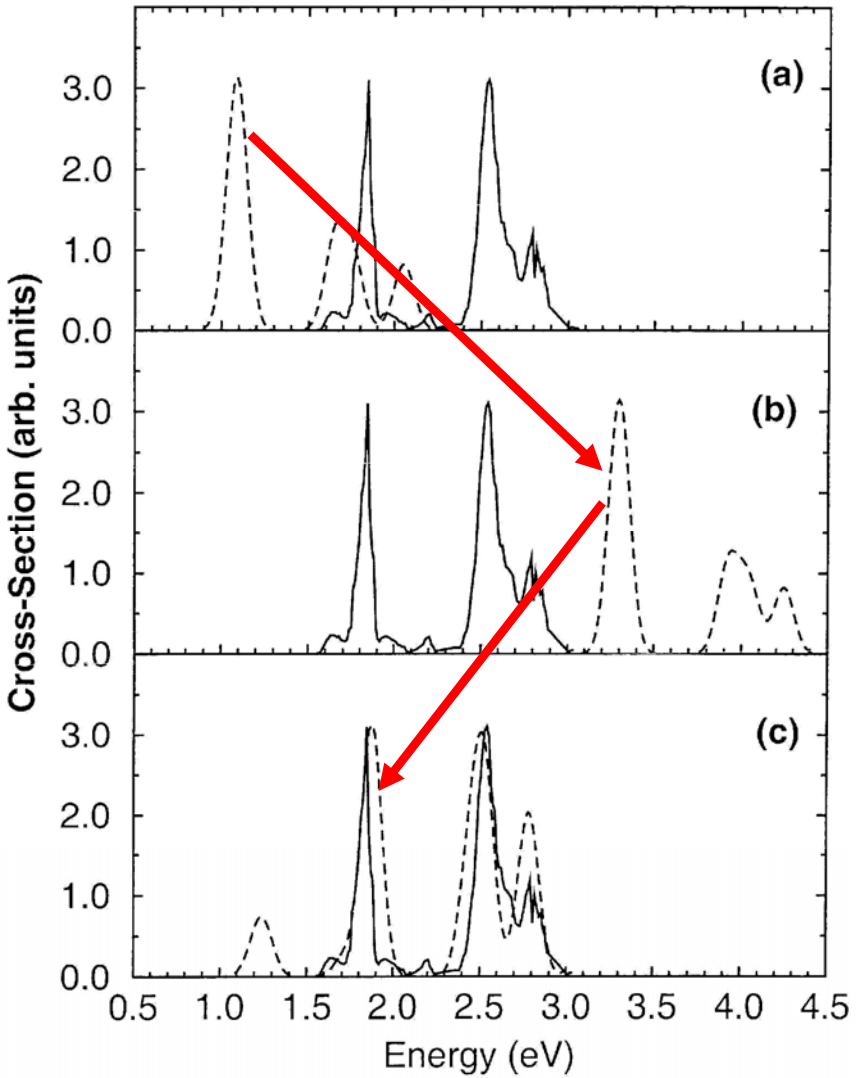
Variation of potential

$$Im[\varepsilon] \sim \Sigma_{vc} |\langle v|D|c\rangle|^2 \qquad \delta (E_c - E_v - \omega)$$

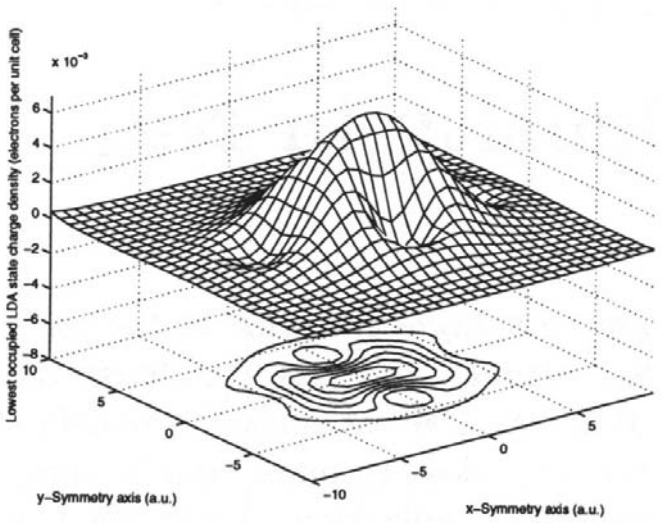
$$Im[\varepsilon] \sim \Sigma_\lambda | \Sigma_{vc} \langle v|D|c\rangle A_\lambda^{vc}|^2 \delta (E_\lambda - \omega)$$

->Mixing of transitions

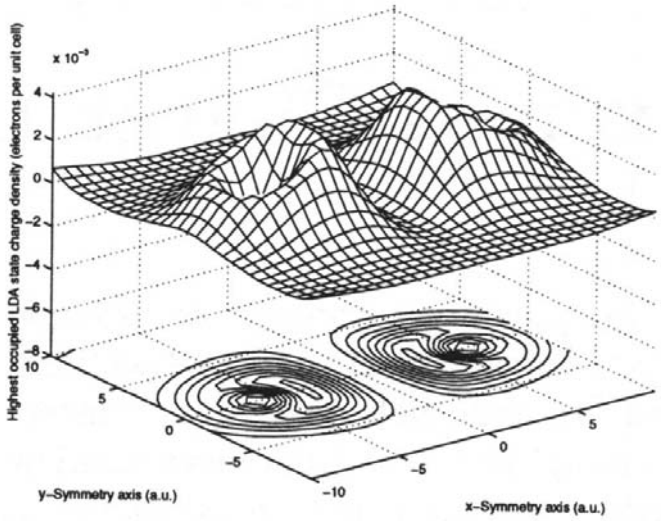
->Modification of excitation energies



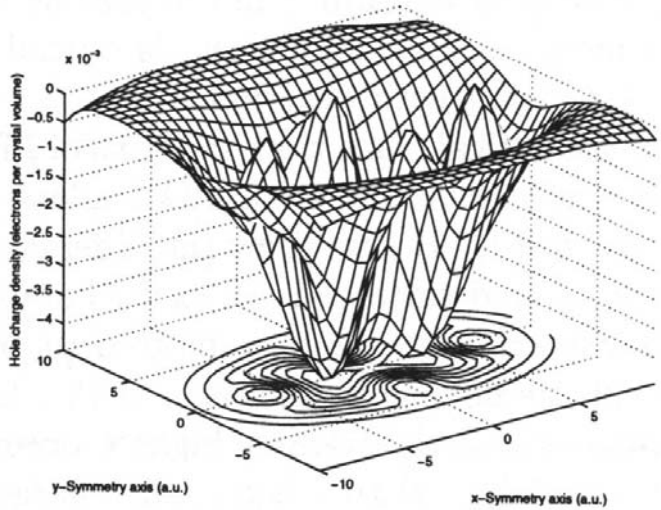
Onida et al 1995, Pulci et al 2000



(a) Charge density of the lowest occupied LDA state.



(b) Charge density of the highest occupied LDA state.



) Charge density of the true hole.

Albrecht et al PhD 1998

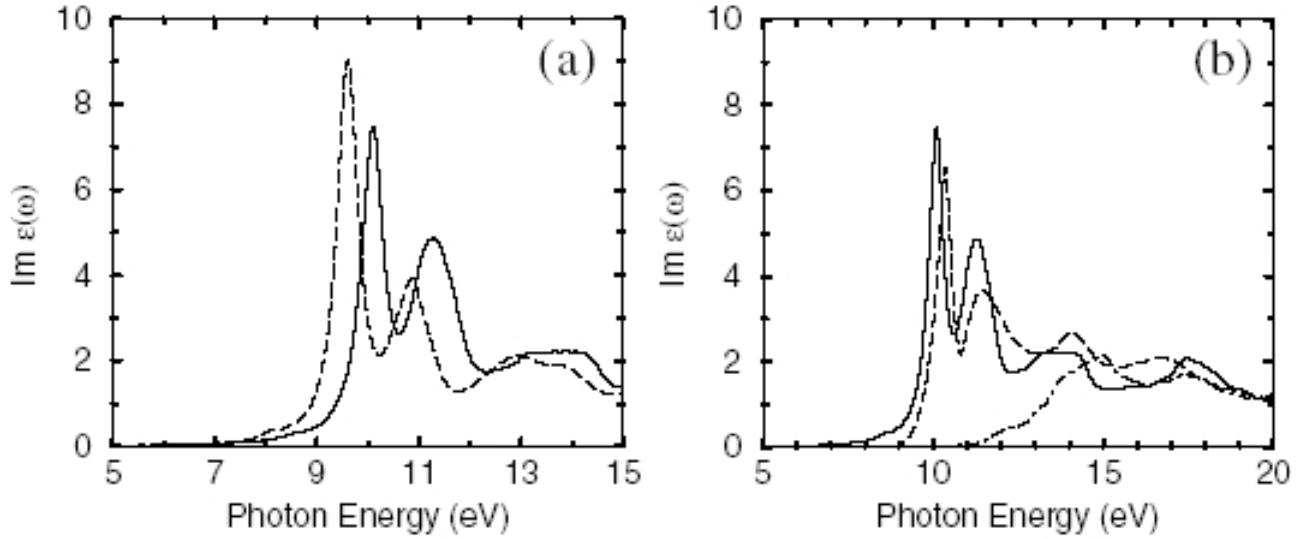


FIG. 2. (a) Absorption spectrum with excitonic effects calculated with RPA (dashed line) and with RPA + excitons (solid line) dielectric screening. (b) Absorption spectrum with excitonic effects calculated with RPA + excitons (solid line) screening as compared to the interband theory (dot-dashed line). Experimental data are given by the dashed line.

Excitons and Optical Properties of α-Quartz

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[2]*Institut für Theoretische Physik II, Universität Münster, Münster, Germany 48149*

(Received 10 April 2000)

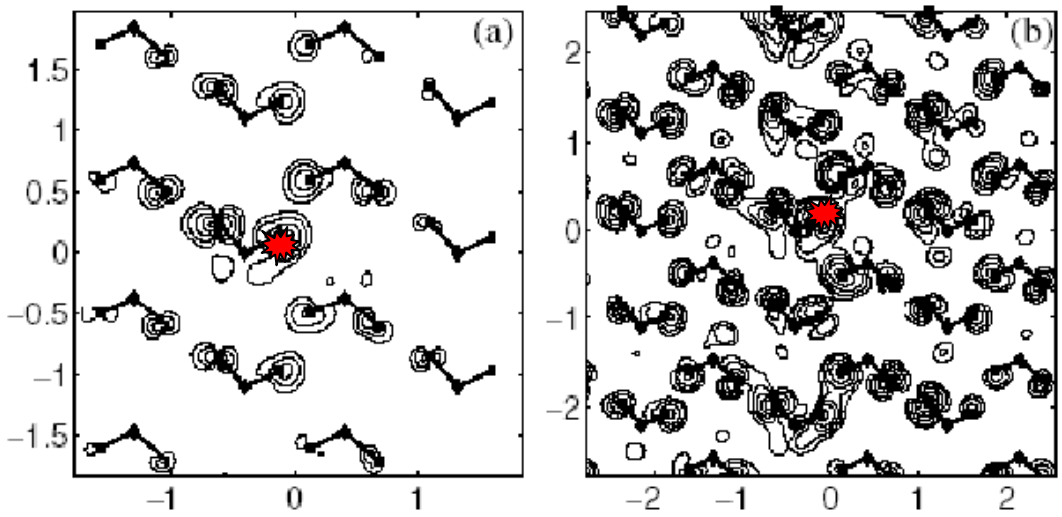
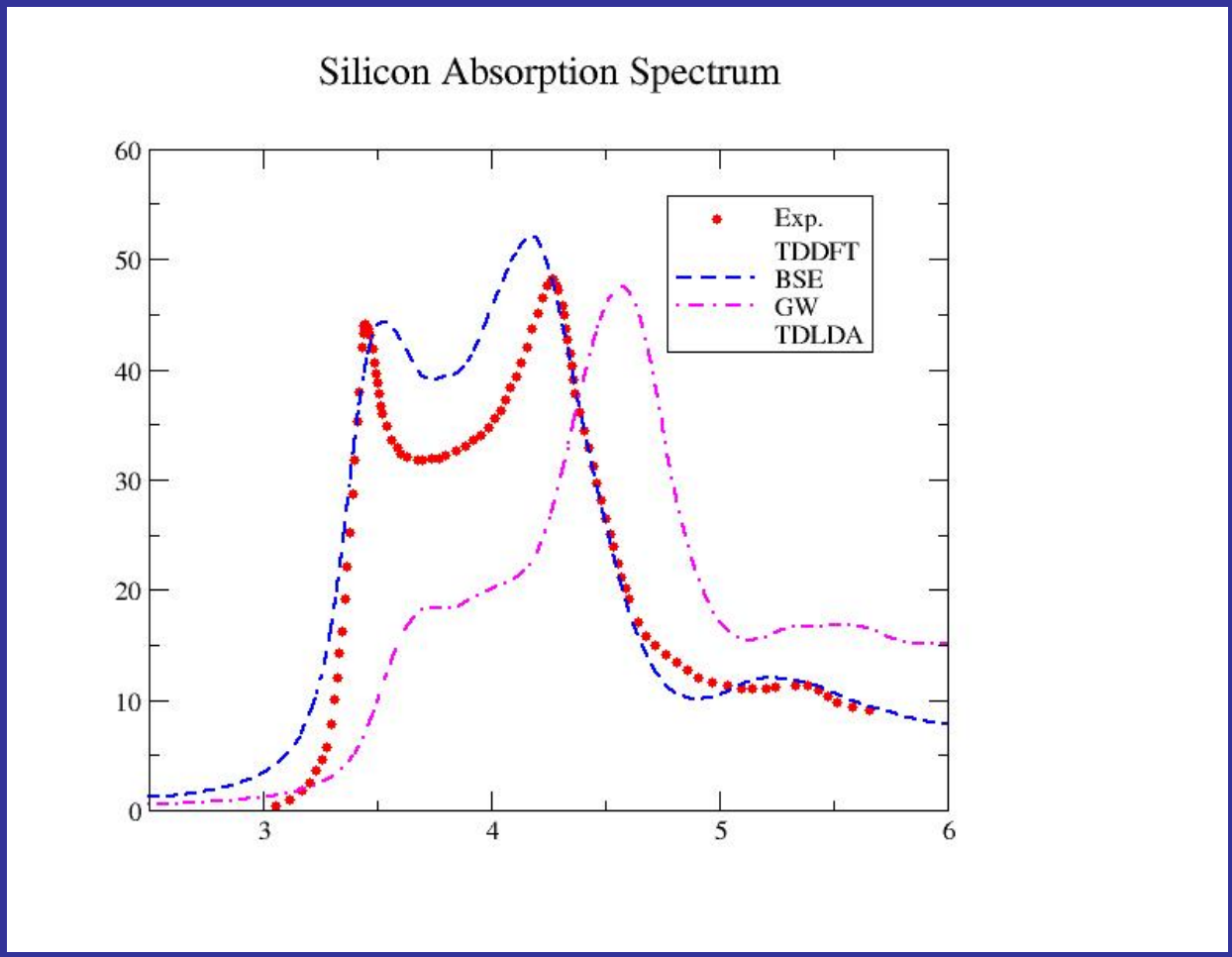


FIG. 4. A log plot of the hole probability density with the electron placed at + of (a) the first peak and (b) the second peak in the optical spectrum. The plot is in the (110) plane. The diamonds correspond to silicon atoms and the squares to oxygen atoms. The scale is in units of the lattice constant.



Hanke+Sham PRL 43, 387 (1979)
Albrecht, Reining, Del Sole, Onida, PRL 80, 4510 (1998)
Etc…….

We want: $\chi(q)$

We calculate: $\chi_{vc}^{v'c'}$

Can calculate vector instead of matrix

Iterative inversion etc.

BSE fine !

“Our” BSE obtained from vertex eq. on GW level

…….plus several approximations.

Diago yields spectra and full analysis,
more efficient solutions available.

Full range from Frenkel to Wannier
to continuum excitons