Electronic Excitations of Cu_2O: within GW Approximation

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Outline

- ◇ **Introduction**
- ◇ **Importance of Semicore States in GW**
- ◇ **Failure of GW in Cu_2O**
- ◇ **Conclusion**

Outline

⇒ **Introduction**

◇ **Importance of Semicore States in GW**

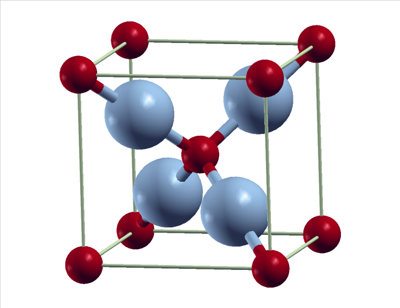
◇ **Failure of GW in Cu_2O**

◇ **Conclusion**

Cu_2O: a simple oxide ?

Cu_2O should be a suitable material to address the issue of 3d valence electrons:

- **♯ non magnetic**
- **♯ simple cubic structure**



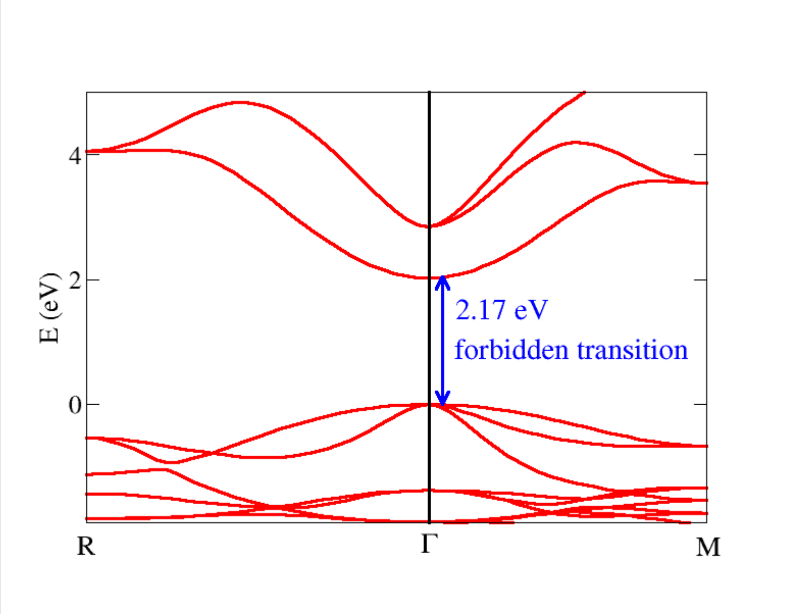
- **♯ closed d shell**

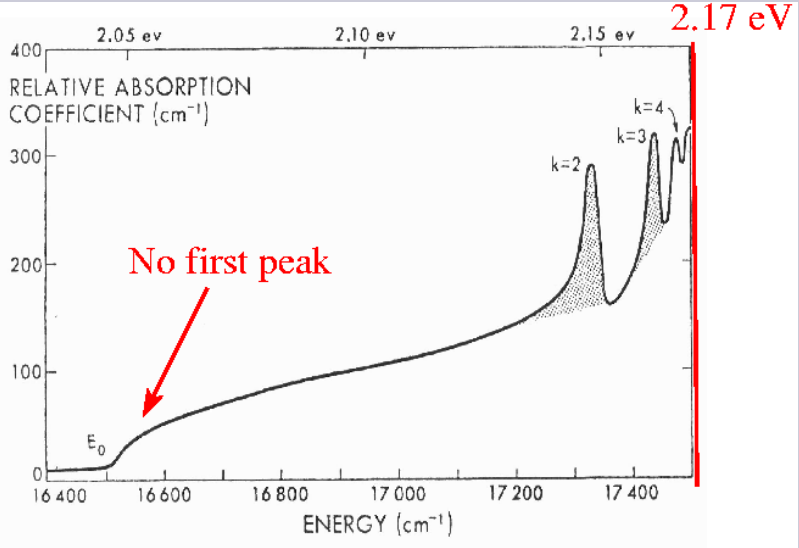
Cu $3s^2 3p^6 3d^{10}$
O $2s^2 2p^6$
$\Rightarrow$ not highly correlated

Cu_2O: A textbook material for excitons

Many excitonic series well studied since 60's

First Exciton Series





Experiment from P. W. Baumeister, *Phys. Rev.*, **121**, 359 (1961).

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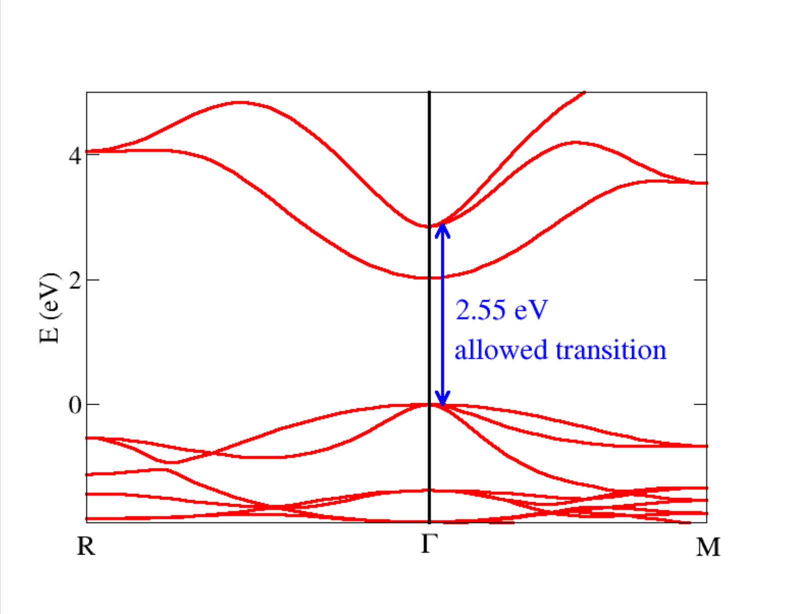
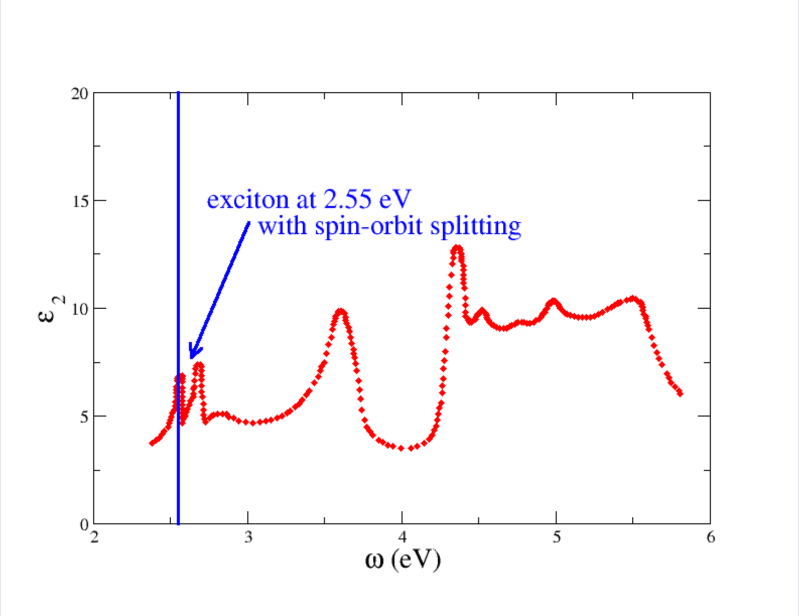
Many excitonic series well studied since 60's

Other Exciton Series





Experiment from M. Balkanski, *Solid State Com.* , **5**, 85 (1966).

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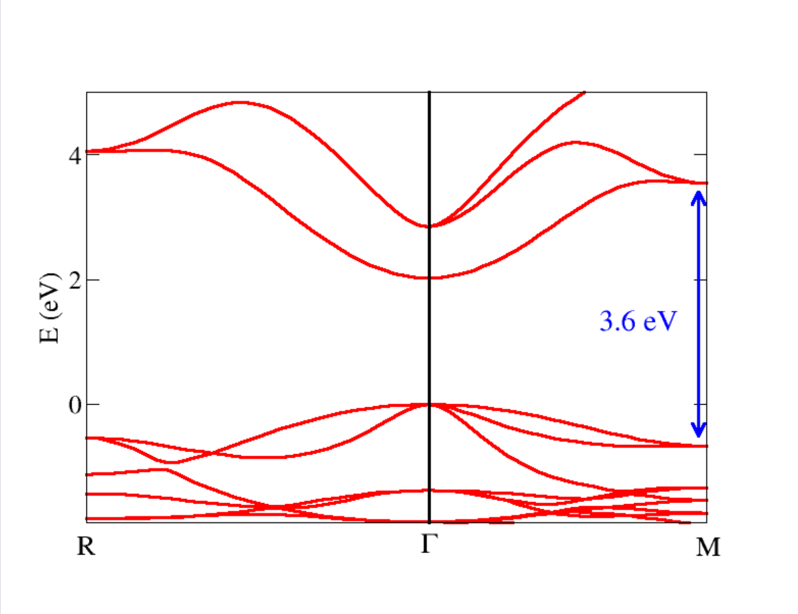
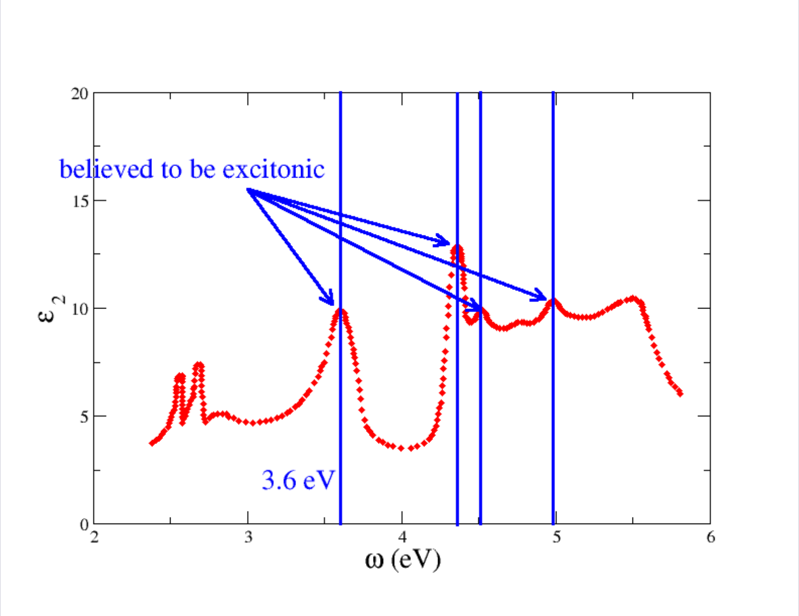
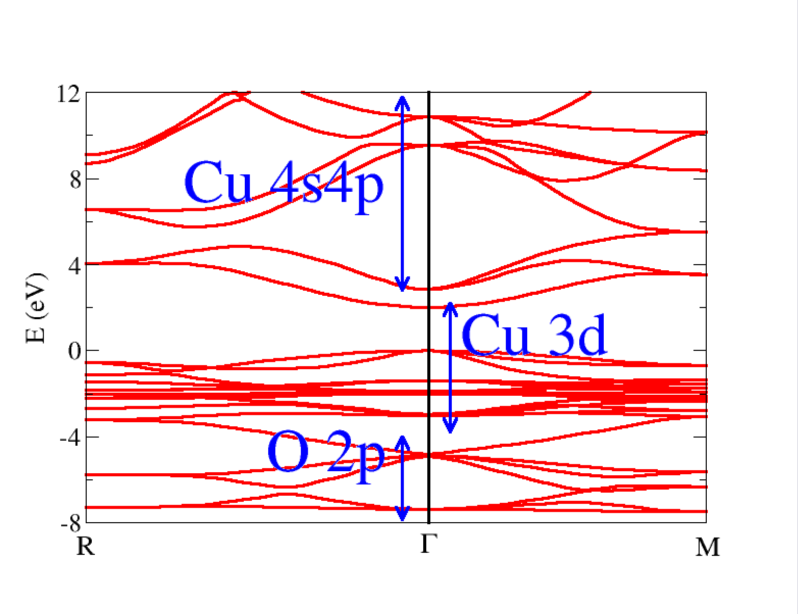
Other Exciton Series





Experiment from M. Balkanski, *Solid State Com.* , **5**, 85 (1966).

Cu_2O: A textbook material for theory



- ◇ **Very localised states: Cu 3d**
  $\Rightarrow$ almost flat bands
- ◇ **Delocalised states: Cu 4s4p**
  $\Rightarrow$ dispersive bands

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- $\diamond$ **Introduction**
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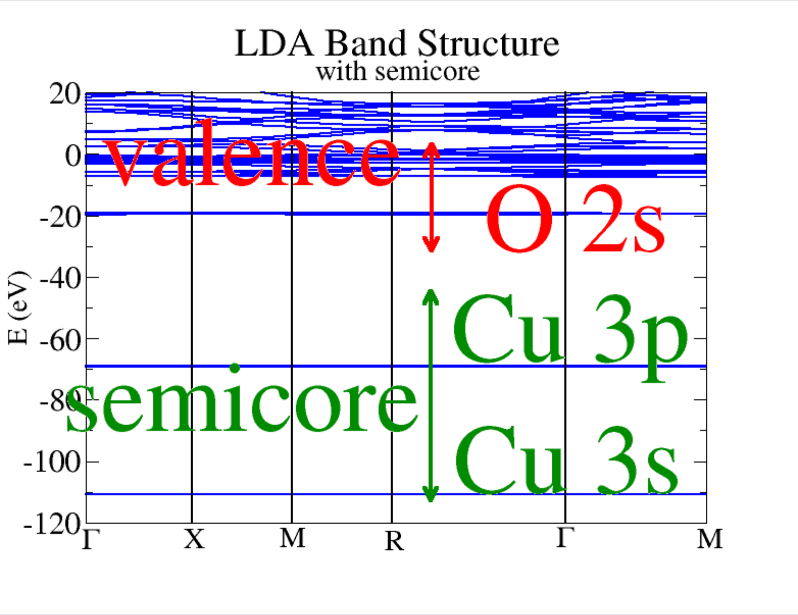
- $\diamond$ **Failure of GW in Cu_2O**
- $\diamond$ **Conclusion**

Should we include semicore states ?

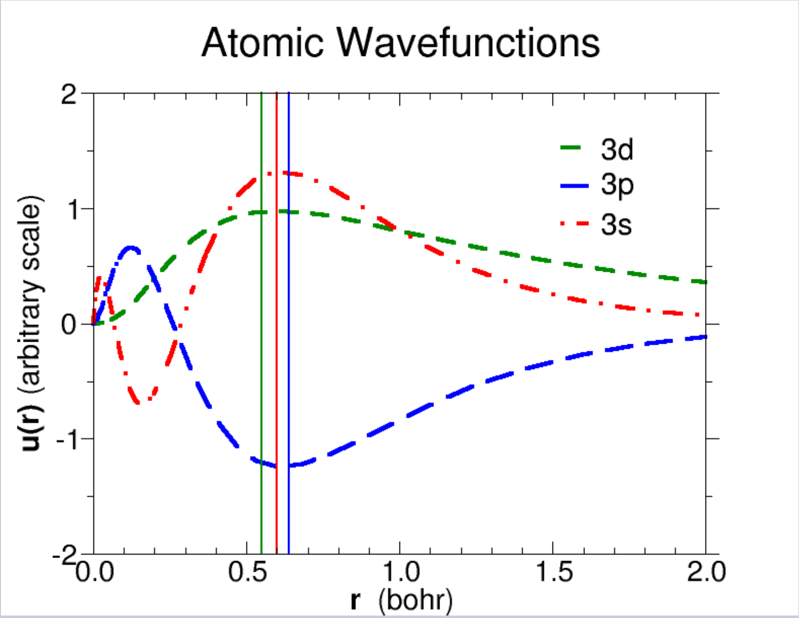
There is an energetic separation.



The semicore is very deep !
$\sim$ 50 eV below valence

Should we include semicore states ?

There is no spatial separation.

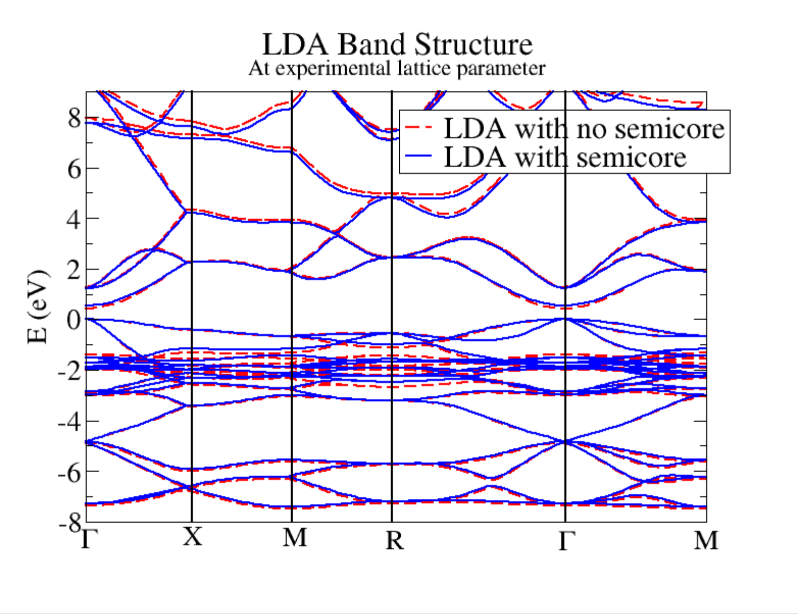


The maxima of the wavefunctions are located at the same place !

Which valence do we choose ?

Effect of semicore on LDA results

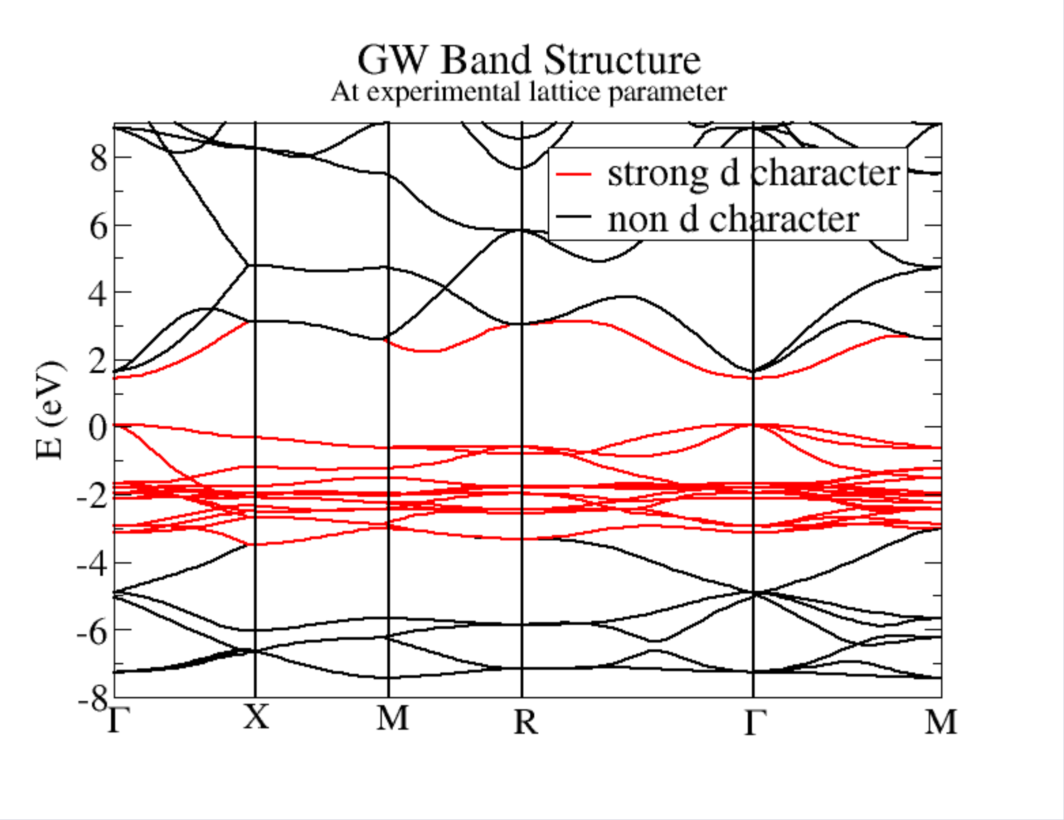
Slight effect on bandstructure



No reason not to trust results without semicore

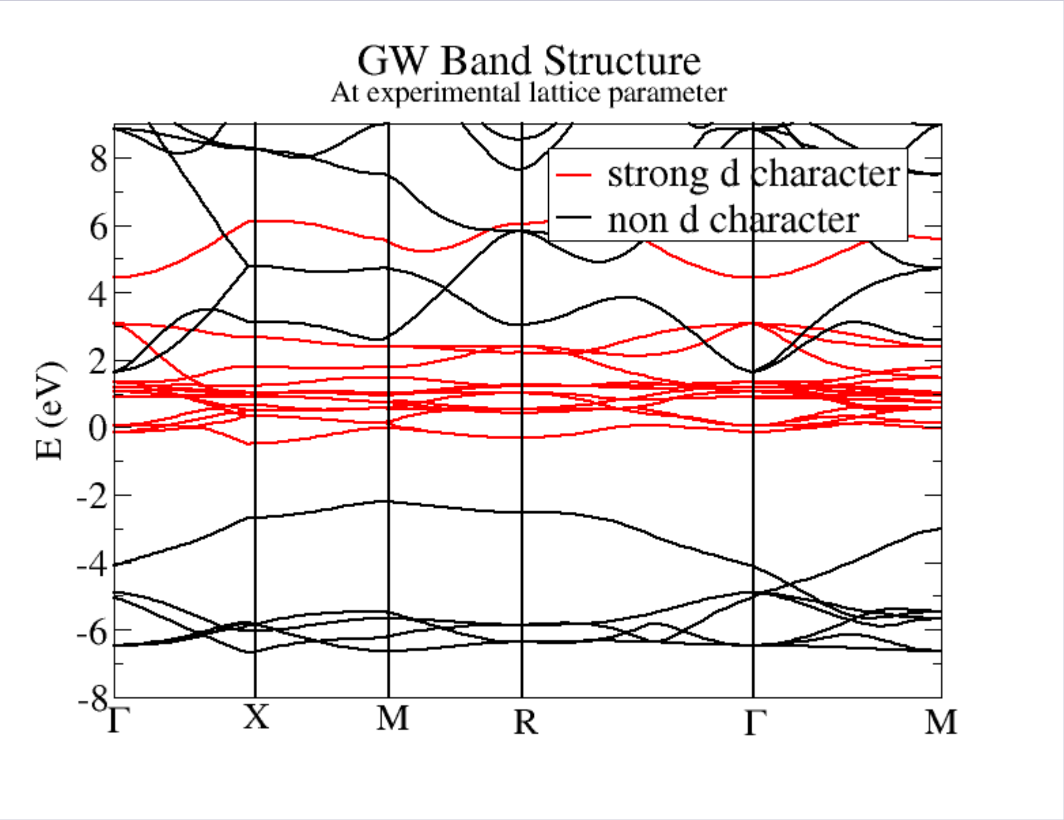
Effect of semicore on GW results

Calculation with semicore



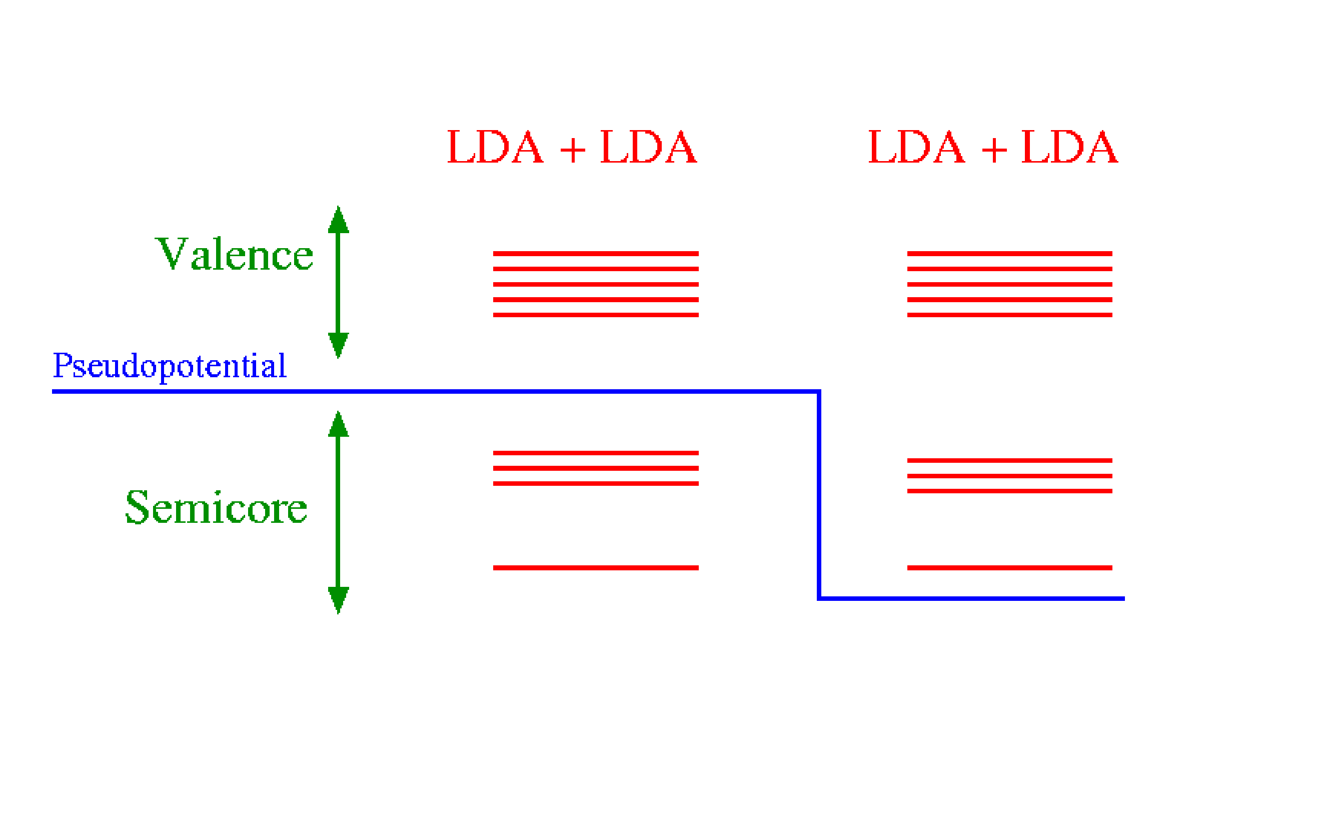
Effect of semicore on GW results

Calculation without semicore



Influence of semicore on valence electrons

LDA calculation



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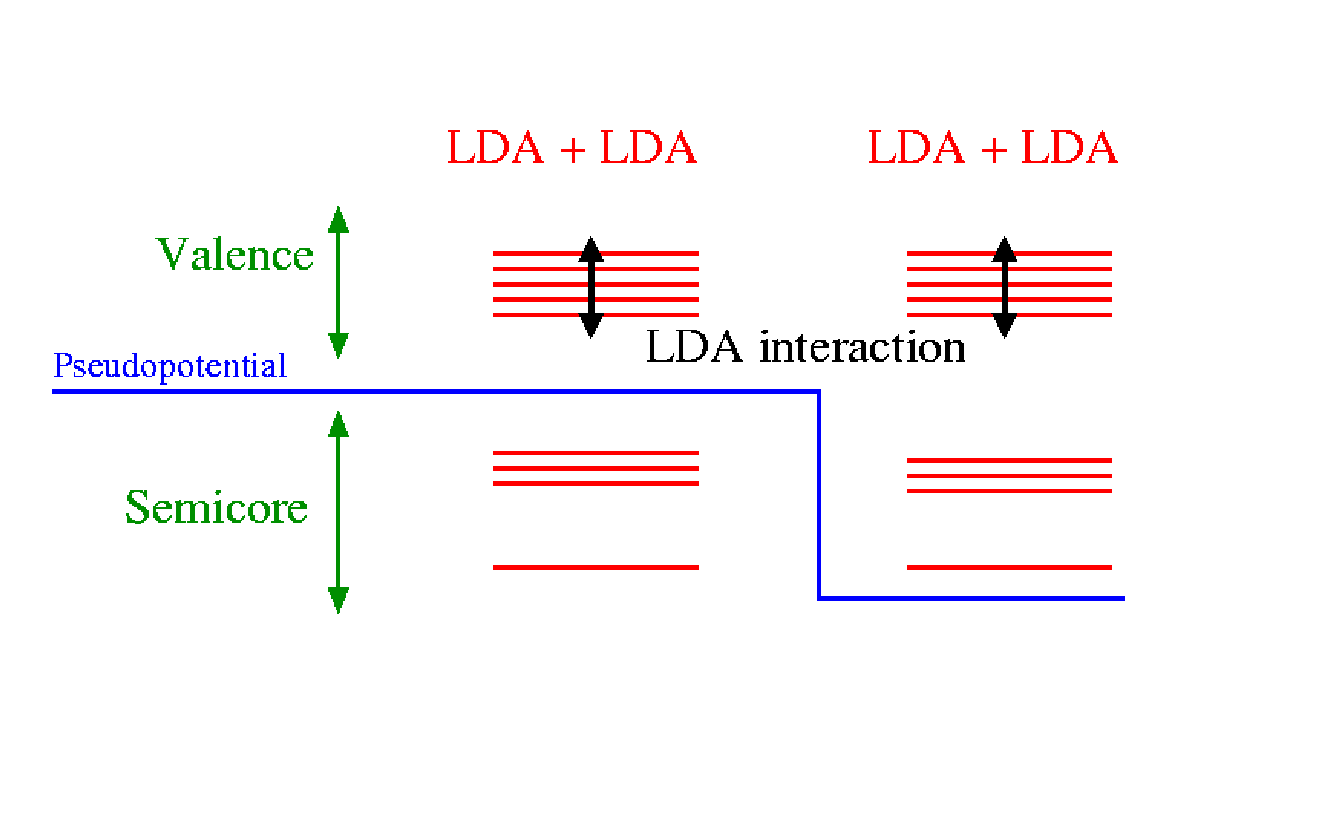

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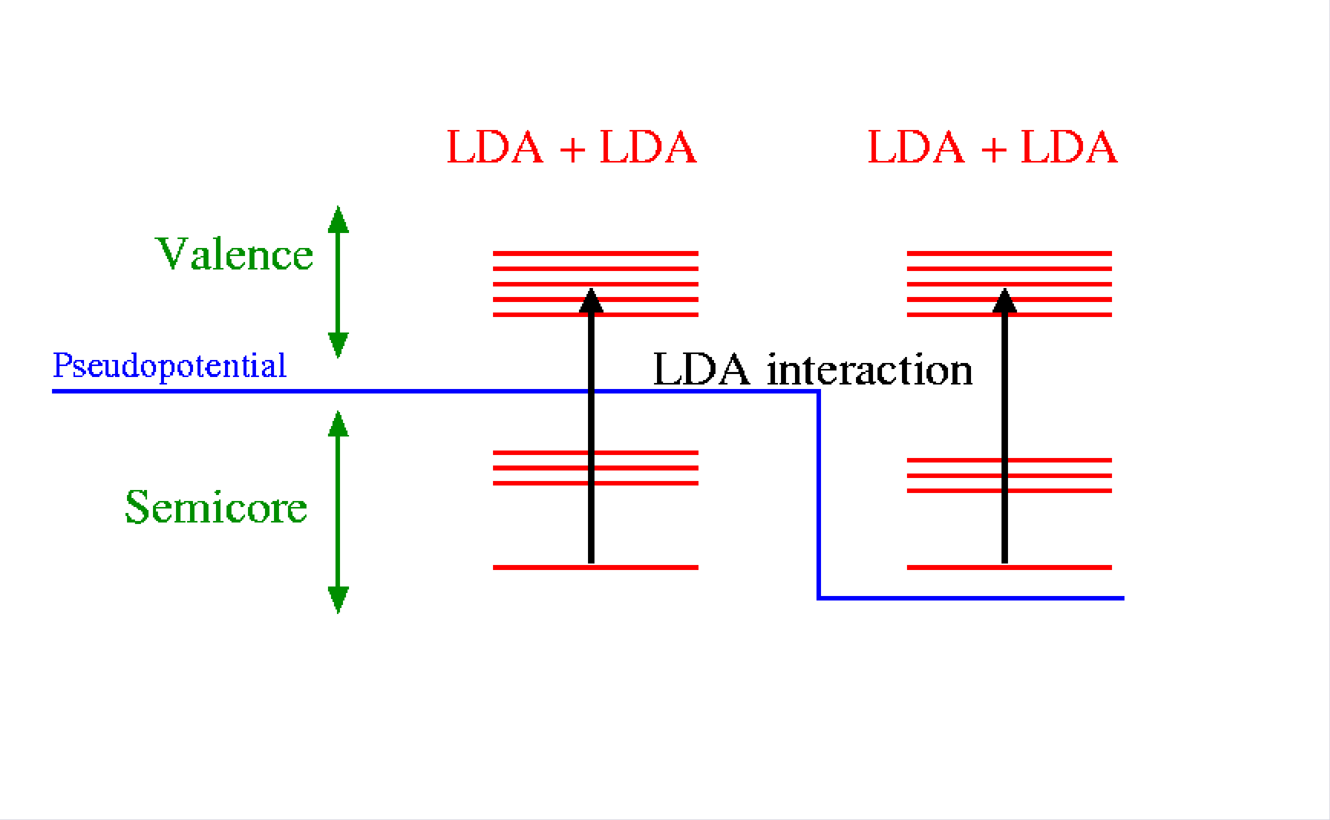
LDA calculation



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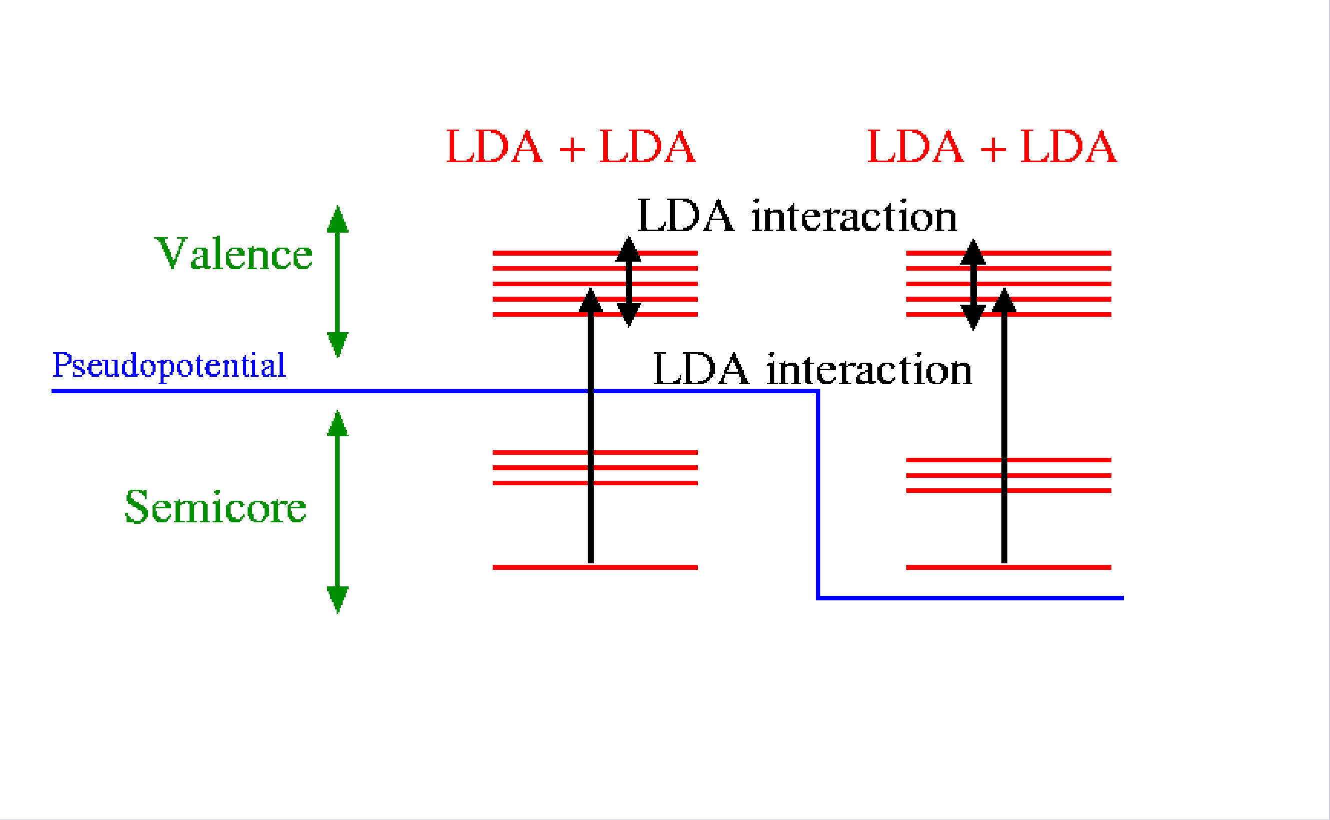
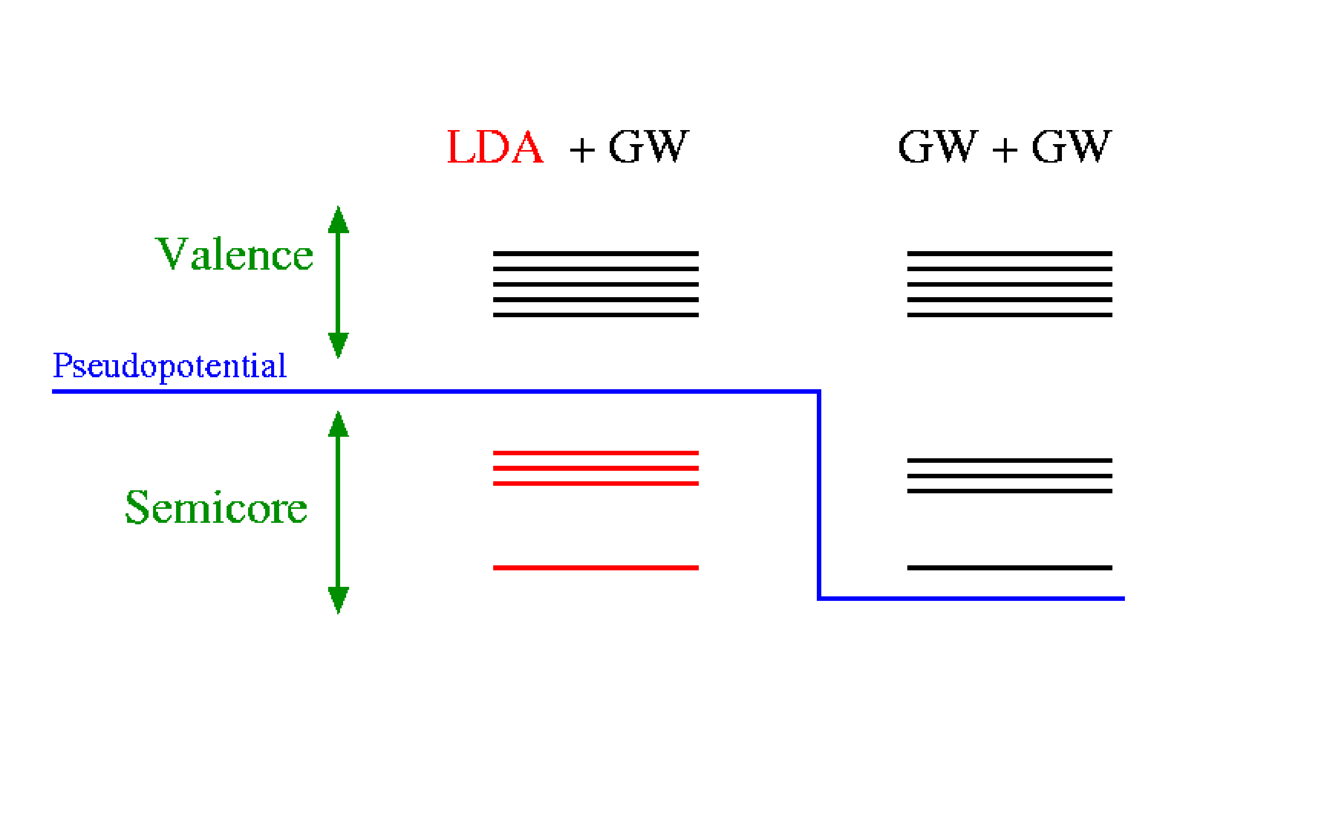


Influence of semicore on valence electrons

GW calculation



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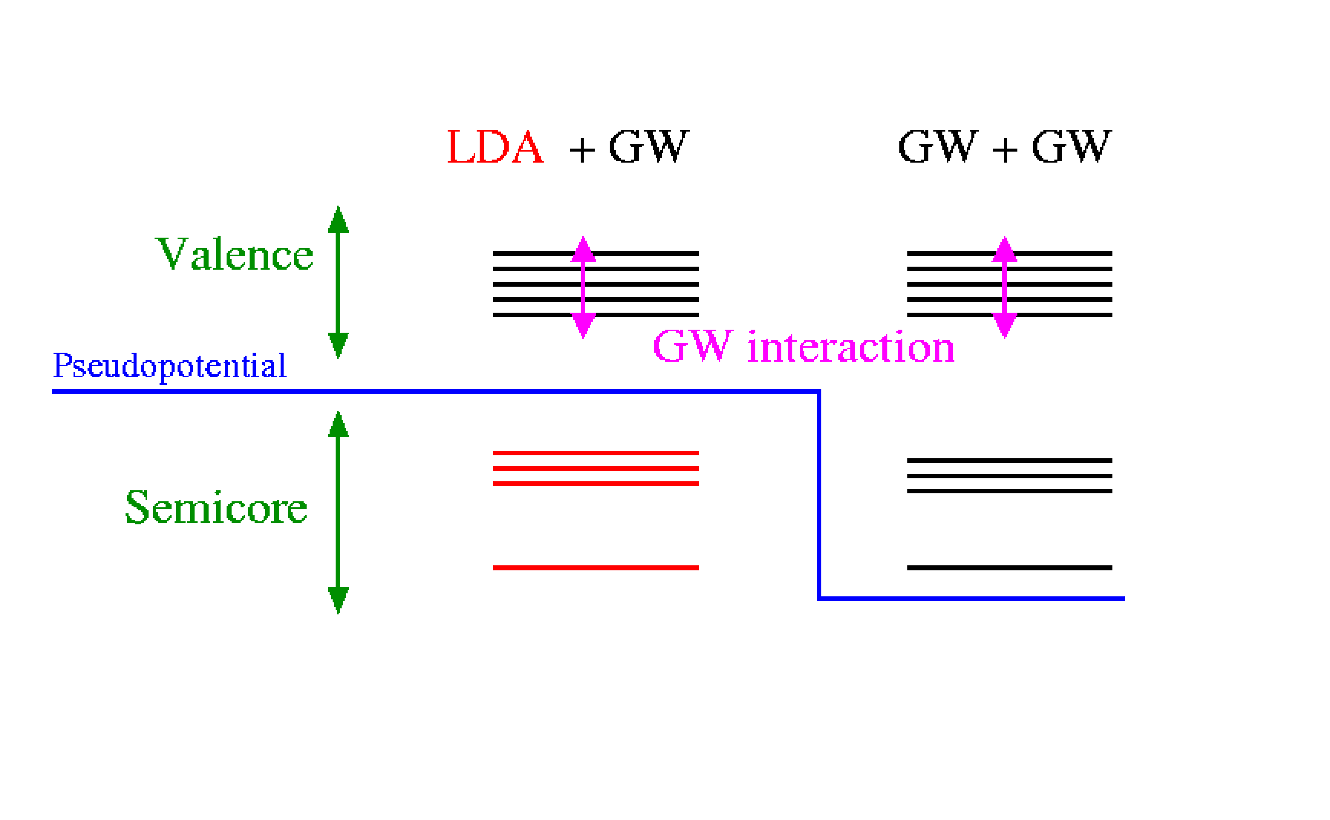

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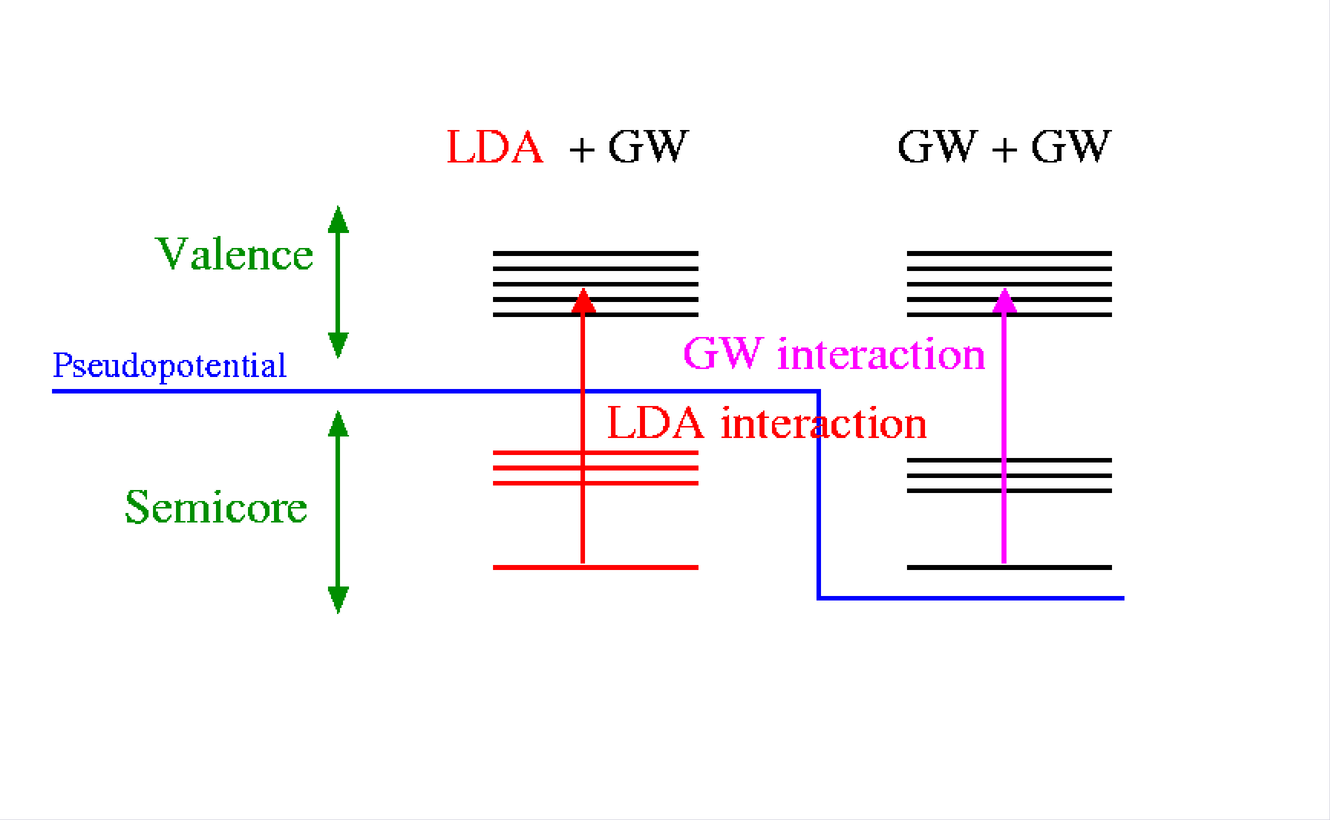

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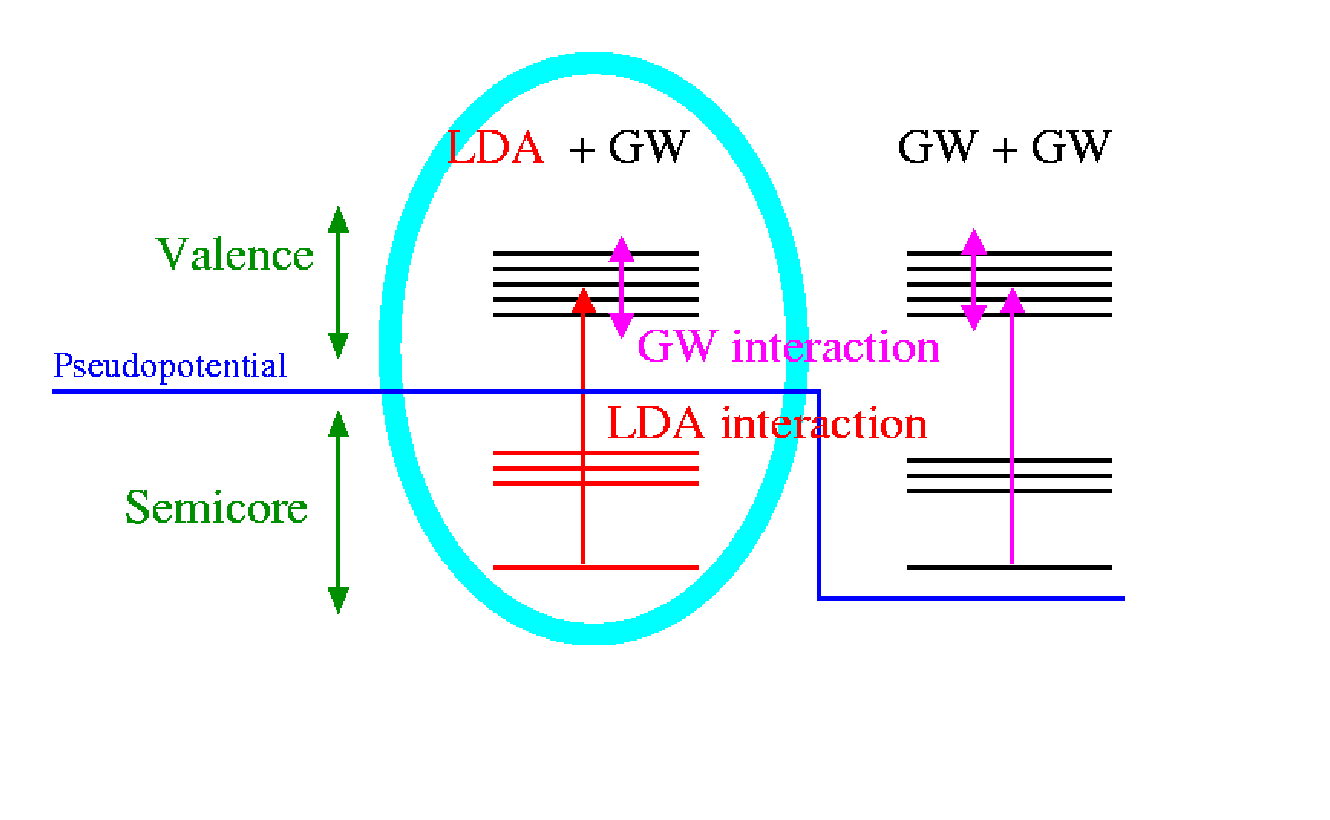

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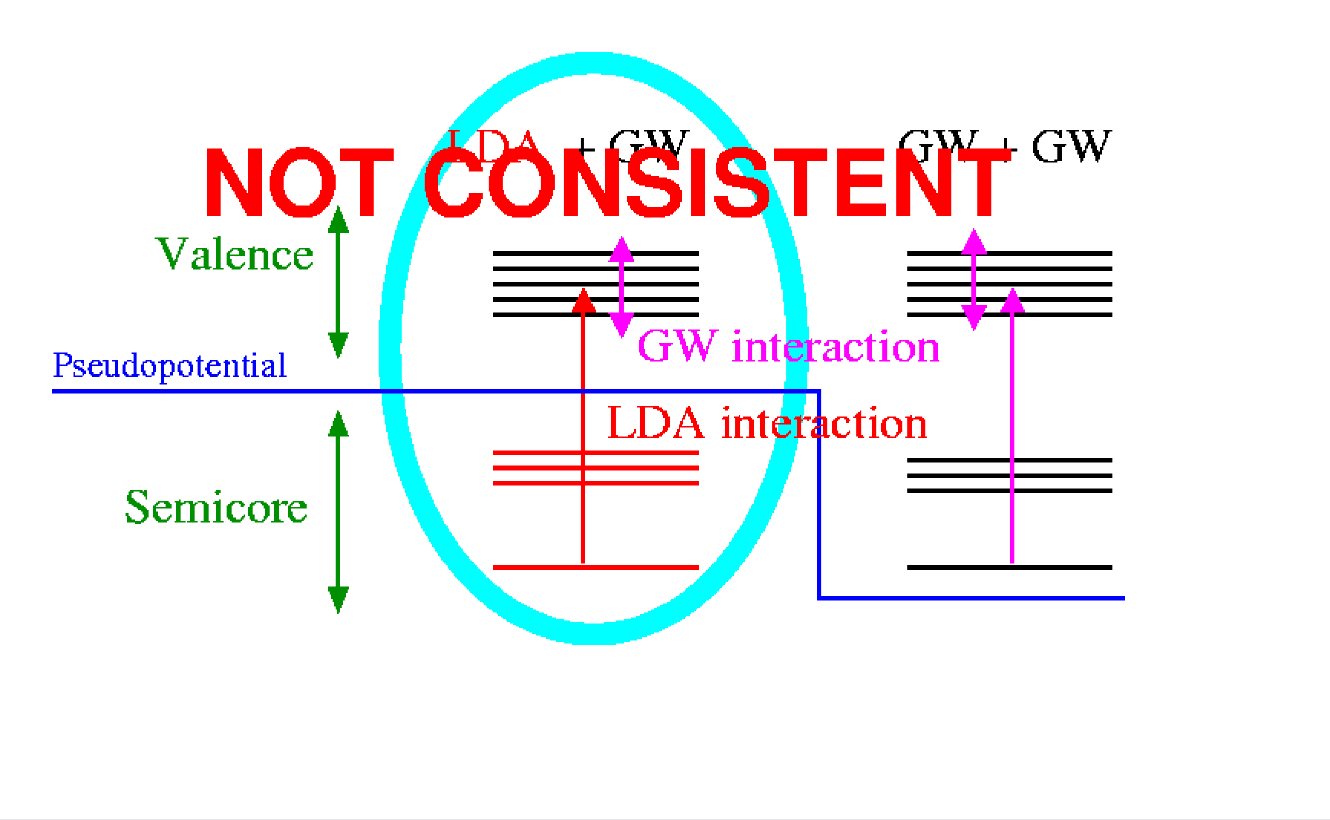

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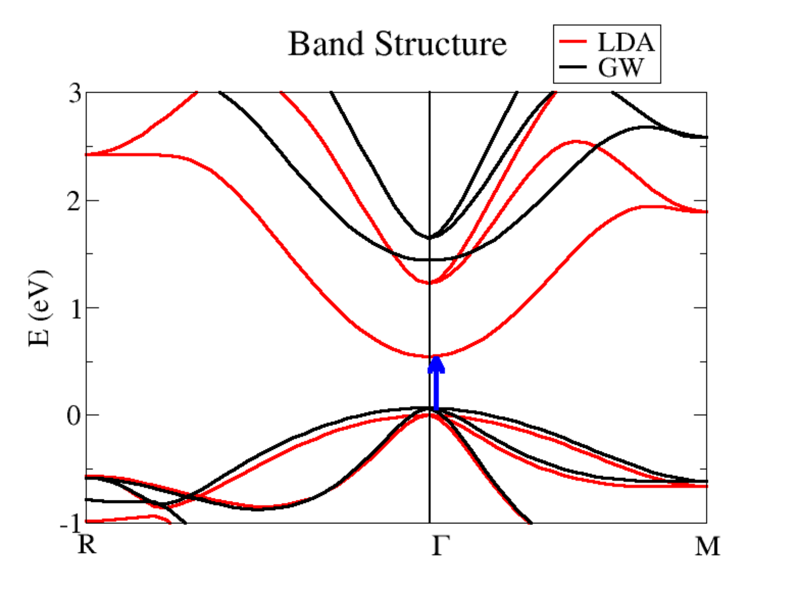
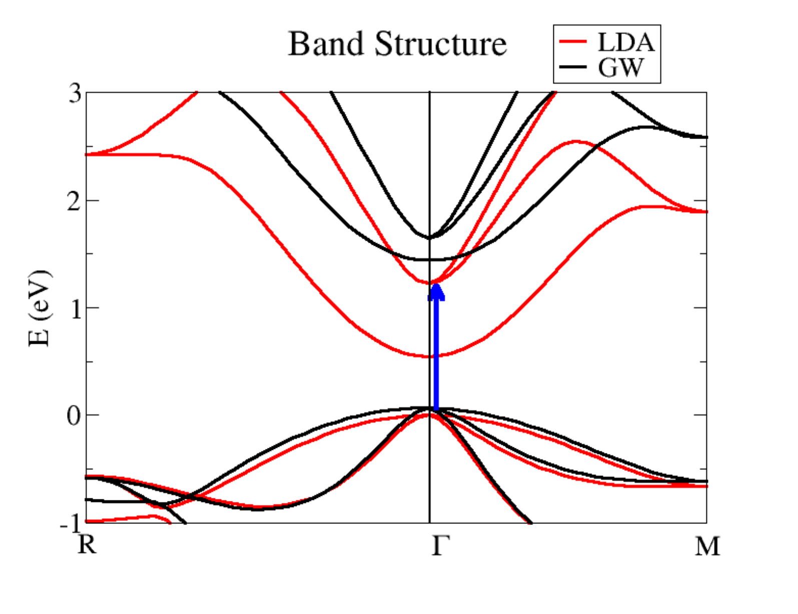
Gap values

	LDA	GW	Exp
Intrinsic Gap	0.54		2.17
Optical Threshold			2.55



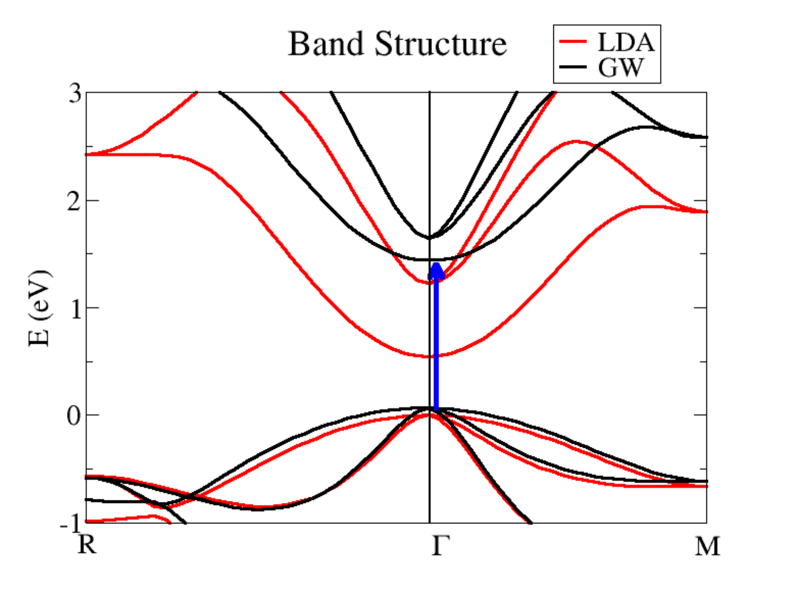
Gap values

	LDA	GW	Exp
Intrinsic Gap	0.54		2.17
Optical Threshold	1.23		2.55



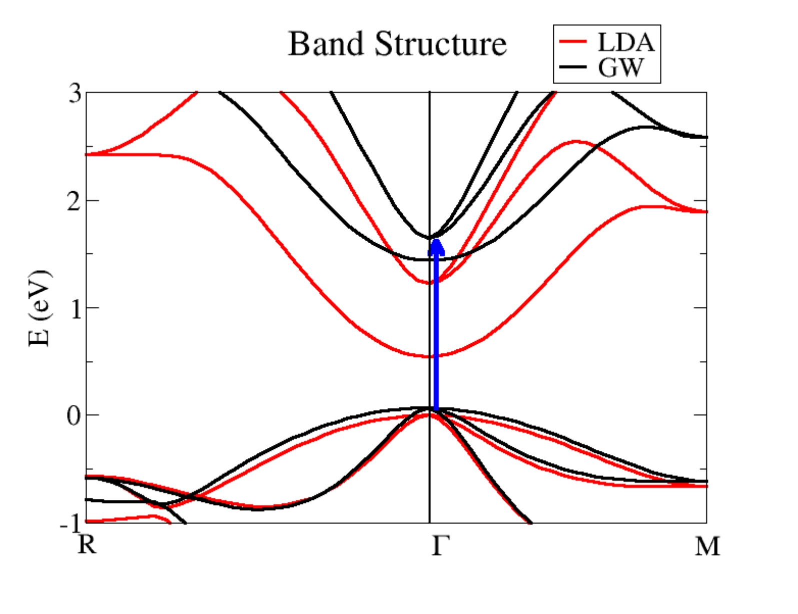
Gap values

	LDA	GW	Exp
Intrinsic Gap	0.54	1.37	2.17
Optical Threshold	1.23		2.55



Gap values

	LDA	GW	Exp
Intrinsic Gap	0.54	1.37	2.17
Optical Threshold	1.23	1.63	2.55



DFT vs Green's function theory

Kohn-Sham Equations:

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}\right] \phi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

Equation of motion of Quasiparticles:

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}\right] \phi_i(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_i)\phi_i(\mathbf{r}') = \epsilon_i \phi_i(\mathbf{r})$$

Practical approximations in standard GW

$$\Sigma(\mathbf{r}_1, \mathbf{r}_2, \omega) = i \int d\omega' G(\mathbf{r}_1, \mathbf{r}_2, \omega') W(\mathbf{r}_1, \mathbf{r}_2, \omega' - \omega)$$

$G(\mathbf{r}_1, \mathbf{r}_2, \omega)$ is assumed to be the LDA Green's function:

$$G(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_i \frac{\phi_i^{LDA}(\mathbf{r}_1)\phi_i^{LDA\star}(\mathbf{r}_2)}{\omega - \epsilon_i^{LDA} \pm i\eta}$$

- **Use of pseudowavefunctions made for LDA not for GW**
  Operators' expectation values might be wrong because of the core region.
- **G^{LDA} might be very different from G^{GW}**
  Lack of self-consistency ?

Practical approximations in standard GW

$W(\mathbf{r}_1, \mathbf{r}_2, \omega)$ is the dynamically screened coulomb interaction:

$$W(\mathbf{r}_1, \mathbf{r}_2, \omega) = \int d\mathbf{r}_3 v(\mathbf{r}_1, \mathbf{r}_3) \varepsilon^{-1}(\mathbf{r}_3, \mathbf{r}_2, \omega)$$

We take into account the full spatial complexity of W, but

- **Its frequency dependence is fit on a single pole.**

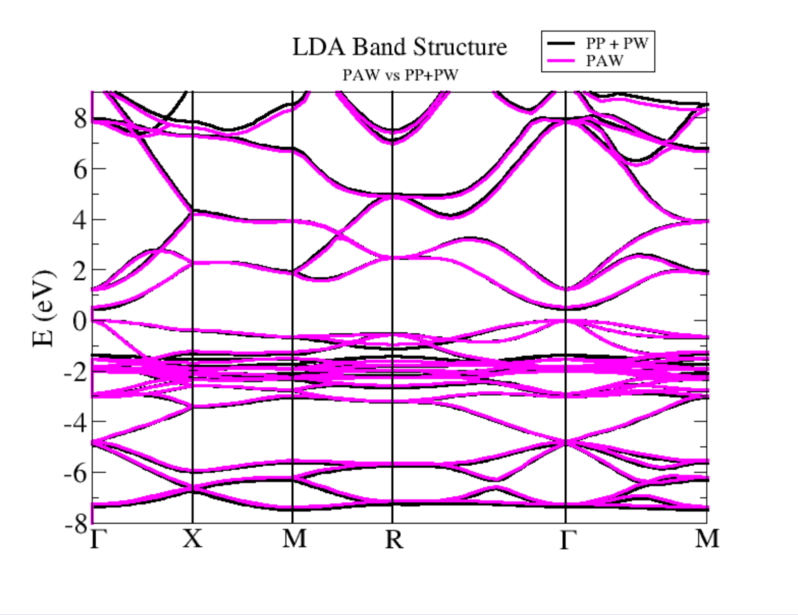
$\Sigma - V_{xc}$ is assumed to be a first order perturbation of H^{LDA}:

$$\epsilon_i^{GW} = \epsilon_i^{LDA} + \langle \phi_i^{LDA} | \Sigma(\epsilon_i^{GW}) - V_{xc} | \phi_i^{LDA} \rangle$$

- **Non diagonal terms $\langle \phi_i^{LDA} | \Sigma(\epsilon_i^{GW}) - V_{xc} | \phi_j^{LDA} \rangle$ might be large if $\phi_i^{GW} \neq \phi_i^{LDA}$**

Failure of PP + PW scheme ?

Comparison with PAW results from Brice Arnaud, University of Rennes



$\Rightarrow$ Eigenvalues: OK

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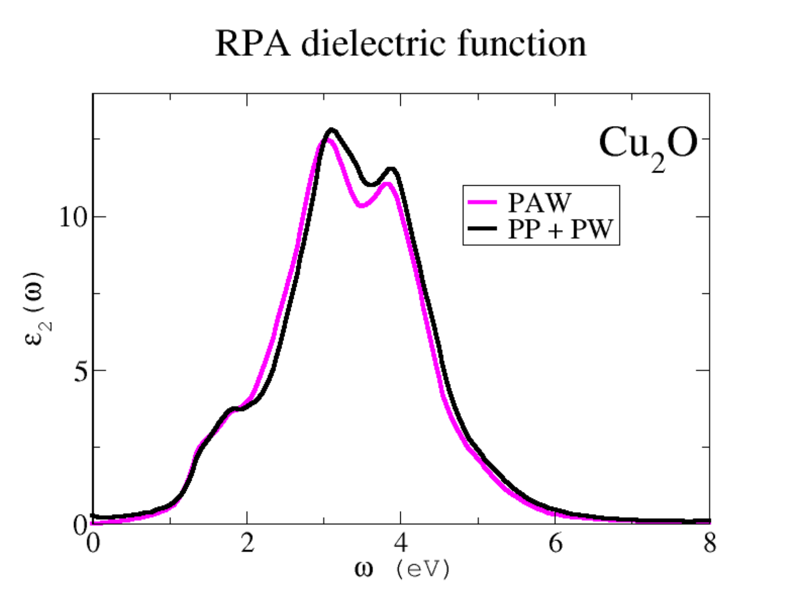


⇒ Eigenfunctions: OK

Plasmon Pole Model in ABINIT

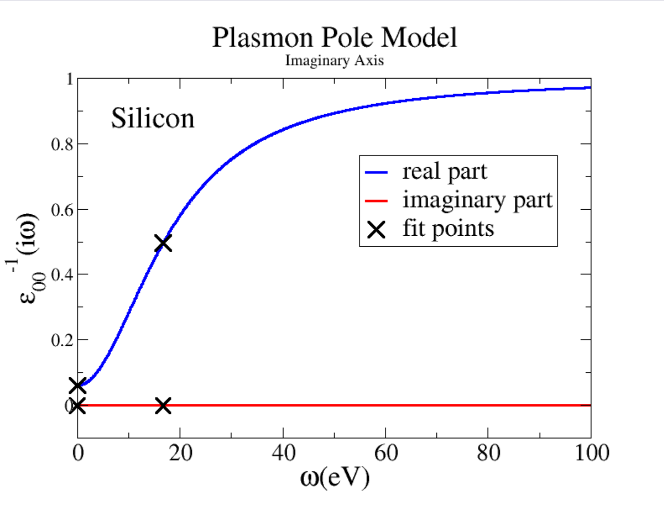
Assuming this ω dependence:

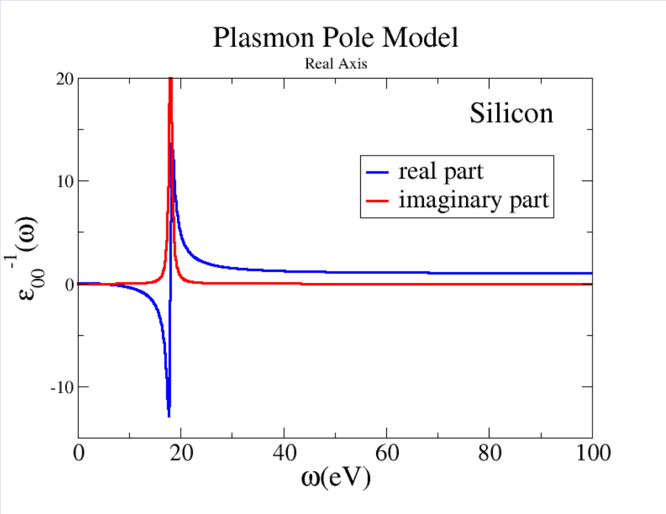
$$\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, i\omega) = \delta_{\mathbf{G},\mathbf{G}'} + \frac{\Omega^2_{\mathbf{G}\mathbf{G}'}(\mathbf{q})}{(i\omega)^2 - \tilde{\omega}^2_{\mathbf{G},\mathbf{G}'}(\mathbf{q})}$$

two-parameter model fit on two frequencies:

$$\omega = 0$$

and $\omega \approx i\omega_{\mathbf{plasma}}$

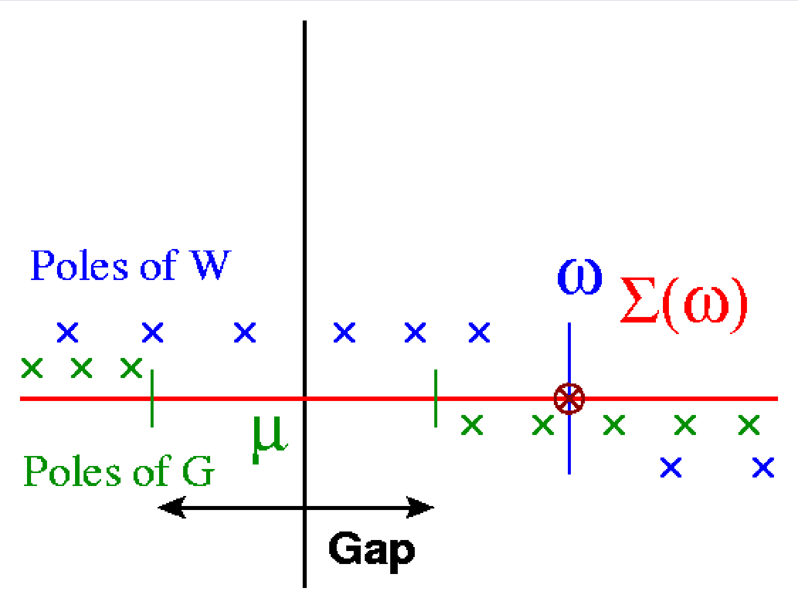




Getting rid of Plasmon Pole Model in ABINIT

Performing convolution along real axis

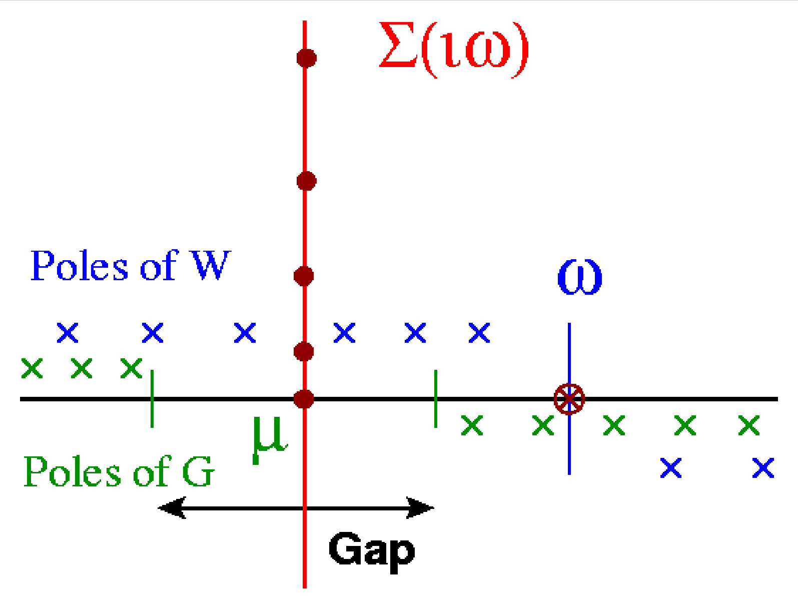
$$\Sigma(\omega) = i \int d\omega' G(\omega') W(\omega' - \omega)$$



Getting rid of Plasmon Pole Model in ABINIT

Performing convolution along imaginary axis

$$\Sigma(i\omega) = \int d\omega' G(i\omega') W(i\omega' - i\omega)$$



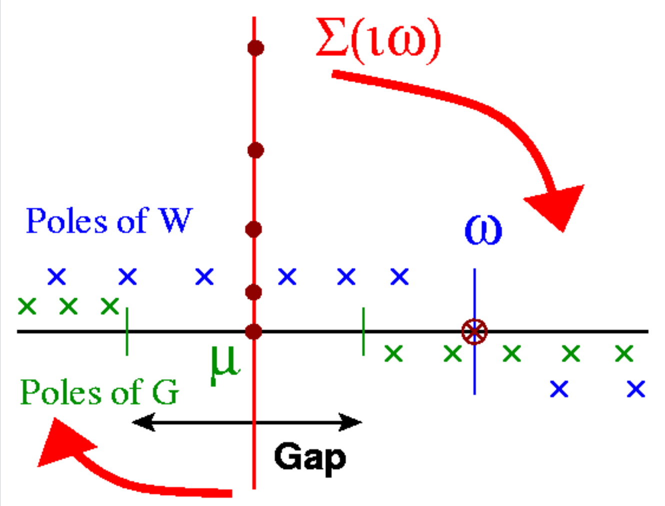
Getting rid of Plasmon Pole Model in ABINIT

Analytic continuation of Σ:

$$P(z) = \frac{a_0 + a_1 z + a_2 z^2 + \ldots + a_N z^N}{b_0 + b_1 z + b_2 z^2 + \ldots + b_M z^M}$$

fit on imaginary points

then, extrapolation to real axis



Details might be found (for instance) in S. Lebegue *et al.*, Phys. Rev. B, **67**, 155208 (2003).

Failure of Plasmon Pole Model ?

Calculating

$$\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, i\omega)$$

and then

$$\langle \phi_i^{LDA} | \Sigma(i\omega) - V_{xc} | \phi_i^{LDA} \rangle$$

	GW with PPM	GW without PPM	Exp
Intrinsic Gap	1.37	1.35	2.17
Optical Threshold	1.63	1.78	2.55

Plasmon Pole Model is accurate around the gap

Are LDA wavefunctions close to GW ones ?

$$\epsilon_i^{LDA} + \langle \phi_i^{LDA} | \Sigma^{GW}(\epsilon_i^{GW}) - V_{xc}^{LDA} | \phi_j^{LDA} \rangle$$

i,j	**42**	**43**	**44**	**48**	**49**	**50**
42	**-0.3064**	**0.0001**	**-0.0001**	**-0.2524**	**-0.1678**	**-0.0220**
43	**0.0001**	**-0.3068**	**0.0000**	**-0.1662**	**0.1368**	**0.0767**
44	**-0.0001**	**0.0000**	**-0.3072**	**-0.0145**	**0.1476**	**-0.2488**
48	**-0.2524**	**-0.1662**	**-0.0145**	**11.2221**	**0.0000**	**0.0000**
49	**-0.1678**	**0.1368**	**0.1476**	**0.0000**	**11.2220**	**0.0000**
50	**-0.0220**	**0.0767**	**-0.2488**	**0.0000**	**0.0000**	**11.2221**

First order perturbation theory:

$$\epsilon^{GW} = -0.3072 \ \textbf{eV}$$

Diagonalization:

$$\Rightarrow \epsilon^{GW} = -0.3112 \ \textbf{eV}$$

and

$$|\langle \phi_i^{LDA} | \phi_i^{GW} \rangle|^2 = 0.998$$

Are LDA wavefunctions close to GW ones ?

$$\epsilon_i^{LDA} + \langle \phi_i^{LDA} | \Sigma^{GW}(\epsilon_i^{GW}) - V_{xc}^{LDA} | \phi_j^{LDA} \rangle$$

i,j	42	43	44	48	49	50
42	-0.3064	0.0001	-0.0001	-0.2524	-0.1678	-0.0220
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First order perturbation theory:

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Diagonalization:

$$\Rightarrow \epsilon^{GW} = -0.3112 \textbf{ eV}$$

and

$$|\langle \phi_i^{LDA} | \phi_i^{GW} \rangle|^2 = 0.998$$

Lack of self-consistency ?

Update of eigenvalues used in G and W
Not quantitative
Just qualitative

	G_0W_0	GW_0	G_0W	Exp
Intrinsic Gap	1.37	1.41	1.50	2.17
Optical Threshold	1.63	1.69	1.92	2.55

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Bethe-Salpeter Calculation