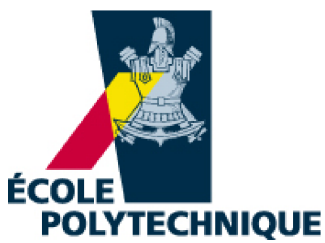
Optical properties of SnO_2

Arjan Berger

Laboratoire des Solides Irradiés
Ecole Polytechnique, Palaiseau, France
European Theoretical Spectroscopy Facility (ETSF)

Moving theory to applications, 22-10, Palaiseau

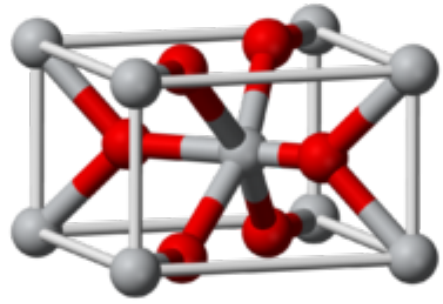


Outline

- SnO_2 facts
- Motivation
- Results
- Conclusions

SnO_2

- Crystal Structure: Rutile
- Band gap: 3.6 eV
- Optical gap: 3.9 eV
- "Color": Transparent
  (visible: 1.5 - 3.5 eV)



Doped with Sb or F ions SnO_2 is a transparent conducting oxides (TCO): electroluminescent devices

Motivation

SnO_2 is a prototype material for the development of TCO's.

In reality not always perfectly transparent:

Study optical properties of $SnO_2 \Longrightarrow$ reliable quasiparticle band structure.

Motivation

GW: powerful tool to calculate quasi-particle energies of solids

$$\Sigma = iGW$$

$$W = \epsilon_{RPA}^{-1} v_c$$

$$\epsilon_{RPA} = 1 - v_c \chi^0$$

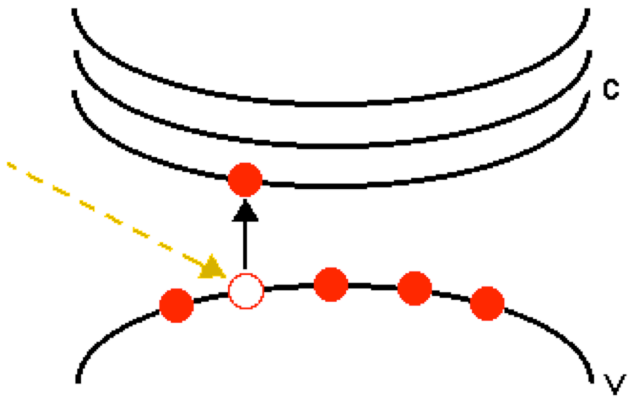
M. van Schilfgaarde, T. Kotani, and S. Faleev, PRL 96, 226402 (2006).

- GW is computationally demanding.
- Large number of empty states in SOS expressions for χ^0 and Σ.

The Polarizability

Standard calculation of χ^0 and Σ: sum over states (SOS)

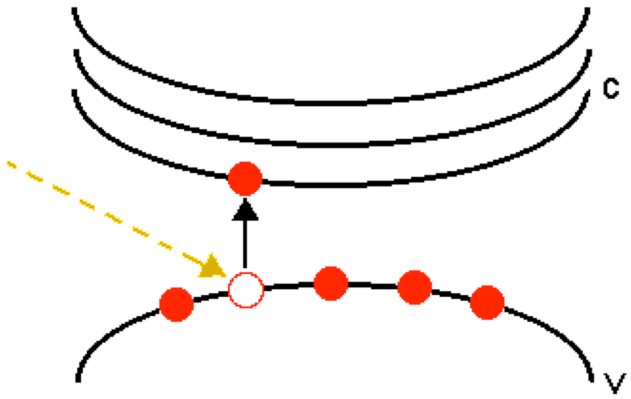
$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \sum_{v}^{occ} \sum_{c}^{empty} \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v\rangle}{\omega - (\epsilon_c - \epsilon_v) + i\eta} + A.R.$$



The Polarizability

Standard calculation of χ^0 and Σ: sum over states (SOS)

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \sum_{v}^{occ} \sum_{c}^{empty} \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v\rangle}{\omega - (\epsilon_c - \epsilon_v) + i\eta} + A.R.$$



Advantages:

- Systematic and controllable
- Easy to implement

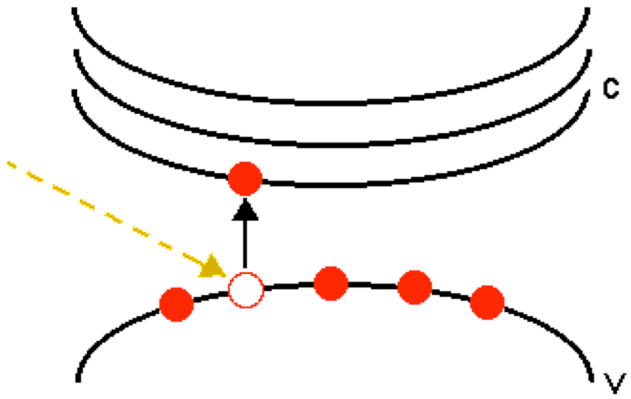
Disadvantages:

- Huge summation over empty states
- Slow (scaling=$N_c N_v N_{\mathbf{G}}^2$)

The Polarizability

Standard calculation of χ^0 and Σ: sum over states (SOS)

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \sum_{v}^{occ} \sum_{c}^{empty} \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v\rangle}{\omega - (\epsilon_c - \epsilon_v) + i\eta} + A.R.$$



Advantages:

- Systematic and controllable
- Easy to implement

Disadvantages:

- Huge summation over empty states
- Slow (scaling=$N_c N_v N_{\mathbf{G}}^2$)

Aim:
- Keep advantages of SOS
- Get rid of disadvantages: occupied states only

Four Criteria for *GW*

- Systematic and controllable
- Easy to implement
- No summation over empty states
- Better scaling properties than SOS

Four Criteria for *GW*

- Systematic and controllable
- Easy to implement
- No summation over empty states
- Better scaling properties than SOS

Other *GW* approaches with less or no empty states:

COHSEX:	L. Hedin, PR A796 (1965)
Extrapolar method:	F. Bruneval and X. Gonze, PRB 78, 085125 (2008).
Sternheimer equation:	L. Reining *et al.*, PRB 56, R4302 (1997) P. Umari *et al.*, PRB 81 115104 (2010) F. Giustino *et al.*, PRB 81 115105 (2010)

Four Criteria for *GW*

- Systematic and controllable
- Easy to implement
- No summation over empty states
- Better scaling properties than SOS

Other *GW* approaches with less or no empty states:

COHSEX:	L. Hedin, PR A796 (1965)
Extrapolar method:	F. Bruneval and X. Gonze, PRB 78, 085125 (2008).
Sternheimer equation:	L. Reining *et al.*, PRB 56, R4302 (1997) P. Umari *et al.*, PRB 81 115104 (2010) F. Giustino *et al.*, PRB 81 115105 (2010)

So far: no *GW* approach which satisfies all criteria simultaneously

Σ_{GW} with sum over occupied states only

The bottleneck in the calculation of Σ_{GW}:

$$\langle n|\Sigma_c^{empty}(\omega)|n\rangle = \sum_{\mathbf{q},\mathbf{G},\mathbf{G}'} \sum_j W^j_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) \sum_c^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c}$$

Σ_{GW} with sum over occupied states only

The bottleneck in the calculation of Σ_{GW}:

$$\langle n|\Sigma_c^{empty}(\omega)|n\rangle = \sum_{\mathbf{q},\mathbf{G},\mathbf{G}'} \sum_j W^j_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) \sum_c^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c}$$

There exists an effective energy $\delta_{nj}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega)$ such that

$$\sum_c^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c} = \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\left(\sum_c^{empty}|c\rangle\langle c|\right)e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \delta_{nj}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega)}$$

Closure relation: $\sum_c^{empty}|c\rangle\langle c| = 1 - \sum_v^{occ}|v\rangle\langle v|$

Σ_{GW} with sum over occupied states only

The bottleneck in the calculation of Σ_{GW}:

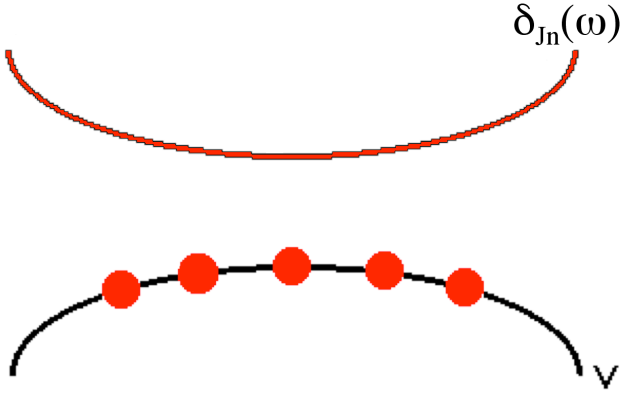
$$\langle n|\Sigma_c^{empty}(\omega)|n\rangle = \sum_{\mathbf{q},\mathbf{G},\mathbf{G}'} \sum_j W^j_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) \sum_c^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c}$$

There exists an effective energy $\delta_{nj}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega)$ such that

$$\sum_c^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c} = \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\left(\sum_c^{empty}|c\rangle\langle c|\right)e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \delta_{nj}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega)}$$

Closure relation: $\sum_c^{empty}|c\rangle\langle c| = 1 - \sum_v^{occ}|v\rangle\langle v|$

$\Longrightarrow$



EET: Effective Energy Technique

A hierarchy of approximations for δ_{nj}

An iterative scheme leads to simple approximations for $\delta_{nj}(\omega)$ ($\mathbf{G} = \mathbf{G}'$):

$$\delta_n^{(0)} = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2}$$

$$\delta_n^{(1)} = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}}$$

$$\delta_{nj}^{(2)}(\omega) = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}} \frac{\omega - \omega_j - \left[\epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}}\right]}{\omega - \omega_j - \left[\epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{jj}}{f_n^{\rho j}}\right]}$$

A hierarchy of approximations for δ_{nj}

An iterative scheme leads to simple approximations for $\delta_{nj}(\omega)$ ($\mathbf{G} = \mathbf{G}'$):

$$\delta_n^{(0)} = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2}$$

$$\delta_n^{(1)} = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}}$$

$$\delta_{nj}^{(2)}(\omega) = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}} \frac{\omega - \omega_j - \left[\epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}}\right]}{\omega - \omega_j - \left[\epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{jj}}{f_n^{\rho j}}\right]}$$

-The $f_n^{\rho\rho}, f_n^{\rho j}, f_n^{jj}, \cdots$ are simple with sums over occupied states only.

$$f_n^{\rho j} = \left[\langle n|i\nabla|n\rangle - \sum_v^{occ} \langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|v\rangle\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}[i\nabla]|n\rangle\right] \cdot (\mathbf{q}+\mathbf{G})$$

-From $\delta_n^{(1)}$ onwards exact for the homogeneous electron gas.
-$\delta_{nj}^{(2)}(\omega)$ simple but nontrivial due to frequency dependence.

Getting δ

Starting from the definition:

$$S \equiv \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c} = \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \delta}$$

Getting δ

Starting from the definition:

$$S \equiv \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c} = \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \delta}$$

Rearranging:

$$\delta = \epsilon_n + \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle(\epsilon_c - \epsilon_n)}{\omega - \omega_j - \epsilon_c} / S$$

Getting δ

Starting from the definition:

$$S \equiv \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c} = \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \delta}$$

Rearranging:

$$\delta = \epsilon_n + \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle(\epsilon_c - \epsilon_n)}{\omega - \omega_j - \epsilon_c} / S$$

The ϵ_i are eigenvalues of $\hat{H}$ with eigenstates $|i\rangle$:

$$\delta = \epsilon_n + \sum_{c} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|[\hat{H}(\mathbf{r}'), e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}]|n\rangle}{[\omega - \omega_j - \epsilon_c]} / S$$

Getting δ

Starting from the definition:

$$S \equiv \sum_c^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} = \sum_c^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\delta}$$

Rearranging:

$$\delta = \epsilon_n + \sum_c^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle(\epsilon_c-\epsilon_n)}{\omega-\omega_j-\epsilon_c}/S$$

The ϵ_i are eigenvalues of $\hat{H}$ with eigenstates $|i\rangle$:

$$\delta = \epsilon_n + \sum_c \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|[\hat{H}(\mathbf{r}'),e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}]|n\rangle}{[\omega-\omega_j-\epsilon_c]}/S$$

Working out the commutator:

$$[\hat{H}(\mathbf{r}),e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}] = e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\left[\frac{|\mathbf{q}+\mathbf{G}|^2}{2}+(\mathbf{q}+\mathbf{G})\cdot i\nabla\right]$$

we obtain

$$\delta = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \sum_c \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}[i\nabla]|n\rangle\cdot(\mathbf{q}+\mathbf{G})}{[\omega-\omega_j-\epsilon_c]}/S$$

The Polarizability

We can apply a similar approach to the polarizability

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \sum_{v}^{occ} \sum_{c}^{empty} \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v\rangle}{\omega - (\epsilon_c - \epsilon_v) + i\eta} + A.R.$$

The Polarizability

We can apply a similar approach to the polarizability

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \sum_{v}^{occ} \sum_{c}^{empty} \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v\rangle}{\omega - (\epsilon_c - \epsilon_v) + i\eta} + A.R.$$

This can be rewritten as:

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \sum_{v} \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \left(\sum_c^{empty} |c\rangle\langle c|\right) e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v\rangle}{\omega - (\delta'_v(\mathbf{q},\mathbf{G},\mathbf{G}',\omega) - \epsilon_v) + i\eta} + A.R.$$

$$\Longrightarrow$$

Band Structure of Solid Argon: G^0W^0

Black: SOS; Red: EET; Blue: LDA

SnO_2: Band gap

	LDA	G^0W^0 (SOS)	G^0W^0 (EET)	Experiment
SnO_2 (E_g)	0.91	2.88	2.94	3.6

SOS: 1600 bands (Σ) EET: 34 valence bands

SnO_2: Band gap

	LDA	G^0W^0 (SOS)	G^0W^0 (EET)	Experiment
SnO_2 (E_g)	0.91	2.88	2.94	3.6

SOS: 1600 bands (Σ) EET: 34 valence bands

- Good agreement between SOS approach and EET.
- G^0W^0 band gaps not in agreement with experiment.

SnO_2: Band gap

	LDA	G^0W^0 (SOS)	G^0W^0 (EET)	Experiment
SnO_2 (E_g)	0.91	2.88	2.94	3.6

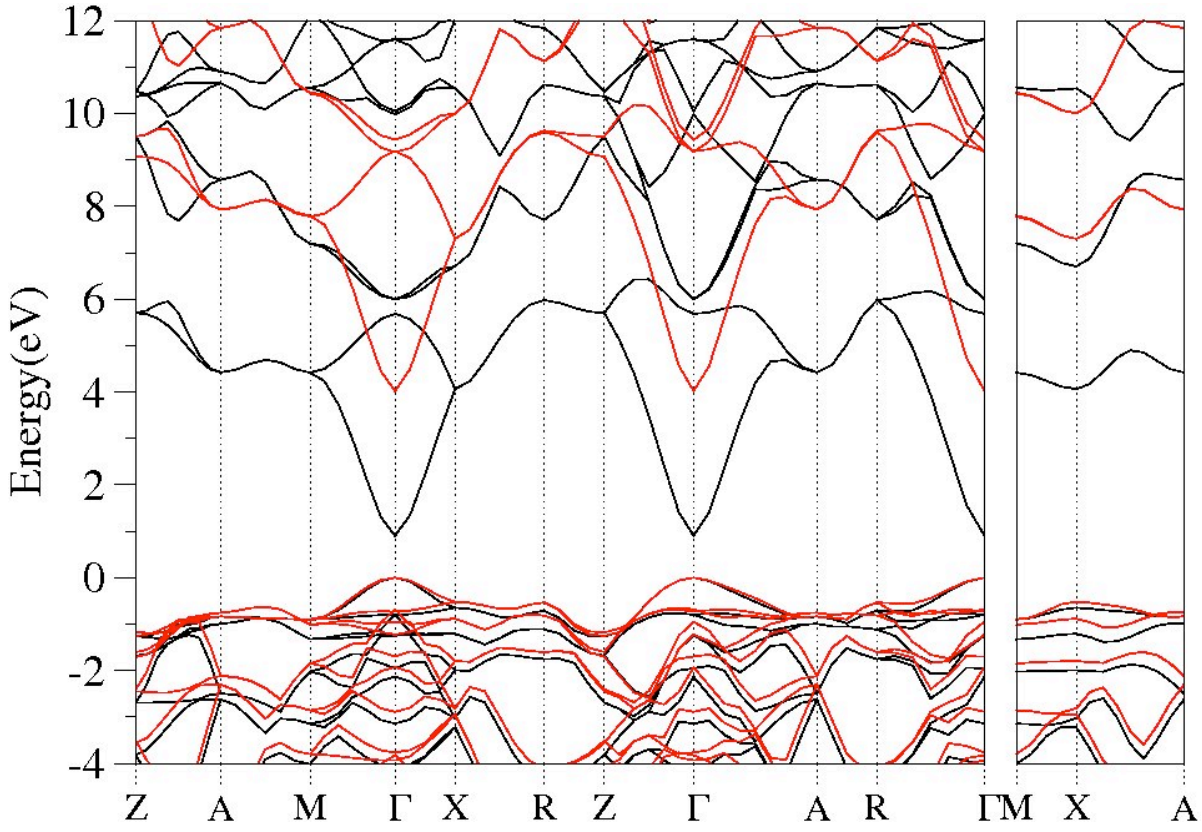
SOS: 1600 bands (Σ) EET: 34 valence bands

- Good agreement between SOS approach and EET.
- G^0W^0 band gaps not in agreement with experiment.

Include self-consistency:
GW = self-consistent COHSEX + G^0W^0 (*Bruneval et al. PRB (2006)*)

	LDA	GW(EET)	Experiment
SnO_2 (E_g)	0.91	3.8	3.6

SnO_2: Band structure



Black: LDA; Red: *GW*(*EET*)

Conclusions and Outlook

- With the EET we can perform GW calculations with occupied states only.
- The approach is simple with immediate speed ups of at least an order of magnitude for any system size.
- Our approach is general and can be applied to any spectral representation.
- EET for GW implemented in ABINIT 6.4
- Potential future applications include:
  - Self-consistency beyond COHSEX: updating only occupied states.
  - RPA total energies
  - optimized effective potentials and kernels.

JAB, L. Reining, F. Sottile, Phys. Rev. B 82, 041103(R) (2010)

SnO_2: Absorption tail