Quasiparticle spectrum and optical properties of SnO_2

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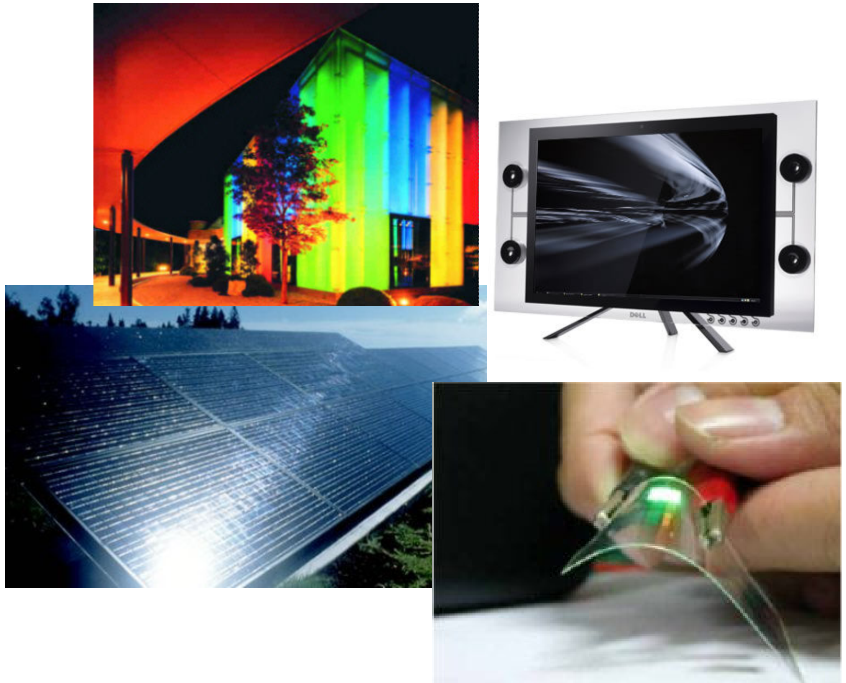
Outline

- Introduction
- Electronic structure
- Optical absorption
- Quasiparticle spectrum of SnO_2
- Pressure effects
- Scalar relativistic pseudopotential
- Optical properties
- Conclusions and outlook

Introduction

Transparent conducting oxides:
- band gap ≥ 2 eV
- resistivity ≤ 10^{-4} Ω cm and μ ≥ 50 cm^2/V s

SnO_2:
- band gap ~ 3.6 eV[1]
- Ta-doped[2] resistivity ~ 2 x 10^{-4} Ω cm … and μ ~ 60 cm^2/V s

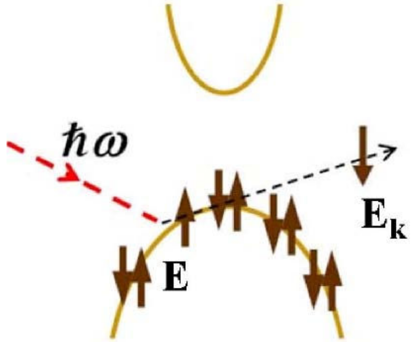


[1]M. Nagasawa and S. Shionoya, Phys. Lett. **22**, 409 (1966).
[2]S. Nakao *et al.*, Appl. Phys. Express **3**, 031102 (2010)

Electronic structure

The electron Green function describes the evolution of an excitation

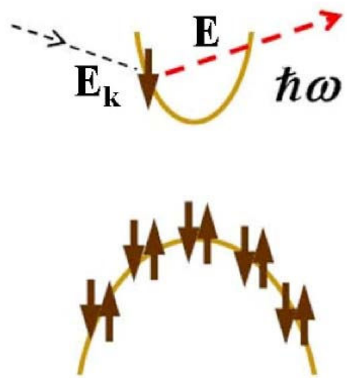
$$G(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = -\frac{i}{\hbar}\langle\Psi_0|T[\hat{\psi}(\mathbf{r}_1, t_1)\hat{\psi}^\dagger(\mathbf{r}_2, t_2)]|\Psi_0\rangle$$



Photoemission: N → N-1

The Green function poles are single-particle excitation energies

$$G(\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{1}{\hbar}\sum_i \frac{\langle\Psi_0^{(N)}|\hat{\psi}(\mathbf{r})|\Psi_i^{(N+1)}\rangle\langle\Psi_i^{(N+1)}|\hat{\psi}^\dagger(\mathbf{r}')|\Psi_0^{(N)}\rangle}{\hbar\omega - \epsilon_i^{(N+1)} + i\eta} + \frac{1}{\hbar}\sum_i \frac{\langle\Psi_0^{(N)}|\hat{\psi}^\dagger(\mathbf{r}')|\Psi_i^{(N-1)}\rangle\langle\Psi_i^{(N-1)}|\hat{\psi}(\mathbf{r})|\Psi_0^{(N)}\rangle}{\hbar\omega - \epsilon_i^{(N-1)} - i\eta}.$$



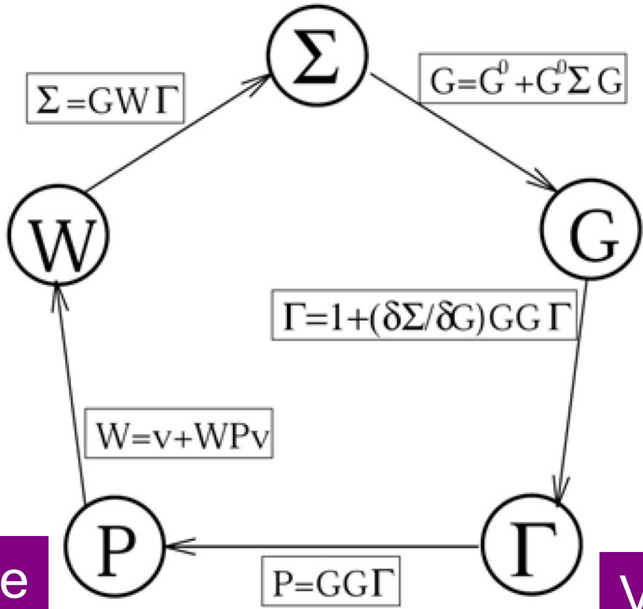
Inverse photoemission:
N → N+1

Hedin equations & GW approximation[1,2]

Self-energy: scattering and energy corrections

Screened Coulomb interaction

Green function: excitation evolution



Polarizability: due to the excitations

Vertex function: electron-hole interactions

[1]L. Hedin, Phys. Rev. **139**, A796 (1965).
[2]W. G. Aulbur, L. Jönsson, and J. W. Wilkins, Solid State Phys. **54**, 1 (1999).

GW scheme

From the Dyson equation

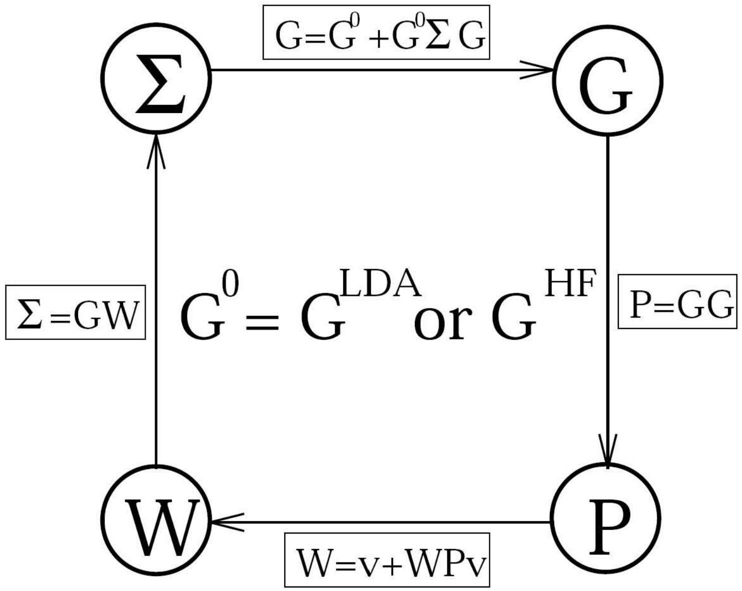
$$\mathcal{H}_0(\mathbf{r})\psi_j(\mathbf{r}) + \int d^3r' \hbar\Sigma^*(\mathbf{r},\mathbf{r}';\epsilon_j)\psi_j(\mathbf{r}') = \epsilon_j\psi_j(\mathbf{r}).$$

DFT-local density approx.

$$\Sigma(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}')V_{\mathrm{xc}}(\mathbf{r})$$

"GW" approximation

$\Gamma = 1$ => $\Sigma = GW$



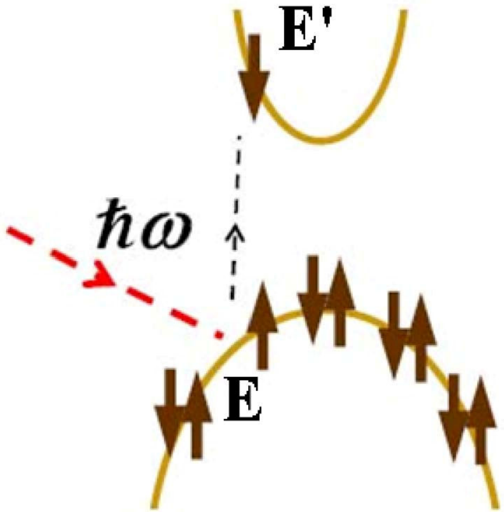
[1]From W. G. Aulbur, L. Jönsson, and J. W. Wilkins, Solid State Phys. **54**, 1 (1999).

Optical absorption

- Macroscopic dielectric function

$$\varepsilon_M(\omega) \equiv \lim_{\mathbf{q}\to 0} \frac{1}{\varepsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)},$$

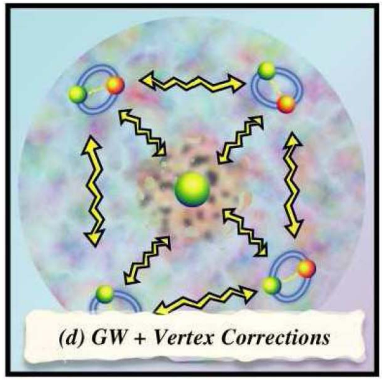
$$= 1 - \lim_{\mathbf{q}\to 0} [v(\mathbf{q})_0 \bar{P}_{\mathbf{G}=\mathbf{G}'=0}(\mathbf{q},\omega)]$$



Photoabsorption: two-particle excitation process ...
but the GW polarizability does not contain electron-hole interactions!

• Bethe-Salpeter

Vertex corrections:



[1]

$$\frac{\delta\Sigma(12)}{\delta G(45)} \simeq i\hbar\delta(14)\delta(25)W(1^{+}2)$$

=> Bethe-Salpeter equation for the polarisabilty

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

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

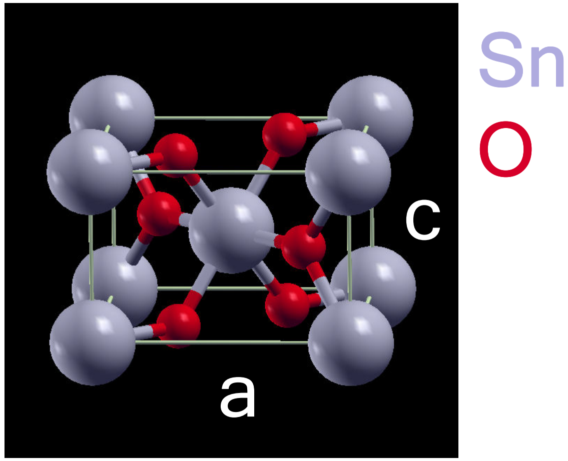
^{4}P = "4-point" polarisability
$^{4}P_{IQP}$ = independent quasiparticle polarisability
v = bare Coulomb interaction
W = dinamically screened Coulomb interaction

[1]From A. J. Morris, M.Sc.Thesis,University of York, 2006.

Quasiparticle spectrum of SnO_2

- DFT calculations

22e PP required: [Ge]$4s^2 4p^6 4d^{10} 5p^2 5s^2$
(Opium code[1]) ... 105 Ha ecut!



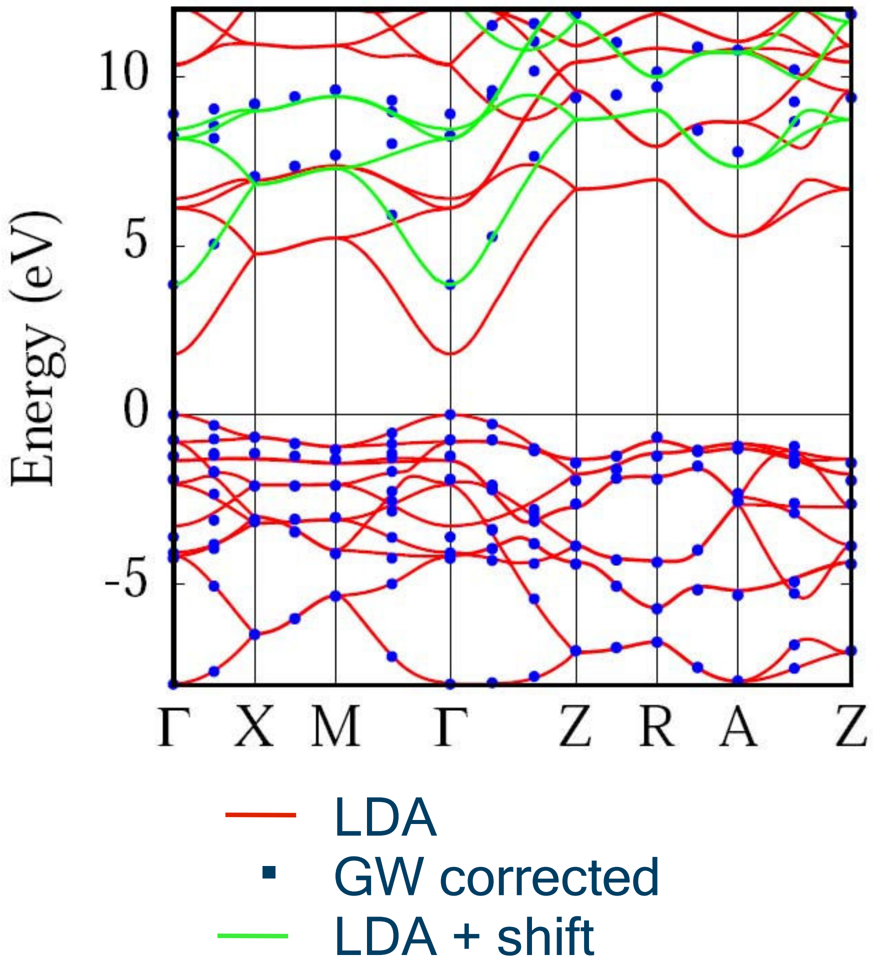
SnO_2 structure:
Rutile ($P4_2mnm$)

Structural properties

	a (Å)	c (Å)	u	B (GPa)
Exp.[2]	4.7374	3.1864	0.30562	212.3[(3)]
Theory	4.7154	3.1864	0.30605	211.7

[1]opium.sourceforge.net/index.html
[2]A. Bolzan *et al.*, Acta Cryst. B**53**, 373 (1997).
[3]E. Chang and E. Graham, J. Geophys. Res. **80**, 2595 (1975).

• Electronic structure



For ref., optical gap at Γ: 3.6 eV

Gap values (eV):

k pt	Γ	X	M	Z
LDA	1.80	5.42	6.17	7.99
GW	3.85	7.69	8.72	10.81
ΔE	2.05	2.27	2.55	2.82

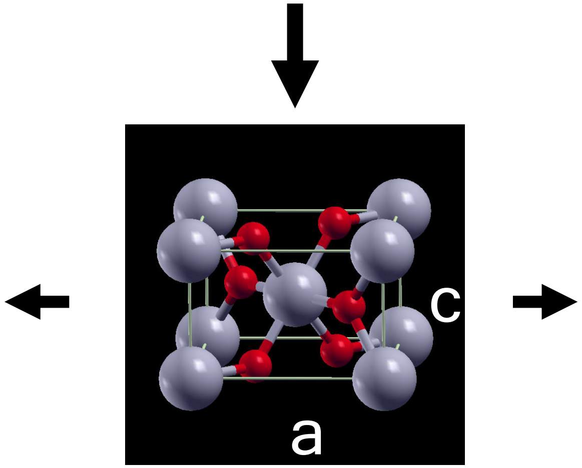
Effective masses (m_e):

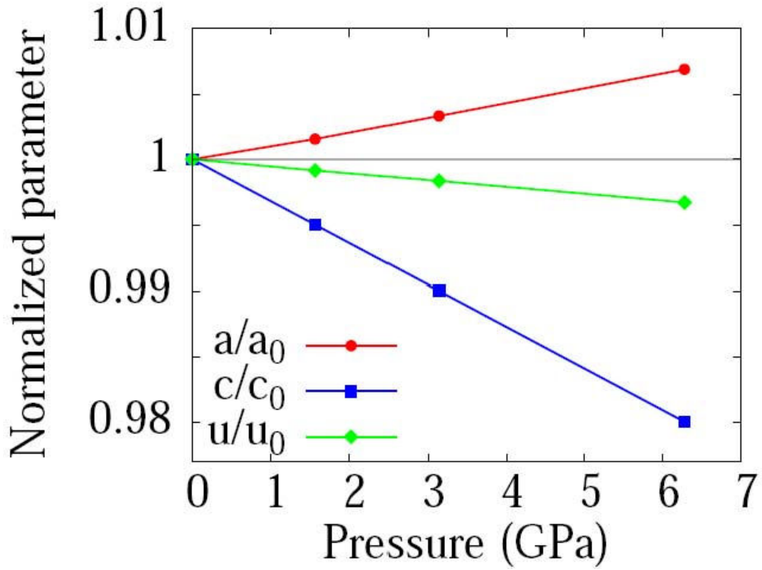
	$m^*_\perp$	$m^*_\parallel$	m^*_p
Exp[1].	0.299	0.234	0.275
Theory	0.253	0.223	0.271

[1]K. Button et al., Phys. Rev. B 4, 4539 (1971).

Pressure effects

Applied uniaxial pressure

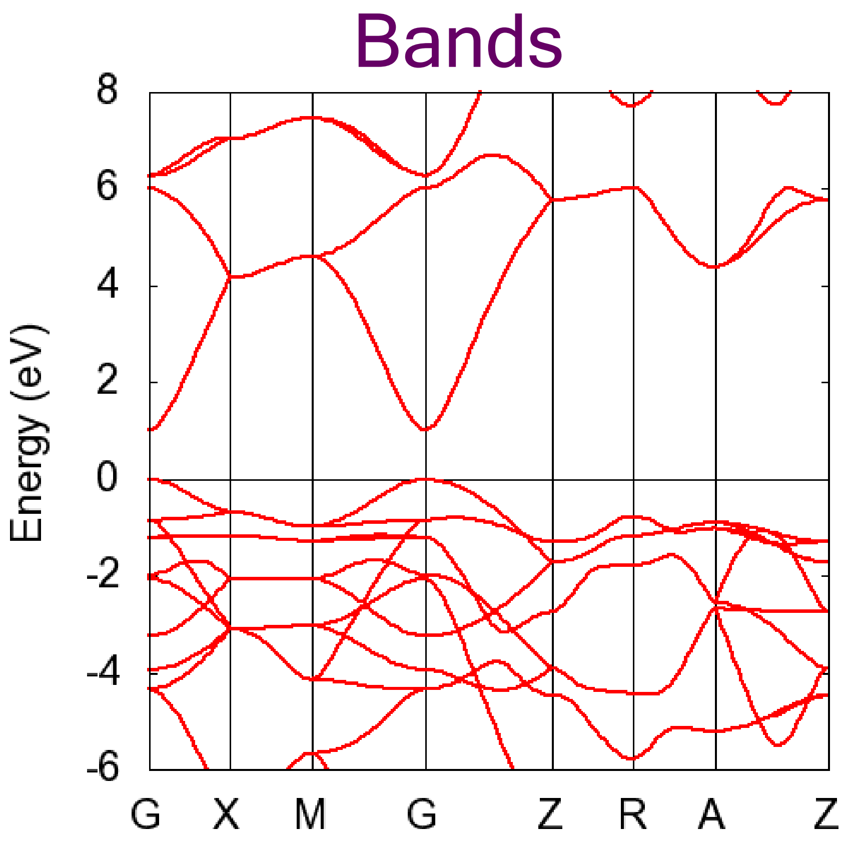


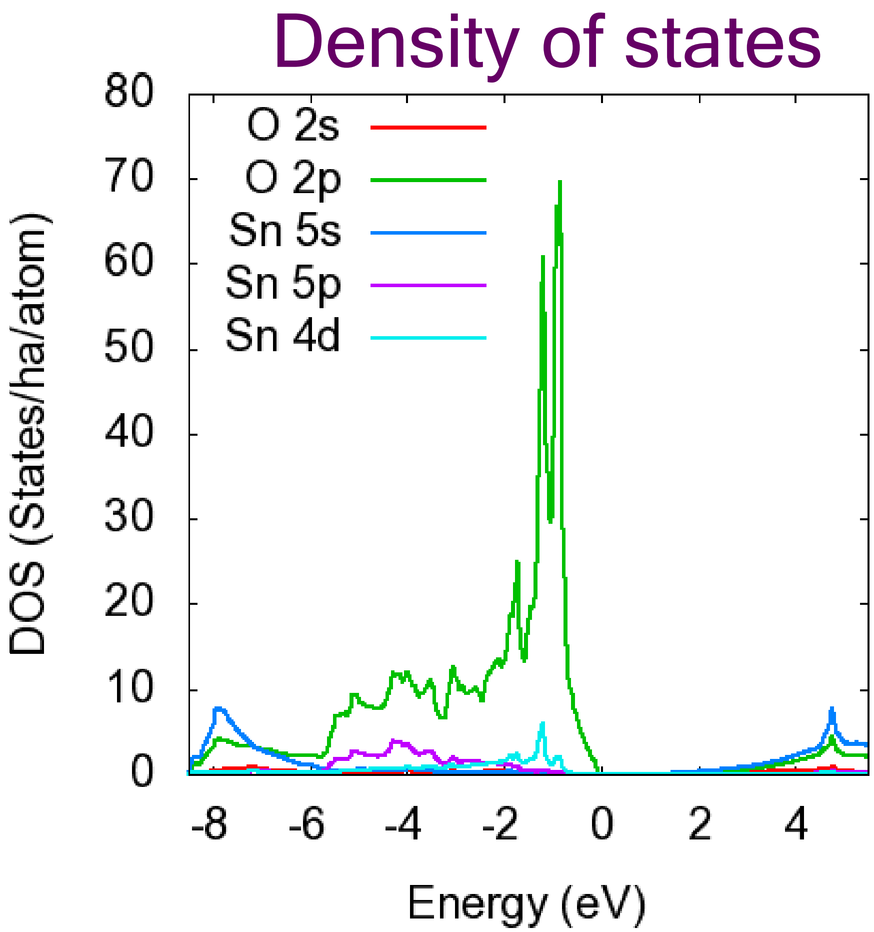


“anaddb”
(35 Gb storage)

	c_{11}	c_{33}	c_{12}	c_{13}	c_{44}	c_{66}	GPa
Exp.[1]	261.7	449.6	177.2	155.5	103.1	207.4	
Theory	274.3	412.5	180.9	149.8	94.3	202.9	
	s_{11}	s_{33}	s_{12}	s_{13}	s_{44}	s_{66}	TPa^{-1}
Theory	6.801	3.186	-3.913	-1.049	10.608	4.929	

[1]E. Chang and E. Graham, J. Geophys. Res. **80**, 2595 (1975).

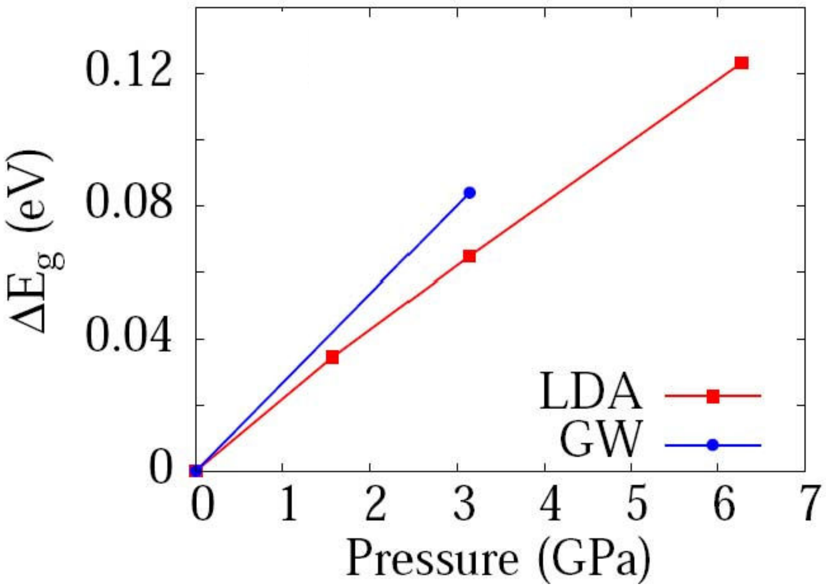

Bands
8
6
4
2
0
-2
-4
-6
Energy (eV)
G
X
M
G
Z
R
A
Z


Density of states
O 2s
O 2p
Sn 5s
Sn 5p
Sn 4d
80
70
60
50
40
30
20
10
0
DOS (States/ha/atom)
-8
-6
-4
-2
0
2
4
Energy (eV)

Pressure and GW

GW corrections at high symmetry k-points

k pt	Γ	X	M	Z
ΔE (P=0)	2.05	2.27	2.55	2.82
ΔE (P=3.1 GPa)	2.08	2.30	2.57	2.84



P_{coeff} GW = 27 meV/GPa

P_{coeff} GW/P_{coeff} GW = 0.74

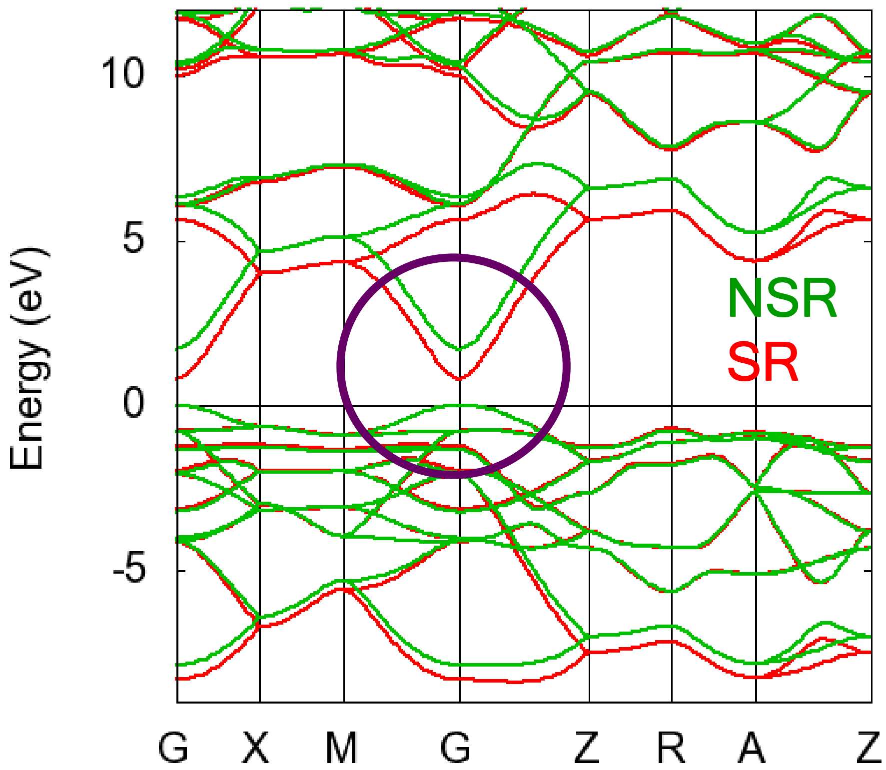
Scalar relativistic pseudopotential

Scalar relativistic effects
⇒ shrinkage of core s and p shells
⇒ change of bandwidths and E_g

Structural parameters

	a (Å)	c (Å)	u
Exp.[2]	4.7374	3.1864	0.30562
Theory	4.7185	3.1849	0.30620

SR E_g = 0.81 eV
(vs 1.80 eV in NSR !)



Elastic constants

	c_{11}	c_{33}	c_{12}	c_{13}	c_{44}	c_{66}
Exp.[1]	261.7	449.6	177.2	155.5	103.1	207.4
Theory	238.7	416.9	177.4	152.8	91.6	204.4
	s_{11}	s_{33}	s_{12}	s_{13}	s_{44}	s_{66}
Theory	9.808	3.281	-6.520	-1.205	10.916	4.892

B_{SR}=202.6 GPa
B_{NSR}=211.7 GPa
B_{exp}=212.3 GPa

GW gaps (eV)

k pt	Γ	X	M	Z
NSR	3.85	7.69	8.72	10.81
SR	2.65	6.75	7.59	9.53

Gaps go down

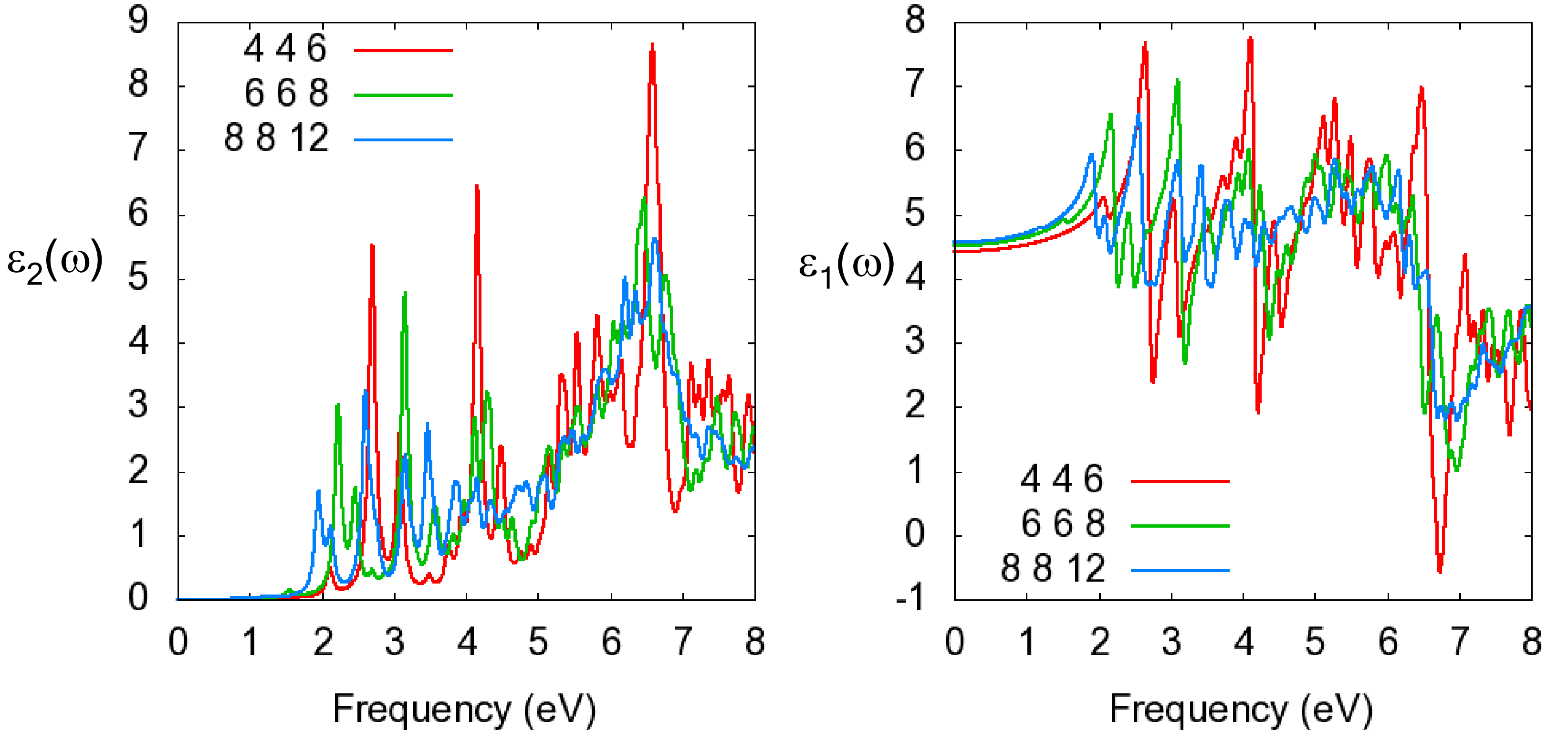
Effective masses (m_e)

	$m^*_\perp$	$m^*_\parallel$	m^*_p
NSR	0.253	0.223	0.271
SR	0.189	0.170	0.204

... and effective masses go down

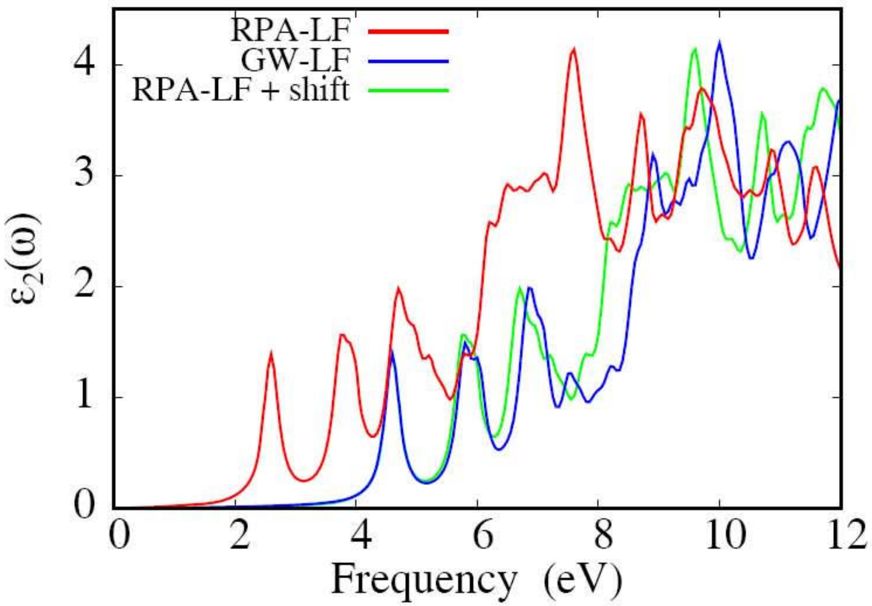
Optical properties

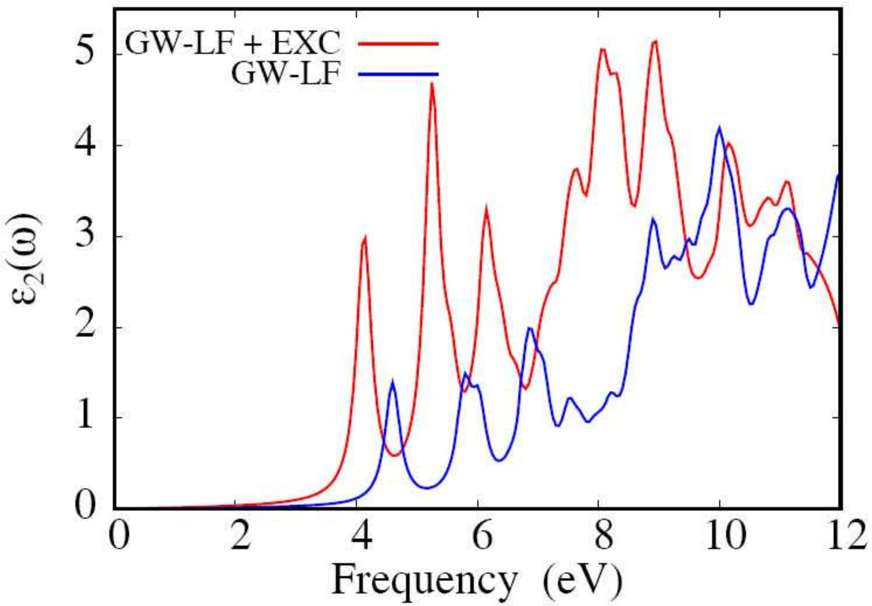
"optic" code



Caution: dense k-point needed (> 5Gb memory/proc.)

Imaginary part of the macroscopic dielectric function: LDA-RPA vs GW-RPA vs Bethe-Salpeter





Absorption edge and structure at higher energies

Absorption edge and structure also at low energies

Conclusions and outlook

- Structural and elastic properties are accurately predicted.
- GW corrections are band and momentum dependent.
- … but require more work: quasi-particle self-consistent calculation (cassiterite_i_SCR = 65 Gb, GW corrections = 11 Gb/proc. with spectral method).
- Bethe-Salpeter shows important excitonic effects.

Future work: Wannier interpolation for GW eigenvalues and LDA for wavefunctions?