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Ab Initio theories to predict ARPES
Hedin's GW and beyond

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European Theoretical Spectroscopy Facility

Nanoquanta
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Many thanks to:

Matteo Gatti, Pierre Darancet,

Fabien Bruneval, Francesco Sottile

and Lucia Reining

Institut NEEL, CNRS, Grenoble, France and

LSI, CNRS - CEA Ecole Polytechnique, Palaiseau France

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Résumé

- Motivation: Electronic Excitations and Spectroscopy
- Many-Body Perturbation Theory and the Hedin's GW approximation -> ARPES
- Non-Equilibrium Green's Function (**NEGF**) theory, GW approximation -> e-e in Quantum Transport
- MBPT using the Density-functional concept: vertex corrections beyond GW.
- Generalized Sham-Schlüter Equation and frequency-dependent effective local potentials.
- Conclusions

The Ground State

Ab initio **DFT** theory well describes (error 1~2%):

- Ground State Total Energy and Electronic Density
- Atomic Structure, Lattice Parameters
- Elastic Constants
- Phonon Frequencies

that is, all the **Ground State** Properties.

Vanadium Oxide, VO_2

		DFT-LDA nlcc	DFT-LDA semic	EXP [Longo et al.]
lattice parameters	a	5.659 Å	5.549 Å	5.7517 ± 0.0030 Å
	b	4.641 Å	4.522 Å	4.5378 ± 0.0025 Å
	c	5.420 Å	5.303 Å	5.3825 ± 0.0025 Å
	α	121.46	121.73°	122.646° ± 0.096

M. Gatti et al.
To be published

Citation Statistics from 110 years of Physical Review

S. Redner, Physics Today June 2005, 49.

DFT Standard Model of Condensed Matter

DFT foundation

Jellium xc calc. and param. for LDA

Table 1. *Physical Review* Articles with more than 1000 Citations Through June 2003

Publication	# cites	Av. age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL **45**, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR **108**, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL **19**, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB **12**, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR **124**, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP **57**, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP **54**, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB **13**, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

LAPW
LMTO

k-points for BZ

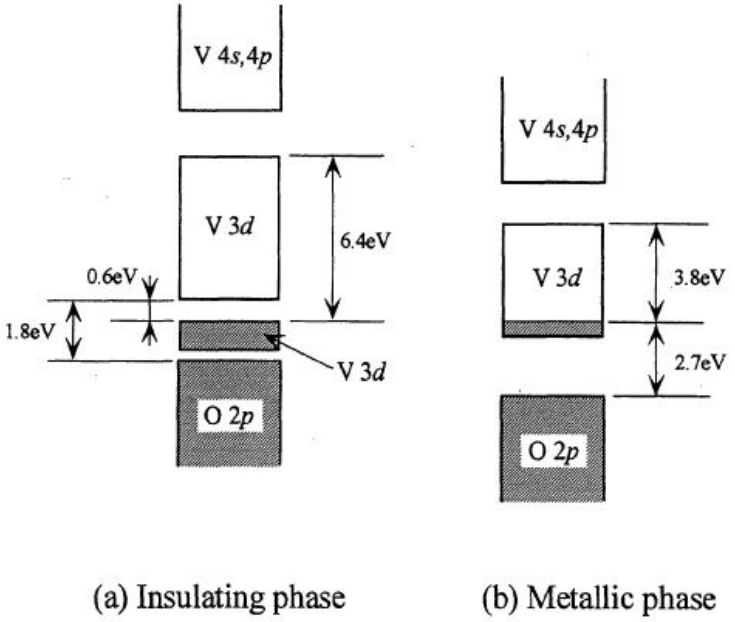
Excited States

But can **DFT** describe the Excited States, such as:

- Band Gap, Band Plot
- Metal/Insulator character
- Spectral Function

?

Vanadium Oxide, VO_2



From H. Abe et al, Jpn. J. Appl. Phys (1997)

Excited States

Answer: NO! DFT **cannot** in principle describe excited states, band gap and so on!

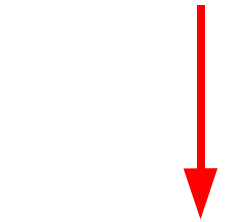
(and it cannot be blamed if it does not succeed)

Nevertheless, be careful:

- DFT for electronic structure -> photoemission spectroscopy
- DFT for optical spectroscopy
- DFT of superconductivity -> superconductivity gap
- DFT-NEGF -> quantum transport

Why we need *ab initio* theories to calculate spectra

1) To understand and explain observed phenomena
2) To offer experimentalists reference spectra
3) To predict properties before the synthesis, the experiment



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Excited States *Ab initio* Theories

- **HF** (Hartree-Fock)**, CI** (Configuration Interaction)
- **QMC** (Quantum Montecarlo)
- **TDDFT** (Time-Dependent Density-Functional Theory)
- **MBPT** (Many-Body Theory) in the Approximation:
  - **GW** ← Photoemission
- **NEGF** (Non-Equilibrium Green's Functions Theory)

Quantum Transport

MBPT and the **GW** approximation

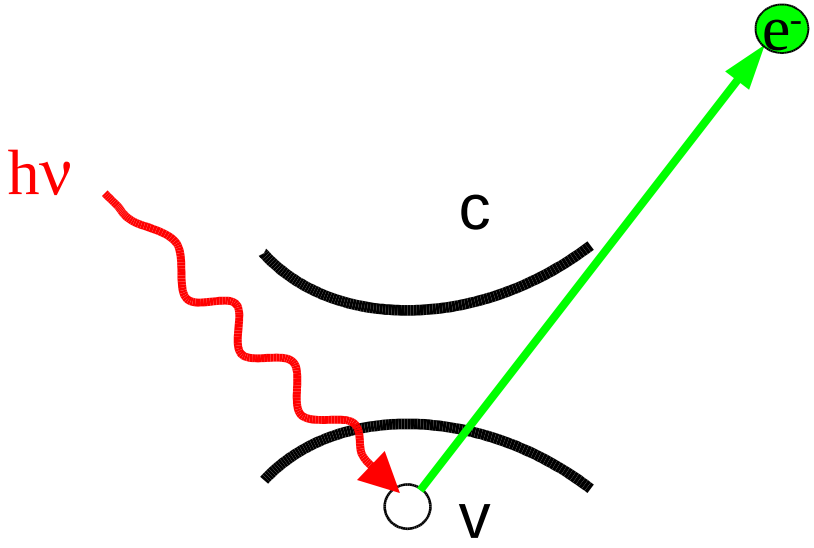
vs

ARPES Photoemission Spectroscopy

(Band Gap, Band Plot, Spectral Function)

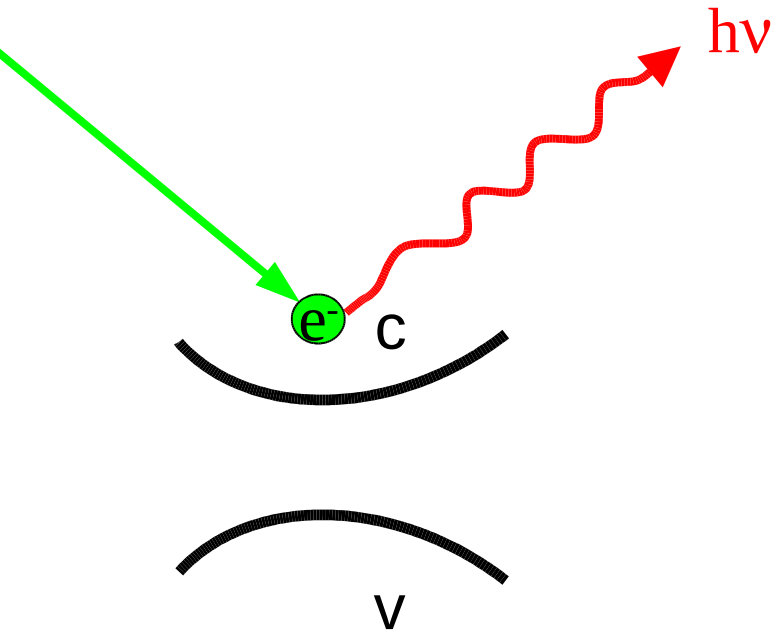
Valerio Olevano, CNRS, Grenoble

Photoemission

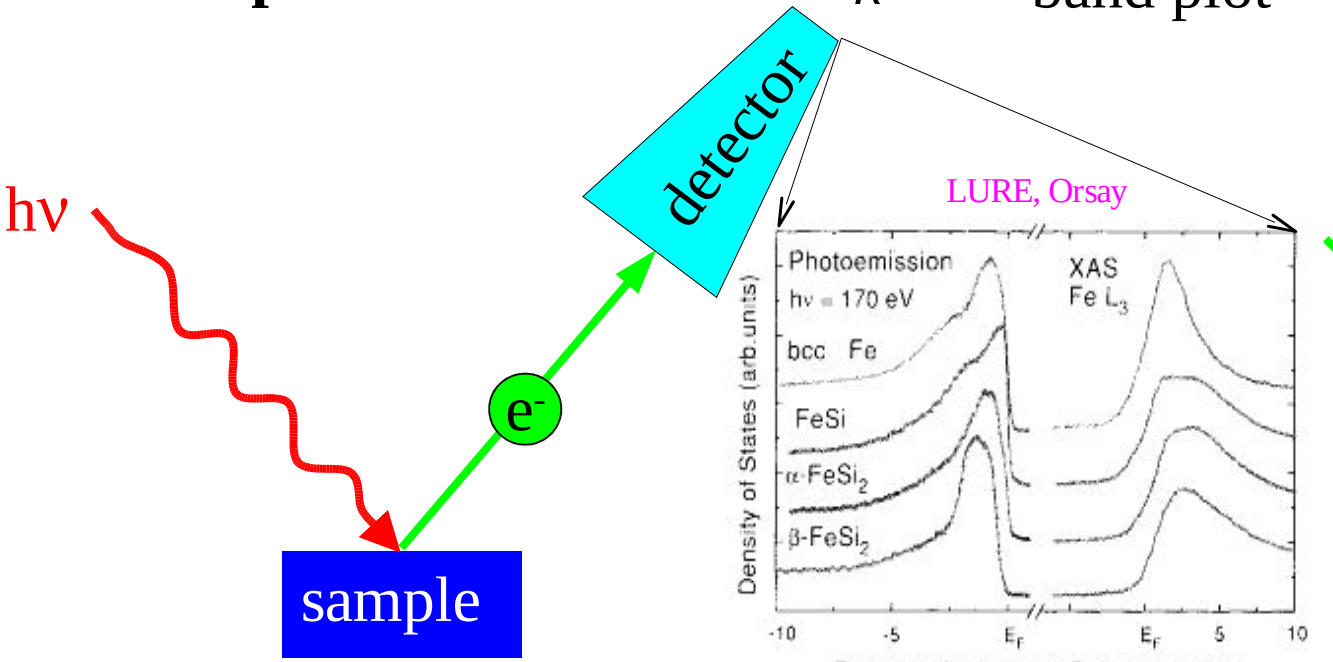


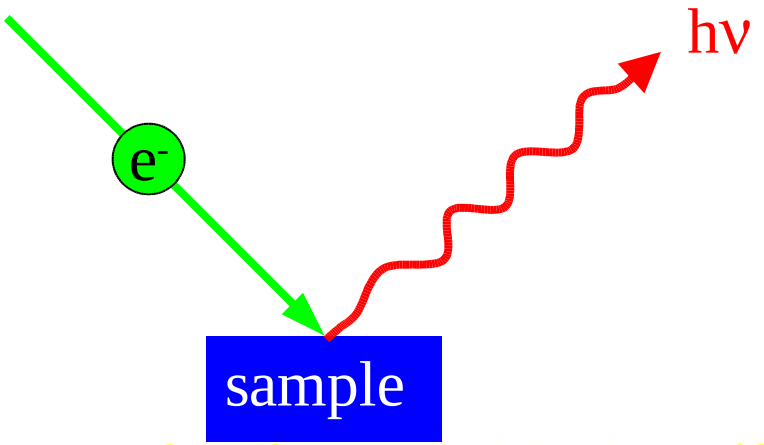
direct photoemission

$$A = \frac{1}{\pi} \left| \Im\, G \right|_{\text{band plot}}^{\text{band gap}}$$



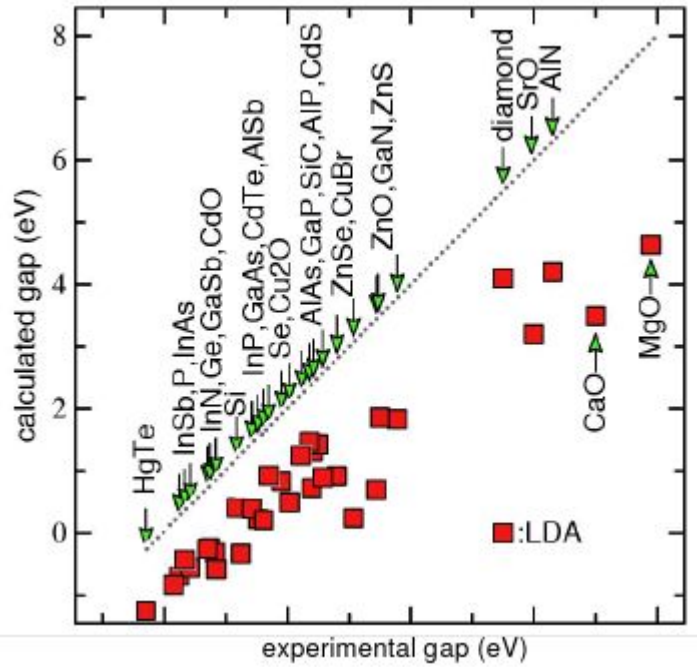
inverse photoemission





Calculating the Band-Gap: inadequacy of HF or DFT

- HF always overestimates the bandgap.
- The Kohn-Sham energies have not an interpretation as removal/addition energies (Kopman Theorem does not hold). If we use them, however we see they are better than HF but the band gap is always underestimated.
- Need to go beyond: MBPT and GW!



	HF	DFT-LDA	EXP
Silicon	5,6	0,55	1,17
Germanium	4,2	0	0,7
Diamond	12,10	4,26	5,48
MgO		5,3	7,83
Sn	2,60	0	0

A. Svane, PRB 1987

What is the MBPT?

- Many-Body "Perturbation" Theory is a **Quantum Field Theory**, based on second quantization of operators and a Green's function formalism.
- Advantages of the Field-Theoretic treatment:
  1. Avoids indices running on the many particles;
  2. Fermionic antisymmetrization automatically imposed;
  3. Treats systems with varying number of particles;
  4. Opens to **Green's functions** or **Propagators** which have condensed inside all the Physics (all the observables) of the system. Spectral Function $A(k,\omega) = \mathrm{Im}\, G(k,\omega)$

$G(x_1,x_2)$ instead of $\Psi(x_1, \ldots, x_N)$

MBPT in brief

- Many-Body “Perturbation” Theory does not work as a Perturbation Theory -the perturbation is not small-
- 1st order MBPT = Hartree-Fock;
- 2^{nd} order not small, the series does not converge -> need to resort to complicated partial resummations of diagrams;
- Better functional and iterative methods: **Hedin equations**.
- Iterative solution of Hedin equations = exact solution of the problem!

Hedin Equations (PR 139, 3453 (1965))

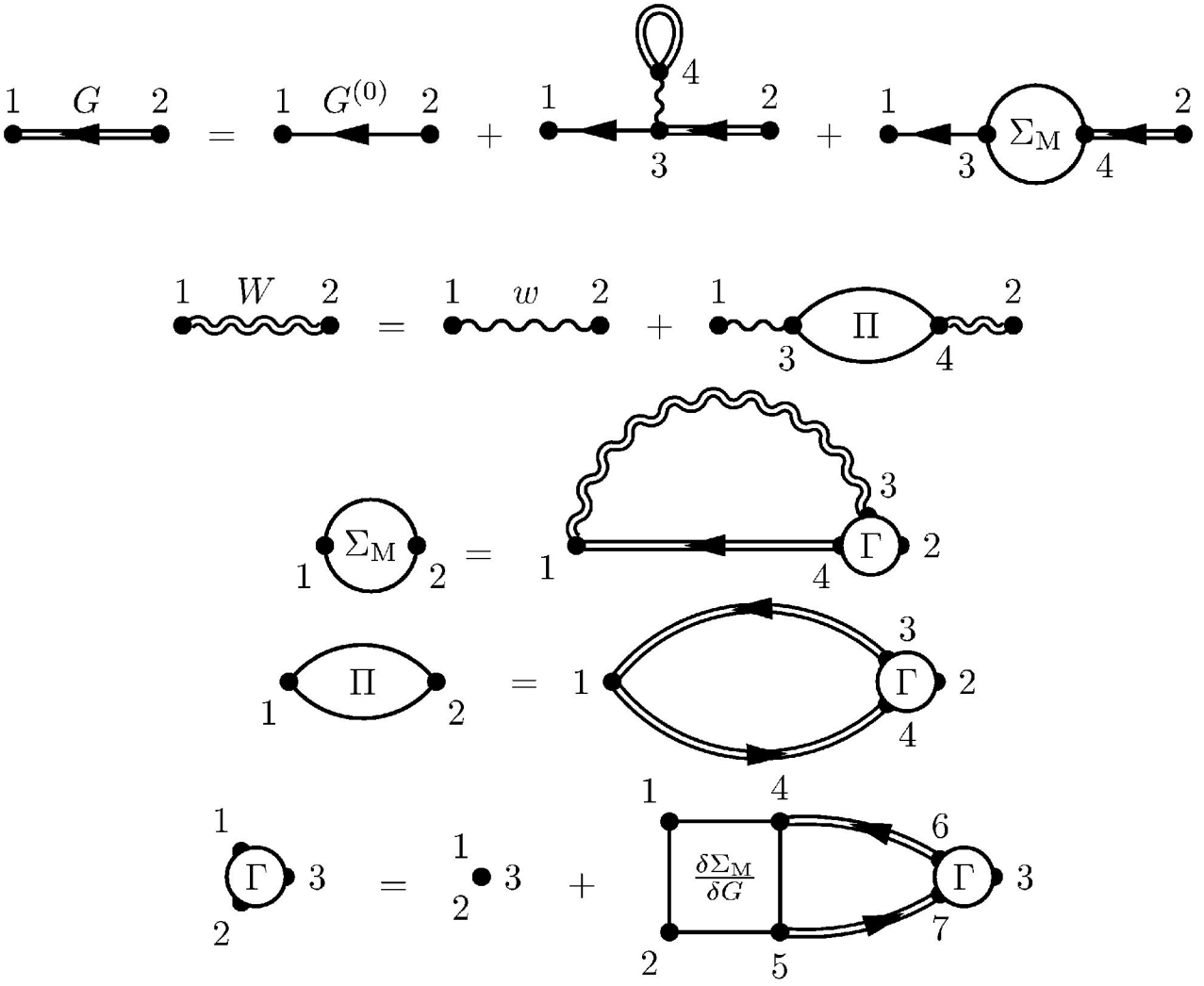
$$G = G^{(0)} + G^{(0)} \Sigma G$$

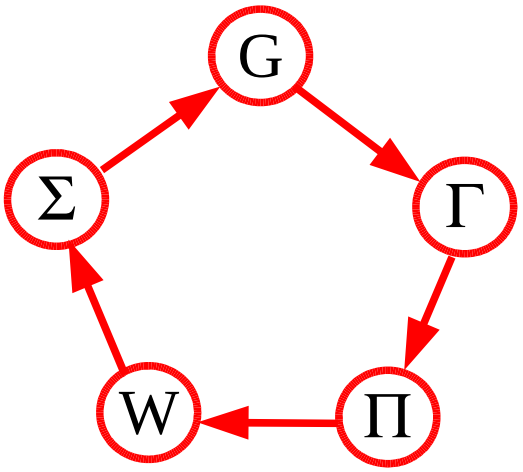
$$W = v + v \Pi W$$

$$\Sigma_M = i G W \Gamma$$

$$\Pi = -i G G \Gamma$$

$$\Gamma = 1 + \frac{\delta \Sigma_M}{\delta G} G G \Gamma$$





- So far, nobody has solved Hedin Equations for a real system
- Need for approximations

Hedin Equations: GW approximation

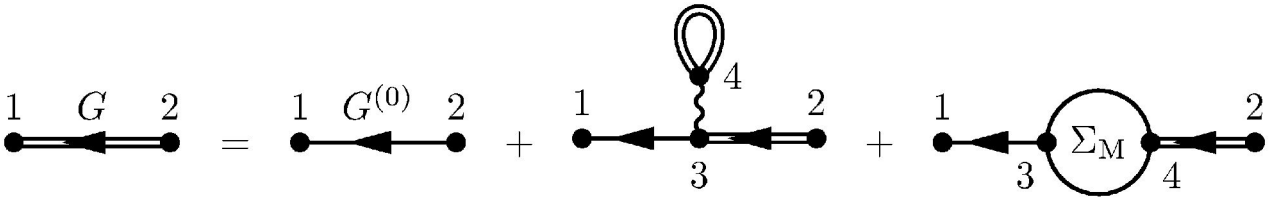
$$G = G^{(0)} + G^{(0)} \Sigma G$$

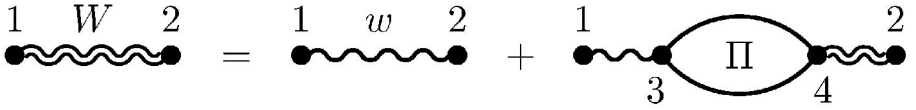
$$W = v + v \Pi W$$

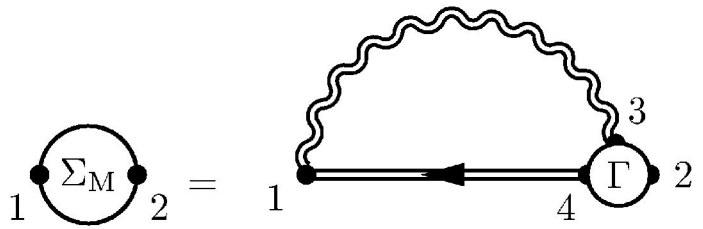
$$\Sigma_M = i G W \Gamma$$

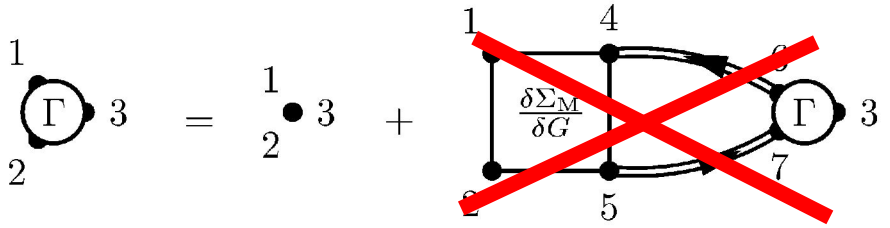
$$\Pi = -i G G \Gamma$$

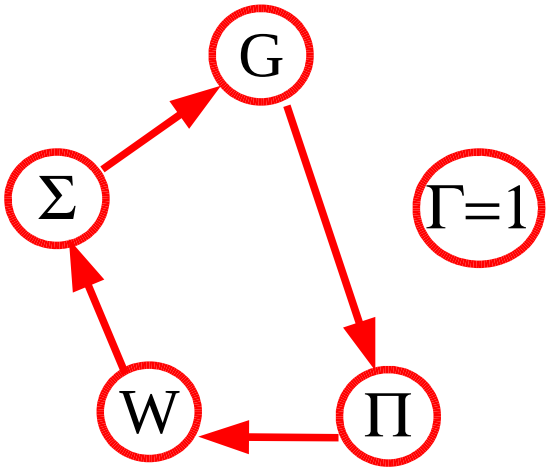
$$\Gamma = 1 + \frac{\delta \Sigma_M}{\delta G} G G \Gamma$$











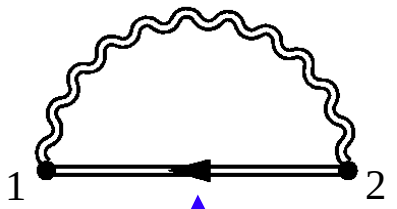
Reviews on GW:
F. Aryasetiawan and O. Gunnarsson, RPP 1998
W.G. Aulbur, L. Jonsson and J.F. Wilkins, 1999

Hedin's GW Approximation for the Self-Energy

GW Self-Energy

Dynamical Screened Interaction W

$$\Sigma^{GW}(x_1, x_2) = iG(x_1, x_2)W(x_1, x_2)$$



Green Function or Electron Propagator G

Hartree-Fock Self-Energy

$$\Sigma_x(x_1, x_2) = iG(x_1, x_2)v(x_1, x_2)$$

Bare Coulombian Potential v

Quasiparticle Energies

KS energies (no physical meaning)

$$\left[-\frac{1}{2}\partial_r^2+v_{ext}(r)+v_H(r)\right]\phi_i(r)+v_{xc}(r)\phi_i(r)=\epsilon_i^{KS}\phi_i(r)$$

Kohn-Sham equation

Exchange-Correlation potential (local)

$$\left[-\frac{1}{2}\partial_r^2+v_{ext}(r)+v_H(r)\right]\phi_i(r)+\int dr'\,\Sigma_x(r,r')\phi_i(r')=\epsilon_i^{HF}\phi_i(r)$$

Hartree-Fock equation

Exchange (Fock) operator **(**non-local)

QP energies

$$\left[-\frac{1}{2}\partial_r^2+v_{ext}(r)+v_H(r)\right]\phi_i(r)+\int dr'\,\Sigma(r,r',\omega=\epsilon_i^{QP})\phi_i(r')=\epsilon_i^{QP}\phi_i(r)$$

Quasiparticle equation

Self-Energy (non-local and energy dependent)

Valerio Olevano, LEPES CNRS, Grenoble

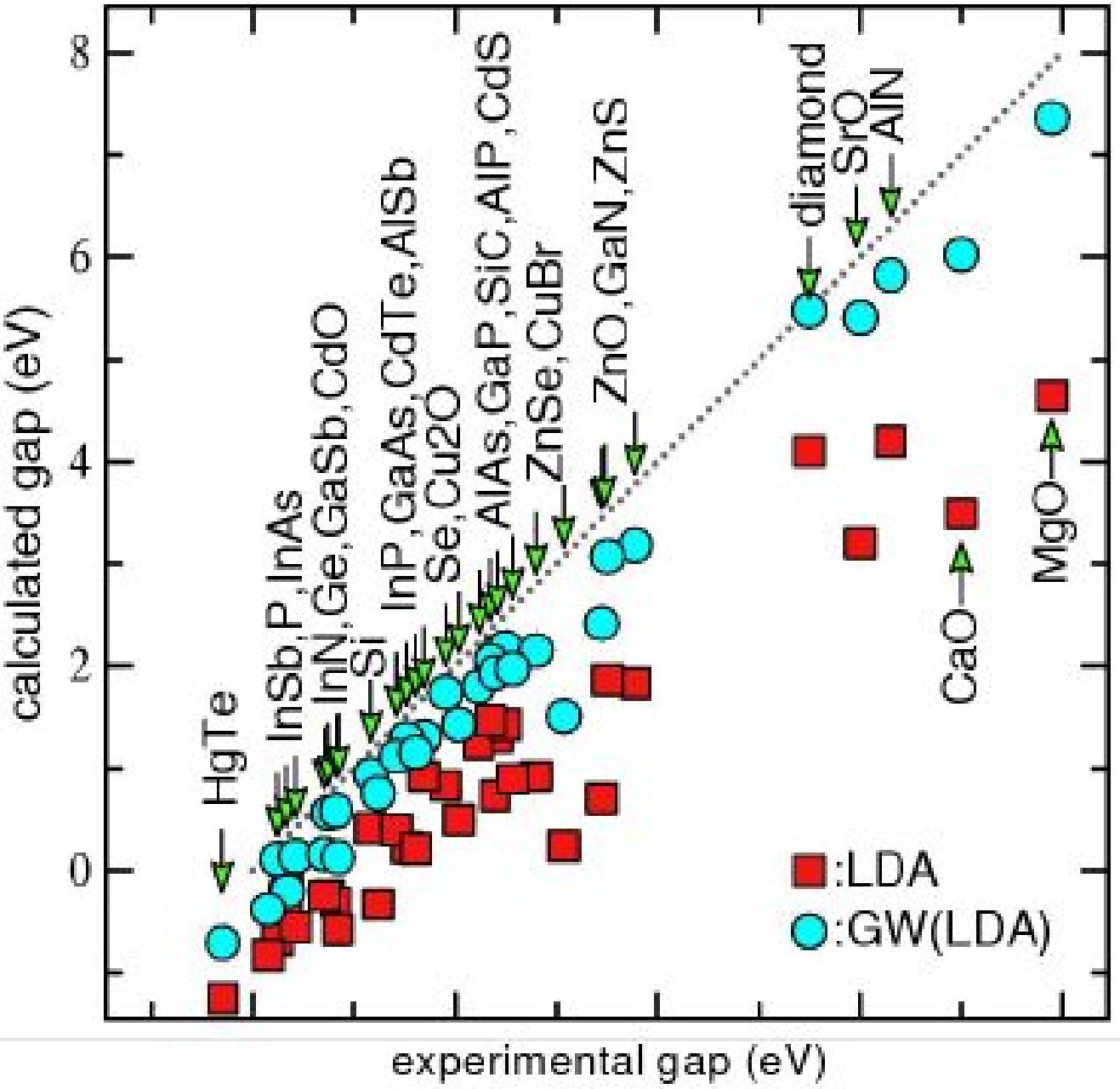
GW and the Photoemission Band Gap

	HF	DFT-LDA	GW	EXP
Silicon	5,6	0,55	1,19	1,17
Germanium	4,2	0	0,6	0,7
Diamond	12,10	4,26	5,64	5,48
MgO		5,3	7,8	7,83
α-Sn	2,60	0		0

Our calculation but reproducing:
M.S. Hybertsen and S.G. Louie (1986)
R.W. Godby, M. Schlueter and L. J. Sham (1987)

- The GW Approximation corrects the LDA band-gap problem (underestimation) and the HF overestimation and it is in good agreement with the Experiment.
- The GW Approximation correctly predicts electron Addition/Removal excitations (Photoemission Spectroscopy).

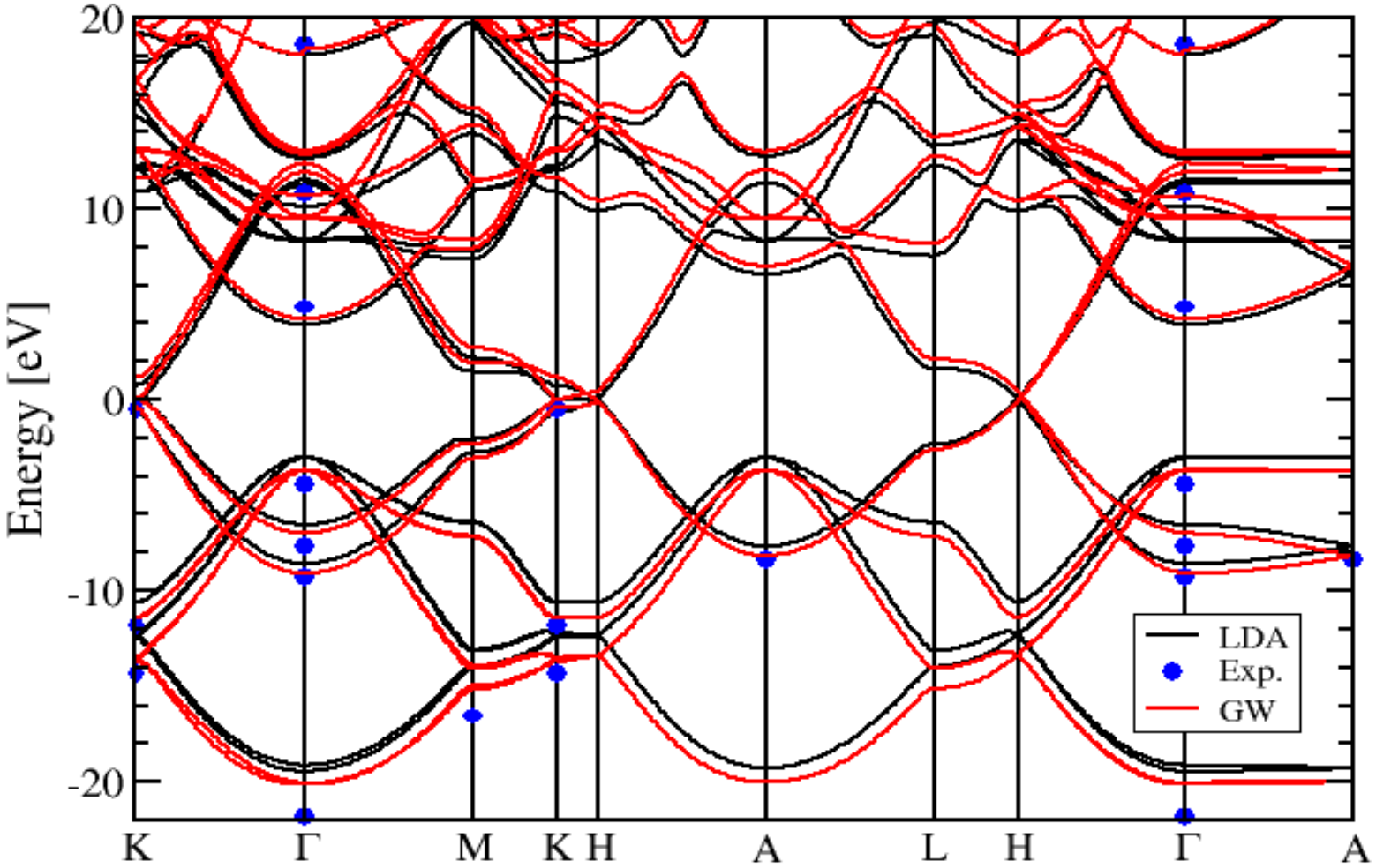
GW and the Photoemission Band Gap



Adapted from Schiffelgard et al. PRL 2006

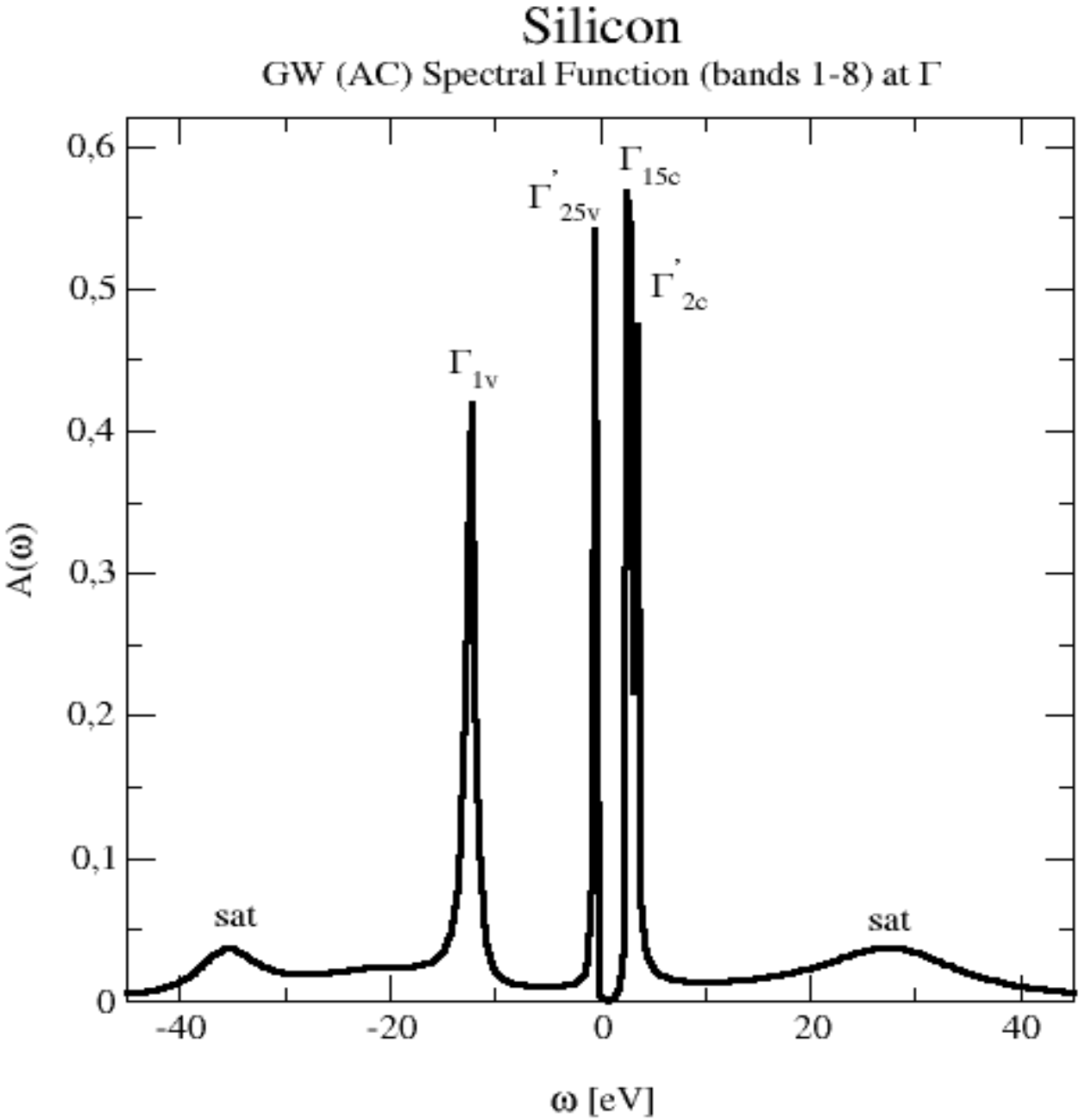
GW band plot

Graphite



J. Serrano et al, unpublished

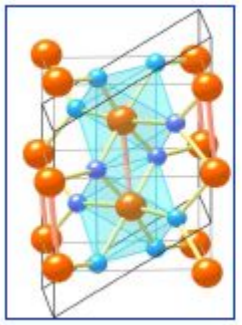
GW spectral function



	GW	EXP
Γ 1v -> Γ'25v	11.73	12.5 ± 0.6
Γ'25v -> Γ 15c	3.23	3.40
Γ'25v -> Γ'2c	3.96	4.2

V. Olevano, unpublished

Vanadium Oxide (VO_2)

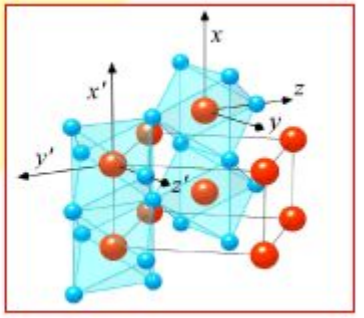


Phase transition at T_C = 340 K

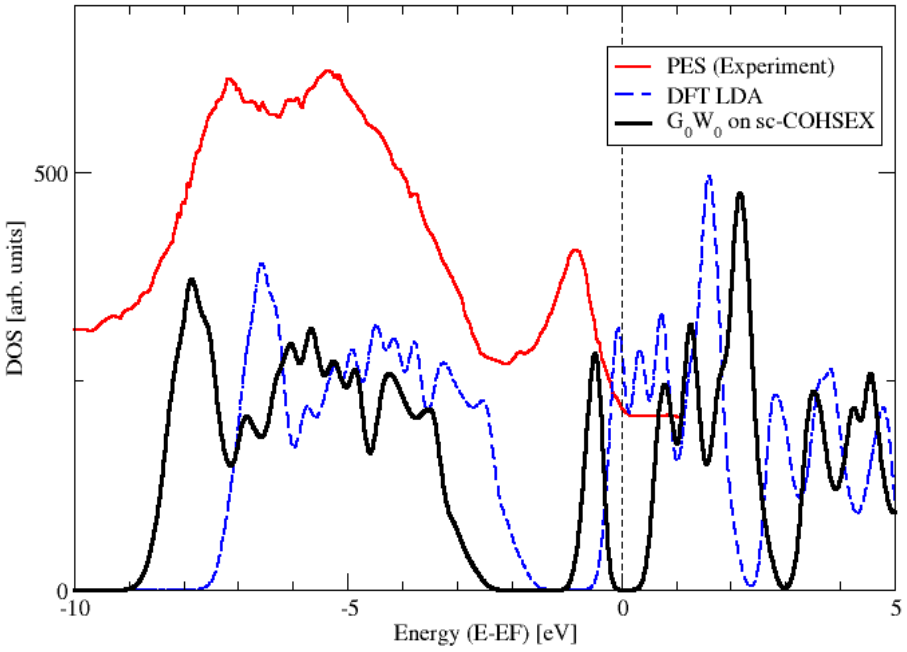
- Monoclinic
- Insulator
- Paramagnetic

- Rutile
- Metal
- Paramagnetic

Mechanism? Role of correlation?
Peierls? or Mott-Hubbard?



Monoclinic VO_2



M. Gatti et al,
to be published

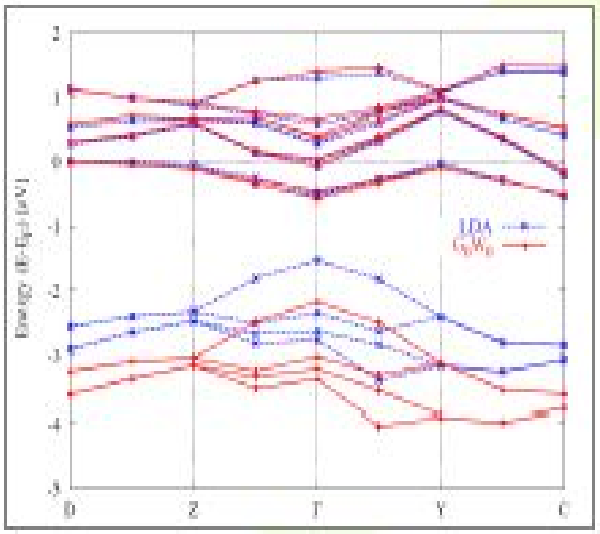
Bandgap	HF	DFT-LDA	SC-COHSEX	GW on SC-COHSEX	EXP
VO2	7,6	0	0,8	0,7	0,6

Vanadium Oxide (VO_2)

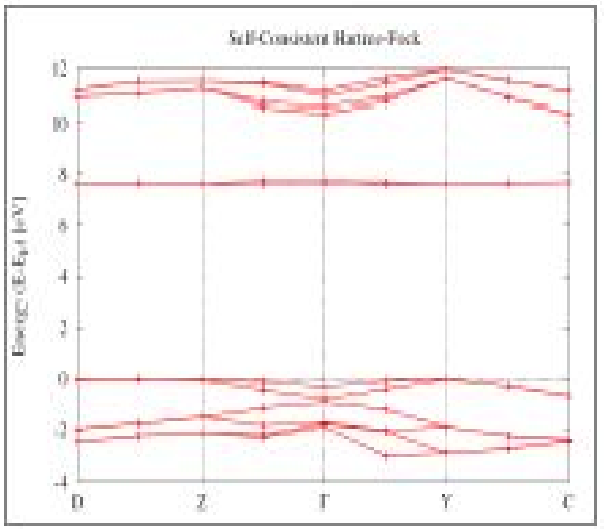
- Need for self-consistency
- But static GW (COHSEX) self-consistent already ok!

M. Gatti et al,
to be published

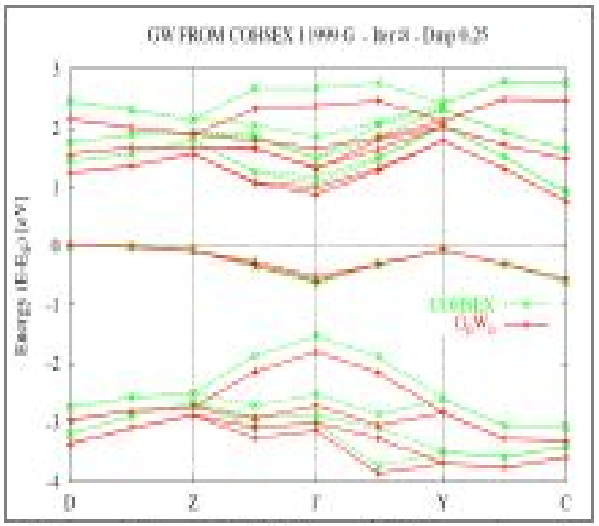
From perturbative G_0W_0 corrections towards self-consistent calculations



Perturbative G_0W_0 (starting from LDA)



Self-consistent Hartree-Fock



Self-consistent COHSEX and G_0W_0 on top of it
(preliminary results)

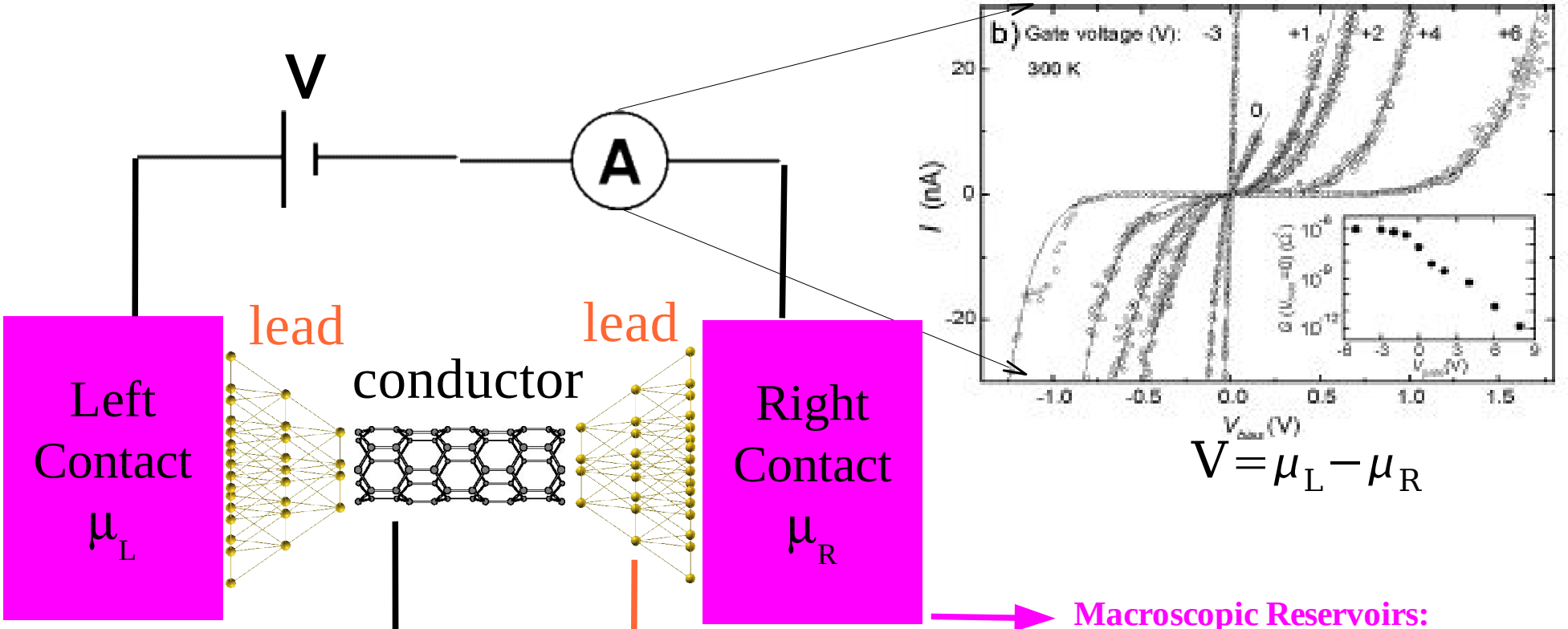
Bandgap	HF	DFT-LDA	GW on DFT	SC-COHSEX	GW on SC-COHSEX	EXP
VO2	7,6	0	0 !!!	0,8	0,7	0,6

Quantum Transport and NEGF

GW approximation and e-e scattering effects

Valerio Olevano, CNRS, Grenoble

Quantum Transport: The Working Bench



$$V = \mu_L - \mu_R$$

Macroscopic Reservoirs:
continuum of states,
thermodynamic equilibrium

Nanoscale Conductor:
finite number of states,
out of equilibrium,
dissipative effects

Mesoscopic Leads:
large but finite number of states,
partial equilibrium,
ballistic

We need:

- a First Principle description of the Electronic Structure
- for Finite Voltage: Open System and Out-of-Equilibrium description.

Non-Equilibrium Green's Function Theory (NEGF)

(improperly called Keldysh)

Much more complete framework, allows to deal with:

- **Many-Body** description of **incoherent** transport(electron-electron interaction, electronic correlations and also electron-phonon);
- **Out-of-Equilibrium** situation;
- Access to **Transient** response (beyond Steady-State);
- Reduces to Landauer-Buttiker for coherent transport.

The theory is due to the works of Schwinger, Baym, Kadanoff and Keldysh

Many-Body Finite-Temperature formalism

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}$$

hamiltonian

many-body

$$\bar{o} = \frac{\sum_i e^{-\beta E_i} \langle \Psi_i | \hat{o} | \Psi_i \rangle}{\sum_i e^{-\beta E_i}} = \mathrm{tr}\left[\hat{\rho}(\hat{H}) \hat{o} \right]$$

observable

$$\hat{\rho}(\hat{H}) = \frac{e^{-\beta \hat{H}}}{\mathrm{tr}[e^{-\beta \hat{H}}]}$$

statistical weight

NEGF formalism

$$\hat{H}(t) = \hat{H} + \hat{U}(t) = \hat{T} + \hat{V} + \hat{W} + \hat{U}(t)$$ hamiltonian

many-body + time-dependence

$$\bar{o}(t) = \mathrm{tr}\left[\hat{\rho}(\hat{H})\,\hat{o}_H(t)\right] \qquad t > t_0$$ observable

$$\hat{\rho}(\hat{H}) = \frac{e^{-\beta\hat{H}}}{\mathrm{tr}\left[e^{-\beta\hat{H}}\right]}$$

statistical weight referred to
the unperturbed Hamiltonian and
the equilibrium situation before t_0

Time Contour

$$\hat{o}_H(t) = \hat{s}(t_0, t)\,\hat{o}(t)\,\hat{s}(t, t_0)$$

Heisenberg representation

$$\hat{s}(t, t_0) = T\left\{\exp\left(-i\int_{t_0}^{t} dt'\,\hat{H}(t')\right)\right\}$$

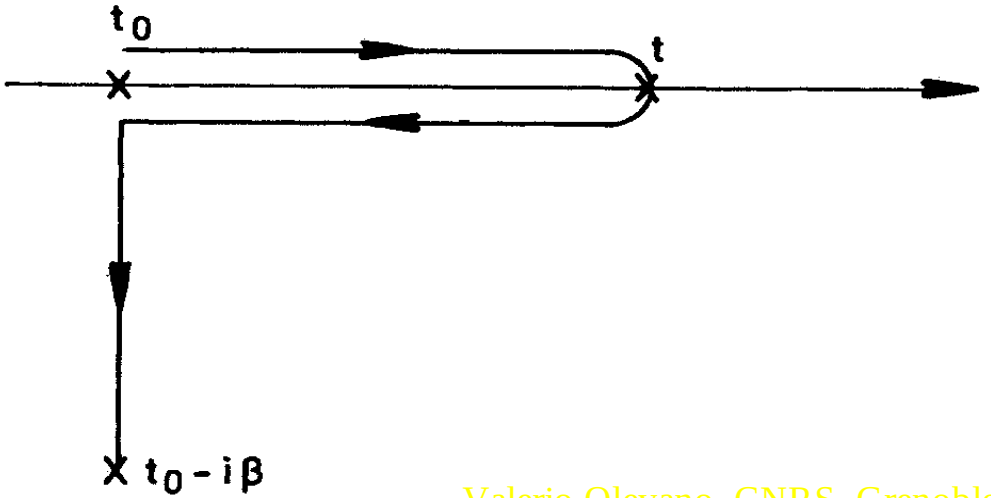
evolution operator

$$\hat{s}(t_0 - i\beta, t_0) = e^{-\beta \hat{H}}$$

trick to put the equilibrium weight into the evolution

$$\bar{o}(t) = \frac{\mathrm{tr}\left[\hat{s}(t_0 - i\beta, t_0)\,\hat{s}(t_0, t)\,\hat{o}(t)\,\hat{s}(t, t_0)\right]}{\mathrm{tr}\left[\hat{s}(t_0 - i\beta, t_0)\right]}$$

$$\bar{o}(t) = \frac{\mathrm{tr}\left[T_C\left[\exp\left(-i\int_C dt'\,\hat{H}(t')\right)\hat{o}(t)\right]\right]}{\mathrm{tr}\left[T_C\left[\exp\left(-i\int_C dt'\,\hat{H}(t')\right)\right]\right]}$$



NEGF Fundamental Kinetic Equations

$$G^r = [\omega - H_c - \Sigma^r]^{-1}$$

$$G^< = G^r \Sigma^< G^a$$

$$G^> = G^r \Sigma^> G^a$$

Caveat!: in case we want to consider also the transient,
then we should add another term to these equations:

$$G^< = G^r \Sigma^< G^a + (1 + G^r \Sigma^r) G^{0<} (1 + \Sigma^a G^a)$$ Keldysh equation

Quantum Transport: composition of the Self-energy

$$\Sigma^{r<>} = \sum_p \Sigma_p^{r<>} + \Sigma_{e-ph}^{r<>} + \Sigma_{e-e}^{r<>}$$

electron-electron interaction -> ?

interaction with the leads

electron-phonon interaction -> SCBA (Frederiksen et al. PRL 2004)

Critical point :

- Choice of relevant approximations for the Self-Energy and the in/out scattering functions

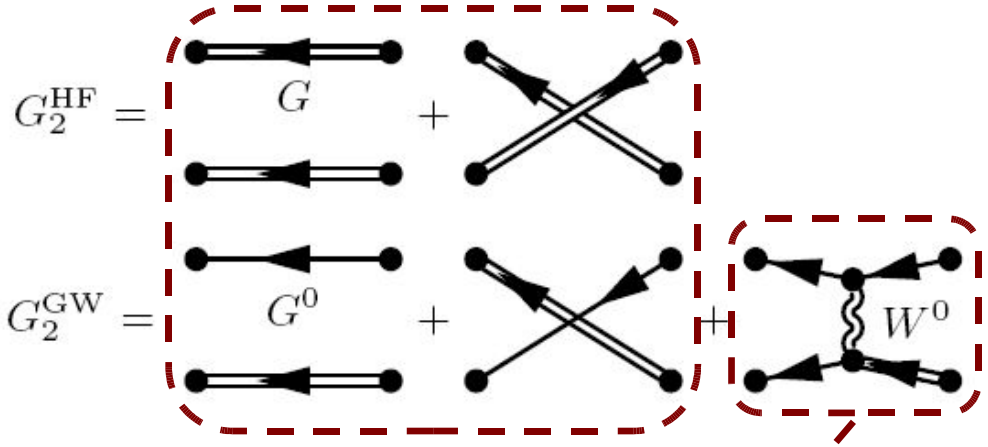
Our Self-Energy: GW. Why GW?

Direct and Exchange terms:

Band Structure Renormalization

Selfconsistent Hartree Fock

G^0W^0



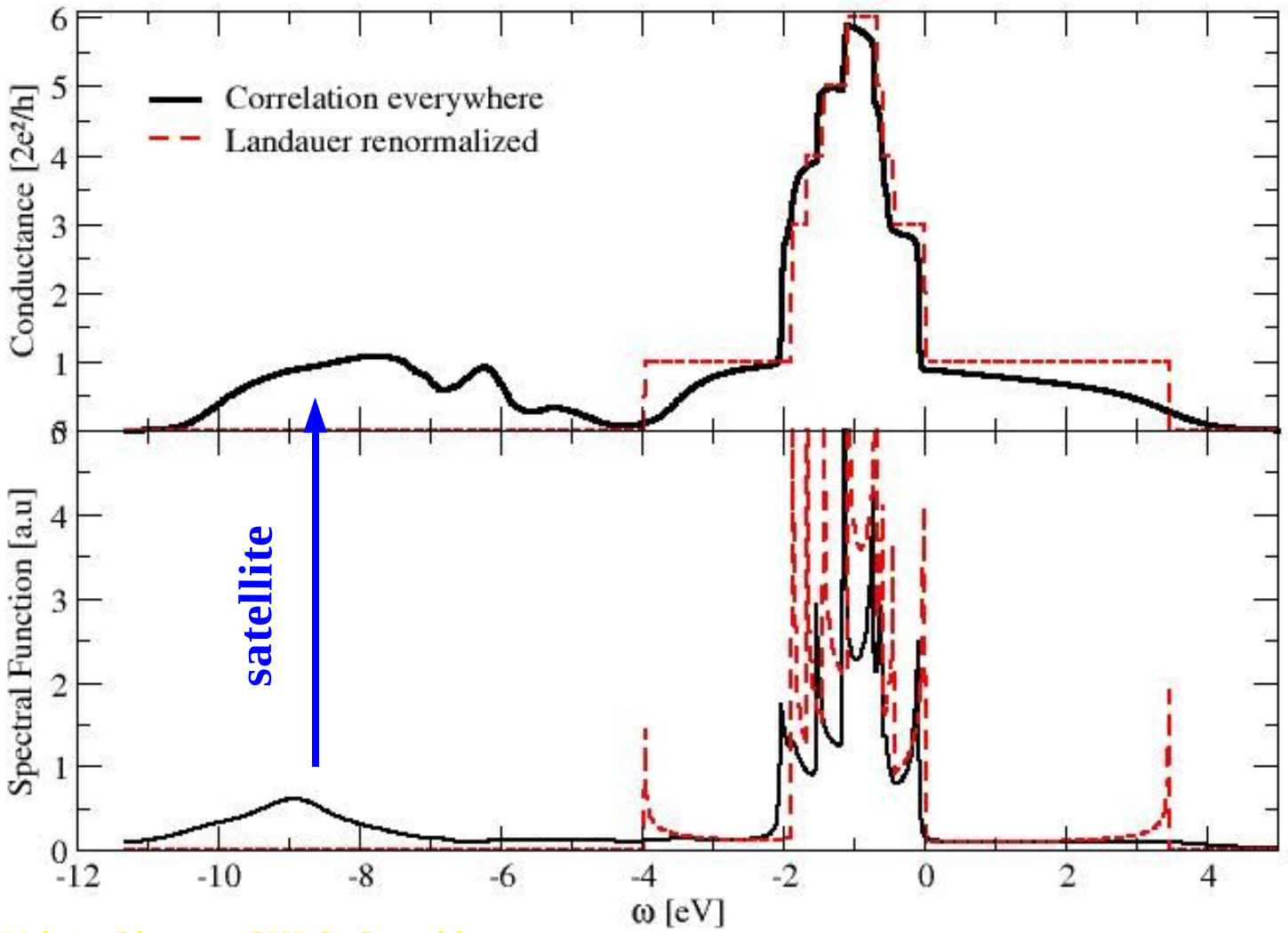
$\Rightarrow \Sigma^{\{>,<\}} = 0$

$\Rightarrow \Sigma^{\{>,<\}} \neq 0$

Collisional Term:
Band structure renormalization for Electronic Correlations +
e-e Scattering ->
Conductance Degrading Mechanisms, Resistance, non-coherent transport

GW and e-e scattering and correlation effects

Gold Atomic Infinite Chain



Loss of Conductance:

→ **Appearance of Resistance**

→ **Appearance of Satellite**

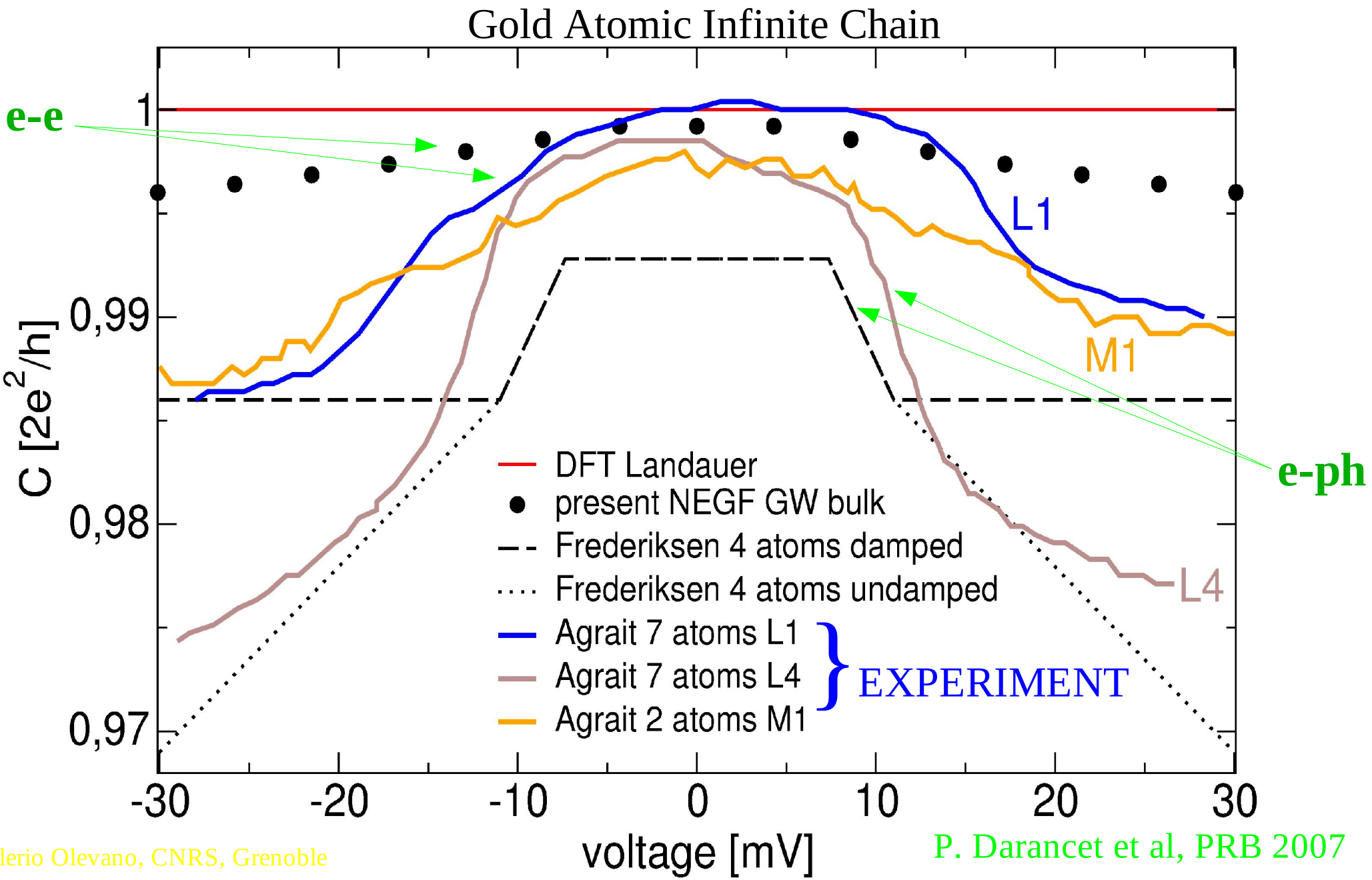
Conductance Channels

Broadening of the peaks:

→ **QP lifetime**

P. Darancet et al, PRB 2007

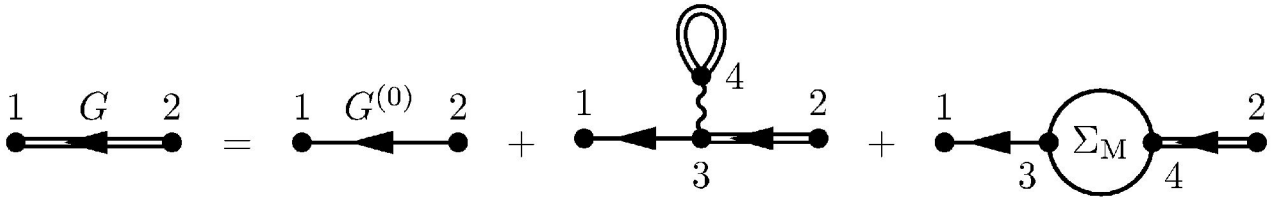
C / V characteristics: GW vs EXP

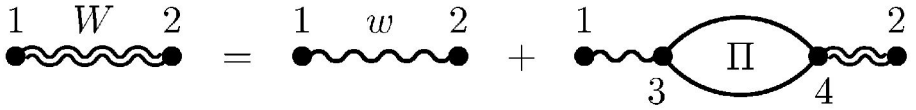


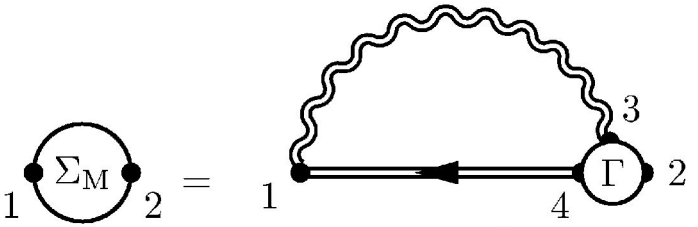
P. Darancet et al, PRB 2007

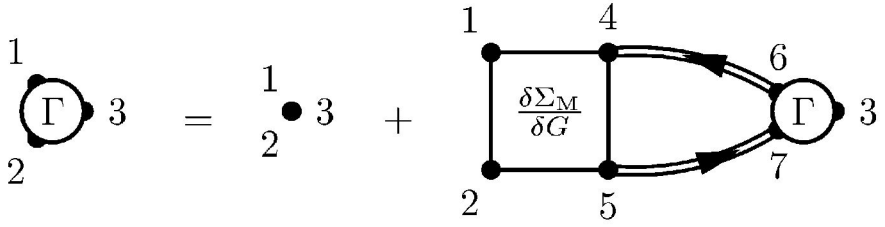
MBPT quantities as density-functionals: vertex corrections beyond GW

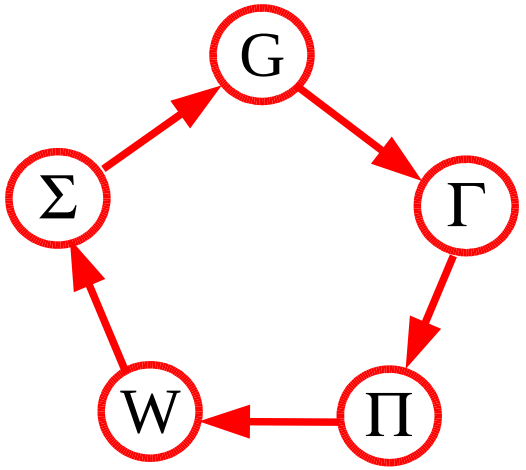
Hedin Equations











$$\Gamma = 1 + \frac{\delta \Sigma_M}{\delta V_c} = 1 + \frac{\delta \Sigma_M}{\delta G}\frac{\delta G}{\delta V_c} = 1 + \frac{\delta \Sigma_M}{\delta G} G G \Gamma$$

MBPT quantities as density-functionals: local vertex corrections beyond GW

$$\Gamma(1,2;3)=1+\frac{\delta\Sigma_M}{\delta V_c}=1+\frac{\delta\Sigma_M}{\delta G}\frac{\delta G}{\delta V_c}=1+\frac{\delta\Sigma_M(1,2)}{\delta G(5,6)}G(5,7)G(6,8)\Gamma(7,8;3)$$

$$\Gamma(1,2;3)=1+\frac{\delta\Sigma_M}{\delta V_c}=1+\frac{\delta\Sigma_M}{\delta \rho}\frac{\delta \rho}{\delta V_c}=1+\frac{\delta\Sigma_M(1,2)}{\delta \rho(4)}\Pi(4,3)$$

Runge-Gross theorem

Remainder Non-local Correction

$$\Gamma(1,2;3)=1+\delta(1,2)f_{xc}^{eff}(2,4)\Pi(4,3)+\Delta\Gamma(1,2;3)$$

Direct gap	LDA	GW	Local Γ	EXP
Si	2.53	3.27	3.28	3.40
Ar	8.18	12.95	12.75	14.2

Direct gap	COHSEX	GW	Local Γ	EXP
Si	3.64	3.30	3.32	3.40
Ar	14.85	14.00	14.76	14.2

F. Bruneval et al., PRL (2005)

Generalized Sham-Schlüter Equation: link between non-locality and frequency dependence

Sham-Schlüter Equation

$$G = G^{KS} + G^{KS}(\Sigma - V_{xc})G$$ Dyson Equation

AND

$$G^{KS}(x,x) = G(x,x) = -i\rho(r)$$ The density of the Kohn-Sham system is by construction equal to the exact density

$$V_{xc} = (G^{KS}G)^{-1}G^{KS}\Sigma G$$ Sham-Schlüter Equation, PRL (1983)

$$V_{xc} = (GG)^{-1}G\Sigma G$$ Linearised SSE

$$V_x^{EXX} = (GG)^{-1}G\Sigma_x G$$ Example: OEP EXact eXchange

Valerio Olevano, CNRS, Grenoble

Generalize SSE

- Spectroscopy calls for the description of new quantities (ex. bandgap), beyond the ground-state density.
- I want the simpler one-body potential V^{SF} able to provide the Green's function G^{SF} of a Fictitious (Kohn-Sham-like) system such as by construction yields the exact density AND the exact photoemission bandgap.
- You can read the bandgap for example just only on the trace of the spectral function.

Generalized Sham-Schlüter Equation

$$G = G^{SF} + G^{SF}(\Sigma - V^{SF})G$$

Dyson Equation

AND

$$G^{SF}(x,x) = G(x,x) = -i\rho(r)$$

The density of the SF system is equal to the exact density

AND

$$\left|\Im\, G^{SF}(r,r,\omega)\right| = \left|\Im\, G(r,r,\omega)\right| = A(r,r,\omega)$$

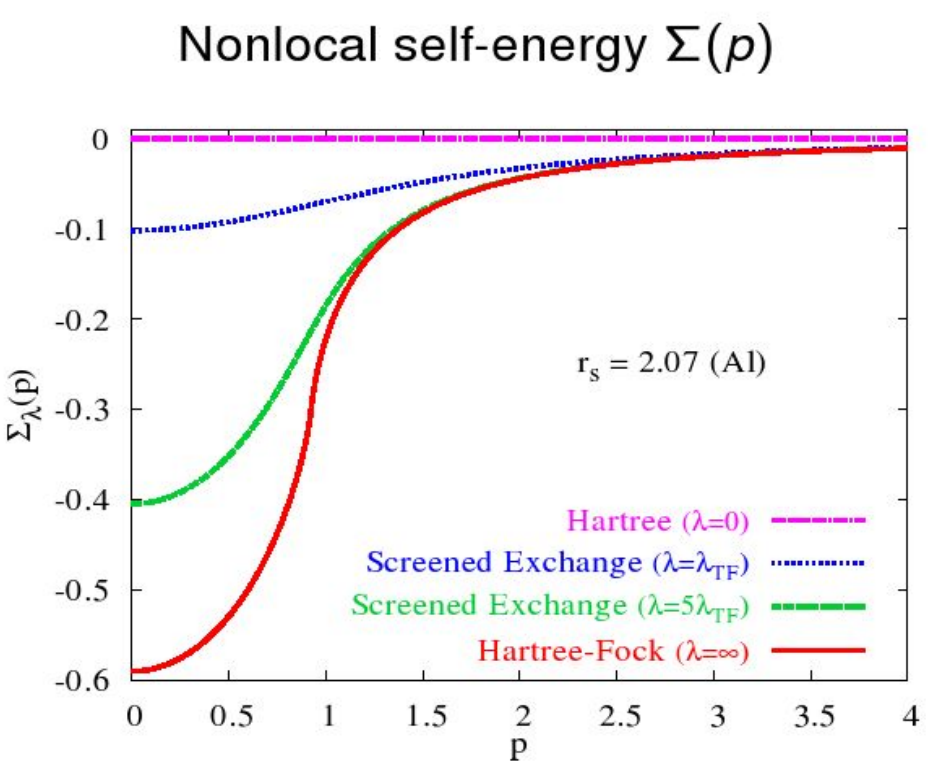
The Trace of the spectral function is the exact one

$$V^{SF}(r,\omega) = \int (\Im\{G^{SF}(r,r_1,\omega)G(r_1,r,\omega)\})^{-1}\Im\{G^{SF}(r_1,r_2,\omega)\Sigma(r_2,r_3,\omega)G(r_3,r_1,\omega)\}$$

Generalized SSE

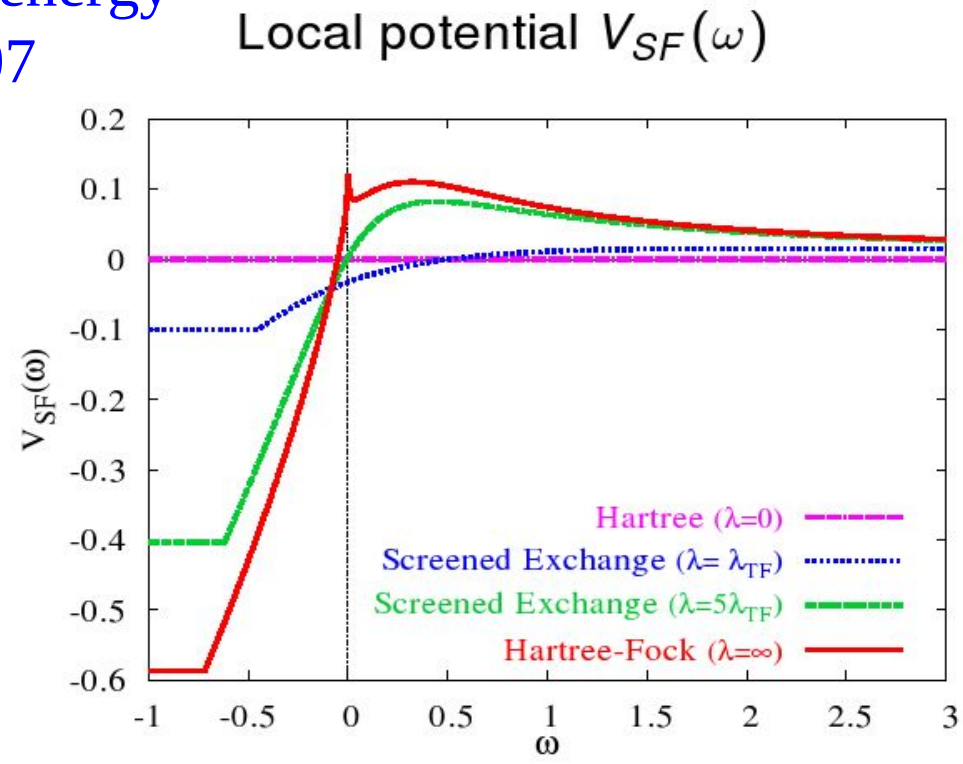
This is the real local and dynamical potential that yields the correct density and the correct bandgap!

Transforming non-locality



Hartree-Fock self-energy on Jellium rs = 2.07

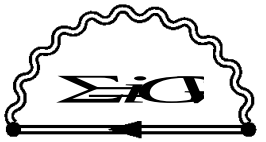
into frequency-dependence



Conclusions

- **GW** Quasiparticle band gaps and band plots are in **good agreement** with Photoemission spectroscopy. But the statistics is not yet quite large. We have still to see the role of self-consistence and to which extent GW works on strongly-correlated systems.
- **NEGF – GW** seems to introduce e-e scattering effects, correlation and lost-of-coherence in Quantum Transport.
- Setting MBPT quantities as **density-functionals** could be a good way to address **vertex corrections beyond GW**.
- Thank to Generalized SSE, we have introduced an effective framework which allows to get rid of the complicated **non-local self-energy** and have a simpler **on-body local potential** which yields the right bandgap. The effective potential is real but needs to be **frequency-dependent**.

The ABINIT-GW code
in few words



- The thing: GW code in Frequency-Reciprocal space on a PW basis.
- Purpose: Quasiparticle Electronic Structure.
- Systems: Bulk, Surfaces, Clusters.
- Approximations: GW, Plasmon-Pole model and RPA on W, non Self-Consistent G^0W^{RPA}, first step of self-consistency on W and G.