The GW Approximation

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European Theoretical Spectroscopy Facility (ETSF)

Belfast, June 2007

Outline

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Towards Hedin's equations

$$\Sigma = iGv\varepsilon^{-1}\tilde{\Gamma}$$

irreducible vertex

$$\begin{aligned}\tilde{\Gamma} &= -\frac{\delta G^{-1}}{\delta V} \\ &= 1 + \frac{\delta \Sigma}{\delta G} GG\tilde{\Gamma}\end{aligned}$$

screened Coulomb interaction

$$W = \epsilon^{-1} v$$

dielectric function

$$\epsilon = 1 - v\tilde{\chi}$$

irreducible polarizability

$$\tilde{\chi} = \frac{\delta \rho}{\delta V} = -iGG\tilde{\Gamma}$$

Hedin's equations

$$
\begin{aligned}
\Sigma &= iGW\tilde{\Gamma} \\
\tilde{\Gamma} &= 1 + \frac{\delta\Sigma}{\delta G} GG\tilde{\Gamma} \\
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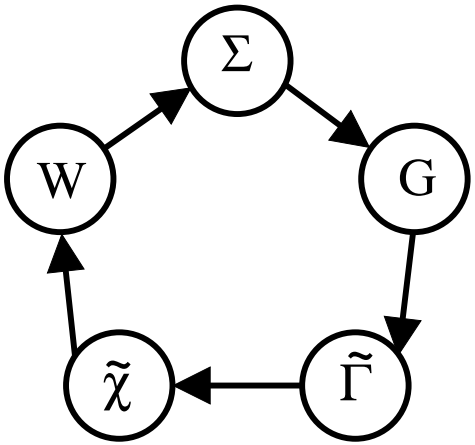
\epsilon &= 1 - v\tilde{\chi} \\
\tilde{\chi} &= -iGG\tilde{\Gamma}
\end{aligned}
$$

Hedin's wheel



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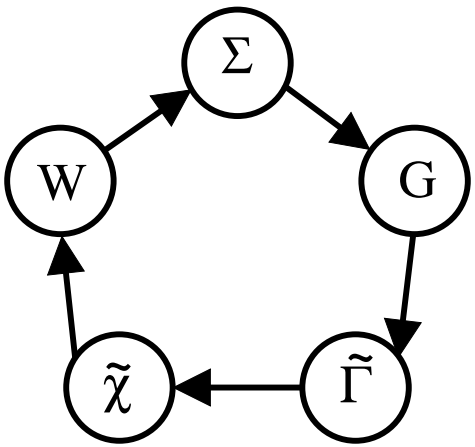

Hedin's wheel

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

$$\Gamma^{(1)} = 1$$

$$\tilde{\chi}^{(1)} = -iGG = \chi_{\mathrm{RPA}}$$

$$\Sigma^{(1)} = iGW$$

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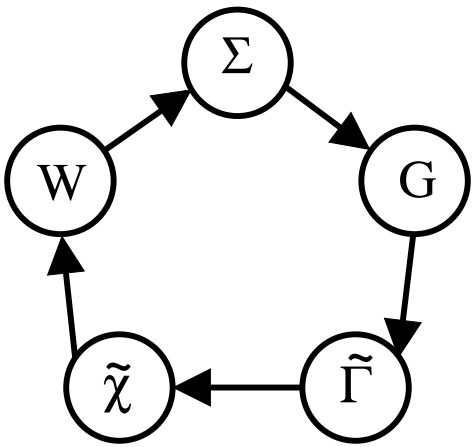
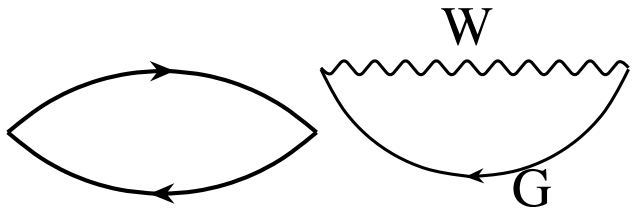


Hedin's wheel



GW origins

PHYSICAL REVIEW VOLUME 139, NUMBER 3A 2 AUGUST 1965

New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem*

LARS HEDIN†
Argonne National Laboratory, Argonne, Illinois
(Received 8 October 1964; revised manuscript received 2 April 1965)

A set of successively more accurate self-consistent equations for the one-electron Green's function have been derived. They correspond to an expansion in a screened potential rather than the bare Coulomb potential. The first equation is adequate for many purposes. Each equation follows from the demand that a corresponding expression for the total energy be stationary with respect to variations in the Green's function. The main information to be obtained, besides the total energy, is one-particle-like excitation spectra, i.e., spectra characterized by the quantum numbers of a single particle. This includes the low-excitation spectra in metals as well as configurations in atoms, molecules, and solids with one electron outside or one electron missing from a closed-shell structure. In the latter cases we obtain an approximate description by a modified Hartree-Fock equation involving a "Coulomb hole" and a static screened potential in the exchange term. As an example, spectra of some atoms are discussed. To investigate the convergence of successive approximations for the Green's function, extensive calculations have been made for the electron gas at a range of metallic densities. The results are expressed in terms of quasiparticle energies $E(\mathbf{k})$ and quasiparticle interactions $f(\mathbf{k},\mathbf{k}')$. The very first approximation gives a good value for the magnitude of $E(\mathbf{k})$. To estimate the derivative of $E(\mathbf{k})$ we need both the first- and the second-order terms. The derivative, and thus the specific heat, is found to differ from the free-particle value by only a few percent. Our correction to the specific heat keeps the same sign down to the lowest alkali-metal densities, and is smaller than those obtained recently by Silverstein and by Rice. Our results for the paramagnetic susceptibility are unreliable in the alkali-metal-density region owing to poor convergence of the expansion for f. Besides the proof of a modified Luttinger-Ward-Klein variational principle and a related self-consistency idea, there is not much new in principle in this paper. The emphasis is on the development of a numerically manageable approximation scheme.

Physics of the GW approximation, I

Splitting of the screened Coulomb interaction:

$$W(\omega) = \epsilon^{-1}(\omega)v = (1 + v\chi(\omega))v = v + W_p(\omega)$$

Splitting of the self-energy:

$$\begin{aligned} \Sigma(\omega) = iGW(\omega) &= iGv + iGW_p(\omega) \\ &= \Sigma_x + \Sigma_c(\omega) \end{aligned}$$

Screening beyond Hartree Fock

Physics of the GW approximation, II

Add a charge - relaxation?

Not if you smear it out in a Bloch function!
What do we add to the system? And where?
$\delta(\mathbf{r} - \mathbf{r}_0)$
Coulomb hole: $0.5(W(r_0, r_0) - v(r_0, r_0))$
Δ SCF in small systems!
Add screened exchange: COHSEX approximation.

Physics of the GW approximation, II

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Outline

Full GW calculation

Calculate the *GW* self-energy:

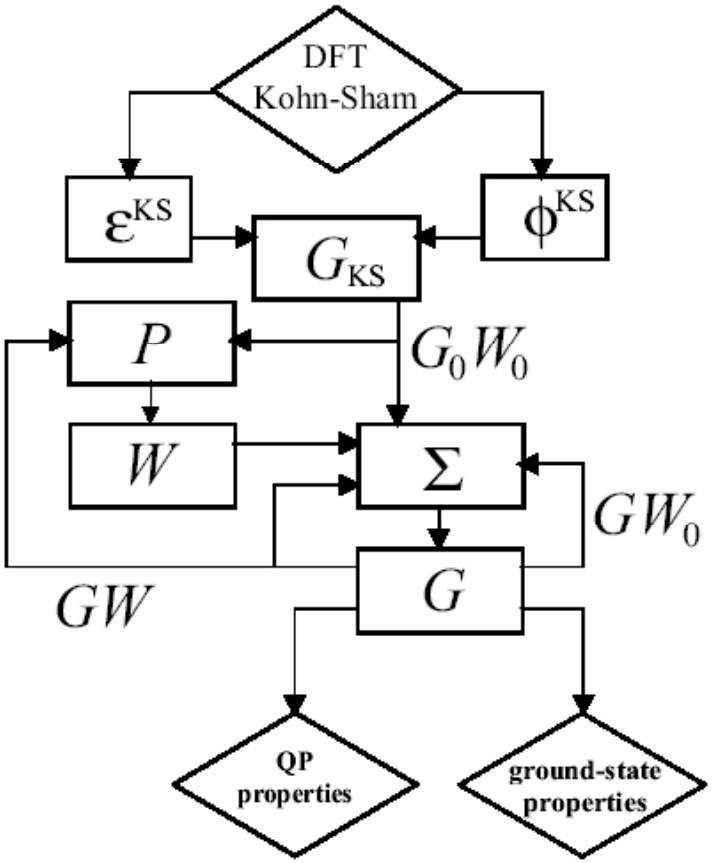
$$\Sigma(1,2) = iG(1,2)W(1^+,2)$$

which is Fourier transformed to frequencies

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

Schematic GW calculation

Start is recipe by Hybertsen and Louie, PRL **55** 1418 (1985) called "G_0W_0" or "best G best W"



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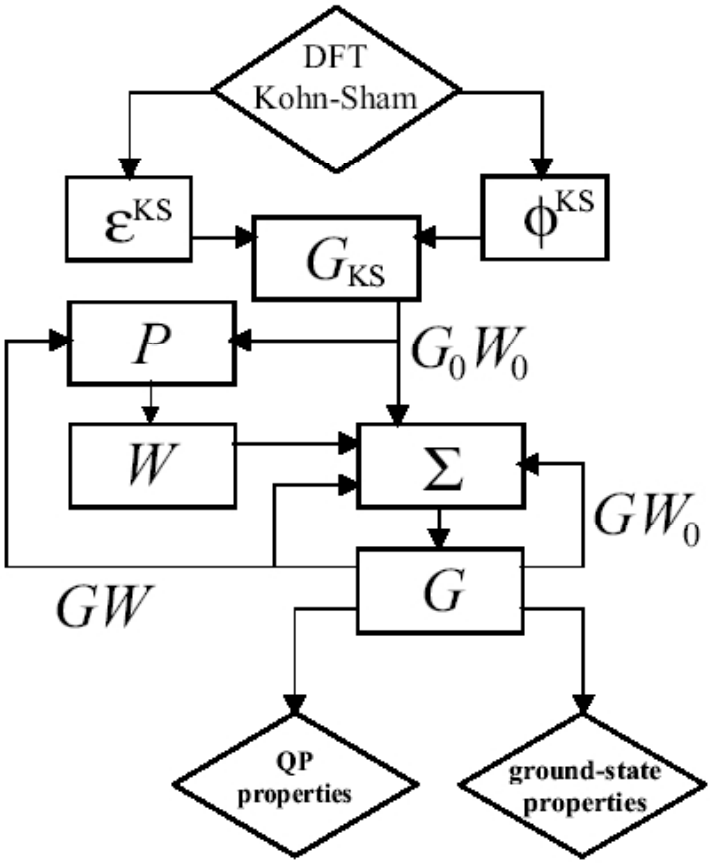

GW for realistic materials

Assumption

$$\phi_i^{GW} \approx \phi_i^{KS}$$

Quasiparticle equations

$$h_0(\mathbf{r}_1)\phi_i^{GW}(\mathbf{r}_1) + \int d\mathbf{r}_2 \Sigma(\mathbf{r}_1, \mathbf{r}_2, \epsilon_i^{GW})\phi_i^{GW}(\mathbf{r}_2) = \epsilon_i^{GW}\phi_i^{GW}(\mathbf{r}_1)$$

Kohn-Sham equations

$$h_0(\mathbf{r}_1)\phi_i^{KS}(\mathbf{r}_1) + v_{xc}(\mathbf{r}_1)\phi_i^{KS}(\mathbf{r}_1) = \epsilon_i^{KS}\phi_i^{KS}(\mathbf{r}_1)$$

Differences

$$\langle \phi_i^{KS} | \Sigma(\epsilon_i^{GW}) - v_{xc} | \phi_i^{KS} \rangle = \epsilon_i^{GW} - \epsilon_i^{KS}$$

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G_0W_0 calculation

To calculate the *GW* self-energy:

$$\Sigma(1,2) = iG(1,2)W(1^+,2)$$

which is Fourier transformed into frequencies

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

We need the following ingredients:

- The KS Green's function: $G(\mathbf{r}_1,\mathbf{r}_2,\omega) = \sum_i \frac{\phi_i^{\mathrm{KS}}(\mathbf{r}_1)\phi_i^{\mathrm{KS}*}(\mathbf{r}_2)}{\omega-\epsilon_i^{\mathrm{KS}}\pm i\eta}$
- The RPA dielectric matrix: $\varepsilon^{\mathrm{RPA}\ -1}_{\mathbf{GG'}}(\mathbf{q},\omega)$

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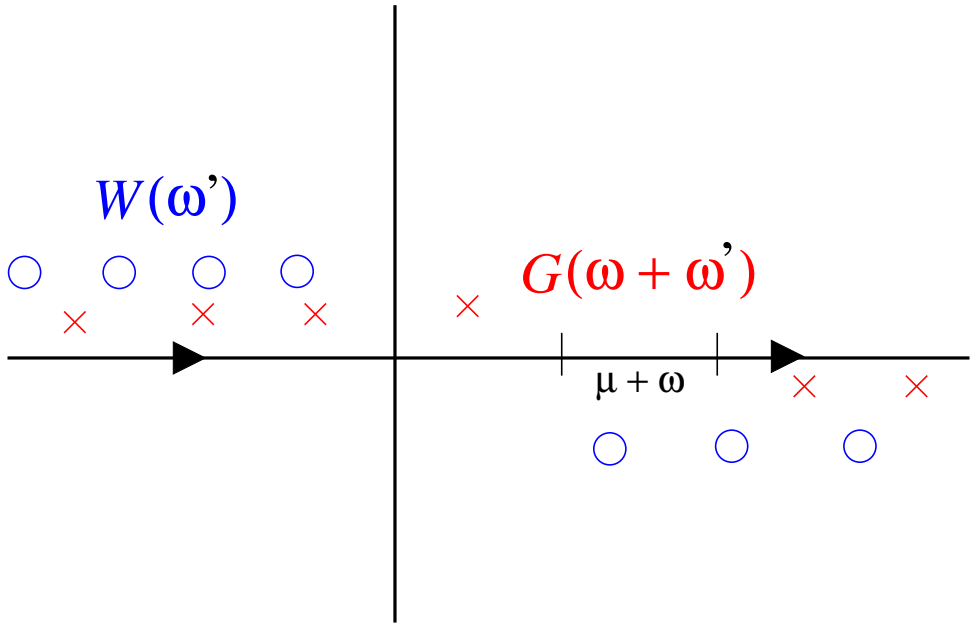
Calculation of RPA screening

We need to know $\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ for all ω's, in order to get Σ.
and the frequency convolution may be problematic because both G and W have poles along the axis



- numerically compute the convolution $\Rightarrow$ accurate, but expensive
- use a model to **mimic** ω-behavior of ε^{-1} $\Rightarrow$ rough, cheap

Plasmon-Pole model

Plasmon-Pole Model

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

The two parameters $\Omega_{\mathbf{G}\mathbf{G}'}(\mathbf{q})$ and $\tilde{\omega}_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$ are fit on *ab initio* calculation of $\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ at two frequencies.
We choose

- $\omega_1 = 0$
- $\omega_2 \approx i\omega_{\text{plasma}}$ pure imaginary frequency

Quasiparticle energy

$$\epsilon_i^{GW} = \epsilon_i^{KS} + \langle i|\Sigma(\epsilon_i^{GW})|i\rangle - \langle i|v_{xc}|i\rangle$$

Taylor expansion of $\Sigma(\epsilon)$ around ϵ_i^{KS}

Final formula used by ABINIT

$$\epsilon_i^{GW} = \epsilon_i^{KS} + Z_i \left[\langle i|\Sigma(\epsilon_i^{KS})|i\rangle - \langle i|v_{xc}|i\rangle\right]$$

where $Z_i = 1/(1 - \partial\Sigma/\partial\epsilon)$

Output from ABINIT for the band gap of silicon

```
k =    0.000   0.000   0.000
Band      E0 <VxcLDA>   SigX SigC(E0)      Z dSigC/dE  Sig(E)    E-E0
   4   5.915 -11.242 -12.433   1.213   0.774  -0.292 -11.225   0.017
   5   8.445 -10.059  -5.864  -3.363   0.774  -0.291  -9.414   0.645

E^0_gap             2.530
E^GW gap            3.158
```

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If you want to do GW calculations.....

www.abinit.org

GW space-time-code

SELF: fisica.uniroma2.it/ self

Outline

Easier?

Observe, I

M. Rohlfing, P. Krueger, and J. Pollmann, Electronic structure of Si(100)2X1, Phys. Rev. B **52**, 1905 (1995).

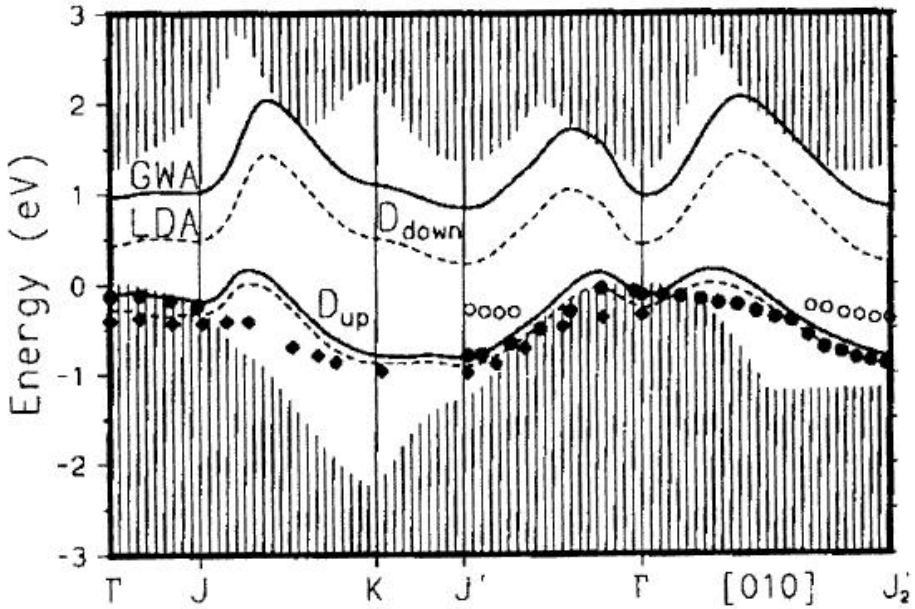
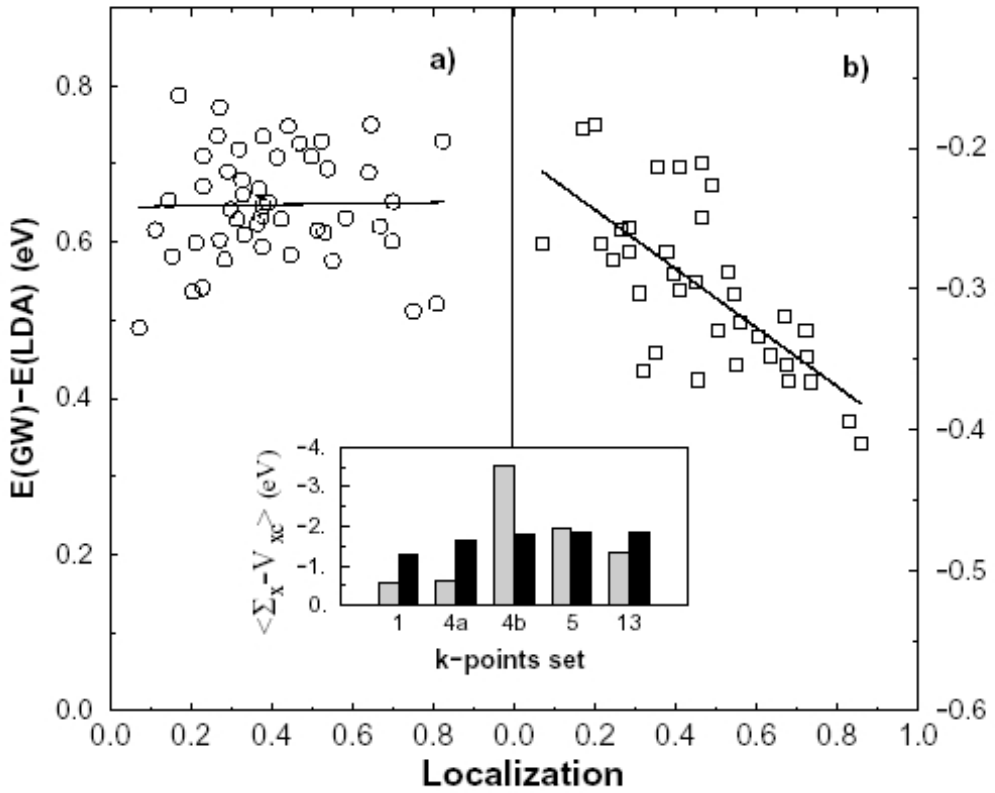


Figure 15. Calculated dangling-bond bands. Full curves, GWA energies; dashed curves, LDA energies. The experimental results are shown by diamonds (Uhrberg *et al* 1981) and circles (full and open) (Johansson *et al* 1990). (After Rohlfing *et al* 1995b).

Observe, II

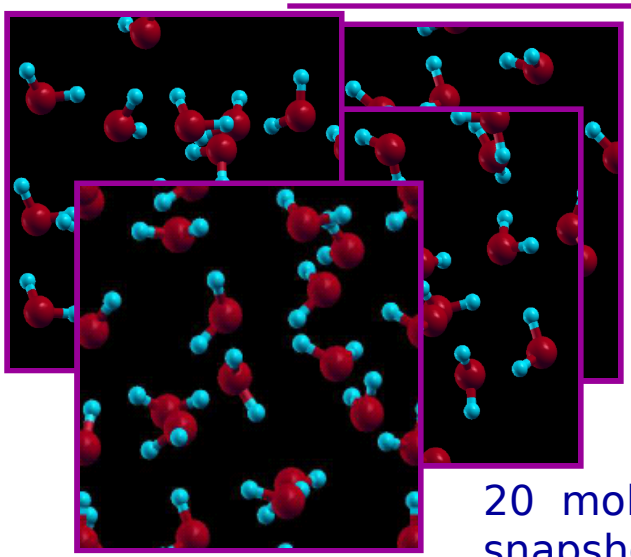
O. Pulci, G. Onida, R. Del Sole, and L. Reining, "Ab-initio calculation of self-energy effects on electronic and optical properties of GaAs(110)", Phys. Rev. Lett. **81**, 5347 (1998).



Observe, III

V. Garbuio, M. Cascella, L. Reining, R. Del Sole, and O. Pulci, "Ab initio calculation of optical spectra of liquids: Many-body effects in the electronic excitations of water", Phys. Rev. Lett. **97**, 137402 (2006)

The sample



Liquid water is a disordered system

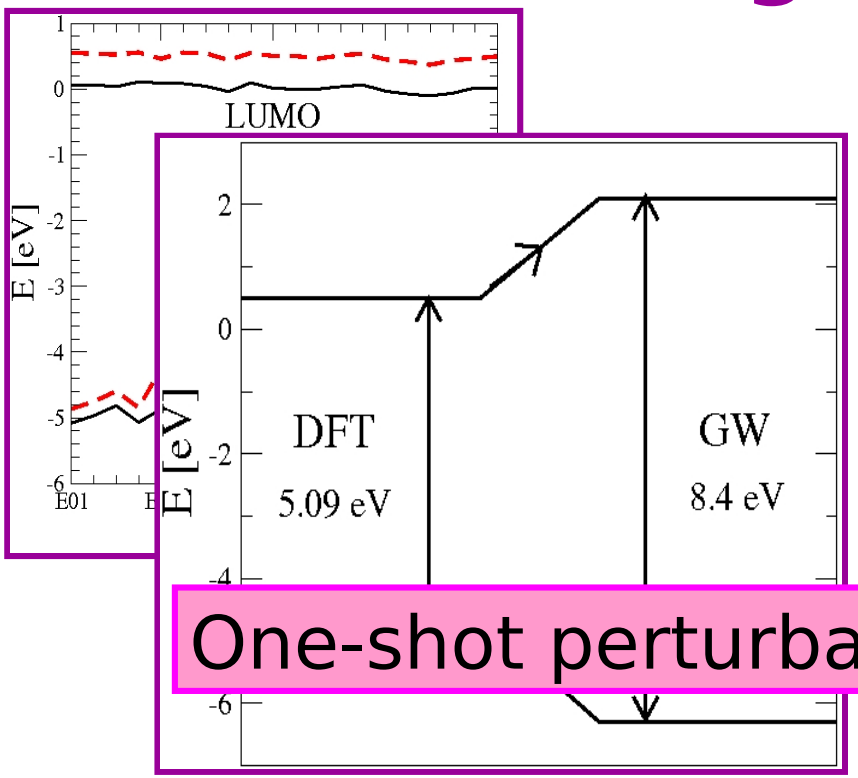
~~Huge unit cell~~

20 molecular dynamics snapshots and average of results

Configurations of 17 molecules in a box with 15 a.u. side obtained with classical molecular dynamics simulations*

Observe, III

Electronic gap



Experimental gap

8.7 ± 0.5 eV

Bernas *et al.*, Chem. Phys. **222**, 151

One-shot perturbative GW

Observe, III

GW corrections independent of configuration!!!

	DFT gap	ΔGW HOMO	ΔGW LUMO	ΔGW gap
E19	5.09	−1.67	1.61	3.28
E08	4.71	−1.64	1.60	3.24
E02	5.29	−1.70	1.60	3.30

Approximate

GW correction $= 9.1/\epsilon$

V. Fiorentini and A. Baldereschi, Phys. Rev. B **51**, 17196 (1995).

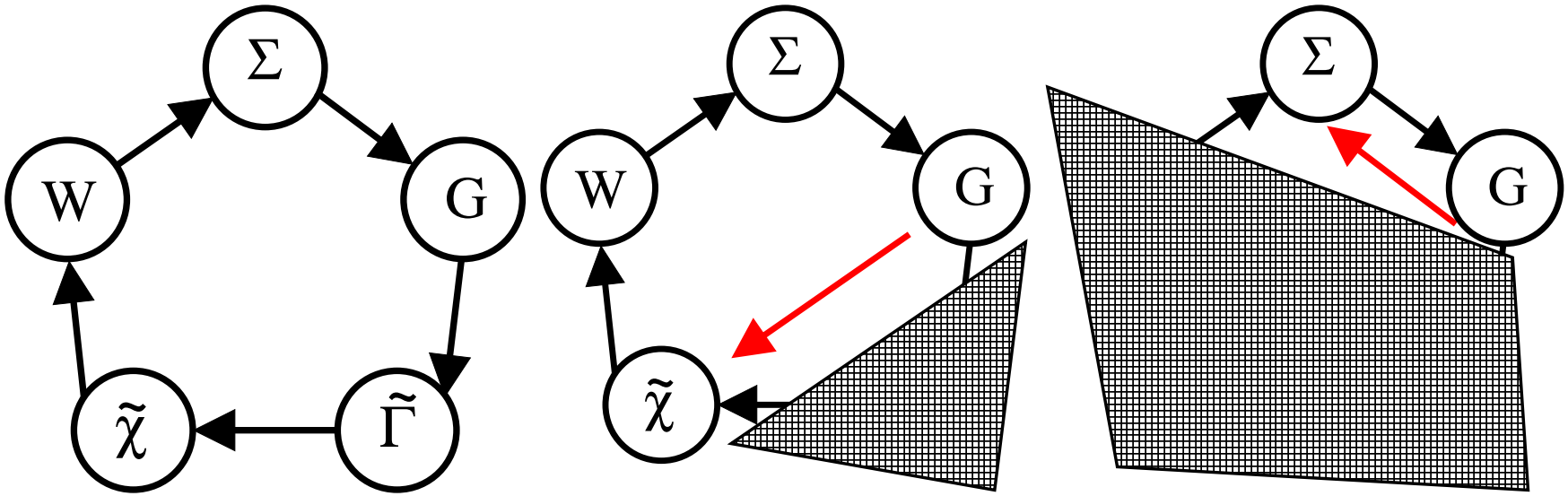
Outline

Basis set dependence

Silicon band gap

LMTO	Kotani	0.84
LAPW	Ku	0.85
PAW	Arnaud	0.92
PAW	Kresse	1.05
FLAPW	Schindlmayr	1.07
PP+PW	me	1.14
Expt.		1.17
PP+PW	Godby2	1.22
PP+PW	Godby1	1.24
PP+PW	Hybertsen	1.29

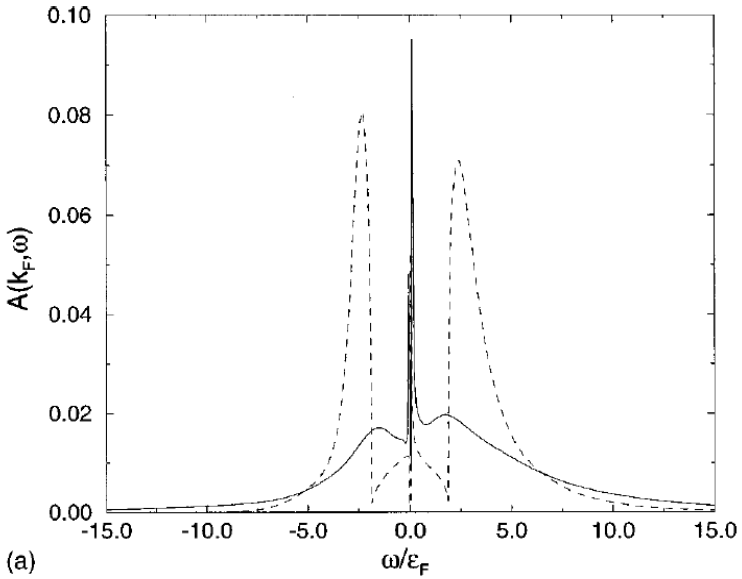
Self-consistency???



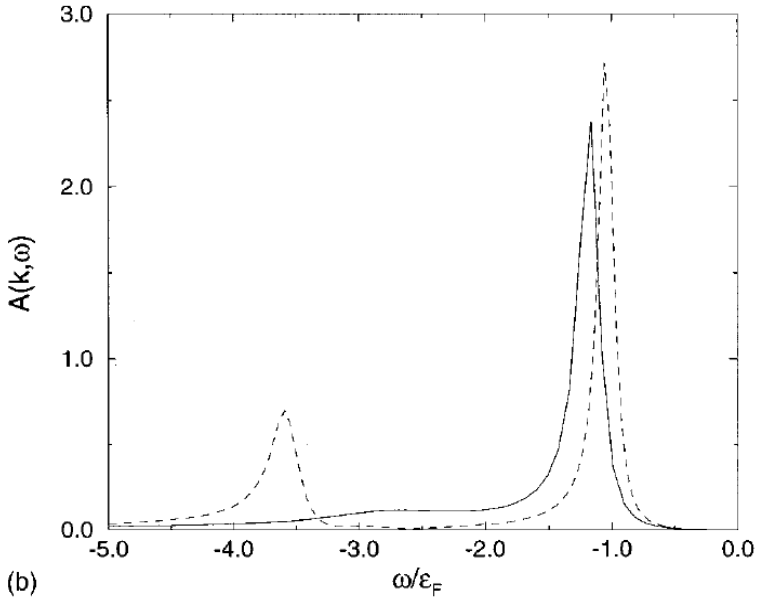
Results for jellium

Spectral function

$\mathbf{k} = \mathbf{k}_F$



$\mathbf{k} = 0$

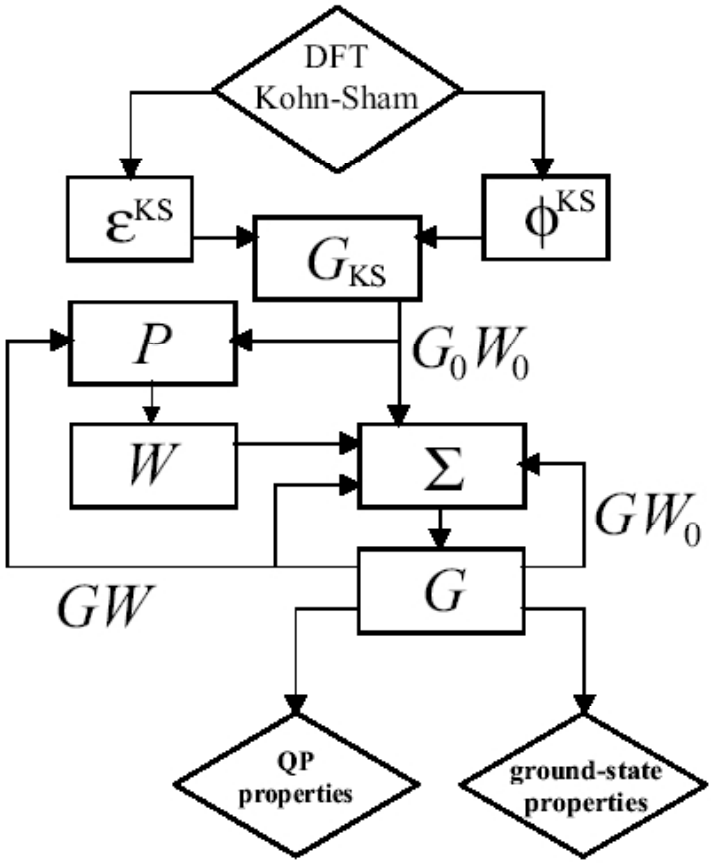


dashed: G_0W_0

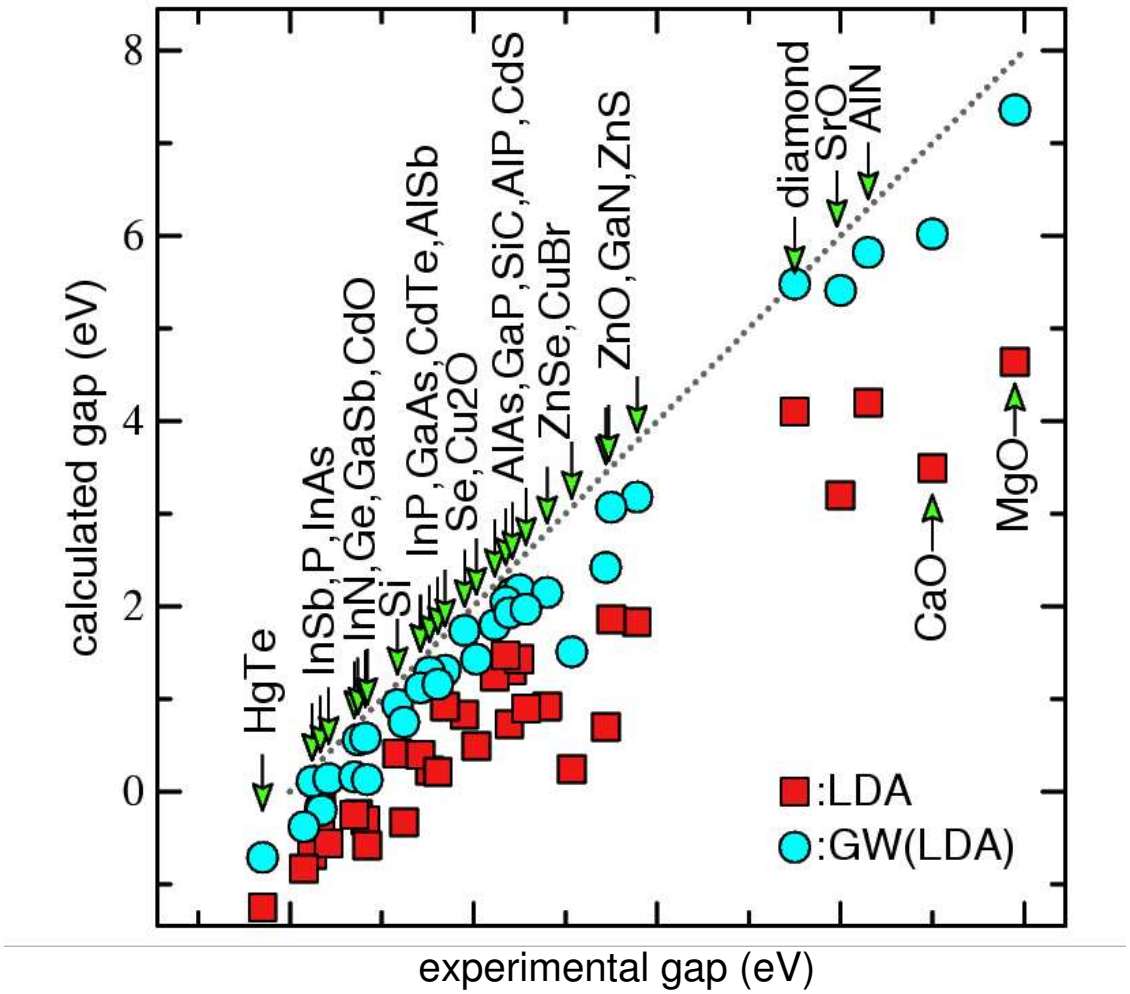
solid: self-consistent GW

from B. Holm and U. von Barth, PRB **57** 2108 (1998).

Self-consistency on the QP wavefunctions and energies?

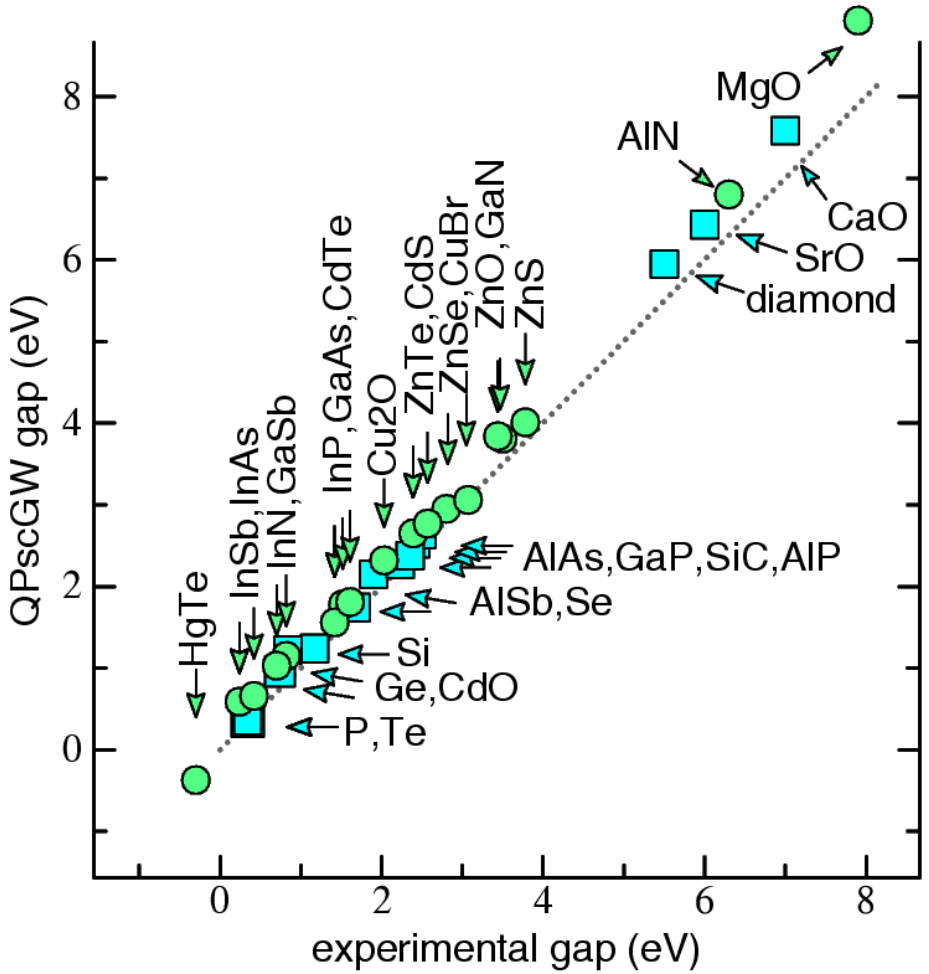


Band gaps of semiconductors



from M. van Schilfgaarde *et al.*, PRL **96** 226402 (2006).

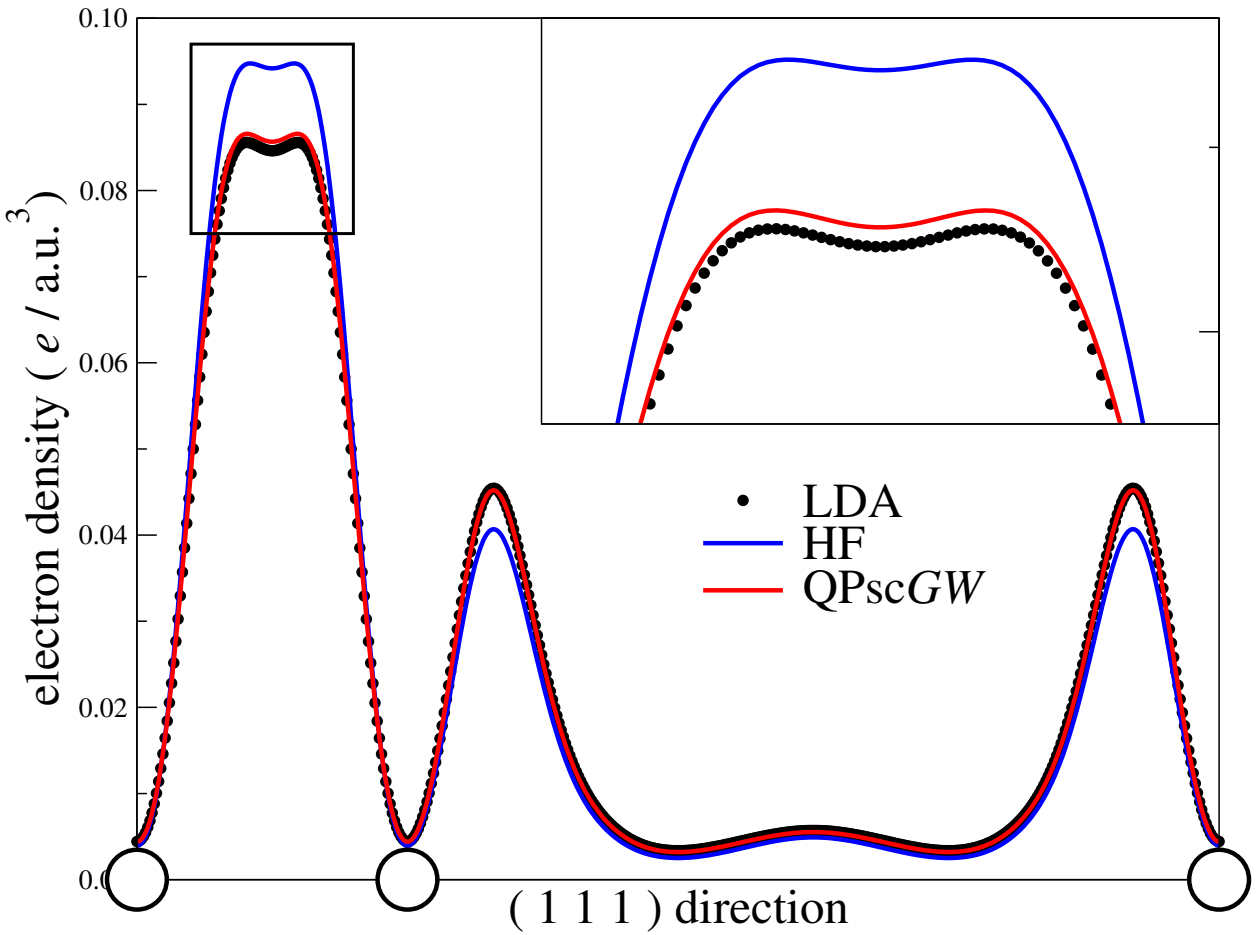
QP self-consistency



from M. van Schilfgaarde *et al.* PRL (2006).

QP self-consistency

Silicon



Bruneval *et al.* PRB **74**, 045102 (2006).

Other issues

...for example, the semi-core!

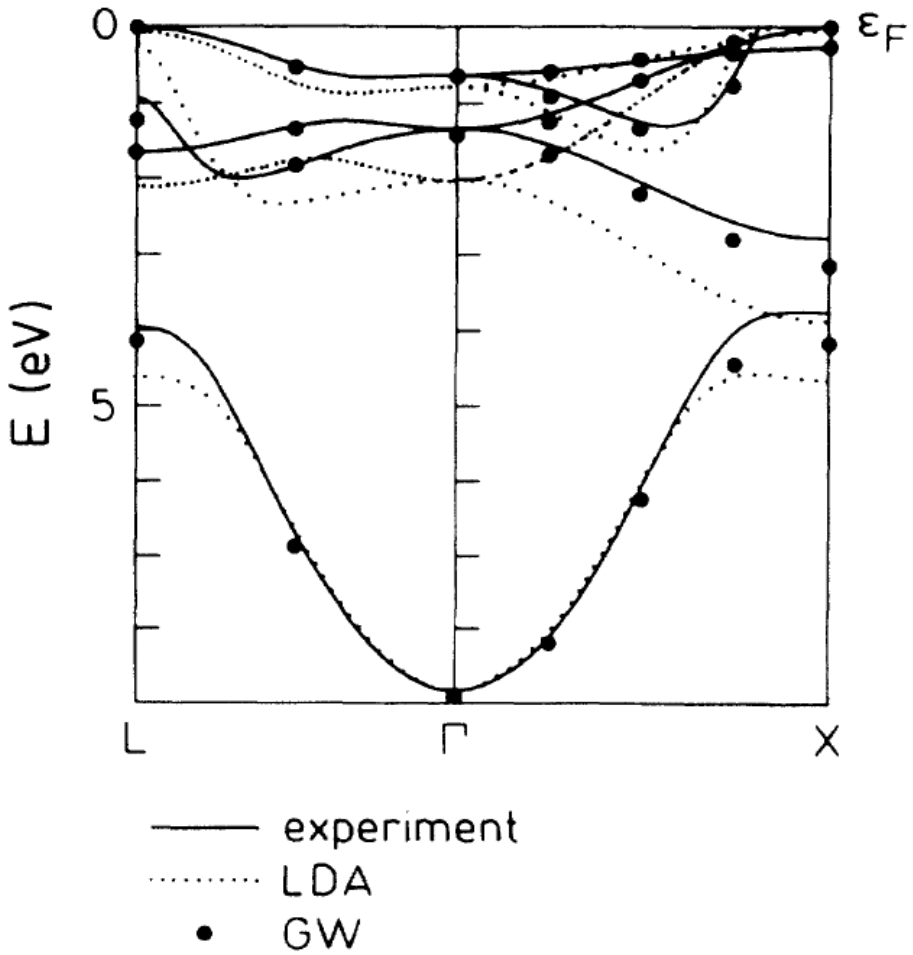
see e.g. Copper:
A. Marini, G. Onida, R. Del Sole, Phys. Rev. Lett. **88**, 016403 (2002)
F. Bruneval, N. Vast, L. Reining, M. Izquierdo, F. Sirotti, and N. Barrett, "Exchange and correlation effects in electronic excitations of Cu2O", Phys. Rev. Lett. **97**, 267601 (2006)

Outline

More results

Result for a complex metal

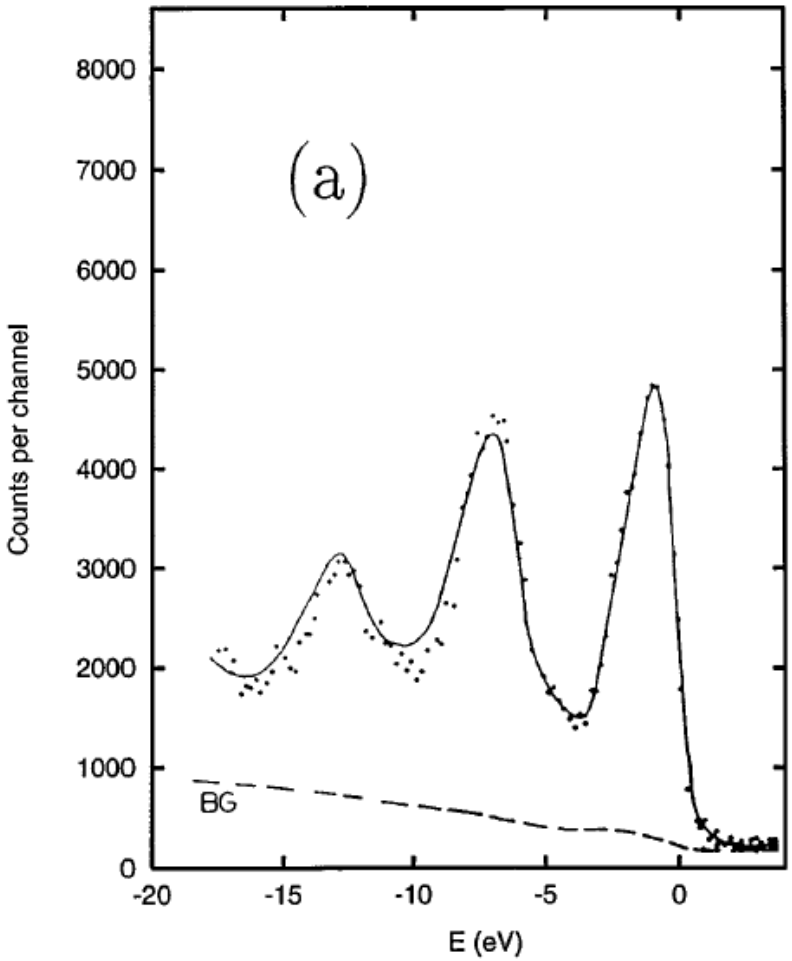
Nickel



from F. Aryasetiawan, PRB **46** 13051 (1992).

Motivation to go beyond.....

Sodium, photoemission



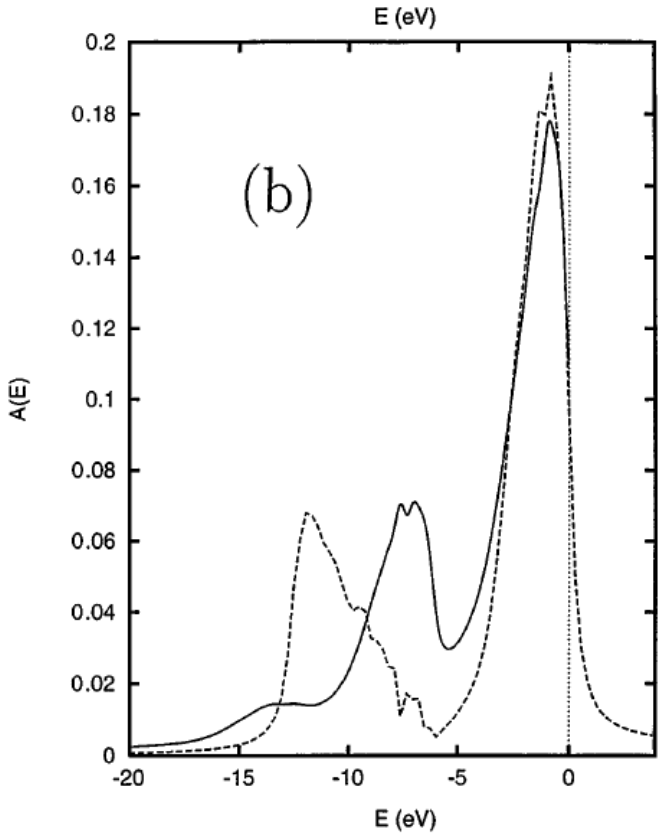


FIG. 1. (a) The experimental spectral function for Na (dots). The solid line is a synthetic spectrum obtained by convoluting the density of states from a band structure calculation and the experimental core level spectrum. BG is the estimated background contribution. The data are taken from Ref. [27]. (b) The total spectral function of Na for the occupied states. The solid and dashed lines correspond to the cumulant expansion and GWA, respectively.

Outline

References

- L. Hedin, Phys. Rev. **139** A796 (1965).
- L. Hedin and Lunqdvist,*Solid State Physics* **23**, (1969)
- F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61** 237 (1998).
- W.G. Aulbur, L. Jonsson, and J.W. Wilkins, Sol. State Phys. **54** 1 (2000).
- G. Strinati, Riv. Nuovo Cimento **11** 1 (1988).
- G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002)
- `www.abinit.org`
- `theory.polytechnique.fr`