

# Site de Grenoble Polygone Scientifique



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Many thanks Titou, Pina, Julien, Michel.



## All-electron space-time formalism for efficient cubic scaling **GW** calculations

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- GW calculations tackle the calculation of electronic energy levels as given by a photoemission experiment (electron addition /removal energies)
- G is the time-ordered one-body Green's function with poles at the proper electron addition/removal energies

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{f_n(\mathbf{r}) f_n^*(\mathbf{r}')}{\hbar\omega - \varepsilon_n + i\eta\hbar \operatorname{sgn}(\varepsilon_n - \mu)}$$

$$\begin{aligned} \varepsilon_n &= (E_n^{N+1} - E_0^N) & (\varepsilon_n > \mu) \\ \varepsilon_n &= (E_0^N - E_n^{N-1}) & (\varepsilon_n > \mu) \end{aligned}$$

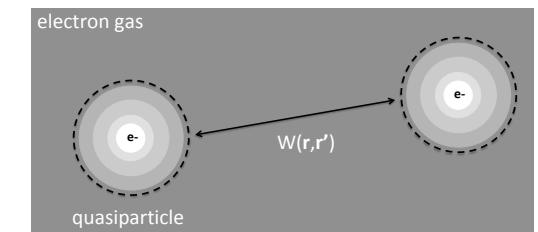
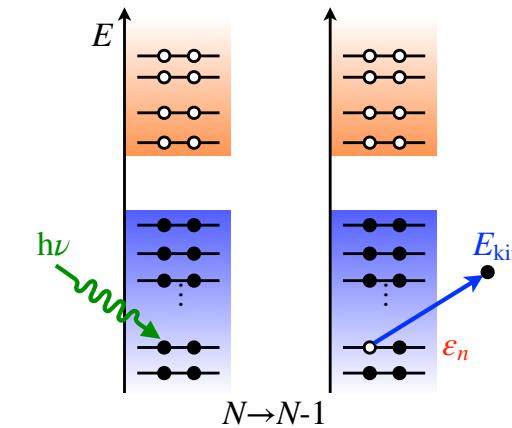
- W is the screened Coulomb potential

$$W(1, 2) = v(1, 2) + \int d34 v(1, 3)\tilde{\chi}(3, 4)W(4, 2)$$

- GW : lowest approximation in W for the exchange-correlation self-energy

$$\Sigma(1, 2) = i \int d34 G(1, 3)W(4, 1^+) \tilde{\Gamma}(4, 2; 3)$$

Vertex  $\tilde{\Gamma}(1, 2, 3) = \delta(1, 2)\delta(1, 3) + \frac{\partial \Sigma(1, 2)}{\partial V(3)}$



$$(V = U + V^H)$$

U = infinitesimal external perturbation

# The GW in practice : frequency representation and Kohn-Sham starting point

Exchange and Correlation

$$\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon) = \frac{i}{2\pi} \int d\omega e^{i\omega 0^+} G(\mathbf{r}, \mathbf{r}'; \varepsilon + \omega) W(\mathbf{r}, \mathbf{r}'; \omega)$$

Energy convolution between G and W

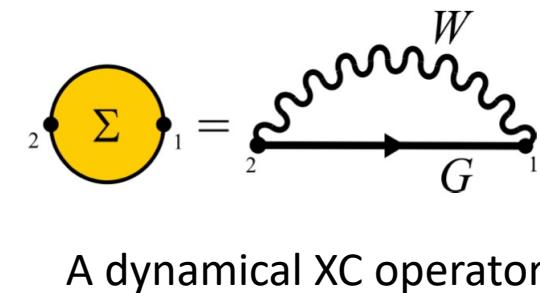
First-order like perturbation to correct Kohn-Sham energies

$$\underline{\varepsilon_n^{GW}} = \varepsilon_n^{KS} + \langle \phi_n^{KS} | \Sigma_{XC}(\underline{\varepsilon_n^{GW}}) - V_{XC}^{DFT} | \phi_n^{KS} \rangle$$

Build the « best » G and W available : start with Kohn-Sham eigenstates possibly with hybrid functional

$$G^{KS}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{\phi_n^{KS}(\mathbf{r}) [\phi_n^{KS}]^*(\mathbf{r}')}{\hbar\omega - \varepsilon_n^{KS} + i0^+ \hbar \operatorname{sgn}(\varepsilon_n^{KS} - \mu)}$$

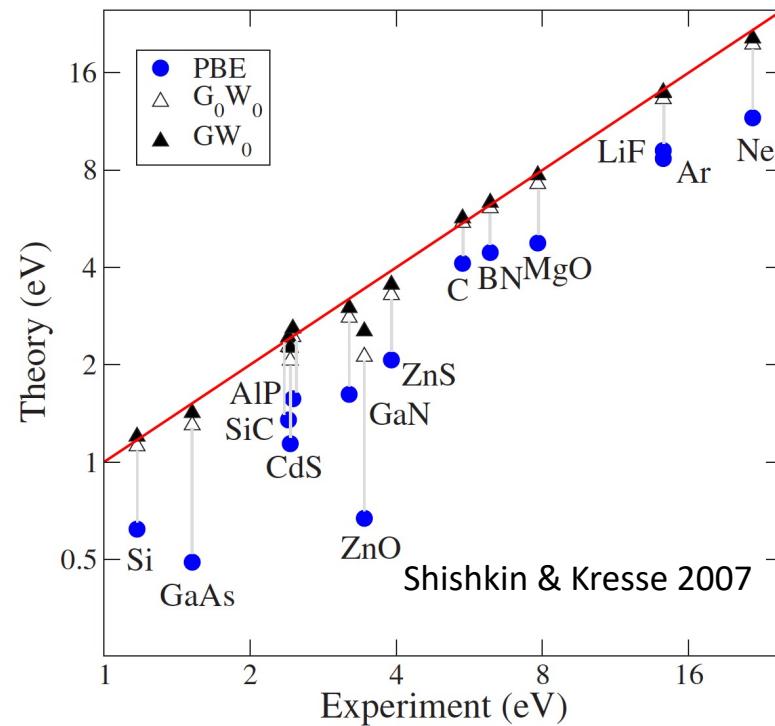
$$\chi_0^{KS}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{mn} (f_m - f_n) \frac{[\phi_m^{KS}(\mathbf{r})]^* \phi_n^{KS}(\mathbf{r}) [\phi_n^{KS}(\mathbf{r}')]^* \phi_m^{KS}(\mathbf{r}')}{\omega - (\varepsilon_m^{KS} - \varepsilon_n^{KS}) + i0^+}$$



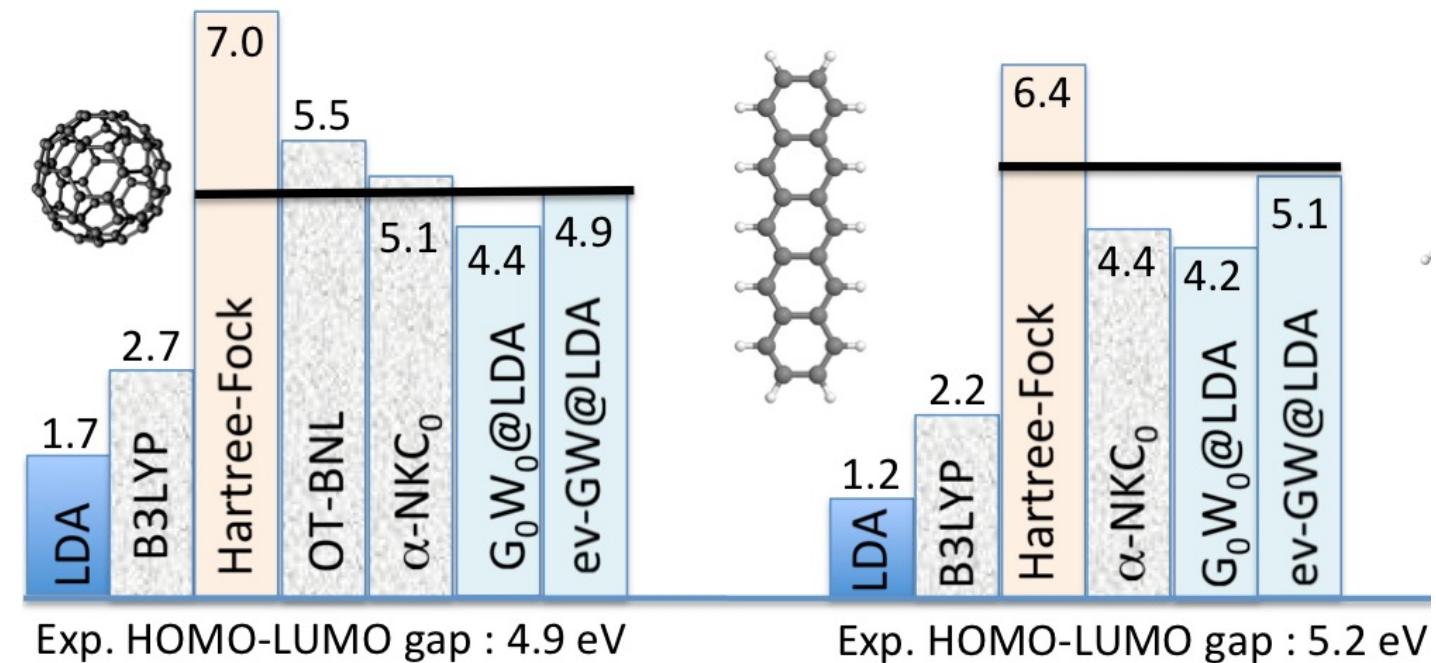
The construction of the susceptibility scales as O(N<sup>4</sup>)

# Standard results in condensed matter physics and chemistry

First ab initio  $GW$  calculation in solids : mid-80s

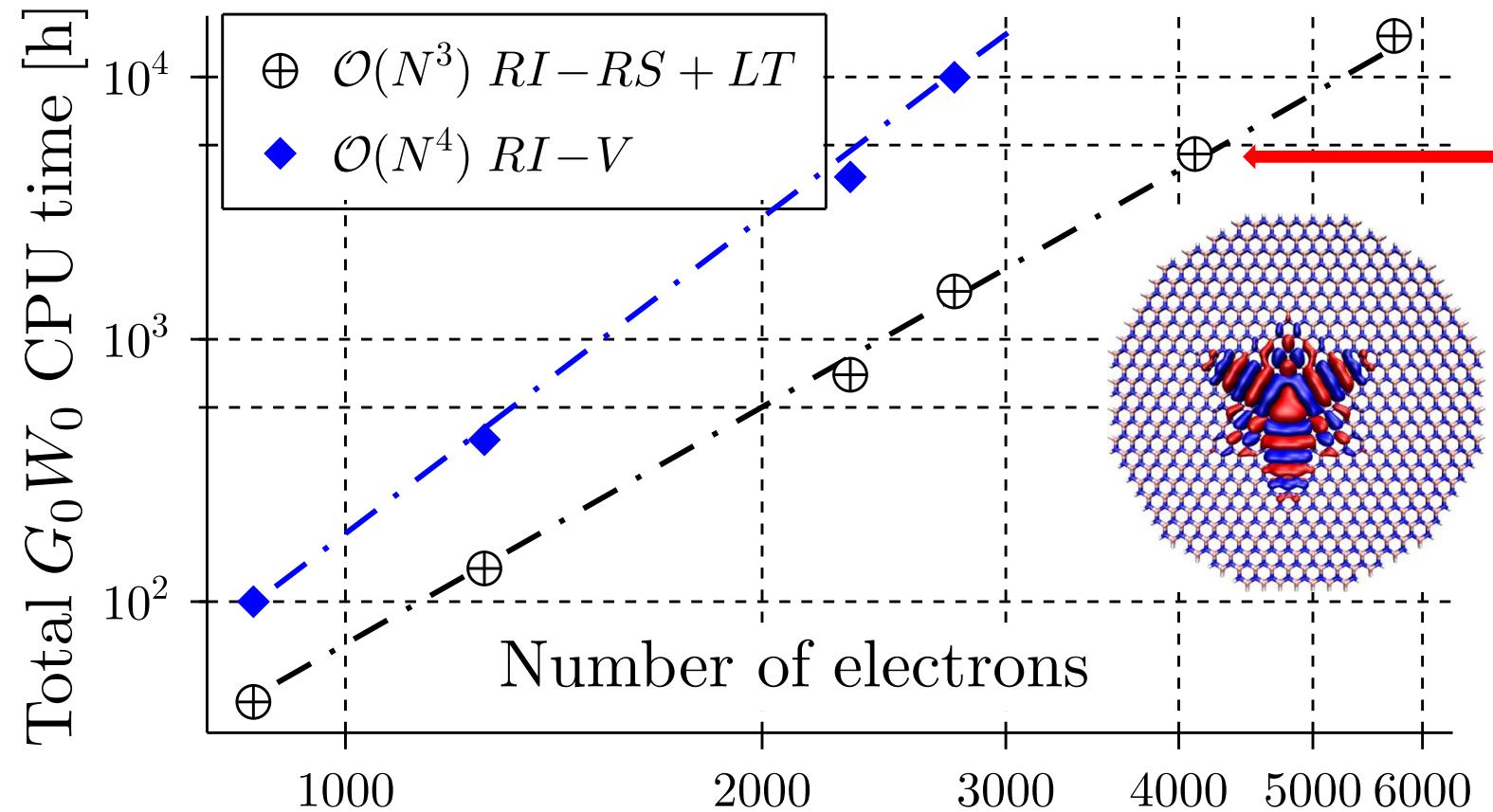


Blase, Attaccalite, Olevano, 2011



Partially self-consistent  $GW$  : insert self-consistently corrected energy levels to (re)build G and W => much more accurate in particular when starting with functionals with no exact exchange.

Fully self-consistent  $GW$  : update as well the eigenstates (or spectral weights in G) => several flavours of self-consistency and much more expensive.



Cubic-scaling algorithm:  
4000 electrons (667 C atoms)  
in less than 5000 hours  
(with meV accuracy).

Standard  $O(N^4)$  approach : 3000 electrons (500 carbon atoms) with 6-311G\* basis and resolution-of-identity (RI-V) within 20000 hours !

=> GW very popular post-DFT approach for electronic structure properties implemented in many physics and chemistry codes (VASP, ABINIT, QuantumEspresso, BerkeleyGW, WEST, Turbomole, CP2K, MolGW, Fiesta, QuAcK, etc.)

$$\chi_0(\mathbf{r}, \mathbf{r}'; \omega) = 2 \sum_{ja} \frac{\phi_j^*(\mathbf{r}) \phi_a(\mathbf{r}) \phi_a^*(\mathbf{r}') \phi_j(\mathbf{r}')}{\omega - (\varepsilon_a - \varepsilon_i)} + c.c.$$



Imaginary time representation

$$\chi_0(\mathbf{r}, \mathbf{r}'; i\tau) = -i G(\mathbf{r}, \mathbf{r}'; i\tau) G(\mathbf{r}', \mathbf{r}; -i\tau)$$

$$G(\mathbf{r}, \mathbf{r}'; i\tau) = -i \sum_j^{\text{occ}} \phi_j(\mathbf{r}) \phi_j(\mathbf{r}') e^{\varepsilon_j \tau} \quad (\tau > 0)$$

$$-i \sum_a^{\text{vir}} \phi_a(\mathbf{r}) \phi_a(\mathbf{r}') e^{\varepsilon_a \tau} \quad (\tau < 0)$$

Almlöf, Häser (1991,1992) :  
Laplace transform idea for MP2 calculations

$$E^{(2)} = -\frac{1}{4} \sum_{ijab} \frac{\langle ab || ij \rangle^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

Laplace transform

$$(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)^{-1} = \int_0^{+\infty} dt e^{-(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)t}$$

Disentangles energies in denominator

The decoupling of the sums between occupied and unoccupied states reduce the calculation of the susceptibility to  $O(N^3)$ . Such an approach has hardly been used in practice but is regaining popularity under various forms.

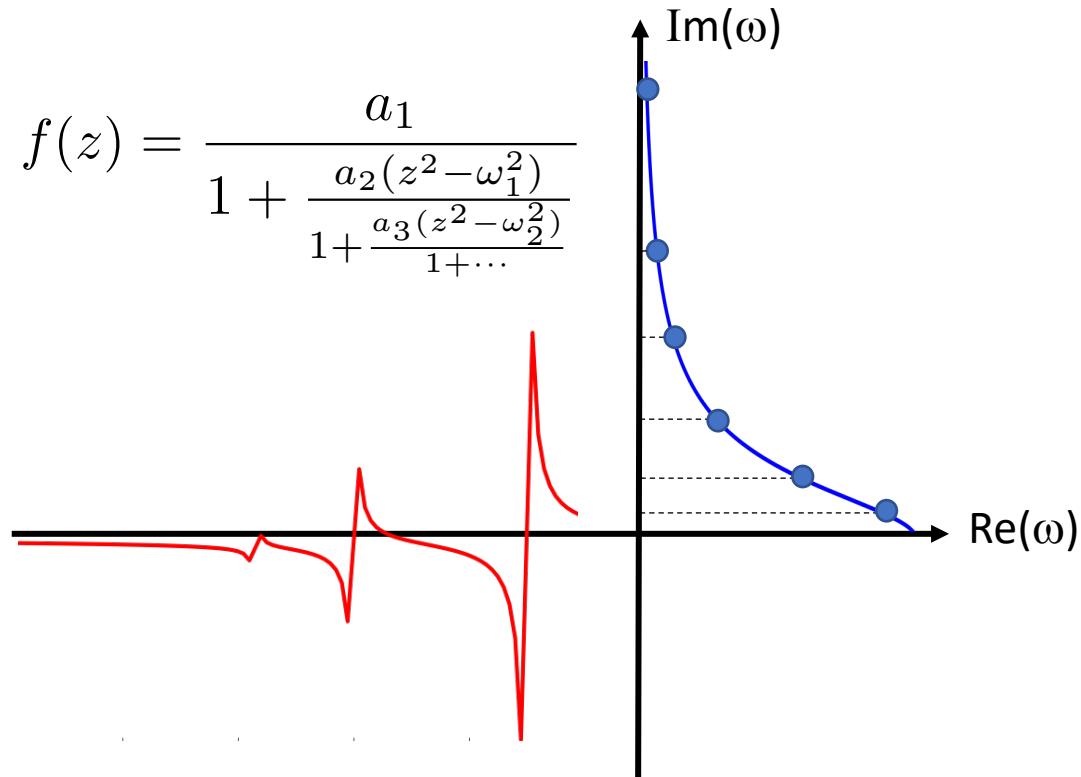
## A first issue : The GW self-energy analytic continuation problem

$$\chi_0(\mathbf{r}, \mathbf{r}'; i\tau) \implies \chi_0(\mathbf{r}, \mathbf{r}'; i\omega) \implies W(\mathbf{r}, \mathbf{r}'; i\omega) \implies \Sigma(\mathbf{r}, \mathbf{r}'; i\omega)$$

Safe and stable procedure : the self-energy is smooth along the imaginary axis

BUT: the analytic continuation to the real-axis is a well-known problem

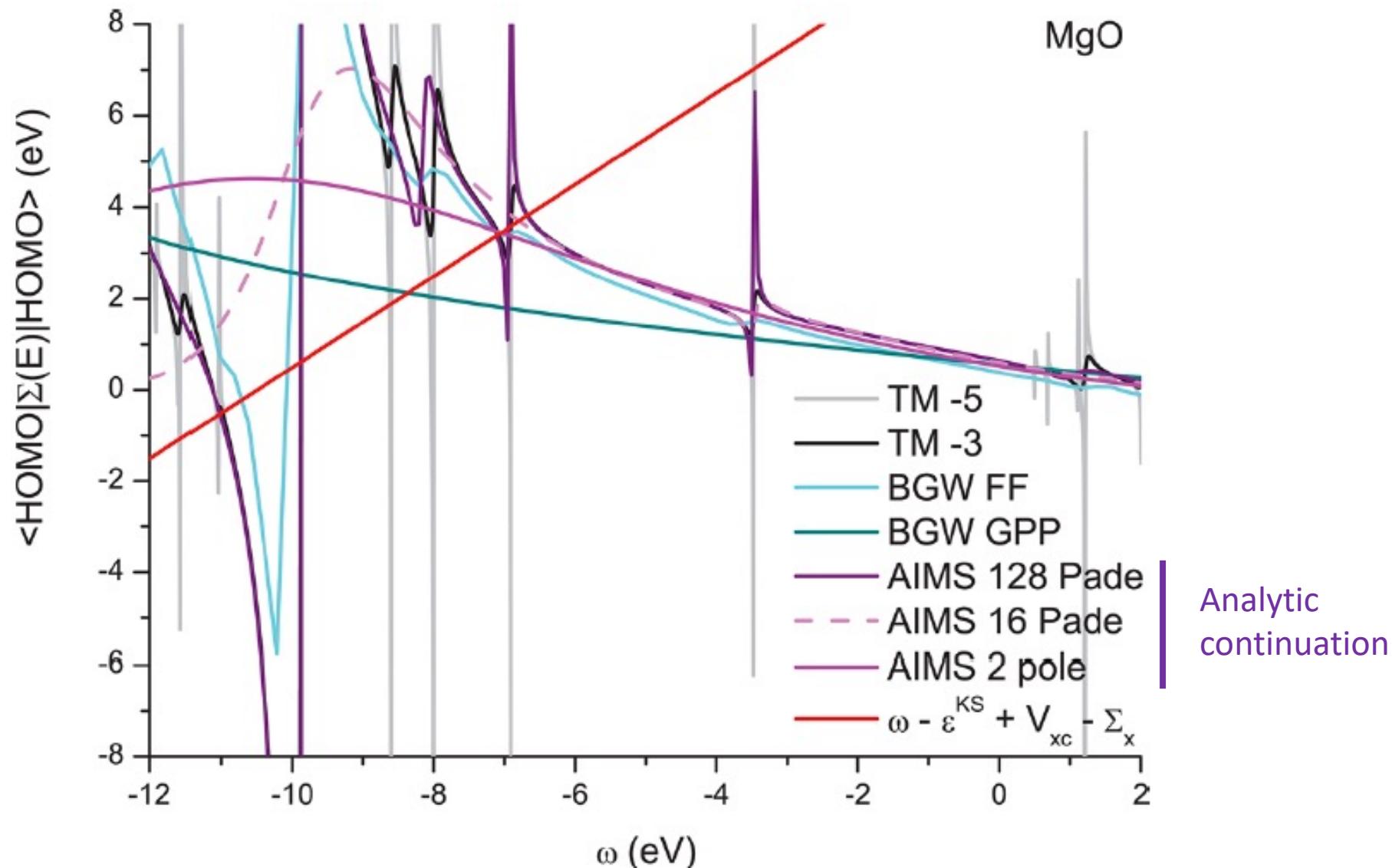
$$f(z) = \frac{a_1}{1 + \frac{a_2(z^2 - \omega_1^2)}{1 + \frac{a_3(z^2 - \omega_2^2)}{1 + \dots}}}$$

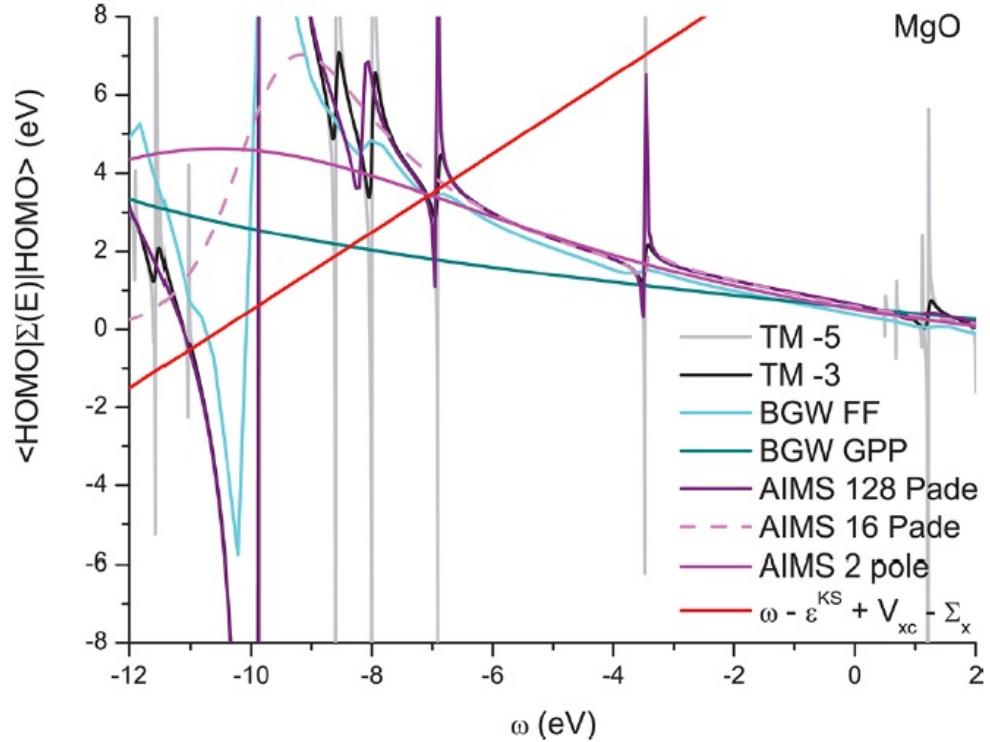


$$\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon) = \frac{i}{2\pi} \int d\omega e^{i\omega 0^+} G(\mathbf{r}, \mathbf{r}'; \varepsilon + \omega) W(\mathbf{r}, \mathbf{r}'; \omega)$$

The number of pole of the self-energies are the poles of  $G$  multiplied by the poles of  $W$  !

## A difficult case (among others)





$$\varepsilon_n^{GW} = \varepsilon_n^{KS} + \langle \phi_n^{KS} | \Sigma_{XC}(\varepsilon_n^{GW}) - V_{XC}^{DFT} | \phi_n^{KS} \rangle$$

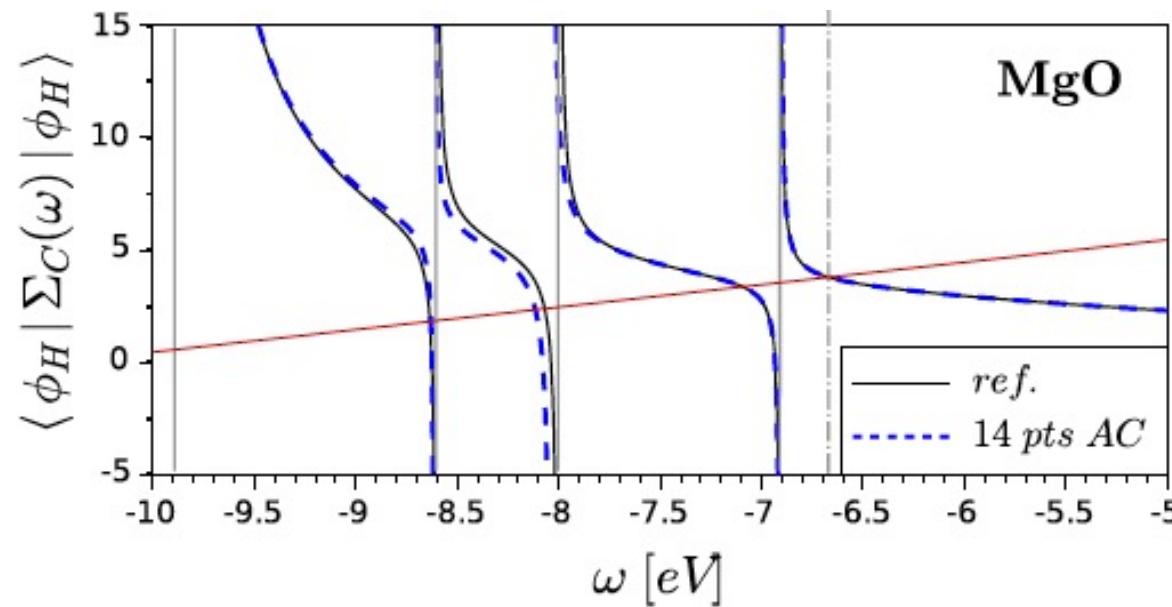
Potentially large errors, including missing states !  
(see "GW100" paper, JCTC 2015)

Solution :  $G$  and its poles on the real axis are known ! The only thing that needs to be continued is the screened Coulomb potential that has much less poles than the self-energy !

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{\omega - \varepsilon_n + i\eta \times \text{sgn}(\varepsilon_n - \mu)}$$

$$\chi_0(\mathbf{r}, \mathbf{r}'; i\tau) \implies \chi_0(\mathbf{r}, \mathbf{r}'; i\omega) \implies W(\mathbf{r}, \mathbf{r}'; i\omega) \implies W(\mathbf{r}, \mathbf{r}'; \omega)$$

Form  $\Sigma(\omega)$



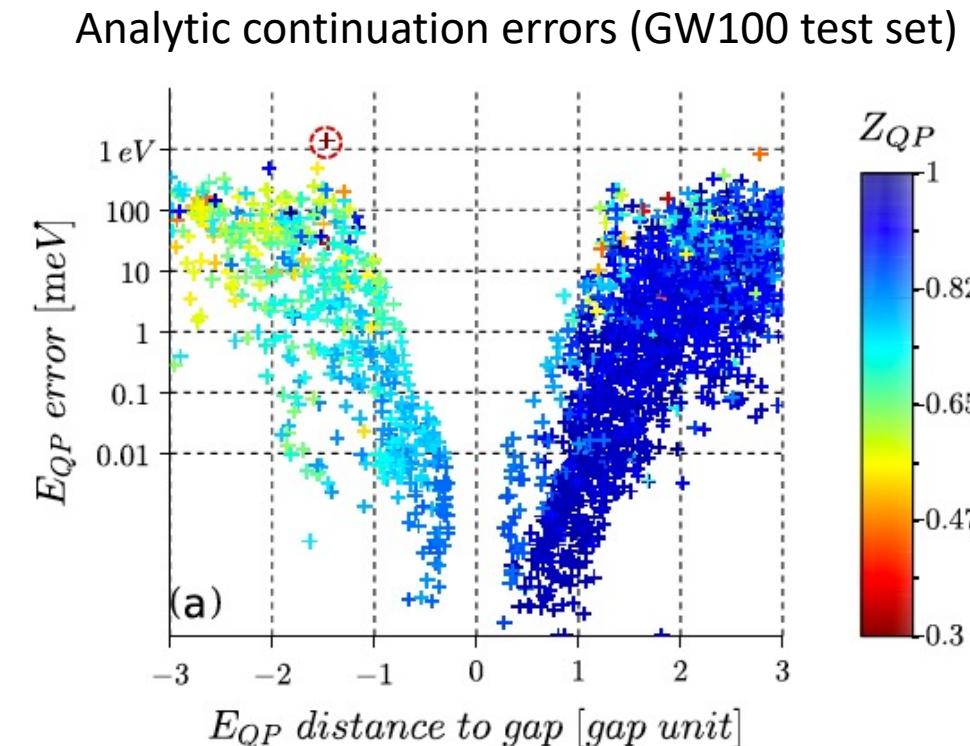
Quasiparticle energy at the crossing of the red line and the correlation self-energy  $\Sigma_C(\omega)$

$$\varepsilon_n^{GW} = \varepsilon_n^{KS} + \langle \phi_n^{KS} | \Sigma_{XC}(\varepsilon_n^{GW}) - V_{XC}^{DFT} | \phi_n^{KS} \rangle$$

↔ Crossing of 2 functions:  $\varepsilon_n^{GW} = \omega$

$$f(\omega) = \omega - \varepsilon_n^{KS} + \langle \phi_n^{KS} | V_{XC}^{DFT} | \phi_n^{KS} \rangle$$

$$g(\omega) = \langle \phi_n^{KS} | \Sigma_{XC}(\omega) | \phi_n^{KS} \rangle$$



Analytic continuation extremely safe close to the gap with few points (10-14) along the imaginary axis.

In physics (planewaves) or quantum chemistry (atomic basis) susceptibility not calculated on a grid :

$$\chi_0(\mathbf{r}, \mathbf{r}'; i\omega) = 2 \sum_{ja} \frac{\phi_j^*(\mathbf{r}) \phi_a(\mathbf{r}) \phi_a^*(\mathbf{r}') \phi_j(\mathbf{r}')}{i\omega - (\varepsilon_a - \varepsilon_i)} + c.c.$$

but using an auxiliary basis (planewaves, atomic orbitals, etc.) that projects on codensities (MOs products) :

$$\langle P_\mu | \chi_0(\mathbf{r}, \mathbf{r}'; i\omega) | P_\nu \rangle = 2 \sum_{ja} \frac{\langle \phi_j \phi_a | P_\mu \rangle \langle P_\nu | \phi_a \phi_j \rangle}{i\omega - (\varepsilon_a - \varepsilon_i)} + c.c.$$

MOs are entangled (not separable) in RI fitting coefficients !

## Standard resolution-of-the-identity (RI) approach

This amounts in quantum chemistry to a resolution-of-the-identity (RI) technique :

$$\phi_n(\mathbf{r})\phi_m(\mathbf{r}) = \sum_{\mu} \mathcal{F}_{\mu}(\phi_n\phi_m)P_{\mu}(\mathbf{r})$$



$$\mathcal{F}_{\mu}^V(\phi_n\phi_m) = \sum_{\nu} [V^{-1}]_{\mu\nu}(P_{\nu}|\phi_n\phi_m)$$

Coulomb fitting

$$[\chi_0^{RI}(i\omega)]_{\mu\nu} = 2 \sum_{ja} \frac{\mathcal{F}_{\mu}(\phi_j\phi_a)\mathcal{F}_{\nu}(\phi_j\phi_a)}{i\omega - (\varepsilon_a - \varepsilon_j)} + c.c.$$

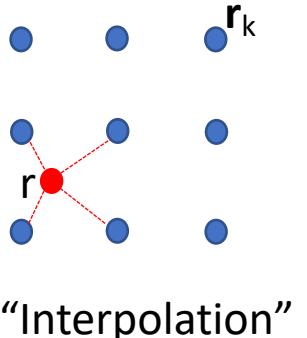
or

$$[\chi_0^{RI}(i\tau)]_{\mu\nu} = -2i \sum_{ja} \mathcal{F}_{\mu}(\phi_j\phi_a)\mathcal{F}_{\nu}(\phi_j\phi_a)e^{\varepsilon_j\tau}e^{-\varepsilon_a\tau}$$

MOs are entangled (not separable) in RI fitting coefficients !

$$\phi_n(\mathbf{r})\phi_m(\mathbf{r}) = \sum_{\mu} \mathcal{F}_{\mu}^V(\phi_n\phi_m)P_{\mu}(\mathbf{r})$$

Fitting coefficient by interpolation (quadrature)



$$\mathcal{F}_{\mu}^{RS}(\phi_j\phi_a) = \sum_k M_{\mu k} \phi_j(\mathbf{r}_k)\phi_a(\mathbf{r}_k)$$

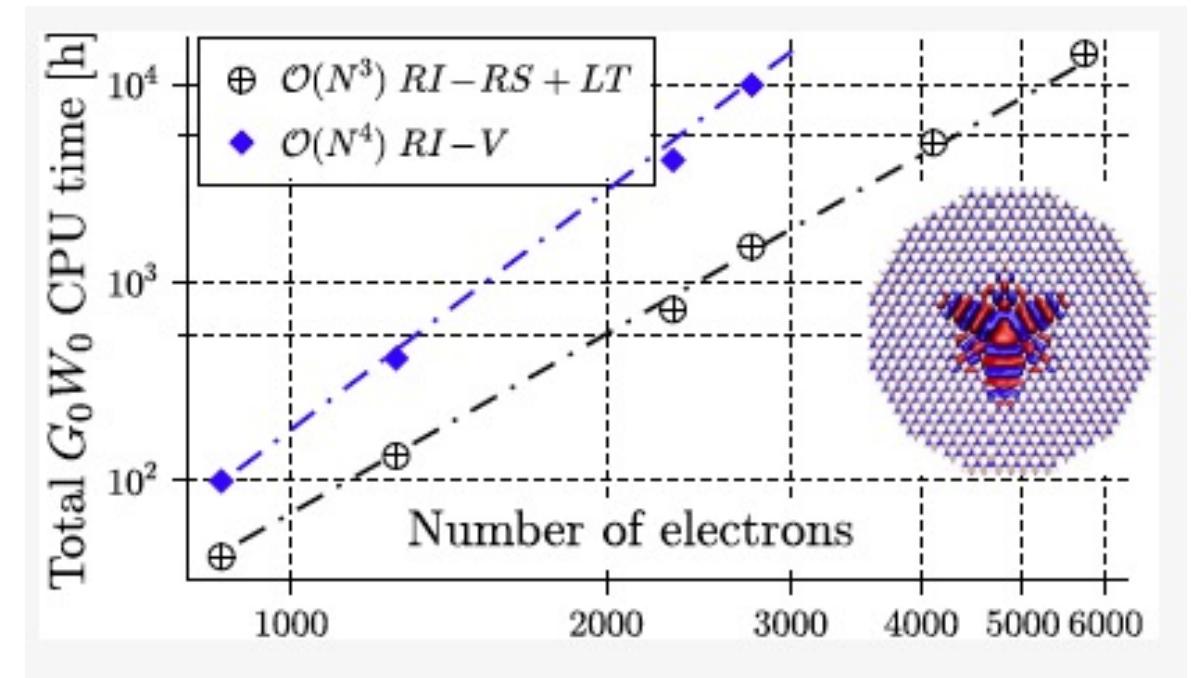
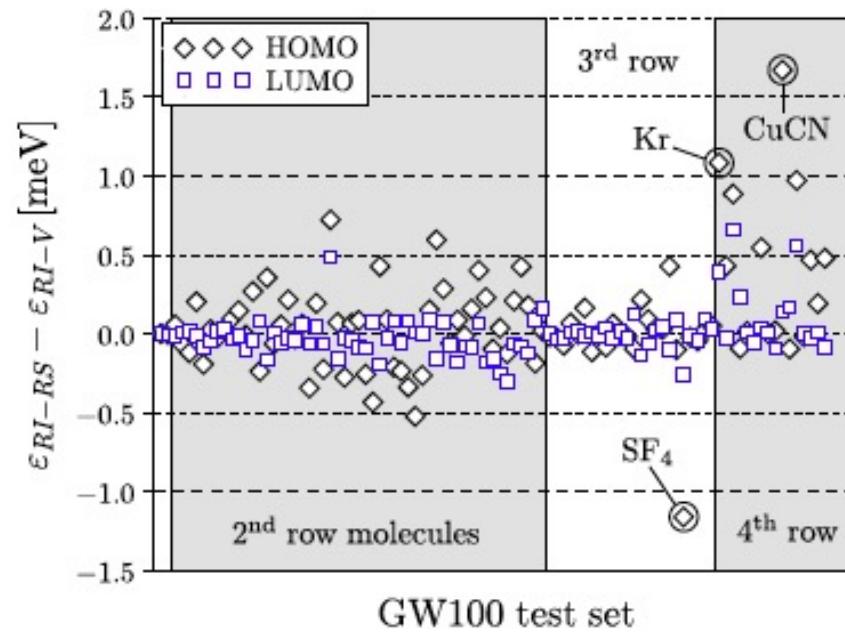
Build  $\{M_{\mu k}, \mathbf{r}_k\}$

$$\underset{\{M_{\mu k}, \mathbf{r}_k\}}{\text{argmin}} \sum_{\mu, ja} \left| \left( \mathcal{F}_{\mu}^{RS}(\phi_j\phi_a) - \mathcal{F}_{\mu}^V(\phi_j\phi_a) \right) P_{\mu} \right|_V^2$$

Least-square minimization  
of optimal quadrature

Build minimal grid that reproduces a RI-V calculation for a given auxiliary basis and a given accuracy (meV)  
=> Typical grid size needed: 300-500 points per atom (3-4 times larger than auxiliary Gaussian basis set)

Standard RI-V results can be obtained with much reduced CPU (cubic scaling) and meV accuracy !  
Crossover with standard quartic scaling approach for systems containing a few dozens of atoms.



- The same technique(s) can be used for cubic-scaling RPA correlation energies

(Duchemin & Blase, JCP 2019)

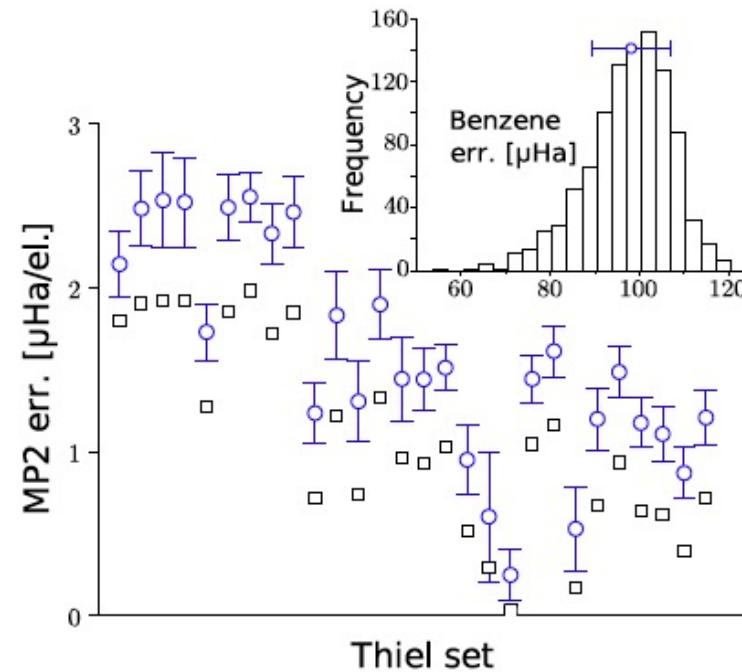
$$E_C^{RPA} = \frac{1}{2\pi} \int_0^\infty d\omega \operatorname{Tr} [\ln(1 - \chi_0(i\omega) \cdot v) + \chi_0(i\omega) \cdot v]$$

- The same technique can be « simply » used to calculate 2-electron Coulomb integrals (applications to HF, MP2, etc.)

$$(ia|jb) = \sum_{\mu\nu} \mathcal{F}_\mu(ia) \cdot (P_\mu|P_\nu) \cdot \mathcal{F}_\mu(jb)$$



$$E_C^{MP2} = - \sum_{ij} \sum_{ab} \frac{(ia|jb)[2(ia|jb) - (ib|ja)]}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$



For Coulomb integrals, similar in spirit to other techniques in quantum chemistry such as chain-of-sphere COS (Neese et al, 2011), Tensor Hyper Contraction techniques (Sherrill et al. 2016), etc.

Towards large scale GW (and Bethe-Salpeter) calculations ...

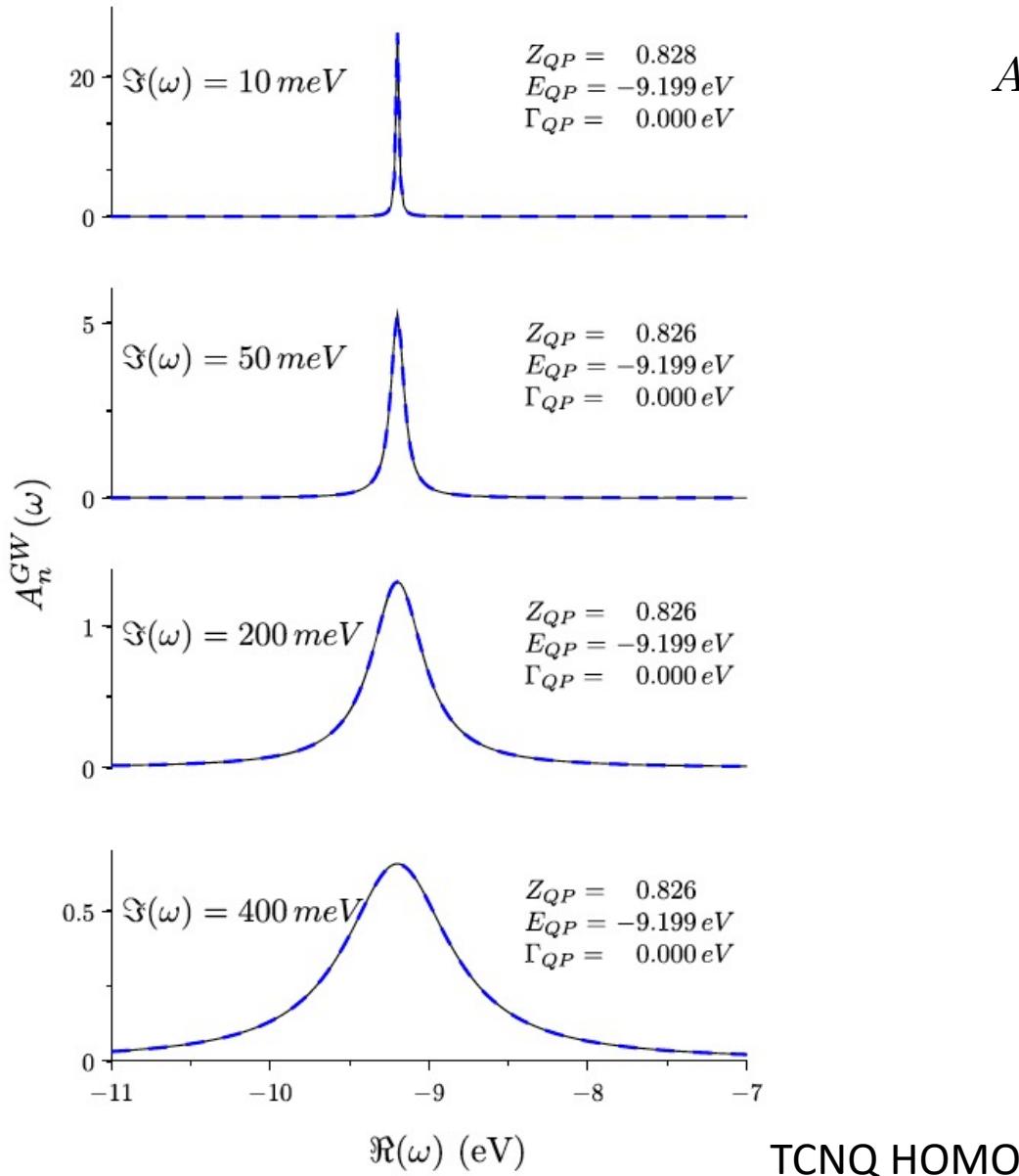
Conclusions : cubic scaling all-electron *GW* calculations can be performed on hundreds of atoms with modest CPU time requirements (reducing the memory needs as well).

- No use of sparsity in AO basis set overlap
- No use of localization of 2-body operators such as  $G(\mathbf{r}, \mathbf{r}'; \omega), \chi_0(\mathbf{r}, \mathbf{r}'; \omega)$ , etc.

## THANKS

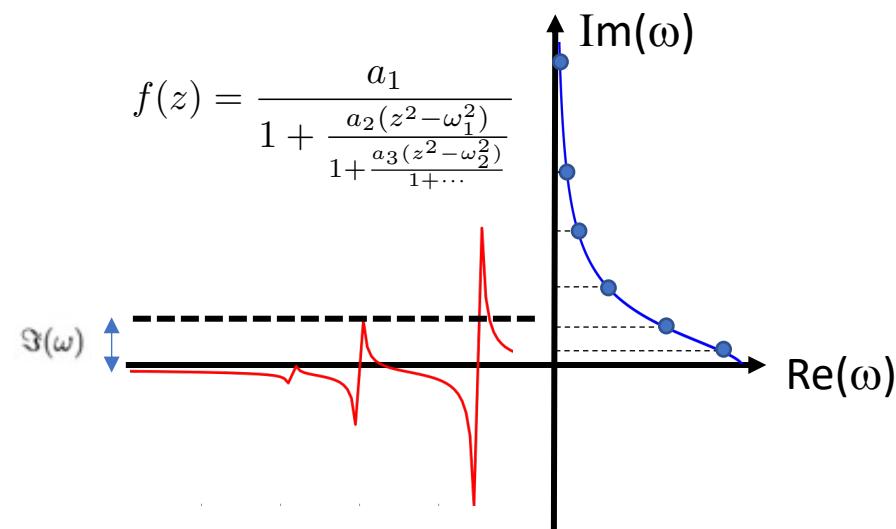
Many thanks again Titou, Pina, Julien, Michel.

## GW spectral function and quasiparticle peak



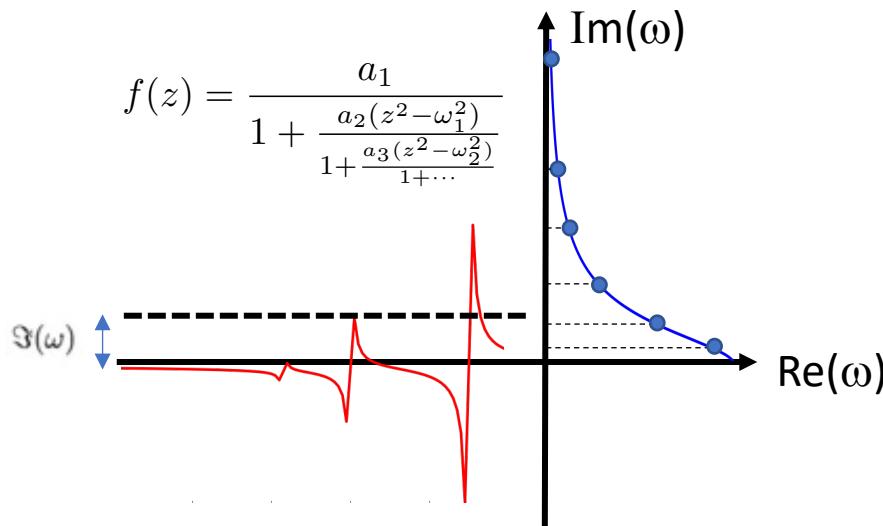
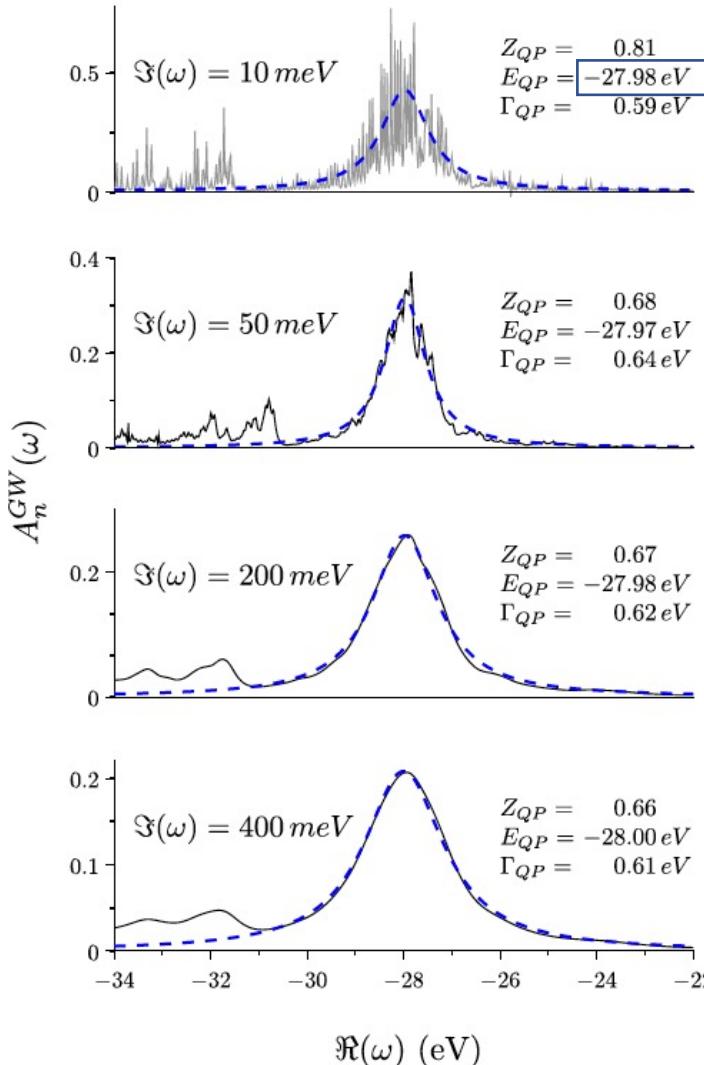
$$A_n^{GW} = \frac{1}{\pi} |Im\langle\phi_n|G(\omega)|\phi_n\rangle|$$

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



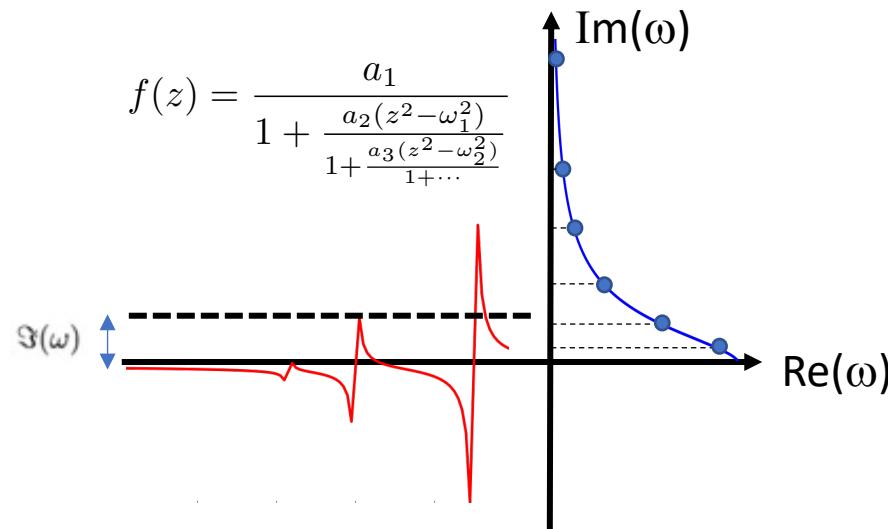
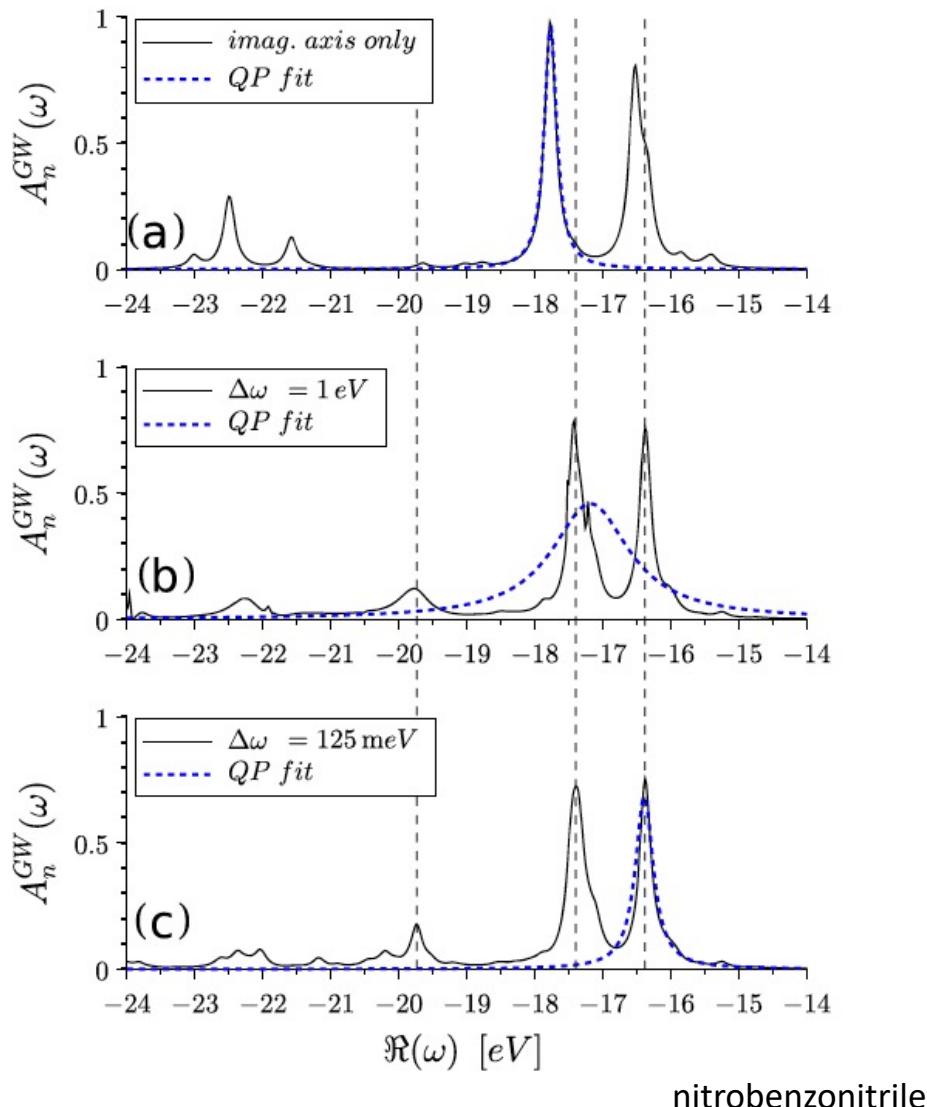
## GW spectral function and quasiparticle peak

$$A_n^{GW}(\omega) = \frac{1}{\pi} |\Im(\langle \phi_n | G(\omega) | \phi_n \rangle)|$$



# GW spectral function and quasiparticle peak

Multiple quasiparticle (?) peaks



## Tensor Hypercontraction Technique

R. M. Parrish, E. G. Hohenstein, T. J. Martinez, and C. D. Sherrill, J. Chem. Phys. 137, 224106 (2012)

$$\operatorname{argmin}_{Z} \sum_{\rho, \rho'} ||(\rho | \rho') - \sum_{kk'} \rho(\mathbf{r}_k) \cdot Z_{kk'} \cdot \rho'(\mathbf{r}_{k'})||^2$$

Similar idea but fit directly 2-electrons Coulomb integrals  $\Rightarrow O(N^4)$  setting of quadrature instead of  $O(N^3)$  in our case.

### Chain-of-sphere approach (COS)

Neese et al. 2009 - present

$$(\mu\kappa | \nu\lambda) \simeq \sum_k W_k \mu(\mathbf{r}_k) \kappa(\mathbf{r}_k) \int d\mathbf{r} \frac{\nu(\mathbf{r}) \lambda(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_k|}$$

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Quadrature on one codensity onlyOne-electron integrals in Gaussian basis

## Imaginary frequency grid points (RPA)

Need to evaluate integrals of the form

$E$  ranges from  $E_{gap}$  to  $\max(\varepsilon_a - \varepsilon_i)$

$$\int_0^\infty d\omega \left( \frac{1}{E - i\omega} - \frac{1}{E + i\omega} \right) = \pi$$

Minimize

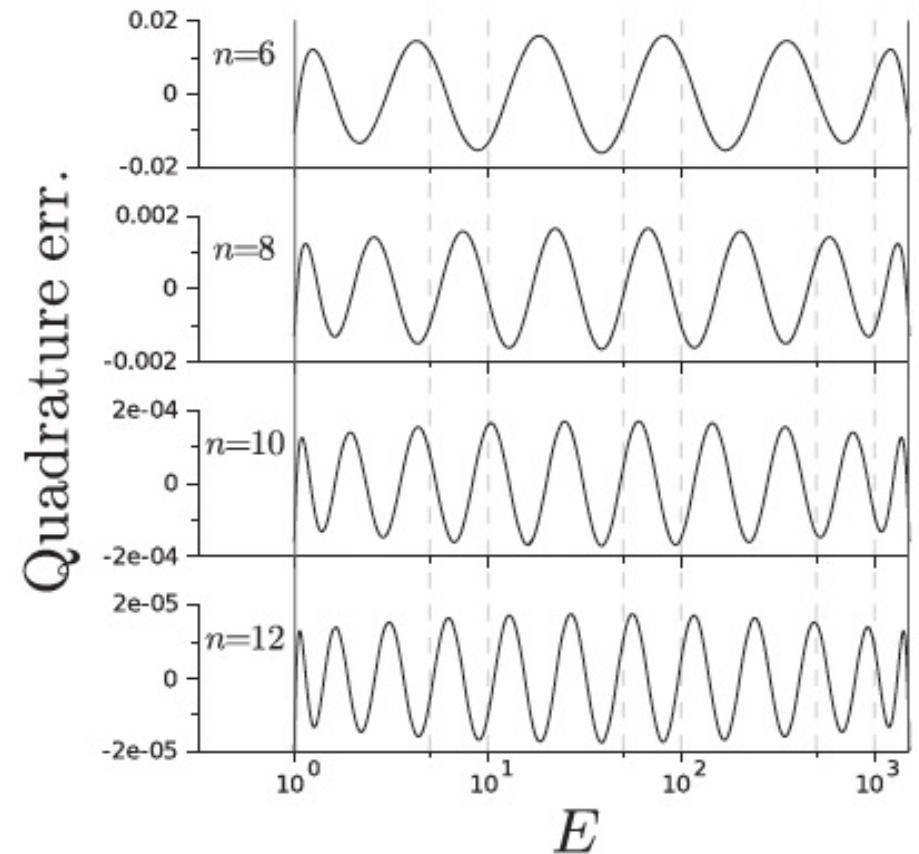
$$\operatorname{argmin}_{w_k, z_k} \left[ \int_{\ln(E_{min})}^{\ln(E_{max})} du \left\| \sum_k w_k \left[ \frac{1}{e^u - iz_k} + \frac{1}{e^u + iz_k} \right] - \pi \right\|^2 \right].$$

Discretized integral

↓  
Discrete frequencies

↓  
weight

Typically 10 to 14 frequencies



## Contour deformation with analytic continuation

$$\begin{aligned}\Sigma_C^{GW}(\mathbf{r}, \mathbf{r}'; E) = & \frac{-1}{2\pi} \int_{-\infty}^{\infty} d\omega G(\mathbf{r}, \mathbf{r}'; E + i\omega)(W - v)(\mathbf{r}, \mathbf{r}'; i\omega) \\ & - \sum_i \phi_i(\mathbf{r})\phi_i(\mathbf{r}')(W - v)(\mathbf{r}, \mathbf{r}'; \underline{\varepsilon_i - E})\theta(\varepsilon_i - E) \\ & + \sum_a \phi_a(\mathbf{r})\phi_a(\mathbf{r}')(W - v)(\mathbf{r}, \mathbf{r}'; \underline{E - \varepsilon_a})\theta(E - \varepsilon_a)\end{aligned}$$



Poles of W shifted by  
Green's function poles

