Réunion general GDR NBODY
(Nearly in) Toulouse, Janvier 2022

Many thanks Titou, Pina, Julien, Michel.

cnrs GDR Groupement de recherche
NBODY Quantum n-body problem in chemistry and physics

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

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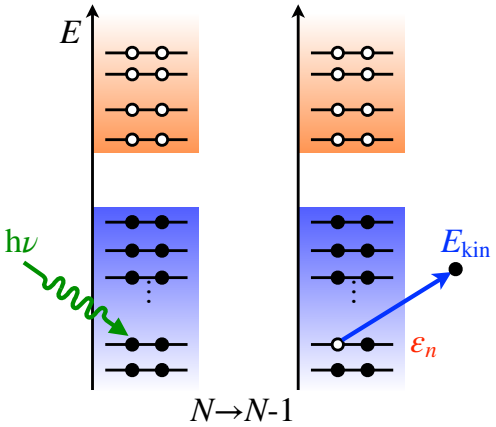
The GW approximation in a nutshell

Lars Hedin, Phys. Rev. 139, A796 (1965)

- GW calculations tackle the calculation of electronic energy levels as given by a photoemission experiment (electron addition /removal energies)

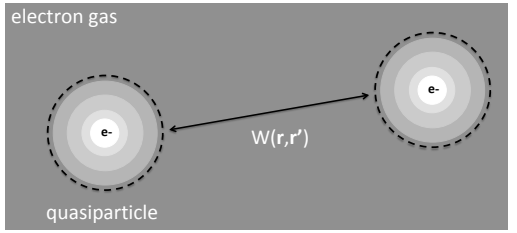
- G is the time-ordered one-body Green's function with poles at the proper electron addition/removal energies



$$G(\mathbf{r},\mathbf{r}';\omega)=\sum_n \frac{f_n(\mathbf{r})f_n^*(\mathbf{r}')}{\hbar\omega-\varepsilon_n+i\eta\hbar\,\mathrm{sgn}(\varepsilon_n-\mu)} \quad \Longleftrightarrow \quad \begin{aligned}\varepsilon_n &= (E_n^{N+1}-E_0^N) \qquad (\varepsilon_n>\mu)\\ \varepsilon_n &= (E_0^N-E_n^{N-1}) \qquad (\varepsilon_n>\mu)\end{aligned}$$

- 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

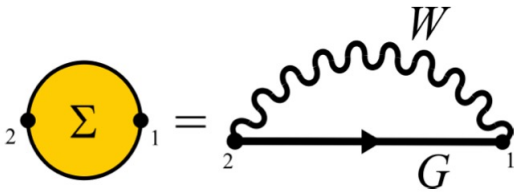
$$\Sigma(1,2)=i\int d34\; G(1,3)W(4,1^+)\tilde{\Gamma}(4,2;3)$$

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

$(V=U+V^H)$

U = infinitesimal external perturbation

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



A dynamical XC operator

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

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

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

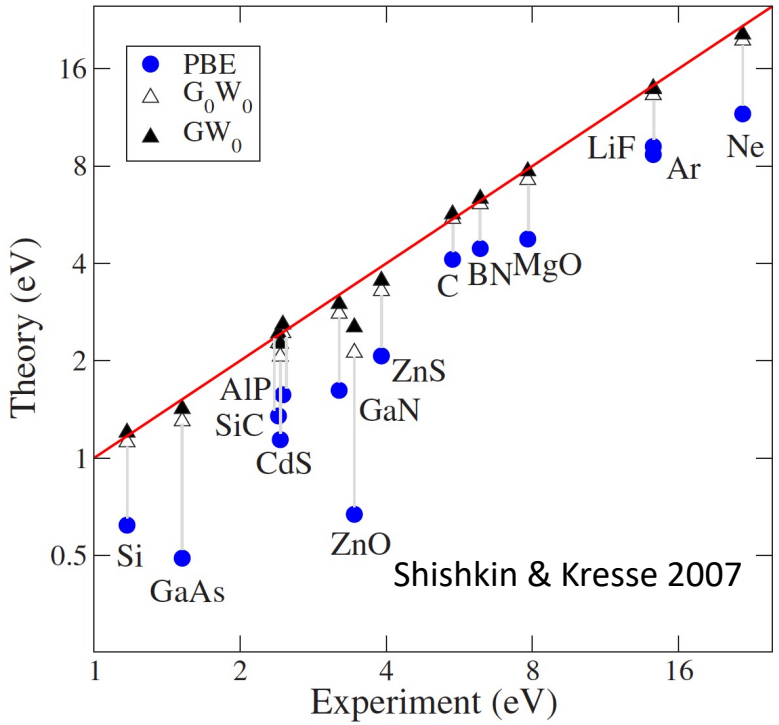
$$G^{KS}(\mathbf{r},\mathbf{r}';\omega) = \sum_n \frac{\phi_n^{KS}(\mathbf{r})[\phi_n^{KS}]^*(\mathbf{r}')}{\hbar\omega - \varepsilon_n^{KS} + i0^+\hbar\,\mathrm{sgn}(\varepsilon_n^{KS}-\mu)}$$

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

The construction of the susceptibility scales as $O(N^4)$

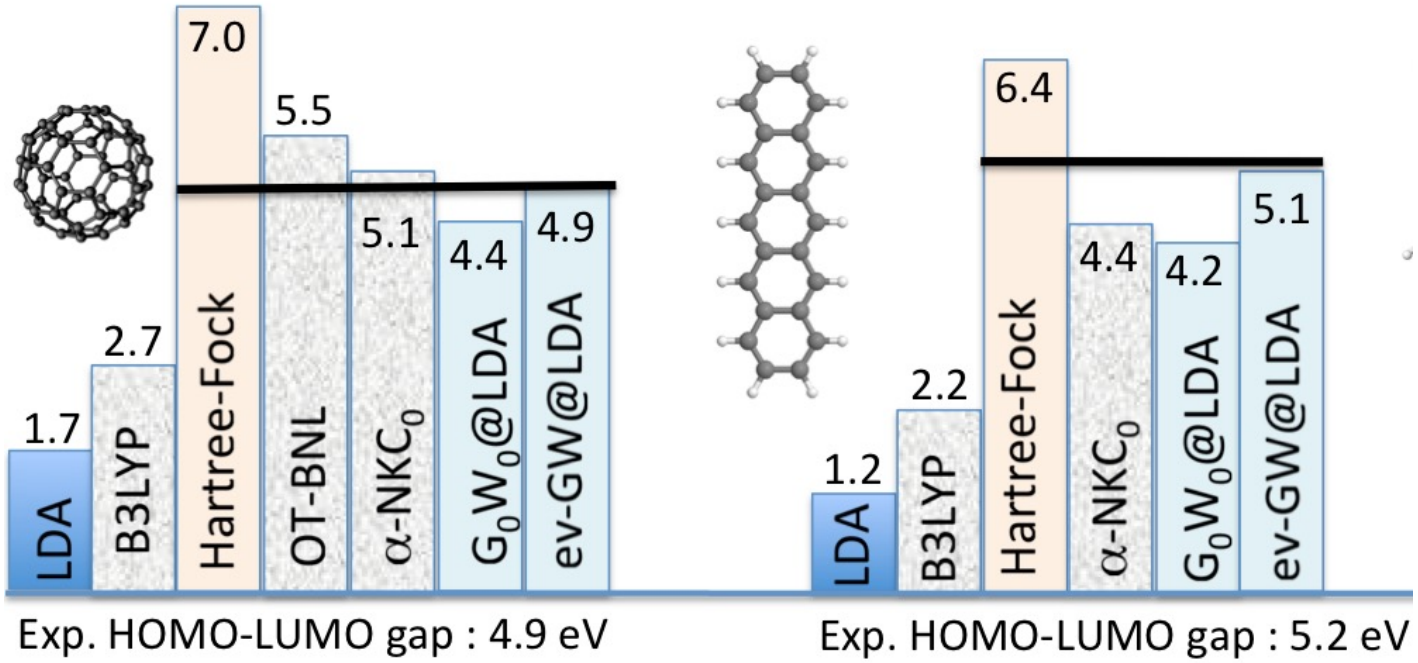
Standard results in condensed matter physics and chemistry

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



Shishkin & Kresse 2007

Blase, Attaccalite, Olevano, 2011

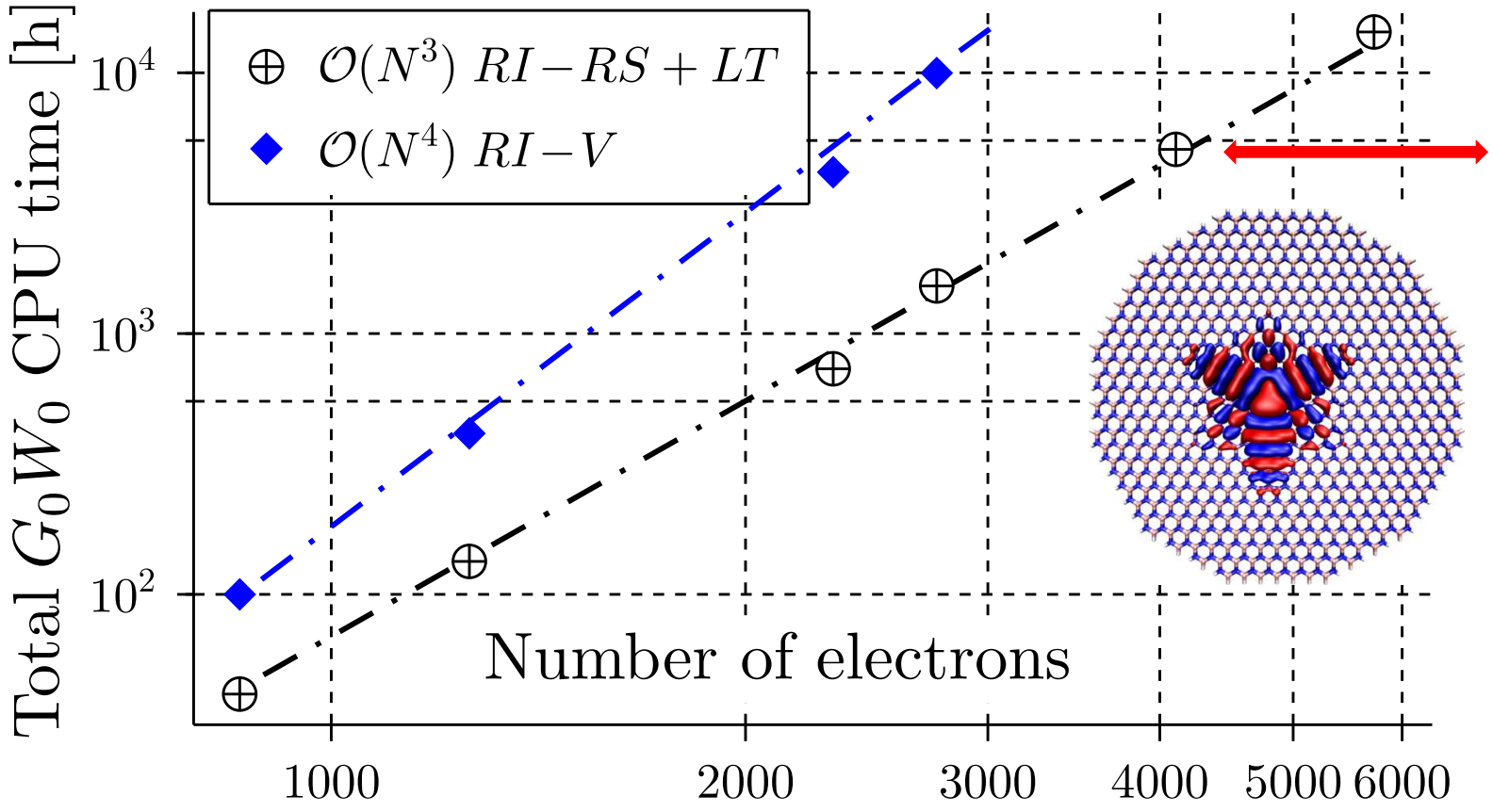


Partially self-consistent *GW* : insert self-consistently corrected energy levels to (re)build G and W => much more accurate in particular when starting with functionals with no exact exchange.

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

From quartic to cubic scaling GW formalism

Duchemin & Blase JCTC 2021



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

Standard *O(N⁴)* 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.)

Cubic-scaling space-time approach (Rojas, Godby, Needs, PRL 1995)

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

Imaginary time representation

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

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

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

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.

See Kresse *et al*. PRB 2016.

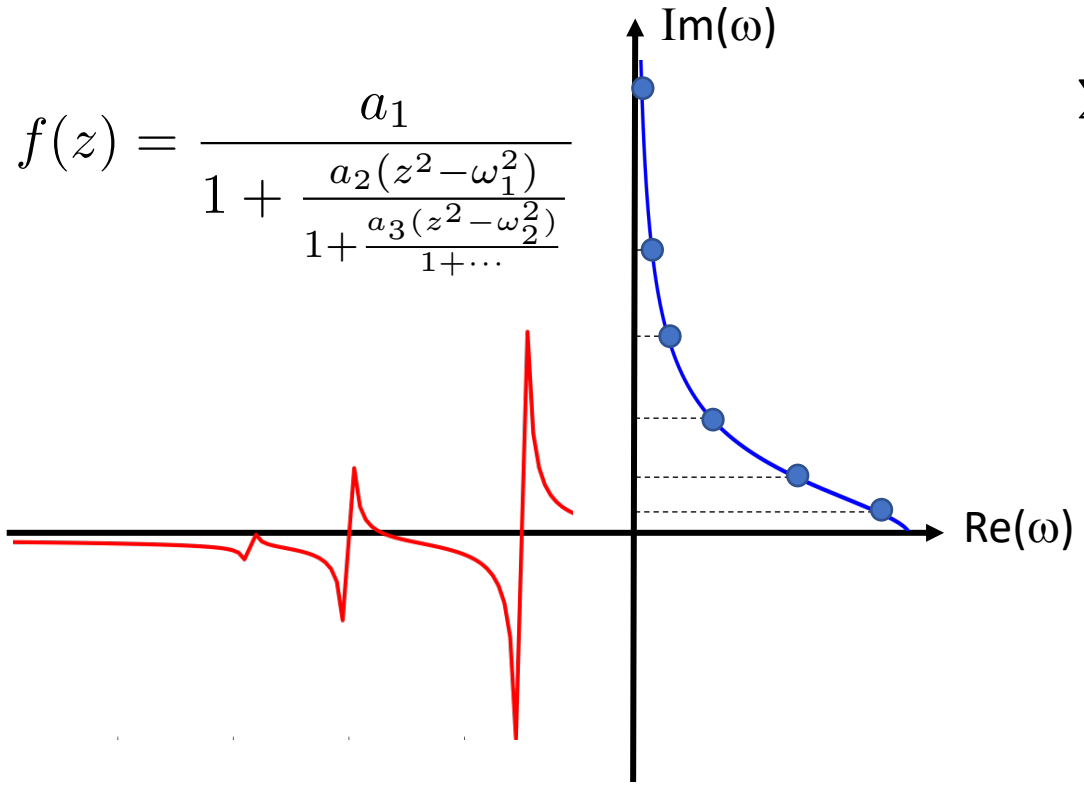
A first issue : The GW self-energy analytic continuation problem

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

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

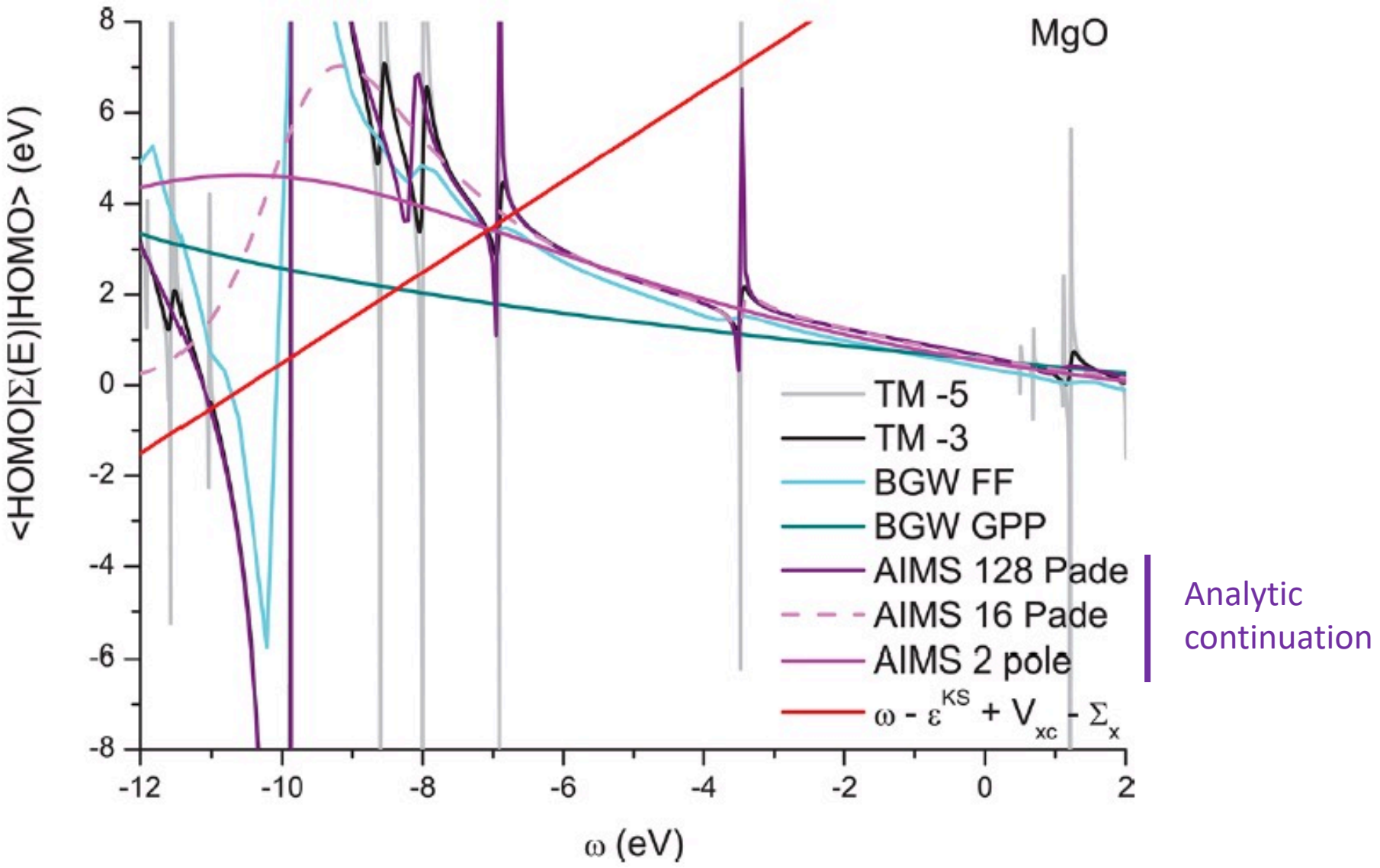
$$f(z) = \cfrac{a_1}{1+\cfrac{a_2(z^2-\omega_1^2)}{1+\cfrac{a_3(z^2-\omega_2^2)}{1+\cdots}}}$$



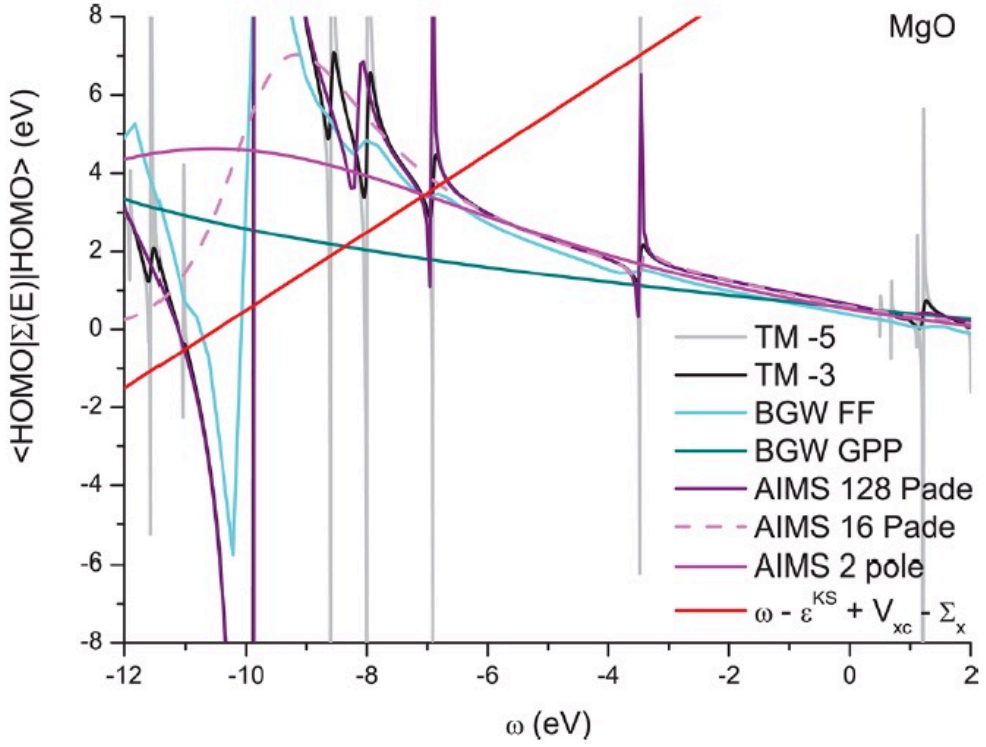
$$\Sigma(\mathbf{r},\mathbf{r}';\varepsilon) = \frac{i}{2\pi}\int d\omega\; e^{i\omega 0^+} G(\mathbf{r},\mathbf{r}';\varepsilon+\omega)W(\mathbf{r},\mathbf{r}';\omega)$$

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

A difficult case (among others)



van Setten *et al*. "GW100: benchmarking…", JCTC 2015



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

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 !

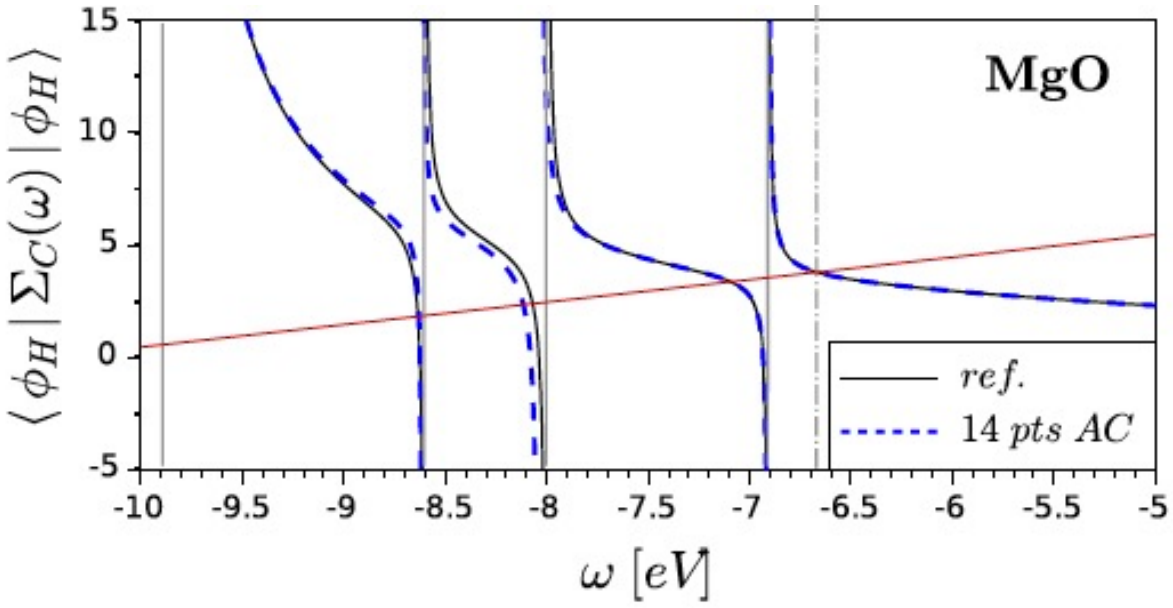
$$G(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{\omega - \varepsilon_n + i\eta \times \mathrm{sgn}(\varepsilon_n - \mu)}$$

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

Form $\Sigma(\omega)$

A stable analytic continuation approach

Duchemin & Blase, JCTC 2020



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

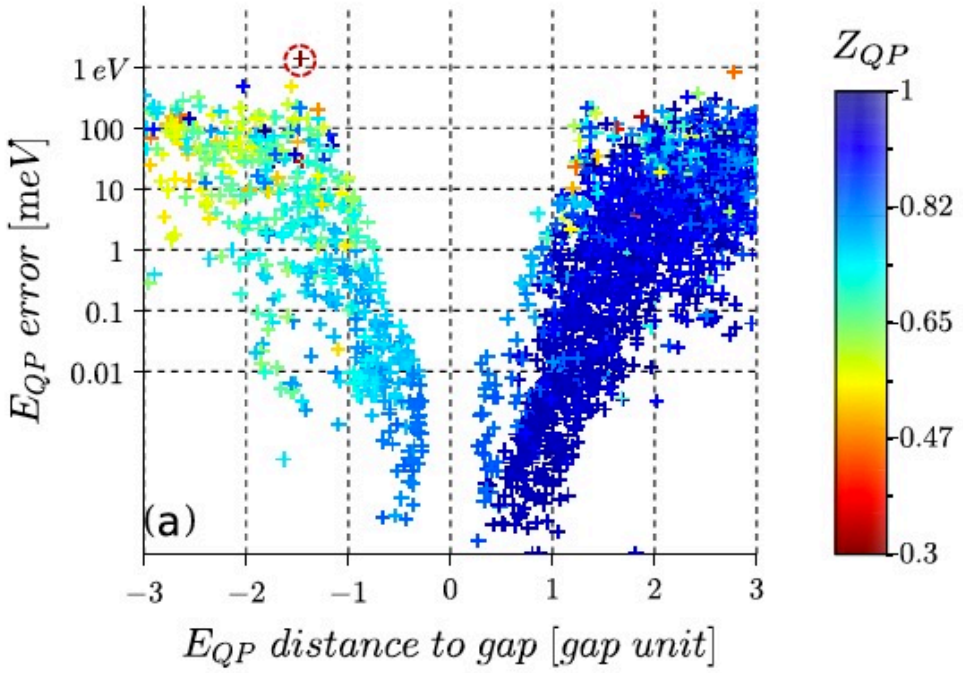
$$\varepsilon_n^{GW} = \varepsilon_n^{KS} + \langle \phi_n^{KS} | \Sigma_{XC}(\varepsilon_n^{GW}) - V_{XC}^{DFT} | \phi_n^{KS} \rangle$$

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 errors (GW100 test set)



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

A second issue : Disentangling the molecular orbitals with separable resolution-of-the-identity (RI)

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

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

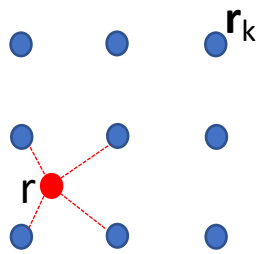
or

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

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

Disentangling the molecular orbitals with separable resolution-of-the-identity (RI)

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

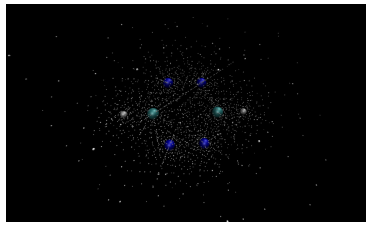


"Interpolation"

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

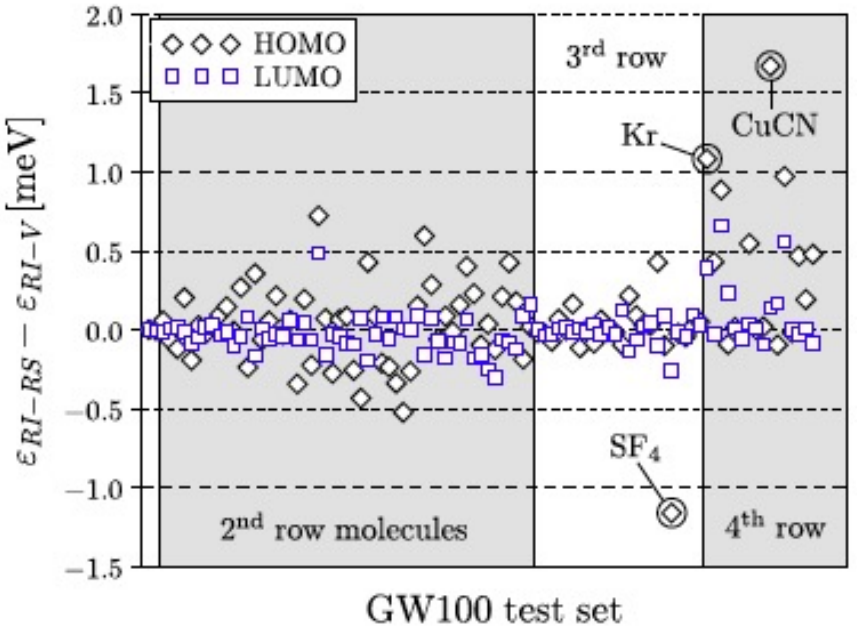
Build minimal grid that reproduces a RI-V calculation for a given auxiliary basis and a given accuracy (meV)

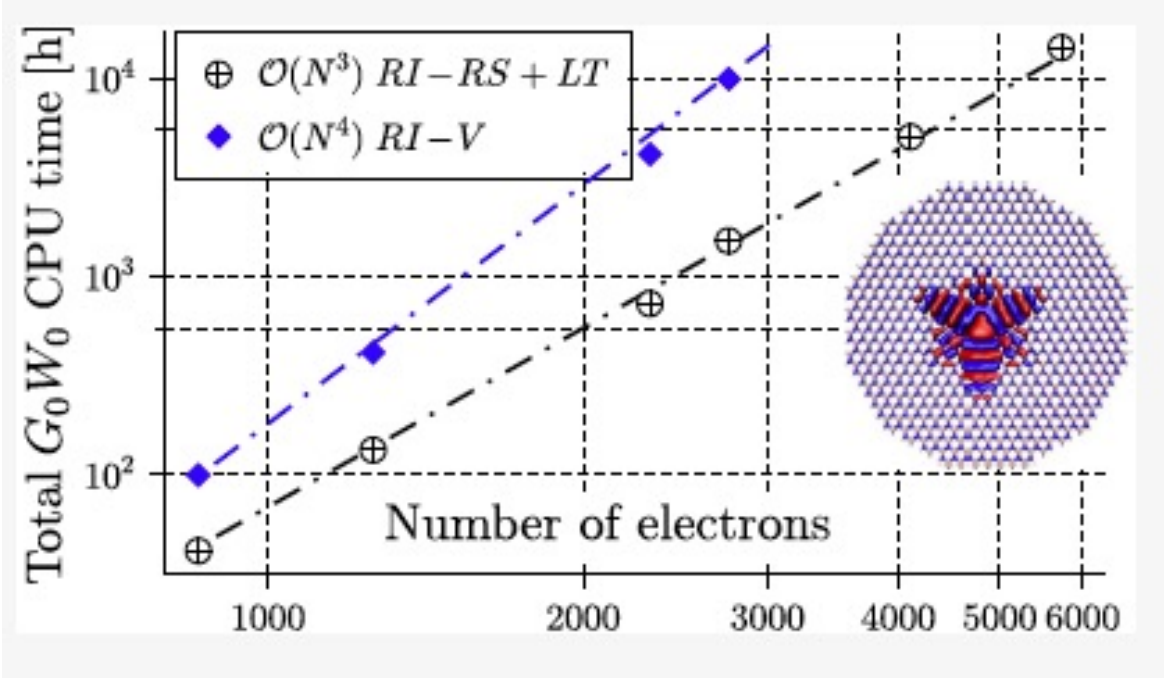
=> Typical grid size needed: 300-500 points per atom (3-4 times larger than auxiliary Gaussian basis set)

See also: ISDF (Interpolative Separable Density Fitting), Lu and Thicke, J. Comput. Phys. 2017

Self-adaptative minimal grid : a few hundred grid points per atom for meV accuracy !

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.





Duchemin & Blase, JCP 2019; JCTC 2021

- The same technique(s) can be used for cubic-scaling RPA correlation energies (Duchemin & Blase, JCP 2019)

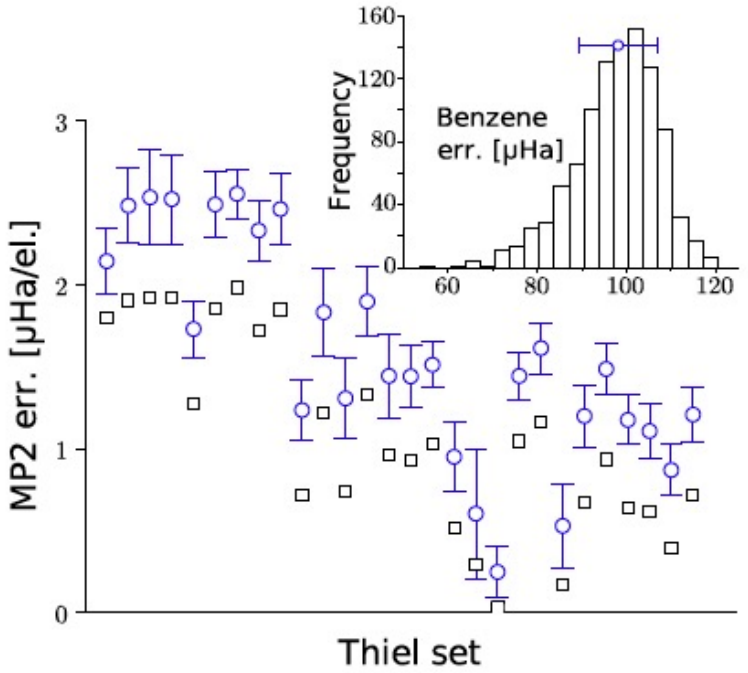
$$E_C^{RPA} = \frac{1}{2\pi}\int_0^\infty d\omega\, Tr\left[\ln(1-\chi_0(i\omega)\cdot v) + \chi_0(i\omega)\cdot v\right]$$

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

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

$$\downarrow$$

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



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 sparcity 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

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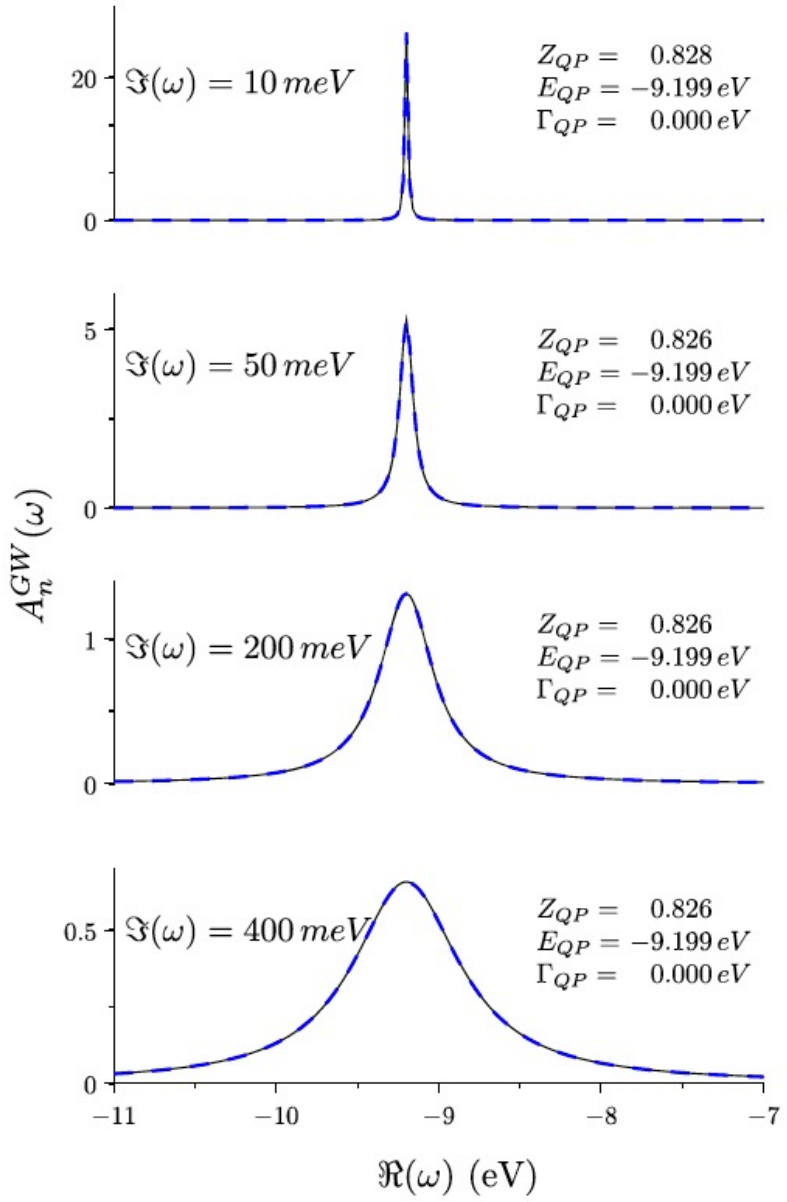
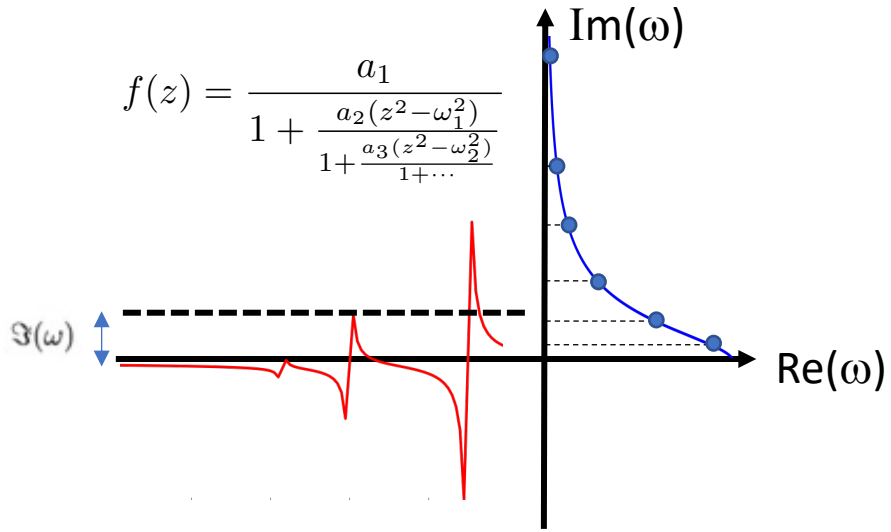
GW spectral function and quasiparticle peak



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

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

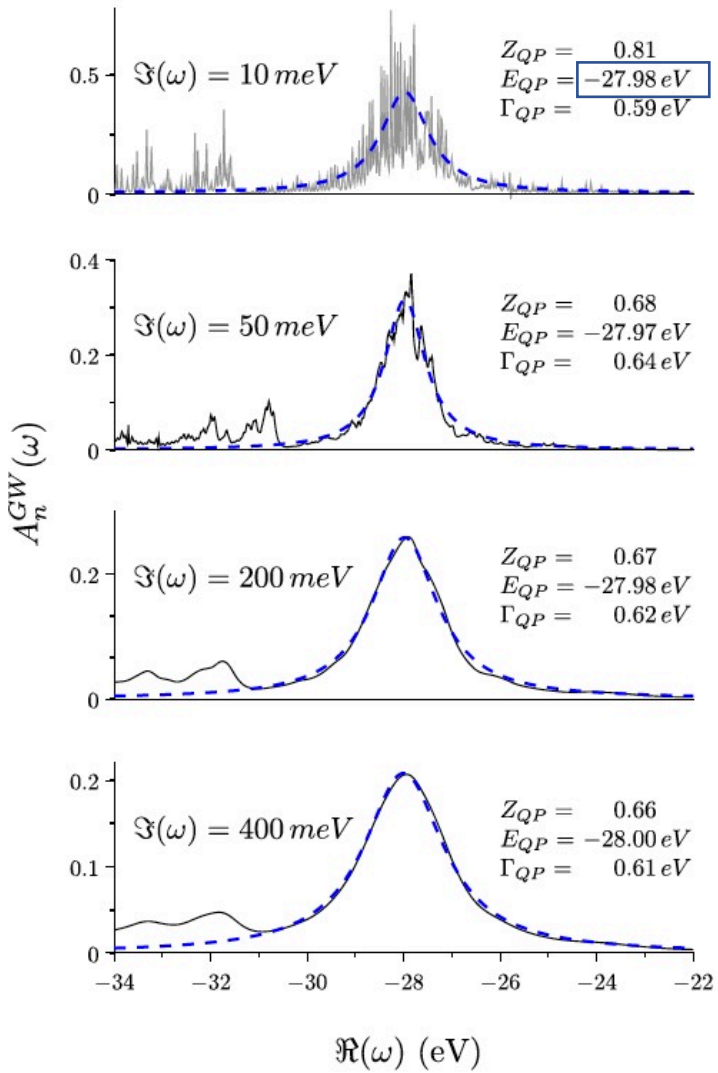
$$f(z) = \frac{a_1}{1 + \frac{a_2(z^2-\omega_1^2)}{1+\frac{a_3(z^2-\omega_2^2)}{1+\cdots}}}$$



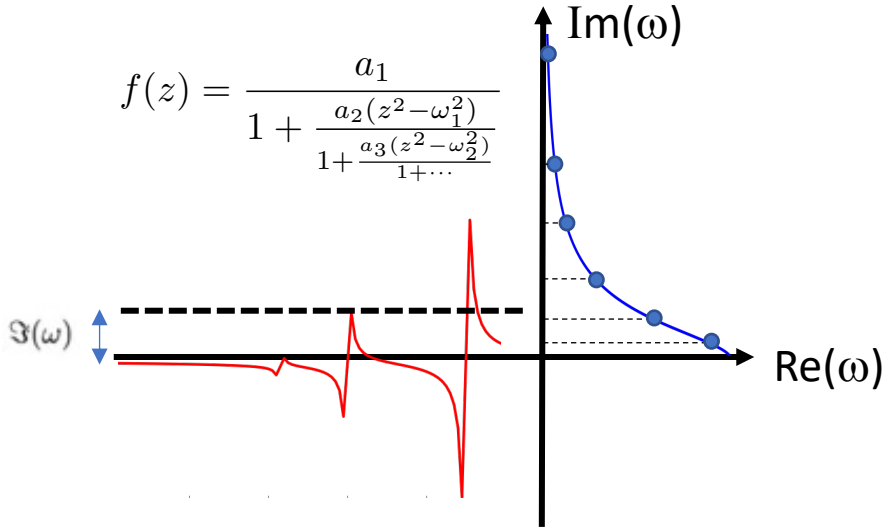
TCNQ HOMO

GW spectral function and quasiparticle peak

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

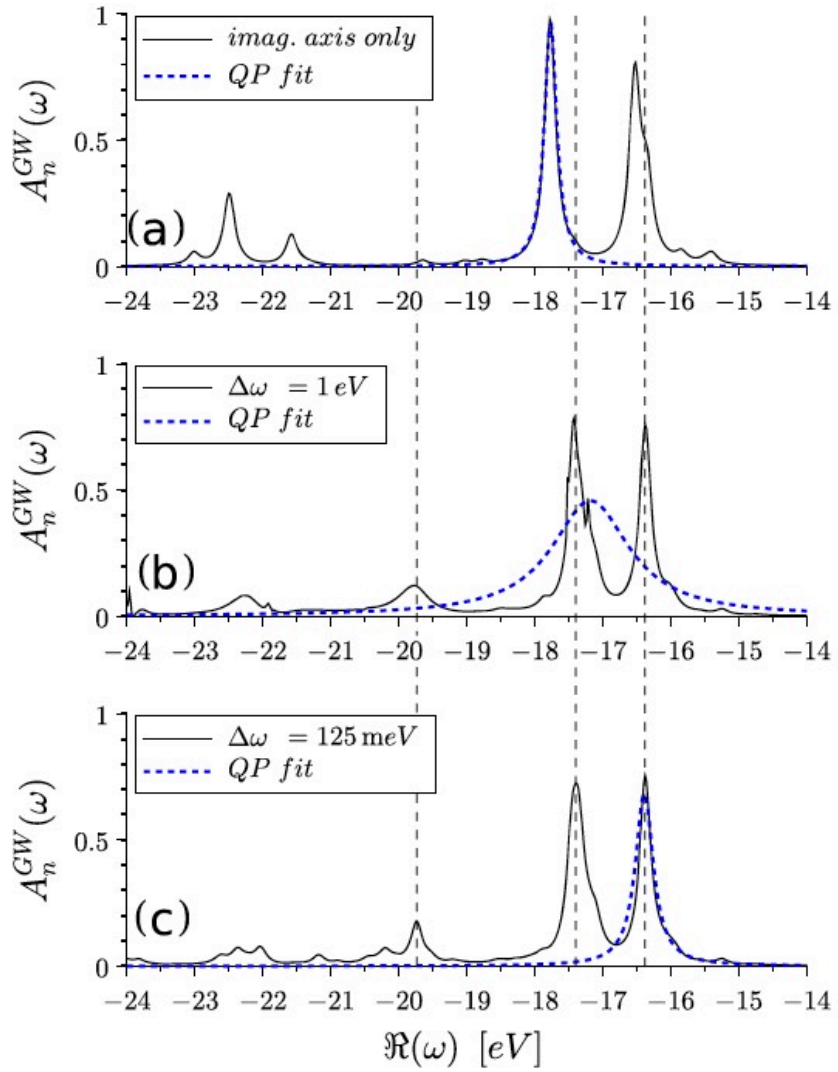


$$f(z) = \frac{a_1}{1 + \frac{a_2(z^2-\omega_1^2)}{1+\frac{a_3(z^2-\omega_2^2)}{1+\cdots}}}$$



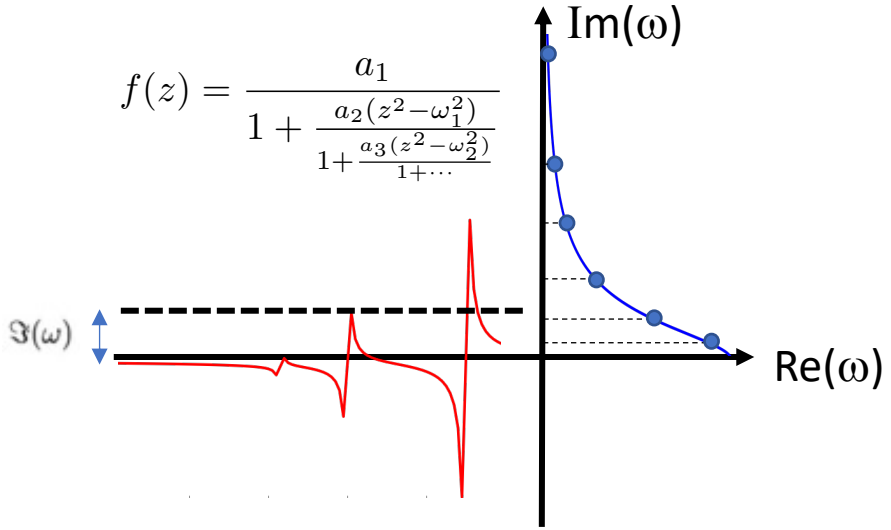
GW spectral function and quasiparticle peak

Multiple quasiparticle (?) peaks



nitrobenzonitrile

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



Tensor Hypercontraction Technique

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

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

Similar idea but fit directly 2-electrons Coulomb integrals => *O(N⁴)* setting of quadrature instead of *O(N³)* in our case.

Chain-of-sphere approach (COS)

Neese et al. 2009 - present

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

Quadrature on one codensity only

One-electron integrals in Gaussian basis

Review : Elisa Rebolini *et al*. JCTC 2016

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

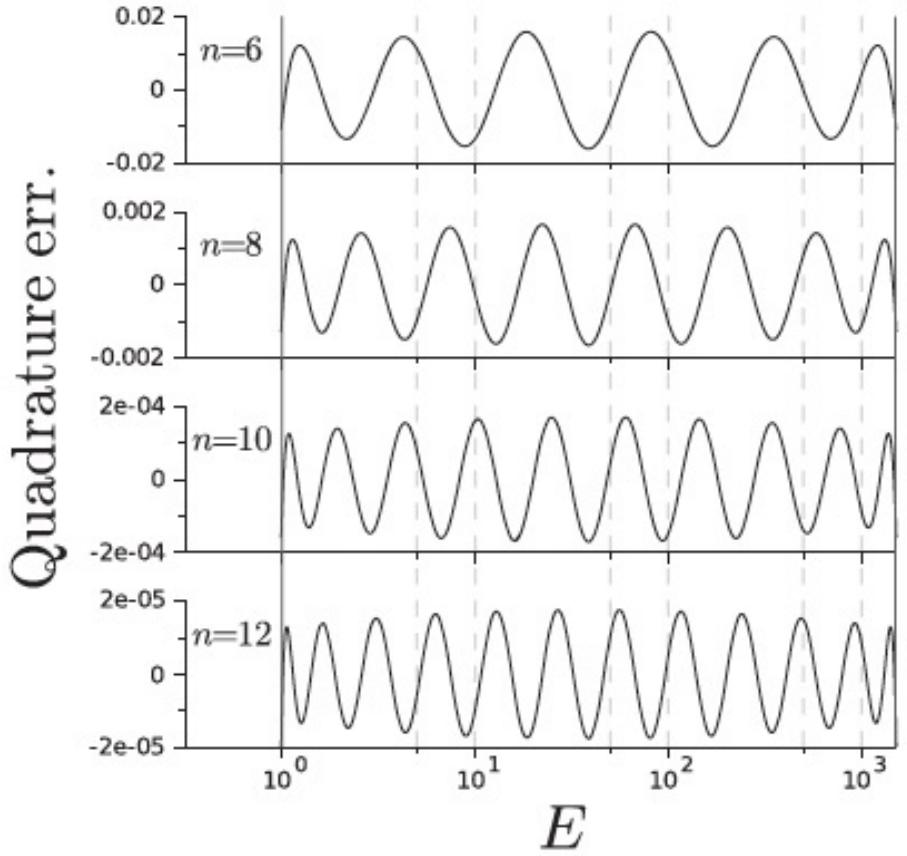
Discretized integral

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

weight

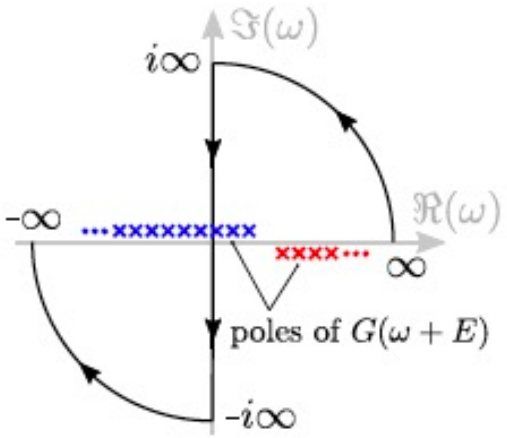
Discrete frequencies

Typically 10 to 14 frequencies



Contour deformation with analytic continuation

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



Poles of W shifted by Green's function poles