An introduction to the *GW* formalism

International summer School in electronic structure Theory: electron correlation in Physics and Chemistry

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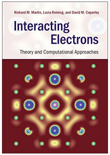
Bibliography



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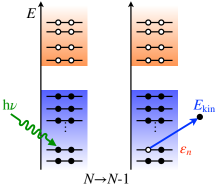
- and PhD manuscripts !!!

(Subtitle) The *GW* formalism: what for ?

The *GW* formalism aims at calculating "electronic energy levels", namely band structures, ionization potentials, electronic affinities, HOMOs, LUMOs, etc.



- the calculated electronic energy levels are well defined electron addition and removal energies (as measured experimentally)
- it is a perturbative approach taking the one-body Green's function as the central variable
- it typically scales as $\mathcal{O}(N^4)$ with blooming efficient and accurate $\mathcal{O}(N^3)$ implementations (can be used for several hundred atoms)
- can be used for finite size and extended, semiconducting or metallic systems

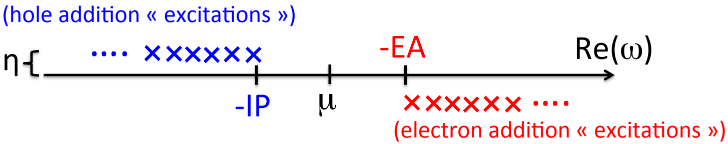
Poles of the time-ordered Green's function G in the complex plane

(Last week reminder) The time-ordered 1-body Green's function

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

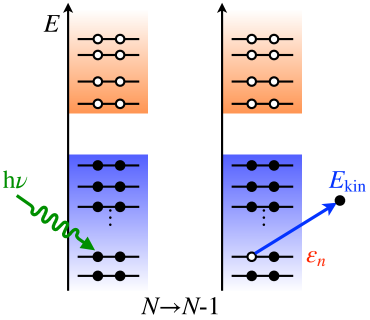
has poles at the:

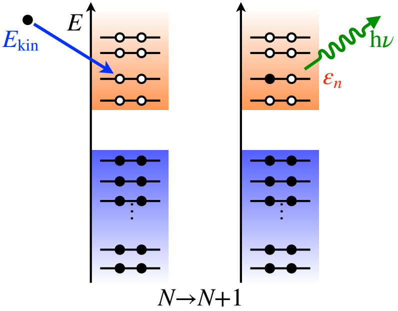
(1) "electron addition energies": $\hbar\omega = (E_n^{N+1} - E_0^N) - i\eta,$
(2) "electron removal energies": $\hbar\omega = (E_0^N - E_n^{N-1}) + i\eta.$



The $\{f_n\}$ are called the Lehman amplitudes $\langle\psi_H^0|\hat\psi_S(\mathbf{r})|\psi_H^{n,N+1}\rangle$ or $\langle\psi_H^{n,N-1}|\hat\psi_S(\mathbf{r})|\psi_H^0\rangle$

Addition/removal energies and photoemission experiments





Energy conservation:
$h\nu + E_0^N = E_{kin} + E_n^{N-1}$

Identify: $\varepsilon_n^{N-1} = E_0^N - E_n^{N-1} \ \ (< \mu)$.

Energy conservation:
$E_{kin} + E_0^N = h\nu + E_n^{N-1}$

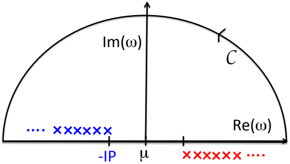
Identify: $\varepsilon_n^{N+1} = E_n^{N+1} - E_0^N \ \ (> \mu)$.

Prolegomena: $\Sigma^X = iGv$ is the exact exchange operator

Let's consider the integral:

$$\frac{i}{2\pi}\int_{\mathcal{C}} d\omega e^{i\omega\eta} G(\mathbf{r},\mathbf{r}';\omega) v(\mathbf{r},\mathbf{r}')$$

with (η) an infinitesimal positive and v the bare Coulomb potential, where the contour $\mathcal{C}$ is in the upper half-plane.



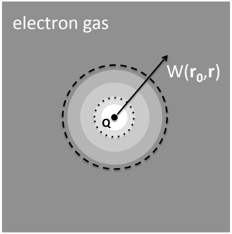
We can then use the residue theorem to obtain:

$$\frac{i}{2\pi}\int_{\mathcal{C}} d\omega e^{i\omega\eta} G(\mathbf{r},\mathbf{r}';\omega) v(\mathbf{r},\mathbf{r}') = \frac{i}{2\pi}(2i\pi)\sum_{n}^{occupied} f_n(\mathbf{r}) f_n^*(\mathbf{r}') v(\mathbf{r},\mathbf{r}')$$

$$= -\sum_{n}^{occupied} \frac{f_n(\mathbf{r}) f_n^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

which is the exact exchange operator (putting back properly the spin !) assuming that Lehman weights (f_n) and one-body orbitals (ϕ_n) can be identified (within e.g. DFT or HF; see last week lecture).

What about W, the screened Coulomb potential ?



Assume you put a charge Q (e.g. an added electron or hole) in an electron gas in $\mathbf{r}_0$. Q will generate a Coulomb potential and an induced charge rearrangement given by:

$$\delta n^{ind}(\mathbf{r}) = \int d\mathbf{r}' \ \chi(\mathbf{r}, \mathbf{r}') \frac{Q}{|\mathbf{r}' - \mathbf{r}_0|}$$

We introduced χ the electronic susceptibility relating the variation of charge to the applied perturbing potential (taken to be static here).

The added charge generates a "depletion "of charge of the same sign in its "vicinity" (cf. the DFT exchange-correlation hole).

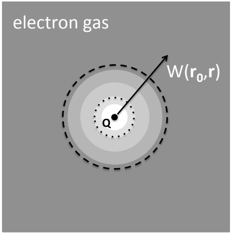
If the charge is a test electron or hole, the ensemble $Q + \delta n(\mathbf{r})$ is called a dressed particle, or quasiparticle. This is really what is added, or removed, in a photoemission experiment !!

What about W, the screened Coulomb potential ?

The field generated by the quasiparticle is that generated by Q plus that generated by $\delta n(\mathbf{r})$.

$$W(\mathbf{r},\mathbf{r}_0) = v(\mathbf{r},\mathbf{r}_0) + \int d\mathbf{r}' \; \frac{\delta n^{ind}(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}$$

$$\delta n^{ind}(\mathbf{r}) = \int d\mathbf{r}' \; \chi(\mathbf{r},\mathbf{r}') \frac{Q}{|\mathbf{r}'-\mathbf{r}_0|}$$



This defines the screened Coulomb potential W (here static).

From the definition of δn^{ind}, one obtains:

$$W(\mathbf{r},\mathbf{r}_0) = v(\mathbf{r},\mathbf{r}_0) + \int d\mathbf{r}' d\mathbf{r}'' \; v(\mathbf{r},\mathbf{r}') \, \chi(\mathbf{r}',\mathbf{r}'') \, v(\mathbf{r}'',\mathbf{r}_0)$$

namely in matrix or operator notations : $\boxed{W = v + v\chi v}$

W is weaker and shorter range than v

At short range ($|\mathbf{r}-\mathbf{r}'| \Longrightarrow 0$) the screened $W(\mathbf{r},\mathbf{r}')$ and bare $v(\mathbf{r},\mathbf{r}')$ Coulomb potential are the same (no electrons to screen an interaction at short range).

At long range, the screened Coulomb potential is exponentially decaying in metals and decays to $v(\mathbf{r},\mathbf{r}')/\epsilon_M$ in a semiconductor with macroscopic dielectric constant ϵ_M. A perturbation theory in terms of W looks therefore "probably better" than a perturbation theory in terms of v.

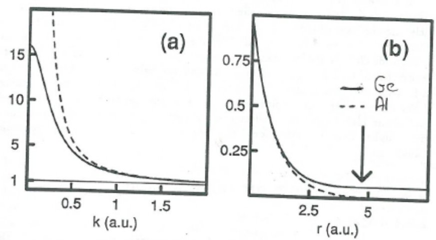


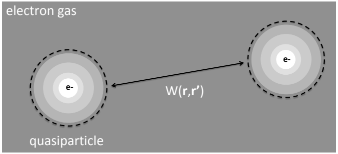
Figure 2.1. (a): Diagonal dielectric functions $\epsilon(k)$ for Al (dashed) and Ge (solid) (b): Ratio $\phi(r)/\phi_0(r)$ between the screened and unscreened potentials of a point charge, from the dielectric functions shown in (a).

Figure from Raffaele Resta, Lecture Notes on "Methods of Electronic Structure Theory", Sissa, Italy. (Left) Reciprocal space representation of the dielectric function $\epsilon(k)$ in Aluminum and Germanium. (Right) Real-space representation of (W/v) as a function of distance in Aluminum (dashed) and Germanium (full line).

Quasiparticles and "screened exchange" (qualitative)

If we summarize :

- a photoemission experiment creates/destroys (namely measures the energy of) a quasiparticle
- quasiparticles interact through the screened Coulomb potential



This suggests a meaningful modification of the exact exchange operator:

$$\Sigma^X = iGv \quad \Longrightarrow \quad \Sigma^{GW} = iGW \quad \text{("screened" exchange).}$$

The operator Σ is called a "self-energy" since the interaction of an electron with its depletion hole is an interaction "internal" to the quasiparticle.

The inverse dielectric function

Generalization : replace the perturbing point charge by a local (in space-time) external electrostatic perturbation $U(1)$ with $1 = (\mathbf{r}_1, t_1)$ inducing a variation of the charge density and Hartree potential:

$$\chi(1,2) = \frac{\partial n(1)}{\partial U(2)} \Longrightarrow \frac{\partial V^H(1)}{\partial U(2)} = \int d3\ v(1,3) \frac{\partial n(3)}{\partial U(2)} \quad \text{with } v(1,3) = \frac{\delta(t_1 - t_3)}{|\mathbf{r}_1 - \mathbf{r}_3|}$$

The variation of the total electrostatic potential $V = U + V^H$ with respect to U defines the inverse dielectric function:

$$\varepsilon^{-1}(1,2) = \frac{\partial V(1)}{\partial U(2)} \quad \text{with} \quad V(1) = U(1) + V^H(1)$$

leading to a general definition of the screened Coulomb potential

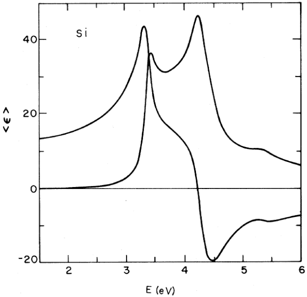
$$W(1,2) = \int d3\ v(1,3) \varepsilon^{-1}(3,2)$$

W and ϵ^{-1} are dynamical :

$$W(1,2) = W(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) \quad \Longrightarrow \quad W(\mathbf{r}_1, \mathbf{r}_2; \omega) \quad \text{by Fourier transform of } (t_2 - t_1).$$

The inverse dielectric function is dynamical

The dynamical character of the screened Coulomb potential can be seen in the measured dielectric constant :



Experimental real part and imaginary part of the dielectric function $\epsilon(\omega)$ of bulk silicon [from PRB **27**, 985 (1983)].

After the discussions, the central equations ...

$$\frac{\partial G(1,2)}{\partial t_1} \text{ (time evolution) } \iff \frac{\partial G(1,2)}{\partial U(3)} \text{ (linear response)}$$

Where we use functional derivative techniques, originally used by Schwinger in quantum electrodynamics and adopted into condensed matter by Lars Hedin.

The one-body time-ordered G equation-of-motion

We want to take the time derivative $\partial/\partial t$ of :

$$\begin{aligned} i\hbar G(\mathbf{r}t,\mathbf{r}'t') &= \theta(t-t') < \psi_H^0|\hat{\psi}_H(\mathbf{r}t)\hat{\psi}_H^\dagger(\mathbf{r}'t')|\psi_H^0 > \\ &\quad - \theta(t'-t) < \psi_H^0|\hat{\psi}_H^\dagger(\mathbf{r}'t')\hat{\psi}_H(\mathbf{r}t)|\psi_H^0 > \end{aligned}$$

Green's function equation of motion (EOM)

The time derivative of the time-ordered Green's function:

$$i\frac{\partial G(\mathbf{r}t,\mathbf{r}'t')}{\partial t} = \delta(t-t')\delta(\mathbf{r}-\mathbf{r}') + \langle N|T\left[\frac{\partial\hat{\psi}(\mathbf{r}t)}{\partial t}\hat{\psi}^{+}(\mathbf{r}'t')\right]|N\rangle$$

requires the EOM of the field operator (in Heisenberg representation) :

$$i\frac{\partial\hat{\psi}(\mathbf{r}t)}{\partial t} = \left[\hat{\psi}(\mathbf{r}t),\hat{H}\right]_{-}$$

with in second-quantization :

$$\hat{H} = \int d\mathbf{r}''\hat{\psi}^{+}(\mathbf{r}'')h_0(\mathbf{r}'')\hat{\psi}(\mathbf{r}'') + \int d\mathbf{r}''d\mathbf{r}'''\hat{\psi}^{+}(\mathbf{r}'')\hat{\psi}^{+}(\mathbf{r}''')\frac{v(\mathbf{r}'',\mathbf{r}''')}{2}\hat{\psi}(\mathbf{r}''')\hat{\psi}(\mathbf{r}'')$$

with h_0 the one-body Hamiltonien (kinetic and ionic potential)

Playing with anti-commutation relations for the field operators, e.g.

$$\left\{\hat{\psi}(\mathbf{r}), \hat{\psi}^{\dagger}(\mathbf{r}')\right\} = \delta(\mathbf{r}-\mathbf{r}')$$

leads to (see Appendix):

$$i\frac{\partial \hat{\psi}(\mathbf{r}t)}{\partial t} = h_0(\mathbf{r})\hat{\psi}(\mathbf{r}t) + \int d\mathbf{r}''\; v(\mathbf{r}-\mathbf{r}'')\hat{\psi}^{\dagger}(\mathbf{r}''t)\hat{\psi}(\mathbf{r}''t)\hat{\psi}(\mathbf{r}t)$$

As a result :

$$\boxed{\begin{aligned}\left(i\frac{\partial}{\partial t} - h_0(\mathbf{r})\right) G(\mathbf{r}t, \mathbf{r}'t') &= \delta(t-t')\delta(\mathbf{r}-\mathbf{r}') \\ &\quad - i\int d\mathbf{r}'' v(\mathbf{r}-\mathbf{r}'')\langle N| T\left[\hat{\psi}^{\dagger}(\mathbf{r}''t^{++})\hat{\psi}(\mathbf{r}''t+)\hat{\psi}(\mathbf{r}t)\hat{\psi}^{\dagger}(\mathbf{r}'t')\right]|N\rangle\end{aligned}}$$

where the t^{++}/t^{+} keep the proper ordering of field operators under the action of T.

The last term involves a 2-body Green's function !

The Green's functions hierarchy

With $(\mathbf{r}t) \to 1 = (\mathbf{r}_1 t_1)$, $(\mathbf{r}' t') \to (2 = \mathbf{r}_2 t_2)$, and $(\mathbf{r}'' t) \to (3 = \mathbf{r}_3 t_3)$ this yields:

$$\boxed{\left(i \frac{\partial}{\partial t_1} - h_0(\mathbf{r}_1) \right) G(1,2) + i \int d3 \; v(1,3) \; G_2(1,3^+;2,3^{++}) = \delta(1,2)}$$

where $v(1,3) = v(\mathbf{r}_1 - \mathbf{r}_3)\delta(t_1 - t_3)$ with:

$$i^2 G_2(1,3;2,4) = \langle N | \, T \left[\hat{\psi}(1)\hat{\psi}(3)\hat{\psi}^\dagger(4)\hat{\psi}^\dagger(2) \right] | N \rangle$$

This is the complicated hierarchy of Green's functions !! : to know the 1-body G, we need to know the 2-body G_2 (and so on ...)

Hopefully, another equation involves the same G_2 !

Green's function variation with respect to an external perturbation U

After looking for the variation of G with respect to time, another equation relates the variation of the G with respect to an external perturbation $U(\mathbf{r}_3 t_3)$:

$$\frac{\partial G(1,2)}{\partial U(3)} = -G_2(1,3;2,3^+) + G(1,2)G(3,3^+)$$

(see e.g. the Nuovo Cimento article by Strinati and Bethe-Salpeter equation lectures).

This important equation allows to get rid of the 2-body G_2 and to build a connection with linear-response theory, namely to the susceptibility χ, the dielectric function ϵ^{-1} and the screened Coulomb potential W !

The GW world : Connection to linear response

Using the equation for the variation of G with respect to U:

$$\frac{\partial G(1,2)}{\partial U(3)} = -G_2(1,3;2,3^+) + G(1,2)G(3,3^+) \quad \text{with } \ 3^+ = (\mathbf{r}_3, t_3 + 0^+)$$

that we can plug in the Green's function EOM:

$$\left(i\partial_{t_1} - h^0(\mathbf{r}_1)\right) G(1,2) + i \int d3 v(1,3) \; G_2(1,3^+;2,3^{++}) = \delta(1,2)$$

to obtain:

$$\left(i\frac{\partial}{\partial t_1} - h^0(\mathbf{r}_1)\right) G(1,2) + i \int d3 v(1,3) \; G(3,3^+) G(1,2) \\ - i \int d3 v(1^+,3) \; \frac{\partial G(1,2)}{\partial U(3)} = \delta(1,2)$$

Note: the (1^+) turns (3) into (3^+) via the Coulomb potential $\delta(t_1^+ - t_3)$ term.

The GW world : Connection to linear response

With the relation $-iG(3,3^+) = \rho(3)$, one obtains the action of the Hartree potential:

$$\left[i \int d3 \; v(1,3) \; G(3,3^+) \right] G(1,2) = -V^H(1) G(1,2)$$

For the complicated "red" contribution, we rewrite :

$$\int d3 \; v(1,3) \; \frac{\partial G(1,2)}{\partial U(3)} = \int d3 d4 \; v(1^+,3) \frac{\partial G(1,4)}{\partial U(3)} \delta(4,2)$$

and use the definition of the inverse G :

$$\int d5 \; G^{-1}(4,5) G(5,2) = \delta(4,2)$$

to obtain an operator acting on G :

$$\int d3 \; v(1^+,3) \; \frac{\partial G(1,2)}{\partial U(3)} = \int d5 \left[\int d3 d4 \; v(1^+,3) \frac{\partial G(1,4)}{\partial U(3)} \; G^{-1}(4,5) \right] G(5,2)$$

The self-energy operator for exchange and correlation

The "beyond Hartree" last contribution can thus be written:

$$i \int d3 \; v(1^+, 3) \, \frac{\partial G(1,2)}{\partial U(3)} = \int d5 \; \Sigma(1,5) G(5,2)$$

with

$$\boxed{\Sigma(1,5) = i \int d34 \; v(1^+, 3) \frac{\partial G(1,4)}{\partial U(3)} G^{-1}(4,5).}$$

This is a formal but important result : all effects beyond the classical Hartree term, namely exchange-and-correlation (XC), can be captured by a non-local energy-dependent operator called the self-energy Σ :

$$\Sigma(\mathbf{r}t, \mathbf{r}'t') \Longrightarrow \Sigma(\mathbf{r}, \mathbf{r}'; t - t') \Longrightarrow \Sigma(\mathbf{r}, \mathbf{r}'; \omega)$$

Recovering a one-body equation for the proper electronic energy levels

Fourier transform to frequency space the Green' function EOM:

$$\left[i\frac{\partial}{\partial t_1} - h^0(\mathbf{r}_1) - V^H(1)\right]G(1,2) - \int d5\,\Sigma(1,5)G(5,2) = \delta(1,2)$$

and plug the spectral representation of the time-ordered 1-body Green's function

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

to obtain a "standard" one-body eigenvalue equation:

$$\boxed{\left[h_0(\mathbf{r}) + V^H(\mathbf{r})\right] f_n(\mathbf{r}) + \int d\mathbf{r}'\;\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_n)f_n(\mathbf{r}') = \varepsilon_n f_n(\mathbf{r})}$$

where the $\{\varepsilon_n\}$ are the proper electron addition/removal energies.

What is really new is that the dynamical XC self-energy operator must be calculated at the energy of the state it acts on.

Towards the GW approximation

All this is nice but very formal : we still need a practical form for Σ !

Take the definition of the self-energy operator :

$$\boxed{\Sigma(1,5) = i \int d34 \; v(1^+,3) \frac{\partial G(1,4)}{\partial U(3)} G^{-1}(4,5).}$$

and use the derivative of the $GG^{-1} = I$ relation :

$$\frac{\partial G(1,4)}{\partial U(3)} = - \int d67 \; G(1,6) \frac{\partial G^{-1}(6,7)}{\partial U(3)} G(7,4)$$

to obtain

$$\Sigma(1,5) = -i \int d3467 \; v(1^+,3) G(1,6) \frac{\partial G^{-1}(6,7)}{\partial U(3)} G(7,4) G^{-1}(4,5)$$

so that integrating over (4) leading to a $\delta(5,7)$ and finally:

$$\boxed{\Sigma(1,5) = -i \int d36 \; v(1^+,3) G(1,6) \frac{\partial G^{-1}(6,5)}{\partial U(3)}}$$

The GWΓ operator (GW + vertex corrections)

Using further the chain rule with $V = U + V^H$ the total electrostatic potential, one obtains:

$$\Sigma(1,5) = -i \int d367\ v(1^+,3) G(1,6) \frac{\partial G^{-1}(6,5)}{\partial V(7)} \frac{\partial V(7)}{\partial U(3)}$$

where

$$\int d3\ v(1^+,3) \frac{\partial V(7)}{\partial U(3)} = \int d3\ v(1^+,3) \epsilon^{-1}(7,3) = W(1^+,7)$$

so that:

$$\boxed{\Sigma(1,5) = i \int d67\ G(1,6) W(1^+,7) \left[-\frac{\partial G^{-1}(6,5)}{\partial V(7)} \right]}$$

The last term is coined the irreducible vertex correction :

$$\tilde{\Gamma}(6,5;7) = -\frac{\partial G^{-1}(6,5)}{\partial V(7)}$$

The GW operator

Introducing the G_0 non-interacting Green's function and the resulting Dyson equation

$$G^{-1} = G_0^{-1} - V - \Sigma$$

(see Lecture last week) one obtains straightforwardly:

$$\tilde{\Gamma}(6,5;7) = \delta(5,6)\delta(5,7) + \frac{\partial \Sigma(6,5)}{\partial V(7)}$$

where the second term is of higher order in W. The GW approximation can be seen as the lowest approximation in W:

$$\Sigma(1,5) \simeq i \int d67\ G(1,6)W(1^+,7)\delta(5,6)\delta(5,7) = iG(1,5)W(1^+,5)$$

a direct product in time representation that becomes a convolution in frequency space:

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

Cycling Dyson-like coupled equations

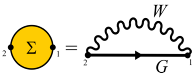
$$\tilde{\Gamma}(6,5;7) = \delta(5,6)\delta(5,7) + \frac{\partial\Sigma(6,5)}{\partial V(7)}$$

$$\Sigma(1,5) = i\int d67\, G(1,6)W(1^+,7)\Gamma(6,5;7)$$

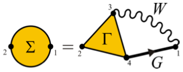
Lowest order $\tilde{\Gamma}$

$$\tilde{\Gamma}(6,5;7) \simeq \delta(5,6)\delta(5,7)$$

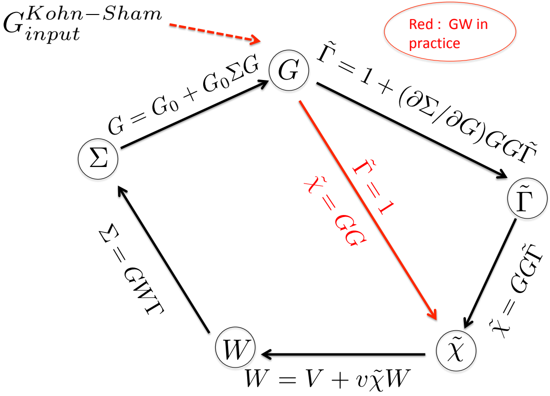
$$\Sigma(1,5) \simeq iG(1,5)W(1^+,5)$$



Higher-order in W



Hedin's coupled equations and self-consistency



Cycling self-consistently around Hedin's pentagon allows in principle to converge to the exact one-body Green's function including correlations at all order.

GW calculations in practice : the G_0W_0 scheme starting from DFT or HF

Build G and independent-particule susceptibility χ_0 from Kohn-Sham (KS) eigenstates:

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

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

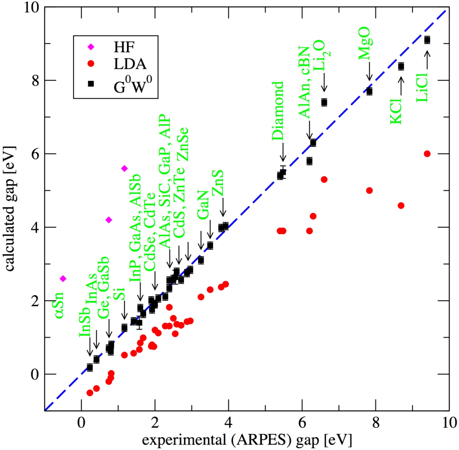
In the Random Phase Approximation (RPA: neglect of V^{XC} variation):

$$W=v+v\chi v=v+v\chi_0W \quad \text{with} \quad \chi=\chi_0+\chi_0v\chi$$

In a first-order-like perturbation scheme, the Kohn-Sham eigenvalues are corrected by replacing the DFT XC potential by the *GW* self-energy:

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

Historical $G_0 W_0$ calculations in solids (band gap)



(courtesy Valerio Olevano, Institut NEEL, Grenoble).

GW calculations in practice : dependence on the DFT starting point

Since the calculation of G, χ_0 and W requires input Kohn-Sham (or HF) one-body orbitals, how does the result depends on the DFT starting point ?

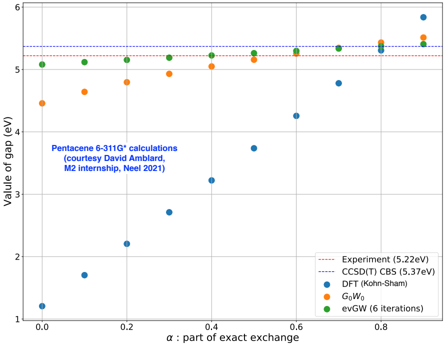


Figure : evolution of PBEh(α) Kohn-Sham HOMO-LUMO gap for pentacene as a function of percentage α of exact exchange and corresponding G_0W_0@PBEh(α) and evGW@PBEh(α) gaps. Calculations performed with Pople 6-311G* basis set (not fully converged). Pentacene geometry and CCSD(T) reference from Rangel, Hamed, Bruneval, Neaton, JCTC 2016.

Simple partial self-consistency on eigenvalues : re-inject corrected quasiparticle energies to reconstruct G and W (the evGW scheme).

GW calculations in practice : convergency

The *GW* formalism is an explicitly correlated approach where correlation are built on the basis of electron-to-hole transition matrix elements : converges much more slowly with basis set size than Kohn-Sham DFT.

A slide for chemists : convergence of IP ($-\varepsilon_{HOMO}$) and AE for acenes ($-\varepsilon_{LUMO}$) within the aug-cc-pVXZ (aXZ) basis sets family

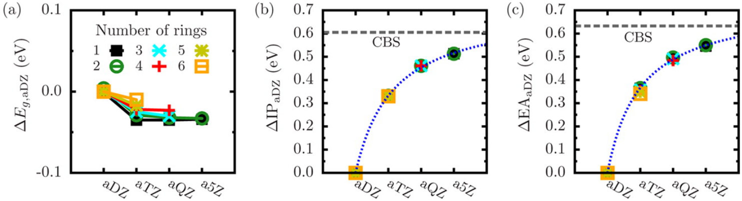


Figure: convergence with basis size for *GW* calculations on acenes (evolution with respect to aug-cc-pVDZ=aDZ values). Rangel, Hamed, Bruneval, Neaton, JCTC 2016.

GW calculations in practice : which solution ?

The self-consistent equation

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

obtained at the crossing of:

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

may not have a unique solution and one has to look at the "spectral weight" (the strength of the Lehman products in the Green's function numerator).

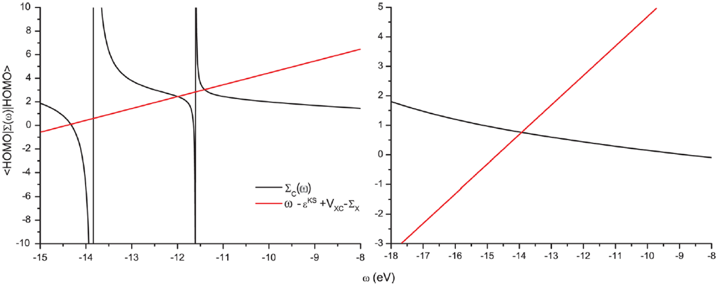


Figure: graphical determination of the quasiparticle energy: (Left) Multiple energy solution, (Right) "usual" simple case. From: van Setten, Caruso, Sharifzadeh et al. JCTC 2015 (the "*GW*100" paper).

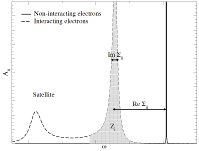
The GW spectral function

The relation $G^{GW} = G^{KS} + G^{KS}(\Sigma - V^{XC})G^{GW}$ allows to obtain the GW spectral function associated within a given state:

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

with the poles of G^{KS} convoluted with those of W !

Model spectral function (Bruneval, PhD thesis)



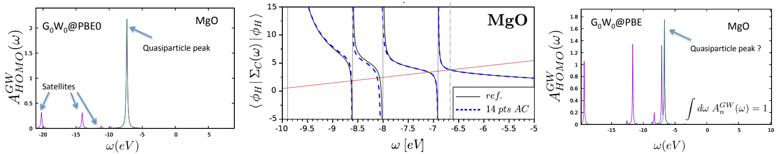


Fig : (Left) MgO HOMO def2-QZVP G_0W_0@PBE0 spectral weight. (Center) MgO HOMO correlation self-energy for a def2-QZVP G_0W_0@PBE calculation. (Right) Corresponding spectral function A_n^{GW} (Duchemin + Blase, JCTC 2020).

The spectral weight confirms or not the existence of a well defined quasiparticle peak capturing an "area under the peak" close to unity. Pathological situations can occur and are starting to be explored (e.g. Véril, Romaniello, Berger, Loos, JCTC 2018).

GW calculations in practice : cost

The *GW* formalism within a planewave basis, or with localized atomic (e.g. Gaussian) basis sets with resolution-of-the-identity techniques is an $O(N^4)$ formalism. However, accurate and efficicient $O(N^3)$ space-time approaches (Rojas, Godby, Needs, PRL 1995) are blooming.

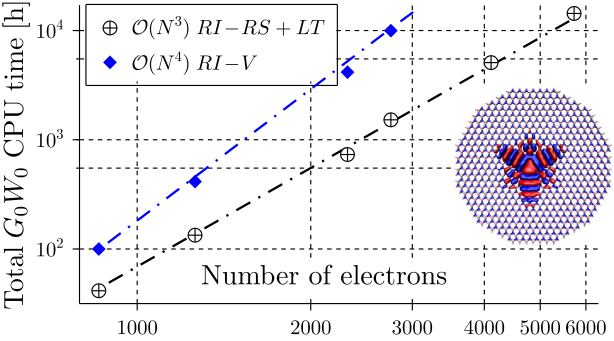
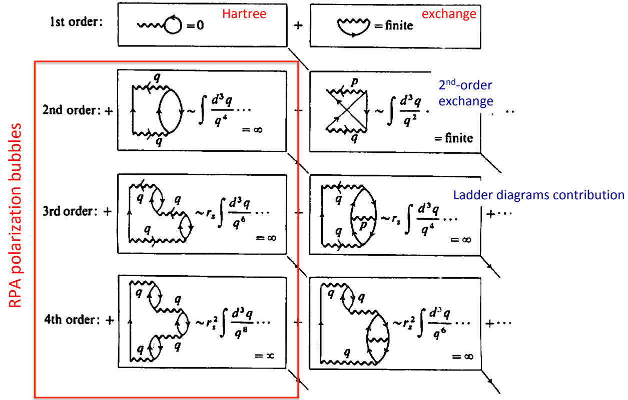


Figure from Duchemin and Blase, JCTC 2021. See also: Foerster, Koval, Sánchez-Portal, JCP 2011; Liu, Kaltak, Klimeš, Kresse, PRB 2016; Wilhelm, Golze, Talirz, Hutter, Pignedoli, JPCL 2018; etc.

A shamefully tiny bit of diagrams

In red, the diagrams contained in *GW* with W_{RPA}



Strongly correlated systems need ladder diagrams (see e.g. Mattuck chapter 10)

Thanks for your attention

A1: The Green's function equation-of-motion (EOM)

We look for the time-derivative of the Green's function :

$$i\partial_t G(\mathbf{r}t,\mathbf{r}'t') = \ \partial_t < N|T\left[\hat{\psi}(\mathbf{r}t)\hat{\psi}^\dagger(\mathbf{r}'t')\right]|N >= \ ???$$

with $N = \psi_H^0$ normalized. As a first step :

$$\begin{aligned}\partial_t\left[\theta(t-t')\langle N|\hat{\psi}(\mathbf{r}t)\hat{\psi}^+(\mathbf{r}'t')|N\rangle\right] = & \quad \delta(t-t')\langle N|\hat{\psi}(\mathbf{r}t)\hat{\psi}^+(\mathbf{r}'t')|N\rangle \\ + & \quad \theta(t-t')\langle N|\partial_t\hat{\psi}(\mathbf{r}t)\hat{\psi}^+(\mathbf{r}'t')|N\rangle\end{aligned}$$

leading after derivation of the "hole"-term to:

$$\begin{aligned}i\partial_t G(\mathbf{r}t,\mathbf{r}'t') = & \quad \delta(t-t')\langle N|\hat{\psi}(\mathbf{r}t)\hat{\psi}^+(\mathbf{r}'t')+\hat{\psi}^+(\mathbf{r}'t')\hat{\psi}(\mathbf{r}t)|N\rangle \\ + & \quad \langle N|T\left[\partial_t\hat{\psi}(\mathbf{r}t)\hat{\psi}^+(\mathbf{r}'t')\right]|N\rangle \\ = & \quad \delta(t-t')\delta(\mathbf{r}-\mathbf{r}')+\langle N|T\left[\partial_t\hat{\psi}(\mathbf{r}t)\hat{\psi}^+(\mathbf{r}'t')\right]|N\rangle\end{aligned}$$

A2: The Green's function equation-of-motion (EOM)

The time-dependent (Heisenberg) field operators obey the standard operators equation of motion ($\hbar = 1$ in atomic units):

$$i\frac{\partial \hat{O}_H}{\partial t} = \left[\hat{O}_H, \hat{H}\right]_- = e^{i\hat{H}t}\left[\hat{O}_S, \hat{H}\right]_- e^{-i\hat{H}t} \quad \text{with} \quad \left[\hat{A}, \hat{B}\right]_- = \hat{A}\hat{B} - \hat{B}\hat{A}$$

with in second-quantization (and Schrödinger representation):

$$\hat{H} = \int d\mathbf{r}''\hat{\psi}^+(\mathbf{r}'')h_0(\mathbf{r}'')\hat{\psi}(\mathbf{r}'') + \int d\mathbf{r}''d\mathbf{r}'''\hat{\psi}^+(\mathbf{r}'')\hat{\psi}^+(\mathbf{r}''')\frac{v(\mathbf{r}'',\mathbf{r}''')}{2}\hat{\psi}(\mathbf{r}''')\hat{\psi}(\mathbf{r}'')$$

with h_0 the one-body Hamiltonien (kinetic and ionic potential), leading in the EOM to terms such as:

$$\left[\hat{\psi}(\mathbf{r}), \hat{\psi}^+(\mathbf{r}'')\hat{\psi}(\mathbf{r}'')\right]_- \quad \text{and} \quad \left[\hat{\psi}(\mathbf{r}), \hat{\psi}^+(\mathbf{r}'')\hat{\psi}^+(\mathbf{r}''')\hat{\psi}(\mathbf{r}''')\hat{\psi}(\mathbf{r}'')\right]_-$$

A3: The Green's function equation-of-motion (EOM)

We use the standard commutation relations, with $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$:

$$\{\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')\} = 0, \quad \{\hat{\psi}^+(\mathbf{r}), \hat{\psi}^+(\mathbf{r}')\} = 0, \quad \{\hat{\psi}^+(\mathbf{r}), \hat{\psi}(\mathbf{r}')\} = \delta(\mathbf{r} - \mathbf{r}')$$

to establish (Exercices) the following useful lemma:

$$\begin{aligned} \left[\hat{\psi}(\mathbf{r}), \hat{\psi}^+(\mathbf{r}'')\hat{\psi}^+(\mathbf{r}''')\hat{\psi}(\mathbf{r}''')\hat{\psi}(\mathbf{r}'')\right]_- &= \delta(\mathbf{r} - \mathbf{r}'')\hat{\psi}^+(\mathbf{r}''')\hat{\psi}(\mathbf{r}''')\hat{\psi}(\mathbf{r}) \\ &+ \delta(\mathbf{r} - \mathbf{r}''')\hat{\psi}^+(\mathbf{r}'')\hat{\psi}(\mathbf{r}'')\hat{\psi}(\mathbf{r}) \end{aligned}$$

As a result:

$$i\frac{\partial \hat{\psi}(\mathbf{r}t)}{\partial t} = h_0(\mathbf{r})\hat{\psi}(\mathbf{r}t) + \int d\mathbf{r}'' \; v(\mathbf{r} - \mathbf{r}'')\hat{\psi}^\dagger(\mathbf{r}''t)\hat{\psi}(\mathbf{r}''t)\hat{\psi}(\mathbf{r}t)$$

A4: The EOM of G ordered

$$\text{Plug}\quad i\frac{\partial\hat{\psi}(\mathbf{r}t)}{\partial t} = h_0(\mathbf{r})\hat{\psi}(\mathbf{r}t) + \int d\mathbf{r}''\; v(\mathbf{r}-\mathbf{r}'')\hat{\psi}^\dagger(\mathbf{r}''t)\hat{\psi}(\mathbf{r}''t)\hat{\psi}(\mathbf{r}t)$$

$$\text{into}\quad i\frac{\partial G(\mathbf{r}t,\mathbf{r}'t')}{\partial t} = \delta(t-t')\delta(\mathbf{r}-\mathbf{r}') + \langle N|T\left[\frac{\partial\hat{\psi}(\mathbf{r}t)}{\partial t}\hat{\psi}^\dagger(\mathbf{r}'t')\right]|N\rangle.$$

The right-hand side contribution yields two terms:

$$A \qquad = -i\langle N|T\left[h_0(\mathbf{r})\hat{\psi}(\mathbf{r}t)\hat{\psi}^\dagger(\mathbf{r}'t')\right]|N\rangle = h_0(\mathbf{r})G(\mathbf{r}t,\mathbf{r}'t')$$

$$B \quad = -i\langle N|T\left[\int d\mathbf{r}''\; v(\mathbf{r}-\mathbf{r}'')\hat{\psi}^\dagger(\mathbf{r}''t^{++})\hat{\psi}(\mathbf{r}''t^{+})\hat{\psi}(\mathbf{r}t)\hat{\psi}^\dagger(\mathbf{r}'t')\right]|N\rangle$$

$$= -i\int d\mathbf{r}'\; v(\mathbf{r}-\mathbf{r}'')\langle N|T\left[\hat{\psi}^\dagger(\mathbf{r}''t^{++})\hat{\psi}(\mathbf{r}''t^{+})\hat{\psi}(\mathbf{r}t)\hat{\psi}^\dagger(\mathbf{r}'t')\right]|N\rangle$$

with $t^{+/++} = t + 0^{+/++}$ for a correct ordering of the $\hat{\psi}^\dagger$ and $\hat{\psi}$ at time t.

The EOM of G ordered

Using the commutation relation of the destruction operators and the rules of the time operators (minus sign when exchanging operators):

$$-T\left[\hat{\psi}^\dagger(\mathbf{r}''t^{++})\hat{\psi}(\mathbf{r}''t^{+})\hat{\psi}(\mathbf{r}t)\hat{\psi}^\dagger(\mathbf{r}'t')\right] = T\left[\hat{\psi}(\mathbf{r}t)\hat{\psi}(\mathbf{r}''t^{+})\hat{\psi}^\dagger(\mathbf{r}''t^{++})\hat{\psi}^\dagger(\mathbf{r}'t')\right]$$

one obtains

$$\begin{aligned} i\frac{\partial G(\mathbf{r}t,\mathbf{r}'t')}{\partial t} &= \delta(t-t')\delta(\mathbf{r}-\mathbf{r}') + h_0(\mathbf{r})G(\mathbf{r}t,\mathbf{r}'t') \\ &\quad -i\int d\mathbf{r}''\ v(\mathbf{r}-\mathbf{r}'')G_2(\mathbf{r}t,\mathbf{r}''t^{+};\mathbf{r}'t',\mathbf{r}''t^{++}) \end{aligned}$$

with the 2-body Green's function propagating two particles:

$$i^2 G_2(1,2;3,4) = \langle N|\,T\left[\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^\dagger(4)\hat{\psi}^\dagger(3)\right]|N\rangle$$