An Introduction to the *GW* Green's function many-body perturbation theory

Ecole thématique RaProche

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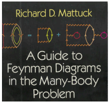
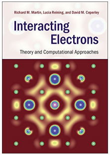
Bibliography

Book: A guide to Feynman Diagrams in the Many-Body Problem.



Richard D. Mattuck

A Guide to Feynman Diagrams in the Many-Body Problem



Richard M. Martin, Lucia Reining, and David M. Ceperley

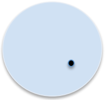
Interacting Electrons

Theory and Computational Approaches

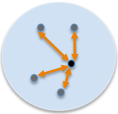
Book: Interacting Electrons: Theory and Computational Approaches, Richard M. Martin, Lucia Reining , David M. Ceperley, Cambridge University Press (2016).

- L. Hedin, Phys. Rev. 139, A796 (1965).
- M. S. Hybertsen and S. G. Louie, Phys. Rev. B 34, 5390 (1986).
- F. Aryasetiawan, O. Gunnarson, Rep. Prog. Phys. 61, 237 (1998).
- B. Farid, in Electron Correlation in the Solid State, edited by N.H. March, Imperial College Press, 1999.

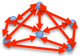
From mean-field to many-body perturbation theory



Mean-field approaches
(DFT, Hartree-Fock, *etc.*)

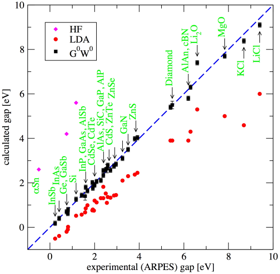


Many-body perturbation theory
(GW, Bethe-Salpeter, CC, ADC, etc.)

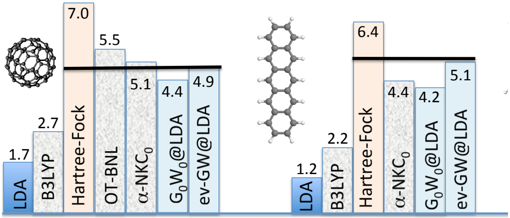


The « exact » many-body problem
(QMC, CI, etc.)

GW formalism for electronic properties : from solids to molecular systems



Band gap of inorganic semiconductors (mid 80s-)



Exp. HOMO-LUMO gap : 4.9 eV

Exp. HOMO-LUMO gap : 5.2 eV

(Blase, Attaccalite, Olevano, 2011)

Extensive benchmarks: van Setten *et al.* (2015); Marom *et al.* (2016); *etc.*

Field-operators in a nutshell

We define the annihilation $\hat{\psi}(x)$ and creation $\hat{\psi}^{\dagger}(x)$ ($x{=}\mathbf{r},\sigma$) field operators that remove/create an electron in **r** with spin σ within an N-electron system and satisfy the proper anti-commutation relations for Fermions, namely with the notation: $\{\hat{A},\hat{B}\}_{+}=\hat{A}\hat{B}+\hat{B}\hat{A}$:

$$\{\hat{\psi}^{\dagger}(x_1),\hat{\psi}^{\dagger}(x_2)\}_{+}=\{\hat{\psi}(x_1),\hat{\psi}(x_2)\}_{+}=0 \quad \textit{and} \quad \{\hat{\psi}^{\dagger}(x_1),\hat{\psi}(x_2)\}_{+}=\delta(x_1-x_2).$$

The many-body Hamiltonian reads with $\hat{h}$ the non-interacting Hamiltonian (kinetic + ionic potential) and v the Coulomb potential :

$$\hat{H}=\int d\mathbf{x}\;\hat{\psi}^{\dagger}(x)\hat{h}(\mathbf{r})\hat{\psi}(x)+\frac{1}{2}\iint dx_1 dx_2\;\hat{\psi}^{\dagger}(x_1)\hat{\psi}^{\dagger}(x_2)v(\mathbf{r}_1-\mathbf{r}_2)\hat{\psi}(x_2)\hat{\psi}(x_1)$$

In the Heisenberg representation (time-dependent operators, stationary eigenstates) these operators create/destroy an electron at a given position and time:

$$\text{e.g.}\qquad \hat{\psi}_H(x,t)=e^{i\hat{H}t/\hbar}\hat{\psi}(x)e^{-i\hat{H}t/\hbar}$$

The time-ordered single-particle Green's function

We DEFINE the time-ordered single-particle Green's function as follows:

$$i\hbar G(1,2) = \frac{< \psi_H^0 | T \left[\hat{\psi}_H(1) \hat{\psi}_H^\dagger(2) \right] | \psi_H^0 >}{< \psi_H^0 | \psi_H^0 >},$$

where $1 = (\mathbf{r}_1, t_1)$ and $2 = (\mathbf{r}_2, t_2)$ are space-time coordinates and:

- $|\psi_H^0 >$ is the ground-state many-body wave function in the Heisenberg representation (time-independent),
- $\hat{\psi}_H(1)$ and $\hat{\psi}_H^\dagger(2)$ are the destruction/creation field operators in the Heisenberg representation (time-dependent),
- T is the time-ordering operator, that orders the operators from left to right according to decreasing time (earliest on the right) with a (-1) factor for each permutation needed (for fermions).

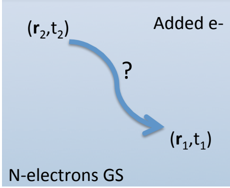
NOTE: we drop the spin variable for simplicity (unpolarized systems).

The electron-propagator ($t_1 > t_2$)

$$i\hbar G(1,2) = \theta(t_1 - t_2) < \psi^0(t_1)|\hat{\psi}(\mathbf{r}_1) e^{-i\hat{H}(t_1-t_2)/\hbar} \hat{\psi}^\dagger(\mathbf{r}_2)|\psi^0(t_2) >$$

- $\hat{\psi}^\dagger(\mathbf{r}_2)|\psi^0(t_2) >$ represents a state with one electron added in $\mathbf{r}_2$ to the N-electron ground-state at time (t_2),
- $\hat{U}(t_1, t_2) = e^{-i\hat{H}(t_1-t_2)/\hbar}$ propagates this state from time (t_2) to (t_1),
- finally, one project this state onto $< \psi^0(t_1)|\hat{\psi}(\mathbf{r}_1)|$ that is the bra of the $\hat{\psi}^\dagger(\mathbf{r}_1)|\psi^0(t_1) >$ with an additional electron in $\mathbf{r}_1$ at time (t_1).

The final projection measures how much the $\hat{\psi}^\dagger(\mathbf{r}_2)|\psi^0(t_2) >$ (N+1)-electron-state overlaps after a ($t_1 - t_2$) delay with the $\hat{\psi}^\dagger(\mathbf{r}_1)|\psi^0(t_1) >$ (N+1)-electron-state. G can be interpreted as a propagator of the "added" electron.



Lehman amplitudes

Let's consider: $i\hbar G^{>}(1,2) = \boxed{\langle \psi^0(t_1)|\hat{\psi}(\mathbf{r}_1)\; e^{-i\hat{H}(t_1-t_2)/\hbar}\hat{\psi}^{\dagger}(\mathbf{r}_2)|\psi^0(t_2)\rangle}$

With $\left\{ E_n^{N+1}, \psi_H^{n,N+1} \right\}$ the eigenstates of the (N+1) electron system:

$$e^{-i\hat{H}(t_1-t_2)/\hbar} = \sum_n e^{-iE_n^{N+1}(t_1-t_2)/\hbar}|\psi_H^{n,N+1}\rangle\langle\psi_H^{n,N+1}|$$

$$\text{and} \quad |\psi^0(t_2)\rangle = e^{-iE_0^N t_2/\hbar}|\psi_H^0\rangle, \qquad \langle\psi^0(t_1)| = \langle\psi_H^0|e^{iE_0^N t_1/\hbar}$$

we obtain (with the "overbar" for the complex conjugate) :

$$\langle\psi^0(t_1)|\hat{\psi}(\mathbf{r}_1)\; \hat{U}(t_1,t_2)\hat{\psi}^{\dagger}(\mathbf{r}_2)|\psi^0(t_2)\rangle = \boxed{\sum_n f_n^{N+1}(\mathbf{r}_1)\overline{f}_n^{N+1}(\mathbf{r}_2)e^{-i\varepsilon_n^{N+1}(t_1-t_2)/\hbar}}$$

$f_n^{N+1}(\mathbf{r}_1) = \langle\psi_H^0|\hat{\psi}(\mathbf{r}_1)|\psi_H^{n,N+1}\rangle$ is called an (addition) Lehman amplitude.

$\varepsilon_n^{N+1} = (E_n^{N+1} - E_0^N)$ is an addition energy.

Lehman amplitudes with hole contribution ($t_2 > t_1$)

We can proceed similarly with the hole-related part of the Green's function to obtain:

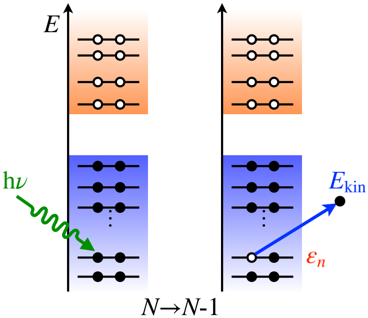
$$\begin{aligned} i\hbar G(1,2) = {} & \theta(t_1 - t_2) \sum_n f_n^{N+1}(\mathbf{r}_1) \overline{f}_n^{N+1}(\mathbf{r}_2) e^{-i\varepsilon_n^{N+1}(t_1 - t_2)/\hbar} \\ & - \theta(t_2 - t_1) \sum_n f_n^{N-1}(\mathbf{r}_1) \overline{f}_n^{N-1}(\mathbf{r}_2) e^{-i\varepsilon_n^{N-1}(t_2 - t_1)/\hbar} \end{aligned}$$

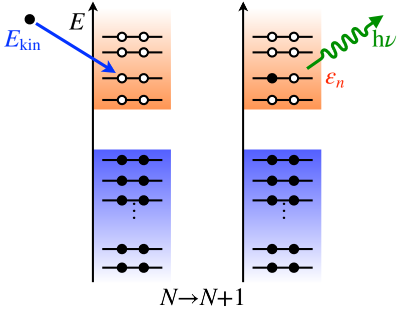
where we have introduce the Lehman removal amplitude and removal energies:

$$f_n^{N-1}(\mathbf{r}) = \langle \psi_H^{n,N-1} | \hat{\psi}(\mathbf{r}) | \psi_H^0 \rangle \quad \text{and} \quad \varepsilon_n^{N-1} = (E_0^N - E_n^{N-1})$$

The time evolution of the Green's function is governed by the electron addition/removal energies from the N-electron ground-state.

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

Time-ordered Green's function in the frequency domain

Defining the Fourier transform : $g(\omega) = \int d\tau e^{i\omega\tau} g(\tau)$, with (use complex integration and residue theorem):

$$\theta(\pm\tau) = \mp \lim_{\eta\to 0^+} \frac{1}{2i\pi} \int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega\tau}}{\omega \pm i\eta}, \quad \text{one obtains (Exercise):}$$

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

where the f_n and ε_n are the addition/removal Lehman amplitudes and energies depending on the sign of $(\varepsilon_n - \mu)$ with μ Fermi level.

The poles of the Green's function are the true addition/removal electronic energies as measured experimentally with a photoemission experiment.

Equation of motion for the Green's function

With a time-independent Hamiltonian, the field operators satisfy the standard equation of motions for operators (Heisenberg representation):

$$i\hbar \frac{d\hat{O}_H}{dt} = \left[\hat{O}_H, \hat{H}\right]$$

Writing the Hamiltonian as a function of the field operators and using the commutation relation between them leads to ($\hbar = 1$ below):

$$\left[i\frac{\partial G(1,2)}{\partial t_1} - \hat{h}(1\right] G(1,2) + i \int d3 \; v(1,3) G_2(1,3^+;2,3^{++}) = \delta(1,2)$$

where G_2 is a two-body equation of motion monitoring the propagation of two particles: $i^2 G(1,3;2,4) = \langle N| T[\hat{\psi}(1)\hat{\psi}(3)\hat{\psi}^\dagger(4)\hat{\psi}^\dagger(2)]|N\rangle$.

This is the hierarchy of Green's function : one need the 2nd order G_2 to know the one-body G, the 3rd order G_3 to get the second-order G_2, etc. Truncating this hierarchy is the central difficulty.

The Hartree-Exchange-Correlation self-energy Σ_{HXC}

This is ugly but one can rewrite the equation of motion for G as follows:

$$\left[i\frac{\partial G(1,2)}{\partial t_1} - \hat{h}(1\right] G(1,2) + i\int d3\, \Sigma_{HXC}(1,3)G(3,2) = \delta(1,2)$$

where $\hat{h}$ accounts for the kinetic energy and the ionic potential and where the Hartree-Exchange-Correlation self-energy Σ_{HXC} reads:

$$\Sigma_{HXC}(1,3) = -i\iint d2d4\; v(1,4)G_2(1,4^+;2,4^{++})G^{-1}(2,3)$$

This is very formal but extremely crucial since it shows that in the equation of motion for G all Hartree and exchange and correlation effects can be described by a two-body time-dependent operator:

$$\Sigma_{HXC}(1,2) = \Sigma_{HXC}(\mathbf{r}_1, \mathbf{r}_2; t_2 - t_1)$$

The quasiparticle equation

The Fourier transform of the equation-of-motion of G leads to:

$$[\omega - h(\mathbf{r}_1)]\, G(\mathbf{r}_1, \mathbf{r}_2; \omega) - \int d\mathbf{r}_3\, \Sigma_{HXC}(\mathbf{r}_1, \mathbf{r}_3; \omega) G(\mathbf{r}_3, \mathbf{r}_2; \omega) = \delta(\mathbf{r}_1 - \mathbf{r}_2)$$

Plugging now the Lehman representation of G:

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

leads formally to the following eigenvalue equation :

$$\boxed{h(\mathbf{r}) f_n(\mathbf{r}) + \int d\mathbf{r}'\, \Sigma_{HXC}(\mathbf{r}, \mathbf{r}'; \varepsilon_n) f_n(\mathbf{r}') = \varepsilon_n f_n(\mathbf{r})}$$

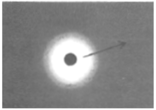
This is a crucial result : the true addition/removal energies are solution of a simple one-body equation (as the Kohn-Sham equation) but now the HXC operator depends on the energy of the state it is acting on.

What is a quasiparticle (qualitatively) ?

We have mapped the true problem of N interacting electrons on a 1-body "quasiparticle" equation with a "self-energy": how is this possible ?

Remember that an electron creates around itself (Coulomb and Pauli repulsion) an exchange-and-correlation hole with its corresponding sum rule : the depletion of charge dynamically created by an electron around itself amounts to one electron ⇒ the electron with its surrounding XC hole is globally neutral !! We call this object the quasiparticle. Since the quasiparticle are globally neutral, they hardly interact with each other ⇒ they can be described by a one-body (independent particles) equation !

The interaction between one electron and the (N-1) other electrons can be recast into an interaction with the corresponding XC hole. As such this interaction is internal to the quasiparticle ⇒ this is a self-energy (Figure from R.D. Mattuck, A guide to Feynman diagrams).



The quasiparticle equation vs Kohn-Sham

Subtracting the Hartree potential to define the dynamical non-local exchange and correlation potential:

$$\Sigma_{XC}(\mathbf{r},\mathbf{r}';\varepsilon_n) = \Sigma_{HXC}(\mathbf{r},\mathbf{r}';\varepsilon_n) - V^{Hartree}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$$

the quasiparticle equation reads:

$$\left[-\nabla^2/2 + v^{ion}(\mathbf{r}) + V^{Hartree}(\mathbf{r})\right] f_n(\mathbf{r}) + \int d\mathbf{r}'\ \Sigma_{XC}(\mathbf{r},\mathbf{r}';\varepsilon_n) f_n(\mathbf{r}') = \varepsilon_n f_n(\mathbf{r})$$

that can be compared to the DFT Kohn-Sham and Hartree-Fock eigenvalue equations with the substitution of $\Sigma_{XC}(\mathbf{r},\mathbf{r}';\varepsilon_n)$ by:

$$\text{(DFT)}\quad V^{XC}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \qquad \text{(HF)}\quad \Sigma_X(\mathbf{r},\mathbf{r}') = -\sum_j^{occp} \frac{\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} |\sigma_j\rangle\langle\sigma_j|$$

Building relations with linear response theory

We can now study the evolution of the system and its Green's function when an external perturbation $U(1) = U(\mathbf{r}_1, t_1)$ is switched on. The variation of the Green's function leads to:

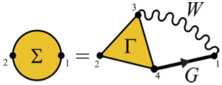
$$\frac{\partial G(1,2)}{\partial U(3)} = G(12)G(33^+) - G_2(1,3;2,3^+)$$

Plugging this definition of G_2 into the definition of Σ_{HXC}, using firther the relation $iG(33^+) = n(3)$ the charge density, one obtains:

$$\begin{aligned}
\Sigma_{XC}(1,2) &= i \iint d3d4\; G(1,3)W(1^+,4)\Gamma(3,2;4) \\
W(1,2) &= \int d3\; \epsilon^{-1}(1,3)v(3,2) \quad \text{screened Coulomb potential} \\
\epsilon^{-1}(1,3) &= \delta(1,3) + \frac{\partial V^{Hartree}(1)}{\partial U(3)} \quad \text{inverse dielectric function}
\end{aligned}$$

The GW approximation (Hedin, 1965)

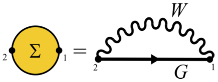
The only ”more-than-2-body” function in the expression of Σ_{XC} is the ”vertex” correction $\Gamma(1,2;3)$ that can be written as follows:



$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \int d(4567)\, \frac{\partial \Sigma_{XC}(1,2)}{\partial G(4,5)} G(4,6) G(7,5) \Gamma(6,7;3)$$

In the GW approximation, one takes $\Gamma(1,2;3) \simeq \delta(1,2)\delta(1,3)$ yielding:

$$\boxed{\Sigma_{XC}^{GW}(1,2) \simeq iG(1,2)W(1,2^{+})}$$



Note that $\partial\Sigma_{XC}/\partial G$ would yield a term proportional to W so that the GW approximation can be seen as a lowest order approximation to Σ_{XC} in terms of the screened Coulomb potential W, not in terms of the bare Coulomb potential v. This is a central point of the GW approximation.

The screened Coulomb potential

Assume we add a test charge Q in $\mathbf{r}_0$ that yields a charge variation:

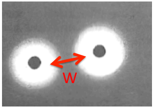
$$\delta n(\mathbf{r}) = \int d\mathbf{r}\; \chi(\mathbf{r},\mathbf{r}') \frac{Q}{|\mathbf{r}-\mathbf{r}_0|} \quad \text{where} \quad \chi \quad \text{is the susceptibility.}$$

Then the total field generated by the charge and δn is:

$$\frac{Q}{|\mathbf{r}-\mathbf{r}_0|} + \int d\mathbf{r}' d\mathbf{r}'' \; \frac{1}{|\mathbf{r}-\mathbf{r}'|} \chi(\mathbf{r}',\mathbf{r}'') \frac{Q}{|\mathbf{r}''-\mathbf{r}_0|}$$

This defines $\boxed{W = v + v\chi v}$ the screened Coulomb potential which is much reduced (!!) as compared to the bare Coulomb potential.

If the test charge is an electron, then W is the potential generated by the electron and its exchange-correlation hole, namely the quasiparticle ⇒ quasiparticles interact through the screened (attenuated) Coulomb potential.



A dynamically screened exchange approximation

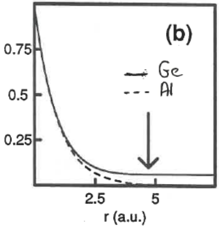
It is "easy" to show that the bare exchange operator can be written :

$$\Sigma_X(1,2) = iG^{HF}(1,2)v(1,2)$$

with v the bare Coulomb potential and G^{HF} the Green's function built with Hartree-Fock eigenstates and eigenvalues.

As such the GW approximation can be seen as a dynamically screened exchange term : the bare Coulomb potential between electrons is replaced by the screened Coulomb potential between quasiparticles.

In metals, W is exponentially decaying; in semiconductors it converges at long-range to v/ϵ_M with ϵ_M the macroscopic dielectric constant (12 in silicon). Figure: plot of $W(\mathbf{r},\mathbf{r}';\omega=0)/v(\mathbf{r},\mathbf{r}')$ as a function of $|\mathbf{r}-\mathbf{r}'|$ for Ge (ϵ_M=16) and Al (courtesy Rafaelle Resta, SISSA).



GW calculations in practice : the $G_0 W_0$ scheme

The input Green's function G and W are built from Kohn-Sham (KS) eigenstates and eigenvalues:

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

and: $\boxed{W = v + v\chi_0^{KS} W}$ (RPA approximation) where χ_0^{KS} is the independent particule susceptibility:

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

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

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

Calculating $\chi_0(\omega)$ in a basis

Besides a few specific implementations (Rojas *et al.* 1999; Liu *et al.* 2016) operators are in most codes not expressed on a real-space grid but use an "auxiliary" basis $\{\beta\rangle$ that spans the "product space" $\{\phi_n \phi_m\}$:

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

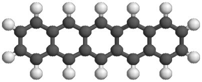
The auxiliary basis can be a planewave basis (most physicists codes), an auxiliary Gaussian basis (quantum chemist's codes) or directly the product space $\{\phi_n \phi_m\}$. With the full $\{\phi_n \phi_m\}$ space, the calculation of χ_0 is exact but scales as $\mathcal{O}(N^6)$ with system size, while with planewaves or Gaussian auxiliary basis sets, the scaling goes down to $\mathcal{O}(N^4)$ but convergency tests on the auxiliary basis are needed.

Standard *GW* calculations scale as $\mathcal{O}(N^4)$ with system size. Cubic-scaling calculations - and even linear-scaling - are starting to appear.

Convergency with the Kohn-Sham basis size

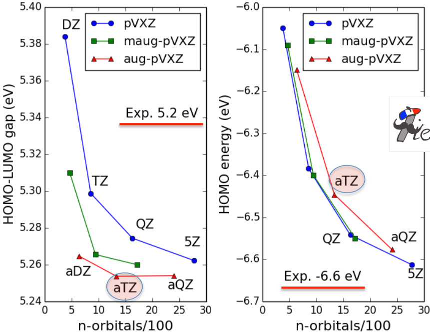
GW is an explicitly correlated technique, namely the correlation energy is built perturbatively from valence-to-conduction "matrix elements". The convergency with the number of unoccupied (conduction) levels can be slow both in the case of Gaussian and planewave basis sets.

G_0W_0@PBEh(α=0.75) calculation on pentacene



With aug-cc-pVTZ basis (1334 basis orbitals)

=> 3 minutes wall time on 256-cores



Starting-point dependency of the $G_0 W_0$ scheme

Since G_0 and W_0 are built from input Kohn-Sham eigenstates:

$$
\begin{aligned}
G_0(\mathbf{r},\mathbf{r}';\omega) &= \sum_n \frac{\phi_n^{KS}(\mathbf{r})[\phi_n^{KS}]^*(\mathbf{r}')}{\hbar\omega - \varepsilon_n^{KS} + i0^+\hbar\ \mathrm{sgn}(\varepsilon_n^{KS} - \mu)} \\
\chi_0^{KS}(\mathbf{r},\mathbf{r}';\omega) &= \sum_{mn}(f_m - f_n)\frac{[\phi_m^{KS}(\mathbf{r})]^*\phi_n^{KS}(\mathbf{r})[\phi_n^{KS}(\mathbf{r}')]^*\phi_m^{KS}(\mathbf{r}')}{\omega - (\varepsilon_m^{KS} - \varepsilon_n^{KS}) + i0^+}
\end{aligned}
$$

the final $G_0 W_0$ quasiparticle energies depend on the input functional.

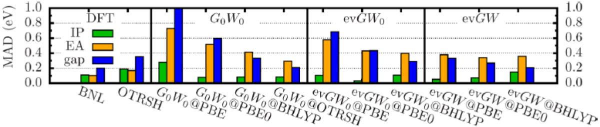


Figure : DFT ΔSCF and *GW* calculations on acenes (benzene, naphtalene, ..., hexacene) [Rangel et al. JCTC 2016]. OTRSH is an "optimally" tuned range-separated hybrid.

Optimaly-tuned starting Kohn-Sham eigenstates

In finite size systems, since ΔSCF DFT calculations provide a "reasonable" estimate of the ionization potential (or electronic affinity) through total energy differences: $IP \simeq |E_0(N) - E_0(N-1)|$, one strategy is to adapt the functional parameters (e.g. range-separation parameter γ) such that the corresponding HOMO energy level is equal to (-IP):

$$\varepsilon^{KS}_{HOMO}(\gamma) = E_0(N;\gamma) - E_0(N-1;\gamma)$$

where the functional contains e.g. the full long-range exchange (Baer-Neuhauser-Livshits=BNL functional) :

$$\hat{V}_X^{LR,\gamma}\phi_i(\mathbf{r}) = -\sum_j^{occ} \phi_j(\mathbf{r}) \int d\mathbf{r}' \frac{\mathrm{erf}(\gamma|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\langle\sigma_i|\sigma_j\rangle$$

Since the corresponding KS eigenstates are already close to the experimental results, this is an excellent starting point to G_0W_0 calculations.

Self-consistency on eigenvalues

Once the Kohn-Sham eigenvalues have been corrected to produce more accurate GW quasiparticle energies, these improved eigenvalues can be injected in the construction of G, or in the construction of G and W, in a self-consistent fashion. Updating the eigenvalues in G is labeled the evGW_0 scheme; updating both G and W is called evGW.

The evGW scheme is accurate and the least starting-point dependent but still the wavefunctions ϕ_n^{KS} are not updated !!

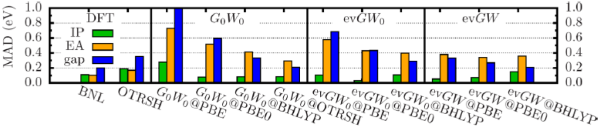


Figure : DFT ΔSCF and GW calculations on acenes [Rangel et al.]

Self-consistency on eigenvalues and wavefunctions

The updating of the eigenstates means diagonalizing the full self-energy operator $\Sigma_{nm} = \langle \phi_n | \Sigma | \phi_m \rangle$ rather than just calculating the "diagonal" $\langle \phi_n | \Sigma - V_{XC} | \phi_n \rangle$.

There is one-conceptual problem: at which energy do we take the self-energy operator ?

$$\Sigma_{nm} = \langle \phi_n | \Sigma(\varepsilon_n \quad \text{or} \quad \varepsilon_m??) | \phi_m \rangle$$

The popular "quasiparticle self-consistency" QPsGW(Schilfgaarde, Kotani, Faleev, PRL 2006) propose the following *ansatz*:

$$\hat{\Sigma} = \sum_{nm} | \phi_n \rangle \frac{\Sigma(\varepsilon_n) + \Sigma(\varepsilon_m)}{2} \langle \phi_m |$$

QPscGW self-consistency in solids

Fundamental gaps of sp compounds from LDA (squares) and G_0W_0@LDA (circles) in top panel, and from QSGW. The spin-orbit coupling was subtracted by hand from the calculations. The G_0W_0@LDA gaps improve on the LDA, but are still systematically underestimated. For QSGW data, zinc-blende compounds with direct transitions are shown as circles; All other gaps are shown as squares. Errors are small and highly systematic, and would be smaller than the figure shows if the electron-phonon renormalization were included.

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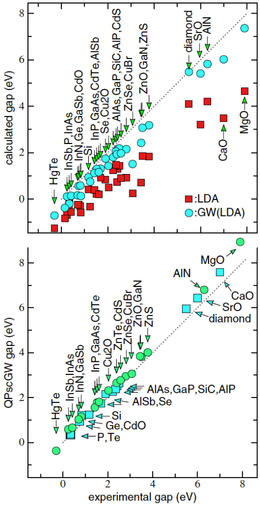

GW formalism: concluding remarks

Together with the "pragmatic" optimally tuned functionals" with $\mathcal{O}(N^4)$ scaling, the *GW* formalism offers an another $\mathcal{O}(N^4)$ (soon $\mathcal{O}(N^3)$ ...) approach that is specifically designed to reproduce electron energy levels !! Calculations on several hundred of atoms are now possible.

Codes : the *GW* formalism is implemented in most major planewave codes (AbInit, VASP, QuantumEspresso, CP2K, etc.) and is starting to emerge in quantum chemistry with standard atomic basis (Gaussians, Slater, numerical radial basis, etc.) formalisms (Turbomole, FHI-Aims, Fiesta, MolGW, etc.)

The *GW* formalism opens the way to the Bethe-Salpeter equation (BSE) approach designed to reproduce optical properties (neutral excitations) as an alternative with same CPU cost as the standard TD-DFT formalism.

Part II (Complement) : optical properties within the Bethe-Salpeter equation formalism : building on the *GW* formalism.

The Bethe-Salpeter equation (BSE) formalism is the equivalent to TD-DFT in the many-body Green's function formalism.

TD-DFT builds its XC kernel from the charge-density derivative of the XC potential while BSE builds it from the Green's function derivative of the XC self-energy.

IN CONSTRUCTION !