GW approximation in ABINIT

F. Bruneval

Service de Recherches de Météllurgie Physique
CEA Saclay
Outline

I. Introduction: going beyond DFT

II. Introduction of the Green's function

III. Exact Hedin's equations and the \textit{GW} approximation

IV. Calculating the \textit{GW} self-energy in practice

V. Applications
Standard DFT has unfortunately some shortcomings

Band gap problem!

after van Schilfgaarde et al PRL 96 226402 (2008)
A pervasive problem

Conductivity for charge transport in semiconductors

Optical absorption

Defect formation energy
Charge transition level

Photoemission

FIG. 1. Single-particle Hartree-Fock and local density approximation eigenvalue spectra (eV) for the SiH₄ molecule.
Gap re-normalization by a (metallic) substrate

**FIG. 1** (color online). Schematic energy level diagram indicating polarization shifts in the frontier energy levels (ionization and affinity) of a molecule upon adsorption on a metal surface.

Benzene deposited on copper, gold, graphite

How do go beyond within the DFT framework?

Not easy to find improvement within DFT framework
There is no such thing as a perturbative expansion
Perdew's Jacob's ladder does not help for the band gap

FIG. 1. Jacob's ladder of density functional approximations to the exchange-correlation energy.

Need to change the overall framework!

F. Bruneval

Jouvence, Quantum Materials 2018
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Many-body perturbation theory

Historically older than the DFT (from the 40-50's)! Big names: Feynman, Schwinger, Hubbard, Hedin, Lundqvist

Green's functions
= propagator

$$G(r_{t}, r'_{t'}) =$$
The Green's function

Exact ground state wavefunction: \( |N,0\rangle \)

Creation, annihilation operator: \( \Psi^\dagger (r \ t), \Psi (r \ t) \)

1. \( \Psi^\dagger (r \ t) |N,0\rangle \) is a (N+1) electron wavefunction not necessarily in the ground state

2. \( \Psi^\dagger (r' \ t') |N,0\rangle \) is another (N+1) electron wavefunction

Let's compare the two of them!
Green's function definition

\[ \langle N, 0 | \Psi(r, t) \Psi^\dagger(r', t') | N, 0 \rangle \]

\[ \text{for } t > t' \]

Mesures how an extra electron propagates from \((r', t')\) to \((r, t)\).
Green's function definition

\[ \langle N,0 | \Psi^\dagger (r\ 't\ ') \Psi (r\ t) | N,0 \rangle \]

\[ = i G^h (r\ 't\ ', r\ t) \text{ for } t' > t \]

Mesures how a missing electron (= a hole) propagates from \( (rt) \) to \( (r't') \).
Final expression for the Green's function

\[ i G(r_t, r'_t') = \langle N, 0 | T [ \Psi(r_t) \Psi^\dagger(r'_t')] | N, 0 \rangle \]

Compact expression that describes both the propagation of an extra electron and an extra hole

\[ G(r_t, r'_t') = G^e(r_t, r'_t') - G^h(r'_t', r_t) \]
Lehman representation

\[ iG(r,r',t-t') = \langle N,0 | T[\Psi(rt)\Psi^+(r't')] | N,0 \rangle \]

Closure relation

\[ \sum_{M,i} |M,i\rangle \langle M,i| \]

Lehman representation:

\[ G(r,r',\omega) = \sum_i \frac{f_i(r)f_i^*(r')}{\omega - \epsilon_i \pm i\eta} \]

where

\[ \epsilon_i = \begin{cases} E(N+1,i) - E(N,0) \\ E(N,0) - E(N-1,i) \end{cases} \]

Exact excitation energies!
Related to photoemission spectroscopy

Energy conservation: before

\[ h\nu + E(N,0) = E_{\text{kin}} + E(N-1, i) \]

after

Quasiparticle energy:

\[ \epsilon_i = E(N,0) - E(N-1, i) = E_{\text{kin}} - h\nu \]
And inverse photoemission spectroscopy

Energy conservation: before after

\[ E_{\text{kin}} + E(N,0) = \hbar \nu + E(N+1,i) \]

Quasiparticle energy:

\[ \epsilon_i = E(N+1,i) - E(N,0) = E_{\text{kin}} - \hbar \nu \]
Exact realization of the Lehman decomposition

\[ \langle m | G^h(\omega) | m \rangle = \sum_i \frac{\langle N 0 | \hat{c}_m^+ | N - 1 i \rangle \langle N - 1 i | \hat{c}_m | N 0 \rangle}{\omega - \epsilon_i - i \eta} \]

\[ \begin{align*}
N &= 2 \\
N - 1 &= 1 \\
m &= 1 \, s
\end{align*} \]

Obtained from FCI calculations

He → He$^+$

Quasiparticle peak

Satellite or shake-up structure
Satellites in reality?

Helium gas
Thompson et al.

Silicon crystal
Guzzo et al. PRL 2011
Other properties of the Green's function

Get the electron density:

\[ \rho(r) = -i G(r, t^-, r, t) \]

Galitskii-Migdal formula for the total energy:

\[ E_{total} = \frac{1}{\pi} \int_{-\infty}^{\mu} d\omega \text{Tr} \left[ (\omega - h_0) \text{Im} G(\omega) \right] \]

Expectation value of any 1 particle operator (local or non-local)

\[ \langle O \rangle = \lim_{t \to t'} \text{Tr} \left[ O G \right] \]
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Equation of motion of Green's functions: Dyson equation

Let us start with a non-interacting Green's function $G_0$
corresponding to a hamiltonian $h_0$

$$\int d\mathbf{r}_2 \delta(\mathbf{r}_1-\mathbf{r}_2)\left[\omega-h_0(\mathbf{r}_2)\right]G_0(\mathbf{r}_2, \mathbf{r}_3, \omega) = \delta(\mathbf{r}_1-\mathbf{r}_3)$$

In short:

$$[\omega-h_0]G_0 = 1 \quad \text{or} \quad G_0^{-1} = [\omega-h_0]$$

Imagine $h_0$ is Hartree and $h_{KS}$ is Kohn-Sham

$$[\omega-h_{KS}]G_{KS} = 1$$

$$[\omega-h_0-v_{xc}]G_{KS} = 1$$

$$[G_0^{-1}-v_{xc}]G_{KS} = 1$$

$$G_{KS} = G_0 + G_0 v_{xc} G_{KS}$$

$$G_{KS} = G_0 + G_0 v_{xc} G_0 + G_0 v_{xc} G_0 v_{xc} G_0 +...$$

Exercice
A first contact with diagrams

\[ G_{KS}(1,2) = G_0(1,2) + \int d3 G_0(1,3) v_{xc}(3) G_{KS}(3,2) \]

Dyson equation connects the Green's functions arising from different approximations.

What about the exact Green's function?
Dyson equation for the exact Green's function

Imagine there exists an operator that generates the exact $G$

$$G(1,2) = G_0(1,2) + \int d(34) G_0(1,3) \Sigma(3,4) G(4,2)$$

This operator is the famous “self-energy”:
- non-local in space
- time-dependent
- non-Hermitian

Everything else now deals with finding expressions for the self-energy!
A hierarchy of equations of motion

In fact there is an exact expression for the self-energy as a function of the two-particle Green's function

\[
\left[ G_0^{-1} - \Sigma \right] G = 1
\]

\[
\left[ G_0^{-1} - G_2 \right] G = 1
\]

\[
G_2(1,2;3,4) = \langle N, 0 | T[\Psi(1)\Psi(2)\Psi^+(3)\Psi^+(4)] | N, 0 \rangle
\]

And try to guess the equation of motion for the two-particle Green's function?

\[
G_2 \text{ needs } G_3
\]

\[
G_3 \text{ needs } G_4
\]

\[
G_4 \text{ needs } G_5
\]

..........
An expression for the self-energy

**Trick due to Schwinger (1951):**
- Introduce a small external potential $U$ (that will be made equal to zero at the end)
- Calculate the variations of $G$ with respect to $U$

$$G_2(1,3;2,3) = \frac{\delta G(1,2)}{\delta U(3)}$$

Obtain a perturbation theory with basic ingredients $G$ and $\nu$
- 1st order is Hartree-Fock
- 2nd order is MP2

However MP2 diverges for metals!

**Trick due to Hubbard+Hedin (late 1950's – early 1960's):**
- Introduce the electrostatic response $V$ to $U$
- Calculate the variations of $G$ with respect to $V$

$$V(1) = U(1) - i \int d2 \nu(1,2) \delta G(2,2)$$

Obtain a new renormalized perturbation theory with basic ingredients $G$ and $W$
- 1st order is $GW$
Shifting from $U$ to $V$

$U(1) = \varepsilon \delta(r-r_1)\delta(t-t_1)$

Everything is functional of $U$

$G[U]$ $

V(1) = U(1) + \int d\mathbf{r} \nu(r_1-r)\delta\rho(r)$

$V$ also includes the electrostatic response

Everything is functional of $V$

$G[V]$
Hedin's coupled equations

6 coupled equations:  

\[ G(1,2) = G_0(1,2) + \int d34 G_0(1,3) \Sigma(3,4) G(4,2) \]  

Dyson equation

\[ \Sigma(1,2) = i \int d34 G(1,3) W(1,4) \Gamma(4,2,3) \]  

self-energy

\[ \Gamma(1,2,3) = \delta(1,2) \delta(1,3) + \int d4567 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(5,7) \Gamma(6,7,3) \]  

vertex

\[ \chi_0(1,2) = -i \int d34 G(1,3) G(4,1) \Gamma(3,4,2) \]  

polarizability

\[ \varepsilon(1,2) = \delta(1,2) - \int d3 \nu(1,3) \chi_0(3,2) \]  

dielectric matrix

\[ W(1,2) = \int d3 \varepsilon^{-1}(1,3) \nu(3,2) \]  

screened Coulomb interaction
Simplest approximation

\[ \Sigma(1,2) = iG(1,2)v(1^+, 2) \]

Fock exchange

\[ G = G_0 + G_0 \Sigma G \]

Dyson equation:

\[ G = G_0 + G_0 \Sigma G_0 + \ldots \]

Not enough: Hartree-Fock is known to perform poorly for solids
Hartree-Fock approximation for band gaps
Hedin's coupled equations

6 coupled equations:

\[ G(1,2) = G_0(1,2) + \int d34 G_0(1,3) \Sigma (3,4) G(4,2) \]  \hspace{1cm} \text{Dyson equation}

\[ \Sigma (1,2) = i \int d34 G(1,3) W(1,4) \Gamma (4,2,3) \]  \hspace{1cm} \text{self-energy}

\[ \Gamma (1,2,3) = \delta (1,2) \delta (1,3) + \int d4567 \frac{\delta \Sigma (1,2)}{\delta G(4,5)} G(4,6) G(5,7) \Gamma (6,7,3) \]

\[ \chi_0(1,2) = -i \int d34 G(1,3) G(4,1) \Gamma (3,4,2) \]

\[ \epsilon(1,2) = \delta (1,2) - \int d3 \nu(1,3) \chi_0(3,2) \]  \hspace{1cm} \text{screened Coulomb interaction}

\[ W(1,2) = \int d3 \epsilon^{-1}(1,3) \nu(3,2) \]
Hedin's coupled equations

6 coupled equations:

\[ G(1,2) = G_0(1,2) + \int d34 G_0(1,3) \Sigma(3,4) G(4,2) \]

\[ \Sigma(1,2) = i \int d34 G(1,3) W(1,4) \Gamma(4,2,3) \]

\[ \Gamma(1,2,3) = \delta(1,2) \delta(1,3) + \int d4567 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(5,7) \Gamma(6,7,3) \]

\[ \chi_0(1,2) = -i \int d34 G(1,3) G(4,1) \Gamma(3,4,2) \]

\[ \varepsilon(1,2) = \delta(1,2) - \int d3 \nu(1,3) \chi_0(3,2) \]

\[ W(1,2) = \int d3 \varepsilon^{-1}(1,3) \nu(3,2) \]

Dyson equation

self-energy

screened Coulomb interaction
Hedin's coupled equations

6 coupled equations:

\[
G(1,2) = G_0(1,2) + \int d34 G_0(1,3) \Sigma(3,4) G(4,2)
\]

Dyson equation

\[
\Sigma(1,2) = i \int d34 G(1,3) W(1,4) \Gamma(4,2,3)
\]

self-energy

\[
\Gamma(1,2,3) = \delta(1,2) \delta(1,3) + \int d4567 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(5,7) \Gamma(6,7,3)
\]

\[
\chi_0(1,2) = -i \int d34 G(1,3) G(4,1) \Gamma(3,4,2)
\]

\[
\epsilon(1,2) = \delta(1,2) - \int d3 \nu(1,3) \chi_0(3,2)
\]

screened Coulomb interaction

\[
W(1,2) = \int d3 \epsilon^{-1}(1,3) \nu(3,2)
\]
Here comes the $GW$ approximation

\[ \Sigma(1,2) = i G(1,2) W(1,2) \]

$GW$ approximation

\[ \chi_0(1,2) = -i G(1,2) G(2,1) \]

RPA approximation

\[ \epsilon(1,2) = \delta(1,2) - \int d^3 v(1,3) \chi_0(3,2) \]

\[ W(1,2) = \int d^3 \epsilon^{-1}(1,3) v(3,2) \]
Let us play with diagrams

\[ \chi_0(1,2) = -i G(1,2)G(2,1) \]

\[ \Sigma(1,2) = i G(1,2)W(1,2) \]

\[ \epsilon(1,2) = \delta(1,2) - \int d3 v(1,3) \chi_0(3,2) \]

\[ W(1,2) = \int d3 \epsilon^{-1}(1,3)v(3,2) \]

\[
\begin{align*}
W &= v + v\chi_0 W \\
&= v + v\chi_0 v + v\chi_0 v\chi_0 v + \ldots \\
\text{Infinite summation over bubble (or ring) diagrams}
\end{align*}
\]
What is $W$?

Interaction between electrons in vacuum:

$$v(r, r') = \frac{1}{4\pi \varepsilon_0} \frac{e^2}{|r - r'|}$$

Interaction between electrons in a homogeneous polarizable medium:

$$W(r, r') = \frac{1}{4\pi \varepsilon_0 \varepsilon_r} \frac{e^2}{|r - r'|}$$

Dielectric constant of the medium

Dynamically screened interaction between electrons in a general medium:

$$W(r, r', \omega) = \frac{e^2}{4\pi \varepsilon_0} \int dr'' \frac{\varepsilon^{-1}(r, r'', \omega)}{|r'' - r'|}$$
$W$ is frequency dependent

$W$ can be measured directly by Inelastic X-ray Scattering

$$\text{Im} \, W(q = 0.80 \text{a.u, } \omega)$$

[Graph showing $S(Q, \omega)$ vs $\omega$ for different curves labeled as 'Exp. present', 'Exp. Schülke', 'TDLDA Ehrnsp.', and 'TDLDA + L/T' for Silicon and Plasmon frequency.]
Summary
Summary: DFT vs Green’s function

Electronic density

\[ \rho(r) \]

Local and static

exchange-correlation potential

\[ v_{xc}(r) \]

Approximations: LDA, GGA, hybrids

Green's function

\[ G(rt, r't') \]

Non-local, dynamic
Depends onto empty states

exchange-correlation operator

\[ \Sigma_{xc}(rt, r't') \]

\[ \Sigma_{GW}(rt, r't') = iG(rt, r', t')W(rt, r't') \]

Approximations: HF, GW approximation

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GW viewed as a “super” Hartree-Fock

Hartree-Fock Approximation

\[ \Sigma_x (r_1, r_2) = \frac{i}{2\pi} \int_{-\infty}^{\mu} d\omega' G(r_1, r_2, \omega') v(r_1, r_2) \]

= bare exchange

GW Approximation

\[ \Sigma_{xc} (r_1, r_2, \omega) = \frac{i}{2\pi} \int d\omega' G(r_1, r_2, \omega + \omega') W(r_2, r_1, \omega') \]

Non Hermitian dynamic

\[ \Sigma_c (r_1, r_2, \omega) \]

+ correlation

GW is nothing else but a “screened” version of Hartree-Fock.
GW approximation gets good band gap

after van Schilfgaarde et al PRL 96 226402 (2008)

No band gap problem anymore!
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Historical recap of GW calculations

- **1965**: Hedin's calculations for the homogeneous electron gas
  Phys Rev *2201 citations*

- **1967**: Lundqvist's calculations for the homogeneous electron gas
  Physik der Kondensierte Materie *299 citations*

- **1982**: Strinati, Mattausch, Hanke for real semiconductors but within tight-binding
  PRB *154 citations*

- **1985**: Hybertsen, Louie for real semiconductors with ab initio LDA
  PRL *711 citations* & PRB *1737 citations*

- **1986**: Godby, Sham, Schlüter for real semiconductors to get accurate local potential
  PRL *544 citations* & PRB *803 citations*

- **~2001**: First publicly available GW code through the ABINIT project

- **2003**: Arnaud, Alouani for extension to Projector Augmented Wave
  PRB *102 citations*

- **2006**: Shishkin, Kresse for extension to Projector Augmented Wave (again)
  PRB *256 citations*
GW approximation in practice

- For periodic solids: Abinit, BerkeleyGW, VASP, Yambo
  based on plane-waves (with pseudo or PAW)

- For finite systems: MOLGW, Fiesta, FHI-AIMS
  based on localized orbitals (Gaussians or Slater or other)
Workflow of a typical GW calculation

\[ G_0 W_0 \text{ vs } GW \]

One-shot GW

DFT

\[ \phi_i^{KS}, \epsilon_i^{KS} \]

occupied AND empty states

calculate W

\[ \phi_i^{KS}, \epsilon_i^{KS} \]

If self-consistent

\[ \phi_i^{GW}, \epsilon_i^{GW} \]

calculate \( G \times W \)

\[ \epsilon_i^{GW}(k) \]

Eigenvalues

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Workflow of a typical GW calculation

\[ G_0 W_0 \ \text{vs} \ \ GW \]

One-shot GW

- DFT
  - \( \phi_i^{KS}, \epsilon_i^{KS} \)
  - \( \phi_i^{KS}, \epsilon_i^{KS} \)

- calculate \( W \)
  - \( \phi_i^{GW}, \epsilon_i^{GW} \)
  - \( \phi_i^{GW}, \epsilon_i^{GW} \)

- calculate \( G \times W \)
  - Eigenvalues
  - \( \epsilon_i^{GW}(k) \)

If self-consistent

\[ \emptyset \]

iscf -2
nband 100

occupied AND empty states

optdriver 3

optdriver 4
How to get $G$?

From Kohn-Sham DFT

Remember

$$\left[ \omega - h_{KS} \right] G_{KS} = 1$$

which means

$$G_{KS}(r, r', \omega) = \sum_i \frac{\phi_i^{KS}(r) \phi_i^{KS*}(r')}{\omega - \epsilon_i^{KS} \pm i \eta}$$

This expression will be used to get $W$ and $\Sigma$. 
How to get $W$?

From the RPA equation

$$\chi_0(1,2) = -i G_{KS}(1,2) G_{KS}(2,1)$$

which translates into

$$\chi_0(r_1, r_2, \omega) = \sum_{i=\text{occ}} \sum_{j=\text{virt}} \phi_i(r_1) \phi_i^*(r_2) \phi_j(r_2) \phi_j^*(r_1)$$

$$\times \left[ \frac{1}{\omega - (\epsilon_j - \epsilon_i) - i \eta} - \frac{1}{\omega - (\epsilon_i - \epsilon_j) + i \eta} \right]$$

This is the Alder-Wiser formula or the SOS formula

It involves empty states!

Then

$$W = v + v \chi_0 W$$

$$W = (1 - v \chi_0)^{-1} v$$

geometric series
Dealing with two-point functions in reciprocal space

Remember 1-point functions are

\[ \phi_k(r) = \frac{1}{\sqrt{\Omega}} \sum_{kG} c_k(G) e^{i(k+G).r} \]

1 vector of coefficients per k-point in the Brillouin zone

Then 2-point functions are

\[ W(r_1, r_2) = \frac{1}{\Omega} \sum_{qGG'} e^{i(q+G).r_1} W_{GG'}(q) e^{-i(q+G').r_2} \]

a matrix of coefficients per q-point in the BZ due to translational symmetry:

\[ W(r_1, r_2) = W(r_1 + R, r_2 + R) \]
W in plane-waves and frequency space

(1) \( \chi_0(r_1, r_2, \omega) = \sum_{i \text{occ}} \phi_i(r_1) \phi_i^*(r_2) \phi_j(r_2) \phi_j^*(r_1) \times \left[ \frac{1}{\omega - (\epsilon_j - \epsilon_i) - i \eta} - \frac{1}{\omega - (\epsilon_i - \epsilon_j) + i \eta} \right] \)

(2) \( \epsilon(1, 2) = \delta(1, 2) - \int d3 \nu(1, 3) \chi_0(3, 2) \)

(3) \( W(1, 2) = \int d3 \epsilon^{-1}(1, 3) \nu(3, 2) \)

(1) \( \chi_{0G^G'}(q, \omega) = \sum_k \sum_{i \text{occ}} \left\langle j k - q \left| e^{-i(q + G).r_1} i k \right| \langle i k \left| e^{i(q + G').r_2} \right| j k - q \right\rangle \times \left[ \frac{1}{\omega - (\epsilon_j - \epsilon_i) - i \eta} - \frac{1}{\omega - (\epsilon_i - \epsilon_j) + i \eta} \right] \)

(2) \( \epsilon_{GG'}(q, \omega) = \delta_{G, G'} - \sum_{G''} \nu_{G G' G''}(q) \chi_{0G''G}(q, \omega) \)

(3) \( W_{GG'}(q, \omega) = \epsilon_{GG'}^{-1}(q, G') \nu_{G'}(q) \)
Self energy evaluation in GW

Correlation part of the GW self energy requires a convolution in frequency:

\[ \Sigma_c(\omega) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega' \ G(\omega + \omega') W_p(\omega') \]

\[ G(\omega) = \sum_i \frac{\phi_i(r) \phi_i^*(r')}{\omega - \epsilon_i \pm i \eta} \]

How do we perform the convolution?
How do we treat the frequency dependence in \( W \)?

How to deal with the frequency dependence in \( W \)?
Time ordered response function:

Many poles which go by pairs: \( \pm (\tilde{\omega}_i - i \eta) \)

Plasmon-pole model:
One pair of poles:
\[\pm (\tilde{\omega} - i \eta)\]

Complex plane:

Silicon:
For a given \( q + G \):
Plasmon-Pole Models in GW

Correlation part of the GW self energy requires a convolution in frequency:

\[ \Sigma_c(\omega) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega' G(\omega + \omega') W_p(\omega') \]

Generalized Plasmon-Pole Model:

\[ \epsilon^{-1}(\omega') - 1 = \frac{\Omega^2}{2\tilde{\omega}} \left[ \frac{1}{\omega' - \tilde{\omega} + i\eta} - \frac{1}{\omega' + \tilde{\omega} - i\eta} \right] \]

2 parameters need two constraints:
- Hybertsen-Louie (HL): \[ \epsilon^{-1}(0) \]
- Godby-Needs (GN): \[ \epsilon^{-1}(0) \]

Position of the pole
Amplitude of the pole

small real number

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GW obtained as a first-order perturbation

\[
G = G_0 + G_0 \Sigma G
\]

\[
G_{KS} = G_0 + G_0 \nu_{xc} G_{KS}
\]

\[
G^{-1} = G_{KS}^{-1} - (\Sigma - \nu_{xc})
\]

Approximation: \( \phi_i^{GW} \approx \phi_i^{KS} \)

\[
G^{-1} = \sum_i |\phi_i\rangle (\omega - \epsilon_i^{GW}) |\phi_i\rangle
\]

\[
G_{KS}^{-1} = \sum_i |\phi_i\rangle (\omega - \epsilon_i^{KS}) |\phi_i\rangle
\]

\[
\epsilon_i^{GW} = \epsilon_i^{KS} + \langle \phi_i | \Sigma (\epsilon_i^{GW}) - \nu_{xc} | \phi_i \rangle
\]
Linearization of the energy dependance

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

Not yet known

Taylor expansion:

\[ \Sigma \left( \epsilon_i^{GW} \right) = \Sigma \left( \epsilon_i^{KS} \right) + \left( \epsilon_i^{GW} - \epsilon_i^{KS} \right) \frac{\partial \Sigma}{\partial \epsilon} + \ldots \]

Final result:

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

where

\[ Z_i = \frac{1}{1 - \langle i \left| \frac{\partial \Sigma}{\partial \epsilon} \right| i \rangle} \]
Typical GW output in ABINIT

\[
\begin{align*}
k_{\text{pt}} & \quad 1 \\
E_{\text{pt}} & \quad 0.000 \\
b_{\text{GW}} & \quad 4 5
\end{align*}
\]

\[
\begin{array}{ccccccccccc}
\text{Band} & k & E_0 & \langle V_{\text{xclDA}} \rangle & \text{SigX} & \text{SigC}(E_0) & Z & d\text{SigC}/dE & \text{Sig}(E) & E-E_0 & E \\
4 & 0.000 & 0.000 & 0.000 & 0.000 & 0.744 & 0.775 & -0.741 & -11.645 & -0.354 & 0.152 \\
5 & 3.080 & -10.095 & -5.870 & -3.859 & 0.775 & 0.775 & -0.290 & -9.812 & 0.283 & 3.363
\end{array}
\]

\[
E_{\text{0\_gap}} = 2.574 \\
E_{\text{GW\_gap}} = 3.212
\]

\[
\epsilon_i^{GW} = \epsilon_i^{KS} + Z_i \langle \varphi_i^{KS} | \sum_{xc} \left( \epsilon_i^{KS} \right) - v_{xc} | \varphi_i^{KS} \rangle
\]
Full quasiparticle solution

\[ A_{ii}(\omega) = \frac{1}{\pi} |\text{Im} G(\omega)| = \frac{\text{Im} \Sigma_{ii}(\omega)}{(\omega - \epsilon_i^{KS} + \text{Re} \Sigma_{ii}(\omega) - \nu_{xc})^2 + \text{Im} \Sigma_{ii}(\omega)^2} \]

Silicon

\[
\begin{align*}
\text{Re} \Sigma(\omega) & \quad \omega - h_{ii} \\
|\text{Im} G| & \quad \omega \text{ (eV)}
\end{align*}
\]

Aluminum

\[
\begin{align*}
\text{Re} \Sigma_{ii}(\omega) & \quad \omega - h_{ii} \\
|\text{Im} G| & \quad \omega \text{ (eV)}
\end{align*}
\]
Outline

I. Introduction: going beyond DFT

II. Introduction of the Green's function

III. Exact Hedin's equations and the GW approximation

IV. Calculating the GW self-energy in practice

V. Applications
GW approximation gets good band gap

No more a band gap problem!

van Schilfgaarde et al PRL 96 226402 (2008)
Spectral function

\[ A(\omega) = \left| \text{Im} G(\omega) \right| / \pi \]
Excitation lifetime

Hole self-energy:

$$\text{Im}\{\langle i | \sum (\epsilon_i) | i \rangle \} = - \sum_{jqGG'} M_{ij}(q + G) M_{ij}^*(q + G') \times \text{Im}(\mathcal{W} - \nu)_{GG'}(q, \epsilon_j - \epsilon_i) \times \theta(\mu - \epsilon_j)\theta(\epsilon_j - \epsilon_i)$$
Exact realization of the Lehman decomposition

\[ \langle m | G^h(\omega) | m \rangle = \sum_i \frac{\langle N0|\hat{c}_m^+|N-1i \rangle \langle N-1i|\hat{c}_m|N0 \rangle}{\omega - \epsilon_i - i\eta} \]

\[ N = 2 \]
\[ N - 1 = 1 \]
\[ m = 1s \]

Obtained from FCI calculations

He → He^+

Quasiparticle peak

Satellite or shake-up structure

Spectral function: $\text{Im}G/\pi$
Clusters de sodium

\[ \text{Na}_4^+ + e^- \Leftrightarrow \text{Na}_4 \]

\[ E_0(\text{Na}_4) - E_0(\text{Na}_4^+) = \begin{cases} 
\epsilon(\text{HOMO}, \text{Na}_4) \\
\epsilon(\text{LUMO}, \text{Na}_4^+) 
\end{cases} \]

\[ \text{Na}_4^+/\text{Na}_4 \]

F. Bruneval  Jouvence, Quantum Materials 2018

Bruneval PRL (2009)
What is the best starting point for $G_0W_0$?

Ionization of small molecules

Hybrids perform better, preferably with a large content of EXX $\sim 50\%$

---

### Table 1. $G_0W_0$ HOMO Energy of the 34 Molecules Employing Different Starting Points with the cc-pVQZ Basis Set

<table>
<thead>
<tr>
<th>starting point</th>
<th>HF</th>
<th>LDA</th>
<th>PBE</th>
<th>PBE0</th>
<th>B3LYP</th>
<th>HSE06</th>
<th>BH&amp;HLYP</th>
<th>CAM-B3LYP tuned</th>
<th>CAM-B3LYP</th>
<th>CCSD(T)</th>
<th>exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$</td>
<td>-5.36</td>
<td>-5.13</td>
<td>-5.12</td>
<td>-5.29</td>
<td>-5.23</td>
<td>-5.19</td>
<td>-5.30</td>
<td>-5.32</td>
<td>-5.38</td>
<td>-5.17</td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>-11.62</td>
<td>-10.61</td>
<td>-10.37</td>
<td>-10.93</td>
<td>-10.82</td>
<td>-10.89</td>
<td>-11.29</td>
<td>-11.49</td>
<td>-11.45</td>
<td>-11.51</td>
<td></td>
</tr>
<tr>
<td>Na$_3$</td>
<td>-4.98</td>
<td>-4.91</td>
<td>-4.89</td>
<td>-4.97</td>
<td>-4.96</td>
<td>-4.91</td>
<td>-4.97</td>
<td>-4.98</td>
<td>-5.01</td>
<td>-4.82</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>-10.85</td>
<td>-10.39</td>
<td>-10.37</td>
<td>-10.53</td>
<td>-10.52</td>
<td>-10.48</td>
<td>-10.65</td>
<td>-10.67</td>
<td>-10.66</td>
<td>-10.68</td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>-11.69</td>
<td>-10.70</td>
<td>-10.64</td>
<td>-10.97</td>
<td>-10.89</td>
<td>-10.88</td>
<td>-11.20</td>
<td>-11.22</td>
<td>-11.17</td>
<td>-11.08</td>
<td>-10.96</td>
</tr>
<tr>
<td>CH$_3$SH</td>
<td>-0.81</td>
<td>-0.18</td>
<td>-0.17</td>
<td>-0.26</td>
<td>-0.25</td>
<td>-0.30</td>
<td>-0.33</td>
<td>-0.33</td>
<td>-0.49</td>
<td>-0.49</td>
<td></td>
</tr>
</tbody>
</table>

---

F. Bruneval & MAL Marques, JCTC (2013)

Jouvence, Quantum Materials 2018
Defect calculation within GW approximation

Up to 215 atoms

Cubic silicon carbide
Photoluminescence of $V_{\text{Si}}$

- $V_{\text{Si}}^{2-}$ and $V_{\text{Si}}^{1-}$
- Conduction band: $E_v + 1.85$ eV
- Valence band: $E_c - 1.58$ eV

Bruneval and Roma PRB (2011)

F. Bruneval
Jouvence, Quantum Materials 2018
3d metal band structure

Nickel

Band Offset at the interface between two semiconductors

Very important for electronics!

Example: Si/SiO$_2$ interface for transistors

GW correction with respect to LDA


F. Bruneval

Jouvence, Quantum Materials 2018
Summary

- The GW approximation **solves the band gap problem!**
- The calculations are extremely heavy, so that we resort to many additional technical approximations: **method named \( G_0 W_0 \)**
- The complexity comes from
  - Dependence upon empty states
  - Non-local operators
  - Dynamic operators that requires freq. convolutions
Reviews - Links

Reviews:

• L. Hedin, Phys. Rev. 139 A796 (1965).


Codes:

• http://www.abinit.org
• http://www.berkeleygw.org/
• https://github.com/bruneval/molgw
Exercice: $H_2$ in minimal basis: GW@HF

Find the location of the poles of the self-energy

Szabo-Ostlun book chapter 3 teaches how to perform HF in this example:

Basis: STO-3G \hspace{1cm} r(H-H) = 1.4 \text{ bohr}

2 basis functions \rightarrow 2 eigenstates:

- **LUMO anti-bonding**
- **HOMO bonding**

In eigenvector basis:

**Hamiltonian:**

\[
C^T H C = \begin{pmatrix}
-0.578 & 0 \\
0 & 0.670
\end{pmatrix}
\]

**Coulomb interaction:**

\[
\begin{align*}
(11\left|\frac{1}{r_1-r_2}\right|11) &= 0.675 \\
(12\left|\frac{1}{r_1-r_2}\right|12) &= 0.181 \\
(22\left|\frac{1}{r_1-r_2}\right|22) &= 0.697
\end{align*}
\]

Atomic units
Exercice: $H_2$ in minimal basis: GW@HF

Find the location of the poles of $W$

Diagonalize the RPA equation

$$
\chi^{-1}(\omega) = \begin{pmatrix}
\omega - (\epsilon_j - \epsilon_i) \\
\frac{f_i - f_j}{2} \\
\langle i j \rangle
\end{pmatrix} - \begin{pmatrix}
\langle i j \rangle \\
\frac{1}{\mathbf{r}} \langle k l \rangle
\end{pmatrix}
$$

$$
\Delta \epsilon = \epsilon_2 - \epsilon_1 = 1.248 \\
v = \langle 12 | 1/r | 12 \rangle = 0.181
$$

$$
\langle 12 | \begin{pmatrix}
\omega - \Delta \epsilon \\
\frac{\omega + \Delta \epsilon}{2} \\
0
\end{pmatrix} - \begin{pmatrix}
v \\
\omega + \Delta \epsilon \\
-2
\end{pmatrix}
\langle 21 \rangle
$$

$$
\Omega = \pm \sqrt{\Delta \epsilon^2 + 4v \Delta \epsilon} = \pm 1.569
$$
Exercice: $H_2$ in minimal basis: GW@HF

\[ \Sigma_c(\omega) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega' \, G(\omega + \omega') \, W_p(\omega') \]

\[ G(\omega) = \sum_i \frac{\phi_i(r) \phi_i(r')}{\omega - \epsilon_i \pm i\eta} \]

\[ W_p(\omega) = \sum_s \frac{L_s(r) R_s(r')}{\omega - \Omega_s \pm i\eta} \]

\[ \Sigma_c(\omega) = \frac{i}{2\pi} \sum_{i \in \{1, 2\}} \sum_{s \in \{1 \rightarrow 2, 2 \rightarrow 1\}} \int_{-\infty}^{+\infty} d\omega' \, \frac{\alpha}{\omega + \omega' - \epsilon_i \pm i\eta} \times \frac{\beta}{\omega' - \Omega \pm i\eta} \]

Integration in the complex plane:

\[ \begin{array}{c|c|c}
\epsilon_1 - \omega & \epsilon_1 & \epsilon_2 \\
\hline
-\Omega & \times & \times \\
\Omega & \times & \times \\
\end{array} \]

Pole table:
Exercice: H$_2$ in minimal basis: GW@HF

\[ \epsilon_2 + \Omega = 2.239 \]
\[ \epsilon_1 - \Omega = -2.147 \]

Real part of the self-energy from MOLGW

\[ \epsilon_{HOMO}^{GW} = -16.23 \text{ eV} \]
\[ \epsilon_{LUMO}^{GW} = 18.74 \text{ eV} \]
Exercice: $H_2$ in minimal basis: GW@HF

Same conclusions hold for a many-state case:

Bulk silicon

Plasmon frequency $\sim 17$ eV
Occupied states $\sim -5 - 0$ eV
Empty states $\sim +2 - ...$ eV
Exercise 1

Green's function in frequency domain

\[ iG(r_1, r_2, \omega) = \theta(t_1 - t_2) \sum_{\text{virt}} \phi_i(r_1) \phi_i^*(r_2) e^{-i \epsilon_i(t_1 - t_2)} - \theta(t_2 - t_1) \sum_{\text{occ}} \phi_i(r_2) \phi_i^*(r_1) e^{-i \epsilon_i(t_2 - t_1)} \]

\[ G(r_1, r_2, \omega) = \int dt_1 dt_2 e^{i \omega(t_1 - t_2)} G(r_1, r_2, t_1, t_2) \]

\[ G(r_1, r_2, \omega) = \sum_{i} \frac{\phi_i(r_1) \phi_i^*(r_2)}{\omega \pm \epsilon_i \pm i \eta} \]
Exercise 2:

Fock exchange from Green's functions

\[ \Sigma_x (1, 2) = i G (1, 2) v (1^+, 2) \]

\[ \Sigma_x (\mathbf{r}_1, \mathbf{r}_2, \omega) = - \sum_{i \text{occ}} \frac{\phi_i (\mathbf{r}_1) \phi_i^* (\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \]
Exercise 3: let's play with Dyson equations

1) The multiple faces of the Dyson equation

\[ \left[ \omega - h_{KS} \right] G_{KS} = 1 \]

\[ \left[ \omega - h_0 - v_{xc} \right] G_{KS} = 1 \]

\[ \left[ G_{0}^{-1} - v_{xc} \right] G_{KS} = 1 \]

\[ G_{KS} = G_0 + G_0 v_{xc} G_{KS} \]

\[ G_{KS} = G_0 + G_0 v_{xc} G_0 + G_0 v_{xc} G_0 v_{xc} G_0 + \ldots \]

\[ G_{KS}^{-1} = G_0^{-1} - v_{xc} \]

2) Combining the Dyson equations

\[ G^{-1} = G_0^{-1} - \Sigma \]

\[ G_{KS}^{-1} = G_0^{-1} - v_{xc} \]

\[ G^{-1} = G_{KS}^{-1} - (\Sigma - v_{xc}) \]

\[ 1 = \left[ G_{KS}^{-1} - (\Sigma - v_{xc}) \right] G \]

\[ 1 = \left[ \omega - h_0 - \Sigma \right] G \]
Exercise 4

Derive the standard Adler-Wiser formula (1963):

\[
\chi_0(1,2) = -i G(1, 2) G(2, 1)
\]

\[
\chi_0(r_1, r_2, \omega) = -\frac{i}{2\pi} \int d\omega' G(r_1, r_2, \omega + \omega') G(r_2, r_1, \omega')
\]

\[
\chi_0(r_1, r_2, \omega) = \sum_{\text{occ}} \sum_{\text{virt}} \phi_i(r_1) \phi_i^*(r_2) \phi_j(r_2) \phi_j^*(r_1) \times \left[ \frac{1}{\omega - (\epsilon_j - \epsilon_i) - i\eta} - \frac{1}{\omega - (\epsilon_j - \epsilon_i) + i\eta} \right]
\]
Exercise 5

Derive that the product in time becomes a convolution in frequency:

\[ \Sigma(r_1, r_2, t_1 - t_2) = i G(r_1, r_2, t_1 - t_2) W(r_2, r_1, t_2 - t_1) \]

\[ G(r_1, r_2, \omega) = \int d(t_1 - t_2) e^{i\omega(t_1 - t_2)} G(r_1 t_1, r_2 t_2) \]

\[ G(r_1, r_2, t_1 - t_2) = \frac{1}{2\pi} \int d\omega e^{-i\omega(t_1 - t_2)} G(r_1, r_2, \omega) \]

\[ \Sigma(r_1, r_2, \omega) = \frac{i}{2\pi} \int d\omega' G(r_1, r_2, \omega + \omega') W(r_2, r_1, \omega') \]
Exercice 6: Feynman diagram drawing

a) Draw all the 1\textsuperscript{st} order diagrams for the self-energy

b) Draw all the 2\textsuperscript{nd} order diagrams for the self-energy

c) What is the difference between the proper and the improper self-energy

d) How self-consistency can simplify the expansion?

Self-energy diagram drawing rules:

1. Diagrams are combinations of arrows (Green’s function) and horizontal lines (Coulomb interaction). Upward arrows are electrons, downward arrows are hole.

2. Diagrams should be connected.

3. Self-energy have an entry point and an exit point (possibly the same).

4. Each intersection should conserve the particle numbers.

5. A valid diagram cannot be cut (by removing an arrow) into another lower order self-energy.