The GW method
Common approximations
& practical implementations

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Charged and neutral excitations

**Charged excitations:** photoemission and inverse photoemission

**Neutral excitations:** absorption
Direct photoemission

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

...plus momentum conservation \( \Rightarrow \) ARPES

Measure the density of occupied states

occupied states

See lecture by Andrea Ferretti
Inverse photoemission

\[ E(N + 1) - E(N) = E_k + h\nu \]

Measure the density of unoccupied states
Electronic structure calculations

Kohn-Sham Equations 1965

\[ \hat{h}_{KS}[n] \psi_j \geq \epsilon_j \psi_j \]

\[ \hat{h}_{KS}[n] = -\frac{1}{2} \nabla^2 + v_{ext}(\mathbf{r}) + v_{Hartree}(\mathbf{r}) + v_{xc}[n](\mathbf{r}) \]

\[ n(\mathbf{r}) = \sum_j \theta(\mu - \epsilon_j) \psi_j^*(\mathbf{r}) \psi_j(\mathbf{r}) \]

\[ E_{GS} = \sum_j \theta(\mu - \epsilon_j) \epsilon_j - U[n] - \int d\mathbf{r} n(\mathbf{r}) v_{xc}[n](\mathbf{r}) + E_{xc}[n] \]

Moderate computational cost

Predict ground state geometries and electronic structures
Band Gap

Adapted from M. van Schilfgaarde et al. PRL 96 (2006)

Huge discrepancy not due to the LDA

Si: 0.47 eV (LDA) vs 1.1 eV (expt)

GaAs: 0.30 eV (LDA) vs 1.4 eV (expt)
Band Gap: definition

Direct photoemission
\[ \epsilon_i = E_{kin} - \hbar \omega \]
\[ \epsilon_i = E_0^N - E_i^{N-1} \]
Total energy difference between the N-particle ground state and the (N-1) particle state that remains after the emission

Inverse photoemission
\[ \epsilon_i = E_i^{N+1} - E_0^N \]

The ejection (removal) of an electron is always a many-body process

\[ E_{gap} = (E_{N+1} - E_N) - (E_N - E_{N-1}) \]

electron affinity  ionization potential
Quasiparticle

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Polarization, screening
Quasiparticle

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electron affinity       ionization potential

Electron injection
Repulsive Coulomb interaction creates a repulsive Coulomb hole around the additional electrons

Direct photemission
an electron leaves the system: also the Coulomb hole disappear

Polarization, screening

Relaxation - Screening - Correlation
Quasiparticle

\[ E_{gap} = (E_{N+1} - E_N) - (E_N - E_{N-1}) \]

electron affinity \hspace{1cm} \text{ionization potential}

\begin{itemize}
  \item Electron injection
    Repulsive Coulomb interaction creates a repulsive Coulomb hole around the additional electrons
  \item Direct photemission
    An electron leaves the system: also the Coulomb hole disappears
\end{itemize}

Relative to the ground-state N-electron system, the addition (removal) of an electron in indirect (direct) photoemission hence creates (annihilates) an ensemble consisting of the bare electron and its oppositely charged Coulomb hole.

\[ \text{electron} + \text{screening cloud} = \text{quasiparticle} \]
Band Gap:

Can we calculate the QP gap directly using total energies from DFT-LDA?
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Can we calculate the QP gap directly using total energies from DFT-LDA?

\[ E_G = \epsilon_{N+1}^N - \epsilon_N^N + \sum_{i}^{N+1} \Delta \epsilon_i^L + \sum_{i}^{N-1} \Delta \epsilon_i^H \]

\[ -E_{\text{Har}}[\Delta \rho^L] - E_{\text{Har}}[\Delta \rho^H] + \int V_{\text{Har}}^N(r)(\Delta \rho^H(r) - \Delta \rho^L(r))dr \]

\[ +E_{\text{XC}}[\rho^{N+1}] + E_{\text{XC}}[\rho^{N-1}] - 2E_{\text{XC}}[\rho^N] \]

\[ -\int V_{\text{XC}}^{N+1}(r)\rho^{N+1}(r)dr - \int V_{\text{XC}}^{N-1}(r)\rho^{N-1}(r)dr + 2\int V_{\text{XC}}^N(r)\rho^N(r)dr \]

From: CE Patrick, Oxford 2011

Kohn-Sham is NOT the QP gap
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Can we calculate the QP gap directly using total energies from DFT-LDA?

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ΔSCF reasonable results for molecules

C. E. Patrick and F. Giustino, PRL 109, 116801 (2012)
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\[ \Delta \text{SCF} \]

reasonable results for molecules

C. E. Patrick and F. Giustino, PRL 109, 116801 (2012)
Theoretical description involving the ejection or injection of electrons requires a framework that links the $N$-particle with the $(N \pm 1)$-particle system.

Many Body Perturbation Theory

$$G(r, r'; t, t')$$

Green Function as a central variable

Contains the excitation energy $\epsilon_i$
excitation lifetime
ground state density
expectation value one-particle operator, Total Energy etc.
Green function

\[ G(r_1 t_1, r_2 t_2) = -i \sum_j f_j(r_1) f_j^*(r_2) e^{-i \epsilon_j (t_1 - t_2)} \left[ \theta(t_1 - t_2) \theta(\epsilon_j - \mu) - \theta(t_2 - t_1) \theta(\mu - \epsilon_j) \right] \]

Fourier Transforming in frequency domain:

\[ G(r_1, r_2, \omega) = \sum_j \frac{f_j(r_1) f_j^*(r_2)}{\omega - \epsilon_j + i \eta \text{sgn}(\epsilon_j - \mu)} \]

\[ \epsilon_j = \frac{E(N + 1, j) - E(N)}{E(N) - E(N - 1, j)} \]

\[ f_j(r_1) = \begin{cases} \langle \Psi_0^N | \hat{\psi}(r_1) | \Psi_j^{N+1} \rangle & \epsilon_j > \mu \\ \langle \Psi_j^{N-1} | \hat{\psi}(r_1) | \Psi_0^N \rangle & \epsilon_j < \mu \end{cases} \]

Green Function has poles at the true many-particle excitation energies
Self Energy

How to obtain G??
Self Energy

How to obtain $G$??

Perturbation theory starts from what is known to evaluate what is not known ...hoping that the difference is small

Let’s say we know $G_0(\omega)$ that corresponds to the Hamiltonian $H_0$

$H = H_0 + H_1$, where the interaction is put in $H_1$

(e.g. non interacting electrons)
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$H = H_0 + H_1$, where the interaction is put in $H_1$

(e.g. non interacting electrons)

Everything that is unknown is put in

$$\Sigma(\omega) = G_0^{-1}(\omega) - G^{-1}(\omega)$$

This is the definition of the Self Energy
Quasiparticle Equation

\[ [\omega - \hat{H}_0]G(\omega) + i \int \Sigma(\omega)G(\omega) = 1 \]

Let’s suppose we know the Self Energy and consider \( G_0 \) the Green function of a mean field system defined by

\[ H_0 = -\frac{\nabla^2}{2m} + V_{ext} + \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(r')}{|r - r'|} d^3r' \]

single-particle Hamiltonian
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Introducing the Lehmann representation for \( G \)

\[ \hat{H}_0(r)f_s(r) + \int \Sigma(r, r'; \epsilon_s)f_s(r')d^3r' = \epsilon_s f_s(r) \]

QP equation: looks similar to KS equation but:
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\( V_{xc} \) part of the potential of a fictitious system

\( \Sigma \) potential felt by an added (removed) electron to (from) the system
Quasiparticle Equation

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- \( V_{xc} \) part of the potential of a fictitious system
- \( \Sigma \) potential felt by an added (removed) electron to (from) the system

\( f_s \) not orthonormal
\( \epsilon_s \) are complex
How to obtain the Self energy: Iteration of Hedin’s Equations and GW

They cannot be solved numerically as they contain functional derivatives, but they can be iterated to derive useful approximations

\[
\Sigma = iGWF \\
G = G_0 + G_0 \Sigma G \\
\Gamma = 1 + \frac{\partial \Sigma}{\partial G} GG\Gamma \\
P = -iGG\Gamma \\
W = v + vPW
\]
How to obtain the Self energy: Iteration of Hedin’s Equations and GW

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\[
\begin{align*}
\Sigma &= iGWT
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\Gamma &= 1 + \frac{\partial \Sigma}{\partial G} GGT
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\end{align*}
\]

We start with \( G = G_0, \Sigma = 0 \)
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\[ G = G_0 + G_0 \Sigma G \]
\[ \Gamma = 1 \]
\[ P = -iGG \]
\[ W = v + vPW \]

Remark:

The vertex \( \Gamma \) has been neglected.

The equations can be solved self-consistently.

Common approximation: \( G = G_0 \)

This is an approximation!!

This is another approximation!!
GW approximation in practice

Goal: \[
\hat{H}_0(r)f_s(r) + \int \Sigma(r, r'; \epsilon_s)f_s(r')d^3r' = \epsilon_sf_s(r) \]

\[\Sigma = iGW\]
GW approximation in practice

Goal: \[ \hat{H}_0(\mathbf{r}) f_s(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_s) f_s(\mathbf{r}') d^3 \mathbf{r}' = \epsilon_s f_s(\mathbf{r}) \]
\[ \Sigma = iGW \]

\[ G = G_0 \] Green function of the non-interacting system
GW approximation in practice

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\[ G = G_0 \] Green function of the non-interacting system

\[ \Sigma^{GW}(r_1, r_2; \tau) = i\hbar G_0(r_1, r_2; \tau) W(r_1, r_2; \tau + \eta) \]

In Fourier space

\[ \Sigma^{GW}(r_1, r_2; \omega) = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} G_0(r_1, r_2; \omega + \omega') W(r_1, r_2; \omega') e^{i\omega' \eta} d\omega' \]
GW approximation in practice

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Polarization and Screening

\[ W = \nu + \nu PW \]

\[ P(r_1, r_2; \tau) = -i\hbar G_0(r_1, r_2; \tau)G_0(r_2, r_1; -\tau) \]
GW approximation in practice

Goal: $\hat{H}_0(r)f_s(r) + \int \Sigma(r, r'; \epsilon_s)f_s(r')d^3r' = \epsilon_s f_s(r)$

$\Sigma = iGW$

$P(r_1, r_2; \tau) = -i\hbar G_0(r_1, r_2; \tau)G_0(r_2, r_1; -\tau)$

Starting point: solve an independent-particle calculation: e.g. LDA

$H_0(r)\phi_j^0(r) + V_{xc}(r)\phi_j^0(r) = \epsilon_j\phi_j^0(r)$

By FT and using Lehmann representation

$P(r_1, r_2; \omega) = \sum_{i}^{occ.\ unocc.} \sum_{j} \phi_i^0(r)\phi_j^0*(r)\phi_i^0*(r')\phi_j^0(r') \times \left( \frac{1}{\hbar\omega + \epsilon_i^0 - \epsilon_j^0 + i\eta} - \frac{1}{\hbar\omega - \epsilon_i^0 + \epsilon_j^0 - i\eta} \right)$

Polarization made of noninteracting electrons and holes
GW approximation in practice

Goal: \[ \hat{H}_0(r) f_s(r) + \int \Sigma(r, r'; \epsilon_s) f_s(r') d^3 r' = \epsilon_s f_s(r) \]

\[ \Sigma = iGW \]

Screened potential

\[ W(r_1, r_2; \omega) = \int \epsilon^{-1}(r_1, r'; \omega) v(r', r_2) dr' = v(r_1, r_2) + \int n_{ind}(r_1, r'; \omega) v(r', r_2) dr' \]

Classical (Hartree) interaction between additional charge and polarization charge

\[ n_{ind}(r_1, r_2; \omega) = \int P^0(r_1, r'; \omega) V^{tot}(r', r_2) dr' \]

\[ \epsilon(r_1, r_2; \omega) = \delta(r_1 - r_2) - \int v(r_1 - r') P^0(r', r_2; \omega) dr' \]

\[ W = v + vPW \]

Using \( P(1, 2) = P^0(1, 2) = G^0(1, 2)G^0(2, 1) \)

Random Phase Approximation (RPA)
Evaluation of the Self-Energy

\[ \Sigma_{GW} = G_0^{KS} W = G_0^{KS} V + G^{KS} (W - V) = \Sigma_{xc}^{GW} + \Sigma_{c}^{GW} \]
Evaluation of the Self-Energy

\[ \Sigma^{GW} = G^{KS}_0 W = G^{KS}_0 V + G^{KS} (W - V) = \Sigma^{GW}_x + \Sigma^{GW}_c \]

\[ \Sigma^{GW}_x (r_1, r_2; \omega) = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} G^{KS}_0 (r_1, r_2; \omega + \omega') v(r_1, r_2) e^{i\omega' \eta} d\omega' \]

can be integrated analytically

\[ \langle \phi^*_i^{KS} | \Sigma^{GW}_x | \phi^*_i^{KS} \rangle = -\frac{e^2}{4\pi\epsilon_0} \sum_j^{\text{occ.}} \int \frac{\phi^*_i^{KS}(r) \phi^*_j^{KS}(r) \phi^*_j^{KS}(r') \phi^*_i^{KS}(r')}{|r - r'|} dr dr' \]

Hartree-Fock exchange term
Evaluation of the Self-Energy

\[ \Sigma^{GW} = G_0^{KS} W = G_0^{KS} V + G^{KS} (W - V) = \Sigma_x^{GW} + \Sigma_c^{GW} \]

\[ \Sigma_x^{GW} (\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} G_0^{KS} (\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') \nu(\mathbf{r}_1, \mathbf{r}_2) e^{i\omega' \eta} d\omega' \]

can be integrated analytically

\[ \langle \phi_i^{KS} | \Sigma_x^{GW} | \phi_i^{KS} \rangle = -\frac{e^2}{4\pi\epsilon_0} \sum_j^{occ.} \int \frac{\phi_i^{KS*}(\mathbf{r}) \phi_j^{KS}(\mathbf{r}) \phi_j^{KS*}(\mathbf{r}') \phi_i^{KS}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \]

\[ \Sigma_c^{GW} (\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} G_0^{KS} (\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') [W(\mathbf{r}_1, \mathbf{r}_2; \omega') - \nu(\mathbf{r}_1, \mathbf{r}_2)] e^{i\omega' \eta} d\omega' \]

have to be computed numerically; most time consuming part

Hartree-Fock exchange term
GW approximation in practice

Different implementations:

Reciprocal Space & Frequency Domain:
M. Hybertsen and S. Louie PRB 34, 5390 (1986)

Real Space and Real Time:

Use of localized basis set:
X. Blase, C. Attaccalite, and V. Olevano PRB 83, 115103 (2011)

Use of Wannier Function:
P. Umari, G. Stenuit and S. Baroni PRB 79, 201104(R) (2009)
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Plane waves representation:

\[
\langle nk|\Sigma_x(r_1, r_2) |n'k'\rangle = -\sum_{n_1} \int_{BZ} \frac{d^3q}{(2\pi)^3} \sum_G v(q + G) \rho_{n,n_1}(q, G) \rho_{n'n_1}^*(q, G) f_{n_1 k_1} \\
\rho_{nn_1}(q + G) = \langle nk|e^{i(q+G)\cdot r}|n'1k_1\rangle
\]

\[
\langle nk|\Sigma_c(r_1, r_2; \omega) |n'k'\rangle = \frac{1}{2} \sum_{n_1} \int_{BZ} \frac{d^3q}{(2\pi)^3} \left\{ \sum_{GG'} v(q + G) \rho_{n,n_1}(q, G) \rho_{n'n_1}^*(q, G') \times \\
\times \int \frac{d\omega'}{2\pi} \epsilon_{GG'}^{-1}(q, \omega') \left[ \frac{f_{n1(k-q)}}{\omega - \omega' - \epsilon_{n1(k-q)}^{LDA} - i\delta} + \frac{1 - f_{n1(k-q)}}{\omega - \omega' - \epsilon_{n1(k-q)}^{LDA} + i\delta} \right] \right\}
\]

What makes GW calculations even at G0W0 level rather “laborious”: 

GW approximation in practice

Plane waves representation:

\[
\langle n\mathbf{k}|\Sigma_x(r_1,r_2)|n'k'\rangle = -\sum_{n_1} \int_{B_\mathbf{Z}} \frac{d^3q}{(2\pi)^3} \sum_G \nu(q+G)\rho_{n,n_1}(q,G)\rho^*_{n',n_1}(q,G)f_{n_1k_1}
\]

\[
\rho_{n_1}(q+G) = \langle n\mathbf{k}|e^{i(q+G)\cdot r}|n_1\mathbf{k}_1\rangle
\]

\[
\langle n\mathbf{k}|\Sigma_c(r_1,r_2;\omega)|n'k'\rangle = \frac{1}{2} \sum_{n_1} \int_{B_\mathbf{Z}} \frac{d^3q}{(2\pi)^3} \left\{ \sum_{GG'} \nu(q+G)\rho_{n,n_1}(q,G)\rho^*_{n',n_1}(q,G') \times \right.
\]

\[
\left. \times \int \frac{d\omega'}{2\pi} \epsilon^{-1}_{G,G'}(q,\omega') \left[ \frac{f_{n_1(k-q)}}{\omega - \omega' - \epsilon_{LDA}^{n_1(k-q)} - i\delta} + \frac{1 - f_{n_1(k-q)}}{\omega - \omega' - \epsilon_{LDA}^{n_1(k-q)} + i\delta} \right] \right\}
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What makes GW calculations even at G0W0 level rather “laborious”:

Careful is needed:

Integration over the Brillouin zone
GW approximation in practice

Plane waves representation:

\[ \langle n k | \Sigma_x (r_1, r_2) | n' k' \rangle = - \sum_{n_1} \left( \int_{Bz} \frac{d^3 q}{(2\pi)^3} \sum_{G} v(q + G) \rho_{n,n_1}(q, G) \rho^*_{n',n_1}(q, G) f_{n_1 k_1} \right) \]

\[ \rho_{n n_1}(q + G) = \langle n k | e^{i(q + G) \cdot r} | n_1 k_1 \rangle \]

\[ \langle n k | \Sigma_c (r_1, r_2; \omega) | n' k' \rangle = \frac{1}{2} \sum_{n_1} \left( \int_{Bz} \frac{d^3 q}{(2\pi)^3} \left\{ \sum_{G G'} v(q + G) \rho_{n,n_1}(q, G) \rho^*_{n',n_1}(q, G') \times \right. \right. \]

\[ \left. \left. \times \int \frac{d \omega'}{2\pi} \frac{1}{\epsilon_{G G'}^{-1}(q, \omega') \left[ \frac{f_{n_1(k-q)}}{\omega - \omega' - \epsilon_{n_1(k-q)}^{LDA} - i\delta} + \frac{1 - f_{n_1(k-q)}}{\omega - \omega' - \epsilon_{n_1(k-q)}^{LDA} + i\delta} \right] } \right\} \right) \]

What makes GW calculations even at G0W0 level rather “laborious”:
Careful is needed:

Integration over the Brillouin zone
Sum over unoccupied states
GW approximation in practice

Plane waves representation:

\[
\langle n\mathbf{k} | \Sigma_x (r_1, r_2) | n'\mathbf{k}' \rangle = - \sum_{n_1} \int_{Bz} \frac{d^3 q}{(2\pi)^3} \sum_G v(q + G) \rho_{n, n_1} (q, G) \rho^*_{n', n_1} (q, G) f_{n_1 k_1} \\
\rho_{nn_1}(q + G) = \langle n\mathbf{k}| e^{i(q+G) \cdot r} | n_1 k_1 \rangle
\]

\[
\langle n\mathbf{k} | \Sigma_c (r_1, r_2; \omega) | n'\mathbf{k}' \rangle = \frac{1}{2} \sum_{n_1} \int_{Bz} \frac{d^3 q}{(2\pi)^3} \left\{ \sum_{GG'} v(q + G) \rho_{n, n_1} (q, G) \rho^*_{n', n_1} (q, G') \times \right. \\
\left. \int \frac{d\omega'}{2\pi} \frac{1}{\epsilon_{GG'} (q, \omega')} \left[ \frac{f_{n1(k-q)}}{\omega - \omega' - \epsilon_{n1(k-q)}^{LDA} - i\delta} + \frac{1 - f_{n1(k-q)}}{\omega - \omega' - \epsilon_{n1(k-q)}^{LDA} + i\delta} \right] \right\}
\]

What makes GW calculations even at G0W0 level rather “laborious”:

Careful is needed:

Integration over the Brillouin zone

Sum over unoccupied states

Integration in energy domain
Exchange Self Energy

(7) Exchange self energy:

\[ \sum_{nk}^{\infty} = \langle nk | \sum (r_1, r_2) | nk \rangle = - \sum_{m} \int_{BZ} \frac{dq}{(2\pi)^3} \sum_{G} v(q+G) \rho_{nm}(k,q,G)^2 f_m(k-q) \]

See (6) See (1)

**G-vectors in the exchange**
Number of RL vectors, or energy in Ry / mHa / etc
Tip: set to less than FFTGvecs

**nk, n’k’ ranges where GW/Σₓ elements are calculated**
first k-point | last k-point | lower band | upper band
This can be split over several lines for multiple groups
Tip: careful use of fewer k-points and bands reduces the calculation time; yambo will interpolate the rest

**%QPkrange**

1 | 5 | 20 | 59 |
4 | 8 | 60 | 80 |
%

**%QPerange (-V qp)**

1 | 32 | 0.0 | -1.0 |
%

**EXXRlvc= 2487001 RL**
Correlation Self Energy

(8) Correlation part of self energy:

\[ \Sigma^c_{nk}(\omega) = \langle nk | \Sigma^c | nk \rangle = i \sum_m \sum_{G,G'} \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \frac{4\pi}{|q + G|^2} \rho^*_nm(k, q, G) \rho_{nm}(k, q, G') \times \int d\omega' G^0_{mk-q}(\omega - \omega') e^{-\frac{1}{G}(q, \omega')} \]

- **GboundRnge:** 1 | 50 |
- **QPerange (-V qp):** 1 | 32 | 0.0 | -1.0 |
- **QPerange (-V qp):** 1 | 32 | 0.0 | -1.0 |
- **NGsBlkXp= 100 RL Response block size**
- **Tip:** If you are interested in gaps, energy differences converge faster

**Bands used in the GW summation**

QP energies usually shows slow convergence

**Tip:** If you are interested in gaps, energy differences converge faster

**nk, n’k’ ranges where GW/Σc elements are calculated**

first k-point | last k-point | lower band | upper band
This can be split over several lines for multiple groups

Tip: careful use of fewer k-points and bands reduces the calculation time; yambo will interpolate the rest
GW approximation in practice: Plasmon-Pole approximation

\[
\langle n\mathbf{k}|\Sigma_c(r_1, r_2; \omega)|n'\mathbf{k}'\rangle = \frac{1}{2} \sum_{n_1} \int_{Bz} \frac{d^3q}{(2\pi)^3} \left\{ \sum_{G G'} v(q + G) \rho_{n, n_1}(q, G) \rho_{n', n_1}^*(q, G') \times \right.
\]
\[
x \int \frac{d\omega'}{2\pi} \frac{1}{\epsilon_{GG'}^{-1}(q, \omega')} \left[ \frac{f_{n1}(k-q)}{\omega - \omega' - \epsilon_{LDA}^{n1(k-q)} - i\delta} + \frac{1 - f_{n1}(k-q)}{\omega - \omega' - \epsilon_{LDA}^{n1(k-q)} + i\delta} \right] \right\}
\]
GW approximation in practice: Plasmon-Pole approximation

\[
\langle n\k | \Sigma_c(r_1, r_2; \omega) | n'\k' \rangle = \frac{1}{2} \sum_{n_1} \int_{Bz} \frac{d^3q}{(2\pi)^3} \left\{ \sum_{G G'} v(q + G) \rho_{n,n_1}(q, G) \rho_{n',n_1}^*(q, G') \times \right. \\
\left. \int \frac{d\omega'}{2\pi} \frac{\epsilon_{GG'}^{-1}(q, \omega')}{\omega - \omega' - \epsilon_{LDA}^{n_1(k-q)} - i\delta} + \frac{1 - f_{n_1(k-q)}}{\omega - \omega' - \epsilon_{LDA}^{n_1(k-q)} + i\delta} \right\}
\]

\[-\Im\{\epsilon^{-1}\} \quad \text{Electron Energy Loss spectrum}\]

All components exhibit a peak, otherwise the amplitude is small

Model Dielectric function: Plasmon-Pole approximation
GW approximation in practice: Plasmon-Pole approximation

\[ \langle n' k' | \Sigma_{c}(r_1, r_2; \omega) | n k \rangle = \frac{1}{2} \sum_{n_1} \int_{Bz} \frac{d^3 q}{(2\pi)^3} \left\{ \sum_{G G'} v(q + G) \rho_{n, n_1}(q, G) \rho_{n', n_1}^*(q, G') \times \right. \]

\[ \left. \times \int \frac{d\omega'}{2\pi} \frac{1}{\epsilon_{G G'}^{-1}(q, \omega')} \left[ \frac{f_{n_1}(k - q)}{\omega - \omega' - \epsilon_{LDA}^{n_1}(k - q) - i\delta} + \frac{1 - f_{n_1}(k - q)}{\omega - \omega' - \epsilon_{LDA}^{n_1}(k - q) + i\delta} \right] \right\} \}

\[ - \Omega \{ \epsilon^{-1} \} \]

Electron Energy Loss spectrum

All components exhibit a peak, otherwise the amplitude is small

Model Dielectric function: Plasmon-Pole approximation

\[ \Im \epsilon_{G G'}^{-1}(q, \omega) = A_{G G'}(q) \{ \delta[\omega - \tilde{\omega}_{G G'}(q)] - \delta[\omega + \tilde{\omega}_{G G'}(q)] \} \]

\[ \Re \epsilon_{G G'}^{-1}(q, \omega) = \delta_{G G'} + \frac{\Omega_{G G'}(q)}{\omega - \tilde{\omega}_{G G'}(q)} \]

The energy integral is now analytic
GW approximation in practice: Plasmon-Pole approximation

\[
\langle n'k' | \Sigma_c(r_1, r_2; \omega) | n'k' \rangle = \frac{1}{2} \sum_{n_1} \int_{Bz} \frac{d^3q}{(2\pi)^3} \left\{ \sum_{GG'} v(q + G) \rho_{n,n_1}(q, G) \rho_{n',n_1}^*(q, G') \right\} \times \\
\times \int \frac{d\omega'}{2\pi} \epsilon^{-1}_{GG'}(q, \omega') \left[ \frac{f_{n_1}(k-q)}{\omega - \omega' - \epsilon_{n1}^{LDA}(k-q) - i\delta} + \frac{1 - f_{n_1}(k-q)}{\omega - \omega' - \epsilon_{n1}^{LDA}(k-q) + i\delta} \right] \right\} - \Im \{ \epsilon^{-1} \}
\]

Electron Energy Loss spectrum

All components exhibit a peak, otherwise the amplitude is small

Model Dielectric function: Plasmon-Pole approximation

\[
\Im \epsilon^{-1}_{GG'}(q, \omega) = A_{GG'}(q) \left\{ \delta[\omega - \tilde{\omega}_{GG'}(q)] - \delta[\omega + \tilde{\omega}_{GG'}(q)] \right\}
\]

\[
\Re \epsilon^{-1}_{GG'}(q, \omega) = \delta_{GG'} + \frac{\Omega_{GG'}(q)}{\omega - \tilde{\omega}_{GG'}(q)}
\]

The energy integral is now analytic

Different recipes to evaluate poles and residues

M. Hybertsen and S. Louie PRB 34, 5390 1986
GW approximation in practice: Plasmon-Pole approximation

Real part along real axis


ZnO case M. Stankovki et al. Phys Rev. B 84, 241201 (2011)

full integration is needed: alternative methods
GW approximation in practice: Plasmon-Pole approximation

Real part along real axis


ZnO case M. Stankovki et al. Phys Rev. B 84, 241201 (2011)

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PPA become questionable when $\epsilon^{-1}_{G\sigma}G_{\sigma'}$ differs from single-pole


full integration is needed: alternative methods
The plasmon pole approximation

\[(9)\text{ Plasmon Pole approximation (PPA): yambo } -\text{p p}\]

Components of the Dielectric matrix approximated has a single pole functions:

\[
\varepsilon_{G,G'}^{-1}(q, \omega) \sim \delta_{G,G'} + R_{G,G'}(q) \left[ (\omega - \Omega_{G,G'}(q) + i0^+)^{-1} - (\omega + \Omega_{G,G'}(q) - i0^+)^{-1} \right]
\]

Residuals \(R_{G,G'}(q)\) and energies \(\Omega_{G,G'}(q)\) are found by imposing the PPA to reproduce the exact function at \(\omega = 0\) and \(\omega = iE_{PPA}\) with \(\epsilon^{-1}\) being a suitable user-defined parameter.

\[
R_{G,G'}(q) = -\frac{\varepsilon_{G,G'}^{-1}(q, \omega=0) \Omega_{G,G'}}{2}
\]

\[
\Omega_{G,G'} = E_{PPA} \sqrt{\frac{\varepsilon_{G,G'}^{-1}(q, \omega=E_{PPA})}{\varepsilon_{G,G'}^{-1}(q, \omega=0) - \varepsilon_{G,G'}^{-1}(q, \omega=E_{PPA})}}
\]

The QP energies should not depend too much on the choice of imaginary plasmon frequency. **Tip:** Choose a value higher in energy than the plasmon peak (EELS spectrum)
GW approximation in practice

Goal: \[ \hat{H}_0(r)f_s(r) + \int \Sigma(r, r'; \epsilon_s)f_s(r')d^3r' = \epsilon_s f_s(r) \]

\[ \Sigma = iGW \]

Once we know \[ \Sigma^{GW} = G^0 W^0 \]
GW approximation in practice

Goal: 
\[ \hat{H}_0(r) f_s(r) + \int \Sigma(r, r'; \epsilon_s) f_s(r') d^3r' = \epsilon_s f_s(r) \]
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Once we know \[ \Sigma^{GW} = G^0 W^0 \]

\[ f_i^{QP}(r) \approx \phi_i^{KS}(r) \]

This is another approximation, very frequently used and not always valid!
GW approximation in practice

Goal:

\[ \hat{H}_0(r) f_s(r) + \int \Sigma(r, r'; \epsilon_s) f_s(r') d^3r' = \epsilon_s f_s(r) \]

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Once we know \[ \Sigma^{GW} = G^0 W^0 \]

\[ f_i^{QP}(r) \approx \phi^K_S(r) \]

This is another approximation, very frequently used and not always valid!

(8a) Dyson Solver: \[ \text{yambo -g n/s} \]

\[ E_{nk}^{QP} = \epsilon_{nk} + \langle \psi_{nk} | \Sigma(E_{nk}^{QP}) - V_{xc} | \psi_{nk} \rangle \]

DysSolver= "n" First order expansion around KS eigenvalue

\[ E_{nk}^{QP} = \epsilon_{nk} + Z_{nk} \langle \psi_{nk} | \Sigma(\epsilon_{nk}) - V_{xc} | \psi_{nk} \rangle \]

\[ Z_{nk} = \left[ 1 - \frac{d\Sigma_{nk}(\omega)}{d\omega} \right]_{\omega=\epsilon_{nk}}^{-1} \]

dScStep = 0.10000 eV # [GW] Energy step to evaluate Z

DysSolver= "s" Secant iterative method


\[ x_n = x_{n-1} - f(x_{n-1}) \frac{x_{n-1} - x_{n-2}}{f(x_{n-1}) - f(x_{n-2})} = \frac{x_{n-2} f(x_{n-1}) - x_{n-1} f(x_{n-2})}{f(x_{n-1}) - f(x_{n-2})} \]
Accelerating convergence wrt number of bands

\[ < n|c(\epsilon_{k,n})|n > = \frac{1}{2\pi N_k \Omega} \int d\omega' \sum_{n_1 \leq N_b} \sum_{qG'} [W_{G'G}(q, \omega') - \delta_{G'G} \nu(q + G)] \]

\times \frac{\rho_{nn_1}(q + G) \rho_{nn_1}^*(q + G')}{\omega' - \epsilon_{k-q,n} + \epsilon_{k,n_1} \pm i\eta} \]

\rho_{nn_1}(q + G) = < k - q, n | e^{i(q + G) \cdot r} | k, n_1 >

F. Bruneval and X. Gonze PRB 78, 085125 2008
Accelerating convergence wrt number of bands

\[ < n k | \Sigma_c(\epsilon_{k,n}) | n k > = \frac{1}{2\pi N_k \Omega} \int d\omega' \sum_{n_1 \leq N_b} \sum_{q, G'} [ W_{G G'}(q, \omega') - \delta_{G G'} \nu(q + G) ] \]
\[ \times \frac{\rho_{nn_1}(q + G) \rho^*_{nn_1}(q + G')}{\omega' - \epsilon_{k-q,n} + \epsilon_{k,n_1} \pm i\eta} \]

\[ \rho_{nn_1}(q + G) = < k - q, n | e^{i(q+G) \cdot r} | k, n_1 > \]

Extrapolar approximation: assume all the stats above Nb have the same "average" high energy: \( \bar{\epsilon} \Sigma \)

F. Bruneval and X. Gonze PRB 78, 085125 2008
Accelerating convergence wrt number of bands

\[
<k| \sum_c (\epsilon_{k,n}) | k > = \frac{1}{2\pi N_k \Omega} \int d\omega' \sum_{n_1 \leq N_b} \sum_{qG'G} \left[ W_{GG'}(q, \omega') - \delta_{GG'} \nu(q + G) \right] \\
\times \rho_{nn_1}(q + G) \rho^*_{nn_1}(q + G') \frac{\omega' - \epsilon_{k-q,n} + \epsilon_{k,n_1} \pm i\eta}{\omega'}
\]

\[
\rho_{nn_1}(q + G) = < k - q, n | e^{i(q+G) \cdot r} | k, n_1 >
\]

Extrapolar approximation: assume all the stats above Nb have the same "average" high energy: \( \bar{\epsilon} \Sigma \)

Extrapolar correction:

\[
\Delta_{k,n_1} = \frac{1}{2\pi N_k \Omega} \int d\omega' \sum_{qG'G} \left[ W_{GG'}(q, \omega') - \delta_{GG'} \nu(q + G) \right] \\
\times \frac{\omega' - \bar{\epsilon} \Sigma + \epsilon_{kn_1} + i\eta}{\omega'} \\
\times [ < k, n | e^{i(G-G')} | k, n > - \sum_{n_1 \leq N_b} \rho_{nn_1}(q + G) \rho^*_{nn_1}(q + G') ]
\]

F. Bruneval and X. Gonze PRB 78, 085125 2008
Accelerating convergence wrt number of bands

CBM and VBM GW correction for bulk silicon

VBM GW correction for TiO2 Nanowire (108 occupied bands)

Non periodic 3D systems: nanostructures

Avoiding spurious replica interactions in non periodic directions
Non periodic 3D systems: nanostructures

Avoiding spurious replica interactions in non periodic directions

Coulomb cutoff technique for supercell calculations

\[ \tilde{V}_c(r) = \begin{cases} 
1/r & \text{if } r \in \mathcal{D} \\
0 & \text{if } r \notin \mathcal{D} 
\end{cases} \]

Different geometries according to the dimensionality
Non periodic 3D systems: nanostructures

Avoiding spurious replica interactions in non periodic directions

Coulomb cutoff technique for supercell calculations

\[ \tilde{V}_c(r) = \begin{cases} 
1/r & \text{if } r \in \mathcal{D} \\
0 & \text{if } r \notin \mathcal{D} 
\end{cases} \]

Different geometries according to the dimensionality

Sphere 0D

\[ \tilde{V}_c(G) = \frac{4\pi}{G^2} [1 - \cos(GR)] \]

Cylinder 1D

\[ \tilde{V}_c(q, G) = \frac{4\pi}{|q_z + G|^2} \left[ 1 + G_\perp R J_1(G_\perp R) K_0(|G_z|R) - |G_z| R J_0(G_\perp R) K_1(|G_z|R) \right] \]

WS 2D

\[ \tilde{V}_c(q, G) = \frac{4\pi}{|q_\parallel + G|^2} \left[ 1 - e^{-|q_\parallel + G_\parallel|L/2} \cos(G_z L/2) \right] \]

Non periodic 3D systems: nanostructures

![Graph showing the relationship between supercell volume and QP Gap (X point) for different interchain distances with and without cutoffed Coulomb interaction.]

1D system: atomic chain

- Bare Coulomb
- Cutoffed Coulomb

QP Gap (X point) [eV]

Interchain distance [a.u.]

Supercell volume [a.u.]^3
GW approximation in practice

Summary: $G^0W^0$

$\epsilon^{-1}$

$\epsilon = 1 - \nu P^0$

RPA

$W^0$

plasmon pole

$G^0W^0$

$E_{iQ}^P$
Some GW results: semiconductor band gaps

GW band gaps: huge improvement wrt the LDA

But for a wrong reason!!!!

M. van Schilfgaarde, Takao Kotani, and S. Faleev PRL 96, 226402 (2006)
Some GW results: semiconductor band gaps

GW band gaps: huge improvement wrt the LDA

Very good agreement with the experiment!!

But for a wrong reason!!!!

M. van Schilfgaarde, Takao Kotani, and S. Faleev PRL 96, 226402 (2006)
Some GW results: metal band structure

Copper Bulk

Breakdown of Plasmon Pole approximation

exchange effect between 3d and 3s and 3p core orbitals are crucial

Three hundred bands (those up to an energy of 74 eV cell), and 243 imaginary time points with (corresponding to a plane-wave energy cutoff of 9 Ry were found to be a plane-wave energy cutoff of 9 Ry. In order to converge our surface calculation, the required parameters for the self-energy can be directly monitored. The ability to solve the full QP equation is then formed at a trial energy, and then iterating the energy of the full energy is then obtained QP eigenfunctions by diagonalizing the QP equation in the LDA eigenfunction basis. The weight in the near-surface region is significantly enhanced relative to the bulk material. In the asymptotic limit far from the surface, we expect the effect of the QP states to self-consistency. The full energy is found. Even for the energy dependence of the density response function and dielectric matrix, it is clear that the state-dependent effective local potential. In particular, in the asymptotic state-dependent local potential. In particular, in the asymptotic state-dependent local potential.

\[ V_{\text{loc}}(\mathbf{r})\Psi_{\text{QP}}(\mathbf{r}) = \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', E_{\text{QP}})\Psi_{\text{QP}}(\mathbf{r}') , \]

Metallic surfaces: Al (111)

Energies and potential by GW

Green Function gives access to Total Energy (Galitskii and Migdal 1958)

\[ E = \langle \hat{T} + \hat{V} \rangle = \langle \hat{H} \rangle = -\frac{i}{2} \int \! \! dr \lim_{\eta \to 0} \lim_{r_2 \to r_1} \left[ i\hbar \frac{\partial}{\partial t} - \frac{\hbar^2 \nabla^2}{2m} \right] G(r_1 t_1, r_2 t_1 + \eta) \]

Ground state properties

Capture VdW behaviour \( \frac{1}{d^2} \) behaviour at large distance

Energies by GW

Total Energy of Na vs lattice parameter

Bulk Silicon band Gap

<table>
<thead>
<tr>
<th>Bulk Silicon Band Gap (eV)</th>
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<tbody>
<tr>
<td>Experiment</td>
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<tr>
<td>LDA</td>
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<td>$G^0W^0$</td>
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<tr>
<td>scGW</td>
</tr>
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</table>

Kutepov et al. PRB 80, 041103 (2009)

Good energy ...comparable with GGA

...but one-electron spectra are worse
Optical absorption?

Independent transitions:

\[
\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle \varphi_j | e \cdot v | \varphi_i \rangle|^2 \delta(E_j - E_i - \omega)
\]
Optical absorption?

Independent transitions:

$$\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle \varphi_j | \mathbf{e} \cdot \mathbf{v} | \varphi_i \rangle|^2 \delta(E_j - E_i - \omega)$$

Something important is missing!!!
(see Maurizia Palummo, Fulvio Paleari lectures)
Conclusive remarks: GW many virtues!!!
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GW: parameter-free method which provides in most of the case accurate results (QP energies, but also total energies, lifetimes)
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GW: Starting point for absorption spectroscopy - excitonic effects: Bethe-Salpeter (see Maurizia Palummo, Fulvio Paleari lectures)
GW: parameter-free method which provides in most of the case accurate results (QP energies, but also total energies, lifetimes)

GW: Starting point for absorption spectroscopy - excitonic effects: Bethe-Salpeter (see Maurizia Palummo, Fulvio Paleari lectures)

$G^0W^0$ today is feasible for medium size systems: algorithms suitable for HPC computation (also hybrids architectures, GPU cards).
If your results do not match the experiments:
If your results do not match the experiments:

Before asking to the forum what I’m doing wrong...
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Check carefully your convergence parameter (the boring part...)
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Even at $G^0W^0$ level, several convergence parameter and approximations have to be carefully checked:
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sum over unoccupied states
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Integration over $Bz$  \hspace{2cm} k-points samplings

sum over unoccupied states

plane wave cutoffs
If your results do not match the experiments:

Before asking to the forum what I’m doing wrong...

Check carefully your convergence parameter (the boring part...)

Even at G<sup>0</sup>W<sup>0</sup> level, several convergence parameter and approximations have to be carefully checked:

Integration over Bz  

k-points samplings  

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psuedopotentials
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**GW**: Many approximations enters in a practical calculations:

- in its widespread $G^0W^0$ flavor it is not self-consistent: strong dependence on the DFT starting point (specially true for molecules. Start from hybrid DFT?)
- Even in partial self consistent flavour usually QP wave function assumed to be the same as the initial KS wave function
- Screening treated at RPA level
- Frequency dependence of the screening usually approximated with a PP model
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**GW successful in the interpretation of spectroscopical properties of many systems but calculations need careful checks and relies on different approximations that can fail.**
Acknowledgments
References

**Seminal papers:**
L. Hedin Phys. Rev. A 139, A796 (1965)

**Reviews:**

**Yambo code implementation:**
Thank you for your attention

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