GW Common Approximations

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Outline

The Dyson Equation

In general the scattering path for an interacting G is given by

$$G = G_0 + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + \dots$$

Or, more compactly,

$$G = G_0 + G_0 \Sigma G$$

- This equation shows the relationship between the interacting system G and the non-interacting G_0

G_0, can be approximated from

- DFT
- HF ...

In typical GW@LDA implementations

- The Dyson equation is not solved in this formulation.
- Its written in a different form.

The Dyson Equation can be written as

$$[-\frac{1}{2}\nabla^2 + V_H + V_{ext}]\Psi_i(\mathbf{x}) + \int \Sigma(\mathbf{x},\mathbf{x}';E_i)\Psi_i(\mathbf{x}')d\mathbf{x}' = E_i\Psi_i(\mathbf{x})$$

This is a single-particle equation of motion, known as the quasiparticle equation

This looks very familiar to KS-DFT,

Its however a non-linear differential equation,

The Dyson and Quasiparticle equations: Perturbation

$$[-\frac{1}{2}\nabla^2 + V_H + V_{ext}]\Psi_i(\mathbf{x}) + \int \Sigma^{GW}(\mathbf{x},\mathbf{x}';E_i)\Psi_i(\mathbf{x}')d\mathbf{x}' = \boxed{E_i^{GW}}\,\Psi_i(\mathbf{x})$$

$$[-\frac{1}{2}\nabla^2 + V_H + V_{ext}]\Psi_i(\mathbf{x}) + V_{xc}\Psi_i = \boxed{E_i^{KS}}\,\Psi_i(\mathbf{x})$$

- Laid out this way, the parallels between the Quasiparticle equation and the KS equation is clear.
- These are true excitation energies
- Excitation energies of fictitious states,

This similarity makes it a small step to use perturbation theory.

$$E_i^{GW} = \epsilon_i^{KS} + \langle\psi_i|\Sigma^{GW}(E_i^{GW}) - V_{xc}|\psi_i\rangle$$

or as commonly implemented, the linearized solution

$$E_i^{GW} = \epsilon_i^{KS} + Z_i\langle\psi_i|\Sigma^{GW}(E_i^{KS}) - V_{xc}|\psi_i\rangle$$

$$Z_i = (1 - \langle\psi_i|\Sigma_i^{GW}(E_i^{KS})|\psi_i\rangle)^{-1}$$

Z: the renomalization factor.

- This gives the proportion of the spectral weight under the quasiparticle peak.

Back to The Self Energy

- Can be decomposed into:
- The exchange term
- and the correlation terms:

$$\Sigma^{GW}(\omega) = iG_0W = iG_0\nu + iG_0(W-\nu) = \Sigma^x - \Sigma^c(\omega)$$

The exchange self-energy: Σ^x

$$\Sigma^x(\mathbf{r_1}, \mathbf{r_2}, \omega) = \frac{i\hbar}{2\pi} \int G_0(\mathbf{r_1}, \mathbf{r_2}, \omega + \omega')\nu(\mathbf{r_1}, \mathbf{r_2}) e^{i\omega'\nu} d\omega'$$

this the Fock term from HF self-energy, and can be rewritten:

$$\Sigma^x(\mathbf{r_1}, \mathbf{r_2}) =< \psi_i | \Sigma^x | \psi_i >= -\frac{e^2}{4\pi\varepsilon_0} \sum_j^{occ} \int \psi_i^*(\mathbf{r_1})\psi_j(\mathbf{r_2})\psi_j^*(\mathbf{r_2})\psi_i(\mathbf{r_2}) d\mathbf{r_1} d\mathbf{r_2}$$

this can be integrated analytically.

and the correlation self-energy: Σ^c

$$\Sigma^c(\mathbf{r_1},\mathbf{r_2},\omega) = \frac{i\hbar}{2\pi}\int G_0(\mathbf{r_1},\mathbf{r_2},\omega+\omega')[W(\mathbf{r_1},\mathbf{r_2},\omega') - \nu(\mathbf{r_1},\mathbf{r_2})]e^{i\omega'\nu}d\omega'$$

Can be re-written as:

$$\Sigma^c(\mathbf{r_1},\mathbf{r_2}) =< \psi_i|\Sigma^c|\psi_i >= -\frac{e^2}{4\pi\varepsilon_0}\sum_j^{occ}\int \psi_i^*(\mathbf{r_1})\psi_j(\mathbf{r_2})\psi_j^*(\mathbf{r_2})\psi_i(\mathbf{r_2})d\mathbf{r_1}d\mathbf{r_2}$$

this can only be computed numerically, this is quite expensive to do.

Lets rewrite both in the plane wave representation:

the exchange part,

$$\Sigma^x_{nk} =< n\mathbf{k}|\Sigma^x(\mathbf{r_1},\mathbf{r_2})|n\mathbf{k} >= -\sum_{n_1}\int_{BZ}\frac{d\mathbf{q}}{(2\pi)^3}\sum_{\mathbf{G}}\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}|\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G})|^2 f_{\mathbf{n_1 k_1}},$$

where, $\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G}) =< n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G}\cdot\mathbf{r})}|\mathbf{n}_1\mathbf{k}_1 >$,

and the correlation part:

$$\begin{aligned}\Sigma^c_{n\mathbf{k}}(\omega) &=< n\mathbf{k}|\Sigma^c(\mathbf{r_1},\mathbf{r_2};\omega)|n\mathbf{k} > \\ &= \sum_{n_1}\int_{BZ}\frac{d\mathbf{q}}{(2\pi)^3}\sum_{\mathbf{G},\mathbf{G}'}\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\rho_{\mathbf{nn_1}}(\mathbf{k},\mathbf{q},\mathbf{G})\rho^*_{\mathbf{nn_1}}(\mathbf{k},\mathbf{q},\mathbf{G}') \\ &\times\int d\omega' G^0_{m\mathbf{k}-\mathbf{q}}(\omega-\omega')\epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega')\end{aligned}$$

There are a few things going on here,

An integral over the Brillouin Zone,

$$\Sigma^x_{nk} =< n\mathbf{k}|\Sigma^x(\mathbf{r_1},\mathbf{r_2})|n\mathbf{k} >= -\sum_{n_1} \boxed{\int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3}} \sum_{\mathbf{G}} \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} |\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G})|^2 f_{\mathbf{n_1k_1}},$$

An integral over the Brillouin Zone,

$$\Sigma^c_{n\mathbf{k}}(\omega) =< n\mathbf{k}|\Sigma^c(\mathbf{r_1},\mathbf{r_2};\omega)|n\mathbf{k} >$$

$$= \sum_{n_1} \boxed{\int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3}} \sum_{\mathbf{G},\mathbf{G}'} \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} \rho_{\mathbf{nn_1}}(\mathbf{k},\mathbf{q},\mathbf{G})\rho^*_{\mathbf{nn_1}}(\mathbf{k},\mathbf{q},\mathbf{G}')$$

$$\times \int d\omega' G^0_{m\mathbf{k}-\mathbf{q}}(\omega-\omega')\epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega')$$

There are a few things going on here,

A Sum over occupied States:

$$\Sigma^x_{nk} = < n\mathbf{k}|\Sigma^x(\mathbf{r_1},\mathbf{r_2})|n\mathbf{k} >= \boxed{-\sum_{n_1}} \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G}} \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} |\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G})|^2 f_{\mathbf{n_1 k_1}},$$

A Sum over unoccupied States:

$$\Sigma^c_{n\mathbf{k}}(\omega) = < n\mathbf{k}|\Sigma^c(\mathbf{r_1},\mathbf{r_2};\omega)|n\mathbf{k} >$$
$$= \boxed{\sum_{n_1}} \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G},\mathbf{G'}} \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} \rho_{\mathbf{nn_1}}(\mathbf{k},\mathbf{q},\mathbf{G}) \rho^*_{\mathbf{nn_1}}(\mathbf{k},\mathbf{q},\mathbf{G'})$$
$$\times \int d\omega' G^0_{m\mathbf{k}-\mathbf{q}}(\omega-\omega') \epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega')$$

There are a few things going on here,

$$\Sigma^{x}_{nk} =< n\mathbf{k}|\Sigma^{x}(\mathbf{r_1},\mathbf{r_2})|n\mathbf{k} >= -\sum_{n_1}\int_{BZ}\frac{d\mathbf{q}}{(2\pi)^3}\sum_{\mathbf{G}}\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}|\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G})|^2 f_{\mathbf{n_1 k_1}},$$

The energy integral,

$$\begin{aligned}\Sigma^{c}_{n\mathbf{k}}(\omega) &=< n\mathbf{k}|\Sigma^{c}(\mathbf{r_1},\mathbf{r_2};\omega)|n\mathbf{k} > \\ &= \sum_{n_1}\int_{BZ}\frac{d\mathbf{q}}{(2\pi)^3}\sum_{\mathbf{G},\mathbf{G}'}\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\rho_{\mathbf{nn_1}}(\mathbf{k},\mathbf{q},\mathbf{G})\rho^{*}_{\mathbf{nn_1}}(\mathbf{k},\mathbf{q},\mathbf{G}') \\ &\times \boxed{\int d\omega'\, G^{0}_{m\mathbf{k}-\mathbf{q}}(\omega-\omega')\epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega')}\end{aligned}$$

There are a few things going on here,

Yambo has to compute all three quantities

- The Exchange part
- The correlation
- the energy integral,
- How?

(7) Exchange self energy - Vxc : $\Sigma^{x}_{n\mathbf{k}} - V^{xc}_{n\mathbf{k}}$ yambo -hf

$$\Sigma^{x}_{n\mathbf{k}} = \boxed{\langle n\mathbf{k}|}\Sigma^{x}(\mathbf{r}_1,\mathbf{r}_2)\boxed{|n\mathbf{k}\rangle} = -\boxed{\sum_{m}}\boxed{\int_{BZ}\frac{d\mathbf{q}}{(2\pi)^3}}\boxed{\sum_{\mathbf{G}}}\boxed{v(\mathbf{q}+\mathbf{G})}\boxed{|\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G})|}^2 f_{m(\mathbf{k}-\mathbf{q})}$$

See (6) See (2)

occupied bands only

DFT k-grid
{q} = {k-k'}

G-vectors in the exchange and xc-potential
Number of RL vectors, or energy in Ry / mHa / etc
Tip : to be converged, possibly leave the maximum value

```
EXXRLvcs= 2487001 RL
```

```
VXCRLvcs= 2487001 RL
```

```
%QPkrange
  1|   5| 20|   59|
  4|   8| 60|   80|
%
%QPerange (-V qp)
  1| 32| 0.0|-1.0|
%
```

nk, n'k' ranges where GW/Σ_x 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
nk,nk' ranges (alternative method)
first k-point | last k-point | lower energy | upper energy

(8) Correlation part of self energy: **yambo -gw0 ppa**

$$\Sigma^c_{n\mathbf{k}}(\omega) = \boxed{\langle n\mathbf{k}}|\Sigma^c|n\mathbf{k}\rangle = i\boxed{\sum_m}\int_{BZ}\frac{d\mathbf{q}}{(2\pi)^3}\boxed{\sum_{\mathbf{G},\mathbf{G}'}}\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G})\rho^*_{nm}(\mathbf{k},\mathbf{q},\mathbf{G}') \times \int d\omega' G^0_{m\mathbf{k}-\mathbf{q}}(\omega-\omega')\epsilon^{-1}_{\boxed{\mathbf{G}\mathbf{G}'}}(\mathbf{q},\omega')$$

```
% GbndRnge
  1 | 50 |
%
```

Bands used in the GW summation
QP energies usually shows slow convergence
Tip: If you are interested in gaps, energy differences converge faster

NGsBlkXp= 100 RL
Response block size
See (9)

```
%QPkrange
  1|   5| 20|  59|
  4|   8| 60|  80|
%
%QPerange (-V qp)
  1| 32| 0.0|-1.0|
%
```

nk, n'k' ranges where GW/Σ_c 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

There are a few things going on here,

Yambo has to compute all three quantities

- ~~The Exchange part~~
- ~~The correlation~~
- the energy integral
- How?

Lets look at that again

The energy integral,

$$\Sigma^c_{n\mathbf{k}}(\omega) = < n\mathbf{k}|\Sigma^c(\mathbf{r_1}, \mathbf{r_2}; \omega)|n\mathbf{k} >$$

$$= \sum_{n_1} \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G},\mathbf{G}'} \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} \rho_{\mathbf{nn_1}}(\mathbf{k},\mathbf{q},\mathbf{G}) \rho^*_{\mathbf{nn_1}}(\mathbf{k},\mathbf{q},\mathbf{G}')$$

$$\times \boxed{\int d\omega' \, G^0_{m\mathbf{k}-\mathbf{q}}(\omega-\omega') \epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega')}$$

The energy integral can be computed once the inverse dielectric function is known. ϵ follows from the reducible response function χ,

$$\epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega) = \delta\mathbf{GG}' + \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\chi_{\mathbf{GG}'}(\mathbf{q},\omega)$$

χ is computed within the RPA, for the GW approximation,

$$\chi_{\mathbf{GG}'}(\mathbf{q},\omega) = [\delta\mathbf{GG}' - \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\chi^0_{\mathbf{GG}''}(\mathbf{q},\omega)]^{-1}\chi^0_{\mathbf{G}''\mathbf{G}'}(\mathbf{q},\omega).$$

and the non-interacting response function $\chi^0_{\mathbf{GG}''}$, can be computed from G_0,

$$\chi^0_{\mathbf{G}''\mathbf{G}'}(\mathbf{q},\omega) = 2\sum_{nn'}\int_{BZ}\frac{d\mathbf{k}}{(\pi)^3}\rho^*_{\mathbf{n}'\mathbf{nk}}(\mathbf{q},\mathbf{G})\rho_{\mathbf{n}'\mathbf{nk}}(\mathbf{q},\mathbf{G}')f_{n\mathbf{k}-\mathbf{q}}(1-f_{n'\mathbf{k}})$$
$$\times\left[\frac{1}{\omega+\epsilon_{n\mathbf{k}-\mathbf{q}}-\epsilon_{n'\mathbf{k}}+i0^+} - \frac{1}{\omega+\epsilon_{n'\mathbf{k}}-\epsilon_{n\mathbf{k}-\mathbf{q}}-i0^+}\right]$$

The PPA

Lets take a look at that energy integral,

$$\int d\omega' \, G^0_{m\mathbf{k}-\mathbf{q}}(\omega-\omega')\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega')$$

- A numerical integration of this would require the inversion of ϵ for many frequency points.
- This is something that's expensive,
- So we typically use the Plasmon Pole Approximation,

In the PPA, ϵ^{-1} is approximated by a single pole function,

$$\epsilon^{-1}\mathbf{G}\mathbf{G}'(\mathbf{q},\omega) \approx \delta_{\mathbf{G}\mathbf{G}'} + R_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\left[\left(\omega - \Omega_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) + i0^+\right)^{-1} \left(\omega + \Omega_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) - i0^+\right)^{-1}\right].$$

the residuals $R_{\mathbf{G}\mathbf{G}'}$ and energies $\Omega_{\mathbf{G}\mathbf{G}'}$, are found in turn by imposing a condition that the PPA reproduces the exact ϵ^{-1} function at two frequencies $\omega = 0$ and a user defined value, $\omega = iE_{PPA}$.

finally, back to the begining, and ready to calculate:

We can now take the Taylor expansion of the SE about the KS energy,

$$G_i(\omega) \approx Z_i \left[\frac{f_i}{\omega - E_i^{GW} + i0^+} + \frac{1 - f_i}{\omega - E_i^{GW} + i0^+} \right]$$

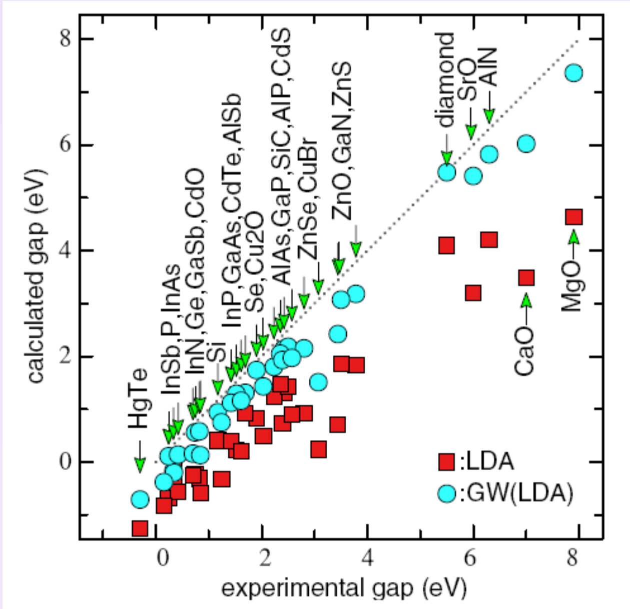
with:

$$E_i^{GW} = \epsilon_i^{KS} + Z_i \langle \psi_i | \Sigma^{GW}(E_i^{KS}) - V_{xc} | \psi_i \rangle$$

and

$$Z_i = (1 - \langle \psi_i | \Sigma_i^{GW}(E_i^{KS}) | \psi_i \rangle)^{-1}$$

After all this work, what do we get?

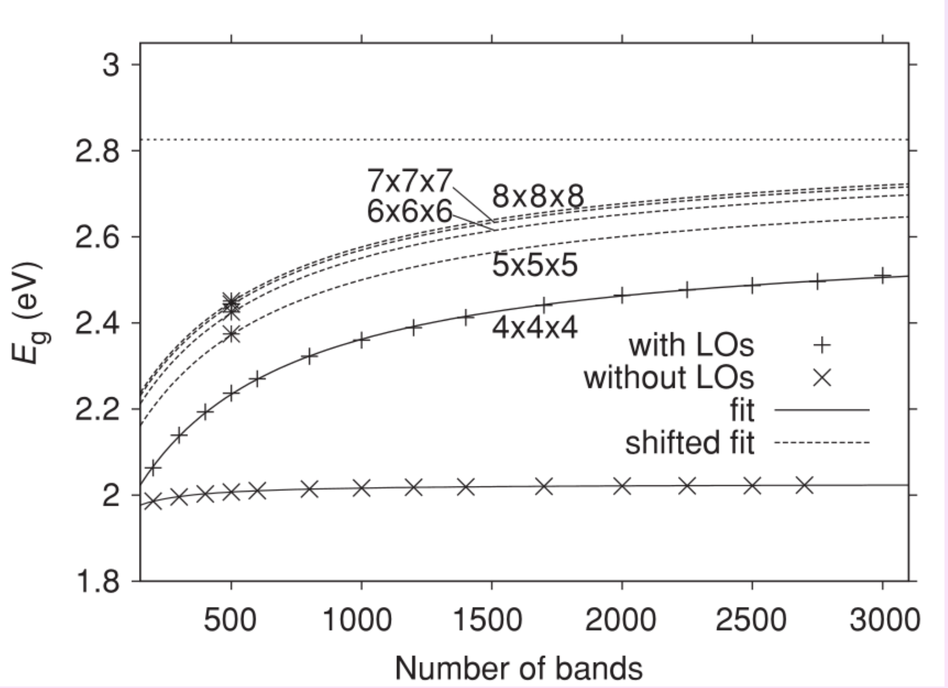


The results, (van Schilfgaarde, 2008)

- This is a good description for one 1-particle G.
- We get back accurate quasiparticle energies, corrected band gaps, lifetime broadening, plasma satellites etc.

$G_0 W_0$ results are quite acceptable, any issues?

- Convergence needs to be perfomed with caution, the typical case is ZnO, (Phys. Rev. B 84, 039906)



False convergence w.r.t. bands

Thanks

- G. Onida, L. Reining and A. Rubio, Rev. Mod. Phys. 2002
- Introduction to Many Body Physics, Piers Coleman,
- Interacting Electrons, David Ceperly, R. Martin, L. Reining.
- Hybertsen and Louie Phys Rev B, 1986.
- Aryasetiawan and O Gunnarsson 1998 Rep. Prog. Phys
- C. Attaccalite, M. Grüning, and A. Marini Phys. Rev. B 84 2011.
- E. Perfetto, D. Sangalli, A. Marini, and G. Stefanucci Phys. Rev. B 94, 2016.
- Stefanucci G., van Leeuwen R. Nonequilibrium Many-Body Theory of Quantum Systems: A Modern Introduction.
- Cheat sheet. (to be introduced.)

Thanks

- You
- TU-K
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- MRSK

MRS-K
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