GW Common Approximations

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The Technical University: RASESMA 2023

February 14, 2023

TECHNICAL UNIVERSITY OF KENYA

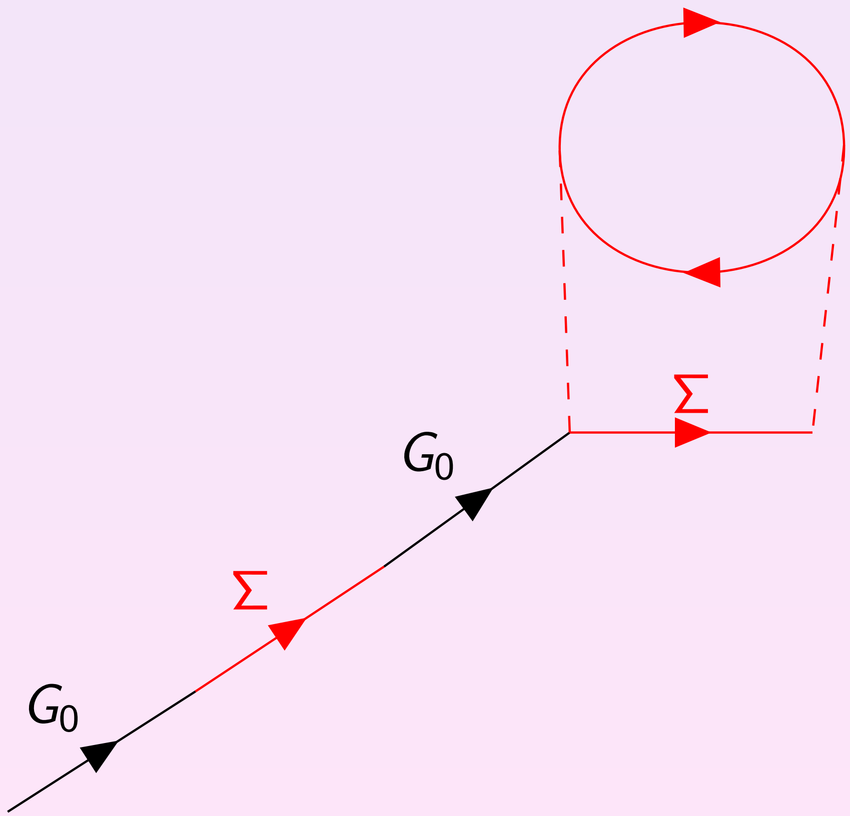
The Abdus Salam International Centre for Theoretical Physics

Outline

The Dyson Equation

- Getting back to the idea of the Greens function as a probability amplitude a propagation process.

- How does the propagation from r_2 to r_1 happen?



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

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

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

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

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

- 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:

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

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,

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

where, $\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G}) =< n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G}\cdot\mathbf{r})}|\mathbf{n_1k_1} >$,

and the correlation part:

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

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,

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

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,

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

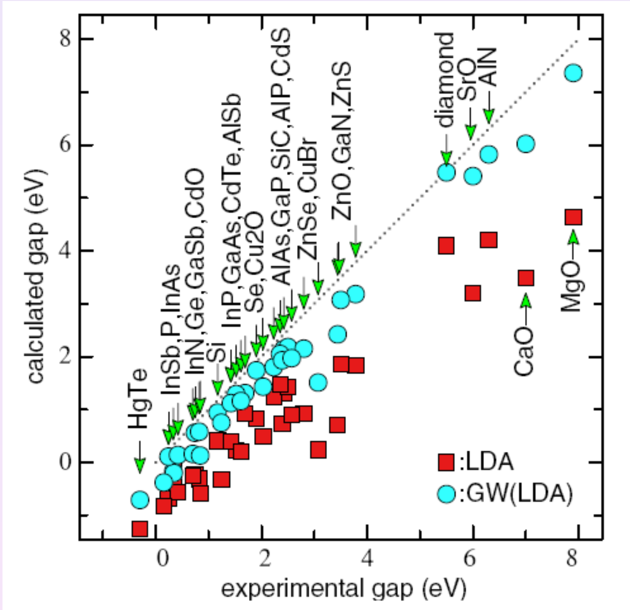
with:

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

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?

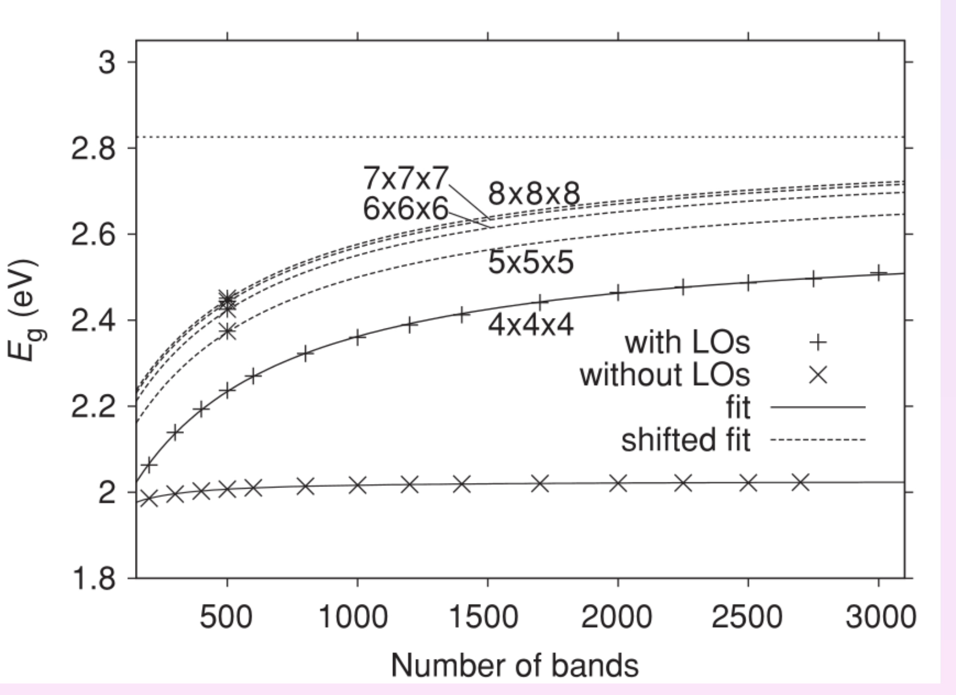


The results, (van Schilfgaarde, 2008)

- 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

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- Stefanucci G., van Leeuwen R. Nonequilibrium Many-Body Theory of Quantum Systems: A Modern Introduction.
- Cheat sheet. (to be introduced.)

Thanks

- You
- TU-K
- CNR-ISM
- KENET
- MRSK

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