A mathematical study of the GW[1] method: the irreducible polarizability within the GW approximation.

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[1]Note: The name "GW" does not stand for anything

We consider a very big electronic system ($N \approx \infty$), with Hamiltonian

$$H_N := -\frac{1}{2}\sum_{i=1}^{N}\Delta_i + \sum_{1\le i<j\le N}\frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} + \sum_{i=1}^{N} V(\mathbf{x}_i)$$

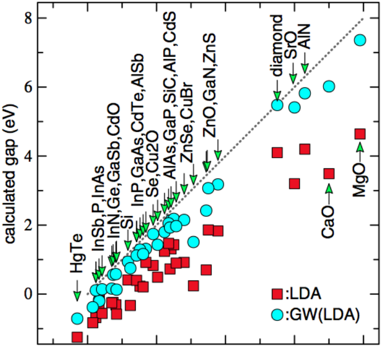
acting on $\mathcal{H}_N := \bigwedge_{i=1}^{N}\mathcal{H}$, with $\mathcal{H} = L^2(\mathbb{R}^3)$.

We would like to understand the optical properties of such a system.

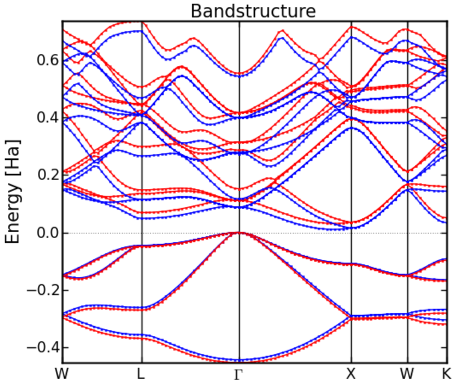
System with N particles   System with $N-1$ particles

It holds $h\nu + E_N^0 = E_{\mathrm{kin}} + E_{N-1}^k$, from which we deduce the gap $E_{N-1}^k - E_N^0$.
There is a dynamical response due to the loss of a particle.

In the limit $N \to \infty$, we expect to recover the correct band gap of crystals.



(a) Band gaps for LDA and GW.



(b) Band structure of Si for LDA, and GW.

A GW calculation gives better results with respect to band gaps.[2]
The GW method is based on Green's functions.

[2] M. van Schilfgaarde, T. Kotani and S. Faleev, Phys. Rev. Let. 96 (2006)

Definition of the Green's functions

Let us fix some notations

We work with fermions, in spin-unpolarized systems.

- The 1-particle Hilbert space is $\mathcal{H} = L^2(\mathbb{R}^3)$.
- The N-particle fermionic Hilbert space is $\mathcal{H}_N = \bigwedge_{i=1}^N L^2(\mathbb{R}^3)$.
- The fermionic Fock space is $\mathcal{F} = \mathbb{C} \oplus \mathcal{H} \oplus \mathcal{H}_2 \oplus \dots$

The Hamiltonian can be written in second quantization as

$$\mathbb{H} = \int_{\mathbb{R}^3} h(\mathbf{x}) \Psi^\dagger(\mathbf{x}) \Psi(\mathbf{x}) \mathrm{d}\mathbf{x} + \iint_{\mathbb{R}^3 \times \mathbb{R}^3} v(\mathbf{x}, \mathbf{y}) \Psi^\dagger(\mathbf{x}) \Psi^\dagger(\mathbf{y}) \Psi(\mathbf{y}) \Psi(\mathbf{x}) \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{y},$$

where we separate the 1-body part of the Hamiltonian $h(\mathbf{x}) \approx -\frac{1}{2}\Delta + V(\mathbf{x})$, and the 2-body part $v(\mathbf{x}, \mathbf{y}) = |\mathbf{x} - \mathbf{y}|^{-1}$.

We define the particle Green's function (here, Θ is the heavyside function):

$$G_p(\mathbf{x}, t, \mathbf{x}', t') = -\mathrm{i}\Theta(t - t')\langle \Psi_N^0 | \Psi(\mathbf{x}) \mathrm{e}^{-\mathrm{i}(t-t')(H_{N+1} - E_N^0)} \Psi^\dagger(\mathbf{x}') | \Psi_N^0 \rangle.$$

Interpretation:

- start from the ground state
- create a particle at x'
- let the system evolves with its extra particle between t' and t $(t - t' > 0)$
- annihilate a particle at x
- compare the new state with the ground state

"Describes the amplitude that a particle added at $(\mathbf{x}, t)$ will be released at $(\mathbf{x}', t')$".

We also define the hole Green's function

$$G_h(\mathbf{x}, t, \mathbf{x}', t') = \mathrm{i}\Theta(t' - t)\langle \Psi_N^0 | \Psi^\dagger(\mathbf{x}') \mathrm{e}^{\mathrm{i}(t-t')(H_{N-1} - E_N^0)} \Psi(\mathbf{x}) | \Psi_N^0 \rangle.$$

"Describes the amplitude that a hole added at $(\mathbf{x}', t')$ will be released at $(\mathbf{x}, t)$".

We finally define the time-ordered Green's function

$$G(\mathbf{x},t,\mathbf{x}',t') = -\mathrm{i}\langle \Psi_N^0 | \mathcal{T}\left\{ \Psi_H(\mathbf{x},t)\Psi_H^\dagger(\mathbf{x}',t') \right\} |\Psi_N^0\rangle$$
$$= G_p(\mathbf{x},t,\mathbf{x}',t') + G_h(\mathbf{x},t,\mathbf{x}',t'),$$

where $\mathcal{T}$ is the fermionic time-ordering operator.
Note that G contains all the information of G_p and G_h.
Finally, note that G_p, G_h and G only depends on $\tau := t - t'$.

The time-ordered Green's function has some interesting properties. We can recover:

- the 1-body density matrix from G:

$$-\mathrm{i}G(\mathbf{x},\mathbf{x}';0^-) = \gamma_N^0(\mathbf{x},\mathbf{x}') := \int_{\mathbb{R}^{3(N-1)}} \Psi_N^0(\mathbf{x},\mathbf{x}_2,\dots\mathbf{x}_N)\overline{\Psi_N^0(\mathbf{x}',\mathbf{x}_2,\dots\mathbf{x}_N)}\mathrm{d}\mathbf{x}_2\dots\mathrm{d}\mathbf{x}_N.$$

- the electronic density $\rho_N^0(\mathbf{x}) = \gamma_N^0(\mathbf{x},\mathbf{x}) = -\mathrm{i}G(\mathbf{x},\mathbf{x},0^-)$.
- the ground-state energy (Galitskii-Migdal formula[3]).
- some information about the optical properties of the system, like $E_{N-1}^k - E_N^0$.

[3] V. M. Galitskii and A. B. Migdal, Sov. Phys.-JETP 7, 96 (1958).

Question: How to calculate the time-ordered Green's function?

The GW approximation: Start with the Hedin's equations[4]

$$G(\mathbf{12}) = G_0(\mathbf{12}) + \int \mathrm{d}\mathbf{34}\, G_0(\mathbf{13})\Sigma(\mathbf{34})G(\mathbf{42}) \qquad \text{(Dyson equation)}$$

$$\Sigma(\mathbf{12}) = \mathrm{i} \int \mathrm{d}\mathbf{34}\, G(\mathbf{13})W(\mathbf{41})\Gamma(\mathbf{423}) \qquad \text{(Self-energy)}$$

$$\Gamma(\mathbf{123}) = \delta(\mathbf{12})\delta(\mathbf{13}) + \int \mathrm{d}\mathbf{4567}\, \frac{\partial \Sigma(\mathbf{12})}{\partial G(\mathbf{45})} G(\mathbf{46})G(\mathbf{57})\Gamma(\mathbf{673}) \qquad \text{(Vertex function)}$$

$$W(\mathbf{12}) = \int \mathrm{d}\mathbf{3}\, \epsilon^{-1}(\mathbf{13})v(\mathbf{32}) \qquad \text{(Screening)}$$

$$\epsilon(\mathbf{12}) = \delta(\mathbf{12}) - \int \mathrm{d}\mathbf{3}\, v(\mathbf{13})P(\mathbf{32}) \qquad \text{(Dielectric)}$$

$$P(\mathbf{12}) = -\mathrm{i} \int \mathrm{d}\mathbf{34}\, G(\mathbf{13})G(\mathbf{41})\Gamma(\mathbf{342}) \qquad \text{(Irreducible polarizability)}$$

The GW approximation consists into setting

$$\frac{\partial \Sigma(\mathbf{12})}{\partial G(\mathbf{45})} = 0, \quad \text{or equivalently} \quad \Gamma(\mathbf{123}) = \delta(\mathbf{12})\delta(\mathbf{13}) \quad \text{(GW approximation)},$$

[4] L. Hedin, Phys. Rev. 139, 3A (1965).

We obtain the GW equations

$$G(\mathbf{12}) = G_0(\mathbf{12}) + \int \mathrm{d}\mathbf{34}\, G_0(\mathbf{13})\Sigma(\mathbf{34})G(\mathbf{42}) \qquad \text{(Dyson equation)}$$

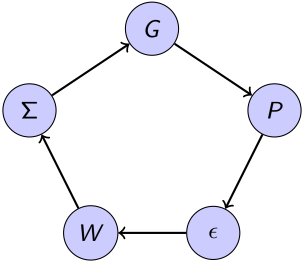
$$\Sigma(\mathbf{12}) = \mathrm{i}G(\mathbf{12})W(\mathbf{21}) \qquad \text{(Self-energy)}$$

$$W(\mathbf{12}) = \int \mathrm{d}\mathbf{3}\,\epsilon^{-1}(\mathbf{13})v(\mathbf{32}) \qquad \text{(Screening)}$$

$$\epsilon(\mathbf{12}) = \delta(\mathbf{12}) - \int \mathrm{d}\mathbf{3}\,v(\mathbf{13})P(\mathbf{32}) \qquad \text{(Dielectric)}$$

$$P(\mathbf{12}) = -\mathrm{i}G(\mathbf{12})G(\mathbf{21}) \qquad \text{(Irreducible polarizability)}$$

Those equations are usually solved with a self-consistent method.



I will not explain all this set of equations, but focus on the last one...

The irreducible polarizability:

$$P(\mathbf{x}, \mathbf{x}', \tau) = -\mathrm{i} G(\mathbf{x}, \mathbf{x}', \tau) G(\mathbf{x}', \mathbf{x}, -\tau)$$

$$P(\mathbf{x},\mathbf{x}',\tau) = -\mathrm{i}G(\mathbf{x},\mathbf{x}',\tau)G(\mathbf{x}',\mathbf{x},-\tau)$$

- We multiply the kernels of the operators ($\neq$ operator multiplication).
- Formally, for $f, g \in \mathcal{H} \times \mathcal{H}$,

$$\begin{aligned}\langle f|P(\tau)|g\rangle &= \iint \overline{f}(\mathbf{x})P(\mathbf{x},\mathbf{x}',\tau)g(\mathbf{x}')\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' = -\mathrm{i}\iint \overline{f}(\mathbf{x})G(\mathbf{x},\mathbf{x}',\tau)g(\mathbf{x}')G(\mathbf{x}',\mathbf{x},-\tau)\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\ &= -\mathrm{i}\mathrm{Tr}\left(\overline{f}G(\tau)gG(-\tau)\right)\end{aligned}$$

This last expression does not involve the kernels

Lemma

For all $\tau \in \mathbb{R}$, the quadratic form $(f,g) \mapsto -\mathrm{i}\mathrm{Tr}\left(\overline{f}G(\tau)gG(-\tau)\right)$ is bounded. As a result, $P(\tau)$ is a well-defined bounded operator.

Idea of the proof: Either $G(\tau)$ or $G(-\tau)$ is the hole Green's function, which is compact.

In a mean-field model (for instance Kohn-Sham model), we can write

$$H_N = \sum_{i=1}^{N} h(\mathbf{x}_i) \quad \text{with} \quad h = -\frac{1}{2}\Delta + V + V_{\mathrm{KS}}.$$

The (time-Fourier transform of the) Green's function is simply the resolvent of h:

$$\widehat{G}(\omega) = (\omega - h)^{-1}.$$

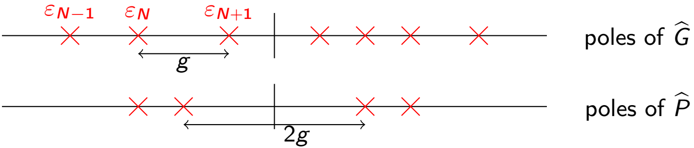
- If we suppose that h is compact resolvent (no dissipation): $h = \sum_{k=1}^{\infty} \varepsilon_k |u_k\rangle\langle u_k|$, then, the (time-Fourier transform of the) irreducible polarizability operator is

$$\boxed{\widehat{P}(\omega) = \sum_{n=1}^{N} \sum_{m=N+1}^{\infty} \frac{2(\varepsilon_m - \varepsilon_n)}{\omega^2 - (\varepsilon_m - \varepsilon_n)^2} |u_n u_m\rangle\langle u_m u_n|.}$$

$$\widehat{P}(\omega) = \sum_{n=1}^{N} \sum_{m=N+1}^{\infty} \frac{2(\varepsilon_m - \varepsilon_n)}{\omega^2 - (\varepsilon_m - \varepsilon_n)^2} |u_n u_m\rangle\langle u_m u_n|.$$

If $g := \varepsilon_{N+1} - \varepsilon_N > 0$ (insulator), then

- $\widehat{P}(\omega)$ is well-defined for $\omega \in (-g, g)$, and is a negative operator.



- There is a widening of gap.
- It holds (Johnson f-sum rule[5]):

$$\forall f, g \in \mathcal{C}_0^\infty \times \mathcal{C}_0^\infty, \quad \lim_{t \to \infty} t^2 \langle f | \widehat{P}(\mathrm{i}t) | g \rangle = -\int \rho \overline{\nabla f} \cdot \nabla g$$

where ρ is the electronic density (here $\rho(x) = \sum_{k=1}^{N} |u_k|^2(x)$).

[5] D.Johnson. Phys. Rev. B, 9,10 (1974).

That was for the mean-field model (with no dissipation). In the general case $P = -\mathrm{i}GG$, we do not have an explicit formula for P. We can still prove

Lemma

Suppose $\widehat{G}$ has a gap of size $g > 0$ (here, $g = 2E_N^0 - E_{N+1}^0 - E_{N-1}^0$). Then,

- *Then, for all $\omega \in (-g, g)$, $\widehat{P}(\omega)$ is a well-defined bounded negative operator.*
- *The Johnson f-sum rule holds true.*

The proof relies on the analytic continuation of the operators on the complex plane, and the use of the so-called Plemelj formulae (or Kramers-Krönig formulae).

Remark:

- The Johnson f-sum rule is important when designing approximation of P.

Conclusion

- We gave a (very rapid) presentation of the GW method.
- We investigated the kernel product $P(\mathbf{x},\mathbf{x}',\tau) = -\mathrm{i}G(\mathbf{x},\mathbf{x}',\tau)G(\mathbf{x}',\mathbf{x},\tau)$.
- In particular, we proved that P is a well-defined operator, which satisfies
  - The widening of gap phenomenon
  - The Johnson f-sum rule.

Future Work

- Do a similar work for the self-energy $\Sigma(\mathbf{x},\mathbf{x}',\tau) = \mathrm{i}G(\mathbf{x},\mathbf{x}',\tau)W(\mathbf{x}',\mathbf{x},\tau)$.
- Give a mathematical framework for the whole GW method.
- Perform a similar study for the Bethe-Salpeter equation[6] ($\approx$ first order approximation for $\dfrac{\partial\Sigma(\mathbf{12})}{\partial G(\mathbf{34})}$).

Thank you for your attention!

[6] H. Bethe, E. Salpeter, Phys. Rev. 84, 6(1951)