An Equation of Motion approach to the GW approximation
What is the key strategy of Density-Functional-Theory to attack the many-body problem?
What is the key strategy of Density-Functional-Theory to attack the many-body problem?

Reduce the degrees of freedom

\[ n(r) = N \sum_s \int d\mathbf{x}_2 \cdots d\mathbf{x}_N |\Psi(r_s \cdots \mathbf{x}_M, \mathbf{x}_{M+1} \cdots \mathbf{x}_N)|^2 \]

(Access only part of the information: ground state properties)
Target charged excitations in electronic system:

Reduce to a 2-point 1 particle 'correlation function'

Target neutral excitations in electronic system:

Reduce to a 4-point 2 particles 'correlation function'

Derive equation of motion for the correlation functions (under certain assumptions)

Look briefly at practical implementations

Discuss the assumptions...
Target charged excitations in electronic system:

Reduce to a 2-point 1 particle 'correlation function'
Let's "watch" the propagation of an added electron:

\[ |\Psi_0^N\rangle \]

with:

\[ \hat{\psi}(r), \hat{\psi}^\dagger(r) \]

field operators of annihilation/creation electron at \( r \)

\[ U(t', t) = \exp \left(-i \hat{H}(t' - t) \right) \]

evolution operator from \( t \) to \( t' \geq t \)

\[ \hat{\psi}(r') U(t', t) \hat{\psi}^\dagger(r) |\Psi_0^N\rangle \]
Probability amplitude for propagation of additional electron from \((r,t)\) to \((r',t')\) in a many electron system:

\[
\langle \Psi_0^N | \hat{\psi}(r')\hat{U}(t', t)\hat{\psi}^\dagger(r)|\Psi_0^N \rangle \equiv \hat{\psi}(r', t')\psi^\dagger(r, t)|\Psi_0^N \rangle
\]

= definition of Green's function:

\[
iG^e(r', t'; r, t) = \langle \Psi_0^N | \hat{\psi}(r', t')\hat{\psi}^\dagger(r, t)|\Psi_0^N \rangle \theta(t' - t)
\]
Probability amplitude for propagation of additional hole from \((r,t)\) to \((r',t')\) in a many electron system:

\[
\langle \Psi_0^N | \hat{\psi}(r') \hat{U}(t', t) \hat{\psi}(r) | \Psi_0^N \rangle \equiv \hat{\psi}(r', t') \psi(r, t) | \Psi_0^N \rangle
\]

= definition of Green's function:

\[
iG^h(r, t; r', t') = \langle \Psi_0^N | \hat{\psi}(r, t) \hat{\psi}(r', t') | \Psi_0^N \rangle \theta(t - t')
\]
We can so define the time-ordered Green's function

\[ G(r', t' ; r, t) = -i \langle \Psi_0^N | \hat{T}[\hat{\psi}(r', t' )\hat{\psi}^\dagger(r, t)] | \Psi_0^N \rangle \]

\[ = G^e(r', t' ; r, t) - G^h(r, t ; r', t') \]

\[ = -i \langle \begin{array}{c|c}
\text{t' > t} & \text{t' < t} \\
\end{array} \rangle + i \langle \begin{array}{c|c}
\text{t' < t} & \text{t' > t} \\
\end{array} \rangle \]

\[ \hat{T} \]

**time ordering operator:** re-arranges a series of field operators in order of ascending time. Each permutation = x(-1)
Which information is contained in the Green's function?

\[ n(rt) = \langle \Psi_0^N | \psi(r, t) \psi(r, t) | \Psi_0^N \rangle = -iG(r, t; r, t + \eta) \]

\[ \eta \quad \text{infinitesimal positive number} \]

It reduces to the ground state density: all ground state observables (by Hohenberg-Kohn theorem)
Which information is contained in the Green's function?

Lehmann representation:

\[ G(r', r) = \sum_s \frac{\psi_s^{N+1}(r') \psi_s^{N+1}(r)^*}{\omega - \varepsilon_{s}^{N+1} + i\eta} + \sum_s \frac{\psi_s^{N-1}(r) \psi_s^{N-1}(r')^*}{\omega - \varepsilon_{s}^{N-1} - i\eta} \]

obtained from GF definition by inserting:

\[ 1 = \sum_s |\Psi_s^{N\pm1}\rangle \langle \Psi_s^{N\pm1}| \]

sum over all states of N+1 (N -1) system

and Fourier transforming (time)
Which information is contained in the Green's function?

Lehmann representation:

\[
G(r', r) = \sum_s \frac{\psi_s^{N+1}(r') [\psi_s^{N+1}(r)]^*}{\omega - \varepsilon_s^{N+1} + i\eta} + \sum_s \frac{\psi_s^{N-1}(r) [\psi_s^{N-1}(r')]^*}{\omega - \varepsilon_s^{N-1} - i\eta}
\]

where

\[
\psi_s^{N+1}(r) = \langle \Psi_0^N | \hat{\psi}(r) | \Psi_s^{N+1} \rangle \quad \text{with} \quad \varepsilon_s^{N+1} = E_s^{N+1} - E_0^N
\]

\[
\psi_s^{N-1}(r) = \langle \Psi_0^N | \hat{\psi}^\dagger(r) | \Psi_s^{N-1} \rangle \quad \text{with} \quad \varepsilon_s^{N-1} = E_0^N - E_s^{N-1}
\]
Which information is contained in the Green's function?

\[ G(\mathbf{r}', \mathbf{r}) = \sum_s \frac{\psi_s^{N+1}(\mathbf{r}') \psi_{s}^{N+1}(\mathbf{r})^*}{\omega - \varepsilon_{s}^{N+1} + i\eta} + \sum_s \frac{\psi_s^{N-1}(\mathbf{r}) \psi_{s}^{N-1}(\mathbf{r}')^*}{\omega - \varepsilon_{s}^{N-1} - i\eta} \]

\[ \varepsilon_{s}^{N+1} = E_{s}^{N+1} - E_0^N \]

\[ \varepsilon_{s}^{N-1} = E_0^N - E_{s}^{N-1} \]

Poles of Green's function give energies of added/removed electron (charged excitations)
How can we obtain the Green's function of a given many electron system?
From the equation of motion (EOM) for the annihilation field operator:

\[ i \partial_t \hat{\psi}(\mathbf{r}, t) = \left[ \hat{\psi}(\mathbf{r}, t), \hat{H} \right] \]

with Hamiltonian (in term of field operators)

\[ \hat{H} = \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) h(\mathbf{r}) \hat{\psi}(\mathbf{r}) + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}) \hat{\psi}(\mathbf{r}') \]

one particle operator = Kinetic + external

two-particle operator (Coulomb)
We obtain an EOM for the Green's function

Using time-ordered Green's function definition:

\[ i \partial_t G(r, t; r', t') = \delta(r - r')\delta(t - t') + h(r)G(r, t; r', t') \]

\[ -i \int dr'' v(r, r'') \langle \Psi_0^N | \hat{T}[\hat{\psi}(r'', t + 2\eta)\psi(r', t + \eta)\psi(r, t)\psi^{\dagger}(r', t')|\Psi_0^N\rangle |_{\eta \to 0^+} \]

which however depends on 2-particles Green's function

\[ G_2(1, 2, 3, 4) = (i)^2 \langle \Psi_0^N | \hat{T}[\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^{\dagger}(4)\hat{\psi}^{\dagger}(3)]|\Psi_0^N\rangle \]

\[ 1 \equiv (r_1, t_1) \]

infinite hierarchy of n-particles Green's function...
Let's introduce the mass operator

\[
i\partial_t G(r, t; r', t') = \delta(r - r')\delta(t - t') + h(r)G(r, t; r', t') + \int dr'' M(r, t; r''t'')G(r'', t; r', t')
\]

We need to find an operative expression

\[
\int dr'' M(r, t; r''t'')G(r'', t; r', t') = -i \int dr'' v(r, r'')\langle \Psi_0^N | \hat{T}[\hat{\psi}^\dagger(r'', t)\hat{\psi}(r'', t)\hat{\psi}(r, t)\hat{\psi}^\dagger(r', t')] | \Psi_0^N \rangle
\]

Many-Body perturbation theory

\[+V \rightarrow 0 \quad \text{Schwinger functional derivative}\]
Following the Schwinger functional derivative method

Change of Green's function to addition of 'fake' external potential

\[ \frac{\delta G(1, 2)}{\delta V(3)} \bigg|_{V=0} = G(1, 2) G(3, 3^+) - G_2(1, 2, 3, 3^+) \]

allows to define:

\[ M(\mathbf{r}, t; \mathbf{r}', t'') = \int d\mathbf{r}' n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'') + \sum \frac{\delta G(34)}{\delta V(5)} G^{-1}(52) \]

\[ \Sigma(12) = v(13) \frac{\delta G(34)}{\delta V(5)} G^{-1}(52) \]

= Hartree Potential + self-energy

and rewrite:

\[ i\partial_t G(\mathbf{r}, t; \mathbf{r}', t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') + \left( h(\mathbf{r}) + v_H(\mathbf{r}) \right) G(\mathbf{r}, t; \mathbf{r}', t') \]

\[ + \int d\mathbf{r}'' \sum \delta(\mathbf{r}, t; \mathbf{r}'', t'') G(\mathbf{r}'', t; \mathbf{r}', t') \]
Taking the Fourier transform (time to frequency space)

\( i \partial_t G(r, t; r', t') = \delta(r - r')\delta(t - t') + h_0(r)G(r, t; r', t') \)

\[ + \int dr'' \Sigma(r, t; r''; t'')G(r'', t; r', t') \]

defining \( (i \partial_t - h_0(1)) G_0(1, 2) = \delta(12) \)

& assuming steady state (dependence on t-t' only)

\[ G(r, t; r'; \omega) = G_0(r, t; r'; \omega) + \int \int dr'' dr''' G_0(r, t; r''; \omega)\Sigma(r'', t''; \omega)G(r'''', r'; \omega) \]

interacting = non-interacting + self-energy corrections
Carrying on with Schwinger functional derivative method eventually obtain Hedin equations set of coupled integro-differential equation for:

\[ G = g_0 + g_0 S g \]
Carrying on with Schwinger functional derivative method eventually obtain Hedin equations:

can be iterated analytically:

\[ v + vPW = W \]

\[ \Sigma = iGW \Gamma \]

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

\[ -iGG \Gamma = P \]

\[ \Gamma = \delta \delta - \frac{\delta \Sigma}{\delta G} G \Gamma G \]
What is the physics we need to "put into" the self-energy?
Let's look at the potential due to an additional electron

Let's neglect interaction between additional electron and electron system:

\[ v(r, r') = \frac{1}{|r - r'|} \]

This gives the Fock self-energy:

\[ \Sigma_x(r, r') = i \int d\omega \, G_0(r, r'; \omega) v(r, r') \]
A test charge in an electron system induces a perturbation in the electron density:

\[ n_{\text{ind}}(\mathbf{r}'', \mathbf{r}; \tau) = \int d\mathbf{r}' R(\mathbf{r}'', \mathbf{r}'; \tau) n(\mathbf{r}', \mathbf{r}) \]

= density response \( \times \) potential change in \( \mathbf{r}' \) due to charge in \( \mathbf{r} \)

\[ R(\mathbf{r}, t; \mathbf{r}', t') = \frac{\delta n(\mathbf{r}, t)}{\delta V(\mathbf{r}', t')} \bigg|_{V=0} \]

where density response = change in density at \( \mathbf{r} \) due to change in potential
In turn the induced charge changes (screens) the Coulomb potential.

Screened potential in \( r' \) due to test charge in \( r \):

\[
W(r', r; \tau) = v(r', r) + \int dr'' v(r', r'') n^{\text{ind}}(r'', r; \tau)
\]

\[
= \int dr'' \epsilon^{-1}(r'', r; \tau) v(r', r'')
\]

= bare Coulomb + potential due to induced charge = inverse dielectric function X bare

with

\[
\epsilon^{-1}(r'', r; \tau) = \delta(r'' - r) + \int dr_1 R(r'', r_1; \tau) v(r_1, r)
\]
Let's look at the potential due to an additional electron when we consider the interaction between additional electron and electron system:

This gives the GW self-energy:

\[
\Sigma_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = i \int d\omega' \ G_0(\mathbf{r}, \mathbf{r}'; \omega') W(\mathbf{r}, \mathbf{r}'; \omega - \omega')
\]
What effect on the calculated band gap do you expect when adding the screening?
What effect on the calculated band gap do you expect when adding the screening?

- $h_0$: Hartree classical mean field potential
- $\Sigma_x$: Fock exchange Pauli correlation
- $\Sigma_c$: screening (less repulsion)
GW approximation for the self-energy can be obtained rigorously from Hedin's equations:

\[ v + vP_0 W = W \]

\[ \Sigma = 0 \]

\[ -iG_0 G_0 = P \]

\[ G = G_0 \]

\[ \Gamma = \delta \delta \]
GW approximation for the self-energy can be obtained rigorously from Hedin's equations.

iteration 1:

\[ \Sigma = iG_0W_0 \]

\[ G = G_0 + G_0\Sigma G \]
How can we implement a feasible computational scheme?
How can we implement a feasible computational scheme?

Recipe from Hedin's equations:

- Independent particle (Hartree)
- \( G_0 \)
- \( P = -iG_0 G_0 \)
- \( W = v + vP_0 W \)
- \( \Sigma = iG_0 W_0 \)
- \( G = G_0 + G_0 \Sigma G \)
- Polarization in the Random Phase Approximation (RPA)
- Screened potential
- \( G_0 \) approximation
- ExTract Excitations from poles
How can we implement a feasible computational scheme?

Recipe from Hedin's equations... problems!

Independent particle (Hartree)

$P = -iG_0 G_0$

$W = v + v P_0 W$

Screened potential

$\Sigma = i G_0 W_0$

$G_0 W_0$ approximation

Polarization in the Random Phase Approximation (RPA)

$G = G_0 + G_0 \Sigma G$

How to solve this???
How can we implement a feasible computational scheme?

**Modified recipe:**

- \( G_0 = G_s \)
- \( P = -iG_0G_0 \)
- \( W = v + vP_0W \)
- \( \Sigma = iG_0W_0 \)
- \( \Sigma = iG_0W_0 \)
- \( G = G_0 + G_0(\Sigma - v_{xc})G \)

**Rationale:**

- \( \phi_s^{KS} \approx \psi_s^{N\pm 1} \)
- \( \langle \phi_i^{KS} | \hat{\Sigma} | \phi_j^{KS} \rangle \approx 0 \)

Excitations from first order Perturbation theory
In more detail one starts from a DFT calculation to obtain the Kohn-Sham eigensolutions and calculate the non-interacting Green's function:

\[
G_0(r, r'; \omega) = \sum_{s}^{\text{occ}} \frac{(\phi_{\text{KS}}(r))^* \phi_{\text{KS}}(r')}{\omega - \varepsilon_{s}^{\text{KS}} - i\eta} + \sum_{s}^{\text{unocc}} \frac{(\phi_{\text{KS}}(r))^* \phi_{\text{KS}}(r')}{\omega - \varepsilon_{s}^{\text{KS}} + i\eta}
\]

solution of EOM:

\[
\left( i\partial_t - h_0(1) - v_{xc} \right) G_0(1, 2) = \delta(12)
\]
Then evaluates the inverse dielectric function and screened potential

Polarisation:

\[
P(r, r'; \omega) = \sum_{i}^{\text{occ}} \sum_{a}^{\text{unocc}} \phi_i(r) \phi_a^*(r) \phi_i^*(r') \phi_a(r') \\
\times \left( \frac{1}{\omega + \varepsilon_i - \varepsilon_a + i\eta} - \frac{1}{\omega - \varepsilon_i + \varepsilon_a - i\eta} \right)
\]

Dielectric matrix:

\[
\epsilon(r, r'; \omega) = \delta(r - r') - \int dr'' v(r, r'') P_0(r'', r'; \omega)
\]

Inverse:

\[
\epsilon^{-1}(r, r'; \omega), \quad W(r, r'; \omega) \quad \text{in a given basis (algebraic problem!)}
\]
Then the self-energy matrix elements

Exchange part (Fock), quite straightforward:

\[
\langle \phi_s | \Sigma_x | \phi_s \rangle = \sum_i \int \int d\mathbf{r} d\mathbf{r}' \frac{\phi_i(\mathbf{r}) \phi^*_i(\mathbf{r}) \phi^*_s(\mathbf{r}') \phi_s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\]

Correlation part (screening), requires integration over frequencies - expensive...

\[
\langle \phi_s | \Sigma_c | \phi_s \rangle \quad \text{non trivial - numerical tricks/approximations needed to efficiently treat/reduce to analytical integral over frequencies}
\]
Finally calculates **perturbatively** the excitation energies

\[
G(r, r'; \omega) = G_0(r, r'; \omega) + \int \int dr'' dr''' G_0(r; r''; \omega) \left( \Sigma(r''; r'''; \omega) - v_{xc}(r'') \delta(r'' - r''') \right) G(r''', t; r', t')
\]

Perturbation to KS solution

At first order:

\[
\phi_s^{KS} \approx \psi_s^{N \pm 1}
\]

\[
\langle \phi_i^{KS} | \hat{\Sigma} | \phi_j^{KS} \rangle \approx 0
\]

\[
E_s = \varepsilon_s + \langle \phi_s | \Sigma(E_s) - v_{xc} | \phi_s \rangle
\]

nonlinear!
Finally calculates **perturbatively** the excitation energies.

\[ E_s = \varepsilon_s + \langle \phi_s | \Sigma(E_s) - v_{xc} | \phi_s \rangle \]

Linearising (Newton):

\[ \Sigma(E_s) \approx \Sigma(\varepsilon_s) + (E_s - \varepsilon_s) \frac{\partial \Sigma(\varepsilon)}{\partial \varepsilon} \]

\[ E_s = \varepsilon_s + Z_s \langle \phi_s | \Sigma(\varepsilon_s) - v_{xc} | \phi_s \rangle \]

\[ Z_s = \left( 1 - \langle \phi_s | \frac{\partial \Sigma(\omega)}{\partial \omega} | \omega = \varepsilon_s | \phi_s \rangle \right)^{-1} \]

*renormalization factor*
How does this approach work?

It corrects the underestimation of the LDA and takes calculated band-gaps close to the experimental values:

\[ E_s = \varepsilon_s + Z_s \langle \phi_s | \Sigma(\varepsilon_s) - v_{xc} | \phi_s \rangle \]

Can you trace back all approximations we made in obtaining the working equations?
Can you trace back all approximations we made in obtaining the working equations?

stopping at first iteration (no vertex, RPA for polarization)

\[ \phi_s^{KS} \approx \psi_s^{N \pm 1} \]

\[ \langle \phi_i^{KS} | \hat{\Sigma} | \phi_j^{KS} \rangle \approx 0 \]

solving Dyson within first-order PT

... more in numerical solutions
G0W0 is not enough... 
...an example

lead telluride

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<th></th>
<th>a (Ang)</th>
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courtesy of Pablo Aguado-Puente
G0W0 is not enough...
...an example

lead telluride

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G0W0 is not enough...
...an example

projection of the bands on atomic-like wave functions:

Te: 5p

Pb: 6p

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G0W0 is not enough...
...an example

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G0W0 is not enough...  
...an example

For the closest k to the L point:  
in black $\Re(\langle n|\Sigma|m\rangle \langle m|\Sigma|n\rangle)$

The previous quantity weighted by the energy difference between states is plotted in red.

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Bibliography:

Interacting electrons: Theory and computational approaches

Application of the Green’s functions method to the study of the optical properties of semiconductors, G. Strinati
RIVISTA DEL NUOVO CIMENTO VOL. 11, N. 12 1988

Electronic Excitations: Density-Functional vs Many-body Green's, G. Onida, L. Reining, A. Rubio

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2. Yambo: an ab initio tool for excited state calculations 