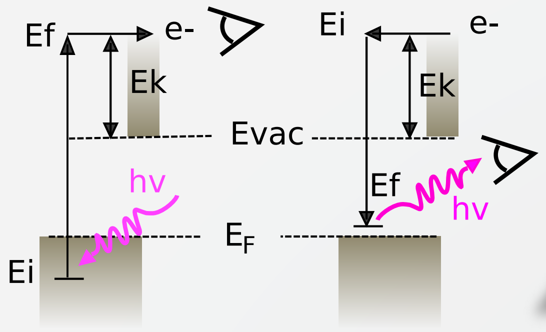
Which is the key strategy of Density-Functional-Theory to attack the many-body problem?

Which is the key strategy of Density-Functional-Theory to attack the many-body problem?

Reduce the degrees of freedom

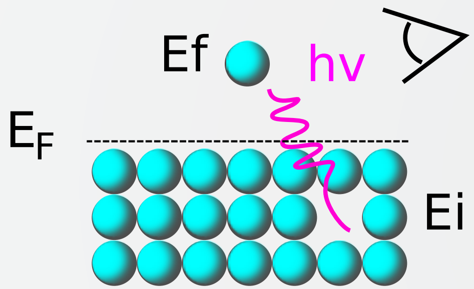
$$n(\mathbf{r}) = N \sum_s \int d\mathbf{x}_2 \cdots d\mathbf{x}_N |\Psi(\mathbf{r}s \cdots \mathbf{x}_M, \mathbf{x}_{M+1} \cdots \mathbf{x}_N)|^2$$

(Access only part of the information: ground state properties)



Target charged excitations in electronic system:

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



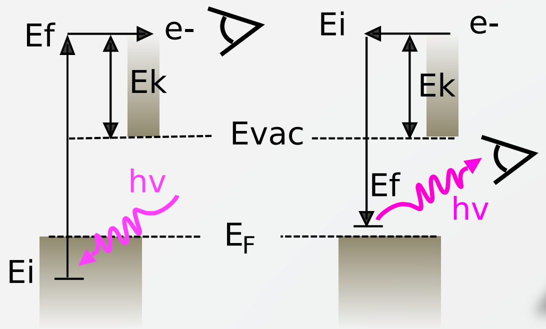
Target neutral excitations in electronic system:

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

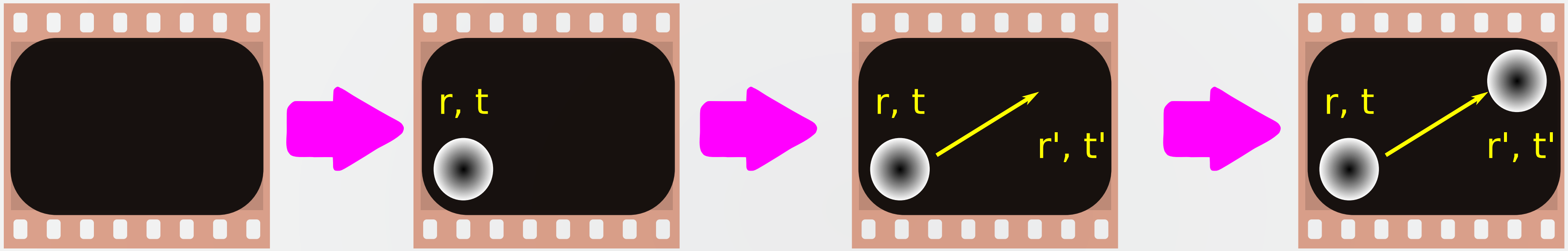
Discuss the assumptions...



Target charged excitations in electronic system:

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

Let's "watch" the propagation of an added electron:



$$|\Psi_0^N\rangle \qquad \hat{\psi}^\dagger(\mathbf{r})|\Psi_0^N\rangle \qquad \hat{U}(t',t)\hat{\psi}^\dagger(\mathbf{r})|\Psi_0^N\rangle \qquad \hat{\psi}(\mathbf{r}')\hat{U}(t',t)\hat{\psi}^\dagger(\mathbf{r})|\Psi_0^N\rangle$$

with:

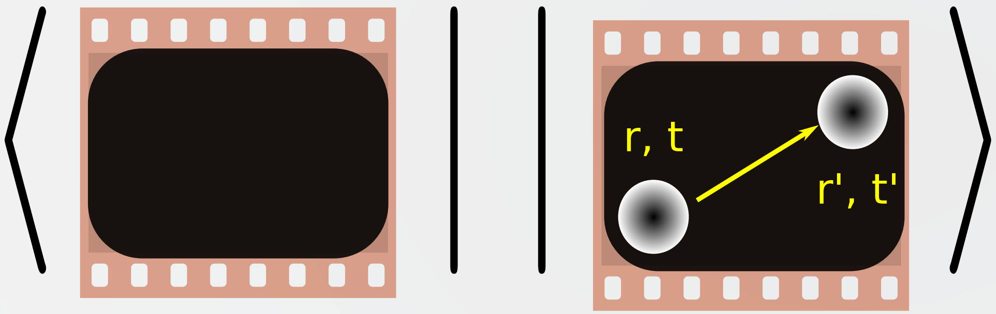
$|\Psi_0^N\rangle$ N-electron ground state

$\hat{\psi}(\mathbf{r}),\ \hat{\psi}^\dagger(\mathbf{r})$ 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'> t

Probability amplitude for propagation of additional electron from (r,t) to (r',t') in a many electron system:

=overlap final/initial states:



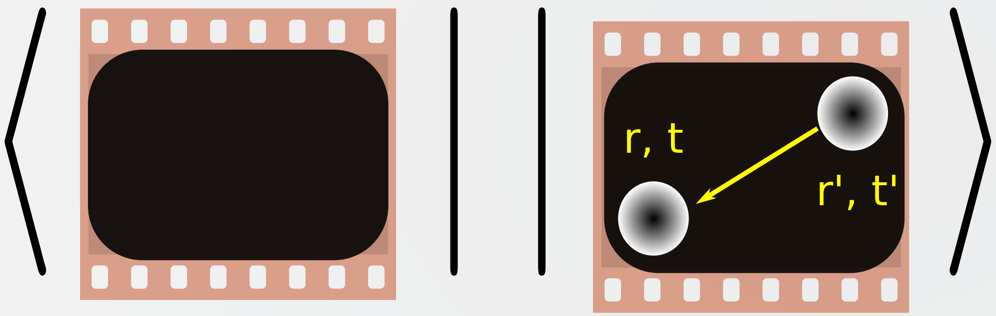
$$\langle \Psi_0^N | \qquad \hat{\psi}(\mathbf{r}')\hat{U}(t',t)\hat{\psi}^\dagger(\mathbf{r})|\Psi_0^N\rangle \equiv \hat{\psi}(\mathbf{r}',t')\psi^\dagger(\mathbf{r},t)|\Psi_0^N\rangle$$

=definition of Green's function:

$$iG^e(\mathbf{r}',t';\mathbf{r},t) = \langle \Psi_0^N|\hat{\psi}(\mathbf{r}',t')\hat{\psi}^\dagger(\mathbf{r},t)|\Psi_0^N\rangle\theta(t'-t)$$

Probability amplitude for propagation of additional hole from (r,t) to (r',t') in a many electron system:

=overlap final/initial states:



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

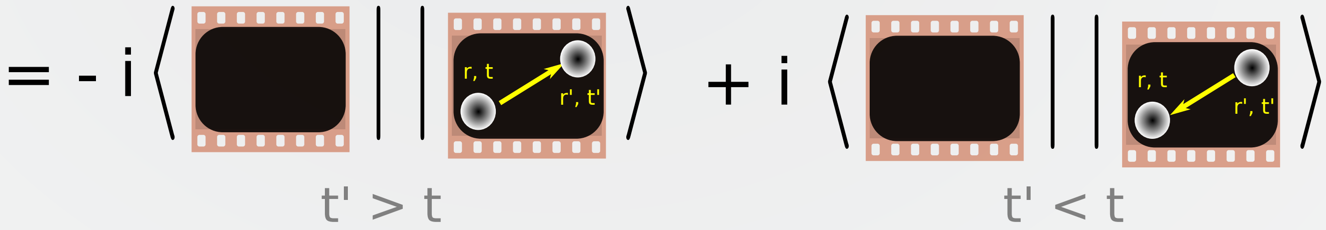
=definition of Green's function:

$$iG^h(\mathbf{r},t;\mathbf{r}',t') = \langle\Psi_0^N|\hat{\psi}^\dagger(\mathbf{r},t)\hat{\psi}(\mathbf{r}',t')|\Psi_0^N\rangle\theta(t-t')$$

We can so define the time-ordered Green's function

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

$$= G^e(\mathbf{r}',t';\mathbf{r},t) - G^h(\mathbf{r},t;\mathbf{r}',t')$$



$\hat{T}$ **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?

$$n(\mathbf{r}t) = \langle \Psi_0^N | \psi^\dagger(\mathbf{r},t)\psi(\mathbf{r},t) | \Psi_0^N \rangle = -iG(\mathbf{r},t;\mathbf{r},t+\eta)$$

η 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:

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

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:

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

where

$$\psi_s^{N+1}(\mathbf{r}) = \langle \Psi_0^N | \hat{\psi}(\mathbf{r}) | \Psi_s^{N+1} \rangle \qquad \varepsilon_s^{N+1} = E_s^{N+1} - E_0^N$$

with

$$\psi_s^{N-1}(\mathbf{r}) = \langle \Psi_0^N | \hat{\psi}^\dagger(\mathbf{r}) | \Psi_s^{N-1} \rangle \qquad \varepsilon_s^{N-1} = E_0^N - E_s^{N-1}$$

Which information is contained in the Green's function?

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

$$\varepsilon_s^{N+1} = E_s^{N+1} - E_0^N \qquad \varepsilon_s^{N-1} = E_0^N - E_s^{N-1}$$

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)

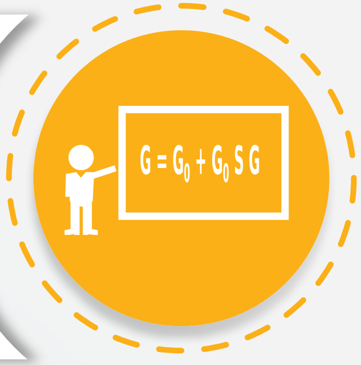
$$\hat{H} = \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) h(\mathbf{r}) \hat{\psi}(\mathbf{r}) +$$

ONE PARTICLE OPERATOR = KINETIC + EXTERNAL

$$\frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') v(\mathbf{r},\mathbf{r}') \hat{\psi}(\mathbf{r}) \hat{\psi}(\mathbf{r}')$$

TWO-PARTICLE OPERATOR (COULOMB)

We obtain an EOM for the Green's function



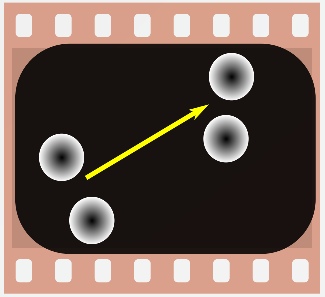
Using time-ordered Green's function definition:

$$i\partial_t G(\mathbf{r},t;\mathbf{r}',t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t') + h(\mathbf{r})G(\mathbf{r},t;\mathbf{r}',t')$$
$$- i\int d\mathbf{r}''\, v(\mathbf{r},\mathbf{r}'')\langle\Psi_0^N|\hat{T}[\hat{\psi}^\dagger(\mathbf{r}'',t)\hat{\psi}(\mathbf{r}'',t)\hat{\psi}(\mathbf{r},t)\hat{\psi}^\dagger(\mathbf{r}',t')|\Psi_0^N\rangle$$

which however depends on 2-particles Green's function

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

$$1 \equiv (\mathbf{r}_1, t_1)$$



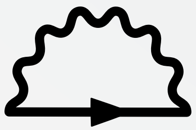
infinite hierarchy of n-particles Green's function...

Let's introduce the mass operator

$$i\partial_t G(\mathbf{r},t;\mathbf{r}',t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t') + h(\mathbf{r})G(\mathbf{r},t;\mathbf{r}',t') + \int d\mathbf{r}''\, M(\mathbf{r},t;\mathbf{r}''t'')G(\mathbf{r}'',t;\mathbf{r}',t')$$

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

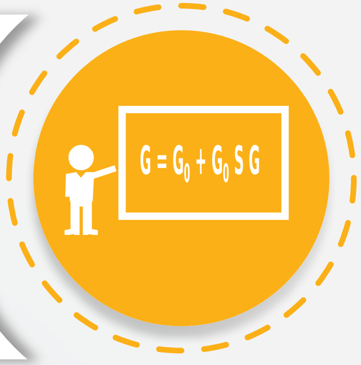
We need to find an operative expression



Many-Body perturbation theory

$+V \to 0$ Schwinger functional derivative

Following the Schwinger functional derivative method



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

$$\left.\frac{\delta G(1,2)}{\delta V(3)}\right|_{V=0} = G(1,2)\underbrace{G(3,3^+)}_{n(3)} - G_2(1,2,3,3^+)$$

allows to define: $$M(\mathbf{r},t;\mathbf{r}''t'') = \underbrace{\int d\mathbf{r}' n(\mathbf{r}') v(\mathbf{r}-\mathbf{r}')}_{v_H(\mathbf{r})} \delta(\mathbf{r}-\mathbf{r}'') + \underbrace{\Sigma(\mathbf{r},t;\mathbf{r}''t'')}_{\Sigma(12)=v(13)\frac{\delta G(34)}{\delta V(5)}G^{-1}(52)}$$

= HARTREE POTENITAL + SELF-ENERGY

and rewrite: $$i\partial_t G(\mathbf{r},t;\mathbf{r}',t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t') + \underbrace{(h(\mathbf{r}) + v_H(\mathbf{r}))}_{h_0(\mathbf{r})} G(\mathbf{r},t;\mathbf{r}',t')$$

$$+ \int d\mathbf{r}'' \, \Sigma(\mathbf{r},t;\mathbf{r}''t'') G(\mathbf{r}'',t;\mathbf{r}',t')$$

Taking the Fourier transform (time to frequency space)

$$i\partial_t G(\mathbf{r},t;\mathbf{r}',t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t') + h_0(\mathbf{r})G(\mathbf{r},t;\mathbf{r}',t') + \int d\mathbf{r}''\,\Sigma(\mathbf{r},t;\mathbf{r}''t'')G(\mathbf{r}'',t;\mathbf{r}',t')$$

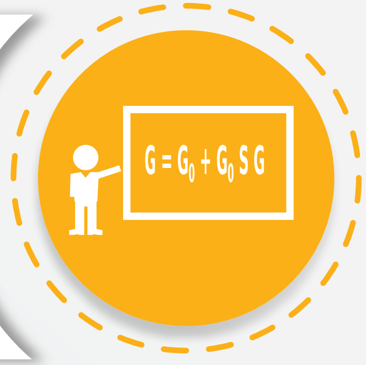
defining $(i\partial_t - h_0(1))\,G_0(1,2) = \delta(12)$

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

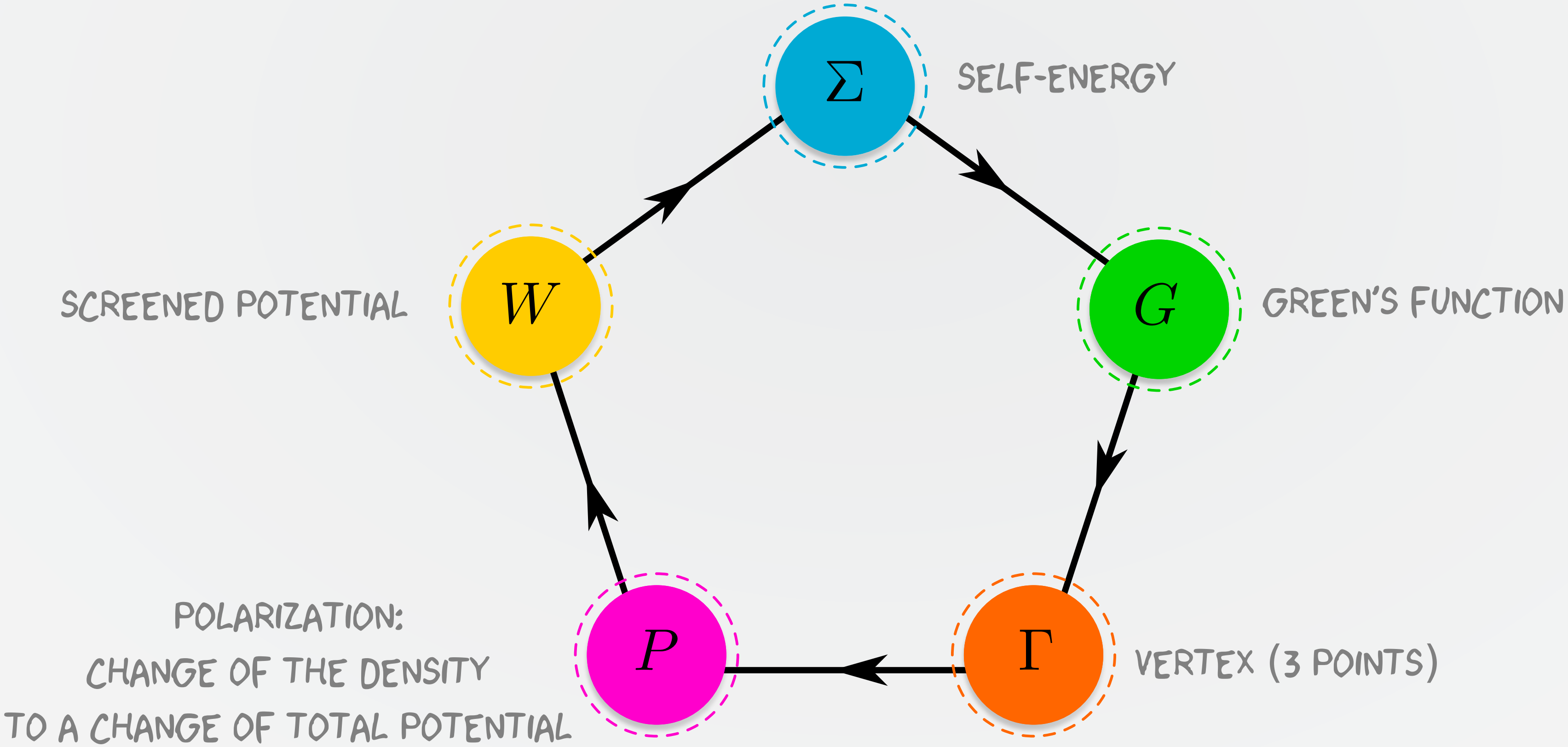
$$G(\mathbf{r},\mathbf{r}';\omega) = G_0(\mathbf{r},\mathbf{r}';\omega) + \iint d\mathbf{r}''d\mathbf{r}'''\,G_0(\mathbf{r};\mathbf{r}'';\omega)\Sigma(\mathbf{r}'',\mathbf{r}''';\omega)G(\mathbf{r}''',\mathbf{r}';\omega)$$

INTERACTING = NON-INTERACTING + SELF-ENERGY CORRECTIONS

Carrying on with
Schwinger functional derivative method
eventually obtain Hedin equations

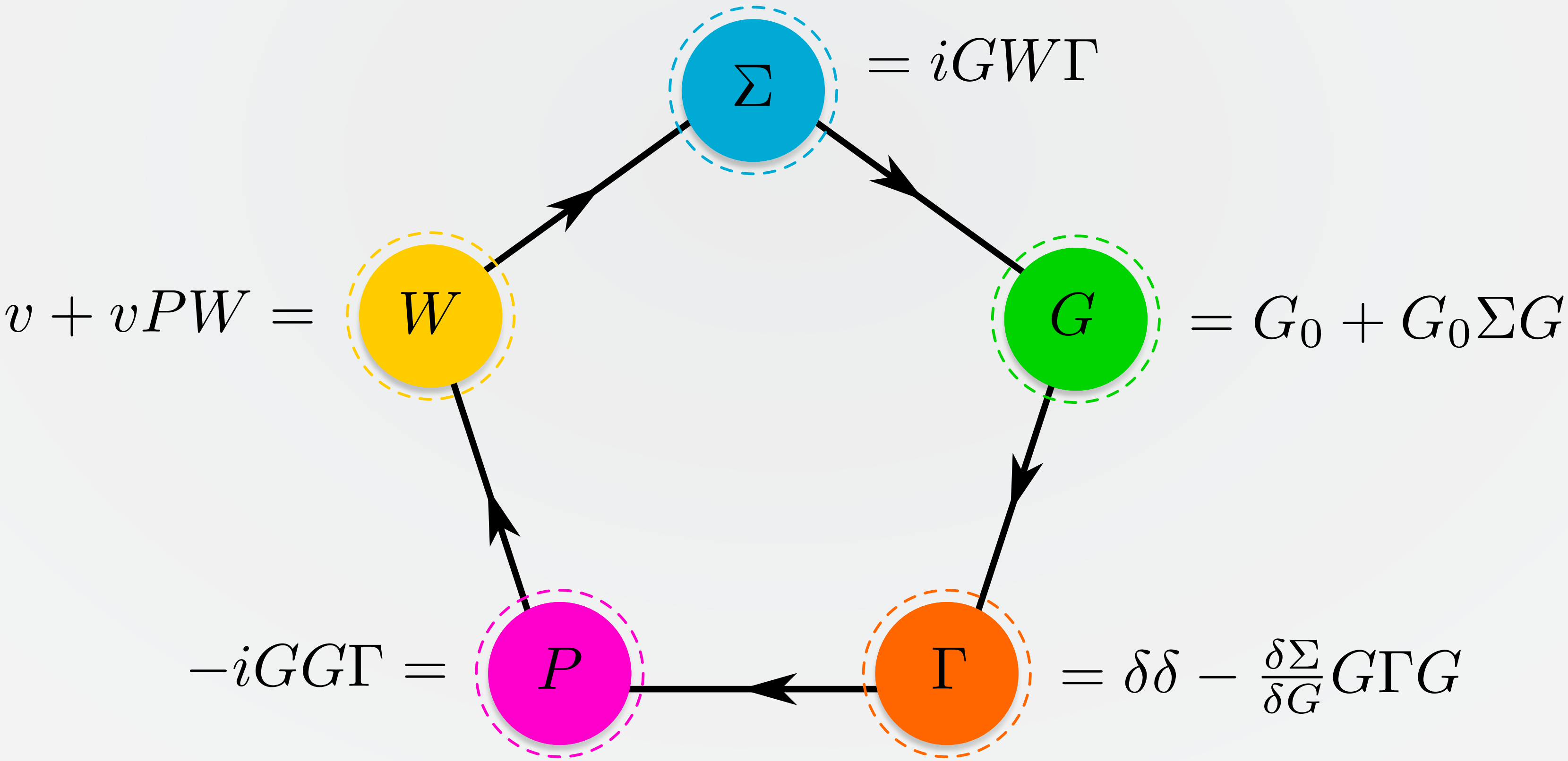


set of coupled integro-differential equation for:



Carrying on with Schwinger functional derivative method eventually obtain Hedin equations

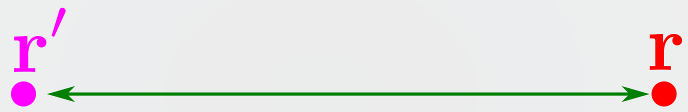
can be iterated analytically:



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:

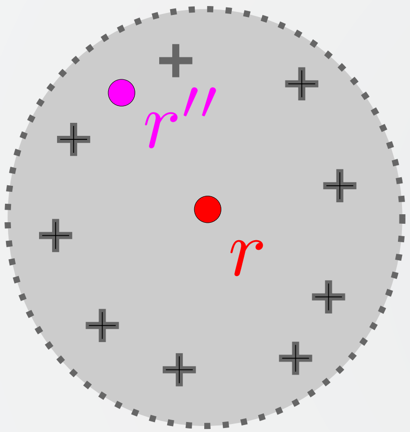


$$v(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

This gives the Fock self-energy:

$$\Sigma_x(\mathbf{r},\mathbf{r}') = i\int d\omega\, G_0(\mathbf{r},\mathbf{r}';\omega)v(\mathbf{r},\mathbf{r}')$$

A test charge in an electron system induces a perturbation in the eletron density



electron gas + positive background

INDUCED CHARGE IN R'' DUE TO CHARGE IN R =

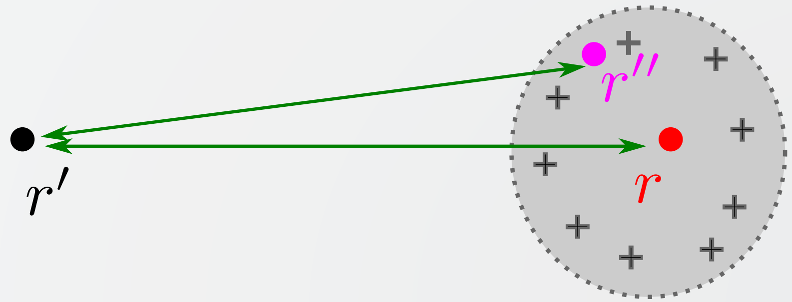
$$n^{\text{ind}}(\mathbf{r}'', \mathbf{r}; \tau) = \int d\mathbf{r}' R(\mathbf{r}'', \mathbf{r}'; \tau) v(\mathbf{r}', \mathbf{r})$$

= DENSITY RESPONSE X POTENTIAL CHANGE IN R' DUE TO CHARGE IN R

where $R(\mathbf{r}, t; \mathbf{r}', t') = \left. \dfrac{\delta n(\mathbf{r}, t)}{\delta V(\mathbf{r}', t')} \right|_{V=0}$

DENSITY RESPONSE = CHANGE IN DENSITY AT R DUE TO CHANGE IN POTENTIAL AT R'

In turn the induced charge changes (screens) the Coulomb potential



SCREENED POTENTIAL IN R' DUE TO TEST CHARGE IN R

$$W(\mathbf{r}',\mathbf{r};\tau) = v(\mathbf{r}',\mathbf{r}) + \int d\mathbf{r}'' v(\mathbf{r}',\mathbf{r}'') n^{\mathrm{ind}}(\mathbf{r}'',\mathbf{r};\tau)$$

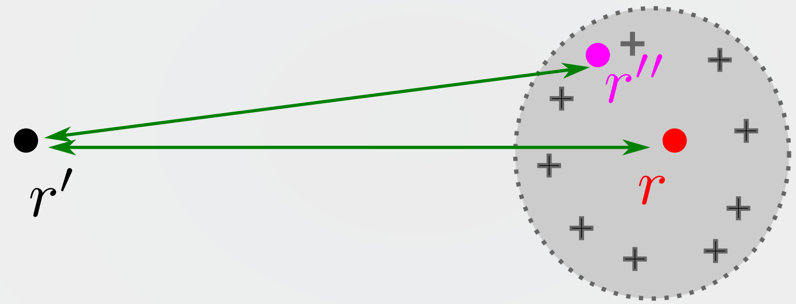
$$= \int d\mathbf{r}'' \epsilon^{-1}(\mathbf{r}'',\mathbf{r};\tau) v(\mathbf{r}',\mathbf{r}'')$$

= BARE COULOMB + POTENTIAL DUE TO INDUCED CHARGE = INVERSE DIELECTRIC FUNCTION X BARE COULOMB POTENTIAL

with $$\epsilon^{-1}(\mathbf{r}'',\mathbf{r};\tau) = \delta(\mathbf{r}''-\mathbf{r}) + \int d\mathbf{r}_1 R(\mathbf{r}'',\mathbf{r}_1;\tau) v(\mathbf{r}_1,\mathbf{r})$$

Let's look at the potential due to an additional electron

when we consider the interaction between
additional electron and electron system:

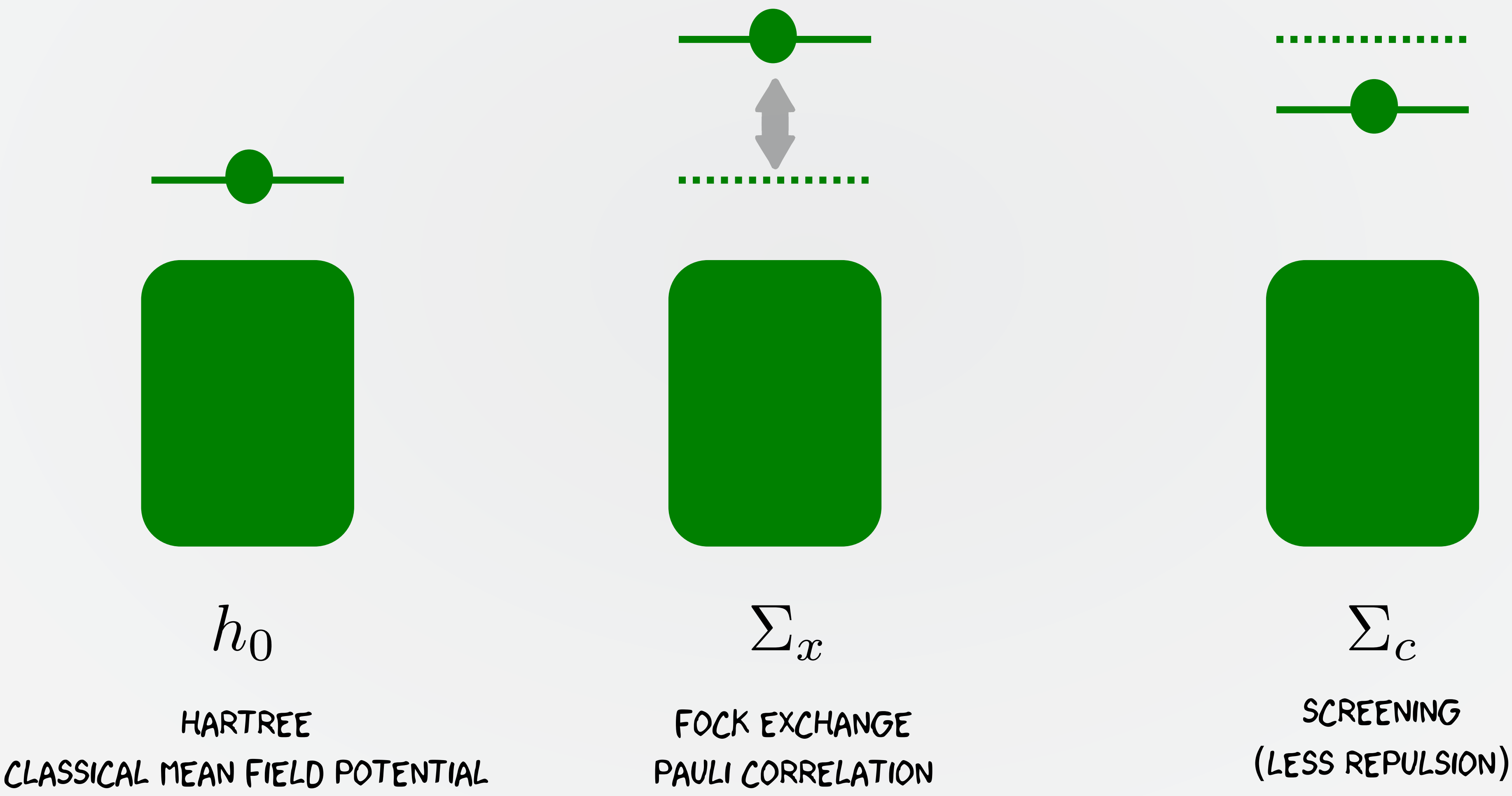


This gives the GW self-energy:

$$\Sigma_{xc}(\mathbf{r},\mathbf{r}';\omega) = i\int d\omega'\, G_0(\mathbf{r},\mathbf{r}';\omega')W(\mathbf{r},\mathbf{r}';\omega-\omega')$$

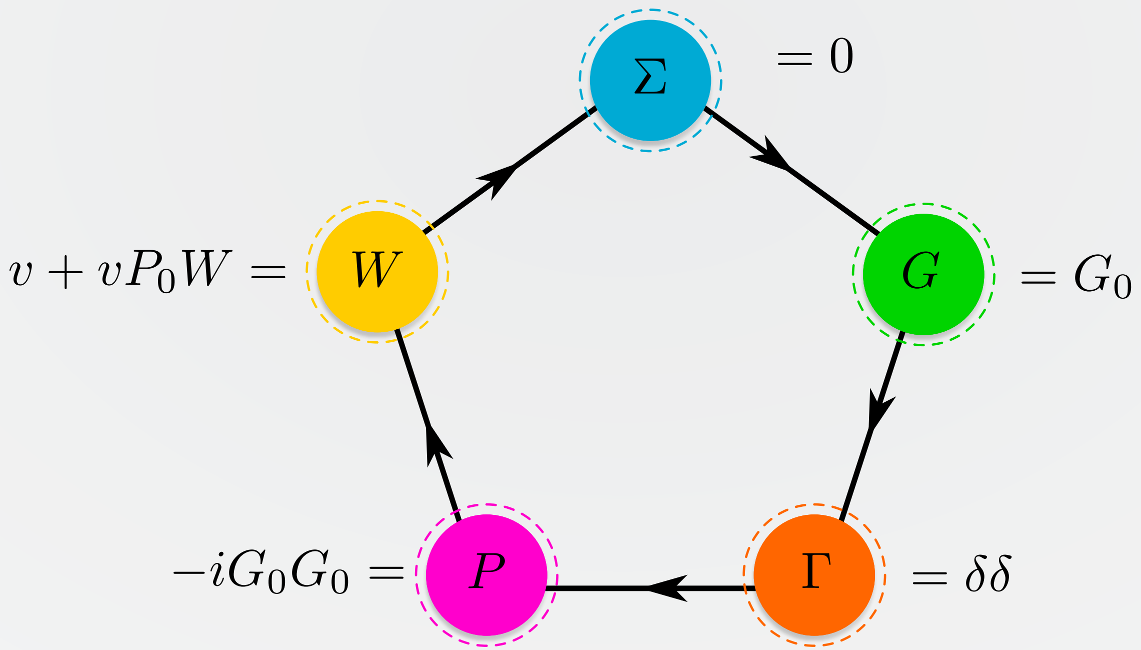
What effect on the calculated band gap do you expect when adding the screening?

What effect on the calculated band gap do you expect when adding the screening?



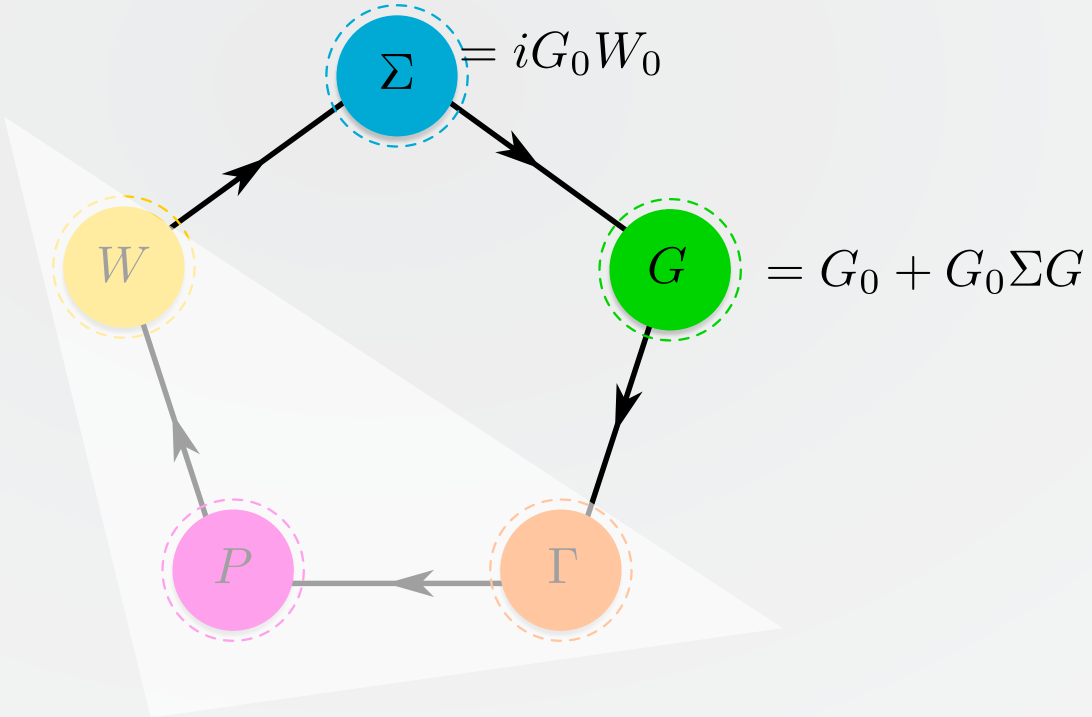
GW approximation for the self-energy can be obtained rigorously from Hedin's equations

iteration 0:



GW approximation for the self-energy can be obtained rigorously from Hedin's equations

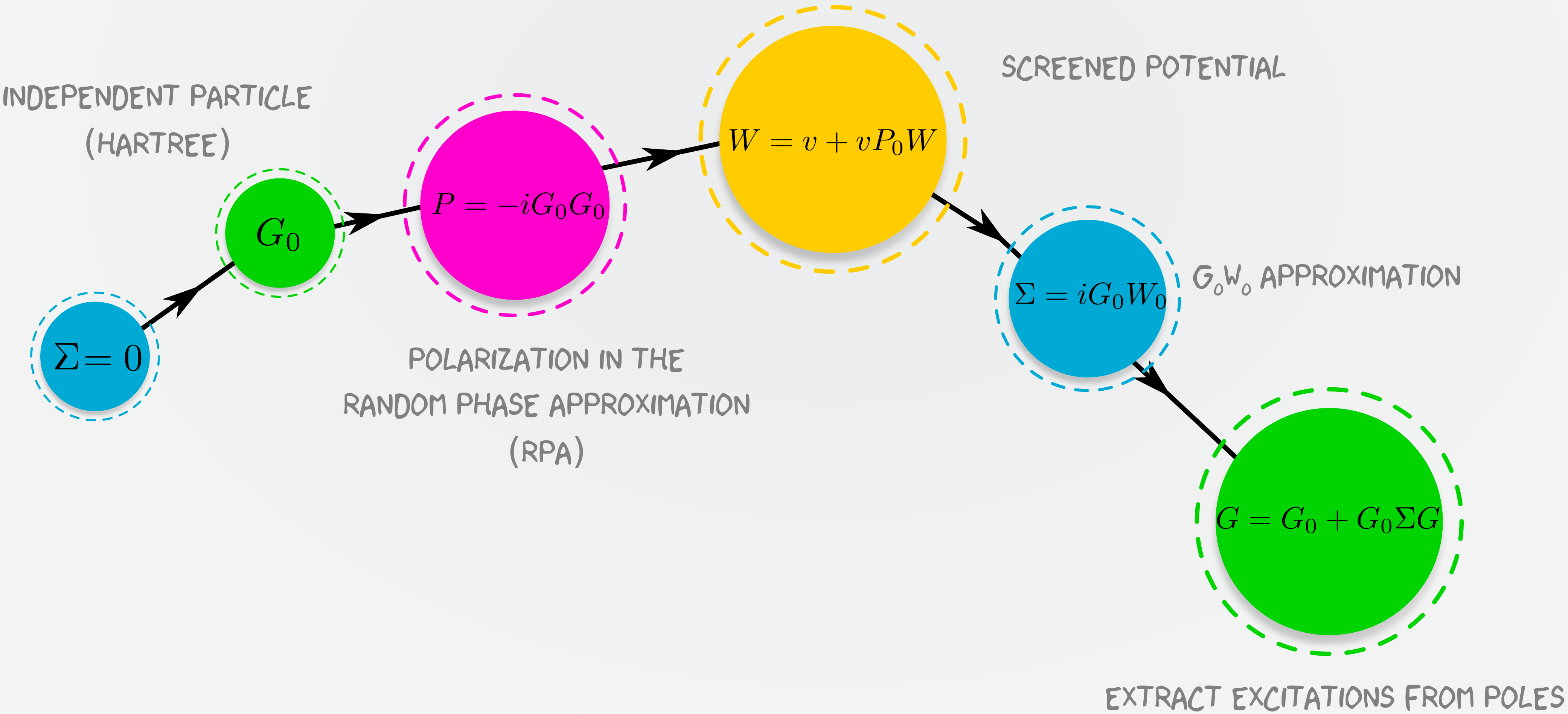
iteration 1:



How can we implement a feasible computational scheme?

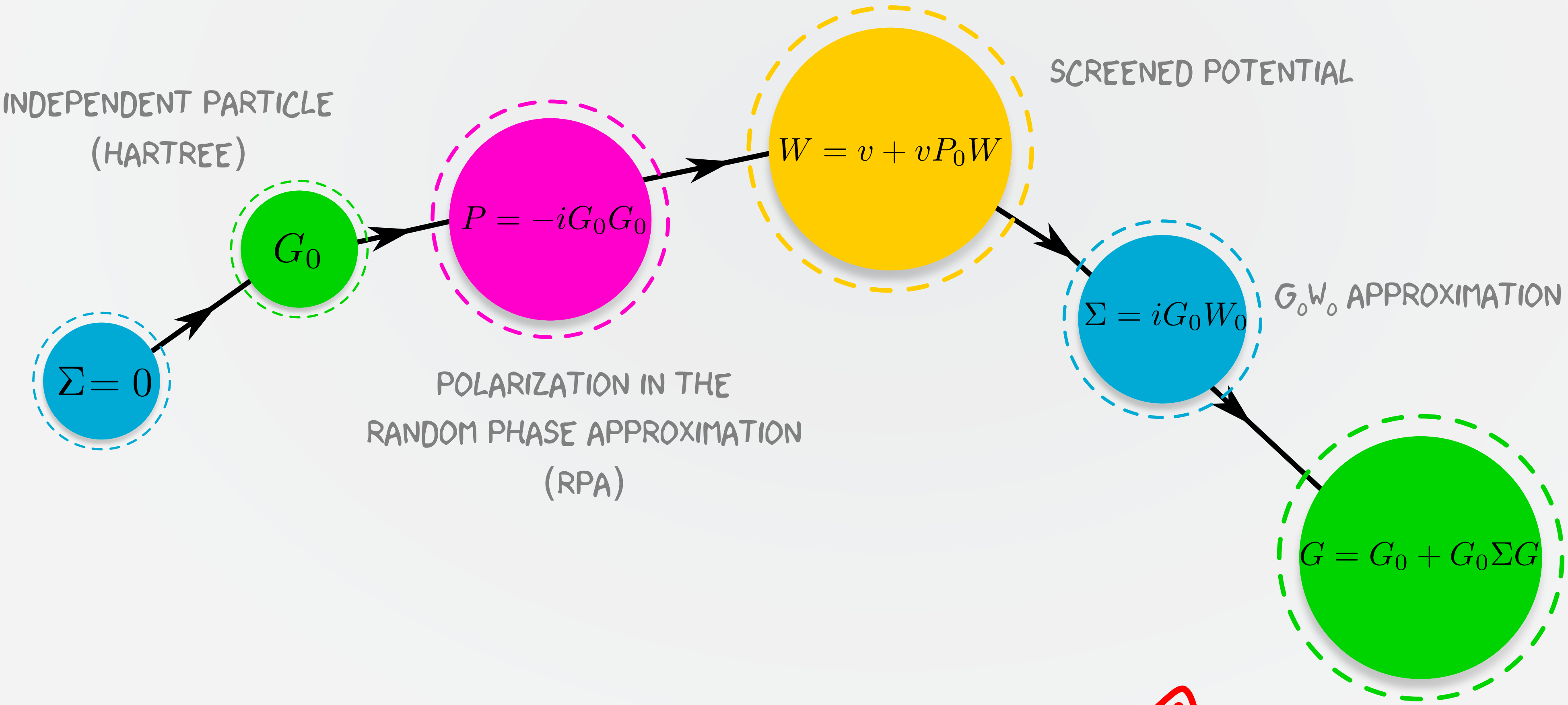
How can we implement a feasible computational scheme?

Recipe from Hedin's equations:



How can we implement a feasible computational scheme?

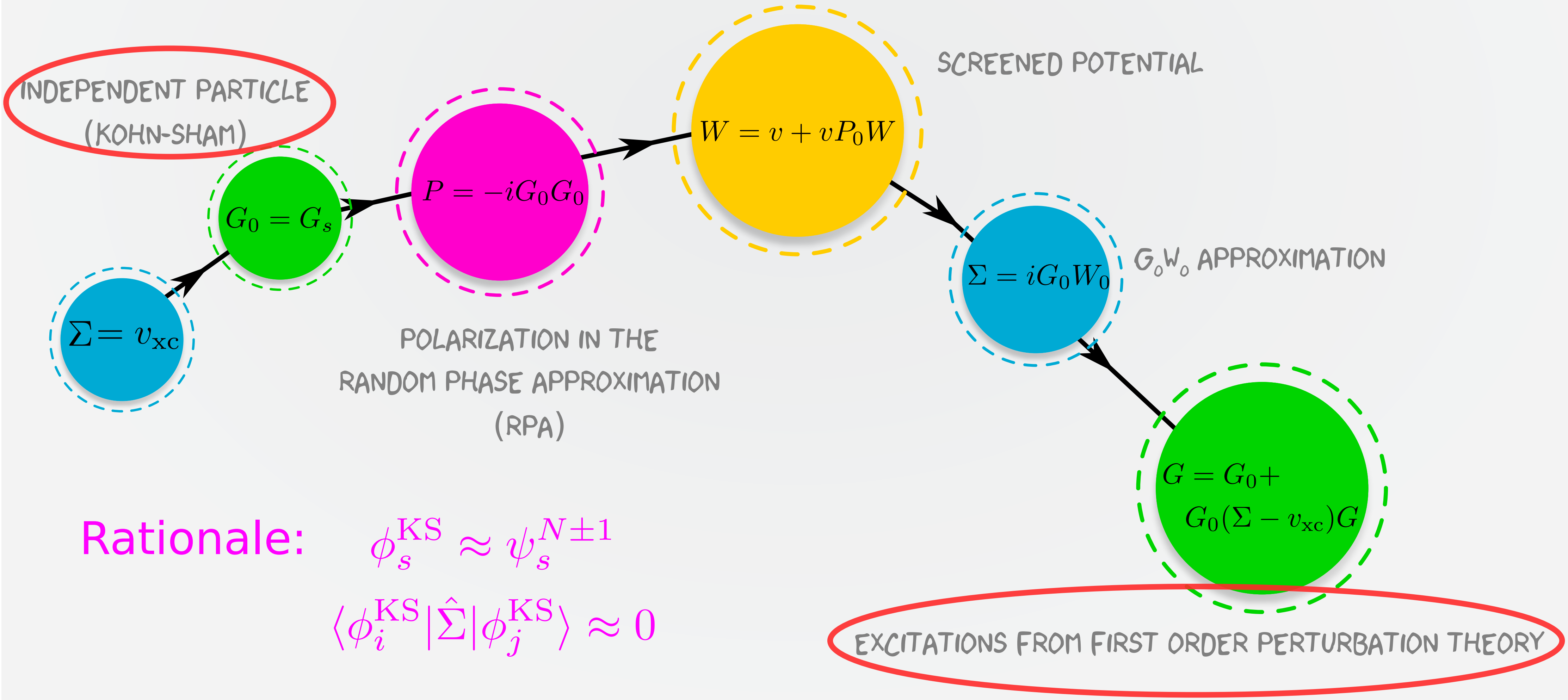
Recipe from Hedin's equations... problems!



How to solve this???

How can we implement a feasible computational scheme?

Modified recipe:



Rationale:

$$\phi_s^{\mathrm{KS}} \approx \psi_s^{N\pm1}$$

$$\langle \phi_i^{\mathrm{KS}} | \hat{\Sigma} | \phi_j^{\mathrm{KS}} \rangle \approx 0$$

In more detail one starts from
a DFT calculation to
obtain the Kohn-Sham eigensolutions

and calculate the non-interacting Green's function:

$$G_0(\mathbf{r},\mathbf{r}';\omega) = \sum_s^{\mathrm{occ}} \frac{(\phi^{\mathrm{KS}}(\mathbf{r}))^* \phi^{\mathrm{KS}}(\mathbf{r}')}{\omega - \varepsilon_s^{\mathrm{KS}} - i\eta} + \sum_s^{\mathrm{unocc}} \frac{(\phi^{\mathrm{KS}}(\mathbf{r}))^* \phi^{\mathrm{KS}}(\mathbf{r}')}{\omega - \varepsilon_s^{\mathrm{KS}} + i\eta}$$

solution of EOM:

$$\left(i\partial_t - \underbrace{h_0(1) - v_{\mathrm{xc}}}_{h^{\mathrm{KS}}} \right) G_0(1,2) = \delta(12)$$

Then evaluates the inverse dielectric function and screened potential

Polarisation:

$$P(\mathbf{r},\mathbf{r}';\omega) = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \phi_i(\mathbf{r})\phi_a^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_a(\mathbf{r}') \times \left(\frac{1}{\omega + \varepsilon_i - \varepsilon_a + i\eta} - \frac{1}{\omega - \varepsilon_i + \varepsilon_a - i\eta} \right)$$

Dielectric matrix:

$$\epsilon(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}') - \int d\mathbf{r}'' v(\mathbf{r},\mathbf{r}'') P_0(\mathbf{r}'',\mathbf{r}';\omega)$$

Inverse: $\epsilon^{-1}(\mathbf{r},\mathbf{r}';\omega),\ W(\mathbf{r},\mathbf{r}';\omega)$ IN A GIVEN BASIS (ALGEBRAIC PROBLEM!)

Then the self-energy matrix elements

EXCHANGE PART (FOCK), QUITE STRAIGHTFORWARD:

$$\langle \phi_s | \Sigma_x | \phi_s \rangle = \sum_i^{\mathrm{occ}} \iint d\mathbf{r} d\mathbf{r}' \frac{\phi_i(\mathbf{r}) \phi_s^*(\mathbf{r}) \phi_i^*(\mathbf{r}') \phi_s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

CORRELATION PART (SCREENING), REQUIRES INTEGRATION OVER FREQUENCIES - EXPENSIVE...

$$\langle \phi_s | \Sigma_c | \phi_s \rangle$$

non trivial - numerical tricks/approximations needed to efficiently treat/reduce to analytical integral over frequencies

Finally calculates **perturbatively** the excitation energies

$$G(\mathbf{r},\mathbf{r}';\omega) = G_0(\mathbf{r},\mathbf{r}';\omega)$$
$$+ \iint d\mathbf{r}''d\mathbf{r}'''\, G_0(\mathbf{r};\mathbf{r}'';\omega)\left(\Sigma(\mathbf{r}'';\mathbf{r}''';\omega) - v_{\mathrm{xc}}(\mathbf{r}'')\delta(\mathbf{r}''-\mathbf{r}'''')\right) G(\mathbf{r}''',t;\mathbf{r}',t')$$

PERTURBATION TO KS SOLUTION

At first order:

$$\phi_s^{\mathrm{KS}} \approx \psi_s^{N\pm1}$$

$$\langle\phi_i^{\mathrm{KS}}|\hat{\Sigma}|\phi_j^{\mathrm{KS}}\rangle \approx \delta_{ij}$$

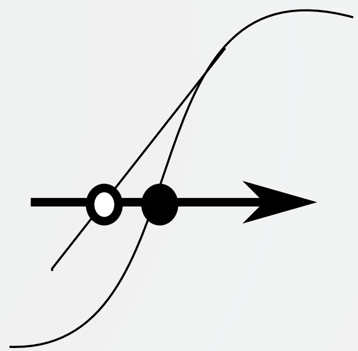
$$E_s = \varepsilon_s + \langle\phi_s|\Sigma(E_s) - v_{xc}|\phi_s\rangle$$

NONLINEAR!

Finally calculates **perturbatively** the excitation energies

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

Linearising (Newton): $\Sigma(E_s) \approx \Sigma(\varepsilon_s) + (E_s - \varepsilon_s)\,\frac{\partial \Sigma(\varepsilon)}{\partial \omega}$

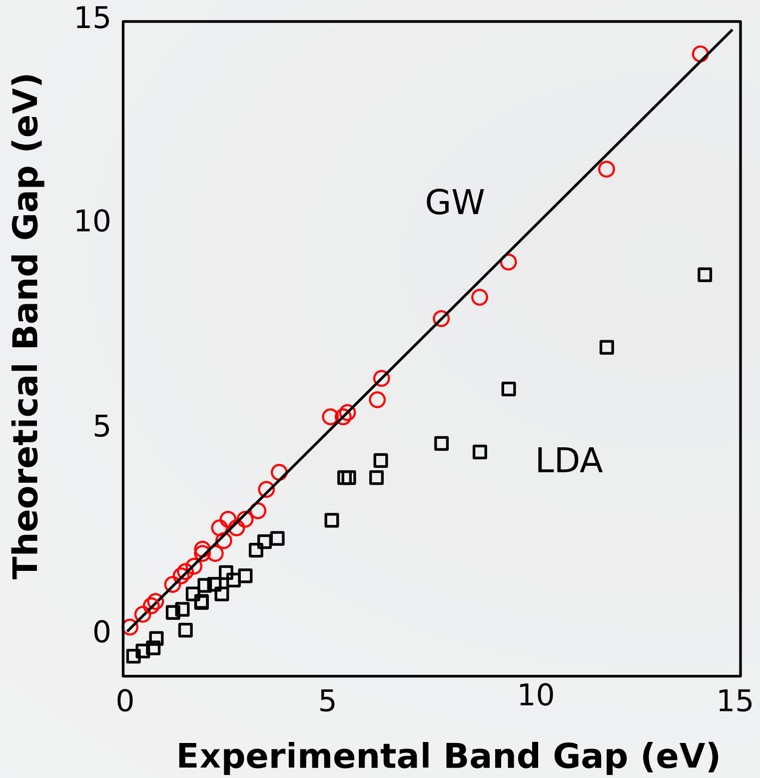


$$E_s = \varepsilon_s + Z_s \langle \phi_s | \Sigma(\varepsilon_s) - v_{xc} | \phi_s \rangle$$

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

RENORMALIZATION FACTOR

How does this approach work?



Hedin, J. Phys. Cond Matt 11, R489 (1999)

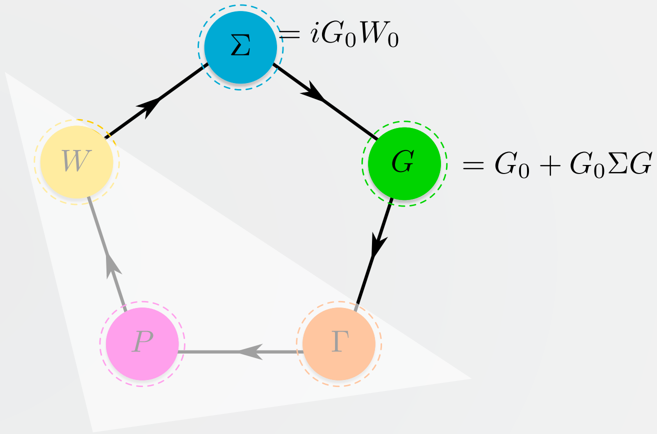
It corrects the underestimation of the LDA and takes calculated band-gaps close to the experimental values

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

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)

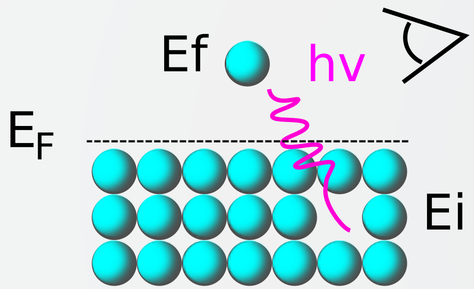


$$\phi_s^{\mathrm{KS}} \approx \psi_s^{N\pm1}$$

$$\langle\phi_i^{\mathrm{KS}}|\hat{\Sigma}|\phi_j^{\mathrm{KS}}\rangle \approx 0$$

solving Dyson
within first-order PT

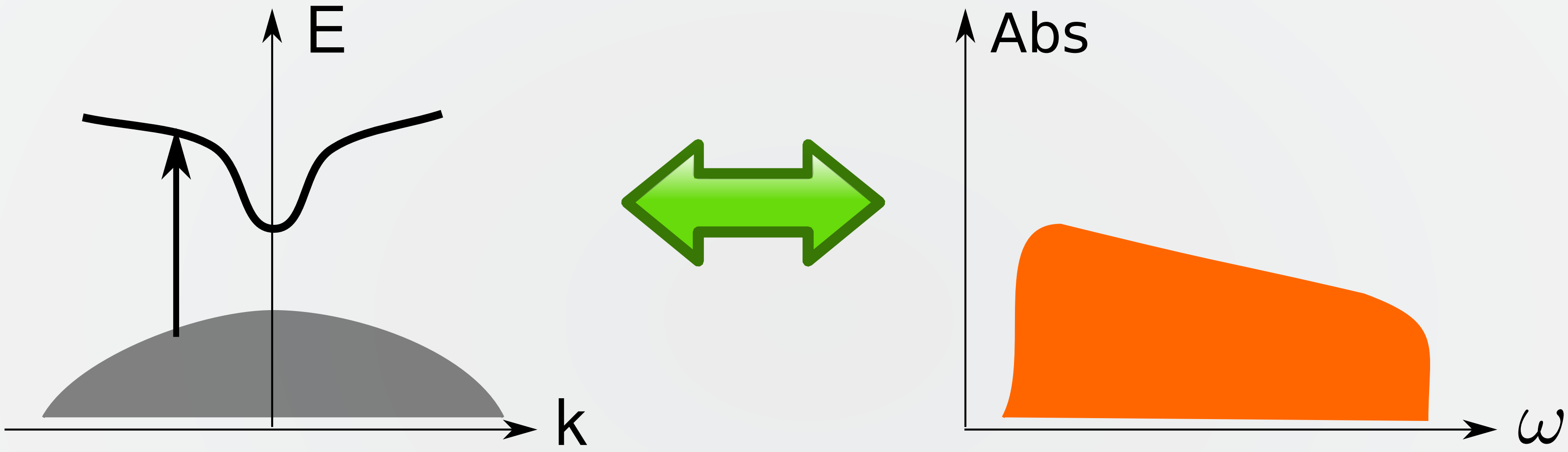
... more in numerical solutions



Target neutral excitations in electronic system:

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

Can we get optical excitations directly from the electronic structure?



Band structure

Optical absorption

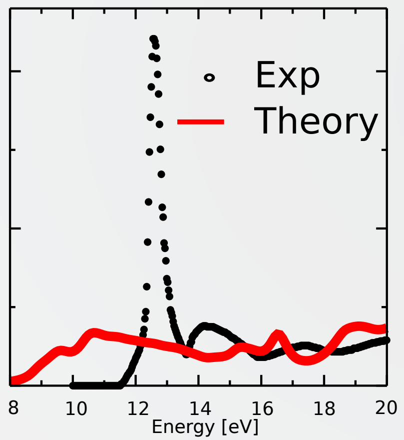
From Fermi-Golden rule + approximation $E_N^{\mathrm{fin}} - E_N^0 = E_{c\mathbf{k}} - E_{v\mathbf{k}}$

$$\mathrm{Abs}(\omega) \propto \sum_{v,c} \int_{\mathrm{BZ}} d\mathbf{k} |\langle v\mathbf{k}|\hat{D}|c\mathbf{k}\rangle|^2 \delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega)$$

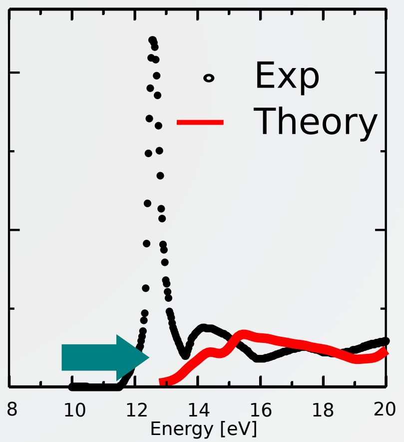
Does this approach give reasonable results?

Test against optical absorption in bulk LiF:

with Kohn-Sham band-structure



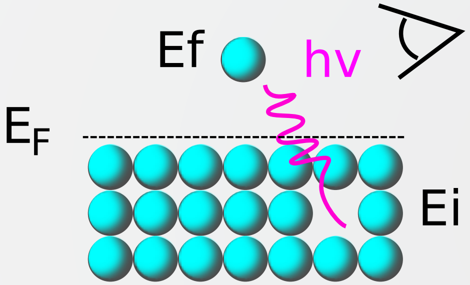
with quasiparticle band-structure



Fermi-Golden rule + approximation $E_N^{\mathrm{fin}} - E_N^0 = E_{c\mathbf{k}} - E_{v\mathbf{k}}$

$$\mathrm{Abs}(\omega) \propto \sum_{v,c} \int_{\mathrm{BZ}} d\mathbf{k} |\langle v\mathbf{k}|\hat{D}|c\mathbf{k}\rangle|^2 \delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega)$$

What physical effect is missing?



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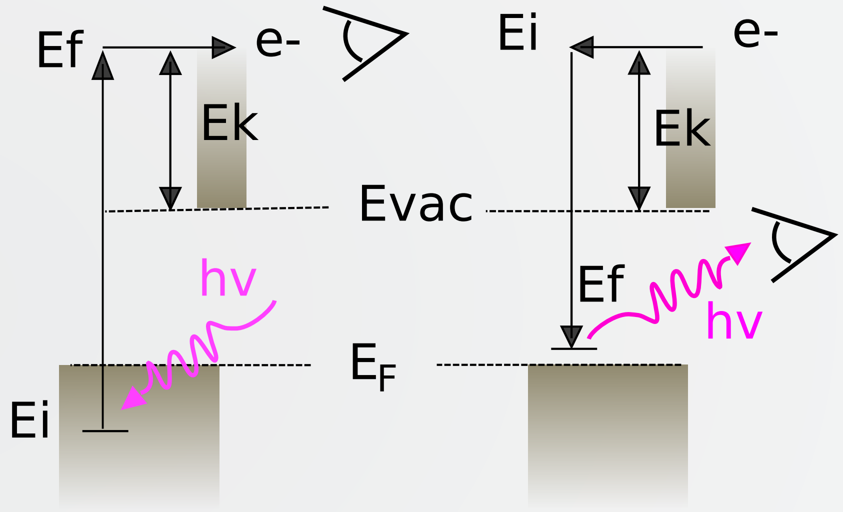


OPTICAL ABSORPTION ≠ SUM OF INVERSE/DIRECT PHOTOEMISSION PROCESSES

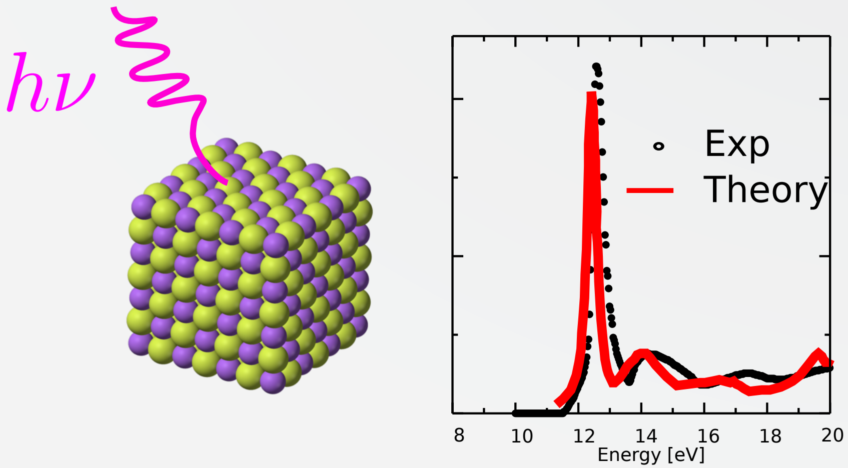
OPTICAL EXCITATION ENERGY ≠ DIFFERENCE OF QUASIPARTICLE ENERGIES

Missing physics is electron-hole interaction: coupling among transitions

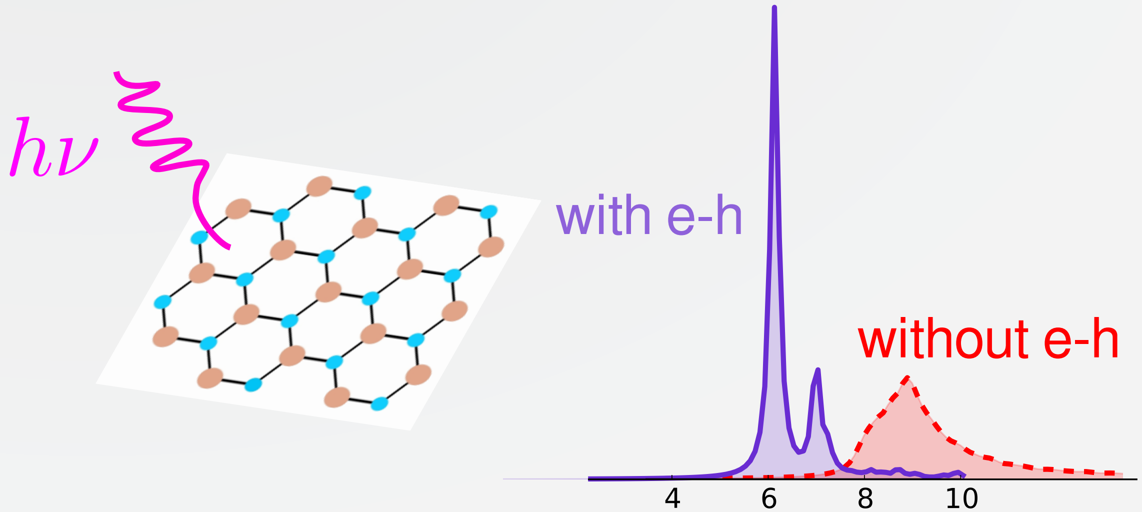
$$E_N^{\mathrm{fin}} - E_N^0 = E_\lambda \neq E_{c\mathbf{k}} - E_{v\mathbf{k}}$$

$$\mathrm{Abs}(\omega) \propto \sum_\lambda \sum_{v,c} \int_{\mathrm{BZ}} d\mathbf{k} \, |A_\lambda^{cv\mathbf{k}} \langle v\mathbf{k}|\hat{D}|c\mathbf{k}\rangle|^2 \delta(E_\lambda - \hbar\omega)$$

back to LiF optical spectrum

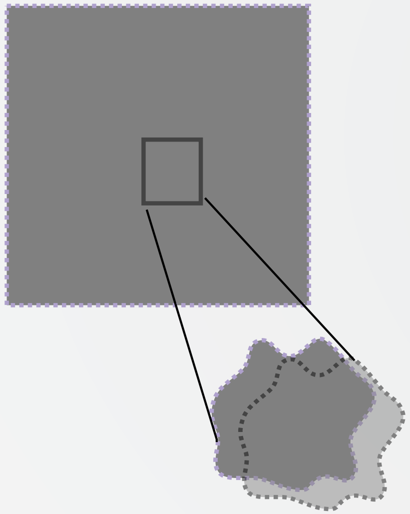


same effects in 2D materials



From which microscopic quantity can we get the optical absorption?

V_{ext} ASSOCIATED WITH LONGITUDINAL PART OF ELECTRIC DISPLACEMENT FIELD



@ MICROSCOPICAL LEVEL:

$$V_{\text{tot}} = V_{\text{ext}} + V_{\text{ind}}$$

$$\equiv v\delta\rho$$

Dielectric function:

IRREDUCIBLE: POLARIZABILITY

$$\epsilon = \frac{\delta V_{\text{ext}}}{\delta V_{\text{tot}}} = 1 - v\frac{\delta\rho}{\delta V_{\text{tot}}} = 1 - vP$$

$$\epsilon^{-1} = \frac{\delta V_{\text{tot}}}{\delta V_{\text{ext}}} = 1 + v\frac{\delta\rho}{\delta V_{\text{ext}}} = 1 + v\chi$$

POLARIZABILITY

Relation between polarizabilities:

$$\chi = P + Pv\chi$$

From which microscopic quantity can we get the optical absorption?

CONNECTION: MACROSCOPIC-MICROSCOPIC DIELECTRIC FUNCTION

$$\mathrm{Abs}(\omega) = \mathcal{I} \lim_{\mathbf{q}\to 0} (\epsilon_M(\mathbf{q},\omega)) = \mathcal{I}\left(\lim_{\mathbf{q}\to 0} \frac{1}{\epsilon^{-1}_{00}(\mathbf{q},\omega)} \right)$$

local fields

Introducing modified polarizability:

$$\bar{P} = P + P\bar{v}\bar{P} \quad \text{with} \quad \bar{v}_{\mathbf{G}} = v_{\mathbf{G}}(1-\delta_{\mathbf{G}0})$$

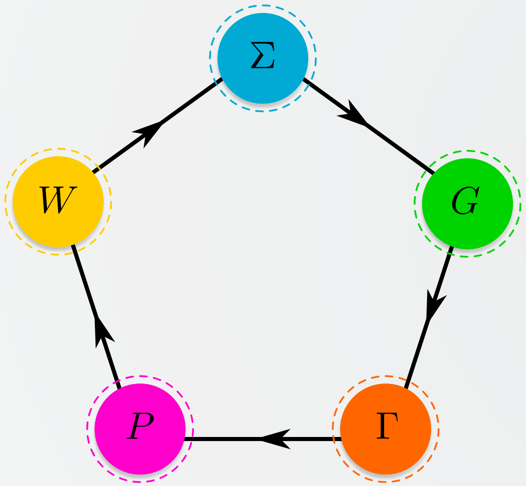
MICROSCOPIC PART

can be conveniently rewritten as:

$$\mathrm{Abs}(\omega) = \mathcal{I}\left(\lim_{\mathbf{q}\to 0} v_0(\mathbf{q})\bar{P}_{00}(\mathbf{q},\omega) \right)$$

Adler, Phys. Rev. 126 (1962); Wiser, Phys. Rev. 129 (1963);Hanke, Adv. Phys. 27 (1978)

How can we (formally) obtain the polarizability?



$$\chi(12) = \frac{\delta\rho(1)}{\delta V_{\text{ext}}(2)} \rightarrow {}^4L(1234) = \frac{\delta G(12)}{\delta V_{\text{ext}}(34)}$$

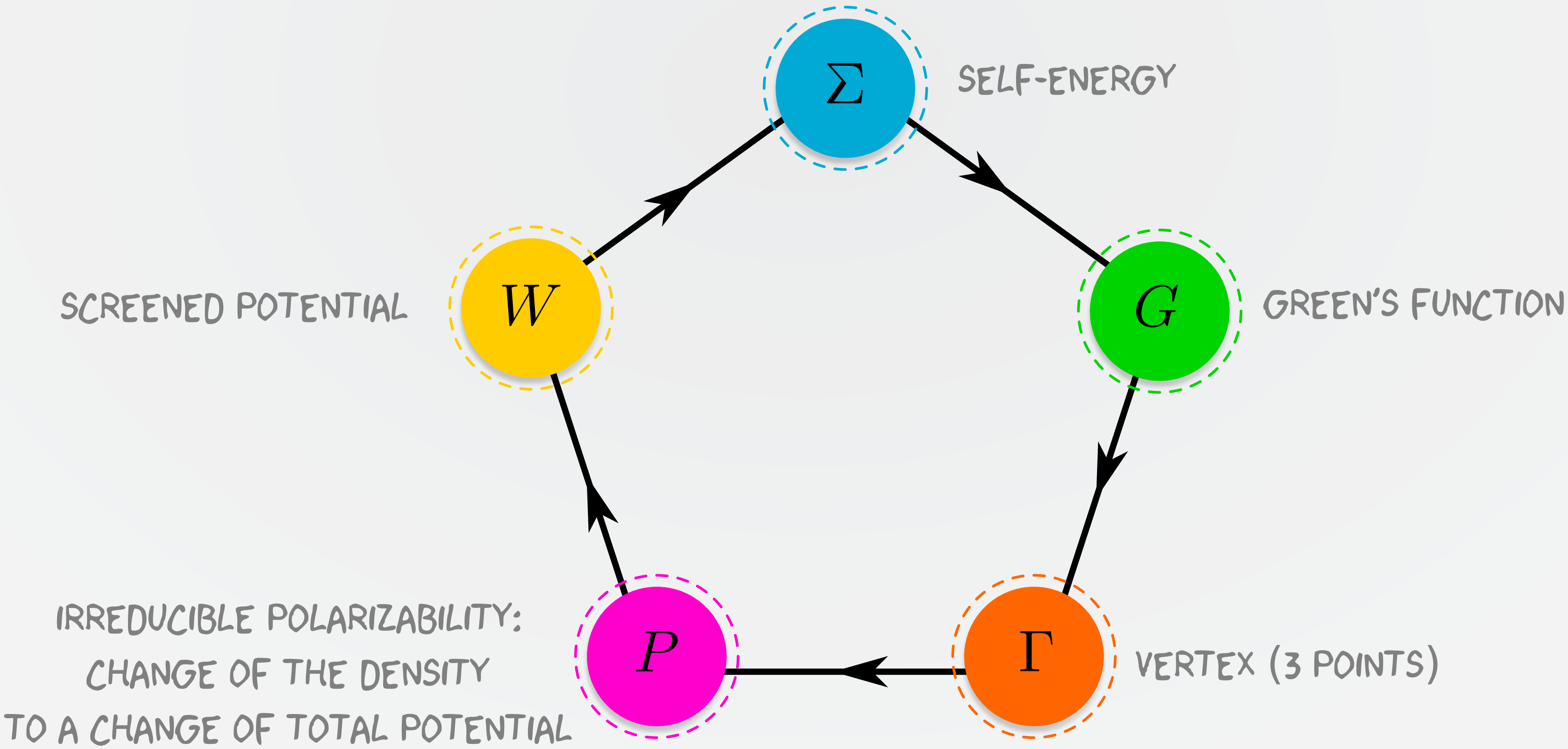
G. Strinati Riv. Nuovo Cim. 11, 12 (1988)

iteration of Hedin's equations which contain P

generalization of the polarizability to 4-point ...

Hedin's equations include the irreducible polarizability

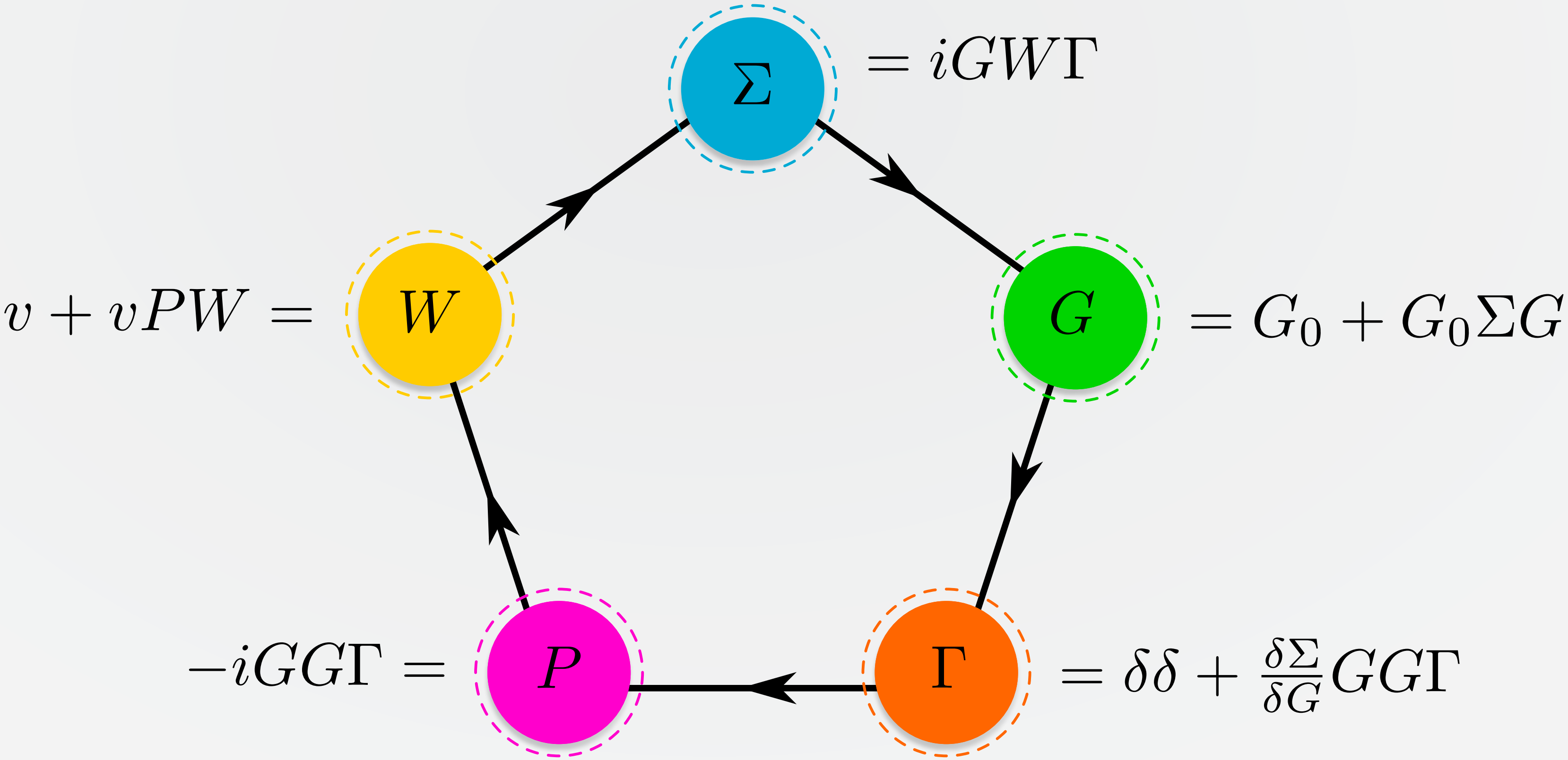
set of coupled integro-differential equation for:



L. Hedin, Phys. Rev. 139 (1965)

Hedin's equations include the irreducible polarizability

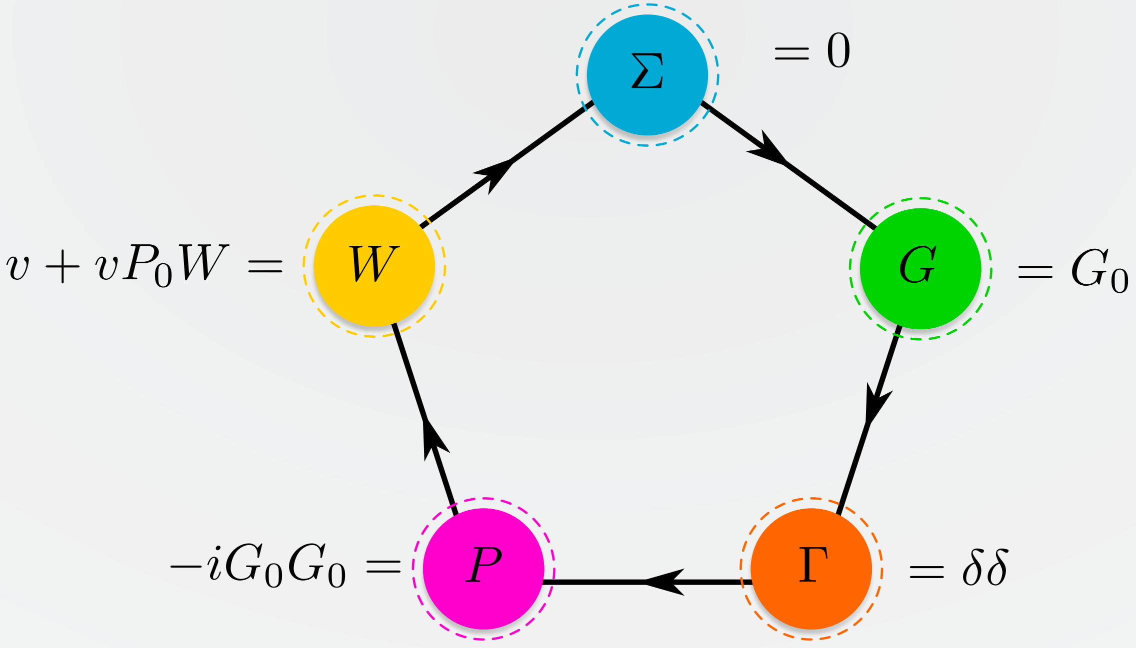
can be iterated analytically:



L. Hedin, Phys. Rev. 139 (1965)

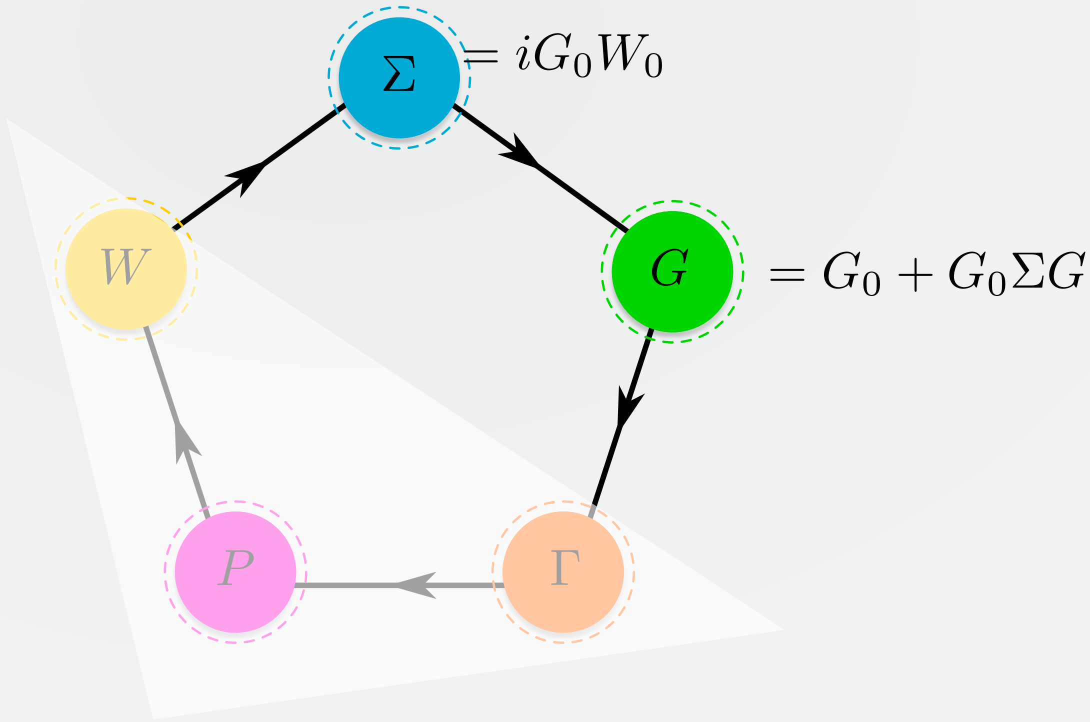
RPA polarization and screening are obtained setting self-energy = 0

iteration 0:



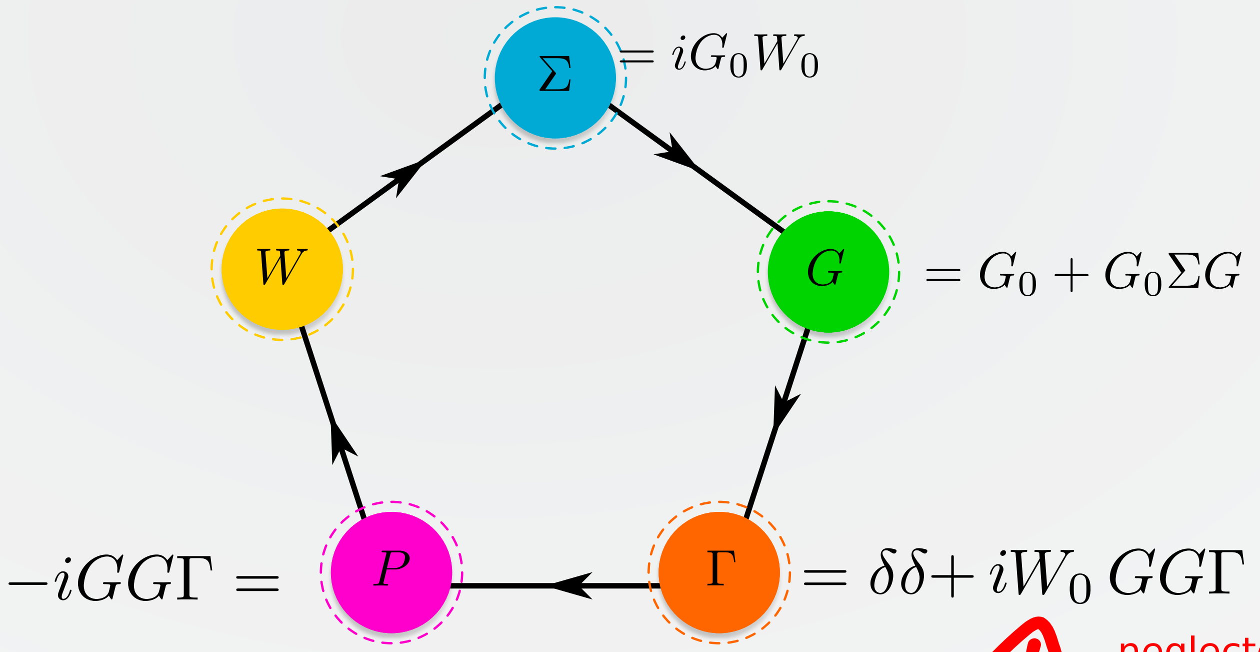
The G_0W_0 approximation to the self energy is obtained as first iteration...

iteration 1:



We can also get the vertex and the polarizability

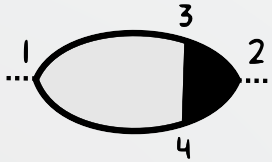
iteration 1:



neglected dependence
of W on G

Let's combine the equations for P and the vertex

$$P(12) = -i \int d(34) G(13) G(41) \Gamma(342)$$

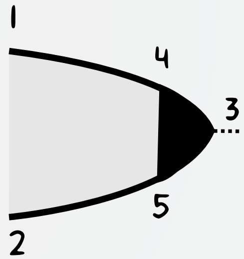


$1 \equiv \mathbf{r}_1, \sigma_1, t_1 \ldots$

$$\Gamma(123) = \delta(12)\delta(13) + iW(1^+2) \boxed{\int d(45) G(14) G(52) \Gamma(453)}$$

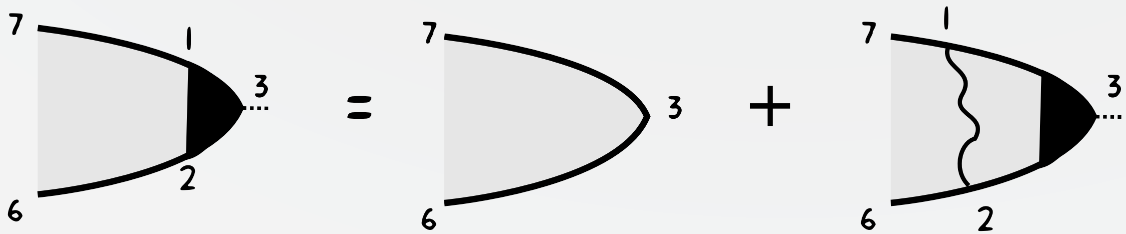
$i\,{}^3P(123)$

3-POINT POLARIZABILITY

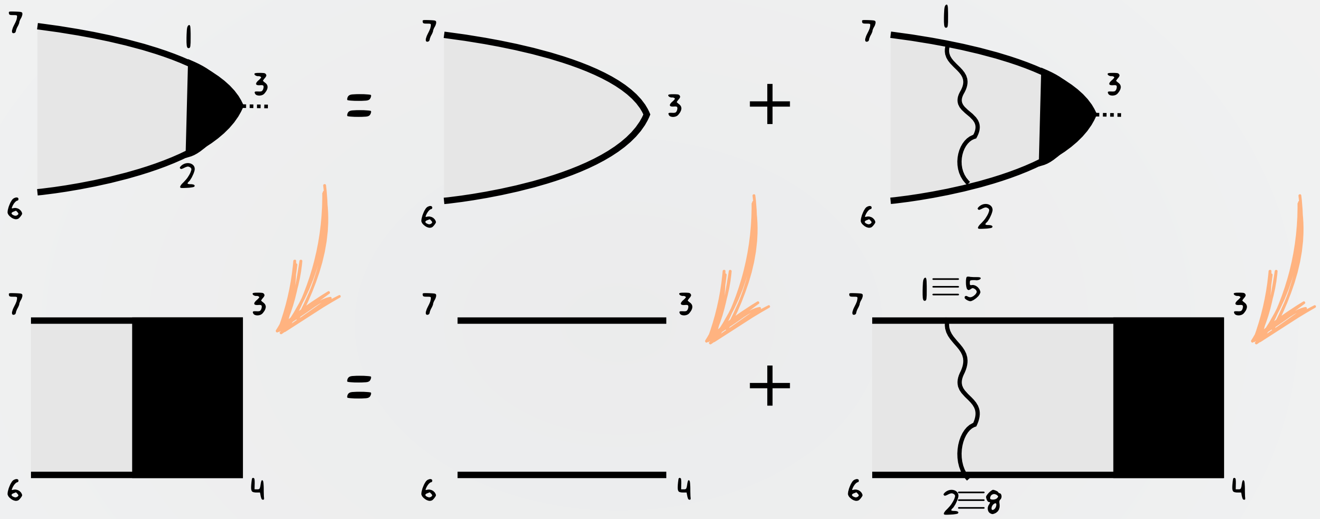


multiplying by -iGG both sides and integrate over (12):

$${}^3P(763) = -iG(73)G(36) + i \int d(12) W(1^+2) G(17) G(62)\, {}^3P(123)$$



Finally we get a Dyson-like equation for a 4-point polarizability



$$ {}^4P(7634) = {}^4P_0(7634) - \int d(1258)\, {}^4P_0(7612)\, {}^4W(1258)\, {}^4P(5834) $$

$$ {}^4P_0(7634) = -i\, G(73) G(64) \qquad {}^4W(1258) = W(1^+2)\delta(15)\delta(28) $$

For the optical absorption we need the modified 4-point polarizability

Symbolic representation of Dyson equation for 4-point irreducible polarizability:

$$^4P = {}^4P_0 + {}^4P_0\,(-{}^4W)\,{}^4P$$

In analogy with the 2-point case we define the 4-point modified polarizability as:

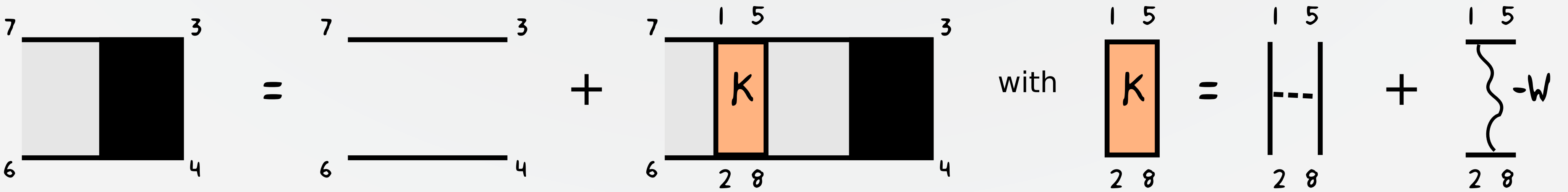
$$^4\bar{P} = {}^4P + {}^4P\,{}^4\bar{v}\,{}^4\bar{P}$$

+ DEF OF THE 4-POINT ANALOGUE OF THE MICROSCOPIC COULOMB POTENTIAL

Combining the two:

$$^4\bar{P} = {}^4P_0 + {}^4P_0\,{}^4\bar{K}\,{}^4\bar{P} \quad \text{with} \quad {}^4\bar{K} = {}^4\bar{v} - {}^4W$$

+ 4-POINT KERNEL



Bethe-Salpeter equation is expressed in terms of the two-particle correlation function

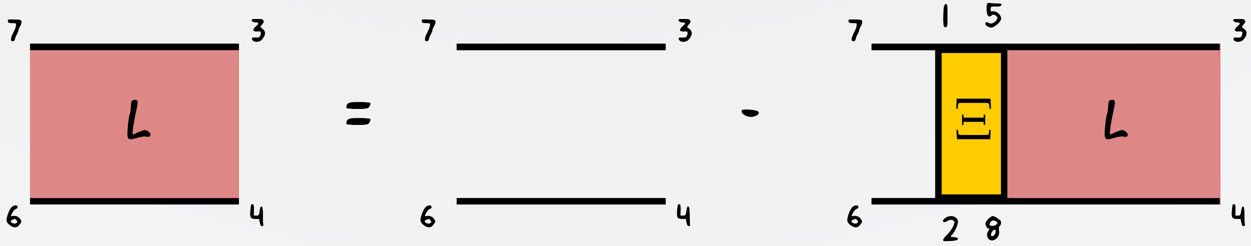
Two-particle correlation function:

$$L(1324) \equiv -G_2(1324) + G(12)G(34)$$

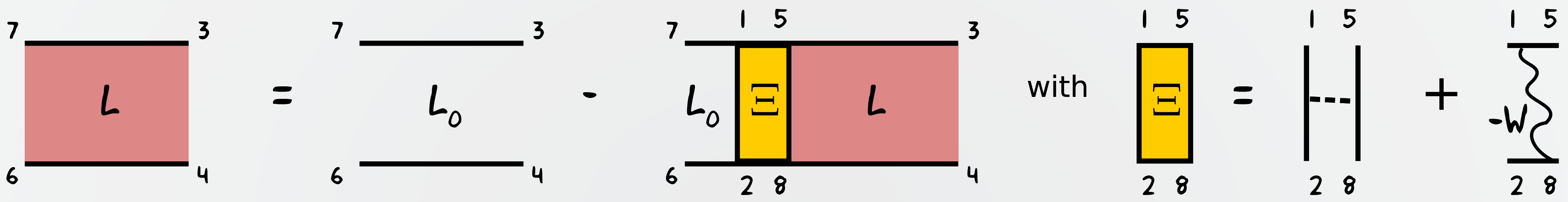
Related to the polarizability: $\bar{L} = -i^{\,4}\bar{P}$ (MODIFIED REDUCIBLE)

Bethe-Salpeter Equation: $\bar{L} = L_0 + L_0\,\Xi\,\bar{L}$

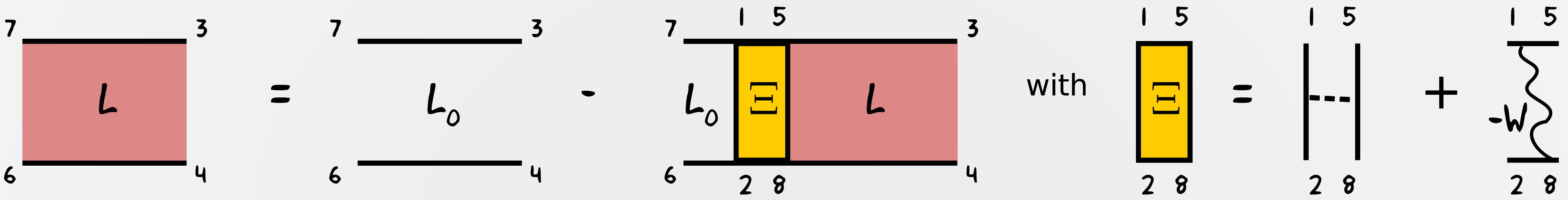
Bethe-Salpeter Kernel: $\Xi = -i^{\,4}K = -i\bar{v} + iW$



Quiz time!!!
Which approximations were introduced so far?



Several approximations entered the equation



Since we iterated Hedin's just twice:

- W is calculated within RPA
- in L_0, G is calculated at G_0W_0 (+ WE ARE SOLVING THE DYSON EQUATION FOR G PERTURBATIVELY)
- We neglected how the screening is changing with G — FUNCTIONAL DERIVATIVE OF SELF-ENERGY

We add a further one:

$$W(\mathbf{r},\mathbf{r}';t,t') \approx W(\mathbf{r},\mathbf{r}')\delta(t-t')$$

STATIC SCREENING!

How can we solve the Bethe-Salpeter in practice?

So far:

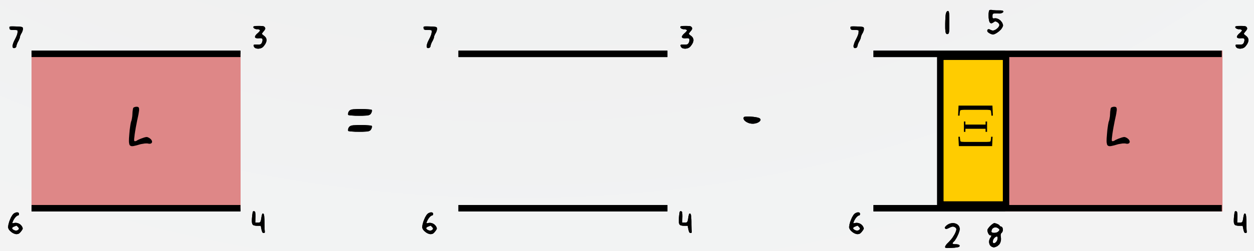
$$\mathrm{Abs}(\omega) = \mathcal{I}\left(\lim_{\mathbf{q}\to 0} v_0(\mathbf{q}) \bar{P}_{00}(\mathbf{q},\omega) \right)$$

$$\bar{P}(12) = {}^4\bar{P}(1122) = -i\bar{L}(1122)$$

From Bethe-Salpeter Equation: $\bar{L} = L_0 + L_0\, \Xi\, \bar{L}$

with Bethe-Salpeter Kernel: $\Xi = -i\, {}^4K = -i\bar{v} + iW$

Four-point quantity....
How can we invert
Dyson equation?



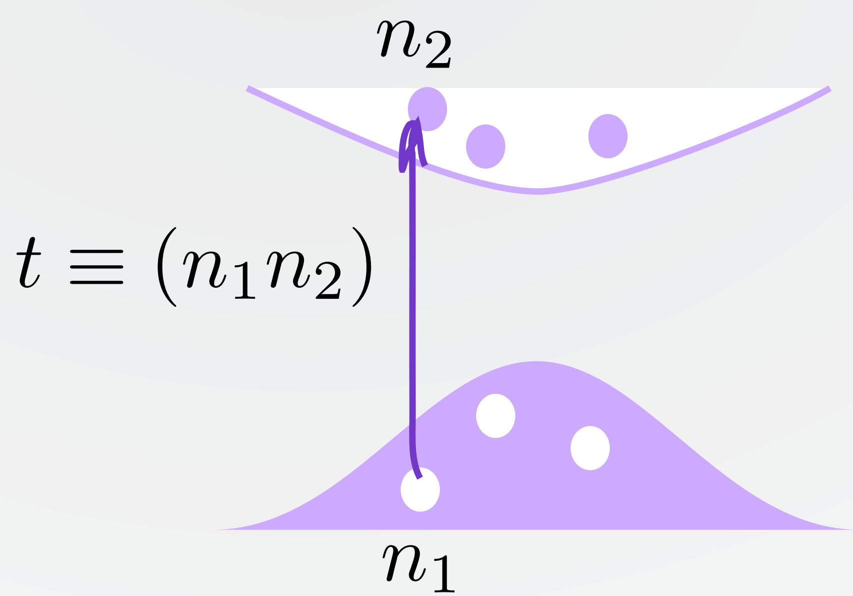
Key idea is to use the "transitions" between quasiparticles as a basis

Any 4-point quantity:

$$A_{tt'} \equiv A_{(n_1 n_2)(n_3 n_4)}$$

$$\equiv \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \psi_{n_1}(\mathbf{r}_1)\psi^*_{n_2}(\mathbf{r}_2) A(1234) \psi^*_{n_3}(\mathbf{r}_3)\psi_{n_4}(\mathbf{r}_4)$$

Where:



Equation rewritten as pseudo-eigenvalue problem for 2-particle Hamiltonian

The modified reducible polarization:

$$\bar{P}_{tt'} = -i\bar{L}_{tt'} = f_t \left[(\omega I - H^{2\mathrm{p}}) \right]^{-1}_{tt'} = \sum_\lambda \frac{A^t_\lambda A^{t'}_\lambda}{\omega - E_\lambda}$$

POLES AT EIGENENERGIES OR H^{2P}

$$H^{2p}_{tt'} A^{t'}_\lambda = E_\lambda A^t_\lambda \qquad \text{with:} \qquad H^{2\mathrm{p}}_{tt'} = \Delta E_t \delta_{tt'} + f_t (v - W)_{tt'}$$

which enters the optical absorption: $\mathrm{Abs}(\omega) = \mathcal{I}\left(\lim_{\mathbf{q}\to 0} v_0(\mathbf{q}) \bar{P}_{00}(\mathbf{q},\omega) \right)$

$$\mathrm{Abs}(\omega) \propto \sum_\lambda \sum_{v,c} \int_{\mathrm{BZ}} d\mathbf{k} \, |A^{cv\mathbf{k}}_\lambda \langle v\mathbf{k}|\hat{D}|c\mathbf{k}\rangle|^2 \delta(E_\lambda - \hbar\omega)$$

CAN BE GENERALIZED FOR NON HERMITIAN

For optical absorption select only the valence to conduction transitions

$$H^{2\mathrm{p}}_{tt'} = \Delta E_t \delta_{tt'} + f_t (v - W)_{tt'}$$

can be rewritten explicitly for valence-conduction transitions as:

SHIFT (ON-DIAGONAL) &
COUPLING (OFF-DIAGONAL)
OF CV TRANSITIONS, E > 0

COUPLING BETWEEN POSITIVE
AND NEGATIVE TRANSITIONS

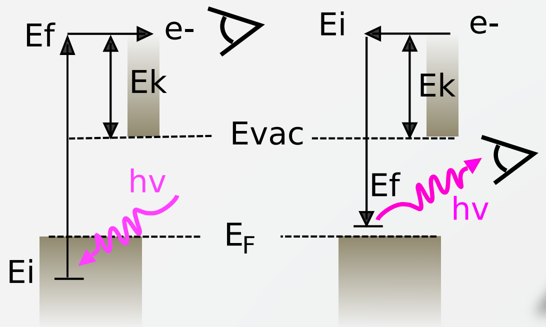
$$H^{2p} = \begin{pmatrix} [\Delta E + (v - W)]_{cv,c'v'} & (v - W)_{cv,v'c'} \\ (v - W)_{vc,c'v'} & [\Delta E + (v - W)]_{vc,v'c'} \end{pmatrix}$$

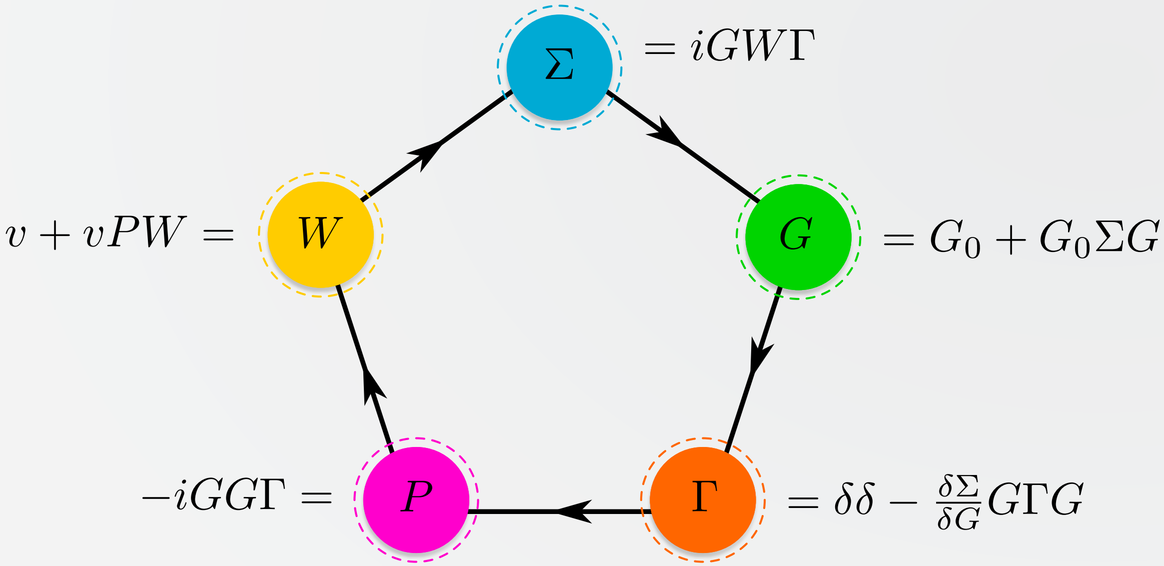
COUPLING BETWEEN POSITIVE
AND NEGATIVE TRANSITIONS

SHIFT (ON-DIAGONAL) &
COUPLING (OFF-DIAGONAL)
OF VC TRANSITIONS, E<0

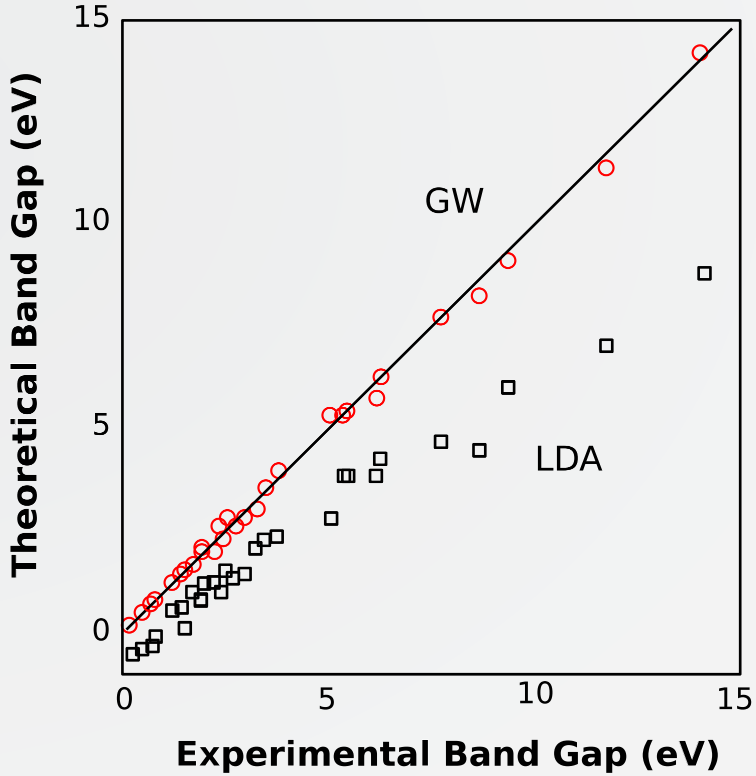
Charged excitations in electronic system:

1-particle Green's function
'solve' set of coupled equations

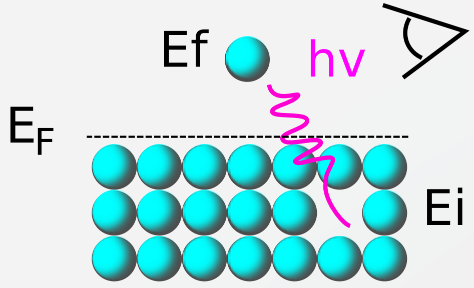




$$E_s = \varepsilon_s + Z_s \langle \phi_s | \Sigma(\varepsilon_s) - v_{xc} | \phi_s \rangle$$



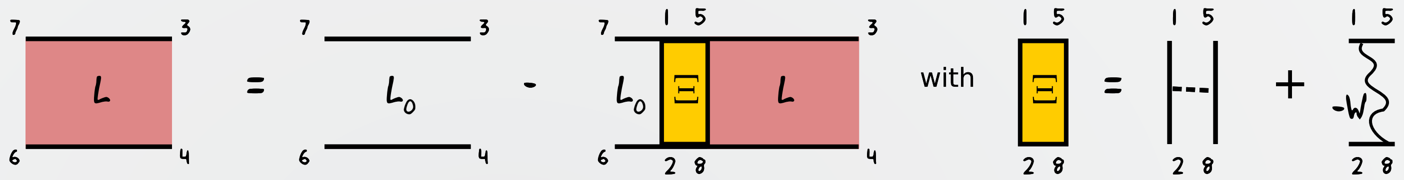
Hedin, J. Phys. Cond Matt 11, R489 (1999)



Neutral excitations in electronic system:

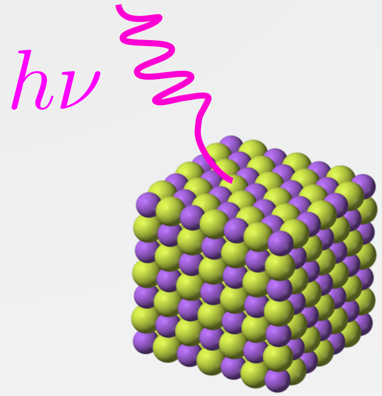
2-particle correlation function
'solve' Bethe-Salpeter equation

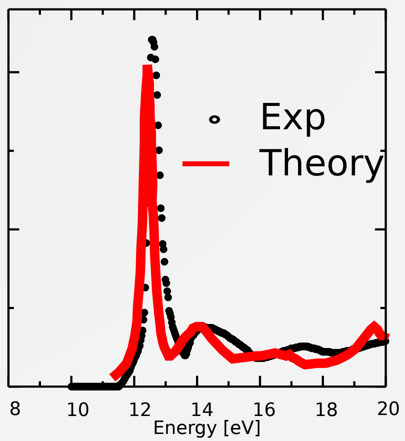
Bethe-Salpeter equation:



eigenproblem for 2-particle Hamiltonian:

$$H^{2p}_{tt'} A^{t'}_{\lambda} = E_{\lambda} A^{t}_{\lambda}$$





$$\text{Abs}(\omega) \propto \sum_{\lambda} \sum_{v,c} \int_{\text{BZ}} d\mathbf{k}\, |A^{cv\mathbf{k}}_{\lambda} \langle v\mathbf{k}|\hat{D}|c\mathbf{k}\rangle|^2 \delta(E_{\lambda} - \hbar\omega)$$

Are the many approximations we made always justified?

Are the many approximations we made always justified?

$$\phi_s^{\mathrm{KS}} \approx \psi_s^{N\pm1}$$

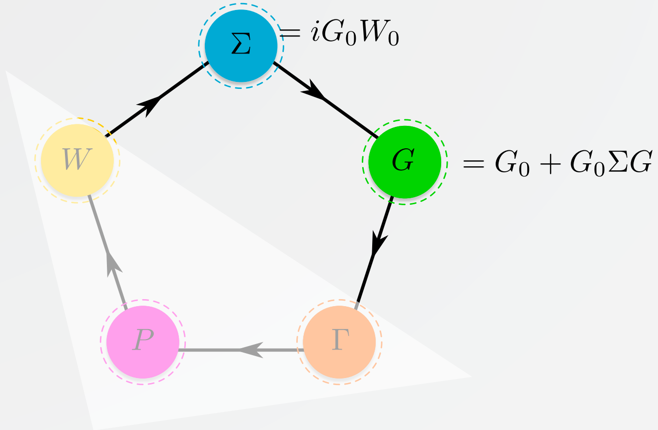
$$\langle \phi_i^{\mathrm{KS}} | \hat{\Sigma} | \phi_j^{\mathrm{KS}} \rangle \approx 0$$

See yesterday's lecture:
-valid only when perturbation is small
-self-consistency: e.g. QSGW, COHSEX

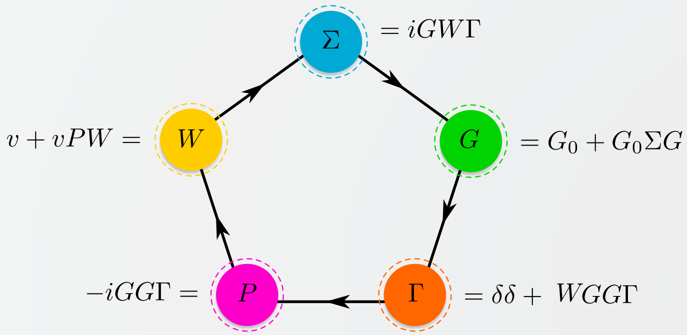
Once we use selfconsistency we 'need' to include vertex because of 'cancellations':

self-consistency gives a larger gap
...thus smaller screening ...thus larger gap...

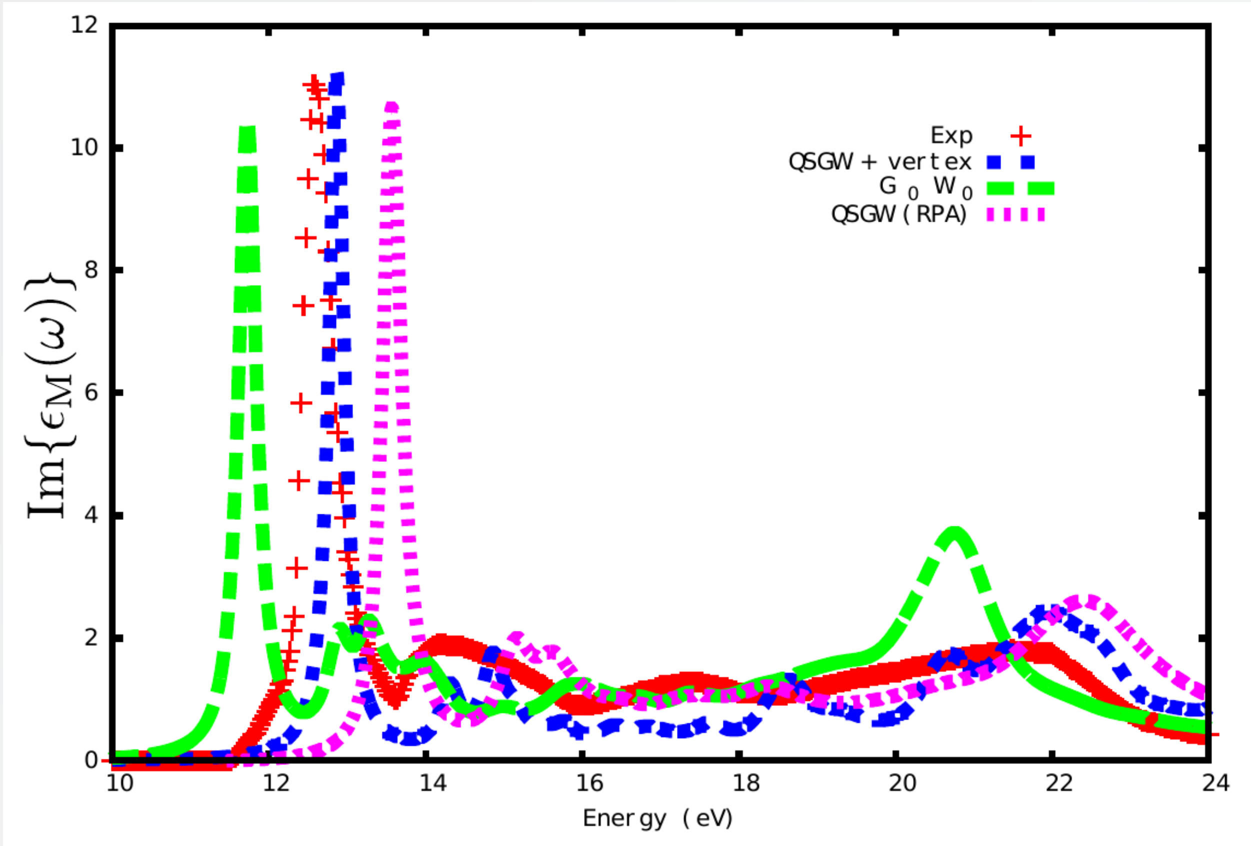
vertex in P enhances the screening
...thus smaller gap



Are the many approximations we made always justified?

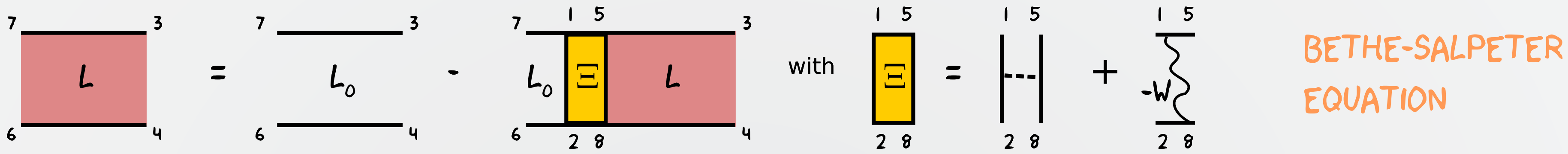


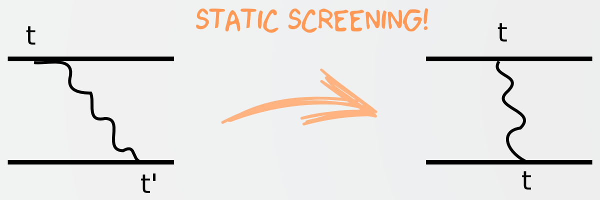
Brian Cunningham's took a further iteration



preliminary results

Are the many approximations we made always justified?



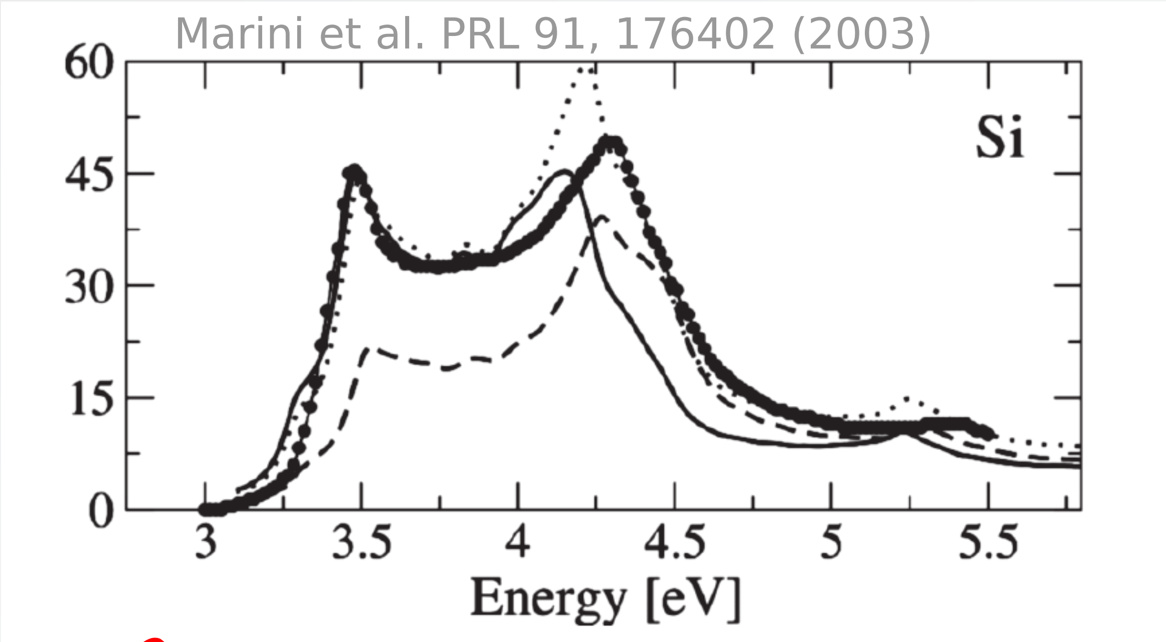


$$W(\mathbf{r},\mathbf{r}';t,t') \approx W(\mathbf{r},\mathbf{r}')\delta(t-t')$$

This approximation is again relying on a cancellation:

- in L_0, no renormalization by Z (if we apply it reduction ~ Z^2)

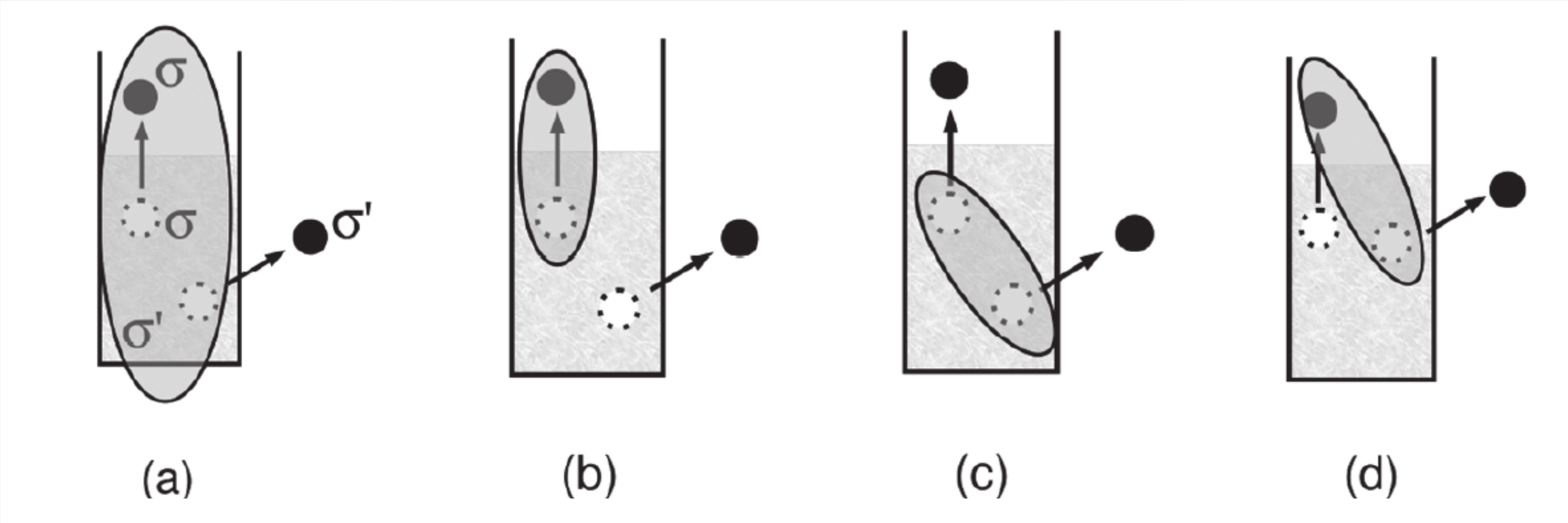
- in the static limit vertex ~1/Z



does not hold for metals...

Are the many approximations we made always justified?

from Interacting electrons - ch. 15



FULL PICTURE	HIGH-DENSITY LIMIT	LOW-DENSITY LIMIT	SPIN-FLIP
	$\Sigma \approx GW$	$\Sigma \approx GT$	$T_{\sigma\sigma'\sigma\sigma'}$

Bibliography:

Interacting electrons: Theory and computational approaches
RM Martin, L. Reining and DM Ceperley - Cambridge University Press (2016)

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

Effects of the Electron–Hole Interaction on the
Optical Properties of Materials: the Bethe–Salpeter Equation, G. Bussi
2004 Phys. Scr. 2004 141

Electronic Excitations: Density-Functional vs
Many-body Green's , G. Onida, L. Reining, A. Rubio
Rev. Modern Phys. 74, 601 (2002)

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