Many-Body Perturbation Theory: the *GW* method

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Electronic *N*-body problem

- Let us consider a system of N interacting electrons in an external potential $V_{\text{ext}}(\mathbf{r})$, such as the one generated by the nuclei.

- It is completely described by its **wavefunction**:

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$$

which is obtained by solving the **Schrödinger equation**:

$$\hat{H}\psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) + \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \psi = E\psi$$

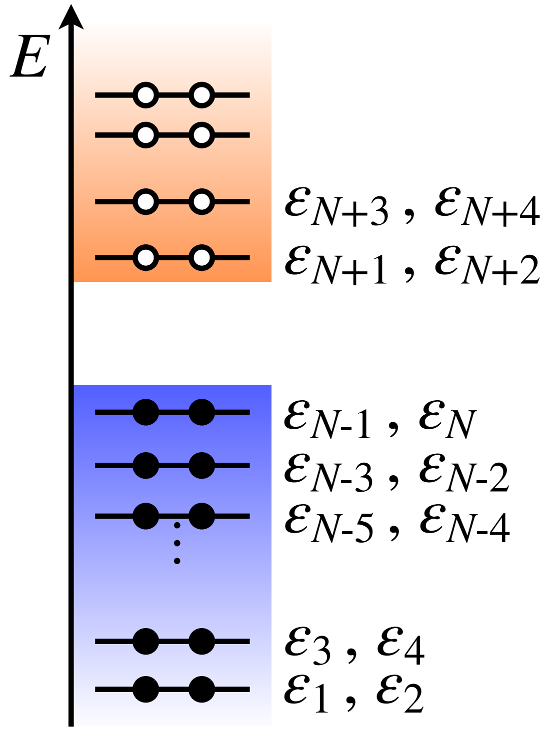
One particle approximations

- If there was no electron-electron interaction, the variables could easily be separated and the N-electrons wavefunction could be replaced by the product of N 1-electron wavefunctions:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)$$

which are the solutions of a 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r})\right]\phi_n(\mathbf{r}) = \varepsilon_n\phi_n(\mathbf{r})$$



- The total energy would simply be:

$$E = \sum_n \varepsilon_n$$

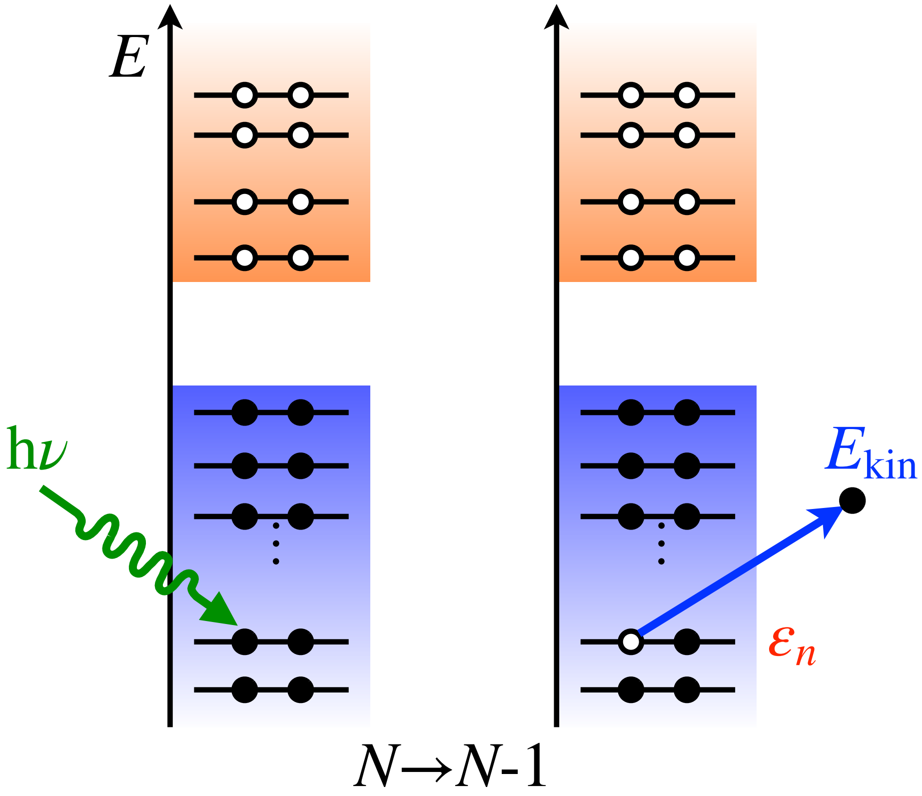
$$E_{N,0} = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_{N\text{-}1} + \varepsilon_N$$

One particle approximations

- By solving the 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r})\right]\phi_n(\mathbf{r}) = \varepsilon_n \phi_n(\mathbf{r})$$

we obtain the band structure ε_n which can be determined experimentally by photoemission or inverse photoemission (valence or conduction bands).



Energy conservation:

before $\rightarrow h\nu + E_{N,0}$

after $\rightarrow E_{\mathrm{kin}} + E_{N\text{-}1,n}$

The binding energy is:

$$E_{\mathrm{kin}} - h\nu = E_{N,0} - E_{N\text{-}1,n} = \varepsilon_n$$

$$E_{N\text{-}1,n} = \varepsilon_1 + \ldots + \cancel{\varepsilon_n} + \ldots + \varepsilon_N$$

One particle approximations

- By solving the 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r})\right]\phi_n(\mathbf{r}) = \varepsilon_n \phi_n(\mathbf{r})$$

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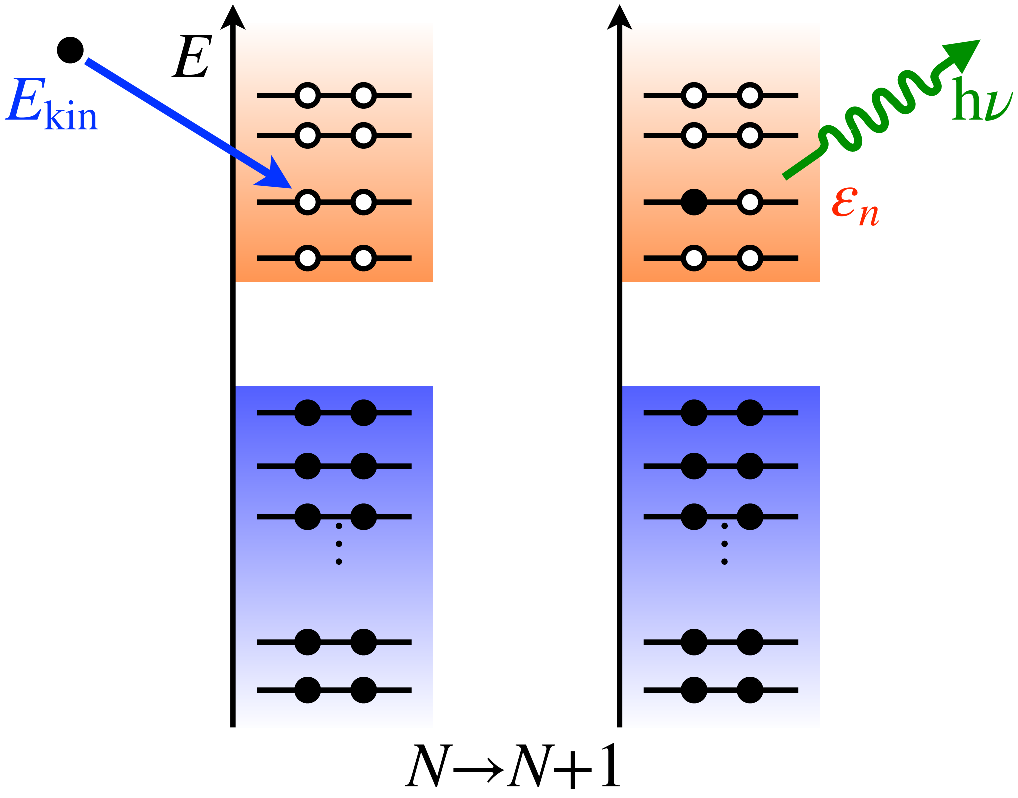


Energy conservation:

before → $E_{\text{kin}} + E_{N,0}$

after → $h\nu + E_{N+1,n}$

The binding energy is:

$$E_{\text{kin}} - h\nu = E_{N+1,n} - E_{N,0} = \varepsilon_n$$

$$E_{N+1,n} = \varepsilon_1 + \ldots + \varepsilon_N + \varepsilon_n$$

Green’s functions theory and quasiparticles

Definition of the 1-particle Green's function

- Green's function theory and the quasiparticle concept constitute an elegant alternative to DFT to solve the many-body problem.
- The 1-particle Green's function $G(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ is

$$\begin{aligned} G(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2) &= -i\langle N,0|T[\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_2,t_2)]|N,0\rangle \\ &= -i\langle N,0|\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_2,t_2)|N,0\rangle\theta(t_1-t_2) \\ &\quad + i\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2,t_2)\hat{\psi}(\mathbf{r}_1,t_1)|N,0\rangle\theta(t_2-t_1) \end{aligned}$$

where T is the **time-ordering operator**:

$$T[\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_2,t_2)] = \begin{cases} \hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_2,t_2) & \text{if } t_1 > t_2 \\ \hat{\psi}^\dagger(\mathbf{r}_2,t_2)\hat{\psi}(\mathbf{r}_1,t_1) & \text{if } t_2 > t_1 \end{cases}$$

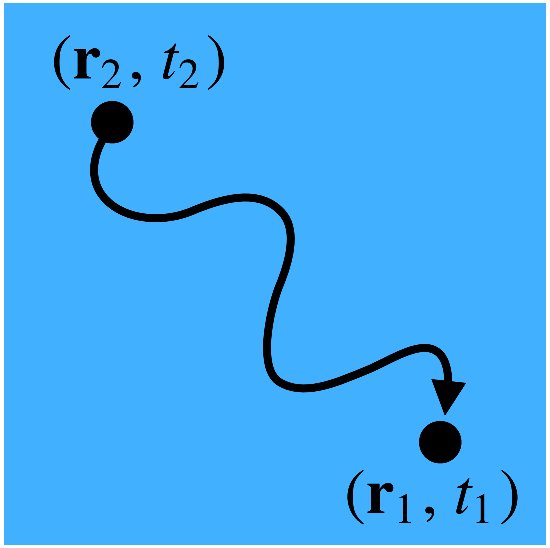
$\theta(t)$ is the Heaviside step function [$\theta(t) = 1$ for $t > 0$ and 0 for $t < 0$], $\hat{\psi}$ and $\hat{\psi}^\dagger$ are the field operators in the Heisenberg representation for annihilation and creation, respectively.

Interpretation of the 1-particle Green's function

- It can be interpreted as the probability amplitude:
  - to detect an electron at point $\mathbf{r}_1$ and time t_1 when an electron has been added to the system at point $\mathbf{r}_2$ and time t_2 (if $t_1 > t_2$),
  - to detect a hole at point $\mathbf{r}_1$ and time t_1 when an electron has been added to the system at point $\mathbf{r}_2$ and time t_2 (if $t_2 > t_1$).

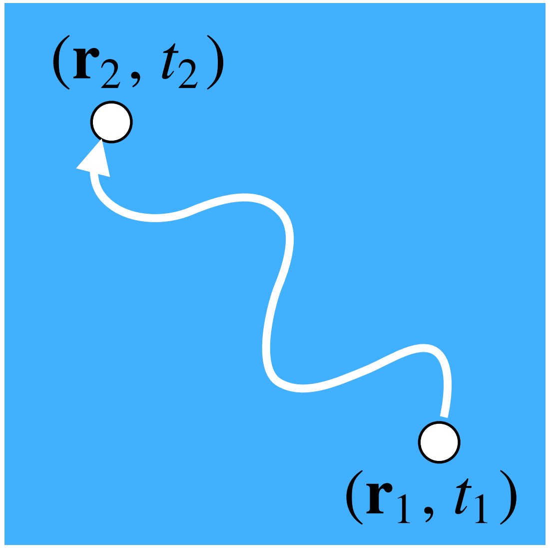
$t_1 > t_2$

$$\langle N,0|\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_2,t_2)|N,0\rangle$$



$t_2 > t_1$

$$\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2,t_2)\hat{\psi}(\mathbf{r}_1,t_1)|N,0\rangle$$



Schrödinger representation

- Assuming that the Hamiltonian is not an explicit function of time, we now move to the Schrödinger representation:

$$\hat{\psi}(\mathbf{r}_1,t_1) = e^{i\hat{H}t}\,\hat{\psi}(\mathbf{r}_1)e^{-i\hat{H}t}$$

- Using the relation: $\hat{H}|N,0\rangle = E_{N,0}|N,0\rangle$ the 1-particle Green's function $G(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2)$ writes:

$$\begin{aligned}G(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2) = &-ie^{iE_{N,0}(t_1-t_2)}\langle N,0|\hat{\psi}(\mathbf{r}_1)e^{-i\hat{H}t_1}e^{i\hat{H}t_2}\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle\theta(t_1-t_2)\\ &+ie^{iE_{N,0}(t_2-t_1)}\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)e^{-i\hat{H}t_2}e^{i\hat{H}t_1}\hat{\psi}(\mathbf{r}_1)|N,0\rangle\theta(t_2-t_1)\end{aligned}$$

- It is now explicitly only a function of the time difference $\tau = t_1 - t_2$, we write:

$$\begin{aligned}G(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2) =&\,G(\mathbf{r}_1,\mathbf{r}_2;\tau)\\ =&-ie^{iE_{N,0}\tau}\langle N,0|\hat{\psi}(\mathbf{r}_1)e^{-i\hat{H}\tau}\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle\theta(\tau)\\ &+ie^{-iE_{N,0}\tau}\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)e^{i\hat{H}\tau}\hat{\psi}(\mathbf{r}_1)|N,0\rangle\theta(-\tau)\end{aligned}$$

Lehman representation

- In order to remove the time operators inside the expectation values, we introduce the complete set of states with M particles: $|M,n\rangle$ where m is a general label to describe the possible excited states.

- Since the states form a complete set, we can write the closure relation:

$$\sum_{M,n} |M,n\rangle\,\langle M,n| = 1$$

and also:

$$\hat{H}\,|M,n\rangle = E_{M,n}\,|M,n\rangle$$

- Introducing the closure relation between the pairs of exponentials in the expression of the 1-particle Green's function, we get:

$$G(\mathbf{r}_1,\mathbf{r}_2;\tau) = -\,i\sum_{M,n} e^{i(E_{N,0}-E_{M,n})\tau}\langle N,0|\hat{\psi}(\mathbf{r}_1)|M,n\rangle\langle M,n|\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle\theta(\tau)$$
$$+\,i\sum_{M,n} e^{-i(E_{N,0}-E_{M,n})\tau}\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)|M,n\rangle\langle M,n|\hat{\psi}(\mathbf{r}_1)|N,0\rangle\theta(-\tau)$$

Lehman representation

- Most often, it is more convenient to work with the Fourier transform of the 1-particle Green's function:

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} G(\mathbf{r}_1,\mathbf{r}_2;\tau)e^{i\omega\tau}d\tau$$

- Thus, we have:

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega) = \sum_{M,n} \frac{\langle N,0|\hat{\psi}(\mathbf{r}_1)|M,n\rangle\langle M,n|\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle}{\omega-(E_{M,n}-E_{N,0})+i\eta}$$

$$+\sum_{M,n} \frac{\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)|M,n\rangle\langle M,n|\hat{\psi}(\mathbf{r}_1)|N,0\rangle}{\omega+(E_{M,n}-E_{N,0})-i\eta}$$

where the infinitesimals $\pm i\eta$ reflect the time ordering.

Lehman representation

- The expectation values $\langle N,0|\hat{\psi}(\mathbf{r}_1)|M,n\rangle$ and $\langle M,n|\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle$ are different from zero only for $M=N+1$; while $\langle M,n|\hat{\psi}(\mathbf{r}_1)|N,0\rangle$ and $\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)|M,n\rangle$ are different from zero only for $M=N-1$.

- Thus, the 1-particle Green's function can be written as:

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega)=\sum_n \frac{\langle N,0|\hat{\psi}(\mathbf{r}_1)|N+1,n\rangle\langle N+1,n|\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle}{\omega-(E_{N+1,n}-E_{N,0})+i\eta}$$

$$+\sum_n \frac{\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)|N-1,n\rangle\langle N-1,n|\hat{\psi}(\mathbf{r}_1)|N,0\rangle}{\omega+(E_{N-1,n}-E_{N,0})-i\eta}$$

Lehman representation

- Let us consider the energy terms appearing at the denominators, they can be rewritten as:

$$E_{N+1,n} - E_{N,0} = (E_{N+1,n} - E_{N+1,0}) + (E_{N+1,0} - E_{N,0})$$

$$E_{N,0} - E_{N-1,n} = (E_{N,0} - E_{N-1,0}) + (E_{N-1,0} - E_{N-1,n})$$

- The difference $E_{N+1,0} - E_{N,0}$ represents the minimum energy needed to add one electron to a system of N electrons.

  It is the **electron affinity** (EA) :

$$\mathrm{EA} = E_{N+1,0} - E_{N,0}$$

- The difference $E_{N,0} - E_{N-1,0}$ represents the minimum energy needed to remove one electron to a system of N electrons.

  It is the **ionization energy** (IE) :

$$\mathrm{IE} = E_{N,0} - E_{N-1,0}$$

Lehman representation

- It can be shown that IE $\leq$ EA, so that if we define:

$$\begin{aligned}\varepsilon_g &= \mathrm{EA} - \mathrm{IE} \\ &= \left(E_{N+1,0} - E_{N,0}\right) - \left(E_{N,0} - E_{N-1,0}\right)\end{aligned}$$

  the quantity ε_g is positive.

- In an atomic or molecular system, we have:
  IE (energy of HOMO) $<$ EA (energy of LUMO).

- In a solid, we define the **chemical potential** μ such that:

$$\mathrm{IE} \leq \mu \leq \mathrm{EA}$$

  In the thermodynamic limit (N, $V \to \infty$, with N/V=cst), we distinguish:

  - metallic systems in which $\varepsilon_g = 0$ (IE$\simeq\mu\simeq$EA)
  - insulating systems in which $\varepsilon_g > 0$ (IE$<\mu<$EA)

Lehman representation

- Coming back to the energy terms appearing at the denominators:

$$E_{N+1,n} - E_{N,0} = \overbrace{(E_{N+1,n} - E_{N+1,0})}^{\geq 0} + \overbrace{(E_{N+1,0} - E_{N,0})}^{\text{EA}}$$

$$E_{N,0} - E_{N-1,n} = \underbrace{(E_{N,0} - E_{N-1,0})}_{\text{IE}} + \underbrace{(E_{N-1,0} - E_{N-1,n})}_{\leq 0}$$

we define the **excitation energies** of the system:

$$\varepsilon_n = \begin{cases} E_{N,0} - E_{N-1,n} & \text{when } \varepsilon_n < \mu \\ E_{N+1,n} - E_{N,0} & \text{when } \varepsilon_n > \mu \end{cases}$$

Lehman representation

- If we define the **Lehman amplitudes** as:

$$\phi_n(\mathbf{r}) = \begin{cases} \langle N-1,n|\hat{\psi}(\mathbf{r})|N,0\rangle & \text{when } \varepsilon_n < \mu \\ \langle N,0|\hat{\psi}(\mathbf{r})|N+1,n\rangle & \text{when } \varepsilon_n > \mu \end{cases}$$

the numerators of the 1-particle Green's function can be rewritten like:

$$\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)|N-1,n\rangle\langle N-1,n|\hat{\psi}(\mathbf{r}_1)|N,0\rangle = \phi_n^*(\mathbf{r}_2)\phi_n(\mathbf{r}_1)$$

$$\langle N,0|\hat{\psi}(\mathbf{r}_1)|N+1,n\rangle\langle N+1,n|\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle = \phi_n(\mathbf{r}_1)\phi_n^*(\mathbf{r}_2)$$

Lehman representation

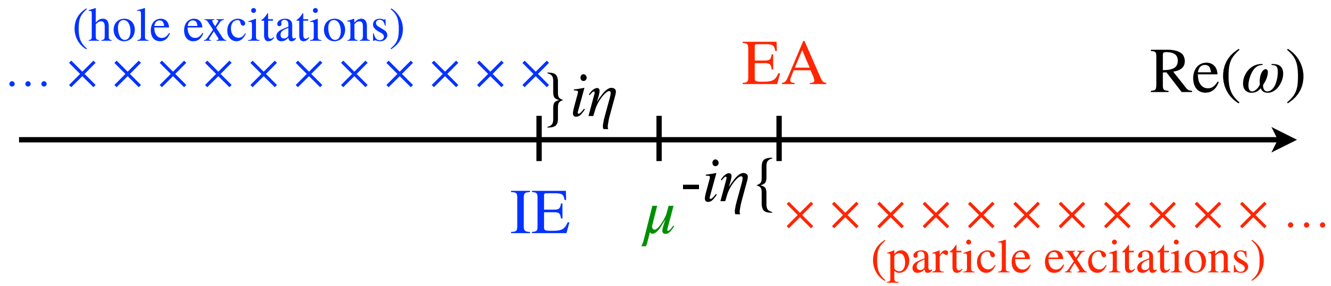
- The 1-particle Green's function can thus be written as :

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega)=\sum_n \frac{\phi_n(\mathbf{r}_1)\phi_n^*(\mathbf{r}_2)}{\omega-\varepsilon_n+i\eta\,\mathrm{sgn}(\varepsilon_n-\mu)}$$

with

$$\varepsilon_n=\begin{cases} E_{N,0}-E_{N-1,n} \\ E_{N+1,n}-E_{N,0}\end{cases} \qquad \phi_n(\mathbf{r})=\begin{cases}\langle N-1,n|\hat{\psi}(\mathbf{r})|N,0\rangle & \text{when } \varepsilon_n<\mu \\ \langle N,0|\hat{\psi}(\mathbf{r})|N+1,n\rangle & \text{when } \varepsilon_n>\mu\end{cases}$$

- Its poles are thus located as follows:

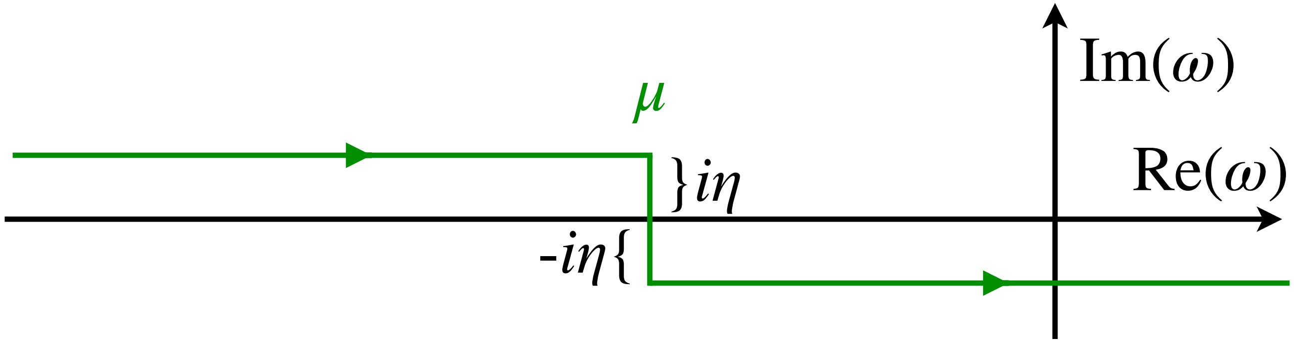


Spectral representation

- The 1-particle Green's function can also be cast into the so-called **spectral representation** like:

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega) = \int_C \frac{A(\mathbf{r}_1,\mathbf{r}_2;\omega')}{\omega-\omega'}d\omega'$$

where the integral is to be taken on the contour C defined as follow:



- The is **spectral function** is simply given by:

$$A(\mathbf{r}_1,\mathbf{r}_2;\omega) = \sum_n \phi_n(\mathbf{r}_1)\phi_n^*(\mathbf{r}_2)\delta(\omega-\varepsilon_n)$$

$$\phi_n(\mathbf{r}) = \begin{cases} \langle N-1,n|\hat{\psi}(\mathbf{r})|N,0\rangle & \text{when } \varepsilon_n < \mu \\ \langle N,0|\hat{\psi}(\mathbf{r})|N+1,n\rangle & \text{when } \varepsilon_n > \mu \end{cases}$$

Spectral representation

- It can be shown that the spectral function satisfy the following sum-rule:

$$\int_{-\infty}^{+\infty} A(\mathbf{r}_1, \mathbf{r}_2; \omega) d\omega = \delta(\mathbf{r}_1 - \mathbf{r}_2)$$

- And, using the Sokhatsky-Weierstrass theorem which states that

$$\lim_{\eta \to 0^+} \int \frac{f(x)}{x \pm i\eta} = \mp i\pi \int f(x)\delta(x) dx + P \int \frac{f(x)}{x} dx$$

where P denotes the Cauchy principal value, we have that

$$A(\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{1}{\pi} \left|\mathrm{Im}[G(\mathbf{r}_1, \mathbf{r}_2; \omega)]\right|$$

Quasiparticles

- In an homogeneous and crystalline system, we have that:

  $$G(\mathbf{r}_1, \mathbf{r}_2; \omega) = G(\mathbf{r}_1 - \mathbf{r}_2; \omega)$$

  it is thus more convenient to perform a momentum transformation of the 1-particle Green's function:

  $$G(\mathbf{k}, \omega) = \int G(\mathbf{r}_1 - \mathbf{r}_2; \omega) e^{-i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} d(\mathbf{r}_1 - \mathbf{r}_2)$$

- Using plane-wave states as a basis for the field operators:

  $$\hat{\psi}(\mathbf{r}) = \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \hat{c}_{\mathbf{k}} \qquad\qquad \hat{\psi}^{\dagger}(\mathbf{r}) = \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{c}^{\dagger}_{\mathbf{k}}$$

  the 1-particle Green's function rewritten as:

  $$G(\mathbf{k}, \omega) = \sum_n \frac{|\phi_{n\mathbf{k}}|^2}{\omega - \varepsilon_n + i\eta\,\mathrm{sgn}(\varepsilon_n - \mu)}$$

  $$\phi_{n\mathbf{k}} = \begin{cases} \langle N-1, n|\hat{c}_{\mathbf{k}}|N, 0\rangle & \text{when } \varepsilon_n < \mu \\ \langle N, 0|\hat{c}_{\mathbf{k}}|N+1, n\rangle & \text{when } \varepsilon_n > \mu \end{cases}$$

Quasiparticles

- The spectral representation thus becomes:

$$G(\mathbf{k},\omega)=\int_C \frac{A(\mathbf{k},\omega')}{\omega-\omega'}d\omega'$$

with

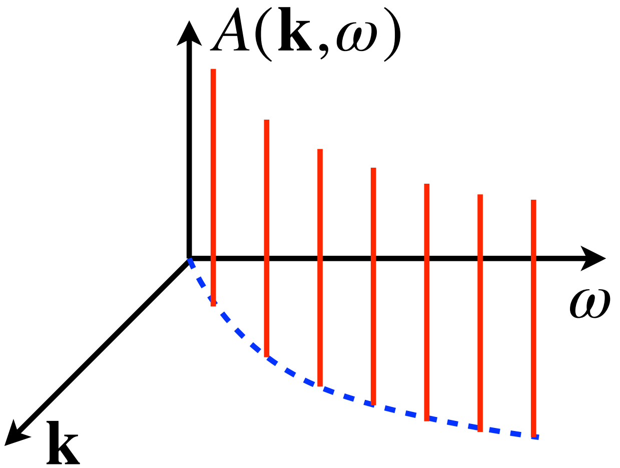
$$A(\mathbf{k},\omega)=\sum_n |\phi_{n\mathbf{k}}|^2\,\delta(\omega-\varepsilon_n)$$

- For non-interacting electrons, we have:

$$\hat{c}^\dagger_{\mathbf{k}}\,|N,0\rangle=|N+1,n,\mathbf{k}\rangle$$
$$\hat{c}_{\mathbf{k}}\,|N,0\rangle=|N-1,n,-\mathbf{k}\rangle$$

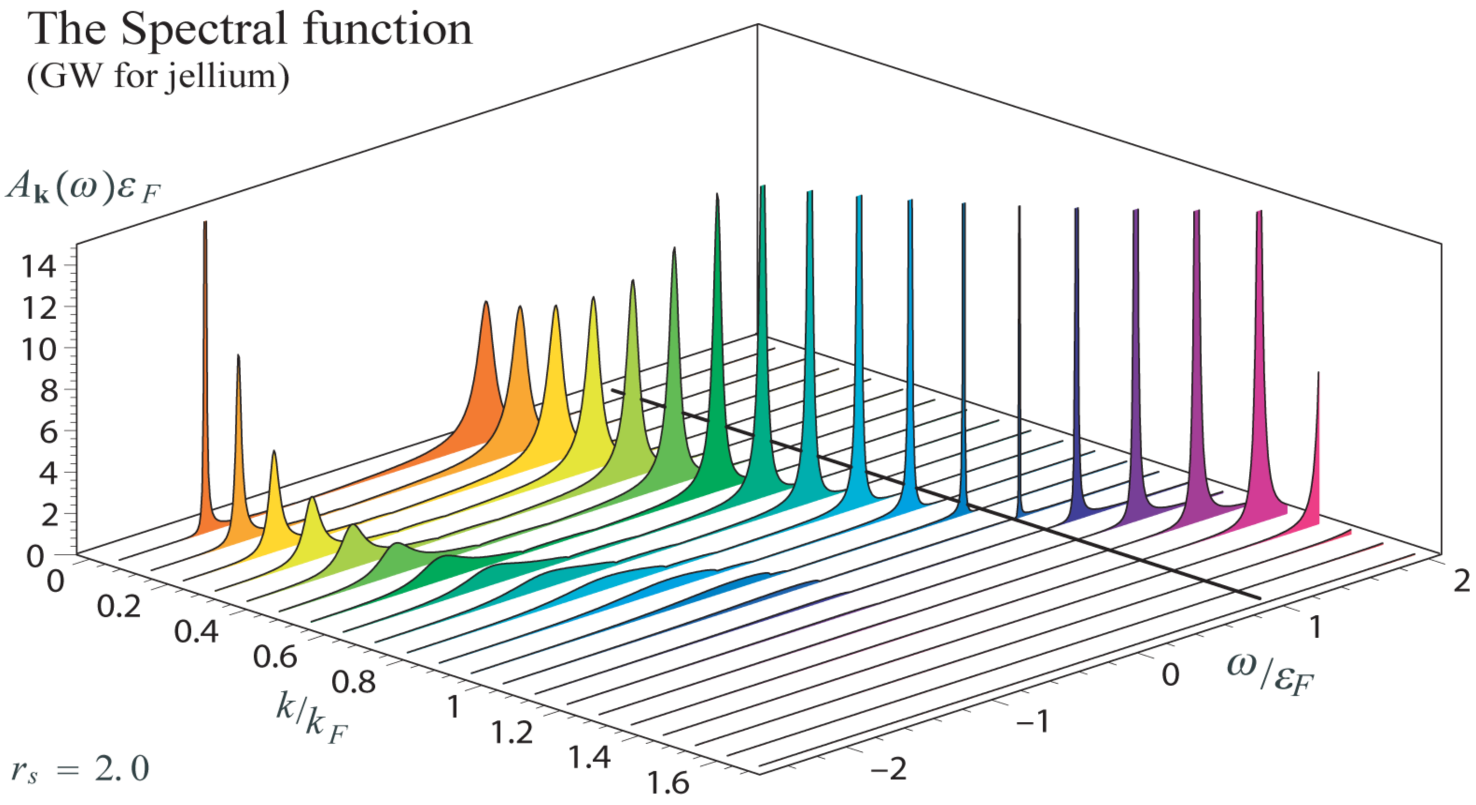
and the spectral function is simply:

$$A(\mathbf{k},\omega)=\sum_n \delta(\omega-\varepsilon_{n\mathbf{k}})$$



Quasiparticles

- For interacting electrons, if there is a strong overlap between $\langle N,0|\,\hat{c}_{\mathbf{k}}$ and $|N+1,n,\mathbf{k}\rangle$ (resp. $\hat{c}_{\mathbf{k}}\,|N,0\rangle$ and $\langle N-1,n,-\mathbf{k}|$), we will say that there exists a **quasi-electron** (resp. **quasi-hole**) of energy $\varepsilon_{n\mathbf{k}}$ ($\varepsilon_{n\text{-}\mathbf{k}}$).



The Spectral function
(GW for jellium)

[courtesy of Martin Stankovski (Université Catholique de Louvain, Belgium)]

Utility of Green's function

- As we have just seen, the 1-particle Green's function contains a lot of information about all the 1-particle excitations.

- It also also to compute the total ground-state energy.
  Indeed, using **Galitskii-Migdal formula**, it can be written:

$$E_{N,0} = \frac{1}{\pi} \int_{-\infty}^{\mu} \mathrm{Tr} \left[\left(\omega - \frac{1}{2}\nabla^2 + V_{\mathrm{ext}} \right) \mathrm{Im}\, G(\omega) \right] d\omega$$

- In fact, we can obtain the expectation value of 1-particle operator (be it local or non-local).

Many-Body Perturbation Theory

Equation of motion of the Green's function

- Starting from the equation of motion for the Heisenberg annihilation and creation field operators ($\hat{\psi}$ and $\hat{\psi}^{\dagger}$) a hierarchy of equations of motion for the Green's function can be derived.

- For the 1-particle Green's function, it gives

$$\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1)\right] G(1,2) + i\int d3\, v(1^+,3) G_2(1,3;2,3^+) = \delta(1,2)$$

where $\hat{H}_0(\mathbf{r}_1) = -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}$ and $v(1,2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\delta(t_1 - t_2)$

Note that we have adopted Hedin's simplified notation:

$1 \equiv (\mathbf{r}_1, t_1)$ and $1^+ \equiv (\mathbf{r}_1, t_1 + \eta)$ where η is a positive infinitesimal.

- The 1-particle Green's function depends on the 2-particles one:

$$G_2(1,2;3,4) = (i)^2 \langle N,0| T[\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}(\mathbf{r}_2,t_2)\hat{\psi}^{\dagger}(\mathbf{r}_3,t_3)\hat{\psi}^{\dagger}(\mathbf{r}_4,t_4)]|N,0\rangle$$

Equation of motion of the Green's function

- If we look at the structure of the equation of motion, we can distinguish:

$$\underbrace{\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1)\right] G(1,2)}_{\text{non-interacting}} + \underbrace{i\int d3\, v(1^+,3)G_2(1,3;2,3^+)}_{\text{interaction terms}} = \delta(1,2)$$

- Since we are specifically interested in the interaction effects, we will assume that the non-interacting part of the equation part can always be solved exactly:

$$[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1)]G_0(1,2) = \delta(1,2)$$

- This defines the **independent-particle Green function** G_0.

  Note that

  (i) the calculation of G_0 is non-trivial for a solid (except jellium);

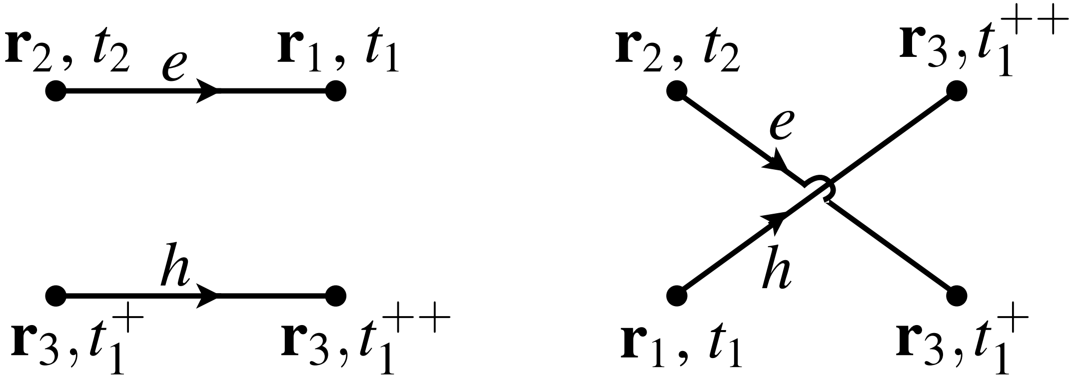
  (ii) some of the larger interaction effects, which produce an effective 1-particle potential, can be included in $\hat{H}_0$

Hartree and Hartree-Fock approximations

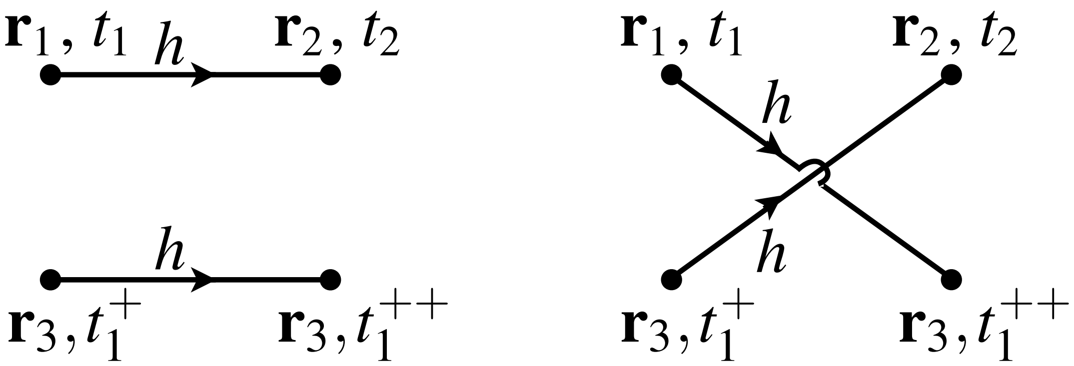
- We first consider the 2-particles Green's function:

$$G_2(1,3;2,3^+)\delta(t_1^+ - t_3) =$$
$$(i)^2\langle N,0|T[\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}(\mathbf{r}_3,t_1^+)\hat{\psi}^\dagger(\mathbf{r}_2,t_2)\hat{\psi}^\dagger(\mathbf{r}_3,t_1^{++})]|N,0\rangle$$

(a) $t_1 > t_2$



(b) $t_2 > t_1$



Hartree and Hartree-Fock approximations

- At this stage, we do not know how the 2 particles propagate, but the obvious first choice is to allow each particle to propagate independently according to the 1-particle Green's functions.
- Thus, we write:

$$G_2(1,3;2,3^+)\delta(t_1^+ - t_3) = \\ \left[G(1,2)G(3,3^+) + G(1,3^+)G(3,2)\right]\delta(t_1^+ - t_3)$$

The first term is the so-called **direct term** and the second one is the **exchange term**.

Hartree and Hartree-Fock approximations

- We first consider the direct term as an approximation to the 2-particles Green's function:

$$G_2(1,3;2,3^+)\delta(t_1^+ - t_3) = G(1,2)G(3,3^+)\delta(t_1^+ - t_3)$$

The equation of motion becomes:

$$\left\{\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1)\right] + i\int d3\, v(1^+,3)G(3,3^+)\right\}G(1,2) = \delta(1,2)$$

- It is degenerated into a simple independent-particle like equation with an added potential, which is nothing but the Hartree potential:

$$V_{\mathrm{H}}(1) = -i\int d3\, v(1^+,3)G(3,3^+) = \int \frac{n(\mathbf{r}_3,t_1)}{\mathbf{r}_1 - \mathbf{r}_3} d\mathbf{r}_3$$

$$\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1) - V_{\mathrm{H}}(1)\right] G(1,2) = \delta(1,2)$$

Hartree and Hartree-Fock approximations

- The next step is to take both the direct and exchange terms as an approximation to the 2-particles Green's function:

$$G_2(1,3;2,3^+)\delta(t_1^+ - t_3) = \left[G(1,2)G(3,3^+) + G(1,3^+)G(3,2)\right]\delta(t_1^+ - t_3)$$

- The direct term obviously gives the Hartree potential again, so the equation of motion becomes:

$$\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1) - V_{\mathrm{H}}(1)\right]G(1,2) + i\int d3\, v(1^+,3)G(1,3^+)G(3,2) = \delta(1,2)$$

- The interaction term is now a non-local operator. It can be shown that it is the Green's function variation of the exchange interaction appearing in the Hartree-Fock approximation.

The self-energy

- The obvious next step would be to carry on like this with the 3-particles Green's function, and so on... but this becomes rapidly far too difficult.

- The trick is to assume that we have solved the infinite series of equations of motions and to look for a solution in the form:

$$\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1) - V(1)\right] G(1,2) - i\int d3\,\Sigma(1,3)G(3,2) = \delta(1,2)$$

  where $V(1)=\phi(1)+V_{\mathrm{H}}(1)$ with $\phi(1)$ being any external potential such as an experimental probe (that will be made equal to zero at the end).

- The operator Σ is called the **self-energy operator**. It includes all the interaction effects.

The self-energy

- To understand the physical meaning of the self-energy operator, we transform the equation of motion in the energy domain:

$$[\omega-\hat{H}_0(\mathbf{r}_1)-V(\mathbf{r}_1,\omega)]G(\mathbf{r}_1,\mathbf{r}_2,\omega) \\ -\int\Sigma(\mathbf{r}_1,\mathbf{r}_3;\omega)G(\mathbf{r}_3,\mathbf{r}_2;\omega)d\mathbf{r}_3=\delta(\mathbf{r}_1-\mathbf{r}_2)$$

or adopting a matrix notation:

$$(\omega\mathbf{1}-\mathbf{H}_0-\mathbf{V})\mathbf{G}-\Sigma\mathbf{G}=\mathbf{1} \qquad \Rightarrow \mathbf{G}^{-1}=\omega\mathbf{1}-\mathbf{H}_0-\mathbf{V}-\Sigma$$

- By comparing with the non-interacting (i.e. without Σ) equation:

$$\mathbf{G}_0^{-1}=\omega\mathbf{1}-\mathbf{H}_0-\mathbf{V}$$

we can write:

$$\mathbf{G}^{-1}=\mathbf{G}_0^{-1}-\Sigma$$

The poles of G are moved in energy by Σ compared to G_0.

Dyson's equation

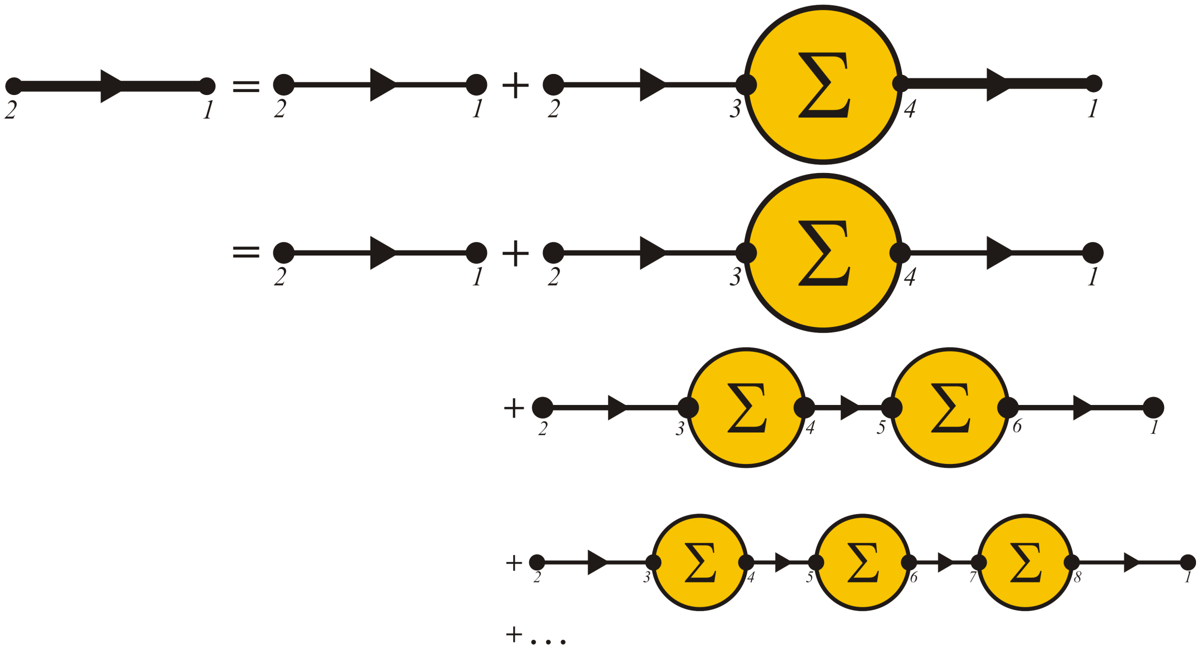
- The equation $\mathbf{G}^{-1} = \mathbf{G}_0^{-1} - \Sigma$ can also be written as:

$$\mathbf{G} = \mathbf{G}_0 + \mathbf{G}_0 \Sigma \mathbf{G}$$

which is known as the **Dyson equation**.

- Coming back to the time domain, we get:

$$G(1,2) = G_0(1,2) + \int G_0(1,3)\Sigma(3,4)G(4,2)\mathrm{d}(3,4)$$



Hedin's equations

- We define the **inverse dielectric function** ϵ^{-1} as the change in δV due to a small variation $\delta\phi$ in the external potential:

$$\epsilon^{-1}(1,2) = \frac{\delta V(1)}{\delta\phi(2)}$$

- We can write:

$$V(1) = \phi(1) + \int v(1,3)n(3)d3 \qquad \phi(1) = V(1) - \int v(1,3)n(3)d3$$

$$\delta V(1) = \delta\phi(1) + \int v(1,3)\delta n(3)d3 \qquad \delta\phi(1) = \delta V(1) - \int v(1,3)\delta n(3)d3$$

$$\epsilon^{-1}(1,2) = \delta(1,2) + \int v(1,3)\underbrace{\frac{\delta n(3)}{\delta\phi(2)}}_{P^{red.}(3,2)}d3 \qquad \epsilon(1,2) = \delta(1,2) - \int v(1,3)\underbrace{\frac{\delta n(3)}{\delta V(2)}}_{P(3,2)}d3$$

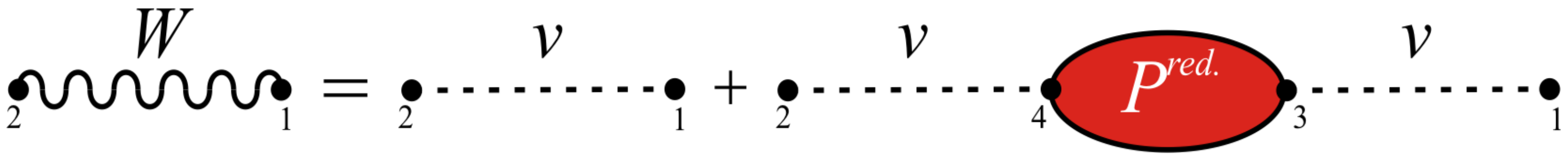
where we have defined the **reducible** and **irreducible polarizability**.

Hedin's equations

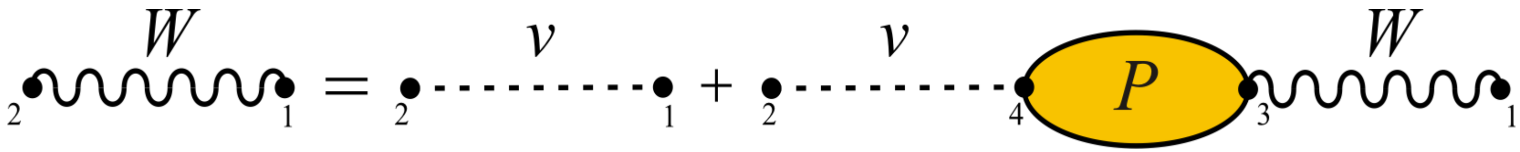
- We also define the **screened Coulomb potential** W :

$$W(1,2) = \int \epsilon^{-1}(1,3)v(3,2)d3$$

$$W(1,2) = v(1,2) + \int v(1,3)P^{red.}(3,4)v(4,2)d(3,4)$$



$$W(1,2) = v(1,2) + \int v(1,3)P(3,4)W(4,2)d(3,4)$$



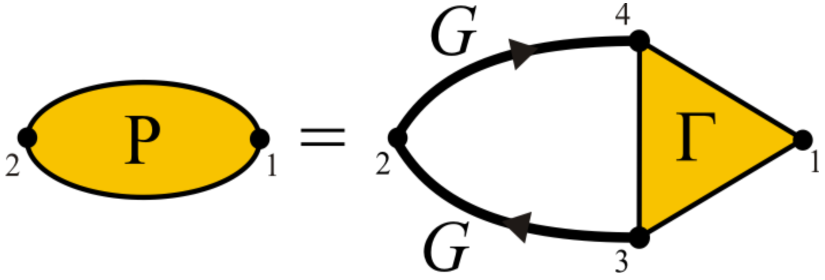
Hedin’s equations

- The expression of the irreducible polarizability

$$P(1,2) = \frac{\delta n(1)}{\delta V(2)} = -i\frac{\delta G(1,1^+)}{\delta V(2)}$$

can be worked out to lead to:

$$P(1,2) = i\int G(2,3)\underbrace{\frac{\delta G^{-1}(3,4)}{\delta V(1)}}_{-\Gamma(3,4,1)}G(4,2^+)d(3,4)$$



where we have defined the **vertex function** Γ.

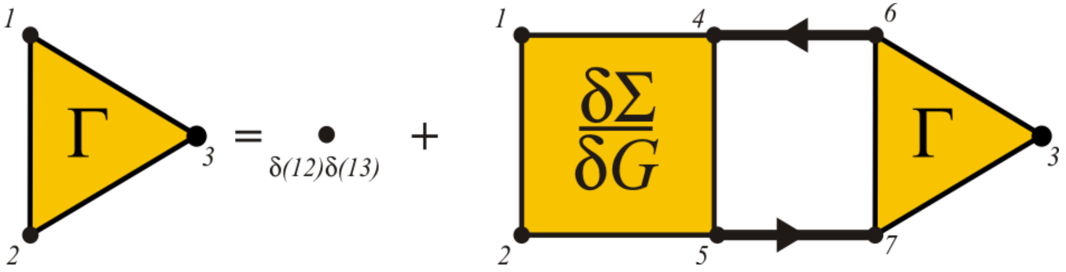
Hedin's equations

- The expression of the vertex function can also be rewritten using:

$$\Gamma(1,2,3) = -\frac{\delta G^{-1}(1,2)}{\delta V(3)} = -\frac{\delta G_0^{-1}(1,2)}{\delta V(3)} + \frac{\Sigma(1,2)}{\delta V(3)}$$

and, after some mathematics, we get:

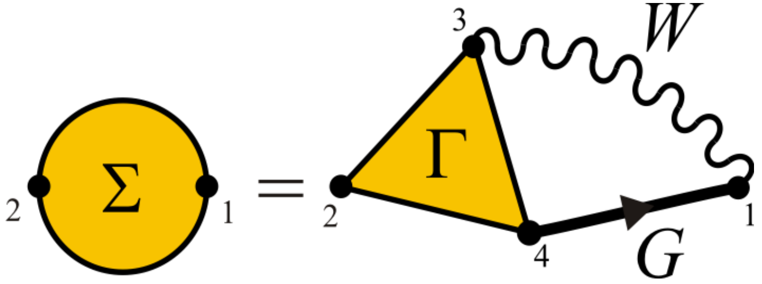
$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(6,7,3)d(4,5,6,7)$$



Hedin's equations

- Finally, after some more mathematics, an expression can be obtained for the self-energy:

$$\Sigma(1,2) = i\int G(1,4)W(1^+,3)\Gamma(4,2,3)d(3,4)$$



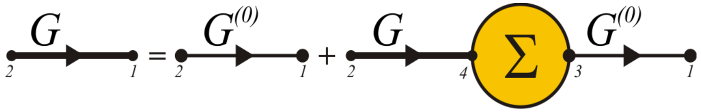
- Using *W* instead of *V* is a critical to achieve a converging series. It was the key finding of Hedin.

- Note that in the Hartree-Fock self-energy is simply given by:

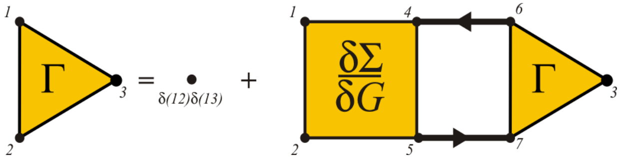
$$\Sigma(1,2) = iG(1,2)v(1,2^+)$$

Hedin's equations

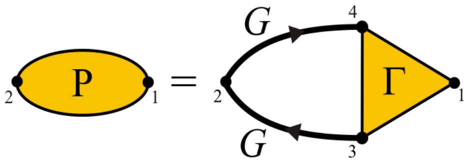
$$G(1,2) = G_0(1,2) + \int G_0(1,3)\Sigma(3,4)G(4,2)\mathrm{d}(3,4)$$



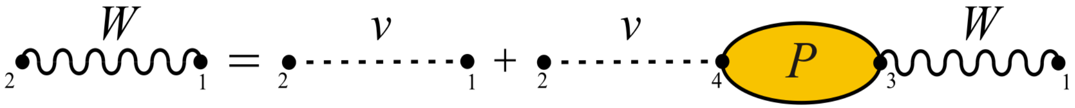
$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(6,7,3)d(4,5,6,7)$$



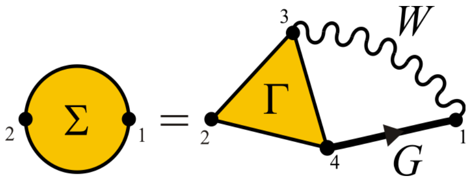
$$P(1,2) = -i \int G(2,3)\Gamma(3,4,1)G(4,2^{+})d(3,4)$$



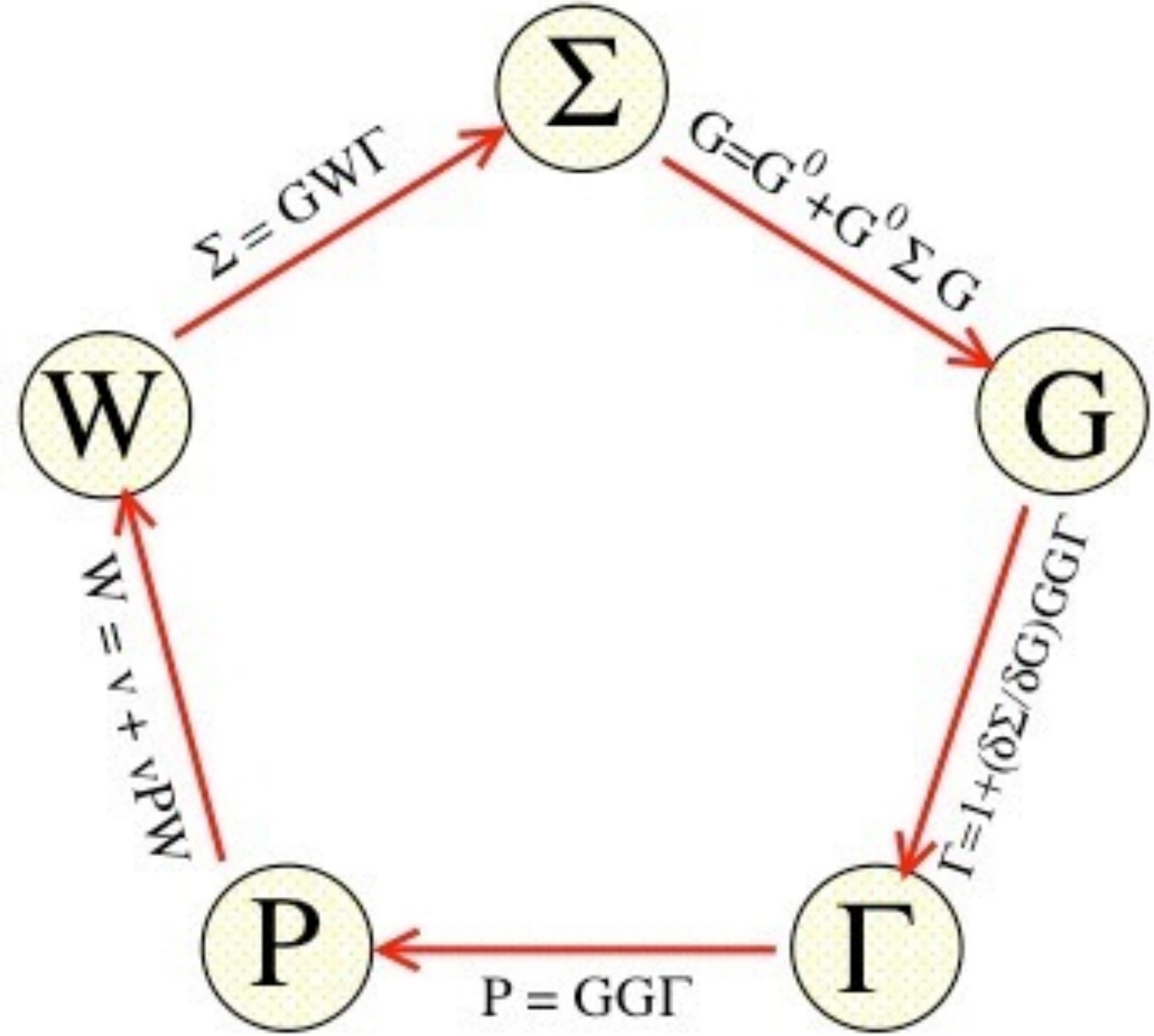
$$W(1,2) = v(1,2) + \int v(1,3)P(3,4)W(4,2)d(3,4)$$



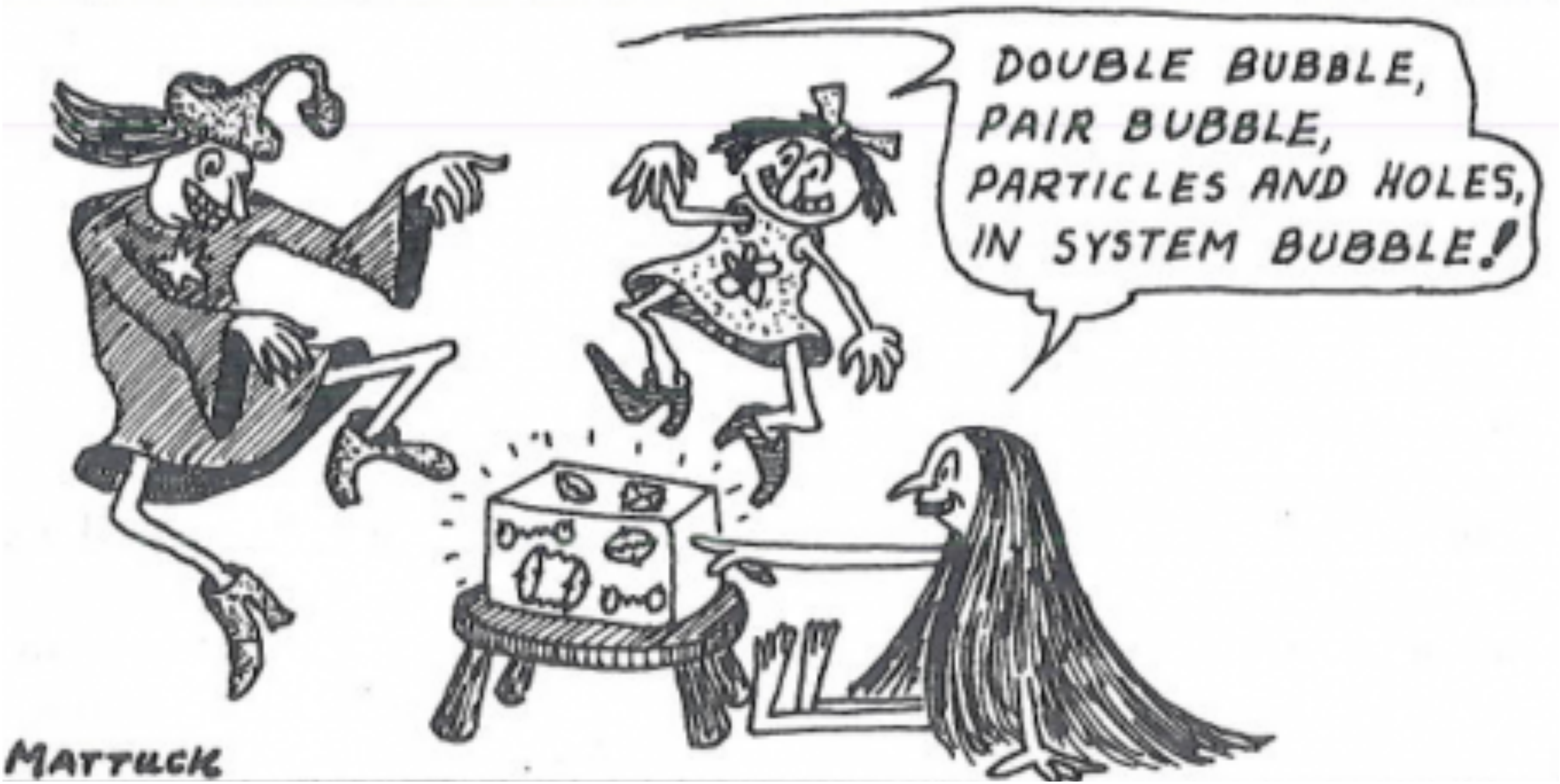
$$\Sigma(1,2) = i \int G(1,4)W(1^{+},3)\Gamma(4,2,3)d(3,4)$$



Hedin's equations



Many-Body Perturbation Theory



[From Richard Mattuck's "Guide to Feynman Diagrams in the Many-Body Problem"]

GW approximation

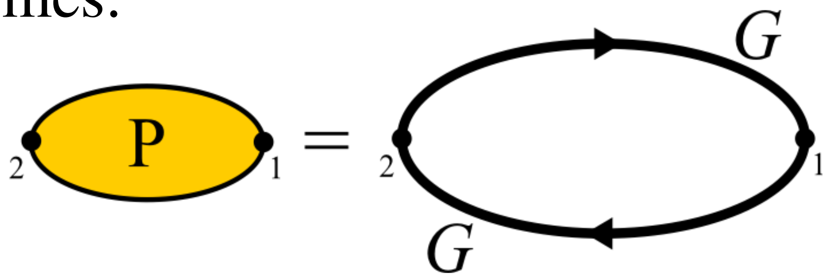
GW approximation

- In order to solve the Hedin's equations, one possible strategy could be to start from the top of the pentagon, with Σ=0.
- The 1-particle Green's function simply reduces to G_0.
- The vertex function is thus:

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3)$$

and the irreducible polarizability becomes:

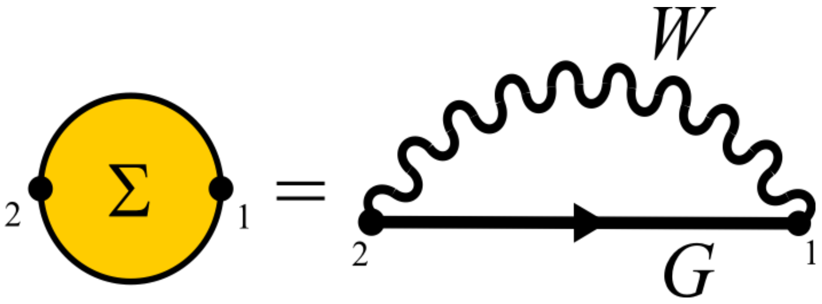
$$P(1,2) = -iG(1,2)G(2,1)$$



- Finally, the self-energy writes:

$$\Sigma(1,2) = iG(1,2)W(1,2^+)$$

hence the name of the approximation.



GW vs. Hartree-Fock approximation

Screened Coulomb interaction

$$W(1,2) = \int \frac{\epsilon^{-1}(\mathbf{r}_3, \mathbf{r}_2, t_1 - t_2)}{|\mathbf{r}_1 - \mathbf{r}_3|} d\mathbf{r}_3$$

GW self-energy

$$\begin{aligned}\Sigma &= i\mathbf{GW} \\ &= i\mathbf{Gv} + i\mathbf{G}(\mathbf{W} - \mathbf{v}) \\ &= \Sigma_x + \Sigma_c(\omega)\end{aligned}$$

non-local

non-hermitian dynamic

Coulomb interaction

$$v(1,2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\delta(t_1 - t_2)$$

Hartree-Fock self-energy

$$\Sigma = i\mathbf{Gv}$$

non-local

hermitian static

Practical *GW* approximation

- Usually, we start from independent-particle Green function G^0 provided by DFT solving the Kohn-Sham equation:

$$G_0(\mathbf{r}_1,\mathbf{r}_2,\omega)=\sum_{n\mathbf{k}}\frac{\phi^{\mathrm{KS}}_{n\mathbf{k}}(\mathbf{r}_1)\left[\phi^{\mathrm{KS}}_{n\mathbf{k}}(\mathbf{r}_2)\right]^*}{\omega-\varepsilon^{\mathrm{KS}}_{n\mathbf{k}}+i\eta\,\mathrm{sgn}(\varepsilon^{\mathrm{KS}}_{n\mathbf{k}}-\mu)}$$

where μ is chemical potential and η a positive infinitesimal.

- The irreducible polarizability is given by the **independent-particle** or **Random Phase Approximation** (RPA) **polarizability**:

$$P_0(\mathbf{r}_1,\mathbf{r}_2,\omega)=\frac{-i}{2\pi}\int G_0(\mathbf{r}_1,\mathbf{r}_2,\omega-\omega')G_0(\mathbf{r}_2,\mathbf{r}_1,\omega)e^{-i\eta\omega'}d\omega'$$

$$P_0(\mathbf{r}_1,\mathbf{r}_2,\omega)=\sum_{n\mathbf{k},m\mathbf{k}'}(f_{n\mathbf{k}}-f_{m\mathbf{k}'})\frac{\phi^{\mathrm{KS}}_{n\mathbf{k}}(\mathbf{r}_1)[\phi^{\mathrm{KS}}_{m\mathbf{k}'}(\mathbf{r}_1)]^*[\phi^{\mathrm{KS}}_{n\mathbf{k}}(\mathbf{r}_2)]^*\phi^{\mathrm{KS}}_{m\mathbf{k}'}(\mathbf{r}_2)}{\omega-(\varepsilon^{\mathrm{KS}}_{n\mathbf{k}}-\varepsilon^{\mathrm{KS}}_{m\mathbf{k}'})-i\eta\,\mathrm{sgn}(\varepsilon^{\mathrm{KS}}_{n\mathbf{k}}-\varepsilon^{\mathrm{KS}}_{m\mathbf{k}'})}$$

$$\varepsilon(\mathbf{r}_1,\mathbf{r}_2,\omega)=\delta(\mathbf{r}_1,\mathbf{r}_2)-\int\frac{P_0(\mathbf{r}_1,\mathbf{r}_3,\omega)}{|\mathbf{r}_3-\mathbf{r}_2|}d\mathbf{r}_3$$

Practical *GW* approximation

- The screened Coulomb interaction is given by:

$$W_0(\mathbf{r}_1,\mathbf{r}_2,\omega)=\int\frac{\varepsilon^{-1}(\mathbf{r}_3,\mathbf{r}_2,\omega)}{|\mathbf{r}_1-\mathbf{r}_3|}d\mathbf{r}_3$$

- Finally, the self-energy is given by:

$$\Sigma(\mathbf{r}_1,\mathbf{r}_2,\omega)=\frac{i}{2\pi}\int G_0(\mathbf{r}_1,\mathbf{r}_2,\omega-\omega')W_0(\mathbf{r}_1,\mathbf{r}_2,\omega)e^{-i\eta\omega'}d\omega'$$

- In principle, this process should be iterated until full self-consistent resolution of Hedin's equations is reached.

- In practice, this is very cumbersome...

- Often, real calculations stop after one round.
  This is the **non-self-consistent *GW* approximation** or **G_0W_0 approximation**.

Quasiparticle equation

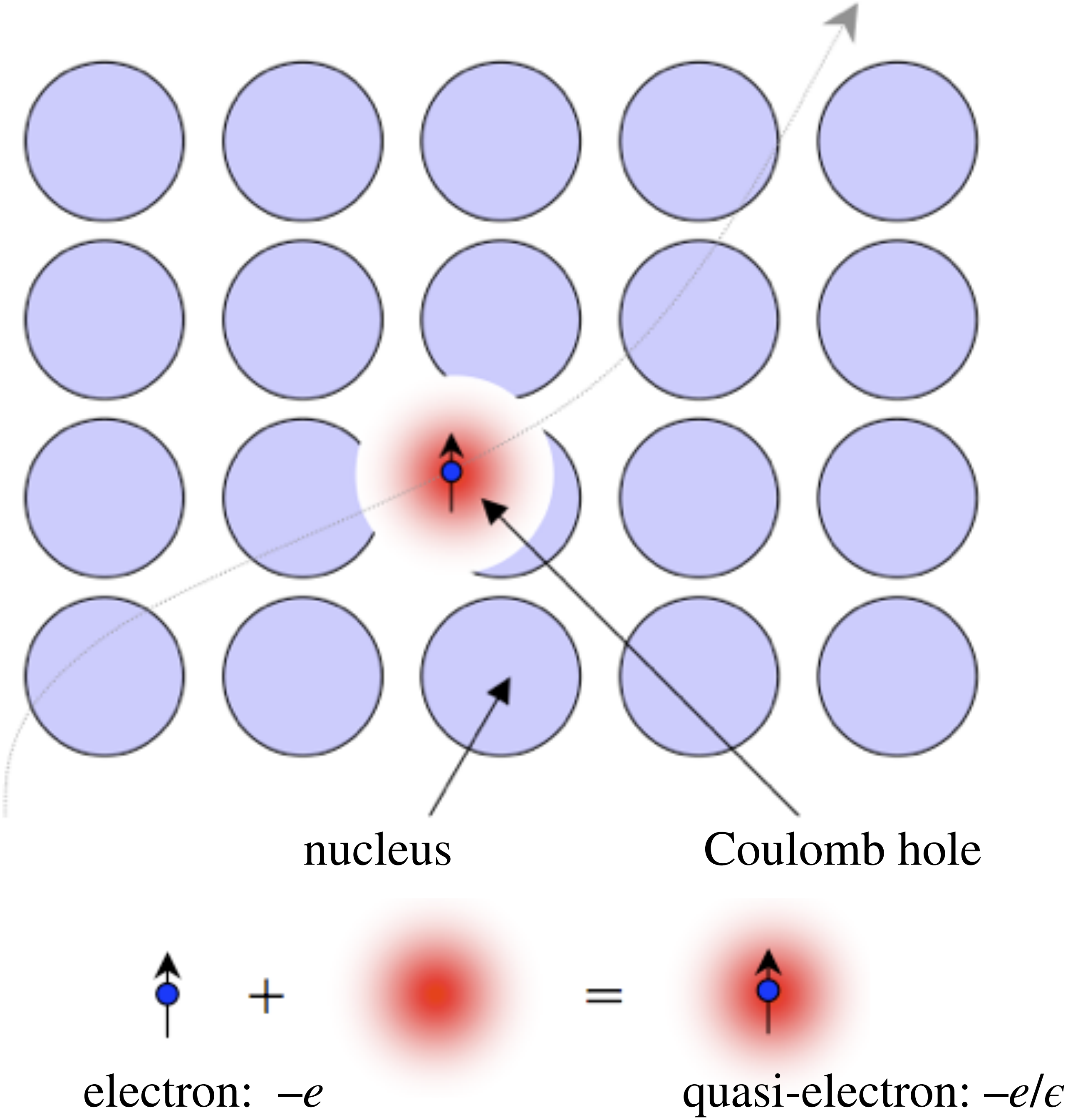
- Often, rather than computing the 1-particle Green's function, we try to solve the **quasiparticle equation**:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}_1} + V_{\text{ext}}(\mathbf{r}_1) + V_{\text{H}}(\mathbf{r}_1)\right] \phi_{n\mathbf{k}}(\mathbf{r}_1,\omega) + \int \Sigma(\mathbf{r}_1,\mathbf{r}_2,\omega)\,\phi_{n\mathbf{k}}(\mathbf{r}_2,\omega)d\mathbf{r}_2 = \varepsilon_{n\mathbf{k}}(\omega)\phi_{n\mathbf{k}}(\mathbf{r}_1,\omega)$$

  for $\omega = \varepsilon_{n\mathbf{k}}(\omega)$.

- In general, the eigenvalues $\varepsilon_{n\mathbf{k}}$ are complex. Their real part can be interpreted as a quasiparticle energy $\varepsilon^{\text{QP}}_{n\mathbf{k}}$ whereas their imaginary part is related to the lifetime of the quasiparticle: $\text{Im}\;\varepsilon_{n\mathbf{k}}(\omega) = 1/\tau^{\text{QP}}$
- An intuitive picture of the quasiparticle concept consists in considering that when a "bare" particle (an electron or a hole) enters in a system of interacting electrons, it perturbs the other particles in its neighborhood and hence it gets "dressed" with a charged (positive or negative) cloud and hence becomes a quasiparticle.

Quasi-electron



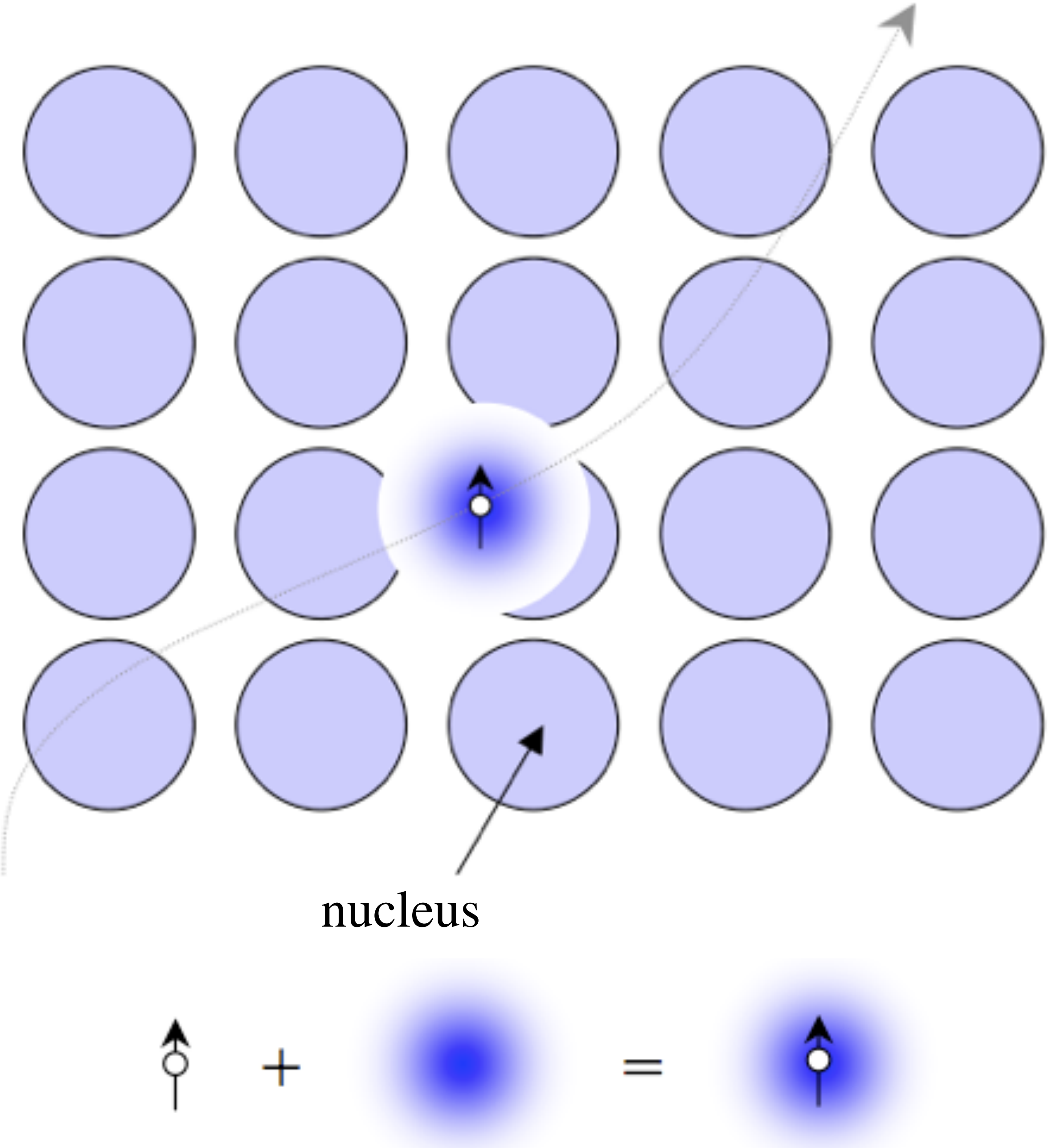
nucleus

Coulomb hole

electron: $-e$

quasi-electron: $-e/\epsilon$

Quasi-hole



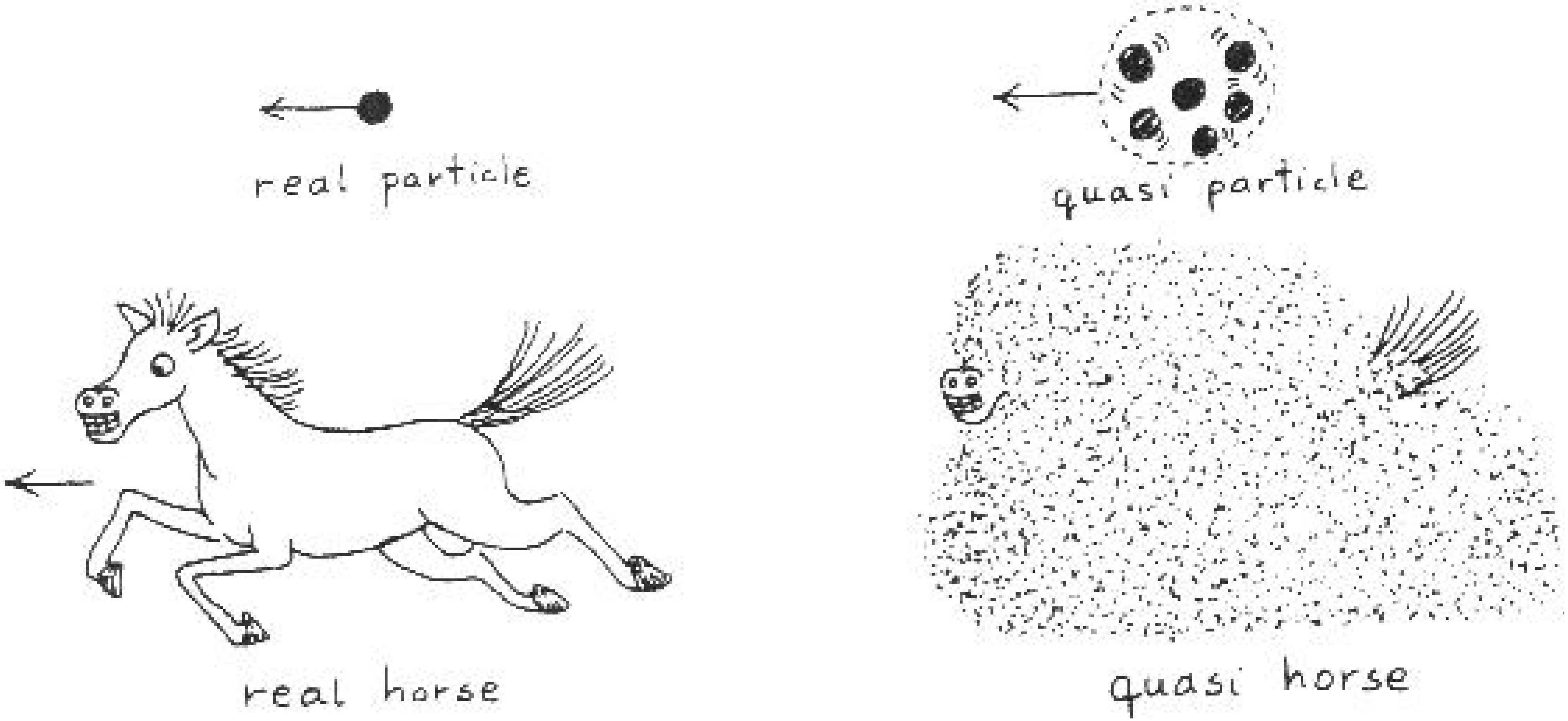
nucleus

$+$ $=$

hole: $+e$

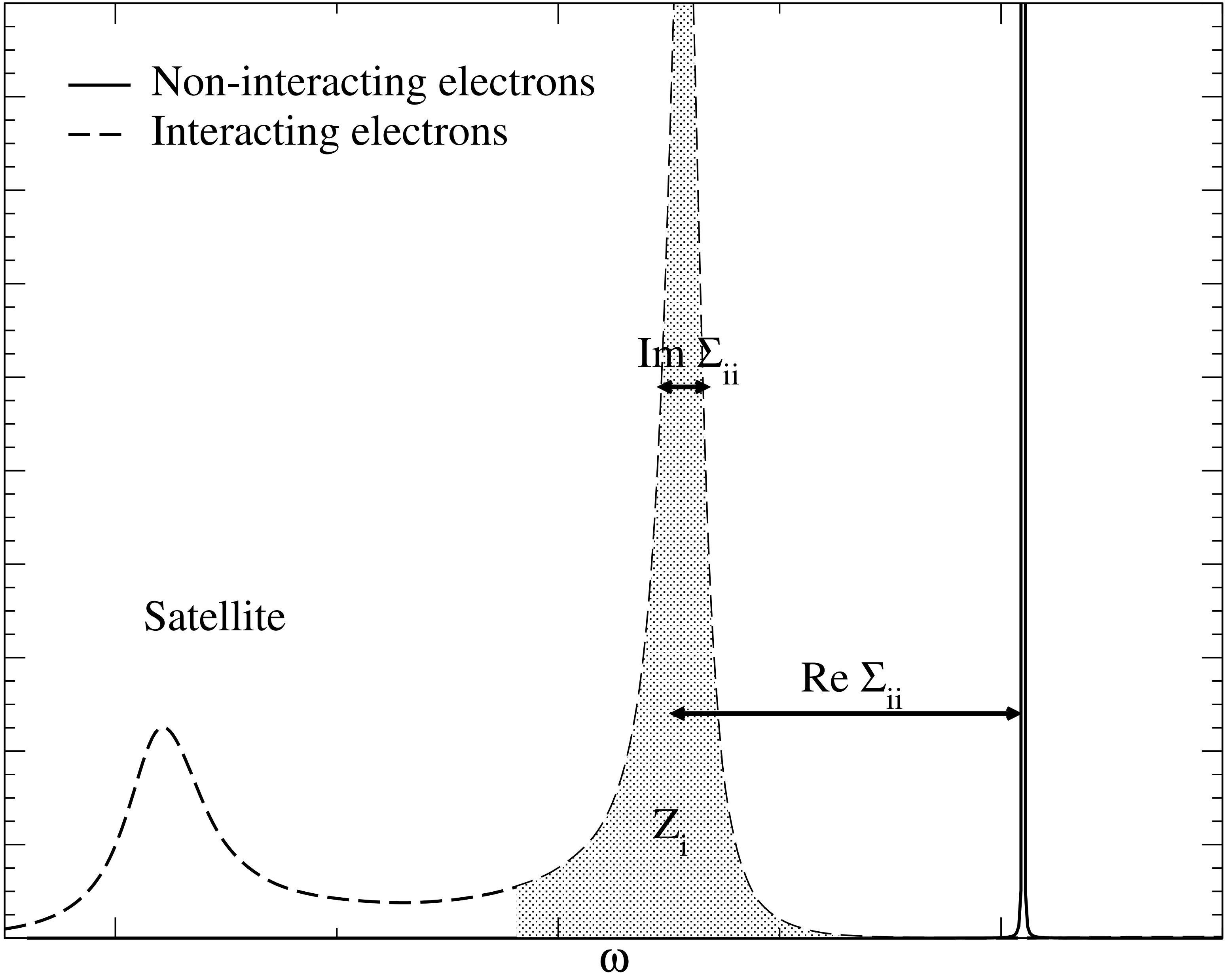
quasi-hole: $+e\,/\epsilon$

Quasi-horse



[From Richard Mattuck's "Guide to Feynman Diagrams in the Many-Body Problem"]

Spectral function



In practice...

- The similarity between the quasiparticle equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r})\right]\phi^{\mathrm{QP}}_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',\omega=\varepsilon^{\mathrm{QP}}_{n\mathbf{k}})\,\phi^{\mathrm{QP}}_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = \varepsilon^{\mathrm{QP}}_{n\mathbf{k}}\,\phi^{\mathrm{QP}}_{n\mathbf{k}}(\mathbf{r})$$

  and the DFT Kohn-Sham one:

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r})\right]\phi^{\mathrm{KS}}_{n\mathbf{k}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})\phi^{\mathrm{KS}}_{n\mathbf{k}}(\mathbf{r}) = \varepsilon^{\mathrm{KS}}_{n\mathbf{k}}\,\phi^{\mathrm{KS}}_{n\mathbf{k}}(\mathbf{r})$$

  suggests to treat the difference between Σ and V_{xc} as a perturbation with respect to the Kohn-Sham calculations.

- In fact, the approximation $\phi^{\mathrm{QP}}_{n\mathbf{k}}(\mathbf{r}) \simeq \phi^{\mathrm{KS}}_{n\mathbf{k}}(\mathbf{r})$ is very reasonable for many materials so that we can write:

$$\epsilon^{\mathrm{QP}}_{n\mathbf{k}} = \epsilon^{\mathrm{KS}}_{n\mathbf{k}} + \left\langle \phi^{\mathrm{KS}}_{n\mathbf{k}} \left| \Sigma(\mathbf{r},\mathbf{r}',\omega=\epsilon^{\mathrm{QP}}_{n\mathbf{k}}) - V_{\mathrm{xc}}(\mathbf{r}) \right| \phi^{\mathrm{KS}}_{n\mathbf{k}} \right\rangle$$

In practice ...

- Since the self-energy Σ operator depends on the energy:

$$\boxed{\epsilon_{n\mathbf{k}}^{\mathrm{QP}}} = \epsilon_{n\mathbf{k}}^{\mathrm{KS}} + \left\langle \phi_{n\mathbf{k}}^{\mathrm{KS}} \left| \Sigma(\mathbf{r},\mathbf{r}',\omega = \boxed{\epsilon_{n\mathbf{k}}^{\mathrm{QP}}}) - V_{\mathrm{xc}}(\mathbf{r}) \right| \phi_{n\mathbf{k}}^{\mathrm{KS}} \right\rangle$$

this non-linear equation should in principle be solved self-consistently.

In practice, the self-energy operator Σ is linearized:

$$\left\langle \Sigma(\omega = \epsilon_{n\mathbf{k}}^{\mathrm{QP}}) \right\rangle = \left\langle \Sigma(\omega = \epsilon_{n\mathbf{k}}^{\mathrm{KS}}) \right\rangle + \left(\epsilon_{n\mathbf{k}}^{\mathrm{QP}} - \epsilon_{n\mathbf{k}}^{\mathrm{KS}} \right) \left\langle \left. \frac{\partial \Sigma(\omega)}{\partial \omega} \right|_{\omega = \epsilon_{n\mathbf{k}}^{\mathrm{KS}}} \right\rangle$$

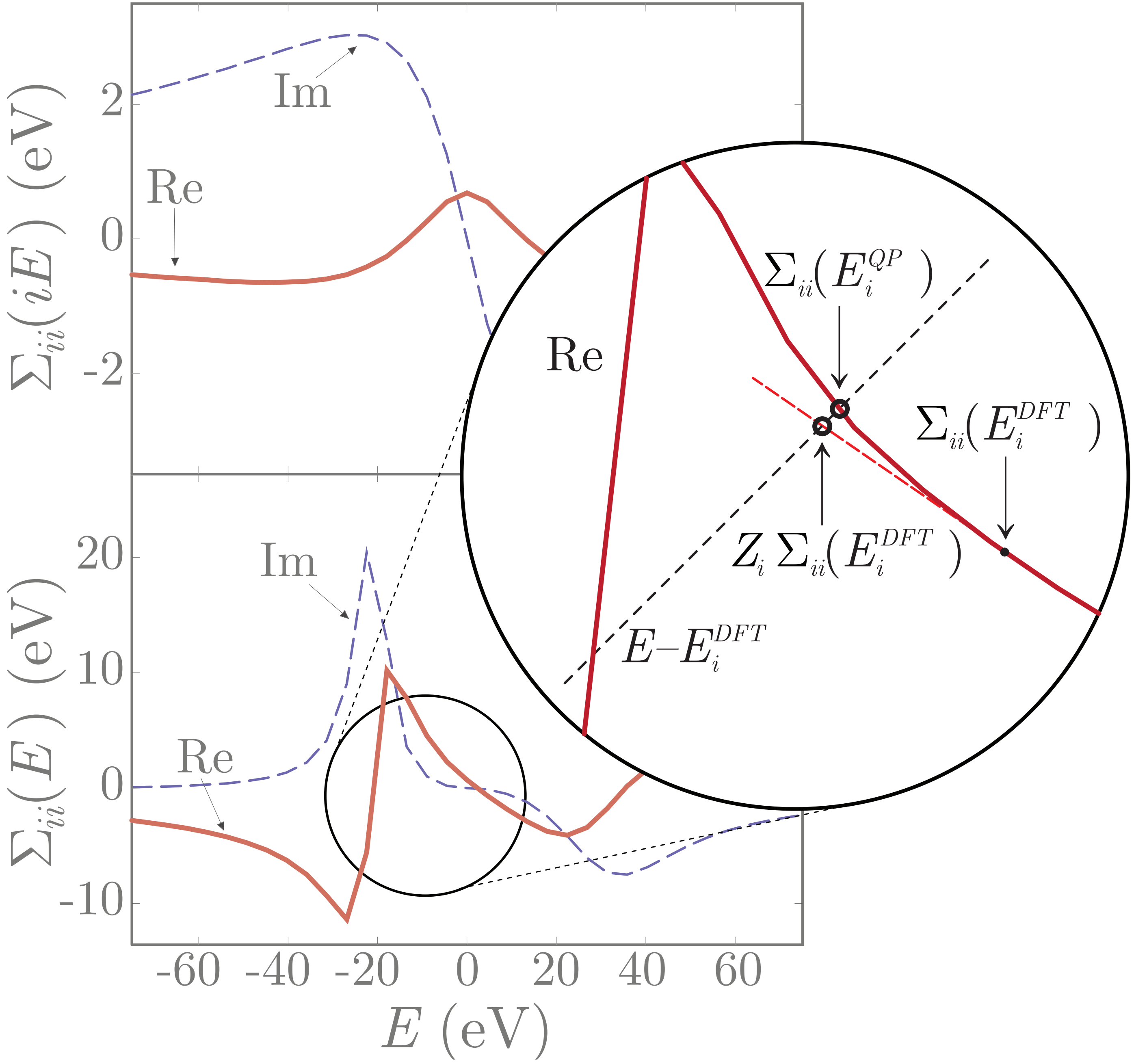
- Hence, defining the renormalization constant $Z_{n\mathbf{k}}$ as:

$$Z_{n\mathbf{k}} = \left(1 - \frac{\partial \left\langle \phi_{n\mathbf{k}}^{\mathrm{KS}} \left| \Sigma(\omega) \right| \phi_{n\mathbf{k}}^{\mathrm{KS}} \right\rangle}{\partial \omega} \right)^{-1}$$

the linearized equation to solve becomes:

$$\epsilon_{n\mathbf{k}}^{\mathrm{QP}} = \epsilon_{n\mathbf{k}}^{\mathrm{KS}} + Z_{n\mathbf{k}} \left\langle \phi_{n\mathbf{k}}^{\mathrm{KS}} \left| \Sigma(\mathbf{r},\mathbf{r}',\omega = \epsilon_{n\mathbf{k}}^{\mathrm{KS}}) - V_{\mathrm{xc}}(\mathbf{r}) \right| \phi_{n\mathbf{k}}^{\mathrm{KS}} \right\rangle$$

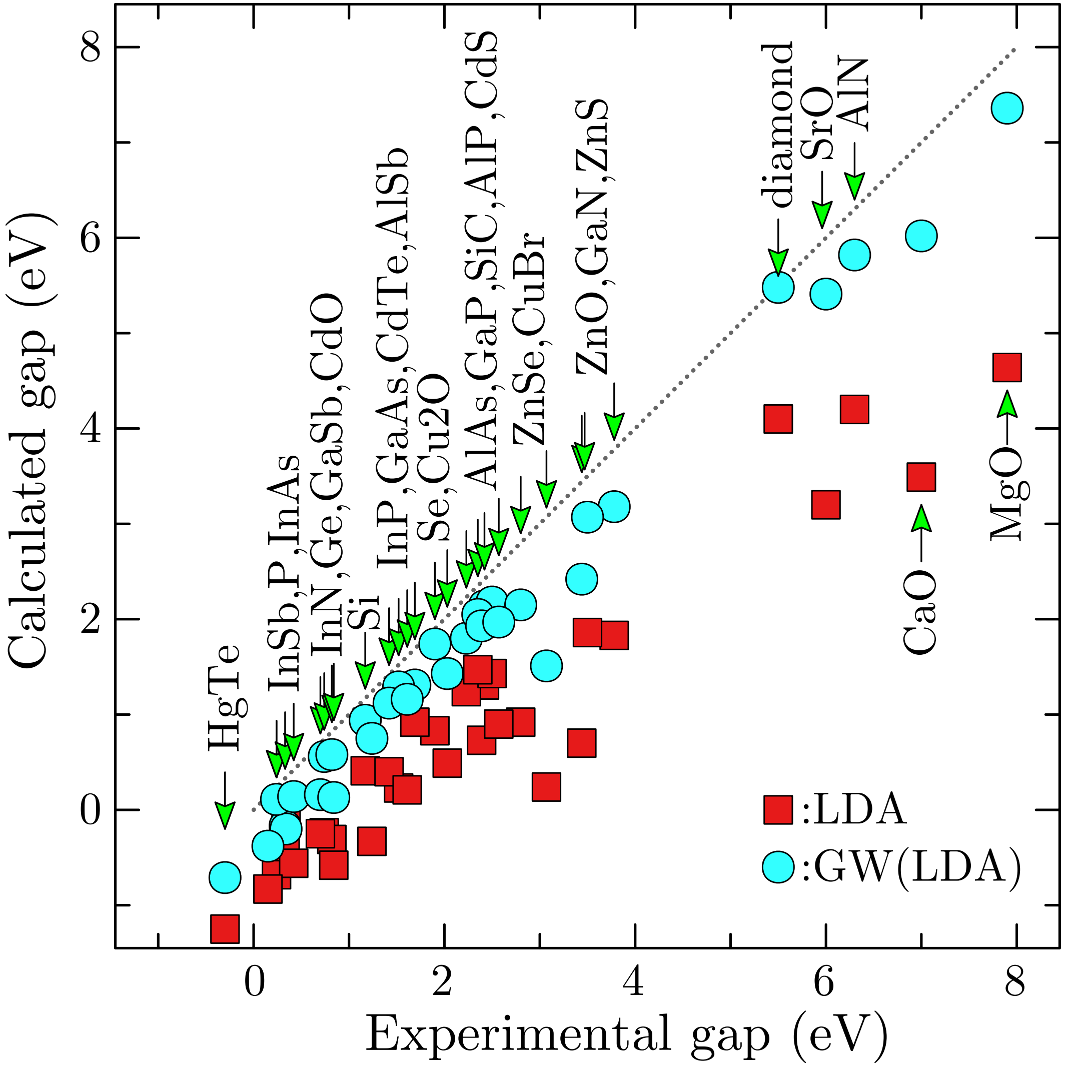
In practice ...



$\Sigma_{ii}(iE)$ (eV)
2
0
-2
Im
Re
$\Sigma_{ii}(E)$ (eV)
20
10
0
-10
Im
Re
-60
-40
-20
0
20
40
60
E (eV)
Re
$\Sigma_{ii}(E_i^{QP})$
$\Sigma_{ii}(E_i^{DFT})$
$Z_i\,\Sigma_{ii}(E_i^{DFT})$
$E - E_i^{DFT}$

The band gap within *GW*

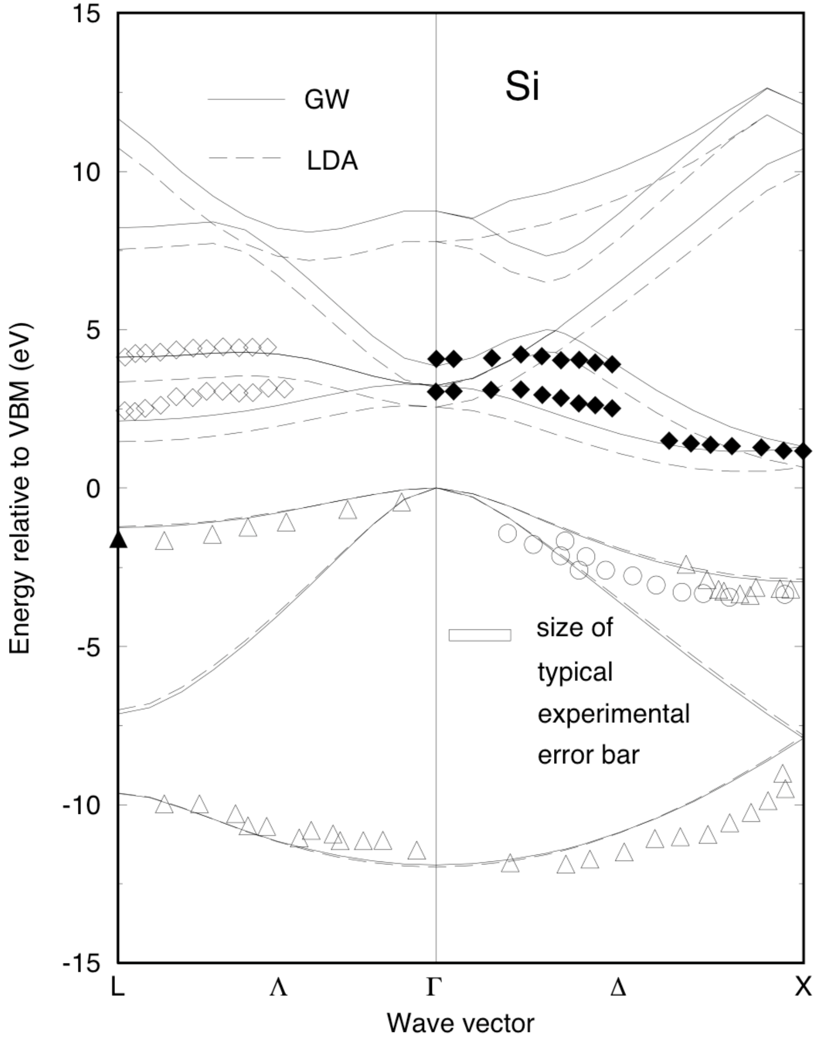
- The agreement with experiments is in much better!



[adapted from van Schilfgaarde *et al.*, PRL **96**, 226402 (2006)]

The band gap within *GW*

- The calculated band structures are in excellent agreement with those measured experimentally.



[from Aulbur *et al.*, Solid State Physics **54**, 1 (2000)]

Self-consistency in the *GW* approximation

- It may happen that the DFT wavefunctions are not adequate, these need to be updated as well in the self-consistent cycle by diagonalizing the self-energy operator. The problem is that the self-energy operator is not hermitian and energy dependent.
- A smart method has thus been devised, the **Quasiparticle Self-consistent GW (QSGW)**, which allows to overcome these problems

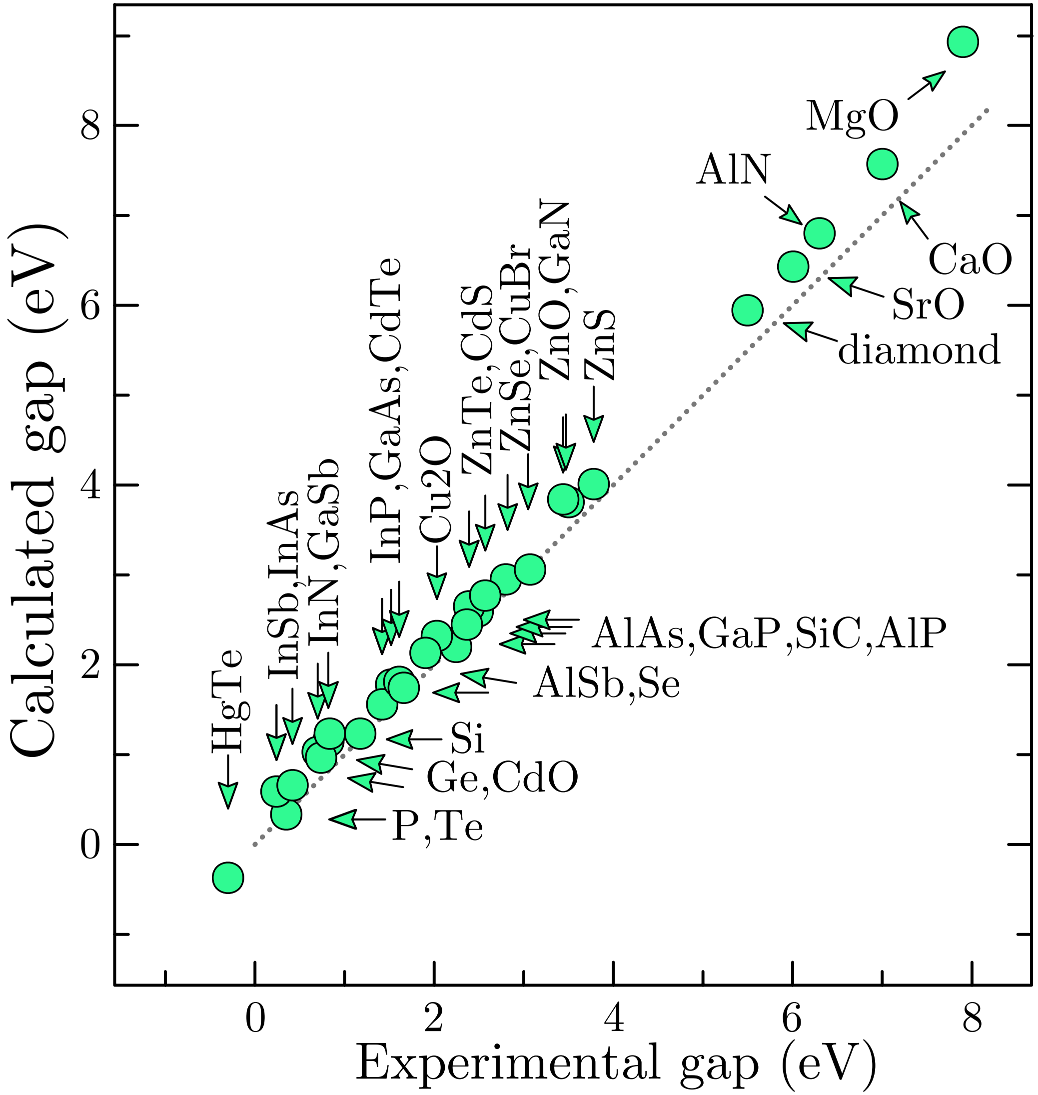
  [S. V. Faleev, M. van Schilfgaarde, and T. Kotani, Phys. Rev. Lett. **93**, 126406 (2004)]:

$$\langle \phi_i | \Sigma | \phi_j \rangle = \frac{1}{2} \Re \left[\langle \phi_i | \Sigma(\varepsilon_i) | \phi_j \rangle + \langle \phi_i | \Sigma(\varepsilon_j) | \phi_j \rangle \right]$$

where $\Re$ means that one only retains the hermitian part of the matrix. Along with self-consistency, the diagonal elements of the self-energy are better and better approximations to the true *GW* diagonal terms, as each of them is finally evaluated for the correct *GW* energy.

Self-consistency in the *GW* approximation

- The QS*GW* band gap is slightly bigger than the experimental one.



[adapted from van Schilfgaarde et al., PRL **96**, 226402 (2006)]

Self-consistency in the *GW* approximation

PRL **99,** 246403 (2007) PHYSICAL REVIEW LETTERS week ending 14 DECEMBER 2007

Accurate Quasiparticle Spectra from Self-Consistent *GW* Calculations with Vertex Corrections

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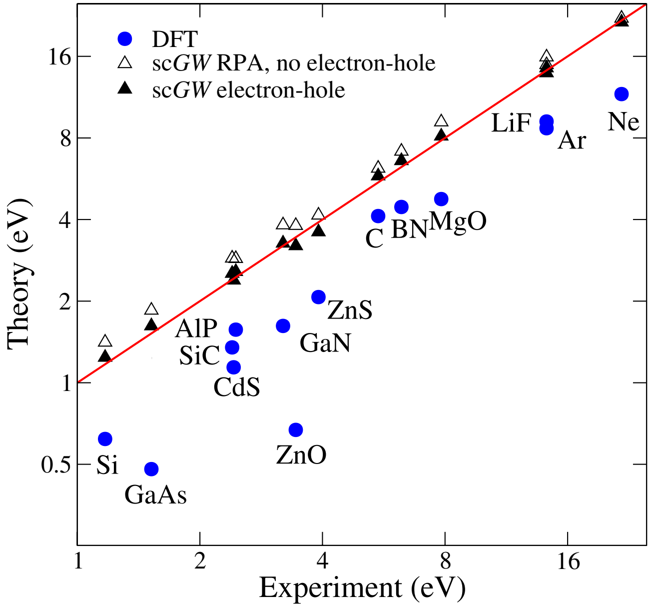
Self-consistent *GW* calculations, maintaining only the quasiparticle part of the Green's function *G*, are reported for a wide class of materials, including small gap semiconductors and large gap insulators. We show that the inclusion of the attractive electron-hole interaction via an effective nonlocal exchange correlation kernel is required to obtain accurate band gaps in the framework of self-consistent *GW* calculations. If these are accounted for via vertex corrections in *W*, the band gaps are found to be within a few percent of the experimental values.



The static screening properties calculated from gradient corrected functionals in the random phase approximation agree very well with the self-consistently determined screening properties in the sc*GW* method. This offers a convenient shortcut and legitimates the often applied GW_0 approximation.

Self-consistency in the *GW* approximation

Self-consistent *GW* calculations for semiconductors and insulators

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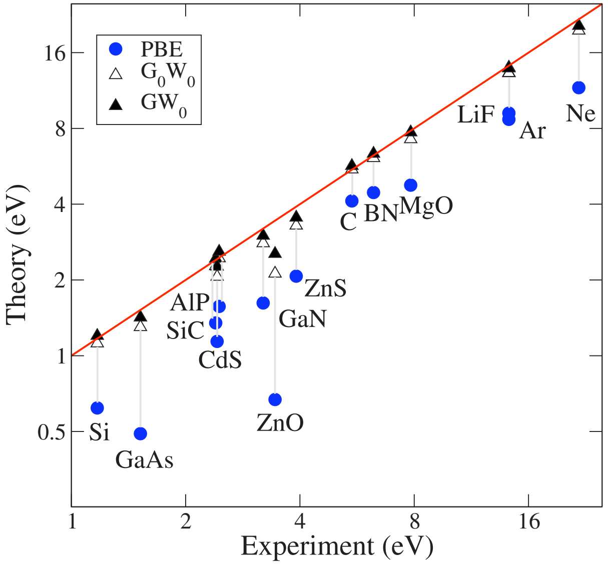
We present *GW* calculations for small and large gap systems comprising typical semiconductors (Si, SiC, GaAs, GaN, ZnO, ZnS, CdS, and AlP), small gap semiconductors (PbS, PbSe, and PbTe), insulators (C, BN, MgO, and LiF), and noble gas solids (Ar and Ne). It is shown that the G_0W_0 approximation always yields too small band gaps. To improve agreement with experiment, the eigenvalues in the Green's function G (GW_0) and in the Green's function and the dielectric matrix (GW) are updated until self-consistency is reached. The first approximation leads to excellent agreement with experiment, whereas an update of the eigenvalues in G and W gives too large band gaps for virtually all materials. From a pragmatic point of view, the GW_0 approximation thus seems to be an accurate and still reasonably fast method for predicting quasiparticle energies in simple *sp*-bonded systems. We furthermore observe that the band gaps in materials with shallow *d* states (GaAs, GaN, and ZnO) are systematically underestimated. We propose that an inaccurate description of the static dielectric properties of these materials is responsible for the underestimation of the band gaps in GW_0, which is itself a result of the incomplete cancellation of the Hartree self-energy within the *d* shell by local or gradient corrected density functionals.



Frequency dependence of *W*

- Within *GW*, the frequency dependence of the dynamically screened Coulomb potential *W* is most often approximated using various plasmon pole models (PPMs):

$$\mathrm{Re}\,\epsilon^{-1}(\omega) = A\delta(\omega - \tilde{\omega}) \qquad\qquad \mathrm{Im}\,\epsilon^{-1}(\omega) = 1 + \frac{\Omega^2}{\omega^2 - \tilde{\omega}^2}$$

  – M.S. Hybertsen and S.G. Louie, Phys. Rev. B 34, 5390 (1986),
  – W. von der Linden and P. Horsch, Phys. Rev. B 37, 8351 (1988),
  – R.W. Godby and R.J. Needs, Phys. Rev. Lett. 62, 1169 (1989),
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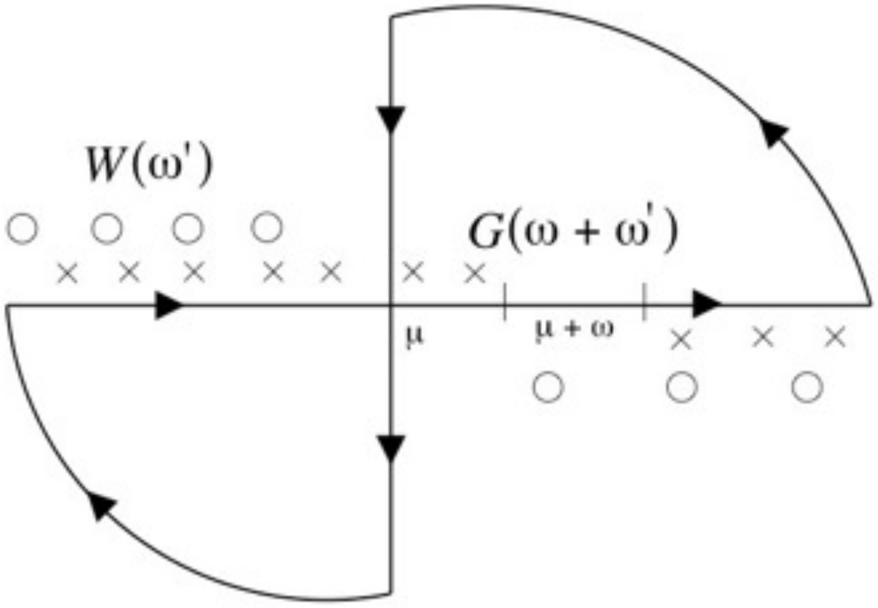
- The advantage is not only to reduce the computational load, but also to obtain an analytic expression for the self-energy.

Frequency dependence of *W*

- Alternatively, the explicit frequency dependence can be obtained using the deformed contour integration technique

  [S. Lebègue, B. Arnaud, M. Alouani and P.E. Bloechl, Phys. Rev. B **67**, 155208 (2003)].

- The integral along the real axis can be calculated from the integral over the contour depicted below: the integral along the imaginary axis requires less points (Σ is smoother) and the sum of the poles of Σ can be evaluated exactly.



× poles of G

○ poles of W

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