# An introduction to the GW method

Johannes Lischner

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## 1 The need to go beyond density-functional theory

### 1.1 Motivation: photoemission spectroscopy and measuring quasiparticle energies

Density-functional theory (DFT) is a hugely successful theory of materials. It can predict many properties in a wide range of materials with high accuracy, including lattice constants, vibrational properties, bulk moduli and cohesive energies. But there are some properties that DFT predicts less accurately, such as band gaps, electron affinities or absorption spectra. To understand why this is the case, let us start by considering a photoemission experiment.

In photoemission spectroscopy, a sample is exposed to photons with an energy $\hbar\omega$ (with $\hbar$ denoting the reduced Planck constant). By the photoelectric effect, photons can transfer so much energy to electrons that they are able to leave the material. Their kinetic energy $E_{kin}$ can then be measured by a detector, see Figure 1. To understand what information can be extracted from a photoemission experiment, consider energy conservation: the sum of the energies of the photon and of the material (containing $N$ electrons) before they interact must be equal to the sum of the energies of the material after the interaction (now containing $N-1$ electrons) and of the escaped electron (often called the photo-electron), i.e.

$$E_{N,0} + \hbar\omega = E_{N-1,\lambda} + E_{kin}. \tag{1}$$

Here, we have assumed that the material is initially in its ground state with energy $E_{N,0}$. After the material has interacted with the photon, it can end up in an excited state $\lambda$ with energy $E_{N-1,\lambda}$.

Rearranging Eq. 1 such that quantities that are measured (the kinetic energy of the photo-electron) or controlled by the experimental setup (the photon energy) are on the left hand side yields

$$\hbar\omega - E_{kin} = -(E_{N,0} - E_{N-1,\lambda}) \equiv -\epsilon_\lambda, \tag{2}$$

where we have defined the quasiparticle energy $\epsilon_\lambda = E_{N,0} - E_{N-1,\lambda}$ which is the difference between the total energy of the $N$-electron system in its ground state and that of the $N-1$-electron system in the excited state $\lambda$. In other words, photoemission spectroscopy measures quasiparticle energies.

“What is a quasiparticle?”, you might ask. Instead of viewing the material after it has lost an electron as an $N-1$-electron system, we can also view it as a system with a single missing electron or hole. This hole behaves in many ways like a real particle: for example, its motion results in an electrical current. Unlike a real particle (say an electron in free space), however, the hole has a finite lifetime: because electrons interact with each other through Coulomb forces, the hole can lose its energy and momentum through an Auger-like decay process in which an electron-hole pair is created in the material. This is why we call it a quasi-particle or quasi-hole.

Another type of quasiparticle is created when an extra electron is added to a material, i.e. when an $N+1$-electron system is created. Again, we can view this system as containing a single quasi-electron. Such quasiparticles are measured in inverse photoemission spectroscopy when a sample is exposed to an electron beam and the outcoming photons are detected. In scanning tunnelling spectroscopy, electrons or holes can hop from a sharp tip onto the surface of a material thereby creating either quasi-electrons or quasi-holes.

## 1.2 Calculating quasiparticle properties

To gain insight into the electronic structure of materials, measured quasiparticle energies are often compared to Kohn-Sham (KS) energies $\epsilon_{KS}$ from DFT calculations which can be obtained by solving the KS equation

$$\left[-\frac{\hbar^2\nabla^2}{2m} + v_{nuc}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})\right]\psi_{KS}(\mathbf{r}) = \epsilon_{KS}\psi_{KS}(\mathbf{r}), \tag{3}$$

where $v_{nuc}(\mathbf{r})$, $v_H(\mathbf{r})$ and $v_{xc}(\mathbf{r})$ denote the potential from the nuclei, the Hartree potential and the exchange-correlation potential, respectively, and $\psi_{KS}(\mathbf{r})$ is the Kohn-Sham wavefunction. This comparison between experimental quasiparticle energies and calculated KS energies might surprise you. First of all, you might remember that DFT is a theory of the electronic ground state, i.e. it produces $E_{N,0}$, but not $E_{N\pm1,\lambda}$ and hence it cannot yield quasiparticle energies. Moreover, the non-interacting KS electrons are merely a convenient mathematical tool for describing the "real" interacting electrons and therefore we should not compare their energies (or wavefunctions) to experiment [1].

Indeed, the quantitative agreement between measured quasiparticle energies and calculated KS energies is often quite poor. For example, (semi-)local exchange-correlation functionals, such as the LDA, underestimate the HOMO-LUMO gap of molecules by several electron volts. A similar underestimation is found for the band gaps of semiconductors and insulators. This inability of DFT to yield accurate results for band gaps in materials is known as the band gap problem of DFT.

To find a route towards overcoming DFT's problem of predicting accurate quasiparticle properties, let us first understand what is going wrong. An important piece of the puzzle is the observation that orbital energies, i.e. the analogue of KS energies, from Hartree-Fock (HF) calculations of *molecules* are often in much better agreement with experimental quasiparticle energies than DFT results. For example, ionization potentials from HF are much closer to experimental values than predictions of semi-local (or even hybrid) exchange-correlation functionals.

In HF, one solves a similar equation as Eq. 3, but with the important difference that the exchange-correlation potential of DFT is replaced by the non-local exact exchange (or Fock) potential

$$v_F(\mathbf{r},\mathbf{r}') = -\sum_n f_n v(\mathbf{r},\mathbf{r}')\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}') \tag{4}$$

with $v(\mathbf{r},\mathbf{r}') = e^2/|\mathbf{r}-\mathbf{r}'|$ (and $e$ denoting the electron charge). Also, $f_n$ denotes the ground state occupancy of state $n$ (in other words, the exchange potential only involves orbitals that are occupied in the ground state). The resulting equation is given by

$$\left[-\frac{\hbar^2\nabla^2}{2m} + v_{nuc}(\mathbf{r}) + v_H(\mathbf{r})\right]\psi_{HF}(\mathbf{r}) + \int d\mathbf{r}' v_F(\mathbf{r},\mathbf{r}')\psi_{HF}(\mathbf{r}') = \epsilon_{HF}\psi_{HF}(\mathbf{r}) \tag{5}$$

with $\epsilon_{HF}$ and $\psi_{HF}(\mathbf{r})$ denoting the HF single-particle energies and wavefunctions, respectively.

A useful relation between the DFT KS energies and the HF single-particle energies can be obtained by subtracting Eq. 3 from Eq. 5 and assuming that $\psi_{HF}(\mathbf{r}) \approx \psi_{KS}(\mathbf{r})$. Multiplying from the left with $\psi_{KS}^*(\mathbf{r})$ and integrating over space yields

$$\epsilon_{HF} = \epsilon_{KS} + \langle\psi_{KS}|v_F - v_{xc}|\psi_{KS}\rangle, \tag{6}$$

where we have used the bra-ket notation for brevity [2]. This result looks exactly like what you would get from first-order perturbation theory with the difference between the Fock exchange potential and the DFT exchange-correlation potential as the perturbation.

While HF works well for quasiparticle properties of molecules, it fails spectacularly for solids: in particular, HF band gaps are often larger than experimentally measured ones by several eV. This shows that HF still lacks an important ingredient needed for predicting accurate quasiparticle properties.

This final ingredient is electronic screening, i.e. the motion of all electrons in the material in response to electric fields. If a charge is inserted into a material, for example by implanting a charged defect, the electrons in the material experience the associated Coulomb potential and rearrange in response to it. The

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[1] The only exception is the KS energy of the HOMO which according to Janak's theorem is equal to minus the ionization potential in *exact* DFT, i.e. if the exact exchange-correlation potential was known.

[2] $\langle\psi_{KS}|v_F - v_{xc}|\psi_{KS}\rangle \equiv \int d\mathbf{r}d\mathbf{r}'\psi_{KS}^*(\mathbf{r})[v_F(\mathbf{r},\mathbf{r}') - v_{xc}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')]\psi_{KS}(\mathbf{r}')$

rearrangement of the electrons leads to a change in the electron density $\delta\rho(\mathbf{r})$ which in turns gives rise to a potential $\delta\phi(\mathbf{r}) = \int d\mathbf{r}' v(\mathbf{r},\mathbf{r}')\delta\rho(\mathbf{r}')$. The total potential is the sum of the "bare" Coulomb potential of the defect and the induced potential created by the rearrangement of the electrons and is often significantly weaker than the "bare" one [3].

Instead of an external charge (such as the one introduced by a defect), we can also consider the charge carried by each electron in the material. The "bare" potential at position $\mathbf{r}$ created by an electron at position $\mathbf{r}'$ is given by $v(\mathbf{r},\mathbf{r}')$. Again, all other electrons rearrange to screen this potential and therefore the total potential is given by

$$W(\mathbf{r},\mathbf{r}') = v(\mathbf{r},\mathbf{r}') + \int d\mathbf{r}'' v(\mathbf{r},\mathbf{r}'')\delta\rho(\mathbf{r}''). \tag{7}$$

As it is the total potential (and not the bare potential $v(\mathbf{r},\mathbf{r}')$) that is experienced by an electron at $\mathbf{r}$, we can say that electrons in a material interact via a screened interaction $W(\mathbf{r},\mathbf{r}')$ instead of the bare interaction $v(\mathbf{r},\mathbf{r}')$ which would be relevant for two electrons interacting with each other in vacuum. Importantly, the screened interaction is often significantly weaker than the bare Coulomb interaction.

The screened interaction is often written in a different form. Linear response theory allows us to express $\delta\rho(\mathbf{r}'')$ due to the presence of an electron at $\mathbf{r}'$ as

$$\delta\rho(\mathbf{r}'') = \int d\mathbf{r}''' \chi(\mathbf{r}'',\mathbf{r}''')v(\mathbf{r}''',\mathbf{r}') \tag{8}$$

with $\chi(\mathbf{r},\mathbf{r}')$ denoting the interacting density-density response function. Inserting this into Eq. 9 yields

$$W(\mathbf{r},\mathbf{r}') = v(\mathbf{r},\mathbf{r}') + \int d\mathbf{r}'' \int d\mathbf{r}''' v(\mathbf{r},\mathbf{r}'')\chi(\mathbf{r}'',\mathbf{r}''')v(\mathbf{r}''',\mathbf{r}') \equiv \int d\mathbf{r}''' \epsilon^{-1}(\mathbf{r},\mathbf{r}''')v(\mathbf{r}''',\mathbf{r}'). \tag{9}$$

Here, $\epsilon^{-1}(\mathbf{r},\mathbf{r}''') = \delta(\mathbf{r}-\mathbf{r}''') + \int d\mathbf{r}'' v(\mathbf{r},\mathbf{r}'')\chi(\mathbf{r}'',\mathbf{r}''')$ denotes the microscopic dielectric matrix which relates the bare Coulomb potential to the screened interaction [4].

So far, we have considered the response of the electrons in a material to a static time-independent perturbation. While this might describe well the situation of an implanted charged defect, it is less appropriate for electrons which can move around the material. Indeed, it is important to consider the material's response to time-dependent perturbations to describe the mutual screening of electrons. In this case, the density-density response function and the screened interaction will become energy-dependent and will be denoted by $\chi(\mathbf{r},\mathbf{r}',E)$ and $W(\mathbf{r},\mathbf{r}',E)$, respectively.

## 1.3 GW: a sneak peak

Now that we have a good understanding of the origin of DFT's (and HF's) failure to produce accurate quasiparticle energies, we are ready to take a sneak peak at the GW approach which is the current state-of-the-art technique for calculating such properties in materials. GW works well for atoms, molecules, clusters and other nanostructures (such as nanotubes, nanoribbons or two-dimensional materials), surfaces and bulk materials. For example, GW produces accurate HOMO-LUMO gaps in molecules and also overcomes the band gap problem of DFT.

In standard GW calculations, quasiparticle energies are obtained by solving an equation that looks similar to Eq. 6, but the Fock potential is replaced by a so-called self-energy $\Sigma_{GW}(\mathbf{r},\mathbf{r}',E)$. The resulting equation is

$$\epsilon_{GW} = \epsilon_{KS} + \langle\psi_{KS}|\Sigma_{GW}(\epsilon_{GW}) - v_{xc}|\psi_{KS}\rangle. \tag{10}$$

Like the Fock potential, the GW self-energy is non-local (i.e. depends on two positions), but in addition it is also energy-dependent. As a consequence, we need to solve for $\epsilon_{GW}$ self-consistently making sure that the self-energy is evaluated at the (a priori unknown) quasiparticle energy.

The GW self-energy is often written as a sum of two terms: the screened-exchange (SX) contribution given by

$$\Sigma_{SX}(\mathbf{r},\mathbf{r}',E) = -\sum_n f_n W(\mathbf{r},\mathbf{r}',E-\epsilon_n)\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}') \tag{11}$$

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[3] This can be seen by considering the potential of a point charge in a homogeneous dielectric. In this case, the "bare" potential is reduced by the dielectric constant of the material.

[4] Setting $\epsilon^{-1}(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')/\epsilon$ with $\epsilon$ being the macroscopic dielectric constant of the material recovers the expected result from macroscopic electrostatics $W(\mathbf{r},\mathbf{r}') = e^2/(\epsilon|\mathbf{r}-\mathbf{r}'|)$.

and a Coulomb-hole (CH) term. We will present the full expression for the CH term later in this chapter. For now, we consider the so-called COHSEX approximation to this term as this makes its physical content more explicit. Within this approximation, the CH contribution to the GW self-energy is given by

$$\Sigma_{CH}(\mathbf{r},\mathbf{r}',E) = \frac{1}{2}\delta(\mathbf{r}-\mathbf{r}')\left[W(\mathbf{r},\mathbf{r}',E=0) - v(\mathbf{r},\mathbf{r}')\right]. \tag{12}$$

One of the appealing aspects of the GW approach is the transparency of the two self-energy terms. The SX term has the same form as the Fock potential (see Eq. 4), but with the bare Coulomb interaction replaced by the screened interaction. This enables GW to produce accurate quasiparticle energies also in solids where HF fails. In contrast to the SX term, the CH contribution within the COHSEX approximation is local and static. By inserting Eq. 9 for the screened interaction, we can see that the CH potential is proportional to the potential associated with $\delta\rho(\mathbf{r})$ which is the change in the electron density induced by the presence of the electron itself. One can describe this situation as the electron "digging a hole for itself".

Finally, it is important to note that GW can predict other quasiparticle properties besides their energies. In particular, it also yields the lifetimes of quasiparticles. Moreover, it can produce other experimental properties that are not related to quasiparticle properties, such as so-called satellite features in the photoemission spectrum that result from the creation of collective plasmon excitations.

Following this somewhat hand-wavy introduction into the GW approach, we will now proceed and try to be more rigorous. In particular, we will derive Eq. 10 from first principles, i.e. starting from the fundamental Hamiltonian of interacting electrons in a material.

## 2 Introduction to Green's functions

### 2.1 Field operators and Green's functions

Quasiparticles are created when electrons are added or removed from an interacting many-electron systems as in an (inverse) photoemission experiment or in scanning tunneling microscopy. The mathematical description of such processes is facilitated by the field operators $\hat{\psi}^\dagger(\mathbf{r},t)$ ($\hat{\psi}(\mathbf{r},t)$) which create (destroy) an electron at position $\mathbf{r}$ and time $t$. Here, we use the Heisenberg picture which means that operators are time-dependent and given by

$$\hat{\psi}(\mathbf{r},t) = e^{i\hat{H}t}\hat{\psi}(\mathbf{r})e^{-i\hat{H}t} \tag{13}$$

with $\hat{H}$ being the fundamental Hamiltonian of the $N$-electron system given by

$$\hat{H} = \hat{H}_0 + \hat{H}_{e-e}. \tag{14}$$

Here, $\hat{H}_0$ is the Hamiltonian of non-interacting electrons (i.e. the kinetic energy contribution and the contribution arising from the interaction with the atomic nuclei) and $\hat{H}_{e-e}$ captures electron-electron interactions.

The spatial dependence of the field operator can be described in terms of a complete set of single-particle orbitals $\psi_n(\mathbf{r})$ (for example, the eigenstates of non-interacting electrons or alternatively the KS orbitals) according to

$$\hat{\psi}^\dagger(\mathbf{r}) = \sum_n \psi_n^*(\mathbf{r})\hat{c}_n^\dagger, \tag{15}$$

where $\hat{c}_n^\dagger$ is the operator that creates an electron in state $\psi_n(\mathbf{r})$.

To convince ourselves that the field operator really creates an electron at a specific position, we act with it on the "vacuum" state $|vac\rangle$ which describes the material without any electrons. This yields

$$\hat{\psi}^\dagger(\mathbf{r})|vac\rangle = \sum_n \psi_n^*(\mathbf{r})|\psi_n\rangle. \tag{16}$$

To analyze the resulting state as a function of position, we project it onto $\langle\mathbf{r}'|$ (recalling that $\psi_n(\mathbf{r}') \equiv \langle\mathbf{r}'|\psi_n\rangle$) and obtain

$$\langle\mathbf{r}'|\hat{\psi}^\dagger(\mathbf{r})|vac\rangle = \sum_n \psi_n^*(\mathbf{r})\langle\mathbf{r}'|\psi_n\rangle = \sum_n \psi_n^*(\mathbf{r})\psi_n(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'), \tag{17}$$

where we used the completeness of the single-particle basis. This is the expected result as it shows us that the electron created by the field operator is completely localized at position $\mathbf{r}$.

Now we are in a position to introduce the Green's function which describes the propagation of electrons or holes through a material. For this reason, the Green's function is often called a propagator. We can calculate the probability amplitude [5] of a hole (added to the ground state $|N,0\rangle$ of an $N$-electron system) propagating from position $\mathbf{r}$ at time $t$ to position $\mathbf{r}'$ at time $t'$ as the expectation value

$$\langle N,0|\hat{\psi}^\dagger(\mathbf{r}',t')\hat{\psi}(\mathbf{r},t)|N,0\rangle. \tag{18}$$

In other words, we first act on the ground state with a field operator to create a hole and then act on this state with another field operator that creates an electron (i.e. removes the hole) at a later time (implying that $t' > t$) and at a different location.

Not surprisingly, the propagation of an electron is given by

$$\langle N,0|\hat{\psi}(\mathbf{r},t)\hat{\psi}^\dagger(\mathbf{r}',t')|N,0\rangle, \tag{19}$$

where we must have that $t > t'$.

The Green's function describes both processes, i.e. the propagation of electrons and holes, and is given by

$$G(\mathbf{r},\mathbf{r}',t,t') = -i\langle N,0|\left\{\Theta(t-t')\hat{\psi}(\mathbf{r},t)\hat{\psi}^\dagger(\mathbf{r}',t') - \Theta(t'-t)\hat{\psi}^\dagger(\mathbf{r}',t')\hat{\psi}(\mathbf{r},t)\right\}|N,0\rangle \equiv -i\langle N,0|\hat{T}\left\{\hat{\psi}(\mathbf{r},t)\hat{\psi}^\dagger(\mathbf{r}',t')\right\}|N,0\rangle, \tag{20}$$

where $\Theta(t)$ denotes the Heaviside step function and we defined the time-ordering operator $\hat{T}$ which orders the field operators in the parenthesis according to their time arguments with the field operator that acts at the earliest time on the very right. When this ordering requires the exchange of two field operators, the expression must be multiplied with a minus to ensure anti-symmetry of the many-electron wavefunction.

To understand what information about quasiparticle properties is contained in the Green's function, let us focus on the part that describes the propagation of a hole and explicitly write out the time-dependence of the field operators. This yields

$$-i\Theta(t'-t)\langle N,0|\hat{\psi}^\dagger(\mathbf{r}',t')\hat{\psi}(\mathbf{r},t)|N,0\rangle = -i\Theta(t'-t)\langle N,0|e^{i\hat{H}t'}\hat{\psi}^\dagger(\mathbf{r}')e^{-i\hat{H}t'}e^{i\hat{H}t}\hat{\psi}(\mathbf{r})e^{-i\hat{H}t}|N,0\rangle. \tag{21}$$

We can simplify this expression by noting that

$$e^{-i\hat{H}t}|N,0\rangle = e^{-iE_{N,0}t}|N,0\rangle. \tag{22}$$

As the field operator acting at $t$ removes an electron from the system, we can insert a complete set of $N-1$-electron states ($\sum_\lambda |N-1,\lambda\rangle\langle N-1,\lambda|$) directly after it and then use that

$$e^{i\hat{H}t}|N-1,\lambda\rangle = e^{iE_{N-1,\lambda}t}|N-1,\lambda\rangle. \tag{23}$$

Collecting all terms yields

$$-i\Theta(t'-t)\sum_\lambda e^{i(E_{N,0}-E_{N-1,\lambda})(t'-t)}\langle N,0|\hat{\psi}^\dagger(\mathbf{r}')|N-1,\lambda\rangle\langle N-1,\lambda|\hat{\psi}(\mathbf{r})|N,0\rangle. \tag{24}$$

A similar expression can be derived for the electron propagation term, but now we have to insert a complete set of states of the $N+1$-electron system. If we add both contributions together and then carry out a Fourier transform from time to frequency space, we obtain our final result

$$G(\mathbf{r},\mathbf{r}',\omega) = \sum_\lambda \frac{\psi_{N-1,\lambda}(\mathbf{r})\psi^*_{N-1,\lambda}(\mathbf{r}')}{\omega-[E_{N,0}-E_{N-1,\lambda}]-i\eta} + \sum_\lambda \frac{\psi_{N+1,\lambda}(\mathbf{r})\psi^*_{N+1,\lambda}(\mathbf{r}')}{\omega-[E_{N+1,\lambda}-E_{N,0}]+i\eta}, \tag{25}$$

where we introduced the quasiparticle wavefunctions $\psi_{N-1,\lambda}(\mathbf{r}) = \langle N-1,\lambda|\hat{\psi}(\mathbf{r})|N,0\rangle$ and $\eta$ is a positive infinitesimal required to ensure the convergence of the Fourier transform of the Heaviside step function. This is known as the Lehmann representation of the Green's function. Importantly, it is an exact result and fully includes the effect of electron-electron interactions. A key insight is that the total energy differences in the denominators are precisely equal to the quasiparticle energies measured in photoemission and

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[5] Recall that in quantum mechanics the probability of a process is obtained by taking the absolute square of the corresponding probability amplitude.

tunnelling experiments. In other words, the quasiparticle energies are the poles of the Green's function in frequency space!

Evaluating Eq. 25 for a material is highly challenging because it requires knowledge of the interacting many-electron wavefunctions (both the ground of the $N$-electron system as well as all excited states of the $N \pm 1$- electron systems) and their energies. Not surprisingly, it is much easier to evaluate this expression when electron-electron interactions are neglected. In this case, $|N, 0\rangle$ and $|N \pm 1, \lambda\rangle$ are single Slater determinants. In particular, $|N, 0\rangle$ is the Slater determinant obtained from the $N$ spin-orbitals with the lowest energies, while $|N - 1, \lambda\rangle$ has an electron missing in one of the spin-orbitals and $|N + 1, \lambda\rangle$ has an extra electron in one of the unoccupied orbitals. As the total energies of these many-electron states is simply the sum of the orbital energies $\epsilon_n$ of all occupied single-electron states $\psi_n(\mathbf{r})$, the quasiparticle energies are simply given by the orbital energies and the quasiparticle wavefunctions by the orbital wavefunctions. The final result is

$$G_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_n f_n \frac{\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')}{\omega - \epsilon_n - i\eta} + \sum_n (1 - f_n) \frac{\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')}{\omega - \epsilon_n + i\eta}. \tag{26}$$

This equation shows that $G_o$ is diagonal in the basis of single-particle states $\psi_n(\mathbf{r})$, i.e.

$$G_{0,nn'}(\omega) \equiv \langle\psi_n|G_0|\psi_{n'}\rangle = \frac{\delta_{nn'}}{\omega - \epsilon_n \pm i\eta}, \tag{27}$$

with the sign depending on whether $n$ is an occupied or an unoccupied state.

## 2.2 Evaluating the interacting Green's function through Feynman diagrams

So far, we have derived an exact expression, the Lehmann represenation, for the interacting Green's function, but evaluating this expression is extremely challenging because it requires knowledge of all many-electron eigenstates (and energies) of the $N \pm 1$ electron systems as well the interacting $N$ electron ground state. However, calculating the non-interacting Green's function is straightforward and we can use this result as the starting point for a perturbation series expension of the interacting Green's function.

Starting from Eq. 14, we treat the $\hat{H}_{e-e}$ as a perturbation and expand the exponential factors that enter the Green's function through the time-dependence of the field operators, such as $\exp(-i\hat{H}t)$, as

$$\exp(-i\hat{H}t) \approx e^{-i\hat{H}_0 t}\left(1 - i\hat{H}_{e-e}t + \frac{(-i\hat{H}_{e-e}t)^2}{2} + ...\right). \tag{28}$$

In addition, we need to expand the interacting $N$-electron ground state. This can be achieved through the use of the Gell-Mann-Low theorem which states that

$$|N, 0\rangle = \exp(-i\int_{-\infty}^{0} dt\hat{H}_\eta(t))|N, 0\rangle_0, \tag{29}$$

where we introduced the time-dependent Hamiltonian $\hat{H}_\eta(t) = \hat{H}_0 + e^{-\eta|t|}\hat{H}_{e-e}$ which is equal to the non-interacting Hamiltonian at $t = \pm\infty$ and equal to the fully interacting Hamiltonian at $t = 0$. Here, $\eta$ is a positive infinitesimal which ensures that the interactions are "switched on" extremely slowly. Finally, $|N, 0\rangle_0$ is the ground-state wavefunction of the non-interacting electrons.

Inserting Eq. 29 into the interacting Green's funtion and expanding $\hat{H}_\eta$ in terms of the electron-electron interaction then allows us to express $G$ as a series of terms which contain different numbers of $\hat{H}_{e-e}$'s. In principle, each term is straightforward to evaluate, but the problem is that so many terms are generated such that the book-keeping becomes a problem.

To deal with this challenge, Richard Feynman came up with a diagrammatic representation of the terms. The building blocks of the diagrams are non-interacting Green's functions $G_0(\mathbf{r}, \mathbf{r}', t, t')$ which are represented by straight lines that connect two space-time points $(\mathbf{r}, t)$ and $(\mathbf{r}', t')$ and Coulomb interactions $v(\mathbf{r}, \mathbf{r}', t, t') = v(\mathbf{r}, \mathbf{r}')\delta(t - t')$ [6] which are represented by "wiggly" lines, see Fig. 1.

Then the interacting Green's function, which is represented by a double straight line can be represented by the set of diagrams shown in Fig. 1.

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[6] Here, we assume that Coulomb interactions act instantaneously and neglect any retardation effects arising from the finite speed of light.

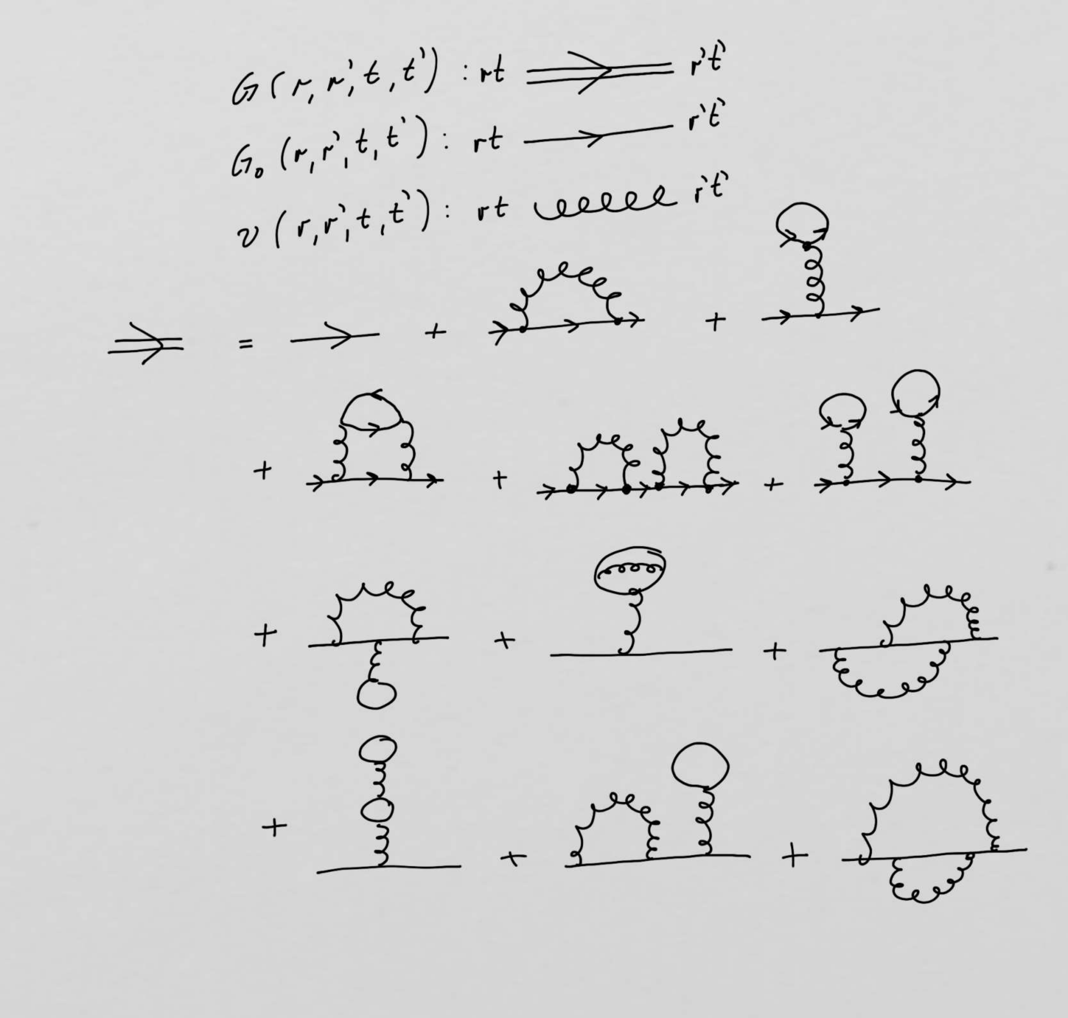

Figure 1: Top: Graphical representations of the interaction and the non-interacting Green's function and the bare Coulomb interaction. Bottom: Lowest-order diagrams for the interacting Green's function.

To evaluate a diagram we label each space-time point where straight lines and wiggly lines meet by a space-time point $(\mathbf{r}_j, t_j)$ and then write down the product of all Coulomb interactions and non-interacting Green's functions that connect the various space-time points. Finally, we integrate over all space-time points except the initial and final one and multiply by a factor of $(-1)^F$ with $F$ denotes the number of closed loops made by straight $G_0$ lines.

As an example, let us evaluate the two first-order terms which contain a single wiggly interaction line. The contribution of the first term is given by

$$\int d^3r_1 \int dt_1 \int d^3r_2 \int dt_2 G_0(\mathbf{r}', t'; \mathbf{r}_2, t_2) v(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) G_0(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) G_0(\mathbf{r}_1, t_1; \mathbf{r}, t) \tag{30}$$

and the contribution of the second term is

$$(-1) \int d^3r_1 \int dt_1 \int d^3r_2 \int dt_2 G_0(\mathbf{r}', t'; \mathbf{r}_1, t_1) v(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) G_0(\mathbf{r}_2, t_2; \mathbf{r}_2, t_2) G_0(\mathbf{r}_1, t_1; \mathbf{r}, t). \tag{31}$$

Here, we multipled the second term by a factor of $-1$ because it contains a closed loop. We will later see that the first term describes the Fock exchange while the second one captures Hartree interactions.

## 2.3 Structure of the diagrammatic series

In principle, we can now start and evaluate term by term of the diagrammatic series and thereby calculate the interacting Green's function with increasing accuracy. Unfortunately, this approach will not yield accurate results for real materials because the Coulomb interaction between electrons is very strong. However, we can exploit the structure of the diagrammatic series to capture the contribution of a subset of terms in all orders of the perturbation expansion.

The first step is to realize that all diagrams (except the zero-th order one which is just a single straight line) start with a straight line and end with a straight line and have "something" in the middle. We can therefore write these diagrams in terms of a shaded bubble which contains the sum of all the stuff that is in the middle between in initial and the final straight lines, see Fig. 2. The diagrams in the shaded bubble are simply the standard Feynman diagrams with the initial and final straight lines "sawn off".

But there is more: when we inspect the diagrams inside the shaded bubble, we see that they fall into two distinct classes. There are some terms that can be separated into two unconnected pieces by "cutting" a single straight line. Examples include the third and the fourth diagrams. The other diagrams that are drawn do not fall into this category and we call them irreducible. The sum of these irreducible diagrams is called the (irreducible) self-energy and is diagrammatically represented by a non-shaded bubble. The shaded bubble can now be expressed as a series of self-energy bubbles, see Fig. 2.

We can insert this result back into the diagrammatic series for the interacting Green's function and obtain the lowest panel of Fig. 2. All terms (except the first one) in this expansion have a similar structure: they start with a straight line, then comes a self-energy bubble and then the "rest". This observation allows us to factor out the common part and write the series as shown in the second line of Fig. 2. Intriguingly, the term in parenthesis is equal to the interacting Green's function and we obtain the final result given by the last line of Fig. 2. This is the famous Dyson equation for the interacting Green's function.

We can again use the Feynman rules to translate this diagram into an mathematical expression according to

$$G(\mathbf{r}, t; \mathbf{r}', t') = G_0(\mathbf{r}, t; \mathbf{r}', t') + \int d^3r_1 \int dt_1 \int d^3r_2 \int dt_2 G_0(\mathbf{r}, t; \mathbf{r}_1, t_1) \Sigma(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) G(\mathbf{r}_2, t_2; \mathbf{r}', t'), \tag{32}$$

where we represented the self-energy diagram by the mathematical symbol $\Sigma(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2)$. Note that the Dyson equation is exact despite its derivation from a perturbation expansion.

We can further simplify this equation by Fourier transforming from time to frequency and expressing $G$, $G_0$ and $\Sigma$ in a basis of single-particle orbitals. In this basis, $G_0$ is diagonal, see Eq. 27. In many materials, it is a very good approximation to assume that also $\Sigma$ is diagonal in this basis. As a consequence, $G$ will also be diagonal and its diagonal components are given by

$$\langle \psi_n | G(\omega) | \psi_n \rangle = \frac{1}{\omega - \epsilon_n - \langle \psi_n | \Sigma(\omega) | \psi_n \rangle}. \tag{33}$$

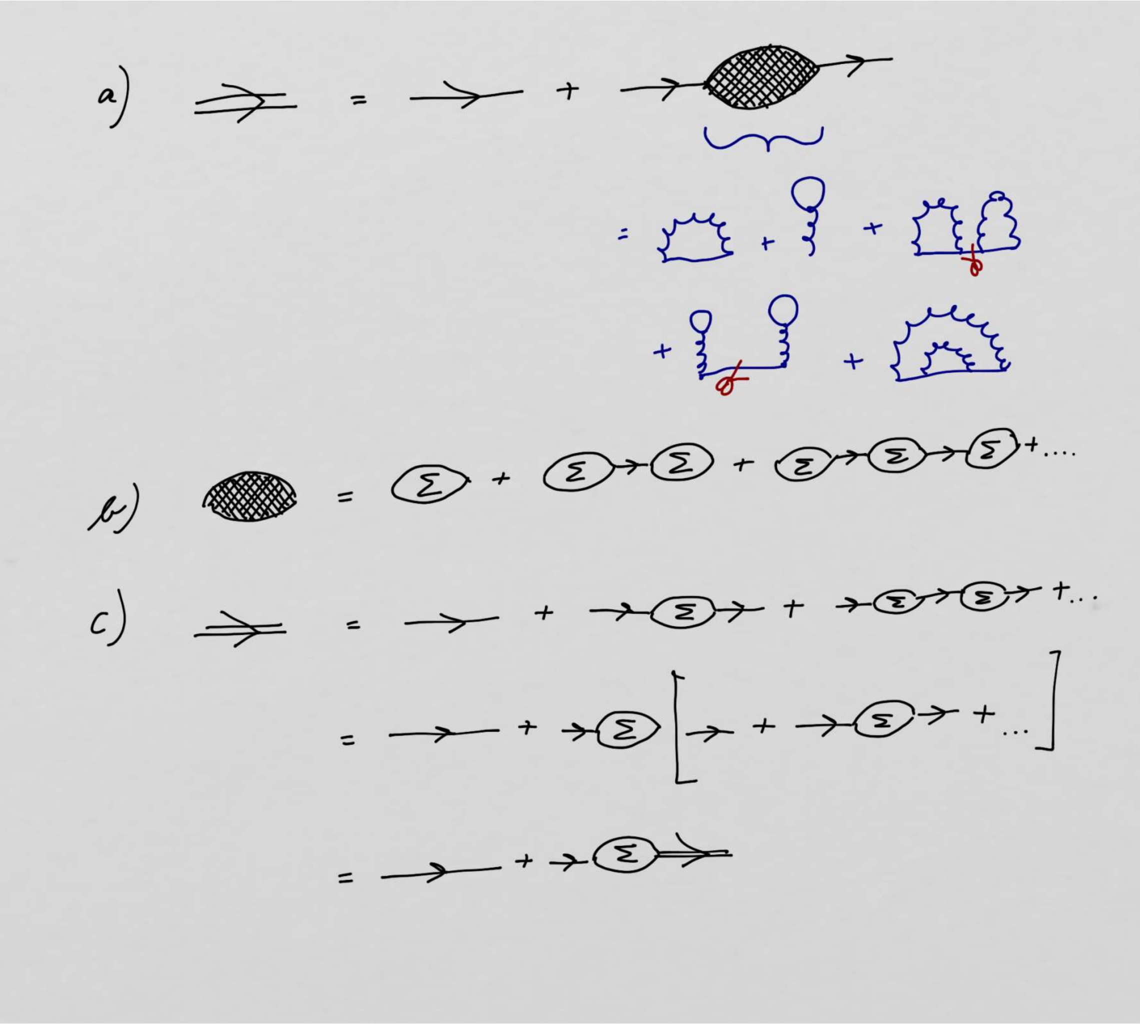

Figure 2: The diagrammatic structure of the interacting Green’s function.

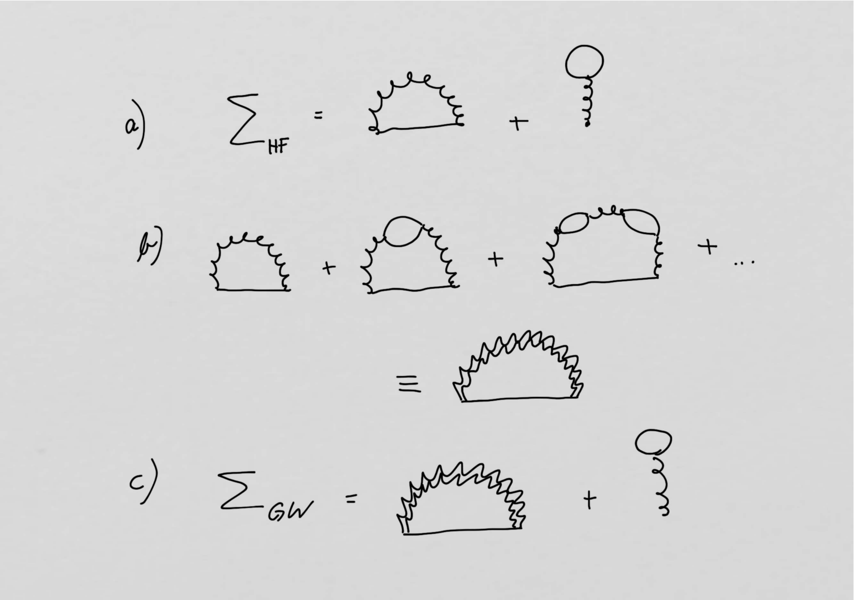

Figure 3: a) Lowest order contributions to the self energy. b) Screening the bare interaction of the Fock diagram. c) xpressing the self energy as a (unscreened) Hartree diagram and a screened exchange diagram.

According to the Lehmann representation, the quasiparticle energies $\epsilon_{QP}$ are given by the poles of the interacting Green's function. These are the frequencies at which the denominator on the right hand side becomes zero, i.e.

$$0 = \epsilon_n^{QP} - \epsilon_n - \langle \psi_n | \Sigma(\epsilon_n^{QP}) | \psi_n \rangle. \tag{34}$$

This can be rearranged into

$$\epsilon_n^{QP} = \epsilon_n + \langle \psi_n | \Sigma(\epsilon_n^{QP}) | \psi_n \rangle. \tag{35}$$

Instead of using the non-interacting Hamiltonian as the starting point for the series expansion, one usually achieves much higher accuracy by using a mean-field Hamiltonian which captures parts of the electron-electron interactions instead. One particularly convenient choice is the Kohn-Sham Hamiltonian. To avoid double counting, one must, however, remove the contributions from electron-electron interactions to $\epsilon_n^{KS}$ resulting in

$$\epsilon_n^{QP} = \epsilon_n^{KS} - \langle \psi_n | v_H + v_{xc} | \psi_n \rangle + \langle \psi_n | \Sigma(\epsilon_n^{QP}) | \psi_n \rangle. \tag{36}$$

## 2.4 Approximate self-energies

We still cannot predict quasiparticle energies in real materials because we do not yet know how to calculate the self-energy which captures the effect of electron-electron interactions. The most straightforward approach is to simply evaluate the lowest order contributions to the self-energy given by the diagrams shown in Fig. 3.

Let us take a closer look at these two contributions to the self-energy. Evaluating the first one yields

$$\Sigma_F(\mathbf{r}, t; \mathbf{r}', t') = G_0(\mathbf{r}, t; \mathbf{r}', t') v(\mathbf{r}, t; \mathbf{r}', t'). \tag{37}$$

Inserting the explicit form of $G_0$ and then Fourier transforming to frequency space produces

$$\Sigma_F(\mathbf{r}; \mathbf{r}', \omega) = v(\mathbf{r}; \mathbf{r}') \sum_n f_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}'), \tag{38}$$

which is just the Fock potential.

Going through the same steps for the second term yields

$$\Sigma_H(\mathbf{r}; \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') \int d^3 r_1\, v(\mathbf{r}, \mathbf{r}_1) \sum_n f_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}), \tag{39}$$

which is just the Hartree potential.

In other words, evaluating only the two lowest-order contributions to the self-energy gives rise to a non-self-consistent Hartree-Fock theory [7]. This is clearly not a very useful theory for describing real materials which indicates that more diagrams must be included in the evaluation of the self-energy.

A much better theory is obtained when one includes all higher-order diagrams which are similar to the Fock diagram but include additional closed loops according to Fig. 3. It is often said that the photon (which mediates the Coulomb interaction) is annihilated creating an electron-hole pair which in turn is annihilated creating a photon. Summing up all these processes allows us to define an effective or screened interaction *W* which is indicated by a double-wiggly line.

Again, there is a nice structure in the equation for the screened interaction which is reminiscent of the Dyson equation for the interacting Green's function. In particular, all diagrams (except the lowest-order one) begin with a wiggly line and a loop which can be factored out. Finally, one notices that the series in the parenthesis is nothing but the screened interaction again.

Translating this diagrammatic equation into a analytical form and Fourier transforming to frequency space gives

$$W(\mathbf{r},\mathbf{r}',\omega) = v(\mathbf{r},\mathbf{r}') + \int d^3r_1 \int d^3r_2 v(\mathbf{r},\mathbf{r}'_1)\chi_0(\mathbf{r}_1,\mathbf{r}_2,\omega)W(\mathbf{r}_2,\mathbf{r}',\omega), \tag{40}$$

where we represented the closed loop by the mathematical symbol $\chi_0$.

Solving this equation for *W* yields

$$W(\mathbf{r},\mathbf{r}',\omega) = \int d^3r_1 \epsilon^{-1}(\mathbf{r},\mathbf{r}_1;\omega)v(\mathbf{r}_1,\mathbf{r}'), \tag{41}$$

where we introduced the dielectric matrix

$$\epsilon(\mathbf{r},\mathbf{r}',\omega) = \delta(\mathbf{r}-\mathbf{r}') - \int d^3r_1 v(\mathbf{r},\mathbf{r}_1)\chi_0(\mathbf{r}_1,\mathbf{r}';\omega). \tag{42}$$

By comparing this equation to Eq. 9 we find that $\chi_0$ can be interpreted as the non-interacting density-density response function (recall that we used the symbol $\chi$ to denote the interacting density-density response function).

By adding the screened Fock diagram to the Hartree diagram we arrive at the $G_0W$ approximation to the self-energy, see Fig. 3. Translating this into an analytical expression yields

$$\Sigma_{G_0W}(\mathbf{r},t;\mathbf{r}',t') = \Sigma_H(\mathbf{r},t;\mathbf{r}',t') + iG_0(\mathbf{r},t;\mathbf{r}',t')W(\mathbf{r},t;\mathbf{r}',t'). \tag{43}$$

The final trick to is to realize that one can capture even more diagrams when the non-interacting Green's function in the screened Fock diagram is replaced by the interacting one. This is the full *GW* self-energy. In practice, however, the full interacting Green's function is usually replaced by a mean-field Green's function; i.e. a Green's function which has the same form as the non-interacting one but with orbitals and energies from a mean-field approach, such as KS DFT or Hartree-Fock.

To evaluate the $G_0W$ diagram, we first Fourier transform to frequency space which produces

$$\Sigma_{G_0W}(\mathbf{r},\mathbf{r}';\omega) = i\int \frac{d\omega'}{2\pi} G_0(\mathbf{r},\mathbf{r}';\omega-\omega')W(\mathbf{r},\mathbf{r}';\omega')e^{-i\eta\omega'}. \tag{44}$$

The frequency integral can be carried out using the method of residues: one obtains contributions from the poles of $G_0$ and contributions from the poles of *W*. This yields

$$\Sigma_{G_0W}(\mathbf{r},\mathbf{r}';\omega) = -\sum_n f_n\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')W(\mathbf{r},\mathbf{r}';\omega-\epsilon_n) - \sum_n \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')\int_0^\infty \frac{d\omega'}{2\pi}\frac{ImW(\mathbf{r},\mathbf{r}';\omega')}{\omega-\omega'-\epsilon_n+i\eta}, \tag{45}$$

where we used the spectral representation of the screened interaction.

In principle, it is straightforward to evaluate this expression (apart from numerical difficulties which will be discussed in the next section). Sometimes, however, additional approximations are made in the second term. In particular, if one assumes that $\omega - \epsilon_n = 0$, one can use the Kramers-Kronig relation to find

$$\int_0^\infty \frac{d\omega'}{2\pi}\frac{ImW(\mathbf{r},\mathbf{r}';\omega')}{-\omega'+i\eta} = -\frac{1}{2}\left[ReW(\mathbf{r},\mathbf{r}',\omega=0) - v(\mathbf{r},\mathbf{r}')\right]. \tag{46}$$

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[7] It is not self-consistent because the orbitals are not the solutions of the Hartree-Fock equation, but the non-interacting ones.

Then the sum over $n$ can be carried out using $\sum_n \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$ and one arrives at Eq. 12.

A less drastic approximation is assume that the imaginary part of $W(\omega')$ in Eq. 45 is proportional to a delta-function which is then used to carry out the integral over frequency analytically. This is known as the plasmon-pole approximation and has been widely used in practical GW calculation for materials.

### 2.5 Practical GW calculations

There are a number of different GW codes which implement different strategies for evaluating quasiparticle properties. Here, I will give a short overview of the steps involved in a "standard" GW calculations, for example using the BerkeleyGW code.

First, one starts with a DFT (or other type of mean-field) calculation to determine the mean-field energies and orbitals. In a GW calculation both the occupied KS states as well as the unoccupied ones are needed for the evaluation of the non-interacting density-density response function and also for the Coulomb-hole part of the self-energy. Of course, it is not possible in a numerical calculation to calculate all unoccupied states so the challenge is to calculate enough of them to obtain converged quasiparticle properties.

The next step is to determine screened interaction which requires the inverse dielectric function. For this, one first constructs the non-interacting density-density response function. Typically, $\chi_0$ is not constructed in real space, but in some basis. For example, BerkeleyGW uses a plane-wave basis. Next, the dielectric matrix is constructed and then inverted. Construction of the dielectric matrix involves the Coulomb interaction, which is very long-ranged. This gives rise to a slow converges with respect to supercell size when periodic boundary conditions are used. To remedy this, truncated Coulomb interactions are often used. Once the inverse dielectric matrix is obtained, it can be used to construct the screened interaction.

Finally, one can determine the self-energy and its matrix elements which allows the determination of quasiparticle properties, such as their energies.