G_0W_0 for Molecules

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ABSTRACT

[This abstract must provide a succinct and informative condensation of your work. Candidates are welcome to prepare a lengthier abstract for inclusion in the dissertation, and provide a shorter one in the CaltechTHESIS record.]

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Chapter 1

NOMENCLATURE

Symbol	Description
i, j, k, l	Occupied orbital indices
a, b, c, d	Virtual orbital indices
p, q, r, s	General MO indices
$\mu, \nu, \lambda, \sigma$	AO indices
$(pq\|rs) = \int \int \psi_p^*(\mathbf{r}_1)\psi_q(\mathbf{r}_1)\frac{1}{r_{12}}\psi_r^*(\mathbf{r}_2)\psi_s(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$	Two-electron spatial integrals
$(pq\|\|rs) = (pq\|rs) - (ps\|rq)$	Antisymmetrized two-electron integrals
$\chi_p(\mathbf{x}) = \psi_p(\mathbf{r})\sigma(\omega)$	Spin-orbital
$[pq\|rs] = \int \int \chi_p^*(\mathbf{x}_1)\chi_q(\mathbf{x}_1)\frac{1}{r_{12}}\chi_r^*(\mathbf{x}_2)\chi_s(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2$	Two-electron spin integrals

All calculations have been done using the PySCF package.[1] The code for this project can be found at `https://github.com/pkozlows/gw_senior_thesis/tree/master`.

Chapter 2

MOTIVATION

The formalism of many-body perturbation theory (MBPT) provides corrections to a mean-field description such as that given by Hartree-Fock or density functional theory (DFT). Hartree-Fock is not used much in practice because it is known to provide a weak treatment of electron correlation chiefly due to the fact that it only considers a single Slater determinant. DFT is often used for systems of large size, as it is fairly accurate and computationally cheap, scaling like $O(N^3)$, where N is the system size. However, it treats electron correlation in an approximate way that is difficult to systematically improve. Specifically, its reliance on approximate functionals gives rise to the notorious self-interaction error; because one is using the electron density to determine the Coulomb repulsion between electrons, this means that one can have the electron interacting with its own contribution to the electron density. In practice, this can potentially lead to a variety of issues, including the underestimation of surface stability (overestimation of surface energies) relevant in surface science studies.[23] To remedy the problems with the mean field approximations, normally one would fall back onto the wave function-based MBPT, such as Moller-Plesset perturbation theory to 2nd order (MP2) and coupled cluster theory (CC). However, their computational scaling is steep, scaling like $O(N^5)$ and $O(N^6)$ or greater, respectively, which can make it difficult to simulate larger systems.[4] To bridge the gap between the cheap mean-field methods and the expensive wave function-based MBPT, there has been an interest in applying Green's function MBPT methods, within the GW approximation, to such systems, which has shown to give accurate corrections to various properties, such as band gaps, on top of a prior (DFT) mean-field calculation, at a moderate computational cost.[5] This is the motivation for my study of the G_0W_0 method, which traditionally scales like $O(N^4)$, within the framework of the GW approximation.

Chapter 3

THEORY

We begin by writing out the time independent Schrödinger equation for the N-electron system

$$\hat{H}\Psi = E\Psi \tag{3.1}$$

with

$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2\right) - \sum_{i=1}^{N}\sum_{\alpha}\frac{Z_\alpha}{r_{i\alpha}} + \sum_{i<j}^{N}\frac{1}{r_{ij}} + C_{nn}. \tag{3.2}$$

An equation 3.1, $\hat{H}$ is the Hamiltonian operator, Ψ is the wave function, and E is the energy of the system. As shown in equation 3.2, the Hamiltonian operator consists of four terms: a kinetic energy term, in which a sum of the kinetic energy $-\frac{1}{2}\nabla_i^2$ of each electron is taken; a nuclear-electron attraction term, in which we have sums running over all of the electrons i and all of the nuclei α with their separation denoted by $r_{i\alpha}$ and the nuclear charge denoted by Z_α; an electron-electron repulsion term, in which we have a sum running over all pairs of electrons i and j with their separation denoted by r_{ij}; and a nuclear-nuclear repulsion term C_{nn}, which we have denoted as a constant since we are working in the Born-Oppenheimer approximation of all electrons moving in a fixed nuclear framework. The objective of many years of research in quantum chemistry has been solving for the electron-electron repulsion term, will we will call V_{ee}. Now, I will introduce some of the mean field methods that have been classically used to tackle this problem at a cheap computational cost.

3.1 Mean Field Methods

Hartree-Fock[6]

The concept behind Hartree-Fock (HF) is that we can assign each electron a given orbital $\chi(\mathbf{r}, \sigma)$, where $\mathbf{r}$ is the spatial coordinate and σ is the spin. Then, we take a Hartree product of these orbitals

$$\Phi_{Hartree} = \chi_1(\mathbf{r}_1, \sigma_1)\chi_2(\mathbf{r}_2, \sigma_2)\cdots\chi_N(\mathbf{r}_N, \sigma_N). \tag{3.3}$$

However, this is not antisymmetric with respect to the exchange of two electrons, so we need to enforce antisymmetry by taking a Slater determinant of these orbitals,

denoting the antisymmetrization operator as $\hat{A}$,

$$\Psi_{HF} = \hat{A} \prod_{i=1}^{N} \chi_i(\mathbf{r}_i, \sigma_i). \tag{3.4}$$

So we have arrived at the Hartree-Fock energy, which is defined as

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle, \tag{3.5}$$

where we have assumed the normalization $\langle \Psi_{HF} | \Psi_{HF} \rangle = 1$. Now we seek to minimize this energy with respect to the constituent orbitals. This may be done by defining the Lagrangian

$$\mathcal{L} = E_{HF} - \lambda \left(\langle \Psi_{HF} | \Psi_{HF} \rangle - 1 \right), \tag{3.6}$$

where λ is a Lagrange multiplier that enforces the normalization condition. We then take the functional derivative of the Lagrangian with respect to the orbitals and set it to zero to find the minimum of the energy

$$\frac{\delta \mathcal{L}}{\delta \chi_i} = 0. \tag{3.7}$$

Carrying out this minimization leads to the eigenvalue equation known as the Hartree-Fock equations

$$F \chi_i = \epsilon_i \chi_i, \tag{3.8}$$

where F is the Fock operator, which is defined as

$$F = h + V_{HF}, \tag{3.9}$$

with h being the one-electron part of the Hamiltonian and V_{HF} being the Hartree-Fock potential. It should be noted that h corresponds to the first and second terms, whereas V_{HF} corresponds to the third term, respectively, of equation 3.2. The Hartree-Fock potential is defined as

$$V_{HF} = \sum_{j=1}^{N} \left(J_j - K_j \right), \tag{3.10}$$

Where J_j is the local Coulomb operator

$$\langle \chi_i(\mathbf{r}_1) | J_j(\mathbf{r}_1) | \chi_i(\mathbf{r}_1) \rangle = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\chi_i^*(\mathbf{r}_1)\chi_i(\mathbf{r}_1)\chi_j^*(\mathbf{r}_2)\chi_j(\mathbf{r}_2)}{r_{12}} = [ii|jj], \tag{3.11}$$

and K_j is the nonlocal exchange operator

$$\langle \chi_i(\mathbf{r}_1)| K_j(\mathbf{r}_1) |\chi_i(\mathbf{r}_1)\rangle = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\chi_i^*(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_j^*(\mathbf{r}_2)\chi_i(\mathbf{r}_2)}{r_{12}} = [ij|ji].$$
(3.12)

We have used the notation for the spin integrals as given in Chapter 1. So when we consider equation 3.10, now performing an additional sum over the spins orbitals being operated on (defined previously, for the general case, as i) in order to treat all unique pairs of occupied spin orbitals, we arrive at the V_{ee}

$$V_{ee} = \frac{1}{2} \sum_i^{occ} \sum_j^{occ} ([ii|jj] - [ij|ji]).$$
(3.13)

We simplify by performing a spin integration to convert to spatial integrals, as defined in Chapter 1

$$V_{ee} = \frac{1}{2} \sum_i^{occ} \sum_j^{occ} \sum_{\sigma=\alpha,\beta} ((ii|jj) - (ij|ji)) = \frac{1}{2} \sum_i^{occ} \sum_j^{occ} 2(ii|jj) - (ij|ji).$$
(3.14)

Notice that the Coulomb term will obtain a factor of 2 after the spin integration, whereas the exchange term will only survive if the spins for i and j are the same. So Hartree-Fock fails to correlate electrons of opposite spin.

Density Functional Theory (DFT)

The central quantity in DFT is the electron density ρ. The motivation for DFT can be seen by considering that the wave function depends on the whereabouts of N electrons, each defined by their own orbital, which in turn has 3 directions within its spatial coordinate $\mathbf{r}$. The electron density, on the other hand, is a function of just 3 variables, x, y, and z. Hohenberg and Kohn were able to take advantage of this fact when they proved that the ground state energy of a system is a unique functional of the electron density.

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_H[\rho] + V_{xc}[\rho] + V_{nn}$$
(3.15)

Where T and V_{ne} are the kinetic and nuclear-electron attraction energies for the first and second terms of equation 3.2, respectively. V_H is the Hartree potential, which is just an alternate name for the Coulomb term of section 3.1, and V_{xc} is the exchange-correlation potential. These two terms cover the V_{HF} from equation 3.10. In addition, the correlation portion of V_{xc} takes into account the electron correlation in an approximate way. Many levels of designing the V_{xc} have been made, as

described by Jacob's Ladder.[7] Finally, V_{nn} is the nuclear-nuclear repulsion term.

What is important to understand is that both the HF and DFT mean field methods yield a reasonable first guess[8] at molecular orbital energies ϵ_p and coefficients $C_{\mu p}$; these molecular orbital coefficients enable one to transform from the basis of atomic μ to molecular orbitals p (via considering the molecular ones as a linear combination of atomic orbitals (LCAO)). We later correct both quantities with MBPT.

3.2 Green's functions

Definitions

One can define the single-particle Green's function G as

$$G\left(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2\right) = -i \left\langle \Psi_0 \left| T \left[\psi\left(\mathbf{r}_1, t_1\right) \psi^\dagger\left(\mathbf{r}_2, t_2\right) \right] \right| \Psi_0 \right\rangle, \qquad (3.16)$$

where ψ is the field operator for creating or destroying a particle at spacetime coordinates $\mathbf{r}$ and t, T is the time-ordering operator that ensures that the ψ at the earlier time is acting on the ket before the ψ at the later time, and Ψ_0 is the ground state wave function. In the same vein, we can define the noninteracting Green's function as

$$G_0\left(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2\right) = -i \left\langle \Phi_0 \left| T \left[\psi\left(\mathbf{r}_1, t_1\right) \psi^\dagger\left(\mathbf{r}_2, t_2\right) \right] \right| \Phi_0 \right\rangle, \qquad (3.17)$$

where now Φ_0 is the ground state wave function of the noninteracting system. The wave function for the noninteracting system can be determined through one of the mean-field methods, which we described earlier. The Dyson equation relating these two quantities is

$$G = G_0 + G_0 \Sigma G, \qquad (3.18)$$

where Σ is the self-energy. The self-energy is a quantity that accounts for the electron correlation that is not captured by the mean-field methods. An intuitive physical picture can be gained from this by considering the example of an electron shot into a gas of electrons, as shown in Figure 3.1a. As it propagates through this medium, it will have an electrostatic repulsion with the electrons in the gas, so it will create holes (depicted in white) as it moves along (pictured in Figure 3.1b). Therefore, it no longer makes sense to think of the bare electron, but rather the quasi-electron along with its "clothing" of holes. To make this more rigorous, we have the equation

$$\epsilon_{\text{quasi}} - \epsilon_{\text{bare}} = \epsilon_{\text{self}}, \qquad (3.19)$$

(a) The electron is shot into the gas

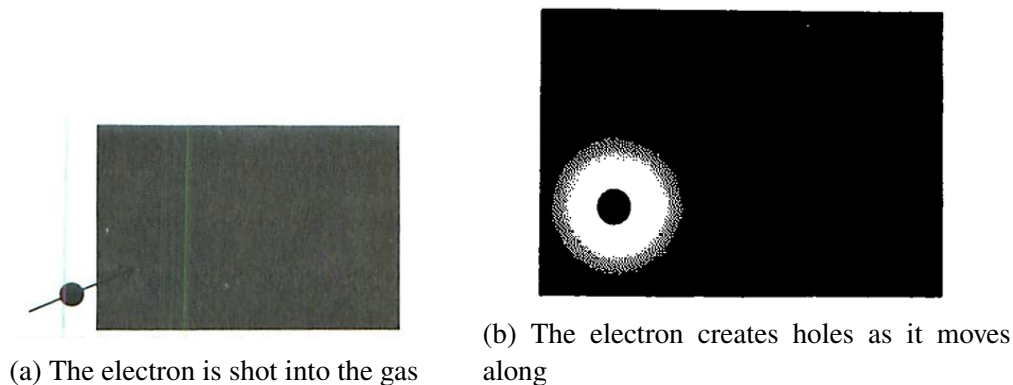(b) The electron creates holes as it moves along

Figure 3.1: Electron gas propagation taken from Mattuck [9]

which is saying that the difference between the quasi-electron energy and the bare electron energy can be thought of as the electron's self-energy, or just the energy of its "clothing". So we can think of ϵ_{bare} and ϵ_{quasi} as originating from the noninteracting and interacting Green's functions G_0 and G, respectively. The self-energy Σ then captures the difference between these two quantities. Typically, Σ is designed to capture all of the quantum mechanical effects of the many body system, including the exchange (partially captured by HF as noted in section 3.1) and correlation effects, so it is often denoted as Σ_{xc}.

The *GW* Approximation

In order to solve the Dyson equation 3.18, we need to make approximations to the self-energy Σ. By introducing the screened Coulomb potential W, which represents the effective electrostatic interaction between electrons (as described above through the concept of the quasi-electron), the polarization function P, which describes the response of the system to the introduction of an electron, and the vertex function Γ, which describes the interaction between the electrons and holes, we can write down
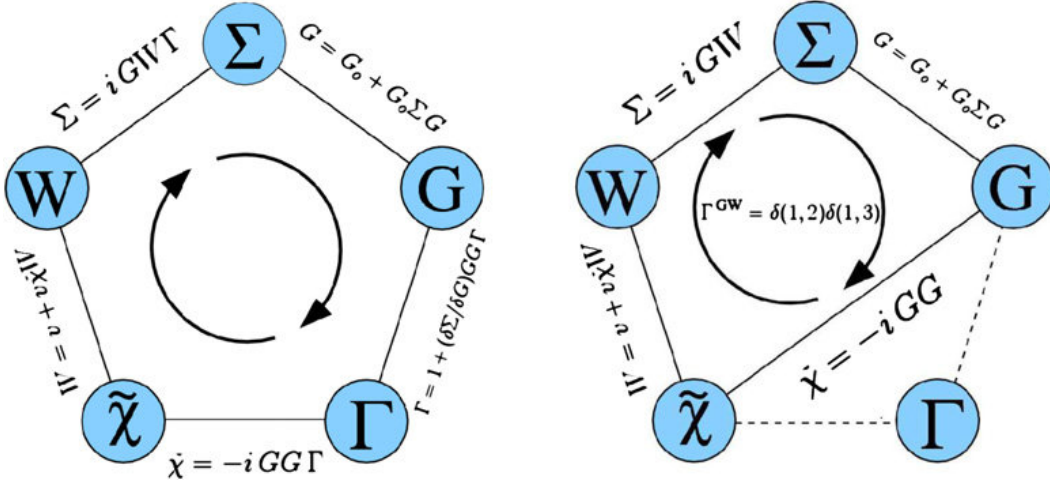
Figure 3.2: Graphical representation of Hedin's equations taken from *Frontiers | The GW Compendium: A Practical Guide to Theoretical Photoemission Spectroscopy* [5]. The left panel shows the full set of equations, whereas the right panel shows the *GW* approximation.

the five Hedin's equations

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

$$P(1,2) = \int d(3,4)G(1,3)G(4,1)\Gamma(3,4;2)$$

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

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

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

(3.20)

where we have made use of the shorthand notation $1 = (\mathbf{r}_1, t_1)$ and V is the bare Coulomb potential. The *GW* approximation is a simplification of these equations, where we neglect the vertex function Γ by setting $\Gamma(1,2,3) = \delta(1,2)\delta(1,3)$. This simplifies the equations for the self-energy and polarization function to

$$\Sigma(1,2) = \int d(1,2)G(1,2)W(1,2)$$

$$P(1,2) = \int d(1,2)G(1,2)G(2,1).$$

(3.21)

The figure 3.2 shows the self-consistency between these equations, with the polarization P represented by $\tilde{\chi}$. Full self-consistency, including the vertex function Γ, is shown in the left panel, whereas the *GW* approximation, which neglects the vertex

function, is shown in the right panel. The G_0W_0 method, which I have studied, only performs one loop of the GW approximation cycle. This is why it is often termed a "one-shot" procedure.

Application in MBPT

Now that we have the recipe to solve for its interacting version, the single-particle Green's function G contains a lot of information that we would be interested in to provide an MBPT correction. In this work, we use it to update mean-field molecular orbital energies ϵ_p^0 to quasiparticle energies ϵ_p^{QP}, which are interpreted as effective molecular orbital energies. We also use it to update the electron density via the linearized G_0W_0 density matrix derived in chapter 5. Finally, we use it to determine the total energy of the molecule with different total energy functionals. It can also be used, among other things, to compute the spectral function, which gives access to ionization potentials and electron affinities.[5]

Chapter 4

G_0W_0 PROCEDURE

4.1 Iterative equation

The linearized procedure that was used in this work to compute quasiparticle energies, is given by

$$\delta_{pq} F_{pq}^{HF}[\gamma^{MF}] + \Sigma_c(\varepsilon_p^{QP}) = \varepsilon_p^{QP}. \tag{4.1}$$

The first term corresponds to taking the diagonal of the Hartree-Fock matrix F_{pq}^{HF} evaluated at a given electron density γ_{MF} These electron densities are obtained from a previous mean-field calculation, so γ_{MF} means either γ_{DFT} or γ_{HF}. The second term evaluates Σ_c for the ε_p^{QP} determined in the previous iteration. The right side of the equality gives the updated ε_p^{QP}.

Equation 4.1 is iterated until self-consistency. We start with an initial guess for ε_p^{QP}, which is given by the mean-field orbital energy ϵ_p. This is used in the first iteration to solve for the right-hand side ε_p^{QP} of Equation 4.1. In the next iteration, we use the previously obtained ε_p^{QP} to determine Σ_c. This process is repeated until we reach a convergence threshold for ε_p^{QP}. One can also use the Newton-Raphson method to solve the iterative equation for ε_p^{QP}.

The Fock Matrix

In section 3.1, we defined the Fock matrix. In the basis of molecular orbitals, it can be written by

$$F_{ij}^{HF} = h_{ij} + \sum_{kl}^{occ} P_{kl} \left((ij|kl) - \frac{1}{2}(ik|jl) \right), \tag{4.2}$$

where h_{ij} is the one-electron part of the Hamiltonian, P_{kl} is the density matrix, and $(ij|kl)$ are the two-electron integrals.

Correlation-Self Energy: Use

Σ_c, tasked with capturing the electron correlation effects, is dynamic, as opposed to the previous Fock term that was discussed, as is updated with a new ε_p^{QP} in each iteration. In the case of the G_0W_0 approximation, we use the common approximation, considering only the diagonal element of Σ_c corresponding to the orbital with index

p. This function is evaluated at the ε_p^{QP} just obtained in the previous iteration. To summarize, we are actually interested in $\Sigma_{pp}^{corr}(\varepsilon_p^{QP})$.

Updated ε_p^{QP}

This is the right side, or the solution, of Equation 4.1.

4.2 Correlation Self-Energy

$$\Sigma_{pp}^{\text{corr}}(\omega) = \sum_{\mu}^{\text{RPA}} \left(\sum_{i}^{\text{occupied}} \frac{\mathbf{V}_{pi}^{\mu}\mathbf{V}_{ip}^{\mu}}{\omega - (\epsilon_i - \Omega_{\mu})} + \sum_{a}^{\text{virtual}} \frac{\mathbf{V}_{pa}^{\mu}\mathbf{V}_{ap}^{\mu}}{\omega - (\epsilon_a + \Omega_{\mu})} \right) \quad (4.3)$$

This is the working equation for the diagonal pp of the correlation self-energy for a given MO. First, we have a sum running over all of the excitations obtained from the previous RPA calculation. Then, we have two terms: one sum running over all of the occupied orbitals and the other sum running over all virtual orbitals. The $\mathbf{V}_{pq}^{\mu}$ and $\mathbf{\Omega}^{\mu}$ are the residues and excitation energies, respectively, from the previous RPA calculation. ω is my input frequency and the ϵ_p are the orbital energies from my previous mean-field calculation.

4.3 Random Phase Approximation

The RPA is a linear response theory that is used to compute the excitation energies and vectors. The working matrix equation is given by[10]

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \mathbf{\Omega}^{(-\mu+\mu)} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}, \quad (4.4)$$

where we define $\mathbf{\Omega}^{(-\mu+\mu)}$ as a diagonal matrix containing the excitation and de-excitation energies, which have the same magnitude $\mathbf{\Omega}^{|\mu|}$. Accordingly, we just use the excitation energies in what follows which we simply denote as $\mathbf{\Omega}^{\mu}$. The matrix $\mathbf{A}$ is defined as

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + 2(ia||jb) \quad (4.5)$$

and $\mathbf{B}$ is

$$\mathbf{B}_{ia,jb} = 2(ia||jb) \quad (4.6)$$

where the anti-symmetrized two-electron integrals are defined in Chapter 1.

$\mathbf{X}$ and $\mathbf{Y}$ correspond to excitations and the de-excitations, respectively.

Direct approximation

Everywhere in this work, we consider the direct approximation, which just means that all instances of anti-symmetrized two-electron integrals are replaced by their direct counterparts, i.e., in Equation 4.5, and Equation 4.6, $(ia||jb) \rightarrow (ia|jb)$.

An alternative formulation that takes advantage of the symmetry obtained through neglect of the deexcitation energies and the direct formulation of the RPA (dRPA) can also be used and is derived in Appendix A as suggested by Furche [11].

Residues

The residue $\mathbf{V}_{pq}^{\mu}$ is obtained by considering a contraction of two tensors. First, we consider the sum of the excitation vectors $\mathbf{X}$ and $\mathbf{Y}$ at the same excitation energy μ: $\mathbf{Z}_{i,a}^{\mu} = \mathbf{X}_{i,a}^{\mu} + \mathbf{Y}_{i,a}^{\mu}$. Then, we define the appropriate integrals for this excitation

$$\mathbf{W}_{p,q,i,a} = \sqrt{2} \sum_{p,q,i,a} (pq|ia). \tag{4.7}$$

This factor of $\sqrt{2}$ comes from the spin integration of the restricted formalism that we use. We define a combined occupied-virtual index ν, so: $\mathbf{Z}_{i,a}^{\mu} = \mathbf{Z}_{\nu}^{\mu}$ and $\mathbf{W}_{p,q,i,a} = \mathbf{W}_{p,q,\nu}$.

And then we form the residue from

$$\mathbf{V}_{pq}^{\mu} = \sum_{\nu} \mathbf{W}_{p,q,\nu} \mathbf{Z}_{\nu}^{\mu}. \tag{4.8}$$

Tamm-Dancoff Approximation

In this method, we neglect the $\mathbf{B}$ matrix of the RPA equation. So the eigenvalue equation becomes

$$\mathbf{AX} = \mathbf{\Omega}^{\mu}\mathbf{X} \tag{4.9}$$

where we still have:

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + 2(ia||jb) \tag{4.10}$$

And then we follow the same procedure as in the RPA to get the residues $\mathbf{V}_{pq}^{\mu}$, where now we have $\mathbf{Z}_{\nu,\mu} = \mathbf{X}_{\nu,\mu}$.

Chapter 5

LINEARIZED G_0W_0 DENSITY MATRIX

As noted earlier, we can get a density matrix out of the interacting Green's function. Then this allows us to obtain new MO coefficients through a rotation of those from the noninteracting Green's function. The form of this density matrix is shown below, and the derivation of it is given in Appendix **??**.

Implementation

These are the working equations in the spin-restricted formalism, which explains why we tack on the factor of 2. First, we consider the fully occupied block

$$\gamma_{ij}^{GW} = 2\delta_{ij} - 2\sum_{a\mu} \frac{\mathbf{V}_{ia}^{\mu}\mathbf{V}_{ja}^{\mu}}{(\epsilon_i - \epsilon_a - \mathbf{\Omega}^{\mu})(\epsilon_j - \epsilon_a - \mathbf{\Omega}^{\mu})}, \tag{5.1}$$

where the $\mathbf{\Omega}^{\mu}$ are the excitation energies and the $\mathbf{V}_{pq}^{\mu}$ are the transition vectors. The sum runs over all virtual orbitals and excitation energies. Next, we have the virtual-virtual block

$$\gamma_{ab}^{GW} = -2\sum_{i\mu} \frac{\mathbf{V}_{ai}^{\mu}\mathbf{V}_{bi}^{\mu}}{(\epsilon_i - \epsilon_a - \mathbf{\Omega}^{\mu})(\epsilon_i - \epsilon_b - \mathbf{\Omega}^{\mu})}, \tag{5.2}$$

where the sum runs over all occupied orbitals and excitation energies. Finally, we have the mixed block

$$\gamma_{ib}^{GW} = \frac{2}{\epsilon_i - \epsilon_b}\left[\sum_{a\mu} \frac{\mathbf{V}_{ia}^{\mu}\mathbf{V}_{ba}^{\mu}}{\epsilon_i - \epsilon_a - \mathbf{\Omega}^{\mu}} - \sum_{j\mu} \frac{\mathbf{V}_{ij}^{\mu}\mathbf{V}_{bj}^{\mu}}{\epsilon_j - \epsilon_b - \mathbf{\Omega}^{\mu}}\right], \tag{5.3}$$

where we have two sums; one over occupied orbitals and excitation energies and the other over virtual orbitals and excitation energies. This all contributes to the form of the density matrix as:

$$2\begin{pmatrix} \gamma_{ij}^{GW} & \gamma_{ib}^{GW} \\ \gamma_{bi}^{GW} & \gamma_{ab}^{GW} \end{pmatrix} \tag{5.4}$$

Where γ_{bi}^{GW} is simply the transpose of γ_{ib}^{GW}, since all elements of this matrix are real. Therefore, this density matrix is Hermitian.

C h a p t e r 6

RESULTS

Graphical vs. Iterative

Equation 4.1 can be solved iteratively, but also graphically in the HF case by plotting Σ_c as a function of the input frequency, which takes on the possible values for ε_p^{QP}. Since F_{pq}^{HF} is diagonal in the canonical HF MO basis, Equation 4.1 can be reformulated as

$$\epsilon_p^{HF} + \Sigma_{pp}^{corr}(\omega) = \omega \rightarrow \Sigma_{pp}^{corr}(\omega) = \omega - \epsilon_p^{HF}. \tag{6.1}$$

As can be seen in figure 6.1, the line at $\omega - \epsilon_p^{HF}$ intersects with Σ_c at the same ε_p^{QP} that we get from our iterative procedure, namely at the $\omega = -12.18eV$. This is a useful check to see if the self-energy, which we defined in section 4.2, has been computed correctly.
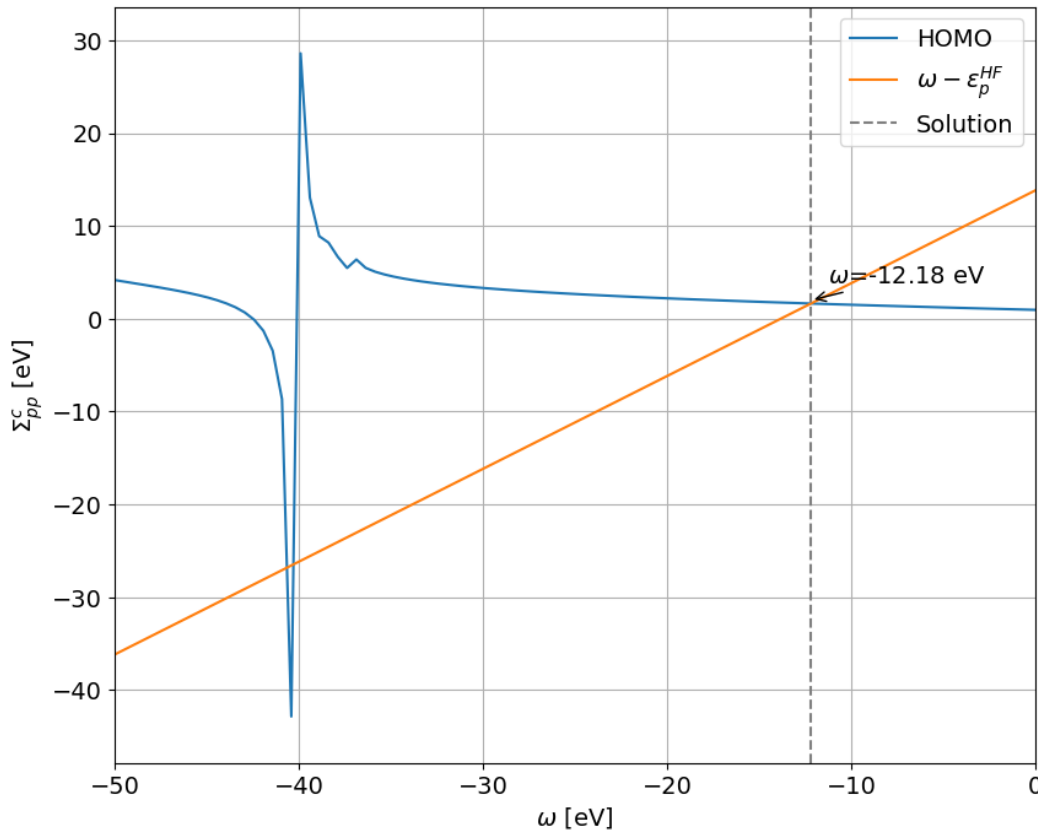

Figure 6.1: Graphical solution of the correlation self-energy for the HOMO of H_2O

Also, at around ω = -40 eV, one can observe a pole structure. This would pose problems for the convergence of my iterative procedure Equation 4.1 if the ε_p^{QP} that I was looking for was close to this ω value.

Testing of equation 4.1

Additional tests for a range of molecules and MOs with my implementation are reported in table 6.1.

Table 6.1: Tests of my dRPA and dTDA implementations of G_0W_0. Energy deviations (in eV) for my implementation of the exact analytic G_0W_0 with dTDA and dRPA for different molecules across a range of orbitals versus that of PySCF.

Orbital	H_2O		HCl		NH_3		LiH		CO	
	dTDA	dRPA	dTDA	dRPA	dTDA	dRPA	dTDA	dRPA	dTDA	dRPA
HOMO - 2	1.78e-15	5.33e-15	1.42e-14	2.13e-12	5.33e-15	1.42e-14	4.21e-10	3.55e-14	1.73e-10	0.00477
HOMO - 1	2.31e-14	1.07e-13	1.30e-12	5.24e-13	3.55e-15	2.33e-10	4.55e-12	2.84e-14	1.73e-10	0.00476
HOMO	4.44e-15	2.84e-13	1.48e-12	5.71e-13	1.67e-11	1.30e-12	1.33e-15	1.96e-10	1.06e-12	2.84e-13
LUMO	3.43e-14	2.65e-14	4.44e-16	1.24e-12	8.60e-14	8.78e-14	1.11e-15	2.66e-15	2.22e-15	0.00679
LUMO + 1	2.14e-13	2.71e-14	2.22e-13	1.04e-10	4.40e-13	8.78e-14	1.12e-12	2.43e-14	3.11e-15	0.00678
LUMO + 2	4.07e-11	6.92e-10	7.11e-15	1.18e-10	3.15e-14	4.97e-14	1.12e-12	3.09e-14	3.99e-14	3.99e-14

The cc-pVDZ basis set was used for all calculations. As can be seen, my deviations from PySCF are near floating point error with the exception of my dRPA calculation for CO.

Plotting natural occupations

The natural occupations are found by diagonalizing the density matrix. They are interpreted as being the number of electrons in a given orbital.[6] Here we considered the one-electron density matrix from multiple methods: restricted Hartree-Fock, which contains no correlation for the single particles, and Full Configuration Interaction (FCI), which contains the exact correlation. As can be seen in Figure 6.2, our implementation of the Linearized G_0W_0 Density Matrix in the direct Random Phase Approximation (dRPA) and direct Tamm-Dancoff Approximation (dTDA) gives a portion of this correlation. When H_2 is at the though bond distance near equate bum, we see in Figure 6.2 that the HOMO is fully occupied with 2 electrons, while the LUMO is unoccupied. This situation is represented by the simple MO diagram in Figure 6.3. As the molecule dissociates, the orbital occupations for the restricted Hartree-Fock method do not change at all, while FCI, containing the exact correlation, gives the expected result of the HOMO and LUMO both having occupations of 1 electron. The dRPA and dTDA fall somewhere in between these two extremes.
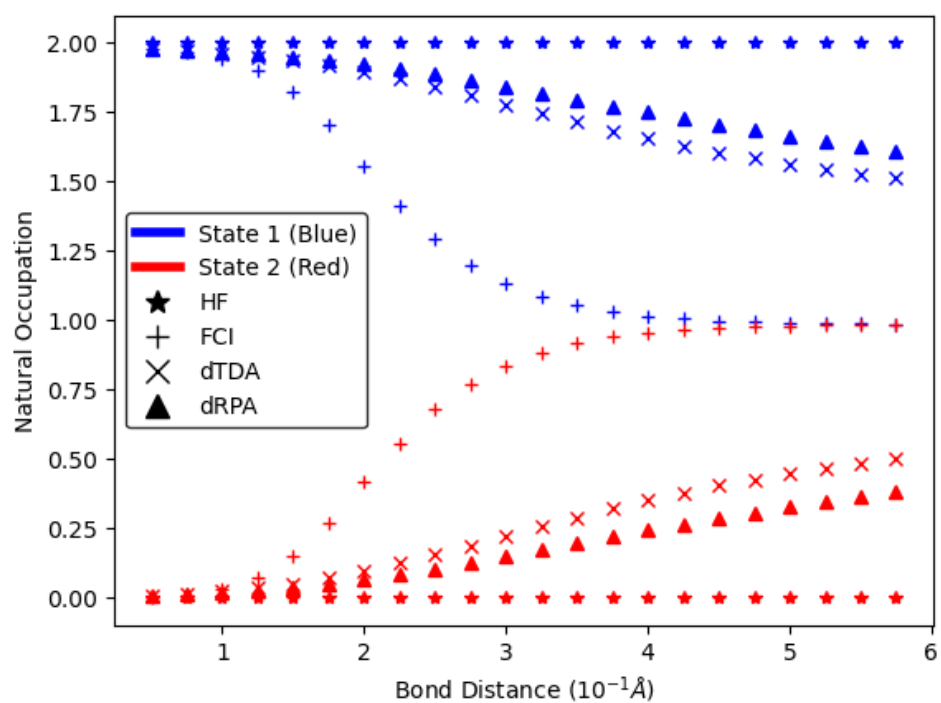
Figure 6.2: Natural occupations of the HOMO (State 1) and LUMO (State 2) of H_2 along the dissociation coordinate
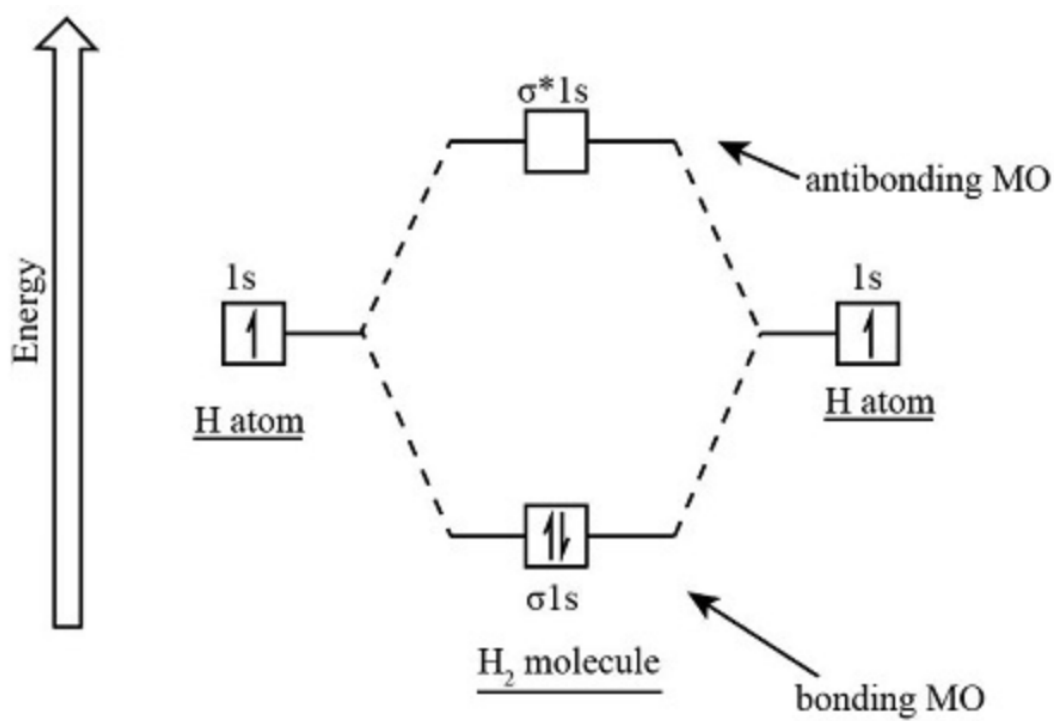
Figure 6.3: MO diagram of H_2 at the equilibrium bond distance. Notice that the HOMO is fully occupied with 2 electrons, while the LUMO is unoccupied. Diagram taken from the web[12]

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A p p e n d i x A

SYMMETRIC FORMULATION OF THE DRPA

Since we know that the excitation and de-excitation energies for the RPA are the same in magnitude, we can simplify the matrix equation to:

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \mathbf{\Omega}^{|\mu|} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}. \tag{A.1}$$

In what follows, we will take $\mathbf{\Omega}$ to mean $\mathbf{\Omega}^{|\mu|}$. The linearity suggests breaking down the problem into a set of linear equations

$$\mathbf{AX} + \mathbf{BY} = \mathbf{\Omega X} \tag{A.2}$$

$$-\mathbf{BX} - \mathbf{AY} = \mathbf{\Omega Y}, \tag{A.3}$$

which can be simplified by the addition of these two equations in A.3

$$(\mathbf{A} - \mathbf{B})(\mathbf{X} - \mathbf{Y}) = \mathbf{\Omega}(\mathbf{X} + \mathbf{Y}) \tag{A.4}$$

which can be rearranged to give

$$(\mathbf{X} + \mathbf{Y}) = \mathbf{\Omega}^{-1}(\mathbf{A} - \mathbf{B})(\mathbf{X} - \mathbf{Y}). \tag{A.5}$$

Doing a pairwise subtraction of the equations in A.3 instead gives

$$(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) = \mathbf{\Omega}(\mathbf{X} - \mathbf{Y}). \tag{A.6}$$

Similarly, we can isolate

$$(\mathbf{X} - \mathbf{Y}) = \mathbf{\Omega}^{-1}(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}). \tag{A.7}$$

Equations A.4 and A.6 can be combined to get

$$\mathbf{\Omega} = (\mathbf{X} - \mathbf{Y})^{\dagger}(\mathbf{A} - \mathbf{B})(\mathbf{X} - \mathbf{Y}) \tag{A.8}$$

and

$$\mathbf{\Omega} = (\mathbf{X} + \mathbf{Y})^{\dagger}(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}). \tag{A.9}$$

Substituting in for $\mathbf{X} + \mathbf{Y}$ from A.5 into equation A.6

$$\mathbf{\Omega}^{-1}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})(\mathbf{X} - \mathbf{Y}) = \mathbf{\Omega}(\mathbf{X} - \mathbf{Y}). \tag{A.10}$$

Multiplication by $\boldsymbol{\Omega}$ gives

$$(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})(\mathbf{X} - \mathbf{Y}) = \boldsymbol{\Omega}^2(\mathbf{X} - \mathbf{Y}). \tag{A.11}$$

Now, we plug the definition in equation A.7 for the $(\mathbf{X} - \mathbf{Y})$ terms

$$(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})\boldsymbol{\Omega}^{-1}(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) = \boldsymbol{\Omega}^2\boldsymbol{\Omega}^{-1}(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}). \tag{A.12}$$

Multiplication through by $\boldsymbol{\Omega}$ gives and $(\mathbf{A} + \mathbf{B})^{-1}$ gives

$$(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) = \boldsymbol{\Omega}^2(\mathbf{X} + \mathbf{Y}). \tag{A.13}$$

At this point we want to define $\mathbf{T} = (\mathbf{A} - \mathbf{B})^{-\frac{1}{2}}(\mathbf{X} + \mathbf{Y})$, so that we can write

$$(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\mathbf{T} = \boldsymbol{\Omega}^2(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\mathbf{T}. \tag{A.14}$$

Dividing through by $(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}$ gives:

$$(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\mathbf{T} = \boldsymbol{\Omega}^2\mathbf{T}. \tag{A.15}$$

We can solve this matrix equation now. We can use this definition for $\mathbf{T}$ to redefine equation A.5

$$(\mathbf{X} + \mathbf{Y}) = (\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\mathbf{T}. \tag{A.16}$$

And then for normalization, we need

$$(\mathbf{X} - \mathbf{Y})^{\dagger}(\mathbf{X} + \mathbf{Y}) = 1. \tag{A.17}$$

So we need

$$(\mathbf{X} - \mathbf{Y}) = (\mathbf{A} - \mathbf{B})^{-1}(\mathbf{X} + \mathbf{Y})\boldsymbol{\Omega}. \tag{A.18}$$

So we can instead use the solution of equation A.15 to obtain the excitation energies $\boldsymbol{\Omega}^{\mu}$ and the excitation vectors $\mathbf{X}^{\mu}$ and $\mathbf{Y}^{\mu}$, the latter of which we will then use to construct our residues $\mathbf{V}_{pq}^{\mu}$.

A p p e n d i x   B

DERIVATION OF THE LINEARIZED G_0W_0 DENSITY MATRIX

This derivation will be carried out in the spin-unrestricted formalism. We have the equation for the density matrix

$$\gamma^\sigma\left(\mathbf{r}_1, \mathbf{r}_2\right) = \gamma_0^\sigma\left(\mathbf{r}_1, \mathbf{r}_2\right) - \frac{\mathrm{i}}{2\pi}\int \mathrm{d}\mathbf{r}_3\,\mathrm{d}\mathbf{r}_4\,\mathrm{d}\omega\mathrm{e}^{\mathrm{i}\omega\eta}G_0^\sigma\left(\mathbf{r}_1, \mathbf{r}_3, \omega\right)\Sigma_c^\sigma\left(\mathbf{r}_3, \mathbf{r}_4, \omega\right)G_0^\sigma\left(\mathbf{r}_4, \mathbf{r}_2, \omega\right)$$
(B.1)

where γ^σ is our new density matrix from the interacting Green's function, and γ_0^σ is the density matrix from the noninteracting Green's function. ω is the frequency and η is a small infinitesimal positive number, which we will later take to be zero. $G_0^\sigma(\omega)$ and $\Sigma_c^\sigma(\omega)$ are the noninteracting Green's function and the correlation self-energy, respectively, now Fourier transformed to the frequency domain. In order to simplify the integral, let us consider

$$I = \int \mathrm{d}\mathbf{r}_3\,\mathrm{d}\mathbf{r}_4 G_0^\sigma\left(\mathbf{r}_1, \mathbf{r}_3\right)\Sigma_c^\sigma\left(\mathbf{r}_3, \mathbf{r}_4\right)G_0^\sigma\left(\mathbf{r}_4, \mathbf{r}_2\right)$$
(B.2)

The noninteracting Green's function in the MO basis is defined as

$$G_0\left(\mathbf{r}_1, \mathbf{r}_2, \right) = \sum_{pq}\phi_p^*(\mathbf{r}_1)G_{pq}\phi_q(\mathbf{r}_2)$$
(B.3)

and likewise for the self-energy

$$\Sigma_c\left(\mathbf{r}_1, \mathbf{r}_2, \right) = \sum_{pq}\phi_p^*(\mathbf{r}_1)\Sigma_{cpq}\phi_q(\mathbf{r}_2)$$
(B.4)

where G_{pq} and Σ_{pq} are the matrix elements of the noninteracting Green's function and the self-energy, respectively. We can rewrite the integral as

$$I_1 = \sum_{pq}\sum_{rs}\sum_{tu}\int \mathrm{d}\mathbf{r}_3\,\mathrm{d}\mathbf{r}_4\phi_p^*(\mathbf{r}_1)G_{pq}\phi_q(\mathbf{r}_3)\phi_r^*(\mathbf{r}_3)\Sigma_{rs}\phi_s(\mathbf{r}_4)\phi_t^*(\mathbf{r}_4)G_{tu}\phi_u(\mathbf{r}_2)$$
(B.5)

We can get rid of the integral over spatial indices by using the orthonormality of the basis functions.

$$I_1 = \sum_{pq}\sum_{r}\sum_{t}\phi_p^*(\mathbf{r}_1)G_{pr}\phi_r(\mathbf{r})\phi_r^*(\mathbf{r})\Sigma_{rt}\phi_t(\mathbf{r}')\phi_t^*(\mathbf{r}')G_{tq}\phi_q(\mathbf{r}_2)$$
(B.6)

We use this and then also rewrite equation B.1 in terms of elements of the density matrix with

$$D_{pq\sigma} = \langle p\sigma \, | \gamma^\sigma | \, q\sigma \rangle \tag{B.7}$$

to get

$$D_{pq\sigma} = \langle p\sigma | \gamma_0^\sigma | q\sigma \rangle - \frac{i}{2\pi} \sum_r \sum_t \int_{-\infty}^{\infty} d\omega e^{i\omega\eta} \langle p\sigma | G_0^\sigma(\omega) | r\sigma \rangle \langle r\sigma | \Sigma_c^\sigma(\omega) | t\sigma \rangle \langle t\sigma | G_0^\sigma(\omega) | q\sigma \rangle . \tag{B.8}$$

Next, we plug in the following definitions for the two different time orderings for the noninteracting Green's function and correlation piece of the self energy

$$G_{0pq}^\sigma = \sum_i \frac{\delta_{pq}\delta_{pi}}{\omega - \epsilon_{i\sigma} - i\eta} + \sum_a \frac{\delta_{pq}\delta_{pa}}{\omega - \epsilon_{a\sigma} + i\eta} \tag{B.9}$$

and

$$\Sigma_{cpq}^\sigma(\omega) = \sum_{is} \frac{w_{pi\sigma}^s w_{qi\sigma}^s}{\omega - \epsilon_{i\sigma} + \Omega_s - i\eta} + \sum_{as} \frac{w_{pa\sigma}^s w_{qa\sigma}^s}{\omega - \epsilon_{a\sigma} - \Omega_s + i\eta} \tag{B.10}$$

into equation B.8 to get

$$D_{pq\sigma} = \langle p\sigma | \gamma_0^\sigma | q\sigma \rangle - \frac{i}{2\pi} \sum_r \sum_t \int_{-\infty}^{\infty} d\omega e^{i\omega\eta} \left(\sum_i \frac{\delta_{pr}\delta_{pi}}{\omega - \epsilon_{i\sigma} - i\eta} + \sum_a \frac{\delta_{pr}\delta_{pa}}{\omega - \epsilon_{a\sigma} + i\eta} \right)$$
$$\left(\sum_{ks} \frac{w_{rk\sigma}^s w_{tk\sigma}^s}{\omega - \epsilon_{k\sigma} + \Omega_s - i\eta} + \sum_{cs} \frac{w_{rc\sigma}^s w_{tc\sigma}^s}{\omega - \epsilon_{c\sigma} - \Omega_s + i\eta} \right) \left(\sum_j \frac{\delta_{tq}\delta_{tj}}{\omega - \epsilon_{j\sigma} - i\eta} + \sum_b \frac{\delta_{tq}\delta_{tb}}{\omega - \epsilon_{b\sigma} + i\eta} \right) . \tag{B.11}$$

Let us distribute the integral, which spawns 8 terms. Also note that the delta functions will get rid of the sums over r and t

$$
\begin{aligned}
I_2 = \int_{-\infty}^{\infty} \mathrm{d}\omega \mathrm{e}^{i\omega\eta} \Bigg(&\sum_{ijks} \left(\frac{w_{ik\sigma}^s w_{jk\sigma}^s}{(\omega - \epsilon_{k\sigma} + \Omega_s - i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{j\sigma} - i\eta)} \right) \\
&+ \sum_{ibks} \left(\frac{w_{ik\sigma}^s w_{bk\sigma}^s}{(\omega - \epsilon_{k\sigma} + \Omega_s - i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{b\sigma} + i\eta)} \right) \\
&+ \sum_{ijcs} \left(\frac{w_{ic\sigma}^s w_{jc\sigma}^s}{(\omega - \epsilon_{c\sigma} - \Omega_s + i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{j\sigma} - i\eta)} \right) \\
&+ \sum_{ibcs} \left(\frac{w_{ic\sigma}^s w_{bc\sigma}^s}{(\omega - \epsilon_{c\sigma} - \Omega_s + i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{b\sigma} + i\eta)} \right) \\
&+ \sum_{ajks} \left(\frac{w_{ak\sigma}^s w_{jk\sigma}^s}{(\omega - \epsilon_{k\sigma} + \Omega_s - i\eta)(\omega - \epsilon_{a\sigma} + i\eta)(\omega - \epsilon_{j\sigma} - i\eta)} \right) \\
&+ \sum_{abks} \left(\frac{w_{ak\sigma}^s w_{bk\sigma}^s}{(\omega - \epsilon_{k\sigma} + \Omega_s - i\eta)(\omega - \epsilon_{a\sigma} + i\eta)(\omega - \epsilon_{b\sigma} + i\eta)} \right) \\
&+ \sum_{ajcs} \left(\frac{w_{ac\sigma}^s w_{jc\sigma}^s}{(\omega - \epsilon_{c\sigma} - \Omega_s + i\eta)(\omega - \epsilon_{a\sigma} + i\eta)(\omega - \epsilon_{j\sigma} - i\eta)} \right) \\
&+ \sum_{abcs} \left(\frac{w_{ac\sigma}^s w_{bc\sigma}^s}{(\omega - \epsilon_{c\sigma} - \Omega_s + i\eta)(\omega - \epsilon_{a\sigma} + i\eta)(\omega - \epsilon_{b\sigma} + i\eta)} \right) \Bigg)
\end{aligned}
$$
(B.12)

At this point, we note the following relation between integrals $\oint_{D_\pm} f(z) = \int_{-R}^{R} f(z) + \int_{C_{R_\pm}} f(z)$. $D_\pm$ is a semicircular domain in either half of the complex plane, $C_{R_\pm}$ is the semicircle in the upper or lower part of the complex plane, and R is the radius of the semicircle. We are able to take $R \to \infty$ and since $f(z) = \mathrm{e}^{i\omega\eta}g(z)$, where $g(z)$ is analytic on D except for a finite number of poles, the integral over the semicircle will vanish by Jordan's lemma, leaving us with $\int_{-R=-\infty}^{R=\infty} f(z) = \oint_{D_\pm} f(z)$.

B.1 Fully occupied block

The contribution over the fully occupied block of the density matrix will be given by the following two terms in equation B.12

$$
\begin{aligned}
I_{ij} = &\sum_{ks} w_{ik\sigma}^s w_{jk\sigma}^s \oint_{D+} \mathrm{d}\omega \mathrm{e}^{i\omega\eta} \frac{1}{(\omega - \epsilon_{k\sigma} + \Omega_s - i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{j\sigma} - i\eta)} \\
&+ \sum_{cs} w_{ic\sigma}^s w_{jc\sigma}^s \oint_{D+} \mathrm{d}\omega \mathrm{e}^{i\omega\eta} \frac{1}{(\omega - \epsilon_{c\sigma} - \Omega_s + i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{j\sigma} - i\eta)}.
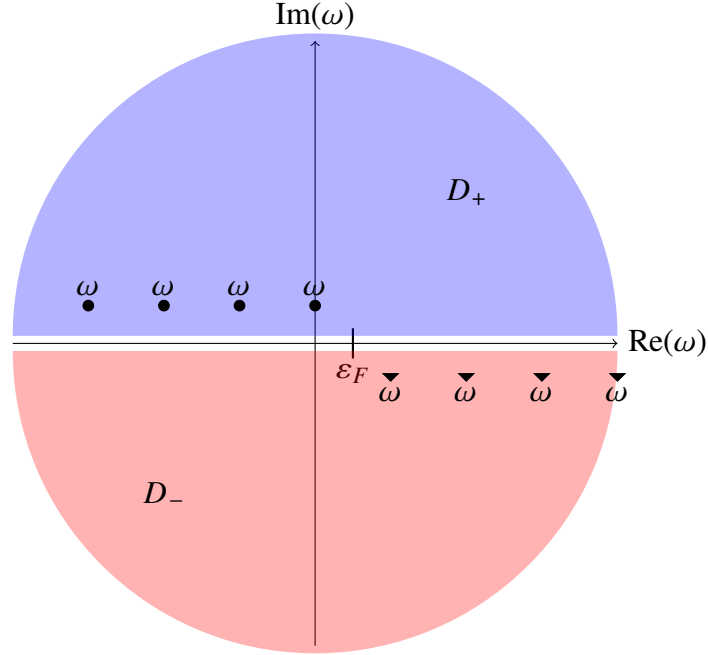\end{aligned}
$$
(B.13)

Figure B.1: Contour for the complex frequency integral. The poles are denoted by the various ω. The Fermi energy is denoted by ε_F. The integration contour D_+ is the semicircle in the upper complex plane, while D_- is the semicircle in the lower complex plane.

Due to the contour D_+ chosen for this case, we have poles for the first term at $\omega_{11} = \epsilon_{k\sigma} - \Omega_s + i\eta$, $\omega_{12} = \epsilon_{i\sigma} + i\eta$, and $\omega_{13} = \epsilon_{j\sigma} + i\eta$. For such simple poles, the Cauchy residue theorem simplifies to

$$\text{Res}_{\omega=\omega_0} f(\omega) = \phi(\omega_0) \tag{B.14}$$

where $\phi_{\omega_0}(\omega) = (\omega - \omega_0)f(\omega)$. For the first of these integrals in the occupied block, we have

$$f_1(\omega) = \frac{e^{i\omega\eta}}{(\omega - \epsilon_{k\sigma} + \Omega_s - i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{j\sigma} - i\eta)}. \tag{B.15}$$

So at the first pole, in the limit $\eta \to 0$, we get

$$\phi_{\omega_{11}}(\epsilon_{k\sigma} - \Omega_s + i\eta) = \frac{1}{(\epsilon_{k\sigma} - \Omega_s - \epsilon_{i\sigma})(\epsilon_{k\sigma} - \Omega_s - \epsilon_{j\sigma})} \tag{B.16}$$

For the other poles, the procedure is similar with

$$\phi_{\omega_{12}}(\epsilon_{i\sigma} + i\eta) = \frac{1}{(\epsilon_{i\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{i\sigma} - \epsilon_{j\sigma})} \tag{B.17}$$

and

$$\phi_{\omega_{13}}(\epsilon_{j\sigma} + i\eta) = \frac{1}{(\epsilon_{j\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{j\sigma} - \epsilon_{i\sigma})}. \tag{B.18}$$

We move on to the second integral in the occupied block. It only has two poles in the fully occupied contour $\omega_{21} = \epsilon_{i\sigma} + i\eta$ and $\omega_{22} = \epsilon_{j\sigma} + i\eta$. We have $f_2(\omega)$ as

$$f_2(\omega) = \frac{e^{i\omega\eta}}{(\omega - \epsilon_{c\sigma} - \Omega_s + i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{j\sigma} - i\eta)}. \tag{B.19}$$

So $\phi_{\omega_{21}}(\omega_{21})$ is

$$\phi_{\omega_{21}}(\epsilon_{i\sigma} + i\eta) = \frac{1}{(\epsilon_{i\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{i\sigma} - \epsilon_{j\sigma})}. \tag{B.20}$$

Now we consider the second pole at $\omega_{22} = \epsilon_{j\sigma} + i\eta$

$$\phi_{\omega_{22}}(\epsilon_{j\sigma} + i\eta) = \frac{1}{(\epsilon_{j\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{j\sigma} - \epsilon_{i\sigma})}. \tag{B.21}$$

We summarize the results in a table B.1.

Adding the two terms together, we get

Table B.1: Summary of Poles and their Residues

Pole Notation	Position ω_0	Residue $\phi_{\omega_0}(\omega_0)$
Series ω_1		
ω_{11}	$\epsilon_{k\sigma} - \Omega_s + i\eta$	$\frac{1}{(\epsilon_{k\sigma}-\Omega_s-\epsilon_{i\sigma})(\epsilon_{k\sigma}-\Omega_s-\epsilon_{j\sigma})}$
ω_{12}	$\epsilon_{i\sigma} + i\eta$	$\frac{1}{(\epsilon_{i\sigma}-\epsilon_{k\sigma}+\Omega_s)(\epsilon_{i\sigma}-\epsilon_{j\sigma})}$
ω_{13}	$\epsilon_{j\sigma} + i\eta$	$\frac{1}{(\epsilon_{j\sigma}-\epsilon_{k\sigma}+\Omega_s)(\epsilon_{j\sigma}-\epsilon_{i\sigma})}$
Series ω_2		
ω_{21}	$\epsilon_{i\sigma} + i\eta$	$\frac{1}{(\epsilon_{i\sigma}-\epsilon_{c\sigma}-\Omega_s)(\epsilon_{i\sigma}-\epsilon_{j\sigma})}$
ω_{22}	$\epsilon_{j\sigma} + i\eta$	$\frac{1}{(\epsilon_{j\sigma}-\epsilon_{c\sigma}-\Omega_s)(\epsilon_{j\sigma}-\epsilon_{i\sigma})}$

$$
\begin{aligned}
I_{ij} = 2\pi i \Bigg(\sum_{ks} w_{ik\sigma}^s w_{jk\sigma}^s &\left(\frac{1}{(\epsilon_{k\sigma} - \Omega_s - \epsilon_{i\sigma})(\epsilon_{k\sigma} - \Omega_s - \epsilon_{j\sigma})} + \frac{1}{(\epsilon_{i\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{i\sigma} - \epsilon_{j\sigma})} \right. \\
&\left. + \frac{1}{(\epsilon_{j\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{j\sigma} - \epsilon_{i\sigma})} \right) \\
&+ \sum_{cs} w_{ic\sigma}^s w_{jc\sigma}^s \left(\frac{1}{(\epsilon_{i\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{i\sigma} - \epsilon_{j\sigma})} + \frac{1}{(\epsilon_{j\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{j\sigma} - \epsilon_{i\sigma})} \right) \Bigg).
\end{aligned}
\tag{B.22}
$$

Getting a common denominator for all of the terms means that the first term simplifies to 0, and the second term gives

$$I_{ij} = -2\pi i \sum_{cs} \frac{w_{ic\sigma}^s w_{jc\sigma}^s}{(\Omega_s + \epsilon_{c\sigma} - \epsilon_{i\sigma})(\Omega_s + \epsilon_{c\sigma} - \epsilon_{j\sigma})}. \tag{B.23}$$

So, the expression for the fully occupied block of the density matrix is

$$D_{ij} = \langle i\sigma | \gamma_0^\sigma | j\sigma \rangle + \frac{2\pi i^2}{2\pi} \sum_{cs} \frac{w_{ic} w_{jc}}{(\Omega_s + \epsilon_{c\sigma} - \epsilon_{i\sigma})(\Omega_s + \epsilon_{c\sigma} - \epsilon_{j\sigma})}. \tag{B.24}$$

The first term is the fully occupied element of the noninteracting density matrix, so this just reduces to δ_{ij} since for this reference system, the occupied occupations are just unity and then we relabel the virtual index $c \to a$.

$$D_{ij} = \delta_{ij} - \sum_{as} \frac{w_{ia} w_{ja}}{(\Omega_s + \epsilon_{a\sigma} - \epsilon_{i\sigma})(\Omega_s + \epsilon_{a\sigma} - \epsilon_{j\sigma})}. \tag{B.25}$$

B.2 Fully Virtual Block

For the fully virtual block, we need to consider third to last and last terms of the integral in equation B.12

$$I_{ab} = \sum_{ks} w_{ak\sigma}^s w_{bk\sigma}^s \int d\omega e^{i\omega\eta} \frac{1}{(\omega - \epsilon_{k\sigma} + \Omega_s - i\eta)(\omega - \epsilon_{a\sigma} + i\eta)(\omega - \epsilon_{b\sigma} + i\eta)}$$
$$+ \sum_{cs} w_{ac\sigma}^s w_{bc\sigma}^s \int d\omega e^{i\omega\eta} \frac{1}{(\omega - \epsilon_{c\sigma} - \Omega_s + i\eta)(\omega - \epsilon_{a\sigma} + i\eta)(\omega - \epsilon_{b\sigma} + i\eta)} \tag{B.26}$$

Due to the contour D_- chosen for this case, we have poles for the first term at just $\omega_{11} = \epsilon_{a\sigma} - i\eta$ and $\omega_{12} = \epsilon_{b\sigma} - i\eta$. Using the Cauchy residue theorem from equation B.14

$$f_1(\omega) = \frac{e^{i\omega\eta}}{(\omega - \epsilon_{k\sigma} + \Omega_s - i\eta)(\omega - \epsilon_{a\sigma} + i\eta)(\omega - \epsilon_{b\sigma} + i\eta)}. \tag{B.27}$$

Plugging in $\omega_{11} = \epsilon_{a\sigma} - i\eta$, we get

$$\phi_{\omega_{11}}(\epsilon_{a\sigma} - i\eta) = \frac{1}{(\epsilon_{a\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{a\sigma} - \epsilon_{b\sigma})}. \tag{B.28}$$

and

$$\phi_{\omega_{12}}(\epsilon_{b\sigma} - i\eta) = \frac{1}{(\epsilon_{b\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{b\sigma} - \epsilon_{a\sigma})}. \tag{B.29}$$

We move on to the second integral in the virtual block. It has now three poles in D_- $\omega_{21} = \epsilon_{c\sigma} + \Omega_s - i\eta$, $\omega_{22} = \epsilon_{a\sigma} - i\eta$, and $\omega_{23} = \epsilon_{b\sigma} - i\eta$. We have $f_2(\omega)$ as

$$f_2(\omega) = \frac{e^{i\omega\eta}}{(\omega - \epsilon_{c\sigma} - \Omega_s + i\eta)(\omega - \epsilon_{a\sigma} + i\eta)(\omega - \epsilon_{b\sigma} + i\eta)}. \tag{B.30}$$

So $\phi_{\omega_{21}}(\omega_{21})$ is

$$\phi_{\omega_{21}}(\epsilon_{c\sigma} + \Omega_s - i\eta) = \frac{1}{(\epsilon_{c\sigma} + \Omega_s - \epsilon_{a\sigma})(\epsilon_{c\sigma} + \Omega_s - \epsilon_{b\sigma})}. \tag{B.31}$$

Now we consider the second pole at $\omega_{22} = \epsilon_{a\sigma} - i\eta$

$$\phi_{\omega_{22}}(\epsilon_{a\sigma} - i\eta) = \frac{1}{(\epsilon_{a\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{a\sigma} - \epsilon_{b\sigma})}. \tag{B.32}$$

Finally, we consider the third pole at $\omega_{23} = \epsilon_{b\sigma} - i\eta$

$$\phi_{\omega_{23}}(\epsilon_{b\sigma} - i\eta) = \frac{1}{(\epsilon_{b\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{b\sigma} - \epsilon_{a\sigma})}. \tag{B.33}$$

The results we got are summarized in the table B.2.

Adding the two terms together, we get

Table B.2: Summary of Poles and their Residues

Pole Notation	Position ω_0	Residue $\phi_{\omega_0}(\omega_0)$
Series ω_1		
ω_{11}	$\epsilon_{a\sigma} - i\eta$	$\frac{1}{(\epsilon_{a\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{a\sigma} - \epsilon_{b\sigma})}$
ω_{12}	$\epsilon_{b\sigma} - i\eta$	$\frac{1}{(\epsilon_{b\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{b\sigma} - \epsilon_{a\sigma})}$
Series ω_2		
ω_{21}	$\epsilon_{c\sigma} + \Omega_s - i\eta$	$\frac{1}{(\epsilon_{c\sigma} + \Omega_s - \epsilon_{a\sigma})(\epsilon_{c\sigma} + \Omega_s - \epsilon_{b\sigma})}$
ω_{22}	$\epsilon_{a\sigma} - i\eta$	$\frac{1}{(\epsilon_{a\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{a\sigma} - \epsilon_{b\sigma})}$
ω_{23}	$\epsilon_{b\sigma} - i\eta$	$\frac{1}{(\epsilon_{b\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{b\sigma} - \epsilon_{a\sigma})}$

$$
\begin{aligned}
I_{ab} = 2\pi i \Bigg(&\sum_{ks} w^s_{ak\sigma} w^s_{bk\sigma} \left(\frac{1}{(\epsilon_{a\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{a\sigma} - \epsilon_{b\sigma})} + \frac{1}{(\epsilon_{b\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{b\sigma} - \epsilon_{a\sigma})} \right) \\
&+ \sum_{cs} w^s_{ac\sigma} w^s_{bc\sigma} \left(\frac{1}{(\epsilon_{c\sigma} + \Omega_s - \epsilon_{a\sigma})(\epsilon_{c\sigma} + \Omega_s - \epsilon_{b\sigma})} \right. \\
&+ \frac{1}{(\epsilon_{a\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{a\sigma} - \epsilon_{b\sigma})} \\
&\left.\left. + \frac{1}{(\epsilon_{b\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{b\sigma} - \epsilon_{a\sigma})} \right) \right)
\end{aligned}
\tag{B.34}
$$

A similar simplification as the one done before, which involves getting a common denominator, gives

$$I_{ab} = -2\pi i \sum_{ks} \frac{w_{ak} w_{bk}}{(\Omega_s + \epsilon_{k\sigma} - \epsilon_{a\sigma})(\Omega_s + \epsilon_{k\sigma} - \epsilon_{b\sigma})}. \tag{B.35}$$

So, the expression for D_{ab} is

$$D_{ab} = \langle a\sigma| \gamma_0^\sigma |b\sigma\rangle + \frac{2\pi i^2}{2\pi} \sum_{ks} \frac{w_{ak} w_{bk}}{(\Omega_s + \epsilon_{k\sigma} - \epsilon_{a\sigma})(\Omega_s + \epsilon_{k\sigma} - \epsilon_{b\sigma})}. \tag{B.36}$$

The noninteracting density matrix does not mix virtual states and we relabel the occupied index $k \to i$, to get

$$D_{ab} = -\sum_{is} \frac{w_{ai}w_{bi}}{(\Omega_s + \epsilon_{i\sigma} - \epsilon_{a\sigma})(\Omega_s + \epsilon_{i\sigma} - \epsilon_{b\sigma})}. \tag{B.37}$$

B.3 Mixed Block

Now, we want to consider one instance of the mixed block i.e. the second and fourth terms of the integral in equation B.12

$$
\begin{aligned}
I_{ib} = &\sum_{ks} w^s_{ik\sigma}w^s_{bk\sigma} \int d\omega e^{i\omega\eta} \frac{1}{(\omega - \epsilon_{k\sigma} + \Omega_s - i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{b\sigma} + i\eta)} \\
&+ \sum_{cs} w^s_{ic\sigma}w^s_{bc\sigma} \int d\omega e^{i\omega\eta} \frac{1}{(\omega - \epsilon_{c\sigma} - \Omega_s + i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{b\sigma} + i\eta)}
\end{aligned}. \tag{B.38}
$$

Due to the contour D_+ chosen for this case, we have poles for the first term which lies in the upper half of the complex plane at $\omega_{11} = \epsilon_{k\sigma} - \Omega_s + i\eta$ and $\omega_{12} = \epsilon_{i\sigma} + i\eta$. Using the Cauchy residue theorem from equation B.14

$$f_1(\omega) = \frac{e^{i\omega\eta}}{(\omega - \epsilon_{k\sigma} + \Omega_s - i\eta)(\omega - \epsilon_{i\sigma} + i\eta)(\omega - \epsilon_{b\sigma} + i\eta)}. \tag{B.39}$$

Plugging in $\omega_{11} = \epsilon_{k\sigma} - \Omega_s + i\eta$, we get

$$\phi_{\omega_{11}}(\epsilon_{k\sigma} - \Omega_s + i\eta) = \frac{1}{(\epsilon_{k\sigma} - \epsilon_{i\sigma} - \Omega_s)(\epsilon_{k\sigma} - \epsilon_{b\sigma} - \Omega_s)}. \tag{B.40}$$

Now we consider the second pole at $\omega_{12} = \epsilon_{i\sigma} + i\eta$

$$\phi_{\omega_{12}}(\epsilon_{i\sigma} + i\eta) = \frac{1}{(\epsilon_{i\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{i\sigma} - \epsilon_{b\sigma})}. \tag{B.41}$$

We move on to the second integral in the mixed block. It has two poles in D_- $\omega_{21} = \epsilon_{c\sigma} + \Omega_s - i\eta$ and $\omega_{22} = \epsilon_{b\sigma} - i\eta$. We have $f_2(\omega)$ as

$$f_2(\omega) = \frac{e^{i\omega\eta}}{(\omega - \epsilon_{c\sigma} - \Omega_s + i\eta)(\omega - \epsilon_{i\sigma} - i\eta)(\omega - \epsilon_{b\sigma} + i\eta)}. \tag{B.42}$$

So $\phi_{\omega_{21}}(\omega_{21})$ is

$$\phi_{\omega_{21}}(\epsilon_{c\sigma} + \Omega_s - i\eta) = \frac{1}{(\epsilon_{c\sigma} + \Omega_s - \epsilon_{i\sigma})(\epsilon_{c\sigma} + \Omega_s - \epsilon_{b\sigma})}. \tag{B.43}$$

Now we consider the second pole at $\omega_{22} = \epsilon_{b\sigma} - i\eta$

$$\phi_{\omega_{22}}(\epsilon_{b\sigma} - i\eta) = \frac{1}{(\epsilon_{b\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{b\sigma} - \epsilon_{i\sigma})}. \tag{B.44}$$

Table B.3: Summary of Poles and their Residues

Pole Notation	Position ω_0	Residue $\phi_{\omega_0}(\omega_0)$
Series ω_1		
ω_{11}	$\epsilon_{k\sigma} - \Omega_s + i\eta$	$\frac{1}{(\epsilon_{k\sigma}-\epsilon_{i\sigma}-\Omega_s)(\epsilon_{k\sigma}-\epsilon_{b\sigma}-\Omega_s)}$
ω_{12}	$\epsilon_{i\sigma} + i\eta$	$\frac{1}{(\epsilon_{i\sigma}-\epsilon_{k\sigma}+\Omega_s)(\epsilon_{i\sigma}-\epsilon_{b\sigma})}$
Series ω_2		
ω_{21}	$\epsilon_{c\sigma} + \Omega_s - i\eta$	$\frac{1}{(\epsilon_{c\sigma}+\Omega_s-\epsilon_{i\sigma})(\epsilon_{c\sigma}+\Omega_s-\epsilon_{b\sigma})}$
ω_{22}	$\epsilon_{b\sigma} - i\eta$	$\frac{1}{(\epsilon_{b\sigma}-\epsilon_{c\sigma}-\Omega_s)(\epsilon_{b\sigma}-\epsilon_{i\sigma})}$

The results we got are summarized in the table B.3.

Adding the two terms together, we get

$$
I_{ib} = 2\pi i \left(\sum_{ks} w^s_{ik\sigma} w^s_{bk\sigma} \left(\frac{1}{(\epsilon_{k\sigma} - \epsilon_{i\sigma} - \Omega_s)(\epsilon_{k\sigma} - \epsilon_{b\sigma} - \Omega_s)} \right. \right.
$$
$$
\left. + \frac{1}{(\epsilon_{i\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \right)
$$
$$
+ \sum_{cs} w^s_{ic\sigma} w^s_{bc\sigma} \left(\frac{1}{(\epsilon_{c\sigma} + \Omega_s - \epsilon_{i\sigma})(\epsilon_{c\sigma} + \Omega_s - \epsilon_{b\sigma})} \right.
$$
$$
\left. \left. + \frac{1}{(\epsilon_{b\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{b\sigma} - \epsilon_{i\sigma})} \right) \right). \tag{B.45}
$$

By getting a common denominator and simplifying terms, we get

$$
D_{ib} = \langle i\sigma | \gamma^\sigma_0 | b\sigma \rangle + \frac{2\pi i^2}{2\pi (\epsilon_{i\sigma} - \epsilon_{b\sigma})} \left[\sum_{ks} \frac{w^s_{ik} w^s_{bk}}{\epsilon_{k\sigma} - \epsilon_{b\sigma} - \Omega_s} - \sum_{cs} \frac{w^s_{ic} w^s_{bc}}{\epsilon_{c\sigma} + \Omega_s - \epsilon_{i\sigma}} \right]. \tag{B.46}
$$

The noninteracting density matrix does not mix occupied with virtual states and we relabel the occupied index $k \to j$ and the virtual index $c \to a$

$$
D_{ib} = \frac{1}{\epsilon_{i\sigma} - \epsilon_{b\sigma}} \left[\sum_{as} \frac{w^s_{ia} w^s_{ba}}{\epsilon_{i\sigma} - \epsilon_{a\sigma} - \Omega_s} - \sum_{js} \frac{w^s_{ij} w^s_{bj}}{\epsilon_{j\sigma} - \epsilon_{b\sigma} - \Omega_s} \right]. \tag{B.47}
$$

Interestingly, for the mixed block, the result you get is exactly the same if you choose the opposite contour D_- for the full frequency integral of B.12. This is what one would expect from an interpretation of Jordan's Lemma.