

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 due to the fact that it only considers the average interaction between electrons and not the explicit one. DFT has a similar computational scaling to Hartree-Fock, but it can deliver accurate results for larger systems. **Site** 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; 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 GW approximation within its one-shot variant G_0W_0 , which practically scales like $O(N^4)$.

Chapter 3

THEORY

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

$$\hat{H}\Psi_0 = E_0\Psi_0 \quad (3.1)$$

with

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

In equation 3.1, \hat{H} is the Hamiltonian operator, while Ψ_0 and E_0 are the ground state wave function and energy of the system, respectively. As shown in equation 3.2, the Hamiltonian operator consists of four terms: a kinetic term, in which a sum of the kinetic operators $-\frac{1}{2}\nabla_i^2$ 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 to solve equation 3.1 with the complication arising from accurately describing the electron-electron repulsion, whose operator we will call \hat{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-Fock⁶

The concept behind Hartree-Fock (HF) is that we can assign each electron a given orbital $\chi_i(\mathbf{r}_i, \sigma_i)$, where \mathbf{r}_i is the spatial coordinate and σ_i is the spin of the i th electron. We then construct the many-electron wave function as a Hartree product of these orbitals

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

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

$$\Psi_{\text{HF}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{r}_1, \sigma_1) & \chi_2(\mathbf{r}_1, \sigma_1) & \cdots & \chi_N(\mathbf{r}_1, \sigma_1) \\ \chi_1(\mathbf{r}_2, \sigma_2) & \chi_2(\mathbf{r}_2, \sigma_2) & \cdots & \chi_N(\mathbf{r}_2, \sigma_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{r}_N, \sigma_N) & \chi_2(\mathbf{r}_N, \sigma_N) & \cdots & \chi_N(\mathbf{r}_N, \sigma_N) \end{vmatrix}. \quad (3.4)$$

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

$$E_{\text{HF}} = \langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle, \quad (3.5)$$

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

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

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

$$\frac{\delta \mathcal{L}}{\delta \chi_i} = 0. \quad (3.7)$$

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

$$\hat{F} \chi_i = \epsilon_i \chi_i, \quad (3.8)$$

where \hat{F} is the Fock operator, which is defined as

$$\hat{F} = \hat{h} + \hat{V}_{\text{HF}}, \quad (3.9)$$

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

$$\hat{V}_{\text{HF}} = \sum_{j=1}^N (\hat{J}_j - \hat{K}_j), \quad (3.10)$$

where N is the number of electrons in the system, \hat{J}_j is the local Coulomb operator

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

and \hat{K}_j is the nonlocal exchange operator

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

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 \hat{V}_{ee}

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

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

$$\hat{V}_{ee} = \frac{1}{2} \sum_i^{\text{occ}} \sum_j^{\text{occ}} \sum_{\sigma=\alpha,\beta} ((i_\sigma i_\sigma | j_\sigma j_\sigma) - (i_\sigma j_\sigma | j_\sigma i_\sigma)) = \sum_i^{\text{occ}} \sum_j^{\text{occ}} 2(ii|jj) - (ij|ji). \quad (3.14)$$

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. In this work, we will work in the spin restricted Hartree-Fock formalism, which considers a single electronic orbital to be doubly occupied, with the two electrons having the same spatial part, but different spin parts.

Density Functional Theory (DFT)

The central quantity in DFT is the electron density $\rho_{\mathbf{r}}$. 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 in the Hartree-Fock theory, 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 density⁷

$$E[\rho_{\mathbf{r}}] = T[\rho_{\mathbf{r}}] + V_{ne}[\rho_{\mathbf{r}}] + V_H[\rho_{\mathbf{r}}] + V_{xc}[\rho_{\mathbf{r}}] + V_{nn}, \quad (3.15)$$

where T and V_{ne} are from the kinetic and nuclear-electron attraction of 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 are designed to give a more accurate treatment of the electron electron repulsion than Hartree-Fock, with the V_{xc} taking into account correlation effects. In practise, the V_{xc} is approximated, but many levels of designing it have been made, as described by Jacob's Ladder.⁸ Finally, V_{nn} is the nuclear-nuclear repulsion term. Kohn and Sham then define a self consistent procedure by which the electron density can be used to define a set of noninteracting orbitals, which is now known as Kohn-Sham DFT (KS-DFT).⁹

What is important to understand is that both the HF and KS-DFT mean field methods yield a reasonable first guess¹⁰ at molecular orbitals χ . We will later correct these orbitals with MBPT.

3.2 Green's functions

Definitions

One can define the single-particle Green's function \mathcal{D} as

$$\mathcal{D}(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = -i \langle N | \hat{T} [\hat{\psi}(\mathbf{r}_1, t_1) \hat{\psi}^\dagger(\mathbf{r}_2, t_2)] | N \rangle, \quad (3.16)$$

where $\hat{\psi}^\dagger$ ($\hat{\psi}$) are the field operators for creating or destroying a particle at spacetime coordinates \mathbf{r}_i and t_i , respectively. \hat{T} is the time-ordering operator that ensures that the field operator at the earlier time is acting on the ket before the field operator at the later time, and N is the N -electron ground state of the system. Now, we make a distinction between the noninteracting and interacting Green's functions, denoted as G_0 and G , respectively. The noninteracting case signifies that the particles in the system are not interacting with each other, with a Green's function given as

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

where now Φ_0 is the ground state wave function composed of noninteracting orbitals as obtained by a mean field calculation. In contrast, the interacting Green's function is defined as

$$G(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = -i \langle \Psi_0 | \hat{T} [\hat{\psi}(\mathbf{r}_1, t_1) \hat{\psi}^\dagger(\mathbf{r}_2, t_2)] | \Psi_0 \rangle, \quad (3.18)$$

where now Ψ_0 is the ground state wave function of a system where the particles can interact with each other. The Dyson equation relating these two quantities can be written symbolically as¹¹

$$G = G_0 + G_0 \Sigma G \rightarrow \Sigma = G^{-1} - G_0^{-1}, \quad (3.19)$$

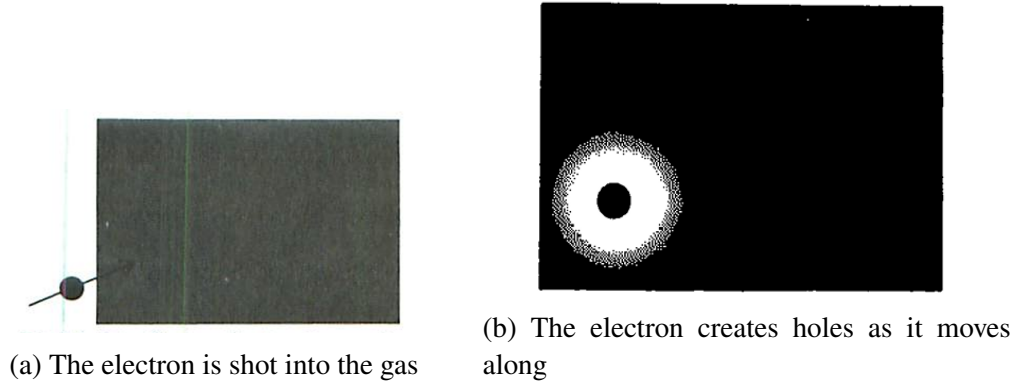


Figure 3.1: Electron gas propagation taken from Mattuck [12]

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 for the self-energy 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

$$\epsilon_{\text{quasi}} - \epsilon_{\text{bare}} = \epsilon_{\text{self}}, \quad (3.20)$$

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, as it is defined as the difference between their inverses, as shown in equation 3.19. Typically, Σ is designed to capture all of the quantum mechanical effects of the many body system and practical realizations of it require computationally efficient approximations, which we will discuss in the next section.

The *GW* Approximation

In order to solve the Dyson equation 3.19, 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 the five Hedin's equations¹³

$$\begin{aligned}
 G(1, 2) &= G_0(1, 2) + \int d(3, 4) G_0(1, 3) \Sigma(3, 4) G(4, 2) \\
 P(1, 2) &= \int d(3, 4) G(1, 3) G(4, 1) \Gamma(3, 4; 2) \\
 W(1, 2) &= V(1, 2) + \int d(3, 4) V(1, 3) P(3, 4) W(4, 2) \\
 \Sigma(1, 2) &= \int d(3, 4) G(1, 3) \Gamma(3, 2; 4) W(4, 1) \\
 \Gamma(1, 2; 3) &= \delta(1, 2) \delta(1, 3) + \int d(4, 5, 6, 7) \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Gamma(6, 7; 3),
 \end{aligned} \tag{3.21}$$

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

$$\begin{aligned}
 \Sigma(1, 2) &= \int d(1, 2) G(1, 2) W(1, 2) \\
 P(1, 2) &= \int d(1, 2) G(1, 2) G(2, 1).
 \end{aligned} \tag{3.22}$$

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 is studied in this work, 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 the interacting single-particle Green's function G , we can use it to obtain a perturbative correction to a variety of properties. In this work, we use it to obtain quasiparticle orbitals χ^{QP} , as an update to the mean-field orbitals χ^{MF} . 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 in chapter ???. It can also be used, among other things, to compute the spectral function, which gives access to ionization potentials and electron affinities.⁵

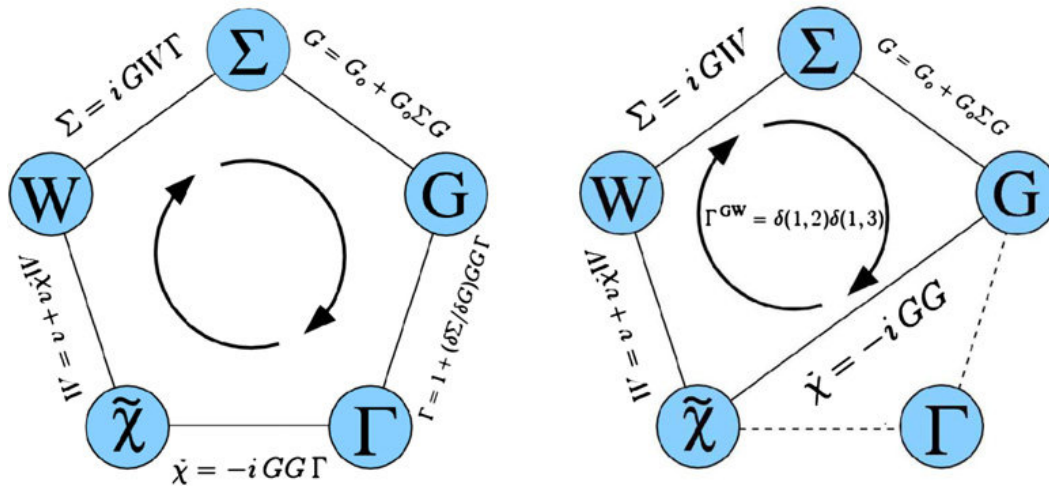


Figure 3.2: Graphical representation of Hedin's equations taken from *Frontiers | The GW Compendium: A Practical Guide to Theoretical Photoemission Spectroscopy* [5]. The left panel shows the full set of equations, whereas the right panel shows the GW approximation.

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 by¹¹

$$\delta_{pq} F_{pq}^{\text{HF}}[\gamma^{MF}] + \Sigma_{pp}^{\text{Corr}}(\varepsilon_p^{\text{QP}}) = \varepsilon_p^{\text{QP}}. \quad (4.1)$$

The first term corresponds to taking the diagonal of the matrix defined by the Hartree-Fock Fock operator, as defined in section 3.1, evaluated at the mean-field density γ^{MF} . The second term determines the correlation self energy dynamically by evaluating Σ^{Corr} for the $\varepsilon_p^{\text{QP}}$ determined in the previous iteration; the common approximation of just considering the diagonal $\Sigma_{pp}^{\text{Corr}}$ is used. The right side of the equality gives the updated $\varepsilon_p^{\text{QP}}$. So, we start by inputting the initial guess for $\varepsilon_p^{\text{QP}}$, which is given by the mean-field orbital energy ϵ_p , into $\Sigma_{pp}^{\text{Corr}}(\varepsilon_p^{\text{QP}})$, and iterate until self-consistency is reached.

4.2 Correlation Self-Energy

$$\Sigma_{pp}^{\text{Corr}}(\omega) = \sum_{\mu}^{\text{RPA}} \left(\sum_i^{\text{occupied}} \frac{V_{pi}^{\mu} V_{ip}^{\mu}}{\omega - (\epsilon_i - \Omega_{\mu})} + \sum_a^{\text{virtual}} \frac{V_{pa}^{\mu} V_{ap}^{\mu}}{\omega - (\epsilon_a + \Omega_{\mu})} \right) \quad (4.2)$$

This is the working equation for the correlation self-energy for a given MO p . First, we have a sum running over all of the excitations μ obtained from the previous RPA calculation, which will be introduced shortly. Then, we have two terms: one sum running over all of the occupied orbitals and the other sum running over all virtual orbitals. The Ω_{μ} are the excitation energies, and the V_{pq}^{μ} defined the coupling between my excitation vectors and electron repulsion integrals, as defined within section 4.3. The ϵ_i and ϵ_a are the orbital energies of the occupied and virtual orbitals, respectively. The ω is the frequency at which we are evaluating the self-energy, which is the quasiparticle energy $\varepsilon_p^{\text{QP}}$ in the iterative equation 4.1.

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 by¹⁴

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} \mathbf{\Omega}, \quad (4.3)$$

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

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + 2(ia||jb) \quad (4.4)$$

and \mathbf{B} is

$$B_{ia,jb} = 2(ia||jb) \quad (4.5)$$

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 4.4, and Equation 4.5, $(ia||jb) \rightarrow (ia|jb)$.

An alternative formulation that takes advantage of the symmetry obtained through neglect of the de-excitation energies will be used in what follows in order to make solving the direct RPA eigenvalue problem, which is the bottleneck of the *GW* calculation, more tractable and is derived in Appendix A as suggested by Furche [15].

Excitation vectors with coupling

The coupled excitation vectors V_{pq}^μ are defined 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 : $Z_{i,a}^\mu = X_{i,a}^\mu + Y_{i,a}^\mu$. Then, we define the appropriate integrals for contraction with this excitation

$$W_{p,q,i,a} = \sqrt{2} \sum_{p,q,i,a} (pq|ia). \quad (4.6)$$

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

And then we form the coupled excitation vectors from

$$V_{pq}^\mu = \sum_v W_{p,q,v} Z_v^\mu. \quad (4.7)$$

Tamm-Dancoff Approximation

In this method, we neglect the **B** matrix of the RPA equation. So the eigenvalue equation becomes

$$\mathbf{A}\mathbf{X} = \mathbf{X}\mathbf{\Omega} \quad (4.8)$$

where we still have:

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + 2(ia||jb) \quad (4.9)$$

And then we follow the same procedure as in the RPA to get the residues V_{pq}^μ , where now we have $Z_{v,\mu} = X_{v,\mu}$.

Chapter 5

LINEARIZED G_0W_0 DENSITY MATRIX

As noted earlier, we can get a new 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 B.

Implementation

First, we consider the fully occupied block

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

where the Ω^μ are the excitation energies and the V_{pq}^μ are the transition vectors. The sum runs over all virtual orbitals and excitation energies. Next, we have the virtual-virtual block

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

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

$$\gamma_{ib}^{GW} = \frac{2}{\epsilon_i - \epsilon_b} \left[\sum_{a\mu} \frac{V_{ia}^\mu V_{ba}^\mu}{\epsilon_i - \epsilon_a - \Omega^\mu} - \sum_{j\mu} \frac{V_{ij}^\mu V_{bj}^\mu}{\epsilon_j - \epsilon_b - \Omega^\mu} \right], \quad (5.3)$$

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

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

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.

Chapter 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

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

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 $\omega = -12.18 \text{ eV}$. This is a useful check to see if the self-energy, which we defined in section 4.2, has been computed correctly. Also, at around $\omega = -40 \text{ eV}$, one can observe a pole structure.

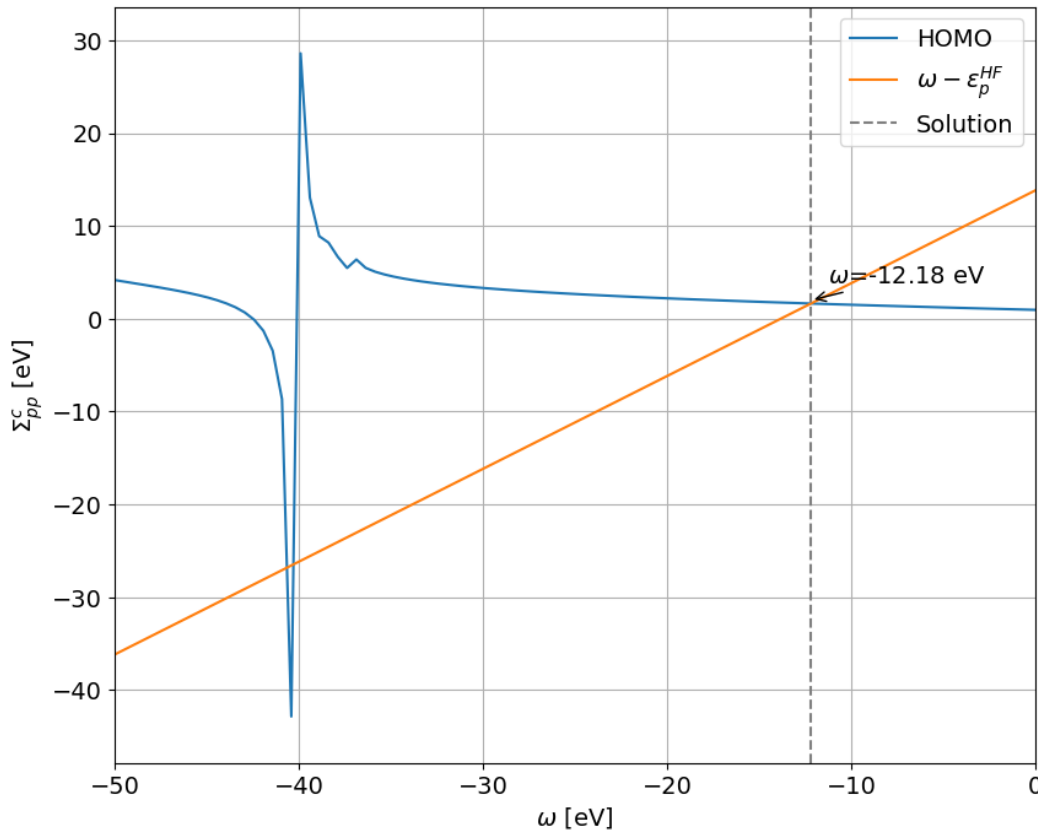


Figure 6.1: Graphical solution of the correlation self-energy for the HOMO of H_2O

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 .

Total energy functionals

One can also get energies of the system with the linearized G_0W_0 density matrix. First, let us two variance of a total and energy functional that can be obtained, called the Klein energy functionals. They are defined as

$$E_{\text{tot}}^1 = T_s[\gamma_0] + V_H[\gamma] + V_x[\gamma] + V_{\text{nuc, elec}}[\gamma] + V_{\text{nuc, nuc}} + E_{\text{corr}}^{\text{Klein}}[\gamma] \quad (6.2)$$

and

$$E_{\text{tot}}^2 = T_s[\gamma] + V_H[\gamma] + V_x[\gamma] + V_{\text{nuc, elec}}[\gamma] + V_{\text{nuc, nuc}} + E_{\text{corr}}^{\text{Klein}}[\gamma_0], \quad (6.3)$$

Where T_s is the kinetic energy, V_H is the Hartree potential, V_x is the exchange potential, $V_{\text{nuc, elec}}$ is the nuclear-electron potential, $V_{\text{nuc, nuc}}$ is the nuclear-nuclear potential, and $E_{\text{corr}}^{\text{Klein}}$ is the correlation energy. $E_{\text{corr}}^{\text{Klein}}$ is defined as

$$E_{\text{corr}}^{\text{Klein}} = \frac{1}{2}\text{Tr}(\Omega^{\text{RPA}} - A^{\text{TDA}}) = \frac{1}{2}\text{Tr}(\Omega^{\text{RPA}}) - \frac{1}{2}\text{Tr}(\Omega^{\text{TDA}}), \quad (6.4)$$

where we have used the invariance of the trace to unitary transformations and cyclic permutations to derive this. Each term in eqns. 6.2 or 6.3 is either evaluated at the noninteracting γ_0 or interacting γ electron density. Note that the only difference

between these two definitions is that the correlation of the interacting and noninteracting systems is 'housed' in the correlation and kinetic functional, respectively. As table 6.3 shows, recognition of this fact shows that Meal, the correlation energy functional defined by Galitskii and Migdal is given by the convolution of the correlations energy with the greens function, as

$$E_{\text{corr}}^{\text{GM}} = -\frac{i}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \int d\mathbf{x}_1 d\mathbf{x}_3 e^{i\omega\eta\Sigma_c}(\mathbf{x}_1\mathbf{x}_3; \omega) G(\mathbf{x}_3\mathbf{x}_1; \omega). \quad (6.5)$$

This can be simplified to

$$E_{\text{corr}}^{\text{GM}} = -2 \sum_{\mu}^{\text{RPA}} \sum_{ia} \frac{(V_{ia}^{\mu})^2}{\epsilon_a - \epsilon_i + \Omega_m} \quad (6.6)$$

As can be seen in table 6.2, my implementation of this correlation energy functional is in good agreement with those from MOLGW and FHI-AIMS.

| | MOLGW | FHI-AIMS | Mine from eqn. 6.6 | Deviation |
|-----------|--------------|-----------------|---------------------------|------------------|
| He | -0.759780 | -0.759737 | -0.759781 | -0.000043 |
| Ne | -0.120554 | -0.120551 | -0.120553 | -0.000002 |

Table 6.2: Galitskii-Migdal correlation energies as defined in 6.6; deviations are calculated with the difference between my implementation and the average of those from MOLGW and FHI-AIMS.

| | Total Energy Diff. | Correlation Energy Diff. | Correlation Contributions Discrepancy |
|-----------------------|---------------------------|---------------------------------|--|
| H₂O | -0.085109 | -0.085097 | 0.000012 |
| NH₃ | -0.074617 | -0.074652 | 0.000035 |
| LiH | -0.055925 | -0.055952 | 0.000027 |

Table 6.3: Differences in total energy, correlation energy, and discrepancy between the former supposed correlation contributions between the Klein functionals of equations 6.2 – 6.3.

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

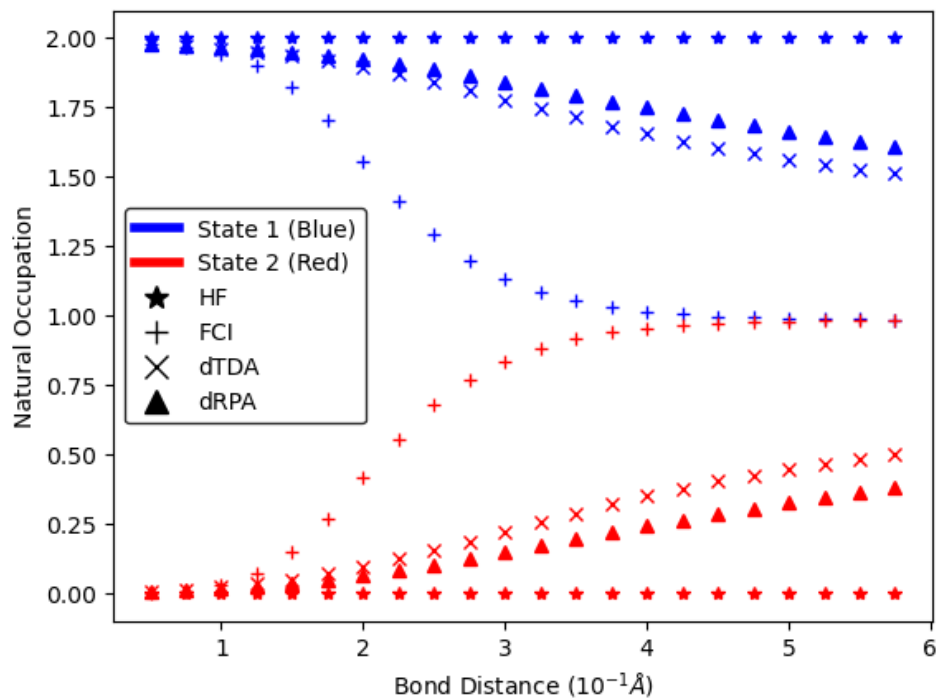


Figure 6.2: Natural occupations of the HOMO (State 1) and LUMO (State 2) of H_2 along the dissociation coordinate

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.

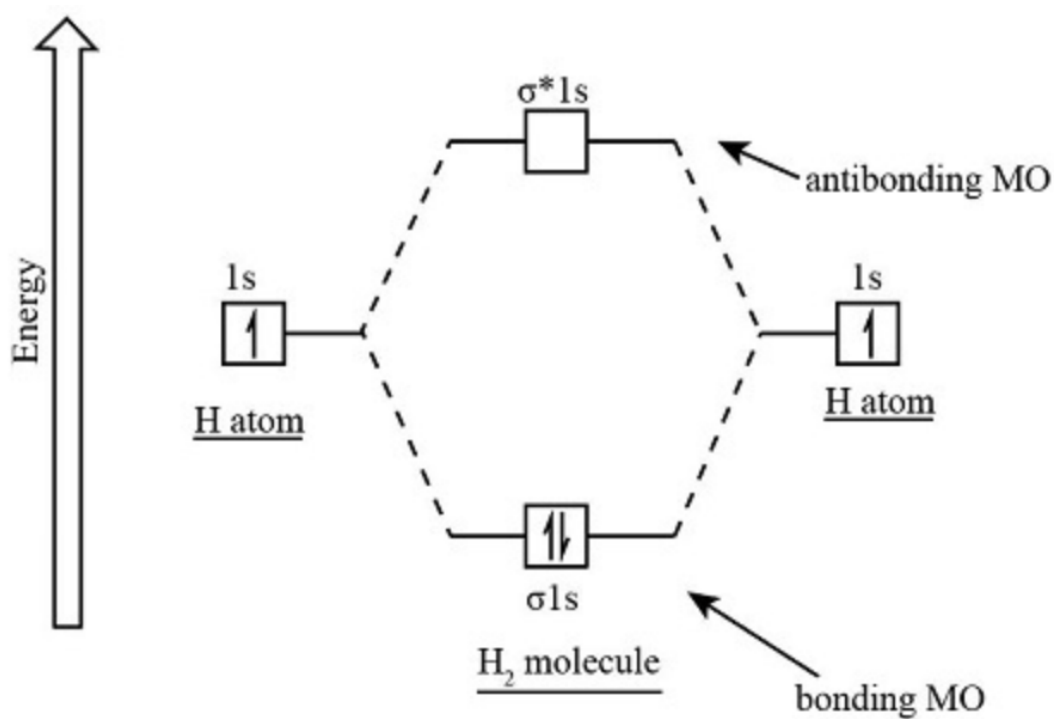


Figure 6.3: MO diagram of H_2 at the equilibrium bond distance. Notice that the HOMO is fully occupied with 2 electrons, while the LUMO is unoccupied. Diagram taken from the web¹⁶

BIBLIOGRAPHY

1. Sun, Q. *et al.* Recent developments in the PySCF program package. *The Journal of Chemical Physics* **153**, 024109. ISSN: 0021-9606. <https://doi.org/10.1063/5.0006074> (2024) (July 2020).
2. Schimka, L. *et al.* Accurate surface and adsorption energies from many-body perturbation theory. en. *Nature Materials* **9**. Publisher: Nature Publishing Group, 741–744. ISSN: 1476-4660. <https://www.nature.com/articles/nmat2806> (2024) (Sept. 2010).
3. Kozłowski, P. Elucidating Catalysis with the “Gold Standard” of Quantum Chemistry. en. *CURJ*. <https://curj.caltech.edu/2021/06/29/elucidating-catalysis-with-the-gold-standard-of-quantum-chemistry/> (2024) (June 2021).
4. McClain, J., Sun, Q., Chan, G. K.-L. & Berkelbach, T. C. Gaussian-Based Coupled-Cluster Theory for the Ground-State and Band Structure of Solids. *Journal of Chemical Theory and Computation* **13**. Publisher: American Chemical Society, 1209–1218. ISSN: 1549-9618. <https://doi.org/10.1021/acs.jctc.7b00049> (2024) (Mar. 2017).
5. *Frontiers | The GW Compendium: A Practical Guide to Theoretical Photoemission Spectroscopy* <https://www.frontiersin.org/articles/10.3389/fchem.2019.00377/full> (2024).
6. Szabo, A. & Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* en. Google-Books-ID: KQ3DAgAAQBAJ. ISBN: 978-0-486-13459-8 (Courier Corporation, June 2012).
7. Hohenberg, P. & Kohn, W. Inhomogeneous Electron Gas. *Physical Review* **136**, B864–B871 (Nov. 1964).
8. Milman, V. *Jacob’s Ladder of DFT* en. Section: science. Aug. 2021. <https://blog.3ds.com/brands/biovia/dft/> (2024).
9. Kohn, W. & Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **140**, A1133–A1138. <https://link.aps.org/doi/10.1103/PhysRev.140.A1133> (4A Nov. 1965).
10. Bruneval, F., Dattani, N. & van Setten, M. J. The GW Miracle in Many-Body Perturbation Theory for the Ionization Potential of Molecules. English. *Frontiers in Chemistry* **9**. Publisher: Frontiers. ISSN: 2296-2646. <https://www.frontiersin.org/articles/10.3389/fchem.2021.749779> (2024) (Dec. 2021).

11. Bruneval, F. Assessment of the Linearized GW Density Matrix for Molecules. *Journal of Chemical Theory and Computation* **15**. Publisher: American Chemical Society, 4069–4078. ISSN: 1549-9618. <https://doi.org/10.1021/acs.jctc.9b00333> (2024) (July 2019).
12. Mattuck, R. *A Guide to Feynman Diagrams in the Many-body Problem* ISBN: 978-0-486-67047-8. <https://books.google.com/books?id=pe-v8zfxE68C> (Dover Publications, 1992).
13. Hedin, L. New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem. *Physical Review* **139**, A796–A823. <https://journals.aps.org/pr/abstract/10.1103/PhysRev.139.A796> (1965).
14. Dreuw, A. & Head-Gordon, M. Single-Reference ab Initio Methods for the Calculation of Excited States of Large Molecules. *Chemical Reviews* **105**. Publisher: American Chemical Society, 4009–4037. ISSN: 0009-2665. <https://doi.org/10.1021/cr0505627> (2024) (Nov. 2005).
15. Furche, F. On the density matrix based approach to time-dependent density functional response theory. *The Journal of Chemical Physics* **114**, 5982–5992. ISSN: 0021-9606. <https://doi.org/10.1063/1.1353585> (2024) (Apr. 2001).
16. *In molecular orbital theory, the 1s orbital in the H2 molecule is?* en. <https://homework.study.com/explanation/in-molecular-orbital-theory-the-1s-orbital-in-the-h2-molecule-is.html> (2024).

Appendix 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:

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

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

$$\mathbf{A}\mathbf{X} + \mathbf{B}\mathbf{Y} = \Omega\mathbf{X} \quad (\text{A.2})$$

$$-\mathbf{B}\mathbf{X} - \mathbf{A}\mathbf{Y} = \Omega\mathbf{Y}, \quad (\text{A.3})$$

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

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

which can be rearranged to give

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

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

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

Similarly, we can isolate

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

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

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

and

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

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

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

Multiplication by Ω gives

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

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

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

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

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

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

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

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

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

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

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

And then for normalization, we need

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

So we need

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

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

Appendix 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

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

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

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

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

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

and likewise for the self-energy

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

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

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

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

$$I_1 = \sum_{pq} \sum_r \sum_t \phi_p^*(\mathbf{r}_1) G_{pr} \phi_r(\mathbf{r}) \phi_r^*(\mathbf{r}) \Sigma_{rt} \phi_t(\mathbf{r}') \phi_t^*(\mathbf{r}') G_{tq} \phi_q(\mathbf{r}_2) \quad (\text{B.6})$$

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

$$D_{pq\sigma} = \langle p\sigma | \gamma^\sigma | q\sigma \rangle \quad (\text{B.7})$$

to get

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

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

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

and

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

into equation B.8 to get

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

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

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

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 $R \rightarrow \infty$ and since $f(z) = e^{i\omega\eta} g(z)$, 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

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

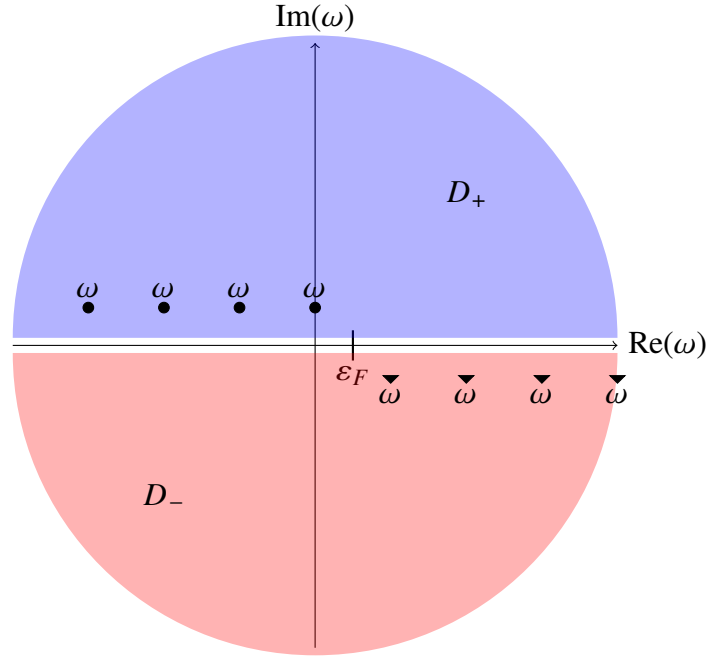


Figure B.1: Contour for the complex frequency integral. The poles are denoted by the various ω . The Fermi energy is denoted by ε_F . The integration contour D_+ is the semicircle in the upper complex plane, while D_- is the semicircle in the lower complex plane.

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

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

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

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

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

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

For the other poles, the procedure is similar with

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

and

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

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

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

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

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

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

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

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} | $\epsilon_{j\sigma} + i\eta$ | $\frac{1}{(\epsilon_{j\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{j\sigma} - \epsilon_{i\sigma})}$ |

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

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

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

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

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

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 $c \rightarrow a$.

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

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

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

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

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

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

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

and

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

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

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

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

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

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

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

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

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

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} | $\epsilon_{b\sigma} - i\eta$ | $\frac{1}{(\epsilon_{b\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{b\sigma} - \epsilon_{a\sigma})}$ |

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

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

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

So, the expression for D_{ab} is

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned}
I_{ib} = 2\pi i \Bigg(& \sum_{ks} w_{ik\sigma}^s w_{bk\sigma}^s \left(\frac{1}{(\epsilon_{k\sigma} - \epsilon_{i\sigma} - \Omega_s)(\epsilon_{k\sigma} - \epsilon_{b\sigma} - \Omega_s)} \right. \\
& + \left. \frac{1}{(\epsilon_{i\sigma} - \epsilon_{k\sigma} + \Omega_s)(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \right) \\
& + \sum_{cs} w_{ic\sigma}^s w_{bc\sigma}^s \left(\frac{1}{(\epsilon_{c\sigma} + \Omega_s - \epsilon_{i\sigma})(\epsilon_{c\sigma} + \Omega_s - \epsilon_{b\sigma})} \right. \\
& + \left. \left. \frac{1}{(\epsilon_{b\sigma} - \epsilon_{c\sigma} - \Omega_s)(\epsilon_{b\sigma} - \epsilon_{i\sigma})} \right) \right) . \quad (B.45)
\end{aligned}$$

By getting a common denominator and simplifying terms, we get

$$D_{ib} = \langle i\sigma | \gamma_0^\sigma | b\sigma \rangle + \frac{2\pi i^2}{2\pi (\epsilon_{i\sigma} - \epsilon_{b\sigma})} \left[\sum_{ks} \frac{w_{ik}^s w_{bk}^s}{\epsilon_{k\sigma} - \epsilon_{b\sigma} - \Omega_s} - \sum_{cs} \frac{w_{ic}^s w_{bc}^s}{\epsilon_{c\sigma} + \Omega_s - \epsilon_{i\sigma}} \right]. \quad (B.46)$$

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

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

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.