

# scGW

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Now that we have the  $G_0$  from Hartree-Fock, our goal will be to compute successive  $G_n$ 's, where  $n = 1, 2, 3, \dots$  until we reach the self-consistent solution. We want to solve the Dyson equation:

$$G_n(1, 2) = G_{n-1}(1, 2) + \int d(3, 4) G_{n-1}(1, 3) \Sigma_n(3, 4) G_n(4, 2). \quad (1)$$

## 1 Polarizability $P$

$$P_n(1, 2) = \int d(1, 2) G_{n-1}(1, 2) G_{n-1}(2, 1). \quad (2)$$

### 1.1 RPA

This must be done by performing an RPA calculation to determine the polarizability  $P$ . The Casida equation that I want to solve is

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}, \quad (3)$$

where we have the transition densities  $\mathbf{X}$  and  $\mathbf{Y}$  with the excitation energies  $\omega$ . We denote occupied and virtual orbital indices as  $i, j, \dots$  and  $a, b, \dots$ , respectively, while general ones are  $p, q, \dots$ . The matrix  $\mathbf{A}$  is defined as

$$A_{ia,jb} = \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i) + (ia||jb) \quad (4)$$

and  $\mathbf{B}$  is

$$B_{ia,jb} = (ia||bj). \quad (5)$$

The virtual and occupied orbital energies are denoted as  $\epsilon_a$  and  $\epsilon_i$ , respectively. Working in the direct interaction approximation, the two-electron integrals are defined as:

$$(ia|jb) = \int \int \phi_i^*(\mathbf{r}_1) \phi_a(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_j^*(\mathbf{r}_2) \phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (6)$$

$$= \frac{4\pi}{\Omega_{vol}} \frac{1}{|\mathbf{G}_b - \mathbf{G}_j|^2} \delta_{\mathbf{G}_a - \mathbf{G}_i, \mathbf{G}_j - \mathbf{G}_b}, \quad (7)$$

where  $\phi_p$  is an atomic orbital. Running a Davidson procedure on the Casida equation 3 will give us the selected low-lying excitation energies  $\omega_\mu$  and the corresponding transition densities  $\mathbf{X}_\mu$  and  $\mathbf{Y}_\mu$ , where  $\mu$  is the index of excitation, which has then been truncated because of Davidson.

## 2 Screened Coulomb interaction $W$

$$W_n(1, 2) = V_0(1, 2) + \int d(3, 4) V_0(1, 3) P_n(3, 4) W_n(4, 2). \quad (8)$$

$V_0$  is the bare Coulomb interaction, which is obtained from the two-electron integrals. We construct the coupled transition densities  $\mathbf{Z}_\mu$  as

$$Z_{ia}^\mu = X_{ia}^\mu - Y_{ia}^\mu \quad (9)$$

Next, we consider the contraction of the coupled transition densities with the two-electron integrals in order to form the actual excitation vectors  $\mathbf{V}^\mu$ :

$$V_{p,q}^\mu = \sum_{i,a} (pq|ia) Z_{ia}^\mu \quad (10)$$

Together with the excitation energies  $\Omega_\mu$ , this constitutes  $W$ .

## 3 Self-energy $\Sigma$

$$\Sigma_n(1, 2) = \int d(1, 2) G_{n-1}(1, 2) W_n(1, 2). \quad (11)$$

We can split the self-energy into a Hartree  $\Sigma_H$ , exchange  $\Sigma_X$ , and correlation  $\Sigma_C$  part:

$$\Sigma = \Sigma_H + \Sigma_X + \Sigma_C. \quad (12)$$

We already found  $\Sigma_H$  and  $\Sigma_X$  in the prior mean-field calculation, so now we are left to find  $\Sigma_C$ , which is defined as

$$\Sigma_{pp}^{\text{corr}}(\omega) = \sum_{\mu}^{\text{RPA}} \left( \sum_i^{\text{occupied}} \frac{V_{pi}^{\mu} V_{ip}^{\mu}}{\omega - (\epsilon_i - \Omega_{\mu})} + \sum_a^{\text{virtual}} \frac{V_{pa}^{\mu} V_{ap}^{\mu}}{\omega - (\epsilon_a + \Omega_{\mu})} \right). \quad (13)$$

Here,  $\omega$  is the input frequency. Note that the amount of excitations  $\mu$  is limited by the Davidson procedure.

## 4 Green's function $G$

$$G_n(1, 2) = G_{n-1}(1, 2) + \int d(3, 4) G_{n-1}(1, 3) \Sigma_n(3, 4) G_n(4, 2). \quad (14)$$

We solve for this using the equation:

$$\varepsilon_p^G = \delta_{pq} F_{pq}^{\text{HF}}[\gamma] + \Sigma_{pp}^{\text{C,n}}(\varepsilon_p^G) \quad (15)$$

where in the first iteration we use  $\gamma \equiv \gamma^{\text{HF}}$ . The  $\varepsilon_p^G$  are the Green's function eigenvalues being solved for in this iterative equation. In order to achieve self-consistency, I would imagine that we want to update  $\gamma$  from the initial density of  $G_0$  to that of  $G_{n-1}$  and also have the self-energy  $\Sigma_C^n$  to be the one from the previous iteration.