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 $n = 1, 2, 3, ...$ until we reach the self-consistent solution. We want to solve the Dyson equation:

$$G_n(1, 2) = G_{n-1}(1, 2) + \int d3 d4 G_{n-1}(1, 3) \Sigma_n(3, 4) G_n(4, 2), \qquad (1)$$

1 Polarizability P

$$P_n(1, 2) = -i G_{n-1}(1, 2) G_{n-1}(2, 1). \qquad (2)$$

1.1 RPA

We denote occupied and virtual orbital indices as $i, j, ...$ and $a, b, ...$, respectively, while general ones are $p, q, ...$ Noting that we will have separate spin channels, The matrix $\mathbf{A}$ has 4 blocks, e.g.,

$$\mathbf{A} = \begin{bmatrix} \mathbf{A}_{\alpha\alpha} & \mathbf{A}_{\alpha\beta} \\ \mathbf{A}_{\beta\alpha} & \mathbf{A}_{\beta\beta} \end{bmatrix}, \qquad (3)$$

where the matrix elements are defined as

$$A_{ia,jb}^{\sigma\sigma'} = \delta_{ij}\delta_{ab}\delta_{\sigma\sigma'}(\epsilon_a - \epsilon_i) + [i_\sigma a_\sigma || b_{\sigma'} j_{\sigma'}]. \qquad (4)$$

and $\mathbf{B}$ is

$$B_{ia,jb}^{\sigma\sigma'} = [i_\sigma a_\sigma || j_{\sigma'} b_{\sigma'}].. \qquad (5)$$

Taking the direct approximation, the two-electron integrals are given by

$$[i_\sigma a_\sigma | j_{\sigma'} b_{\sigma'}] = \int \int d\mathbf{x}_1 d\mathbf{x}_2 \phi_{i_\sigma}^*(\mathbf{x}_1) \phi_{a_\sigma}^*(\mathbf{x}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{j_{\sigma'}}(\mathbf{x}_2) \phi_{b_{\sigma'}}(\mathbf{x}_2)$$

(6)

Note that we can only have an excitation at a certain spatial index if the spin is the same. We can use the Cholesky decomposition to approximate these integrals. We can express the two-electron integrals in terms of the Cholesky vectors as

$$(pq|rs) = \sum_\zeta L_{pq}^\zeta L_{rs}^\zeta = \sum_{\mu\nu\lambda\sigma} \sum_\zeta C_{\mu p} C_{\nu q} C_{\lambda r} C_{\sigma s} L_{\mu\nu}^\zeta L_{\lambda\sigma}^\zeta.$$

(7)

The Casida equation is then

$$\left[\begin{pmatrix} \begin{pmatrix} A_{\alpha\alpha} & A_{\alpha\beta} \\ A_{\beta\alpha} & A_{\beta\beta} \end{pmatrix} & \begin{pmatrix} B_{\alpha\alpha} & B_{\alpha\beta} \\ B_{\beta\alpha} & B_{\beta\beta} \end{pmatrix} \\ \begin{pmatrix} -B_{\alpha\alpha} & -B_{\alpha\beta} \\ -B_{\beta\alpha} & -B_{\beta\beta} \end{pmatrix} & \begin{pmatrix} -A_{\alpha\alpha} & -A_{\alpha\beta} \\ -A_{\beta\alpha} & -A_{\beta\beta} \end{pmatrix} \end{pmatrix} \right] \left[\begin{pmatrix} X_{\alpha\alpha} & X_{\alpha\beta} \\ X_{\beta\alpha} & X_{\beta\beta} \\ Y_{\alpha\alpha} & Y_{\alpha\beta} \\ Y_{\beta\alpha} & Y_{\beta\beta} \end{pmatrix} \right] = \omega \left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -1 & 0 \\ 0 & -1 \end{pmatrix} \right] \left[\begin{pmatrix} X_{\alpha\alpha} & X_{\alpha\beta} \\ X_{\beta\alpha} & X_{\beta\beta} \\ Y_{\alpha\alpha} & Y_{\alpha\beta} \\ Y_{\beta\alpha} & Y_{\beta\beta} \end{pmatrix} \right],$$

(8)

where we have the transition densities $\mathbf{X}$ and $\mathbf{Y}$ with the excitation energies ω.

2 Screened Coulomb interaction W

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

(9)

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

$$Z_{ia}^\mu = X_{ia}^\mu + Y_{ia}^\mu$$

(10)

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

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

(11)

Together with the excitation energies Ω_μ, this constitutes W.

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3 Self-energy Σ

$$\Sigma_n(1,2) = \int d(1,2)G_{n-1}(1,2)W_n(1,2). \tag{12}$$

We can split the self-energy into a Hartree Σ_H, exchange Σ_X, and correlation Σ_C part:

$$\Sigma = \Sigma_H + \Sigma_X + \Sigma_C. \tag{13}$$

We already found Σ_H and Σ_X in the prior mean-field calculation, so now we are left to find Σ_C, which is defined as

$$\Sigma_{pp}^{\text{corr}}(\omega) = \sum_{\mu}^{\text{RPA}} \left(\sum_i^{\text{occupied}} \frac{V_{pi}^{\mu} V_{ip}^{\mu}}{\omega - (\epsilon_i - \Omega_{\mu})} + \sum_a^{\text{virtual}} \frac{V_{pa}^{\mu} V_{ap}^{\mu}}{\omega - (\epsilon_a + \Omega_{\mu})} \right). \tag{14}$$

Here, ω is the input frequency. Note that the amount of excitations μ is limited by the Davidson procedure.

4 Green's function G

$$G_n(1,2) = G_{n-1}(1,2) + \int d(3,4)G_{n-1}(1,3)\Sigma_n(3,4)G_n(4,2). \tag{15}$$

We solve for this using the equation:

$$\varepsilon_p^{\text{G}} = \delta_{pq} F_{pq}^{\text{HF}}[\gamma] + \Sigma_{pp}^{\text{C,n}}(\varepsilon_p^{\text{G}}) \tag{16}$$

where in the first iteration we use $\gamma \equiv \gamma^{\text{HF}}$. The ε_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 γ from the initial density of G_0 to that of G_{n-1} and also have the self-energy Σ_C^n to be the one from the previous iteration.

5 Hubbard model

In order to determine these MO integrals for the Hubbard model, at first we only care about the repulsion between two electrons with opposite spin on the same site, with the proportional coefficient being U. The ERIs in the atomic basis are $(\mu\mu|\mu\mu)$, so if we want to transform this into the MO basis

with $(ia|jb)$, we need $(ia|jb) = U_\mu C_{\mu i} C_{\mu a} C_{\mu j} C_{\mu b}$, where U_μ is the on-site repulsion and $C_{\mu i}$ is the coefficient of the i-th MO in the μ-th atomic orbital. I was thinking about this with Aadi, and we realized that the Hartree-Fock term calculation might be the same as a Hartree one; the exchange matrix K would be the same as the Coulomb J, but I guess this would be true only in the restricted formalism. My correlation self-energy is off by an order of magnitude, so I suspect that I might not be generating my integrals correctly. For the ab initio system, we have something like this for the correlation self-energy:

$$\Sigma_{pq}^{c}\left(\varepsilon_{s}^{H}\right) = \sum_{jbkc}\sum_{I}\left(\sum_{i}\frac{(ip|jb)(iq|kc)}{\varepsilon_{s}^{H}-\Omega_{I}-\varepsilon_{i}^{H}-i\eta}\right.$$
$$\left.+\sum_{a}\frac{(ap|jb)(aq|kc)}{\varepsilon_{s}^{H}+\Omega_{I}-\varepsilon_{a}^{H}+i\eta}\right)M_{jbkc}^{I} \tag{17}$$

Our job is to specify this for the Hubbard model, where the integrals are $(ip|jb) = U_\mu C_{\mu i} C_{\mu p} C_{\mu j} C_{\mu b}$.

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I want to prove equivalence between

$$\sum_{jbkc}\sum_{a}\sum_{\mu}(ap|jb)(aq|kc)M_{jbkc}^{\mu}$$

and

$$\sum_{a}\sum_{\mu}V_{pa}^{\mu}V_{aq}^{\mu}$$

, where we know that

$$M_{jbkc}^{\mu} = X_{jb}^{\mu}X_{kc}^{\mu} + X_{jb}^{\mu}Y_{kc}^{\mu} + Y_{jb}^{\mu}X_{kc}^{\mu} + Y_{jb}^{\mu}Y_{kc}^{\mu}. \tag{18}$$

where X_{ia}^{μ} and Y_{ia}^{μ} are the transition densities from diagonalizing the Casida equation in the RPA. We started by deriving V_{pq}^{μ} in the unrestricted formalism. Recall that

$$V_{pq}^{\mu} = \sum_{i,a}(pq|ia)Z_{ia}^{\mu} \tag{19}$$

where $Z_{ia}^{\mu} = X_{ia}^{\mu} + Y_{ia}^{\mu}$. We can then expand

$$V_{pa}^{\mu}V_{aq}^{\mu} = \sum_{jbkc}(pa|jb)(aq|kc)Z_{jb}^{\mu}Z_{kc}^{\mu}. \tag{20}$$

4

7 Cholesky decomposition

We want to approximate the two-electron integrals in the Hubbard model with the Cholesky decomposition. In order to express something like $(ia|jb)$ in terms of the Cholesky decomposition, we need to first define

$$L_{\mu\nu}^p = \delta_{\mu\nu}\sqrt{U_\mu}, \tag{21}$$

Note that in the Hubbard model, we have $dim(p) = 1$. Then we can form

$$L_{ia}^p = \sum_{\mu\nu} C_{\mu i} C_{\nu a} L_{\mu\nu}^p. \tag{22}$$

And then in order to build the A matrix of the Casida equation, we can write

$$A_{ia,jb} = \sum_p L_{ia}^p L_{jb}^p = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|jb). \tag{23}$$

8 Use of the Cholesky vectors

we want to solve a Casida equation of the form

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}, \tag{24}$$

where we have the transition densities $\mathbf{X}$ and $\mathbf{Y}$ with the excitation energies ω. The definition of elements of the matrix $\mathbf{A}$ is given by

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|bj) \tag{25}$$

and $\mathbf{B}$ is

$$B_{ia,jb} = (ia|jb). \tag{26}$$

We can express the two-electron integrals in terms of the Cholesky vectors as

$$(pq|rs) = \sum_\zeta L_{pq}^\zeta L_{rs}^\zeta = \sum_{\mu\nu\lambda\sigma} \sum_\zeta C_{\mu p} C_{\nu q} C_{\lambda r} C_{\sigma s} L_{\mu\nu}^\zeta L_{\lambda\sigma}^\zeta. \tag{27}$$

so that we can write

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \sum_p L_{ia}^p L_{bj}^p. \tag{28}$$

and

$$B_{ia,jb} = \sum_p L_{ia}^p L_{jb}^p.$$ (29)

and then when we evaluate the self energies we also need them for the V_{pq}^μ:

$$\Sigma_{pq}^C(\omega) = \sum_\mu \left(\sum_i \frac{V_{pi}^\mu V_{iq}^\mu}{\omega - (\epsilon_i - \Omega_\mu)} + \sum_a \frac{V_{pa}^\mu V_{aq}^\mu}{\omega - (\epsilon_a + \Omega_\mu)} \right).$$ (30)

where V_{pq}^μ is constructed conventionally as

$$V_{pq}^\mu = \sum_{ia} (pq|ia) Z_{ia}^\mu \implies = \sum_{ia} \sum_\zeta L_{pq}^\zeta L_{ia}^\zeta Z_{ia}^\mu.$$ (31)

and finding Z is just $Z_{ia}^\mu = X_{ia}^\mu + Y_{ia}^\mu$, where X_{ia}^μ and Y_{ia}^μ are the transition densities from diagonalizing the Casida equation in the RPA. For the exchange self-energy, we have

$$\Sigma_{pq}^x = -\sum_i (pi|iq) = -\sum_i \sum_\zeta L_{pi}^\zeta L_{iq}^\zeta.$$ (32)