

# G0W0

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## 1 Implementation

I want to discuss two equations today:

$$\Sigma_{pp}^{\text{correlation}}(\omega) = \sum_{\mu}^{\text{RPA}} \left( \sum_j^{\text{occupied}} \frac{V_{pj}^{\mu} V_{pj}^{\mu}}{\omega - (\varepsilon_j - \Omega_{\mu})} + \sum_b^{\text{virtual}} \frac{V_{pb}^{\mu} V_{bp}^{\mu}}{\omega - (\varepsilon_b + \Omega_{\mu})} \right) \quad (1)$$

and the iterative procedure:

$$\delta_{pq} F_{pq}^{\text{HF}}[\gamma^{\text{HF}}] + \Sigma_p^{\text{corr}}(\varepsilon_p^{\text{QP}}) = \varepsilon_p^{\text{QP}} \quad (2)$$

My current understanding is that for now we have initially

$$\varepsilon_p^{\text{QP}} = \varepsilon_p^{\text{HF}} \quad (3)$$

which is just the molecular orbital energies from my initial HF calculation. Also, something like

$$\delta_{pq} F_{pq}^{\text{HF}}[\gamma^{\text{HF}}] \quad (4)$$

is just a diagonal matrix with the molecular orbital energies from my HF calculation. I know that we are making a whole lot of approximations, so what do you recommend that I play with next?

## 2 Spin Integration

We previously discussed that for the electron repulsion integrals in terms of spin orbitals

$$(ia|jb) \rightarrow (i_{\alpha}a_{\alpha}|j_{\beta}b_{\beta}), (i_{\beta}a_{\beta}|j_{\alpha}b_{\alpha}); (i_{\alpha}a_{\alpha}|j_{\alpha}b_{\alpha}), (i_{\beta}a_{\beta}|j_{\beta}b_{\beta}) \quad (5)$$

We label them as 1, 2, 3, and 4 respectively. So we have a singlet and triplet CSF respectively

$$|\Psi_S\rangle = \frac{1}{\sqrt{2}} (|1\rangle + |2\rangle) \quad (6)$$

and

$$|\Psi_T\rangle = \frac{1}{\sqrt{2}} (|3\rangle - |4\rangle) \quad (7)$$

In these CSFs, the total spin is conserved. How can I start to think about getting different factors from here e.g. 2 for

$$A_{iajb} = \delta_{ij}\delta_{ab} (\varepsilon_a - \varepsilon_i) + (\underline{ia}|\underline{jb}) \quad (8)$$

to

$$A_{iajb} = \delta_{ij}\delta_{ab} (\varepsilon_a - \varepsilon_i) + 2(ia|jb) \quad (9)$$

and  $\sqrt{2}$  for

$$W_{p,q,i,a} = \sum_{\underline{p,q,i,a}} (\underline{pq}|\underline{ia}) \quad (10)$$

to

$$W_{p,q,i,a} = \sqrt{2} \sum_{p,q,i,a} (pq|ia) \quad (11)$$

I assume an understanding of this concept will also be helpful for making  $F_{pq}[\gamma^{DFT}]$ . Right now I am just using  $F_{pq}[\gamma^{HF}]$ , which is just a simple diagonal approximation.

### 3 Fock Matrix

My current understanding of the Fock operator in the diagonal approximation is

$$f_{pp}(\mathbf{r}) |\phi_p\rangle = H_{\text{core}}(\mathbf{r}) |\phi_p\rangle + 2 * J - K \quad (12)$$

I assume that all of the pieces here I can just get from  $\gamma_{DFT}$ . I recall you said earlier that I should also take spin into account i.e. just calling *mf.get\_fock()* wont work. Could you try to cover this again?

## 4 Filipp Furche

I have come to the idea that doing research with him this summer is going to be a good idea. I will get a exposure to a different quantum chemistry code and will meet new people. I took a brief look at what he does and I saw that he does a thought of applications, but I also saw that he does something with RPA theory. So far I have not been able to get far enough in the project to get exposure to the RPa, but it seems like something that I would want to dive deeper into diving the summer. Do you have any thoughts about what I would want to ask him to do?