G0W0

Patryk Kozlowski

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1 Implementation

I want to discuss two equations today:

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

and the iterative procedure:

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

My current understanding is that for now we have initially

$$\varepsilon_p^{\text{QP}} = \varepsilon_p^{\text{HF}} \tag{3}$$

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

$$\delta_{pq} F_{pq}^{\text{HF}}[\gamma^{\text{HF}}] \tag{4}$$

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

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

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

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

and

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

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

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

to

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

and $\sqrt{2}$ for

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

to

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

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

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

I assume that all of the pieces here I can just get from γ_{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?