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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.]

PUBLISHED CONTENT AND CONTRIBUTIONS

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- (1) Cahn, J. K. B.; Baumschlager, A.; Brinkmann-Chen, S.; Arnold, F. H. *Protein Engineering Design and Selection* **2016**, *19*, 31–38,
J.K.B.C participated in the conception of the project, solved and analyzed the crystal structures, prepared the data, and participated in the writing of the manuscript.
- (2) Cahn, J. K. B.; Brinkmann-Chen, S.; Spatzal, T.; Wiig, J. A.; Buller, A. R.; Einsle, O.; Hu, Y.; Ribbe, M. W.; H., A. F. *Biochemical Journal* **2015**, *468*, 475–484,
J.K.B.C participated in the conception of the project, solved and analyzed the crystal structures, prepared the data, and participated in the writing of the manuscript.

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Chapter 1

NOMENCLATURE

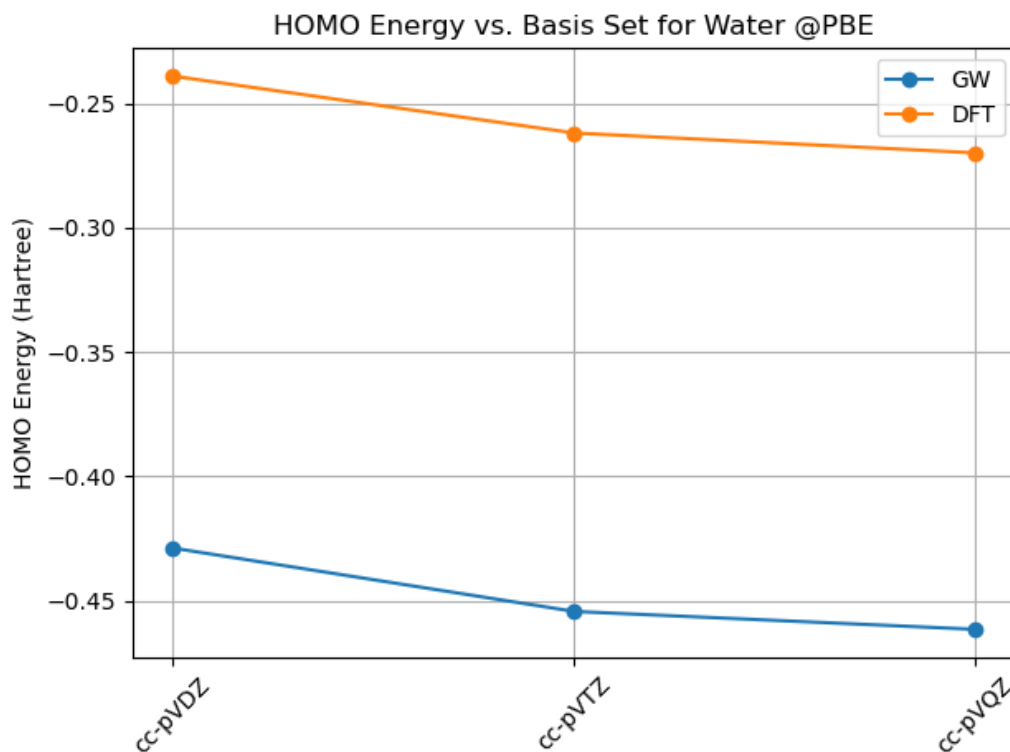
This all uses the Hartree-Fock formalism.

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
χ_p	Spin orbital basis
ψ_p	Spatial orbital basis
$(\underline{pq} \underline{rs}) = \int \int \chi_p^*(\mathbf{r}_1) \chi_q(\mathbf{r}_1) \frac{1}{r_{12}} \chi_r^*(\mathbf{r}_2) \chi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$	Two-electron integrals before spin integration
$(pq rs) = \int \int \psi_p^*(\mathbf{r}_1) \psi_q(\mathbf{r}_1) \frac{1}{r_{12}} \psi_r^*(\mathbf{r}_2) \psi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$	Two-electron integrals after spin integration
$(pq rs) = (pq rs) - (pq sr)$	Antisymmetrized two-electron integrals

Chapter 2

MOTIVATION

G_0W_0 , within the formalism of many-body perturbation theory, can provide corrections to a mean-field description such as that given by Hartree-Fock or density functional theory (DFT). Because the latter two methods treat the correlation between electrons in an average way, they can give rise to a self-interaction error; in practice, this can mean a variety of things, including the underestimation of surface stability (overestimation of surface energies) found in my previous work.¹ I have also included a plot that shows the difference in the HOMO energy with different basis choices for GW and regular DFT with a PBE starting point. As can be seen, G_0W_0 captures more of the electronic correlation, thus lowering the orbital energy.



Chapter 3

G_0W_0 PROCEDURE

3.1 Iterative equation

The procedure that was used to compute the quasiparticle energies is given by the below equation:

$$\delta_{pq} F_{pq}^{HF} [\gamma^{DFT}] + \Sigma_{pp}^{corr}(\epsilon_p^{QP}) = \epsilon_p^{QP} \quad (3.1)$$

We explain the notation starting from left to right. The first term corresponds to taking the diagonal δ_{pq} of the Hartree-Fock matrix F_{pq}^{HF} evaluated at a given electron density γ . These electron densities are obtained from a previous mean-field calculation, either γ_{DFT} or γ_{HF} . The second term evaluates the real part of the correlation self-energy for the ϵ_p^{QP} determined in the previous iteration. The right side of the equality gives the updated quasiparticle energy.

The above equation is solved self-consistently. We start with an initial guess for the quasiparticle energies, which is given by the mean-field orbital energy. This is used to solve for the right-hand side quasiparticle energy of equation 2.1. In the next iteration, we use the previously obtained quasiparticle energy to formulate Σ^{corr} . This process is repeated until we reach a convergence threshold for the quasiparticle energy. We note the distinction between this and self-consistent GW (scGW); in G_0W_0 , the iterative procedure only considers one quasiparticle energy at a time (with self-energy Σ_{pp}^{corr}), whereas scGW does not make this kind of diagonal approximation for the self-energy.

The Fock Matrix

In the basis of atomic orbitals, this is given by:

$$F_{\mu\nu}^{HF} = h_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\nu|\lambda\sigma) - \frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\lambda|\nu\sigma) \quad (3.2)$$

where $h_{\mu\nu}$ is the one-electron part of the Hamiltonian, $P_{\lambda\sigma}$ is the density matrix, and $(\mu\nu|\lambda\sigma)$ is one of the two-electron integrals.⁵ This is the simple form of the Hartree-Fock matrix that we want to use here and not the DFT Fock matrix. We transform this Fock matrix into the MO basis with:

$$F_{pq} = \sum_{\mu} \sum_{\nu} C_{\mu p}^* F_{\mu\nu} C_{\nu q} \quad (3.3)$$

where C is the matrix of MO coefficients. Another useful identity is for the density matrix in terms of the MO coefficients from the mean-field calculation:

$$P_{\mu\nu} = 2 \sum_{i=1}^{N/2} C_{\mu i} C_{\nu i}^* \quad (3.4)$$

We note that the sum runs only over the $N/2$ occupied *spatial* orbitals.

Real Correlation-Self Energy

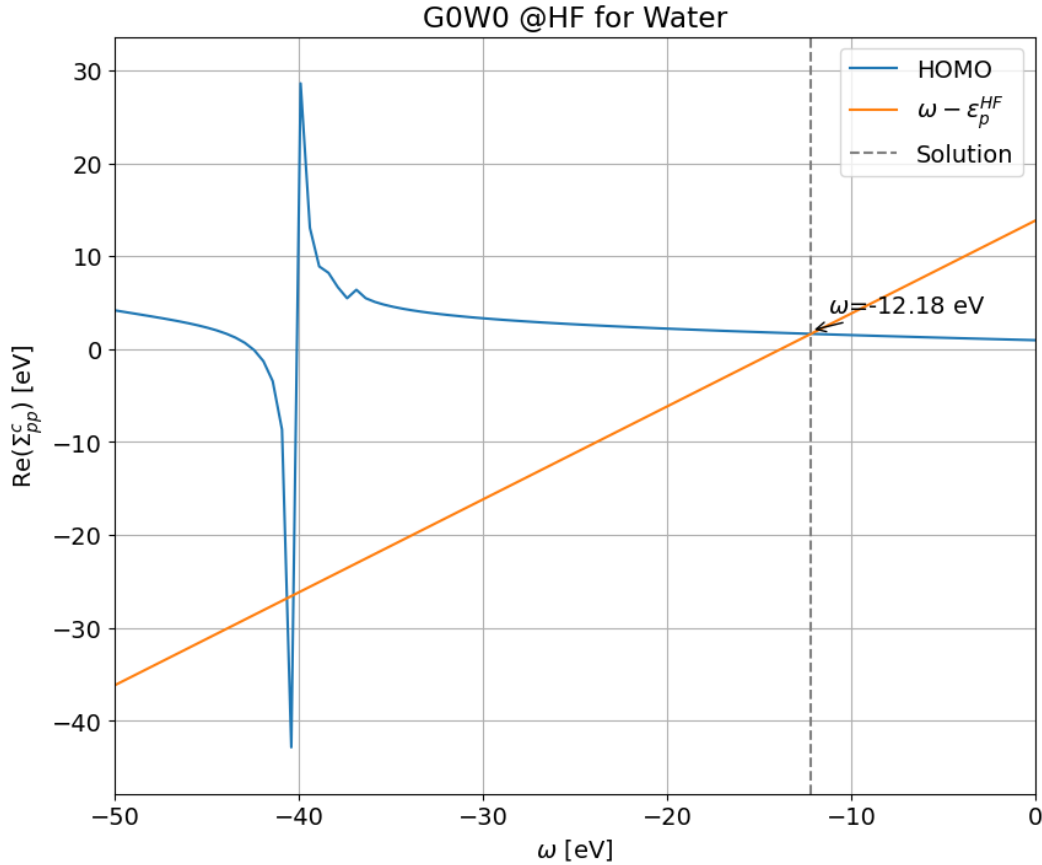
This is the second term in the iterative equation. It is dynamic, as opposed to the previous Fock term that was discussed, as it is updated with a new quasiparticle energy in each iteration. In the case of the G_0W_0 approximation, we are only interested in the diagonal element of Σ^{corr} corresponding to the orbital with index p . This function is evaluated at the QP energy ε_p^{QP} just obtained in the previous iteration. We will go into greater detail about the form of Σ^{corr} in the next chapter.

Quasiparticle Energy

This is the right side, or the solution, of this equation.

Graphical solution

I have been working with the HOMO of the water molecule with HF@PBE as my mean field object. I have plotted my self-energy computed for a wide range of frequencies. The line at $\omega - \varepsilon_p^{HF}$ should intersect with my self-energy at the same quasiparticle energy that I get from my iterative procedure, and indeed this is the case. Also, at around $\omega = -40$ eV, one can observe a pole structure. This is a derivate



discontinuity in my self-energy that would pose problems for my iterative procedure if the quasiparticle energy of the orbital that I was looking for was close to this value.

3.2 Real correlation Self-Energy

$$\Sigma_{pp}^{\text{corr}}(\omega) = \sum_{\mu}^{\text{TD-DFT}} \left(\sum_i^{\text{occupied}} \frac{V_{pi}^{\mu} V_{ip}^{\mu}}{\omega - (\varepsilon_i - \Omega_{\mu})} + \sum_a^{\text{virtual}} \frac{V_{pa}^{\mu} V_{ap}^{\mu}}{\omega - (\varepsilon_a + \Omega_{\mu})} \right) \quad (3.5)$$

I have implemented the diagonal of the real part of the correlation self-energy. The V^{μ} and Ω_{μ} are the excitation vectors and energies, respectively, from a previous

TD-DFT routine; the direct Tamm-Dancoff approximation (dTDA) and the direct Random Phase Approximation (dRPA) were used here. ω is my input frequency and the ε are the orbital energies from my previous mean-field calculation.

3.3 Time dependent DFT

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 by:³

$$\begin{bmatrix} A & B \\ -B & -A \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} \quad (3.6)$$

where A is

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (\underline{ia}||\underline{jb}) \quad (3.7)$$

and B is

$$\mathbf{B}_{ia,jb} = (\underline{ia}||\underline{jb}) \quad (3.8)$$

ω is a matrix with the excitation energy eigenvalues Ω_μ on the diagonal. After performing the spin integration in the restricted Hartree-Fock formalism:

$$(\underline{ia}||\underline{jb}) = \sum_{\alpha,\beta} (\underline{ia}||\underline{jb}) = 2(\underline{ia}||\underline{jb}) \quad (3.9)$$

we get for \mathbf{A} and \mathbf{B} :

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + 2(\underline{ia}||\underline{jb}) \quad (3.10)$$

$$\mathbf{B}_{ia,jb} = 2(\underline{ia}||\underline{jb}) \quad (3.11)$$

The excitation vectors \mathbf{V}^μ are taken by considering a contraction of two tensors. First, we consider the sum of \mathbf{X} and \mathbf{Y} at the same excitation energy μ : $\mathbf{Z}_{i,a,\mu} = \mathbf{X}_{i,a,\mu} + \mathbf{Y}_{i,a,\mu}$. Then we contract this with the two-electron integrals:

$$\mathbf{W}_{p,q,i,a} = \sum_{\underline{p,q,i,a}} (\underline{pq}||\underline{ia}) = \sqrt{2} \sum_{p,q,i,a} (pq||ia) \quad (3.12)$$

We defined a combined occupied-virtual index ν , so: $\mathbf{Z}_{i,a,\mu} \rightarrow \mathbf{Z}_{\nu,\mu}$ and $\mathbf{W}_{p,q,i,a} \rightarrow \mathbf{W}_{p,q,\nu}$.

I probably want to carry out the deviation for this factor of $\sqrt{2}$ which was something like the following. Have I set this up correctly?

Spin integration

$|\Phi_i^a\rangle$ has the CSF

$$|\Phi_{singlet}\rangle = \frac{1}{\sqrt{2}}(|\Phi_{i\alpha}^{a\alpha}\rangle + |\Phi_{i\beta}^{a\beta}\rangle) \quad (3.13)$$

We want to consider something like:

$$\langle\Phi_0|\frac{1}{4}\sum_{pqrs}V_{pqrs}a_p^\dagger a_q^\dagger a_s a_r \frac{1}{\sqrt{2}}(a_a^\dagger a_i^\alpha + a_a^\dagger a_i^\beta)|\Phi_0\rangle \quad (3.14)$$

Consolidating constants out front and distributing the CSF terms:

$$\frac{1}{4\sqrt{2}}V_{pqrs}\langle\Phi_0|a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i^\alpha|\Phi_0\rangle + \frac{1}{4\sqrt{2}}V_{pqrs}\langle\Phi_0|a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i^\beta|\Phi_0\rangle \quad (3.15)$$

And then we form the excitation vector from:

$$\mathbf{V}_{pq}^\mu = \sum_v \mathbf{W}_{p,q,v} \mathbf{Z}_{v,\mu} \quad (3.16)$$

Tamm-Dancoff Approximation

In this method, we neglect the \mathbf{B} matrix of the RPA equation. So the eigenvalue equation becomes

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X} \quad (3.17)$$

where we still have:

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + 2(ia||jb) \quad (3.18)$$

And then we follow the same procedure as in the RPA to get \mathbf{V}_{pq}^μ , where now we have $\mathbf{Z}_{v,\mu} = \mathbf{X}_{v,\mu}$.

Direct approximation

Everywhere in this code, we were considering the direct approximation, which just means that all instances of anti-symmetrized two-electron integrals are replaced by their non-symmetrized counterparts (i.e. containing just the Coulomb part with $(ia||jb) \rightarrow (ia|jb)$).

Chapter 4

LINEARIZED G_0W_0 DENSITY MATRIX

Implementation

I was able to implement these working equations.⁴ First, we consider the fully occupied block for a certain spin:

$$D_{ij\sigma}^{GW} = \delta_{ij} - \sum_{\omega s} \frac{w_{ia\sigma}^s w_{j\omega\sigma}^s}{(\epsilon_{i\sigma} - \epsilon_{a\sigma} - \Omega_s)(\epsilon_{j\sigma} - \epsilon_{a\sigma} - \Omega_s)} \quad (4.1)$$

where the Ω_s are the excitation energies and the w_{ij}^s are the excitation vectors for a single spin σ . The sum runs over all virtual orbitals and all excitation energies. The ϵ are the orbital energies from the mean-field calculation. Next, we have the virtual-virtual block:

$$D_{ab\sigma}^{GW} = - \sum_{is} \frac{w_{ai\sigma}^s w_{bi\sigma}^s}{(\epsilon_{i\sigma} - \epsilon_{i\sigma\sigma} - \Omega_s)(\epsilon_{i\sigma} - \epsilon_{b\sigma} - \Omega_s)} \quad (4.2)$$

Finally, we have the mixed block:

$$D_{ib\sigma}^{GW} = \frac{1}{\epsilon_{i\sigma} - \epsilon_{b\sigma}} \left[\sum_{as} \frac{w_{ia\sigma}^s w_{ba\sigma}^s}{(\epsilon_{i\sigma} - \epsilon_{a\sigma} - \Omega_s)} - \sum_{js} \frac{w_{ij\sigma}^s w_{bj\sigma}^s}{(\epsilon_{j\sigma} - \epsilon_{b\sigma} - \Omega_s)} \right] \quad (4.3)$$

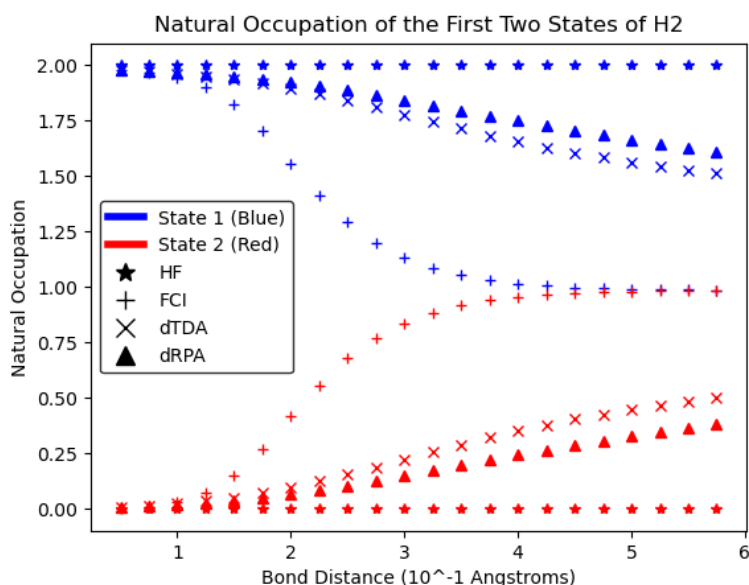
This all contributes to the form of the density matrix as:

$$2 \begin{pmatrix} D_{ij\sigma}^{GW} & D_{ib\sigma}^{GW} \\ D_{bi\sigma}^{GW} & D_{ab\sigma}^{GW} \end{pmatrix} \quad (4.4)$$

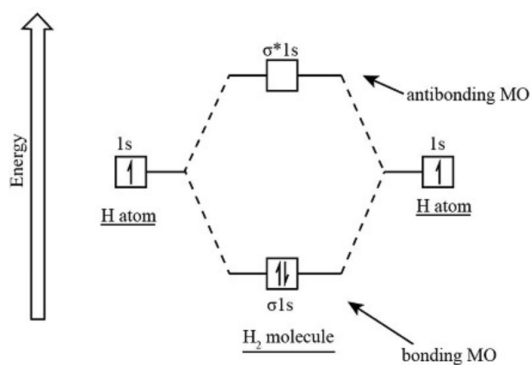
Where $D_{bi\sigma}^{GW}$ is simply the transpose of $D_{ib\sigma}^{GW}$, since all elements of this matrix are real. Therefore, this density matrix is Hermitian. The formulas given are only for a certain spin σ . So after we sum over both possible spins, we get the factor of 2.

Plotting natural occupations

The natural occupations can be found by the diagonalizing the density matrix. They can be interpreted as being the amount of electrons in a given orbital.⁵ Here we considered the one-electron density matrix from multiple methods; We started with Hartree-Fock, which contains no correlation, then we considered our implementation of the direct Random Phase Approximation (dRPA) and the direct Tamm-Dancoff Approximation (dTDA). Finally, we considered Full Configuration Interaction (FCI) as a reference, as it contains the exact correlation. It should be



noted that we considered natural occupations of the HOMO (State 1) and LUMO (State 2) of H₂, which has the simple MO diagram.



Chapter 5

THIS IS THE SIXTH CHAPTER

Chapter 6

THIS IS THE SEVENTH CHAPTER

Chapter 7

THIS IS THE EIGHTH CHAPTER

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Appendix A

QUESTIONNAIRE

*Appendix B***CONSENT FORM**

POCKET MATERIAL: MAP OF CASE STUDY SOLAR
SYSTEMS