

G_0W_0 for molecules

Patryk Kozlowski

Caltech

June 7, 2024

Motivation

Objective: solve time-independent Schrödinger equation for N electron system in the Born-Oppenheimer approximation

$$\hat{H}\Psi_0 = E_0\Psi_0 \quad (1)$$

Motivation

Objective: solve time-independent Schrödinger equation for N electron system in the Born-Oppenheimer approximation

$$\hat{H}\Psi_0 = E_0\Psi_0 \quad (1)$$

where

$$\hat{H} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 \right) - \sum_{i=1}^N \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{i<j}^N \frac{1}{r_{ij}} + C_{nn} \quad (2)$$

Common electronic structure tools

- ▶ Mean-field theories
 - ▶ **Hartree-Fock**: Assumes only average electron-electron interactions
 - ▶ **Density Functional Theory**: Lack of systematic improvability due to the approximate exchange-correlation functional

Common electronic structure tools

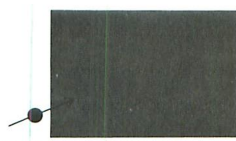
- ▶ Mean-field theories
 - ▶ **Hartree-Fock**: Assumes only average electron-electron interactions
 - ▶ **Density Functional Theory**: Lack of systematic improvability due to the approximate exchange-correlation functional
- ▶ Wavefunction-based methods
 - ▶ **Coupled cluster theories like CCSD(T)**: Highly accurate, but computationally intractable for large systems

Common electronic structure tools

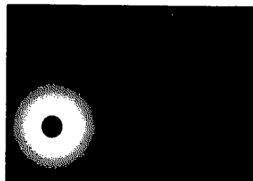
- ▶ Mean-field theories
 - ▶ **Hartree-Fock**: Assumes only average electron-electron interactions
 - ▶ **Density Functional Theory**: Lack of systematic improvability due to the approximate exchange-correlation functional
- ▶ Wavefunction-based methods
 - ▶ **Coupled cluster theories like CCSD(T)**: Highly accurate, but computationally intractable for large systems
- ▶ Green function methods
 - ▶ **GW approximation**: The gap-filling method; decent accuracy for cheap computational cost
 - ▶ variation of this ($G_0 W_0$) studied here

Self-Energy

Figure: Electron gas propagation¹



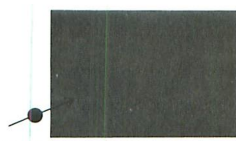
(a) The **bare** electron is shot into the gas



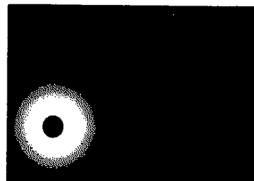
(b) The **quasi**-electron dynamically creates holes

Self-Energy

Figure: Electron gas propagation¹



(a) The **bare** electron is shot into the gas



(b) The **quasi**-electron dynamically creates holes

Qualitatively

$$\epsilon_{\text{self}} = \epsilon_{\text{quasi}} - \epsilon_{\text{bare}}, \quad (3)$$

The **self-energy** Σ can be thought of as the difference between the quasi and bare electron

$G_0 W_0$ iterative procedure³ for ϵ_p^{QP}

$$\epsilon_p^{\text{MF}} + \Sigma_p^{\text{corr}}(\epsilon_p^{\text{QP}}) = \epsilon_p^{\text{QP}} \quad (4)$$

1. start with the mean-field guess ϵ_p^{MF}
2. add self-energy, evaluated at ϵ_p^{QP} from the previous iteration
3. iterate until self-consistency in ϵ_p^{QP} is reached

G_0W_0 iterative procedure³ for ϵ_p^{QP}

$$\epsilon_p^{\text{MF}} + \Sigma_p^{\text{corr}}(\epsilon_p^{\text{QP}}) = \epsilon_p^{\text{QP}} \quad (4)$$

1. start with the mean-field guess ϵ_p^{MF}
2. add self-energy, evaluated at ϵ_p^{QP} from the previous iteration
3. iterate until self-consistency in ϵ_p^{QP} is reached

Table: Deviation in ϵ_p^{QP} (in eV) for G_0W_0 between my implementation and PySCF²

| Orbital | H_2O | NH_3 | LiH | CO |
|----------|----------|----------|----------|----------|
| HOMO - 2 | 5.33e-15 | 1.42e-14 | 3.55e-14 | 0.00477 |
| HOMO - 1 | 1.07e-13 | 2.33e-10 | 2.84e-14 | 0.00476 |
| HOMO | 2.84e-13 | 1.30e-12 | 1.96e-10 | 2.84e-13 |
| LUMO | 2.65e-14 | 8.78e-14 | 2.66e-15 | 0.00679 |
| LUMO + 1 | 2.71e-14 | 8.78e-14 | 2.43e-14 | 0.00678 |
| LUMO + 2 | 6.92e-10 | 4.97e-14 | 3.09e-14 | 3.99e-14 |

Linearized G_0W_0 density matrix⁵: Part 1

Natural occupations: number of electrons in a given orbital.⁴

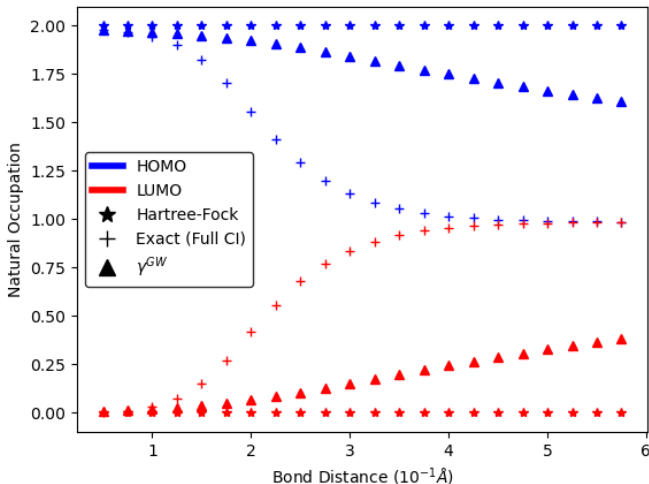


Figure: HOMO and LUMO of H_2 along the dissociation coordinate

Reference

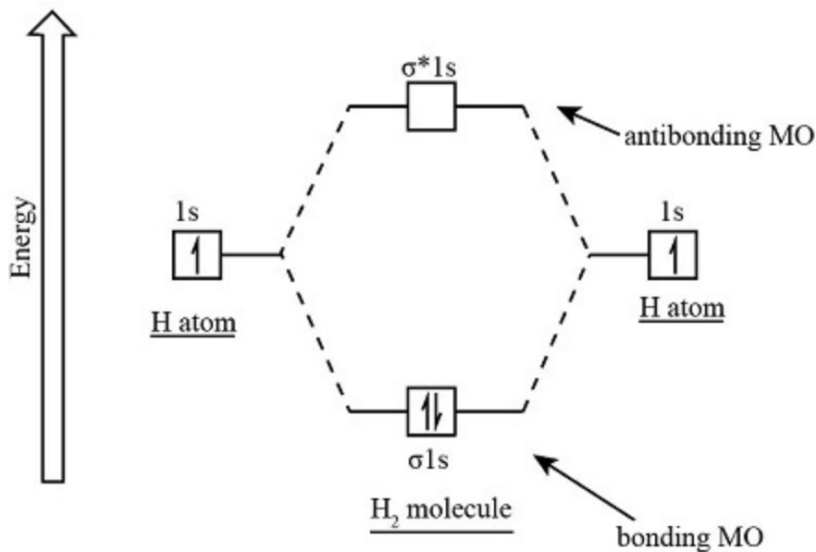


Figure: MO diagram of H₂ at the equilibrium bond distance⁶

Total energies from the linearized G_0W_0 density matrix

Galitskii-Migdal E^{corr} : convolution of the correlation self-energy Σ_c with the Green's function \mathcal{D}

$$E_{\text{corr}}^{\text{GM}} = -\frac{i}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \int d\mathbf{x}_1 \mathbf{x}_3 e^{i\omega\eta} \Sigma_c(\mathbf{x}_1 \mathbf{x}_3; \omega) \mathcal{D}(\mathbf{x}_3 \mathbf{x}_1; \omega) \quad (5)$$

Table: Deviation in total energies (in eV) from the CCSD(T) reference for Hartree-Fock and γ^{GW} of the linearized G_0W_0 density matrix (using E^{corr} from equation 5).

| Molecule | HF $\Delta\text{CCSD(T)}$ | γ^{GW} $\Delta\text{CCSD(T)}$ |
|------------------|---------------------------|---|
| H ₂ O | 5.93 | 0.696 |
| NH ₃ | 5.60 | 0.544 |
| LiH | 0.846 | 0.0361 |

Acknowledgements

I would like to thank the medical professionals who are the reason that I can be here, the guys at Cursorless who helped me learn to voice code, my adviser, Professor Garnet Chan, and mentor, Dr. Johannes Tolle, for guiding me in my research, and my family, and particularly my mom, for being the biggest supporters in my rehabilitation and academic journey.

Bibliography

1. Mattuck, R. *A Guide to Feynman Diagrams in the Many-body Problem*. ISBN: 978-0-486-67047-8.
<https://books.google.com/books?id=pe-v8zfxE68C>
(Dover Publications, 1992).
2. Sun, Q. *et al.* Recent developments in the PySCF program package. *The Journal of Chemical Physics* **153**, 024109. ISSN: 0021-9606. <https://doi.org/10.1063/5.0006074> (2024) (July 2020).
3. Bruneval, F. Assessment of the Linearized GW Density Matrix for Molecules. *Journal of Chemical Theory and Computation* **15**. Publisher: American Chemical Society, 4069–4078. ISSN: 1549-9618. <https://doi.org/10.1021/acs.jctc.9b00333> (2024) (July 2019).
4. Szabo, A. & Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. en. Google-Books-ID: KQ3DAgAAQBAJ. ISBN: 978-0-486-13459-8 (Courier Corporation, June 2012).