# $G_0W_0$ for molecules

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August 9, 2024

# Motivation

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

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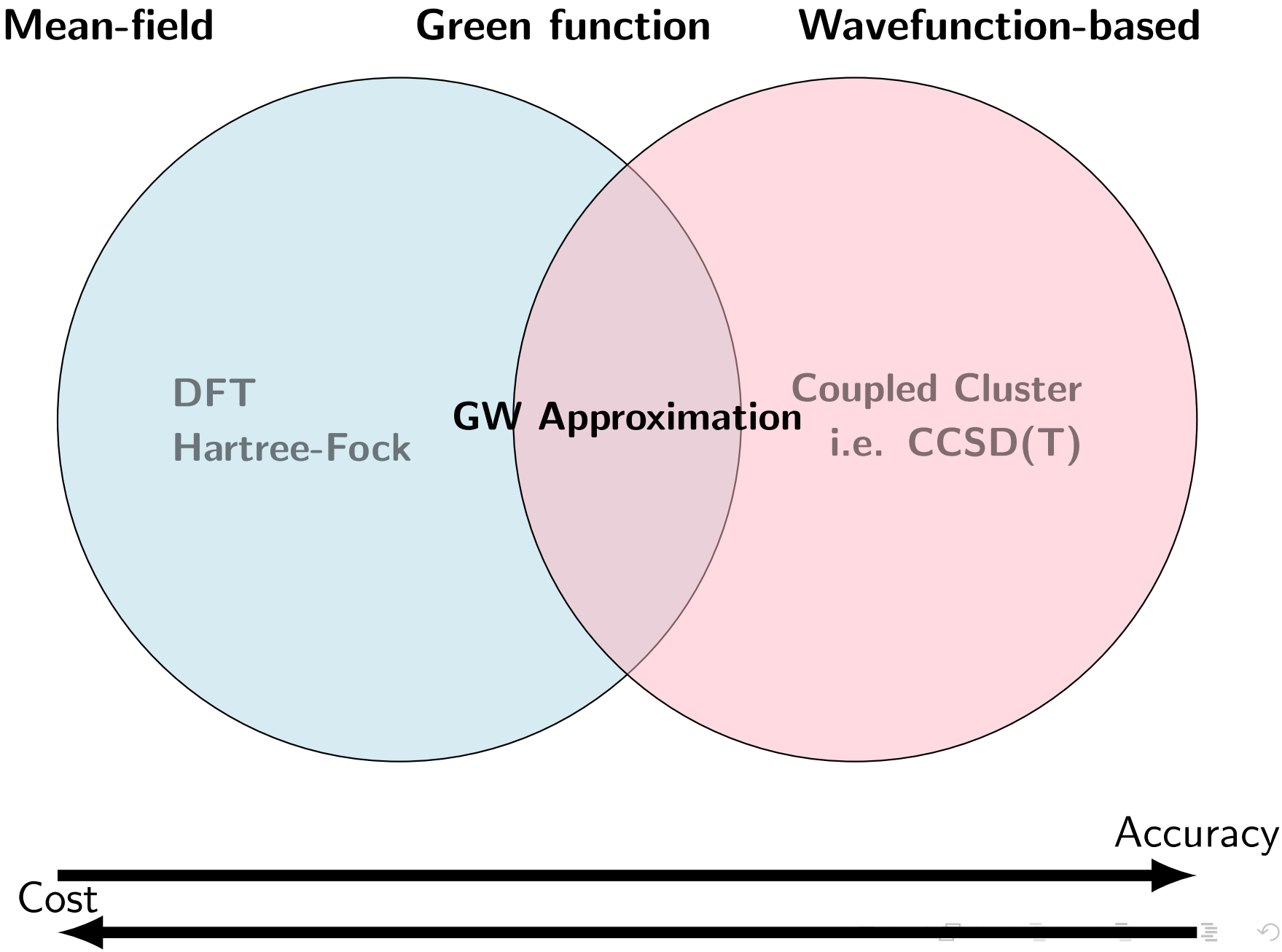
where

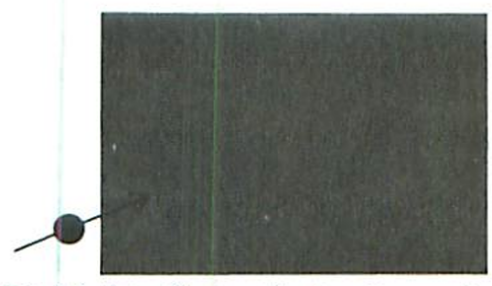
$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2\right) - \sum_{i=1}^{N}\sum_{\alpha}\frac{Z_\alpha}{r_{i\alpha}} + \sum_{i<j}^{N}\frac{1}{r_{ij}} + C_{nn} \tag{2}$$

# Common electronic structure tools

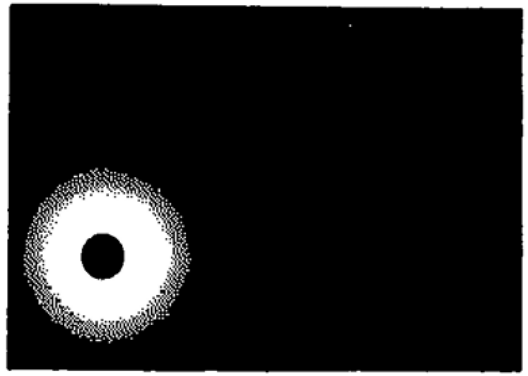


# Self-Energy

Figure: Electron gas propagation[1]



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



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

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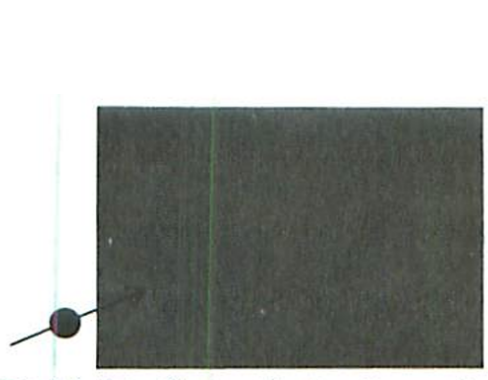

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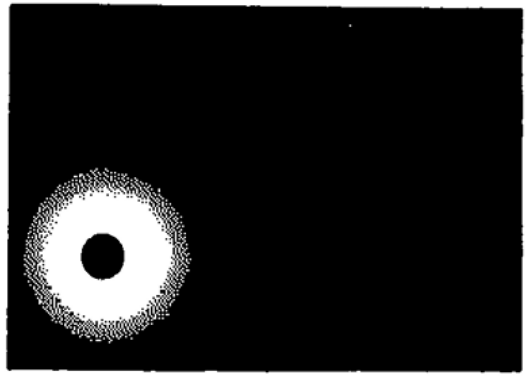

(b) The **quasi**-electron dynamically creates holes

Qualitatively

$$\epsilon_{\text{self}} = \epsilon_{\text{quasi}} - \epsilon_{\text{bare}}, \tag{3}$$

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

# $G_0W_0$ iterative procedure[3] for $\varepsilon_p^{\mathrm{QP}}$

$$\epsilon_p^{\mathrm{MF}} + \Sigma_p^{\mathrm{corr}}(\varepsilon_p^{\mathrm{QP}}) = \varepsilon_p^{\mathrm{QP}} \tag{4}$$

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

# Linearized $G_0W_0$ density matrix[3]:

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

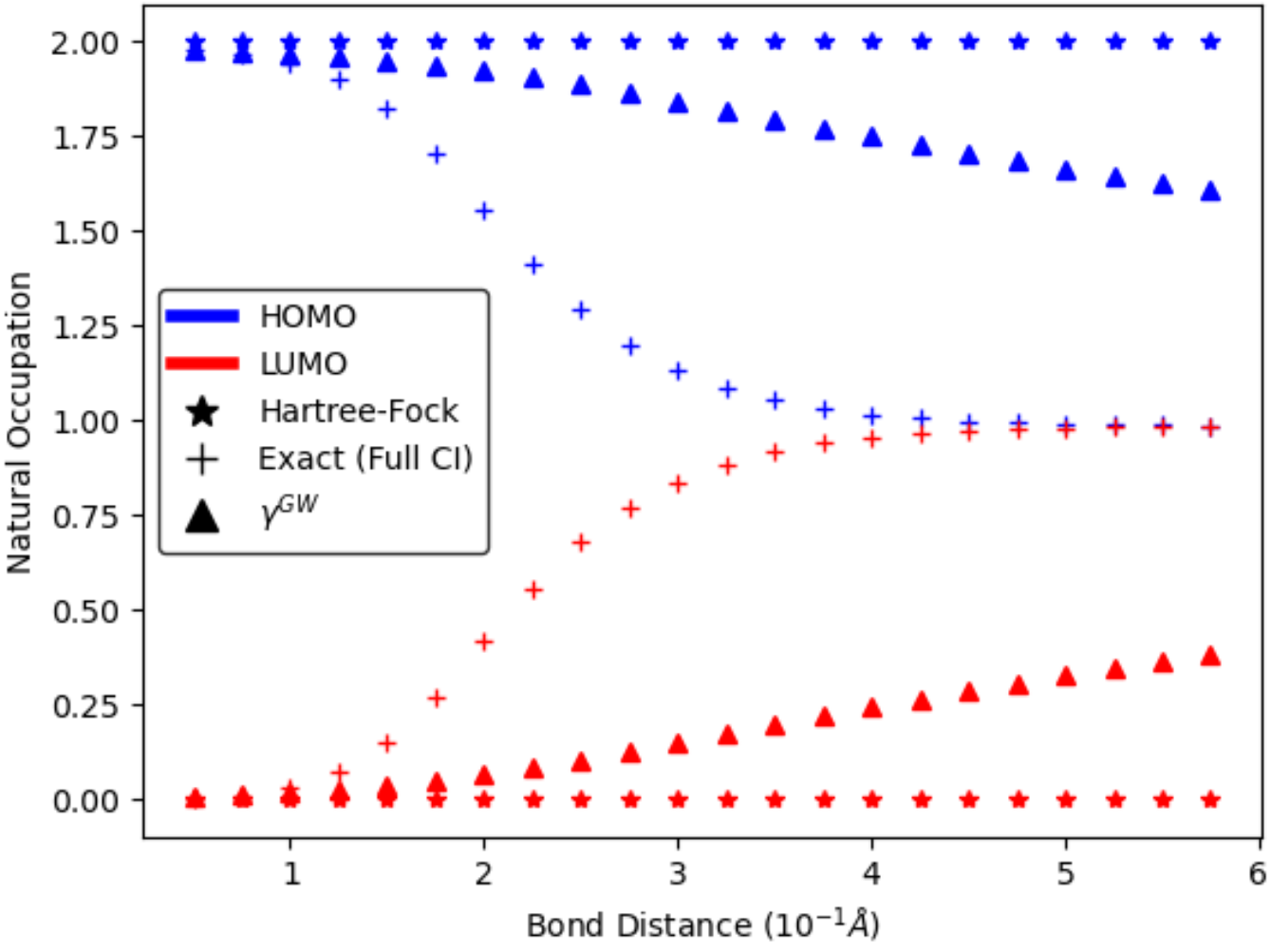


Figure: HOMO and LUMO of $H_2$ along the dissociation coordinate

# Bibliography


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