APPROXIMATING THE MANY BODY PROBLEM THROUGH REFINING COUPLED CLUSTER THEORY

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Thouless Theorem

$$|\Phi\rangle = e^{\widehat{T_1}}|\Phi_0\rangle$$

Greens and Spectral Functions

$$G(x, x_0) = G(rt, r_0 t_0) = -i\Theta(t - t_0)\langle 0|\{\psi(rt), \psi^\dagger(r_0 t_0)\}|0\rangle$$

$$A(\omega) = -\frac{1}{\pi} Im|G(\omega)|$$

Time-dependent approach to the calculation of spectral functions

K. Schönhammer and O. Gunnarsson, Phys Rev B 18, 6606 (1978)

- Time dependent generalization of coupled-cluster theory

- Goal: Calculate the spectral weight function of a many body Hamiltonian with respect to some given Slater determinant, $|\Phi_o\rangle$
- Two ways

  Frequency domain

$$\rho(\epsilon) = \langle \Phi_o | \delta(\epsilon - H) | \Phi_o \rangle = \sum |\langle \Phi_o | E_i \rangle|^2 \delta(\epsilon - E_i)$$

- Time domain

  - $$\rho(\epsilon) = \frac{1}{\pi} Im[i \int_0^\infty e^{i(\epsilon - i0)t} \langle \Phi_o | e^{-iHt} | \Phi_o \rangle$$

Methods for solving a many-body Schrodinger Equation

- Hedin GW Approximation (GWA)
- Configuration Interaction
- Cumulant Expansion
- Coupled-Cluster Theory

Why Coupled Cluster Theory?

What is Coupled Cluster Theory?

- Extension of Hartree Fock Ab Initio Method
- Exact solution to TISE $H|\Psi\rangle = E|\Psi\rangle$
  - *H* is the Hamiltonian
  - $|\Psi\rangle$ is the exact ground state wave function
  - *E* is the exact ground state energy
  - CC Ansatz: $|\Psi\rangle = e^{\hat{T}}|\Psi_0\rangle$

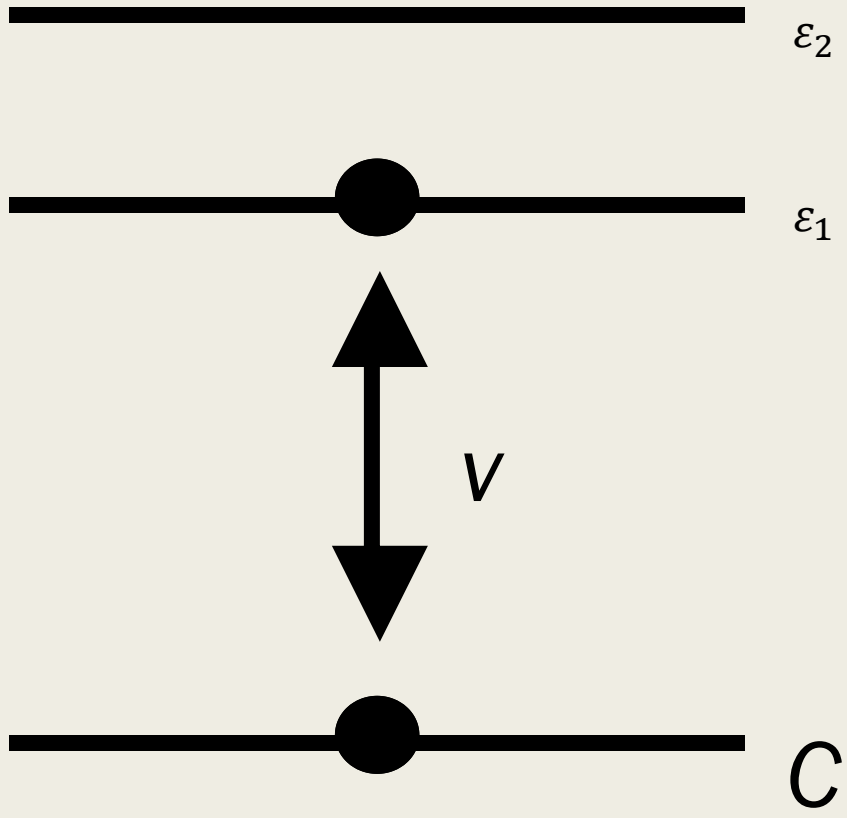
Hartee Fock

- Minimizes energy expectation value of orbitals
  - *Solving set of coupled 1-electron eigenvalue equations*

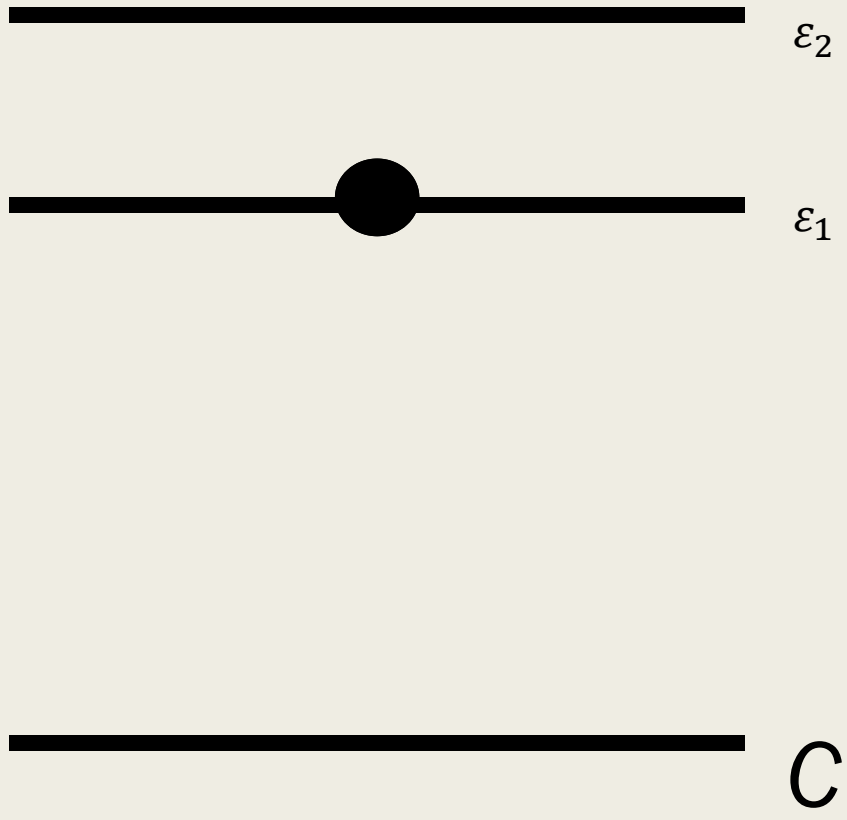
$$\hat{f}\psi_i = \varepsilon_i\psi_i$$

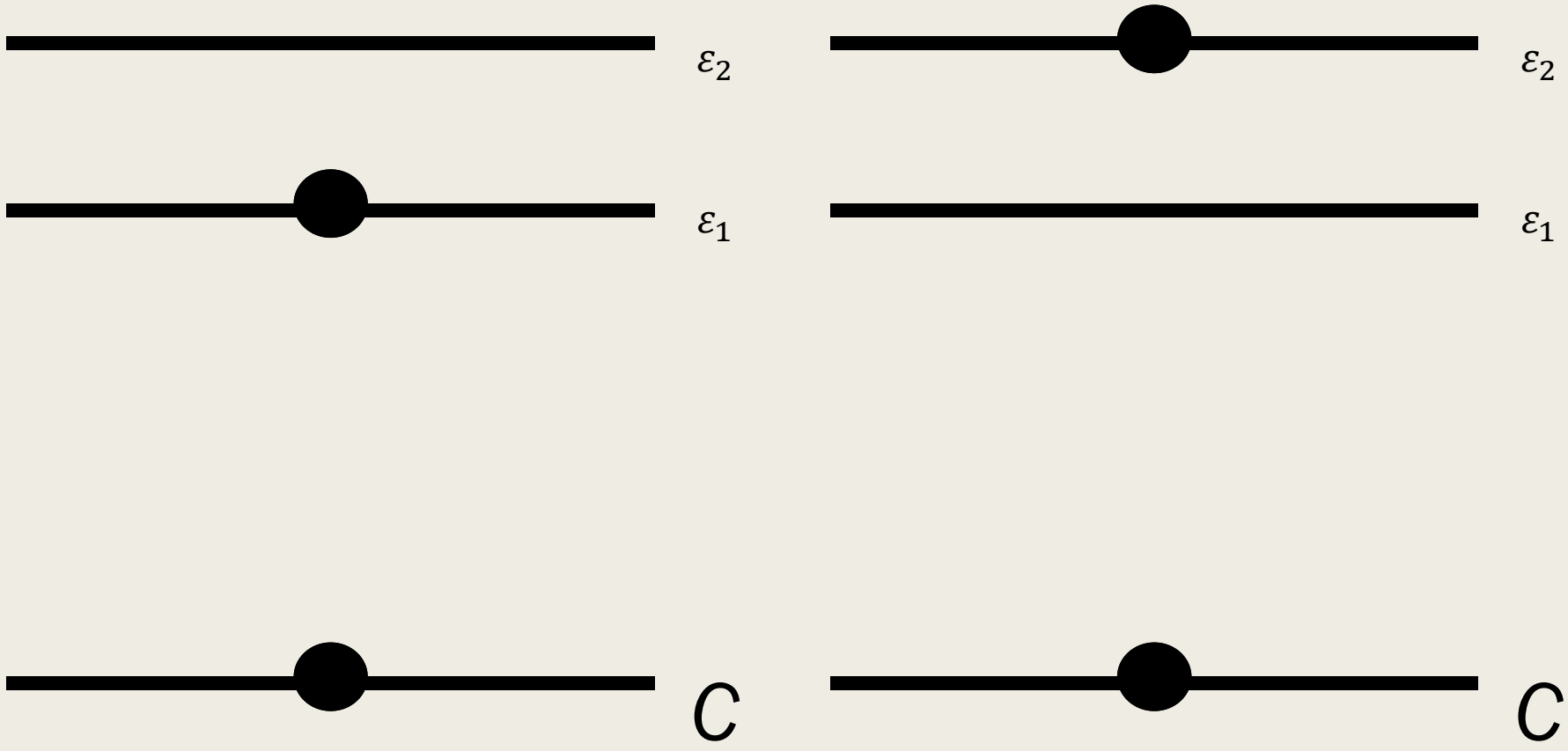
- Great Initial Approximation
  - *99% of total electronic energy*
  - *95% of the wave function*

3-State/ 2-Electron Model

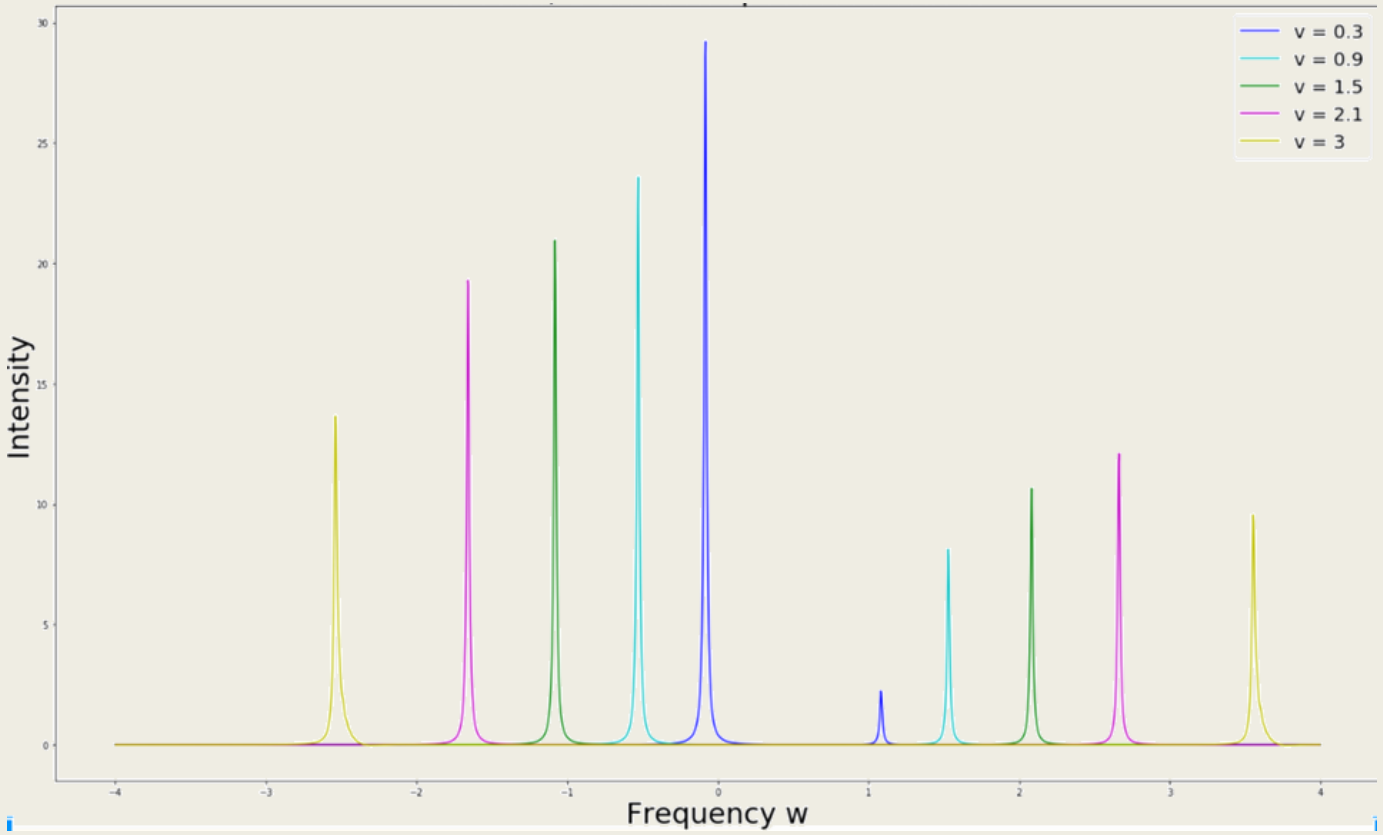


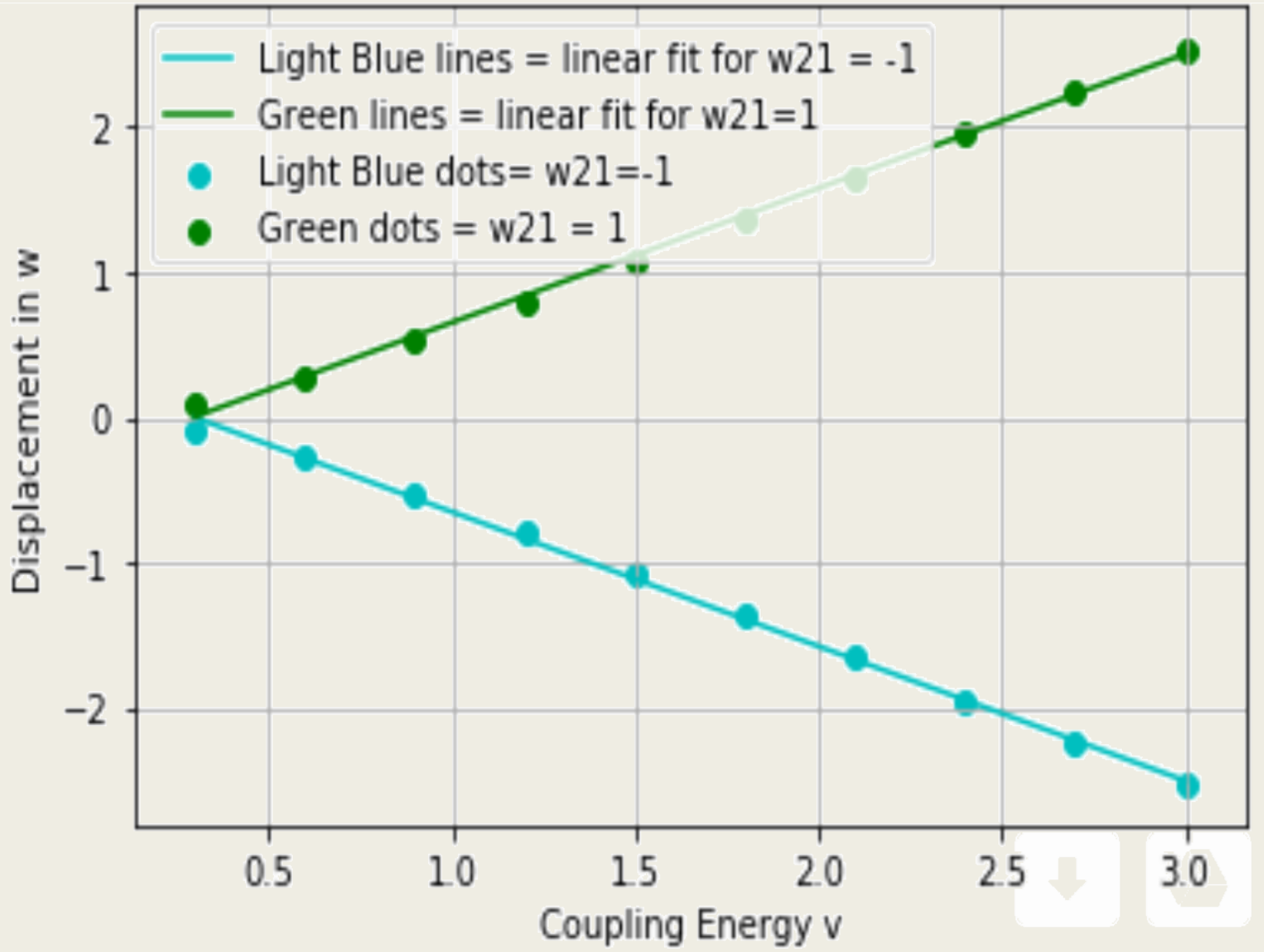
3-State/ 2-Electron Model



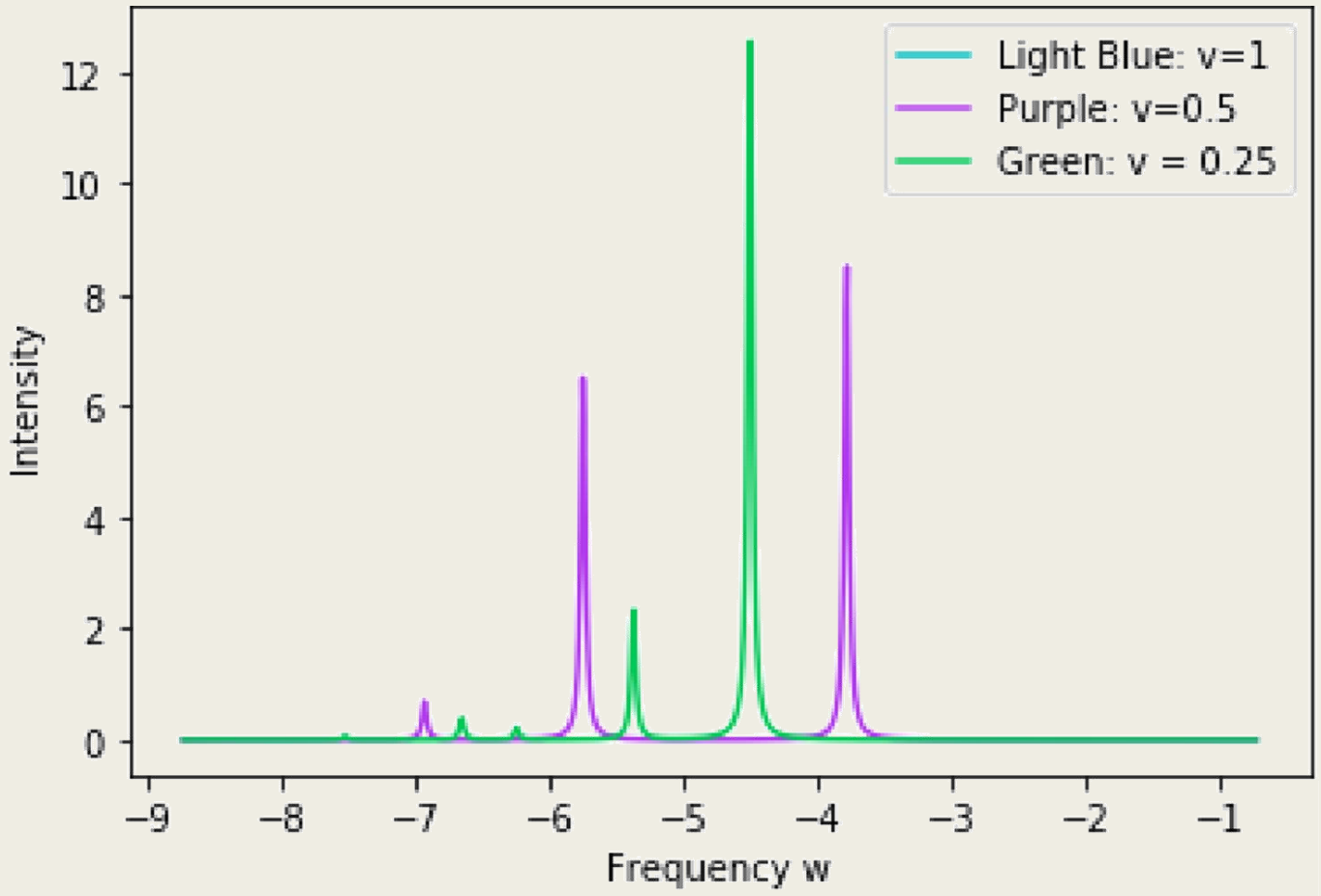

ε_2
ε_1
C
ε_2
ε_1
C

3-State/2-Electron Spectral Functions




Light Blue lines = linear fit for w21 = -1
Green lines = linear fit for w21=1
Light Blue dots= w21=-1
Green dots = w21 = 1
Displacement in w
Coupling Energy v
2
1
0
−1
−2
0.5
1.0
1.5
2.0
2.5
3.0

4-State/2-Electron



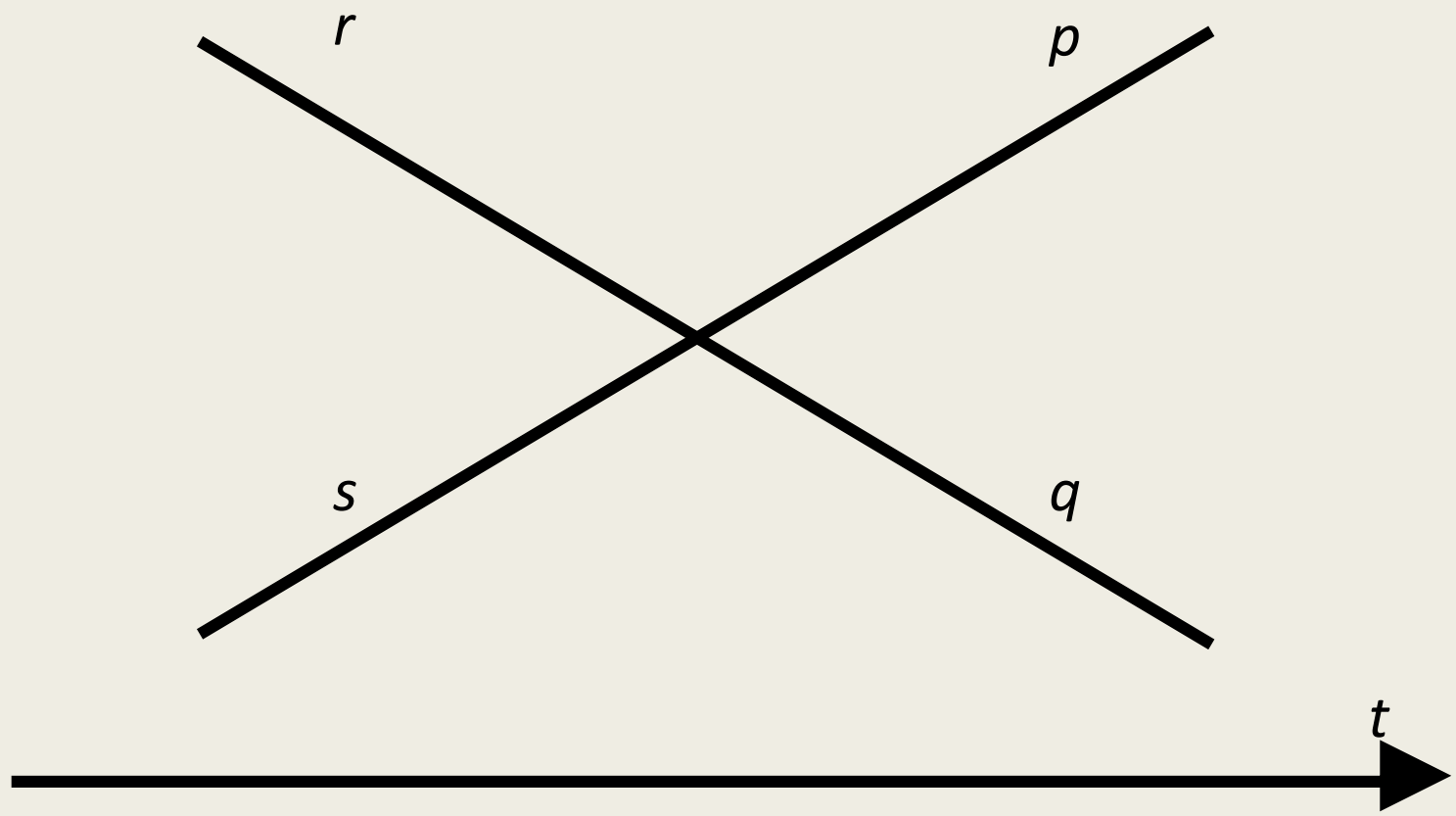
What is the Coupling Potential v_{pq}^{rs}?

- Describes the coulombic potential between different, interacting electrons.
- Approximate value comes from the Hartee Fock method

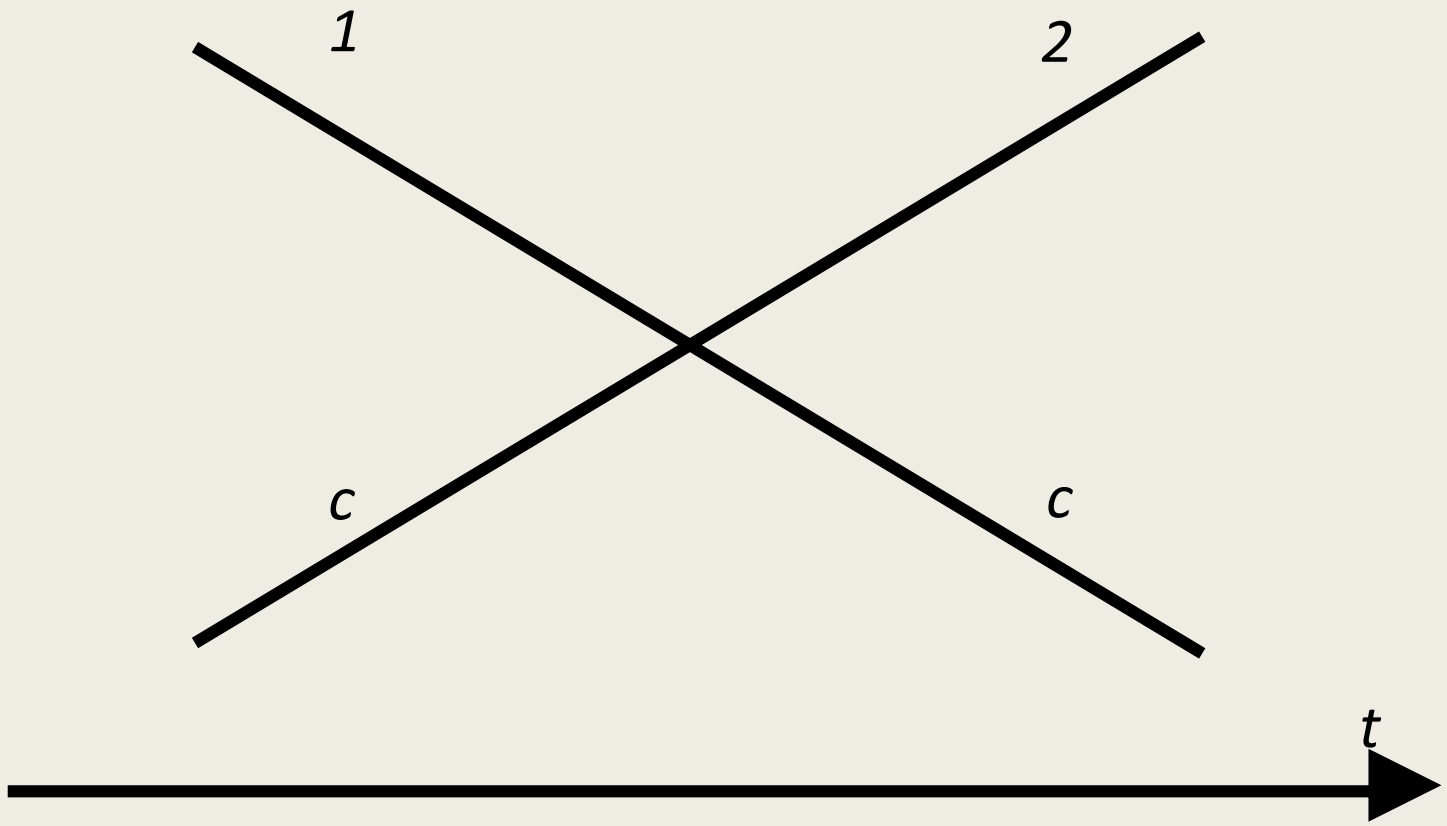
$$v_{pq}^{rs} = \langle pq||rs\rangle = \langle pq|rs\rangle - \langle pq|sr\rangle$$

$$\langle pq|rs\rangle = \iint_{-\infty}^{\infty} d\overrightarrow{r_1} d\overrightarrow{r_2} \frac{\varphi_p^*(\overrightarrow{r_1})\varphi_q^*(\overrightarrow{r_2})\varphi_r(\overrightarrow{r_1})\varphi_s(\overrightarrow{r_2})}{|\overrightarrow{r_2} - \overrightarrow{r_1}|}$$

Intuition behind v_{pq}^{rs}



Intuition behind v_{2c}^{1c}

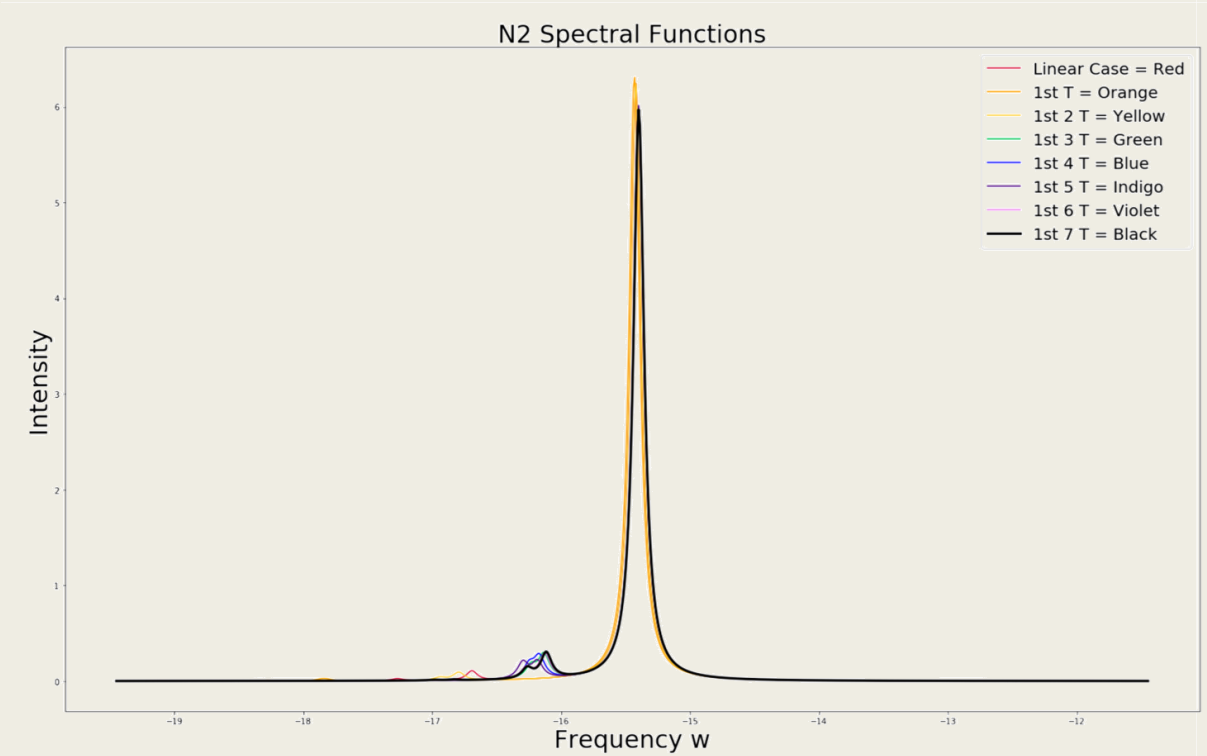


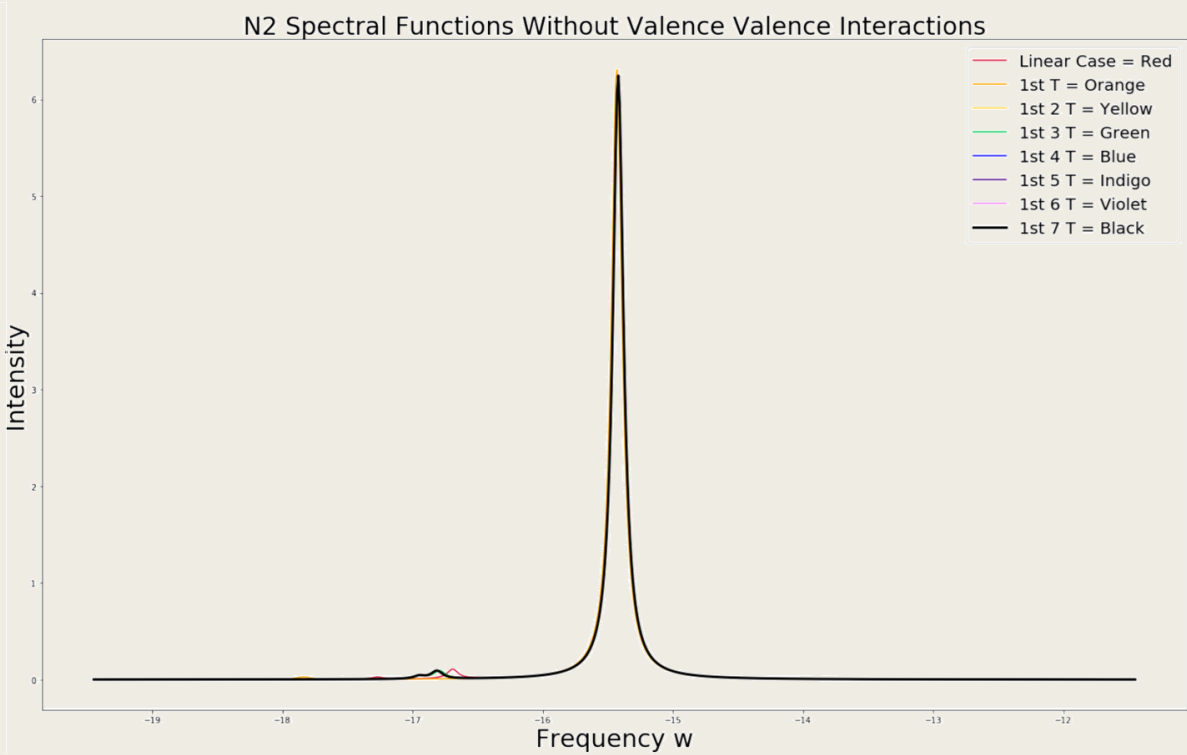
v_{pq}^{rs} Role in Coupled Cluster Method

$$H\left|\Phi^{N-1}\right> = \left(\hat{h}_{nuc} + \hat{V}\right)\left|\Phi^{N-1}\right>$$
$$= (\hat{h}_{nuc} + f^N - f^N)|\Phi^{N-1}>$$
$$= (h_{HF}^N - f^N + f^{N-1} + \hat{V})|\Phi^{N-1}>$$

$$\hat{V} = \sum_{pqrs} v_{ps}^{rs} a_p^* a_q^* a_r a_s$$

Realistic Model of N_2





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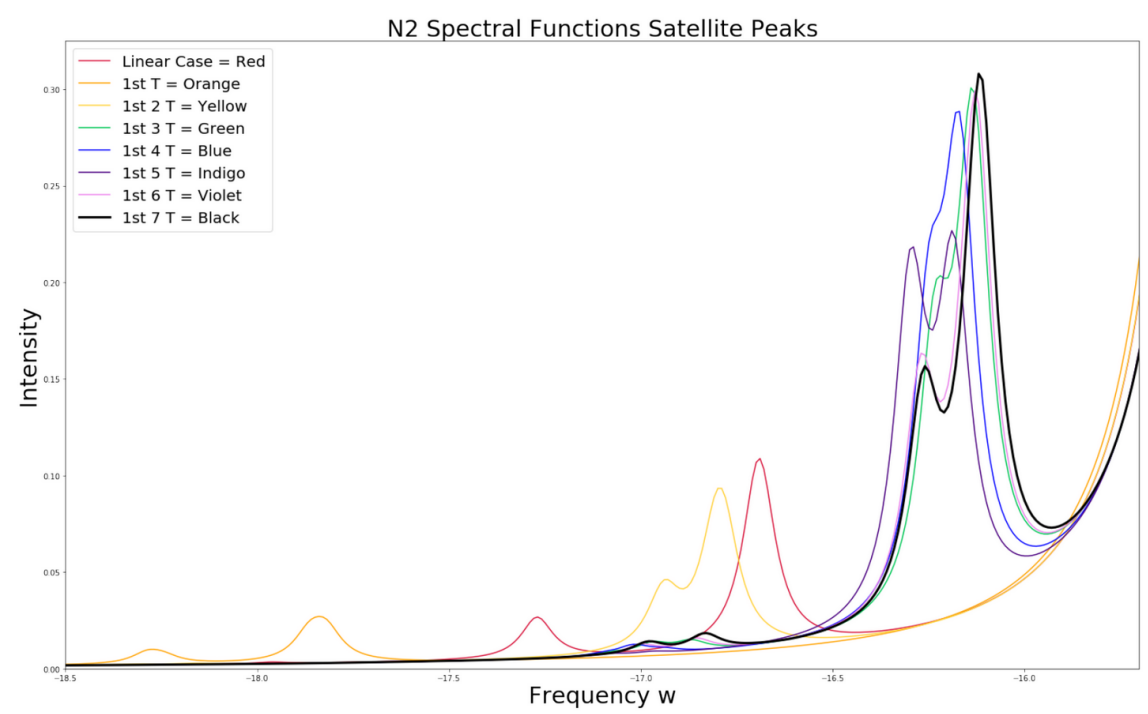

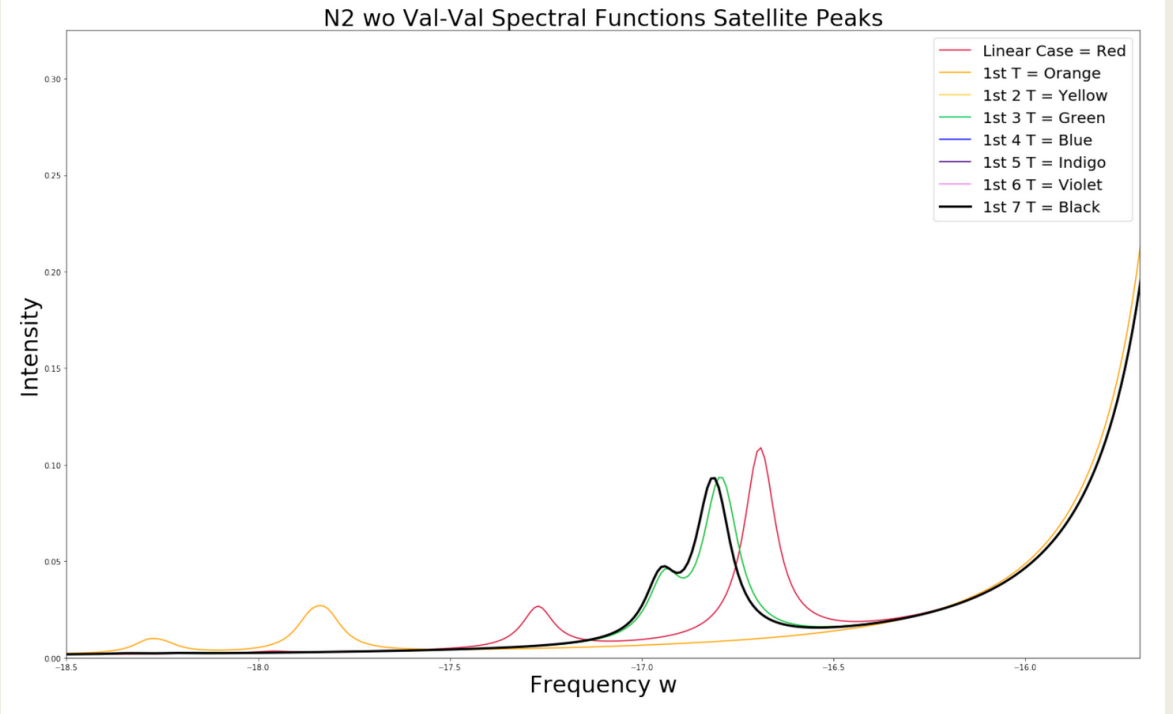

Going Forward

- Goal is to get proof of principle
  - *Prototype Calculations*
    - approximations that have about 20% accuracy
- Better understanding of electron interactions
- Faster calculations of larger systems
- More complicated system simulations

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