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Laboratoire de Chimie et Physique Quantiques

DOCI solutions with pCCD optimized orbitals for H_4

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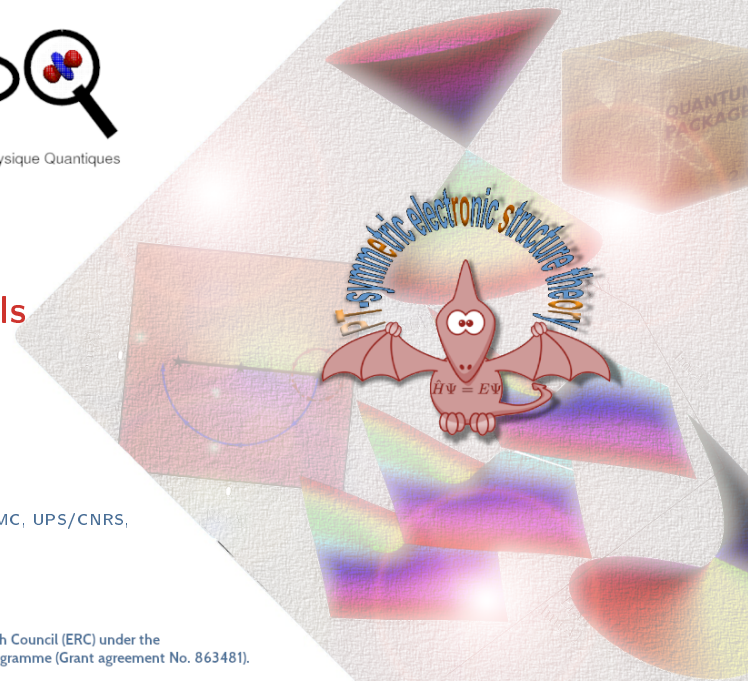
https://lcpq.github.io/pterosor



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Usual exponential ansatz:

$$|\Psi\rangle = e^{T}|0\rangle$$

where the excitation operator

$$T = \sum_{ia} t_i^a P_a^\dagger P_i$$

and singlet paired operators

$$P_q^\dagger = c_{q\alpha}^\dagger c_{q\beta}^\dagger$$

Substitution into the Schroedinger equation leads to

$$E = \langle 0|e^{-T} H e^{T}|0\rangle$$
$$0 = \langle 0|P_i^\dagger P_a e^{-T} H e^{T}|0\rangle$$

Equations for energy and t-amplitudes:

$$
\begin{aligned}
E =& \langle 0|H|0\rangle + \sum_{ia} t_i^a v_{aa}^{ii} \\
0 =& v_{ii}^{aa} + 2\left(f_a^a - f_i^i - \sum_j v_{aa}^{jj} t_j^a - \sum_b v_{bb}^{ii} t_j^a\right) t_i^a \\
& - 2\left(2v_{ia}^{ia} - v_{ai}^{ai} - v_{aa}^{ii} t_i^a\right) t_i^a \\
& + \sum_b v_{bb}^{aa} t_i^b + \sum_j v_{ii}^{jj} t_j^a + \sum_{jb} v_{bb}^{jj} t_j^a t_i^b
\end{aligned}
$$

where f_q^p is an element of the Fock operator and $v_{rs}^{pq} = \langle \phi_p \phi_q | V_{ee} | \phi_r \phi_s \rangle$ is a two-electron integral.

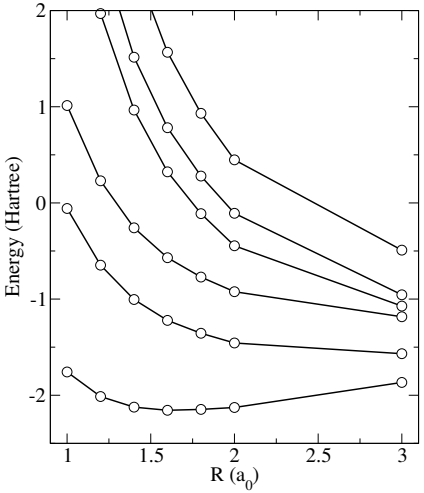

Figure: DOCI solutions for HF orbitals

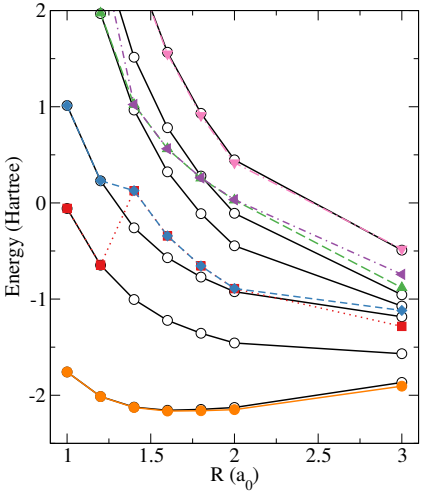

Figure: DOCI solutions for HF orbitals (black) and for pCCD optimized orbitals (colored)

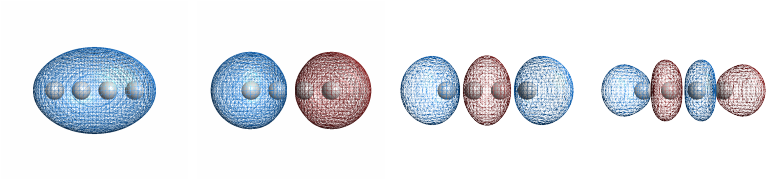

Figure: HF orbitals

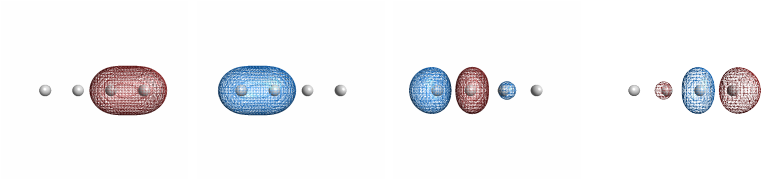

Figure: pCCD optimized orbitals

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