Orbital Optimization in APG

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for the Gemini[1,2]

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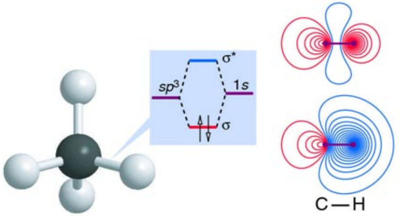
AP1roG for CH_4

- AP1roG in pSE (STO-6G)

$$\prod_{\alpha=1}^{N=5}\left(S_\alpha^\dagger + \sum_{i=6}^{9} G_{\alpha i} S_i^\dagger\right)|\theta\rangle$$

- OO = hybridisation (Lewis)



$$G = \left(\begin{array}{ccccc|cccc} 1 & 0 & 0 & 0 & 0 & -.001 & -.001 & -.001 & -.001 \\ 0 & 1 & 0 & 0 & 0 & -.007 & -.007 & -.007 & -.093 \\ 0 & 0 & 1 & 0 & 0 & -.007 & -.007 & -.093 & -.007 \\ 0 & 0 & 0 & 1 & 0 & -.007 & -.093 & -.007 & -.007 \\ 0 & 0 & 0 & 0 & 1 & -.093 & -.007 & -.007 & -.007 \end{array}\right)$$

E [mH]	fCI	Δ_{HF}	Δ_{DOCI} (MO)	Δ_{DOCI}(OO)	Δ_{AP1roG}(OO)
STO-6G	-40190.572	80.110	55.106	17.457	17.464
6-31G	-40301.051	120.549	99.477	44.596	44.603

Orbital Optimization: variational vs projective (AP1roG)

Unitary transfo's

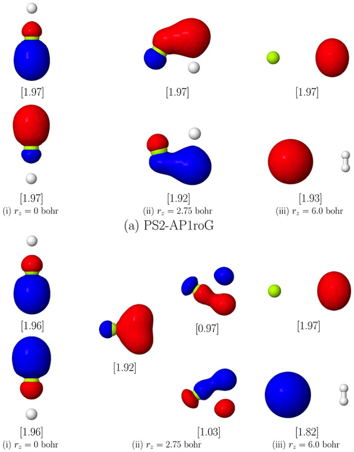
$$\hat{U} = e^{\hat{\kappa}}, \quad \hat{\kappa} = \sum_{pq} \kappa_{pq} a_p^\dagger a_q$$

1. Variational: Lagrangian

$$\mathcal{L} = \langle \Phi_0 | e^{\hat{\kappa}} H e^{-\hat{\kappa}} | \text{AP1roG} \rangle + \sum_{ia} \lambda_i^a \langle \Phi_i^a | (e^{\hat{\kappa}} H e^{-\hat{\kappa}} - E) | \text{AP1roG} \rangle$$

2. Projective: generalized Brillouin

$$\langle \text{AP1roG} | [a_q^\dagger a_p - a_p^\dagger a_q, e^{\hat{\kappa}} H e^{-\hat{\kappa}}] | \text{AP1roG} \rangle = 0$$



(a) PS2-AP1roG

(b) vOO-AP1roG

Orbital Optimization: seniority minimizing orbitals

- Seniority operator counts unpaired particles

$$\hat{\Omega} = \sum_{i=1}^{L} (n_i + n_{\bar{i}} - 2S_i^\dagger S_i)$$

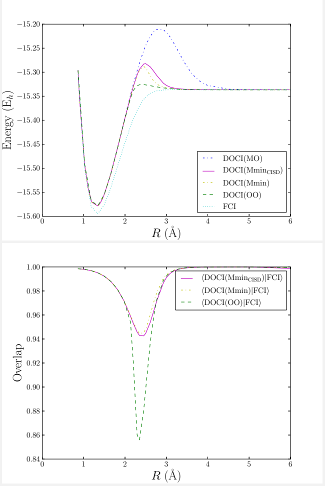
- Orbital dependent
- Given $|\Psi\rangle$, there is a basis (Mmin)

$$\Omega_{\text{Mmin}} = \min_{\hat{\kappa}} \langle \Psi | e^{\hat{\kappa}} \hat{\Omega} e^{-\hat{\kappa}} | \Psi \rangle$$

- Equilibrium static/dynamical ✍

✍ M. Van Raemdonck, et. al. (2015)
J. Chem. Phys. 143, 104106

Overlaps BeH_2



Orbital Optimization: local vs global

? How to walk this $\binom{L}{2}$ dim world

1 Gradient descent: local updates

$$e^{\varepsilon\kappa} \approx 1 + \varepsilon\hat{\kappa} + \mathcal{O}(\varepsilon^2)$$

2 Jacobi: semi-global scan ✍

$$E[\theta] = P_2(\cos 2\theta, \sin 2\theta)$$

3 Simulated Annealing: pinball

✍ W. Poelmans et. al. (2015) J. Chem. Theor. Comp. 11, 4064

1-body rotation

$$e^{\kappa} = \begin{pmatrix} U_{11} & U_{12} & \dots & U_{1L} \\ U_{21} & U_{22} & \dots & U_{2L} \\ \vdots & \vdots & \ddots & \vdots \\ U_{L1} & U_{L2} & \dots & U_{LL} \end{pmatrix}$$

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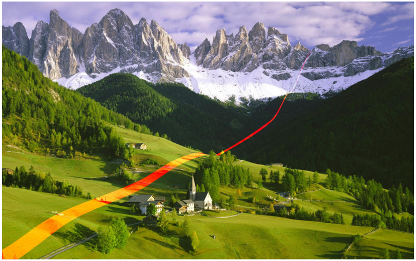
$$e^{\kappa} = \begin{pmatrix} 1 & 0 & \dots & 0 \\ 0 & \cos\theta & \dots & -\sin\theta \\ \vdots & \vdots & \ddots & \vdots \\ 0 & \sin\theta & \dots & \cos\theta \end{pmatrix}$$



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