Orthogonally Constrained Orbital Optimization and the Electronic Structure

Loris Delafosse

Faculty of Physics & Engineering, University of Strasbourg

May 29, 2024

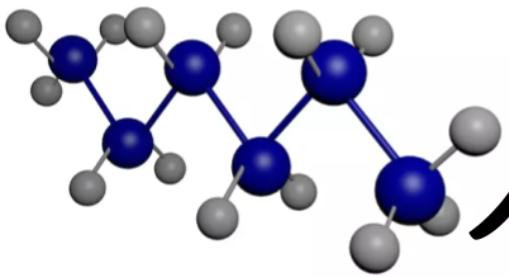
Plan

1. The electronic structure problem

2. Developing a new method for excited state calculations

Plan

Position of the problem

$$\psi \left(\right.$$  $$\left. \right)$$

$$\hat{H} = \sum_{i \text{ electrons}} \left(\frac{\hat{P}_i^2}{2} - \sum_{j \text{ nuclei}} \frac{Z_j}{r_{ij}} \right) + \sum_{ij \text{ electrons}} \frac{1}{r_{ij}}$$

The CASSCF method - variational ansatz

Complete Active Space Self-Consistent Field

$$|\Psi(\mathbf{c}, \boldsymbol{\kappa})\rangle = \mathrm{e}^{-\hat{\kappa}} |\psi_{\mathbf{c}}\rangle = \mathrm{e}^{-\hat{\kappa}} \frac{|\psi\rangle + \hat{\not{\Pi}} |\mathbf{c}\rangle}{\sqrt{1 + \langle \mathbf{c}| \hat{\not{\Pi}} |\mathbf{c}\rangle}}$$

$$\hat{\not{\Pi}} = \mathbb{I} - |\psi\rangle\langle\psi|$$

$$|\mathbf{c}\rangle = \sum_{\underline{i}} c_{\underline{i}} |\underline{i}\rangle$$

The CASSCF method - Lagrangian

Complete Active Space Self-Consistent Field

$$E(\mathbf{c}, \boldsymbol{\kappa}) = \langle \Psi(\mathbf{c}, \boldsymbol{\kappa}) | \hat{H} | \Psi(\mathbf{c}, \boldsymbol{\kappa}) \rangle$$

- we compute the Gradient and Hessian of this Lagrangian
- we find the values $(\mathbf{c}, \boldsymbol{\kappa})$ that minimize E

+ Complete Active Space: we truncate the Hilbert space

The CASSCF method - Hessian and Gradient

$$G^E_{pq} = \left.\frac{\partial E}{\partial \kappa_{pq}}\right|_{(\mathbf{c},\boldsymbol{\kappa})=\mathbf{0}}$$

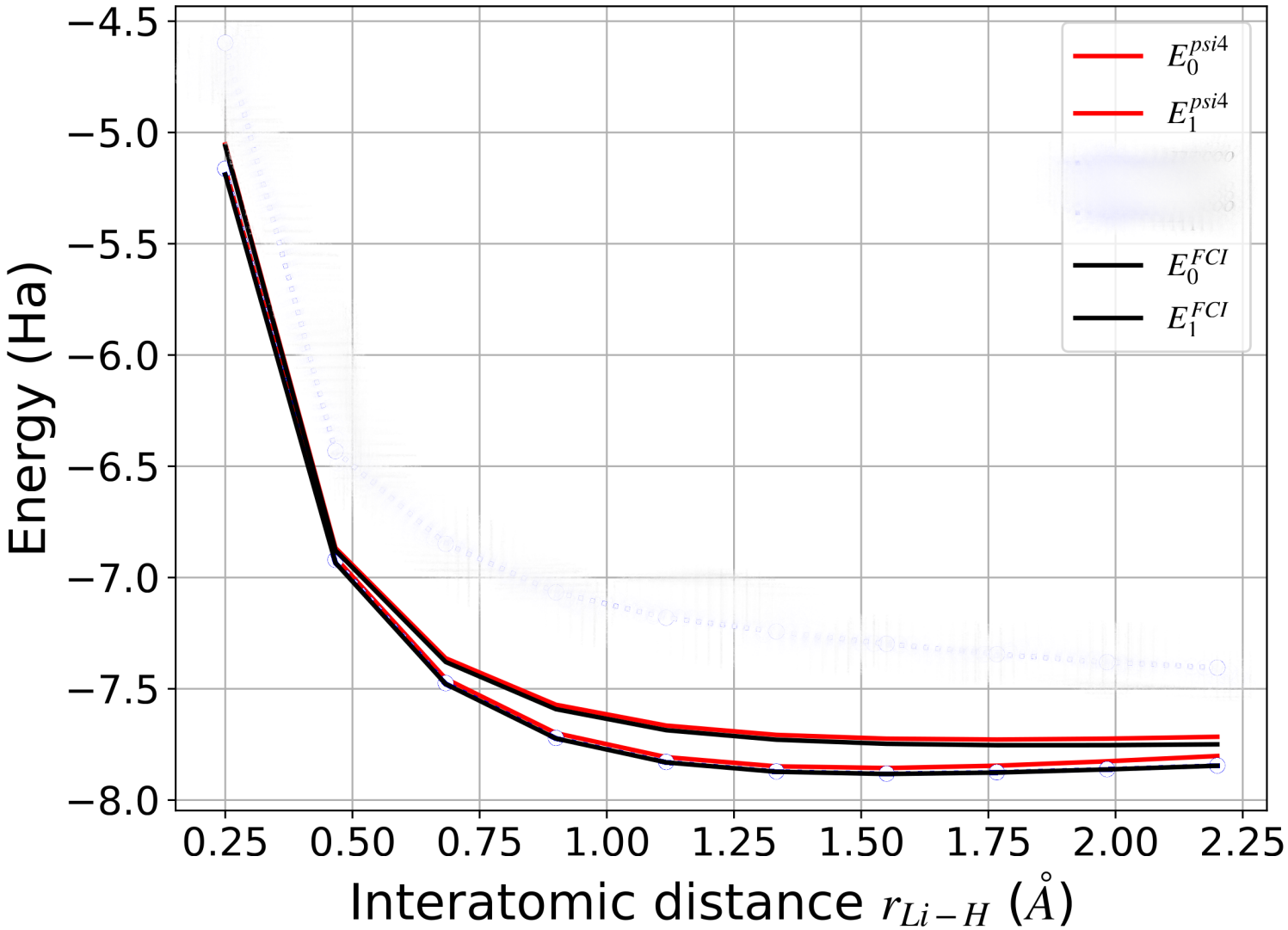
$$H^E_{pqrs} = \left.\frac{\partial^2 E}{\partial \kappa_{pq}\partial \kappa_{rs}}\right|_{(\mathbf{c},\boldsymbol{\kappa})=\mathbf{0}}$$

$$G^E_{\underline{i}} = \left.\frac{\partial E}{\partial c_{\underline{i}}}\right|_{(\mathbf{c},\boldsymbol{\kappa})=\mathbf{0}}$$

$$H^E_{\underline{ij}} = \left.\frac{\partial^2 E}{\partial c_{\underline{i}}\partial c_{\underline{j}}}\right|_{(\mathbf{c},\boldsymbol{\kappa})=\mathbf{0}}$$

$$H^E_{pq\underline{i}} = \left.\frac{\partial^2 E}{\partial \kappa_{pq}\partial c_{\underline{i}}}\right|_{(\mathbf{c},\boldsymbol{\kappa})=\mathbf{0}}$$

Typical results



Plan

1 The electronic structure problem

2 Developing a new method for excited state calculations

The idea behind OCOO

How do we find the first excited state?

- we find the ground state ψ^0
- we minimize the energy with an additional constraint: orthogonality!

$$\mathcal{L}(\mathbf{c}, \boldsymbol{\kappa}) = \langle \Psi(\mathbf{c}, \boldsymbol{\kappa}) | \hat{H} | \Psi(\mathbf{c}, \boldsymbol{\kappa}) \rangle + \lambda_0 \left| \left\langle \psi^0 \middle| \Psi(\mathbf{c}, \boldsymbol{\kappa}) \right\rangle \right|^2$$

and then we find the second excited state, the third, and so on...

General form for the OCOO Lagrangian

$$\mathcal{L}(\mathbf{c},\boldsymbol{\kappa}) = \langle\Psi(\mathbf{c},\boldsymbol{\kappa})|\hat{H}|\Psi(\mathbf{c},\boldsymbol{\kappa})\rangle + \sum_{A=0}^{n-1}\lambda_A\left|\left\langle\psi^A\middle|\Psi(\mathbf{c},\boldsymbol{\kappa})\right\rangle\right|^2$$

$$= \langle\Psi(\mathbf{c},\boldsymbol{\kappa})|\hat{H}|\Psi(\mathbf{c},\boldsymbol{\kappa})\rangle + \sum_{A=0}^{n-1}\lambda_A\langle\Psi(\mathbf{c},\boldsymbol{\kappa})|\hat{\Pi}^A|\Psi(\mathbf{c},\boldsymbol{\kappa})\rangle$$

$$\text{with } \hat{\Pi}^A = \left|\psi^A\middle\rangle\middle\langle\psi^A\right|$$

Overlap Hessian and Gradient

$$G^A_{pq} = 2S^{\psi,\psi^A}\gamma^{\psi,\psi^A}_{[pq]}$$

$$H^A_{pqrs} = 2\,\mathrm{T}^{pq}_{rs}\left[S^{\psi,\psi^A}\left(\Gamma^{\psi,\psi^A}_{[pq][rs]} + \delta_{[r|[q}\gamma^{\psi,\psi^A}_{p]|s]}\right) + \gamma^{\psi,\psi^A}_{[pq]}\gamma^{\psi,\psi^A}_{[rs]}\right]$$

$$G^A_{\underline{i}} = 2S^{\psi,\psi^A}C^A_{\underline{i}} - 2\mathcal{L}^A_{(\boldsymbol{\xi}=\mathbf{0})}C^{\mathrm{ref}}_{\underline{i}}$$

$$H^A_{\underline{ij}} = 2C^A_{\underline{i}}C^A_{\underline{j}} - 2\mathcal{L}^A_{(\boldsymbol{\xi}=\mathbf{0})}\delta_{\underline{ij}} - 2C^{\mathrm{ref}}_{(\underline{i}}G^A_{\underline{j})}$$

$$H^A_{pq\underline{i}} = 2C^A_{\underline{i}}\gamma^{\psi,\psi^A}_{[pq]} - 2S^{\psi,\psi^A}\gamma^{\psi^A,\underline{i}}_{[pq]} - 2C^{\mathrm{ref}}_{\underline{i}}G^A_{pq}$$

The Mystery of the Lagrange Multipliers

$$\hat{H} = \sum_{A=0}^{\infty} E_A \left|\psi^A\right\rangle\!\left\langle\psi^A\right|$$

$$\begin{aligned}\mathcal{L}(\boldsymbol{\xi}) &= \sum_{A=0}^{\infty} E_A \left\langle \Psi(\boldsymbol{\xi}) | \hat{\Pi}^A | \Psi(\boldsymbol{\xi}) \right\rangle + \sum_{A=0}^{n-1} \lambda_A \left\langle \Psi(\boldsymbol{\xi}) | \hat{\Pi}^A | \Psi(\boldsymbol{\xi}) \right\rangle \\ &= \left\langle \Psi(\boldsymbol{\xi}) \middle| \sum_{A=0}^{n-1} (E_A + \lambda_A) \hat{\Pi}^A + \sum_{A=n}^{\infty} E_A \hat{\Pi}^A \middle| \Psi(\boldsymbol{\xi}) \right\rangle\end{aligned}$$

Bibliography

- Helgaker, T. Jørgensen, P. Olsen, J. *Molecular Electronic-Structure Theory*. John Wiley & Sons, Ltd (2000). ISBN: 9781119019572
- Yalouz, S. *et al.* Analytical Nonadiabatic Couplings and Gradients within the State-Averaged Orbital-Optimized Variational Quantum Eigensolver. *J. Chem. Theory Comput.* **18** (2022). DOI: 10.1021/acs.jctc.1c00995
- Yalouz, S. Robert, V. Orthogonally Constrained Orbital Optimization: Assessing Changes of Optimal Orbitals for Orthogonal Multireference States. *J. Chem. Theory Comput.* **19** (2023). DOI: 10.1021/acs.jctc.2c01144
- Yalouz, S. QuantNBody. https://github.com/syalouz/quantnbody

Annex I

$$|\psi\rangle = |\Psi(\mathbf{0},\mathbf{0})\rangle = \sum_{\underline{i}} C_{\underline{i}}^{\mathrm{ref}} |\underline{i}\rangle \tag{6}$$

(the reference state we want to optimize)

$$\hat{\not{\Pi}} = \mathbb{1} - |\psi\rangle\langle\psi| \tag{7}$$

$$|\mathbf{c}\rangle = \sum_{\underline{i}} c_{\underline{i}} |\underline{i}\rangle \tag{8}$$

$$\hat{\kappa} = \sum_{p>q} \kappa_{pq} \hat{E}_{[pq]} \tag{9}$$

$$\hat{E}_{pq} = \hat{a}_{p\sigma}^{\dagger} \hat{a}_{q\sigma} = \hat{E}_{qp}^{\dagger} \tag{10}$$

$$\hat{e}_{pqrs} = \hat{e}_{rspq} = \hat{a}_{p\sigma}^{\dagger} \hat{a}_{r\tau}^{\dagger} \hat{a}_{s\tau} \hat{a}_{q\sigma} = \hat{e}_{qpsr}^{\dagger} = \hat{e}_{srqp}^{\dagger} \tag{11}$$

Annex II

$$\gamma_{pq}^{\psi,\psi} = \langle\psi|\hat{E}_{pq}|\psi\rangle = \gamma_{qp}^{\psi,\psi} \tag{18}$$

$$\Gamma_{pqrs}^{\psi,\psi} = \langle\psi|\hat{e}_{pqrs}|\psi\rangle = \Gamma_{qpsr}^{\psi,\psi} \tag{19}$$

Hence, we have the following expressions for the orbital Gradient and Hessian:

$$G_{pq}^{E} = 2F_{[pq]} \tag{20}$$

$$H_{pqrs}^{E} = 2h_{[q|[s}\gamma_{p]|r]}^{\psi,\psi} - \delta_{[s|[q}F_{p]|r]} + \delta_{[q|[s}F_{r]|p]} + 2Y_{[pq][rs]} \tag{21}$$

with:

$$F_{mn} = \sum_{q} h_{nq}\gamma_{mq}^{\psi,\psi} + \sum_{qrs} g_{nqrs}\Gamma_{mqrs}^{\psi,\psi} \tag{22}$$

$$Y_{pqrs} = \sum_{mn}\left(g_{qmns}\Gamma_{pm(rn)}^{\psi,\psi} + g_{qsmn}\Gamma_{prmn}^{\psi,\psi}\right) \tag{23}$$

where $(h_{pq})_{pq}$ and $(g_{pqrs})_{pqrs}$ are the molecular one- and two-electron integrals.

Annex III

$$\begin{aligned} \gamma_{pq}^{\psi^1,\psi^0} &= \left\langle \psi^1 \middle| \hat{E}_{pq} \middle| \psi^0 \right\rangle \\ &= \left\langle \psi^0 \middle| \hat{E}_{qp} \middle| \psi^1 \right\rangle = \gamma_{qp}^{\psi^0,\psi^1} \end{aligned} \tag{24}$$

$$\begin{aligned} \Gamma_{pqrs}^{\psi^1,\psi^0} = \Gamma_{rspq}^{\psi^1,\psi^0} &= \left\langle \psi^1 \middle| \hat{e}_{pqrs} \middle| \psi^0 \right\rangle \\ = \left\langle \psi^0 \middle| \hat{e}_{srqp} \middle| \psi^1 \right\rangle &= \Gamma_{srqp}^{\psi^0,\psi^1} = \Gamma_{qpsr}^{\psi^0,\psi^1} \end{aligned} \tag{25}$$

Annex IV

$$\boldsymbol{\xi} = -\left(\mathbf{H}^E\right)^{-1}\mathbf{G}^E \tag{28}$$

with:

$$\mathbf{G}^E = \begin{pmatrix} \mathbf{G}^c \\ \mathbf{G}^o \end{pmatrix} \tag{29}$$

$$\mathbf{H}^E = \begin{pmatrix} \mathbf{H}^{cc} & \mathbf{H}^{co} \\ \mathbf{H}^{oc} & \mathbf{H}^{oo} \end{pmatrix} \tag{30}$$

Annex V

2-electron excitation operators with at least one virtual index are all zero. 2-electron excitation operators without virtual indices but with at least one inactive index can be computed by using:

$$\hat{e}_{pqrs} = \hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps} \tag{46}$$

together with Eq. (44).
Then the RDMs take the form:

$$\gamma_{iq}^{\psi,\psi} = 2\delta_{iq} \tag{47}$$

$$\Gamma_{pqis}^{\psi,\psi} = 2\delta_{is}\gamma_{pq}^{\psi,\psi} - \delta_{iq}\gamma_{ps}^{\psi,\psi} \tag{48}$$

All RDM elements involving a virtual index are zero.

Annex VI

Then, the total Gradient and Hessian consist in a sum:

$$\mathbf{G}^{\text{tot}} = \mathbf{G}^{E} + \sum_{A=0}^{n-1} \lambda_A \mathbf{G}^{A} \tag{62}$$

$$\mathbf{H}^{\text{tot}} = \mathbf{H}^{E} + \sum_{A=0}^{n-1} \lambda_A \mathbf{H}^{A} \tag{63}$$

and the optimized parameters are:

$$\boldsymbol{\xi} = -\left(\mathbf{H}^{\text{tot}}\right)^{-1} \mathbf{G}^{\text{tot}} \tag{64}$$

The various components of the Gradients and Hessians can be computed through:

Annex VII

Imposing $\lambda_A = -E_A$ appears as a way to eliminate the energies we already know in the Hamiltonian, creating a new system in which these known states are eliminated. Then, the Lagrangian is nothing but the expectation value of the reduced Hamiltonian:

$$\hat{H}_r = \sum_{A=n}^{\infty} E_A \hat{\Pi}^A \tag{73}$$

whose ground state is now $|\psi^n\rangle$.
Rigorously, writing $|\Psi(\boldsymbol{\xi})\rangle = \sum_A k_A |\psi^A\rangle$:

$$\mathcal{L}(\boldsymbol{\xi}) = \langle\Psi(\boldsymbol{\xi})|\hat{H}_r|\Psi(\boldsymbol{\xi})\rangle \tag{74}$$

$$= \sum_{A=n}^{\infty} E_A |k_A|^2 \geq E_n \sum_{A=n}^{\infty} |k_A|^2 \geq E_n \tag{75}$$

because $E_n < 0$ and $0 \leq \sum_{A=n}^{\infty} |k_A|^2 \leq 1$. The equality case happens when $|\Psi(\boldsymbol{\xi})\rangle = |\psi^n\rangle$.

This adapted version of Ritz' theorem shows that $(\lambda_A)_A = -(E_A)_A$ correctly solves the variational problem, and thus is a correct choice of Lagrange multipliers.