A geometric picture of linear response theory for variational methods

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Excited states

What is an excited state?

- higher-energy solution of Schrödinger equation

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$\Longrightarrow$ natural minimisation problem for approximating ground state:

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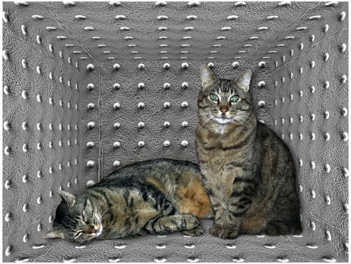

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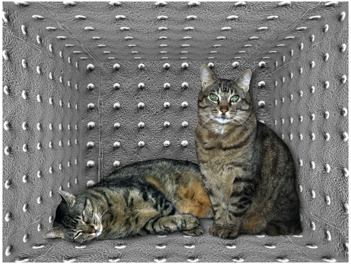

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introduction of artifacts!

Let's start from mathematics...

Linear response - FCI

Time-dependent Schrödinger equation $i\frac{d\Psi}{dt}(t) = \hat{H}\Psi(t)$

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2. Linearise equation of motion around ground state

$$i\frac{\mathrm{d}\Psi^{(1)}}{\mathrm{d}t}(t) = (\hat{H} - E_0)\Psi^{(1)}(t) \Leftrightarrow i\frac{\mathrm{d}\Gamma^{(1)}}{\mathrm{d}t}(t) = [\hat{H}, \Gamma^{(1)}(t)]$$

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$$(\hat{H} - E_0)\Psi = \omega\Psi, \;\; \Psi \perp \Psi^{(0)} \implies \omega = E_1 - E_0, E_2 - E_0, \ldots$$

Classical Hamiltonian dynamics

- Potential energy $V : \mathbb{C}^n \to \mathbb{R}$
- Decomposition of $\boldsymbol{x} \in \mathbb{C}^n$ as $\boldsymbol{x} = \boldsymbol{q} + i\boldsymbol{p}$, with $\boldsymbol{q}, \boldsymbol{p} \in \mathbb{R}^n$
- Classical Hamiltonian $H(\boldsymbol{q}, \boldsymbol{p}) := V(\boldsymbol{q} + i\boldsymbol{p})$ on the phase space $\mathbb{R}^{2n}$

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or equivalently $\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t}(t) = i \,\mathrm{grad}_{\mathbb{R}^{2n}} V(\boldsymbol{x}(t))$.

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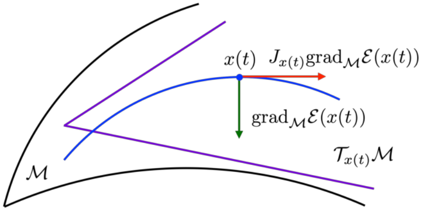
- Potential energy $V : \mathcal{M} \to \mathbb{R}$, with $\mathcal{M}$ embedded in complex space
- Classical Hamiltonian $V(\boldsymbol{x})$ on $\mathcal{M}_{\mathbb{R}}$ ($\mathcal{M}$ seen as real)

Smooth energy functional $\mathcal{E} : \mathcal{M} \to \mathbb{R}$



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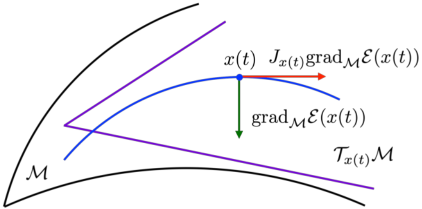

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with $\mathcal{J}_{x(t)} : \mathcal{T}_x\mathcal{M}_\mathbb{R} \to \mathcal{T}_x\mathcal{M}_\mathbb{R}$ complex structure, satisfying $\mathcal{J}_{x(t)}^2 = -\mathrm{Id}_{\mathcal{T}_x\mathcal{M}_\mathbb{R}}$

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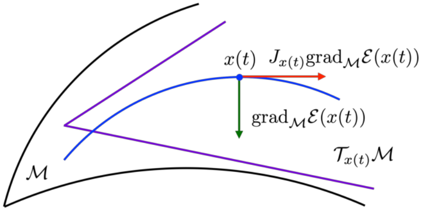

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TD-Schrödinger equation as classical Hamiltonian dynamics

$$\frac{\mathrm{d}\Gamma(t)}{\mathrm{d}t} = \mathcal{J}_{\Gamma(t)}\text{grad}_{\mathcal{M}_{\mathbb{R}}}\mathcal{E}(\Gamma(t)) = -i[\hat{H}, \Gamma(t)]$$

with $\Gamma(t) \in \mathcal{M}_{\mathbb{R}} = \mathcal{M}_{\text{exact}}$ and $\mathcal{J}_{\Gamma(t)}(Q) := i[\Gamma, Q]$.

Kähler manifolds

How to find $\mathcal{J}$ for general manifolds?

Kähler manifold

Kähler manifold $\mathcal{M}$: complex manifold of dimension $n = \dim_{\mathbb{C}}(\mathcal{M})$, endowed with positive-definite Hermitian form $\langle \bullet, \bullet \rangle_{\bullet}$, allowing to endow $\mathcal{M}_{\mathbb{R}}$ (real $2n$-dimensional) with

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- Riemannian structure $g_x(u, v) := \text{Re}(\langle u, v \rangle_x), \forall u, v \in \mathcal{T}_x\mathcal{M}_{\mathbb{R}}, x \in \mathcal{M}_{\mathbb{R}}$
- Symplectic structure $\omega_x(u, v) := \text{Im}(\langle u, v \rangle_x), \forall u, v \in \mathcal{T}_x\mathcal{M}_{\mathbb{R}}, x \in \mathcal{M}_{\mathbb{R}}$
- Symplectic operator $\mathcal{J}_x : \mathcal{T}_x\mathcal{M}_{\mathbb{R}} \to \mathcal{T}_x\mathcal{M}_{\mathbb{R}}, \mathcal{J}_x^2 = -Id_{\mathcal{T}_x\mathcal{M}_{\mathbb{R}}}$

such that

$$g_x(u, v) = \omega_x(u, \mathcal{J}_x(v)), \forall u, v \in \mathcal{T}_x\mathcal{M}_{\mathbb{R}}, x \in \mathcal{M}_{\mathbb{R}}$$

Kähler manifolds for linear response

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$$\frac{\mathrm{d}x^{(1)}(t)}{\mathrm{d}t} = \mathcal{J}_{x^{(0)}} \mathrm{Hess}_{\mathcal{M}_{\mathbb{R}}} \mathcal{E}(x^{(0)}) x^{(1)}(t) \quad \text{on} \quad \mathcal{T}_{x^{(0)}} \mathcal{M}_{\mathbb{R}}$$

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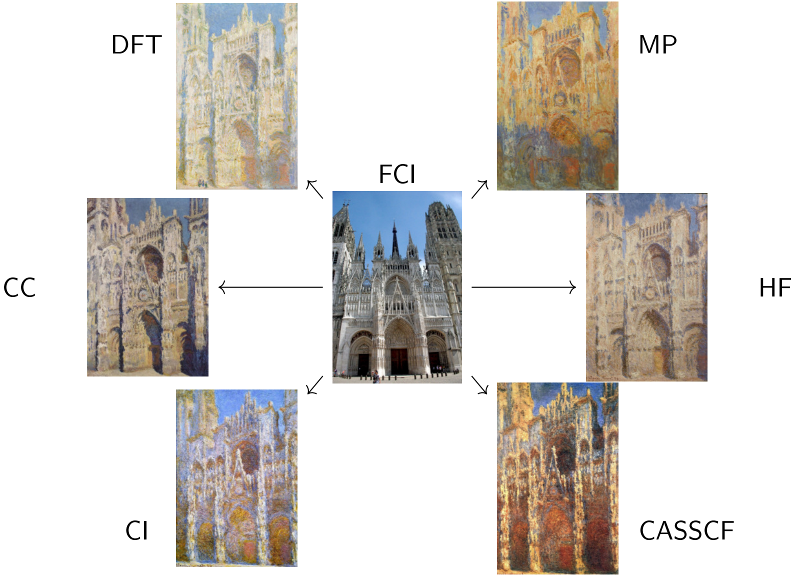
4. Excitation energies through computation of symplectic eigenvalues of $\mathrm{Hess}_{\mathcal{M}_{\mathbb{R}}} \mathcal{E}(x^{(0)})$ on $\mathcal{T}_{x^{(0)}} \mathcal{M}_{\mathbb{R}}$.

Methods

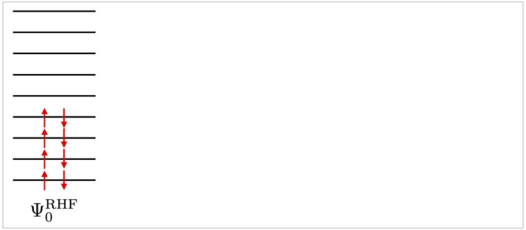
FCI

Methods



Hartree-Fock manifold

Single-determinant ansatz



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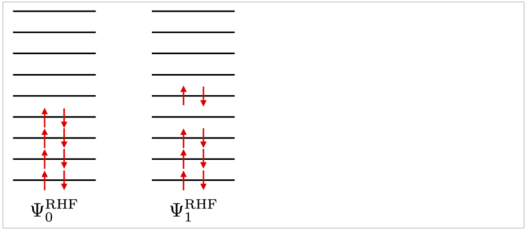

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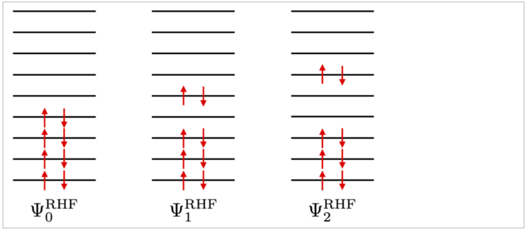

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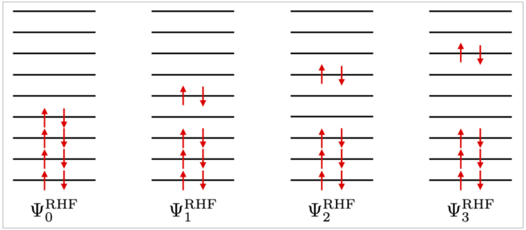

Grassmann manifold

$$\mathrm{Gr}(N,\mathcal{N}_b) = \{P \in \mathbb{C}_{\mathrm{sym}}^{\mathcal{N}_b\times\mathcal{N}_b} | P^2 = P, \mathrm{Tr}(P) = N\}$$

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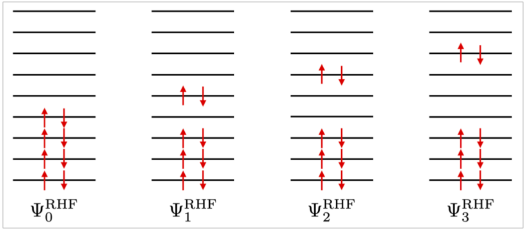

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electrons (N)

basis functions ($\mathcal{N}_b$)

Hartree-Fock manifold

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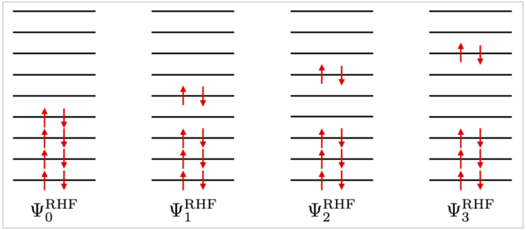

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→ density matrix

Linear response - HF

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$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B} & -\boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix}$$

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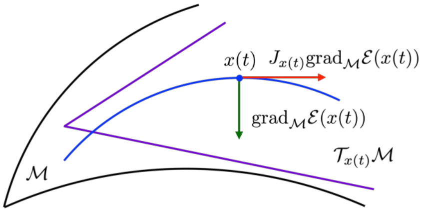
where $\boldsymbol{A}$ and $\boldsymbol{B}$ depend on orbital energies and 2-electron integrals.

Casida's equation



- Find canonical basis of $\mathcal{T}_{P_0}\mathcal{M}_{\mathbb{R}}$

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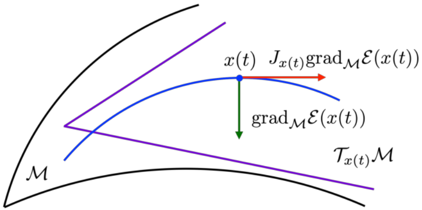

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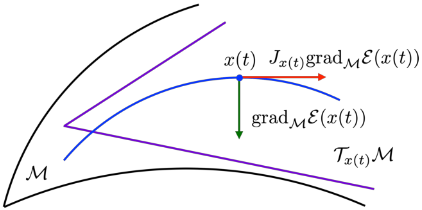
- In this basis,

$$\mathrm{Hess}_{\mathcal{M}_{\mathbb{R}}}\mathcal{E}(P_0) = \begin{pmatrix} \boldsymbol{A}+\boldsymbol{B} & 0 \\ 0 & \boldsymbol{A}-\boldsymbol{B} \end{pmatrix}$$

$\boldsymbol{A}$ and $\boldsymbol{B}$ defined as in Casida

Casida's equation



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- LR excitation energies $\rightarrow$ symplectic eigenvalues of $\mathrm{Hess}_{\mathcal{M}_{\mathbb{R}}}\mathcal{E}(P_0)$

$\Longrightarrow$ eigenvalues of symmetric matrix (J. Williamson, Am. J. Math., 58, 1936)

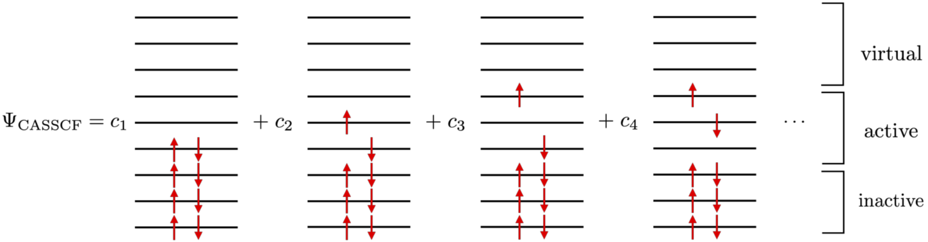
$$\tilde{\Omega} := \left((\boldsymbol{A}+\boldsymbol{B})^{1/2}(\boldsymbol{A}-\boldsymbol{B})(\boldsymbol{A}+\boldsymbol{B})^{1/2}\right)^{1/2}$$

Equivalent to Casida's equation!

CASSCF

- Describe multi-reference states $\Longrightarrow$ single determinant not sufficient

Complete active space self-consistent field (CASSCF) theory



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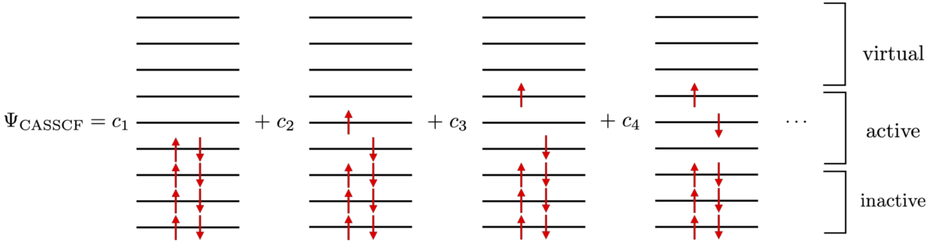

$$\phi_p^C := \sum_{\mu=1}^{N_b} C_{\mu p}\chi_\mu, \quad p = 1, \dots, N_b \qquad |\Psi_{c,C}\rangle = \sum_{I=1}^{N_{\text{det}}} c_I |I^C\rangle$$

orbital rotation

lin. comb. of Slater Determinants

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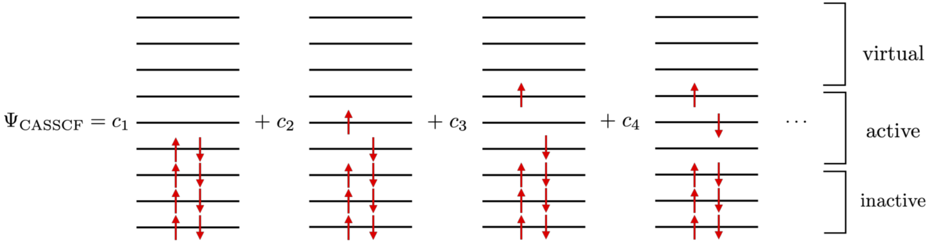
Complete active space self-consistent field (CASSCF) theory



$$\phi_p^C := \sum_{\mu=1}^{N_b} C_{\mu p} \chi_\mu, \quad p = 1, \ldots, N_b \qquad |\Psi_{c,C}\rangle = \sum_{I=1}^{N_{\text{det}}} c_I |I^C\rangle$$

- Partition of orbital space into inactive, active and virtual orbitals

CASSCF

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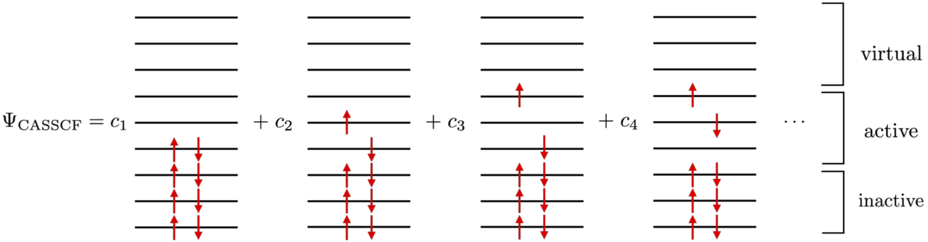

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CASSCF excited states

Linear Response

– From dynamical equations (TD)

– Strong ground-state dependence

– Poor for charge-transfer or Rydberg states

P. Normann, K. Ruud, and T. Saue, John Wiley & Sons (2018)
H.-J. Werner, W. Meyer, J. Chem. Phys. 74, 5794–5801 (1981)
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– Optimised orbitals for each state

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– Shared orbitals for considered states

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– Bad approximation if states are very different

P. Normann, K. Ruud, and T. Saue, John Wiley & Sons (2018)
H.-J. Werner, W. Meyer, J. Chem. Phys. 74, 5794–5801 (1981)
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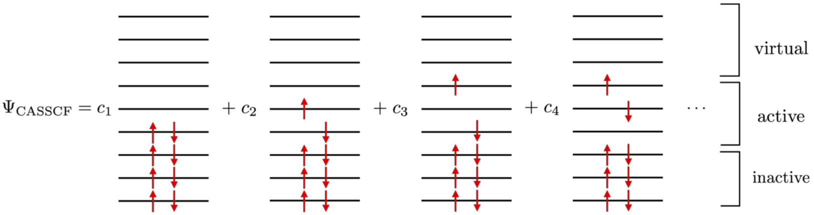
CASSCF manifold



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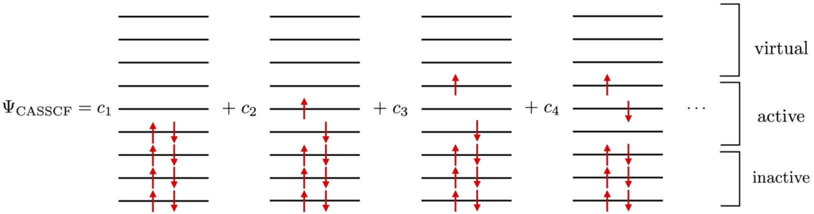

State characterised by (c, C)

- rotation in configuration space $\to$ coefficients vector c ($|c| = 1$)
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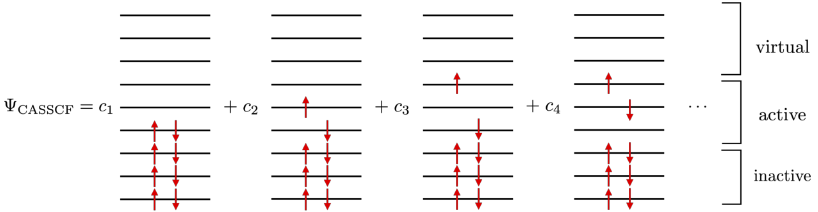

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$$\mathcal{M} := \left\{ (c, C) \in (\mathbb{S}_{\mathbb{C}}^{N_{\text{det}}-1} \times U(N_{\text{b}})) \mid \text{rank}\left(\gamma_{c,C}^{\text{act}}\right) = N_{\text{a}} \right\}$$

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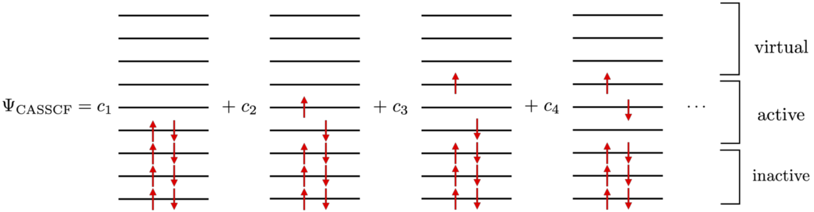

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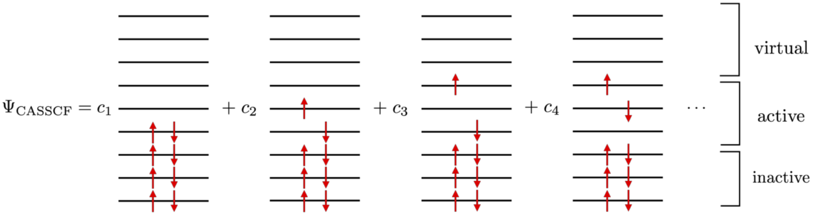

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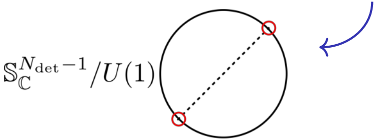

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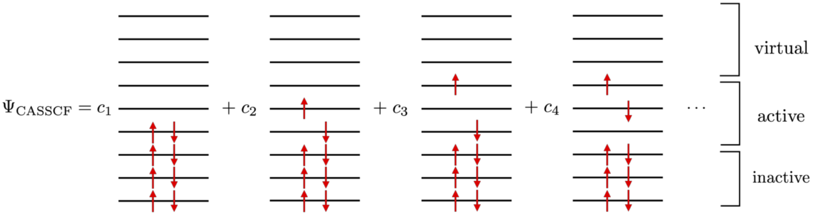

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$U(N_{\text{i}})$: equivalence int. orb.

$U(N_{\text{a}})$: equivalence act. orb.

$U(N_{\text{e}})$: equivalence virt. orb.

CASSCF manifold

Caveat!

Rotation of orbitals may compensate rotation of configurations $\Longrightarrow$ two spaces cannot be treated separately!

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Manifold geometry needed for linear response!

M. Lewin, J. Math. Chem., 44, 967–980 (2018)

CASSCF-LR

Conventional CASSCF-LR derivations involve *ad hoc* technicalities, to obtain

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B} & -\boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} \boldsymbol{\Sigma} & \boldsymbol{\Delta} \\ \boldsymbol{\Delta} & \boldsymbol{\Sigma} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix}$$

$\implies$ non-intelligible manifold geometry!

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In canonical basis of $\mathcal{T}_{P_0}\mathcal{M}_{\mathbb{R}}$ gives

$$\mathrm{Hess}_{\mathcal{M}_{\mathbb{R}}}\mathcal{E}(P_0)[\boldsymbol{v}] = \begin{pmatrix} \boldsymbol{A}+\boldsymbol{B} & 0 \\ 0 & \boldsymbol{A}-\boldsymbol{B} \end{pmatrix} \begin{pmatrix} \boldsymbol{v}^+ \\ \boldsymbol{v}^- \end{pmatrix}$$

CASSCF-LR

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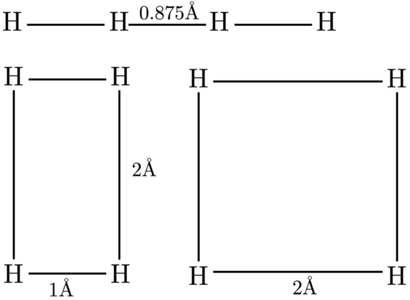
$\implies$ CASSCF-LR excitation energies are symplectic eigenvalues of $\tilde{\Omega}$:

$$\tilde{\Omega} = \left((\boldsymbol{A}+\boldsymbol{B})^{1/2}(\boldsymbol{A}-\boldsymbol{B})(\boldsymbol{A}+\boldsymbol{B})^{1/2}\right)^{1/2}.$$

Model system H_4



- H_4 known to have multiple SCF solutions
- Generally, multiple local minima, maxima and saddle points
  → HF nonlinear approximation
  → symmetry breaking (UHF)
  → bad single-reference approximation

H. G. A. Burton and D. J. Wales, J. Chem. Theory Comput. 17, 151-169 (2021)

Comparison between LR and CP

Comparison in perturbative framework

$$\hat{H} = \hat{h} + \lambda \hat{V}$$

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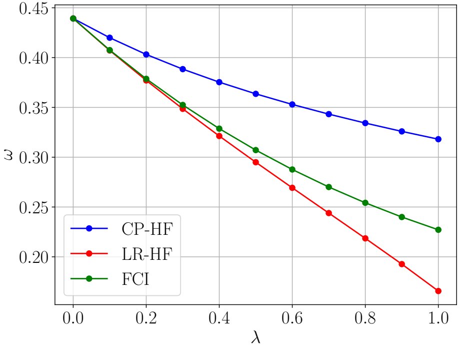
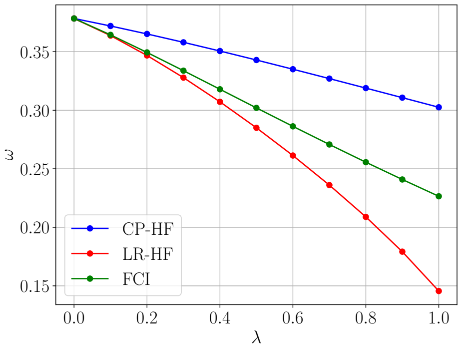
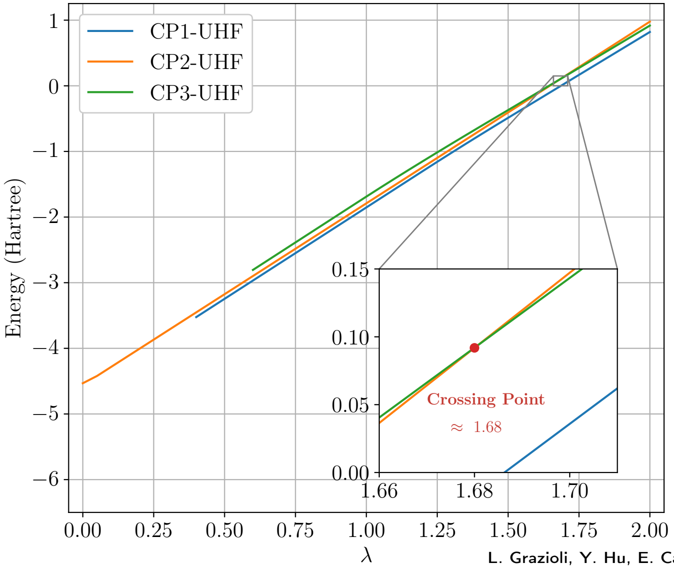


H_4 linear geometry, 3-21G



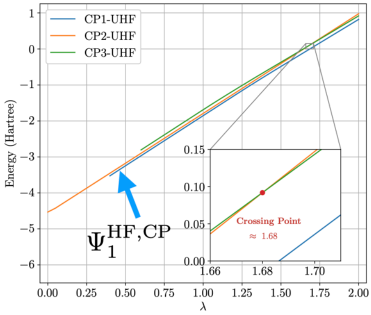
H_4 rectangular geometry, 3-21G

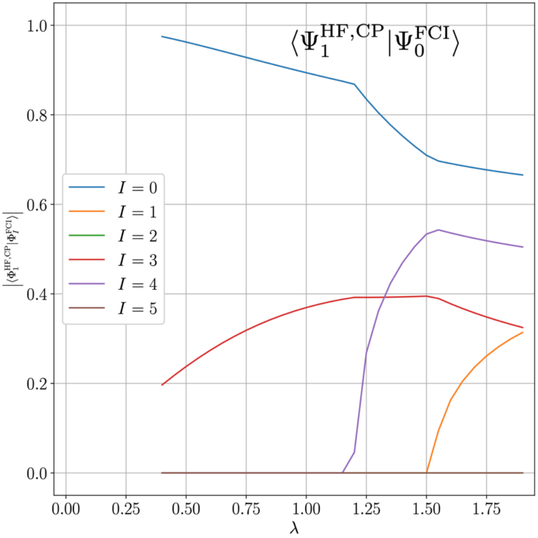
H_4 index-1 saddle points



L. Grazioli, Y. Hu, E. Cancès, arXiv:2506.16420, 2025

H_4 index-1 saddle points

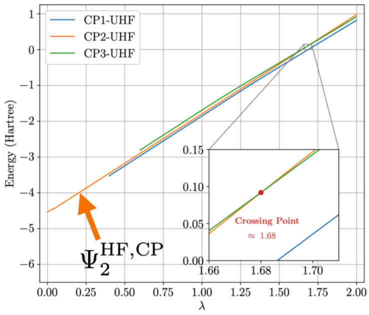


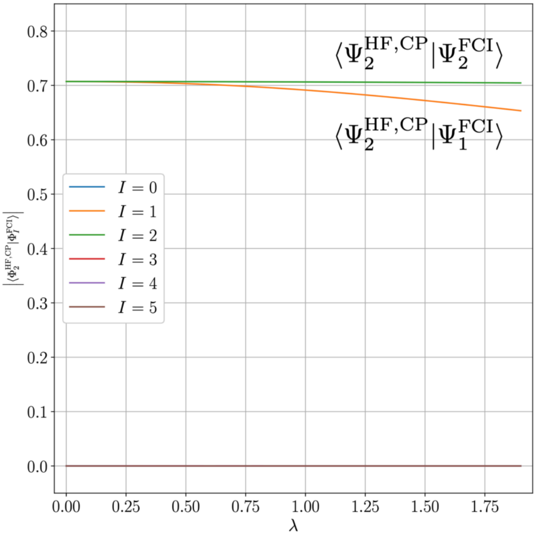


Spurious saddle point close to Ψ_0^{FCI}!

L. Grazioli, Y. Hu, E. Cancès, arXiv:2506.16420, 2025

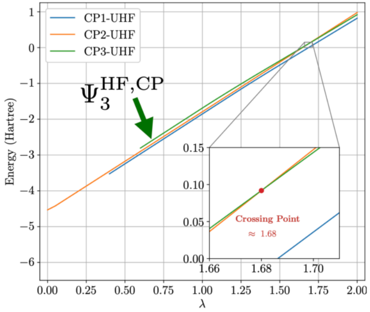
H_4 index-1 saddle points

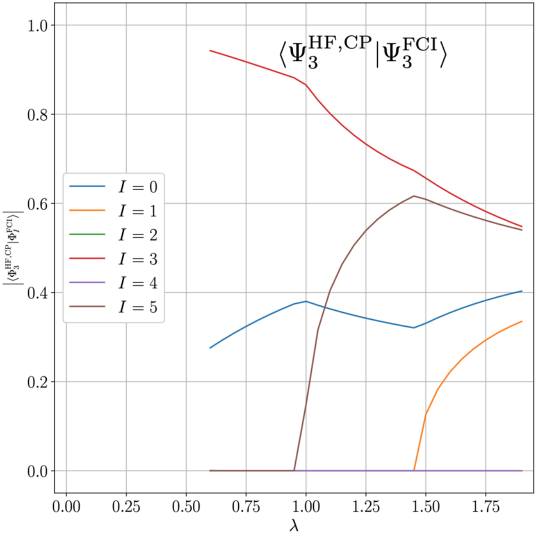




Symmetry-broken state $\Psi_2^{HF,CP}$, lin. comb. Ψ_1^{FCI} (triplet) and Ψ_2^{FCI} (singlet)

H_4 index-1 saddle points





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L. Grazioli, Y. Hu, E. Cancès, arXiv:2506.16420, 2025. Accepted J. Chem. Phys.

Conclusions

Universal derivation of LR equations based on Kähler manifolds; derivation for HF and CASSCF

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Universal derivation of LR equations based on Kähler manifolds; derivation for HF and CASSCF

Next steps

– comparison between linear response, state specific and state average results for CASSCF
– testing on bigger molecules
– implementation of second-order methods for faster convergence
– extend to other methods in quantum chemistry

L. Grazioli, Y. Hu, E. Cancès, arXiv:2506.16420, 2025. Accepted in J. Chem. Phys.

Eric Cancès
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Tony Lelièvre
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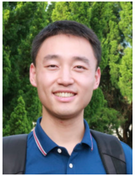
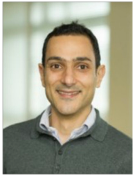
European Research Council
Established by the European Commission



Yukuan Hu
(ENPC)



Panos Parpas
(ICL)

Tommaso Nottoli
(UniPi)

EMC²
Extreme-scale Mathematically-based Computational Chemistry

Thank you for your attention!

LR-UHF vs CP-UHF

$$\omega^{\text{LR-UHF},(1)}_{\text{HOMO-LUMO}} = \sum_{i=1}^{N_p-1} (N_p+1, N_p+1||i,i)_{\beta\beta} - \sum_{i=1}^{N_p-1} (N_p, N_p||i,i)_{\beta\beta}$$
$$+ \sum_{i=1}^{N_p} (N_p+1, N_p+1|i,i)_{\beta\alpha} - \sum_{i=1}^{N_p} (N_p, N_p|i,i)_{\beta\alpha}$$
$$-(N_p, N_p+1|N_p+1, N_p)_{\beta\alpha}$$

$$\omega^{\text{CP-UHF},(1)}_{\text{HOMO-LUMO}} = \sum_{i=1}^{N_p-1} (N_p+1, N_p+1||i,i)_{\beta\beta} - \sum_{i=1}^{N_p-1} (N_p, N_p||i,i)_{\beta\beta}$$
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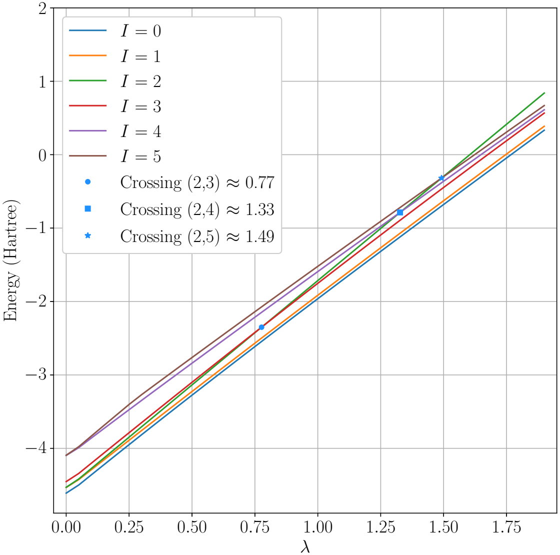
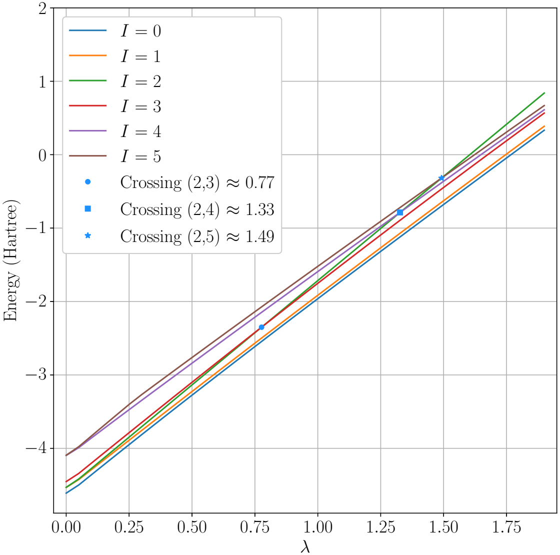
H_4 index-1 saddle points



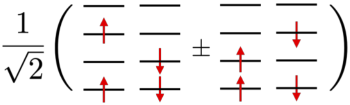
- FCI states are spin-eigenfunctions

H_4 index-1 saddle points



- FCI states are spin-eigenfunctions
- degeneracies at $\lambda = 0$ for singlet and triplet states with $S_z = 0$

$$\frac{1}{\sqrt{2}}\left(\quad \pm \quad \right)$$



Different approaches

CISD	LR for variational models
Compute HF ground state $\Phi_0 \in \operatorname{argmin}_\Phi E^{\mathrm{HF}}(\Phi)$ $x_0 \in \operatorname{argmin}_{x \in \mathcal{M}} \mathcal{E}(x)$	Compute a ground state of the model

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Identity CISD subspace canonical basis $\mathcal{H}^{\mathrm{CISD}} = \mathrm{Span}(\Phi_0, \Phi_i^a, \Phi_{ij}^{ab})$ $T_{x_0}\mathcal{M}_{\mathbb{R}} = \mathrm{Span}_{\mathbb{R}}(u_1, \ldots, u_n, -J_{x_0}u_1, \ldots, -J_{x_0}u_n)$	Identify the canonical basis of $T_{x_0}\mathcal{M}_{\mathbb{R}}$

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Build matrix of $\widehat{H}$ in this basis $\mathfrak{H}_0^{\text{CISD}} = \begin{pmatrix} E_0^{\text{HF}} & \langle\Phi_0\vert\widehat{H}\vert\Phi_i^a\rangle & \langle\Phi_0\vert\widehat{H}\vert\Phi_{ij}^{ab}\rangle \\ * & \langle\Phi_i^a\vert\widehat{H}\vert\Phi_j^b\rangle & \langle\Phi_i^a\vert\widehat{H}\vert\Phi_{jk}^{bc}\rangle \\ * & * & \langle\Phi_{ij}^{ab}\vert\widehat{H}\vert\Phi_{kl}^{cd}\rangle \end{pmatrix}$ $\mathfrak{H}_0^{\text{LR}} = \begin{pmatrix} \mathfrak{h}_{qq} & \mathfrak{h}_{qp} \\ \mathfrak{h}_{qp}^T & \mathfrak{h}_{pp} \end{pmatrix}$	Build the matrix of $\text{Hess}_\mathcal{M}\mathcal{E}(x_0)$ in this basis

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Compute HF ground state $\Phi_0 \in \operatorname{argmin}_\Phi E^{\text{HF}}(\Phi)$ $x_0 \in \operatorname{argmin}_{x\in\mathcal{M}} \mathcal{E}(x)$	Compute a ground state of the model
Identity CISD subspace canonical basis $\mathcal{H}^{\text{CISD}} = \text{Span}(\Phi_0, \Phi_i^a, \Phi_{ij}^{ab})$ $T_{x_0}\mathcal{M}_\mathbb{R} = \text{Span}_\mathbb{R}(u_1, \dots, u_n, -J_{x_0}u_1, \dots, -J_{x_0}u_n)$	Identify the canonical basis of $T_{x_0}\mathcal{M}_\mathbb{R}$
Build matrix of $\widehat{H}$ in this basis $\mathfrak{H}_0^{\text{CISD}} = \begin{pmatrix} E_0^{\text{HF}} & \langle\Phi_0\|\widehat{H}\|\Phi_i^a\rangle & \langle\Phi_0\|\widehat{H}\|\Phi_{ij}^{ab}\rangle \\ * & \langle\Phi_i^a\|\widehat{H}\|\Phi_j^b\rangle & \langle\Phi_i^a\|\widehat{H}\|\Phi_{jk}^{bc}\rangle \\ * & * & \langle\Phi_{ij}^{ab}\|\widehat{H}\|\Phi_{kl}^{cd}\rangle \end{pmatrix}$ $\mathfrak{H}_0^{\text{LR}} = \begin{pmatrix} \mathfrak{h}_{qq} & \mathfrak{h}_{qp} \\ \mathfrak{h}_{qp}^T & \mathfrak{h}_{pp} \end{pmatrix}$	Build the matrix of $\text{Hess}_\mathcal{M}\mathcal{E}(x_0)$ in this basis
Compute eigenvalues of $\mathfrak{H}_0^{\text{CISD}}$	Compute symplectic eigenvalues of $\mathfrak{H}_0^{\text{LR}}$