Implications of pinned occupation numbers for natural orbital expansions

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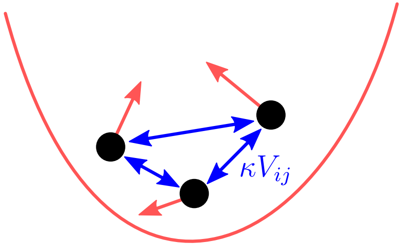
In collaboration with:
Christian Schilling (LMU, Munich), Carlos L Benavides-Riveros (MPIPKS Dresden), Adam Sawicki (CTP PAS, Warsaw), David Gross & Alexandre Lopes (University of Cologne),

Implications of pinned occupation numbers for natural orbital expansions: I & II (2020), New Journal of Physics. 22, 023001 & 023002

Motivation – consider a fermionic interacting system

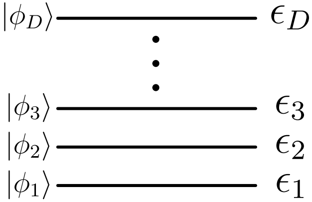


$$H(\kappa) = h + \kappa V$$

- h – single-particle Hamiltonian
- V – interaction
- $\kappa > 0$ – interaction strength

No interactions – Hartree-Fock state

If $\kappa = 0$, then $H \equiv h$.



$$h = \sum_{i=1}^{D} \epsilon_i |\phi_i\rangle\langle\phi_i|$$

N-fermion ground state:

$$|HF(h)\rangle = f^\dagger_{\phi_1} \dots f^\dagger_{\phi_N} |vac\rangle =: |\phi_1, \dots, \phi_N\rangle.$$

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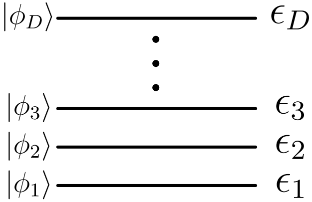

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If $\kappa > 0$, then the ground state is in principle a superposition of all the configurations

$$|\Phi_N(\kappa)\rangle = \sum_{i_1 < \dots < i_N} c_{i_1,\dots,i_N}(\kappa) |\phi_{i_1}, \dots, \phi_{i_N}\rangle \in \Lambda^N \left(\mathbb{C}^D\right).$$

Back to $\kappa = 0$

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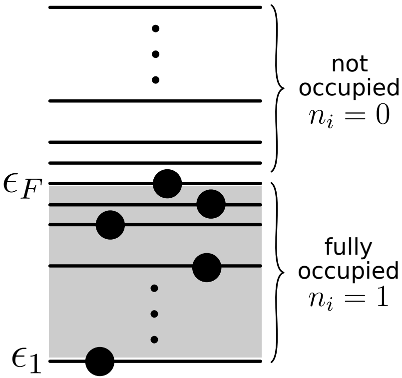
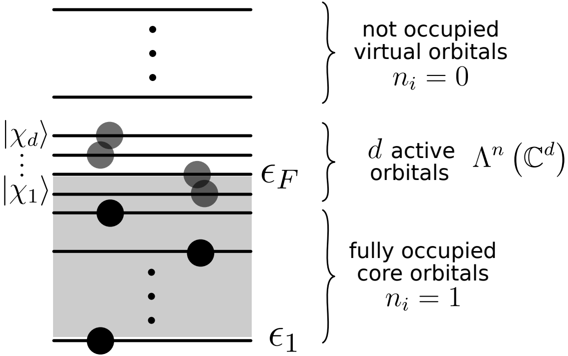


Complete active space ansatz

$$H(\kappa) = h + \kappa V, \quad \kappa << 1$$



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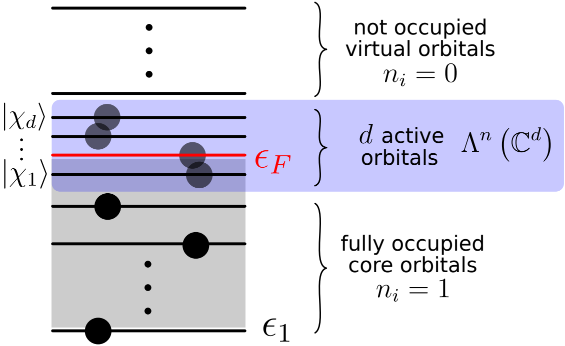

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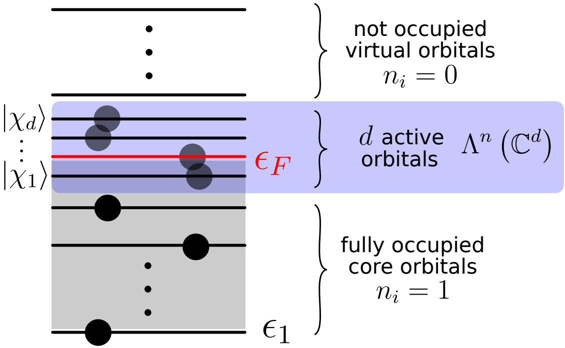

Complete active space ansatz

$$|\Psi_n\rangle = \sum_{1<i_1<\cdots<i_n<d} c_{i_1,\ldots,i_n} |\chi_{i_1},\ldots,\chi_{i_n}\rangle \in \Lambda^n\left(\mathbb{C}^d\right).$$

Complete active space self consistent field ansatz

$$|\Psi_n\rangle = \sum_{i_1<\cdots<i_n} c_{i_1,\ldots,i_n} |\chi_{i_1},\ldots,\chi_{i_n}\rangle \in \Lambda^n\left(\mathbb{C}^d\right).$$

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- optimisation over the coefficients $c_{i_1,\ldots,i_n}$,
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Multi configurational self consistent field ansatz:

- only a subset of all configurations $|\chi_{i_1}, \ldots, \chi_{i_n}\rangle$ enters the ansatz $|\Psi_n\rangle$,
- optimisation over the the coefficients and the active orbitals $|\chi_1\rangle, \ldots, |\chi_d\rangle$.

Multi configurational self consistent field ansatz optimisation

$$|\Psi_n\rangle = \sum_{(i_1,\ldots,i_n)\in\mathcal{I}} c_{i_1,\ldots,i_n} |\chi_{i_1},\ldots,\chi_{i_n}\rangle, \quad |\chi_k\rangle = \sum_l U_{kl}|\psi_k\rangle,$$

$$E_{MCSCF} = \min_{c_{i_1,\ldots,i_n},U} \langle\Psi_n|H|\Psi_n\rangle.$$

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Potential issues:

- computing $\langle\Psi_n|H|\Psi_n\rangle$ in different orbital bases,
- convergence of the minimisation,
- **large number of configurations** $\binom{d}{n}$**.**

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This talk

A **systematic** construction of ansatz states that involves **few configurations** relative to the active Hilbert space size $\binom{d}{n}$.

Natural orbitals & natural occupation numbers

The one-fermion reduced density matrix

$$\rho_{ij}\left(|\Psi_n\rangle\right) = \langle\Psi_n|f^\dagger_{\chi_j} f_{\chi_i}|\Psi_n\rangle.$$

The $d \times d$ matrix $\rho\left(|\Psi_n\rangle\right)$ can be diagonalised:

$$\rho\left(|\Psi_n\rangle\right) = \sum_{k=1}^{d} n_k |k\rangle\langle k|$$

so that $n_1 \geq n_2 \geq \cdots \geq n_d$.

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- Numbers $n_1, \ldots, n_d$ are the **natural occupation numbers**.
- Orbitals $|1\rangle, \ldots, |d\rangle$ are the **natural orbitals**.

Pauli constraints

Consider the map:

$$\Lambda^n\left(\mathbb{C}^d\right) \ni |\Psi_n\rangle \to \rho\left(|\Psi_n\rangle\right) \to (n_1, \ldots, n_d), \quad n_1 \geq n_2 \geq \cdots \geq n_d.$$

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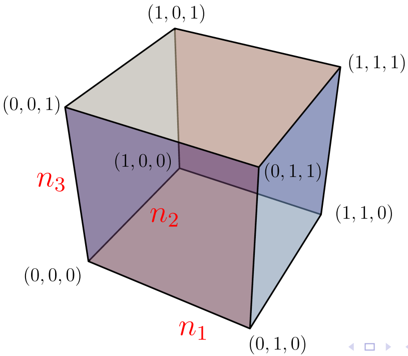
Question: What is the image of the map $|\Psi_n\rangle \to (n_1, \ldots, n_d)$?

It is contained in the d-dimensional hypercube $0 \leq n_k \leq 1$, $k = 1, \ldots, d$.



Pauli constraints and CASSCF

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This leaves the effective Hibert space

$$\Lambda^n \left(\mathbb{C}^d \right)$$

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Strategy: Start with small n, d and incrementally increase the size of the active space and the number of active electrons.

Generalised Pauli constraints

The Pauli constraints $0 \leq n_k \leq 1$ **are not the only ones!** (On top of ordering $n_1 \geq \cdots \geq n_d$ and normalisation $n_1 + \cdots + n_d = n$).

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- If $n = 3$ and $d = 6$, then we have further constraints by Borland and Dennis (1972).

$$n_1 + n_6 = n_2 + n_5 = n_3 + n_4 = 1\,,$$
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Breakthrough by Klyachko (2005) – the image of $|\Psi_n\rangle \to (n_1, \ldots, n_d)$ is a **convex polytope** + an algorithm for finding the polytope. **Current record**: $n = 5$, $d = 11$.

Borland-Dennis polytope (1972) – $\Lambda^3\left(\mathbb{C}^6\right)$

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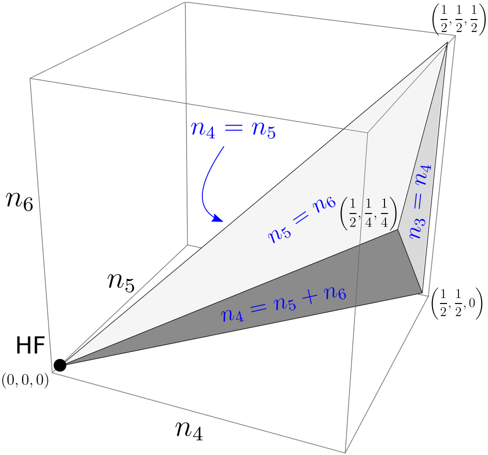
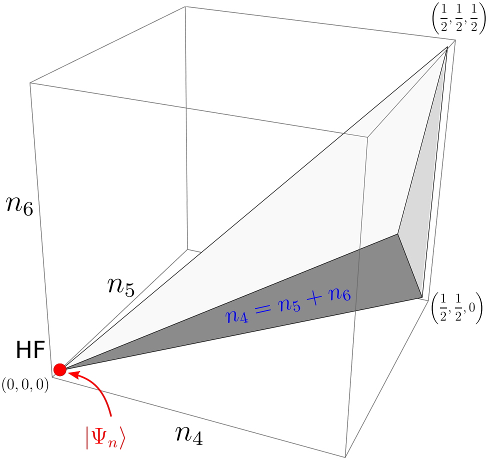


$$n_4 \leq n_5 + n_6, \quad n_1 \geq n_2 \geq \ldots \geq n_6 \geq 0.$$

Hartree-Fock method



$$|\Psi_n\rangle \to (1,1,1,0,0,0) = HF$$

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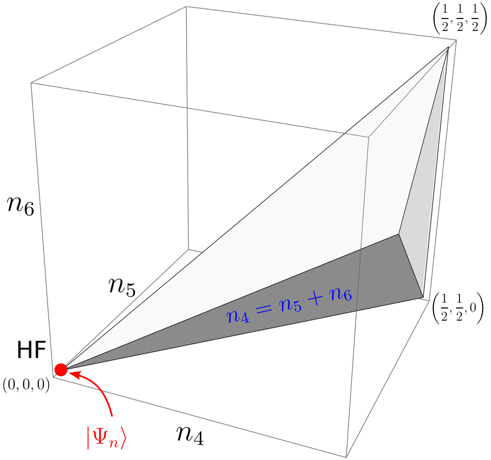
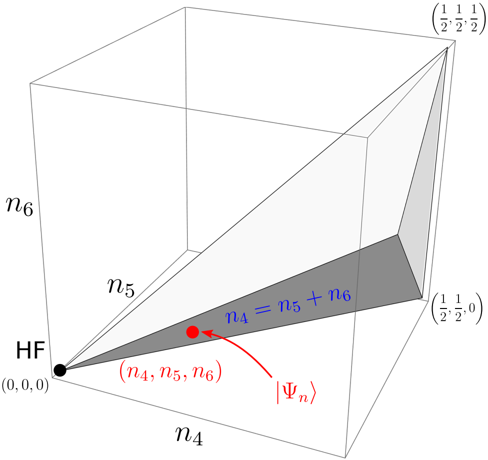


$$|\Psi_n\rangle \to (1,1,1,0,0,0) = HF \implies |\Psi_n\rangle = |1,2,3\rangle.$$

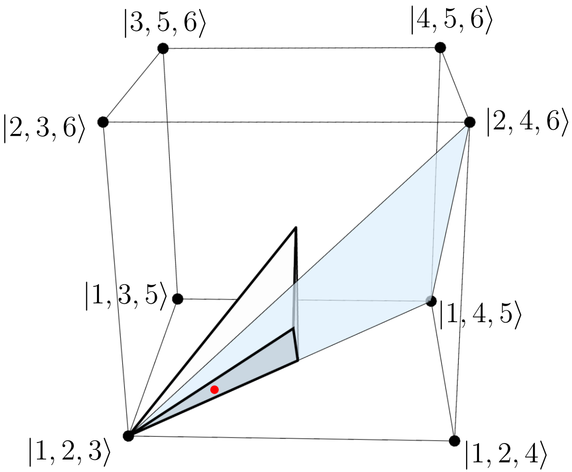
Pinning-based multiconfigurational ansatz



What if $|\Psi_n\rangle \to (n_1, \ldots, n_6)$ saturates a **generalised** Pauli constraint?

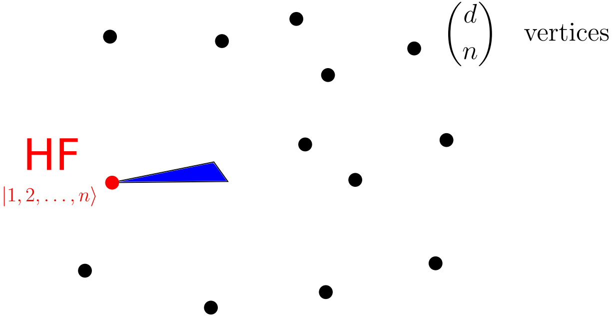
$$n_4 = n_5 + n_6$$

Pinning-based multiconfigurational ansatz



$$|\Psi_n\rangle = c_1|1,2,3\rangle + c_2|1,4,5\rangle + c_3|2,4,6\rangle.$$

Pinning-based multiconfigurational ansatz – general setting



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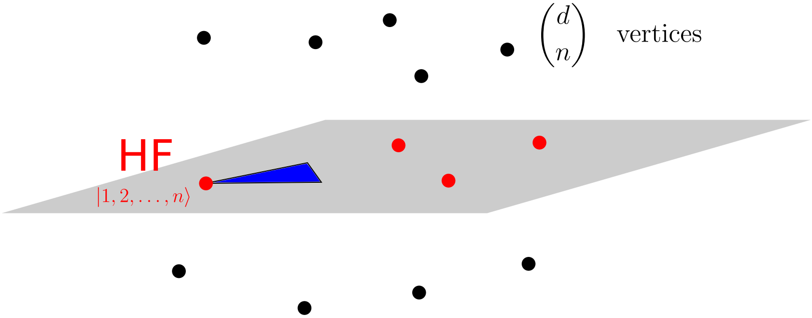

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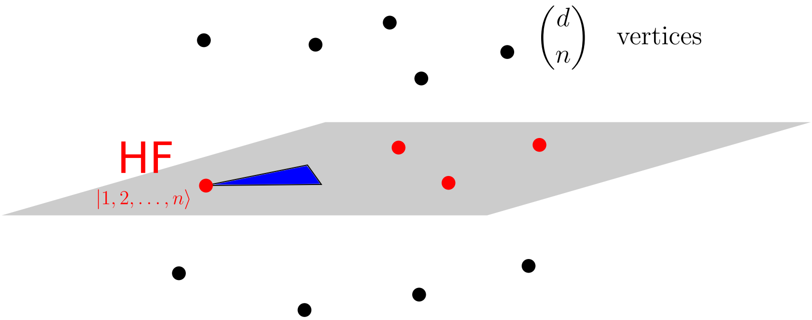
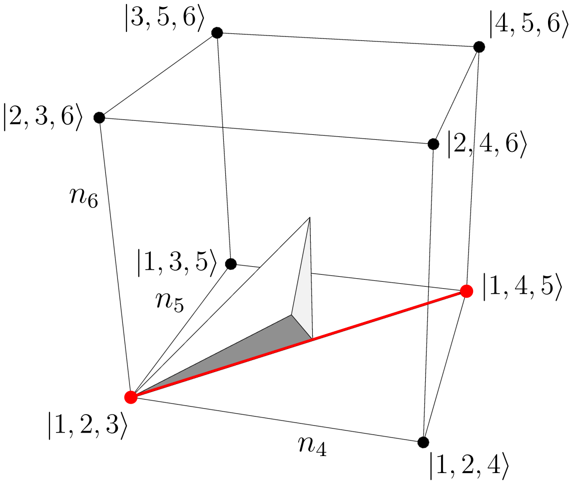


Theorem (C Schilling et al 2020 & T Maciazek et al 2020)

If occupation numbers saturate a generalised Pauli constraint, then the configurations entering the n-fermion state lie on the hyperplane containing that face.

Ansatz associated with an extremal edge

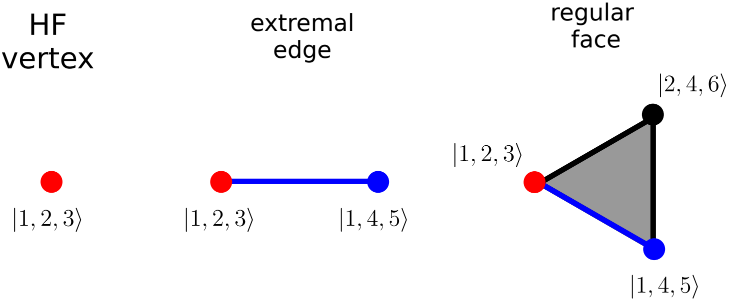


$$|\Psi_n\rangle = c_1|1,2,3\rangle + c_2|1,4,5\rangle.$$

This is CASSCF with $n_1 = 1$ and $n_6 = 0$!

A family of MCSCF ansatz states

For $d = 6$ and $n = 3$ we have constructed a **nested family of MCSCF ansatz states**.



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$CASSCF$

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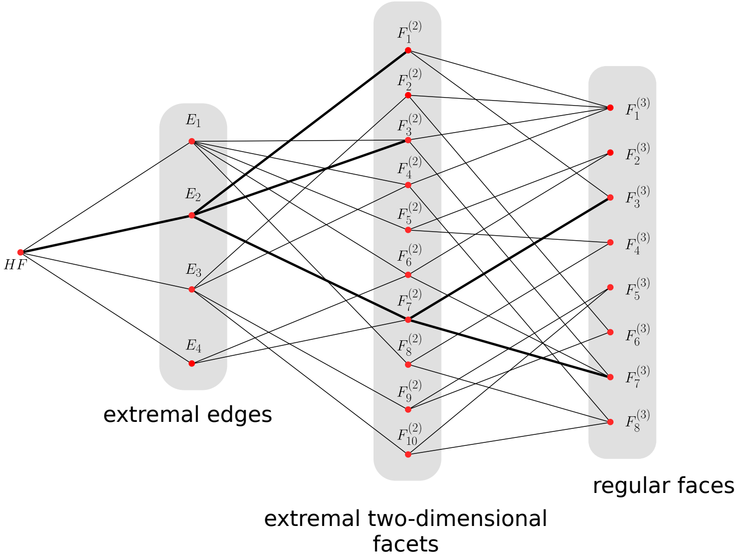
MCSCF ansatz states in higher dimensions



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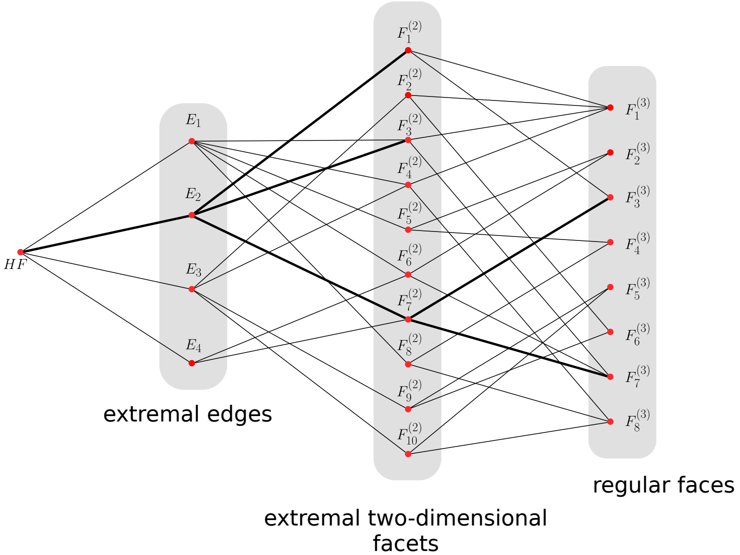

Numerics – work in progress... (T. Maciazek, C. Schilling, P. Knowles).

MCSCF ansatz states – properties

So defined ansatz states contain very few configurations.

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Example $N = 3$ and $d = 8$. Consider a regular face of the polytope:

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Try: $|2, 4, 6\rangle$, i.e.

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Configuration $|2, 4, 6\rangle$ **does not** enter the ansatz!

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Task: Find configurations $|i_1, i_2, i_3\rangle$ satisfying

$$19n_1 + 11n_2 - 21n_3 - 13n_4 - 5n_5 - 5n_6 + 3n_7 + 11n_8 = 9.$$

Try: $|1, 5, 6\rangle$, i.e.

$$n_2 = n_3 = n_4 = n_7 = n_8 = 0, \quad n_1 = n_5 = n_6 = 1.$$

$19\cdot 1 + 11\cdot 0 - 21\cdot 0 - 13\cdot 0 - 5\cdot 1 - 5\cdot 1 + 3\cdot 0 + 11\cdot 0 = 19 - 5 - 5 = 9.$

Configuration $|1, 5, 6\rangle$ **does** enter the ansatz!

MCSCF ansatz states – properties

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The configurations that saturate the inequality are: $|1,2,3\rangle$, $|1,5,6\rangle$, $|1,3,8\rangle$, $|2,5,7\rangle$, $|5,7,8\rangle$, $|2,4,8\rangle$, $|1,4,7\rangle$, $|2,6,7\rangle$, $|6,7,8\rangle$.

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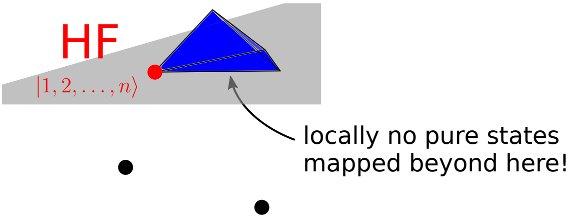
Only 9 configurations out of the total of $\binom{8}{3} = 56$.

Methods



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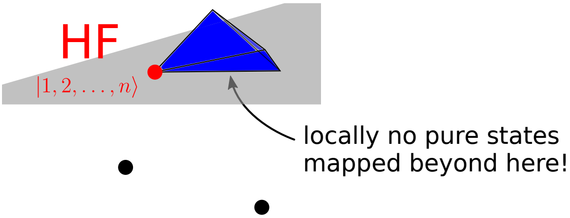

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- differential-geometric and group-theoretic methods,
- the the map $|\Psi_n\rangle \to (n_1, \ldots, n_d)$ is **singular** on the regular boundary of the polytope,
- kernel of the derivative matrix is nontrivial $\Longrightarrow$ constraints for $|\Psi_n\rangle$.

Summary

- A construction of families of MCSCF variational ansatz states implied by the (quasi)pinning of the natural occupation numbers to the boundary of the spectral polytope.

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Outlook:

- Imposing spin conservation symmetries allows to include more spin-orbitals.
- Numerical applications.

Spin-adapted MCSCF ansatz states

So far, we have considered spinless fermions or **spin-orbitals**

$$|\chi_{1\uparrow}\rangle, |\chi_{1\downarrow}\rangle, \ldots, |\chi_{r\uparrow}\rangle, |\chi_{r\downarrow}\rangle, \quad d = 2r.$$

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The orbital one-electron reduced density matrix (a $r \times r$ matrix) is given by

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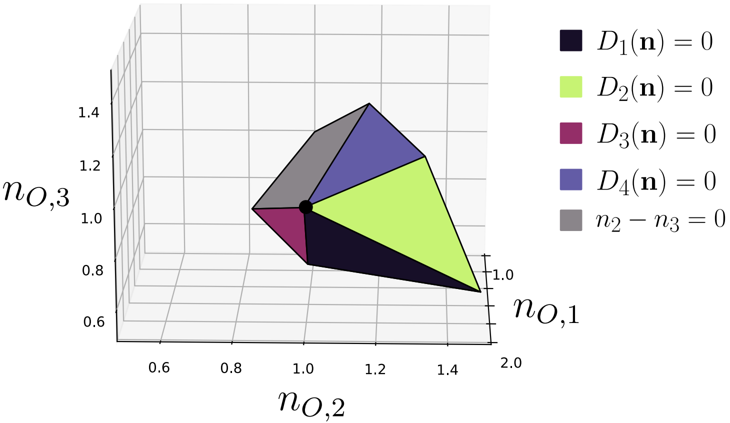
The image of $|\Psi_n\rangle \to (n_{O,1}, \ldots, n_{O,r})$ is again a convex polytope (depends on n, r, S, S_z).

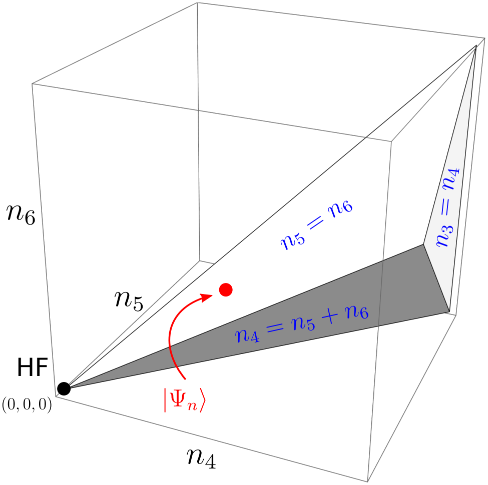
Four-electron triplet $r = 4$ (courtesy of M Altunbulak)



So far, polytopes up to $r = 7$ (so 14 spin-orbitals).

Singular faces

Is there an ansatz associated with the face $n_5 = n_6$?



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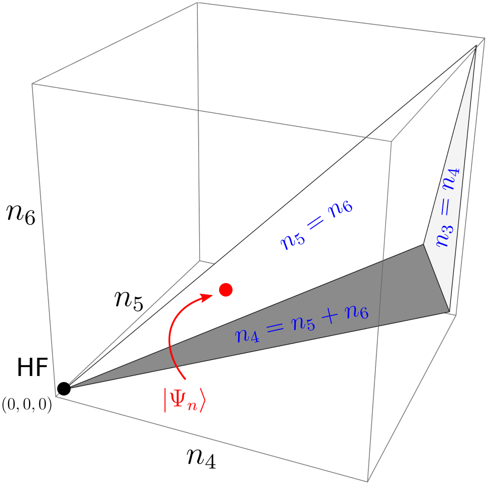
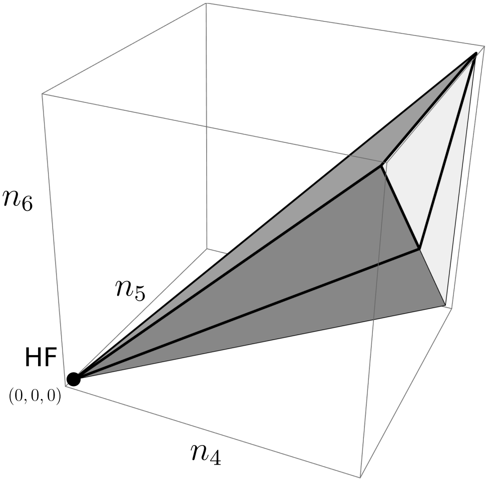


There are states mapped beyond this face, so **no ansatz**!

Reflected polytope $n_5 \leftrightarrow n_6$

Face $n_5 = n_6$ is not extremal.



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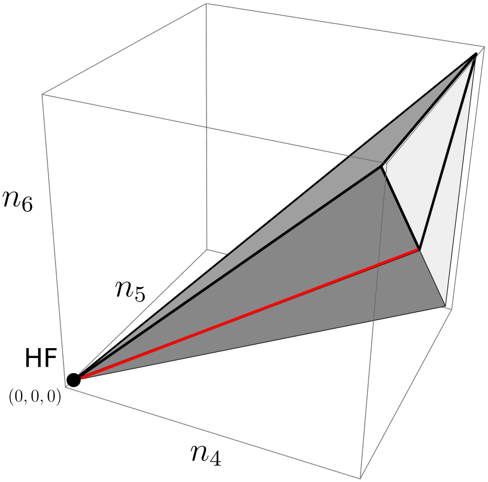
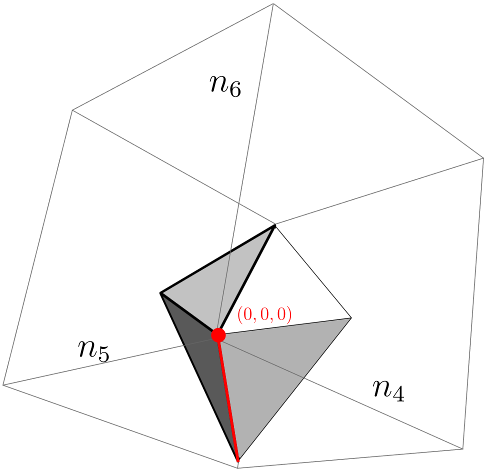


One of the edges is not extremal as well.

Reflected polytope $n_4 \leftrightarrow n_5$

Face $n_4 = n_5$ is not extremal.



This edge is extremal $\Longrightarrow$ another ansatz!

Degenerate natural occupation numbers

If $|\Psi_n\rangle \to (n_1, \ldots, n_d)$ and $n_i = n_{i+1}$, then the choice of natural orbitals $|i\rangle$ and $|i+1\rangle$ is not unique.

$$|i\rangle \to a|i\rangle + b|i+1\rangle, \quad |i+1\rangle \to c|i\rangle + d|i+1\rangle.$$

Theorem 2* (C Schilling et al 2020 & T Maciazek et al 2020)

Assume $|\Psi_n\rangle \to (n_1, \ldots, n_d)$ with degenerate $(n_1, \ldots, n_d)$ belonging to exactly one regular face of the polytope given by the inequality

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* correct under a technical combinatorial assumption which we have checked to be satisfied for any system where the generalised Pauli constraints are explicitly known.