Ensemble reduced density matrix functional theory for excited states and hierarchical generalization of Pauli's exclusion principle

Julia Liebert

12.10.2022

In collaboration with:

Christian Schilling, Federico Castillo, Jean-Philippe Labbé

Motivation

1RDM:

$$\boxed{\hat{\gamma} = N\mathrm{Tr}_{N-1}[\hat{\Gamma}] \equiv \sum_\alpha \lambda_\alpha |\alpha\rangle\langle\alpha|}$$

natural occupation numbers

natural orbitals

Conjugate variables: $\hat{h} \leftrightarrow \hat{\gamma}$

Motivation

1RDM: $$\boxed{\hat{\gamma} = N\mathrm{Tr}_{N-1}[\hat{\Gamma}] \equiv \sum_\alpha \lambda_\alpha |\alpha\rangle\langle\alpha|}$$

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Conjugate variables: $\hat{h} \leftrightarrow \hat{\gamma}$

Hamiltonian: $\hat{H}(\hat{h}) = \hat{h} + \boxed{\hat{W}}$ fixed!

Motivation

1RDM: $$\boxed{\hat{\gamma} = N\mathrm{Tr}_{N-1}[\hat{\Gamma}] \equiv \sum_\alpha \lambda_\alpha |\alpha\rangle\langle\alpha|}$$

natural occupation numbers

natural orbitals

Conjugate variables: $\hat{h} \leftrightarrow \hat{\gamma}$

Hamiltonian: $\hat{H}(\hat{h}) = \hat{h} + \boxed{\hat{W}}$ fixed!

$$\Rightarrow \boxed{E(\hat{h}) = \min_{\hat{\gamma}}[\mathrm{Tr}_1[\hat{h}\hat{\gamma}] + \mathcal{F}(\hat{\gamma})]}$$

universal functional

[T. L. Gilbert, Phys. Rev. B **12**, 2111 (1975),
M. Levy, Proc. Natl. Acad. Sci. U.S.A **76**, 6062 (1979),
S.M. Valone, J. Chem. Phys. **73**, 1344 (1980)]

$\Rightarrow$ Explicitly allows for fractional occupation numbers! ☺

DFT

1-RDMFT

DFT

- Ground states ✓

1-RDMFT

- Ground states ✓

DFT

- Ground states ✓
- Excited states?
  - → Time-dependent DFT ✓

    [E. Runge, E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).]
  - → Ensemble DFT ✓

    [E. K. U. Gross, L. N. Oliveira, W. Kohn, Phys. Rev. A **37**, 2809 (1988).]

1-RDMFT

- Ground states ✓
- Excited states?
  - → Time-dependent 1-RDMFT ✓

    [K. Pernal and K. J. H. Giesbertz, Spinger (2015).]
  - → Ensemble 1-RDMFT ✗

    ⇒ **Goal of this talk**

    [C. Schilling, S. Pittalis, Phys. Rev. Lett. **127**, 023001 (2021),
    J. Liebert, F. Castillo, J.-P. Labbé, C. Schilling, J. Chem. Theory Comput. **19**, 124 (2022)]

Outline

1) Foundation of excited state 1-RDMFT

2) Domain of $\mathcal{F}_{\boldsymbol{w}}$: Generalizing Valone

3) Hierarchy of exclusion principle constraints

1) Foundation of excited state 1-RDMFT

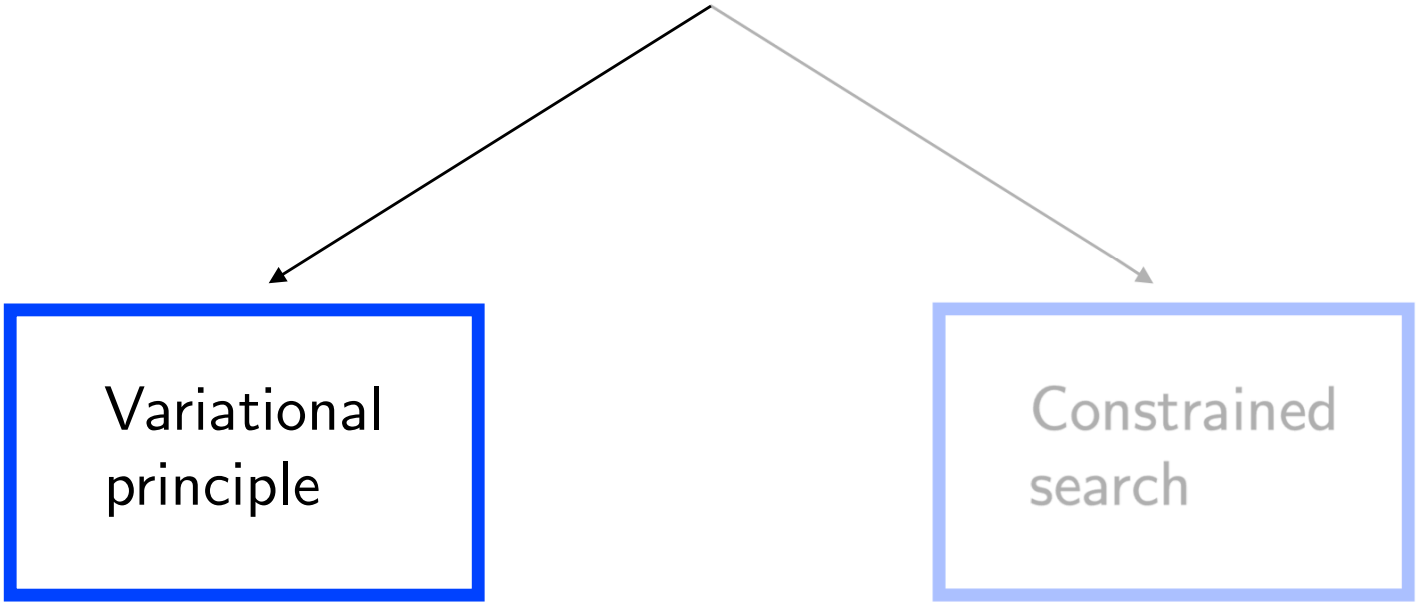
2 key ingredients

Variational principle

Constrained search

1) Foundation of excited state 1-RDMFT

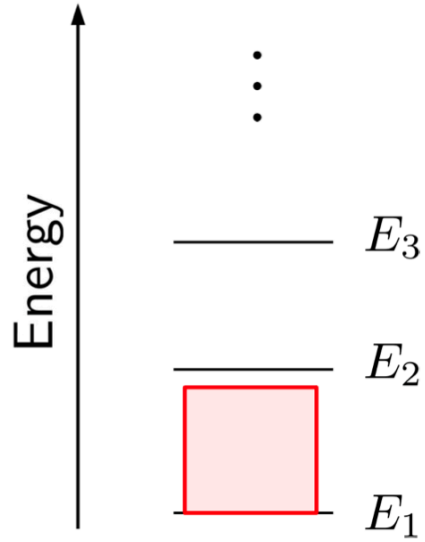
2 key ingredients



GOK variational principle

Rayleigh-Ritz: $E_1 = \min_{|\Psi\rangle} \langle \Psi | \hat{H} | \Psi \rangle$

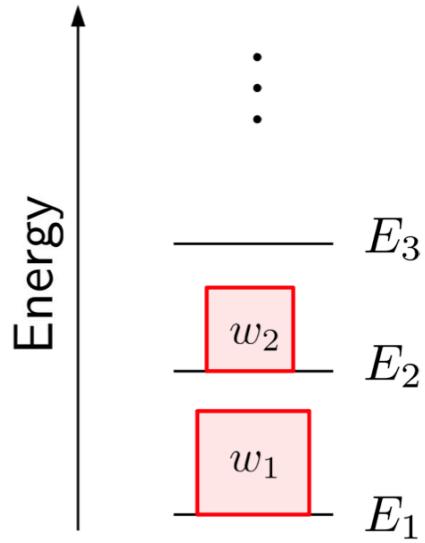
ground state energy



[E. K. U. Gross, L. N. Oliveira, W. Kohn, Phys. Rev. A **37**, 2805 (1988).]

GOK variational principle

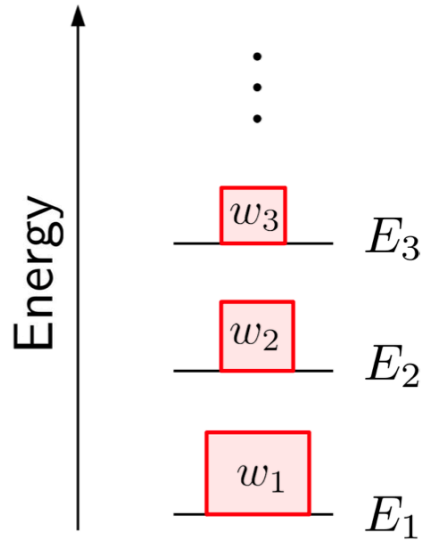
$$w_1 E_1 + w_2 E_2 = \min_{w_1|\Psi_1\rangle\langle\Psi_1| + w_2|\Psi_2\rangle\langle\Psi_2|} \mathrm{Tr}_N[(w_1|\Psi_1\rangle\langle\Psi_1| + w_2|\Psi_2\rangle\langle\Psi_2|)\hat{H}]$$



[E. K. U. Gross, L. N. Oliveira, W. Kohn, Phys. Rev. A **37**, 2805 (1988).]

GOK variational principle

$$E_{\boldsymbol{w}} = \sum_{j=1} w_j E_j = \min_{\hat{\Gamma}\in\mathcal{E}^N(\boldsymbol{w})} \mathrm{Tr}_N[\hat{\Gamma}\hat{H}], \quad \hat{\Gamma} \in \mathcal{E}^N(\boldsymbol{w}) \Leftrightarrow \mathrm{spec}^{\downarrow}(\hat{\Gamma}) = \boldsymbol{w}$$



[E. K. U. Gross, L. N. Oliveira, W. Kohn, Phys. Rev. A **37**, 2805 (1988).]

1) Foundation of excited state 1-RDMFT

2 key ingredients

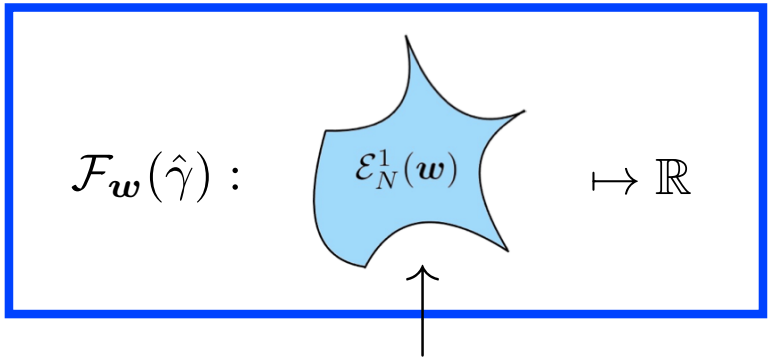
Variational principle

Constrained search

Constrained search

$$
\begin{aligned}
E_{\boldsymbol{w}} &= \min_{\hat{\Gamma}\in\mathcal{E}^N(\boldsymbol{w})} \mathrm{Tr}_N\left[(\hat{h}+\hat{W})\hat{\Gamma}\right] \\
&= \min_{\hat{\gamma}\in\mathcal{E}^1_N(\boldsymbol{w})} \left[\mathrm{Tr}_1[\hat{h}\hat{\gamma}] + \min_{\hat{\Gamma}\mapsto\hat{\gamma}} \mathrm{Tr}_N[\hat{W}\hat{\Gamma}]\right] \\
&\equiv \min_{\hat{\gamma}\in\mathcal{E}^1_N(\boldsymbol{w})} \left[\mathrm{Tr}_1[\hat{h}\hat{\gamma}] + \mathcal{F}_{\boldsymbol{w}}(\hat{\gamma})\right]
\end{aligned}
$$

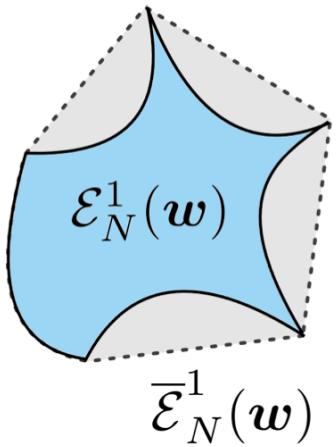
[M. Levy, Proc. Natl. Acad. Sci. U.S.A **76**, 6062 (1979),
E. H. Lieb, J. Quantum Chem. **24**, 243 (1983)]



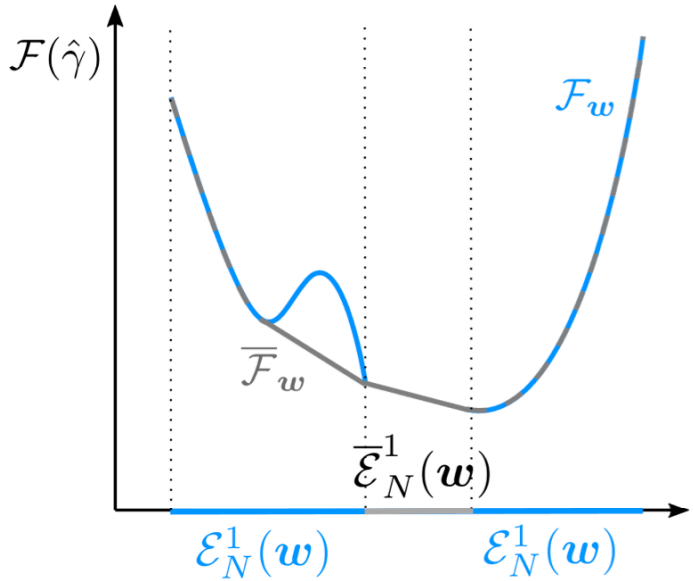
Too complicated!

2) Domain of $\mathcal{F}_{\boldsymbol{w}}$: Generalizing Valone

Key idea: Exact convex relaxation



$$\overline{\mathcal{E}}_N^1(\boldsymbol{w}) = \mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w}))$$

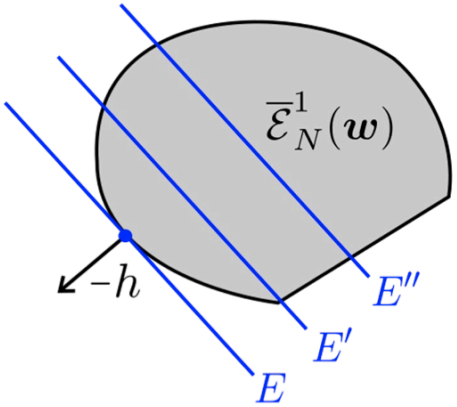


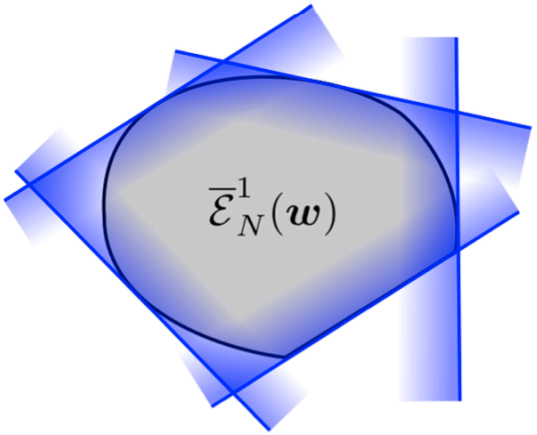
$$\overline{\mathcal{F}}_{\boldsymbol{w}}(\hat{\gamma}) = \mathrm{conv}(\mathcal{F}_{\boldsymbol{w}})$$

$\Rightarrow$ Turns excited state 1-RDMFT into a feasible method

[C. Schilling, S. Pittalis,Phys. Rev. Lett. **127**, 023001 (2021),
J. Liebert, F. Castillo, J.-P. Labbé, C. Schilling, J. Chem. Theory Comput. **19**, 124 (2022).]

1) Duality principle:





$\Rightarrow$ Minimize over linear functional $\langle \hat{h}, \hat{\gamma} \rangle_1 \equiv \mathrm{Tr}_1[\hat{h}\hat{\gamma}]$

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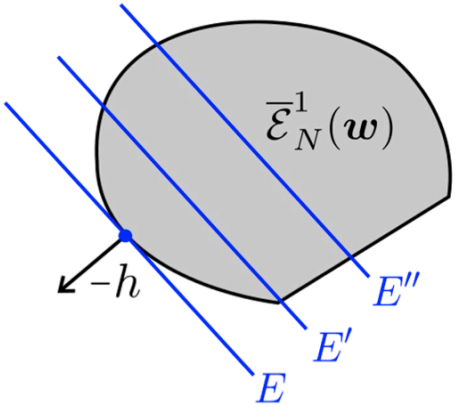
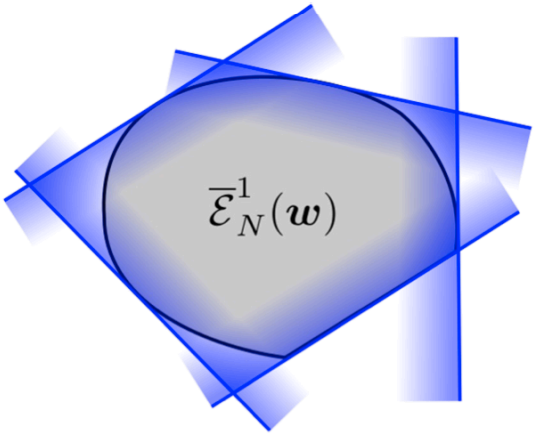




$\Rightarrow$ Minimize over linear functional $\langle \hat{h}, \hat{\gamma} \rangle_1 \equiv \mathrm{Tr}_1[\hat{h}\hat{\gamma}]$

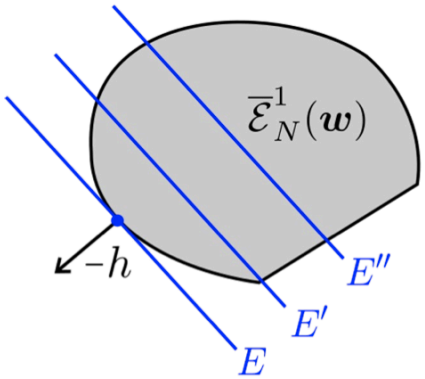
2) Unitary invariance:

$$\hat{u}_1 \overline{\mathcal{E}}_N^1(\boldsymbol{w}) \hat{u}_1^\dagger = \overline{\mathcal{E}}_N^1(\boldsymbol{w}) \quad \forall \text{ unitaries } \hat{u}_1$$

$\Rightarrow$ $\boxed{\Sigma(\boldsymbol{w}) = \mathrm{spec}(\overline{\mathcal{E}}_N^1(\boldsymbol{w}))}$ is sufficient

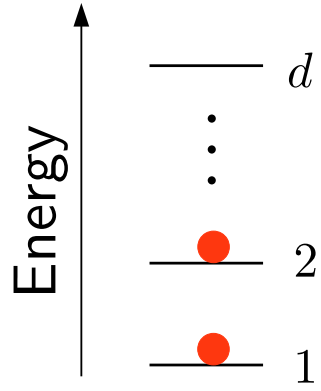
Spectral polytope

Mathematical problem



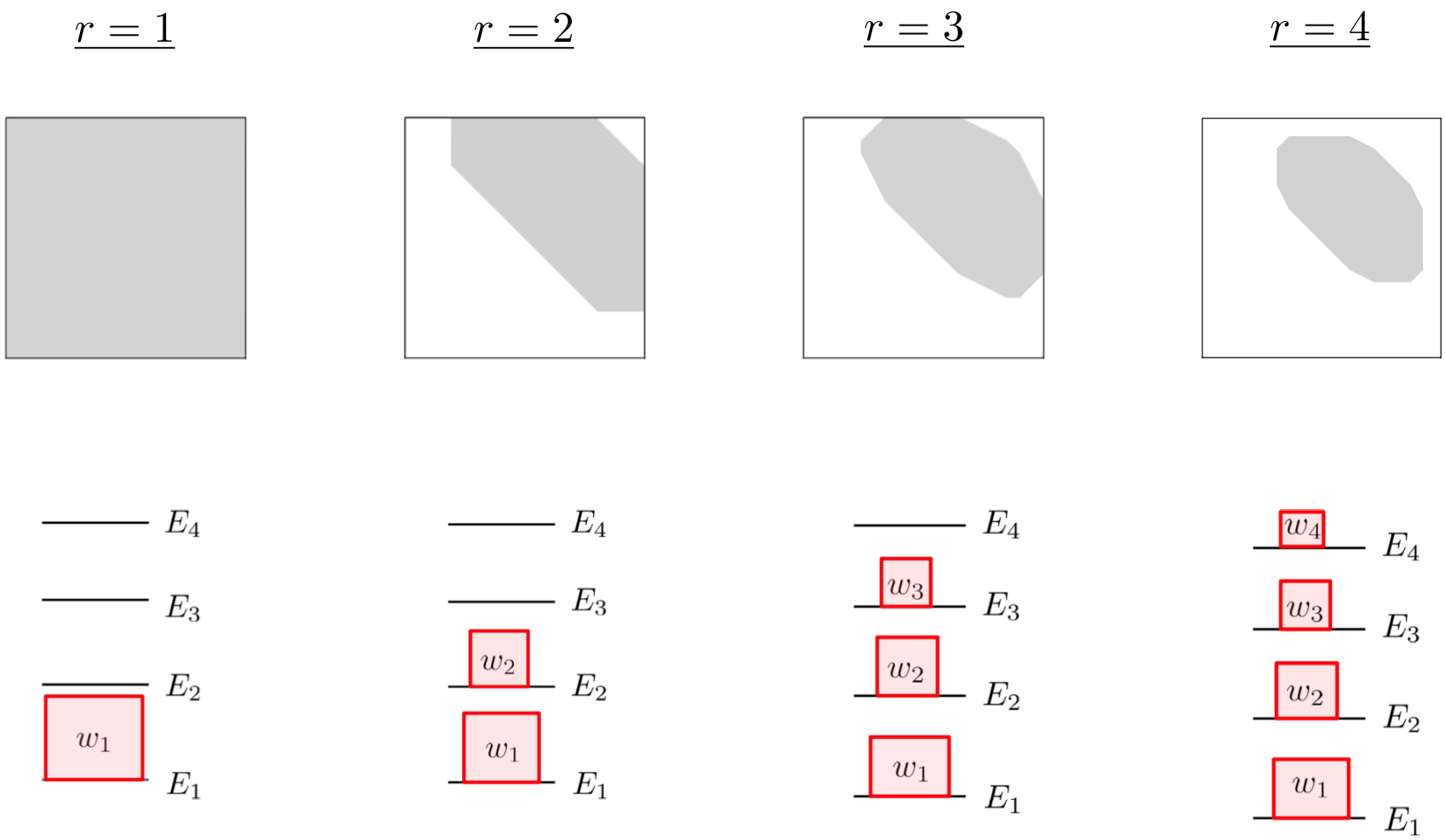
Minimize $\mathrm{Tr}_1[\hat{h}\hat{\gamma}]$ for all $\hat{h}$

Physical problem



Describe excitation spectrum of non-interacting fermions

3) Hierarchy of exclusion principle constraints



[J. Liebert, F. Castillo, J.-P. Labbé, C. Schilling, J. Chem. Theory Comput. **19**, 124 (2022),
F. Castillo, J.-P. Labbé, J. Liebert, A. Padrol, E. Philippe, C. Schilling, arXiv:2105.06459, submitted (2021)]

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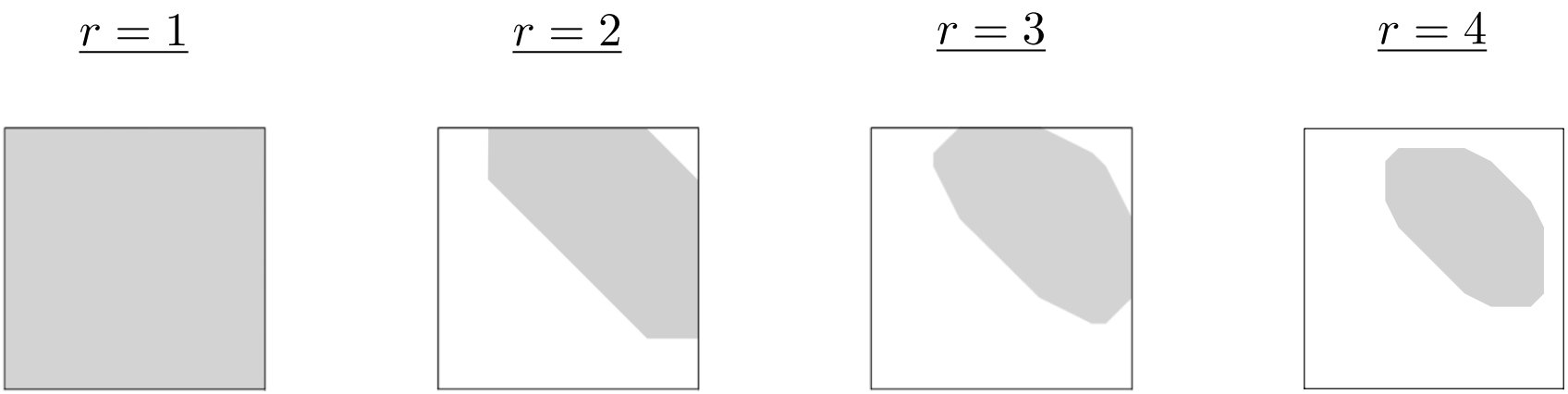

$$
\begin{cases}
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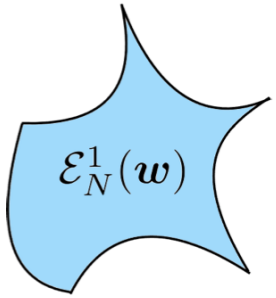
\lambda_1^{\downarrow} \leq 1 \\
\lambda_1^{\downarrow} + \lambda_2^{\downarrow} + \ldots + \lambda_N^{\downarrow} \leq N - 1 + w_1
\end{cases} \\
2 \sum_{j=1}^{N-1} \lambda_j^{\downarrow} + \lambda_N^{\downarrow} + \lambda_{N+1}^{\downarrow} \leq 2(N-1) + w_1 + w_2 \\
\vdots
\end{cases}
$$

[J. Liebert, F. Castillo, J.-P. Labbé, C. Schilling, J. Chem. Theory Comput. **19**, 124 (2022),
F. Castillo, J.-P. Labbé, J. Liebert, A. Padrol, E. Philippe, C. Schilling, arXiv:2105.06459, submitted (2021)]

	Unfeasible	**Feasible**
$\boldsymbol{w} = (1, 0, \ldots)$	Klyachko Generalized Pauli constraints $\Rightarrow$ Complicated!	
$\boldsymbol{w} \neq (1, 0, \ldots)$	 $\Rightarrow$ More complicated than $\boldsymbol{w} = (1, 0, \ldots)$	

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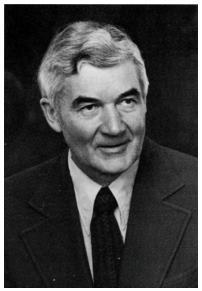
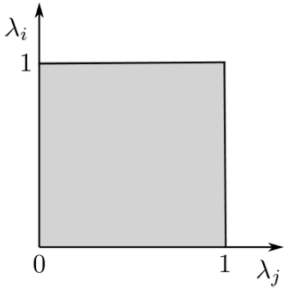
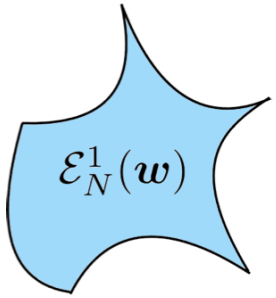
$\boldsymbol{w} = (1, 0, \ldots)$	Klyachko Generalized Pauli constraints $\Rightarrow$ Complicated!	Coleman   $0 \leq \lambda_i \leq 1$ $\Rightarrow$ Pauli's simple exclusion principle
$\boldsymbol{w} \neq (1, 0, \ldots)$	 $\Rightarrow$ More complicated than $\boldsymbol{w} = (1, 0, \ldots)$	

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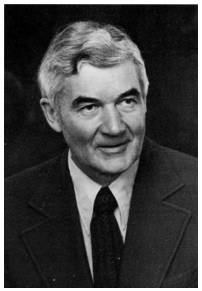
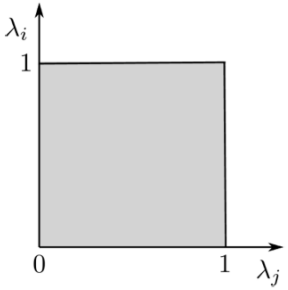
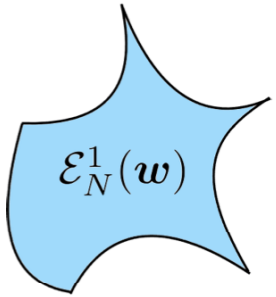
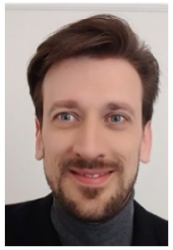
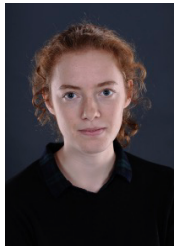
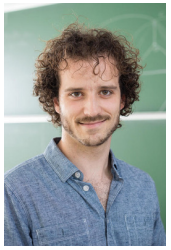
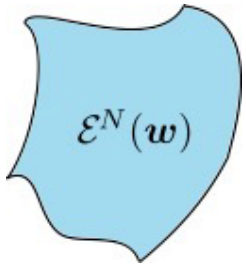
$\boldsymbol{w} = (1, 0, \ldots)$	Klyachko Generalized Pauli constraints $\Rightarrow$ Complicated!	Coleman   $0 \leq \lambda_i \leq 1$ $\Rightarrow$ Pauli's simple exclusion principle
$\boldsymbol{w} \neq (1, 0, \ldots)$	 $\Rightarrow$ More complicated than $\boldsymbol{w} = (1, 0, \ldots)$	   **Independent of N and d!** $\Rightarrow$ Generalization of Pauli's exclusion principle to mixed states

Relation to quantum marginal problem

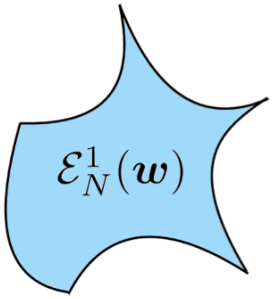
Breakthrough result by Klyachko:

N



$\downarrow$

1



$\Rightarrow$ **Too complicated!**

[A. Klyachko, J. Phys. Conf. Ser. **36**, 72 (2006),
M. Altunbulak, A. Klyachko, CMP **282**, 287 (2008)]

Relation to quantum marginal problem

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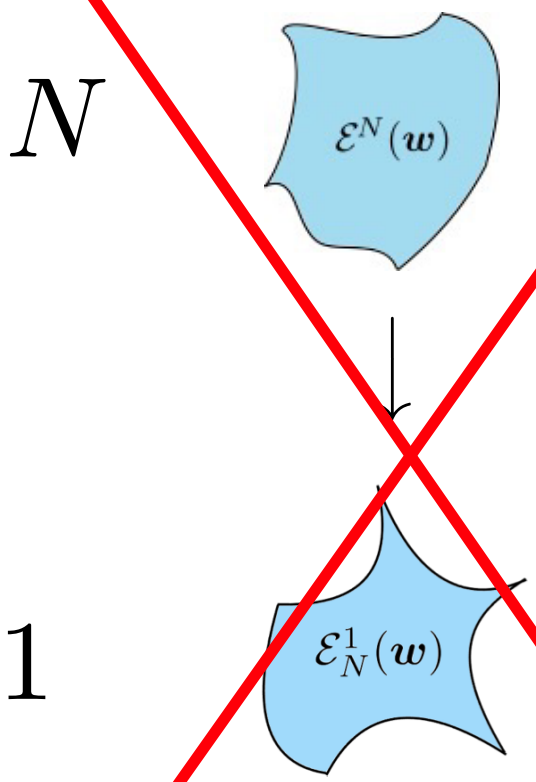

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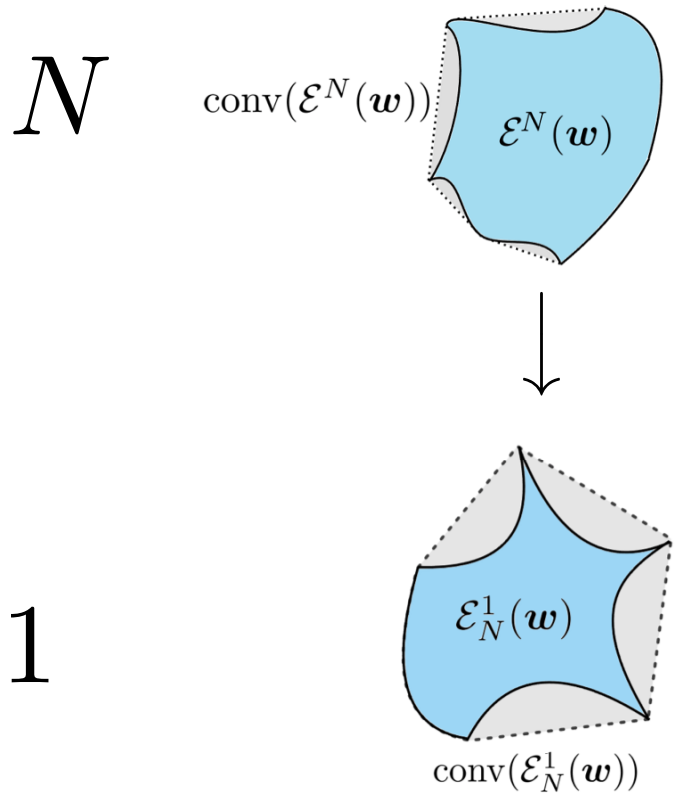
Here: Convex problem



$\Rightarrow$ **Efficient solution!**

[F. Castillo, J.-P. Labbé, J. Liebert, A. Padrol, E. Philippe, C. Schilling, arXiv:2105.06459, submitted (2021).]

Relation to quantum marginal problem

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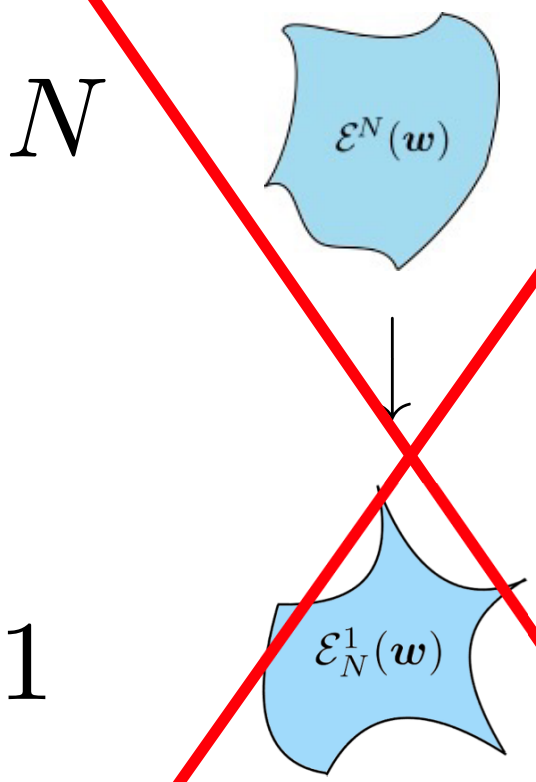

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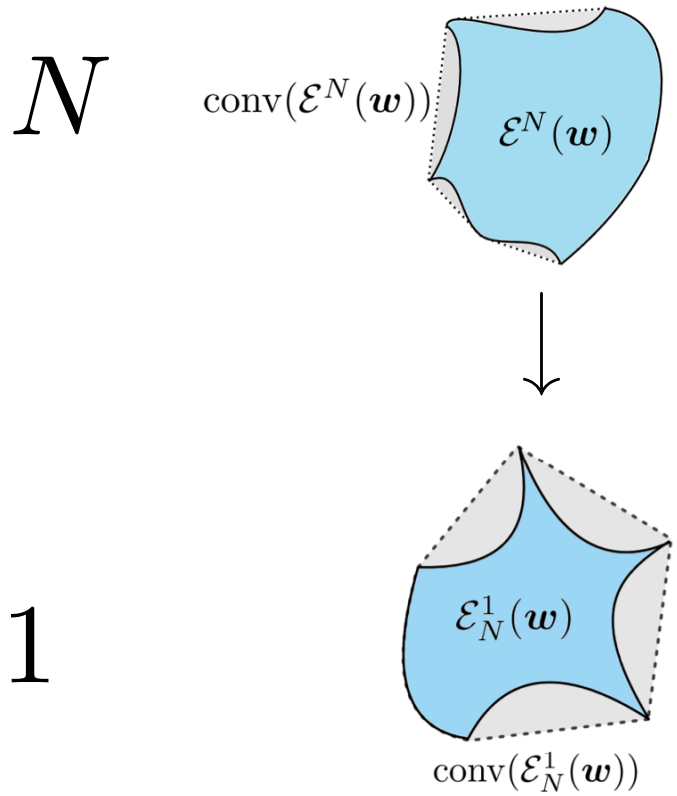

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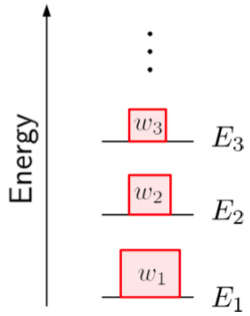
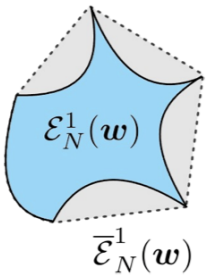
Summary

- Foundation of excited state 1-RDMFT

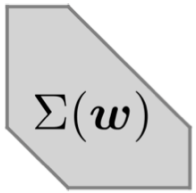


- Key ingredient: Exact convex relaxation

  $\Rightarrow$ Rationalizing Valone



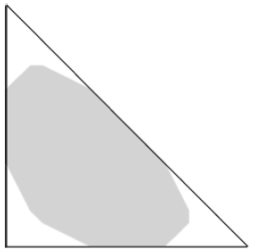
- Hierarchy of generalized exclusion principle constraints



Outlook

- Repeat all steps for bosons

  $\Rightarrow$ **Exclusion principle for bosons!**



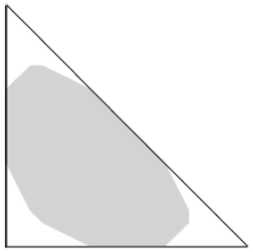
J. Liebert, C. Schilling,An exact one-particle theory of bosonic excitations: From a generalized Hohenberg-Kohn theorem to convexified N-representability, arXiv:2204.12715 (2022),

J. Liebert, C. Schilling, Deriving density-matrix functionals for excited states,arXiv:2210.00964 (2022)

Outlook

- Repeat all steps for bosons

  $\Rightarrow$ **Exclusion principle for bosons!**



J. Liebert, C. Schilling,An exact one-particle theory of bosonic excitations: From a generalized Hohenberg-Kohn theorem to convexified N-representability, arXiv:2204.12715 (2022),

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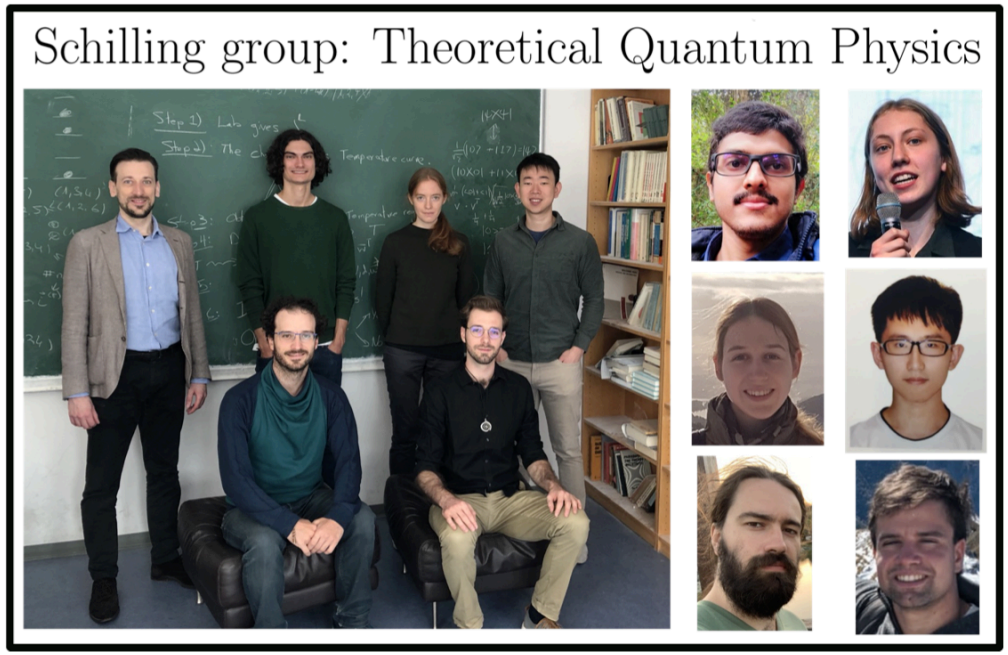
Application of exclusion principle constraints beyond functional theory

Development of w-ensemble functionals

Work in progress

Thank you!



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