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

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Electron correlation problem

N interacting fermions

$\rightarrow$ ground state energy?

wave function methods versus functional theories

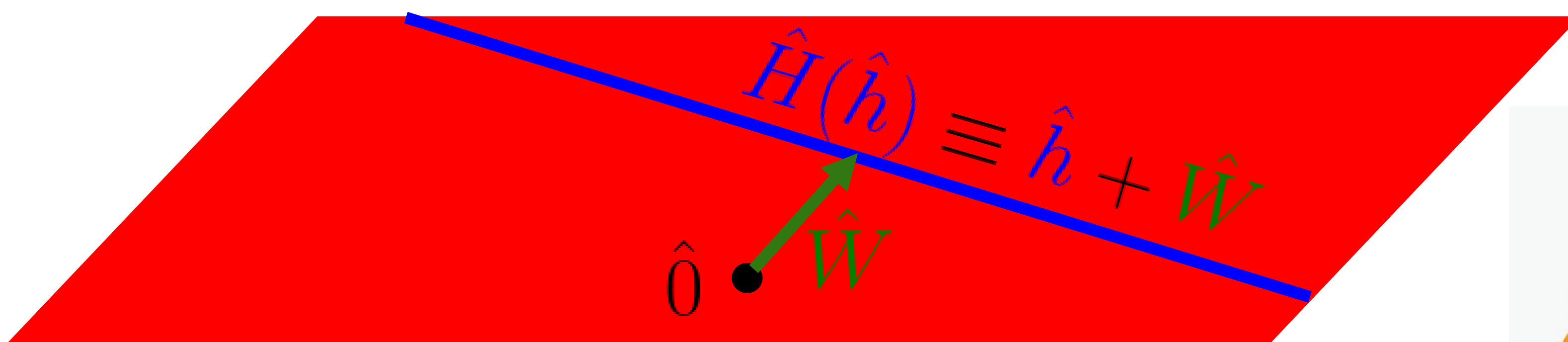
most economic!

$$E = \min_{|\Psi_N\rangle} \langle \Psi_N|\hat{H}|\Psi_N\rangle$$

$\forall \hat{H} \;\rightarrow$ overkill !?

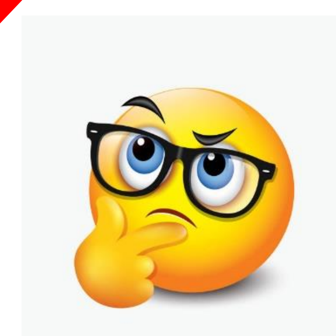
interaction $\hat{W}$ fixed

$$E_{\hat{W}}(\hat{h}) = \min_{\hat{\gamma}}\Big[\underbrace{\langle \hat{h}, \hat{\gamma}\rangle}_{\text{conjugate variables}} + \mathcal{F}_{\hat{W}}(\hat{\gamma})\Big]$$



all Hermitian operators on $\mathcal{H}_N$

exponentially large!



$\rightarrow$ universal functional $\mathcal{F}(\hat{\gamma})$?

$\rightarrow$ relation to Pauli principle ?

Levy-Lieb constrained search:

[M. Levy, Proc. Natl. Acad. Sci. U.S.A 76, 6062 (1979),
E. H. Lieb, J. Quantum Chem. 24, 243 (1982)]

$$E(\hat{h}) = \min_{|\Psi_N\rangle} \langle \Psi_N | \hat{h} + \hat{W} | \Psi_N \rangle$$

1-particle Hamiltonian

$$= \min_{\hat{\gamma}} \min_{|\Psi_N\rangle \mapsto \hat{\gamma}} \left[\mathrm{Tr}_1[\hat{h}\hat{\gamma}] + \langle \Psi_N | \hat{W} | \Psi_N \rangle \right]$$

$$\equiv \min_{\hat{\gamma}} \left[\mathrm{Tr}_1[\hat{h}\hat{\gamma}] + \mathcal{F}(\hat{\gamma}) \right] \quad \rightarrow \quad \boxed{\mathrm{RDMFT}}$$

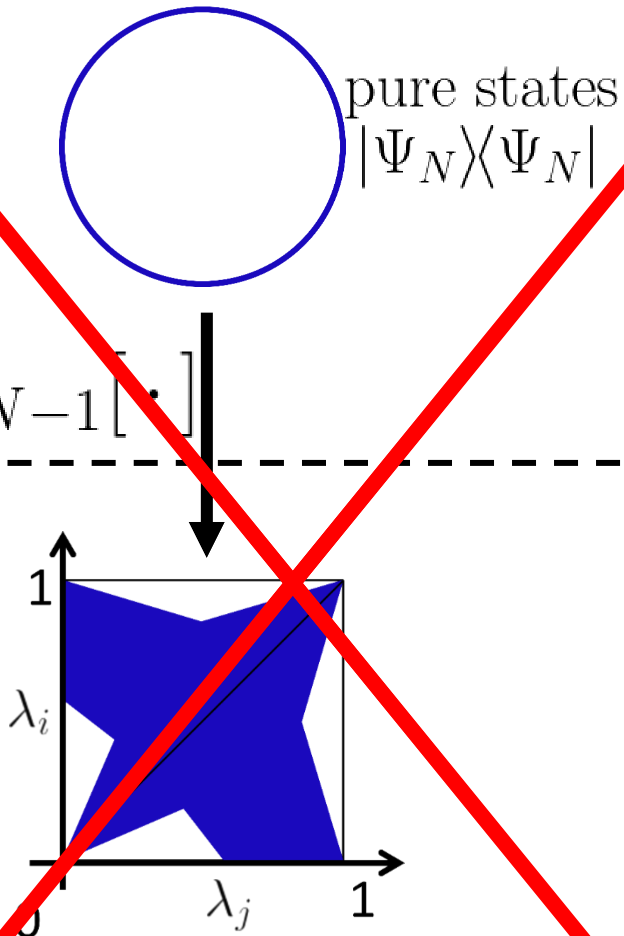
variational principle + structure $\hat{H}(\hat{h}) \equiv \hat{h} + \hat{W}$

$\Rightarrow$ functional theory

domain of $\mathcal{F}(\hat{\gamma})$?

Levy-Lieb: $\mathcal{F}(\hat{\gamma}) = \min_{\hat{\Gamma}_N \mapsto \hat{\gamma}} \mathrm{Tr}_N[\hat{W}\,\hat{\Gamma}_N]$

N

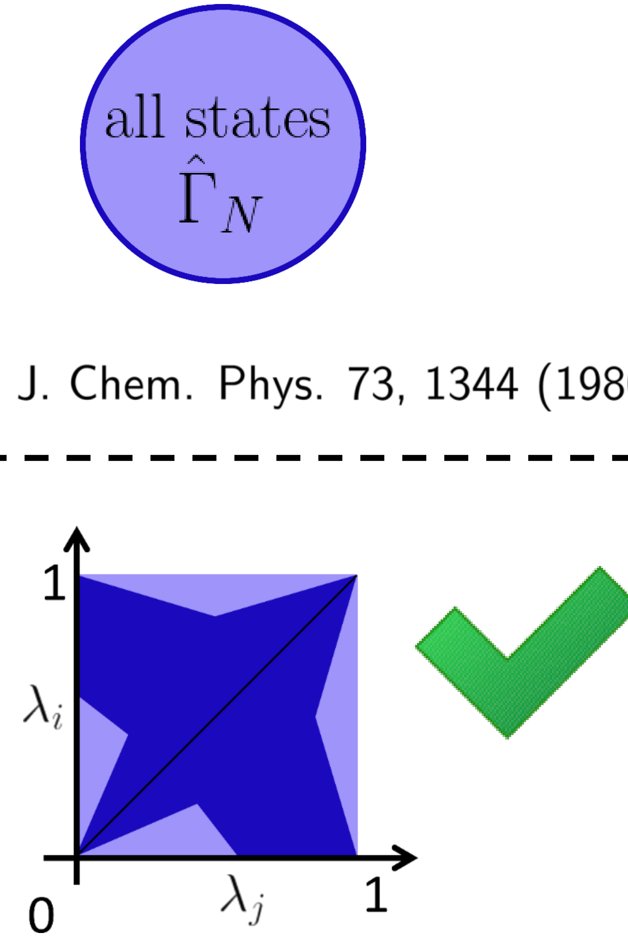


$N\mathrm{Tr}_{N-1}[\,\cdot\,]$

1

“generalized Pauli constraints”

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



[S.M. Valone, J. Chem. Phys. 73, 1344 (1980)]

“Pauli constraints”

$\boxed{0 \leq \lambda_i \leq 1}$ simple

Outline

1) Functional theory for excited states

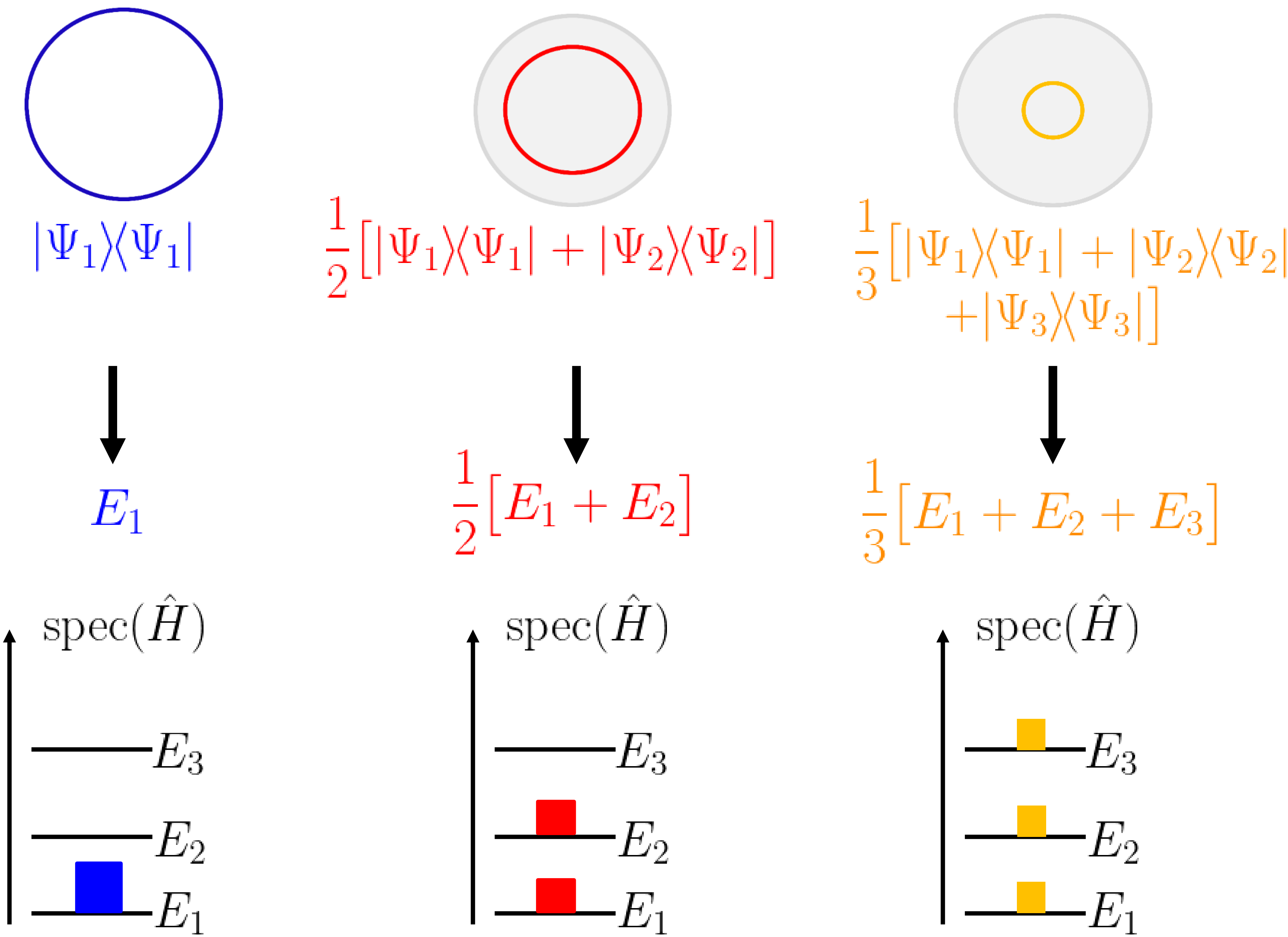
2) Generalized exclusion principle

1) Functional theory for excited states

variational principle for

excited states?

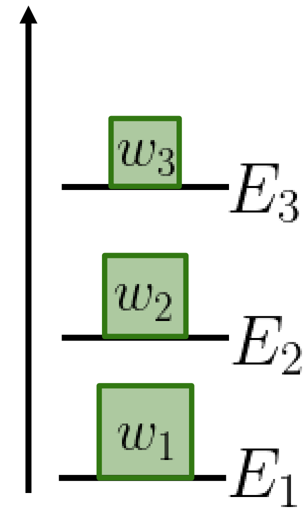
minimization of $\mathrm{Tr}[\hat{H}\hat{\Gamma}]$ over



GOK variational principle

$$E_{\boldsymbol{w}} \equiv \sum_j w_j E_j = \min_{\hat{\Gamma}_N \in \mathcal{E}^N(\boldsymbol{w})} \mathrm{Tr}[\hat{H}\hat{\Gamma}_N]$$

$\mathrm{spec}(\hat{\Gamma}_N) = \boldsymbol{w}$



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

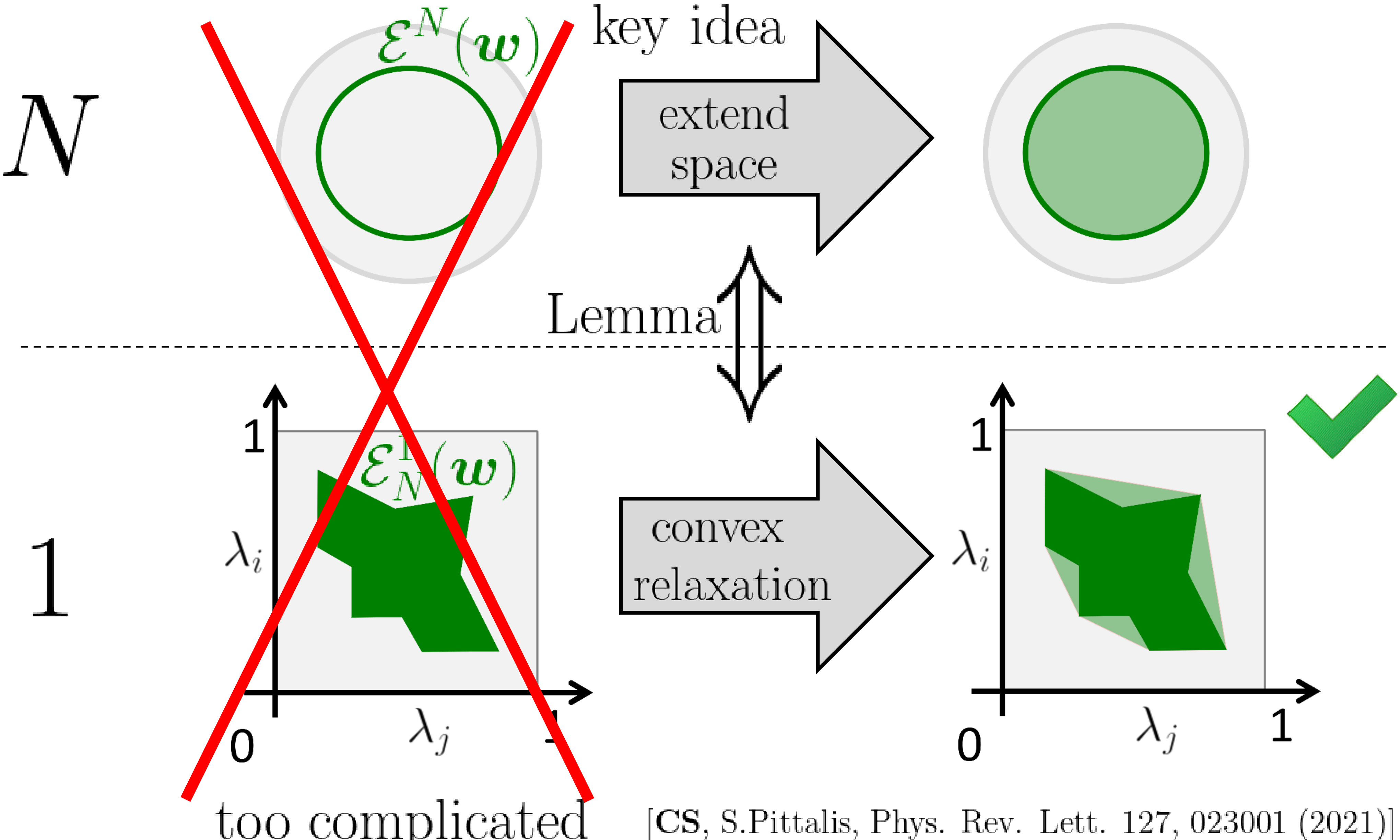
application to $\mathcal{H}_N \equiv \wedge^N \mathcal{H}_1$
+Levy-Lieb constrained search

$$\boxed{\boldsymbol{w}\text{-ensemble RDMFT}}$$

universal functional $\mathcal{F}_{\boldsymbol{w}}(\hat{\gamma})$
on the domain $\mathcal{E}^1_N(\boldsymbol{w}) = N\mathrm{Tr}_{N-1}[\mathcal{E}^N(\boldsymbol{w})]$

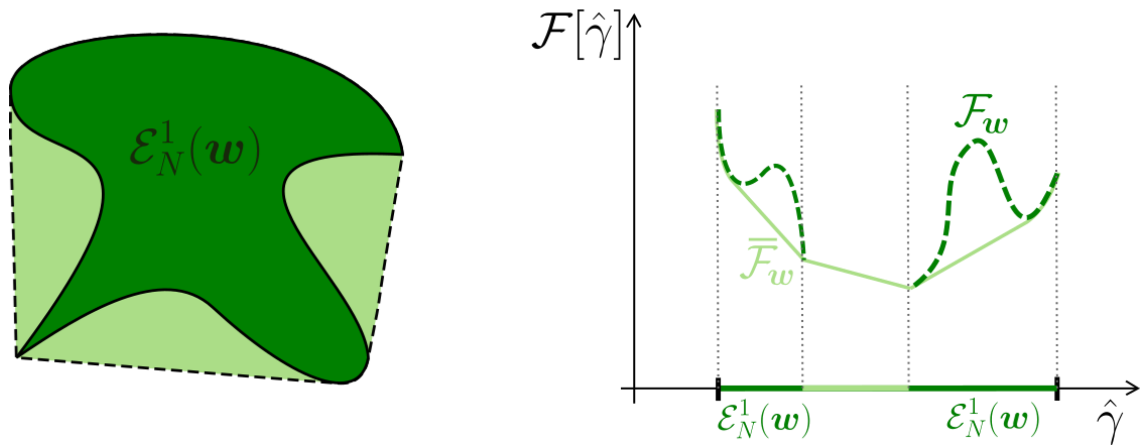
[**CS**, S.Pittalis, Phys. Rev. Lett. 127, 023001 (2021)]
[J.Liebert, F.Castillo, J.-P.Labbé, **CS**, J. Chem. Theory Comput. 18, 124 (2022)]

$\boldsymbol{w}$-RDMFT



[**CS**, S.Pittalis, Phys. Rev. Lett. 127, 023001 (2021)]

exact convex relaxation:



(i) extend $\mathcal{F}_{\boldsymbol{w}}$ to $\mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w}))$:

$$\mathcal{F}_{\boldsymbol{w}} \equiv \infty \text{ on } \mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w})) \setminus \mathcal{E}_N^1(\boldsymbol{w})$$

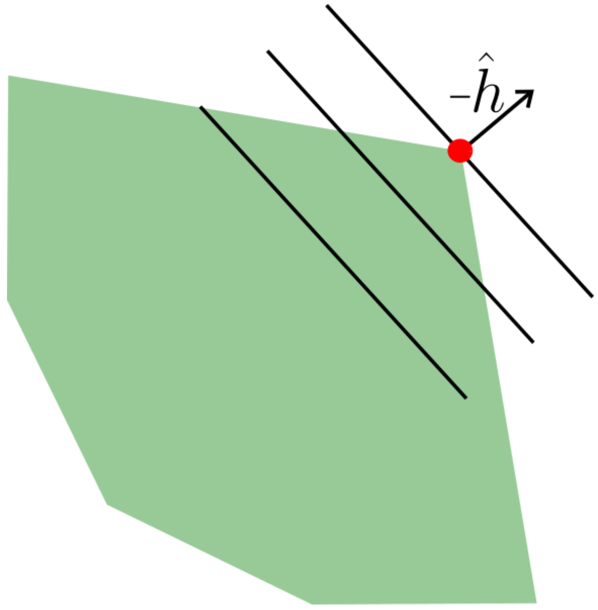
(ii) replace $\mathcal{F}_{\boldsymbol{w}} \to \overline{\mathcal{F}}_{\boldsymbol{w}} := \mathrm{conv}(\mathcal{F}_{\boldsymbol{w}})$

"lower convex envelope"

2) Generalized exclusion principle

goal: efficient description of $\mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w}))$

$\rightarrow$ duality principle:



minimization of linear functional $\mathrm{Tr}_1[\hat{h}\hat{\gamma}]$ on $\mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w}))$

$\Downarrow$

extremal point of $\mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w}))$

unitary invariance:

$$\hat{u}\,\mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w}))\,\hat{u}^\dagger = \mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w}))$$

$$\Downarrow$$

restriction to $\mathrm{spec}^{\downarrow}\big(\mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w}))\big)$

i.e., $\hat{h} \equiv \sum_{j=1}^{d} h_j |j\rangle\langle j|$ with fixed eigenbasis

and $h_1 \leq h_2 \leq \ldots \leq h_d$

mathematical problem

minimization of linear functional $\mathrm{Tr}_1[\hat{h}\hat{\gamma}]$ on $\mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w}))$ for all $\hat{h}$

$$\min_{\hat{\gamma}\in\mathrm{conv}(\mathcal{E}_N^1(\boldsymbol{w}))} \mathrm{Tr}_1[\hat{h}\hat{\gamma}]$$

=

indeed, since: ←

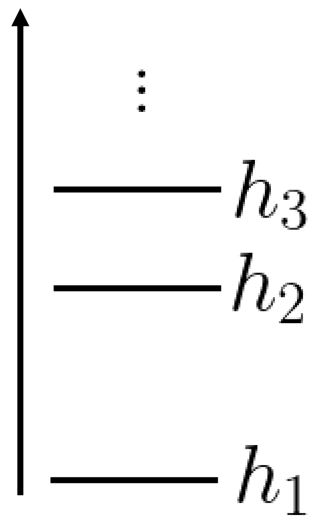
$$\min_{\hat{\Gamma}_N\in\mathrm{conv}(\mathcal{E}^N(\boldsymbol{w}))} \mathrm{Tr}_N[\hat{h}\hat{\Gamma}_N]$$

=

physical problem

understanding excitation spectrum of non-interacting fermions

easy!



$$
\begin{array}{ccccccc}
\hat{h} & \mapsto & \hat{\Gamma}_N & \mapsto & \hat{\gamma} & \xmapsto{\mathrm{spec}^{\downarrow}(\cdot)} & \boldsymbol{v} \\
 & & \rotatebox[origin=c]{90}{$\in$} & & & & \\
 & & \mathcal{E}^N(\boldsymbol{w}) & & & &
\end{array}
$$

try out all $\hat{h}$ to get all vertices $\boldsymbol{v}$

of spectral polytope

$$\hat{h} \mapsto \hat{\Gamma}_N? :$$

Well, $\hat{\Gamma}_N \equiv \sum_k w_k |\boldsymbol{i}_k\rangle\langle\boldsymbol{i}_k|$

where $\boldsymbol{i} \equiv (i_1, i_2, \ldots, i_N), 1 \leq i_1 < \ldots < i_N \leq d$

and $|\boldsymbol{i}\rangle \equiv f^\dagger_{i_1} \cdots f^\dagger_{i_N}|0\rangle$ "configuration"

it remains to find energetic ordring of various $\boldsymbol{i}$

for more details please see:

[**CS**, S.Pittalis, Phys. Rev. Lett. 127, 023001 (2021)]

[J.Liebert, F.Castillo, J.-P.Labbé, **CS**, J. Chem. Theory Comput. 18, 124 (2022)]

[F.Castillo, J.-P.Labbé, J.Liebert, A.Padrol, E.Philippe, **CS**, arXiv:2105.06459]

hierarchy of exclusion principles

- $\boldsymbol{w} = (w_1, 0, \ldots)$

$$\boxed{\lambda_1^{\downarrow} \leq 1}$$

- $\boldsymbol{w} = (w_1, w_2, 0, \ldots)$

$$+ \quad \boxed{\sum_{j=1}^{N} \lambda_j^{\downarrow} \leq N - 1 + w_1}$$

- $\boldsymbol{w} = (w_1, w_2, w_3, 0, \ldots)$

$$+ \quad \boxed{2\sum_{j=1}^{N-1} \lambda_j^{\downarrow} + \lambda_N^{\downarrow} + \lambda_{N+1}^{\downarrow} \leq 2N - 2 + w_1 + w_2}$$

arbitrary r? more complicated!

[F.Castillo, J.-P.Labbé, J.Liebert, A.Padrol, E.Philippe, **CS**, arXiv:2105.06459]

r	1	2	3	4	5	6	7	8	9
$\#ineq$	1	2	3	4	8	13	23	42	88

- inequalities "independent" of N and d

  $\Rightarrow$ infinite basis set limit possible!

Summary

- GOK variational principle + constrained search
  $\Rightarrow$ $\boldsymbol{w}$-RDMFT for excitation energies

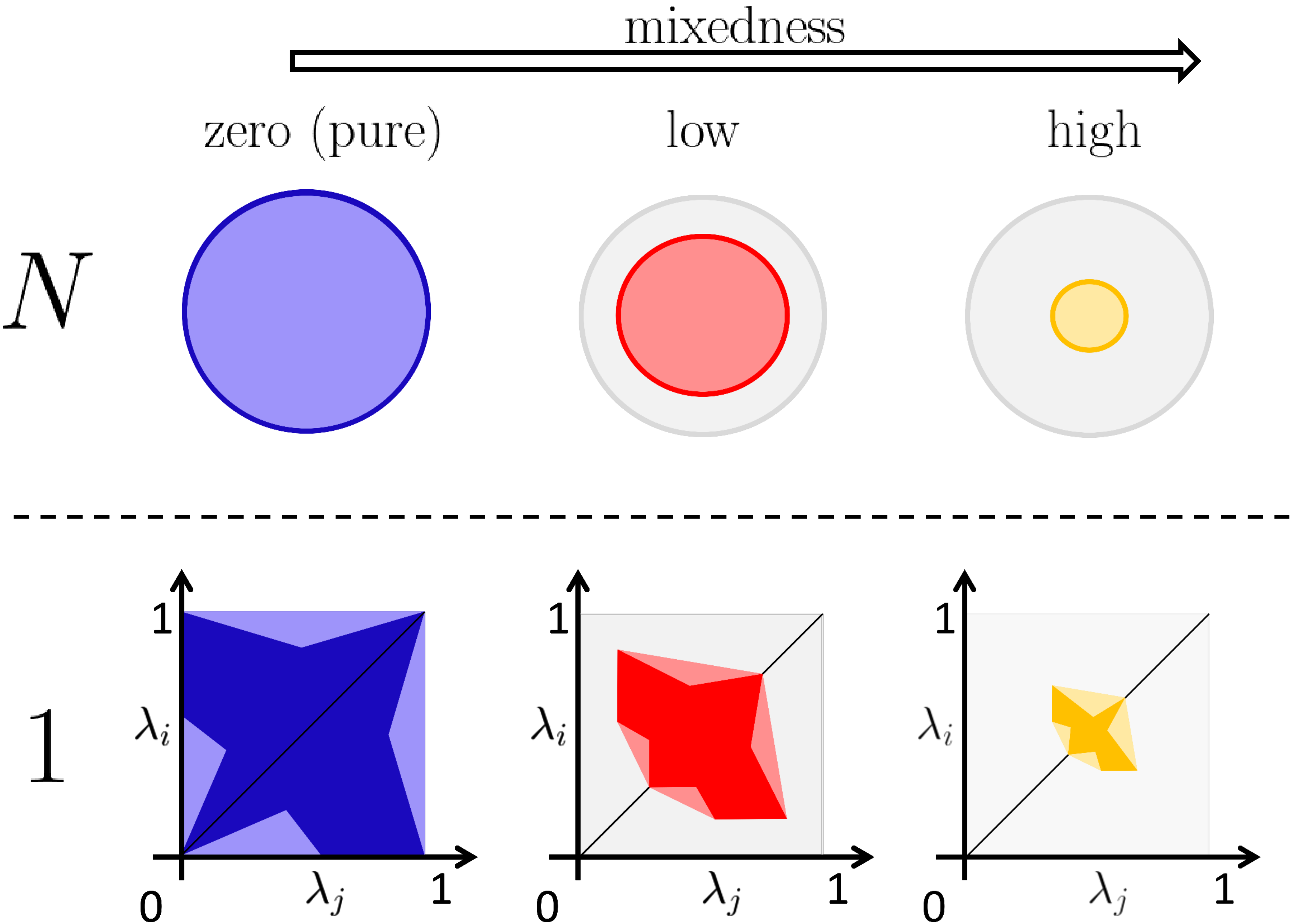
- convex relaxation $\Rightarrow$ feasible $\boldsymbol{w}$-RDMFT
  [**CS**, S.Pittalis, Phys. Rev. Lett. 127, 023001 (2021)]
  [J.Liebert, F.Castillo, J.-P.Labbé, **CS**, J. Chem. Theory Comput. 18, 124 (2022)]
  $\Rightarrow$ complete hierarchy of exclusion principles
  [F.Castillo, J.-P.Labbé, J.Liebert, A.Padrol, E.Philippe, **CS**, arXiv:2105.06459]

- same story again for bosons!
  [J.Liebert, **CS**, arXiv:2204.12715]

- universal functional? long-term endeavour

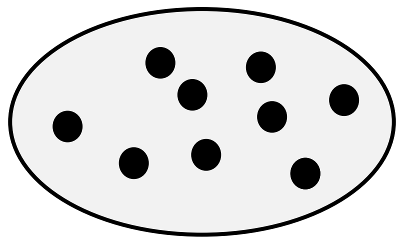
Outlook

(work in progress)


mixedness
zero (pure)
low
high
N
1
λ_i
λ_j
0
1

general idea:

physical system Σ



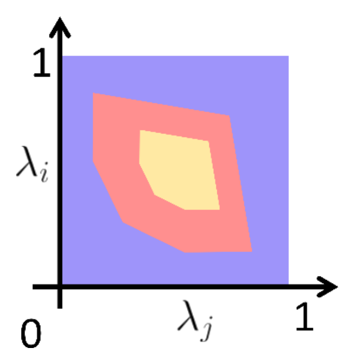
ρ_Σ

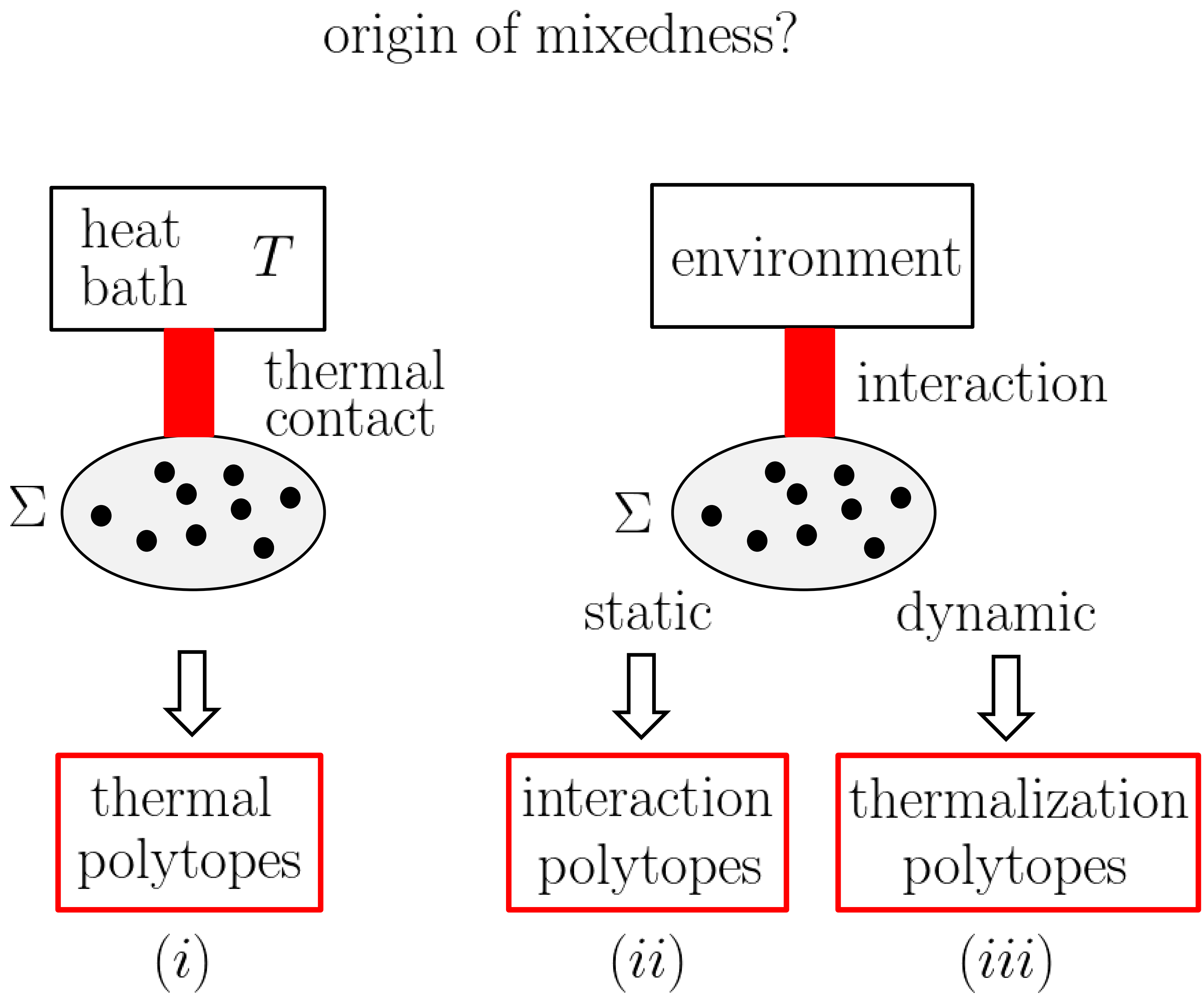
mixedness $\boldsymbol{w}$

measurement of occupation numbers

restricts range !

$\vec{\lambda} \in$




origin of mixedness?
heat bath T
thermal contact
Σ
environment
interaction
Σ
static
dynamic
thermal polytopes
interaction polytopes
thermalization polytopes
(i)
(ii)
(iii)

Postdoc/PhD positions available

Thank you!