Algebraic Varieties in Quantum Chemistry

Bernd Sturmfels
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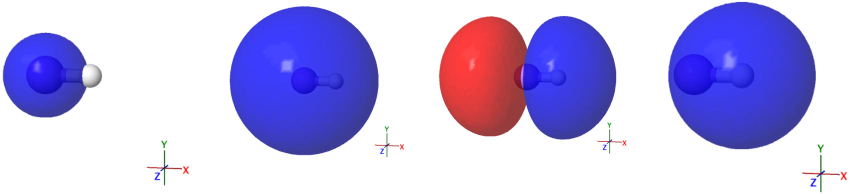

Paper with Fabian Faulstich and Svala Sverrisdóttir
Mathematics in Science, CMSA, Harvard, *October 27, 2023*

Linear Algebra

Fix integers $n \geq d > 1$. $1 \leq i_1 < i_2 < \cdots < i_d \leq n$.

Vector space $\wedge_d \mathbb{R}^n$ has standard basis $e_I = e_{i_1} \wedge e_{i_2} \wedge \cdots \wedge e_{i_d}$,

Column vectors $\psi = \sum_{I \in \binom{[n]}{d}} \psi_I e_I$ are called *quantum states*.

A scientist gives us a symmetric matrix $H \in \mathbb{R}^{\binom{n}{d} \times \binom{n}{d}}$, called

Hamiltonian, and asks us to solve the eigenvalue problem

$$H\psi = \lambda\psi.$$

This is easy, isn't it?

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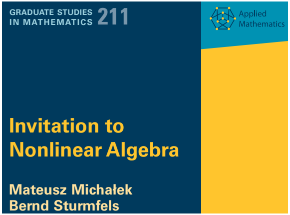
Coupled Cluster Theory replaces
a large problem of Linear Algebra
with a small problem
of Nonlinear Algebra.



GRADUATE STUDIES IN MATHEMATICS 211

Applied Mathematics

Invitation to Nonlinear Algebra

Mateusz Michałek
Bernd Sturmfels

Math ...

Our Abstract

We develop algebraic geometry for coupled cluster (CC) theory of quantum many-body systems. The high-dimensional eigenvalue problems that encode the electronic Schrödinger equation are approximated by a hierarchy of polynomial systems.

The exponential parametrization of the eigenstates gives rise to truncation varieties. These generalize Grassmannians in their Plücker embedding.

$$\psi_{12}\psi_{34} - \psi_{13}\psi_{24} + \psi_{14}\psi_{23} = 0$$

$$\begin{pmatrix} \star & \star & \star & \star \\ \star & \star & \star & \star \end{pmatrix}$$

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$$\begin{pmatrix} \star & \star & \star & \star \\ \star & \star & \star & \star \end{pmatrix}$$

We explain how to derive Hamiltonians, we offer a detailed study of truncation varieties and their CC degrees, and we present the state of the art in solving the CC equations.

… in Science

Opening paragraph from our paper

Electronic structure theory is a powerful quantum mechanical framework for investigating the intricate behavior of electrons within molecules and crystals. At the core lies the interaction between particles, specifically electron-electron and electron-nuclei interactions. Embracing the essential quantum physical effects, this theory is the foundation for *ab initio* electronic structure calculations …

With its diverse applications in chemistry and materials science, electronic structure theory holds vast implications for the mathematical sciences. Integrating methods from algebra and geometry into this field leads to the development of precise and scalable numerical methods, enabling extensive *in silico* studies of chemistry for e.g. sustainable energy, green catalysis, and nanomaterials.

The synergy between fundamental mathematics and electronic structure theory offers potential for groundbreaking advances in addressing these global challenges.

Sounds promising?

A Tale of Two Vectors Spaces

$\mathcal{H} = \wedge_d \mathbb{R}^n$ Vectors ψ are quantum states

Reference state $e_{[d]}$ = first basis vector

$\mathcal{V} = \wedge_d \mathbb{R}^n$ Vectors x are cluster amplitudes

The *exponential parametrization* is a nonlinear bijection

$$\mathcal{V} \to \mathcal{H}\,,\; x \mapsto \psi, \qquad \text{where} \quad \psi = \exp(T(x))\, e_{[d]}.$$

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$$\mathcal{V} \to \mathcal{H}\,,\ x \mapsto \psi, \qquad \text{where} \quad \psi = \exp(T(x))\, e_{[d]}.$$

- $T(x)$ is a strictly lower-triangular $\binom{n}{d} \times \binom{n}{d}$ matrix.
- Its entries are x_K or $-x_K$ or 0.
- The matrix $T(x)$ is nilpotent. We have $T(x)^{d+1} = 0$.
- The matrix exponential $\exp(T(x))$ is idempotent.
- Its entries are polynomials in x of degree $\leq d$.

$d = 2, n = 5$

$$T(x) = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ x_{13} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ x_{14} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ x_{15} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -x_{23} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -x_{24} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -x_{25} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ x_{34} & -x_{24} & x_{23} & 0 & -x_{14} & x_{13} & 0 & 0 & 0 & 0 \\ x_{35} & -x_{25} & 0 & x_{23} & -x_{15} & 0 & x_{13} & 0 & 0 & 0 \\ x_{45} & 0 & -x_{25} & x_{24} & 0 & -x_{15} & x_{14} & 0 & 0 & 0 \end{bmatrix}$$

$$\exp(T(x)) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ x_{13} & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ x_{14} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ x_{15} & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -x_{23} & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ -x_{24} & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ -x_{25} & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ x_{14}x_{23} - x_{13}x_{24} + x_{34} & -x_{24} & x_{23} & 0 & -x_{14} & x_{13} & 0 & 1 & 0 & 0 \\ x_{15}x_{23} - x_{13}x_{25} + x_{35} & -x_{25} & 0 & x_{23} & -x_{15} & 0 & x_{13} & 0 & 1 & 0 \\ x_{15}x_{24} - x_{14}x_{25} + x_{45} & 0 & -x_{25} & x_{24} & 0 & -x_{15} & x_{14} & 0 & 0 & 1 \end{bmatrix}$$

Lower-triangular Matrix

The entry of $T(x)$ in row J and column I is zero
unless $I \backslash J \subseteq [d]$ and $(J \backslash I) \cap [d] = \emptyset$.

If this holds then

$$T(x)_{J,I} \; = \; \pm \, x_K \qquad \text{where } K = ([d] \cup J) \backslash I$$

with a combinatorially defined sign.

Rows and columns of $T(x)$ are ordered by increasing level.
The *level* of a coordinate ψ_I or x_I is the cardinality of $I \backslash [d]$.

Example ($d = 3, n = 6$)

Quantum states ψ and cluster amplitudes x or have 20 coordinates:
Level 0: 123
Level 1: 124, 125, 126, 134, 135, 136, 234, 235, 236
Level 2: 145, 146, 156, 245, 246, 256, 345, 346, 356,
Level 3: 456

Exponential Parametrization $\mathcal{V} \to \mathcal{H}\,,\ \psi = \exp(T(x))\, e_{[d]}$

$\psi =$ the leftmost column of the matrix $\exp(T(x))$.

$d = 3, n = 6$

$$\psi_{123} = 1$$
$$\psi_{124} = x_{124}$$
$$\psi_{125} = x_{125}$$
$$\psi_{126} = x_{126}$$
$$\psi_{134} = -x_{134}$$
$$\psi_{135} = -x_{135}$$
$$\psi_{136} = -x_{136}$$
$$\psi_{234} = x_{234}$$
$$\psi_{235} = x_{235}$$
$$\psi_{236} = x_{236}$$
$$\psi_{145} = x_{145} - x_{124}x_{135} + x_{125}x_{134}$$
$$\psi_{146} = x_{146} - x_{124}x_{136} + x_{126}x_{134}$$
$$\psi_{156} = x_{156} - x_{125}x_{136} + x_{126}x_{135}$$
$$\psi_{245} = -x_{245} + x_{124}x_{235} - x_{125}x_{234}$$
$$\psi_{246} = -x_{246} + x_{124}x_{236} - x_{126}x_{234}$$
$$\psi_{256} = -x_{256} + x_{125}x_{236} - x_{126}x_{235}$$
$$\psi_{345} = x_{345} - x_{134}x_{235} + x_{135}x_{234}$$
$$\psi_{346} = x_{346} - x_{134}x_{236} + x_{136}x_{234}$$
$$\psi_{356} = x_{356} - x_{135}x_{236} + x_{136}x_{235}$$

$$\psi_{456} = x_{456} + x_{124}x_{356} - x_{125}x_{346} + x_{126}x_{345} - x_{134}x_{256} + x_{135}x_{246} - x_{136}x_{245} + x_{145}x_{236} - x_{146}x_{235}$$
$$+ x_{156}x_{234} - x_{124}x_{135}x_{236} + x_{124}x_{136}x_{235} + x_{125}x_{134}x_{236} - x_{125}x_{136}x_{234} - x_{126}x_{134}x_{235} + x_{126}x_{135}x_{234}$$

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$\psi_{145} = x_{145} - x_{124}x_{135} + x_{125}x_{134}$
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$\psi_{156} = x_{156} - x_{125}x_{136} + x_{126}x_{135}$
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Proposition

The map $\mathcal{V} \to \mathcal{H}$ has a polynomial inverse. Namely, x_I equals $\pm\,\psi_I$ plus a polynomial in ψ-coordinates of strictly lower level.

$x_{123} = 1,\ x_{124} = \psi_{124},\ \ldots\ ,\ \psi_{236} = x_{236}$

$x_{145} = \psi_{145} - \psi_{124}\psi_{135} + \psi_{125}\psi_{134},\ \ldots\ ,\ \psi_{356} = x_{356} - x_{135}x_{236} + x_{136}x_{235}$

$$x_{456} = \psi_{456} - \psi_{124}\psi_{356} + \psi_{125}\psi_{346} - \psi_{126}\psi_{345} + \psi_{134}\psi_{256} - \psi_{135}\psi_{246} + \psi_{136}\psi_{245} - \psi_{145}\psi_{236} + \psi_{146}\psi_{235}$$
$$- \psi_{156}\psi_{234} + 2(\psi_{124}\psi_{135}\psi_{236} - \psi_{124}\psi_{136}\psi_{235} - \psi_{125}\psi_{134}\psi_{236} + \psi_{125}\psi_{136}\psi_{234} + \psi_{126}\psi_{134}\psi_{235} - \psi_{126}$$

Combinatorics

All coordinates of the exponential parametrization $\mathcal{H} \to \mathcal{V}$ arise by relabeling from the master polynomial $\psi_I(x)$, where $I = [2d]\backslash[d]$.

$$\begin{array}{rcl} x_{34}(\psi) & = & \psi_{34} - \psi_{13}\psi_{24} + \psi_{14}\psi_{23} \\ x_{456}(\psi) & = & \psi_{456} - \psi_{124}\psi_{356} + \cdots - 2\psi_{126}\psi_{135}\psi_{234} \\ x_{5678}(\psi) & = & \psi_{5678} - \psi_{1235}\psi_{4678} + \cdots - 2\psi_{1278}\psi_{1346}\psi_{2345} \ + \cdots - 6\psi_{1238}\psi_{1247}\psi_{1346}\psi_{2345} \\ x_{67890}(\psi) & = & \psi_{67890} - \psi_{12346}\psi_{57890} + \cdots - 2\psi_{12890}\psi_{13457}\psi_{23456} + \cdots \\ & & + 6\psi_{12390}\psi_{12458}\psi_{13457}\psi_{23456} + \cdots + 24\psi_{12349}\psi_{12358}\psi_{12457}\psi_{13456}\psi_{23450} \end{array}$$

Number of terms in the master polynomial:

$3, 16, 131, 1496, 22482, 426833 \quad \text{for} \ d = 2, 3, 4, 5, 6, 7.$ (A023998)

Combinatorics

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$$\begin{aligned}
x_{34}(\psi) &= \psi_{34} - \psi_{13}\psi_{24} + \psi_{14}\psi_{23} \\
x_{456}(\psi) &= \psi_{456} - \psi_{124}\psi_{356} + \cdots - 2\psi_{126}\psi_{135}\psi_{234} \\
x_{5678}(\psi) &= \psi_{5678} - \psi_{1235}\psi_{4678} + \cdots - 2\psi_{1278}\psi_{1346}\psi_{2345} \ + \cdots - 6\psi_{1238}\psi_{1247}\psi_{1346}\psi_{2345} \\
x_{67890}(\psi) &= \psi_{67890} - \psi_{12346}\psi_{57890} + \cdots - 2\psi_{12890}\psi_{13457}\psi_{23456} + \cdots \\
&\quad + 6\psi_{12390}\psi_{12458}\psi_{13457}\psi_{23456} + \cdots + 24\psi_{12349}\psi_{12358}\psi_{12457}\psi_{13456}\psi_{23450}
\end{aligned}$$

Number of terms in the master polynomial:

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Similarly, all coordinates of the inverse map $\mathcal{V} \to \mathcal{H}$ arise by relabeling from the master polynomial $x_I(\psi)$, where $I = [2d]\backslash[d]$.

Theorem

We have explicit formulas for the master polynomials $\psi_I(x)$ and $x_I(\psi)$ as integer linear combinations of monomials that represent the uniform block permutations on $[2d]$. [Orellana et al, 2022]

Truncation Varieties

Fix a subset σ of $[d]$. Restrict the map $\mathcal{H} \to \mathcal{V}$ to the subspace whose coordinates x_I whose level is in σ.

Image of this restriction is the *truncation variety*

$$V_\sigma \ \subset \ \mathbb{P}(\mathcal{V}) \ = \ \mathbb{P}^{\binom{n}{d}-1}.$$

Remark: $\dim(V_\sigma) \ = \ \#\{I : \mathrm{level}(I) \in \sigma\}$

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Example (d=3, n=6)

The six truncation varieties V_σ in $\mathbb{P}^{19}$ are

$\{2\}$ $V_{\{2\}} \simeq \mathbb{P}^9$ = zero set of ten coordinates ψ_I of level 1 or 3.

$\{3\}$ Line $V_{\{3\}} \simeq \mathbb{P}^1$ spanned by the points e_{123} and e_{456}.

$\{2,3\}$ $V_{\{2,3\}} \simeq \mathbb{P}^{10}$ = zero set of nine coordinates ψ_I of level 1.

$\{1,2\}$ Cubic hypersurface $V_{\{1,2\}}$ defined by master polynomial $\bar{x}_{456}(\psi)$.

$\{1,3\}$ $V_{\{1,3\}}$ has dim 10, degree 41, defined by 25 quadrics.

$\{1\}$ Grassmannian $V_{\{1\}} = \mathrm{Gr}(3,6)$, dim 9, degree 42, 35 quadrics.

Ideals, Varieties and Algorithms

Theorem

The restriction of V_σ *to the affine chart* $\{\psi_{[d]} = 1\}$ *in* $\mathbb{P}^{\binom{n}{d}-1}$ *is a complete intersection, defined by* $x_I(\psi) = 0$ *for* $\mathrm{level}(I) \notin \sigma$.

The homogeneous prime ideal of V_σ *is the saturation*

$$\mathcal{I}(V_\sigma) \;=\; \big\langle\, \bar{x}_I(\psi) \,:\, \mathrm{level}(I) \notin \sigma \big\rangle \,:\, \langle\, \psi_{[d]} \,\rangle^{\infty}.$$

How to be linear ?

Theorem

The truncation variety V_σ *is a linear subspace of* $\mathbb{P}^{\binom{n}{d}-1}$ *if and only if the index set* σ *is additively closed,*

i.e. if $i, j \in \sigma$ *with* $i + j \in [d]$ *then* $i + j \in \sigma$.

Grassmannians

Theorem ($\sigma = \{1\}$)

The truncation variety $V_{\{1\}}$ *in* $\mathbb{P}^{\binom{n}{d}-1}$ *equals the* *Grassmannian* $\mathrm{Gr}(d,n)$ *in its Plücker embedding.*

Punchline: The V_σ are generalizations of Grassmannians.

Proposition (Duality)

Fix $\sigma \subset [d]$ *and* $n \geq 2d$. *There is a linear isomorphism between two copies of* $\mathbb{P}^{\binom{n}{d}-1}$ *which switches the truncation varieties* V_σ *for* (d,n) *and for* $(n-d,n)$.

A Variety of Varieties

Example ($d = 3, n = 7$)

The six varieties in $\mathbb{P}^{34}$ correspond to the six columns in this table:

σ	$\{1\}$	$\{2\}$	$\{3\}$	$\{1,2\}$	$\{1,3\}$	$\{2,3\}$
dim	12	18	4	30	16	22
degree	462	1	1	43	405	1
mingens	$[0, 140]$	$[16]$	$[30]$	$[0, 0, 7]$	$[0, 76, 10]$	$[12]$
$\mathrm{CCdeg}_{3,7}$	2883	19	5	1195	3425	23

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Example ($d = 4, n = 8$)

The 14 varieties live in $\mathbb{P}^{69}$. Five are linear spaces:
$V_{\{3\}} \simeq \mathbb{P}^{16}$, $V_{\{4\}} \simeq \mathbb{P}^{1}$, $V_{\{2,4\}} \simeq \mathbb{P}^{37}$, $V_{\{3,4\}} \simeq \mathbb{P}^{17}$, $V_{\{2,3,4\}} \simeq \mathbb{P}^{53}$.
The nine others:

σ	$\{1\}$	$\{2\}$	$\{1, 2\}$	$\{1, 3\}$	$\{1, 4\}$	$\{2, 3\}$	$\{1, 2, 3\}$	$\{1, 2, 4\}$	$\{1, 3, 4\}$
dim	16	36	52	32	17	52	68	53	33
mingens	$[0, 721]$	[32,1]	[0,0, 63]	[0,237,200]	[0,668]	[16, 1]	[0,0,0,1]	[0,46,120]	[0,236,200
degree	24024	2	442066	24024	24203	2	4	221033	12012
$\mathrm{CCdeg}_{4,8}$	154441	73	??	??	177503	105	273	??	245239

Coupled Cluster Equations

$$(H\psi)_\sigma = \lambda\, \psi_\sigma$$
$$\text{for } \psi \in V_\sigma$$

The *coupled cluster degree* $\mathrm{CCdeg}_{d,n}(\sigma)$

is the number of complex solutions in $\mathbb{P}^{\binom{n}{d}-1}$

for generic symmetric matrices H.

Back to **Science**: *Where does H come from ?*

Electronic Schrödinger Equation

$$\mathbb{H}\,\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_d) \;=\; \lambda\,\Psi(\mathbf{r}_1,\mathbf{r}_2\ldots,\mathbf{r}_d).$$

Ψ is an unknown function in positions $\mathbf{r}_i \in \mathbb{R}^3$ of d electrons.

By Pauli's Exclusion Principle, Ψ is skew-symmetric. The Hamiltonian is

$$\mathbb{H} \;=\; -\frac{1}{2}\sum_{i=1}^{d}\Delta_{\mathbf{r}_i} \;-\; \sum_{i=1}^{d}\sum_{j=1}^{d_{\mathrm{nuc}}}\frac{Z_j}{|\mathbf{r}_i-\mathbf{R}_j|} \;+\; \sum_{1\le i<j\le d}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}.$$

Δ is the Laplacian, and $\mathbf{R}_j \in \mathbb{R}^3$ are fixed nuclei. Nuclear charge Z_j is the number in the periodic table. We have $d_{\mathrm{nuc}} \le d = \sum_{j=1}^{d_{\mathrm{nuc}}} Z_j$.

Example (Lithium hydride)

The molecule LiH has $d_{\mathrm{nuc}}=2$ atoms: lithium Li and hydrogen H. # electrons is $d = Z_1 + Z_2 = 3 + 1 = 4$. Two nuclei at locations $\mathbf{R}_1$ and $\mathbf{R}_2$. Four electrons have variable locations $\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4$.

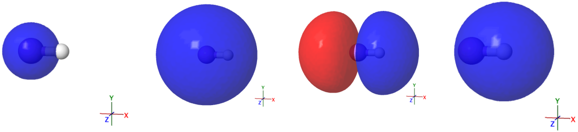
So, Ψ is a function of 12 scalar unknowns.

Discretization

Restrict the Hamiltonian $\mathbb{H}$ to a k-dim'l space of nice functions $\mathbb{R}^3 \to \mathbb{R}$, where $k \geq d$. Basis of *atomic orbitals* $\{\chi_1, \chi_2, \ldots, \chi_k\}$ from `www.basissetexchange.org`

Example (LiH, $d = k = 4$)

Select $k = 4$ atomic orbitals, three for lithium and one for hydrogen:



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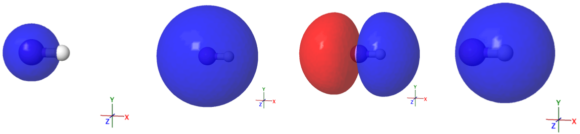
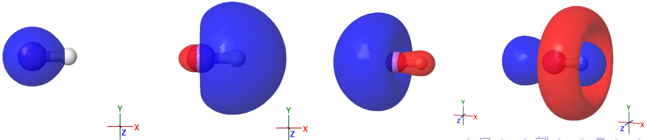


Electronic spin doubles the number of functions, and the LCAO method leads to $n = 2k$ *molecular orbitals*. Hence for LiH we have $d = 4, n = 8$.



Computing H from $\mathbb{H}$

Basis of molecular orbitals: $\{\xi_1, \xi_2, \ldots, \xi_n\}$.
Inner product on molecular orbit space: must incorporate spin

$$\langle \xi_i, \xi_j \rangle = \int_{\mathbb{R}^3} \xi_i(\mathbf{r}) \xi_i(\mathbf{r}) d\mathbf{r}$$

Galerkin basis of $\binom{n}{d}$ skew-symmetric d-particle functions:

$$\Phi_I \; = \; \frac{1}{\sqrt{d!}} \, \xi_{i_1} \wedge \cdots \wedge \xi_{i_d}, \quad \text{where } I = \{i_1, \ldots, i_d\}.$$

Inner product:

$$\langle \Phi_I, \Phi_J \rangle \; = \; \sum_{\substack{\mu \in S_I \\ \nu \in S_J}} \prod_{p=1}^{d} \langle \xi_{\mu(i_p)}, \xi_{\nu(j_p)} \rangle$$

Compute entries of the $\binom{n}{d} \times \binom{n}{d}$ matrix H by integration:

$$H_{I,J} \; = \; \langle \Phi_I, \mathbb{H} \Phi_J \rangle.$$

For Lithium hydride, Hamiltonian H is a symmetric 70 × 70 matrix.

Coupled Cluster Equations

$$(H\psi)_\sigma \;=\; \lambda\,\psi_\sigma$$

$$\text{for}\;\; \psi \in V_\sigma$$

Coupled Cluster Equations

$$(H\psi)_\sigma = \lambda\,\psi_\sigma$$

$$\text{for } \psi \in V_\sigma$$

Example $(d = 2, n = 5, \sigma = \{1\})$

Determinantal formulation for $V_\sigma = \mathrm{Gr}(2,5)$:

$$\operatorname{rank}\begin{bmatrix} 0 & \psi_{12} & \psi_{13} & \psi_{14} & \psi_{15} \\ -\psi_{12} & 0 & \psi_{23} & \psi_{24} & \psi_{25} \\ -\psi_{13} & -\psi_{23} & 0 & \psi_{34} & \psi_{35} \\ -\psi_{14} & -\psi_{24} & -\psi_{34} & 0 & \psi_{45} \\ -\psi_{15} & -\psi_{25} & -\psi_{35} & -\psi_{45} & 0 \end{bmatrix} \leq 2 \;\textit{ and }\; \operatorname{rank}\begin{bmatrix} (H\psi)_{12} & \psi_{12} \\ (H\psi)_{13} & \psi_{13} \\ (H\psi)_{14} & \psi_{14} \\ (H\psi)_{15} & \psi_{15} \\ (H\psi)_{23} & \psi_{23} \\ (H\psi)_{24} & \psi_{24} \\ (H\psi)_{25} & \psi_{25} \end{bmatrix} \leq 1$$

Hamiltonian H is a 10×10 matrix.

$\#$ solutions in $\mathbb{P}^9$ equals $\mathrm{CCdeg}_{2,5}(\{1\}) = \mathbf{27} = 2 \cdot \mathbf{14} - 1$.

Degree Bound

Theorem

The number of isolated solutions satisfies

$$\mathrm{CCdeg}_{d,n}(\sigma) \quad \leq \quad \big(\dim(V_\sigma)+1\big)\deg(V_\sigma).$$

Example $(d=2, n=5, \sigma=\{1\})$

For $\mathrm{Gr}(2,5)$, the inequality is strict: $27 \ \leq \ 7 \cdot 5 = 35$.

Corollary

Suppose V_σ *is a linear space. Then* $(H\psi)_\sigma = H_{\sigma,\sigma}\psi_\sigma$*, and*

$$\mathrm{CCdeg}_{d,n}(\sigma) \ = \ \dim(V_\sigma)+1.$$

The CC equations describe the usual eigenvalue problem for the symmetric matrix $H_{\sigma,\sigma}$*. In particular, all complex solutions are real.*

Catalan Numbers

2, 5, 14, 42, 132, 429, 1430

Fix $d = 2, \sigma = \{1\}$.

The degree of the Grassmannian $\mathrm{Gr}(2, n)$ *is the Catalan number*

$$C_{n-2} \;=\; \frac{1}{n-1}\binom{2n-4}{n-2}.$$

Theorem (arXiv today)

The CC degree of the Grassmannian $\mathrm{Gr}(2, n)$ *equals*

$$2 \cdot C_{n-1} \,-\, 1 \;=\; \frac{4}{n}\binom{2n-3}{n-1} \,-\, 1.$$

CCdeg: 9, 27, 83, 263, 857, 2859

Bound: 10, 35, 126, 462, 1716, 6435

This was Conjecture 5.5 in the paper with Fabian and Svala.
Proved in the **new paper** with Svala and Viktoriia Borovik.

Master Polynomial Revisited

Proposition

If $n = 2d$ and $\sigma = \{1, 2, \ldots, d-1\}$, then the bound is off by $d-1$:

$$\begin{aligned} \mathrm{CCdeg}_{d,2d}(V_\sigma) \;&=\; \big(\dim(V_\sigma)+1\big)\deg(V_\sigma) \;-\; (d-1) \\ &=\; d\binom{2d}{d} - 2d + 1. \end{aligned}$$

Here the truncation variety is a hypersurface.

Example ($d = 3$)

Six truncation varieties in $\mathbb{P}^{19}$ revisited:

σ	$\{1\}$	$\{2\}$	$\{3\}$	$\{1,2\}$	$\{1,3\}$	$\{2,3\}$
dim	9	9	1	18	10	10
degree	42	1	1	3	41	1
bound	420	10	2	57	451	11
$\mathrm{CCdeg}_{3,6}$	250	10	2	**55**	420	11

Previous Literature

Work presented here improves significantly over

- F. Faulstich and M. Oster: *Coupled cluster theory: towards an algebraic geometry formulation*, SIAM J Appl Algebra Geom, 2024.

Section 6 reports that the CCSD model for three electrons in six spin-orbitals $(d = 3, n = 6, \sigma = \{1,2\})$ *supersedes the abilities of state-of-the-art algebraic geometry software*. Theorem 4.10 offers upper bound $2^{27} = 134217728$ for $\mathrm{CCdeg}_{3,6}(\sigma)$.

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Theorem

Our formulation of the CC equations is equivalent to the classical equations in [FO] if and only if σ is an arithmetic progression, i.e. $\sigma = \{m, 2m, \ldots, km\}$ for some integers $m, k \geq 1$ with $km \leq d$.

This covers all models CCS, CCD, CCSD, CCSDT studied in the vast computational chemistry literature. *Sample reference:* [K. Kowalski and P. Piecuch: *Complete set of solutions of multireference coupled-cluster equations: The state-universal formalism*, Physical Review A (2000)]

Numerical Solutions

We solved the CC equations for a range of models with

`HomotopyContinuation.jl`

[P. Breiding and S. Timme: *HomotopyContinuation.jl: A package for homotopy continuation in Julia*, Mathematical Software – ICMS 2018]

[P. Breiding, K. Rose and S. Timme: *Certifying zeros of polynomial systems using interval arithmetic*, ACM Trans. Math. Software **49** (2023)]

Example ($d = 3, n = 8$)

The six CC models for three electrons in eight spin-orbitals:

σ	$\{1\}$	$\{2\}$	$\{3\}$	$\{1,2\}$	$\{1,3\}$	$\{2,3\}$
$\lvert\widetilde{\sigma}\rvert + 1$	16	31	11	46	26	41
$\deg(V_\sigma)$	6006	1	1	3894	4195	1
$\mathrm{CCdeg}_{3,8}$	38610	31	11	145608	58214	41
$\#\mathrm{real}$	430	31	11	1376	658	41
$\mathrm{solve(sec)}$	619	8	3	26757	1948	7
$\mathrm{certify(sec)}$	7	3	0	41	8	0

Scientists Like Figures

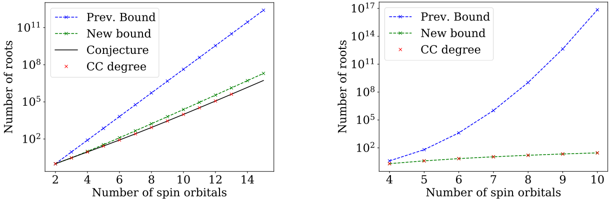
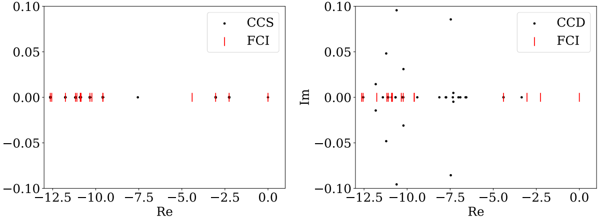


Figure 4: Bounds to the number of roots of CCS (left panel) and CCD (right panel).

chemistry (cf. Section 4) is not generic, but has special structure. Therefore, the obtained number of solutions for the target system can be much smaller than the CC degree.



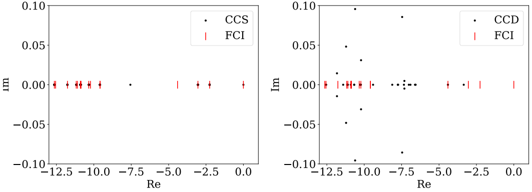
(a) CCS (only real)

(b) CCD

Figure 5: Energy spectra from exact diagonalization (FCI) and from CCS and CCD.

Example 6.4 (Lithium hydride ($d = 4$, $n = 8$)). We use the Hamiltonian from Example 4.3.

Lithium Hydrite



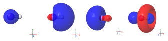
(a) CCS (only real)

(b) CCD

Figure 5: Energy spectra from exact diagonalization (FCI) and from CCS and CCD.

CCS model for $d = 4$, $n = 8$

We use the Hamiltonian (70×70 *matrix) derived from*



Solving generic start system for $\sigma = \{1\}$ *takes 82 minutes and yields* 154441 *solutions – the CC degree for* $\mathrm{Gr}(4, 8)$.

Tracking all paths yields 3 *non-singular solutions, all real. We also find* 104641 *singular solutions. Only* 399 *of them yield real energies. Use these for comparison to exact eigenvalues. Takes* 11 *minutes and* 32 *seconds.*

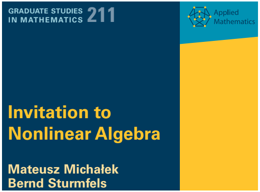
Figure 5 compares the exact eigenvalue spectrum with the energies obtained from CCS and CCD. Interesting observation: these appear to approximate different subsets of eigenvalues that cover the whole spectrum..... etc...etc...

Conclusions

$$(H\psi)_\sigma = \lambda \psi_\sigma$$
$$\text{for } \psi \in V_\sigma$$

HomotopyContinuation.jl

- Algebraic Geometry and Combinatorics are essential ingredients for Mathematics in Science.
- Polynomial equations with $\sim$ 100,000 zeros can now be solved routinely, with certification.
- Everybody loves Grassmannians and Catalan numbers.
- Quantum chemistry offers very interesting problems.
- Our equations make sense for any projective variety V



GRADUATE STUDIES IN MATHEMATICS 211

Applied Mathematics

Invitation to Nonlinear Algebra

Mateusz Michałek
Bernd Sturmfels

Thank You
for Listening

Math in Science

Our Abstract

We develop algebraic geometry for coupled cluster (CC) theory of quantum many-body systems. The high-dimensional eigenvalue problems that encode the electronic Schrödinger equation are approximated by a hierarchy of polynomial systems at various levels of truncation. The exponential parametrization of the eigenstates gives rise to truncation varieties. These generalize Grassmannians in their Plücker embedding. We explain how to derive Hamiltonians, we offer a detailed study of truncation varieties and their CC degrees, and we present the state of the art in solving the CC equations.

$$\psi_{12}\psi_{34} - \psi_{13}\psi_{24} + \psi_{14}\psi_{23} = 0$$

$$\begin{pmatrix} \star & \star & \star & \star \\ \star & \star & \star & \star \end{pmatrix}$$