Perturbative Quantum Chemistry

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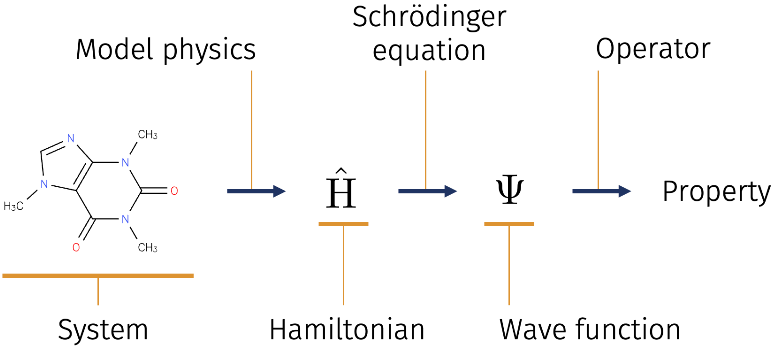
🌐 nablachem.org/talks

Solved?



Model physics

Schrödinger equation

Operator

$\hat{H}$

Ψ

Property

System

Hamiltonian

Wave function

Scale

Each single point is hard

- $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$
- Common methods scale N^3 or worse

Chemical space is vast

- 10^{60}
- sampling: random-molecule.org[1]

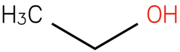
Methane

CH_4

N_2

$N \equiv N$

Ethanol



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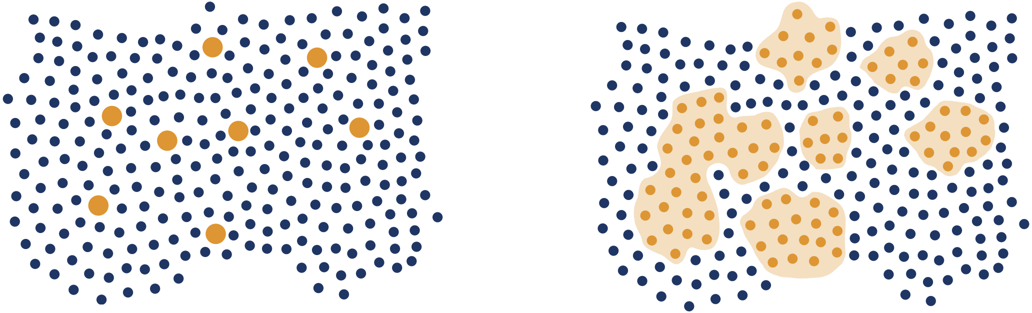
[1] D J Monterrubio-Chanca, GFvR, *J Chem Theory Comput*, 2025.

Scale

Speed does not matter

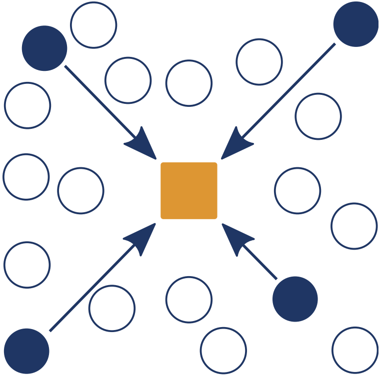
even enumeration is impossible



Ideas

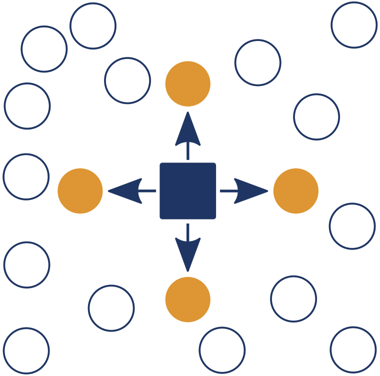
Machine Learning

Interpolation



Quantum Alchemy

Extrapolation



Properties

change in geometry (R), external electric field (F), external magnetic field (M), nuclear magnetic field (I)

n_R	n_F	n_B	n_I	**Property**
1	0	0	0	Energy gradient **g**
2	0	0	0	Harmonic vibrational frequencies ω_i
0	1	0	0	Electric dipole moment μ
0	2	0	0	Electric polarizability α
0	0	1	0	Magnetic (dipole) moment μ
0	0	2	0	magnetic susceptibility χ
0	0	0	1	ESR hyperfine coupling constant a_i
1	1	0	0	Intensities of fundamental IR transitions
0	1	1	0	Circular dichroism (CD)
0	0	1	1	Nuclear magnetic shielding (→ chemical shift in NMR)

Quantum Alchemy

Connect two iso(-valence-)electronic systems[1,2,3]

$$\hat{H}(\lambda) = \overbrace{\lambda}^{\text{Mixing parameter}}\, \underbrace{\hat{H}_\mathrm{t}}_{\text{Target Hamiltonian}} + (1-\lambda)\, \underbrace{\hat{H}_\mathrm{r}}_{\text{Reference Hamiltonian}} \tag{1}$$

Taylor approximant in λ

- Potentially many coefficients
- Hopefully converges early

Idea

Few highly accurate calculations instead of many intermediate ones

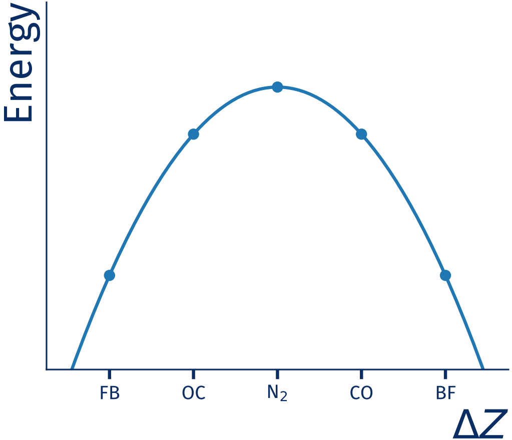
$$\hat{H} = \hat{H}(\underbrace{Z_i, \mathsf{R}_i}_{4N}, \overbrace{N_e}^{\text{1D, close to } \sum_I Z_I}, \underbrace{\sigma}_{\text{1D}}) \tag{2}$$

1| E. B. Wilson, J. Chem. Phys. 1962 2| GFvR, O. A. von Lilienfeld, Phys. Rev. Res., 2020.
3| GFvR, J. Chem. Phys., 2021.

Quantum Alchemy: Example

Intermediate values

- Fractional nuclear charges
- Physically valid, yet unobservable



Quantum Alchemy: Different uses

Quantitative prediction

- closed form (!)
- cheap to evaluate
- use as constraint for models

Interpretation

- decouple global physical effect
- discover dominant trends
- discover sparsity patterns

$$\overset{\text{Property}}{Q}(\underbrace{\boldsymbol{\Delta Z}}_{\text{Changes in nuclear charges}}) \simeq \sum_{|\alpha| \leq \underbrace{k}_{\text{Truncation of expansion, 2 or 3}}} \frac{\partial^{|\alpha|} \sigma_I(\mathbf{a})}{\partial Z_1^{\alpha_1} \cdots \partial Z_n^{\alpha_n}} \frac{\boldsymbol{\Delta Z}^{\alpha}}{\alpha!} \tag{3}$$

Tested

Methods

- Hartree-Fock
- DFT
- CCSD

Codes

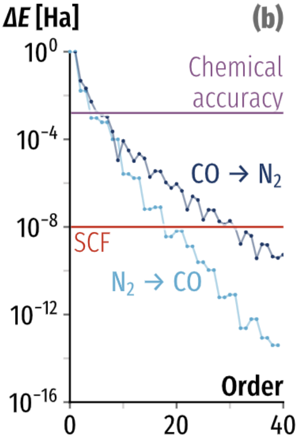
- Molecules
  - Gaussian, Psi4, PySCF, MRCC, ORCA
- Materials
  - cp2k, CPMD
- AD
  - Quax, dqc, DiffiQult, PySCF-AD

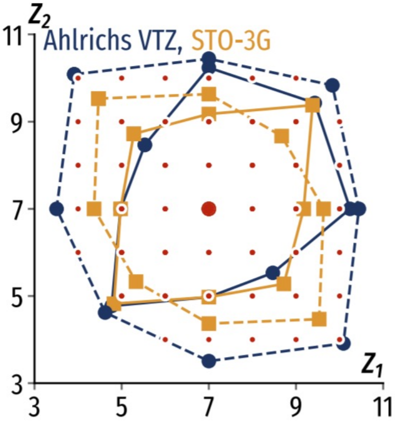
Properties

- Total Energy [1,2]
- Electron density [1,2]
- Orbital eigenvalues [2]
- Dipole moments [2]
- Non-covalent interactions [1]
- Binding energies [1,2]
- Deprotonation energies [3]
- Ionisation Energy, Electron Affinity [4]
- Photoelectron circular dichroism [5]
- ...

1| GFvR, A von Lilienfeld, Phys. Rev. Res., 2020 2| GFvR, J. Chem. Phys., 2021 3| GFvR, A von Lilienfeld, Phys. Chem. Chem. Phys., 2020 4| E Eikey, A Maldonado, C Griego, GFvR, J Keith, J. Chem. Phys., 2022 5| GFvR, A Artemyev, B Lagutin, P Demekhin, J. Chem. Phys., 2024

Convergence



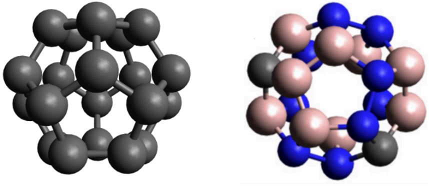


GFvR, *J. Chem. Phys.*, *2021.*

Quantitative examples

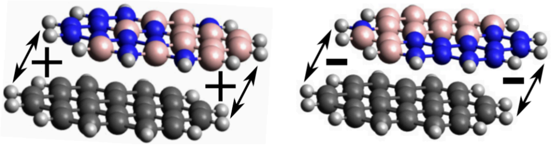
Covalent Interaction

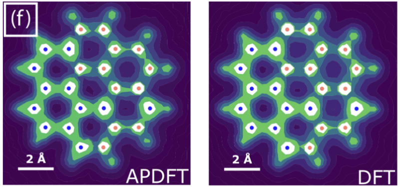
- $3.1 \cdot 10^6$ targets
- 80.000x faster



Non-covalent Interactions

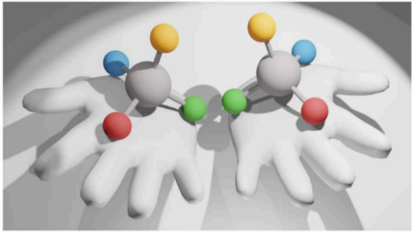
- $2.8 \cdot 10^{10}$ targets
- 20.000x faster

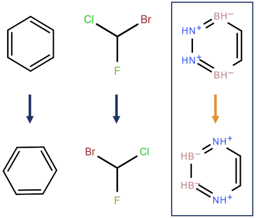


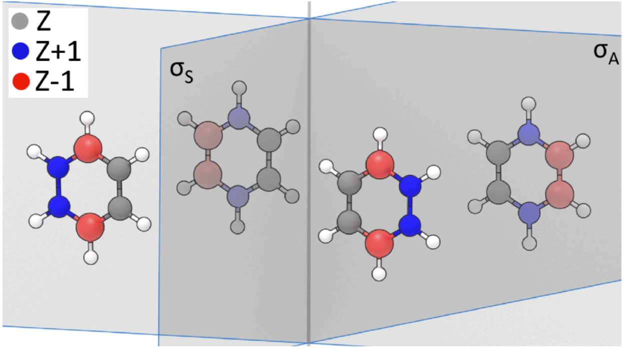


GFvR, O. A. von Lilienfeld, Phys. Rev. Res., 2020.

Symmetries: Alchemical Enantiomers





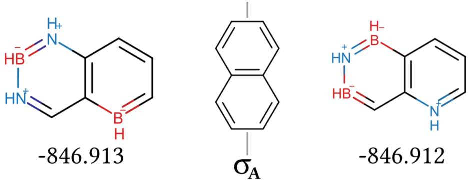


GFvR, O. A. von Lilienfeld, Science Adv. 2021.

Symmetries: Alchemical Enantiomers

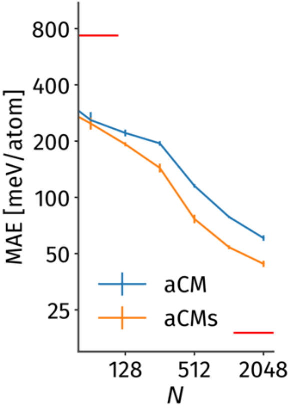
Fundamental symmetry

- Electronic energy only
- Include derivatives



Approximate Symmetry

saves training data



GFvR, O. A. von Lilienfeld, Science Adv. 2021.

Interpretability PECD

Angular emission

- Expensive to calculate
- Highly coupled degrees of freedom: multidimensional expansion

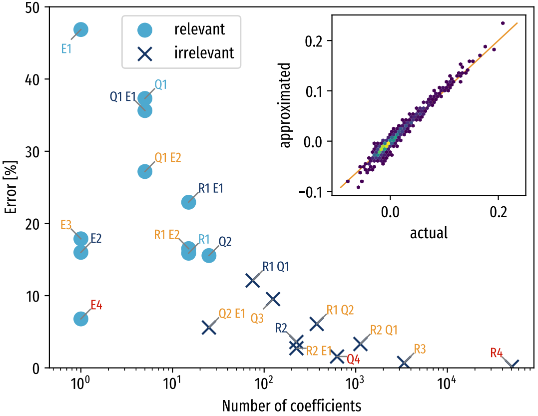
cross section

anisotropy parameter

$$\frac{d\sigma^{\pm}}{d\Omega} = \frac{\sigma}{4\pi}\left[1 \pm \beta_1 P_1(\cos\theta) - \frac{1}{2}\beta_2 P_2(\cos\theta)\right] \quad (4)$$

emission angle

dichroic parameter



GFvR, A Artemyev, B Lagutin, P Demekhin, J. Chem. Phys., 2024.

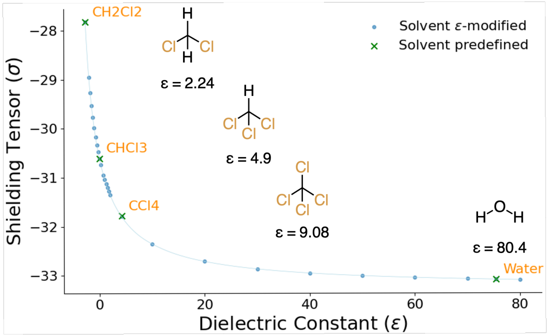
Interpretability NMR

NMR shift σ

- Used for identification of atoms-in-molecules
- Formally: $4N - 7$ degrees of freedom
- Typically short-range
- strong solvent interaction $\sigma(\mathsf{R}_I, Z_I|\mathsf{w})$

Interpretation

- $i \neq j : \frac{\partial^2 \sigma}{\partial Z_i \partial Z_j} = 0$
- H shift: at most second order in Z_i
- C shift: at most third order in Z_i
- Can often be simplified: $\partial_{\mathsf{w}} \sigma \approx \partial_{\varepsilon} \sigma$

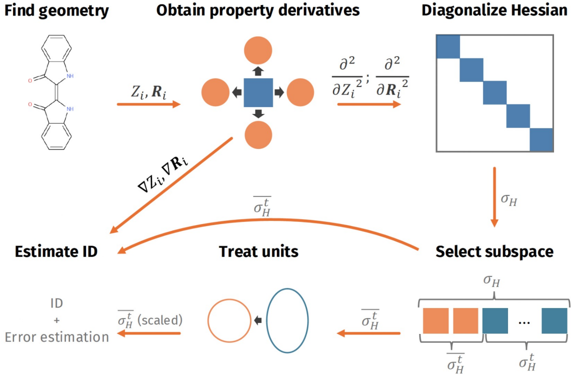


Nicolas Grimblat, GFvR, *in preparation*.

Dimensionality Estimation

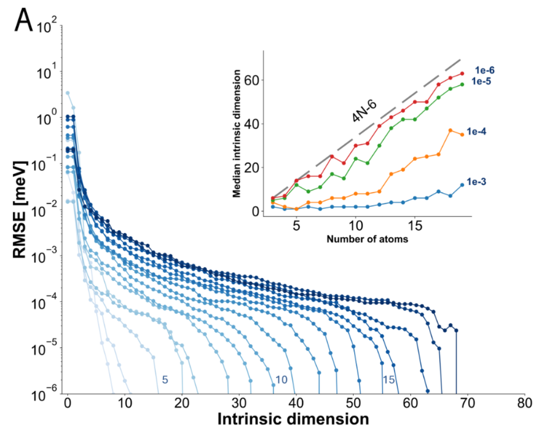
(Local) Intrinsic Dimension

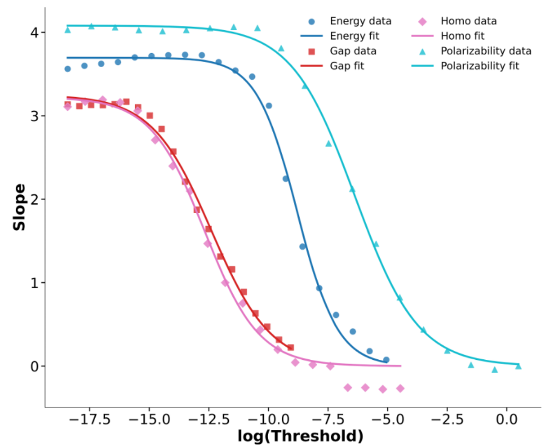
- Minimal number of orthogonal basis vectors s.t. $\langle Q \rangle_\Omega < t$ in local environment Ω
- $\neq$ intrinsic dimension of point cloud



A Banjafar, GFvR, J Chem Phys, 2025.

Dimensionality Estimation





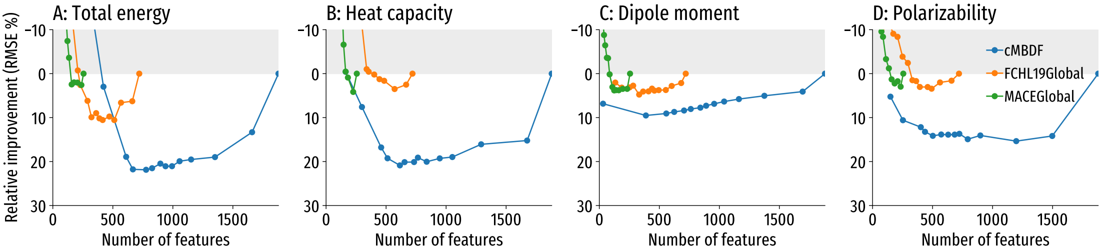
A Banjafar, GFvR, J Chem Phys, 2025.

Dimensionality Reduction

Kernel Ridge Regression

Data-efficient, needs molecular representation

$$\underbrace{y}_{\text{prediction}}(\underbrace{\mathbf{x}'}_{\text{representation}}) = \sum_i \overbrace{\alpha_i}^{\text{model weights}} \overbrace{k}^{\text{kernel function}}(\mathbf{x}_i, \mathbf{x}') \tag{5}$$



A Banjafar, GFvR, *in preparation.*

Quantum Alchemy: Limitations

Derivatives are hard

- Finite differences: expensive, unstable
- Hellmann-Feynman: basis set inaccurate
- Coupled-perturbed: finite order
- Automatic differentiation: memory
    - DiffiQult, quax, dqc, PySCF-AD

Pseudopotentials

Discrete Elements, parameters not differentiable

Gaussian basis sets not cooperative

- Elements are discrete, derivatives are not
- Density converges slowly with basis quality

Convergence

- Finite radius
- Not all systems are made equally

Summary

Symmetries

Reducing ("folding") search space

Physics-driven

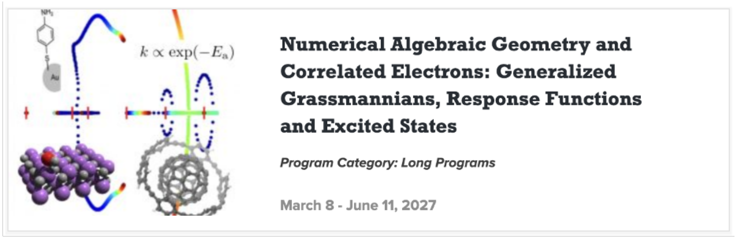
Predictive power

Closed-Form

Explainable and shows structure

Efficient

Re-use knowledge, no one-by-one



Numerical Algebraic Geometry and Correlated Electrons: Generalized Grassmannians, Response Functions and Excited States

Program Category: Long Programs

March 8 - June 11, 2027

PhD position available

Quantum Alchemy for materials

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