Computational Material Design and the Curse of Dimensionality

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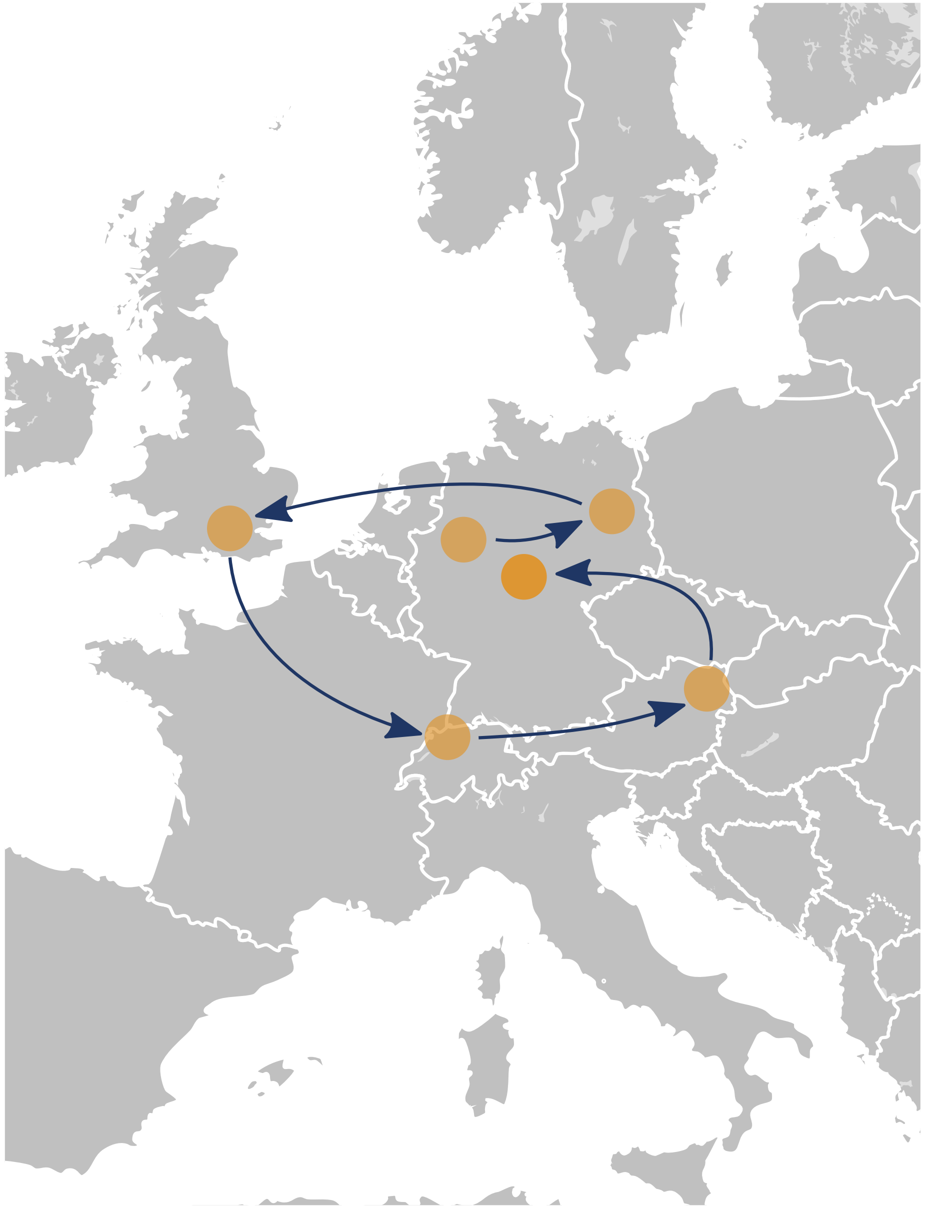
About me



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universität wien

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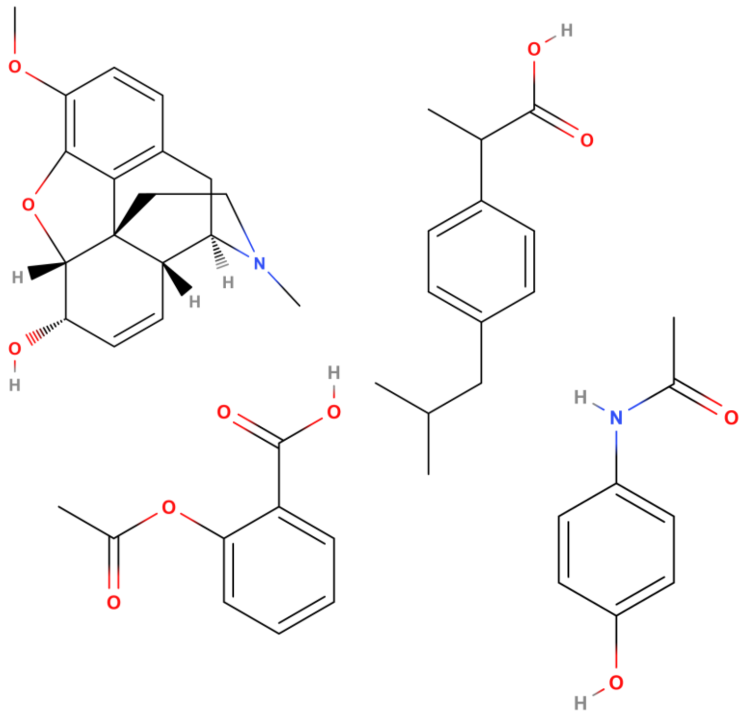
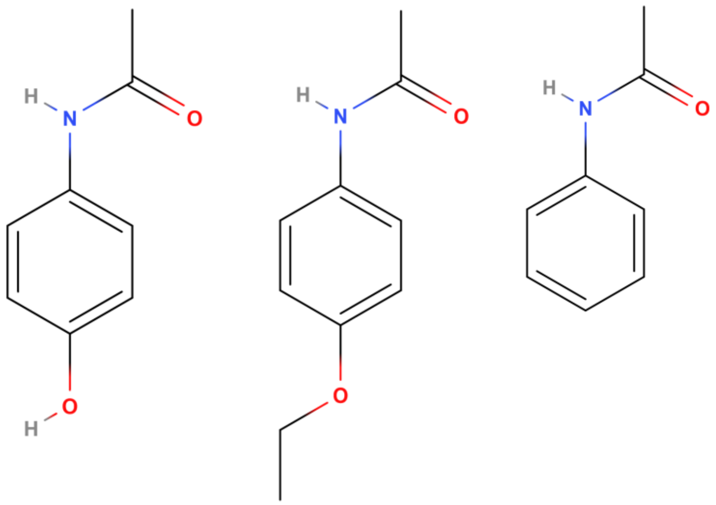
Introduction



Global Search Problem

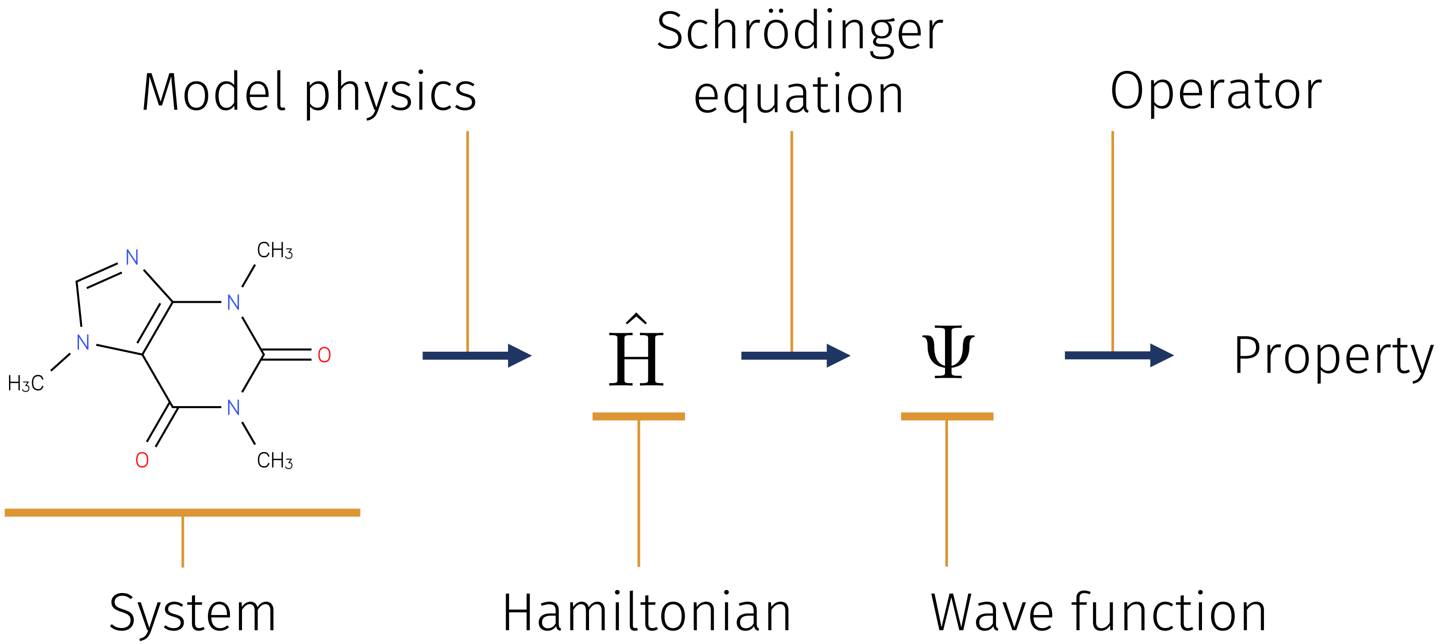
Which class of compounds?



Local Search Problem

Which particular species within that class?

Solved?


Model physics
Schrödinger
equation
Operator
N
CH3
N
N
O
H3C
N
O
CH3
Ĥ
Ψ
Property
System
Hamiltonian
Wave function

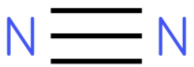
Wave Function

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_n)$$

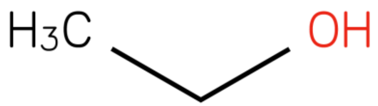
Methane

CH_4

N_2



Ethanol



Solved by approximations in computational chemistry?

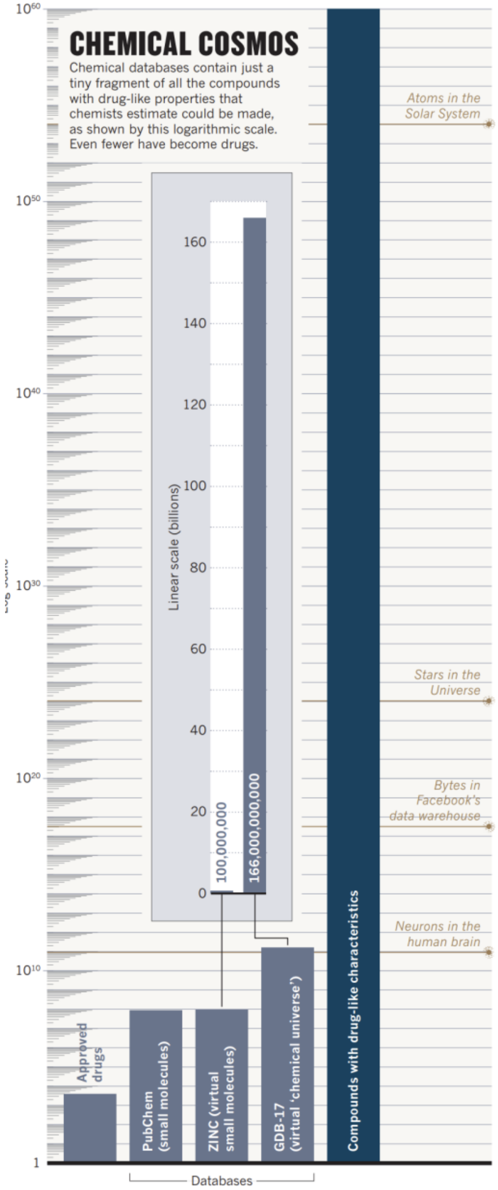
Scaling of Molecules

Commercial databases

- 164 million molecules
- 15k added daily

Scale

- One person: 1 million compounds/second
- 10 billion people on earth
- 10^{26} universe ages to go through



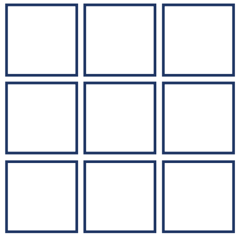
A. Mullard, *Nature*, 2017.

Scaling of Materials

Face centered cubic and 70 elements only

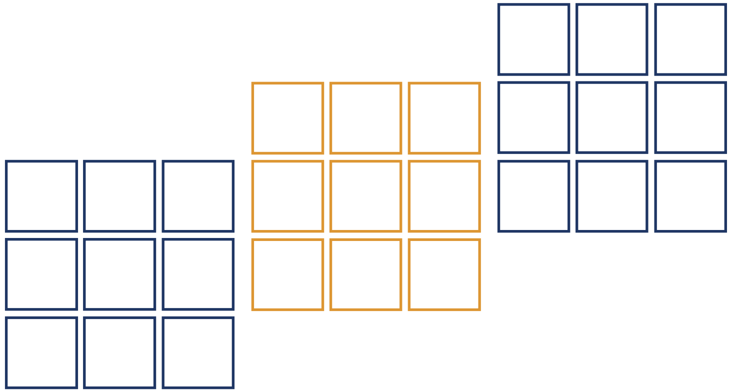
9 primitive cells

- Binary 10^7
- Ternary: 10^{13}
- Quaternary: 10^{15}



27 primitive cells

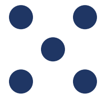
- Binary: ~ 10^{17}
- Ternary: ~ 10^{29}
- Quaternary: ~ 10^{36}



K. Shinohara, A. Seko, T. Horiyama, M. Ishihata, J. Honda, I. Tanaka, *J Chem Phys*, **2020**.

3D Geometries

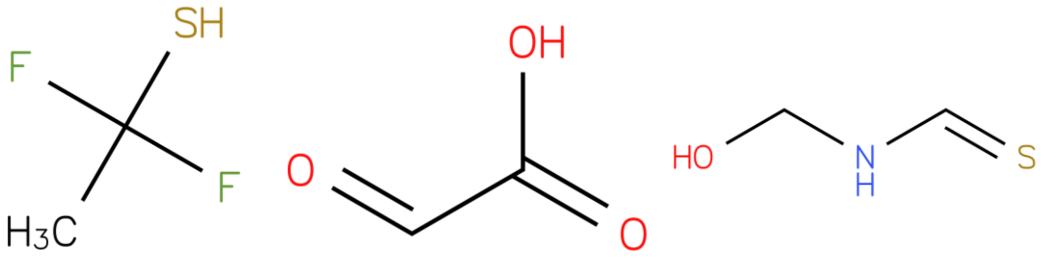
Take some atoms from {C, O, N, F, S}, H-saturated



349:

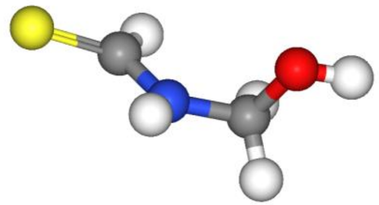
$C_2H_4F_2S$
$C_2H_2O_3$
C_2H_5NOS
...

9,917:



...

~52k:



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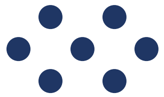
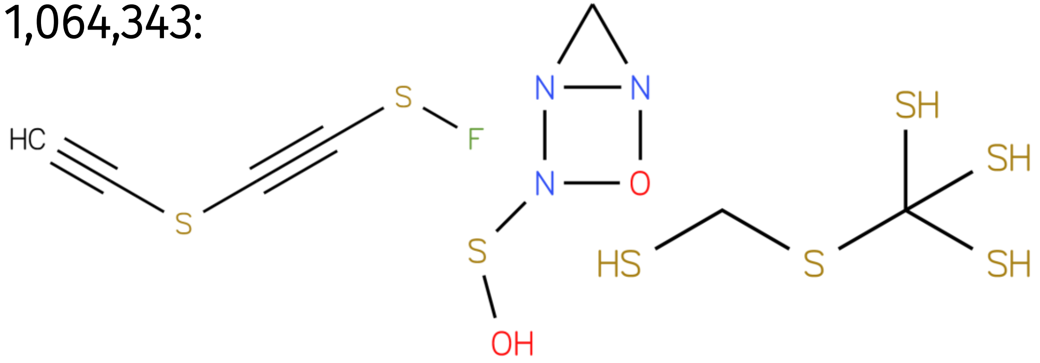


1,050:

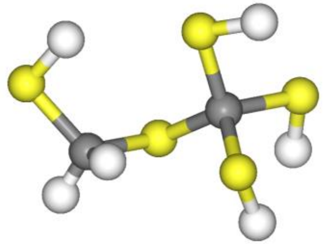
C_4HFS_2
$CH_3N_3O_2S$
$C_2H_6S_5$
...

1,064,343:



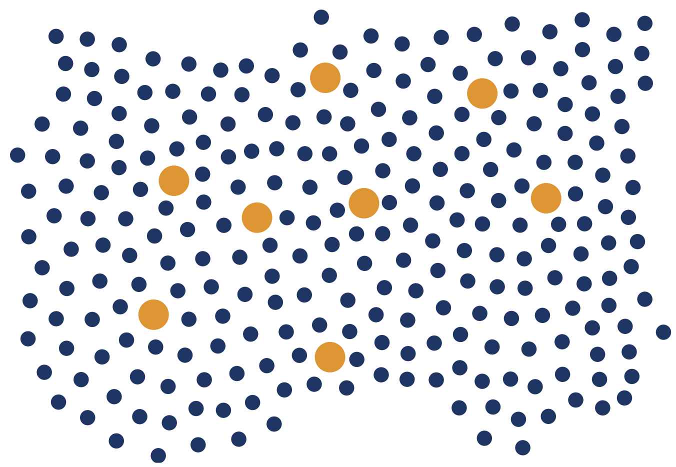
...

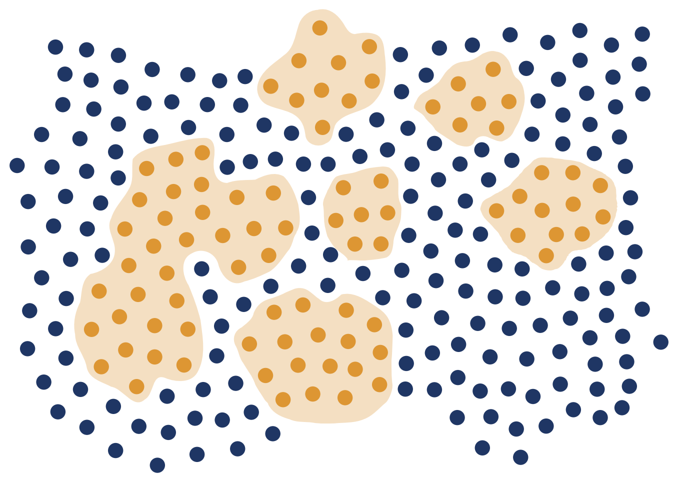
~23M:



...

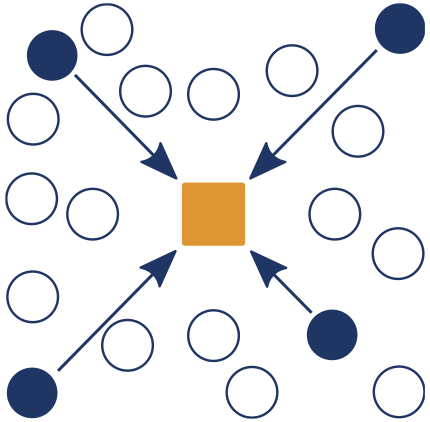
Speed does not matter:
even enumeration is impossible.





Approaches

Machine Learning



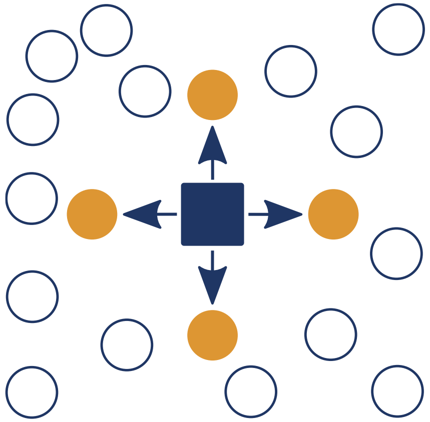
Foundations | Statistical modelling

Accuracy | Systematically improvable through data and training

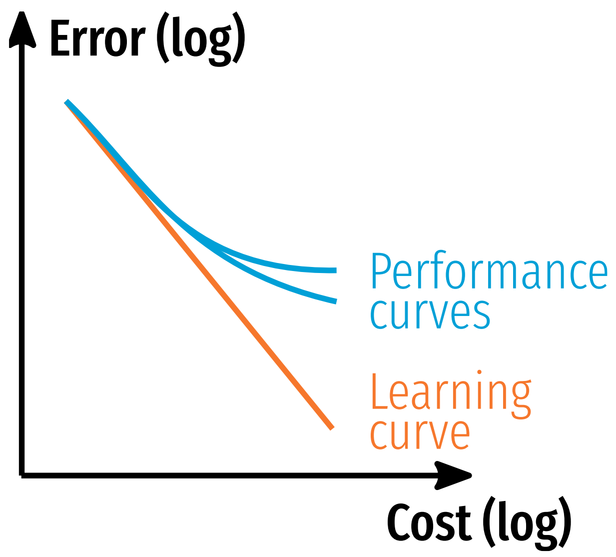
Specialty | Universal, scale-bridging, data-driven approach

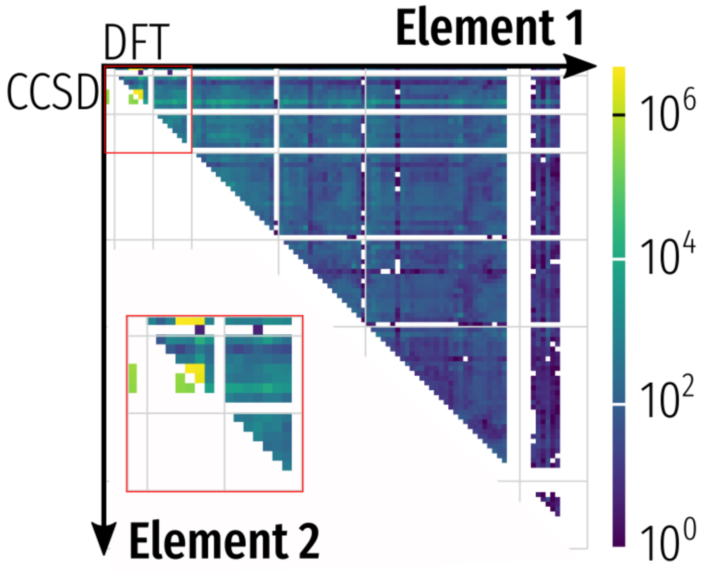
Limitation | Requires training data, no black box

Quantum Alchemy



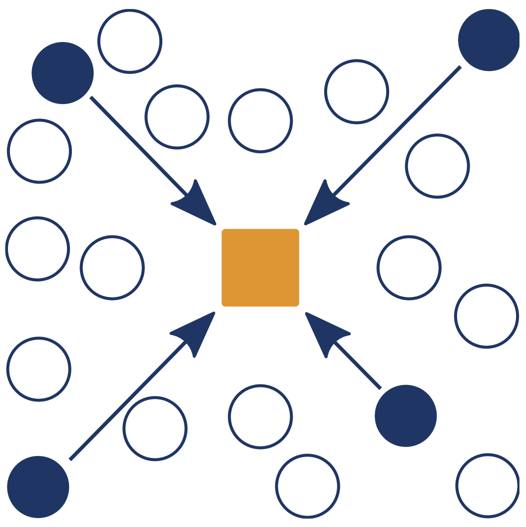
Data Availability





Low-Data Regime

Machine Learning

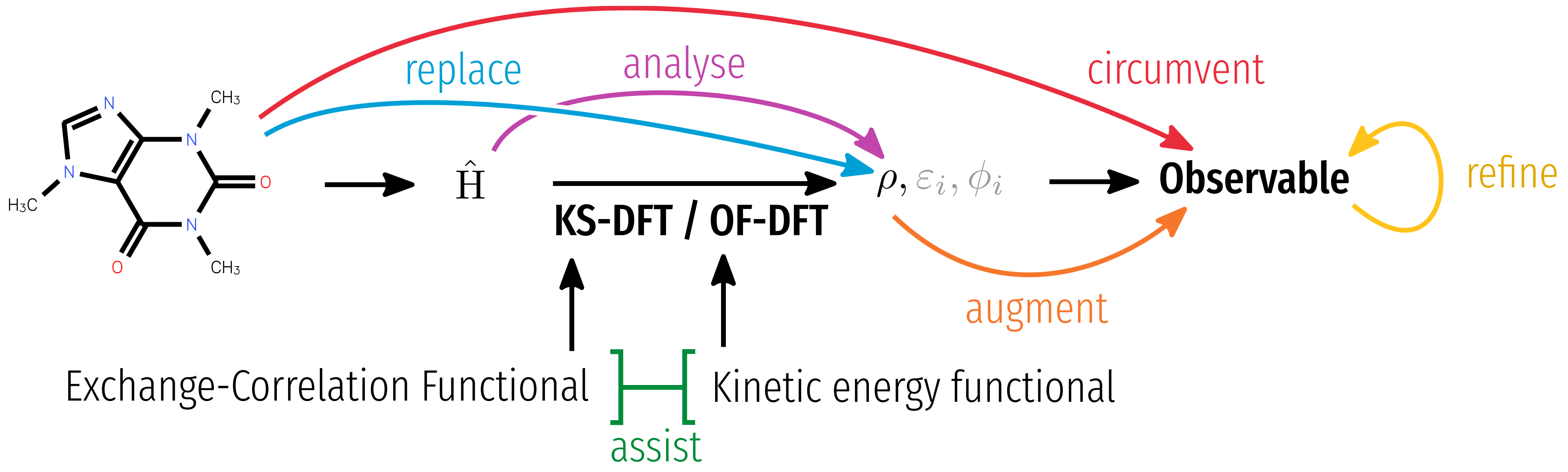


Kernel-Ridge-Regression

- Efficient in the low-data regime (around 1k points)
- Ingredients
  - Representation $\mathbf{M}$
  - Similarity measure $k(\mathbf{M}_i, \mathbf{M}_j)$
  - Observed properties $\mathbf{y}$
- Training
  - Pairwise similarities $\mathbf{K}$
  - Model coefficients $\boldsymbol{\alpha} = (\mathbf{K} + \lambda \mathbf{I})^{-1}\mathbf{y}$
- Predictions
  - Compare to training $\tilde{q}(\mathbf{M}) = \sum_i \alpha_i k(\mathbf{M}, \mathbf{M}_i)$

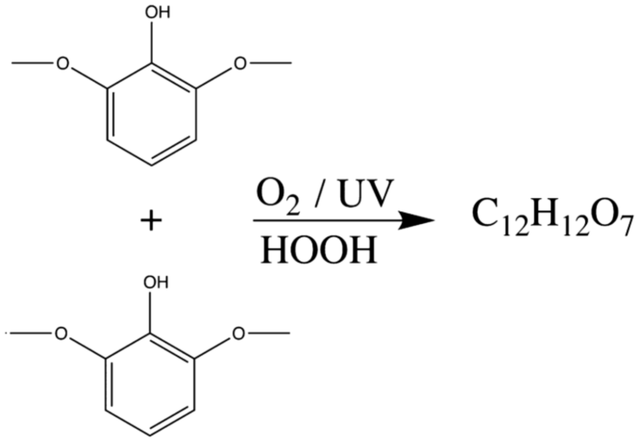
V. N. Vapnik: The Nature of Statistical Learning Theory, *Springer* **2000**.
B. Schölkopf, A. J. Smola: Learning with Kernels, *MIT Press*, **2001**.

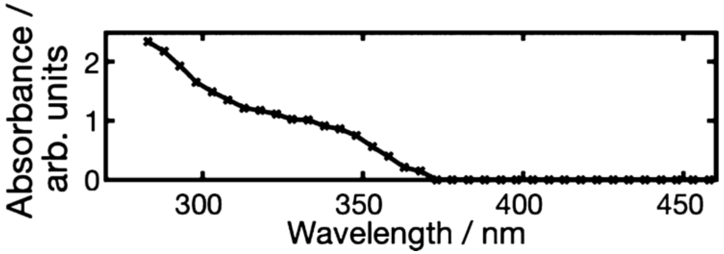
Strategies


CH3
N
N
N
O
N
H3C
O
CH3
Ĥ
KS-DFT / OF-DFT
ρ, εi, φi
Observable
replace
analyse
circumvent
refine
augment
Exchange-Correlation Functional
Kinetic energy functional
assist

Filter by Spectrum

Experiment

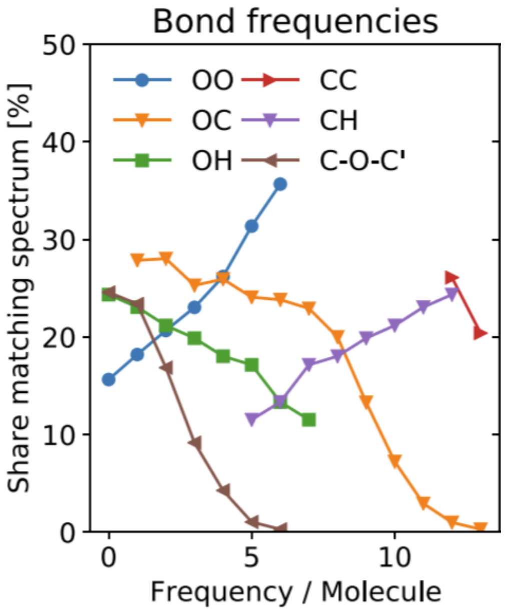




Search space

Molecular graphs: 264 M

Stable molecules: 123 M



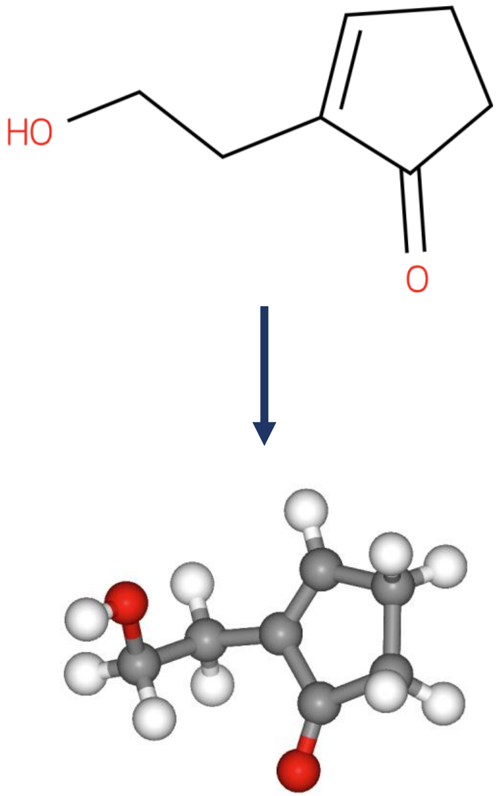
Millions at once!

Guide experiment

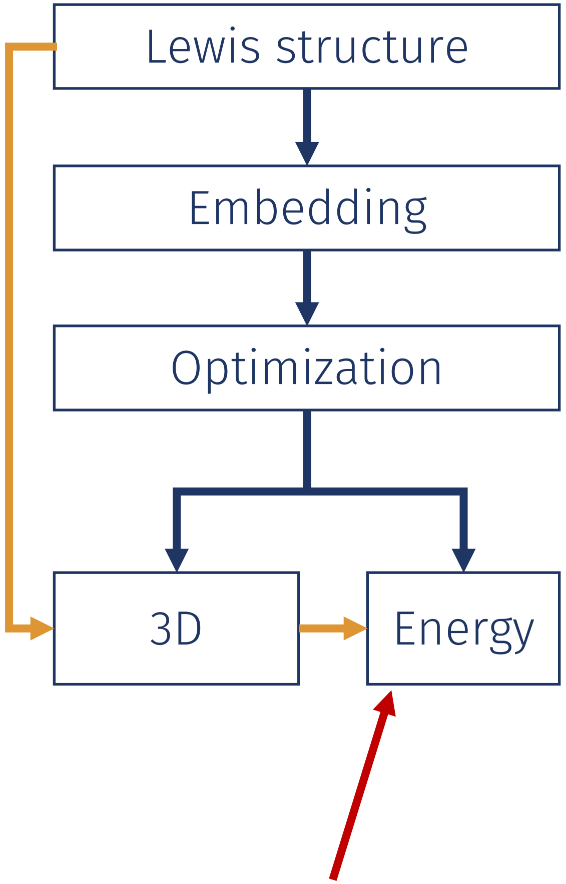
How many molecules are left and which feature to measure next?

E. Tapavicza, **GFvR**, D. O. De Haan, M. Contin, C. George, M. Riva, O. A. von Lilienfeld, *Environ. Sci. Technol.* **2021**.

Filter by Geometry



Traditional / G2S



ML: 100.000x faster,
can filter graphs

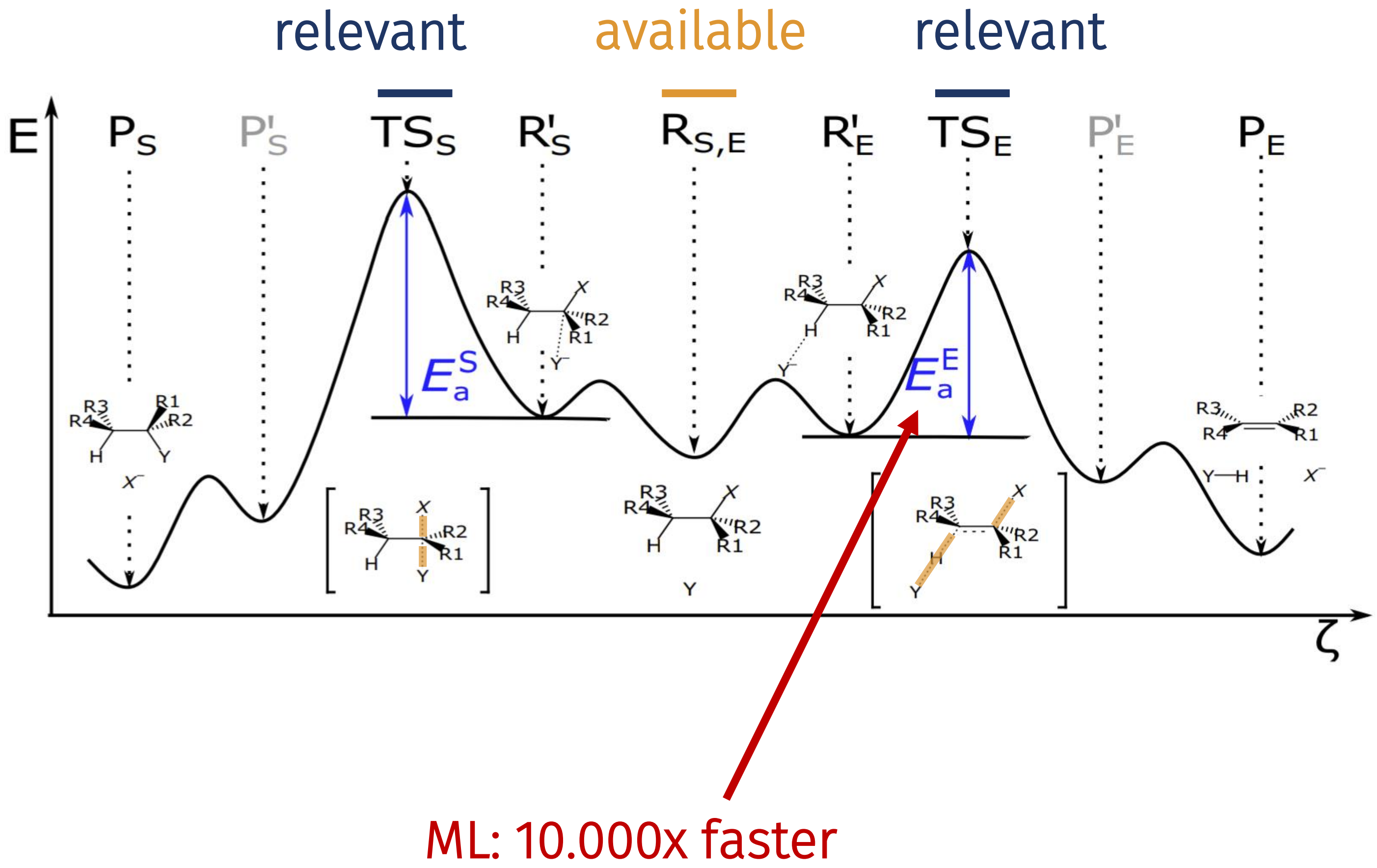
G2S

- Closer to DFT than common methods
  - Small molecules

- Applicable to complex chemical spaces
  - Transition state geometries
  - Carbenes
  - Elpasolite crystals

D. Lemm, **GFvR**, O. A. von Lilienfeld, *Nat. Commun.* **2021**.

Filter by Barriers

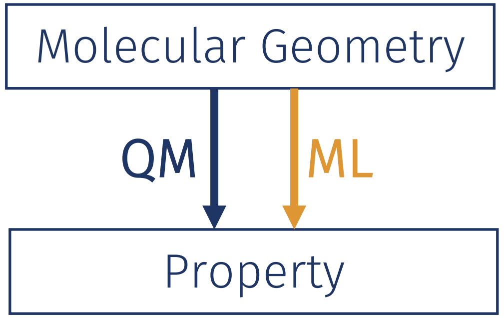


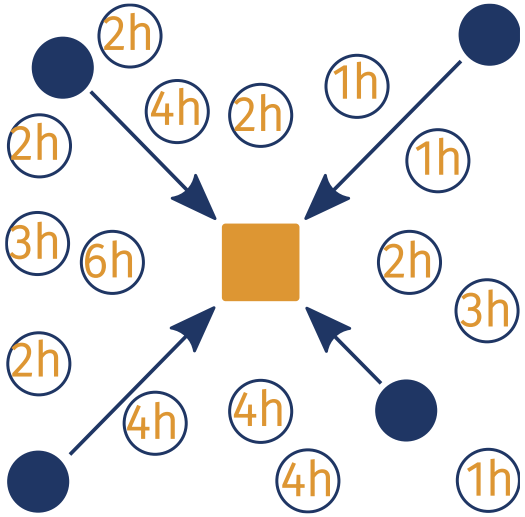
Competing reactions: E2, S_N2

- 4.5k reactions in one new dataset
- Learning activation energies from reactants only reaching 2.5 kcal/mol with 800 data points
- Learning geometries of transition states
  - direct
    0.05 Angstrom for distances
  - G2S
    0.45 Angstrom heavy-atom RMSD

GFvR, S.N. Heinen, M. Bragato, O. A. von Lilienfeld, *Mach. Learn.: Sci. Technol.* 2020.
S.N. Heinen, GFvR, O. A. von Lilienfeld, *J. Chem. Phys.*, 2021.

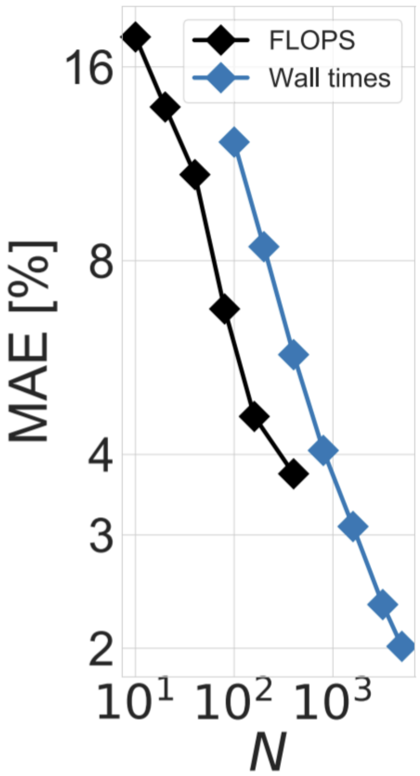
Filter by Cost





Computational effort as molecular property

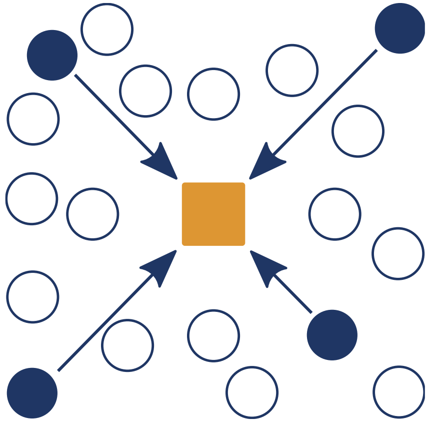
- Improves models
- Accuracy depends on problem
  - Single points: 2%
  - Transition state search: 25%
  - Geometry optimisations: 40%



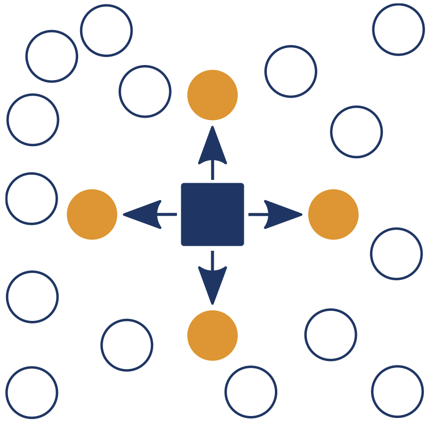
S.N. Heinen, M. Schwilk, **GFvR**, O. A. von Lilienfeld, *Mach. Learn.: Sci. Technol.* **2020**.

Approaches

Machine Learning



Quantum Alchemy



Foundations | Perturbation theory

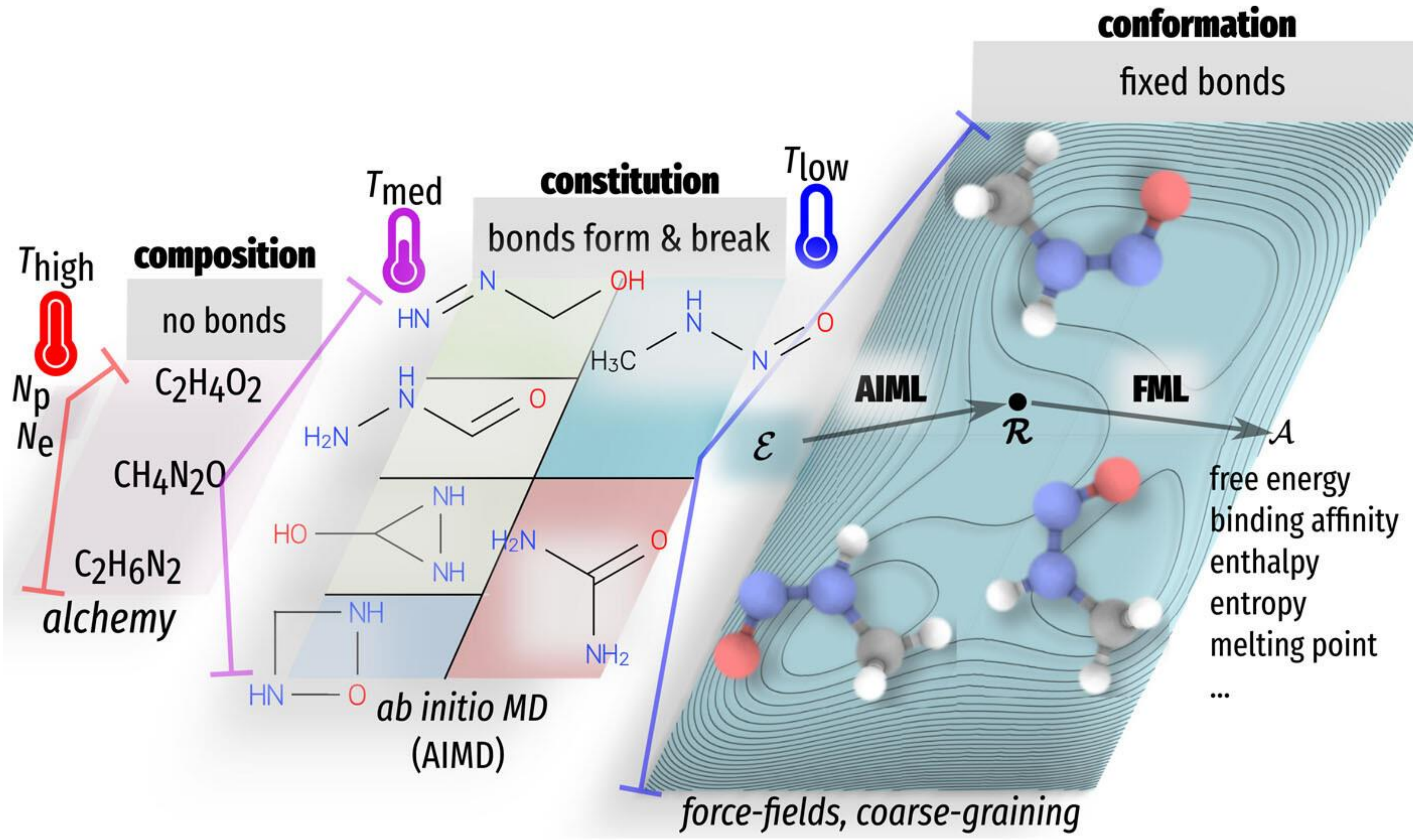
Accuracy | Systematically improvable through higher orders terms

Specialty | Combinatorial scaling with chemical diversity

Limitation | Finite range in chemical space

Joseph Wright, 1771

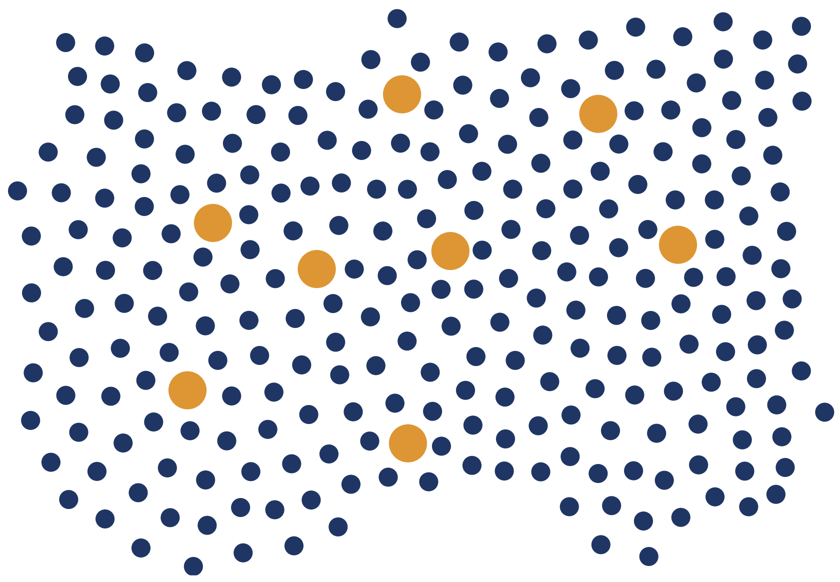
Discrete points?



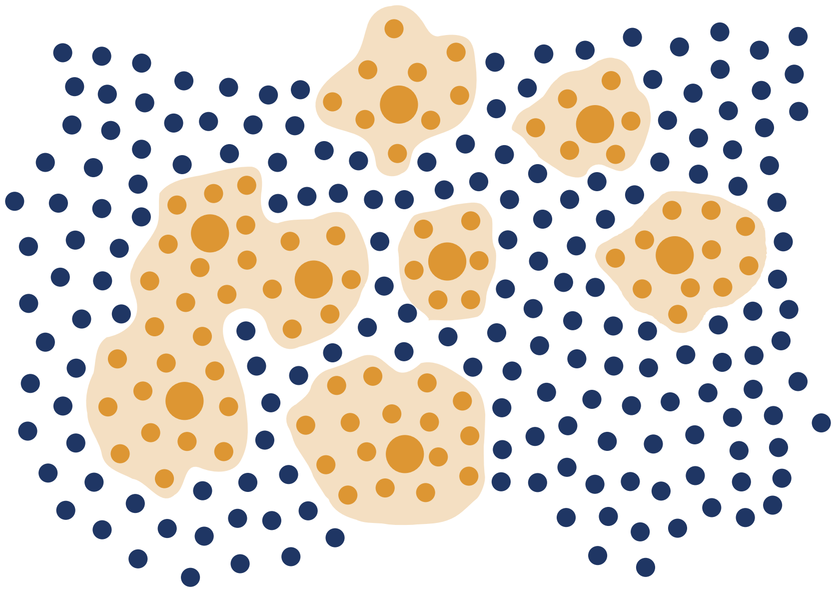
J. Weinreich, D. Lemm, GFvR, O.A. von Lilienfeld, *J. Chem. Phys.*, 2022.

Motivation

Without Perturbation



With Perturbation



Systems/Molecules

- Any
- Known
- Approximated

Motivation

Perspective shift

Few highly accurate calculations instead of many intermediate ones

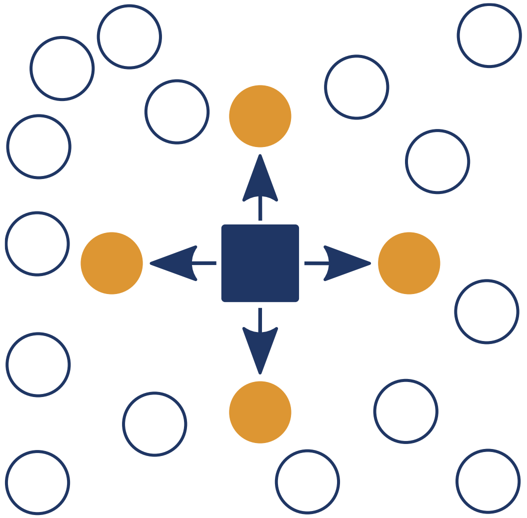
$$\hat{\mathrm{H}} = \hat{\mathrm{H}}(\underbrace{Z_i, \mathbf{R}_i}_{4N}, \underbrace{N_e}_{1D,\ \text{close to } \sum_i Z_i}, \underbrace{\sigma}_{1D})$$

4N

1D, close to $\sum_i Z_i$

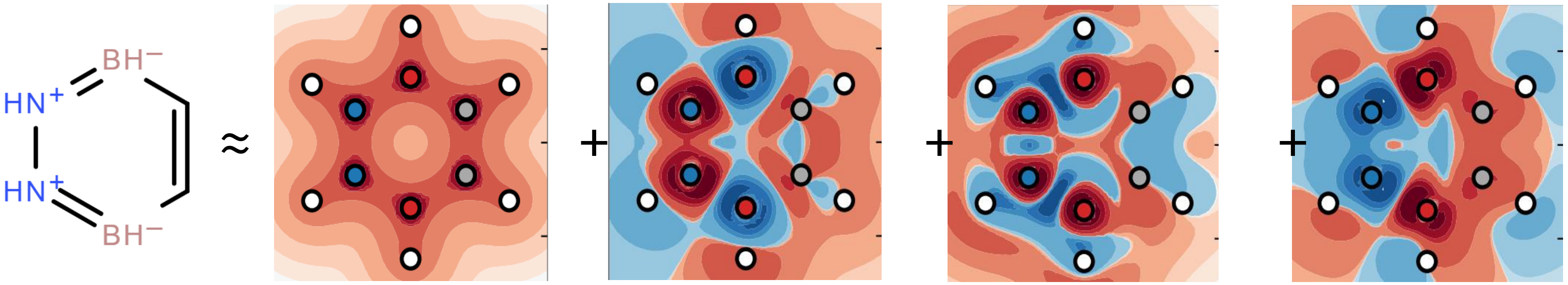
1D

Quantum Alchemy



Taylor expansion

- Energy function of
  - Geometry — Forces, Vibrations
  - Nuclear charges — Alchemical changes
- Idea: obtain dominant leading derivatives, predict many systems



E. B. Wilson, *J. Chem. Phys.* 1962.
GFvR, O. A. von Lilienfeld, *Phys. Rev. Res.*, 2020.

Quantum Alchemy

Interpolate between molecular isoelectronic Hamiltonians

$$\hat{H}(\lambda) \equiv \lambda \hat{H}_{\mathrm{t}} + (1-\lambda)\hat{H}_{\mathrm{r}}$$

Taylor expansion around reference molecule

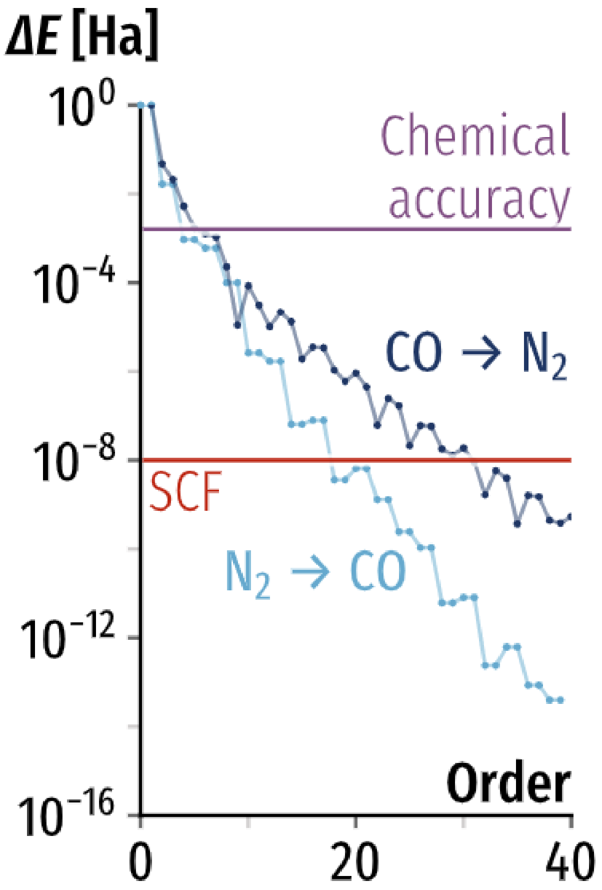
$$E_{\mathrm{t}} = E_{\mathrm{r}} + \Delta E^{\mathrm{NN}} + \int_{\Omega} d\mathbf{r} \sum_{n=0}^{\infty} \frac{1}{(n+1)!} \, \Delta v \frac{\partial^n \rho_\lambda(\mathbf{r})}{\partial \lambda^n}\bigg|_{\lambda=0}$$

- Gives consistent energies, densities, forces, …
- Uses the same derivatives for all predictions

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

xkcd.com/2605

Convergence



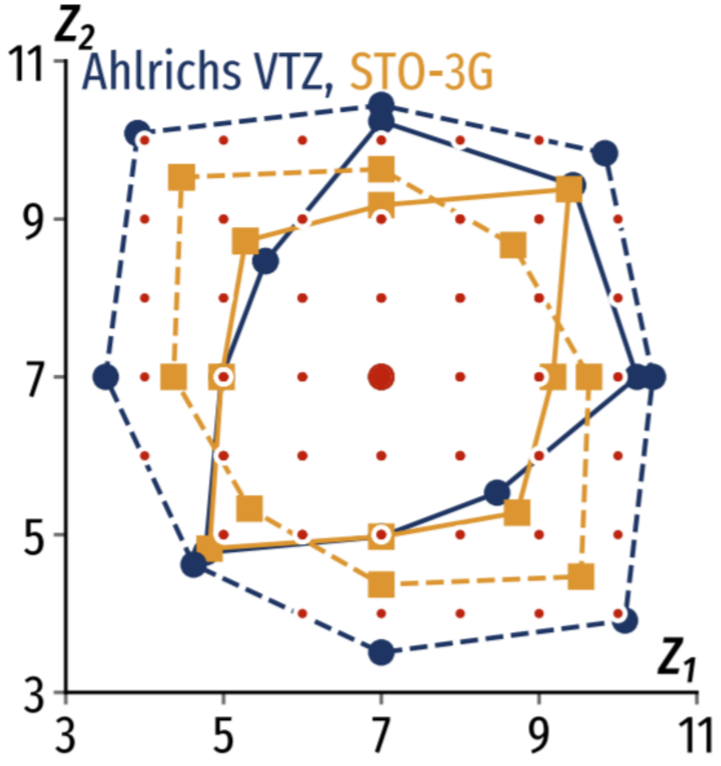
HF/STO-3G

Taylor expansion

- First terms accurate enough
  - Truncate early
- Converges to the right value
- Large convergence radius
- Scales with chemical space

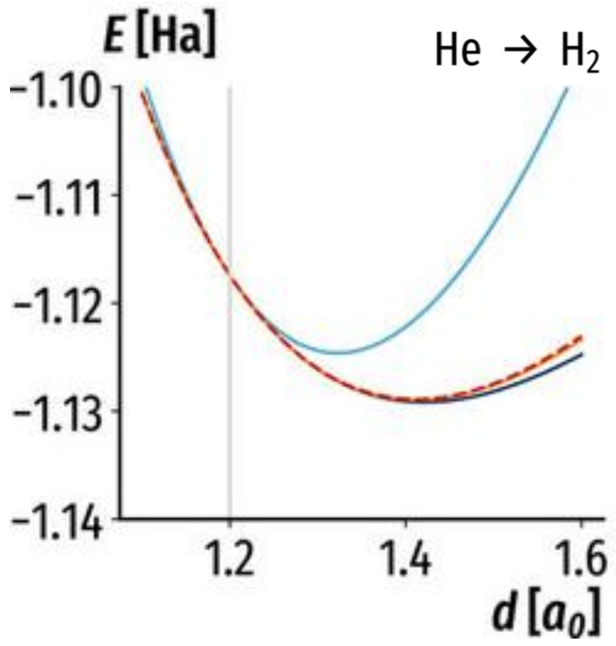
Limits

- Only few orders feasible
- Iterative in chemical space



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

Geometry Relaxation



Taylor expansion

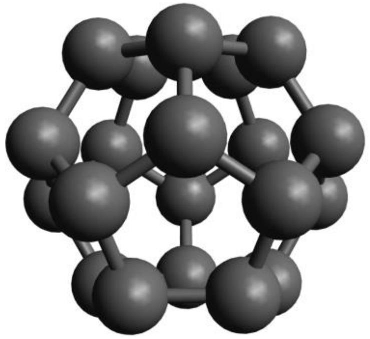
- Large changes still converge (more slowly)
- Geometric response can be recovered

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

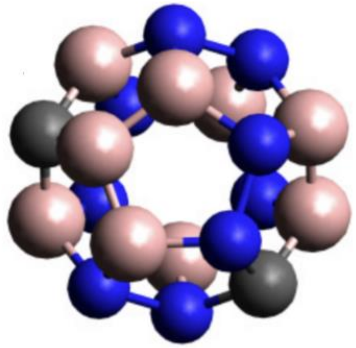
Covalent Interactions

Scaling with chemical space

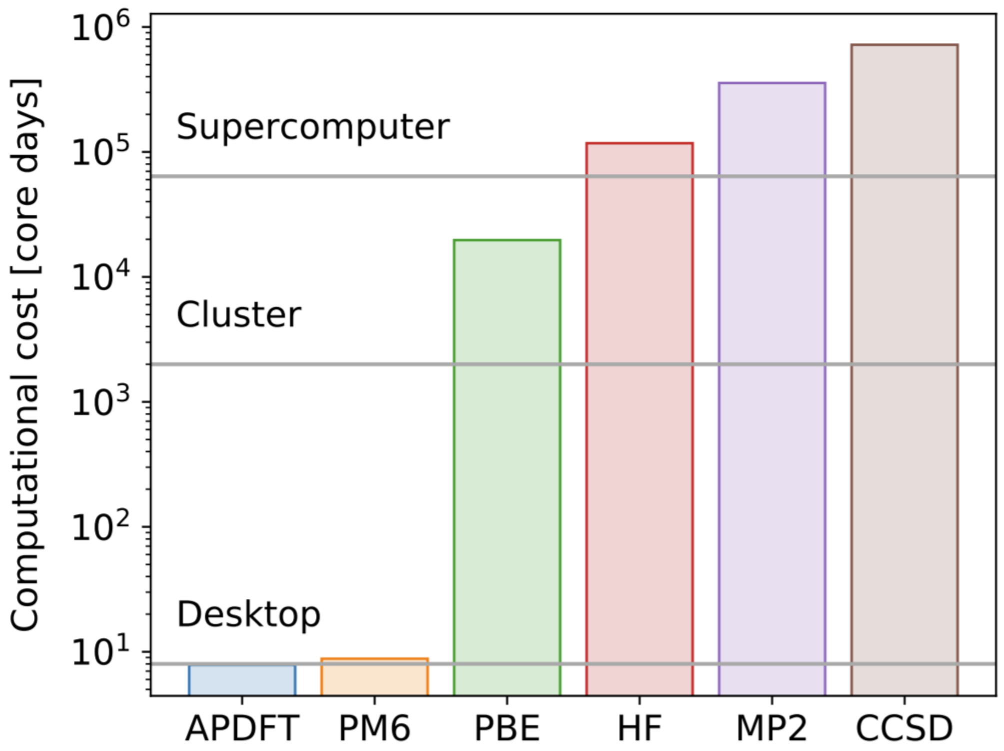
- 1 derivative for second order
- 5 derivatives for third order



C_{20}



$3.1 \cdot 10^6$ targets



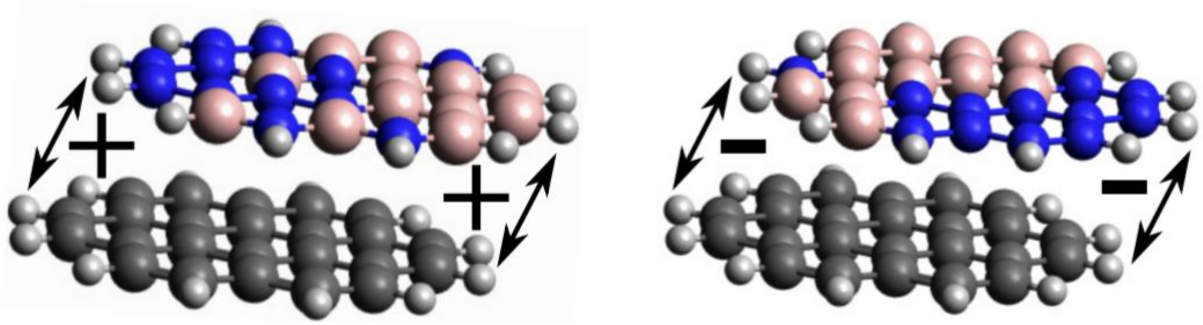
QA: 80.000x faster

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

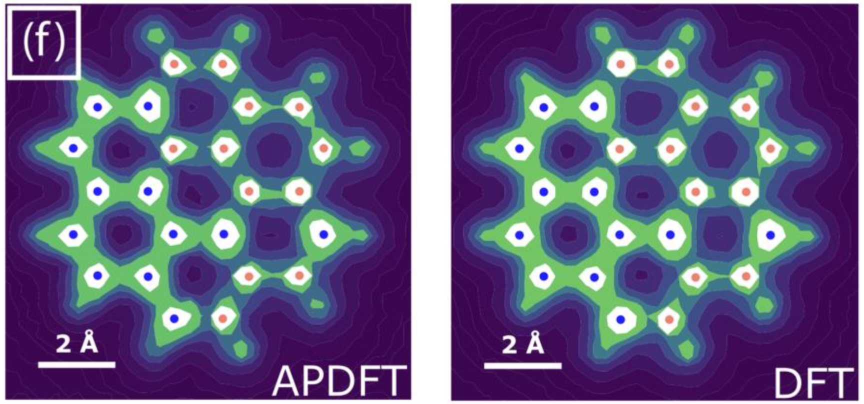
Non-covalent Interactions

BN-doped coronene dimer

- Identify most/least attractive doping pattern
- Design case



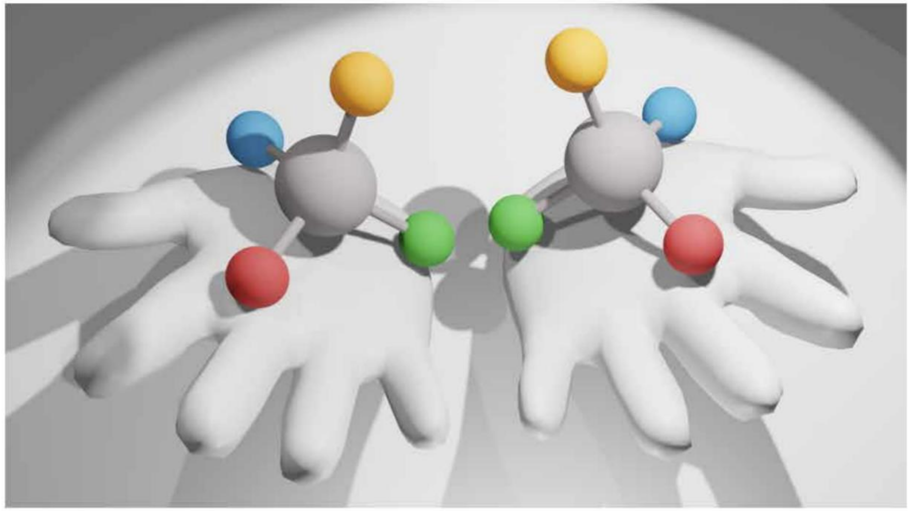
QA: 20.000x faster

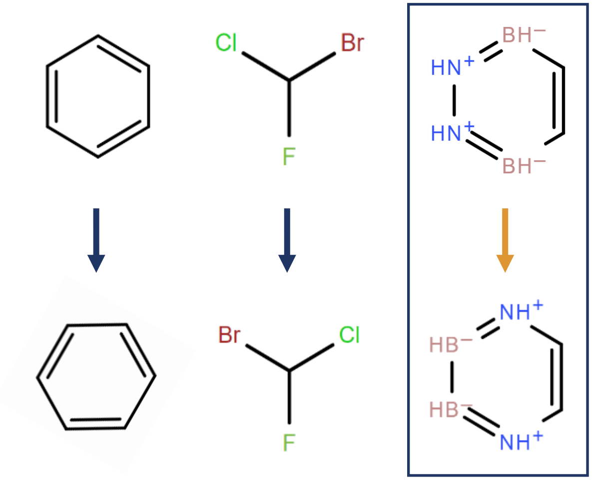


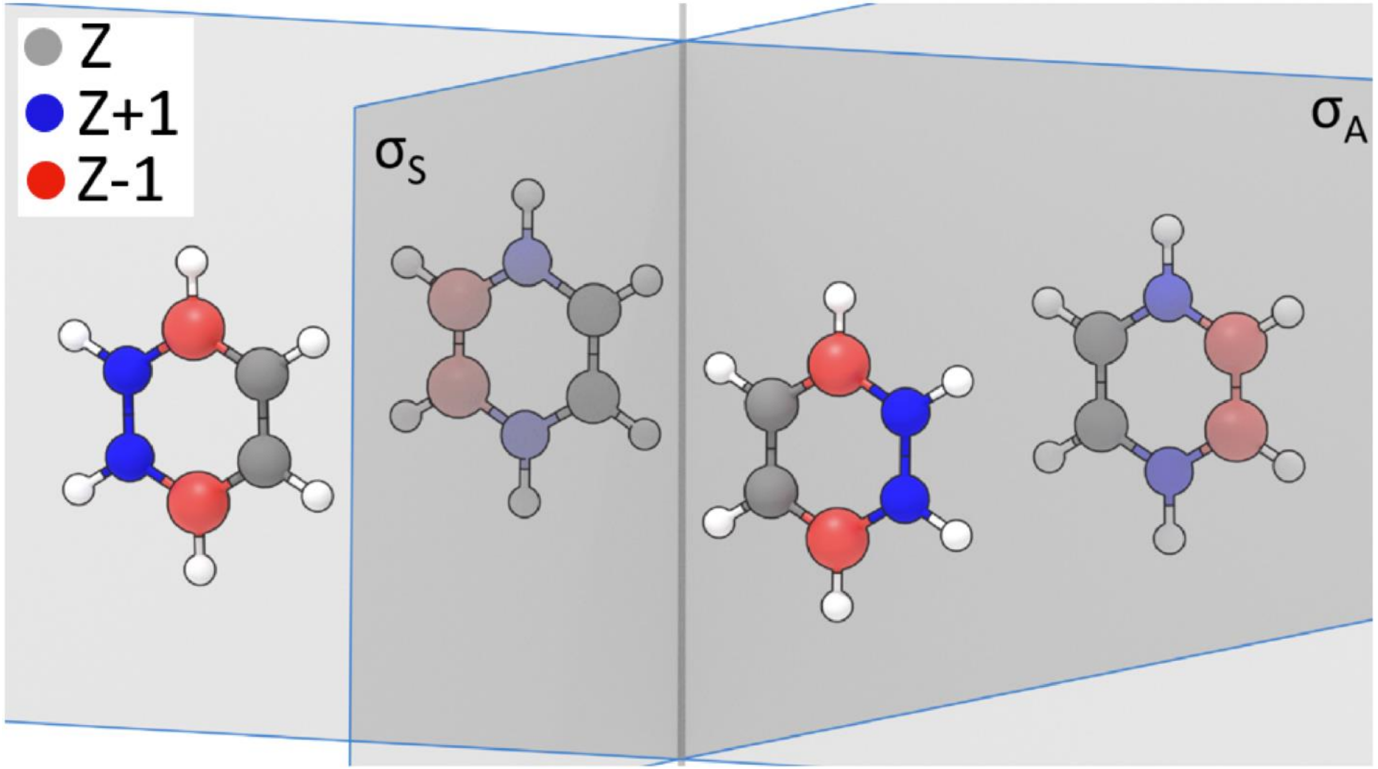
$2.8 \cdot 10^{10}$ targets

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

Alchemical Enantiomers





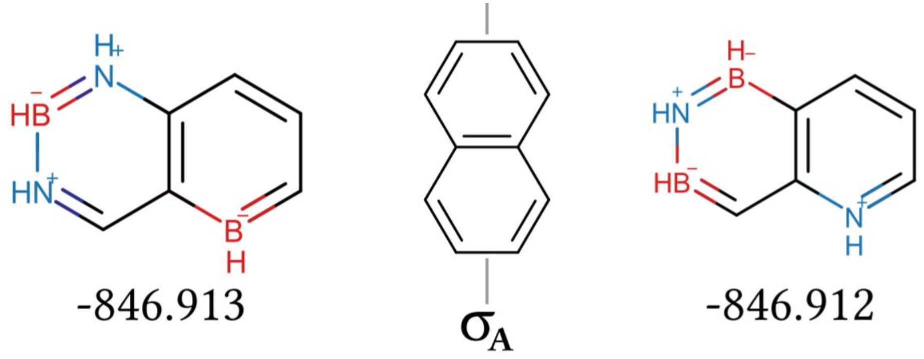


GFvR, O. A. von Lilienfeld, *Science Adv.* 2021.

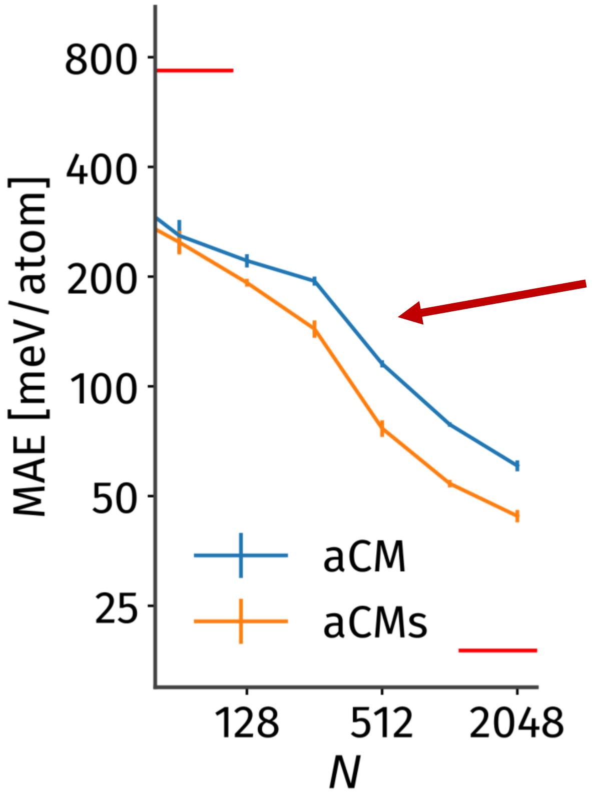
Alchemical Enantiomers

Fundamentally new symmetry

Electronic energy only



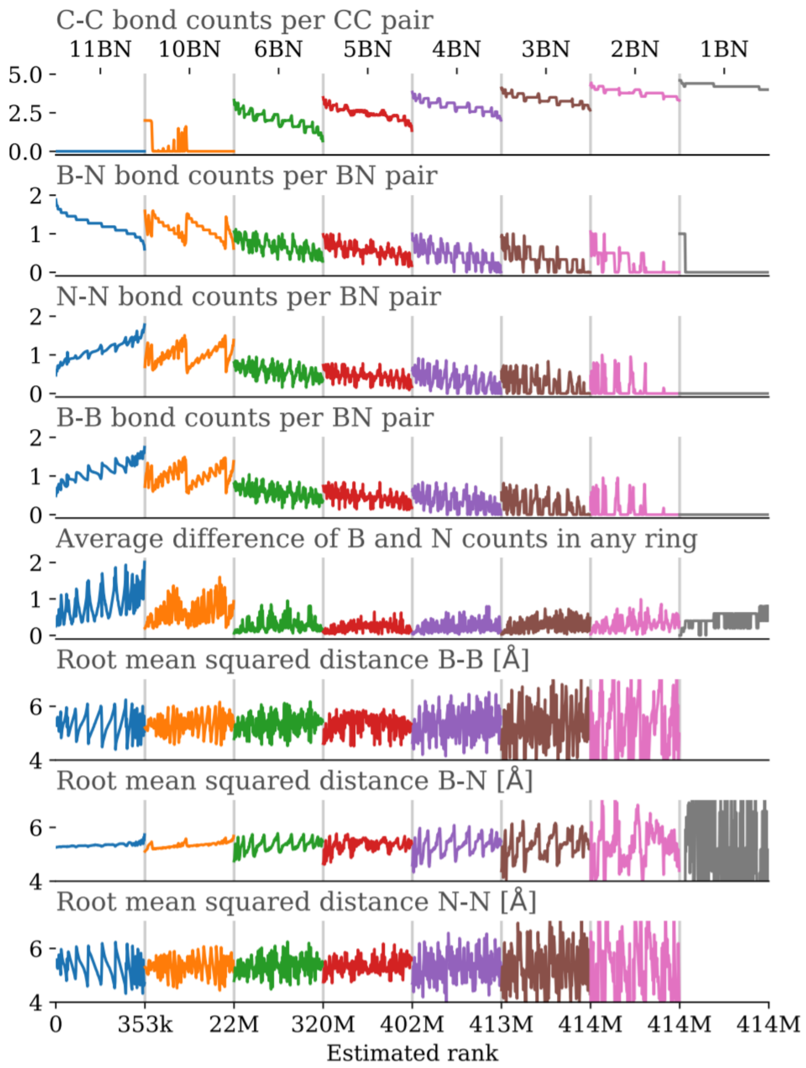
Speed up machine learning

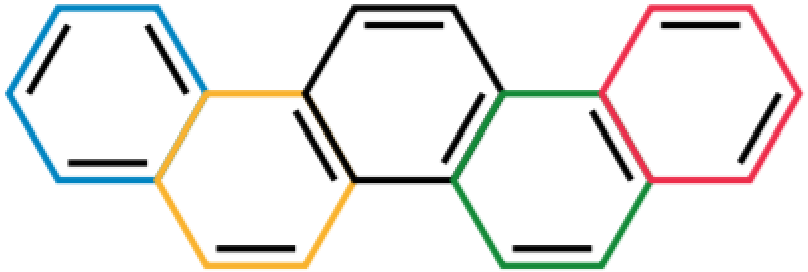


ML+QA: half the data

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

Alchemical Enantiomers





x 414 M

QA: Millions at once!

Design rules in order of decreasing strength

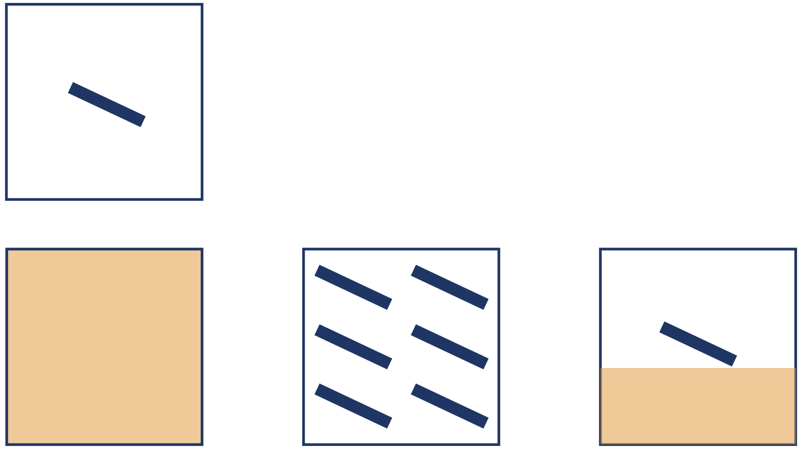
- Add BN pairs
- Maximize CC bonds
- Substitute sites shared between rings
- Maximize BN bonds
- Avoid N substitutions on rings sharing a larger amount of bonds with other rings
- Balance BN substitutions in each ring

Not a single QM calculation required!

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

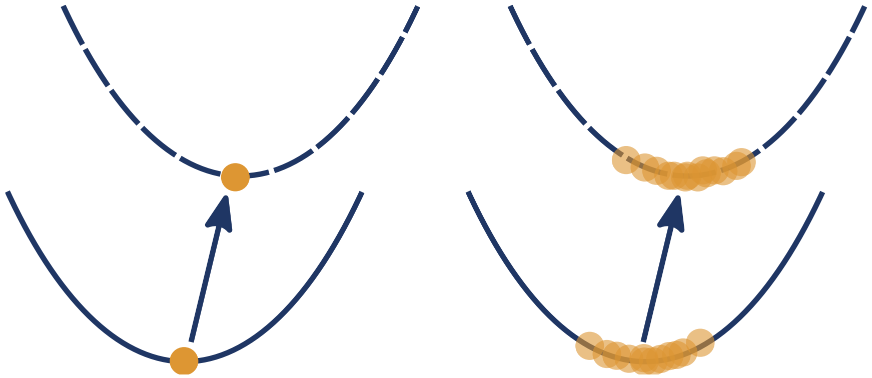
Future Steps

Include materials



also in collaboration with CINSaT members

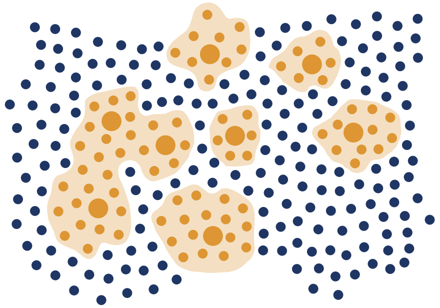
Include ensembles

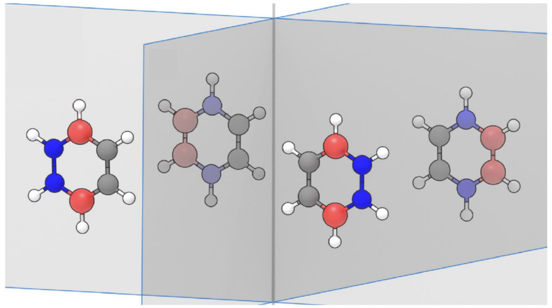


Method

- Basis sets and pseudopotentials need alchemy built-in
- Exploit pen&paper structure for fundamental aspects
- Push differentiable quantum chemistry
- Simplify use

Summary





Efficient | Re-use knowledge, no one-by-one

Symmetries | Reducing (“folding”) search space

Constraints | Exclude whole regions

Differentiable Chemistry | Arbitrary derivatives

Representations | Better data efficiency

Thanks
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Quantum Alchemy

Interpolate between molecular isoelectronic Hamiltonians

$$\hat{H}(\lambda) \equiv \lambda \hat{H}_\mathrm{t} + (1-\lambda)\hat{H}_\mathrm{r} \qquad \lambda \in [0,1]$$

Taylor expansion around reference molecule

$$E_\mathrm{t} = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial^n}{\partial \lambda^n} \left\langle \psi_\lambda \middle| \hat{H}(\lambda) \middle| \psi_\lambda \right\rangle \Big|_{\lambda=0} = E_\mathrm{r} + \sum_{n=1}^{\infty} \frac{1}{n!} \frac{\partial^n E(\lambda)}{\partial \lambda^n} \Big|_{\lambda=0}$$

Hellmann-Feynman theorem

$$\partial_\lambda E = \left\langle \psi_\lambda \middle| \hat{H}_\mathrm{t} - \hat{H}_\mathrm{r} \middle| \psi_\lambda \right\rangle = \Delta E^\mathrm{NN} + \int_\Omega d\mathbf{r}\, \underbrace{(v_\mathrm{t}(\mathbf{r}) - v_\mathrm{r}(\mathbf{r}))}_{\equiv \Delta v} \rho_\lambda(\mathbf{r})$$

O. A. von Lilienfeld, *J. Chem. Phys.* **2009**.

Alchemical Perturbation Density Functional Theory (APDFT)

$$E_{\mathrm{t}} = E_{\mathrm{r}} + \Delta E^{\mathrm{NN}} + \int_\Omega d\mathbf{r} \sum_{n=0}^{\infty} \frac{1}{(n+1)!} \Delta v \frac{\partial^n \rho_\lambda(\mathbf{r})}{\partial \lambda^n}\Bigg|_{\lambda=0}$$

$$\rho_t = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial^n \rho}{\partial \lambda^n}\Bigg|_{\lambda=0}$$

- Gives consistent energies, densities, forces, …
- Uses the same derivatives for all predictions

ferchault/APDFT

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