Quantum Alchemy and PECD

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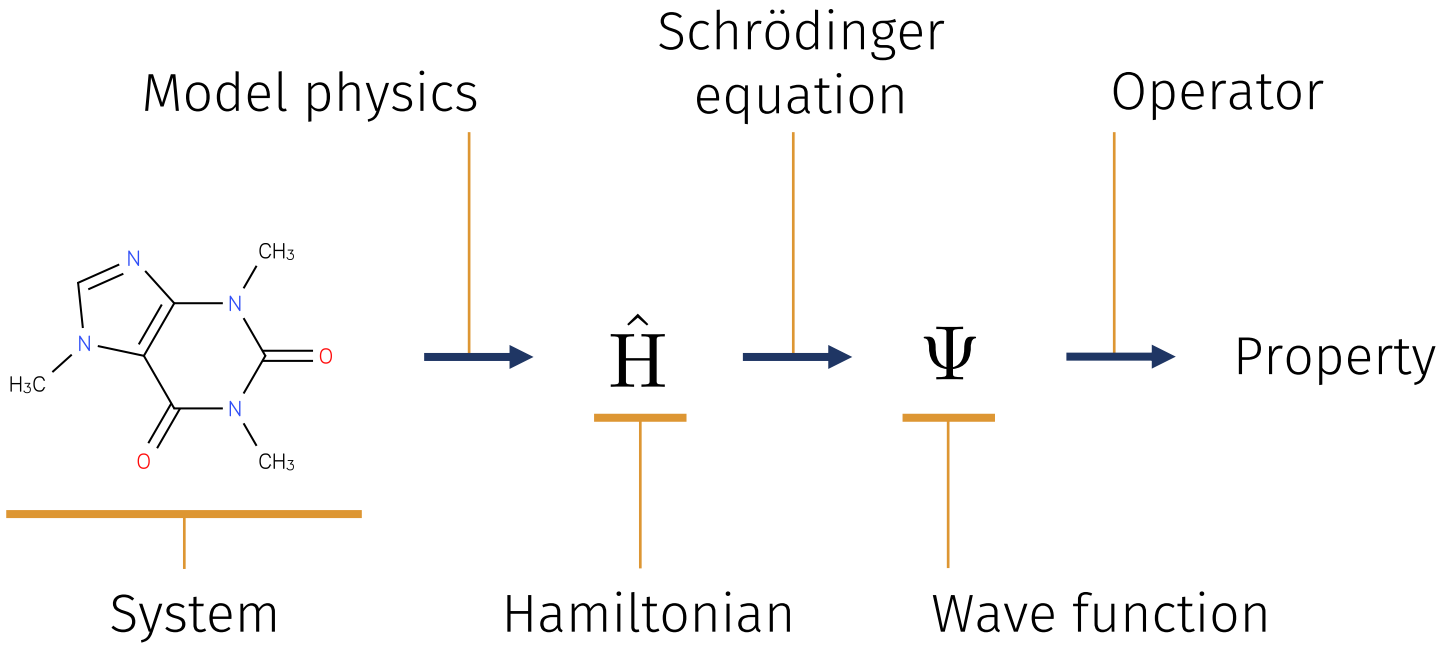
Solved?


Model physics
Schrödinger equation
Operator
$\hat{H}$
Ψ
Property
System
Hamiltonian
Wave function

Quantum Alchemy

Idea

Treat system changes perturbatively[1,2]
Build a Taylor/Padé approximant[3] : **often 100.000 times faster**

Steps

Choose system

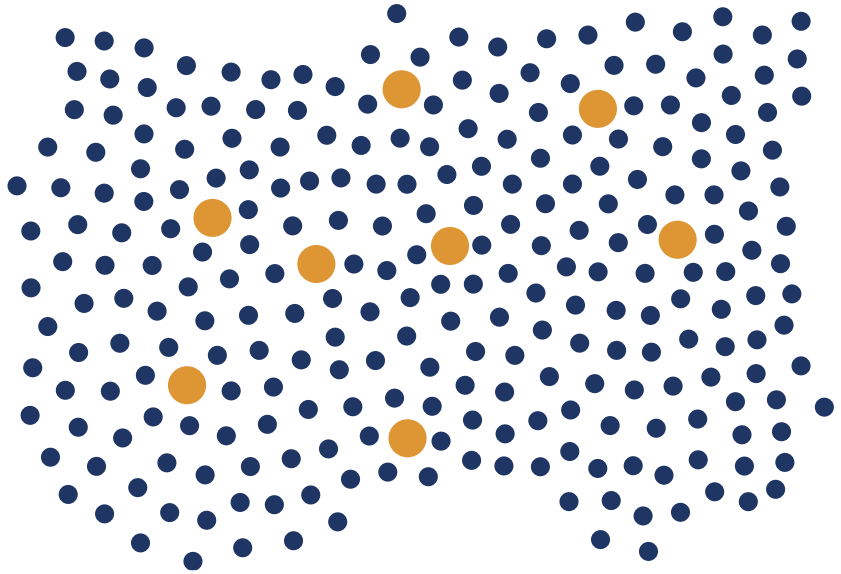
Alter system, calculate property response functions

Predict many modified systems

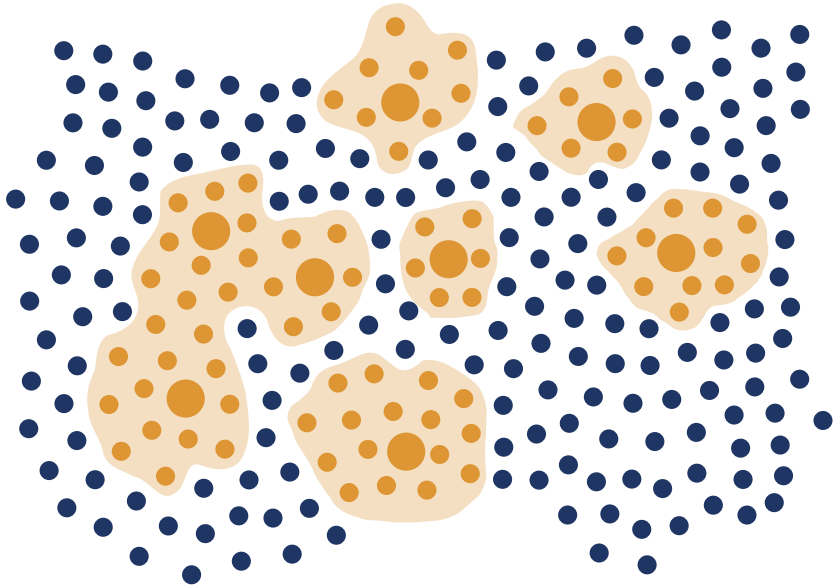
1 | E. B. Wilson, *J. Chem. Phys.* 1962. 2 | GFvR, O. A. von Lilienfeld, *Phys. Rev. Res.*, 2020. 3 | GFvR, *J. Chem. Phys.*, 2021.

Motivation

Without Perturbation



With Perturbation



Systems
- Any
- Known
- Approximated

Motivation

Perspective shift

Few highly accurate calculations
instead of many intermediate ones

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

Requirements

Differentiable / Analytic

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

Converge quickly

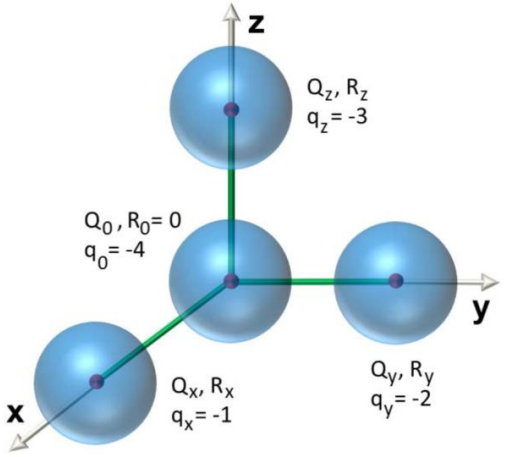
Angular emission in photoelectron circular dichroism?

1 | GFvR, O. A. von Lilienfeld, *Phys. Rev. Res.*, 2020. 2 | GFvR, *J. Chem. Phys.*, 2021. 3 | GFvR, O. A. von Lilienfeld, *Phys. Chem. Chem. Phys.*, 2020. 4 | E Eikey, A Maldonado, C Griego, GFvR, J Keith, *J. Chem. Phys.*, 2022.

PECD Angular Emission

Angular emission

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



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

dichroic parameter

anisotropy parameter

Data

- 85 pairs of β_i
- Center: Q_{xyz}=2.5, R_{xyz} = 3, photoelectron = 6 eV

$$\beta_i(\boldsymbol{x}) \simeq \sum_{|\alpha|\leq k} \frac{\partial^{|\alpha|}\beta_i(\mathbf{a})}{\partial x_1^{\alpha_1}\cdots\partial x_n^{\alpha_n}} \frac{(\mathbf{x}-\mathbf{a})^{\alpha}}{\alpha!}$$

GFvR, A.A. Artemyev, B.M. Lagutin, P.V. Demekhin, *submitted*.

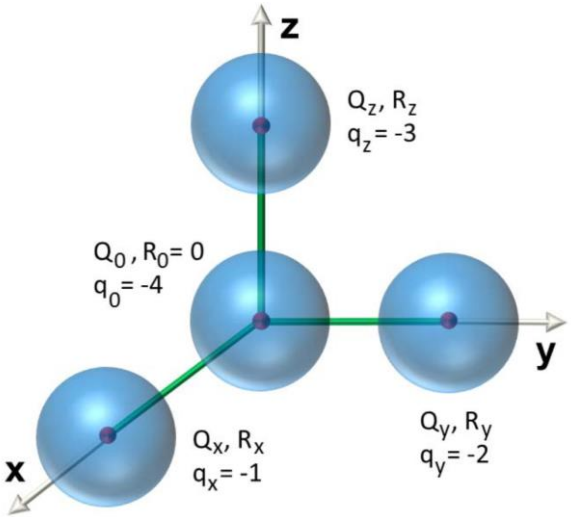
Optimization

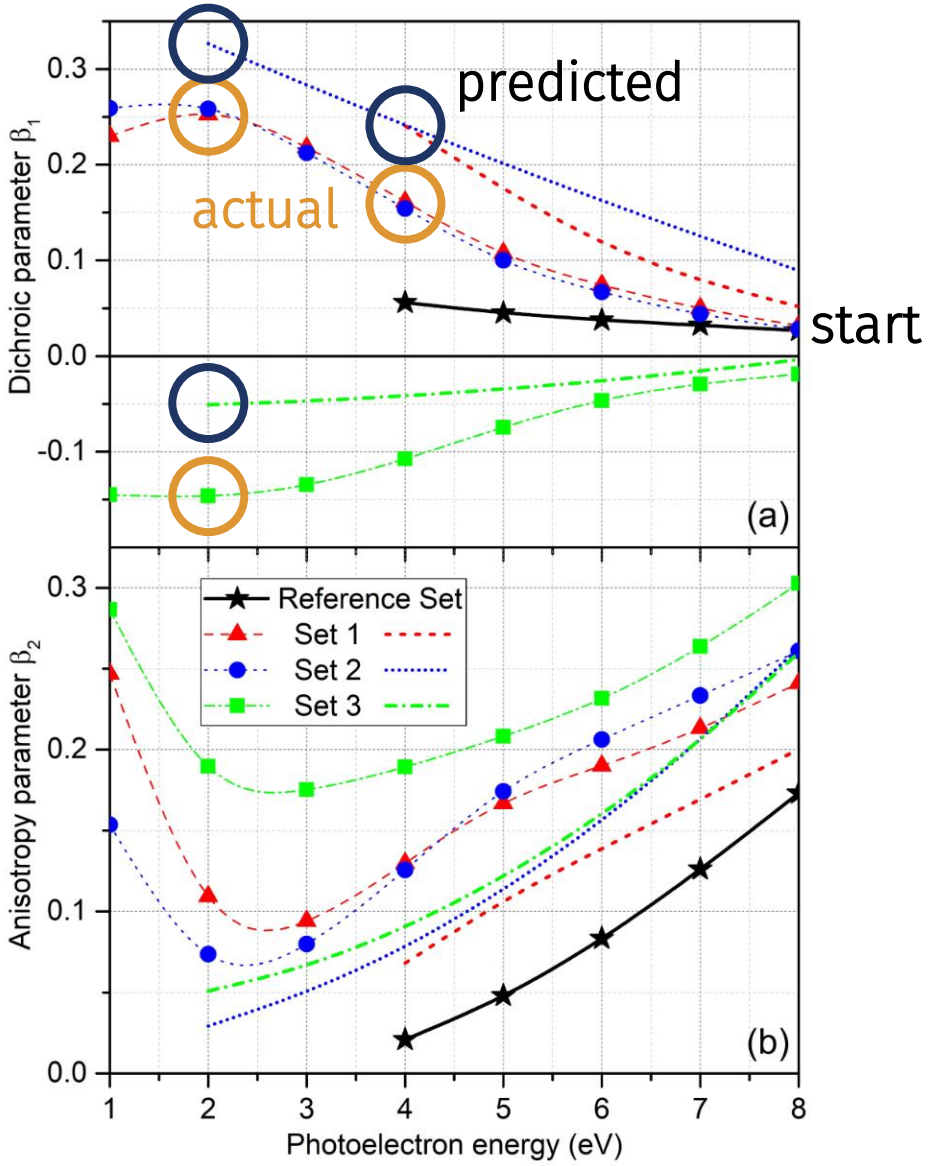
Objective

- Modify **all** Q_i, R_i, photoelectron energy
- Find extremal β_1, predict matching β_2

Results

- max β_1: 5.6% → 25.8%
- Min β_1: 5.6% → -14.7%





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Interactions

Group terms

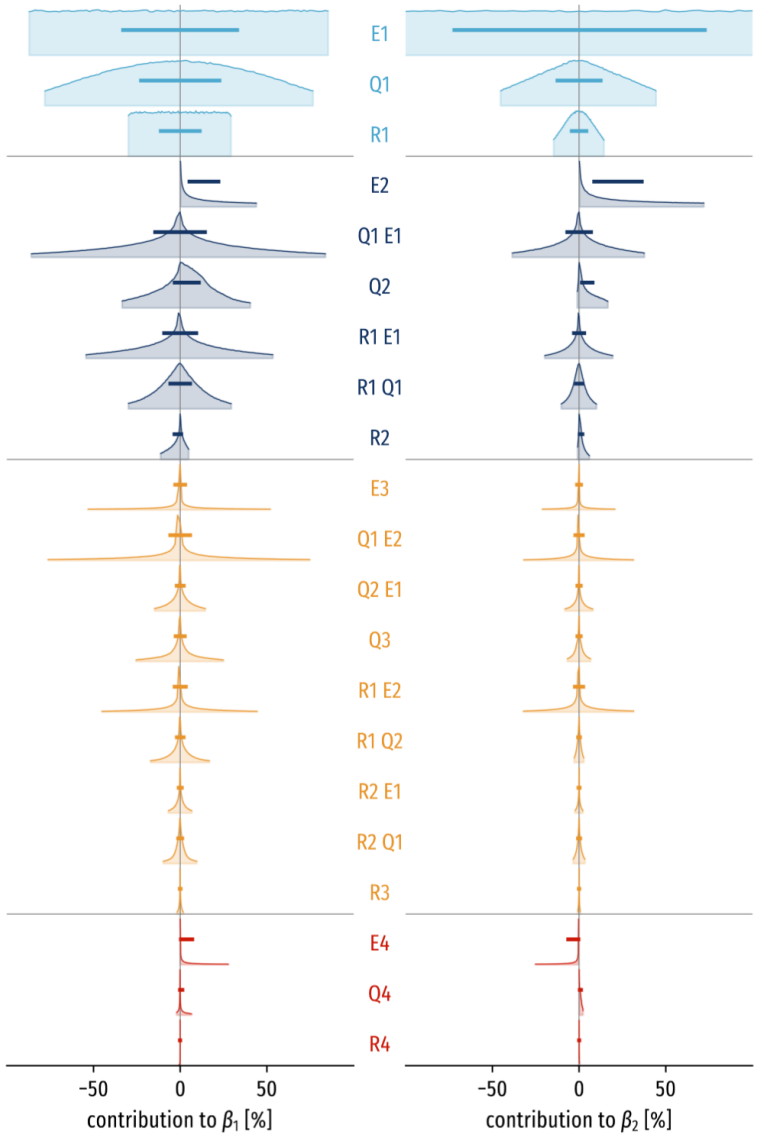
- Q_i: Q
- R_i,: R
- photoelectron energy: E
- Mixed: count groups

$$\frac{\partial \beta_i}{\partial R_x} \qquad \frac{\partial^2 \beta_i}{\partial Q_y^2} \qquad \frac{\partial^2 \beta_i}{\partial R_x Q_y}$$

$\in$ R1 $\in$ Q2 $\in$ R1 Q1

Results

- Converges quickly
- Few third order terms contribute
- Almost no spatial-spatial coupling



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Towards Molecules

Relate to cost

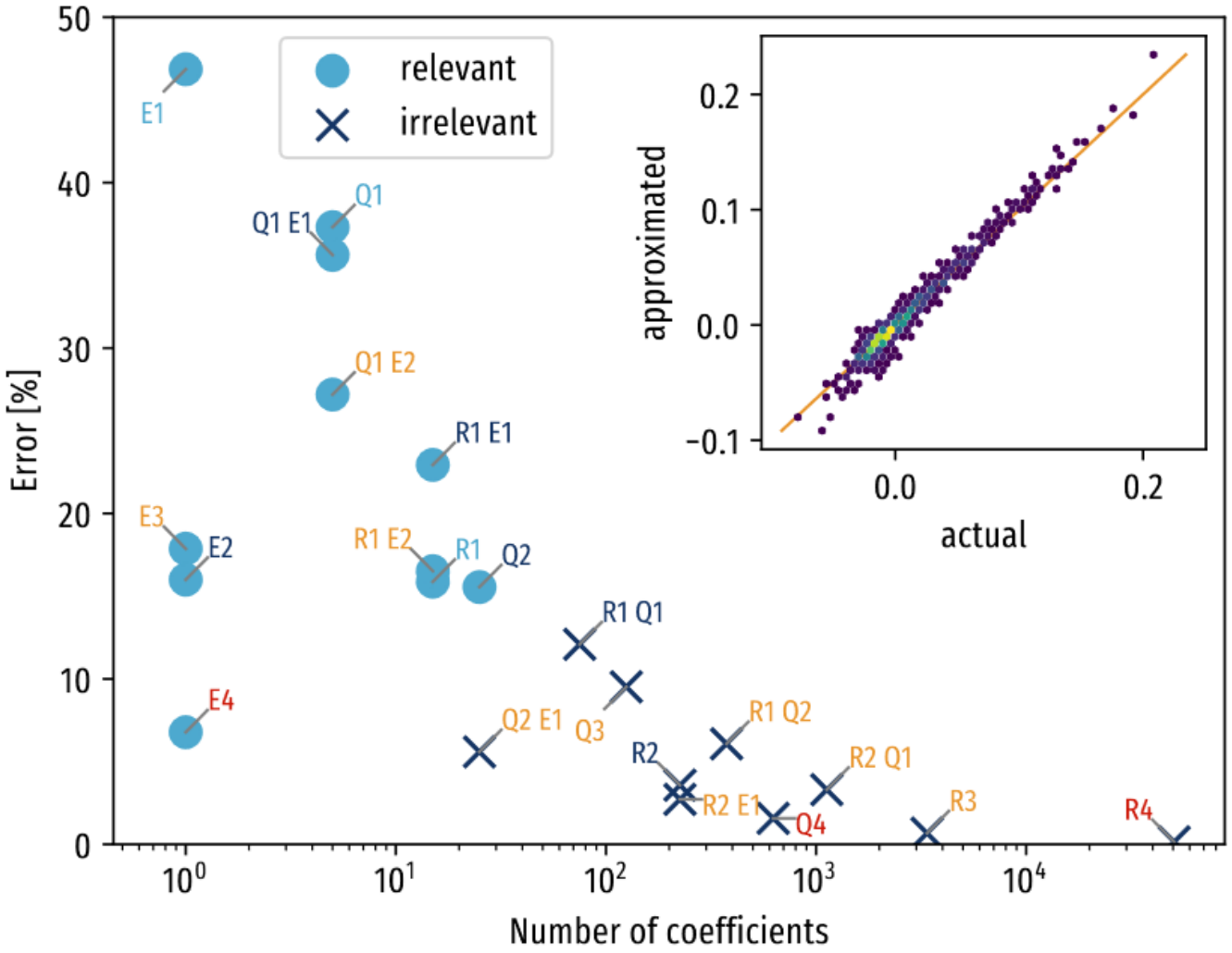
- Expensive terms also irrelevant
- For molecules, subset only
- Allows for efficient stencil design

Estimated speedup „as is“

$$\frac{3^N}{N^2 + 12N - 1}$$

Lessons learned

- Many terms not relevant
- Smaller displacement
- Iterative procedure necessary
- Inclusion of limit expressions?
- Variable transformations?



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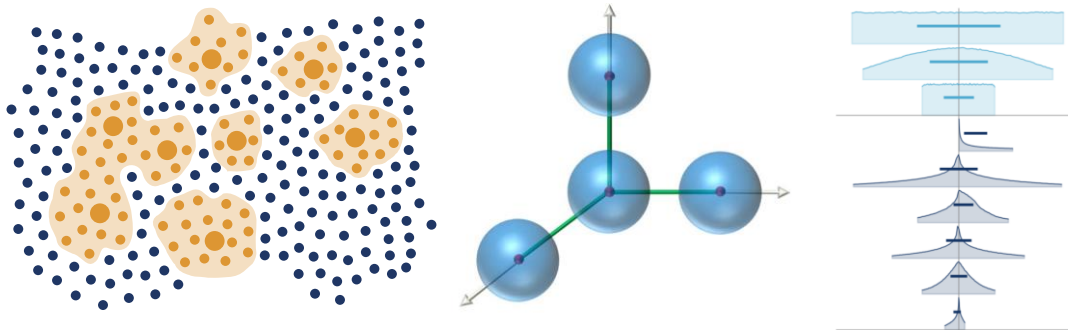
Summary



Thanks
Anton Artemyev
Boris Lagutin
Philipp Demekhin

Accessible | Can be treated perturbatively

Interpretable | Investigate interaction relevance

Efficient | Even for few atom systems

Design | Iterative refinement for molecules

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