Spectral Learning for Solving Molecular Schrödinger equations

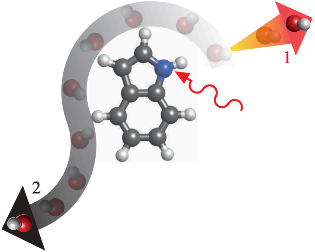
Yahya Saleh

Department of Mathematics, Universität Hamburg
Controlled Molecule Imaging Group
Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron
DESY, Hamburg, Germany

Molecular quantum dynamics

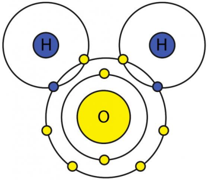
Time-dependent Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = (H_{\mathrm{mol}} + H_{\mathrm{ext}})\psi$$



Time-independent Schrödinger equation

$$\underbrace{\left(-\frac{1}{2}\Delta + V\right)}_{H_{\mathrm{mol}}}\psi_i = E_i\psi_i, \quad \Omega \subseteq \mathbb{R}^{3N}$$



M. S. Robinson, J. Küpper, *Phys. Chem. Chem. Phys.* **26**, 1587 (2024).

Solving molecular time-independent Schrödinger equations

$$H\psi_n = E_n\psi_n \qquad n = 0, 1, \ldots, M-1$$
$$H : D(h) \to L^2$$

$$H\psi_n = E_n\psi_n \underbrace{\longrightarrow}_{\psi_n \approx \tilde{\psi}_{n,\theta}} \mathbf{H}\cdot\mathbf{C} = \tilde{E}\mathbf{S}\cdot\mathbf{C}, \qquad \mathbf{H}^{nm} = \langle\tilde{\psi}_m|H\tilde{\psi}_n\rangle, \mathbf{S}^{nm} = \langle\tilde{\psi}_m|\tilde{\psi}_n\rangle$$

Objective

$$\min_\theta \mathrm{Tr}(\tilde{\mathbf{H}})$$

D. Gottlieb and S. A. Orszag, Numerical analysis of spectral methods: theory and applications, SIAM, 1977.
J. Hermann, Z. Schätzle, F. Noé, *Nat. Chem.* **12**, 891 (2020).

Solving molecular time-independent Schrödinger equations

$$H\psi_n = E_n\psi_n \qquad n = 0, 1, \ldots, M-1$$
$$H : D(h) \to L^2$$

$$H\psi_n = E_n\psi_n \underbrace{\longrightarrow}_{\psi_n \approx \tilde{\psi}_{n,\theta}} \mathbf{H}\cdot\mathbf{C} = \tilde{E}\mathbf{S}\cdot\mathbf{C}, \qquad \mathbf{H}^{nm} = \langle\tilde{\psi}_m|H\tilde{\psi}_n\rangle, \mathbf{S}^{nm} = \langle\tilde{\psi}_m|\tilde{\psi}_n\rangle$$

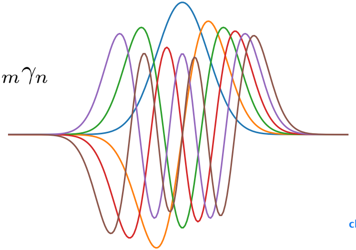
Objective

$$\min_\theta \mathrm{Tr}(\tilde{\mathbf{H}})$$

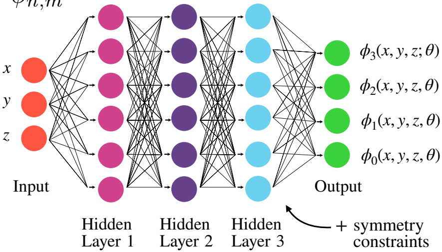
D. Gottlieb and S. A. Orszag, Numerical analysis of spectral methods: theory and applications, SIAM, 1977.
J. Hermann, Z. Schäzle, F. Noé, *Nat. Chem.* **12**, 891 (2020).

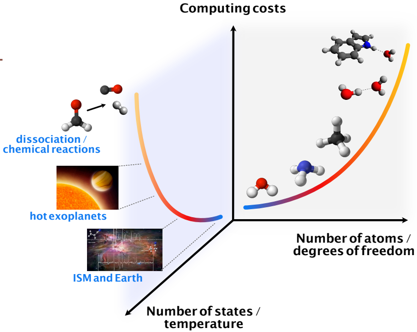
Choices of trial functions $\tilde{\psi}_n$

$$\tilde{\psi}_{n,m} = \sum_{n<N} c_{n,m} \gamma_n$$

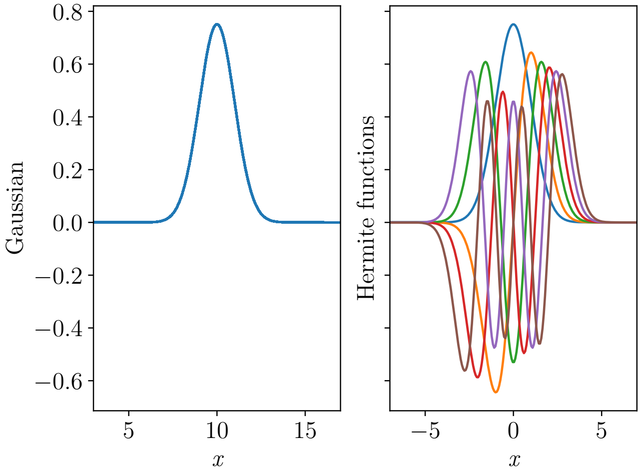


$$\tilde{\psi}_{n,m} = \phi_{n,m}$$

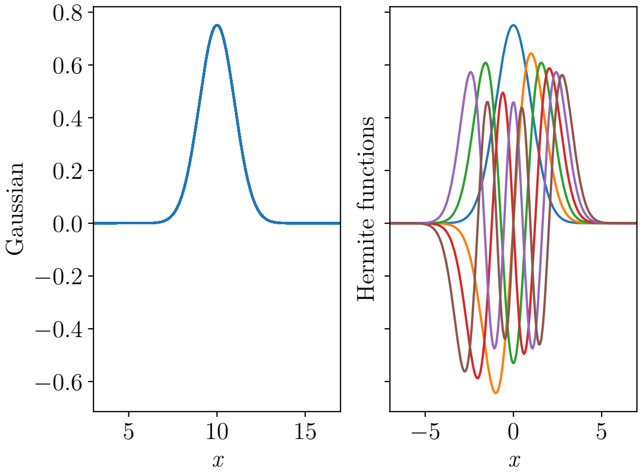




A motivating example for a way forward

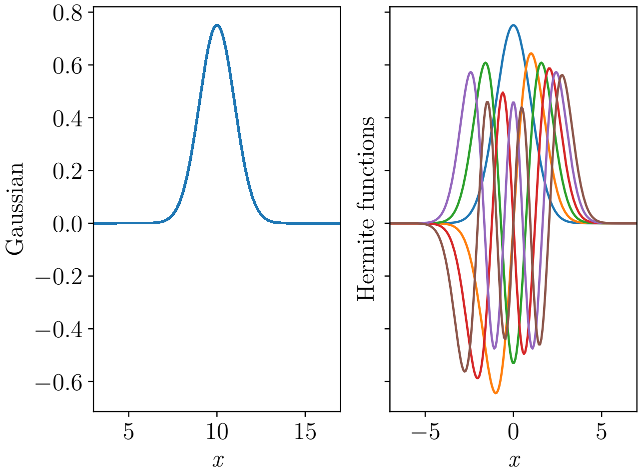


A motivating example for a way forward



One needs: $N \gg \frac{e}{2} a^2$. Solution: $(\phi_1 \circ \underbrace{(x - 10)}_{h}, \ldots, \phi_N \circ (x - 10))$

A motivating example for a way forward



One needs: $N \gg \frac{e}{2}a^2$. Solution: $(\phi_1 \circ \underbrace{(x-10)}_{h}, \ldots, \phi_N \circ (x-10))$

Learning problem-specific basis sets

$$\left(\gamma_n\right)_{n=0}^{\infty}\text{orthonormal basis of } L^2 \longrightarrow \left(\gamma_n \circ h\right)_{n=0}^{\infty}, \quad \left(\gamma_n \circ h \,|\det J_h|^{1/2}\right)_{n=0}^{\infty}$$

h is a differentiable mapping that induces a well-posed composition operator $C_h : L^2 \to L^2$ defined by $C_h f = f \circ h$

Theorem 1.
$\left(\gamma_n \circ h\right)_{n=0}^{\infty}$ is a Riesz basis, resp. $\left(\gamma_n \circ h \,|\det J_h|^{1/2}\right)_{n=0}^{\infty}$ is an orthonormal basis

if and only if

h is invertible and $\det J_h$ is essentially upper bounded.

Y. Saleh, A. Iske, A.Yachmenev, J. Küpper, *Proc. Appl. Math. Mech.* **23**, e202200239 (2023).

$$\left(\gamma_n\right)_{n=0}^{\infty} \text{orthonormal basis of } L^2 \longrightarrow \left(\gamma_n \circ h\right)_{n=0}^{\infty}, \quad \left(\gamma_n \circ h \,|\det J_h|^{1/2}\right)_{n=0}^{\infty}$$

h is a differentiable mapping that induces a well-posed composition operator $C_h : L^2 \to L^2$ defined by $C_h f = f \circ h$

Theorem 1.
$\left(\gamma_n \circ h\right)_{n=0}^{\infty}$ is a Riesz basis, resp. $\left(\gamma_n \circ h \,|\det J_h|^{1/2}\right)_{n=0}^{\infty}$ is an orthonormal basis

if and only if

h is invertible and $\det J_h$ is essentially upper bounded.

Y. Saleh, A. Iske, A.Yachmenev, J. Küpper, *Proc. Appl. Math. Mech.* **23**, e202200239 (2023).

From spectral methods to spectral learning

Spectral methods $\longrightarrow$ Spectral learning

$$\psi_m \approx \tilde{\psi}_m = \sum_{n<N} c_n \gamma_n \longrightarrow \psi_m \approx \tilde{\psi}_m = \sum_{n<N} c_n \gamma_n \circ h$$

To optimize h

$$\min_h l\big(\psi_m, \tilde{\psi}_m(h)\big)$$

Y. Saleh, *Active and spectral learning for enhanced and computationally scalable quantum molecular dynamics*, Dissertation, Universität Hamburg (2023).

Application: approximating Schwartz functions

- Objective function $f \in \mathcal{S}$.
- $\gamma_n = \phi_n$.
- $\tilde{f}$ approximation in the linear span of $(\phi_n \circ h)_{n<N}$.

Theorem 2. **Assume**

- h is such that $(\phi_n \circ h)_n$ is a basis for $L^2(\mu)$.
- $\chi \circ h^{-1} \in \mathcal{S}$ for all $\chi \in \mathcal{S}$.

Then

$$\|f - \tilde{f}\|_{L^2(\mu)} \leq c(d, N)\|Df \circ h^{-1}\|_{L^1(\mu)}$$

Corollary $\tilde{E}_k \to E_k$ as $N \to \infty$ for special TISEs .

Y. Saleh, *Active and spectral learning for enhanced and computationally scalable quantum molecular dynamics*, Dissertation, Universität Hamburg (2023).

Application: approximating Schwartz functions

- Objective function $f \in \mathcal{S}$.
- $\gamma_n = \phi_n$.
- $\tilde{f}$ approximation in the linear span of $(\phi_n \circ h)_{n<N}$.

Theorem 2. **Assume**

- h is such that $(\phi_n \circ h)_n$ is a basis for $L^2(\mu)$.
- $\chi \circ h^{-1} \in \mathcal{S}$ for all $\chi \in \mathcal{S}$.

Then

$$\|f - \tilde{f}\|_{L^2(\mu)} \leq c(d, N)\|Df \circ h^{-1}\|_{L^1(\mu)}$$

Corollary $\tilde{E}_k \to E_k$ as $N \to \infty$ for special TISEs .

Y. Saleh, *Active and spectral learning for enhanced and computationally scalable quantum molecular dynamics*, Dissertation, Universität Hamburg (2023).

Application: approximating Schwartz functions

- Objective function $f \in \mathcal{S}$.
- $\gamma_n = \phi_n$.
- $\tilde{f}$ approximation in the linear span of $(\phi_n \circ h)_{n<N}$.

Theorem 2. **Assume**

- h is such that $(\phi_n \circ h)_n$ is a basis for $L^2(\mu)$.
- $\chi \circ h^{-1} \in \mathcal{S}$ for all $\chi \in \mathcal{S}$.

Then

$$\|f - \tilde{f}\|_{L^2(\mu)} \leq c(d, N)\|Df \circ h^{-1}\|_{L^1(\mu)}$$

Corollary $\tilde{E}_k \to E_k$ as $N \to \infty$ for special TISEs .

Y. Saleh, *Active and spectral learning for enhanced and computationally scalable quantum molecular dynamics*, Dissertation, Universität Hamburg (2023).

Faster convergence *via* spectral learning

Theorem 2. **Assume**

- h is such that $(\phi_n \circ h)_n$ is a basis for $L^2(\mu)$.
- $\chi \circ h^{-1} \in \mathcal{S}$ for all $\chi \in \mathcal{S}$.

Then

$$\|f - \tilde{f}\|_{L^2(\mu)} \leq c(d, N)\|Df \circ h^{-1}\|_{L^1(\mu)}$$

Remark 1.: $h = \mathrm{id}$ standard results are recovered[1].
$\mathfrak{H}$: class of functions satisfying Thm. 1 and Thm. 2.

Theorem 3. The optimization problem

$$\inf\{\|Df \circ h^{-1}\|_{L^1(\mu)} \mid h \in \mathfrak{H}\}$$

admits a minimizer h^*, $h^* \neq \mathrm{Id}$.

[1] C. Lubich, from quantum to classical molecular dynamics (2008)

Y. Saleh, *Active and spectral learning for enhanced and computationally scalable quantum molecular dynamics*, Dissertation, Universität Hamburg (2023).

Faster convergence *via* spectral learning

Theorem 2. **Assume**

- h is such that $(\phi_n \circ h)_n$ is a basis for $L^2(\mu)$.
- $\chi \circ h^{-1} \in \mathcal{S}$ for all $\chi \in \mathcal{S}$.

Then

$$\|f - \tilde{f}\|_{L^2(\mu)} \leq c(d, N)\|Df \circ h^{-1}\|_{L^1(\mu)}$$

Remark 1.: $h = \mathrm{id}$ standard results are recovered[1].

$\mathfrak{H}$: class of functions satisfying Thm. 1 and Thm. 2.

Theorem 3. The optimization problem

$$\inf\{\|Df \circ h^{-1}\|_{L^1(\mu)} \mid h \in \mathfrak{H}\}$$

admits a minimizer h^*, $h^* \neq \mathrm{Id}$.

[1] C. Lubich, from quantum to classical molecular dynamics (2008)

Y. Saleh, *Active and spectral learning for enhanced and computationally scalable quantum molecular dynamics*, Dissertation, Universität Hamburg (2023).

Faster convergence *via* spectral learning

Theorem 2. **Assume**

- h is such that $(\phi_n \circ h)_n$ is a basis for $L^2(\mu)$.
- $\chi \circ h^{-1} \in \mathcal{S}$ for all $\chi \in \mathcal{S}$.

Then

$$\|f - \tilde{f}\|_{L^2(\mu)} \leq c(d, N)\|Df \circ h^{-1}\|_{L^1(\mu)}$$

Remark 1.: $h = \mathrm{id}$ standard results are recovered[1].

$\mathfrak{H}$: class of functions satisfying Thm. 1 and Thm. 2.

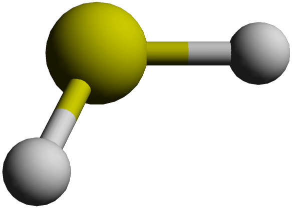
Theorem 3. The optimization problem

$$\inf\{\|Df \circ h^{-1}\|_{L^1(\mu)} \mid h \in \mathfrak{H}\}$$

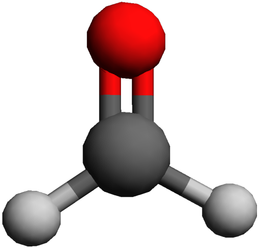
admits a minimizer h^*, $h^* \neq \mathrm{Id}$.

[1] C. Lubich, from quantum to classical molecular dynamics (2008)

Application to solving Schrödinger equations



Hydrogen sulfide (**H_2S**)
3-dimensional system

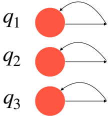


Formaldehyde (**H_2CO**)
6-dimensional system

- Solve $H\psi_m = E_m\psi_m \qquad m = 0, \ldots, M-1$
- Trial and test function $\tilde{\psi}_{m,\theta} = \sum_{n<N} c_{n,m}\gamma_n \circ h_\theta |\det J_{h_\theta}|^{1/2}$
- Optimization

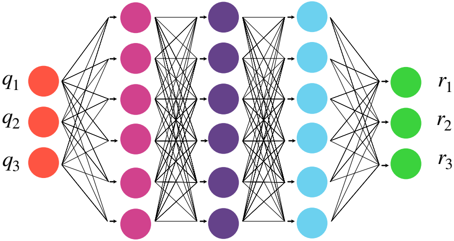
$$\min_{c_n,\theta} \mathrm{Tr}\langle \psi_\theta | H\psi_\theta \rangle$$

Modelling h_θ



$h_\theta^{-1}(r_1, r_2, r_3) \longleftrightarrow h_\theta(q_1, q_2, q_3)$

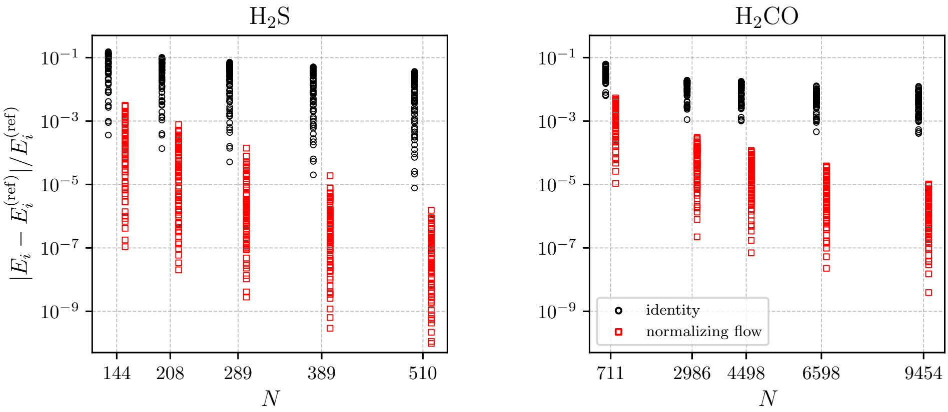
Identity mapping
Standard spectral methods are recovered



$h_\theta^{-1}(r_1, r_2, r_3) \longleftrightarrow h_\theta(q_1, q_2, q_3)$

Normalizing flow
Induces a spectral learning paradigm

Convergence as a function of N



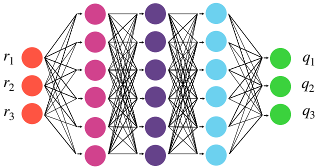
Y. Saleh, A. F. Corral, A. Iske, A.Yachmenev, J. Küpper, arXiv:2308.16468 (2023).

Analogy to normalizing flows for generative ML

Generative ML

$P_0 =$ Gaussian

+



$h^{-1}(q_1, q_2, q_3; \boldsymbol{\theta}) \longleftrightarrow h(r_1, r_2, r_3; \boldsymbol{\theta})$

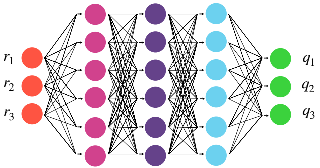
$\Downarrow$

$P^\theta = P_0 \circ h_\theta =$ Augmented Gaussian

Spectral learning

$(\phi_n)_n =$ basis of L^2

+

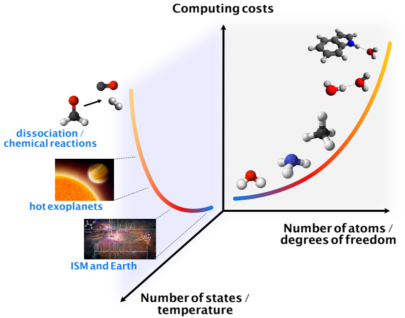


$h^{-1}(q_1, q_2, q_3; \boldsymbol{\theta}) \longleftrightarrow h(r_1, r_2, r_3; \boldsymbol{\theta})$

$\Downarrow$

$(\phi_n^\theta)_n = (\phi_n \circ h_\theta)_n =$ Augmented basis

Summary



- $\left(\gamma_n\right)_{n=0}^{\infty} \rightsquigarrow \left(\gamma_n \circ h\right)_{n=0}^{\infty}$
- Spectral methods to spectral learning.
- Orders of magnitude improved accuracy for vibrational eigenvalues of molecules.

Y. Saleh, A. Iske, A.Yachmenev, J. Küpper, *Proc. Appl. Math. Mech.* **23**, e202200239 (2023).
Y. Saleh, A. F. Corral, A. Iske, A.Yachmenev, J. Küpper, (2023), in preparation.
Y. Saleh, A. Iske, A.Yachmenev, J. Küpper, (2023), in preparation.

Acknowledgements

CFEL Controlled Molecule Imaging Group

Jochen Küpper

Sebastian Trippel
Hubertus Bromberger
Nayab M. Chaudhry
Wuwei Jin
Matthew Robinson
Andrey Samartsev
Mukhtar Singh
Ivo Vinklárek
Nidin Vadassery

Amit Samanta
Xuemei Cheng
Armando Estillore
Lukas Haas
Jingxuan He
Surya Kiran Peravali

Muhamed Amin

Andrey Yachmenev
Álvaro Fernández
Yahya Saleh

Karol Długołęcki
Barbora Vagovič

Department of mathematics, UHH

Armin Iske

Klaus Goetz
Kristof Albrecht

Stephanie Blanke
Juliane Entzian
Álvaro Fernández
Frank Gholampour
Yahya Saleh
Vladislav Sukharnikov

Tigran Andrikyan
Florian Hammer
Nico Hudaff
Max Lewerenz
Susanna Saarinen

Söncke Evers
Lennar Ohlsen
Frieke Krusch

CUI The Hamburg Center for Ultrafast Imaging

DASHH Data Science in Hamburg HELMHOLTZ Graduate School for the Structure of Matter

Bundesministerium für Bildung und Forschung

erc European Research Council

Universität Hamburg

DFG
EXC Center for Ultrafast Imaging
EXC Advanced Imaging of Matter
SPP 1840 Quantum Dynamics in Tailored Light Fields

Alexander von Humboldt Stiftung/Foundation

HELMHOLTZ ASSOCIATION

DESY.