Differentiable Quantum Chemistry

Guido Falk von Rudorff, University of Kassel

vonrudorff@uni-kassel.de nablachem.org/talks ferchault @ferchault

Core idea

- Self-consistent cycle can be a pure function
- Build call tree, apply chain rule

- Technical challenges:
  - Requires re-implementation
  - Crossing language borders is hard
  - Some syntactic sugar is unsupported
  - Slow, can be boosted with “Harris functional” like step
- Chemistry challenges:
  - Some derivatives not well defined (e.g. w.r.t. basis set)

Example Forward Mode

$$
\begin{aligned}
z &= f(x_1, x_2) \\
&= x_1 x_2 + \sin x_1 \\
&= w_1 w_2 + \sin w_1 \\
&= w_3 + w_4 \\
&= w_5
\end{aligned}
$$

Operations to compute value	Operations to compute derivative
$w_1 = x_1$	$\dot{w}_1 = 1$ (seed)
$w_2 = x_2$	$\dot{w}_2 = 0$ (seed)
$w_3 = w_1 \cdot w_2$	$\dot{w}_3 = w_2 \cdot \dot{w}_1 + w_1 \cdot \dot{w}_2$
$w_4 = \sin w_1$	$\dot{w}_4 = \cos w_1 \cdot \dot{w}_1$
$w_5 = w_3 + w_4$	$\dot{w}_5 = \dot{w}_3 + \dot{w}_4$

- Most natural
- Compute intensive: needs seed (0, 1) for next variable, so each gradient costs the same as the original function

Example Reverse Mode

$$
\begin{aligned}
z &= f(x_1, x_2) \\
&= x_1 x_2 + \sin x_1 \\
&= w_1 w_2 + \sin w_1 \\
&= w_3 + w_4 \\
&= w_5
\end{aligned}
$$

- More memory, faster compute
- Multiple derivatives at once
- Can be done on
  - other primitives
  - control structures
- Works with matrices

$$\frac{dz}{dz} = 1$$

$$z = w_5 \Rightarrow \frac{dz}{dw_5} = 1$$

$$\frac{dz}{dw_4} = \frac{dz}{dw_5}\frac{dw_5}{dw_4} = 1 \times 1 = 1$$

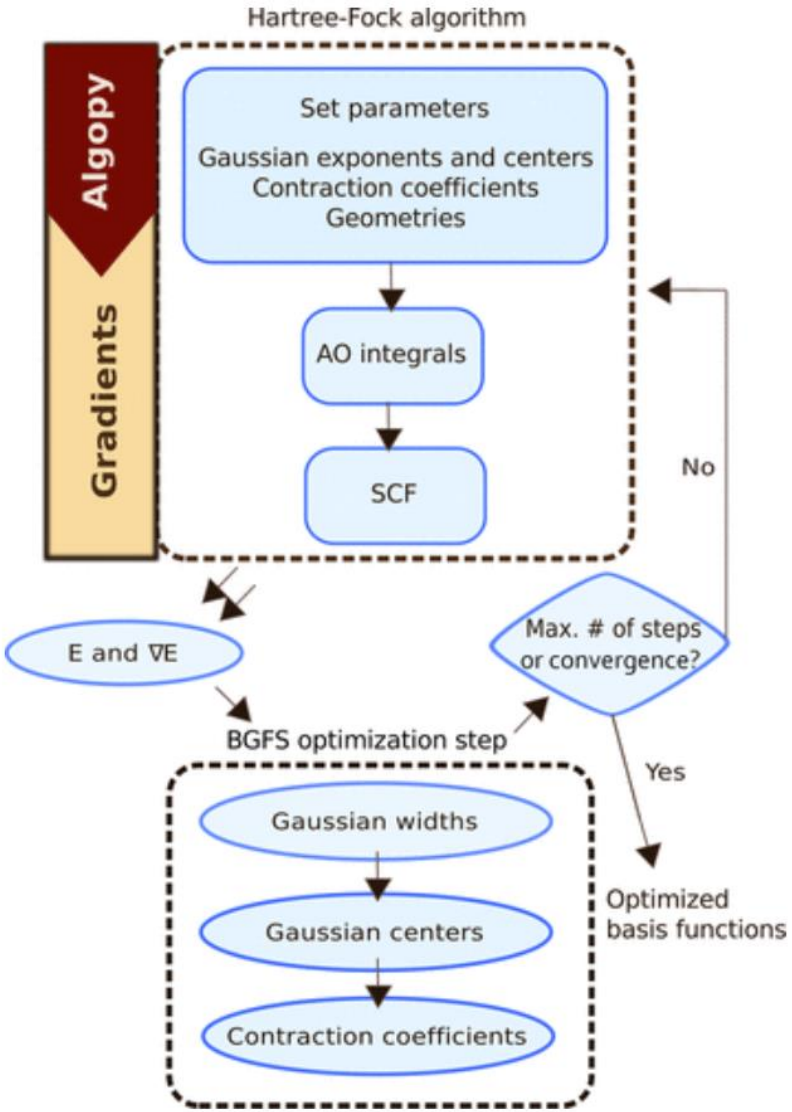
$$\frac{dz}{dw_3} = \frac{dz}{dw_5}\frac{dw_5}{dw_3} = 1 \times 1 = 1$$

$$\frac{dz}{dw_2} = \frac{dz}{dw_3}\frac{dw_3}{dw_2} = 1 \times w_1 = w_1$$

$$\frac{dz}{dw_1} = \frac{dz}{dw_3}\frac{dw_3}{dw_1} + \frac{dz}{dw_4}\frac{dw_4}{dw_1} = w_2 + \cos(w_1)$$

DiffiQult

- Forward mode proof-of-concept
- Reason: matrix diagonalisation for degenerate eigenvalues not available in reverse mode
- Optimizes everything
- HF



ACS central science

ACS AuthorChoice

Research Article

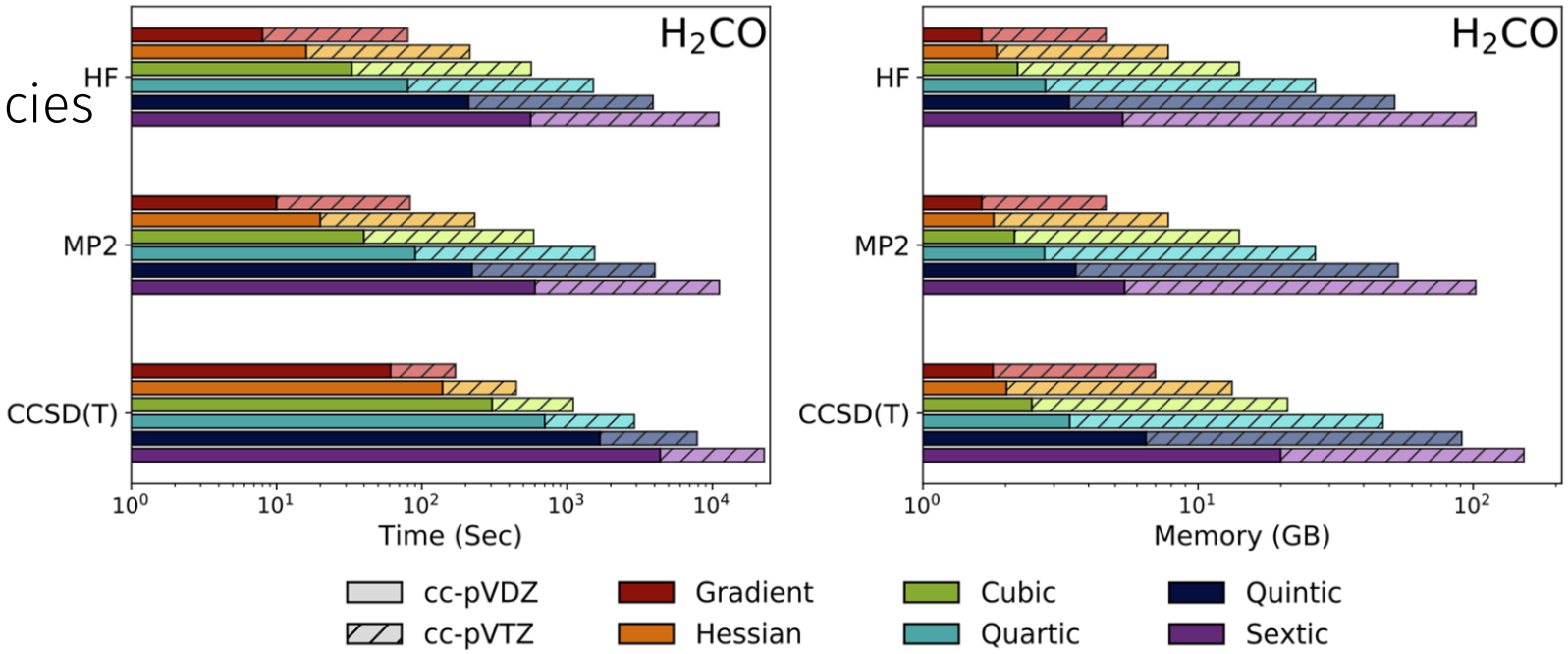
Cite This: ACS Cent. Sci. 2018, 4, 559−566

Automatic Differentiation in Quantum Chemistry with Applications to Fully Variational Hartree−Fock

Teresa Tamayo-Mendoza,[†] Christoph Kreisbeck,[*,†] Roland Lindh,[‡] and Alán Aspuru-Guzik[*,†,§]

Quax

- Forward mode
- Somewhat stable for degeneracies
- Focuses on spatial derivatives
- HF, MP2, CCSD(T)



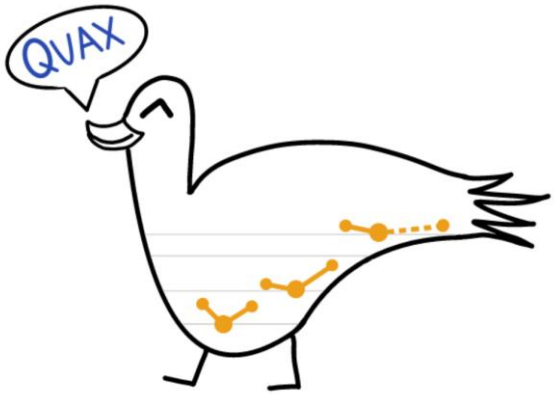
THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JPCL Letter

Arbitrary-Order Derivatives of Quantum Chemical Methods via Automatic Differentiation

Adam S. Abbott, Boyi Z. Abbott, Justin M. Turney, and Henry F. Schaefer, III*

Cite This: *J. Phys. Chem. Lett.* 2021, 12, 3232–3239 Read Online

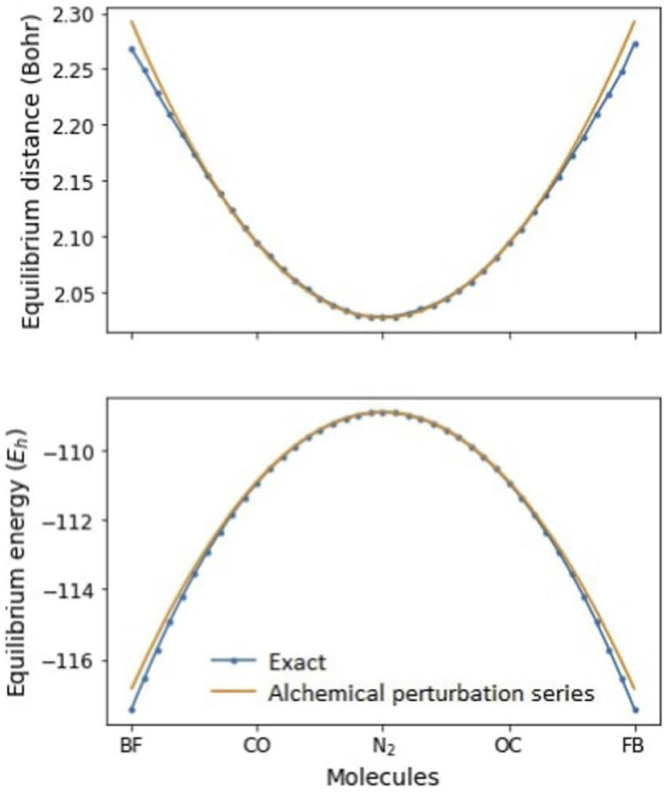


DQC

- Reverse mode (!)
- Focuses on different properties
- HF, DFT
- Includes alchemical derivatives

TABLE I. Execution speed comparison between DQC (SCF iterations) and PySCF.

Cases	DQC	PySCF
H_2O (HF/cc-pVDZ)	96 ms	245 ms
H_2O (PW92/cc-pVDZ)	530 ms	430 ms
C_4H_5N (HF/cc-pVTZ)	108 s	17 s
C_4H_5N (PW92/cc-pVTZ)	101 s	25 s
C_4H_5N (density fit PW92/cc-pVTZ)	30 s	22 s
$C_6H_8O_6$ (density fit PW92/cc-pVDZ)	87 s	57 s



DQC: A Python program package for differentiable quantum chemistry

Cite as: J. Chem. Phys. **156**, 084801 (2022); doi: 10.1063/5.0076202
Submitted: 22 October 2021 • Accepted: 31 January 2022 •
Published Online: 22 February 2022

View Online Export Citation CrossMark

Muhammad F. Kasim,[1,a)] Susi Lehtola,[2] and Sam M. Vinko[1,3,b)]

PySCF-AD

- Most advanced
- Out-of-core only
- No integral symmetries
- Reverse-Mode
- Takes special care of SCF derivatives
- Based on JAX