Finding density functionals with ML

Kieron Burke and many friends
UC Irvine
Departments of Physics and of Chemistry

Themes

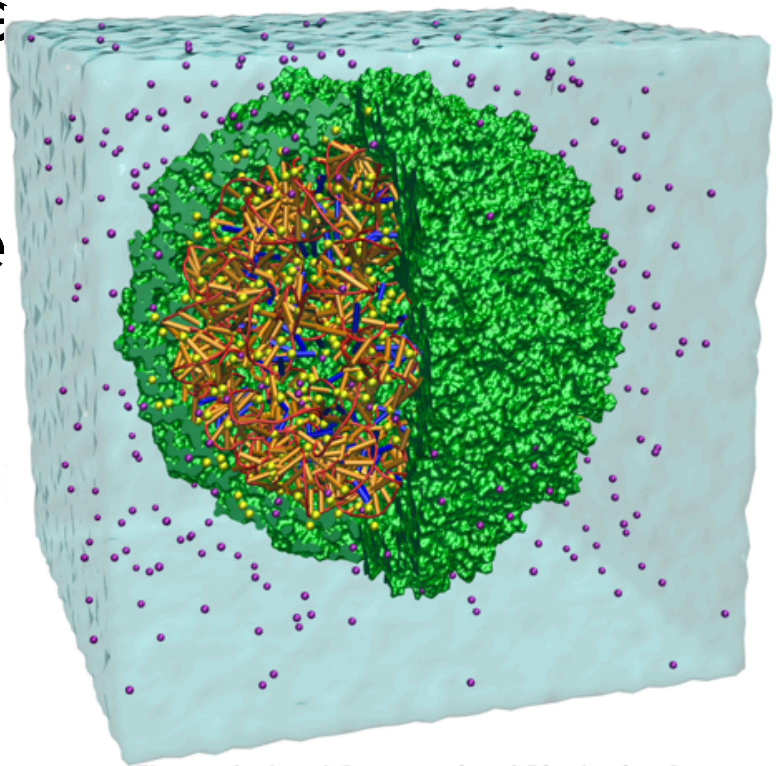
- DFT (electronic structure) in a nutshell

- Along comes ML

- New opportunities?

Standard atomistic simulations: Molecular dynamics

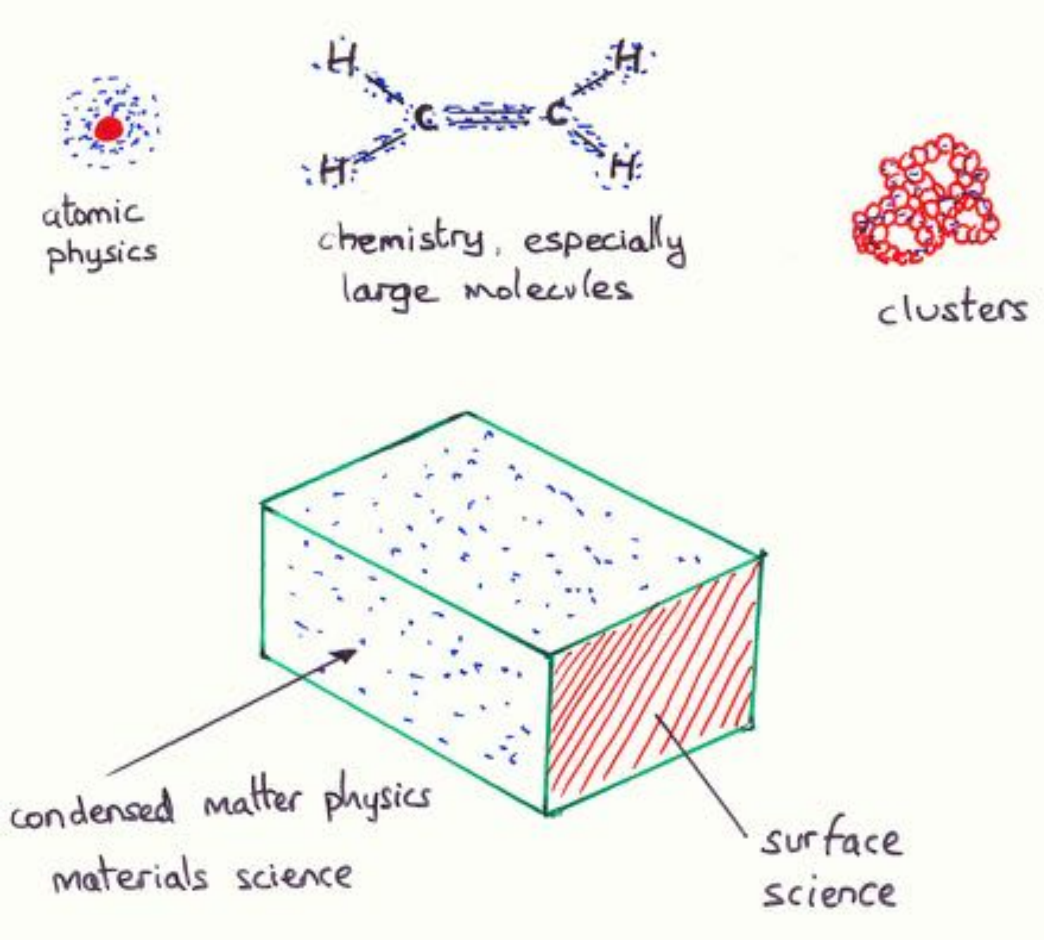
- Solve Newton’s equations for nuclei at given temperature and pressure
- Use simple force fields be
- Can do a million atoms fo
- But, cannot break bonds!



Theoretical and Computational Biophysics Group
Beckman Institute
University of Illinois at Urbana-Champaign

Electronic Structure Problem: Diversity

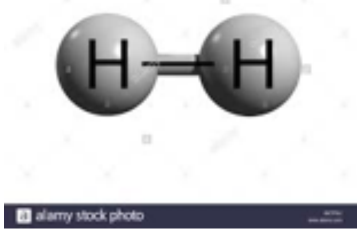
- For all everyday matter

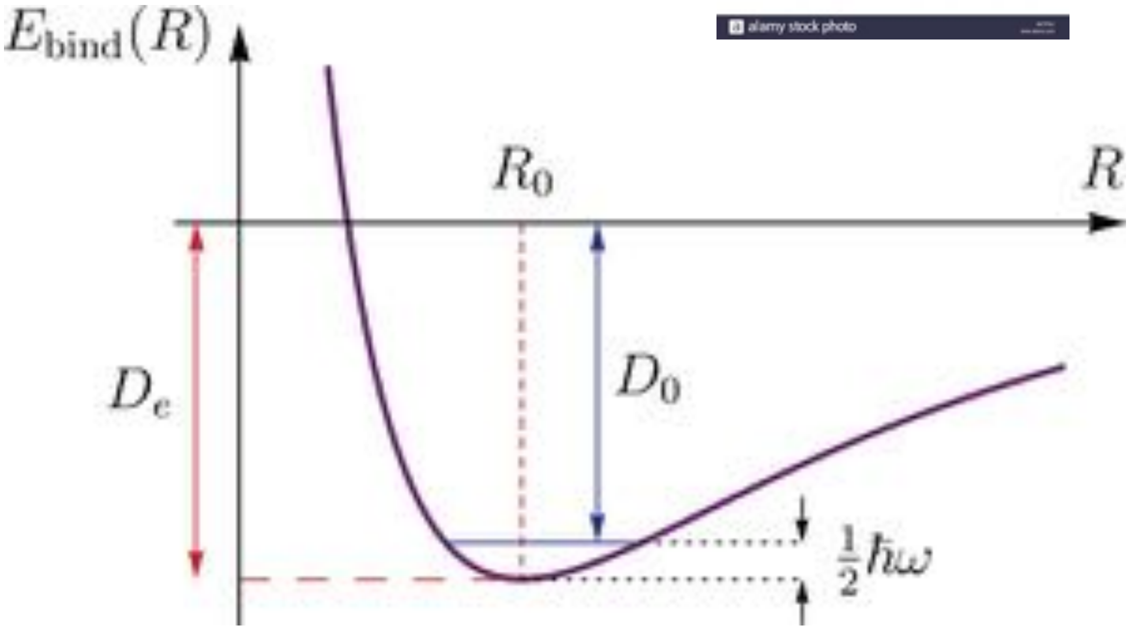


Basic Electronic Structure Problem

- Just want E(R)

<-R->





Why electronic structure problem is evil

- Quantum mechanics really needed for electrons
- It’s a many-body problem: Every electron sees every other one, as well as nucleus.
- Chemical accuracy is about 1 in 10^7 for electronic energy of 500 atoms.
- *Ab initio* quantum chemistry: When # electrons doubles, computer cost increases by 128.

Mathematical form of problem

- Differential equation in 3N coordinates:

$$\{\hat{T} + \hat{V}_{\rm ee} + \hat{V}\}\,\Psi = E\,\Psi,$$

Hamiltonian for N electrons in the presence of external potential $v(\mathbf{r})$:

$$\hat{H} = \hat{T} + \hat{V}_{\rm ee} + \hat{V},$$

where the kinetic and elec-elec repulsion energies are

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2, \qquad \hat{V}_{\rm ee} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

and difference between systems is N and the one-body potential

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i)$$

Often $v(\mathbf{r})$ is electron-nucleus attraction

$$v(\mathbf{r}) = -\sum_{\alpha}\frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|}$$

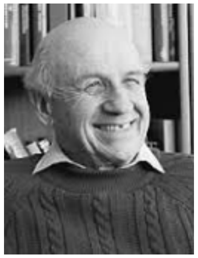
where α runs over all nuclei, plus weak applied $\mathbf{E}$ and $\mathbf{B}$ fields.

$$E = \min_{\Psi}\langle\Psi|\hat{T} + \hat{V}_{\rm ee} + \hat{V}|\Psi\rangle$$

The greatest free lunch ever: DFT

- 1964: Hohenberg and Kohn proved a theorem showing lowest energy can be found by search over electronic densities (much simpler than wavefunction)

- 1965: Created Kohn-Sham (KS) equations of fake non-interacting electrons (not many-body anymore) which, when solved, yield lowest E and density alone.



KS equations (1965)

Define *fictitious* non-interacting electrons satisfying:

$$\left\{-\frac{1}{2}\nabla^2 + v_{\rm S}(\mathbf{r})\right\}\phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r}), \qquad \sum_{j=1}^{N} |\phi_j(\mathbf{r})|^2 = n(\mathbf{r}).$$

where $v_{\rm S}(\mathbf{r})$ is *defined* to yield $n(\mathbf{r})$.

Define $T_{\rm S}$ as the kinetic energy of the KS electrons, U as their Hartree energy and

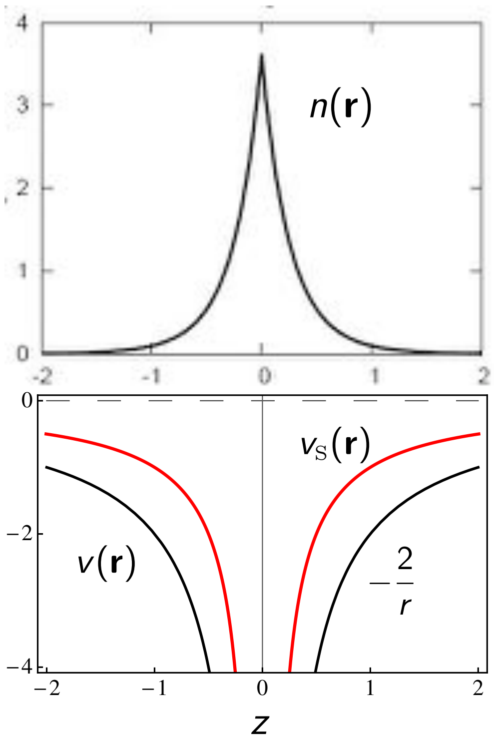
$$\boxed{F = T + V_{\rm ee} = T_{\rm S} + U + E_{\rm XC}}$$

the remainder is the exchange-correlation energy.

Most important result of exact DFT:

$$v_{\rm S}(\mathbf{r}) = v(\mathbf{r}) + \int d^3r \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\rm XC}[n](\mathbf{r}), \qquad \boxed{v_{\rm XC}(\mathbf{r}) = \frac{\delta E_{\rm XC}}{\delta n(\mathbf{r})}}$$

Knowing $E_{\rm XC}[n]$ gives closed set of self-consistent equations.



The kicker

- Need a formula for a small fraction of electronic energy, called XC energy, in terms of density, containing all quantum many-body effects.

- First formula (1965) good for solids, but not accurate enough for chemistry.

- Next formulas (1990) give useful accuracy for chemistry and materials.

Today's commonly-used XC approximations

- Local density approximation (LDA)
  - Uses only n(**r**) at a point.

$$E_{\rm X}^{\rm LDA}[n] = A_{\rm X} \int d^3r\; n^{4/3}(\mathbf{r})$$

$$A_{\rm X} = -(3/4)(3/\pi)^{1/3} = -0.738.$$

- Generalized gradient approx (GGA)
  - Uses both n(**r**) and |∇n(**r**)|
  - Should be more accurate, corrects overbinding of LDA
  - Examples are PBE and BLYP

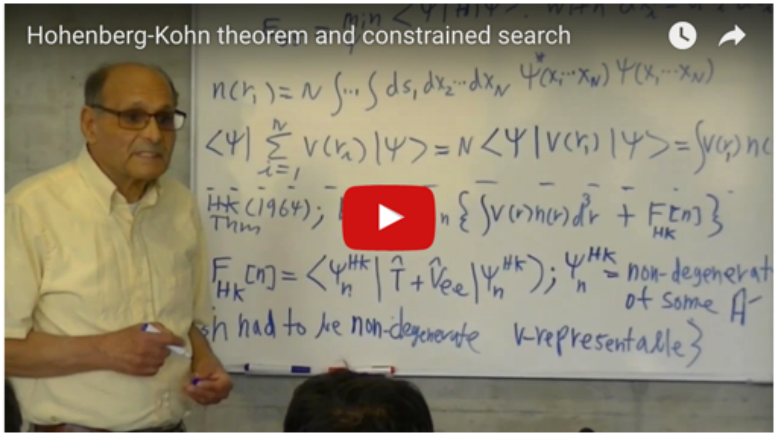
$$E_{\rm XC}^{\rm GGA} = \int d^3r\; e_{\rm XC}^{\rm GGA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$$

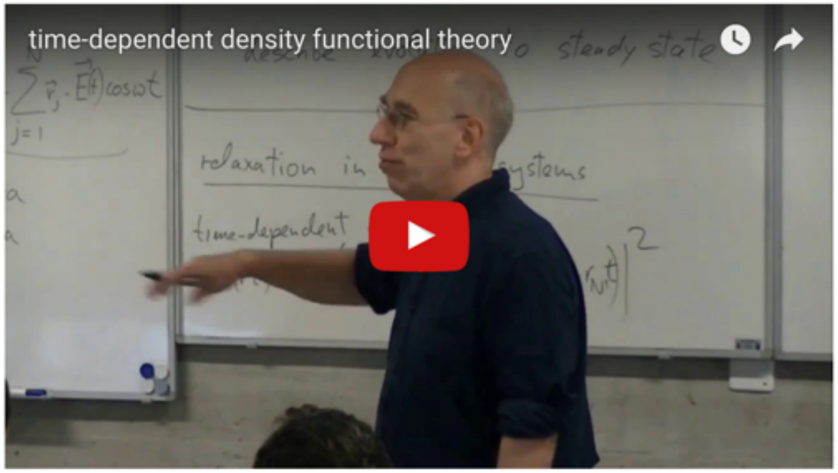
- Hybrid:
  - Mixes some fraction of HF with GGA
  - Examples are B3LYP and PBE0

$$E_{\rm XC}^{\rm hyb} = a\,(E_{\rm X} - E_{\rm X}^{\rm GGA}) + E_{\rm XC}^{\rm GGA}$$

Modern research to find XC energy

Youtube: Teaching the theory in DFT



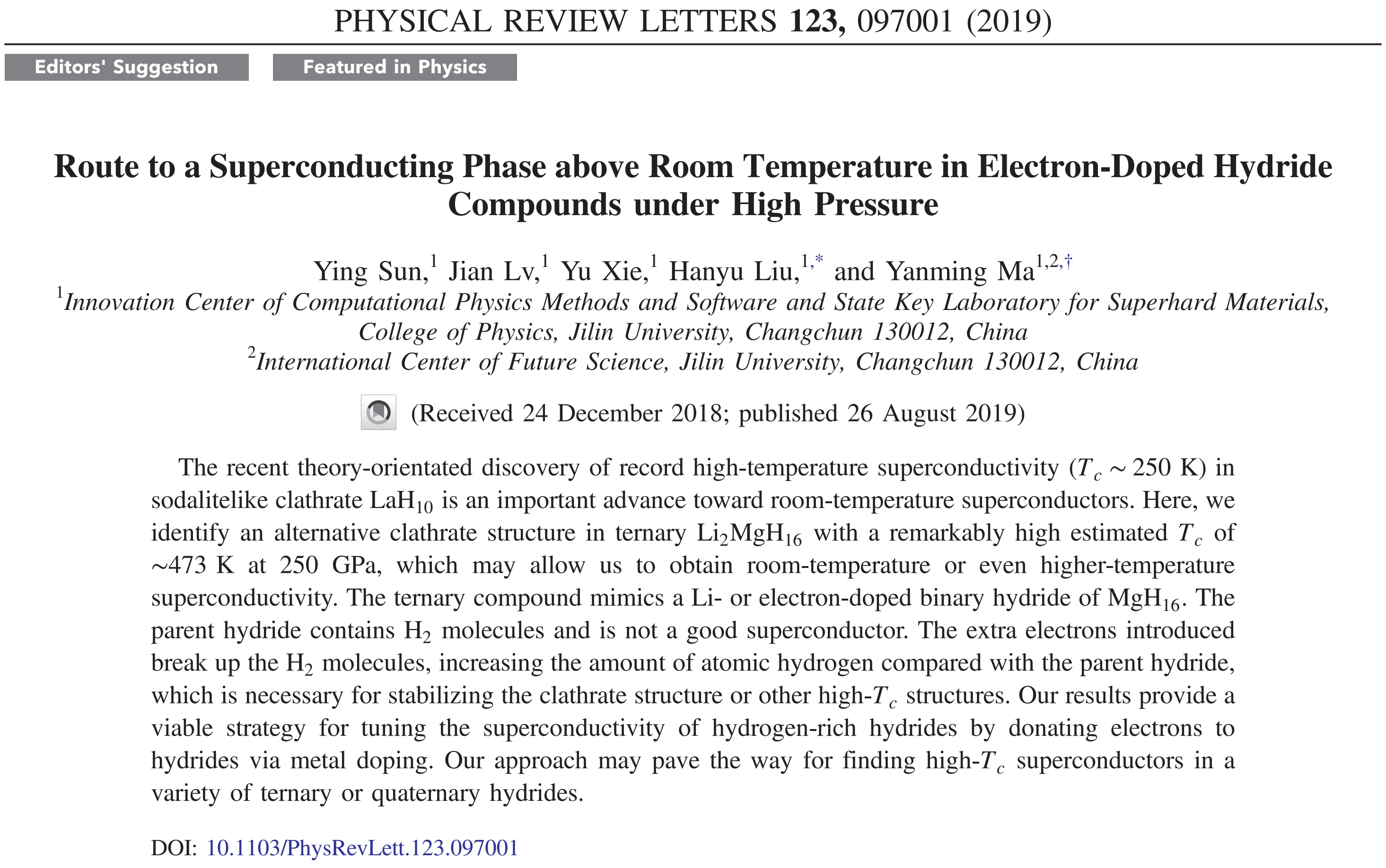


Alphabet soup

Applications

- Computers, codes, algorithms always improving
- Making bona fide predictions
- E.g., a new better catalyst for Haber-Bosch process ('fixing' ammonia from air) was predicted after about 25,000 failed experiments (Norskov's group)
- Now scanning chemical and materials spaces using big data methods for materials design (materials genome project).
- World's hottest superconductor (203K) is hydrogen sulfide, predicted by DFT calculations, then made.
- Latest generation of intel chips (needed for Mac airbook) is half-size and Pb-free with help of DFT.

Highest temperature superconductors



PHYSICAL REVIEW LETTERS **123,** 097001 (2019)

Editors' Suggestion Featured in Physics

Route to a Superconducting Phase above Room Temperature in Electron-Doped Hydride Compounds under High Pressure

Ying Sun,[1] Jian Lv,[1] Yu Xie,[1] Hanyu Liu,[1,*] and Yanming Ma[1,2,†]
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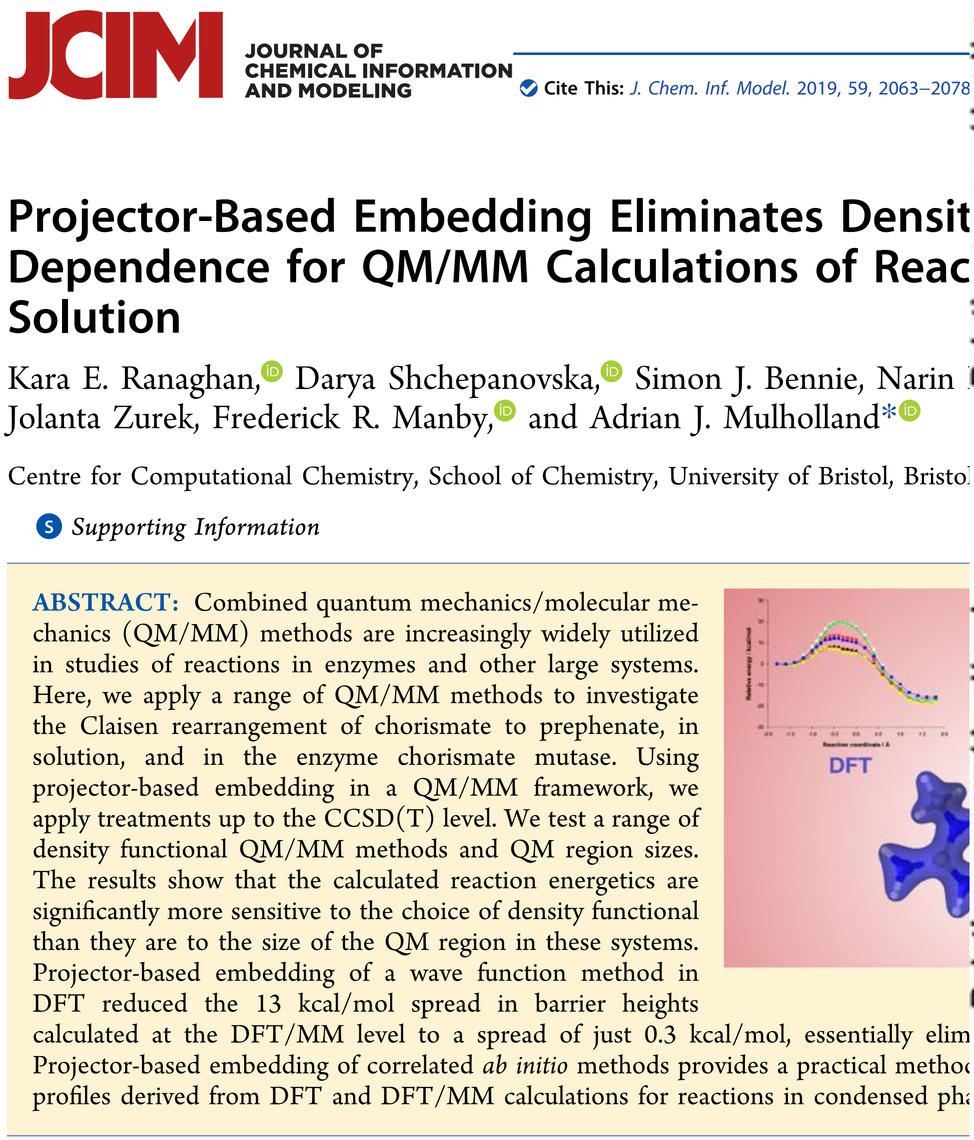
College of Physics, Jilin University, Changchun 130012, China
[2]*International Center of Future Science, Jilin University, Changchun 130012, China*

(Received 24 December 2018; published 26 August 2019)

The recent theory-orientated discovery of record high-temperature superconductivity ($T_c \sim 250$ K) in sodalitelike clathrate LaH_{10} is an important advance toward room-temperature superconductors. Here, we identify an alternative clathrate structure in ternary Li_2MgH_{16} with a remarkably high estimated T_c of ~ 473 K at 250 GPa, which may allow us to obtain room-temperature or even higher-temperature superconductivity. The ternary compound mimics a Li- or electron-doped binary hydride of MgH_{16}. The parent hydride contains H_2 molecules and is not a good superconductor. The extra electrons introduced break up the H_2 molecules, increasing the amount of atomic hydrogen compared with the parent hydride, which is necessary for stabilizing the clathrate structure or other high-T_c structures. Our results provide a viable strategy for tuning the superconductivity of hydrogen-rich hydrides by donating electrons to hydrides via metal doping. Our approach may pave the way for finding high-T_c superconductors in a variety of ternary or quaternary hydrides.

DOI: 10.1103/PhysRevLett.123.097001

In quantum chemistry



JCIM JOURNAL OF CHEMICAL INFORMATION AND MODELING

Cite This: *J. Chem. Inf. Model.* 2019, 59, 2063–2078

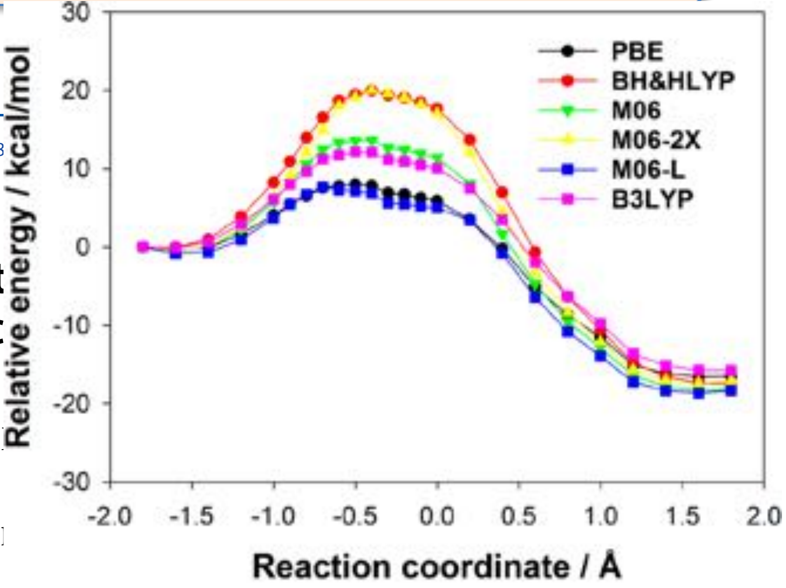
Projector-Based Embedding Eliminates Densit Dependence for QM/MM Calculations of Reac Solution

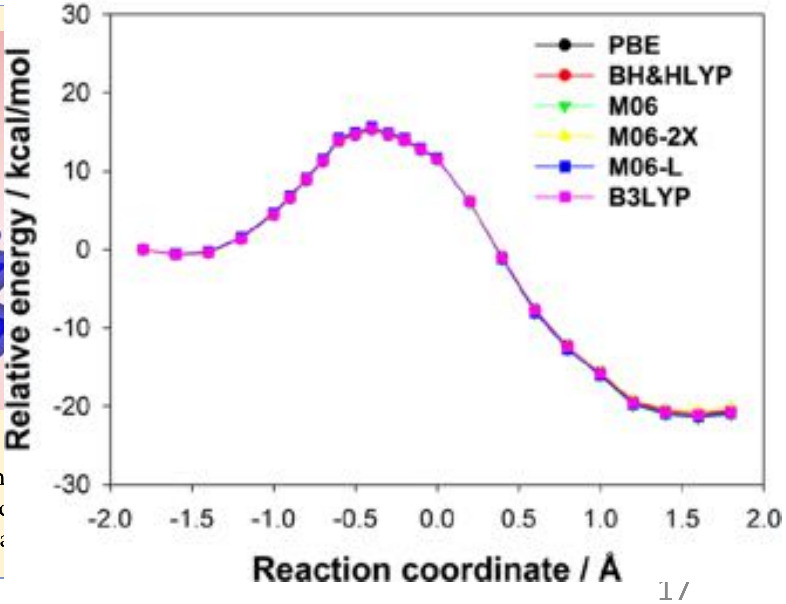
Kara E. Ranaghan, Darya Shchepanovska, Simon J. Bennie, Narin Jolanta Zurek, Frederick R. Manby, and Adrian J. Mulholland*

Centre for Computational Chemistry, School of Chemistry, University of Bristol, Bristol

Supporting Information

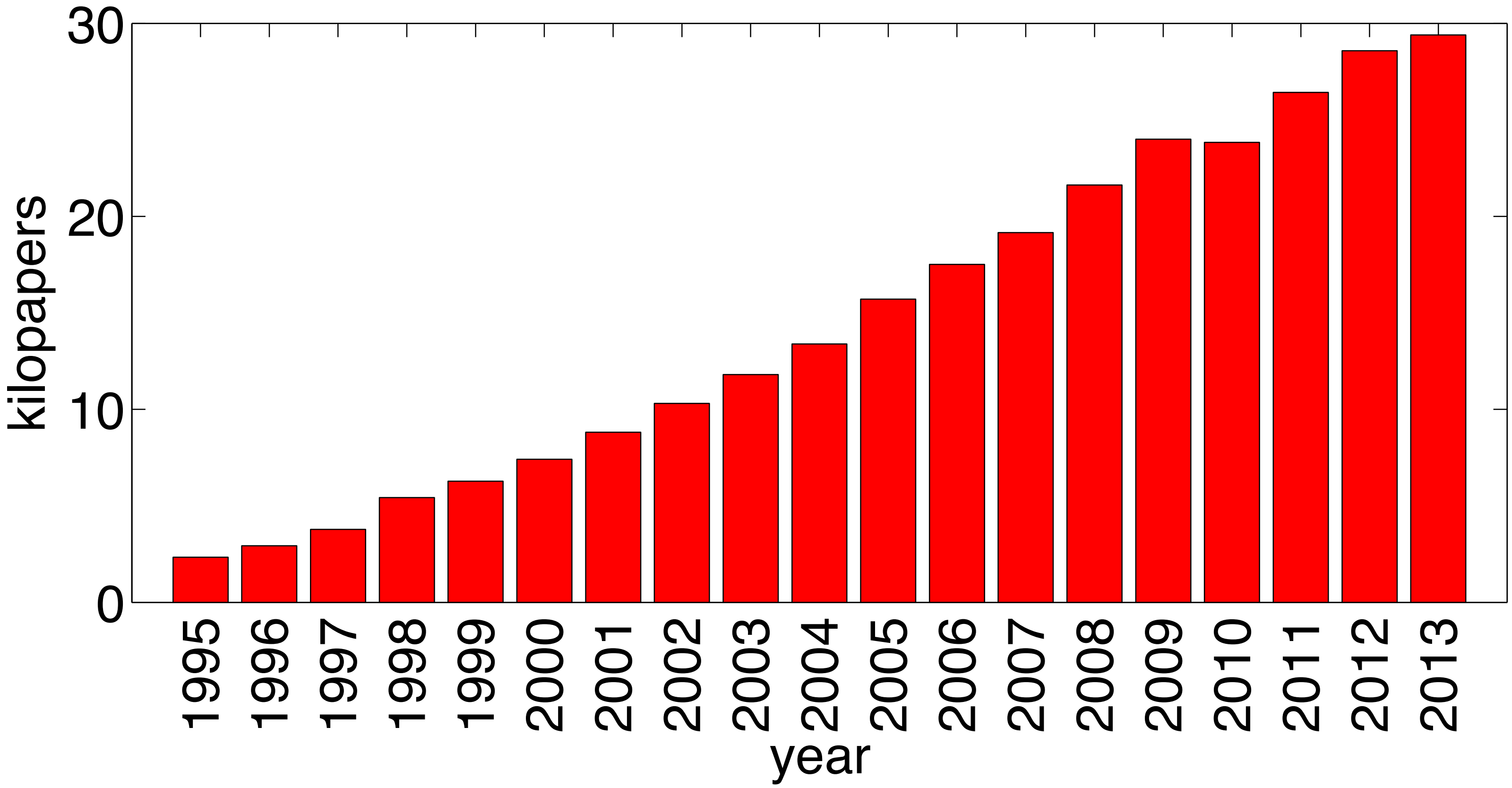
ABSTRACT: Combined quantum mechanics/molecular mechanics (QM/MM) methods are increasingly widely utilized in studies of reactions in enzymes and other large systems. Here, we apply a range of QM/MM methods to investigate the Claisen rearrangement of chorismate to prephenate, in solution, and in the enzyme chorismate mutase. Using projector-based embedding in a QM/MM framework, we apply treatments up to the CCSD(T) level. We test a range of density functional QM/MM methods and QM region sizes. The results show that the calculated reaction energetics are significantly more sensitive to the choice of density functional than they are to the size of the QM region in these systems. Projector-based embedding of a wave function method in DFT reduced the 13 kcal/mol spread in barrier heights calculated at the DFT/MM level to a spread of just 0.3 kcal/mol, essentially elim Projector-based embedding of correlated *ab initio* methods provides a practical metho profiles derived from DFT and DFT/MM calculations for reactions in condensed pha





Electronic Structure Problem: Impact

- Absurdly useful: Nvidia estimates 1/6th world's supercomputers run DFT calculations.



Difficulties with this research

- Truly multidisciplinary in a deep way – very hard to understand each other's methods and goals

- Not the latest shiny toy, e.g., not quantum computing or machine learning

- But just a little progress in this field can have enormous impact overnight.

Paying the price of the KS equations

- By using fake electrons, cost increases by factor of 8 when size doubles.
- Limits current sizes to 500 atoms on a single machine in a day.
- If we could avoid this, might be able to do 10^6 atoms.
- Again, a rule exists, $T_S[n]$, and some folks try to find it, but never accurately and generally enough.

Machine learning

Machine learning in electronic structure

- Explosion of interest in last 5 years
- Machine learning/big data/data science very broad terms
- Some examples:
  - Searching databases of materials calculations to find optimal functionality
  - Searching chemical compound space (SCHNET, ANI,..)
  - Accelerated sampling
  - Designing interatomic potentials (Behler,,Csanyi,..)

]**Editorial: Special Topic on Data-enabled Theoretical Chemistry** Matthias Rupp, O. Anatole von Lilienfeld, Kieron Burke, Journal of Chemical Physics Guest Editorial: Special Topic on Data-Enabled Theoretical Chemistry 148, 241401 (2018)

Original team for ML DFT (2010)

- Most with Klaus Mueller of TU Berlin, computer science.

Klaus-Robert Müller

- ML now being applied directly to, e.g., molecular energies from geometries for drug design, many by Matthias Rupp

Matthias Rupp

- Our efforts are focused on finding $T_s[n]$ from examples, work by John Snyder (Humboldt fellow at TU Berlin/MPI Halle)

John Snyder

Demo problem in DFT

- N non-interacting same-spin fermions confined to 1d box

- Define class of potential:

$$v(x) = -\sum_{i=1}^{3} a_i \exp(-(x-b_i)^2/(2c_i^2))$$

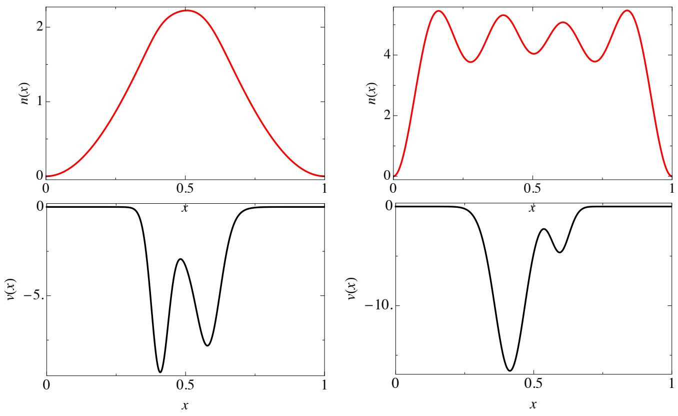
- Represent the density on a grid with spacing $\Delta x = 1/(G-1)$

- ML-DFA for KE:

$$\hat{T}(\mathbf{n}) = \bar{T}\sum_{j=1}^{M} \alpha_j k(\mathbf{n}_j, \mathbf{n})$$

$$k[n,n'] = \exp\left(-\int dx\, (n(x)-n'(x))^2)/(2\sigma^2 \right))$$

Generate 2000 potentials. Solve for up to 4 electrons.



Performance for T_s

kcal/mol

N	M	λ	σ	$\overline{\lvert\Delta T\rvert}$	$\lvert\Delta T\rvert^{\text{std}}$	$\lvert\Delta T\rvert^{\text{max}}$
1	40	2.4×10^{-5}	238	3.3	3.0	23.
	60	1.0×10^{-5}	95	1.2	1.2	10.
	80	6.7×10^{-6}	48	0.43	0.54	7.1
	100	3.4×10^{-7}	43	0.15	0.24	3.2
	150	2.5×10^{-7}	33	0.060	0.10	1.3
	200	1.7×10^{-7}	28	0.031	0.053	0.65
2	100	1.3×10^{-7}	52	0.13	0.20	1.8
3	100	2.0×10^{-7}	74	0.12	0.18	1.8
4	100	1.4×10^{-7}	73	0.078	0.14	2.3
1-4†	400	1.8×10^{-7}	47	0.12	0.20	3.6

LDA ~ 223 kcal/mol, Gradient correction ~ 159 kcal/mol

We don’t just need the energy

- The KS equations are solving the following equation for us:

$$\frac{\delta T_{\mathrm{S}}}{\delta n(\mathbf{r})} = -v(\mathbf{r}) - v_{\mathrm{H}}[n](\mathbf{r}) - v_{\mathrm{XC}}[n](\mathbf{r})$$

- If we had an explicit approximation for $T_S[n]$, we could solve this directly.

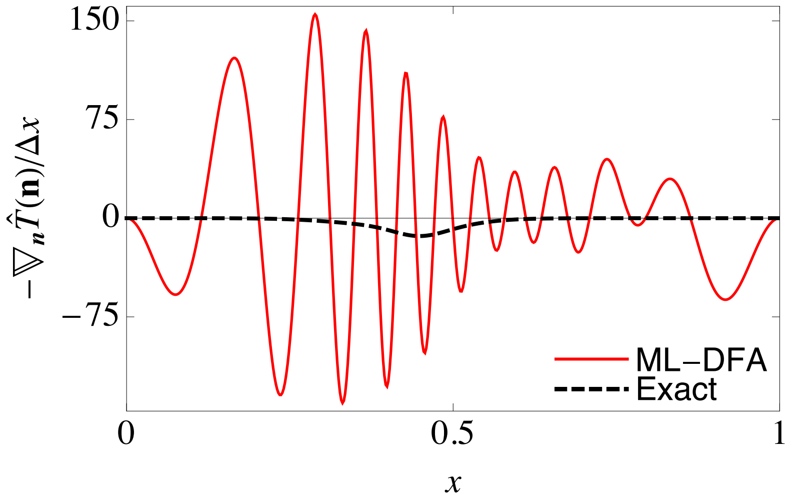
functional derivative?

Exact

ML-DFA

$$\frac{\delta T[n]}{\delta n(x)} = \mu - v(x) \quad \longleftrightarrow \quad \frac{1}{\Delta x}\nabla_{\mathbf{n}}\hat{T}(\mathbf{n}) = \sum_{j=1}^{M}\alpha'_j(\mathbf{n}_j-\mathbf{n})k(\mathbf{n}_j,\mathbf{n})$$

$$\alpha'_j = \alpha_j/(\sigma^2\Delta x)$$



- Functionals are defined on infinite-dimensional spaces
- With finite interpolation, can always find bad directions
- Can we make a cruder definition that will work for our purposes?

Principal component analysis

$$X = (\mathbf{n}_{j_1} - \mathbf{n}, \ldots, \mathbf{n}_{j_m} - \mathbf{n})^\top$$

$$C = \frac{1}{m} X^\top X$$

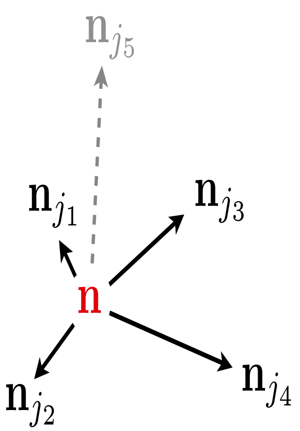
$$\downarrow$$

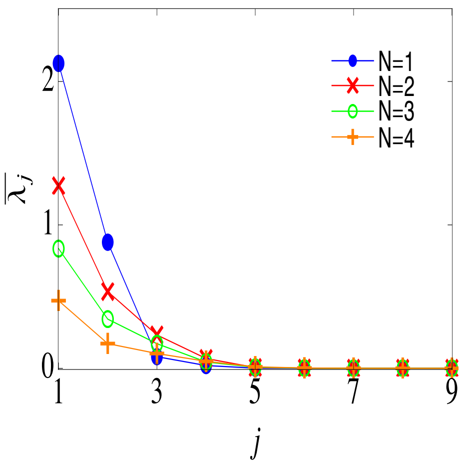
$$\lambda_j, \mathbf{x}_j$$

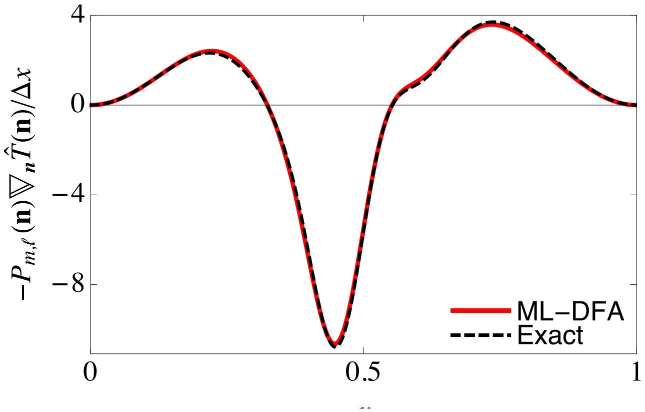
$$\downarrow$$

$$P_{m,\ell}(\mathbf{n}) = V^\top V$$

$$V = (\mathbf{x}_1, \ldots, \mathbf{x}_\ell)^\top$$







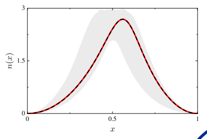
Lessons

- Exact noise-free data infinitely available for $T_s[n]$, every cycle of every KS calculation in the world provides examples.
- Need very accurate derivatives to get accurate density from Euler equation.
- Can find ways to bypass this.
- Functionals can be made arbitrarily accurate with sufficient data.

Finding Density Functionals with Machine Learning John C. Snyder, Matthias Rupp, Katja Hansen, Klaus-Robert Müller, Kieron Burke, Phys. Rev. Lett. **108**, 253002 (2012)

Road map back to reality

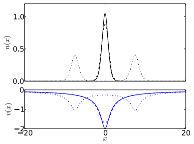
Roadmap to 3d land



1d box — model selection, projected functional derivatives, OF-DFT

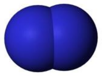
bond breaking, self-consistent densities

1d diatomics

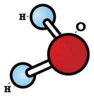


dimensionality, basis sets, representation, inversion symmetry

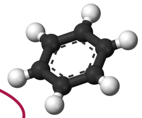
3d atoms, diatomics



full symmetries, scaling

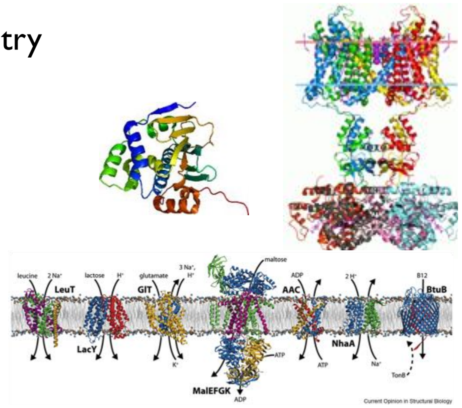


3d molecules

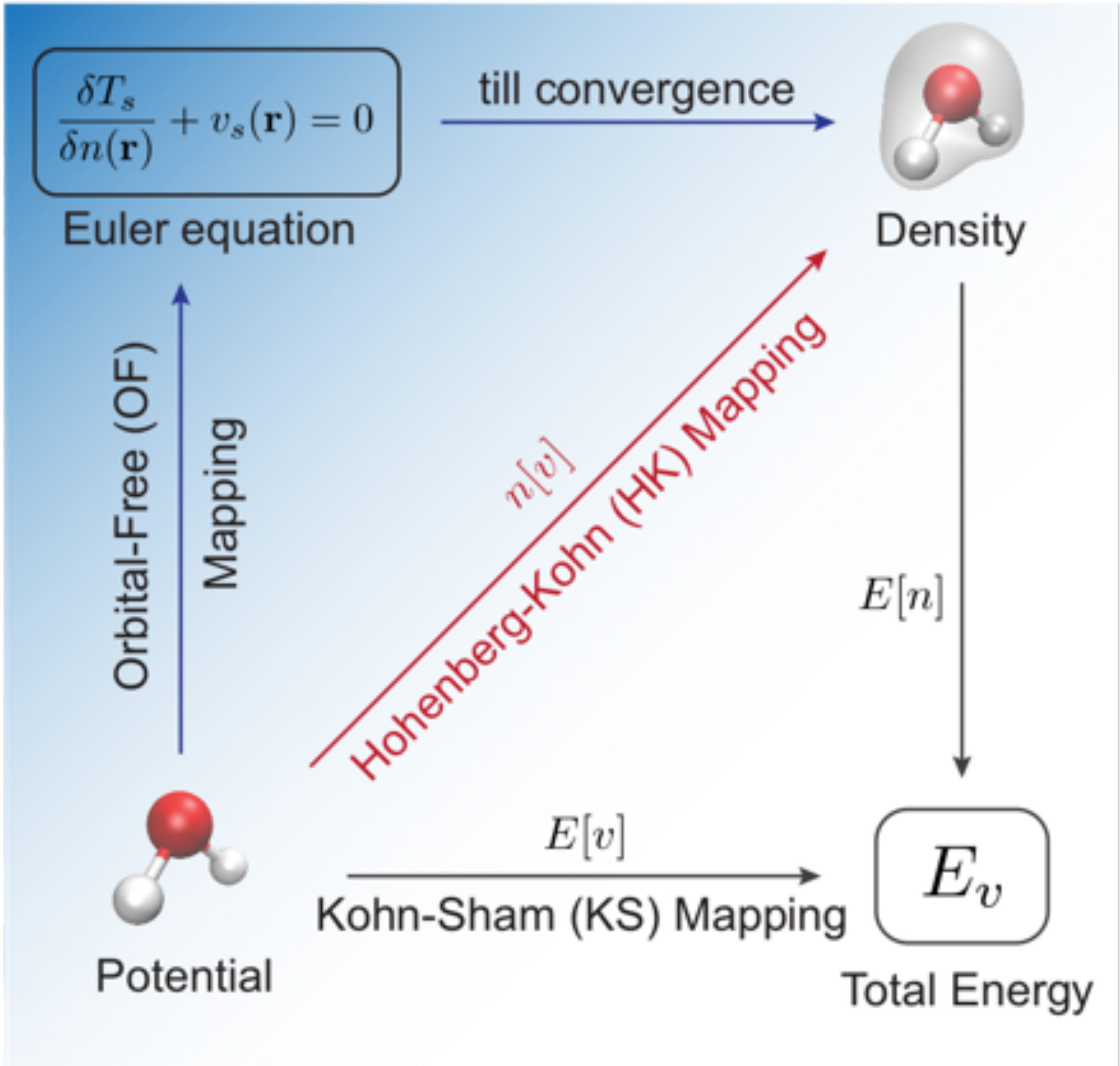


scalability, data accumulation
ab-initio MD, active learning

large systems, real applications



By-passing KS



MD simulations testing ML method

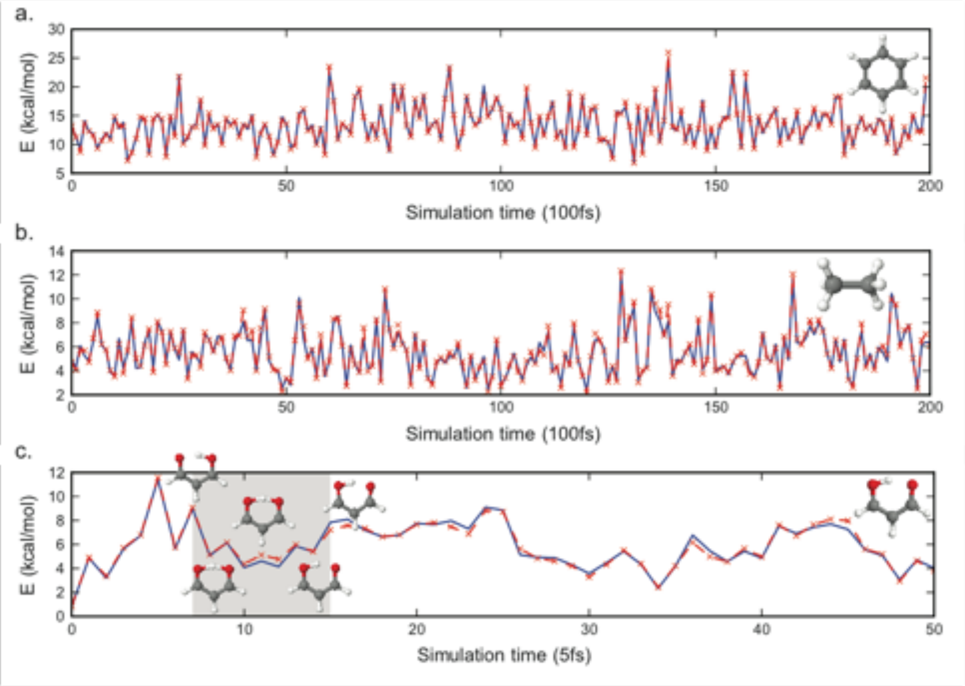
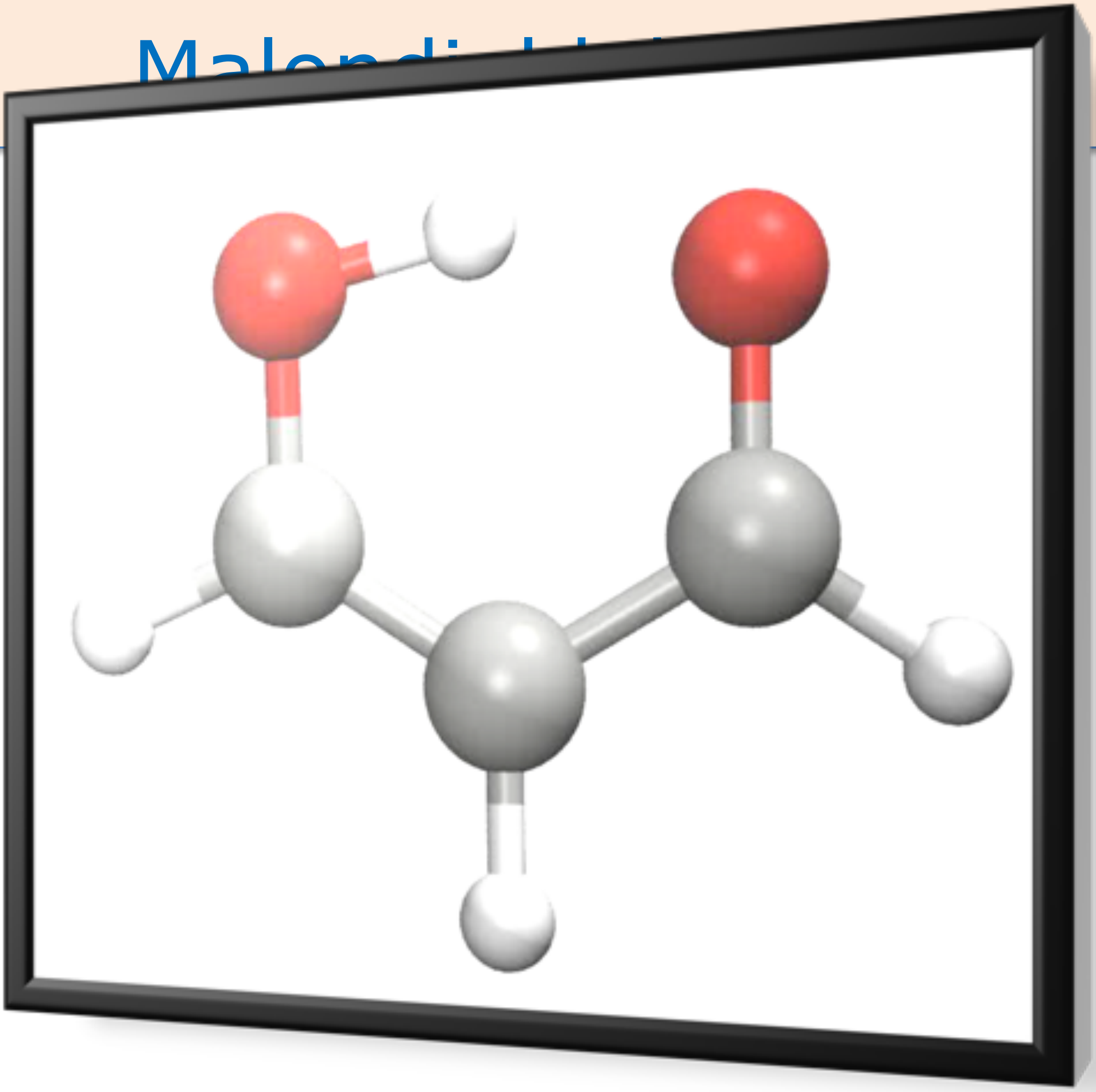


Figure 3. Energy errors of ML-HK along MD trajectories. PBE values in blue, ML-HK values in red. **a.** A 2 ps classical trajectory of benzene. **b.** A 2 ps classical trajectory of ethane. **c.** A 0.25 ps ab-initio trajectory of malonaldehyde. The ML model correctly predicts energies during a proton transfer in frames 7 to 15 without explicitly including these geometries in the training set.

	Benzene		Ethane		Malonaldehyde	
Training trajectories	MAE	max	MAE	max	MAE	max
300K	0.395742	1.92642	0.212137	1.33947	0.206795	0.725515
300K + 350K	0.260517	1.76190	0.236088	1.38227		
300K + 400K	0.370876	2.1162	0.101054	0.576107		

Table V. Errors (ΔE_D in kcal/mol) on the MD datasets for different training trajectory combinations.

Malondi



[174] By-passing the Kohn-Sham equations with machine learning Felix Brockherde, Leslie Vogt, Li Li, Mark E Tuckerman, Kieron Burke, Klaus-Robert Müller, Nature Communications 8, 872 (2017).

Lessons

- Our 1d gradient methods become prohibitively expensive in 3d.
- Instead of using $T_s[n]$, learn $n[v](r)$.
- Much smarter than learning $E[v_s]$
- Works for H_2 and H_2O and …
- ..MD of malonaldehyde using ML forces with Leslie Vogt and Mark Tuckerman.
- Created non-local orbital-free density functional running much faster than solving KS equations

Our papers (all on dft.uci.edu)

Nonlinear gradient denoising: Finding accurate extrema from inaccurate functional derivatives John C. Snyder, Matthias Rupp, Klaus-Robert Müller, Kieron Burke, *International Journal of Quantum Chemistry* **115**, 1102--1114 (2015).

Understanding kernel ridge regression: Common behaviors from simple functions to density functionals Kevin Vu, John C. Snyder, Li Li, Matthias Rupp, Brandon F. Chen, Tarek Khelif, Klaus-Robert Müller, Kieron Burke, *International Journal of Quantum Chemistry* **115**, 1115--1128 (2015).

Understanding machine-learned density functionals Li Li, John C. Snyder, Isabelle M. Pelaschier, Jessica Huang, Uma-Naresh Niranjan, Paul Duncan, Matthias Rupp, Klaus-Robert Müller, Kieron Burke, *International Journal of Quantum Chemistry* n/a--n/a (2015).

Kernels, Pre-Images and Optimization John C. Snyder, Sebastian Mika, Kieron Burke, Klaus-Robert Müller, *Chapter in Empirical Inference - Festschrift in Honor of Vladimir N. Vapnik* (2013).

Orbital-free Bond Breaking via Machine Learning John C. Snyder, Matthias Rupp, Katja Hansen, Leo Blooston, Klaus-Robert Müller, Kieron Burke, *J. Chem. Phys.* **139**, 224104 (2013).

Finding Density Functionals with Machine Learning John C. Snyder, Matthias Rupp, Katja Hansen, Klaus-Robert Müller, Kieron Burke, *Phys. Rev. Lett.* **108**, 253002 (2012).

Bypassing the Kohn-Sham equations with machine learning Felix Brockherde, Leslie Vogt, Li Li, Mark E Tuckerman, Kieron Burke, Klaus-Robert Müller, Nature Communications 8, 872 (2017).

Pure density functional for strong correlations and the thermodynamic limit from machine learning Li Li, Thomas E. Baker, Steven R. White, Kieron Burke, Phys. Rev.B (2016).

Can exact conditions improve machine-learned density functionals? Jacob Hollingsworth, Li Li, Thomas E. Baker, Kieron Burke, The Journal of Chemical Physics 148, 241743 (2018).

Our latest trick

Theory

$$E = E^{\mathrm{DFT}}[n^{\mathrm{DFT}}] + \Delta E[n^{\mathrm{DFT}}],$$

RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 52, NUMBER 3 SEPTEMBER 1995

Correlation-energy density-functional formulas from correlating first-order density matrices

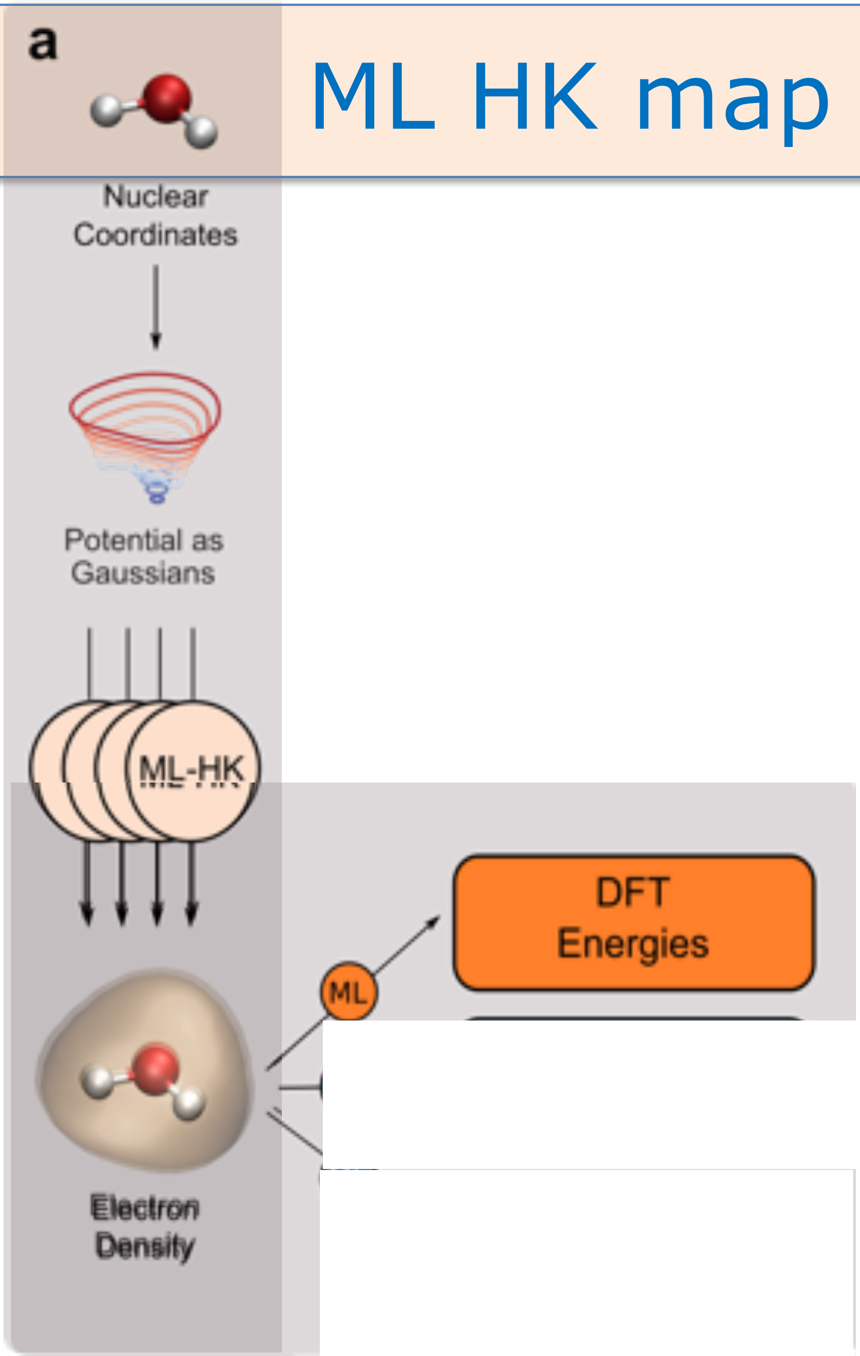
Mel Levy and Andreas Görling

Department of Chemistry and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

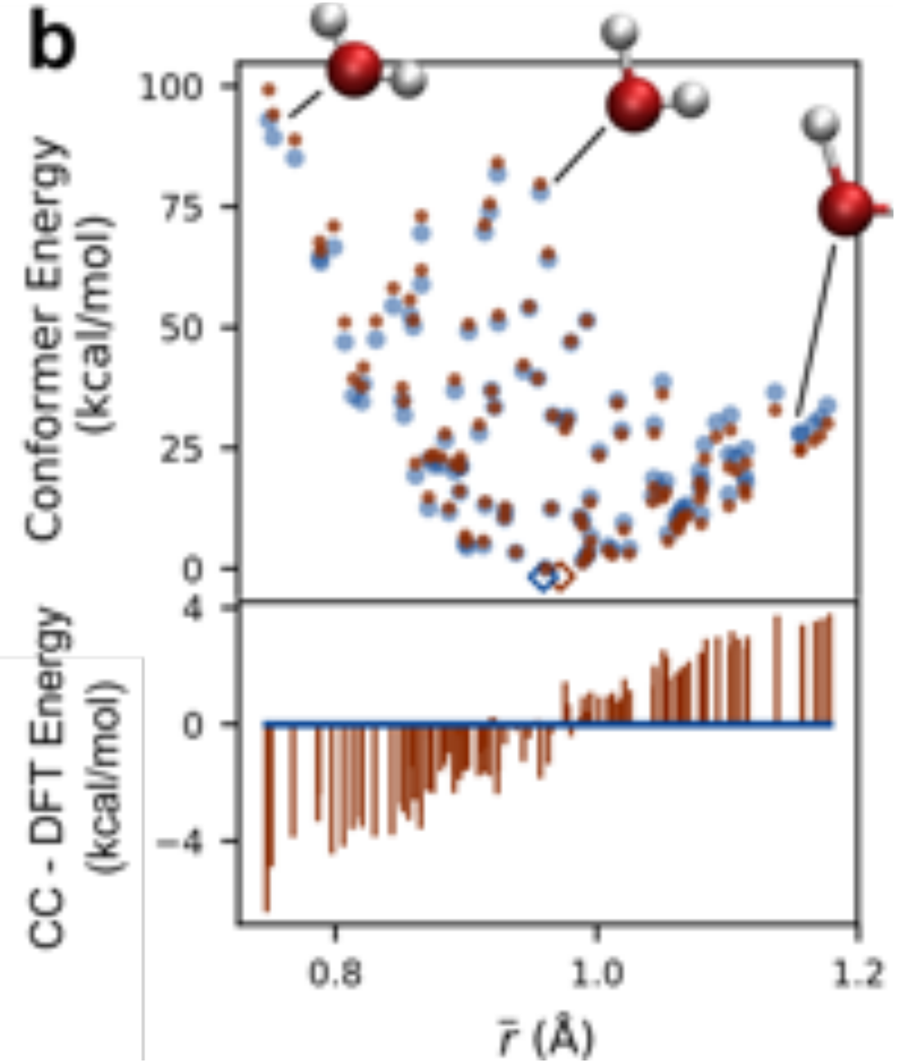
(Received 12 June 1995)

$$n(\mathbf{r}) = \frac{\delta E[v]}{\delta v(\mathbf{r})}$$

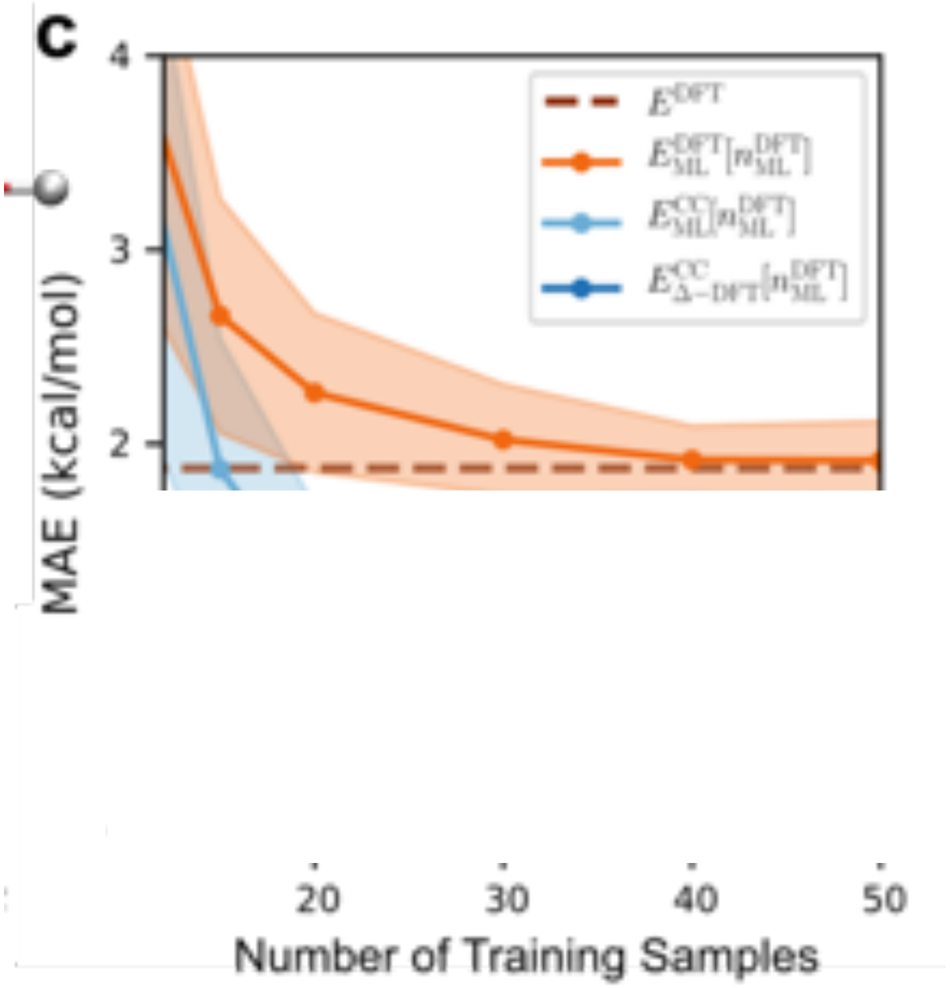
ML HK map


a
Nuclear Coordinates
Potential as Gaussians
ML-HK
Electron Density
ML
DFT Energies

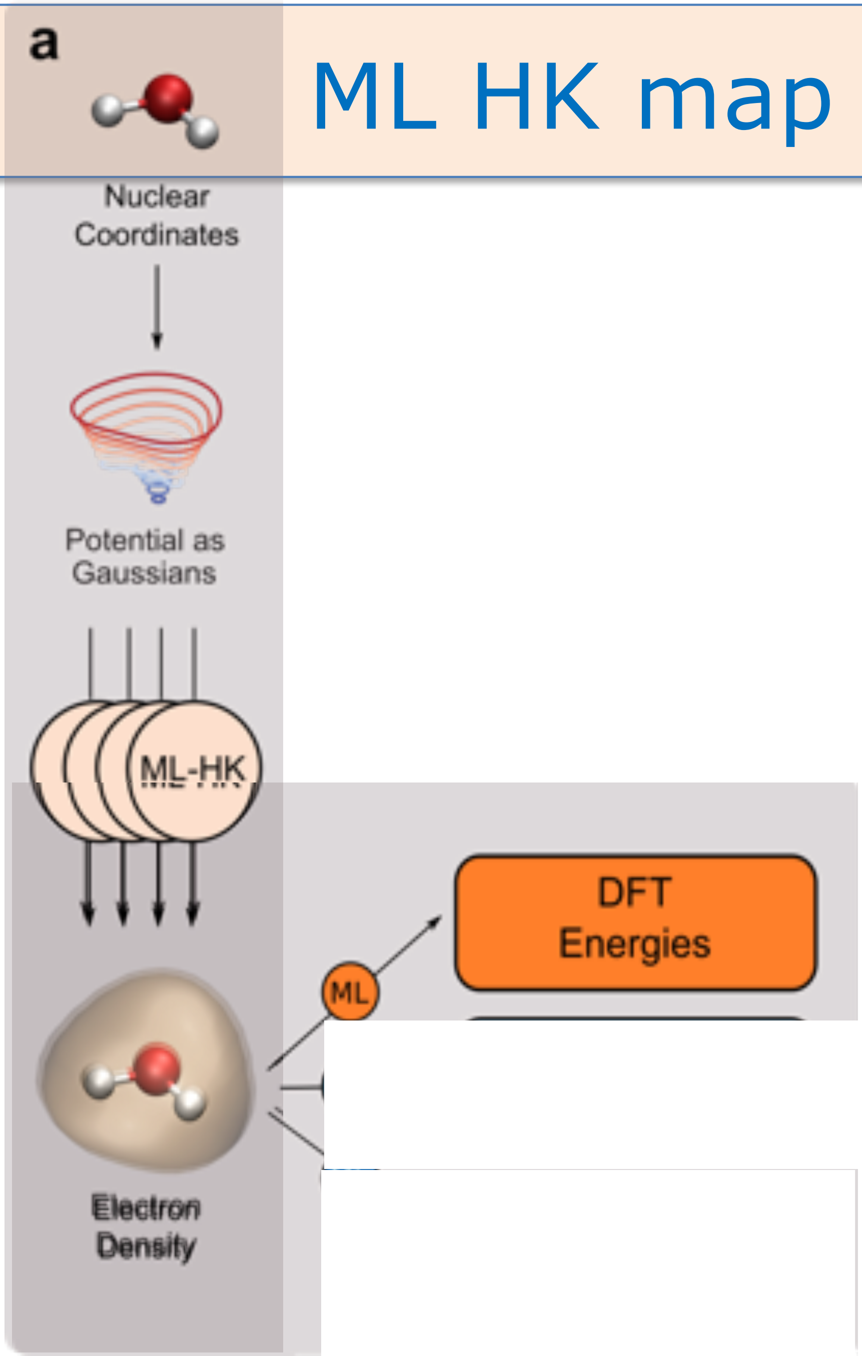
Range of PBE errors



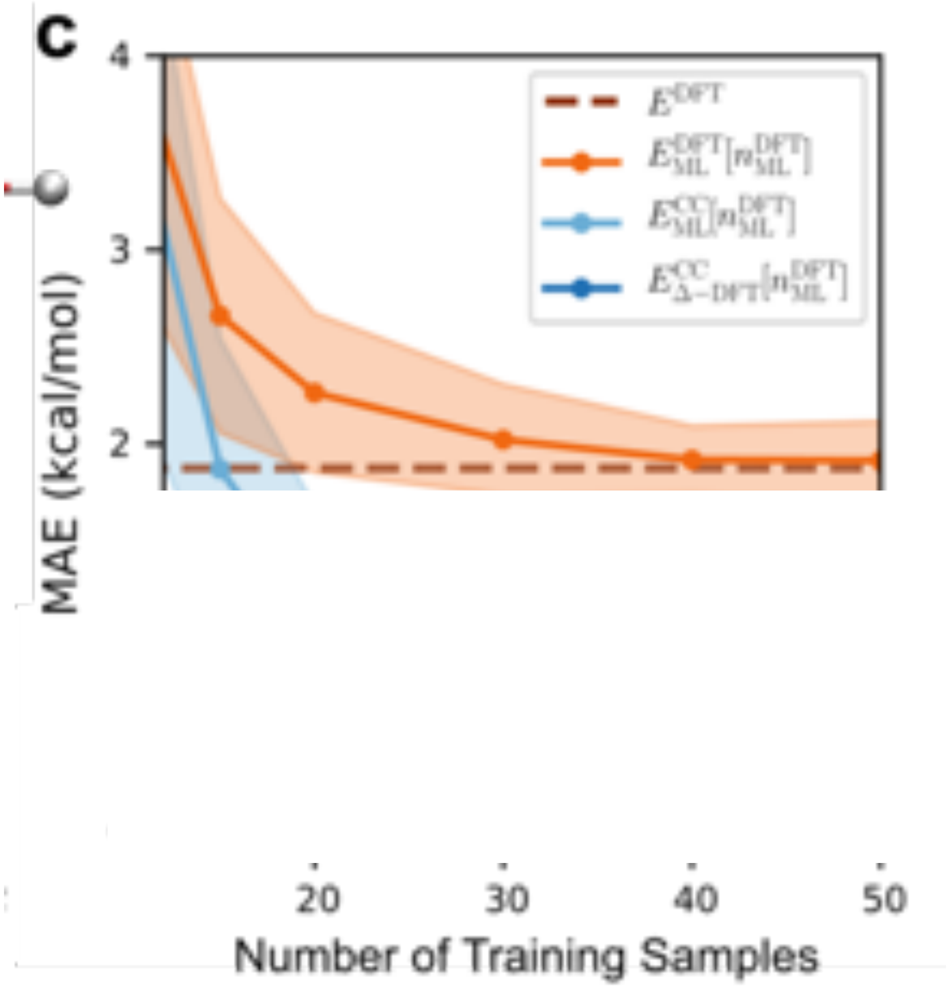
Learning curves



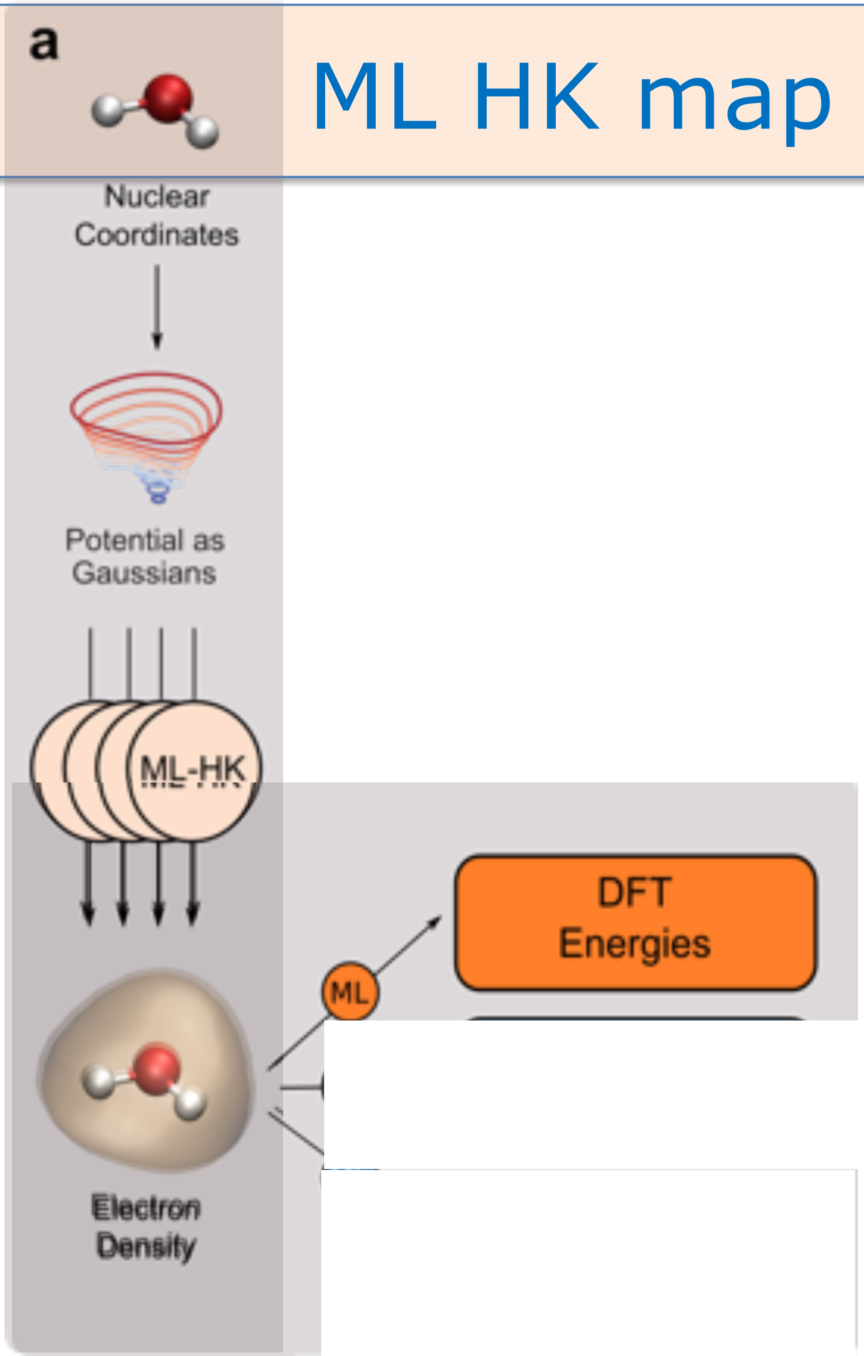
ML HK map


a
Nuclear Coordinates
Potential as Gaussians
ML-HK
Electron Density
ML
DFT Energies

Learning curves



ML HK map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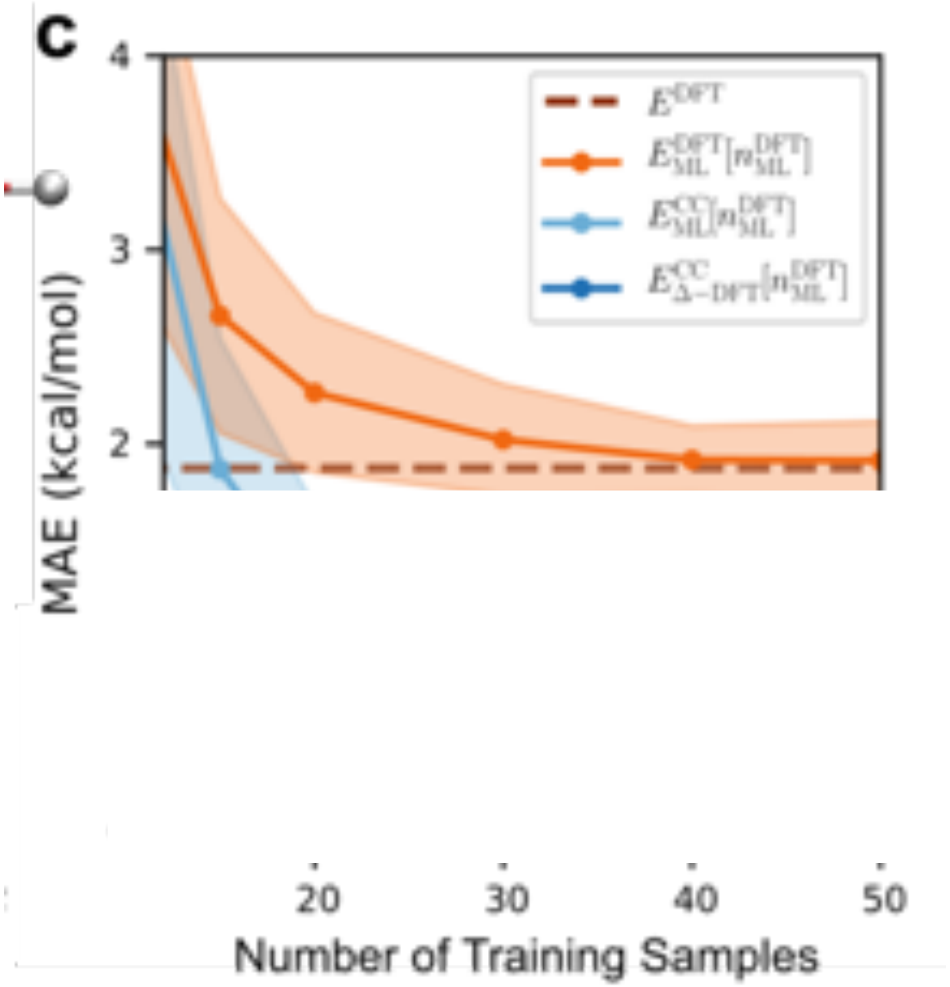
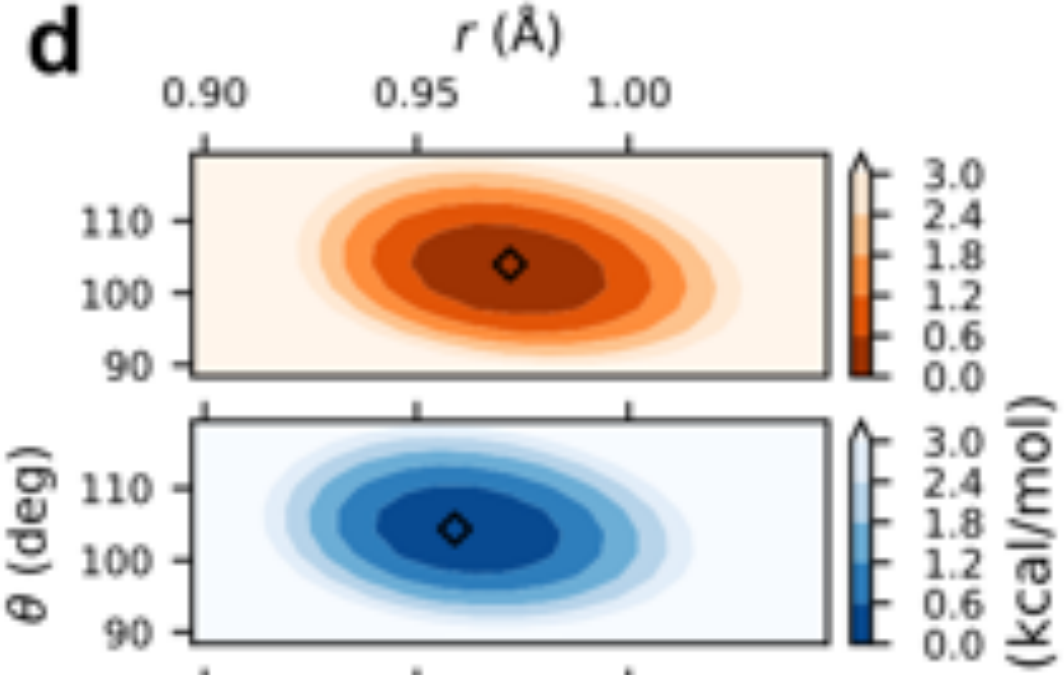
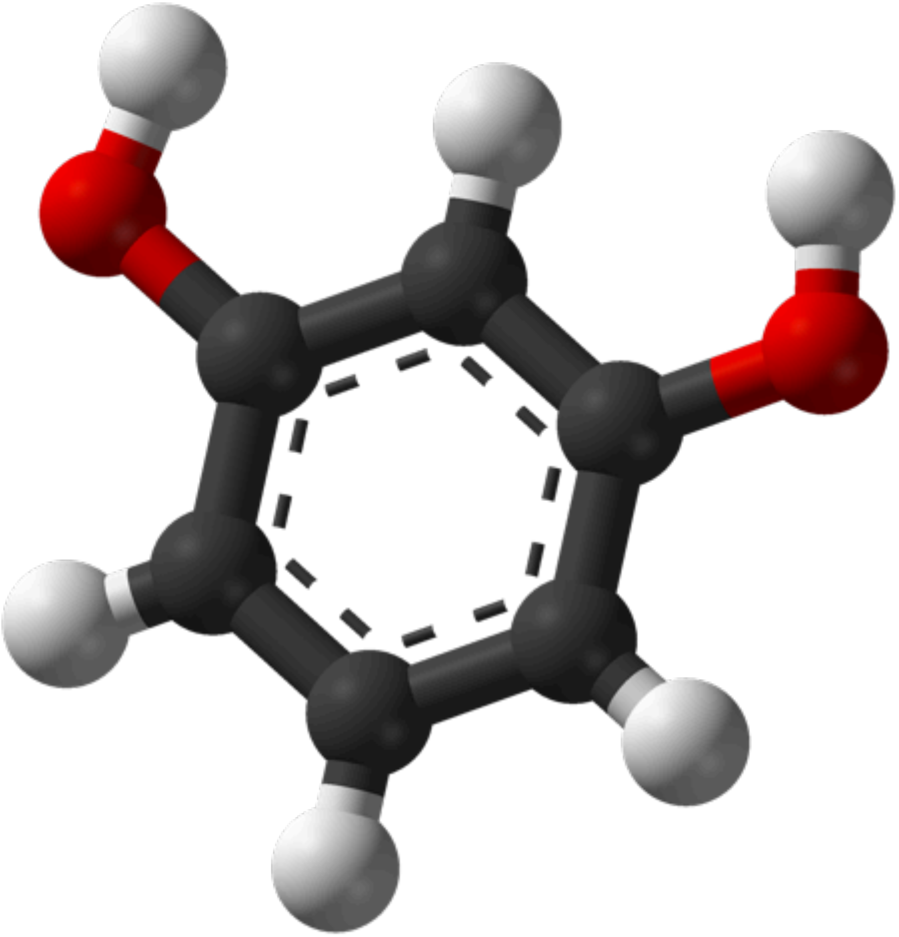
Learning curves



Potential energy surfaces



Resorcinol



Resorcinol dynamics

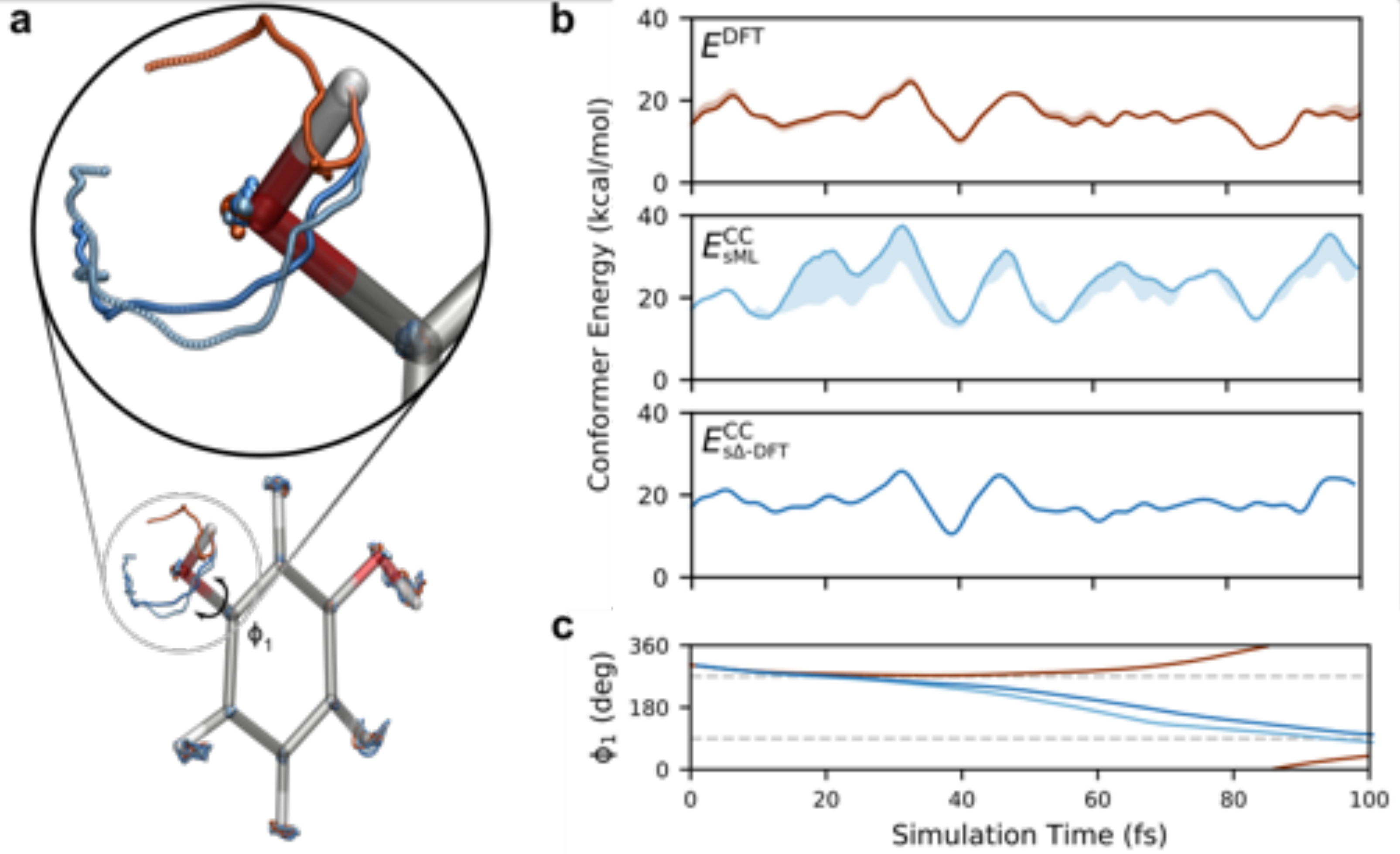


Figure 3: Resorcinol dynamics from an initi positions explored during 100 fs NVE MD traj RESPA-corrected forces (light blue), and $E^{\mathrm{CC}}_{\mathrm{s\Delta\text{-}DFT}}[n_{\mathrm{sML}}]$ (blue), b) the conformer energy along each trajectory (solid lines), with the error relative to CC shown as a shaded line width, and c) the evolution of the C-C-O-H dihedral angle for each trajectory with dashed grey lines indicating the barrier between conformers. For this figure, all DFT calculations use PBE and all CC energies are from CCSD(T).

Density Functionals with Quantum Chemical Accuracy: From Machine Learning to Molecular Dynamics Mihail Bogojeski, Leslie Vogt-Maranto, Mark E. Tuckerman, Klaus-Robert Mueller, Kieron Burke, ChemRXiv, (2019).

Opportunities for ML in physics using DFT

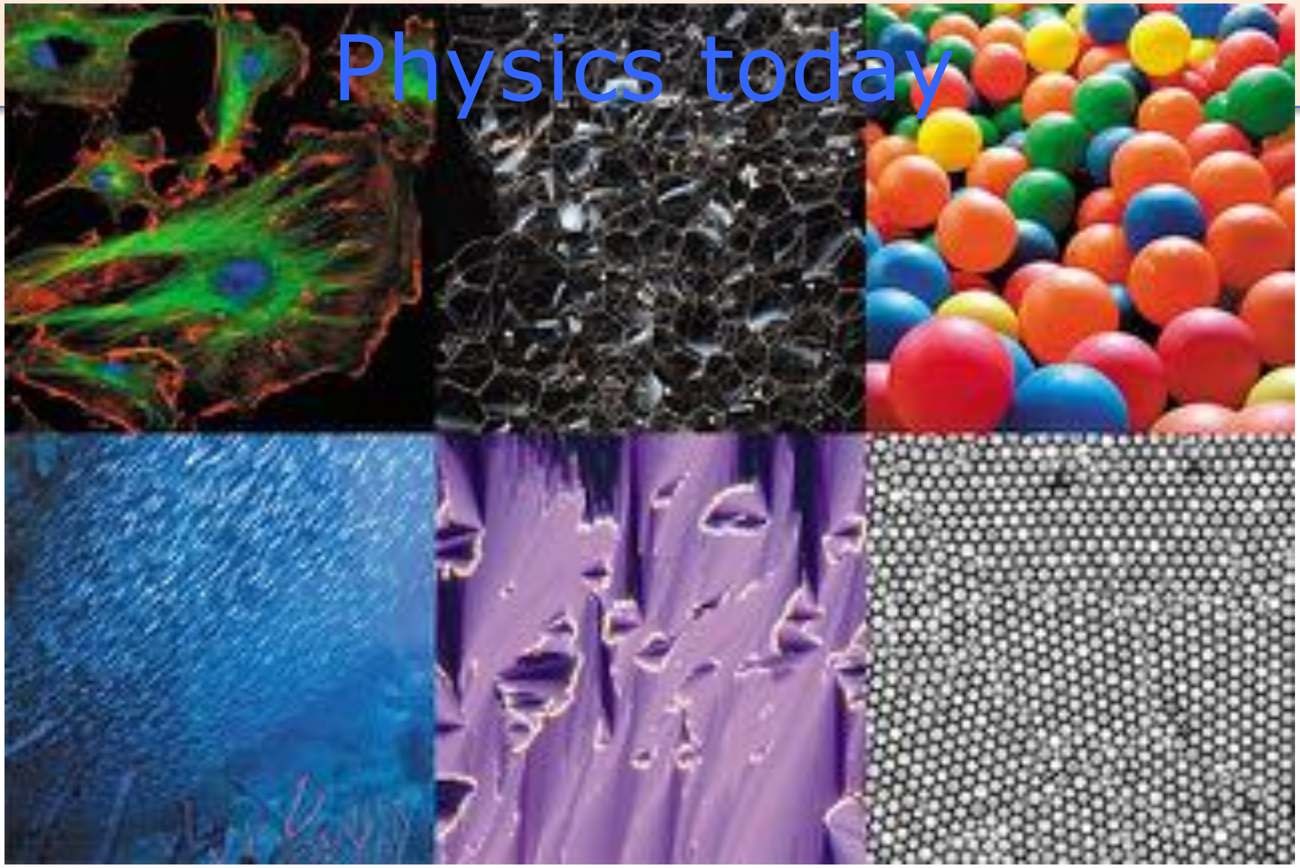
DFT is a working procedure for coarse-graining!

But it needs good functional approximations.

Classical DFT – faster than MD

- Can prove HK theorem for equilibrium classical statistical mechanics (Bob Evans, *Advances in Physics 28 (2), 143-200, 1979.)*
- Thus can solve self-consistent equations directly for equilibrium density
- But every liquid has a different interaction and so a different functional.
- Can look at wetting, phase transitions, nucleation, etc.
- But often very crude for realistic systems due to crude functional approximations.

Physics today



Clockwise from top left: Biological, Public Domain; Foams, CC BY-SA 2.5 André Karwath; Packings CC BY 2.0 Julie Kertesz; Colloids, CC BY-SA 3.0; Liquid Crystals, CC BY-SA 4.0 Alexprague; Fish school, CC BY-SA 2.0 Matthew Hoelscher.

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DOI: 10.1063/PT.3.4135

ARTICLE

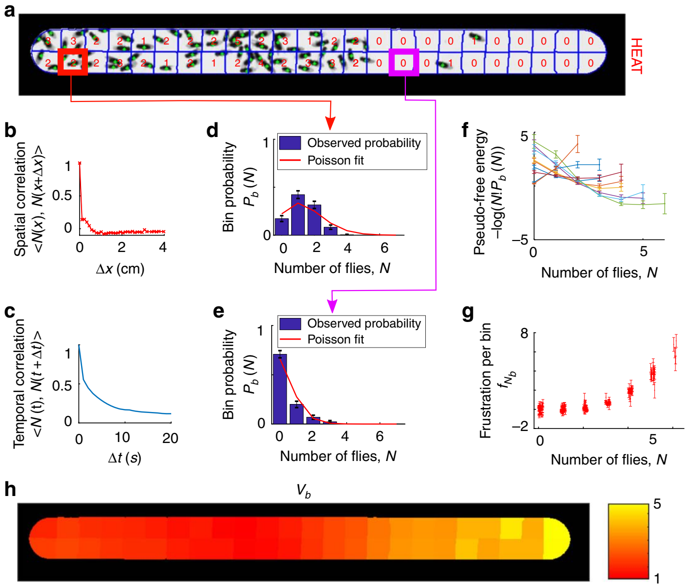
DOI: 10.1038/s41467-018-05750-z

OPEN

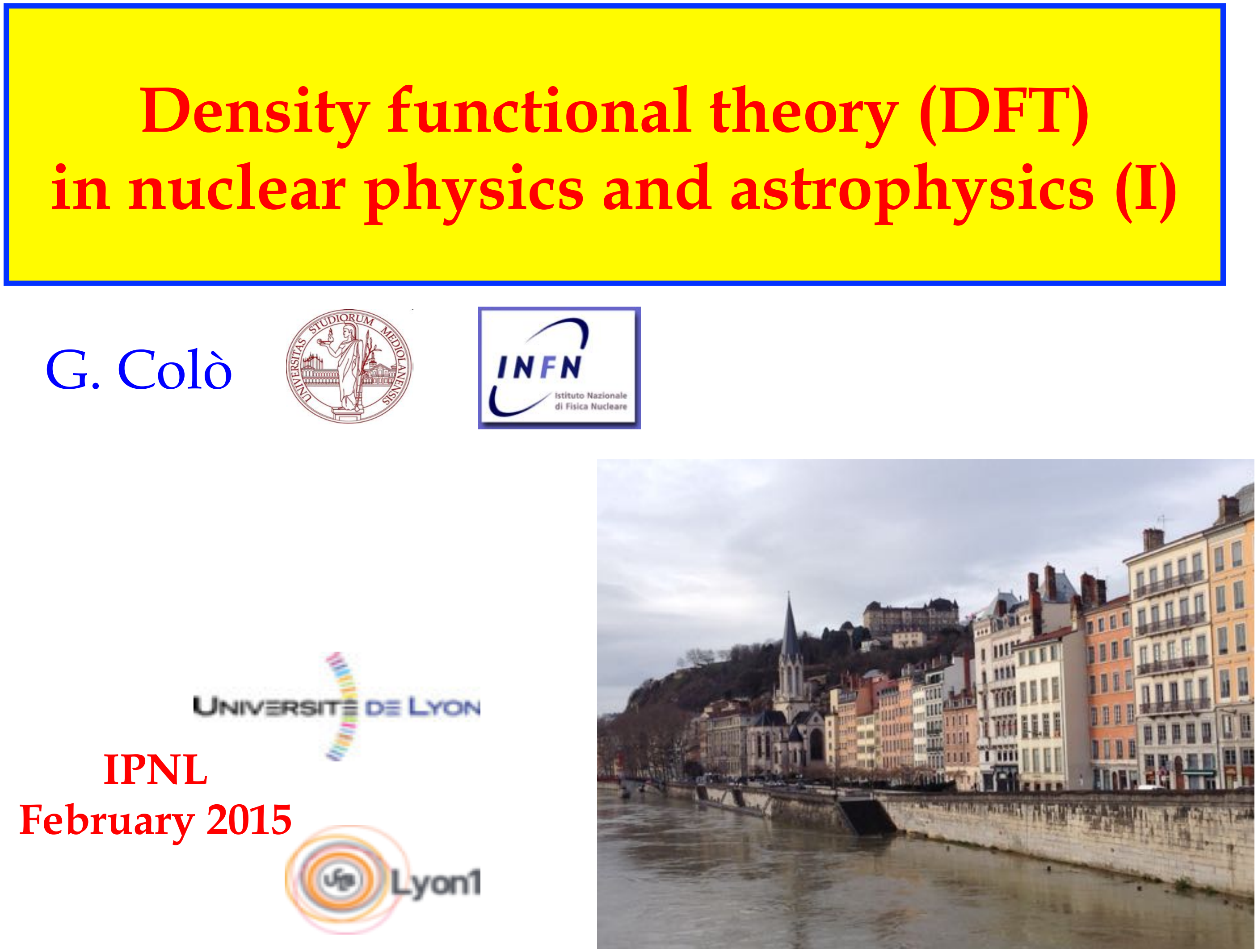
Density-functional fluctuation theory of crowds

J. Felipe Méndez-Valderrama[1], Yunus A. Kinkhabwala[2], Jeffrey Silver[3], Itai Cohen[4] & T.A. Arias[4]

Extraction of functionals for model system of walking flies. To test whether this approach applies to actual populations, we consider a model crowd consisting of wild-type male *Drosophila melanogaster* from an out-bred laboratory stock. It is well know that flies exhibit complex spatial preferences[30,31] and social behaviors[32,33]. Here we seek to determine whether a large crowd of individuals with such complex behaviors indeed can be described within our vexation and frustration framework. The flies are confined in 1.5 mm tall transparent chambers where they can walk freely but cannot fly or climb on top of each other. We record overhead videos of the flies, bin the arena, and use custom Matlab-based tracking algorithms (Methods) to measure the individual bin counts N_b in each video frame. To explore a variety of behaviors, we use arenas of different shapes[30] and apply heat gradients[34] across the arenas to generate different spatial preferences. We find that the flies fully adjust to such changes in their environments after 5 min. We also find that the behavior of the flies changes slowly over a time scale of hours (Methods). We thus take care to make our observations over 10 minute windows during time periods where the behavior is stable.



DFT of nuclear forces



Density functional theory (DFT)
in nuclear physics and astrophysics (I)

G. Colò

INFN
Istituto Nazionale di Fisica Nucleare

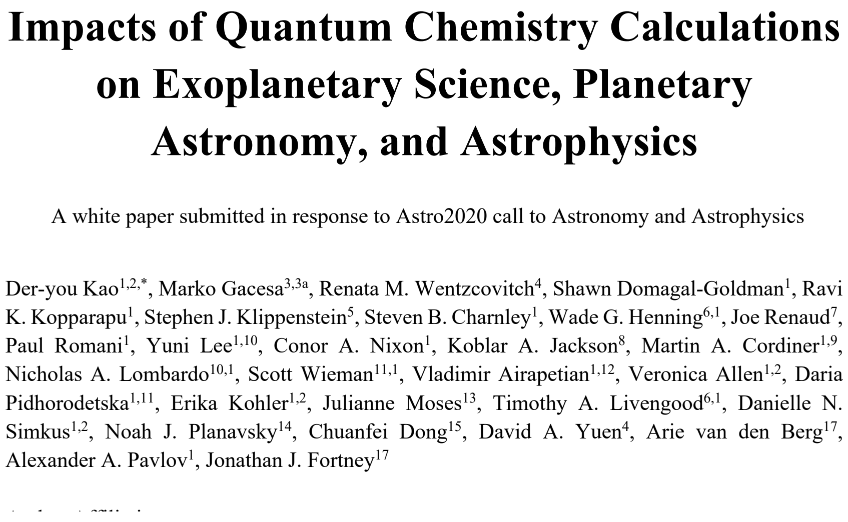
UNIVERSITÉ DE LYON

IPNL
February 2015

Lyon1

Warm dense matter

- Controlled fusion at NIF
- Planetary interiors
- Matter under extreme temperature and pressure
- Take theorems of DFT and heat up
- At high enough temperatures, electrons behave classically

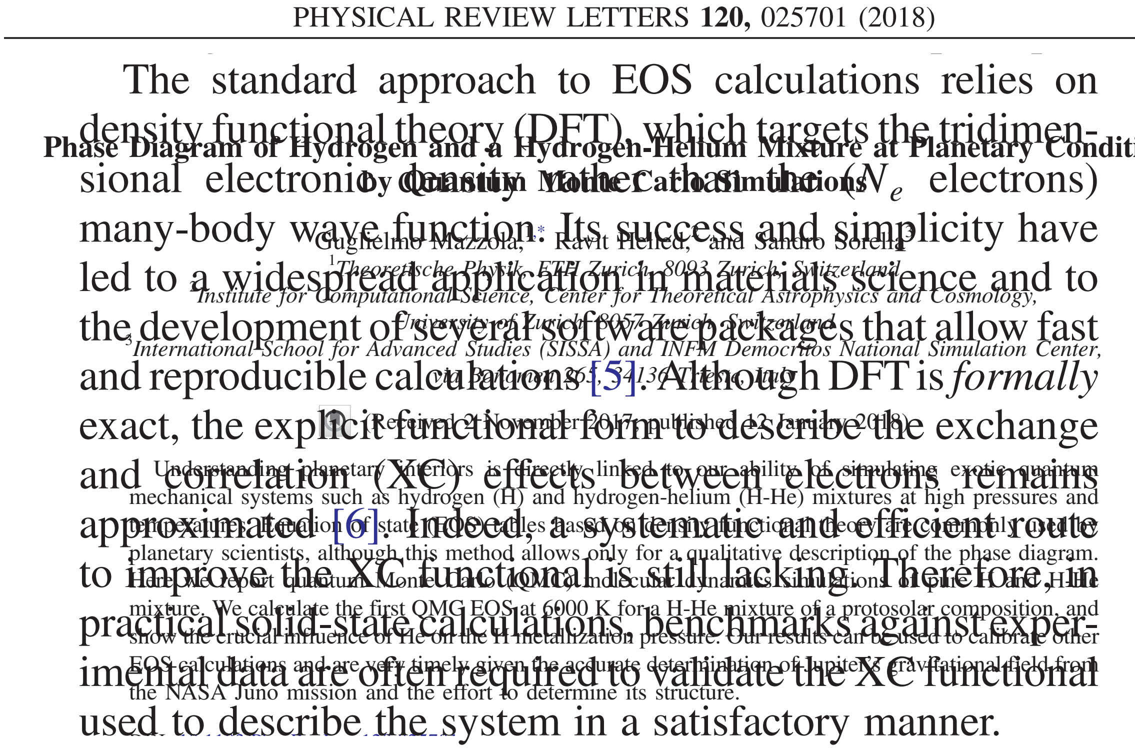


Impacts of Quantum Chemistry Calculations on Exoplanetary Science, Planetary Astronomy, and Astrophysics

A white paper submitted in response to Astro2020 call to Astronomy and Astrophysics

Der-you Kao[1,2,*], Marko Gacesa[3,3a], Renata M. Wentzcovitch[4], Shawn Domagal-Goldman[1], Ravi K. Kopparapu[1], Stephen J. Klippenstein[5], Steven B. Charnley[1], Wade G. Henning[6,1], Joe Renaud[7], Paul Romani[1], Yuni Lee[1,10], Conor A. Nixon[1], Koblar A. Jackson[8], Martin A. Cordiner[1,9], Nicholas A. Lombardo[10,1], Scott Wieman[11,1], Vladimir Airapetian[1,12], Veronica Allen[1,2], Daria Pidhorodetska[1,11], Erika Kohler[1,2], Julianne Moses[13], Timothy A. Livengood[6,1], Danielle N. Simkus[1,2], Noah J. Planavsky[14], Chuanfei Dong[15], David A. Yuen[4], Arie van den Berg[17], Alexander A. Pavlov[1], Jonathan J. Fortney[17]

Interior of Jupiter



PHYSICAL REVIEW LETTERS 120, 025701 (2018)

Phase Diagram of Hydrogen and a Hydrogen-Helium Mixture at Planetary Conditions by Quantum Monte Carlo Simulations

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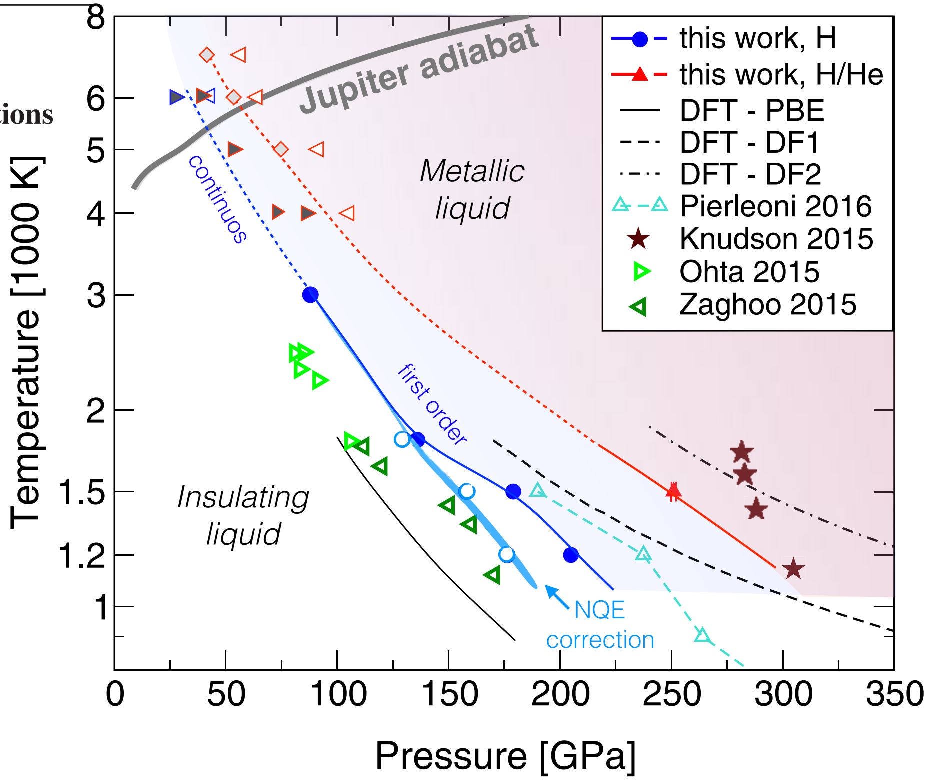
(Received 2 November 2017; published 12 January 2018)

Understanding planetary interiors is directly linked to our ability of simulating exotic quantum mechanical systems such as hydrogen (H) and hydrogen-helium (H-He) mixtures at high pressures and temperatures. Equation of state (EOS) tables based on density functional theory are commonly used by planetary scientists, although this method allows only for a qualitative description of the phase diagram. Here we report quantum Monte Carlo (QMC) molecular dynamics simulations of pure H and H-He mixture. We calculate the first QMC EOS at 6000 K for a H-He mixture of a protosolar composition, and show the crucial influence of He on the H metallization pressure. Our results can be used to calibrate other EOS calculations and are very timely given the accurate determination of Jupiter's gravitational field from the NASA Juno mission and the effort to determine its structure.

The standard approach to EOS calculations relies on density functional theory (DFT), which targets the tridimensional electronic density rather than the (N_e electrons) many-body wave function. Its success and simplicity have led to a widespread application in materials science and to the development of several software packages that allow fast and reproducible calculations [5]. Although DFT is *formally* exact, the explicit functional form to describe the exchange and correlation (XC) effects between electrons remains approximated [6]. Indeed, a systematic and efficient route to improve the XC functional is still lacking. Therefore, in practical solid-state calculations, benchmarks against experimental data are often required to validate the XC functional used to describe the system in a satisfactory manner.

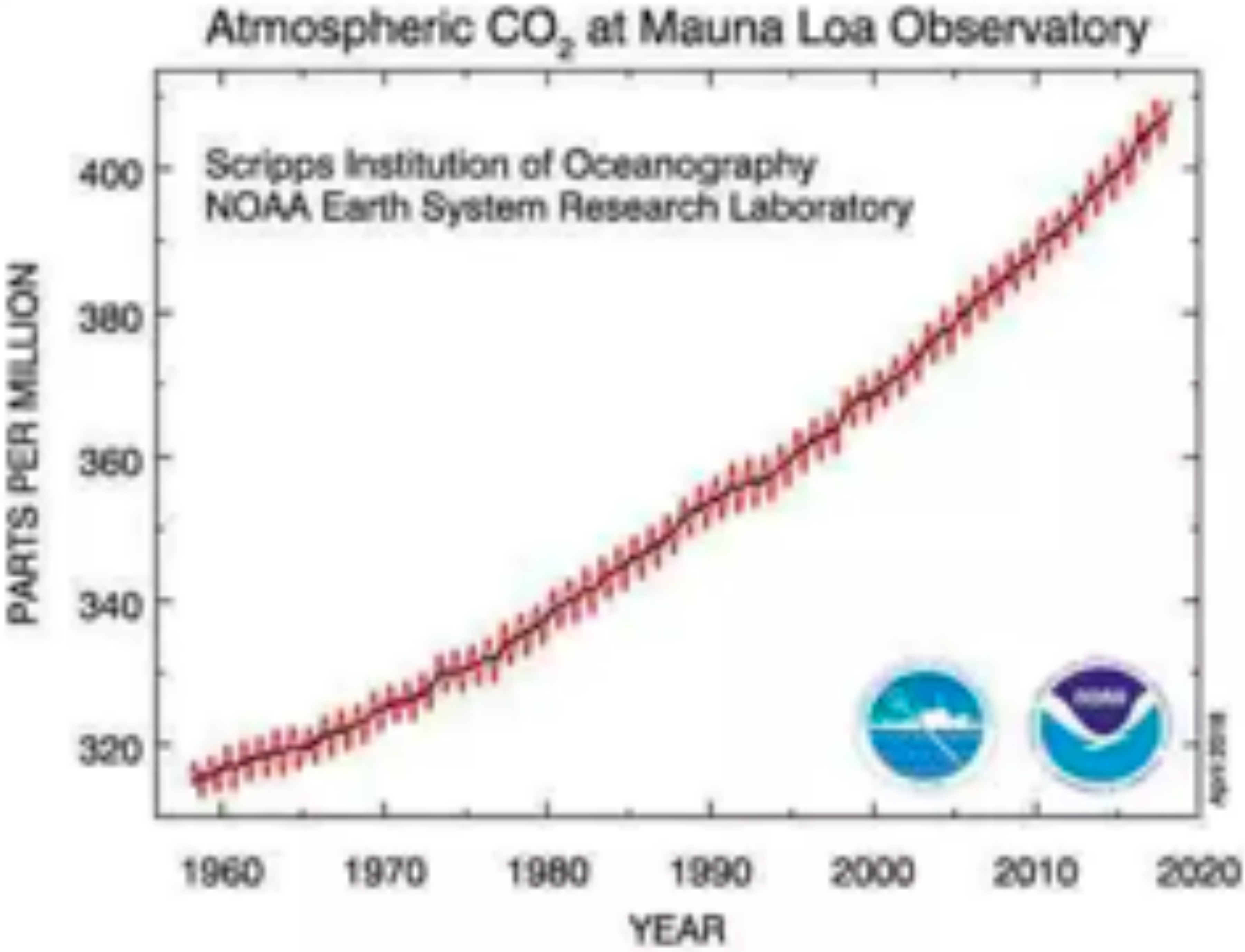


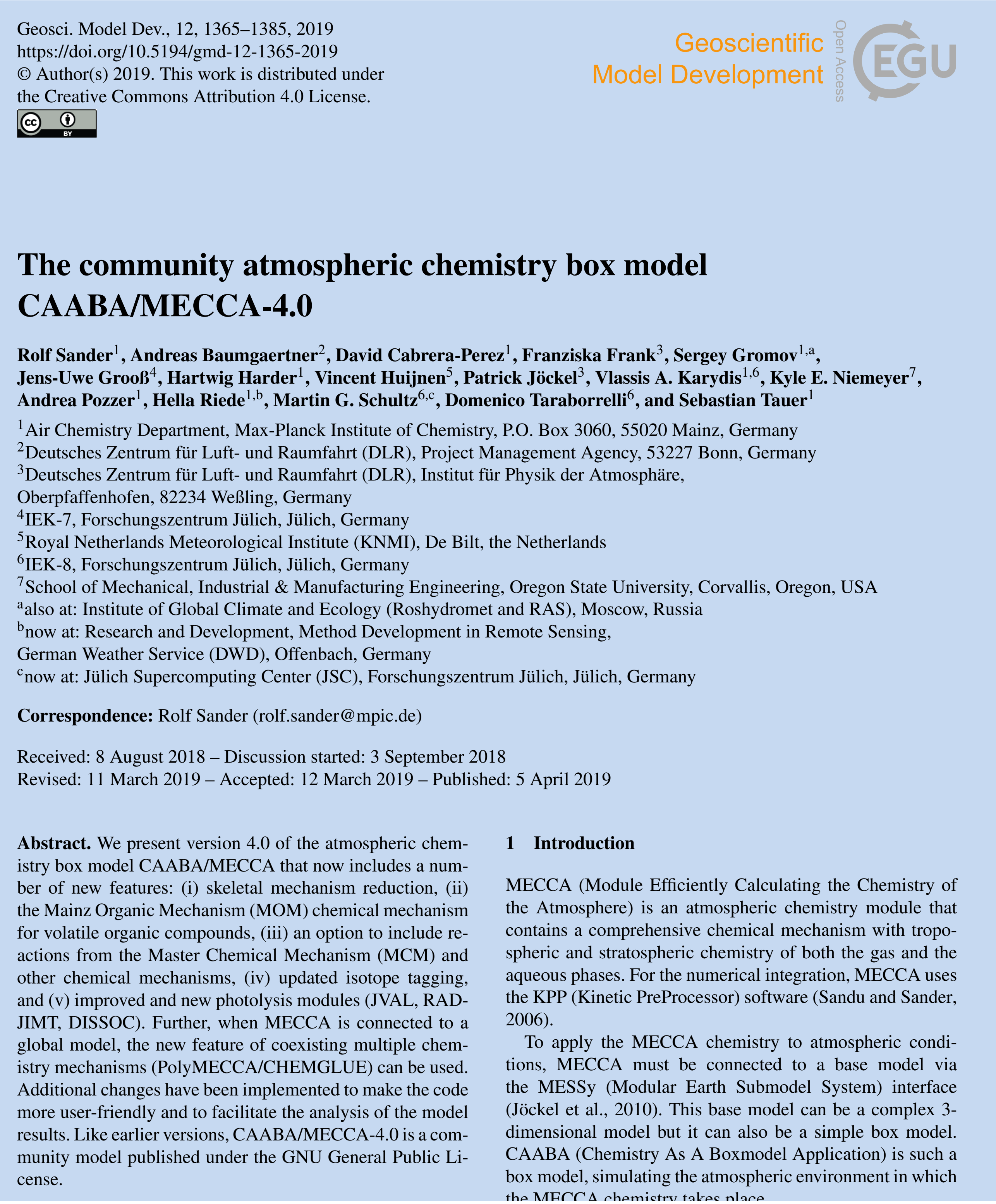
Relations between WDM and classical DFT

- Mermin theorem applies to equilibrium electrons at all temperatures
- Implies entropic contributions to XC and non-interacting functionals
- As T->0, becomes ground-state theory
- As T -> infinity, becomes classical theory of charged liquid!

Essence of HK theorem

- Prior to 1964, essentially believed one needs the many-body wavefunction to find properties of system.
- HK theorem says density alone, in principle, determines all properties.
- Extreme compression of information
- KS scheme leverages this for electronic problem.


Atmospheric CO₂ at Mauna Loa Observatory
Scripps Institution of Oceanography
NOAA Earth System Research Laboratory
PARTS PER MILLION
400
380
360
340
320
1960
1970
1980
1990
2000
2010
2020
YEAR



Geosci. Model Dev., 12, 1365–1385, 2019
https://doi.org/10.5194/gmd-12-1365-2019

Geoscientific
Model Development
Open Access

The community atmospheric chemistry box model CAABA/MECCA-4.0

Rolf Sander[1], Andreas Baumgaertner[2], David Cabrera-Perez[1], Franziska Frank[3], Sergey Gromov[1,a], Jens-Uwe Grooß[4], Hartwig Harder[1], Vincent Huijnen[5], Patrick Jöckel[3], Vlassis A. Karydis[1,6], Kyle E. Niemeyer[7], Andrea Pozzer[1], Hella Riede[1,b], Martin G. Schultz[6,c], Domenico Taraborrelli[6], and Sebastian Tauer[1]

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Revised: 11 March 2019 – Accepted: 12 March 2019 – Published: 5 April 2019

Abstract. We present version 4.0 of the atmospheric chemistry box model CAABA/MECCA that now includes a number of new features: (i) skeletal mechanism reduction, (ii) the Mainz Organic Mechanism (MOM) chemical mechanism for volatile organic compounds, (iii) an option to include reactions from the Master Chemical Mechanism (MCM) and other chemical mechanisms, (iv) updated isotope tagging, and (v) improved and new photolysis modules (JVAL, RADJIMT, DISSOC). Further, when MECCA is connected to a global model, the new feature of coexisting multiple chemistry mechanisms (PolyMECCA/CHEMGLUE) can be used. Additional changes have been implemented to make the code more user-friendly and to facilitate the analysis of the model results. Like earlier versions, CAABA/MECCA-4.0 is a community model published under the GNU General Public License.

1 Introduction

MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere) is an atmospheric chemistry module that contains a comprehensive chemical mechanism with tropospheric and stratospheric chemistry of both the gas and the aqueous phases. For the numerical integration, MECCA uses the KPP (Kinetic PreProcessor) software (Sandu and Sander, 2006).

To apply the MECCA chemistry to atmospheric conditions, MECCA must be connected to a base model via the MESSy (Modular Earth Submodel System) interface (Jöckel et al., 2010). This base model can be a complex 3-dimensional model but it can also be a simple box model. CAABA (Chemistry As A Boxmodel Application) is such a box model, simulating the atmospheric environment in which the MECCA chemistry takes place

ACS EARTH AND SPACE CHEMISTRY

Cite This: *ACS Earth Space C*

Direct Kinetic and Atmospheric Mod
Intermediate Reactions with Acetone

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Supporting Information

ABSTRACT: Mounting evidence suggests that Criegee intermediate
tropospheric oxidants of both organic and inorganic gases, sup
oxidation chemistry initiated by OH radicals. Here, the rate coe
reaction of the simplest Criegee intermediate CH_2OO with aceton
$(CH_3)_2CO$), was measured using laser flash photolysis and ca
spectroscopy methods under tropospherically relevant conditions c
temperature. The pressure dependence of $k(CH_2OO + (CH_3)_2CO)$ =
10^{-13} $[N_2]/((3.7 \pm 1.4) \times 10^{16} + [N_2])$ cm^3 $molecule^{-1}$ s^{-1} was mea
100 Torr range, returning a high-pressure limit value of (4.7 ± 0.1
$molecule^{-1}$ s^{-1} at 293 K. A temperature dependence of $k(CH_2OO$ + (
cm^3 $molecule^{-1}$ s^{-1} was observed in the 250−310 K range. The globa
to model the speciated Criegee intermediate field using the recently r
various reactions of Criegee intermediates. The incorporation of the
predicts decreases in acetone concentration of as much as 10−40 pp

KEYWORDS: *Criegee intermediates, acetone, atmospheric chemistry, gl*

conditions.

3.2. ME Modeling of the $CH_2OO + (CH_3)_2CO$ Reaction.

The observable rate coefficients for the $CH_2OO + (CH_3)_2CO$ reaction as a function of temperature and pressure were calculated using Rice−Ramsperger−Kassel−Marcus/ME simulations, as described by Elsamra et al.[17] Briefly, the reaction is predicted to proceed by the formation of a van der Waals complex before passing over a submerged barrier to form a SOZ, as shown in Figure 4. Only one cycloaddition pathway is possible because of the symmetric substitution of the carbonyl carbon atoms in both reactants. The molecular geometries and energies, calculated by Jalan et al.[31] using RCCSD(T)-F12a/VTZ-F12//B3LYP/MG3S methods, were input to Arkane, a one-dimensional ME solver previously named Cantherm that is part of the RMG-Py package.[33] The $k(T, P)$ values output by

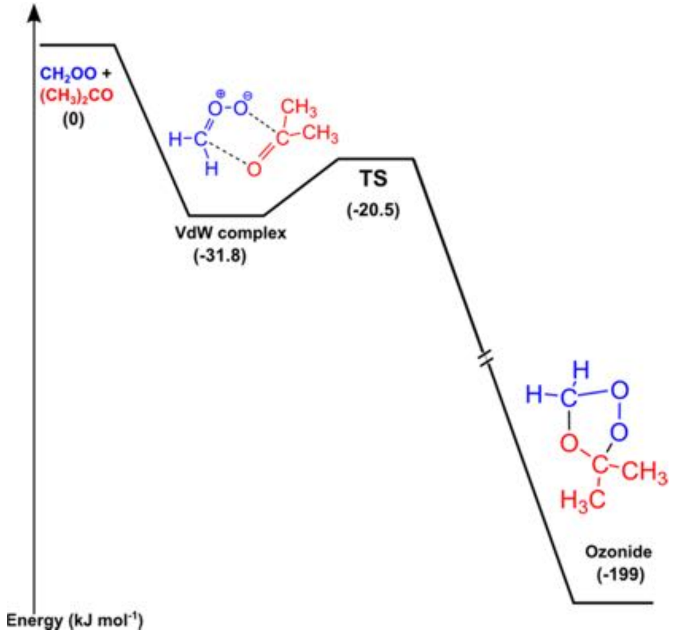
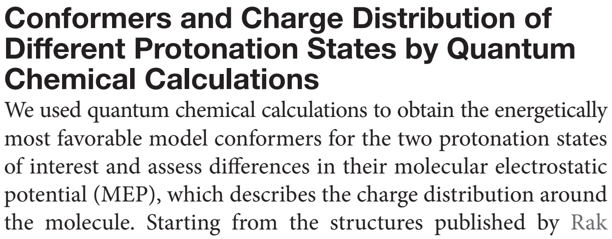


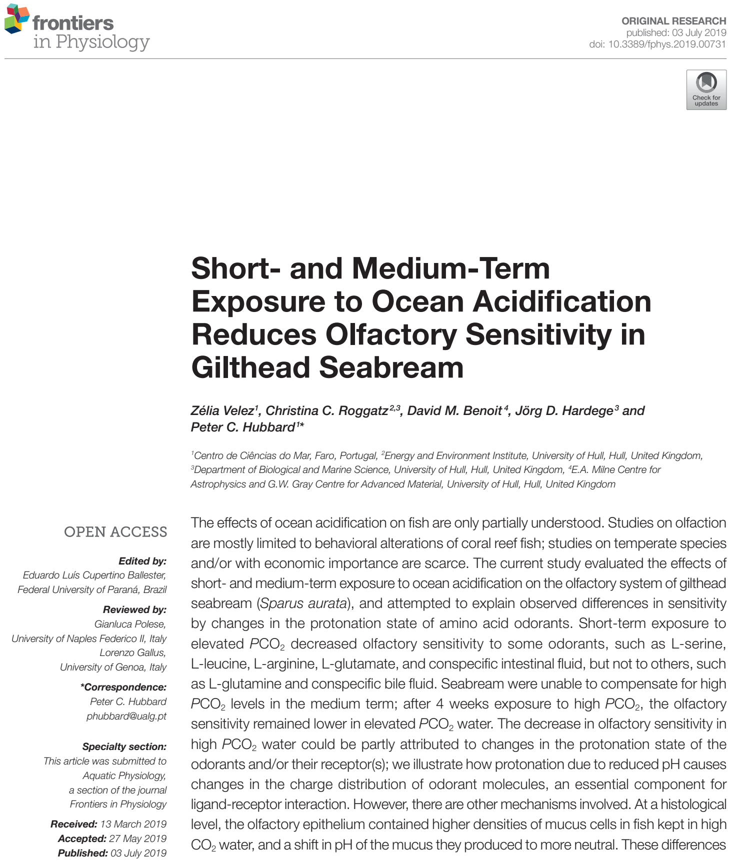
Figure 4. Minimum energy pathway for the reaction of CH_2OO with $(CH_3)_2CO$. The stationary point energies were calculated at the RCCSD(T)-F12a/VTZ-F12//B3LYP/MG3S level of theory and were obtained from the previous study by Jalan et al.[31]

Gilt-head Seabream



Conformers and Charge Distribution of Different Protonation States by Quantum Chemical Calculations

We used quantum chemical calculations to obtain the energetically most favorable model conformers for the two protonation states of interest and assess differences in their molecular electrostatic potential (MEP), which describes the charge distribution around the molecule. Starting from the structures published by Rak



frontiers in Physiology

ORIGINAL RESEARCH
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Check for updates

Short- and Medium-Term Exposure to Ocean Acidification Reduces Olfactory Sensitivity in Gilthead Seabream

Zélia Velez[1], *Christina C. Roggatz*[2,3], *David M. Benoit*[4], *Jörg D. Hardege*[3] *and Peter C. Hubbard*[1]*

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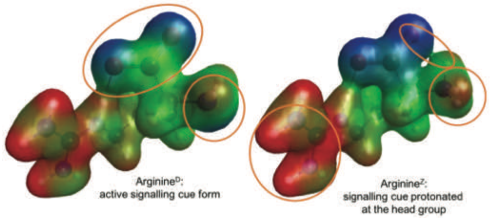
The effects of ocean acidification on fish are only partially understood. Studies on olfaction are mostly limited to behavioral alterations of coral reef fish; studies on temperate species and/or with economic importance are scarce. The current study evaluated the effects of short- and medium-term exposure to ocean acidification on the olfactory system of gilthead seabream (*Sparus aurata*), and attempted to explain observed differences in sensitivity by changes in the protonation state of amino acid odorants. Short-term exposure to elevated PCO_2 decreased olfactory sensitivity to some odorants, such as L-serine, L-leucine, L-arginine, L-glutamate, and conspecific intestinal fluid, but not to others, such as L-glutamine and conspecific bile fluid. Seabream were unable to compensate for high PCO_2 levels in the medium term; after 4 weeks exposure to high PCO_2, the olfactory sensitivity remained lower in elevated PCO_2 water. The decrease in olfactory sensitivity in high PCO_2 water could be partly attributed to changes in the protonation state of the odorants and/or their receptor(s); we illustrate how protonation due to reduced pH causes changes in the charge distribution of odorant molecules, an essential component for ligand-receptor interaction. However, there are other mechanisms involved. At a histological level, the olfactory epithelium contained higher densities of mucus cells in fish kept in high CO_2 water, and a shift in pH of the mucus they produced to more neutral. These differences



Maybe we can?

- If we make T_S much more accurate and reliable, can suddenly do much larger simulations, so much more relevant
- If we make E_{XC} much more accurate and reliable, we can do many more simulations of more challenging systems
- Huge impact if ML improves functionals for classical DFT, nuclear DFT, or thermal DFT
- Can we do this in 10 years, not 100?
- Maybe we must!

Summary

- Direct solution of Schrodinger equation too expensive to be practical in many situations.
- Density functional theory (DFT) allows larger and more diverse systems to be modelled, but with uncontrollable errors.
- DFT chemical and materials modeling already plays important role in modern materials and drug design.
- Two very important possibilities:
  - Much bigger DFT simulations, more realistic
  - Much more accurate, systematic DFT calculations
- Other (smaller) areas need better functionals
- Thanks to IPAM and NSF and DOE.