Introduction: **Computational Chemistry and Materials Modeling**

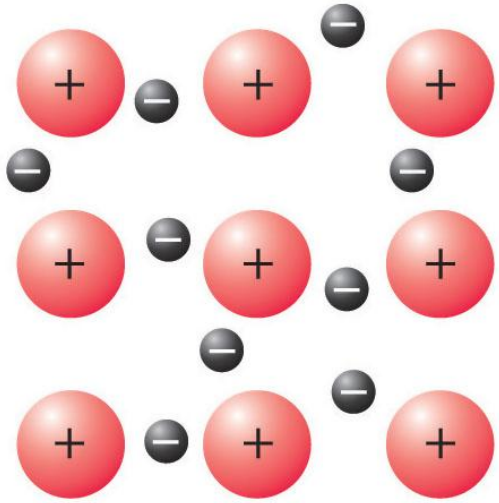
- What is this course about?
- General guidelines for Computational Materials Science
- Case studies: from basic applications to student projects
- Course logistics

Andriy Zhugayevych (lecturer)
Dmitry Aksenov (lecturer)
Sergey Levchenko (lecturer)
Alexander Shapeev (lecturer)
Guest Lecturers (e.g. use of Abinit, FHI-aims, USPEX)

What is this course about?

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

P A M Dirac, Proc Royal Soc London 123, 714 (1929)

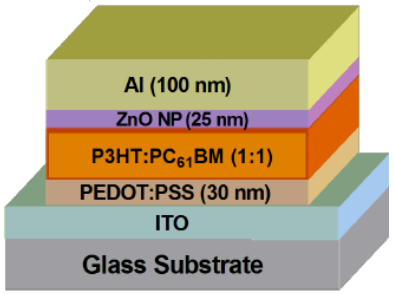


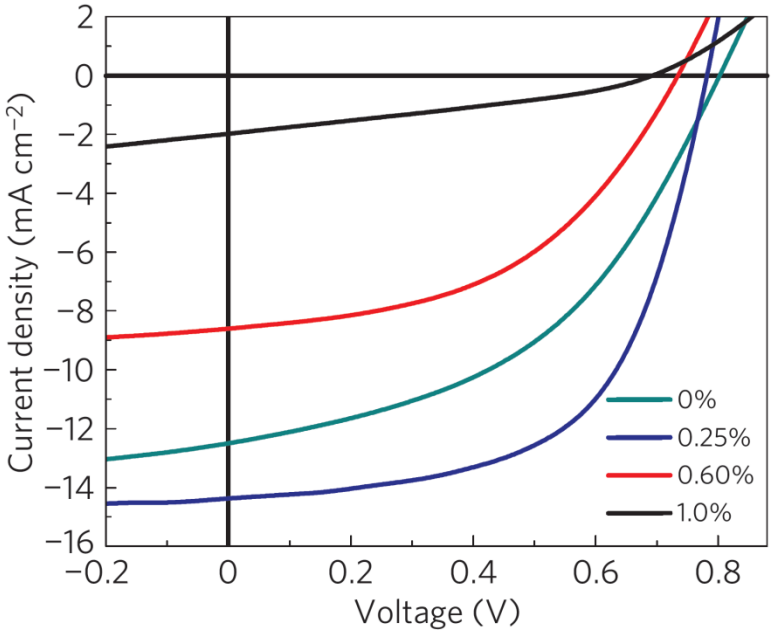
- Computational Chemistry
  = solving Coulomb problem for >10 particles
- Materials Modeling
  = relating that solution to real world

Who is this course intended for?

Theoreticians and experimentalists studying materials with atomic resolution (most of recent high-technology devices)

Example





- You would like to understand the overall shape of an I-V curve
  → you don't need this course

- You would like to understand the difference in these I-V curves
  → you do need this course

Level of coverage

Our approach

• Pragmatic & practical guide to start working in the research lab (theory/experiment) right away

Out of scope

• Other scales than atomistic

• Underlying quantum chemistry, condensed matter theory, and computational mathematics

• Technical implementation

• Limited-use and highly specialized methods

Primary Learning Outcomes

- Professionally perform most common calculations including understanding of what you are doing
- Understand the results of calculations including quality assessment
- Avoid common mistakes and slips
- Hands-on experience in use of software/hardware including solution of common technical problems
- **Support or start your research project**

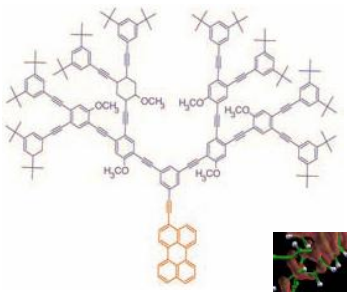
Demand for computational materials scientists

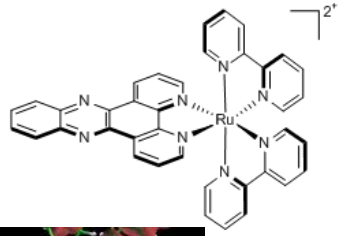
Area of expertise: knowledge of materials science + experience in computational chemistry

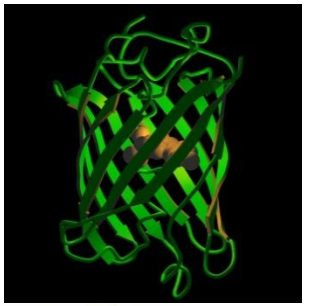
- **Any research group in modern materials science performs or needs theoretical modeling**
- Research institutions: Skoltech, MSU, MIPT, MIT, LANL, IMEC, UC, UT…
- Computational materials science at Skoltech: Artem Oganov, Andriy Zhugayevych, Alexei Buchachenko, Alexandr Shapeev, Sergey Levchenko, Xavier Gonze…
- Los Alamos National Lab (Sergei Tretiak): visiting postdocs and summer internship students (e.g. 2017 CCMM student Nikita Rybin)
- R&D Labs: Samsung, Boeing, IBM, Philips, 3M…
- Software developers: Gaussian, VASP, Abinit, Turbomole, Q-chem, Psi-K, MOPAC, LAMMPS, Molpro, FHI-aims, MedeA, NEXMD, Continuum Analytics https://aip.scitation.org/doi/10.1063/5.0023185 JCP special issue 2020

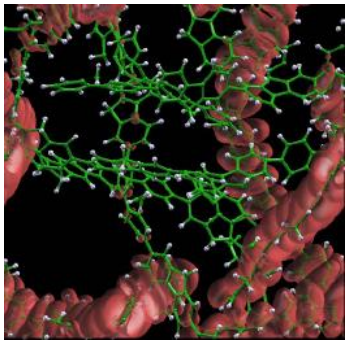
Materials examples

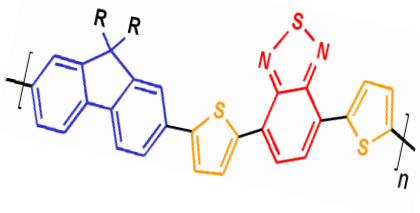
- *Molecules, biomolecules, metal-organic complexes;*
- *Organic semiconductors (conjugated polymers)*
- *Carbon nanostructures (graphene, nanotubes)*
- *Semiconductor quantum dots;*
- *Metal clusters;*
- *Organic molecular and semiconductor crystals, perovskites.*

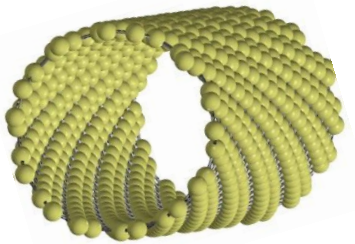


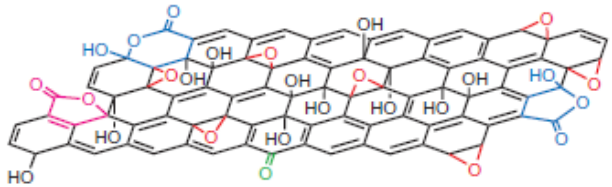


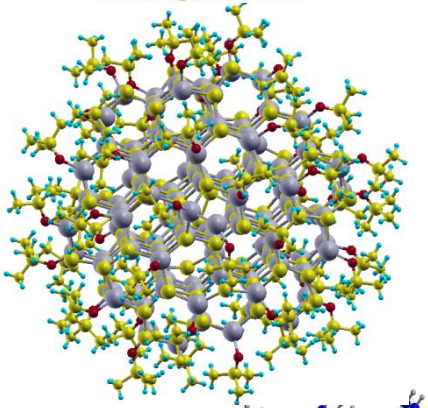


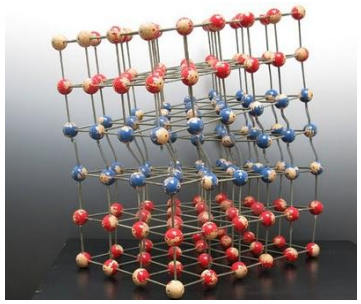


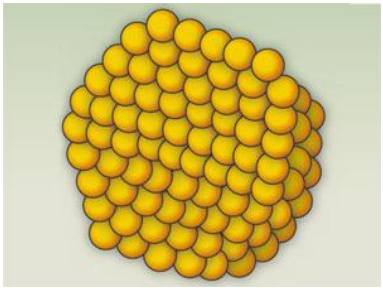


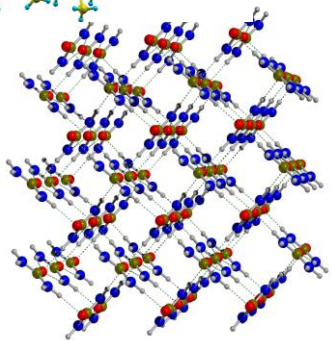












When materials modeling is useful; interactions with experiment

- *Tool to obtain detailed information on specific properties;*
- *Generally much 'cheaper' than experiment;*
- *Interpretation of experimental data;*
- *Suggestions of specific structural modifications for synthesis;*
- *Formulation of the trends (i.e. structure-property relationships);*
- *Discovery of new emergent properties;*
- *Discovery of new molecular materials.*

Examples

- *New drug design;*
- *Materials for green energy technologies (e.g. photovoltaics);*
- *Materials for energy storage (e.g. batteries);*
- *Atmospheric chemistry, reactions, pollutions;*
- *Biochemistry and fundamental biological processes (e.g. photosynthesis, metabolism, perspiration);*
- *Electronics, spintronics, valleytronics, optoelectronics;*
- *Quantum computing, artificial intelligence;*
- *…*

General guidelines for Computational Materials Science

- ***How to approach the computational 'black box'?***
- ***Should I calculate or measure?***
- ***Which methods should I use? Understanding scales.***

Approaching the 'black box':

Molecular structures

Materials properties

How to deal with it?

- ***Basic understanding of what is going on inside;***
- ***Interpretation of experimental data;***
- ***Understanding of dominating physical phenomena;***
- ***Rational choice of optimal electronic structure methodology;***
- ***Efficient analysis of the numerical results;***
- ***Developing physical intuition: 'does it make sense?'***

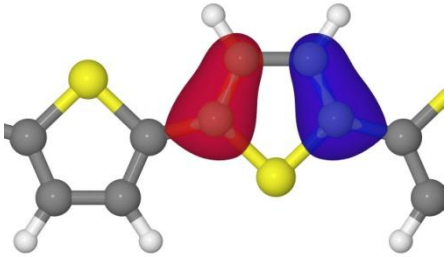
Measure vs model

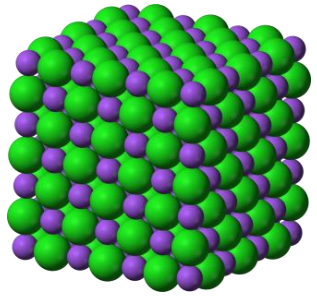
	Measure	Compute
Research costs	✗	✓
Research time	✗	✓
Accuracy	?	?
Reliability	✓	?
Relevance for practical use	✓	✗

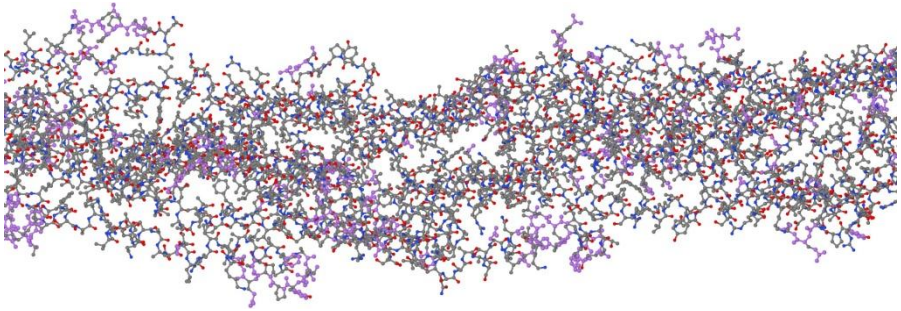
Which approach to choose?

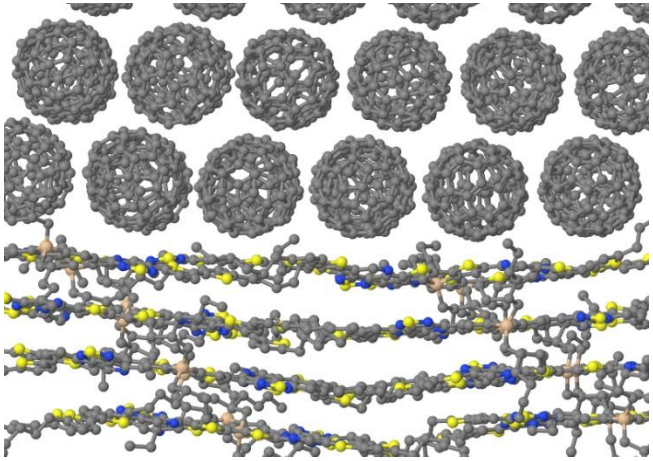
Methods vs scales

- $<10^{2\text{-}3}$ atoms (molecule, unit cell)
  - Density Functional Theory
  - Gaussian, VASP
- $<10^{4\text{-}5}$ atoms, <1ns
  - Semiempirical, O(N)-DFT
  - MOPAC
- $< 10^{9}$ atoms
  - Molecular Mechanics, QM/MM
  - LAMMPS
- Coarse-grained (not atomistic)
  - Effective Hamiltonian, Kinetic Monte Carlo, continuum models …
  - ALPS, CADs, …





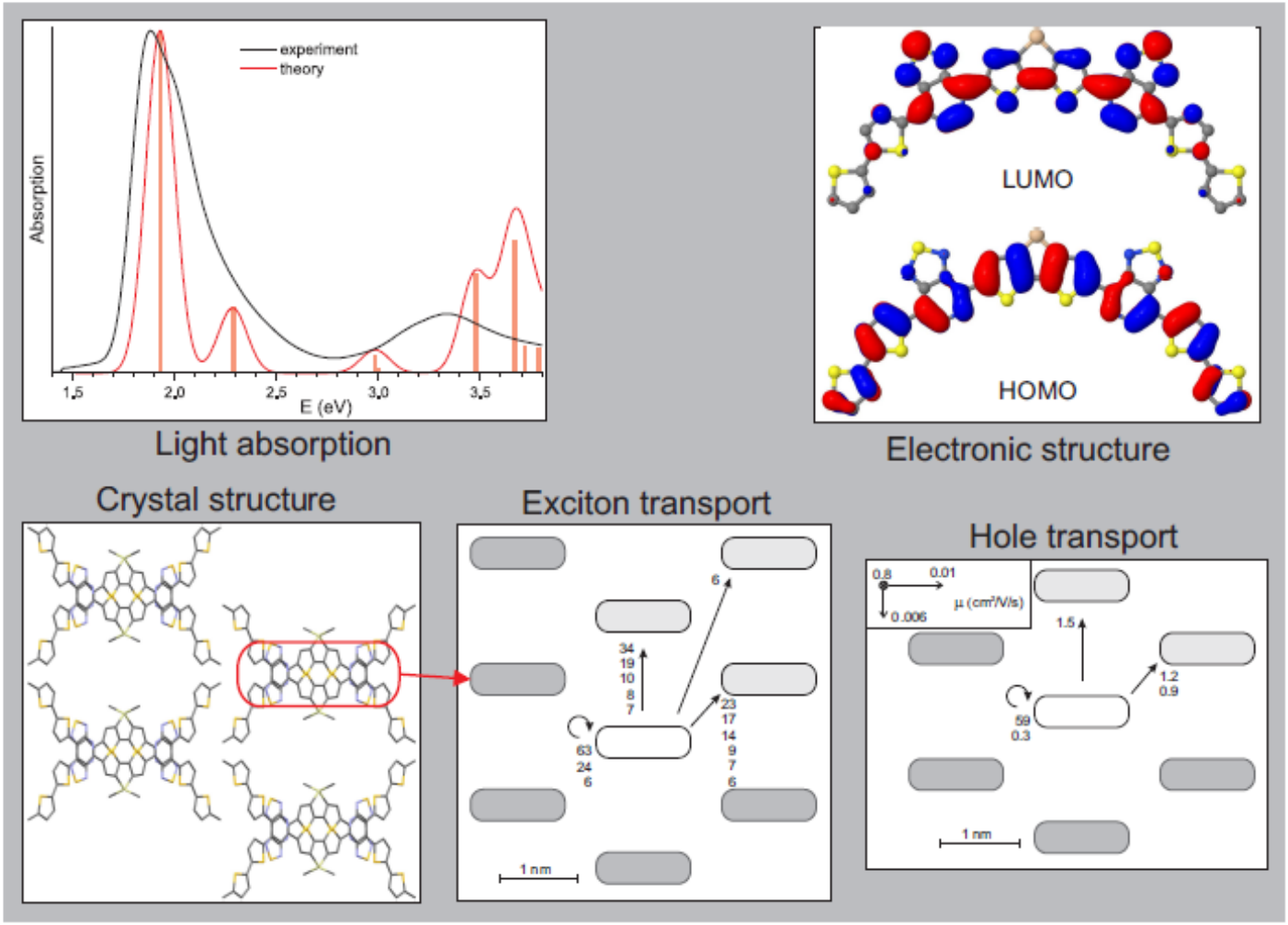




Case study: Calculation of material properties

Solar cells: where is the bottleneck in power conversion efficiency?

Current efficiency of solar cells with donor-acceptor donor and non-fullerene acceptors (NFA) exceeds 17%



Exciton diffusion length $\sim$ 100 nm, hole mobility $\sim$ 1 $cm^2/V{\cdot}s$

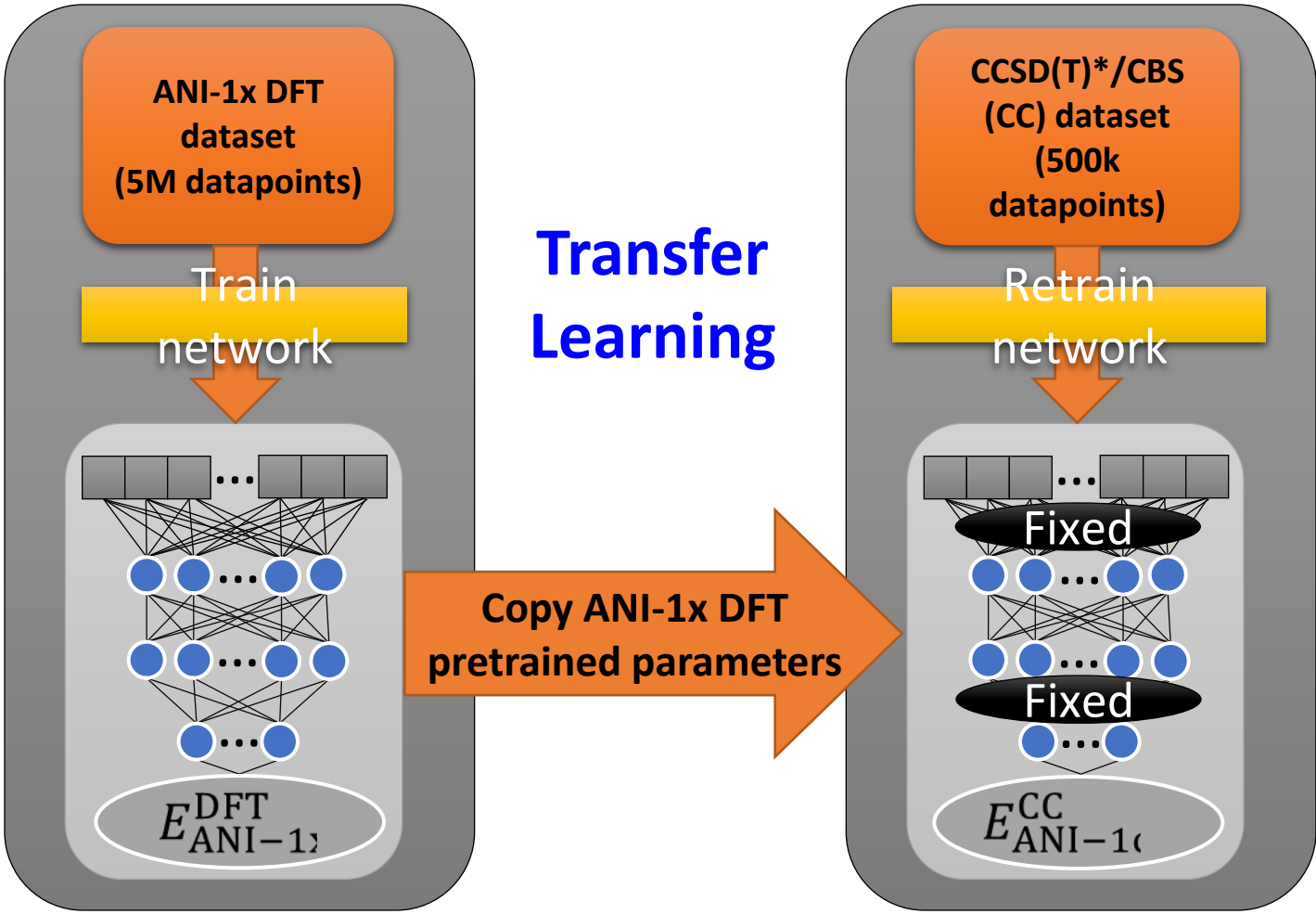
Single-crystal properties of the given molecule are perfect for photovoltaics

A.Z., O Postupna, R C Bakus II, G C Welch, G C Bazan, S Tretiak, J Phys Chem C 117, 4920 (2013)

Nover

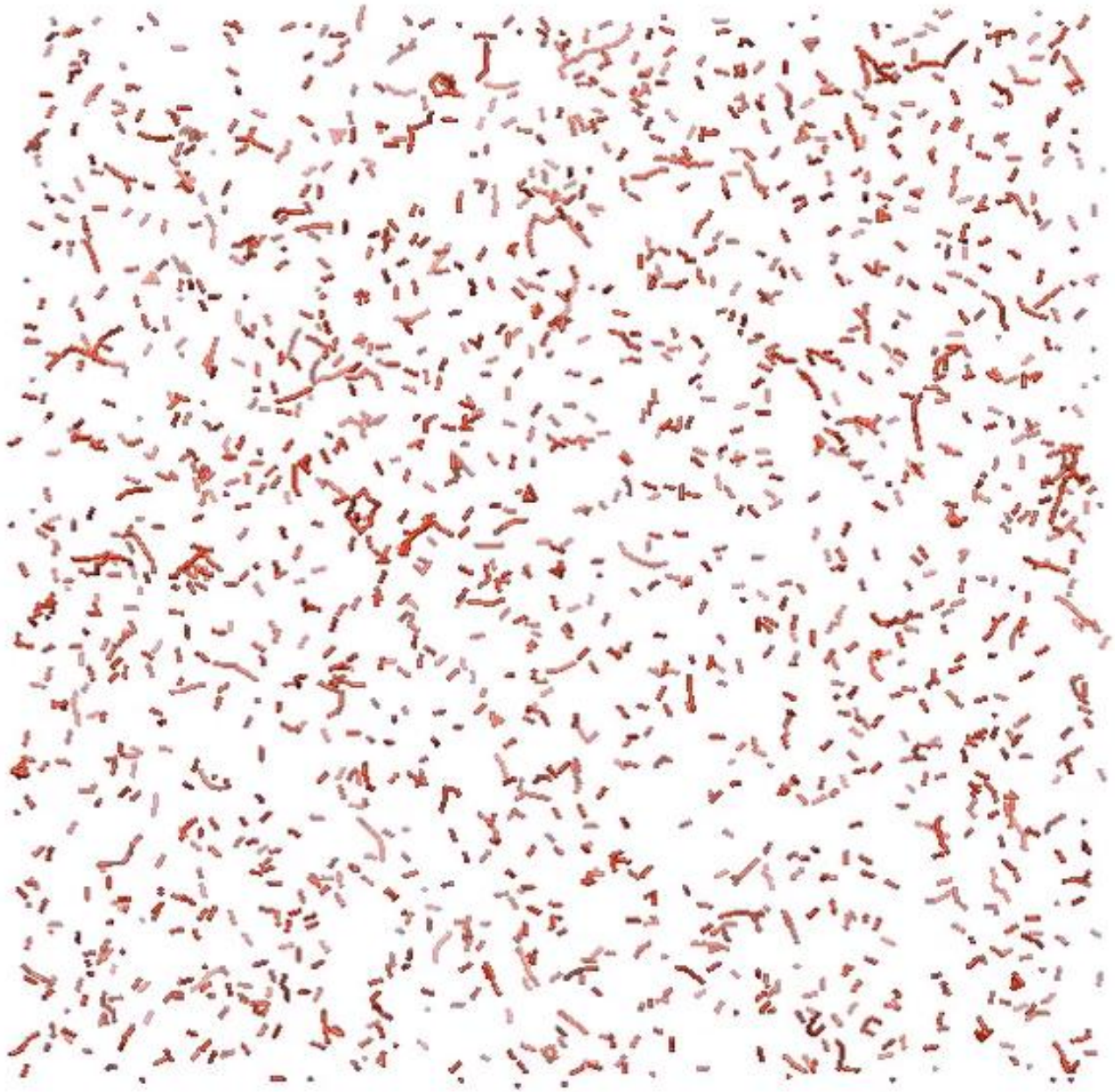
Case study: Machine learning and Data Science (new to this course!)

- Subsample 10% of ANI-1x training data (0.5M of 5M)
- Recompute CCSD(T)/CBS level
- 340k parameters fixed, re-train 60k
- 10^7 faster than DFT



J.S. Smith, B.T. Nebgen, R. Zubatyuk, N. Lubbers, C. Devereux, K. Barros, S. Tretiak, O. Isayev, A.E. Roitberg, "Approaching coupled cluster accuracy with a general-purpose neural network potential through transfer learning" Nature Comm. 10, 2903 (2019)

Example ML force field reactive dynamics

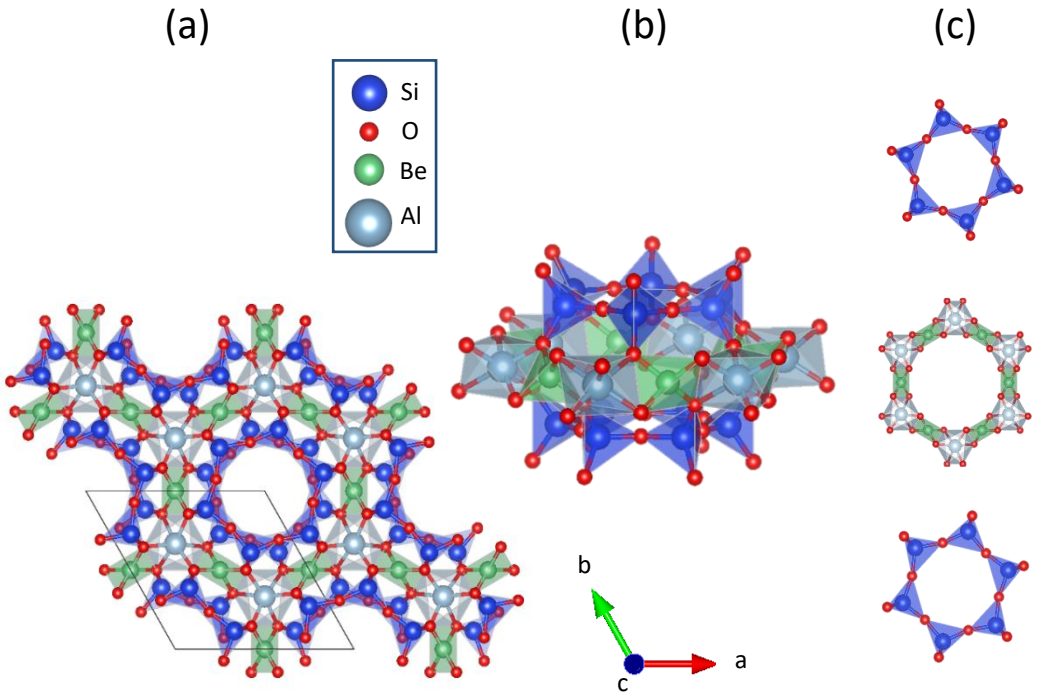


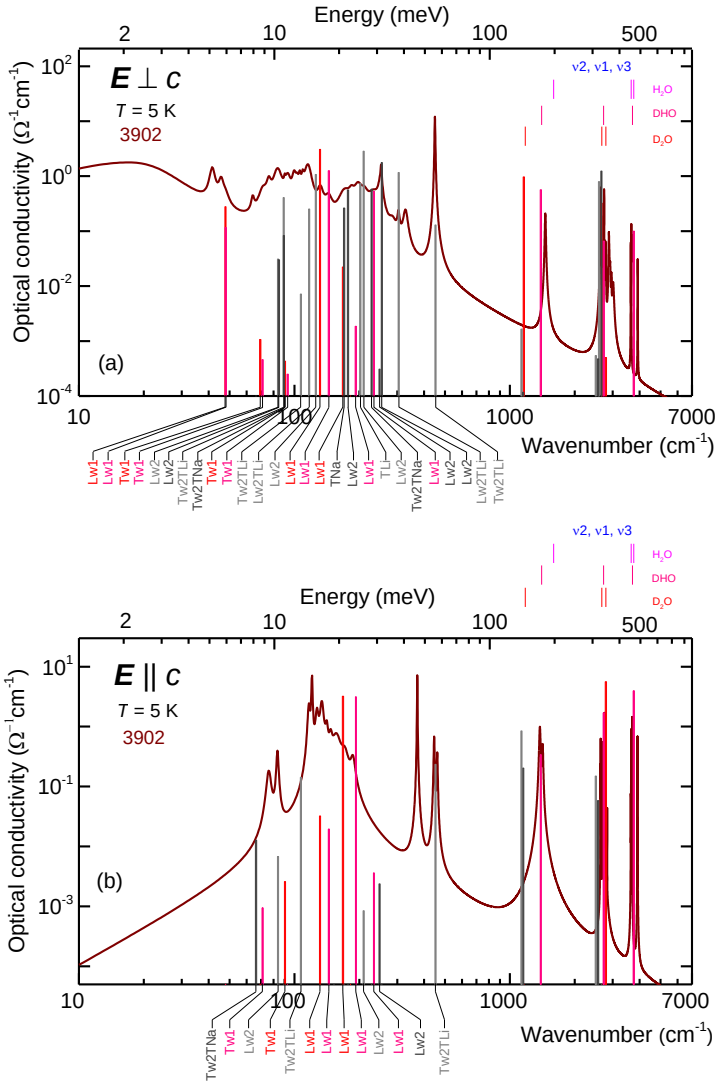
Carbon nanoparticles/sheets nucleation [4000 atoms in 60Å box at 2500K] 5ns MD simulation

(made by Justin Smith, LANL)

Student project: Ferroelectric water

Mikhail Belyanchikov, 2015, advisor A. Zhugayevych, S. Tretiak & Boris Gorshunov (MIPT)





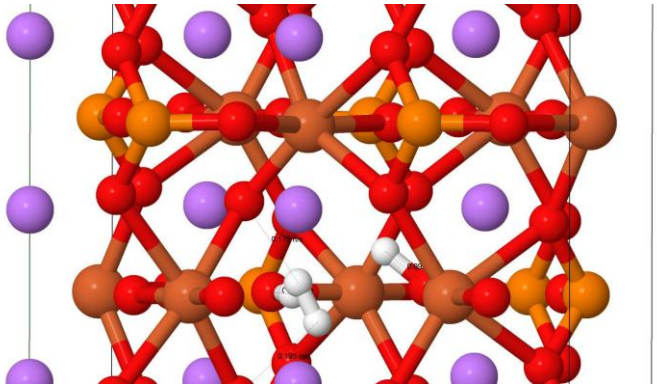
M. A. Belyanchikov, E. S. Zhukova, S. Tretiak, A. Zhugayevych, M. Dressel, F. Uhlig, J. Smiatek, M. Fyta, V. G. Thomas, and B. P. Gorshunov, "Vibrational states of nano-confined water molecules in beryl based on optical experiments and first principles calculations" Phys. Chem. Chem. Phys. 19, 30740 (2017)

+ follow-up publications

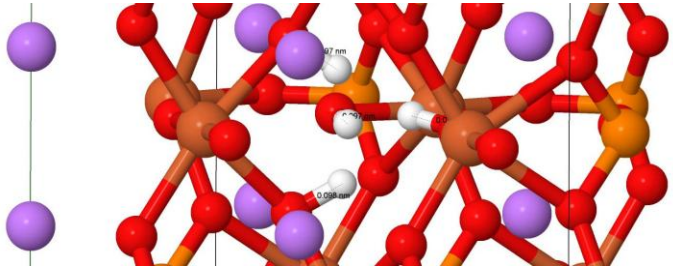
Student project: defects in $LiFePO_4$

Irina Varlamova, 2018, advisor D. Aksenov

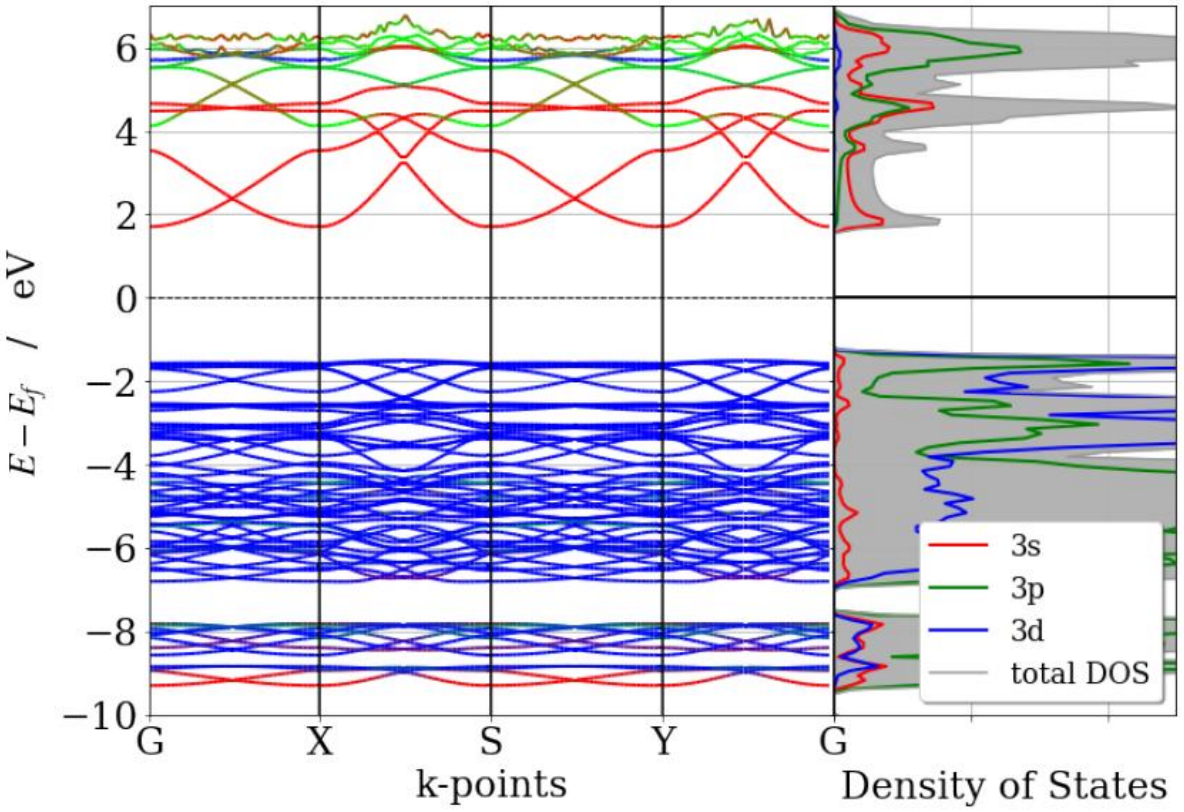
H_2 molecule at P-vacancy



Inside H defects



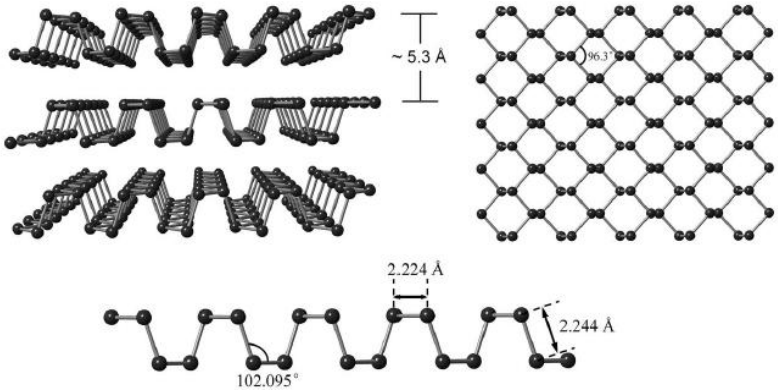
Band structure and DOS of $LiFePO_4$ with respect to Fe



D Aksyonov, I Varlamova, I Trussov, A Savina, A Senyshyn, K Stevenson, A Abakumov, A Zhugayevych, S Fedotov, Hydroxyl Defects in LiFePO4 Cathode Material: DFT+U and an Experimental Study, Inorg Chem 60, 5497 (2021) – Nature-index journal

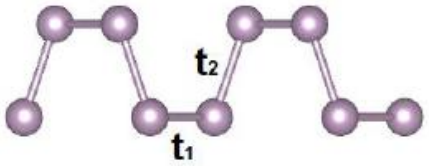
Student project: black phosphorus

Vasiliy Vasilchenko, 2018, advisor A. Zhugayevych



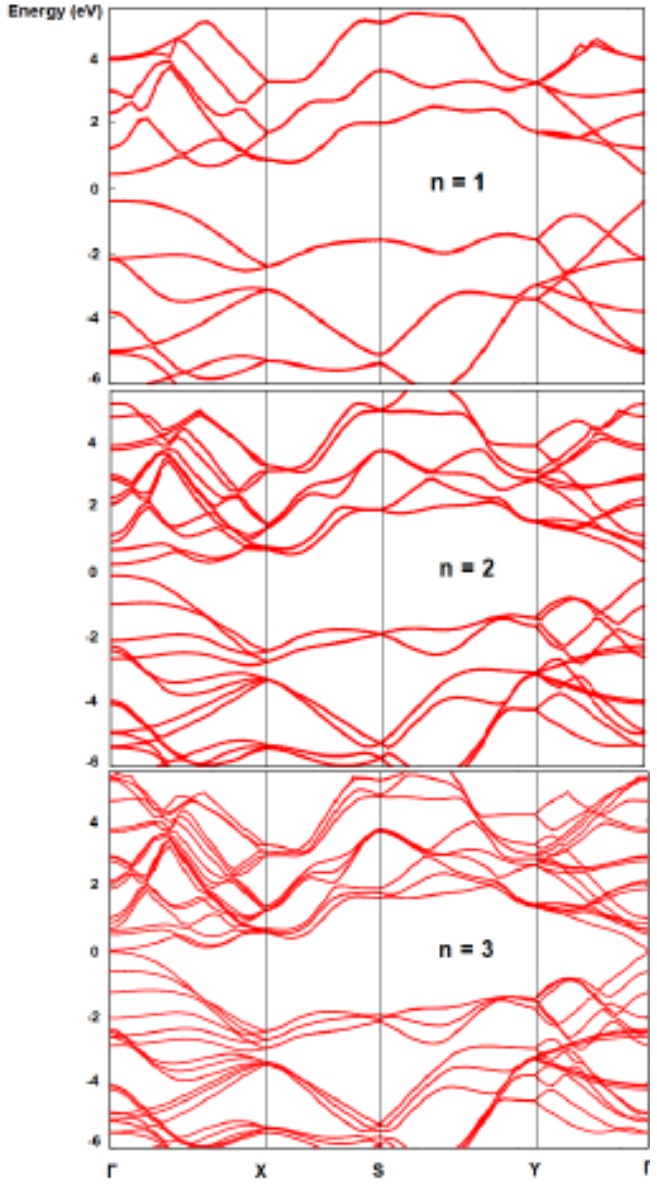
Derived tight binding Hamiltonian

$$\begin{bmatrix} 0 & t_1 + t_1 e^{ik_x} & 0 & t_2 e^{-ik_y} \\ t_1 + t_1 e^{-ik_x} & 0 & t_2 & 0 \\ 0 & t_2 & 0 & t_1 + t_1 e^{-ik_x} \\ t_2 e^{ik_y} & 0 & t_1 + t_1 e^{ik_x} & 0 \end{bmatrix}$$



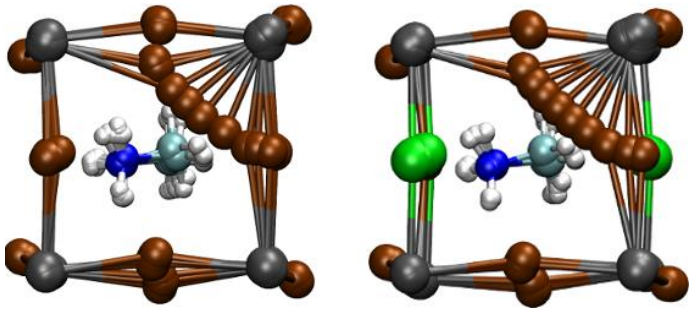
V Vasilchenko, S Levchenko, V Perebeinos, A Zhugayevych, Small Polarons in Two-Dimensional Pnictogens: A First-Principles Study, J Phys Chem Lett 12, 4674 (2021) – Nature-index journal

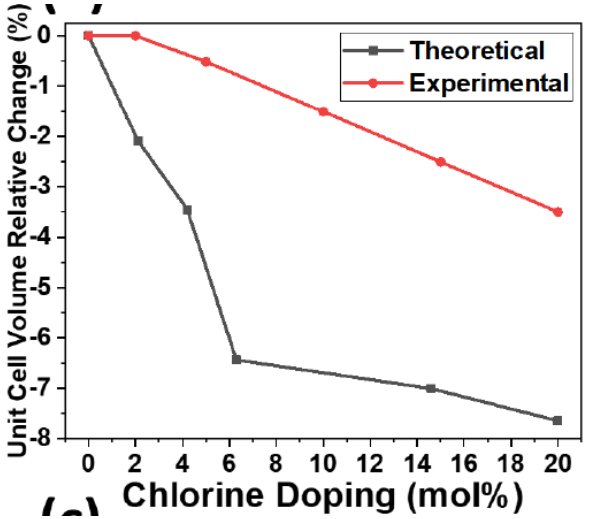
Calculated band structure of 1-, 2- and 3-layer phosphorene



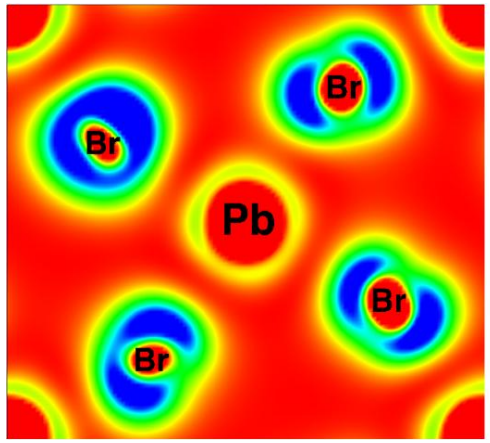
Academic mobility project: Anion Mixing in Halide perovskites

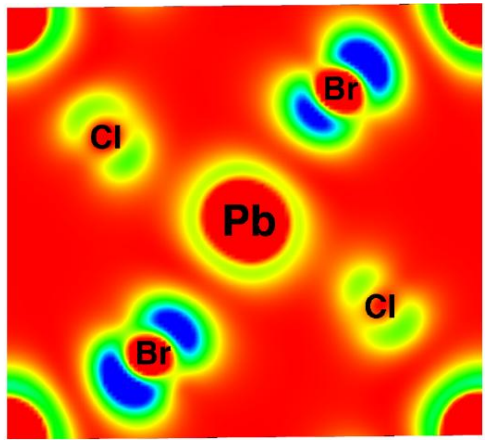
Nikita Rybin, 2017 CCMM course, 2018 academic mobility, advisor S. Tretiak (at LANL)





Experiment and theory suggest that halide mixing suppresses bromide ion migration, and thus improves Gamma-Ray detection performance of halide perovskites





N. Rybin, D. Ghosh, J. Tisdale, S. Shresta, M. Yoho, D. Vo, JC. Katan, J. Even, W. Nie, A. J. Neukirch, and S. Tretiak, *"Effects of Chlorine Mixing on Optoelectronics, Ion Migration, and Gamma-Ray Detection in Bromide Perovskites"* Chem. Mater. **32**, 1854 (2020).

Summary: when theoretical modeling is essential

- Tool to obtain detailed information on specific properties (intrinsic properties of a material)
- Generally much “cheaper” than experiment
- Interpretation of experimental data (conductivity mechanism)
- Suggesting specific structural modifications for synthesis (tune emission color)
- Establishing structure-property relationships (polar substrate – low electron mobility in graphene)
- Discovery of new materials/properties (graphene)

Before jumping into a final project research read these guidelines on methodology

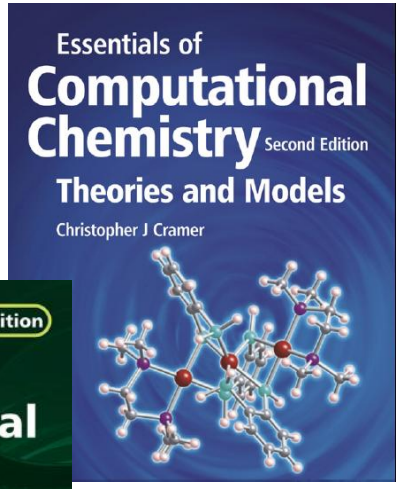
1. Define what you want to accomplish, how much time it will take, and make a plan of the attack
2. Start with literature review
3. Understand physics/chemistry of the problem
4. If you are novice, try to repeat some published results
5. Create/refine computational protocol
6. Do benchmarking (vs. experiment or compare methods)
7. **Main part**: Run calculations and analyze results
8. Iterate all steps progressively until convergence (2-3 iterations are usually needed)

Common methodological mistakes

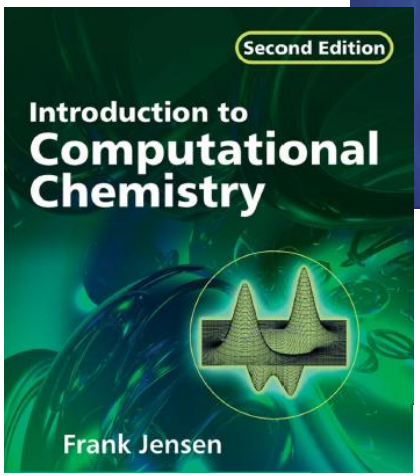
1. Skipping planning → unfinished project
2. Skipping literature review → reinventing the wheel
3. Not understanding physics/chemistry of the problem → performing irrelevant calculations
4. Working without a computational protocol → generating non-reproducible results
5. Skipping benchmarking → generating useless data
6. Skipping critical analysis of your data and results → low scholar quality of your work – unsuitable for publication
7. Doing things non-iteratively → large overheads for recalculations with the refined computational protocol

Recommended textbooks:

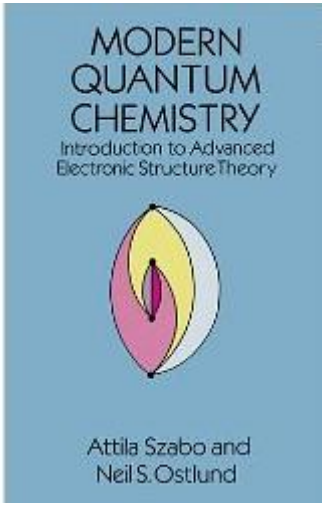
(1) "Essentials of Computational Chemistry: Theories and Model" by Christopher J. Cramer.



(2) "Introduction to Computational Chemistry" by Frank Jensen.



(3) "Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory" by Attila Szabo and Neil S. Ostlund.



See complete list at
http://zhugayevych.me/edu/CC/Ref.htm

What is your next step?
Course Advance Materials Modeling (AMM)
Term 4 (Gonze, Levchenko, Shapeev, others)

Special topics in DFT
Beyond DFT
Statistical physics
Crystalline defects
Transport properties
Optical properties
Ab initio molecular dynamics
Photoexcited dynamics
Machine learning and data analytics

Some wisdom

"I cannot teach anybody anything. I can only make them think" (Socrates)

"Three things will never come back to you: the time, the word and the opportunity. Therefore, do not loose your time, carefully pick up your words and actively chase the opportunities" (Confucius)

"Success is not final, failure is not fatal: it is the courage to continue that counts" (Churchill)

Course logistics and resources

- Course web-site (schedule, syllabus, homework, literature etc)

http://zhugayevych.me/edu/CC/index.htm

Individual studies:

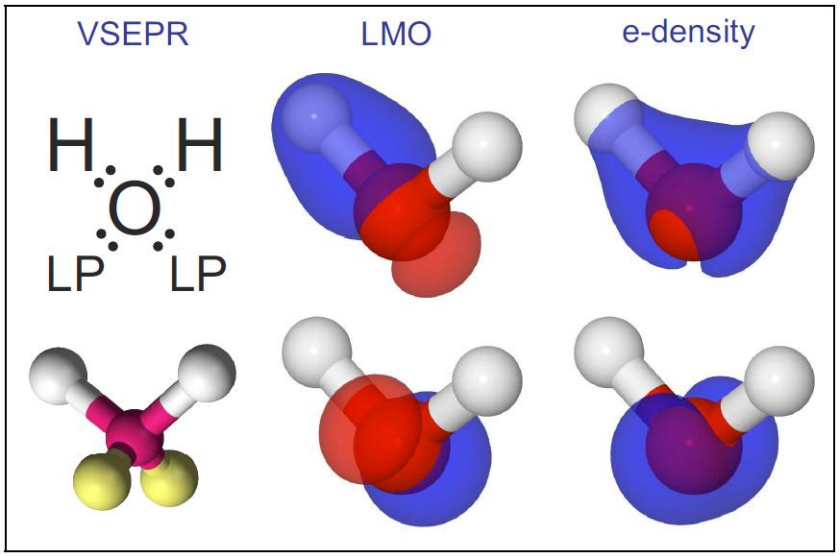
- ***Reading.***

Required: *Cramer (Ch. 1, 17 pages)*

Additional: *Jansen (Ch. 1, 22 pages)*

Web: "what is molecular modeling/electronic structure methods/computational chemistry?"

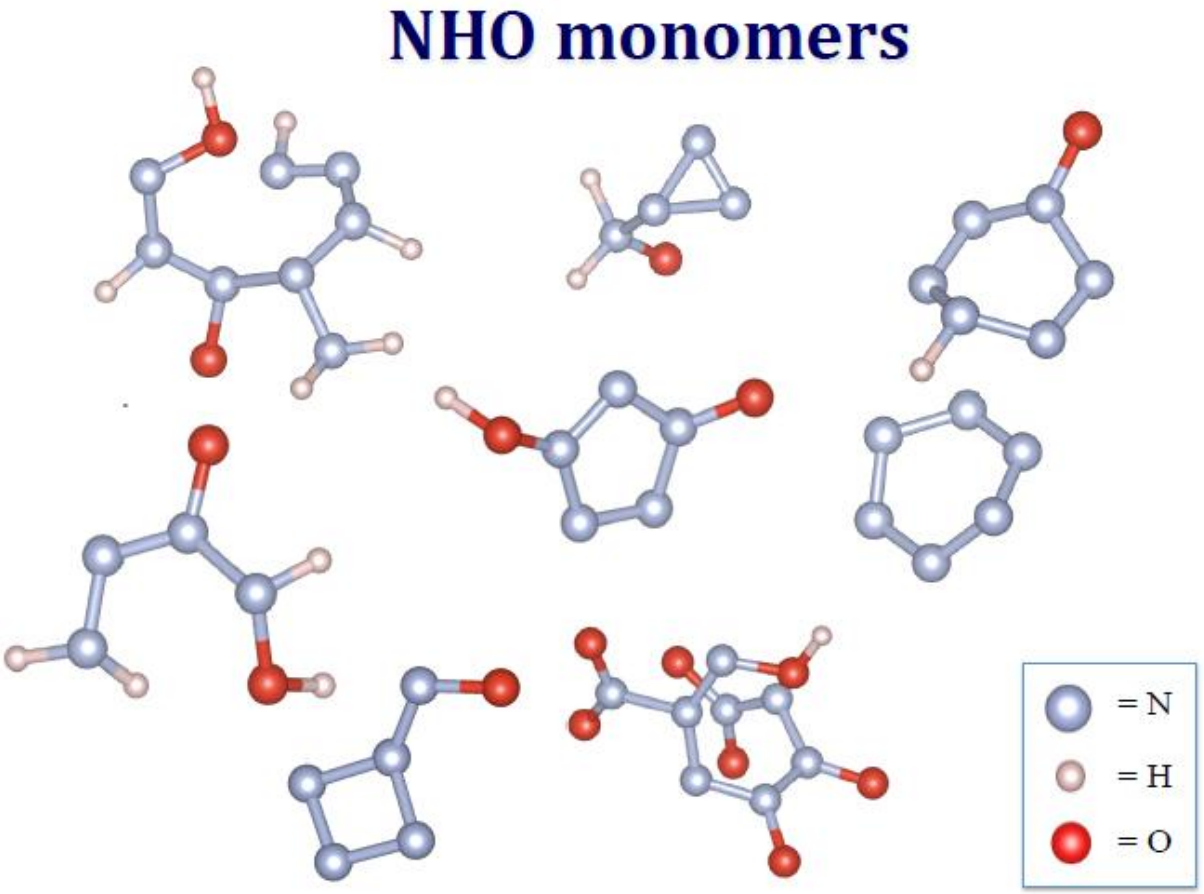
Case study: Understanding chemical rules



- Valence shell electron pair repulsion (VSEPR) theory – are lone pairs (LP) real or virtual?
- Hypervalency in SF_6 – 3c4e bonding or sp^3d^2-hybridization?
- Directional noncovalent interactions in π-conjugated molecules and electron-rich covalent solids – secondary bonds?
- Why bond in F_2 "weaker" than in Cl_2?
- Why N atom has smaller electron affinity than P?

Student project: Is there a life on Jupiter?

Anastasia Naumova, 2015, advisor Artem Oganov



A. Mikhaylov, P. Zhmurov, A. Naumova, Y. Khoroshutina, A. Sukhorukov, S Ioffe, Stereoselective Synthesis of Spirocyclic Nitronates by SnCl4-promoted Reaction of Nitroalkenes with C-2 Substituted 4-methylidene-1,3-dioxolane. Mendeleev Communications. 25. 449 (2015)