Building Predictive Chemistry Models

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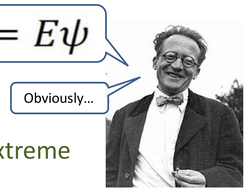
Getting chemistry from quantum mechanics

- Schrodinger's equation (1926)
- Probability of electron position can be extrapolated to predict behavior of atoms
- Prove chemical theory ground up
- Allows study of compounds that only exist in extreme conditions (no experimental data)

$\hat{H}\psi = E\psi$



Problem: Solving

- Difficult, need supercomputers.
- 500 atoms takes ~2 weeks
- Fewer atoms = no large scale application

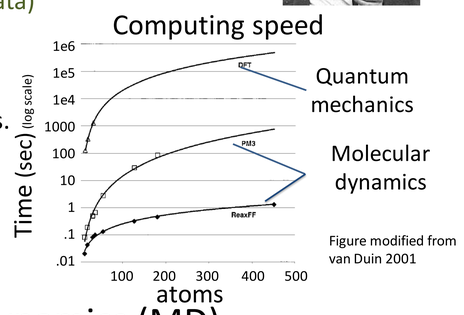
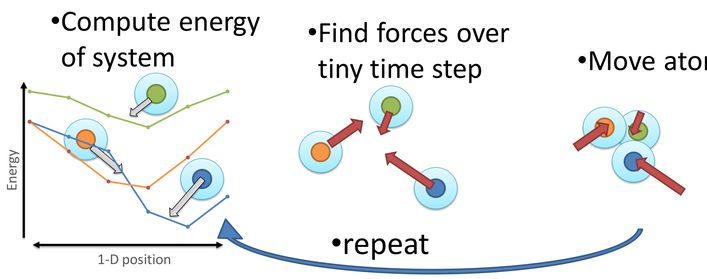


Figure modified from van Duin 2001

Solution: Molecular Dynamics (MD)

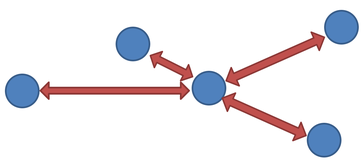
- Approximate QM with Newtonian-like forces
- "Force Field"- equation that finds these forces



- 1,000x – 100,000x faster
- Billions of atoms instead of 100s
- Code not "smart". Needs to be "taught" each element.
- Force field equation has many unknowns

ReaxFF

- ReaxFF: "reaction force field". A particular MD model (equation) that adapts interactions depending on environment
- All bonds and non-bond forces based on distance



- Net force between each atom pair found
- As atoms move apart bonds gradually lose pull. Even distant atoms slightly bonded.

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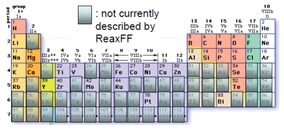
Force Field Training

- Many versions of ReaxFF incorporating different elements
- Now extending Si-O-H ReaxFF to include Cu
- Run QM calculations to verify and improve Cu-Si-O-H ReaxFF
- **Why:** validates ReaxFF as meaningful predictions of reality

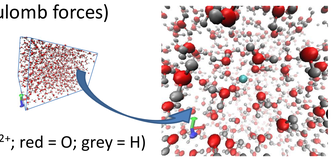


Elements described by ReaxFF
Photo from van Duin 2008

Test 1: Molecules

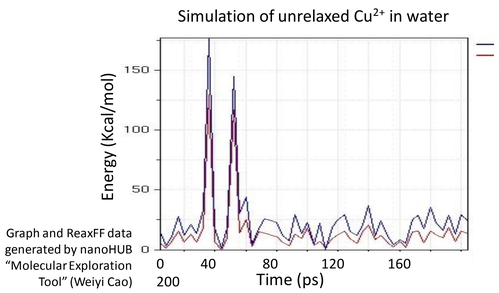
Copper Complexes in Water

- What: When dissolved, H_2O groups around Cu^{2+} in distinct patterns (van der Waals & coulomb forces)
- Why: Test ReaxFF's ability to model these non-bonding forces
- How:
  - Create virtual "water box" (Blue = Cu^{2+}; red = O; grey = H)
  - Find energy using QM and MD every time step to compare



Graph: simulation in time

- Used nanoHUB "Molecular Exploration Tool" by Weiyi Cao to generate ReaxFF data and graph (see "Molecular Exploration Tool" poster)
- MD predicts behavior very close to QM. *Model works!*



Graph and ReaxFF data generated by nanoHUB "Molecular Exploration Tool" (Weiyi Cao)

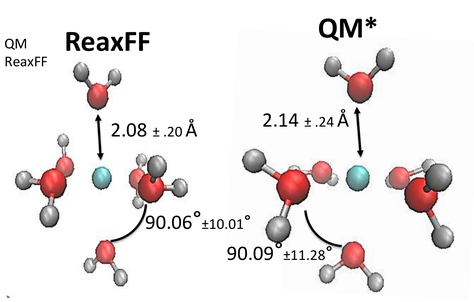
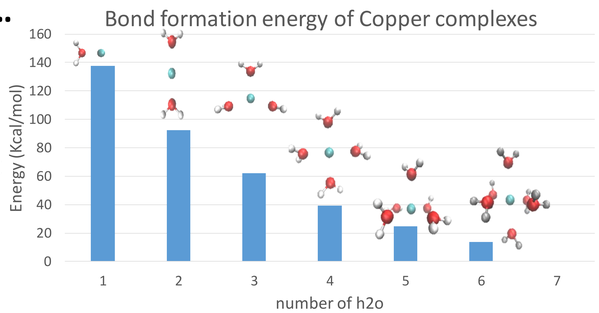


Figure: relaxed geometry

- Using QM at one moment allow atoms to move around until stable
- QM predicts experimental geometry. *Confirms theory!*
- ReaxFF matches QM (Cu-O bond length and O-Cu-O angles). *Model works!*

Going Further…

- Look at under coordinated Cu (fewer H_2O's) to see why they don't exist
- How much more stable is 6 H_2O's than 5? (11 Kcal/mol)



Test 2: Solids

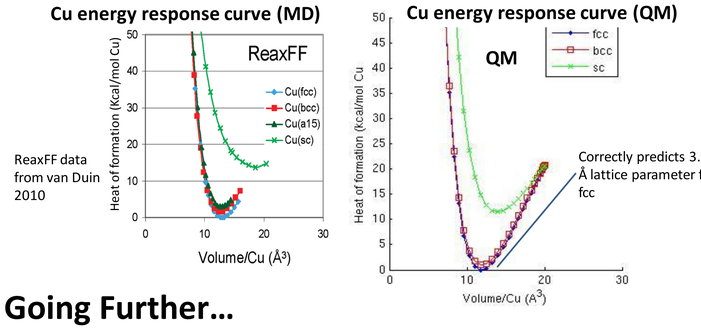
Solid Copper metal (bulk)

- What: In nature copper is face-centered cubic (fcc) lattice
- Why: Test ReaxFF's ability to model solids
- How:
  - Simplify with symmetrical lattice
  - Stretch the simulated metal
  - Find energy for different volumes
  - Look at properties (elastic constants, response curves)

fcc lattice

Results: Energy Response Curves

- ReaxFF response curves mimic QM



ReaxFF data from van Duin 2010

Correctly predicts 3.61 Å lattice parameter for fcc

Going Further…

- Computing elastic constants with QM difficult, Requires many simulations. (Each point on energy curve separate simulation)
- Developed automated method to compute Bulk modulus using SeqQuest and PUQ.
- Why:
  - Shows QM calculation's accuracy
  - Can train ReaxFF's elastic predictions
  - Useful for studying materials that can't be Tested experimentally (Cu in non-fcc lattice)
- Developing into tool that will be made available online on nanoHUB.org

Bulk modulus predictions	
experimental	140 GPa
QM	143 Gpa

References

- Van Duin, Adri, Siddharth Dasgupta, Francois Lorant, and William Goddard III. "ReaxFF: A Reactive Force Field for Hydrocarbons". *J. Phys. Chem. A.* 2001. web.
- Van Duin, Adri, Vayacheslav Bryantsec, Mamadou Diallo, William Goddard, Obaidur Rahaman, Douglas Doren, David Raymand, Kersti Hermansson. "Development and Validation of a ReaxFF Reactive Force Field for Cu Cation/Water Interactions and Copper Metal/Metal Oxide/Metal Hydroxide Condensed Phases". *J. Phys. Chem. A.* 2010. web.
- Van Duin, Adri. "Reactive force field: concepts of ReaxFF". CH-121 lecture. 2008. web.

*These QM simulations done using Gaussian09, a DFT simulation code, using the UB3LYP functional
** These QM simulations done using seqQuest, a DFT simulation code, using GGA functional