Toward Computational Materials Design

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Computational Materials Design

• Develop tools to **design** new materials rather than merely understanding existing ones.
• Incorporate **combinatorial-ish** rapid scans of multiple structures, elements, etc.
• Getting close to materials design
  – QM and MM methods still have to get better
  – Design process is not combinatorial
  – Beginning to develop the approaches to use for the design process
  – In 20 years…
Multiscale Modeling

Time Scales

Length Scales

Multiscale Modeling

Segment Averages

Meso-MD Segments

EOS Kinetics/Diffusion

Reality?

MD Atoms F=ma

QM Electrons H=E

Force Fields

Multiscale Modeling

Multiscale Modeling

Multiscale Modeling

Multiscale Modeling
Rapid Prototyping Strategy

1. Determine mechanism/behavior of material in question.
2. Determine bottlenecks and critical points in the behavior above.
3. Formulate new materials and test against critical points in 2.
   • Lather, rinse, repeat
4. Validate against experiment, higher level theory, etc.
QM-RP Application: Methane Activation

• Methane
  – Produced in large quantities at oil wells
  – Gaseous: Need to convert to liquid to transport
  – Most of this methane goes wasted

• Syngas/Fisher-Tropsch
  – Convert methane to Syngas (CO/H₂) (not efficient)
  – Syngas to alkanes via Fischer-Tropsch (not efficient)

• Ideal situation
  – Convert methane to methanol via low-temperature catalytic process.
Why CH₄ ⇌ CH₃OH is hard

• CH bonds are stronger in CH₄ than in CH₃OH
  – 114 vs 103 kcal/mol
  – Thus, any catalyst that converts CH₄ to CH₃OH will probably continue on to CO₂
Periana Pt Catalyst

• Pros
  – 72% conversion to mixture of $\text{CH}_3\text{OH} + \text{CH}_3\text{OSO}_3\text{H}$ in 2.5 hrs at 220 C
  – Relatively low temperature

• Cons
  – Conc. Sulfuric Acid
  – $\text{SO}_3$ oxidizing agent
  – Separation/hydrolysis of $\text{CH}_3\text{OSO}_3\text{H}$

• Desire
  – Reaction that works in water

Periana Catalytic Cycle
Mechanism of the C-H Activation Step

- **Electrophilic Substitution**
- **Oxidative Addition**

Reaction Pathways:

1. **A** (0 kcal/mol) to **B**
2. **B** to **T1** (Elongation)
3. **T1** to **T2**
4. **T2** to **T2b** (Activation)
5. **T2b** to **C**

Key Chemical Species:
- Pt
- Cl
- N
- H
- O
- S
- SO₃H

Energy Diagram:

- Energy levels are indicated at each step with kcal/mol.

Overall Process:

- Initial state at A (0 kcal/mol)
- Activation step at T2b (+35.4 kcal/mol)
- Final product at C (+10.2 kcal/mol)
Water Poisoning

\[ \Delta H(0 \text{ K}) = -6.8 \text{ kcal/mol} \]

\[ \text{PtClOSO}_3\text{H} + \text{H}_2\text{O} \text{ (at } \infty \text{)} \] → \[ \text{PtClOH}_2 \] + \[ \text{HSO}_4^- \text{ (at } \infty \text{)} \]
Rapid Prototyping Test 1

- Compute the energy of the M-CH₃ compound; should be < 10 kcal/mol.
For candidates that pass test 1, compute the reaction with a single water; new candidates should be stable ($\Delta E_{H2O} > 0$).
Rapid Prototyping Test 3

- For candidates that pass tests 1-2, compute the barrier $\square E^\ddagger_{AC}$; new candidates should be < 33 kcal/mol.
Rapid Prototyping Test 4

- For candidates that pass tests 1-3, compute energetics for oxidation and functionalization steps.

- Candidates that pass all tests are candidates for experimental validation.
Catalyst Candidates #1

Pt(II), 16 electron complexes with N,O,N (a) and O,O,O (b) coordinating atoms. Again, as the $\Delta E$(A-C) energies are 22.5 and 18.0 kcal/mol, respectively, these systems do not pass QM-RP test 1, and are not pursued further.
NCN structures with (a) Os(II) (14 electrons) and (b) Pt(II) (18 electrons). Structure (a) has a $\Delta$E(A-C) of 32.7 kcal/mol, which does not pass QM-RP test 1, but structure (b) has $\Delta$E(A-C), which does pass QM-RP test 1.
• Transition state for C-H bond activation for the structure from the previous slide. The barrier is 48.9 kcal/mol, and thus does not pass QM-RP test 2.
Best QM-RP Catalyst Candidate

![Diagram showing the catalytic process with energy levels and reactants/products labeled with chemical structures and energies in kcal/mol.]

- **W**: +0.7 kcal/mol
- **A**: 0.0 kcal/mol
- **A'**: +27.9 kcal/mol
- **B**: +26.7 kcal/mol
- **D**: 0.0 kcal/mol
- **C**: +34.6 kcal/mol
- **E**: +49.4 kcal/mol

Reactants:
- **HCl**
- **CH₄**

Products:
- **Cl⁻**
- **N⁺**
- **O⁻**

Chemical Structures:
- **Ir**
- **N⁺**
- **O⁻**
- **Cl⁻**
- **HCl**
- **CH₄**

Energy Levels:
- **+0.7 kcal/mol**
- **+27.9 kcal/mol**
- **+26.7 kcal/mol**
- **+34.6 kcal/mol**
- **+49.4 kcal/mol**
Catalysis-RP Future Directions

- Continue work on CH$_4$
  - Roy looking at a few structures
- Move on to fuel cell design
  - High T DECO Fuel Cells
  - Optimize Catalyst to prevent coking
  - Understand behavior of TPB
CMDF Energetic Materials Simulation

• Predictive simulation of HE
  – Integrate software tools across multiple physical scales
  – First principles based simulation
  – Validate against existing experiments
  – Predict behavior of novel materials
Detailed Nitramine Reaction Mechanism
ReaxFF: QM-honest Classical FF

- Classical FF accurately describes QM results
  - TS and Pathways
  - Automatically fit to QM structures, energies

- \( E = E_{\text{val}} + E_{\text{coul}} + E_{\text{vdw}} \)

- Bonds can break and reform
  - Bond-order-dependent valence terms

- Charge equilibration for long-range charge transfer

- Generic: every O is the same, regardless of CH\(_2\)O or Al\(_2\)O\(_3\)
ReaxFF Reproduces RDX QM Data

Energy (kcal/mol)

NO$_2$ dissociation
concerted

HONO elimination

ReaxFF (thin lines)
QM (thick lines)
Species Profiles from ReaxFF

- Can use ReaxFF for shock or cook-off
- Every product in the simulation is also observed experimentally
- ReaxFF can simulate complicated multicomponent reactions at high T,P

![Graph showing species profiles with time (ps) on the x-axis and population on the y-axis.](image)
Move from Simulation to Design

• Detailed reaction mechanisms too expensive
  – Too many man hours to work for arbitrary new materials

• Use ReaxFF to simulate reaction chemistry
  – Validate against quantum chemistry

• Distill multiple ReaxFF trajectories to reduced reaction mechanism

• Use reduced mechanism in Cantera flame simulation
  – Also need transport and thermochemistry parameters
  – Collaboration with Dave Goodwin, Caltech
CMDF Sample Code for HE

```python
RDX = load_bgf("rdx_uc.bgf")
RDX444 = periodic supercell(RDX,(4,4,4))
for T in [100,500,1000]:
    RDX444.set_temperature(T)
    Traj[T]=RunDynamics(material=RDX444,time=10)
Species = AnalyzeFragments(Traj)
Mech1D = SimpleMech(Species,reactant="rdx",
                    product="n2")
for frag in Species:
    Thermo[frag] = SimThermo(frag)
    Transport[frag] = SimTransport(frag)
Cantera1DFlame(Mech1D,Thermo,Transport,
               MoleFrac=("rdx",1))
```