Using LAMMPS to map potential energy surfaces for rapid ionic liquid forcefield development

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Ionic liquids are (room temperature) molten salts.

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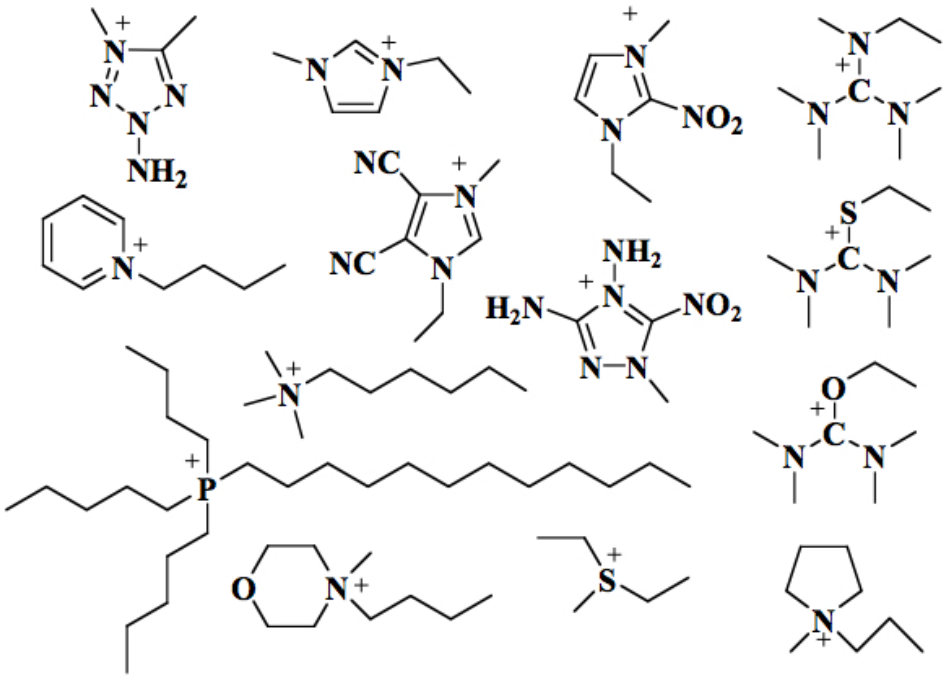
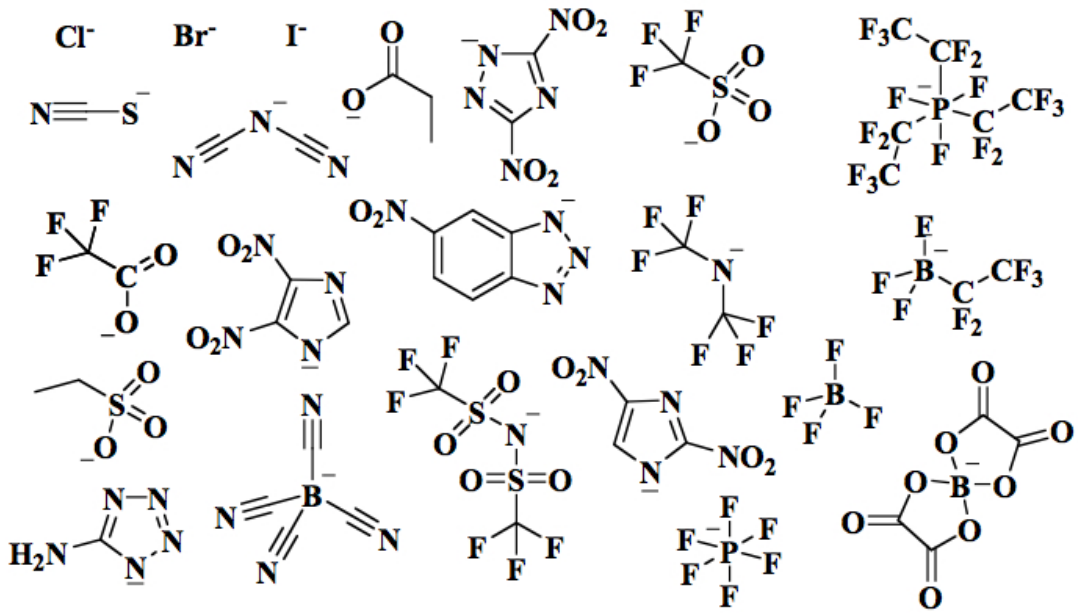
ILs have practically unlimited variety.



Thousands of cations and anions are available.

10^{many} possible ILs with widely varying properties . . .

Which one is "best"?



Molecular simulation can predict many properties.

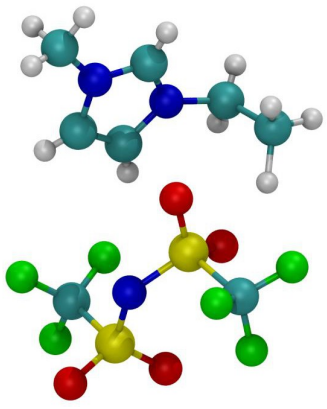
- density
- heat capacity
- heat of vaporization
- viscosity
- thermal conductivity
- diffusivity
- . . . and more

But first, we need a forcefield.

Classical molecular simulation

soft billiard balls, connected by springs, bouncing around in a box

Force field specifies how soft, how springy.



$$\Phi = \sum_{bonds} k_x(x - x_0)^2 + \sum_{angles} k_\theta(\theta - \theta_0)^2$$
$$+ \sum_{dihedrals} k_\phi \left[1 + cos(n\phi - \phi_0)\right]$$
$$+ \sum_{impropers} k_\psi(\psi - \psi_0)^2$$
$$+ \sum_{i=1}^{N-1} \sum_{j>1}^{N} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\epsilon_0 r_{ij}} \right\}$$

different force field $\rightarrow$ different system $\rightarrow$ different results

Assigning force field parameters for a new molecule

Extremes:

- Generate from scratch
  - years of calculations
- Assemble from previous forcefields
  - tedious and typo-prone
  - questionable consistency ("FrankenCHARMM")

Compromise:

1. Take most terms from a big pharma force field database.
2. Re-fit atomic charges and dihedral parameters.
   - molecule-specific
   - strong influence on system behavior

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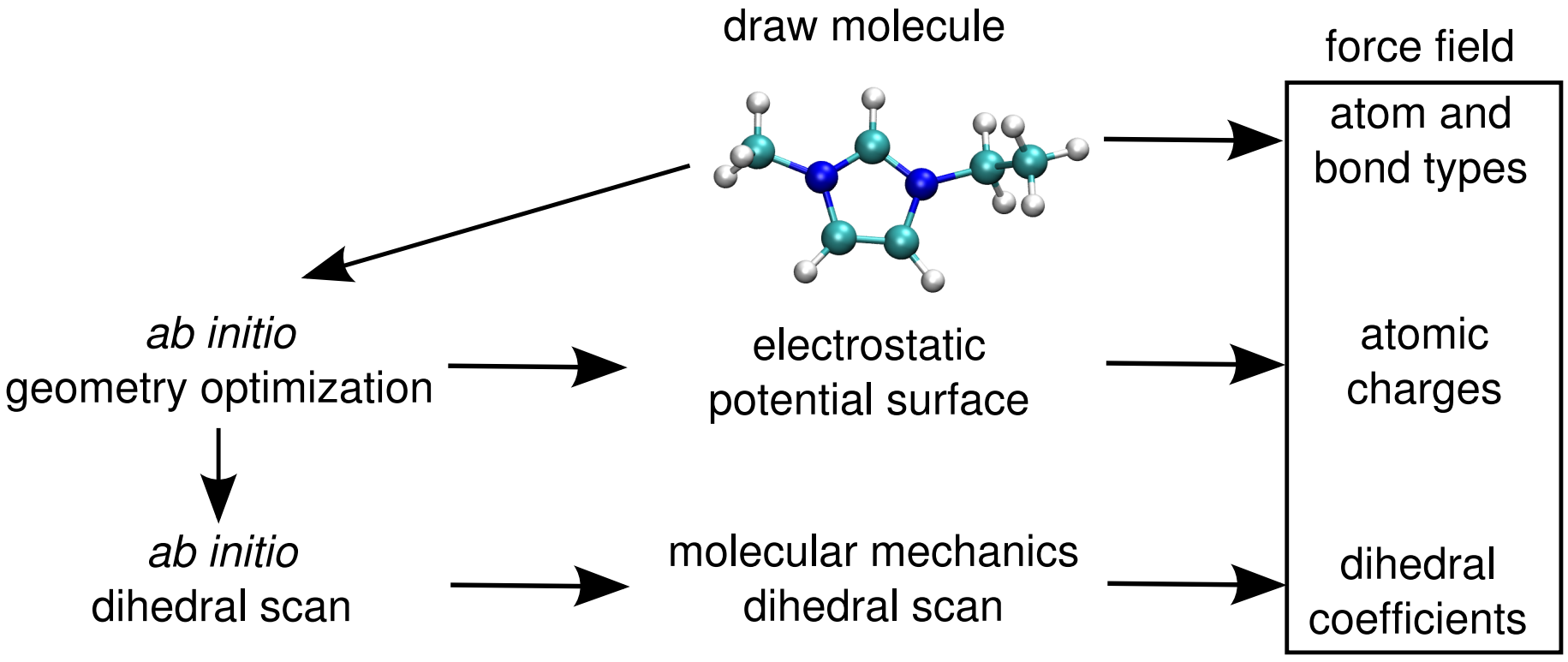
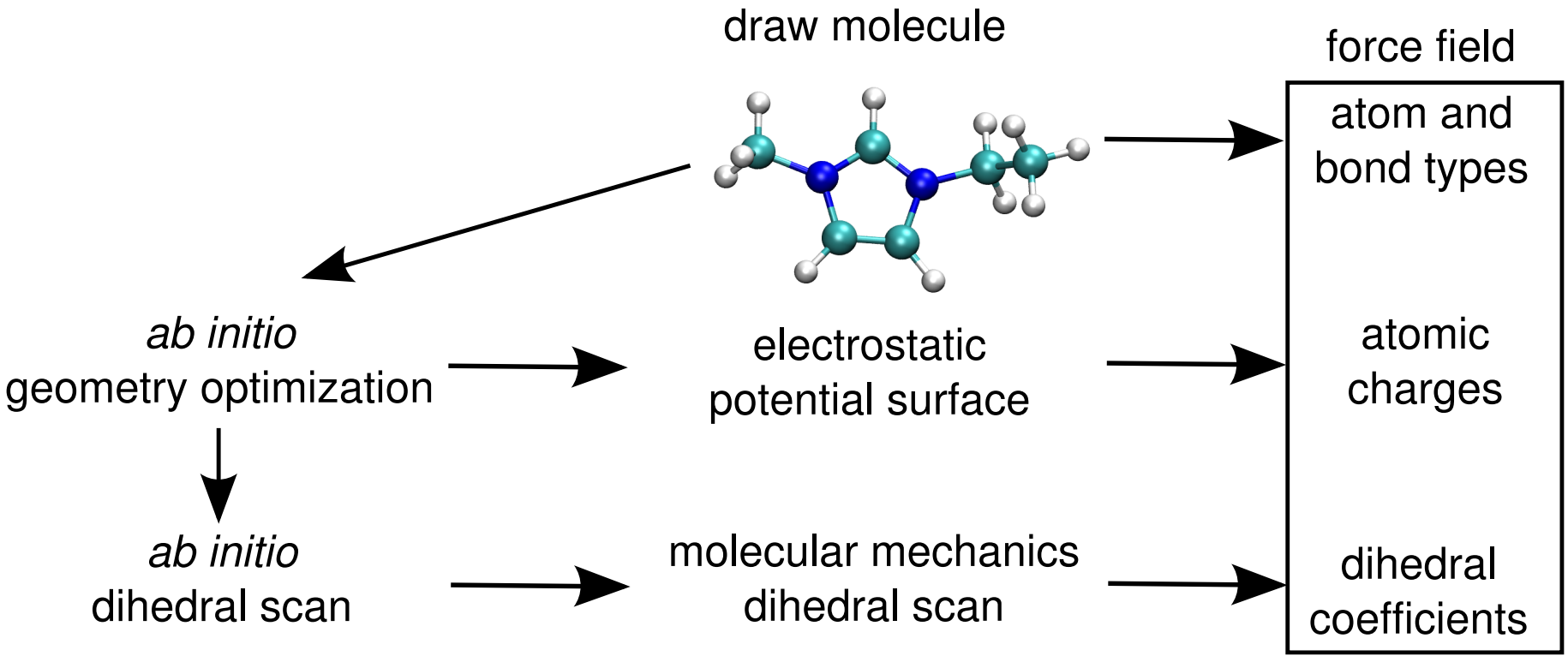


development details

time: 2-4 days (if scripted and nothing "interesting" shows up)
tools: Avogadro (drawing), Antechamber/GAFF/RESP (atom/bond types, charges), Gaussian (*ab initio*), LAMMPS (MM dihedrals), PSwarm (non-linear fitting)

Assigning force field parameters



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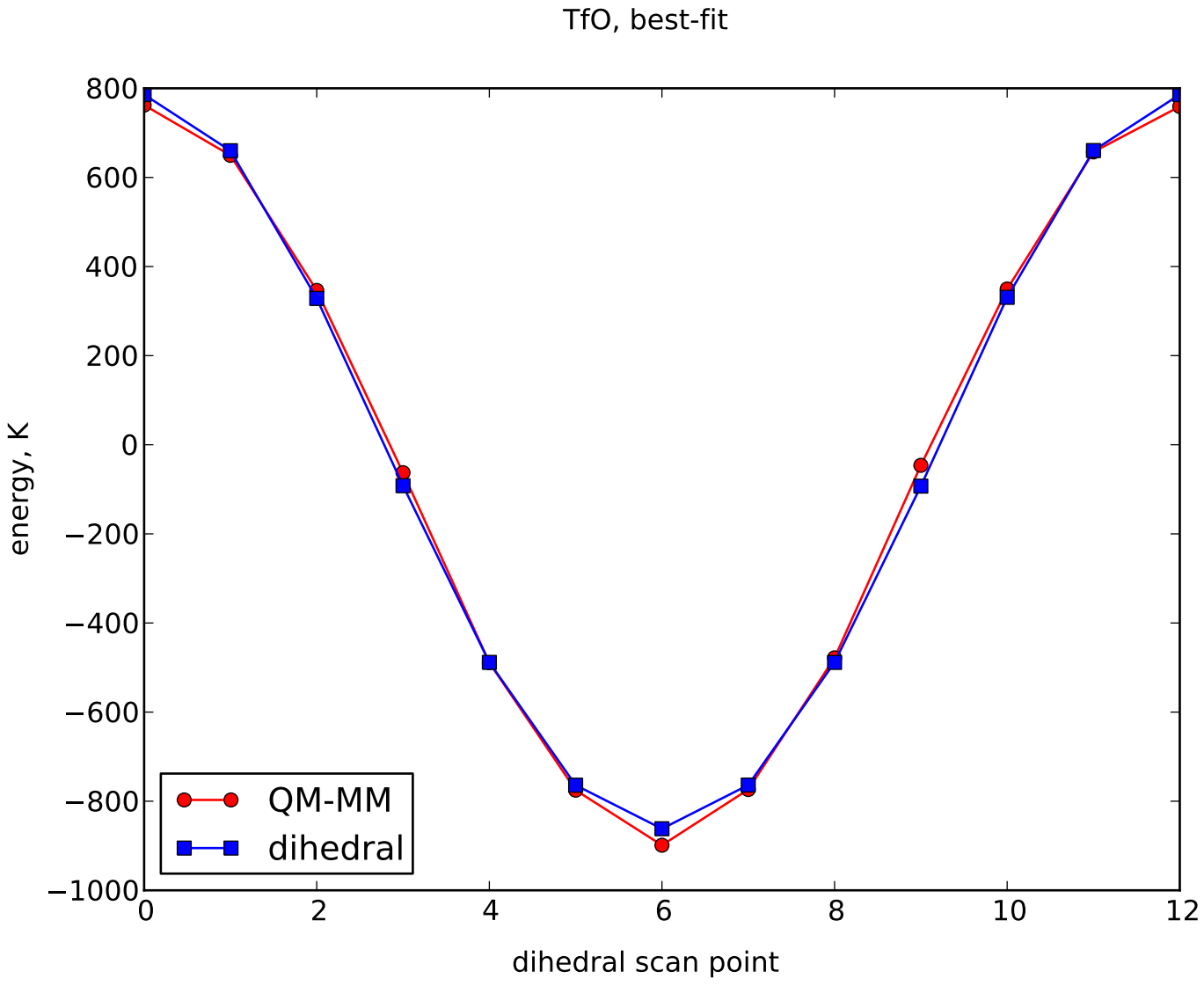
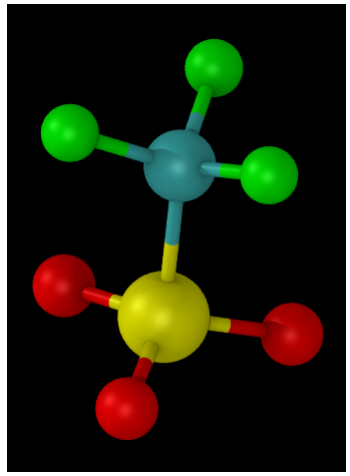
Fitting dihedral parameters

1. Calculate quantum mechanics energy vs. angle
   - Restrain dihedral of interest to 0, 10, 20, ... degrees
   - Allow other degrees of freedom to relax
2. Calculate molecular mechanics energy vs. angle (without dihedral energy term)
   - Restrain dihedral of interest to 0, 10, 20, ... degrees
   - Allow other degrees of freedom to relax
3. Calculate difference between QM and MM energies
4. Fit dihedral term(s) to this difference

Triflate dihedral parameters are easy to fit





triflate is simple and well-behaved

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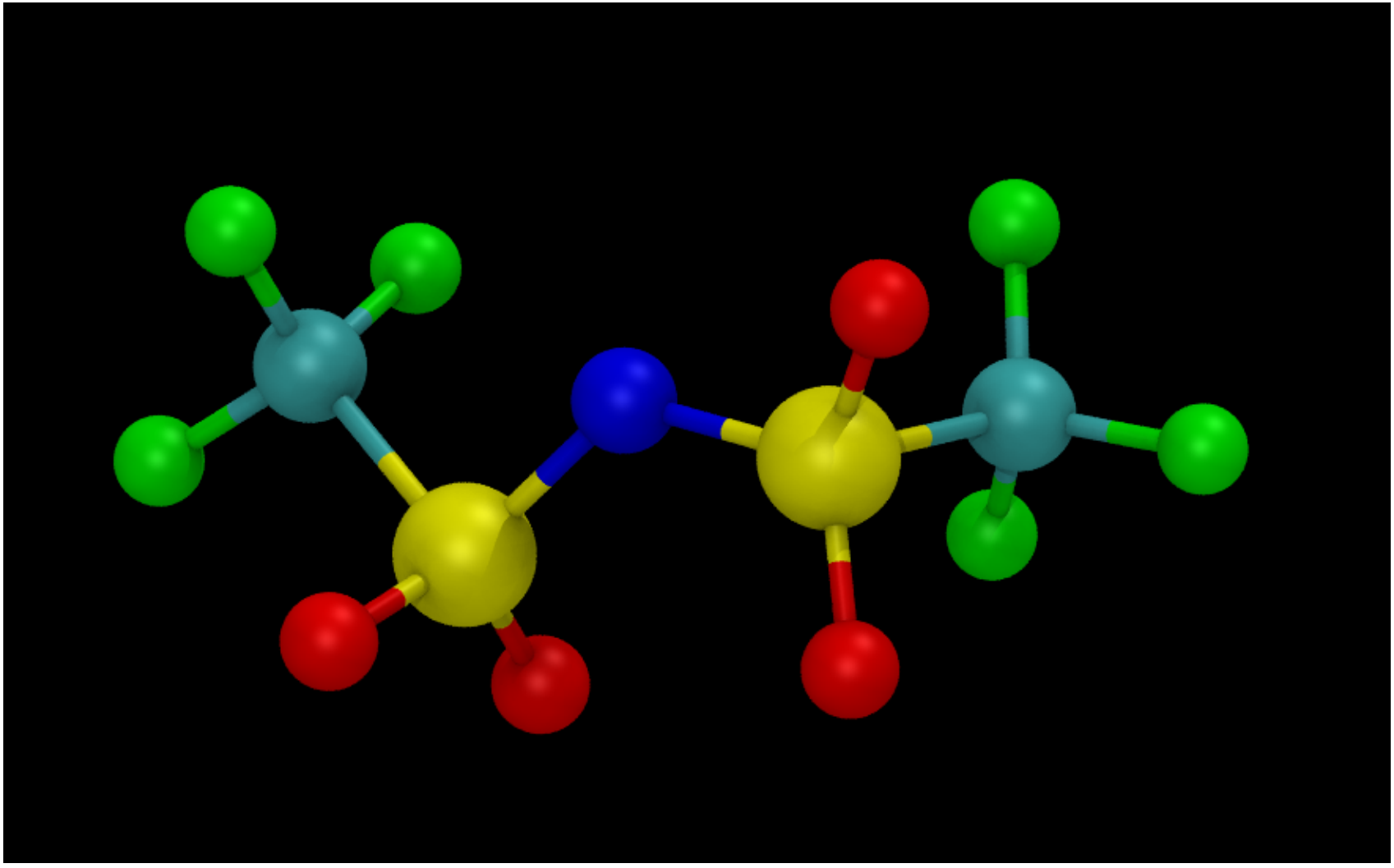
Bistriflimide C-S-N-S dihedrals are coupled



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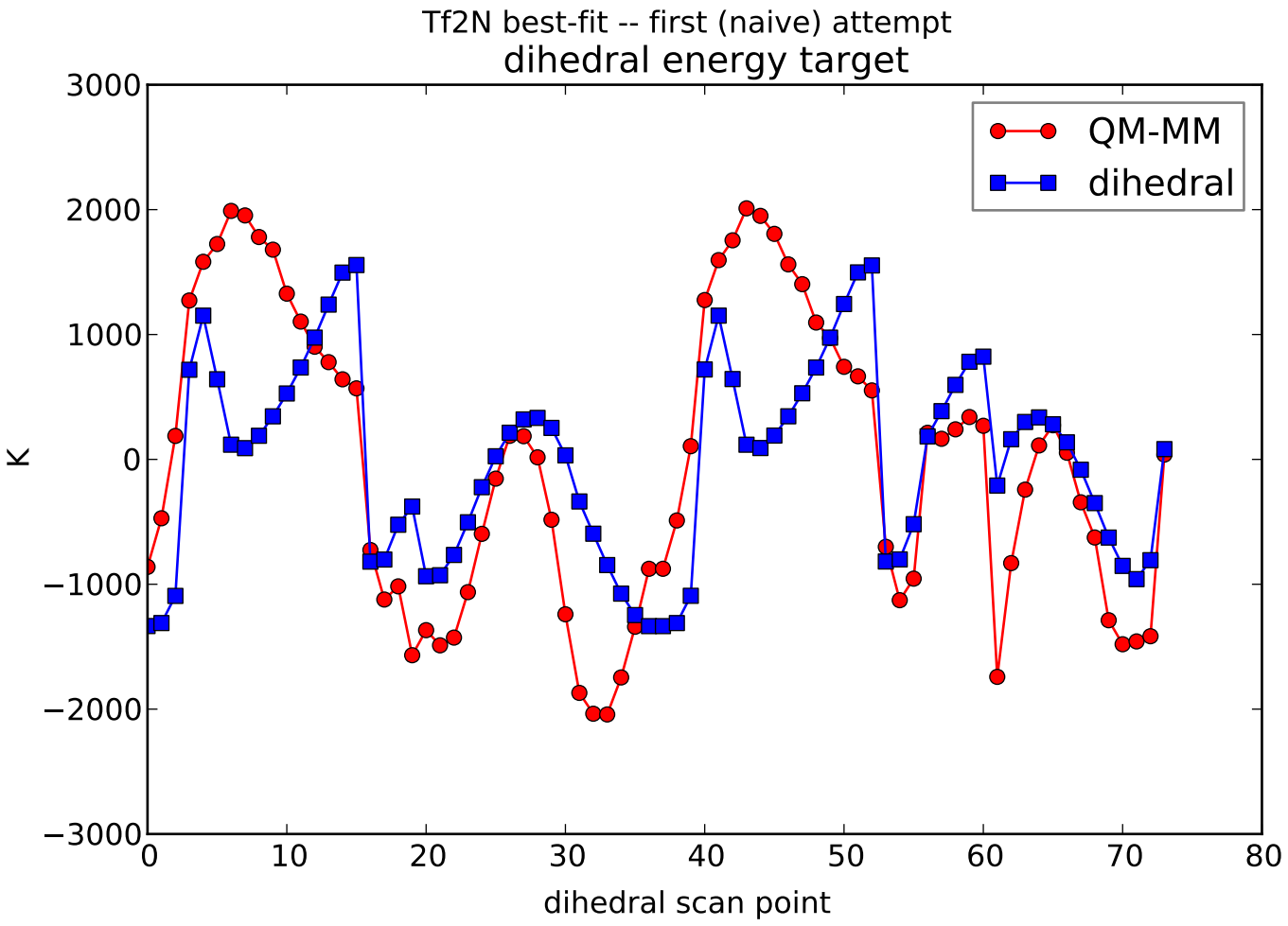
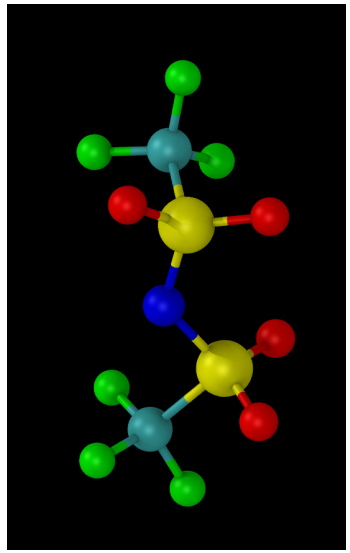
Naive 1D best-fit bistriflimide C-S-N-S parameters





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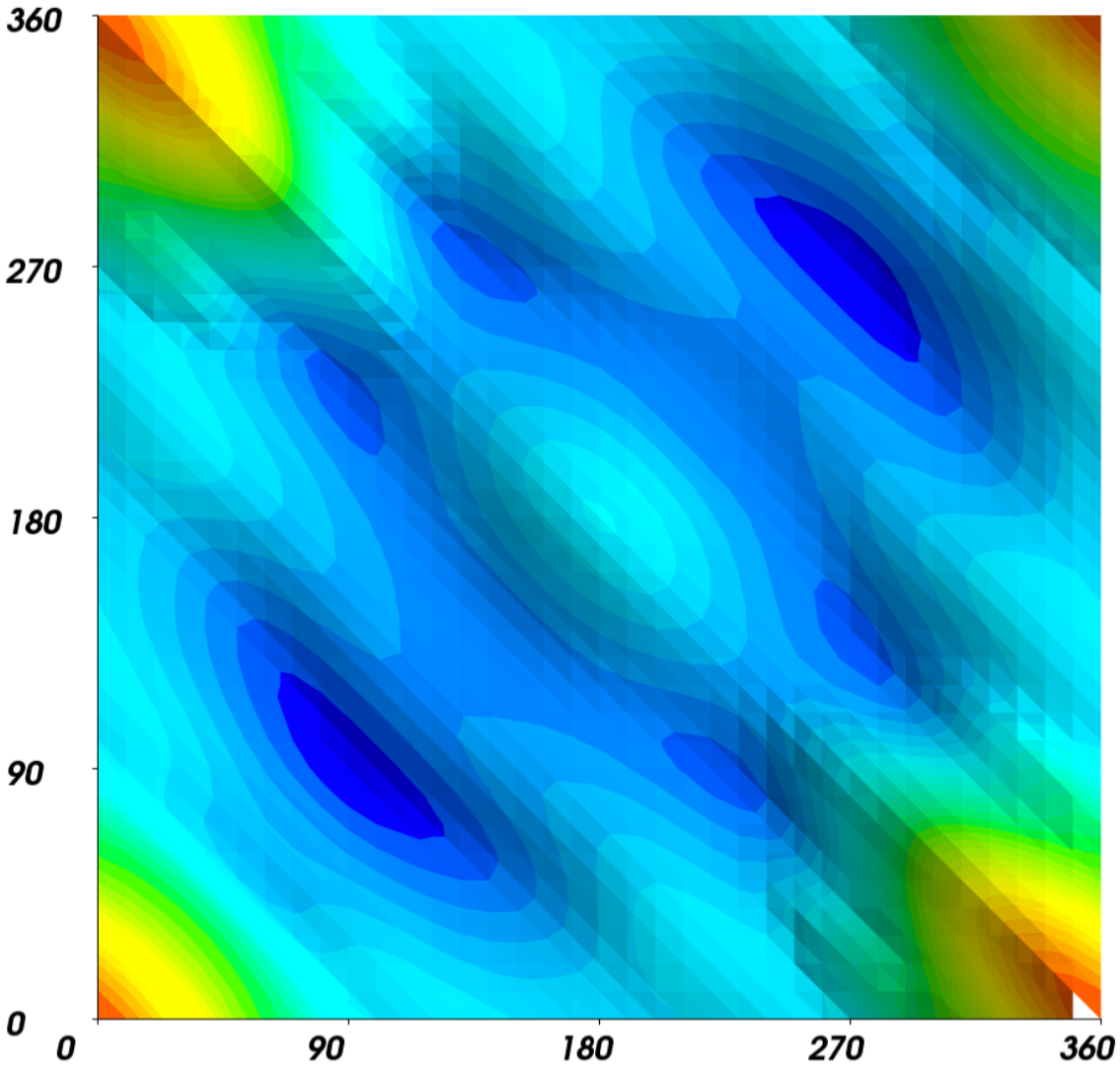
Scan 2D bistriflimide C-S-N-S potential energy surface

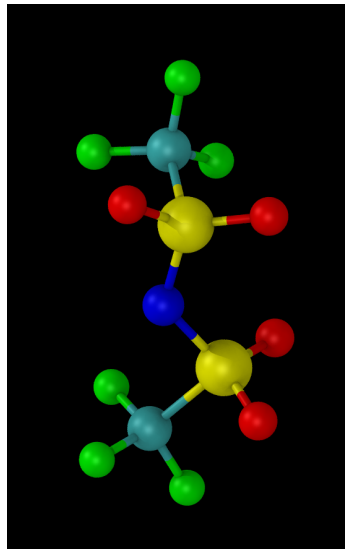
```
#!/bin/sh
# Run LAMMPS inside two nested loops

for a1 in $(seq 0 10 360); do
  for a2 in $(seq 0 10 360); do

    lmp_serial -in 2dscan.in -log ${a1}_${a2}.out \
        -var angle1 $a1 -var angle2 $a2

  done
done
```

Minimize energy with two restrained dihedrals

```
fix NVE all nve

fix TFIX all langevin ${hi_temp} ${lo_temp} 100 24601
fix REST all restrain 0.0 ${k_restrain} &
    dihedral 2 1 3 8 ${angle1} 3 1 2 9 ${angle2}
fix_modify REST energy yes
run ${numsteps}

fix TFIX all langevin ${lo_temp} ${lo_temp} 100 24601
fix REST all restrain ${k_restrain} ${k_restrain} &
    dihedral 2 1 3 8 ${angle1} 3 1 2 9 ${angle2}
fix_modify REST energy yes
run ${numsteps}

unfix REST
run 0
print "final_result ${angle1} ${angle2} ${pe}"
```

2D bistriflimide C-S-N-S potential energy surface





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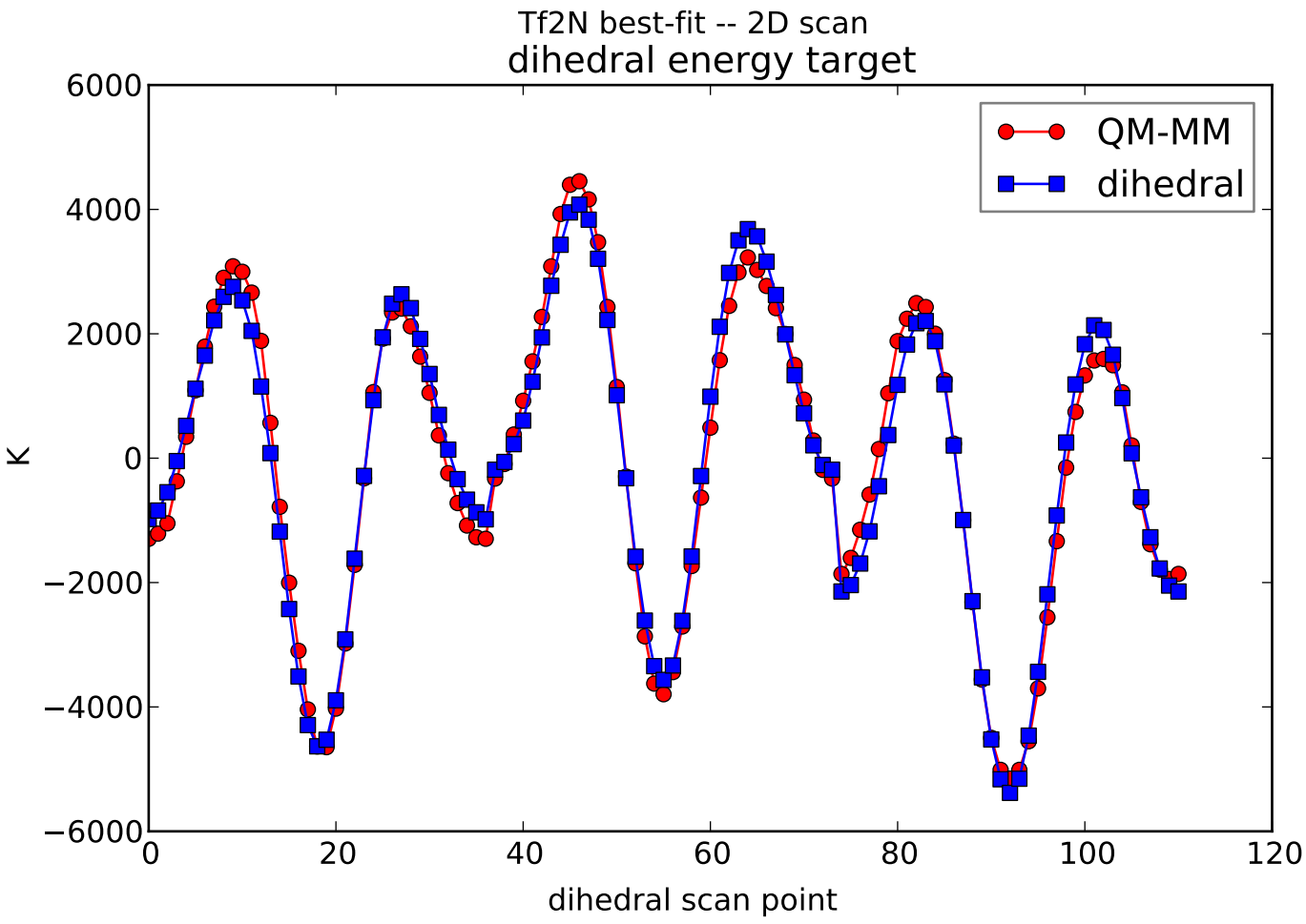
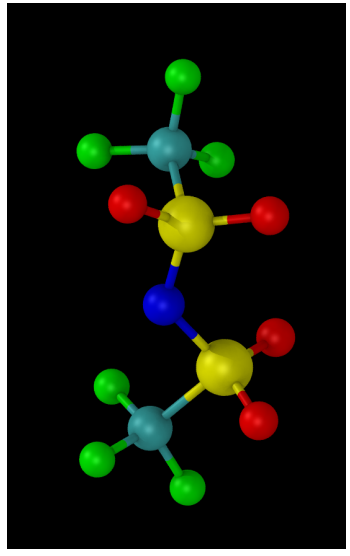
2D best-fit bistriflimide C-S-N-S parameters





Summary

- Rapid force field implementation enables simulation-assisted materials development.
- Reasonable force fields can be assembled relatively efficiently.
- 'fix restrain' allows easy minimization with restrained bonds (see LAMMPS email list archives for code)

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