Quantum Chemistry for Separations

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Scoring Extractants: Distribution Coefficients From Free Energy Changes

Exchange reaction:

$$\left[Ln\left(H_2O\right)_9\right]^{3+} + \left[An\left(L\right)_2\left(H_2O\right)_6\right]^{-} \rightarrow \left[An\left(H_2O\right)_9\right]^{3+} + \left[Ln\left(L\right)_2\left(H_2O\right)_6\right]^{-}$$

characterized by **free energy change ΔG=ΔH-TΔS**
equilibrium constant K

These are related by $\boxed{e^{-\beta\Delta G} \propto K}$

- Caveat
  - Almost no empirical potentials available
  - Current molecular mechanic potentials are not good enough to describe the chemistry of *f*-elements

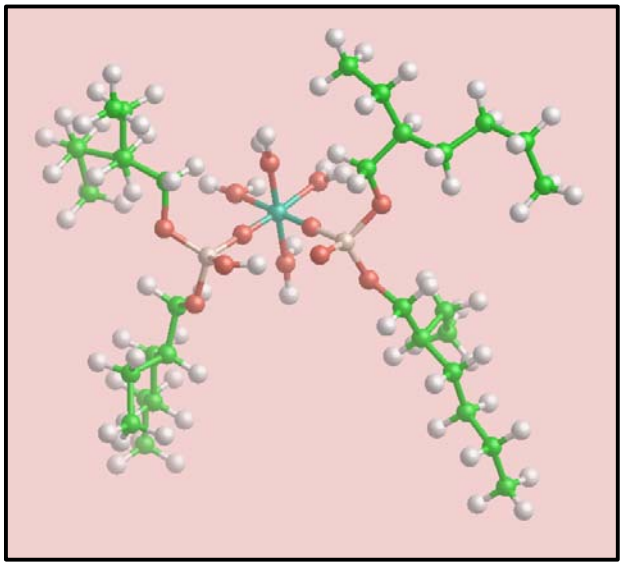
Use Quantum Chemistry techniques

Our goal is to build quantum chemical approximations to ΔG for candidate ligands (*L*)

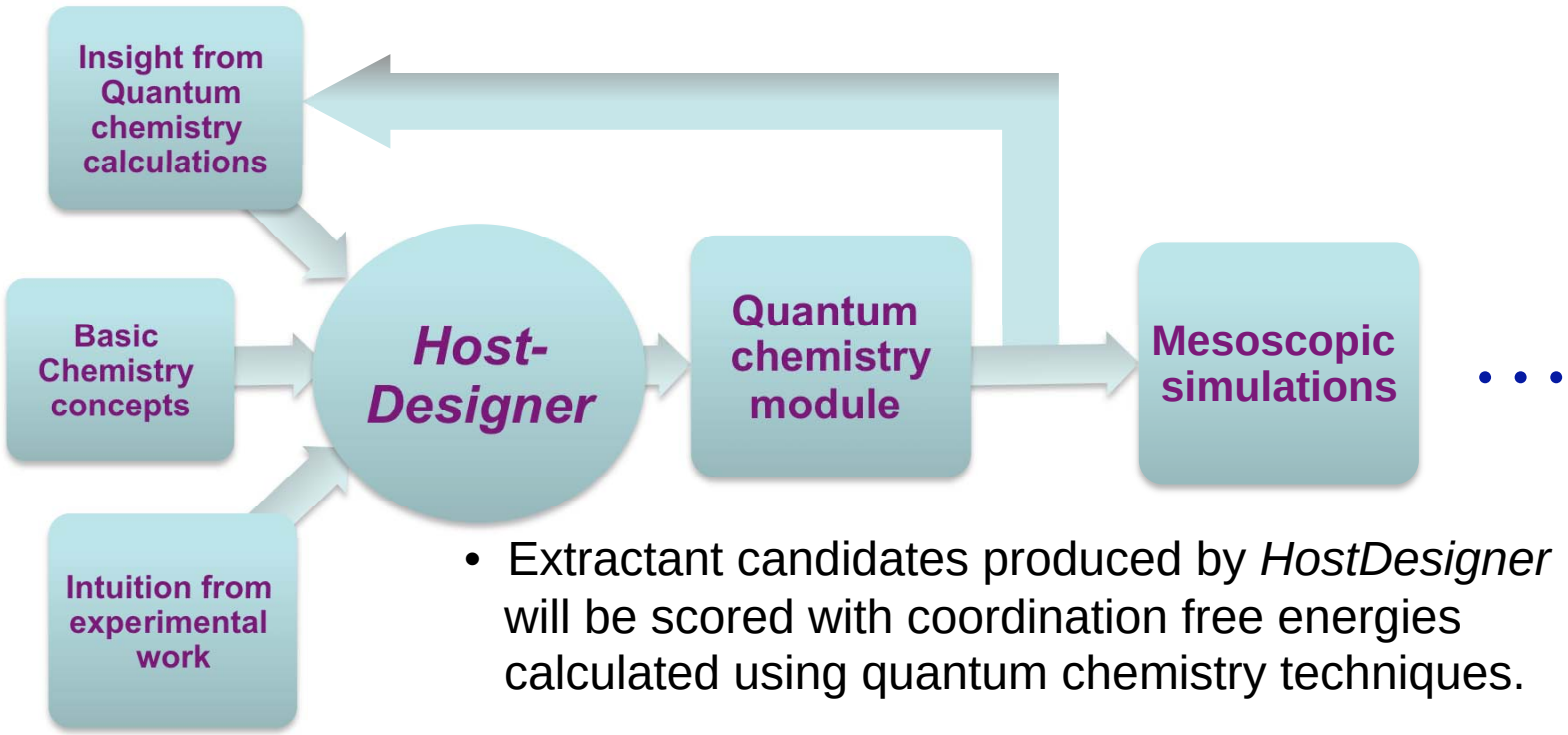
ΔH: total energy of minimal energy structure
ΔS: vibrational frequencies at minimal energy structure

M(III)	M'(III)	ΔG(kcal/mol)	
		BT	BTA
Am	La	-56.0	-52.7
Am	Ce	-37.9	-53.3
Cm	La	-36.4	-43.8
Cm	Ce	-18.3	-44.3
La	Ce	+18.1	-0.5
Am	Cm	-19.6	-8.8

$[Eu(HDEHP)_2(H_2O)_4]^{2+}$

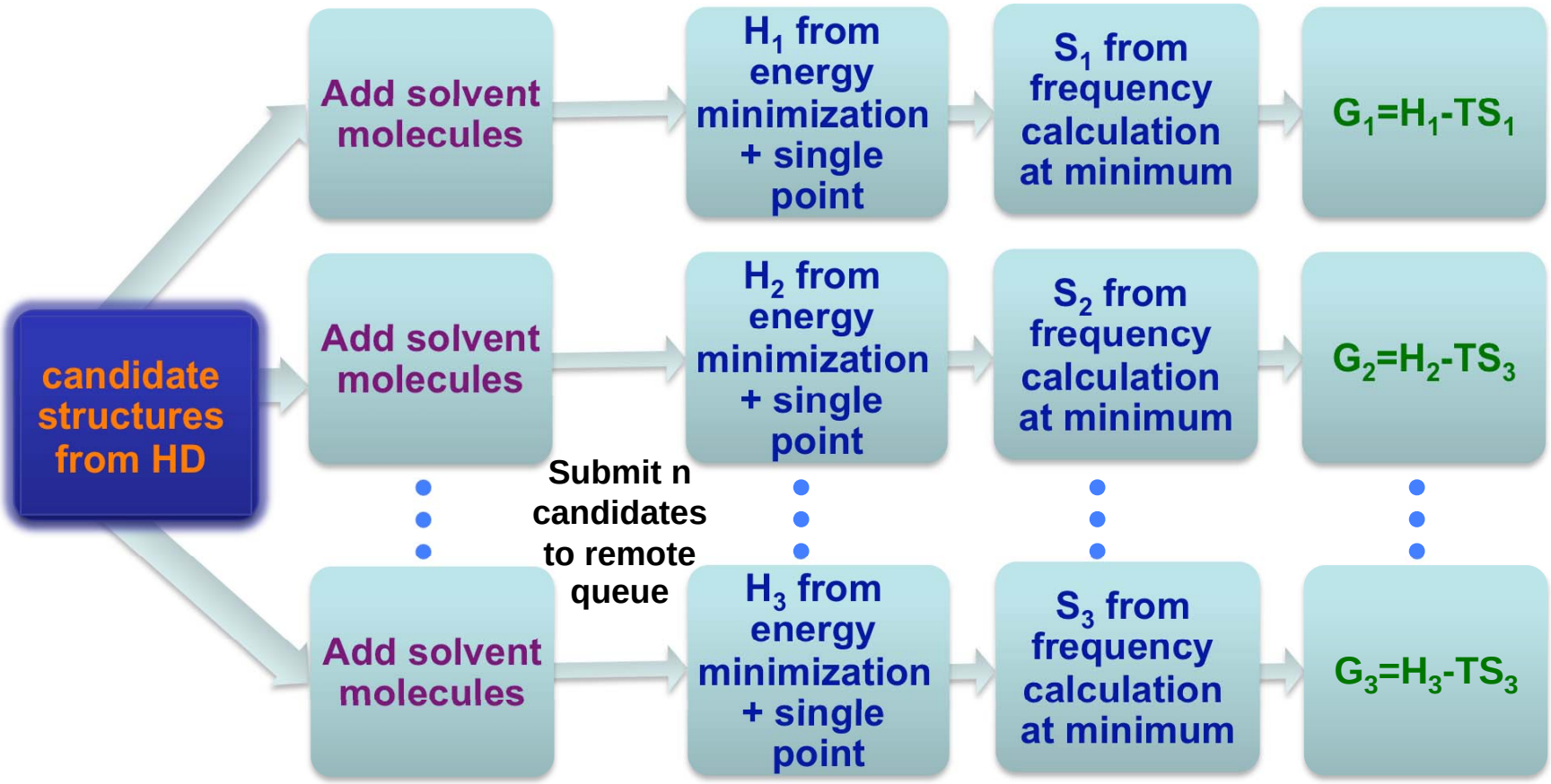


Hierarchical Approach to Extractant Screening



- Extractant candidates produced by *HostDesigner* will be scored with coordination free energies calculated using quantum chemistry techniques.
- Insight obtained from the quantum chemistry calculations of electronic structure will be fed back into *HostDesigner* as input information.
- Most successful candidates move on to mesoscopic studies (Molecular Dynamics, continuum flow)

Automated QM Screening: Schematic



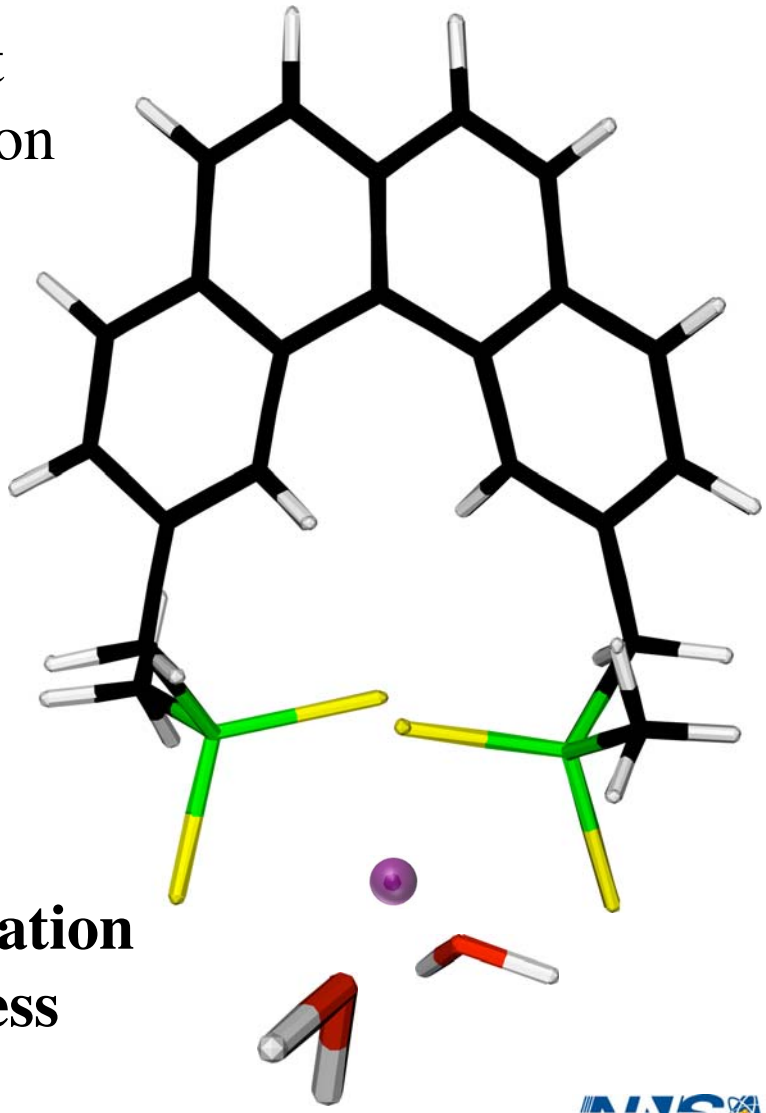
- Jobs launched in parallel
- Script "sleeps" on desktop, wakes up periodically to check jobs running in remote queue

Filling Out the Coordination Shell

- HD complexes don't include solvent
- Atomic specificity in first coordination shell is essential => implicit solvent not good enough

- Manual addition possible, but time-consuming
- Automated addition useful, but hard

- location?
- orientation?
- generality?



Shouldn't have to waste optimization steps correcting bad initial guess

Current status of implementation

- Python interface between HostDesigner and quantum chemistry codes

- HostDesigner targets are analyzed and a 1st approximation solvent arrangement added prior to Qchemistry calculation

- Structural optimization (including solvent molecules) and calculation of free energy

- Current implementation can be controlled from any desktop workstation

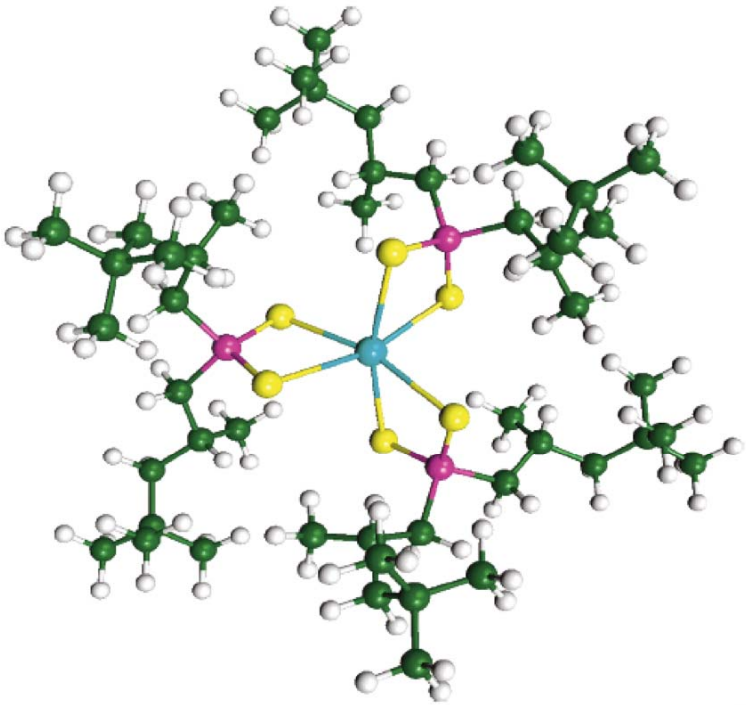
- Quantum chemistry calculations are run remotely in a chosen supercomputer anywhere on the internet

Future implementation

- Automatic address of convergence issues
  - Basis sets
  - Near degeneracies lead to difficulties in converging electronic structure
  - Soft modes
  - Explicit versus implicit solvent models

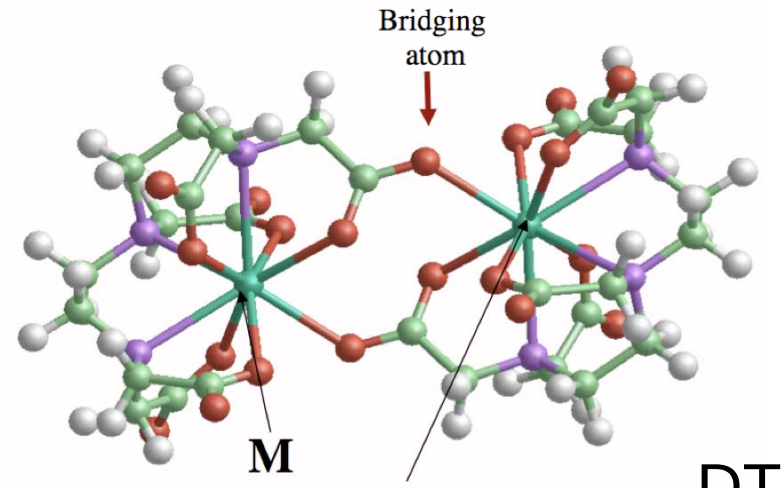
- Analysis of possible coordination environments

Other approaches to HD involve multiple ligands

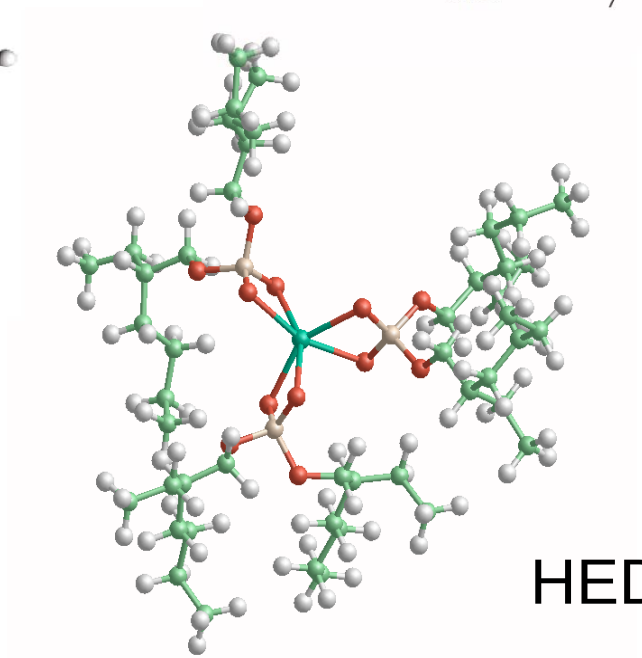


cyanex

Cao et al. Inorg. Chem. (2010)



DTPA



HEDHP