EMORY Emerson Center for Scientific Computation

Program

I. OVERVIEW

1. Modern methods of computational chemistry (MM, ab initio, DFT and Hybrid methods).
2. Introduction to the Emerson Center's facilities
3. Intro (cont.)

II. Molecular mechanics and Molecular Dynamics

4. Molecular Mechanics and Molecular Dynamics methods
5. Applications and Practical sessions on Problem solving

III. Transition Metal Chemistry and Catalysis

6. Computational approaches to the Transition Metal Chemistry
7. Computational Catalysis (including Organic, Inorganic and Enzymatic)
8. Practical sessions on Problem solving.

IV. PhotoChemistry and Excited State Studies

9. Introduction, Overview of Methodology, and some Typical Examples
10. A problem solving session on Spectroscopy, Radicals and PhotoChemistry

EMORY Emerson Center for Scientific Computation

Lecture 5

Part I:

- **A Practical Session on water dimer with AMBER**
- **Visualization of trajectories with VMD**
- **Numerical Analysis with VMD**

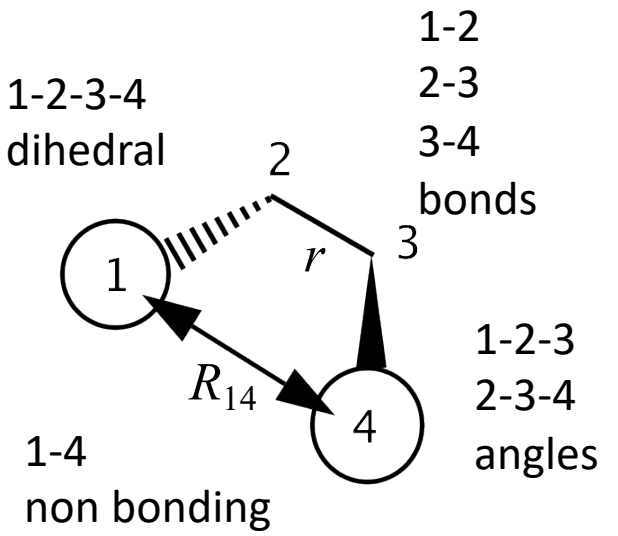
Part II:

- **Monte Carlo Search Techniques in AMBER**

A Generic Force Field: Parameters, Atom types, and Connectivities

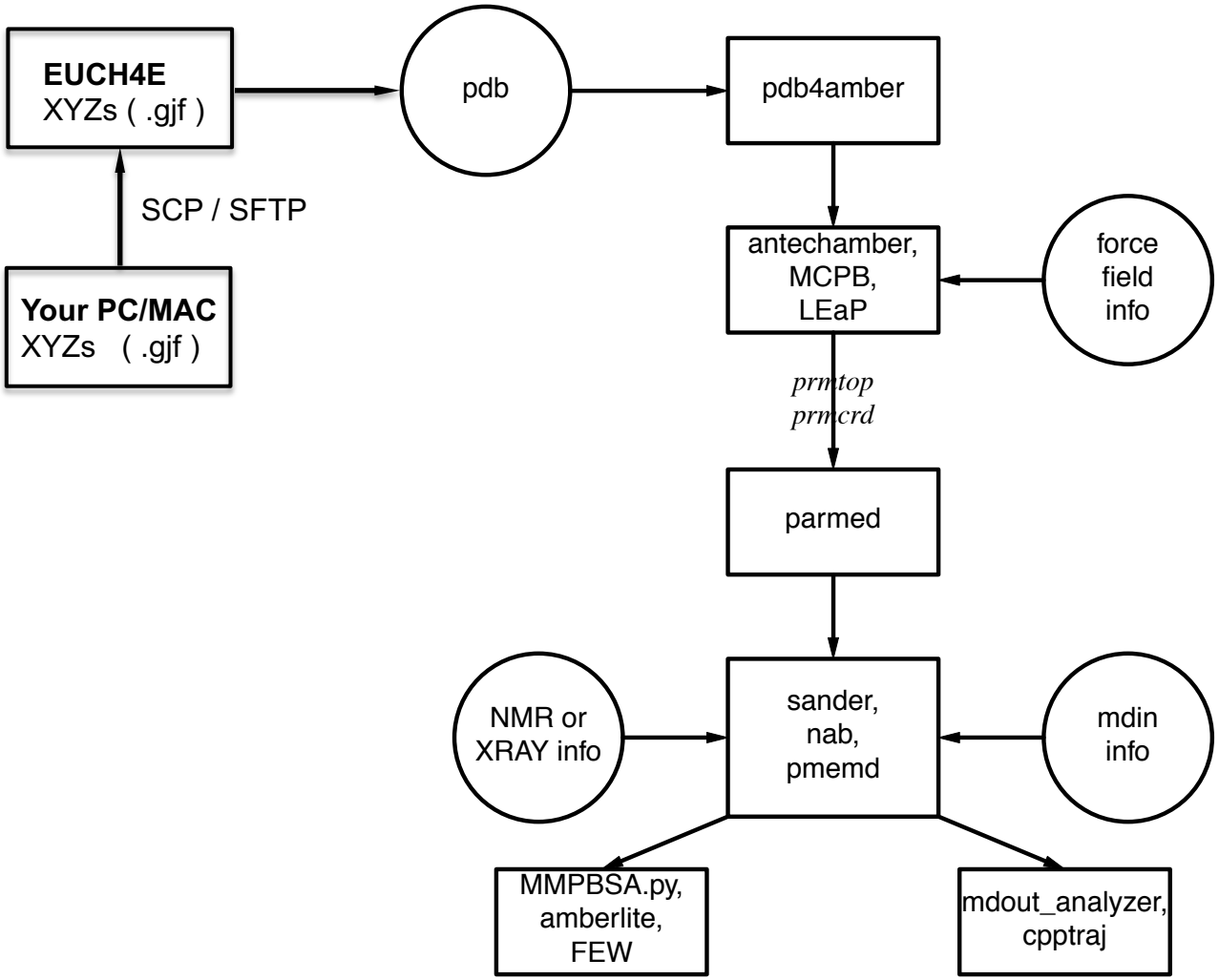
$$
\begin{aligned}
E_{total} &= \sum_{bonds} k_b (r - r_0)^2 \\
&+ \sum_{angles} k_\theta (\theta - \theta_0)^2 \\
&+ \sum_{dihedrals} V_n [1 + \cos(n\phi - \gamma)] \\
&+ \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} + \frac{q_i q_j}{\varepsilon R_{ij}} \right]
\end{aligned}
$$

$k_b \quad r_0$	bonds
$k_q \quad \theta_0$	angles
$V_n \quad \gamma$	dihedrals
A_{ij}, B_{ij}	van der Waals
q_i	partial charges

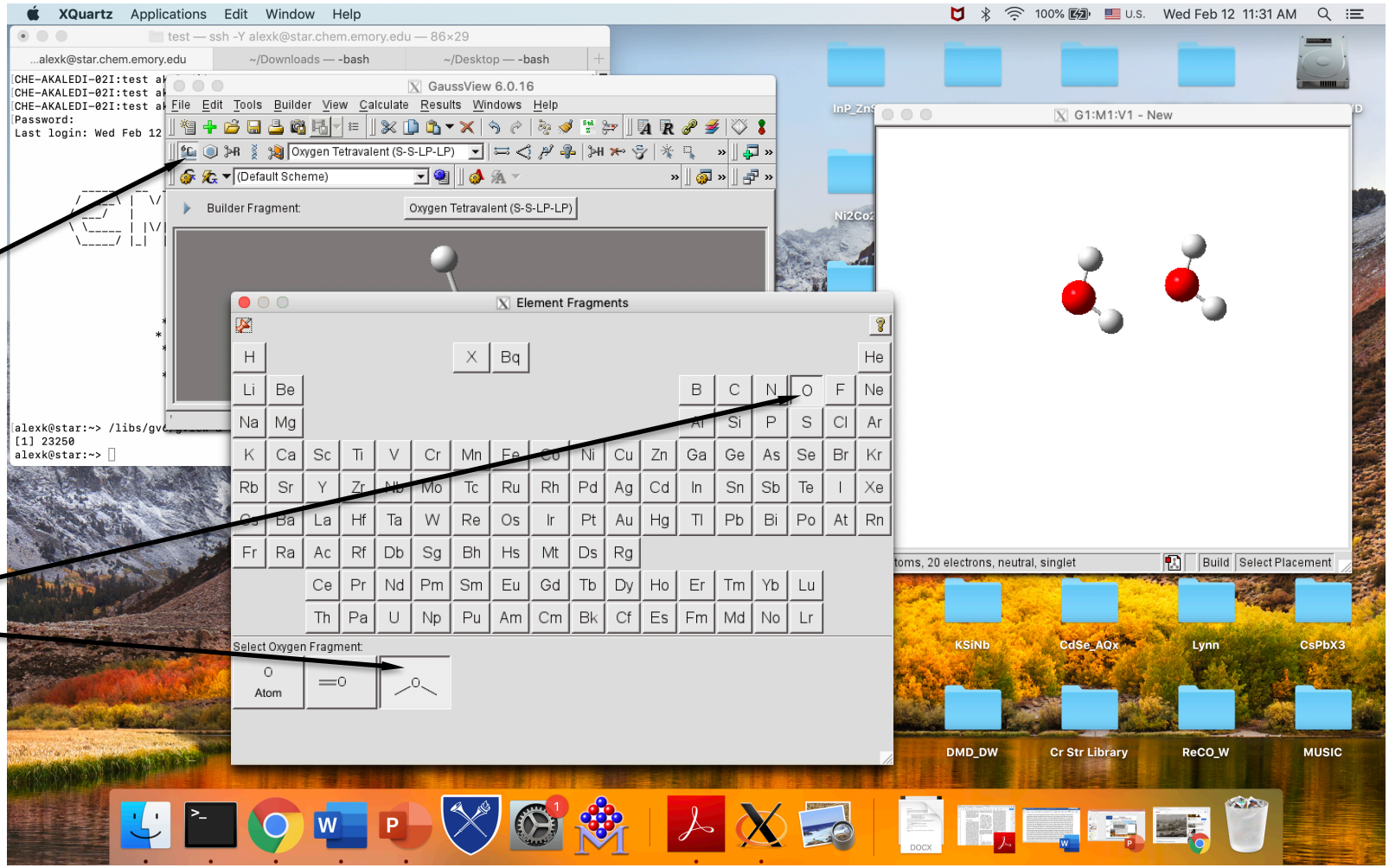


note the atom types and connectivities

standard information flow in AMBER



GaussView: making a water dimer



double click

choose *sp3* O

AMBER:
start GV + make water dimer

1) start GaussView; make water dimer using the “Fragment” Tool

   Calculate -> Gaussian Calculation Setup -> General
   deselect connectivity -> Retain

2) save file as Gaussian Input: File->Save water_dimer.gjf

3) MAC/PC USERS (command line method):

```
scp water_dimer.gjf eclab@euch4e.chem.emory.edu:./star/YOUR_ID/
```

   PC USERS (alternative method):
   Download and use WinSCP, an open source scp client
   https://winscp.net/eng/index.php

AMBER:
setup procedure on EC servers

4) ssh -Y eclab@euch4e.chem.emory.edu

```
/home/chemistry/ch_res/eclab/: ssh -Y star
eclab@star:~> cd YOUR_ID
eclab@star:~> ls
water_dimer.gjf
eclab@star:~> cat water_dimer.gjf
```

5) process GAUSSIAN INPUT into PDB using AMBER

```
> antechamber -i water_dimer.gjf -fi gcrt \

             -o water_dimer.pdb -fo pdb
```

AMBER: setup procedure on EC servers

6) generate atomic charges

```
> antechamber -i water_dimer.pdb -fi pdb \
              -o water_dimer.mol2 -fo mol2 -c bcc
```

7) check all parameters (any missing ones will be reported)

```
> parmchk -i water_dimer.mol2 -f mol2 -p \
  $AMBERHOME/dat/leap/parm/gaff.dat -o water_dimer.frcmod
```

AMBER:
setup procedure on EC servers

8) start TLEAP interface to make parameter and XYZ files:

water_dimer.prmtop -- parameter topology file
water_dimer.prmcrd -- initial XYZ file

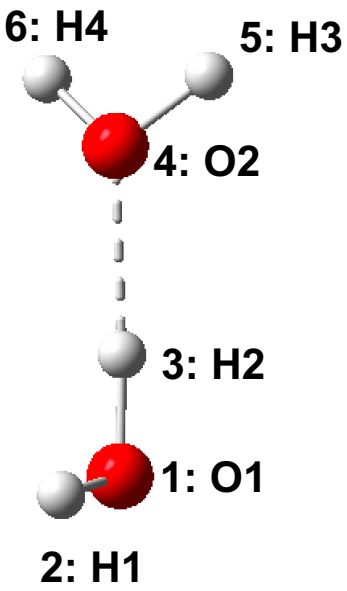
```
> tleap
  > source /libs/amber11/dat/leap/cmd/leaprc.gaff
  > file = loadMol2 water_dimer.mol2
  > loadAmberParams water_dimer.frcmod
  > saveAmberParm file water_dimer.prmtop water_dimer.prmcrd
  > Quit
```

AMBER atom type asignment: contents of **ATOMTYPE.INF** file

```
-ring property (III)-
atom[ 1] (O1  ) is not in any ring (nr[1]=1)
atom[ 2] (H1  ) is not in any ring (nr[2]=1)
atom[ 3] (H2  ) is not in any ring (nr[3]=1)
atom[ 4] (O2  ) is not in any ring (nr[4]=1)
atom[ 5] (H3  ) is not in any ring (nr[5]=1)
atom[ 6] (H4  ) is not in any ring (nr[6]=1)

-electronic property-
atom [ 1] (O1  ) is an electron-withdrew atom
atom [ 2] (H1  ) is not an electron-withdrew atom
atom [ 3] (H2  ) is not an electron-withdrew atom
atom [ 4] (O2  ) is an electron-withdrew atom
atom [ 5] (H3  ) is not an electron-withdrew atom
atom [ 6] (H4  ) is not an electron-withdrew atom

-connectivity property-
atom[ 1] (O1  )     2    H1
atom[ 1] (O1  )     3    H2
atom[ 2] (H1  )     1    O1
atom[ 3] (H2  )     1    O1
atom[ 4] (O2  )     5    H3
atom[ 4] (O2  )     6    H4
atom[ 5] (H3  )     4    O2
atom[ 6] (H4  )     4    O2
```



AMBER: internal structure of **.prmtop** file

```
%FLAG ATOM_NAME
%FORMAT(20a4)
O1  H1  H2  O2  H3  H4
%FLAG CHARGE  * 18.222
%FORMAT(5E16.8)
 -1.46507292E+01  7.32536460E+00  7.32536460E+00 -1.46507292E+01  7.32536460E+00
  7.32536460E+00
%FLAG MASS
%FORMAT(5E16.8)
  1.60000000E+01  1.00800000E+00  1.00800000E+00  1.60000000E+01  1.00800000E+00
  1.00800000E+00
%FLAG BOND_FORCE_CONSTANT  (kcal/mol)/Å²
%FORMAT(5E16.8)
  3.69600000E+02
%FLAG BOND_EQUIL_VALUE    Å
%FORMAT(5E16.8)
  9.74000000E-01
%FLAG ANGLE_FORCE_CONSTANT  (kcal/mol)/rad²
%FORMAT(5E16.8)
  4.19300000E+01
%FLAG ANGLE_EQUIL_VALUE   rad
%FORMAT(5E16.8)
  1.82910584E+00
%FLAG LENNARD_JONES_ACOEF
%FORMAT(5E16.8)
  5.81803229E+05  0.00000000E+00  0.00000000E+00
%FLAG LENNARD_JONES_BCOEF
%FORMAT(5E16.8)
  6.99746810E+02  0.00000000E+00  0.00000000E+00
%FLAG AMBER_ATOM_TYPE
%FORMAT(20a4)
oh  ho  ho  oh  ho  ho
```

GEOMETRY OPTIMIZATION

9) create/copy input, “min.in”, for structure optimization

```
cp ~/min.in ~/YOUR_ID
```

```
#title: optimization
&cntrl
maxcyc=1000, imin=1, cut=12.0, ntb=0, ntpr=1
```

10) perform a geometry optimization (command line interactive)

```
> sander -O -i min.in -o min.out -p water_dimer.prmtop \
          -c water_dimer.prmcrd -r water_dimer.xyz
```

MOLECULAR DYNAMICS

9b) create/copy input, “md.in”, for a molecular dynamics run

```
cp ~/md.in ~/YOUR_ID
```

```
#title: md run

&cntrl

imin=0, irest=0, cut=12.0, ntb=0,

nstlim=100000, dt=0.001,                femtosecond

ntt=2, tempi=300.0, temp0=300.0,         Kelvin

ntpr=10,ntwx=10
```

MOLECULAR DYNAMICS

10b) perform an MD simulation (command line interactive)

```
> sander -O -i md.in -o md.out -p water_dimer.prmtop \
  -c water_dimer.prmcrd -r water_dimer.xyz -x water_dimer.crd
```

Using the queue for larger MD jobs

```
#!/bin/ksh
# @ initialdir = /star/chemistry/ch_res/eclab/YOU
# @ requirements = (Arch == "R6000") && (OpSys == "AIX53")
# @ class = stars
# @ notify_user = YOUR_ID@emory.edu
# @ group = ch_res
# @ error = error
# @ queue
#
sander -O -i md.in -o md.out -p water_dimer.prmtop -c
water_dimer.prmcrd -r water_dimer.xyz -x water_dimer.crd
```

Visualization & Analysis

- Visual Molecular Dynamics **VMD** (UIUC by K. Schulten & group)
- Spectral densities
- Radial Distribution Functions
- X11 graphics session...

Starting Graphics Session on STAR

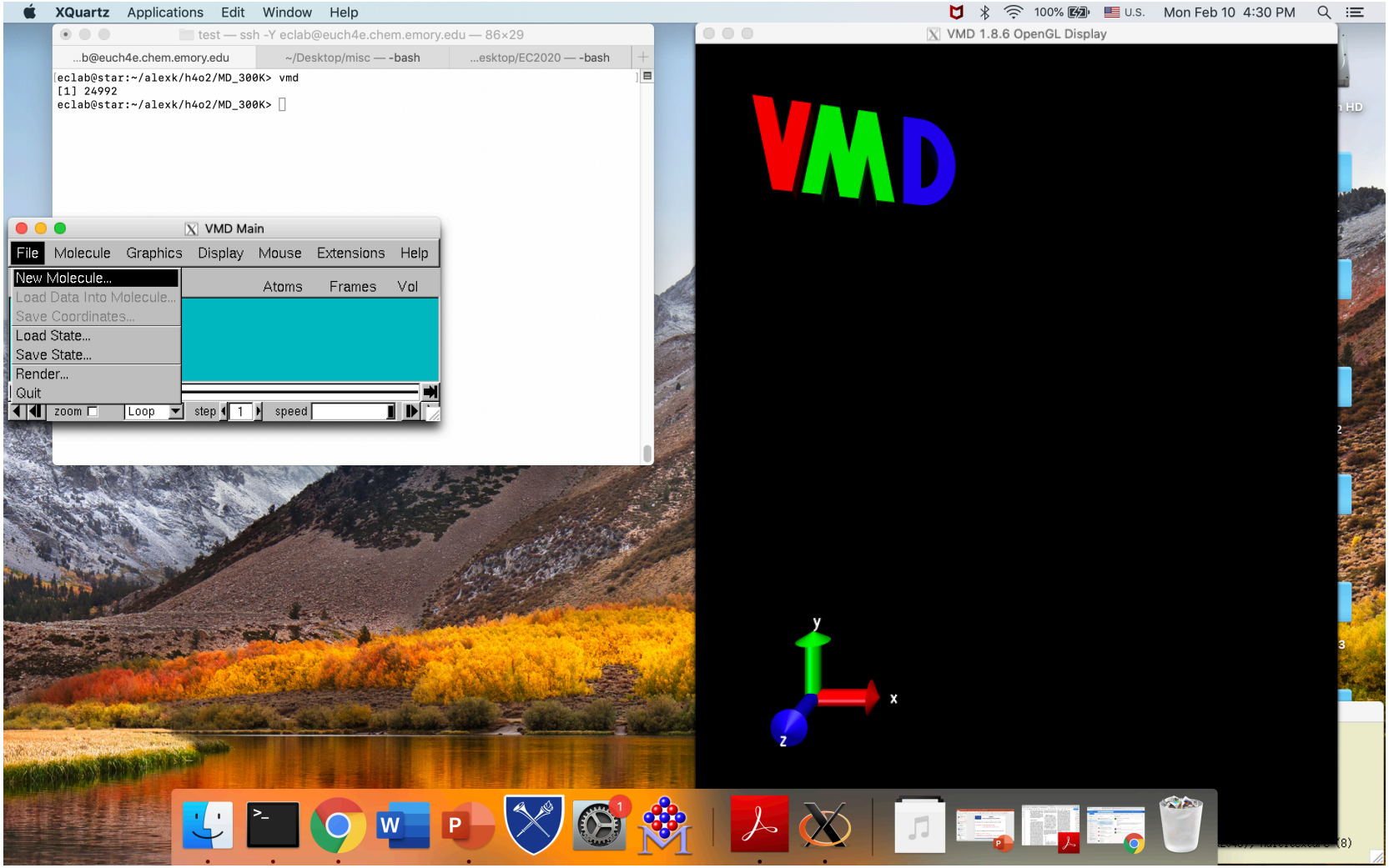
- MAC users: Xquartz 2.7.8 recommended

  www.xquartz.org/releases/index.html

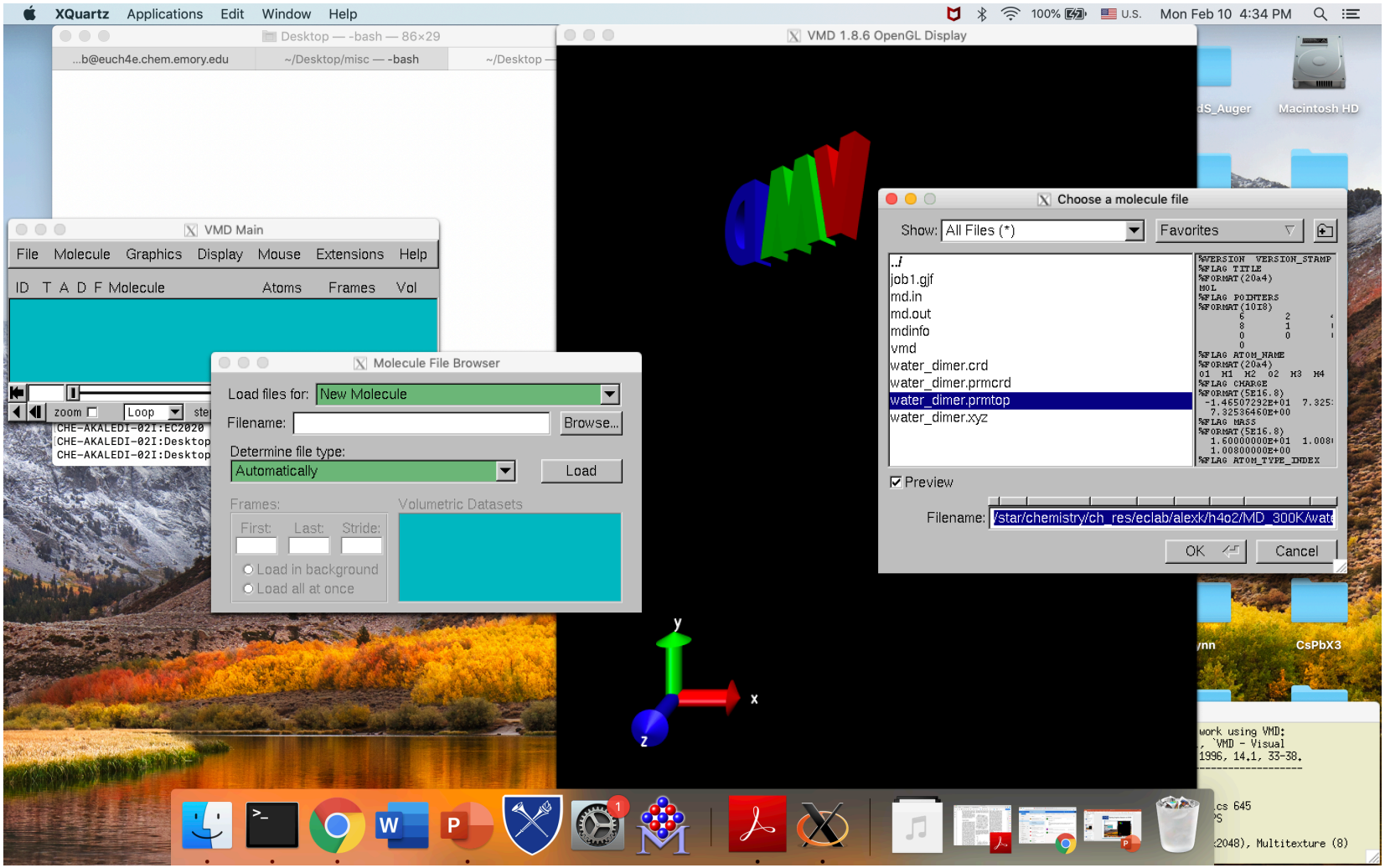
- PC users: Xlaunch or Xming

> vmd

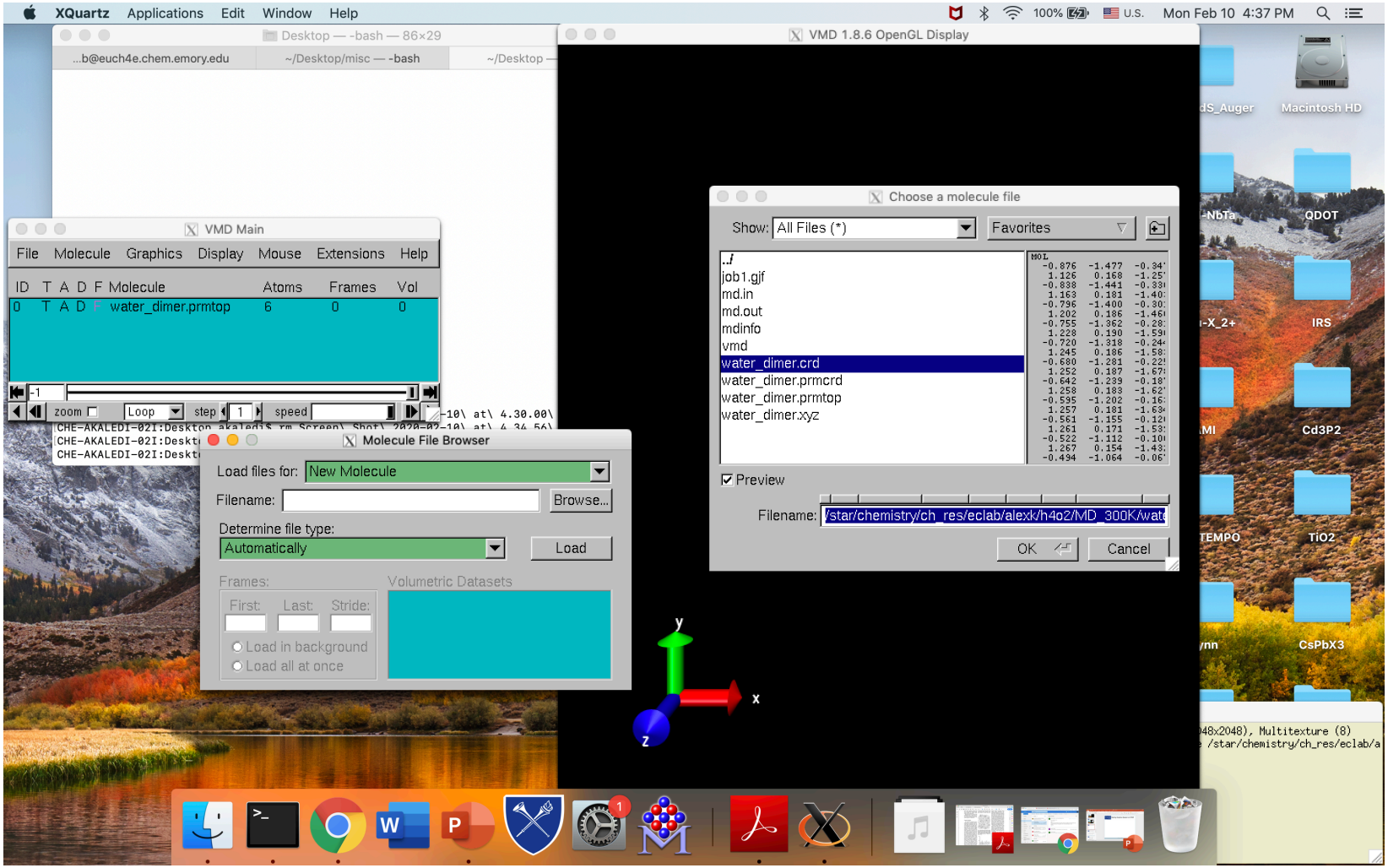
VMD Session on STAR defining a New Molecule



VMD Session on STAR loading parameters



VMD Session on STAR loading trajectory

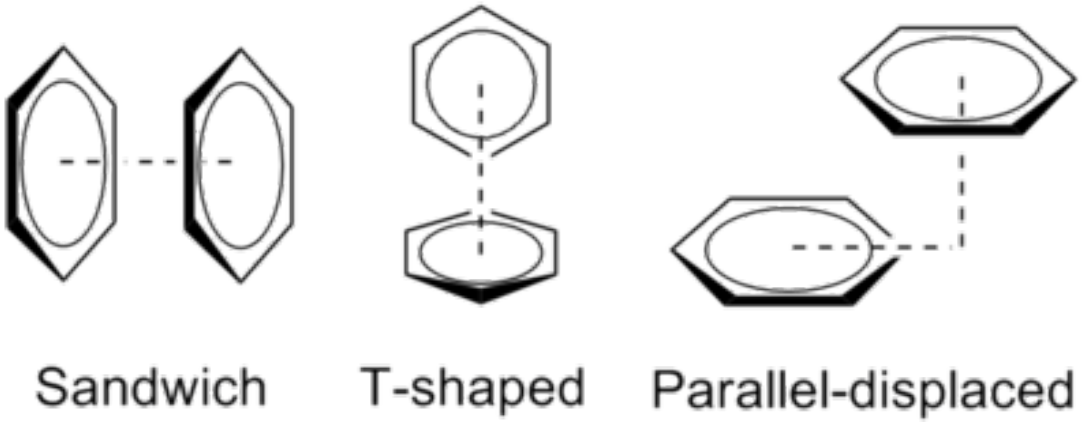


Part II: other applications

- The challenge of π-π stacking interactions

- Advanced Methods of Structure search

Exemplary π-π stacking interactions



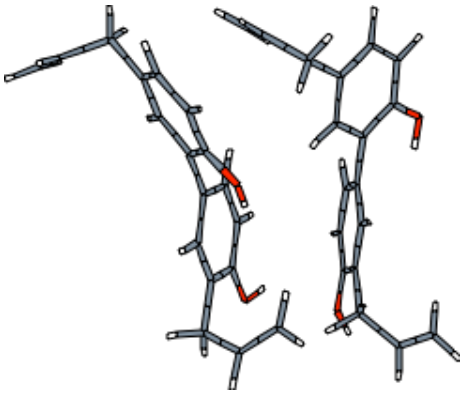
The dominant component of fragment interaction energy is the dipole induction, also known as electrostatic dispersion.

These interactions are described by dynamically correlated methods (CI/MP2) while a generic DFT fails to yield a correct description.

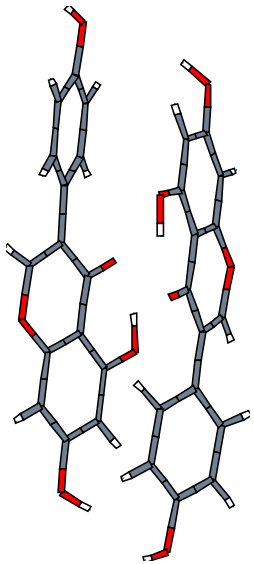
On the other hand, the **non-bonding** potentials parameterized in AMBER provide a remarkably accurate description of the above systems.

examples of π-π stacking systems calculated with AMBER

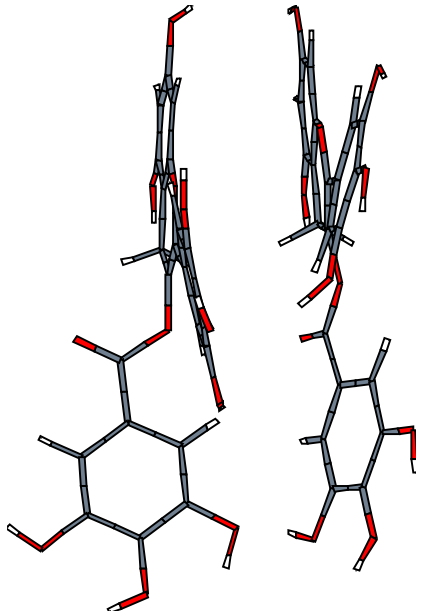
dimer-A



dimer-B



dimer-C



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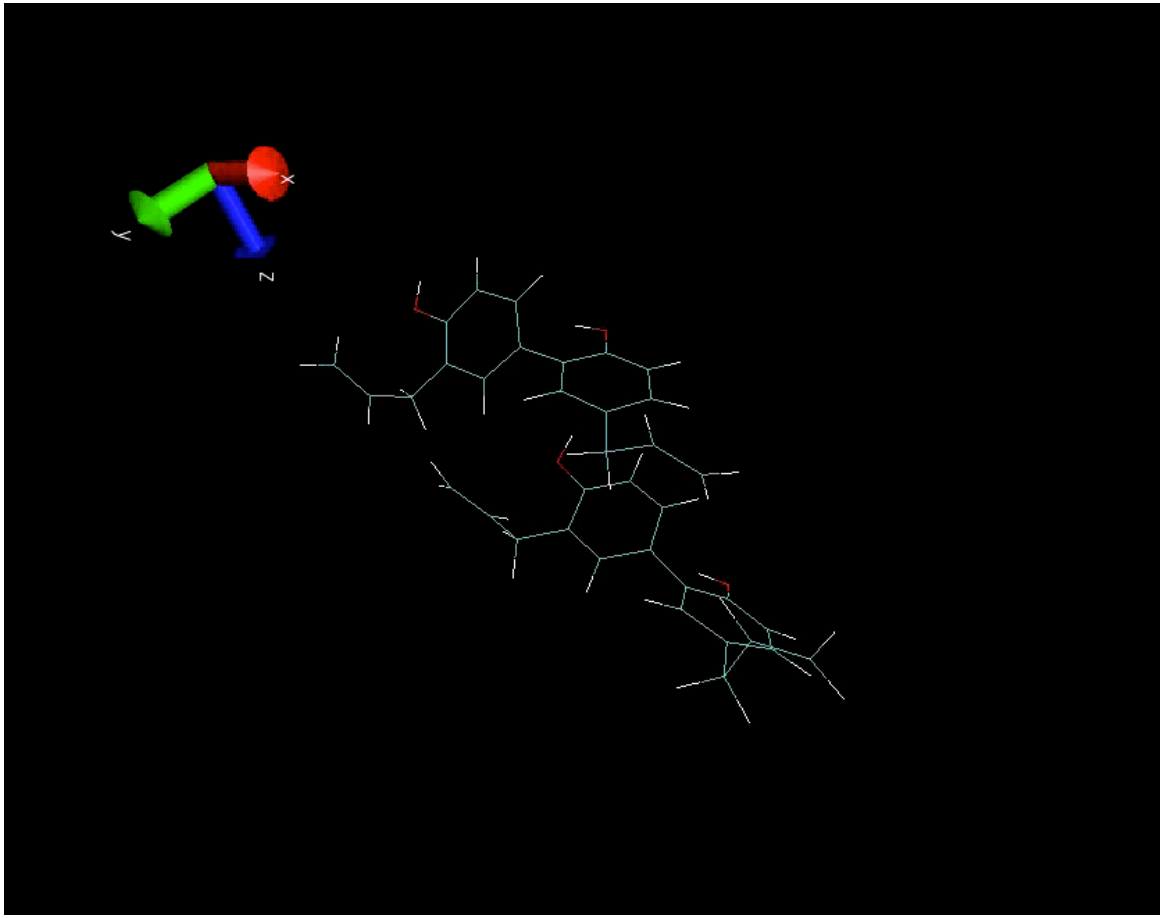
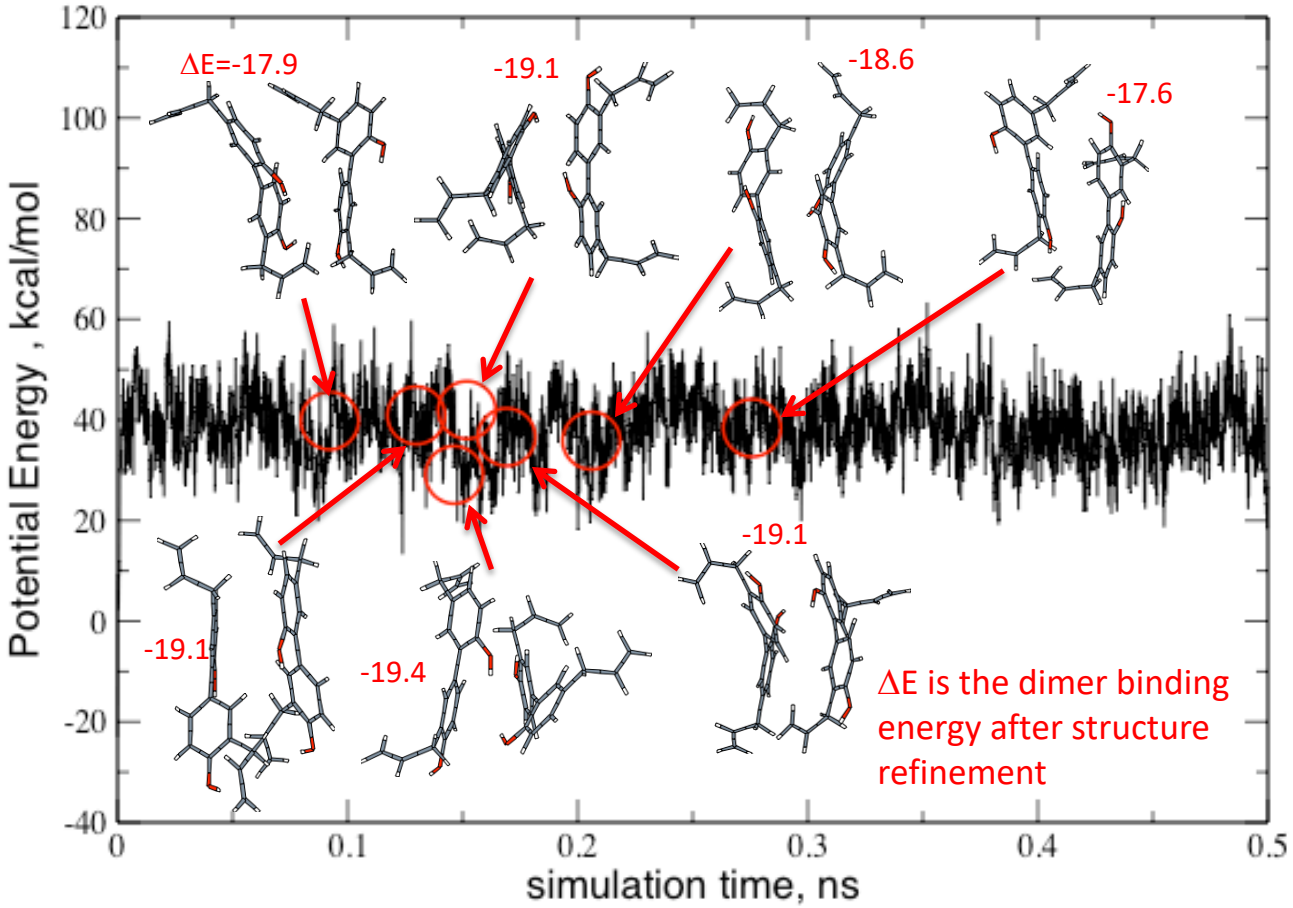
visualization of the molecular dynamics of dimer-**C** in gas phase at 300K



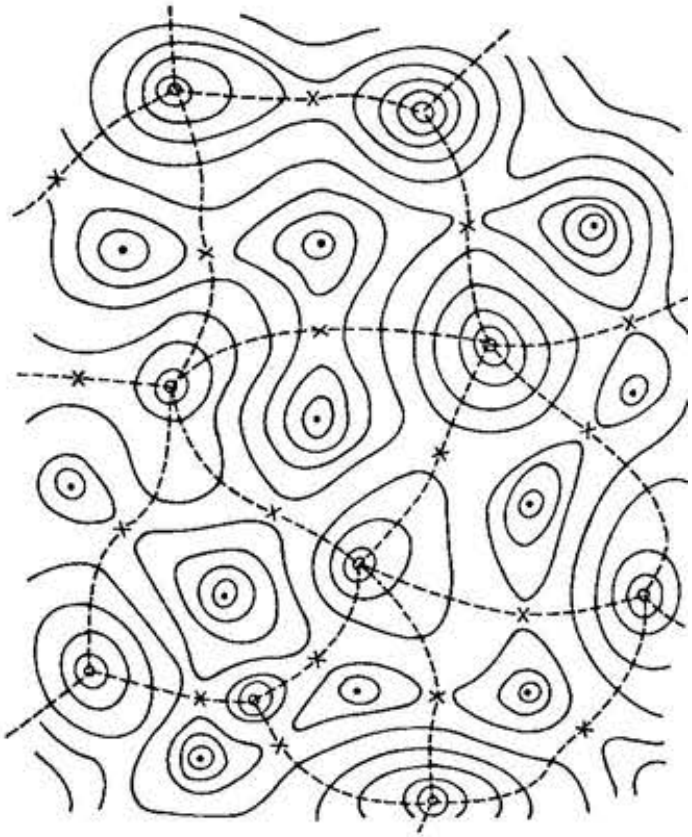
Analysis of the molecular dynamics of dimer-**C** in gas phase at 300K



Improved search techniques

- MD trajectories tend to ”fly over” low energy structures due to inertia (kinetic energy)
- Thus, long time propagation is required to find low energy structures
- Long-time MD may be computationally prohibitive
- What other methods may avoid this problem?

Potential Energy "Landscape"



Schematic representation of the potential energy surface for an N-atom system.

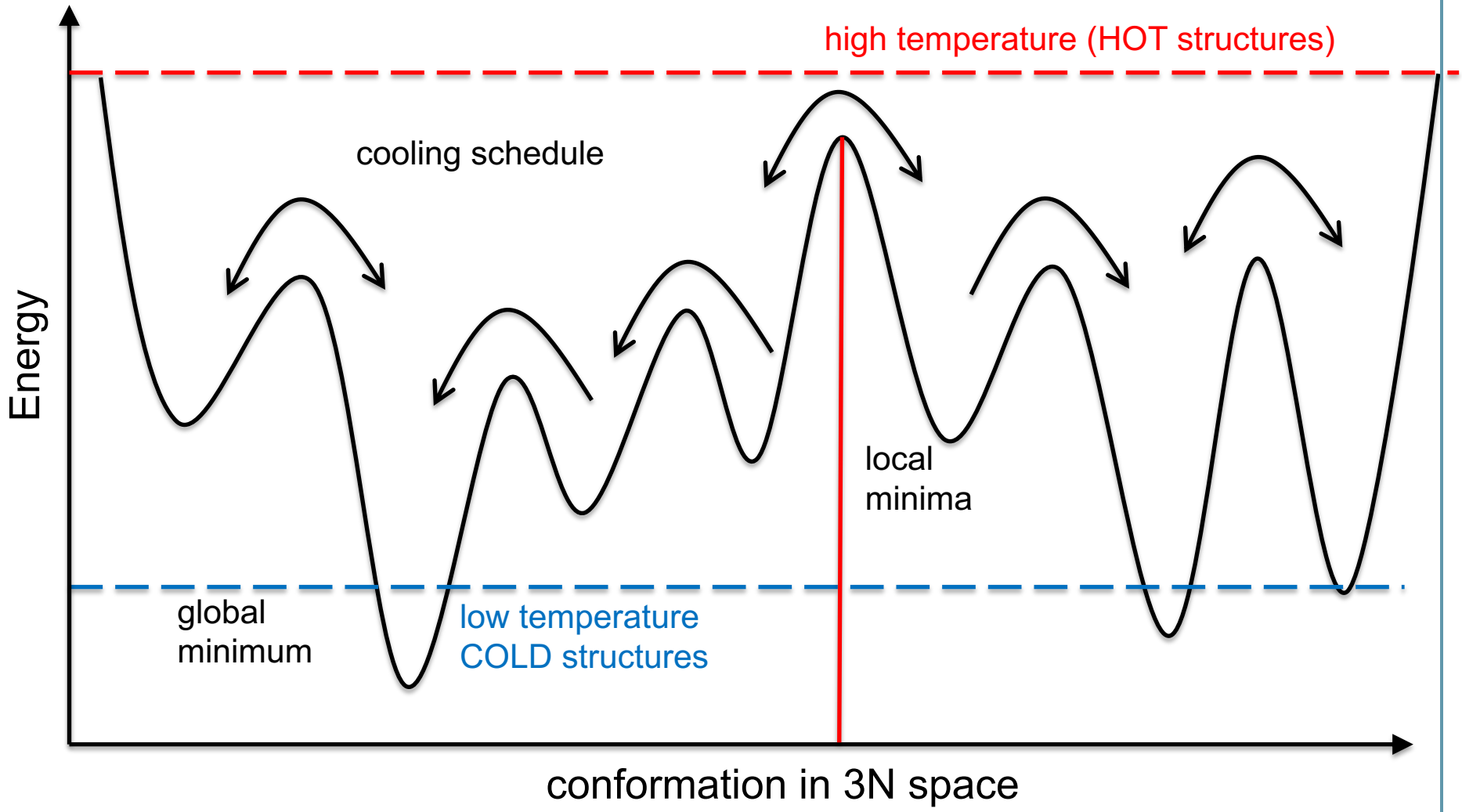
Minima are shown as filled circles and saddle points as crosses.

Potential energy is constant along the continuous curves.

Regions belonging to different minima are indicated by dashed curves.

F. H. Stillinger, T. A. Weber "Packing Structures and Transitions in Liquids and Solids" *Science* 225, 983-989, 1984.

Monte Carlo (MC) methods: simulated annealing (SA) MD search



multichannel SA-MD MC search

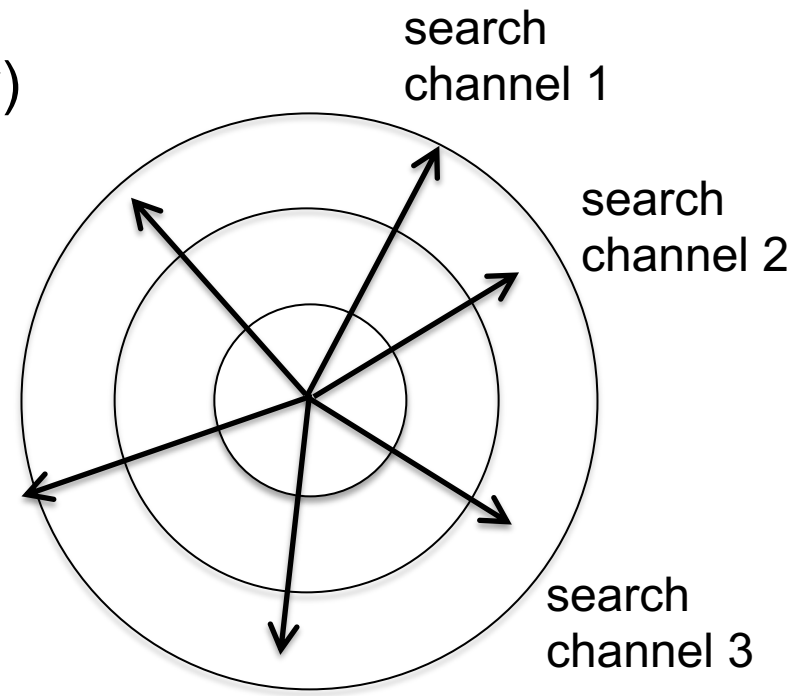
1) start at some initial (high E) structure

2) send out a random trajectory (arrow)

3) heat system to 500 - 600K

4) cool gradually to 0K

5) a final set of structures will be a good sample of low energy minima



Summary of Amber MM tools

- AMBER's versatile definitions allow to set up calculations of general molecular systems
- MD simulations are easily run for all typical ensembles
- Systems of 10^4-10^5 order of atoms are possible to model
- Visualization and analysis is performed with VMD
- Advanced Monte Carlo techniques allow for extensive Energy Landscape exploration