Toward a multilevel QM/MM methodology for performing molecular dynamic simulations of complex reactive processes

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Outline

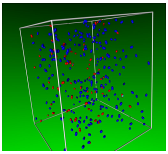
- Context and motivation
- Overview of complex reactions
- Challenges/Opportunities of complex chemical reactions
- Time-dependent group methodology
- Accelerated MD with Chemistry (***AMolDC***) outline
- Illustrative simulations
- Computational scaling
- Summary

Context/Motivation of Research

How can we take first principles (*ab initio*) methods for the molecular dynamics (MD) simulations of:

$A + BC \rightarrow$	$BC' + A'$	
	$AB + C$	**3 atoms**
	$AC + B$	**6 species**
	$A + B + C$	**5 channels**
	ABC	

and extend it to:



$C_2H_4 + O_2 \rightarrow$ **products**

or

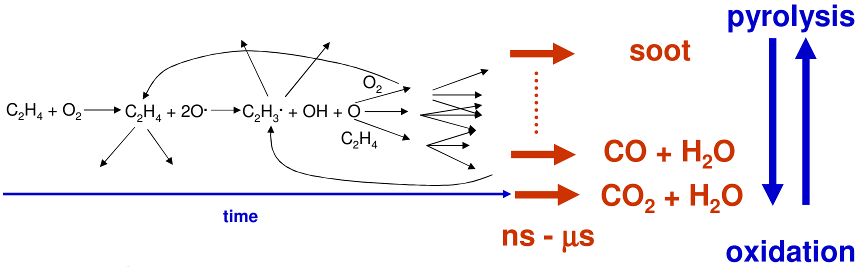
$HMX(\beta) \rightarrow HMX(\delta)$

$HMX(\delta) \rightarrow HMX(NO_2)$

$HMX(NO_2) \rightarrow N_2O + NO + CO +$ **(intermediate products)**

$N_2O + NO + CO \rightarrow N_2 + CO_2 +$ **(final gas products)**

Overview of Complex Reactions



$C_2H_4 + O_2 \rightarrow C_2H_4 + 2O\cdot \rightarrow C_2H_3\cdot + OH + O$

O_2

C_2H_4

soot

$CO + H_2O$

$CO_2 + H_2O$

time

ns - µs

pyrolysis

oxidation

~10^2 elementary steps

exponential growth of species with steps: OH, C_2H_3, C_2H_3OO, H_3CCH_2, …

~10^3 unique chemical species

Combustion and detonation processes
Oxidation and pyrolysis of fuels
HMX/RDX decomposition

Current Theory (Kinetics)

- postulated kinetic mechanism
- fit rate constants **or**
- experiments of elementary reactions **or**
- *ab initio* MD **or**
- transition state theory

J. Phys. Chem. A, Vol. 101, No. 20, 1997 **3733**

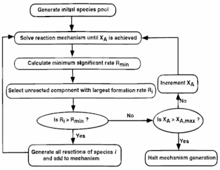


Figure 2. Flow diagram illustrating the iterative reaction scheme generation.

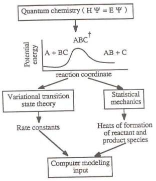


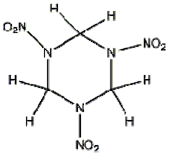
Fig. 1 Schematic representation of link between first-principles quantum chemistry and combustion modeling input.

```
REACTIONS
!
! H2,O2, H,OH and O reactions
!
H2+OH=H2O+H           2.14E8    1.51     3430.0 ! [Emdee et al. 1992]
H2+O2=OH+OH          1.70E13     0.0    47780.0 ! [Miller and Melius
1992]
H+O2=OH+O           1.91E14     0.0    16440.0 ! [Emdee et al. 1992]
H+O2+M=HO2+M          1.41E18   -0.80       0.0 ! [Baulch et al. 1994]
for N2
  H2/1.25/  H2O/6.0/  CO2/1.90/            ! relative to N2, based on Baulch
et al. 1972
2H+M=H2+M           1.00E18    -1.0       0.0 ! [Miller and Melius 1992]
2H+H2=2H2          9.20E16    -0.6       0.0 ! [Miller and Melius 1992]
2H+H2O=H2+H2O         6.00E19   -1.25       0.0 ! [Miller and Melius
1992]
2H+CO2=H2+CO2         5.49E20    -2.0       0.0 ! [Miller and Melius
1992]
H+OH+M=H2O+M          2.21E22    -2.0       0.0 ! [Baulch et al. 1992] for
N2
  H2/1.25/  H2O/6.0/  CO2/1.90/            ! relative to N2, based on Baulch
et al. 1972
H+O+M=OH+M           6.02E16    -0.6       0.0 ! [Miller and Melius 1992]
  H2O/5.0/
OH+H2O2=H2O+HO2       7.08E12     0.0     1430.0 ! [Emdee et al.
1992]
OH+OH=O+H2O          1.23E4     2.62    -1878.0 ! [Emdee et al. 1992]
O+HO2=OH+O2          1.74E13     0.0     -400.0 ! [Emdee et al. 1992]
O+H2=OH+H           5.13E4     2.67     6290.0 ! [Emdee et al. 1992]
O+O+M=O2+M           5.04E13     0.0    -1790.0 ! [Tsang and Hampson
1986] corrected for N2
  H2/1.25/  H2O/6.0/  CO2/1.90/            ! relative to N2, based on Baulch
et al. 1972
O+OH+M=HO2+M          1.00E17     0.0       0.0 ! [Zhang and McKinnon
1995]
!
!
! HO2 peroxyl reactions
!
HO2+H=H2O+O          3.00E13     0.0     1070.0 ! [Baulch et al. 1992]
HO2+H=H2+O2          6.61E13     0.0     2130.0 ! [Emdee et al. 1992]
HO2+H=OH+OH          1.40E14     0.0     1073.0 ! [Miller and Melius
1992]
HO2+OH=H2O+O2         7.50E12     0.0       0.0 ! [Miller and Melius
1992]
HO2+HO2=H2O2+O2       2.00E12     0.0       0.0 ! [Miller and Melius
1992]
!
!
! H2O2 reactions
!
H2O2+M=OH+OH+M        1.21E17     0.0    45510.0 ! [Baulch et al.
1992] for N2
  H2/1.25/  H2O/6.0/  CO2/1.90/            ! relative to N2, based on Baulch
et al. 1972
H2O2+H=HO2+H2         4.79E13     0.0     7950.0 ! [Emdee et al. 1992]
H2O2+H=OH+H2O         1.00E13     0.0     3590.0 ! [Emdee et al. 1992]
H2O2+O=OH+HO2         9.55E6      2.0     3970.0 ! [Emdee et al. 1992]
H2O2+O=O2+H2O         9.55E6      2.      3970.0 ! [Emdee et al. 1992]
!
!
```

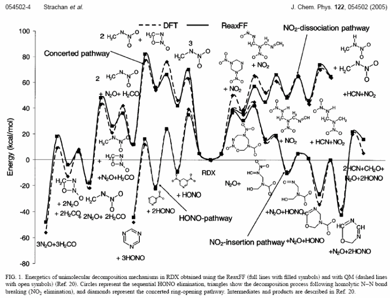
Current Theory (Dynamics)

Classical MD simulations with ReaxFF for potential

RDX decomposition



products



054502-4 Strachan *et al.* J. Chem. Phys. **122**, 054502 (2005)

FIG. 1. Energetics of unimolecular decomposition mechanisms in RDX obtained using the ReaxFF (full lines with filled symbols) and with QM (dashed lines with open symbols) (Ref. 20). Circles represent the sequential HONO elimination, triangles show the decomposition process following homolytic N–N bond breaking (NO_2 elimination), and diamonds represent the concerted ring-opening pathway. Intermediates and products are described in Ref. 20.

RDX/Estane decomposition

Challenges/Opportunities of MD Studies

Challenges for *ab initio* MD studies:

1. System Size
   - ~10^3 unique species
   - NAtoms ~10^3
2. PESs
   - Reactive and non-reactive PESs
   - large dimensionality
3. Time Scale
   - ns → μs

Opportunities:

1. Mechanism
   - Species
   - Branching ratios
2. Kinetics
   - Dynamics determining kinetics rather than kinetics determining dynamics
3. Energetics

Bath gas collisional processes

O_2—O_2, CO—CO_2, …

Reactive processes

$C_2H_3 + O_2 \rightarrow C_2H_3O_2$, …

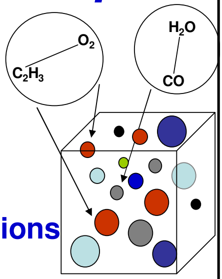
$$\frac{\partial E_e}{\partial x_i} = tr\left\{P \cdot \left[2T' + 2V'_{n,e} + J' + K'\right] - 2S'PFP\right\} + V'_{n,n}$$

Computational scaling factors: *O(N)* to *O(N^7)*

$N_{evaluations}$ ~ 1×10^5 for 100 ps

MD by Time Dependent Groups

$$V_{Total}(t) = \underbrace{\sum_{i}^{group} \sum_{\alpha}^{N_i} V_{i\alpha}(t)} + \underbrace{\frac{1}{2} \sum_{l}^{group} \sum_{\alpha}^{N_l} \sum_{m \neq l}^{group} \sum_{\beta}^{N_m} V_{l\alpha,m\beta}(t)}$$



Group interactions
(QM/QM/QM…)

- Governed by spatial cutoffs
- Differing levels of *ab initio* theory over differing groups

  - ➢ Fast-access PES database
  - ➢ Interpolation

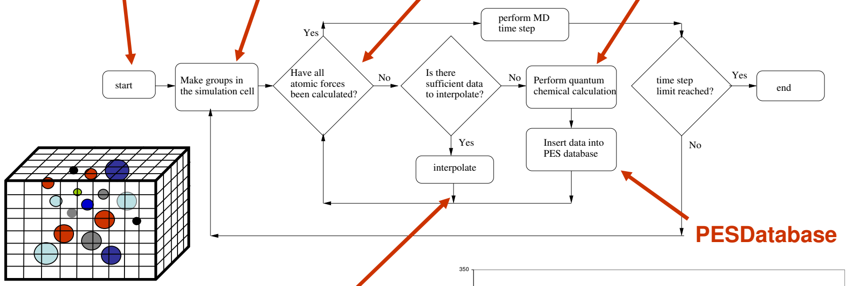
Group-group interactions
(MM)

- Outside of spatial cutoffs
- Less important to reactive systems

  - ➢ force fields
  - ➢ low level *ab initio*

Salazar, M.R. J. Phys. Chem. A **2005, *109*, 11515.**

Accelerated MD with Chemistry (AMolDC)



Input initial coordinates, T, and P

MakeGroups

Sum over groups

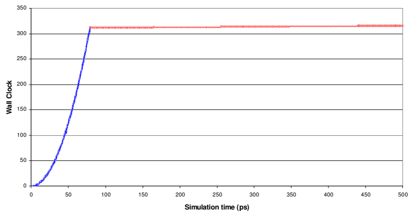
Direct dynamics

PESDatabase

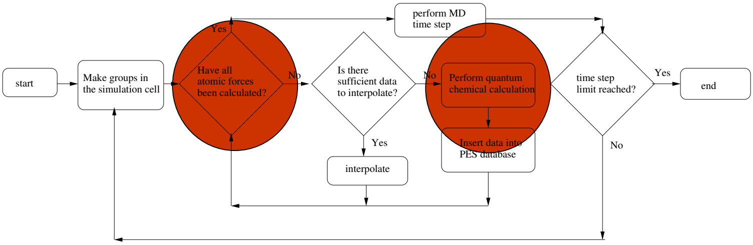
Link-listed subcells

Interpolation

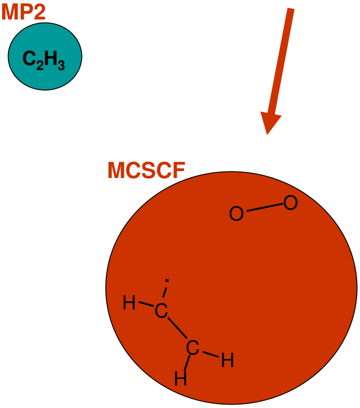
$$V_{Total}(t) = \sum_{i}^{group} \sum_{\alpha}^{N_i} V_{i\alpha}(t) + \frac{1}{2} \sum_{l}^{group} \sum_{\alpha}^{N_l} \sum_{m\neq l}^{group} \sum_{\beta}^{N_m} V_{l\alpha,m\beta}(t)$$

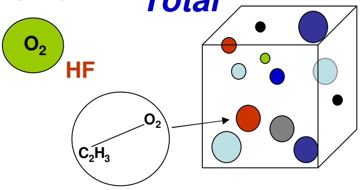


Calculate Forces



Discontinuities of V_{Total}

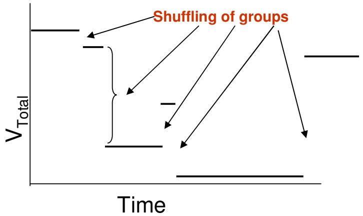




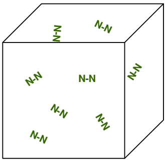
at spatial cutoff

$V(C_2H_3) + V(O_2) \neq V(C_2H_3 + O_2)$, but

$\nabla V \approx 0$,therefore, $\Delta T \approx 0$

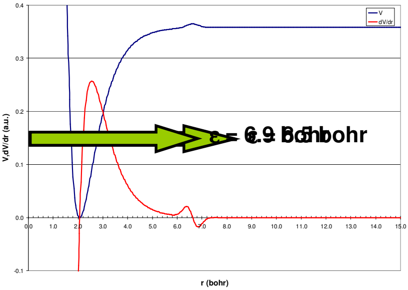


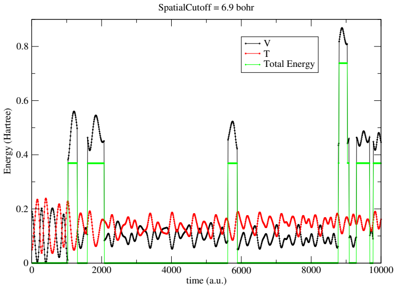
Illustrative Simulations



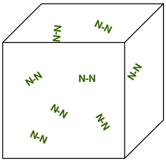
N_2 system
Reflective walls
Variable simulation cell size
T=1000K
P~10^3 atm
Variable spatial cutoff (ε)

N_{Atoms} = 12, P~1.3×10^3 atm



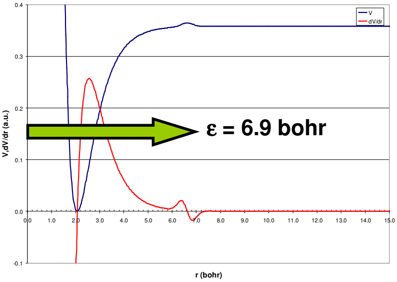


Illustrative Simulations (cont.)

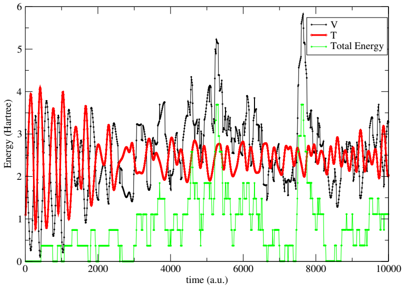


N_2 system
Reflective walls
Variable simulation cell size
T=1000K
P~10^3 atm
Variable spatial cutoff (ε)

N_{Atoms} = 300, P~1.3×10^3 atm

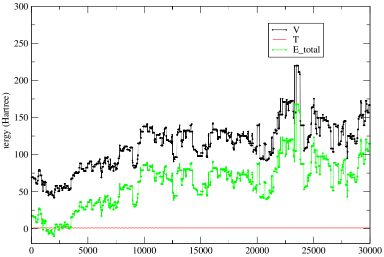

ε = 6.9 bohr

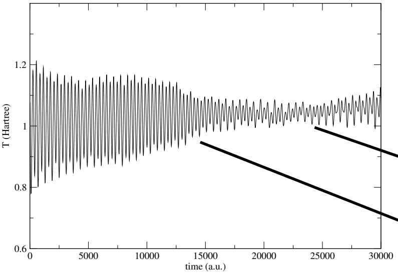
Spatial Cutoff = 6.9 bohr



Canonical (NVT) Simulations

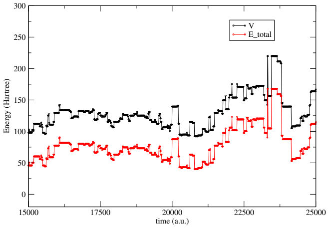
220 Atom simulation
P ~ 1000 atm
T = 1000 K
Time step = 0.25 fs

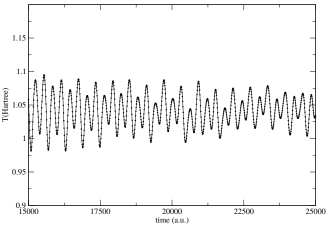


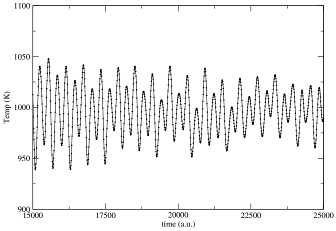


Focus on thermalized region

Canonical (NVT) Simulations

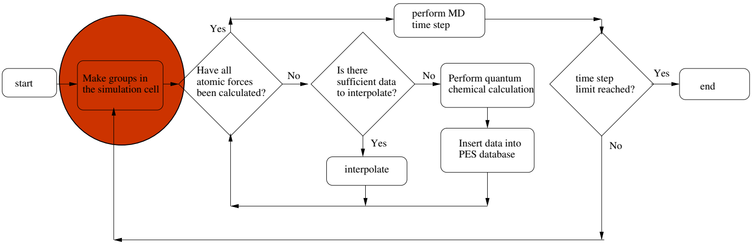






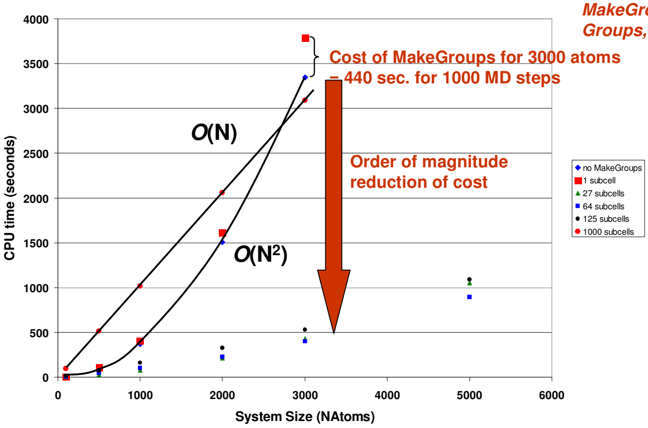
Exceedingly discontinuous potential and total energy;
however,
smooth and continuous kinetic energy,
smooth and continuous temperature,
and, therefore,
canonical (NVT) simulations.

MakeGroups


start
Make groups in the simulation cell
Have all atomic forces been calculated?
Yes
No
perform MD time step
Is there sufficient data to interpolate?
No
Yes
interpolate
Perform quantum chemical calculation
Insert data into PES database
time step limit reached?
Yes
No
end

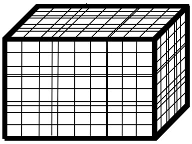
Computational Scaling of MakeGroups Module

MakeGroups(NSubCells,NGroups, Groups,Members)

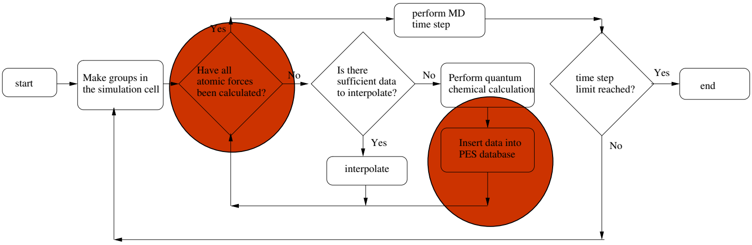


Cost of MakeGroups for 3000 atoms = 440 sec. for 1000 MD steps

Order of magnitude reduction of cost



PESDatabase



start

Make groups in
the simulation cell

Have all
atomic forces
been calculated?

Yes

No

Is there
sufficient data
to interpolate?

No

Yes

interpolate

Perform quantum
chemical calculation

Insert data into
PES database

perform MD
time step

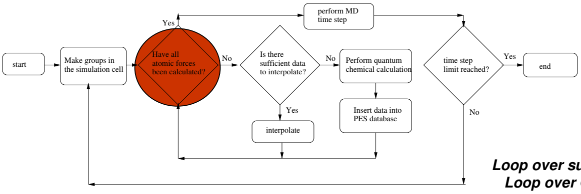
time step
limit reached?

Yes

No

end

PESDatabase Module



start

Make groups in the simulation cell

Have all atomic forces been calculated?

Yes

No

Is there sufficient data to interpolate?

No

Yes

interpolate

Perform quantum chemical calculation

Insert data into PES database

perform MD time step

time step limit reached?

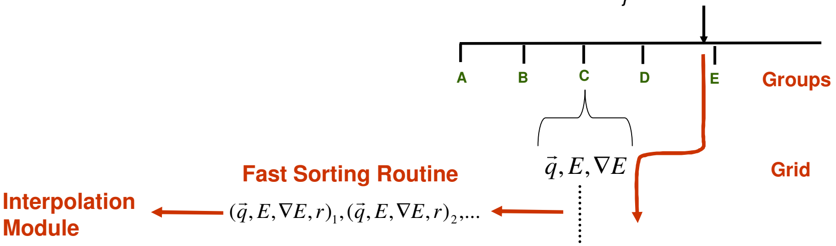
Yes

No

end

```
Loop over subcells {
   Loop over Groups in subcells {
      $\vec{q}(P; Group = C_2H_3O)$
   }
}
```

PESDatabase for Complex Systems



A B C D E

Groups

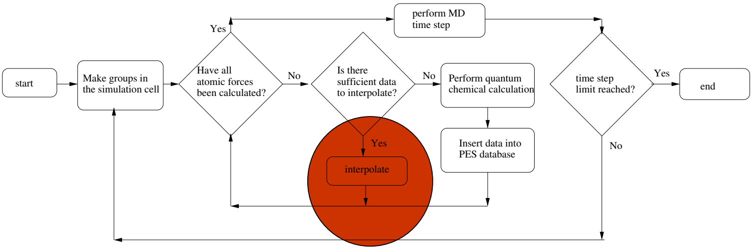
$\vec{q}, E, \nabla E$

Grid

Fast Sorting Routine

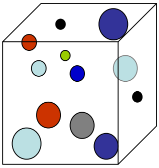
$(\vec{q}, E, \nabla E, r)_1, (\vec{q}, E, \nabla E, r)_2, \ldots$

Interpolation Module



Interpolation

Interpolation Methodology Challenges



- **diverse interactions**
  - **collisional processes**
  - **reactive processes**
- **diverse chemical species**
  - **free radicals**
  - **excited electronic states**
  - **closed shell species**
- **diverse PES topologies**
  - **flat asymptotic region**
  - **barriers, TS regions**
- **diverse grid spacings**

Solution:

Completely general adaptive interpolation methodology

Local, Optimized Interpolants

Local vs. global interpolation

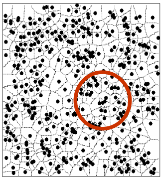


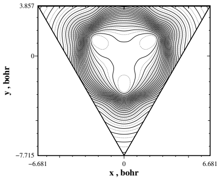
Fig. 2, M. Salazar

$$E(p)=\sum_{i=1}^{N} c_i\left[d_{ip}{}^2+r\right]^{\frac{1}{2}}$$

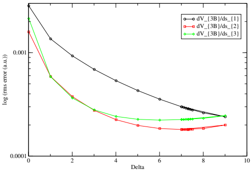
$$\begin{bmatrix}\sqrt{d_{11}^2+r} & . & . & \sqrt{d_{1N}^2+r}\\ & . & & \\ & & . & \\ \sqrt{d_{N1}^2+r} & & & \sqrt{d_{NN}^2+r}\end{bmatrix}\begin{bmatrix}c_1\\ .\\ .\\ c_N\end{bmatrix}=\begin{bmatrix}E_1\\ .\\ .\\ E_N\end{bmatrix}$$

speed vs. accuracy

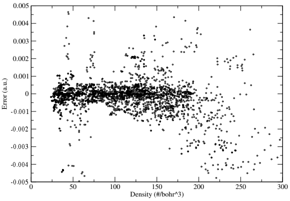
Optimization of local interpolants



M.R. Salazar, *Chem. Phys. Lett.*, 359, 460 (2002).



F. Colavecchia, W.J. Stevens, J.P. Burke, M.R. Salazar, G.A. Parker, and R.T Pack, *J Chem. Phys.*, 118, 5484 (2003).



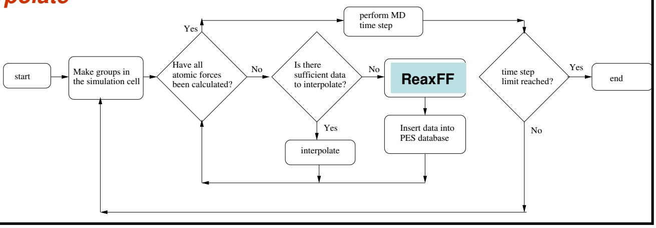
Highly repulsive $Al^+ + H_2$

ReaxFF with AMolDC

Need a smooth FF that can facilitate reactive events
Link ReaxFF with PESDatabase and interpolation

Investigations:

1. **Accuracy of interpolants as function of:**
   - **Dimensionality**
   - **Grid density**
2. **Computational timings of:**
   - ***PESDatabase***
   - ***Interpolate***

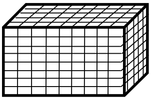


Summary

1. **Reactive PESs**
   - Varying levels of theory that **change over the groups (QM/QM/QM…/MM)**
   - Reactive → higher levels
   - Collisional → lower levels

$$V_{Total}(t) = \sum_{i}^{group} \sum_{\alpha}^{N_i} V_{i\alpha}(t) + \frac{1}{2} \sum_{l}^{group} \sum_{\alpha}^{N_l} \sum_{m \neq l}^{group} \sum_{\beta}^{N_m} V_{l\alpha,m\beta}(t)$$

2. **System Size**
   - Assembly of total potential by time-dependent groups
   - *MakeGroups*
     - Linked-listed subcell division
   - *PESDatabase*



3. **Time Scale**
   - *PESDatabase*
   - *Interpolate*
     - Multidimensional, local, optimized interpolants