# Parameterization of a reactive force field using a Monte Carlo algorithm

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Particular Strength Strengt

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TU

### Thermochemical energy storage



Energy storage density of thermochemical materials is about 10 times higher than that of water.



# Thermochemical energy storage

Problem: Changes in the crystallinity of the material, Slow kinetics, Reusability etc.



Dehydration

Hydration





# Thermochemical energy storage



#### ► Aim:

- · To study hydration and dehydration reactions
- To characterize the structural changes
- To understand the mechanism of water release during dehydration



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# **Molecular dynamics**

- Atoms are assumed to be point mass particles which obey Newton's laws of motion
- All particles interact with each other through some potential,  $U(r_1, r_2, \cdots, r_N)$
- Force acting on any particle at any time is calculated as,  $F = -\nabla U(r_1, r_2, \cdots r_N)$
- Positions are updated by integrating the equation of motion, F = ma

Force Field

Energy,  $E = E(r_1, r_2, \cdots r_N)$ 

Force,  $F = -\nabla E(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ 

### Condensed water between two Pt slabs



Details: NVT ensemble,  $\rho_{water} = 1001.22 kg/m^3$ 



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# ReaxFF force field

$$E_{system} = E_{vdWaals} + E_{Coulomb} + E_{bond} + E_{val} + E_{tors}$$
$$+ E_{over} + E_{under} + E_{H-bond} + E_{lp}$$
$$+ E_{conj} + E_{pen} + E_{coa} + E_{C2} + E_{triple}$$

#### Characteristics of ReaxFF

- Dynamic charges are calculated using EEM
- van Der Waal's interaction is calculated using a Morse-type potential
- Energy surface is made continuous
- Connected interactions include
  - Bonded interaction (two body)
  - Valence angle interaction (three body)
  - Torsion interaction (four body)
  - Hydrogen bond interaction





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### What makes ReaxFF reactive?

- ReaxFF calculates bond order between every pair of atoms
- Bond order is a function of distance of separation
- Every connected interaction is made a function of this bond order
- Thus all the bonds become dynamic

$$\begin{split} \mathrm{BO}_{\mathrm{ij}}^{\prime} = & \mathrm{BO}_{\mathrm{ij}}^{\prime\sigma} + \mathrm{BO}_{\mathrm{ij}}^{\prime\pi} + \mathrm{BO}_{\mathrm{ij}}^{\prime\pi\pi} \\ = & \exp\left[\mathrm{P}_{\mathrm{bo1}} \cdot \left(\frac{\mathrm{r}_{\mathrm{ij}}}{\mathrm{r}_{\mathrm{o}}^{\sigma}}\right)^{\mathrm{P}_{\mathrm{bo2}}}\right] + \exp\left[\mathrm{P}_{\mathrm{bo3}} \cdot \left(\frac{\mathrm{r}_{\mathrm{ij}}}{\mathrm{r}_{\mathrm{o}}^{\pi}}\right)^{\mathrm{P}_{\mathrm{bo4}}}\right] \\ & + \exp\left[\mathrm{P}_{\mathrm{bo5}} \cdot \left(\frac{\mathrm{r}_{\mathrm{ij}}}{\mathrm{r}_{\mathrm{o}}^{\pi\pi}}\right)^{\mathrm{P}_{\mathrm{bo6}}}\right] \end{split}$$



# Bond energy in Reax force field

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Bond energy

$$\begin{split} \mathbf{E}_{bond} = & -\mathbf{D}_{e}^{\sigma} \cdot \mathbf{BO}_{ij}^{\sigma} \cdot \exp\left[\mathbf{P}_{be1}\left(1 - \left(\mathbf{BO}_{ij}^{\sigma}\right)^{\mathbf{P}_{be2}}\right)\right] \\ & -\mathbf{D}_{e}^{\pi} \cdot \mathbf{BO}_{ij}^{\pi} - \mathbf{D}_{e}^{\pi\pi} \cdot \mathbf{BO}_{ij}^{\pi\pi} \end{split}$$



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# $\mathrm{E}_{\mathrm{conj}}$ and $\mathrm{E}_{\mathrm{coa}}$ in ReaxFF





# $E_{pen}$ for valence angle in ReaxFF





# $E_{C2}$ for valence angle in ReaxFF





#### First Hohenberg-Kohn Theorem



 $v_{ext}(r) \Leftrightarrow |\Psi_0\rangle \Leftrightarrow n_0(r) = \langle \Psi_0 \mid \hat{n}(r) \mid \Psi_0 \rangle$ 

The theorem states that, one has a one-to-one correspondence between the external potential  $V_{ext}$  in the Hamiltonian, the (non-degenerate) ground state  $|\Psi_0\rangle$  resulting from the Schrödinger equation and the associated ground state (electron) density  $n_0$ .



#### First Hohenberg-Kohn Theorem



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# $E[n] = \langle \Psi[n] \mid \hat{H} \mid \Psi[n] \rangle$



- Thus, the many-body problem of N electrons with 3N spatial coordinates is reduced to a problem involving only 3 spatial coordinates.
- The second theorem states that the ground state correponds to the density which minimizes the total energy of the system.

 $E_0 < E[n]$ 

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# Parameterization of ReaxFF force field

- Quantum Chemical (DFT) data is used to parameterize the force field
- A training data set is prepared which contains the following informations
  - Atomic charges (Mulliken)
  - Equilibrium bond lengths
  - Equilibrium bond angles
  - Torsion angles
  - Energies of the DFT optimized geometries
  - Heat of formation
- Error in the force field is then calculated

$$Err(p_1, p_2, \cdots p_n) = \sum_{i=1}^n \left[ \frac{x_{i,QM} - x_{i,ReaxFF}}{\sigma_i} \right]^2$$



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### Parabolic search algorithm





## Drawbacks of parabolic search algorithm

- Only one parameter is searched at a time
- The procedure has to repeated over several rounds
- It will only find a local minimum
- Needs a good starting point

Shapes of typical ReaxFF Error surface



# A double well potential with a linear term

$$U(x) = x^4 - 0.75x^2 + 0.01x$$





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# Equilibrium distribution of states

The distribution has a global maximum near the left well.



# Metropolis Monte Carlo (MMC) method

- Calculate the error of the starting force field, Errold
- Make a new proposition (move) for the parameters
- Calculate the error of the new force field, Errnew
- Calculate the difference in the Error, i.e.

 $\Delta Err = Err_{new} - Err_{old}$ 

Accept the move with a probability given by,

$$P = min[1, exp(-\beta\Delta Error)], where, \beta = \frac{1}{k_BT}$$

Repeat the algorithm



## Error vs $\beta$ for a Simulated Annealing run





## Comparison between MMC and ParSearch

#### For five random starting force fields





Table : Initial and final errors of the five simulations. The average < Error > and the coefficient of variation,  $\frac{std(sigma)}{< Error >}$ , of the final errors are shown.

Trial	$Error_{initial}  imes 1E - 6$	$\textit{Error}_{\textit{final}}  imes 1E - 6$	
		ParSearch	MMC
1	4.3	0.9	0.31
2	1.1	0.4	0.44
3	8.1	2.5	0.31
4	2.0	1.4	0.26
5	4.3	1.3	0.42
< Error >		1.3	0.35
std(Error) <error></error>		0.6	0.21





# Equation of state for MgSO<sub>4</sub>



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# Equation of state for MgSO<sub>4</sub>.7H<sub>2</sub>O



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# **Binding energy**

Binding energy of one water molecule on the (100) surface of MgSO<sub>4</sub>



Binding Energy with one water molecule MgSO4

Distance

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# Hydrogen bonds in $MgSO_4$ hydrates



The hydrogen bonds slows down the kinetics of dehydration as can be seen from the two sets of dehydration curves (one with hydrogen bonds and the other without hydrogen bonds) in the figure.

# Dissaperance of step-edge sites



The movement of step-edge sites in Co-nanoparticles are studied using ReaxFF.



# Conclusion

- Metropolis MC algorithm is used to parameterize the ReaxFF force field.
- The method shows good improvement over the traditional optimization scheme.
- The stochastic nature of the method allows one to arrive at the global minima in the parameter space.



# Thank You!!

