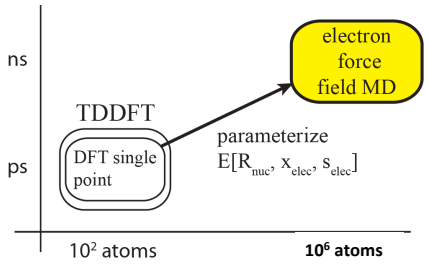
Large-scale Explicit Electron Molecular Dynamics and Applications to Materials/ Phenomena in Extreme Conditions [in LAMMPS]



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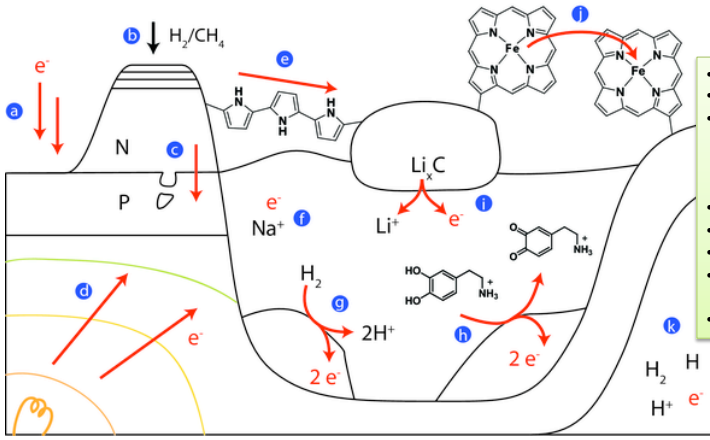
Outline

- Motivation for modeling excited electronic states
- The eflectron force field (eFF) (user-eff)
  - Original published applications of eFF (z<6)
  - eFF on hypervelocity impact (HVI)
- Extending eFF to higher Z's: effective cores
  - Theory
  - Si fracture dynamics
  - ECPs for Carbon, Oxygen, Aluminum
- Summary

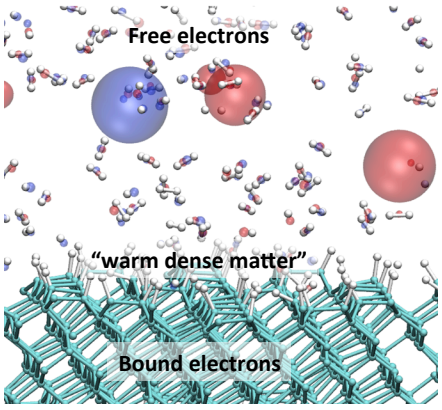
Excited electrons drive essential chemistry

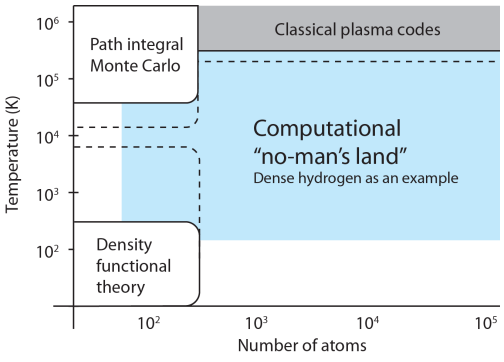


- e⁻ etching
- CVD diamond layers
- e⁻ transport across semiconductor junctions, cellular respiration, organics
- Thermo-electrics
- Solvated electron
- ½ FC or Li battery rx
- Electrochemical sensors (dopamine)
- Plasmas

Want to study electron dynamics in solids, liquids, and plasmas

Interfaces between materials and excited phases

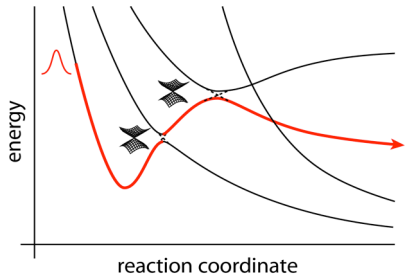




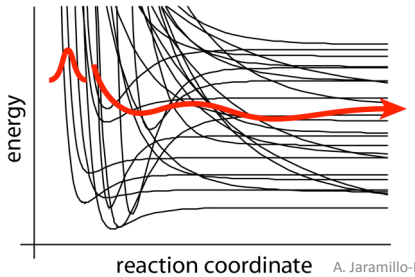
Important to understand but challenging to model

Bridges electronic structure and plasma physics methods

Simulation of large scale excited electron dynamics



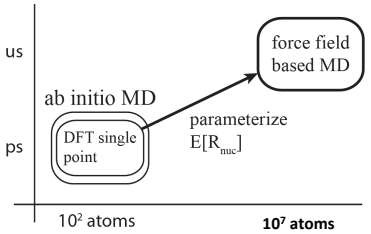
For small systems, determine stationary states and take random hops between them.



How do we simulate large systems with many states and curve crossings?

Impossible with QM

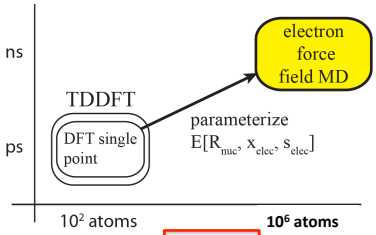
Electron force fields for simulating excited electrons



Conventional force field
ground state dynamics of nuclei

point nuclei, Born-Oppenheimer approximation

Julius Su, 2007



Electron force field
excited state dynamics of nuclei and electrons

point nuclei, FS Gaussian wave packet electrons

$$U = E_{KE}(r,s) + E_{NN}(R) + E_{Ne}(R,r,s) + E_{ee}(r,s) + E_{Pauli}(\uparrow\downarrow,S)$$

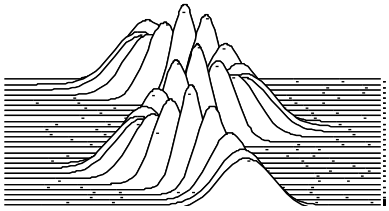
Makes large scale **non-adiabatic** simulations practical

Dynamics of spherical Gaussian wave packets

Wave packet whose **size and position varies with time**:

$$\Psi(\mathbf{x}) \propto \exp\left[-\left(\frac{1}{s^2} - \frac{2p_s}{s}\frac{i}{\hbar}\right)(\mathbf{x}-\mathbf{r})^2\right] \cdot \exp\left[\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}\right]$$

Assume a *locally harmonic* potential, stays Gaussian over time:



$$\frac{d\mathbf{r}}{dt} = \frac{\mathbf{p}}{m} \qquad \frac{d\mathbf{p}}{dt} = -\nabla E$$

$$\frac{ds}{dt} = \frac{p_s}{(3/4)m} \qquad \frac{dp_s}{dt} = -\frac{\partial E}{\partial s}$$

Schrodinger's equation gives simple equations of motion

Heller, semiclassical dynamics – J. Chem. Phys **1975** 62(4) 1544-1555

Fermionic molecular dynamics – Rev. Mod. Phys. **2000** 72 655-688

Electron force field energy expression

(1) Classical electrostatics plus (2) **quantum potentials**:

$$U = E_{KE}(r,s) + E_{NN}(R) + E_{Ne}(R,r,s) + E_{ee}(r,s) + E_{Pauli}(\uparrow\downarrow,S)$$

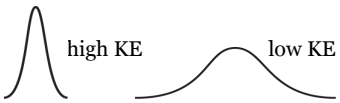
Electrostatics of Gaussian charge densities and nuclei

$$\frac{1}{x_{ij}}\,\mathrm{Erf}\left(\frac{\sqrt{2}\,x_{ij}}{\sqrt{s_i^2+s_j^2}}\right)$$

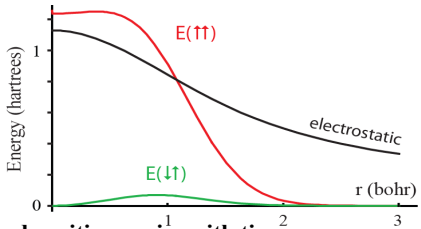
distance

elec. size

Wavefunction kinetic energy
Heisenberg principle



Pairwise Pauli repulsion
Spin-dependent, 3 parameters



Similar formulations

Boal and Glosli, nuclear reactions
Phys Rev C **1988** 38(4):1870-1878

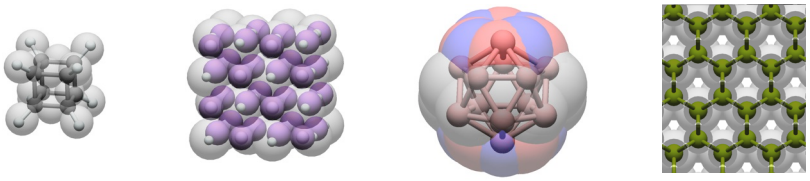
Klakow et al, hydrogen plasma
J. Chem. Phys **1994** 101(12):10766-10774

Wave packet whose **size and position varies with time**

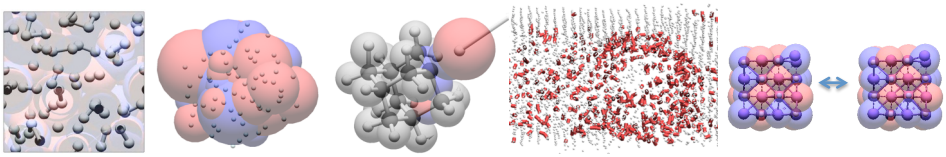
Our expression is the first applicable to a wide range of molecules

eFF Describes Many Materials and Excitations Consistently

Bonding: covalent, ionic, multicenter, metallic



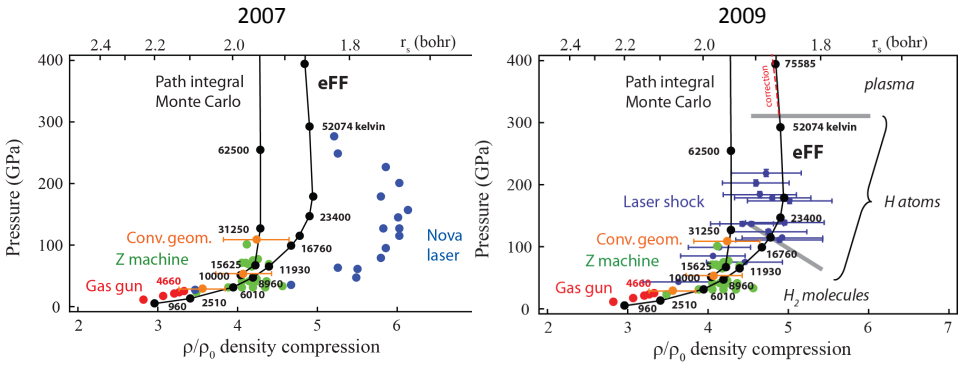
Excitation: thermal, laser, core ionization, proton impact, hypervelocity impact



Makes it feasible to study large heterogeneous excited systems

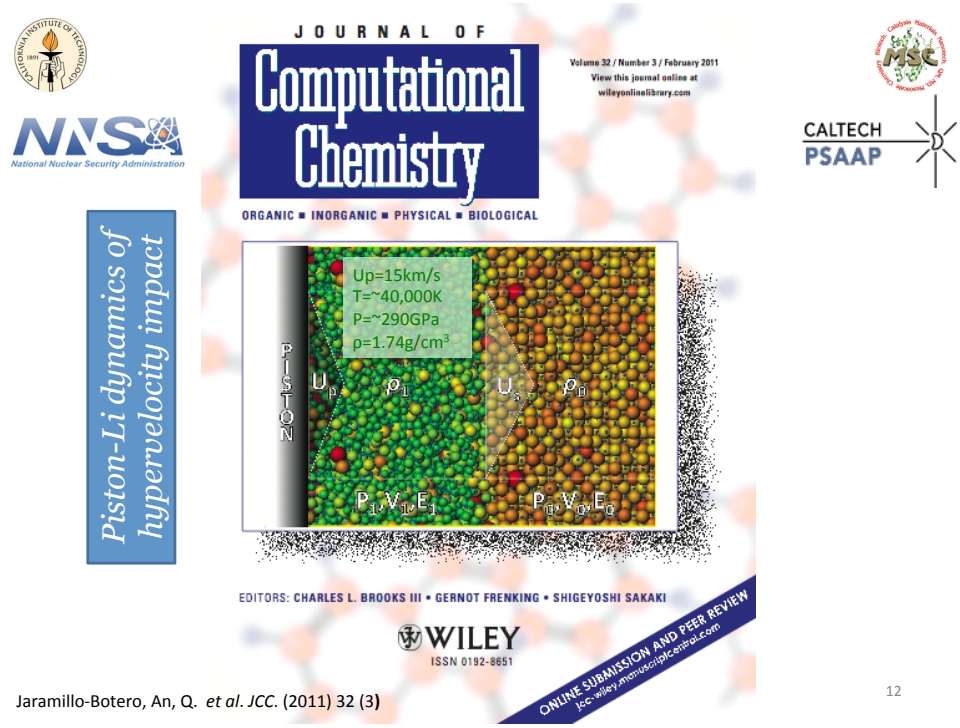
EFF VALIDATED FOR EXTREME CONDITIONS (H, Li, Be, C)

Hugoniot curves from shock compression of D_2



Good agreement with most recent experiments and theory

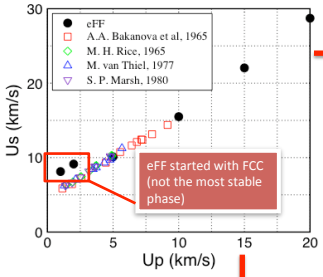
Su, J. T. and Goddard, W. A. III, warm dense hydrogen – Phys. Rev. Lett. **2007** 99:185003



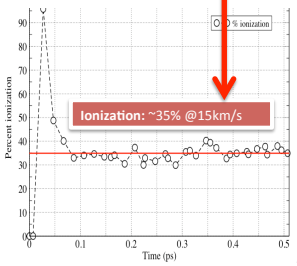
Piston-Li dynamics of hypervelocity impact

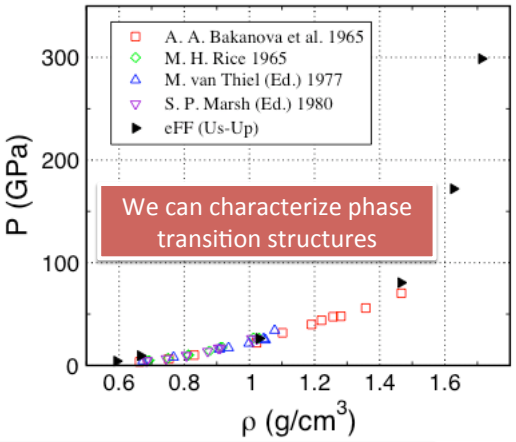
Jaramillo-Botero, An, Q. *et al. JCC.* (2011) 32 (3)

Lithium dynamic single shock Hugoniot



$P=\rho_0 U_s U_p$ and $\rho=\rho_0[U_s/(U_s-U_p)]$



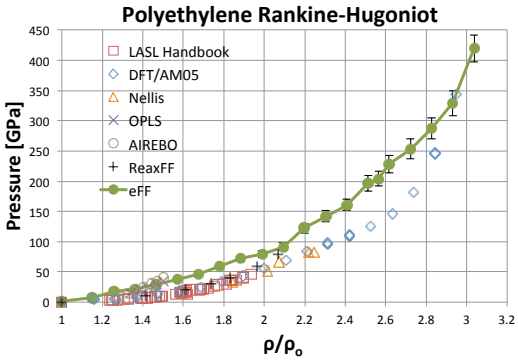


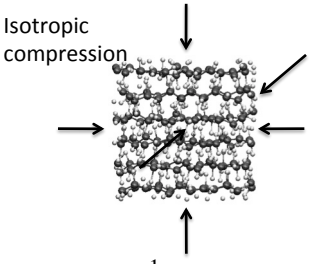
Excellent agreement with experiment up to 1.5 g/cc

Jaramillo-Botero, Qi A. *et al. JCC.* (2011) 32 (3)

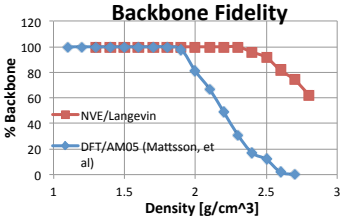
PE Hydrostatic Shock Hugoniot

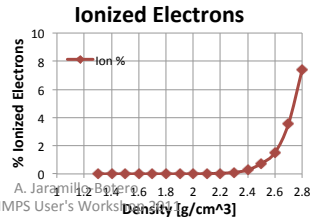
Thermodynamic Hugoniot Determination





$$U - U_0 = \frac{1}{2}(P + P_0)(V_0 - V)$$





eFF is able to produce a good shock Hugoniot and reveal ionization properties

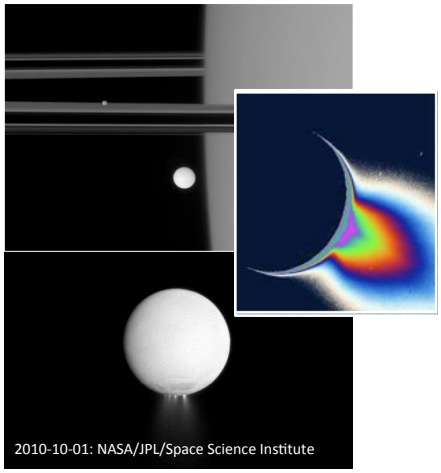
With Patrick Theofanis

Cassini-Huygens (NASA's mission to Saturn)

PREDICTING MATTER FRAGMENTATION DURING HYPERVELOCITY IMPACTS (HVI)

Cassini Data Analysis: Hypervelocity impact of molecules

- Water-rich cryovolcanic plume venting from Saturn's Enceladus moon (south polar region)
- On-ship INMS picks gas cloud composition
- Composition dependent on flyby velocity, suggesting:
  - Species produced by dissociation/fragmentation through impact on,
  - and reaction with, the walls of the INMS antechamber.

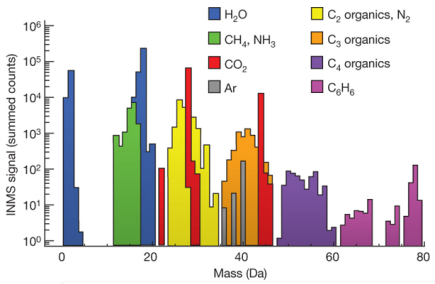


Need to decode data sent back to earth by Cassini, considering mission flyby velocity conditions

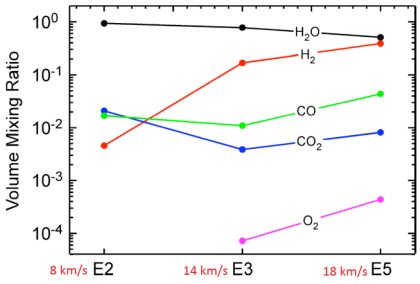
Jaramillo-Botero, *et al. LPSC.* (2011)

Cassini INMS Data Analysis

Molecular species detected



Velocity dependence

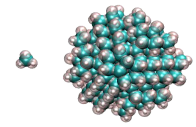


This could be indicative of a possible water ocean in Enceladus and the existence of an internal heat source to fuel the cryovolcanic plume

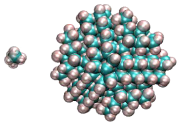
We need to understand the plume species-INMS interactions and the species evolution as a function of vehicular velocity, i.e. explain what they have not been able to decode (CDAP)

Jaramillo-Botero, *et al. LPSC.* (2011)

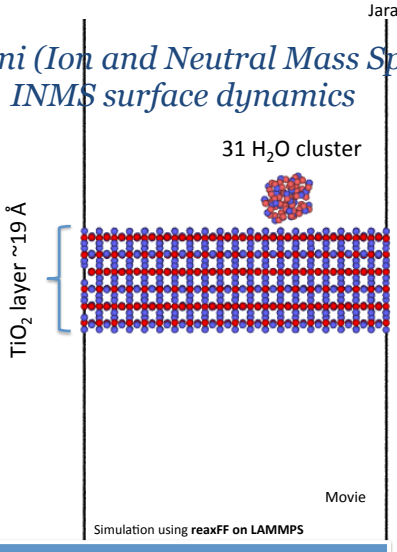
Cassini (Ion and Neutral Mass Spec) INMS surface dynamics

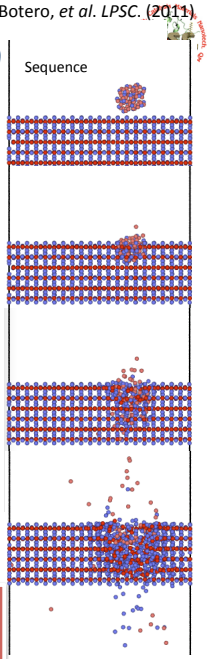


pEFF LAMMPS: Methane @15km/s



pEFF LAMMPS: Methane @20km/s





ReaxFF: Ice-I impact damages TiO2 surface at 25km/s

Ice impact at 25km/s (100K) leads to perforation of thin 6-layer TiO2 film, producing among other species H, O2, O, H2, Ti, and TiO. No water molecules left. The resulting surface exposes Ti atoms, changing reactivity. pEFF simulations capture fundamental processes associated with molecule-surface collisions. H2 increase at E5 from H2O

Carbon, Oxygen, Silicon, and Aluminum

EXTENDING EFF TO HIGHER Z's: EFFECTIVE CORE PSEUDOPOTENTIALS

Effective Core Pseudopotentials (ECP)

- Spherical Gaussian representation of electrons make it difficult to describe *p* and higher order angular momentum orbitals

- **eFF1: fast large-scale excited state method:** trouble with multiple bonds and lone pairs
- **eFF2: proper description of *p* electrons:** expensive, Pauli between *s*-electrons underestimated

- Develop effective core potential (ECP) for original eFF (eFF1) for *p*-block: Combine merits of both eFF1 and eFF2

eFF1 ECP Formulation

ECP in eFF1 is used to account for Pauli and approximated as

$$E_{ECP} \propto S^2$$

s-s overlap ECP has been successfully applied to Si

$$E_{ss} = \boldsymbol{a} \exp\left(-\frac{\boldsymbol{b} r_{12}^2}{\boldsymbol{c} + s_{val}^2} \right)$$

For C, N, O, more complicated functions needed: *s-p* overlap ECP

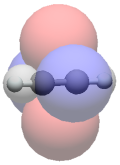
$$E_{sp} = \boldsymbol{a} \left(\frac{2}{\boldsymbol{b}/s_{val} + s_{val}/\boldsymbol{b}} \right)^5 (r_{12} - \boldsymbol{c} s_{val})^2 \exp\left[-\frac{\boldsymbol{d}(r_{12} - \boldsymbol{c} s_{val})^2}{\boldsymbol{e} + s_{val}^2} \right]$$

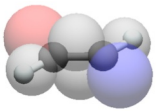
Improved version coming (3 only physical parameters, V: valence, C: core)

$$E_{ECP} = \Delta T = \frac{S_{VC}^S}{1 - S_{VC}} (T_{VV} + T_{CC}) - \frac{S_{VC}}{1 - S_{VC}^2} 2T_{VC}$$

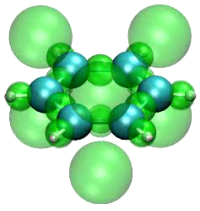
s-p ECP for Carbon: Gallery

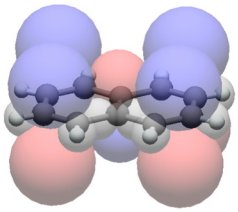
$H_2C{=}CH_2$

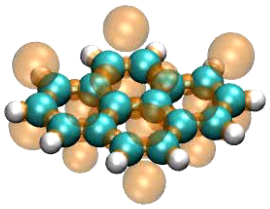




HC≡CH more stable than ·HC=CH· by 132 kcal/mol







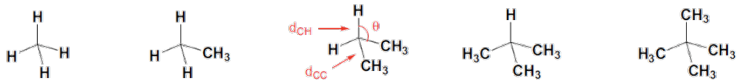
The most stable configurations of benzene, naphthalene and pyrene: all of them are stable and remain planar at 2,000 K

With Hai Xiao

Carbon: Fitting Set and Goals (1)

1. Moderately variable C-C and C-H bond lengths

	d_{CC} (pm)			d_{CH} (pm)			Θ (degree)		
	exact	eFF1	ECP	exact	eFF1	ECP	exact	eFF1	ECP
CH_4				109.4	114.3	105.6	109.5	109.5	109.5
$CH_3(CH_3)$	153.6	150.1	152.0	109.1	117.3	106.5	110.9	110.8	111.3
$CH_2(CH_3)_2$	152.6	151.3	152.6	109.6	122.9	107.6	109.5	107.9	110.6
$CH(CH_3)_3$	152.5	152.9	153.0	110.8	142.4	108.7	109.4	101.8	109.9
$C(CH_3)_4$	153.4	157.3	153.2	111.4	117.8	106.7			
Diamond	154.5	168.1	155.1						



2. Correct C-C bond energy

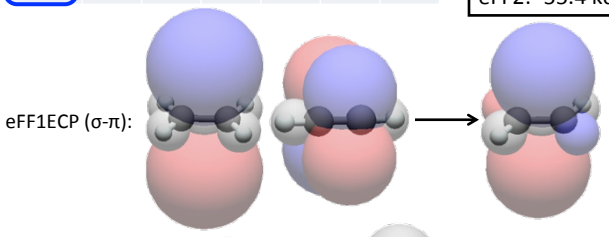
H_3C-CH_3: exact 89.7 kcal/mol; eFF1 163.5 kcal/mol; ECP 89.7 kcal/mol

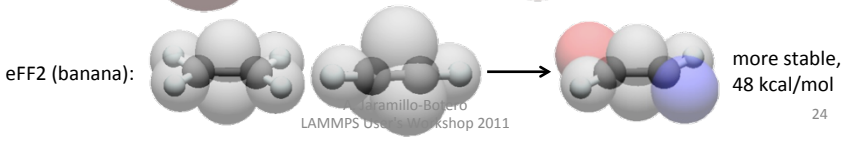
Carbon: Fitting Set and Goals (2)

3. Stable multiple bonds with reasonable bond lengths

	d_{CC} (pm)			d_{CH} (pm)		
	exact	eFF1	ECP	exact	eFF1	ECP
H_3C-CH_3	153.6	150.1	152.0	109.1	117.3	106.5
H_2C=CH_2	133.9	151.7	137.7	108.6	108.9	97.2
HC≡CH	120.3	138.3	115.4	106.3	105.2	91.8

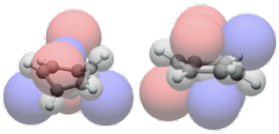
H_2C=CH_2 + H_2 → H_3C-CH_3
ΔE -- exact: -38.2 kcal/mol
eFF1: -141.6 kcal/mol
eFF1ECP: -38.2 kcal/mol
eFF2: -55.4 kcal/mol





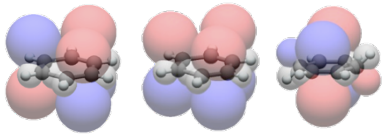
Multiple Double Bonds: Benzene

eFF1 (diradicals):



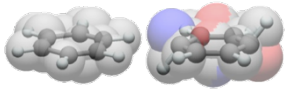
0.0 kcal/mol 53.7 kcal/mol

eFF1ECP (planar):

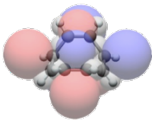


0.0 kcal/mol 3.6 kcal/mol 74.4 kcal/mol

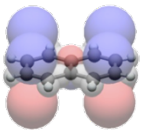
eFF2 (planar):



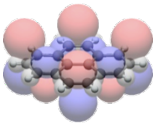
0.0 kcal/mol 12.0 kcal/mol



Cyclooctatetraene (nonplanar)



Naphthalene (planar)

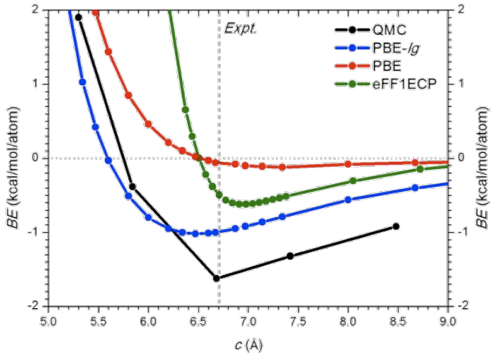


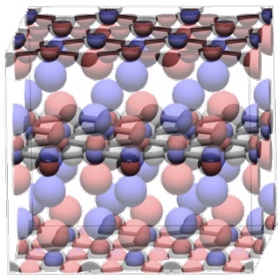
Pyrene (planar)

intrinsic problem of eFF -- no conjugation due to localized orbitals: alternating single and double bonds (150.6 pm, 137.4pm vs 139.7 pm); benzene to 1,3-Cyclohexadiene, -154.3 kcal/mol (vs 5.2 kcal/mol)

Proper description of non-planar vs. planar

Interlayer π-π Interaction: Graphite





eFF1ECP gives surprisingly good LPs (a = 2.550 Å, c = 6.943 Å vs. expt. a = 2.461 Å, c = 6.708 Å), only 3.6% and 3.5% larger, although the binding energy is underestimated (-0.62 kcal/mol vs. expt. 0.8-1.2 kcal/mol).

Problem: unstable w.r.t. diamond; π electrons → bonding between layers with small c

QMC results: L. Spanu, S. Sorella, G. Galli. *Phys. Rev. Lett.* **2009**, *103*, 196401.

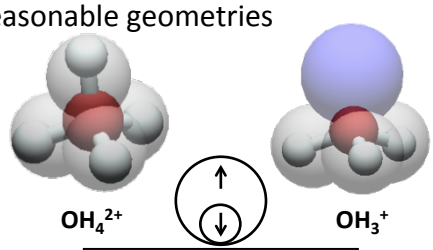
PBE/PBE-*lg* results: Y. Liu, W. A. Goddard III. *J. Phys. Chem. Lett.* **2010**, *1*, 2550-2555.

Oxygen: Fitting Set and Goals

1. Stable lone pairs on OH_n with reasonable geometries

eFF1ECP fitting results (HF/AVTZ data)

	O-H (pm)	H-O-H (degree)
H_4O^{2+}	82.9 (102.2)	109.5 (109.5)
H_3O^+	106.6 (96.1)	106.6 (114.0)
H_2O	111.4 (94.1)	112.1 (106.4)
HO	125.2 (95.2)	---

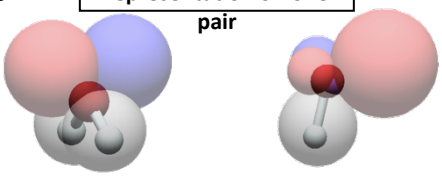


open shell representation of lone pair

2. Correct O-H/O-H^+ bonding energies

eFF1ECP fitting results (HF/AVTZ data)

	ΔE (kcal/mol)
$H_4O^{2+} = H_3O^+ + H^+$	-54.3 (-56.2)
$H_3O^+ = H_2O + H^+$	175.1 (175.4)
$H_2O = HO + H$	139.0 (87.4)

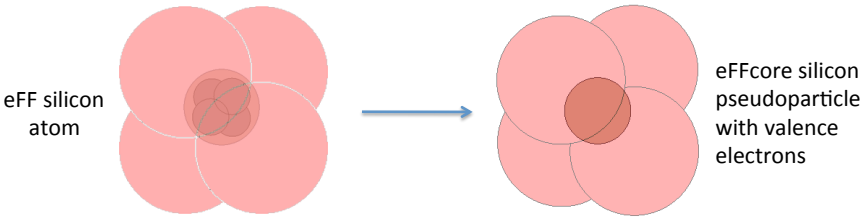


Funded by DOE-NNSA (PSAAP)

EFFCORE SIMULATIONS OF DYNAMIC FRACTURE IN CRYSTALLINE SILICON

eFFcore Silicon Model

eFFcore: Si core pseudoparticles + valence electrons only



Pseudoparticle potentials:

$$E_{core-elec} = \sum_{i,j} \frac{Z_i Z_j}{R_{ij}} Erf\left(\frac{\sqrt{2}R_{ij}}{\sqrt{r_{core,i}^2 + r_{elec,j}^2}}\right) \quad E_{core-core} = \sum_{i<j} \frac{Z_i Z_j}{R_{ij}} Erf\left(\frac{\sqrt{2}R_{ij}}{\sqrt{r_{core,i}^2 + r_{core,j}^2}}\right)$$

$$E_{core-nuc} = \sum_{i,j} \frac{Z_i Z_j}{R_{ij}} Erf\left(\frac{\sqrt{2}R_{ij}}{r_{core,j}^2}\right) \quad E_{Pauli} = a\,Exp\left(\frac{-b\,r^2}{c + s^2}\right)$$

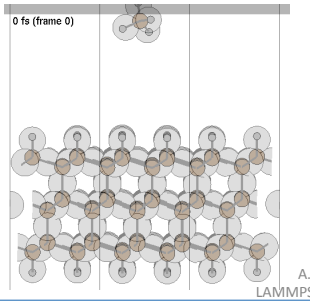
eFFcore Silicon Model

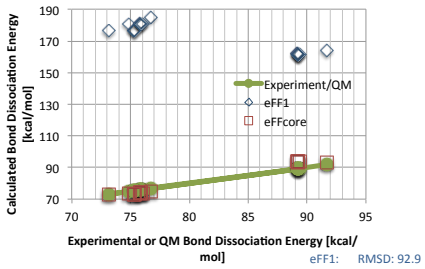
Validation by emergent properties

Si_6H_{12} Conformer Energies [kcal/mol]

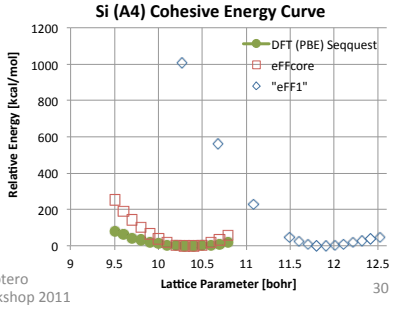
Method	chair	sofa	twist	boat	RMSD
B3LYP/ 6-311G**	0	3.11	1.78	2.10	0
eFF1	0	2.61	0.67	0.81	1.01
eFFcore	0	1.27	1.40	1.40	0.55

66% reduction of particles per simulation
50x longer dynamic time step possible



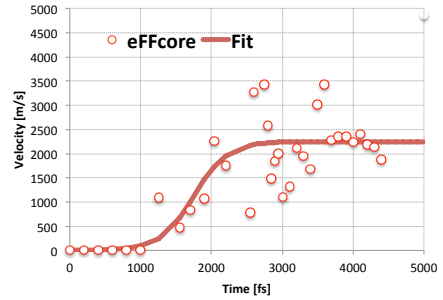


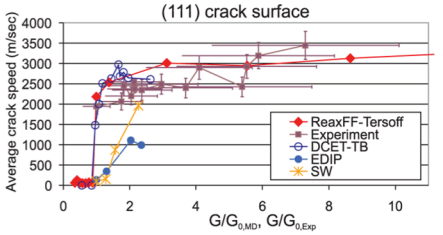
eFF1: RMSD: 92.9
eFFcore: RMSD: 2.84



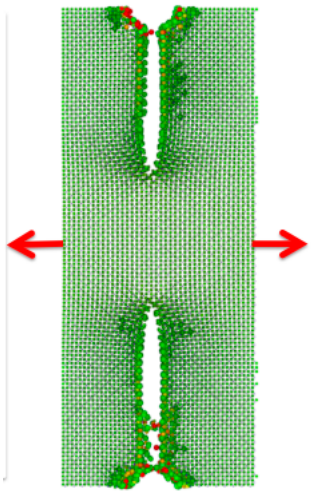
*Si [112] direction crack propagation **step** velocity*

Crack Tip Velocity Profile





Crack tip velocity plateaus ~**2200 m/s**
Experiment: 2300 - 3500 m/s[1]

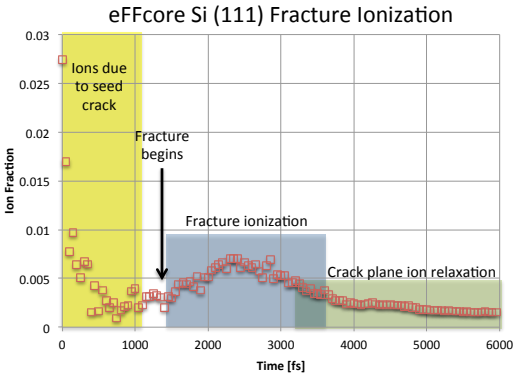


[1] Hauch, *et al. Phys. Rev. Lett.* (1999) **82**, 3824
[2] Buehler, *et al. Phys. Rev. Lett.* (2007) **99**, 165502

Theofanis, Jaramillo-Botero and Goddard, *submitted to PRL* (2011)

Structural Degradation

Dynamic ionization



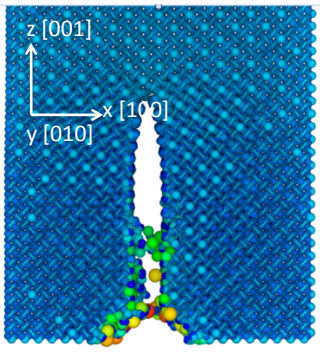
100,800 electrons in model

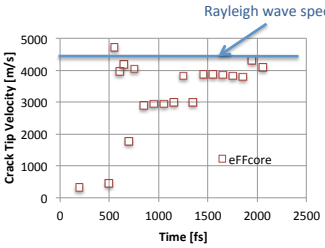
- Seed crack leaves dangling bonds and causes ionization
- The seed crack surface relaxes as load is increased on the system
- Eventually fracture causes additional ionization
- Ions on cleaved surfaces relax and surface relaxation occurs

eFFcore Simulation Model

(100) cleavage plane

Low temperature, low strain rate fracture





Delamination
(color-coded e energy)

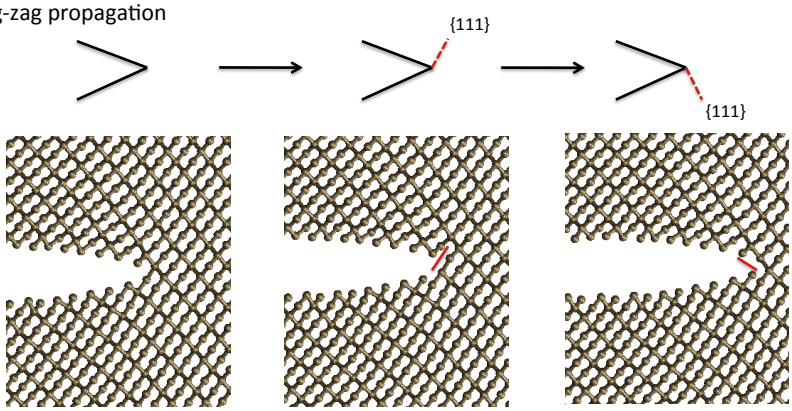
- Crack tip rapidly accelerates to ~4 km/s and plateaus- This is observed experimentally*
- Low energy cracks produce atomically sharp tips

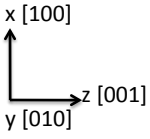
*Phys. Rev. Lett. 1999, v82, pp.3823; Phys. Rev. Lett. 2000, v85, pp788; Phys. Stat. Sol. 1997, v164, R5.

Crack Propagation Mechanism

(100) cleavage plane

Zig-zag propagation





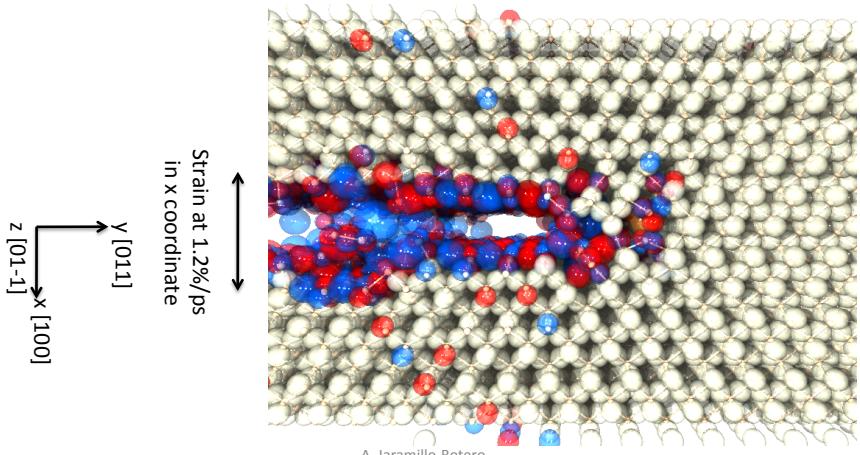
- At low temperatures (300 K) the crack is atomically sharp
- Crack extends by alternating microfractures into the low E {111} plane
- No observation of dislocation nucleation or cleavage decohesion
- Expect blunting at high temperatures to lead to dislocation emission

(100)x(011)x(01-1) Crack Model

(100) cleavage plane

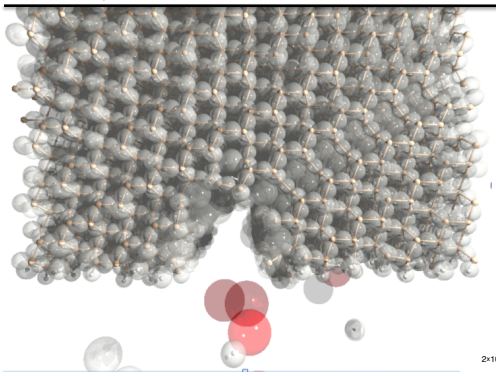
Low temperature, low strain rate fracture

Actual cell dimensions: 3.8 x 25 x 3.8 nm
18,200 silicon nuclei; 72,800 electrons

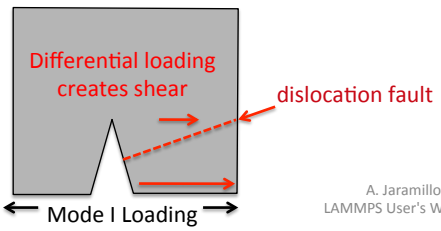


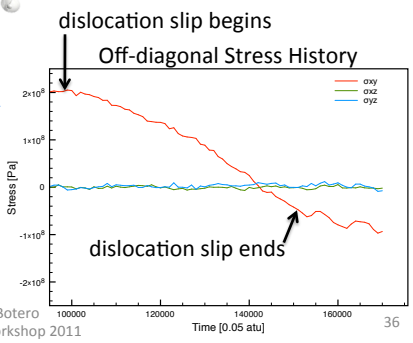
111 Dislocation Nucleation

Caused by shear strain



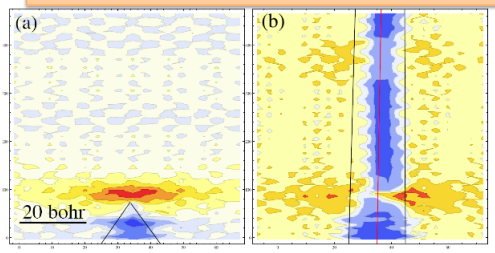
- Differential loading in the uniaxial strain dimension due to seed crack introduces shear strain
- Small amounts of shear are known to nucleate dislocations



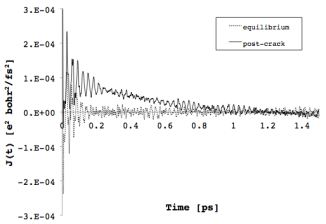


Increased conductivity during fracture

This indicates that the production of mobile charge carriers as a direct result of fracture accounts for the experimentally observed fracture current bursts.



The evolution of electrostatic potential calculated on a grid is given at (a) 0 fs and (b) 15 ps. Warm colors denote positive potential and cool colors signify negative potential. The crack edges are given by solid black lines and the midline of the crack is provided in red. The electrostatic field is also distorted along a narrow front perpendicular to the crack tip direction.



The electric current velocity correlation functions for the {111} system at equilibrium and after a crack has occurred.

$$J(t) = \langle \mathbf{j}(t) \cdot \mathbf{j}(0) \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle q_i q_j \mathbf{v}_i(t) \cdot \mathbf{v}_j(0) \rangle = Z(t) + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \langle q_i q_j \mathbf{v}_i(t) \cdot \mathbf{v}_j(0) \rangle = Z(t) + \Delta(t)$$

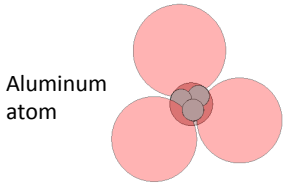
Theofanis, Jaramillo-Botero, and Goddard, submitted to PRL, 7-2011

Preliminary results

EFF ECP FOR ALUMINUM

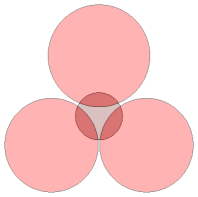
eFFcore Aluminum Model

eFFcore: Si core pseudoparticles + valence electrons only



Aluminum atom

Z = 13
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$



Z = 3
$3s^2\ 3p^1$

Aluminum core pseudoparticle with valence electrons

Pseudoparticle potentials:

$$E_{core-elec} = \sum_{i,j} \frac{Z_i Z_j}{R_{ij}} Erf\left(\frac{\sqrt{2}R_{ij}}{\sqrt{r_{core,i}^2 + r_{elec,j}^2}}\right) \quad E_{core-core} = \sum_{i<j} \frac{Z_i Z_j}{R_{ij}} Erf\left(\frac{\sqrt{2}R_{ij}}{\sqrt{r_{core,i}^2 + r_{core,j}^2}}\right)$$

$$E_{core-nuc} = \sum_{i,j} \frac{Z_i Z_j}{R_{ij}} Erf\left(\frac{\sqrt{2}R_{ij}}{r_{core,j}^2}\right) \quad E_{Pauli} = a\,Exp\left(\frac{-b\,r^2}{c + s^2}\right)$$

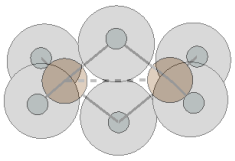
a, b, c, and r_{core} are parameters to be fit

eFFcore Aluminum Model

Small aluminum hydrides

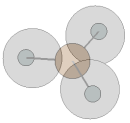
Al_2H_6

Bond/Angle	B3LYP	M06	eFF1	eFFcore
Energy [hartrees]	-488.5105208	-488.436265	-398.670056	-6.154032
Al-Al	2.583	2.61382	2.2	2.67142
Al-H	1.577	1.573	1.597	1.48241
Al-bridgeH	1.745,1.709	1.744,1.742	1.616	1.78306
Al-Al-bridgeH	42.105, 41.051	41.386,41.441	47.111	41.486
H-Al-H	127.493	128.168	116.71	128.647
H-Al-bridgeH	109.3	109.042	110.858	108.94
H-bridgeH	2.681	2.702	2.65	2.66321



AlH_3

Bond/Angle	B3LYP	M06	eFF1	eFFcore
Energy [hartrees]	-244.2291676	-244.1904645	-199.228403	-3.050437
Al-H	1.584	1.581	1.604	1.51932
H-Al-H	120	120	120	120



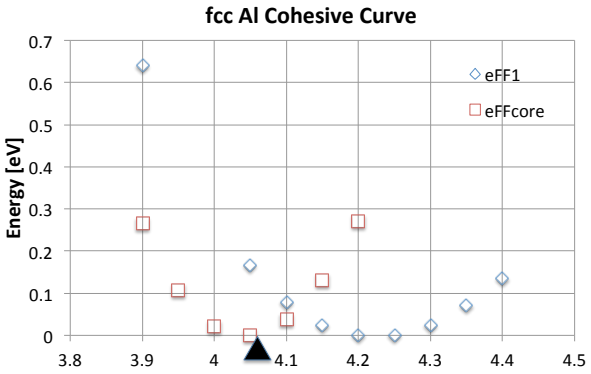
Bond Energies	B3LYP	M06	eFF1	eFFcore
al2h6 -> 2 alh3	32.74698671	34.72389299	133.8163776	33.35714421

Distances in Å, angles in degrees

Geometries and bond energies improved over eFF1, good performance versus QM

eFFcore Aluminum Model

Bulk aluminum



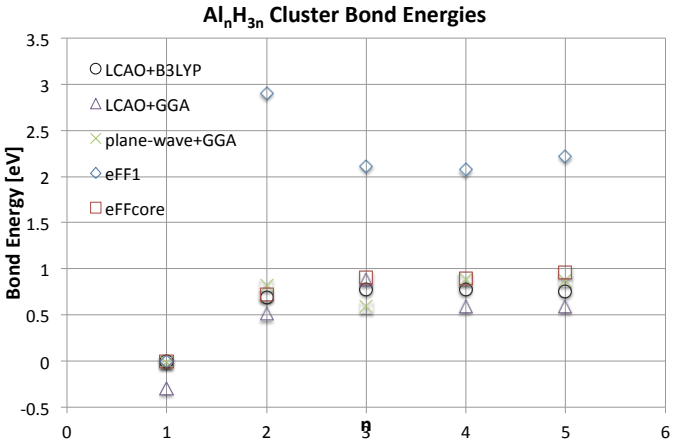
▲ = Experimental lattice constant

	Experiment	eFF1	eFFcore
Bulk Modulus [GPa]	76	44	108

Better lattice constant, bulk modulus still too stiff

eFFcore Aluminum Model

Al_nH_{3n} Clusters



n > 2 clusters were not included in fitting set so this is an excellent demonstration of eFFcore's ability

*QM values from: Kawamura *et al*, *Phys. Rev. A* (2003) **67** 063205

Parameter Comparison

Three trained elements so far

Fit technique: genetic algorithm.

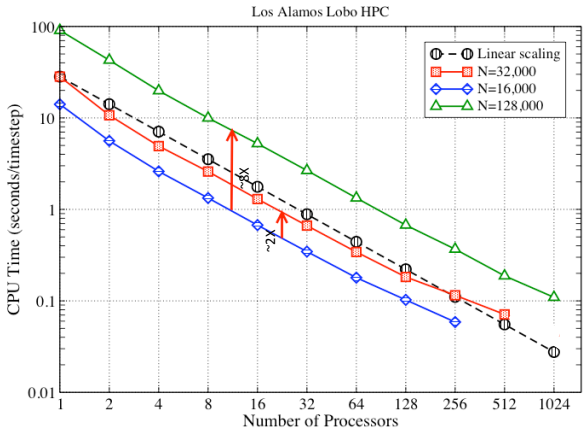
- Parameters computed from small library of finite molecules and periodic systems
- Score based on bond lengths, angles, energies, and cohesive curves
- Allow GA to minimize score from fitness function

Element	a	b	c	r_{core} [bohr]
C	0.735	0.909	0.616	0.154
Al	0.486	1.049	0.207	1.660
Si	0.321	2.283	0.815	1.691

- Al & Si core sizes are roughly the same
- Carbon parameters aren't completely trained
  - Either get good bond energies or good geometries
- Aluminum parameters work well except on surfaces
  - More work needed here

AVAILABLE AS USER-EFF package in LAMMPS

eFF parallel performance (all-electron case)



Good weak and strong parallel scaling
Multi-ps to ns for millions of electrons

Jaramillo-Botero, *et al. JCC.* (2011) 32 (3)

Summary

- Original eFF limited ~Z<6 - we have now extended support for higher Z's with p-character thru ECP
- eFFcore for Si, C, O, Al validated through bond energies, geometries, bulk properties & dynamics
- Achieve significant reduction in number particles per atom simulation (e.g. 66% in Si)
- Improve timestep for NVE dynamics (50x)
- eFFcore faithfully reproduces brittle fracture dynamics of silicon, and models brittle to ductile transition
- Preliminary results for electronic transport properties thru Green-Kubo approach (validated for Si high-rate fracture)
- user-eFF in LAMMPS demonstrates parallel scalabilty, and support up to millions of atoms over 10-100's ps dynamics

Acknowledgements

- Hai Xiao (ECP)
- Patrick Theofanis (Si, Al)
- Qi An (Li)
- Chi Feng (C60)
- Julius Su (eFF1)
- William A. Goddard III
- Robert Hodyss and Luther Beegle (JPL, Cassini)

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