Large-scale Quantum Non-Adiabatic Electron Dynamics

USER-EFF (GHA+AMPERE) package in LAMMPS

Thanks to Steve Plimpton and Organizers for the invitation

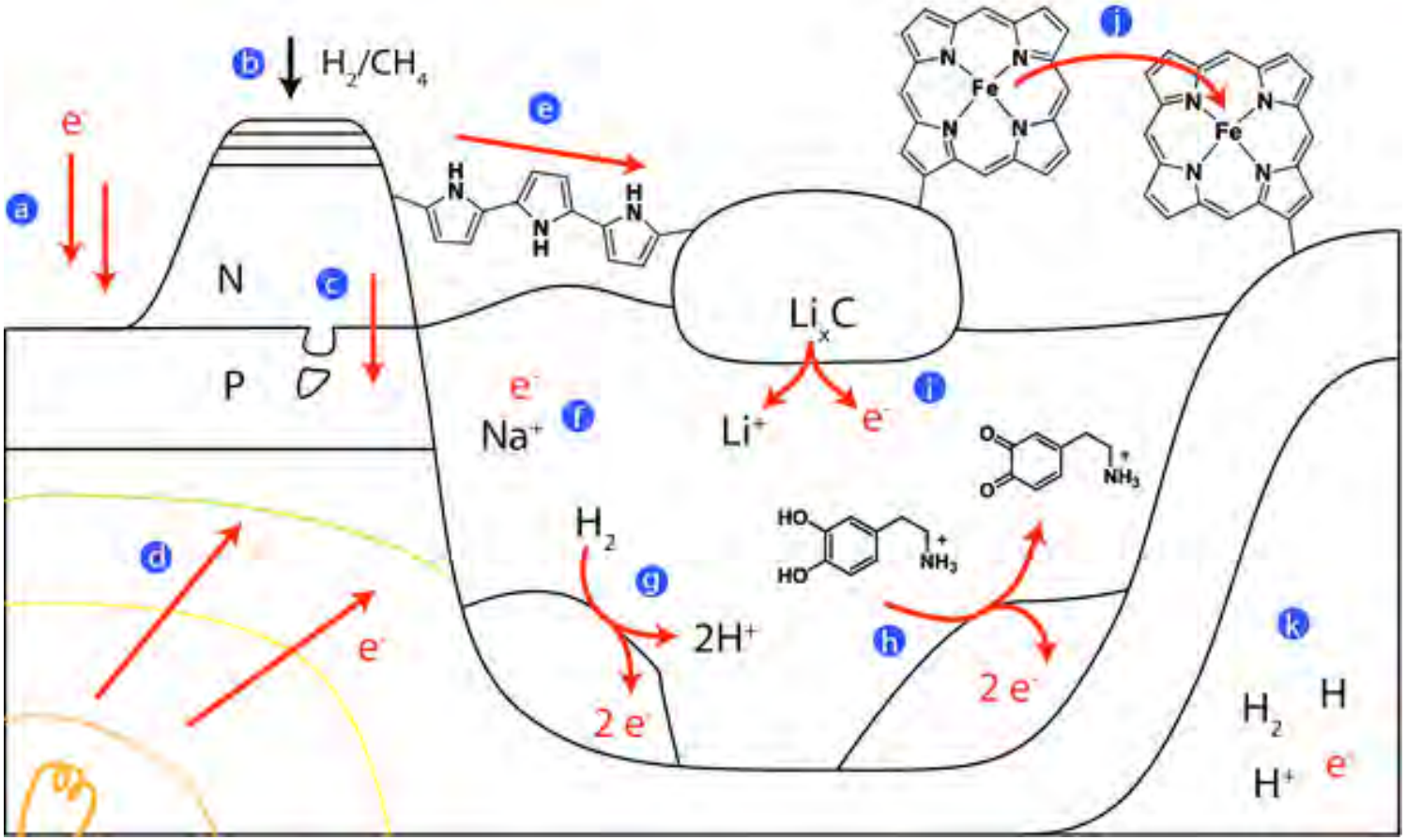
Andres Jaramillo-Botero

Hai Xiao, Sijia Dong, William A Goddard III

Chemistry and Chemical Engineering Division

Caltech

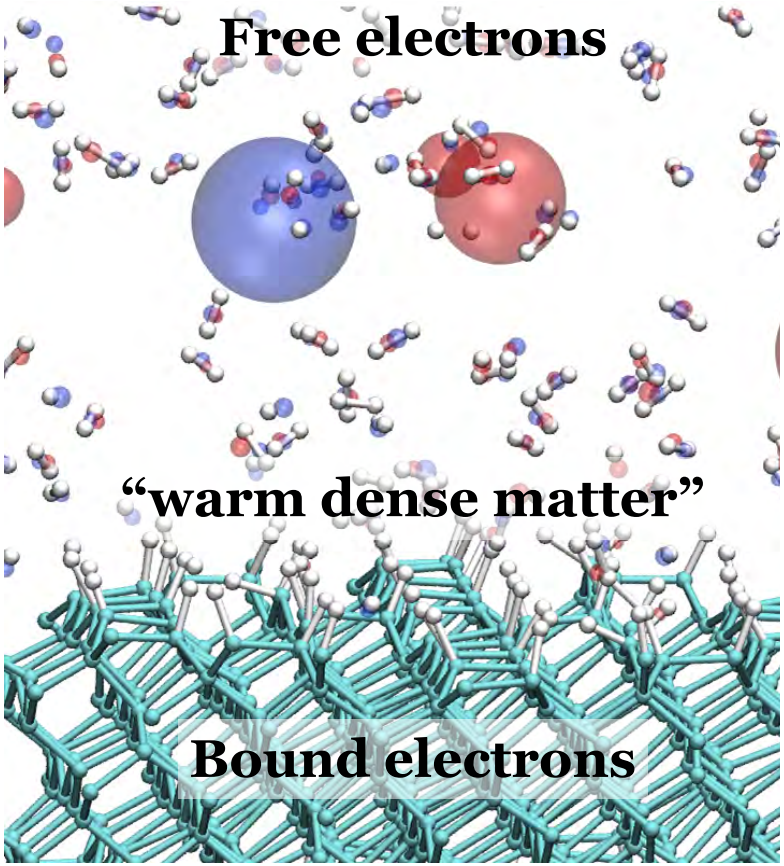
Excited electrons drive essential chemistry

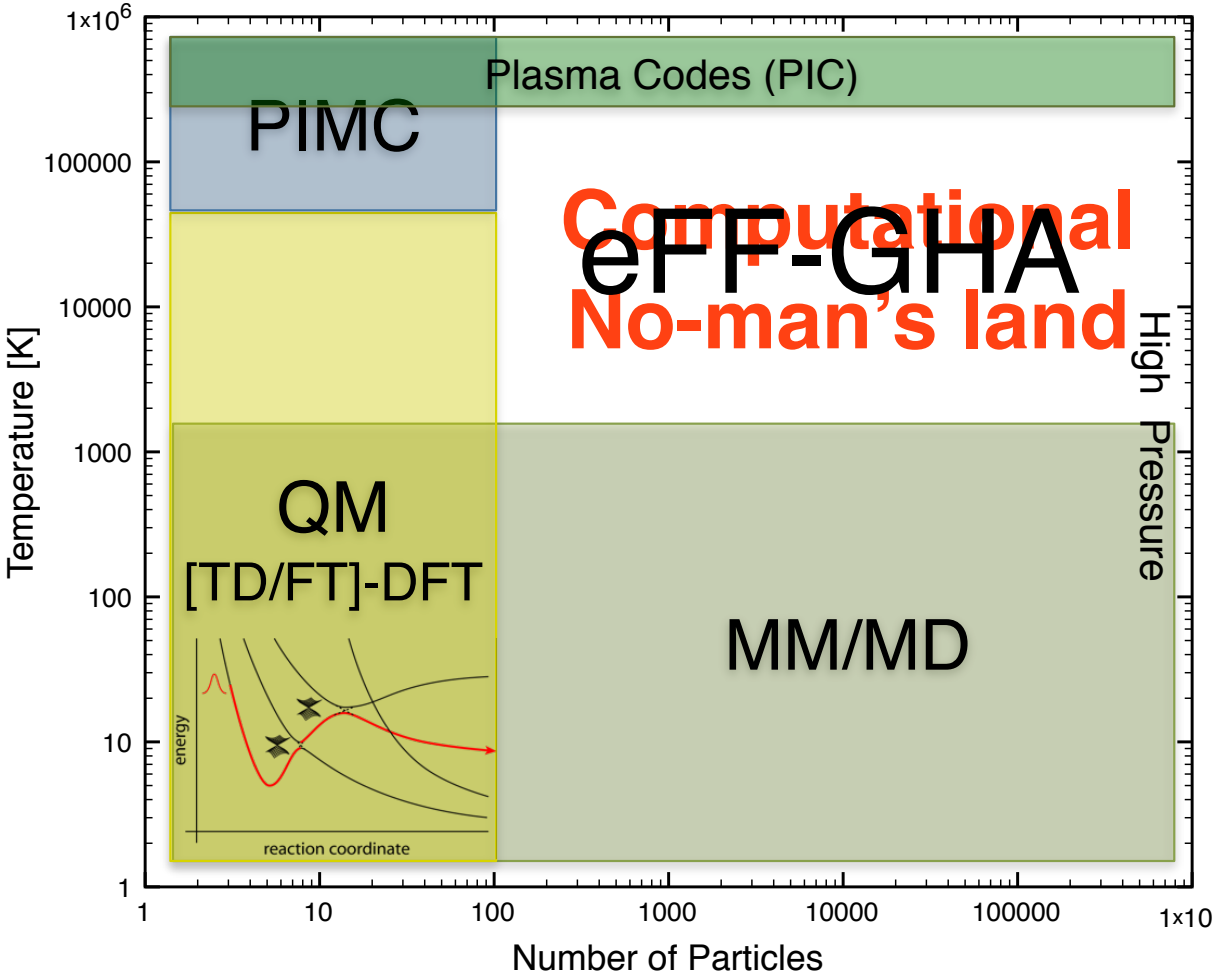


Schematic from Julius Su

Study electron dynamics in solids, liquids, and plasmas.
Understand conditions that cause irreversible material changes.

Computational No-Man's Land

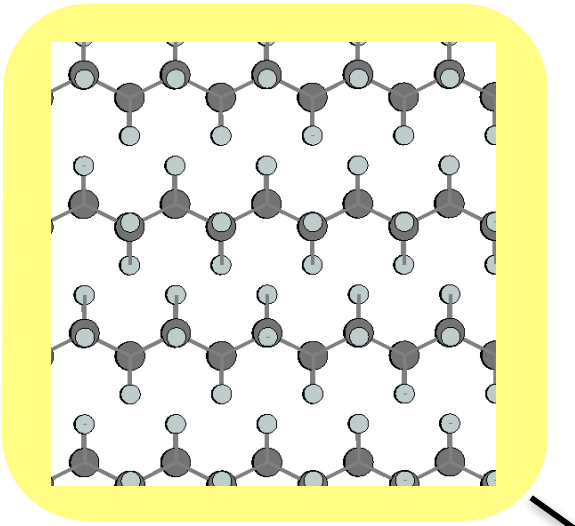




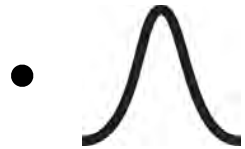
Dynamics of Large Systems with High Number of Excited States: Critical to understand but challenging for theory and experiment

Mixing classical nuclei and Gaussian electrons

Classical



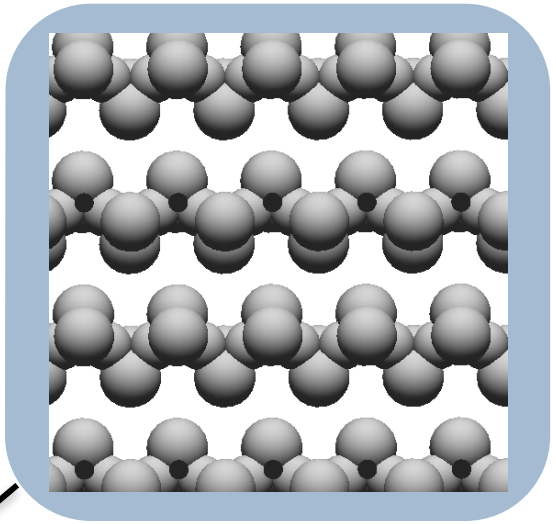
10^7 atoms



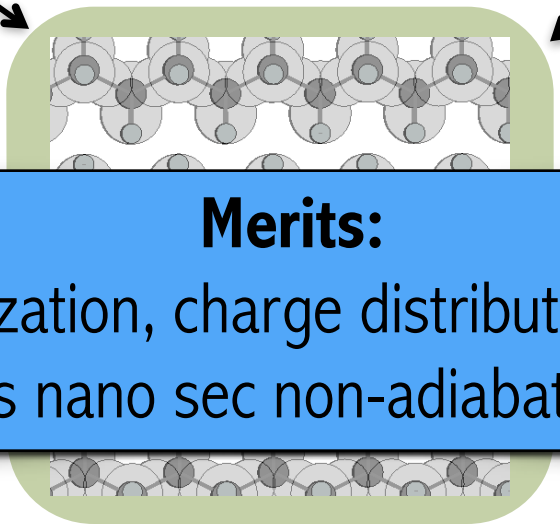
Nuclei as point charges,
FS Gaussian wave
packet electrons
(with spin, radius, charge, xyz)

Mixed Q-C

Quantum



10^2 atoms



10^6 atoms

Merits:

No typing, explicit hybridization, charge distribution, LP, non-adiabatic, etc.
Millions of atoms over 10's nano sec non-adiabatic dynamics (linear scaling)

Wave packet dynamics in Electron Force Field (eFF)

(1) Electrons as FSGO. Wave packet whose **size+position varies with *t***:

$$\psi \propto \exp\left[-\left(\frac{1}{s^2}-\frac{2p_s}{s}\frac{i}{\hbar}\right)(\mathrm{x}-\mathrm{r})^2\right]\cdot\exp\left[\frac{i}{\hbar}\mathrm{p}\cdot\mathrm{r}\right] \longrightarrow i\hbar\frac{\partial}{\partial t}\psi=\hat{H}\psi$$

(2) *Locally harmonic* potential that stays Gaussian over time:

Simple EOMs

$$\frac{dr}{dt}=\frac{\mathrm{p}}{m};\ \frac{d\mathrm{p}}{dt}=-\nabla E \qquad \frac{ds}{dt}=\frac{p_s}{(3/4)m};\ \frac{dp_s}{dt}=-\frac{\partial E}{\partial s}$$

Heller, semiclassical dynamics – J. Chem. Phys **1975** 62(4) 1544-1555
Fermionic molecular dynamics – Rev. Mod. Phys. **2000** 72 655-688

(3) "Pairwise" energy expression with semi-classical *T*, *C* and Pauli:

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

Wavefunction KE
Heisenberg principle

Electrostatics *of Gaussian charge densities and nuclei*

Pauli repulsion
Spin-dependent

(4) Evolve EOMs classically

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

Su and Goddard, PRL, 2007
Jaramillo-Botero et al, JCC, 2011

Spherical Gaussians (FSG) and Pauli in eFF

1 e-=FSG wave packet and n-electron wave function=Hartree product of all FSGs

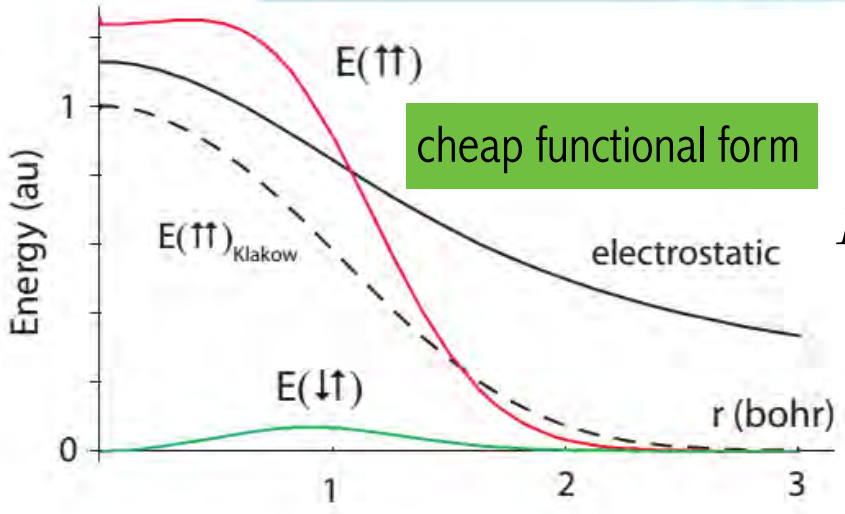
$$\Psi = \prod_i \psi(\vec{r}_i)$$

Electron size is a dynamical variable and its position is not constrained to a nuclear center

Pauli exclusion creates an exchange energy (orthogonalization):

$$E_{\text{exch}}[\{\phi_i\}] = E(\mathcal{A}(\phi_1 \cdots \phi_N)) - E(\phi_1 \cdots \phi_N)$$

Slater determinant Hartree product

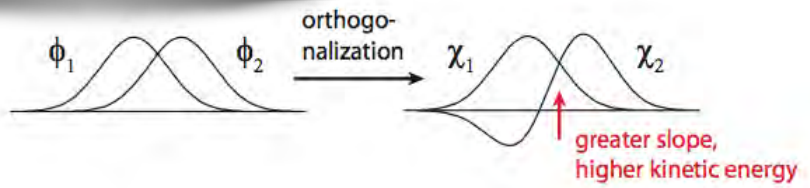


cheap functional form

local anti-symmetrization penalty

$$E(\uparrow\uparrow) \propto \left\langle 12-21 \middle| \hat{T} \middle| 12-21 \right\rangle - \left\langle 12 \middle| \hat{T} \middle| 12 \right\rangle$$

kinetic energy dominates

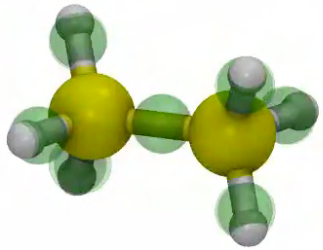


JCP, **2009**, *131*, 244501

eFF Effective Core Potentials (eFF-ECP)

Core-valence Pauli interaction, proportional to wave-packet overlap

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



Find appropriate overlap expression for an 's' electron or a cuasi 'p'

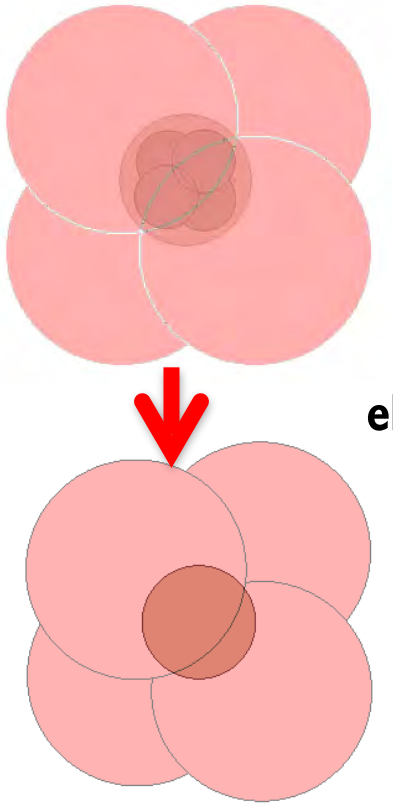
1. s-s overlap (e.g. Na, C, Al, Si) – 3 par.

$$E = a\,exp\left(-\frac{br^2}{c+s^2}\right)$$

2. s-p overlap (e.g. C, N, O) – 6 par.

$$E = a\left(\frac{2}{b/s + s/b}\right)(r-cs)^2\,exp\left[-\frac{d(r-cs)^2}{e+s^2}\right]$$

Xiao, Jaramillo-Botero, Theofanis and Goddard, Mechanics of Materials, Elsevier, 2015



eFF silicon atom

Z = 14

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

15 particles per Si

eFF-ECP silicon atom

Z = 4

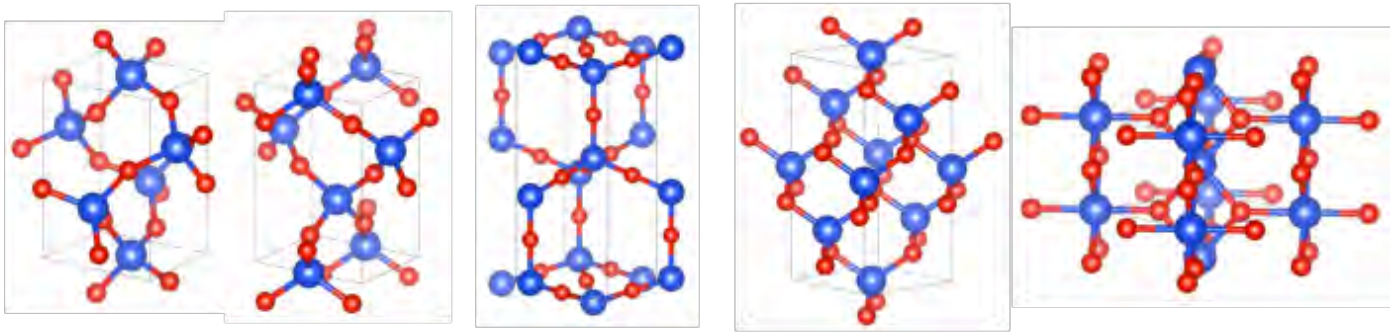
$3s^2\ 3p^2$

5 particles per Si

ECPs based on wavepacket overlap

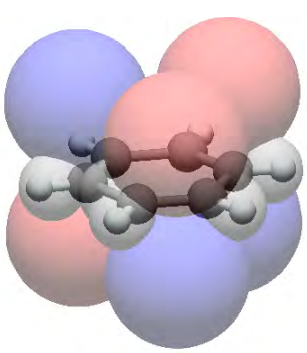
$(\alpha\text{-quartz} \xrightarrow{846\ K} \beta\text{-quartz} \xrightarrow{1140\ K} \beta\text{-tridymite} \xrightarrow{2010\ K} \beta\text{-cristobalite}) \xrightarrow{7.5\sim8.5\ GPa}$ stishovite

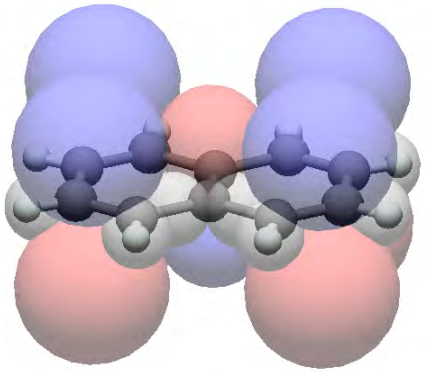
$H_2C{=}CH_2$

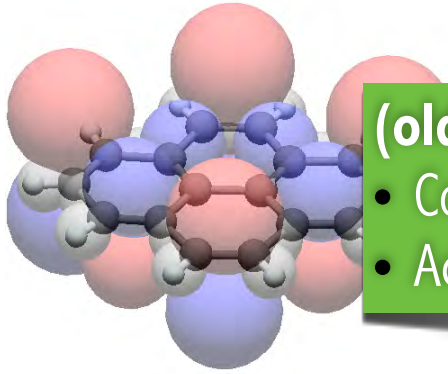


140.2°	150.3°	180.0°	106.3°	98.4°/130.8°
129.3°	139.0°	179.8°	98.6°	99.9°/130.0°

Si-O-Si angle from **PBE** and **eFF-ECP**







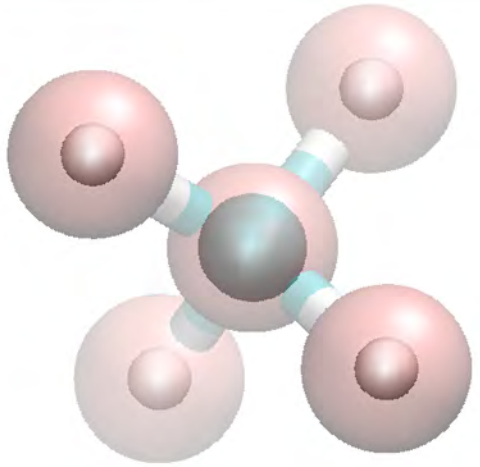
(old) Effective Core Potentials

- Correct multiple bonds and LPs
- Accurate geometries (ionic to cov)

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

USER-EFF package in LAMMPS

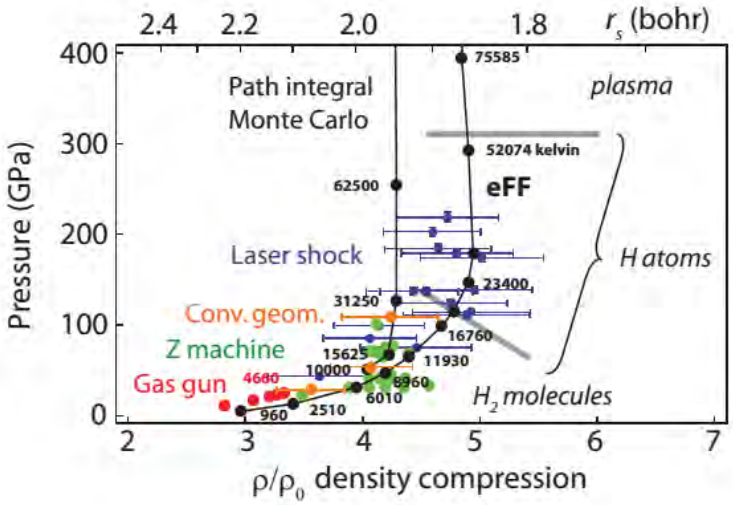
```
15 atoms
3 atom types

-500.0 500.0 xlo xhi
-500.0 500.0 ylo yhi
-500.0 500.0 zlo zhi

Masses

1 12.01070 # C nuclei mass
2 1.000794 # H nuclei mass
3 0.000549 # electron mass

Atoms
#id|type|q|spin|eradius|x|y|z|
1  1  6.0  0  0.0  0.0  0.0  0.0
2  2  1.0  0  0.0  1.0  1.0  1.0
3  2  1.0  0  0.0  -1.0  -1.0  1.0
4  2  1.0  0  0.0  1.0  -1.0  -1.0
5  2  1.0  0  0.0  -1.0  1.0  -1.0
6  3  0.0  -1  0.5  0.0  0.0  0.0
7  3  0.0  -1  1.0  1.0  1.0  1.0
8  3  0.0  -1  1.0  -1.0  -1.0  1.0
9  3  0.0  -1  1.0  1.0  -1.0  -1.0
10  3  0.0  -1  1.0  -1.0  1.0  -1.0
11  3  0.0  1  0.5  0.0  0.0  0.0
12  3  0.0  1  1.0  1.0  1.0  1.0
13  3  0.0  1  1.0  -1.0  -1.0  1.0
14  3  0.0  1  1.0  1.0  -1.0  -1.0
15  3  0.0  1  1.0  -1.0  1.0  -1.0
```

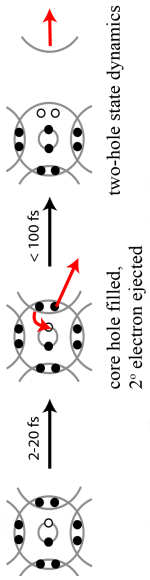


```
units          electron
newton         on
boundary       f f f

atom_style     electron
read_data      data.ch4

pair_style     eff/cut 100.0
pair_coeff     * *

compute        effTemp all temp/eff

min_style      cg
compute        er all property/atom spin eradius erforce
dump           2 all custom 10 ch4.min.lammpstrj id type q c_er[1] c_er[2] x y z fx fy fz c_er[3]
minimize       0 1e-6 2000 4000
```

eFF succesful applications

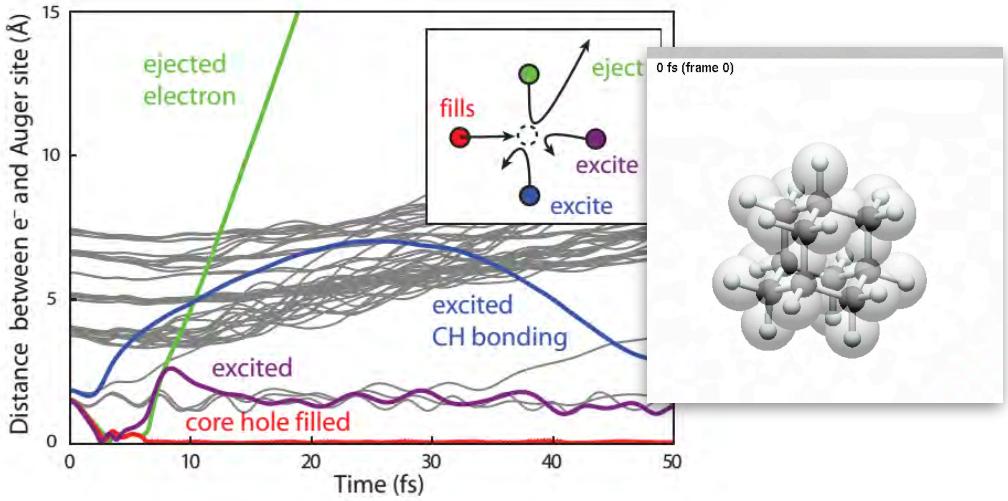
Hugoniot curve of H_2





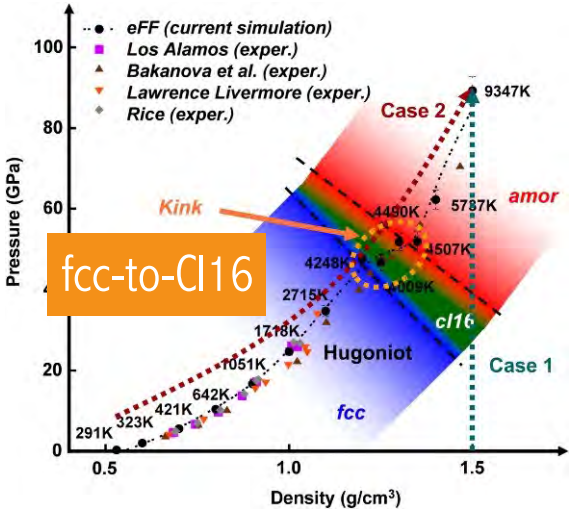
PRL, **2007**, *99*, 185003; *JCP*, **2009**, *131*, 244501

Auger process in hydrocarbon nanoparticle



PNAS, **2009**, *106*, 1001; *JCP*, **2009**, *131*, 244501

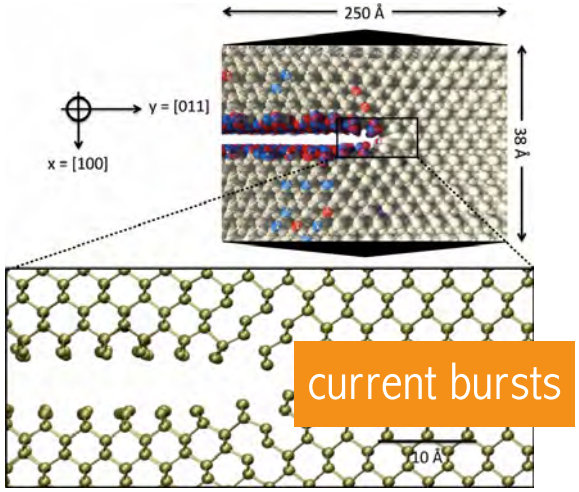
Hugoniot curve of Li



fcc-to-Cl16

PNAS, **2011**, *108*, 15101

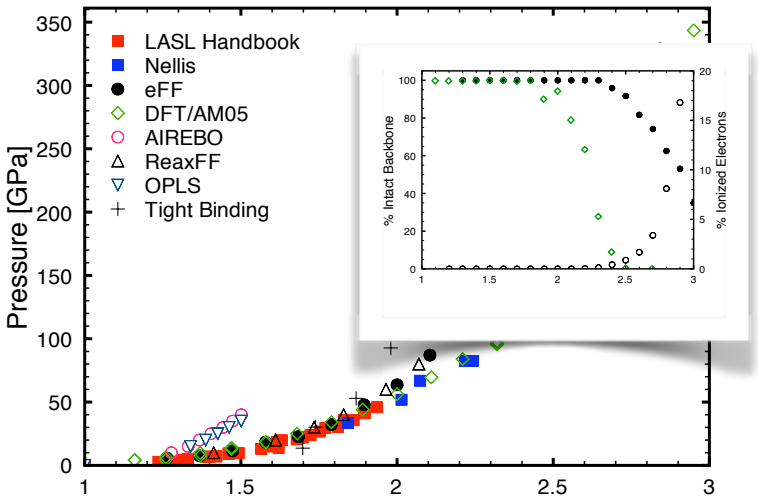
Electrons in brittle fracture of Si



current bursts

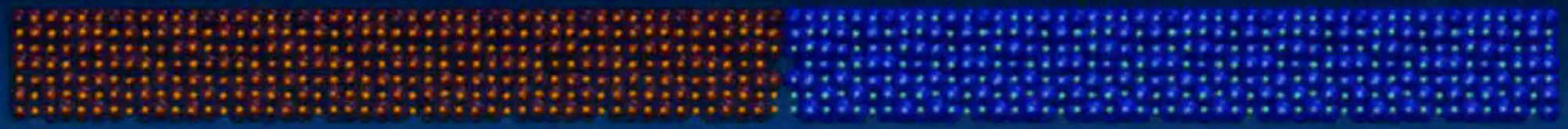
PRL, **2012**, *108*, 045501

Hugoniot and conductivity of PE



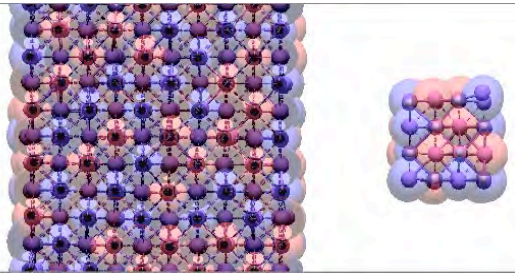
*PRB 85, 094109, **2012***

Non-adiabatic Shock Dynamics

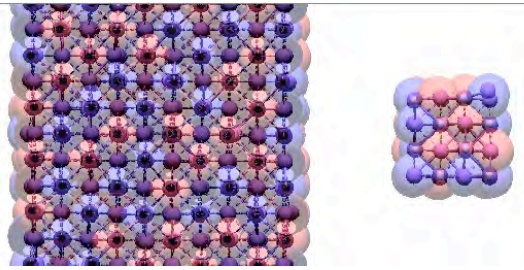


20km/s Li-slab on Li-slab

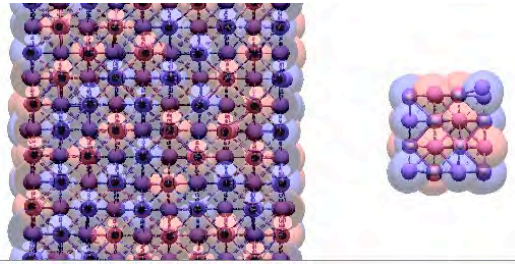
2 km/sec,
welding



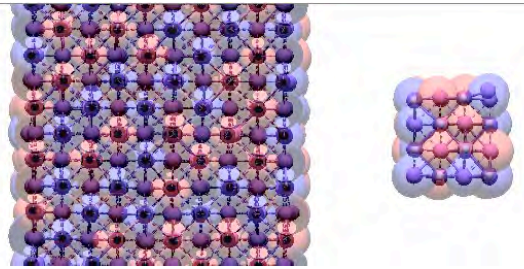
10 km/sec,
fluid layer

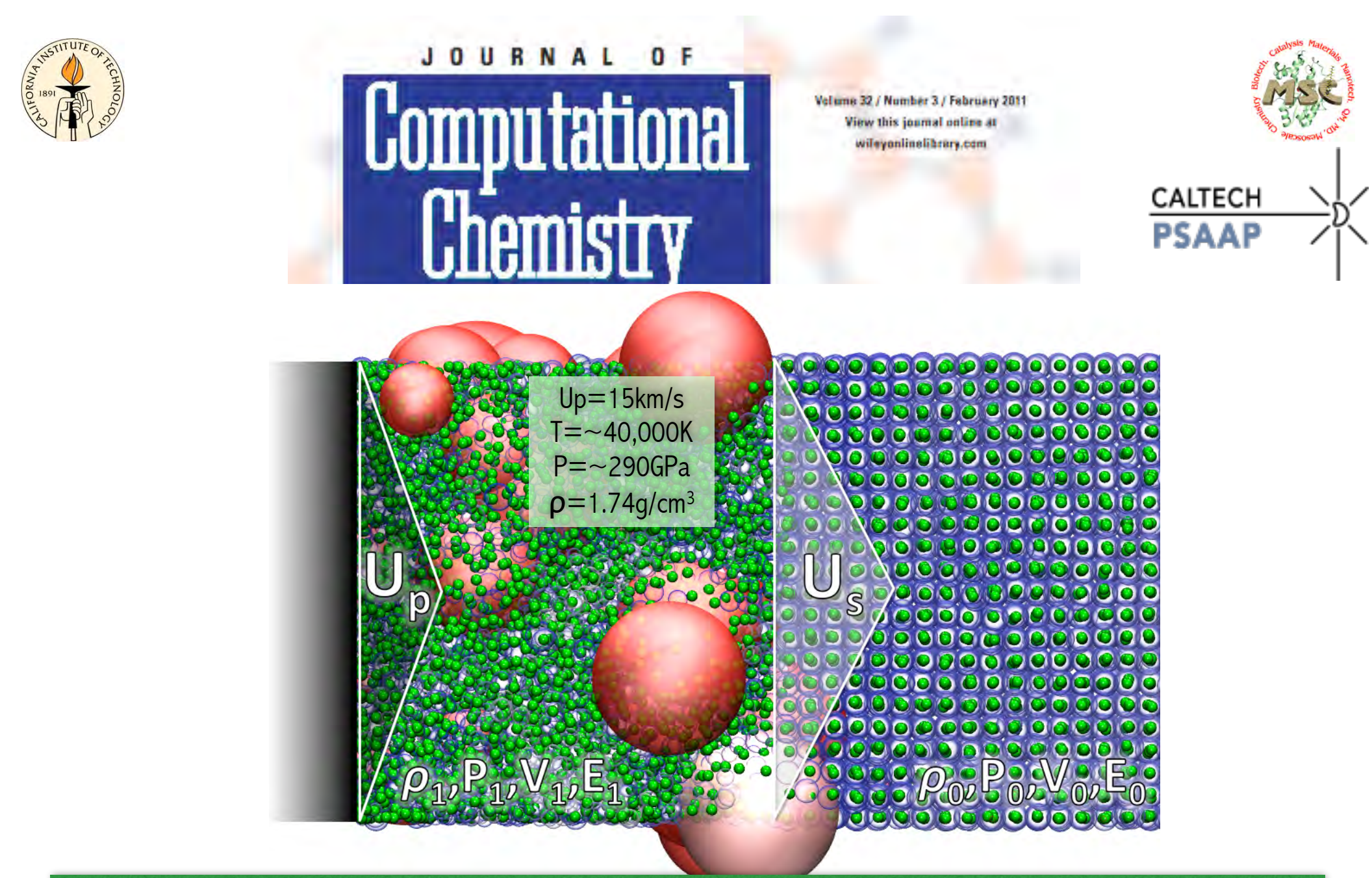


5 km/sec,
melting



20 km/sec,
plasma

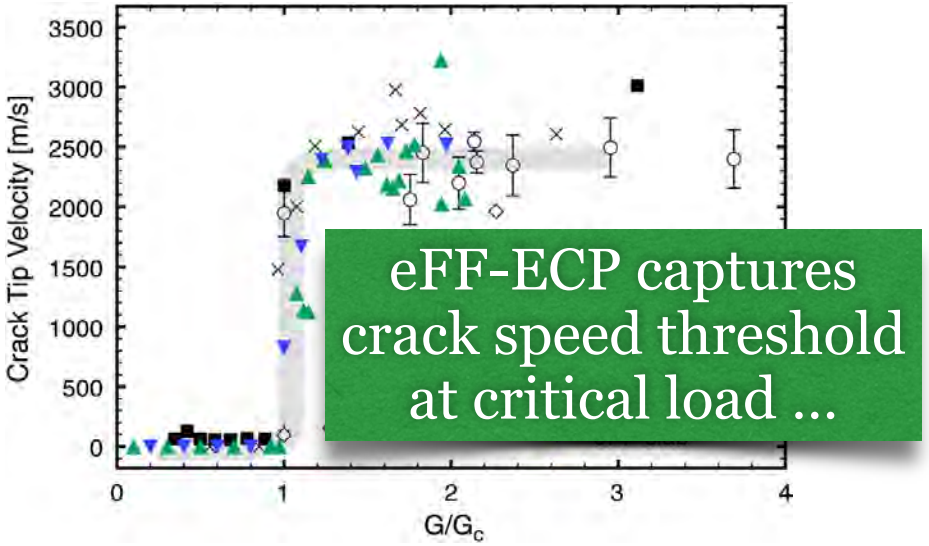




Accurate **dynamic** Rankine Hugoniot from Up/Us relationship

Jaramillo-Botero, An, Su, Goddard (JCC 2011)

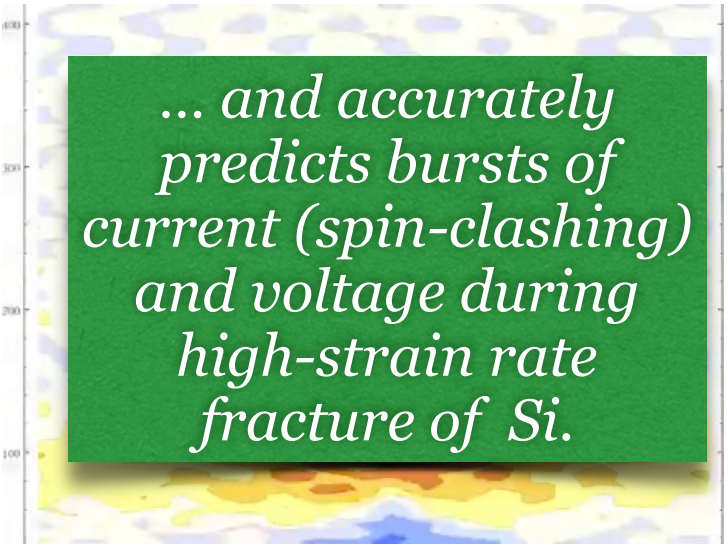
Si brittle fracture: crack speed and emissions



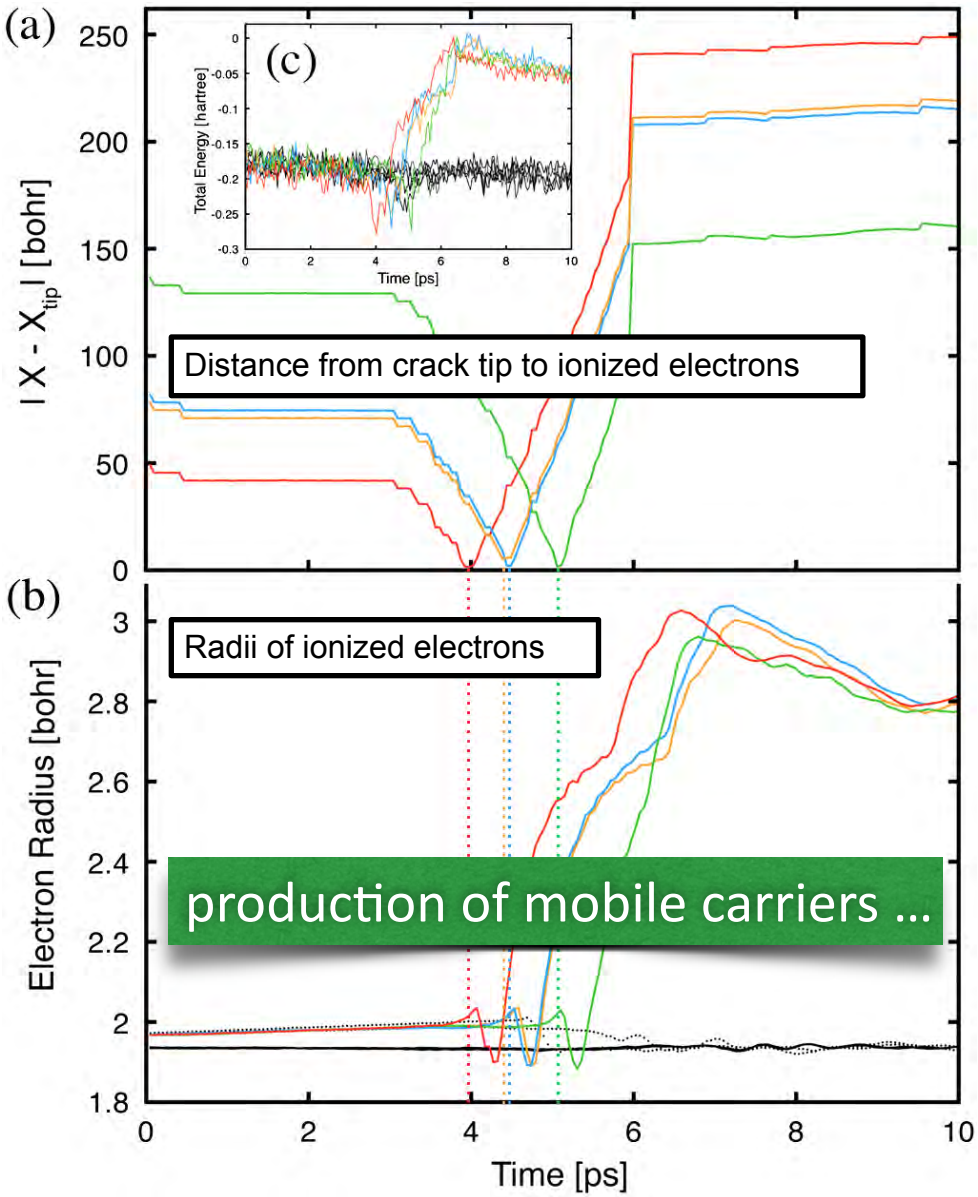
eFF-ECP captures crack speed threshold at critical load …

Crack tip velocity vs energy release rate for (111) - normalized by critical energy release rate determined at the onset of fracture

Validated against experiments in Phys. Rev. Lett. 73, 1170 (1994).



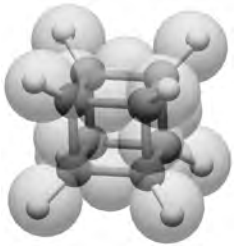
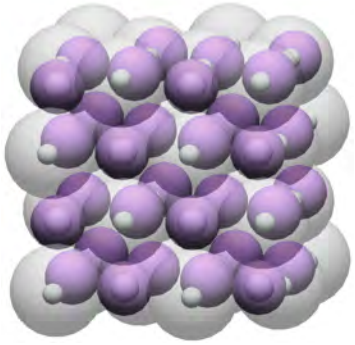
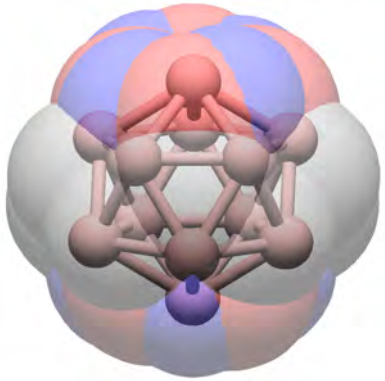
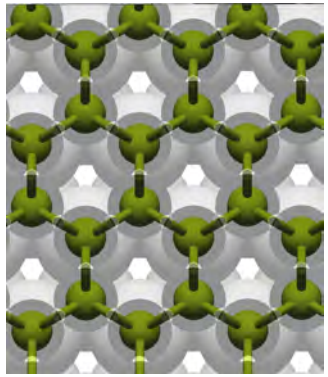
… and accurately predicts bursts of current (spin-clashing) and voltage during high-strain rate fracture of Si.



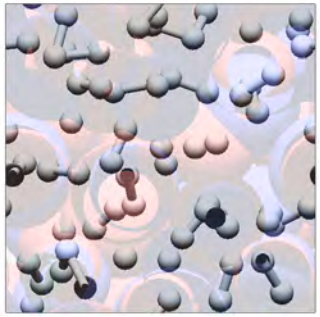
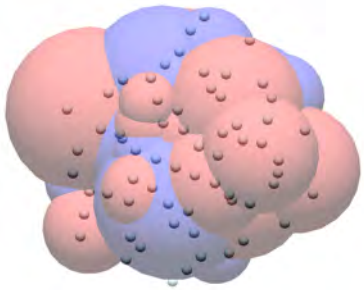
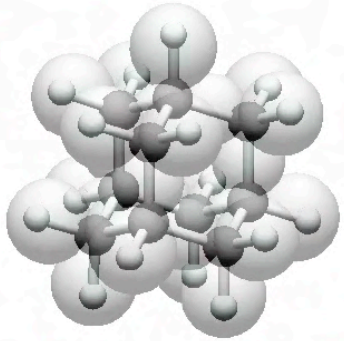
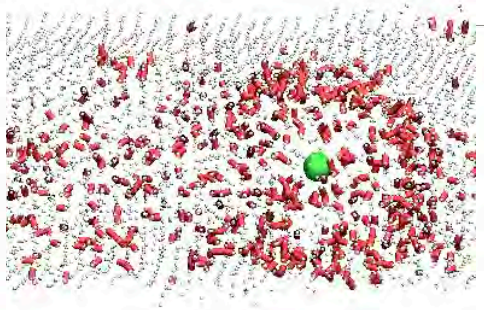
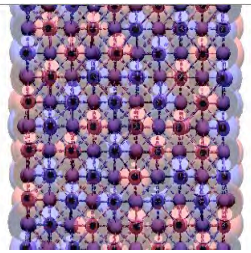
Theofanis, Jaramillo-Botero, and Goddard *PRL*, **2012**, *108*, 045501

First Applicable to a Wide Range of Materials, Molecules and States (~low Z)

Bonding: covalent, ionic, multicenter, metallic

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


Feasible to study large heterogeneous excited systems

eFF shortcomings

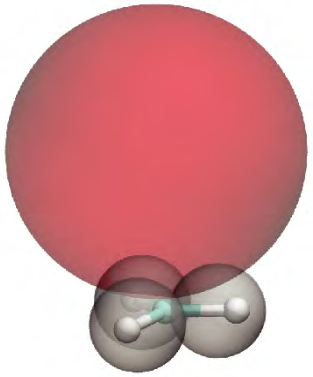
Source of problem

1. FSG per electron

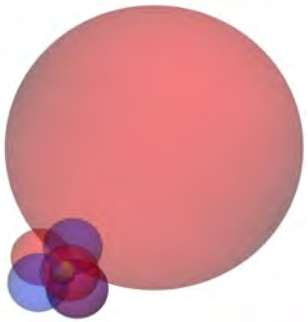
- Difficult higher order angular momentum orbitals, multiple bonds and LPs
- No conjugation due to localized Gaussians
- No cusp condition (e.g. H2)
- No nodal structures (higher Zs)

2. Pauli potential design

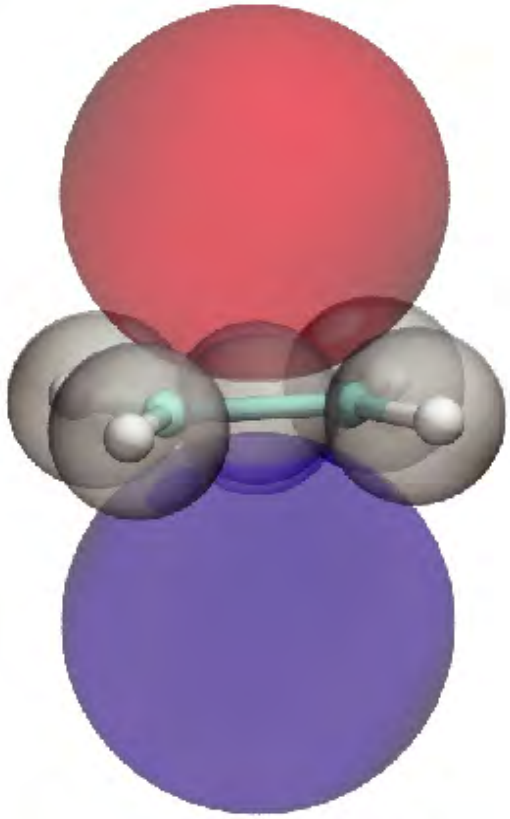
- KE dominates (e.g. zero in pi bonds)
- Difficult atom-specific parameterization
- No correlation for opposite spins
- Direct sum of pair Pauli energy, incorrect



methyl radical
IP =64 (227) kcal/mol



fluorine atom
IP = 190 (402) kcal/mol



ethylene
pi bond is too large

GHA+AMPERE: a rigorous eFF successor

Gaussian Hartree Approximated QM (GHA-QM)

→ New set of Pauli potentials to describe any FSG-represented electron systems with **exact QM level of accuracy**

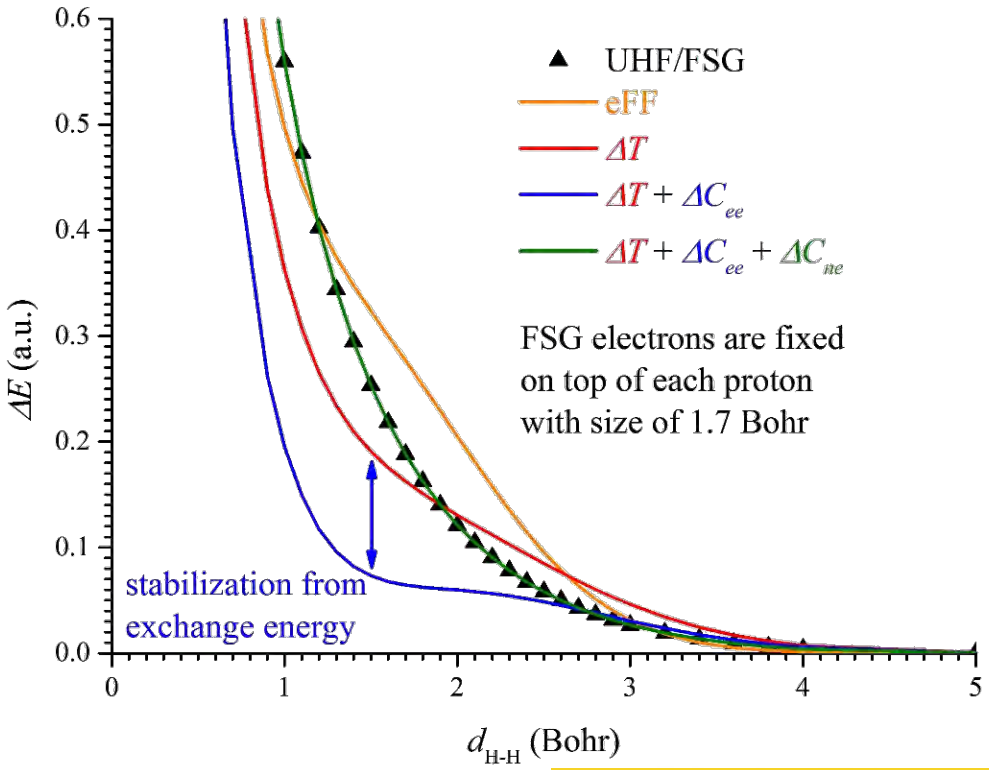
Angular Momentum Projected Effective coRe pseudopotEntial (AMPERE)

→ Compensate for deficiency of FSG: **cusp condition and explicit nodal structures**.
Similar to PP for plane waves.
Also designed for H cusp condition.

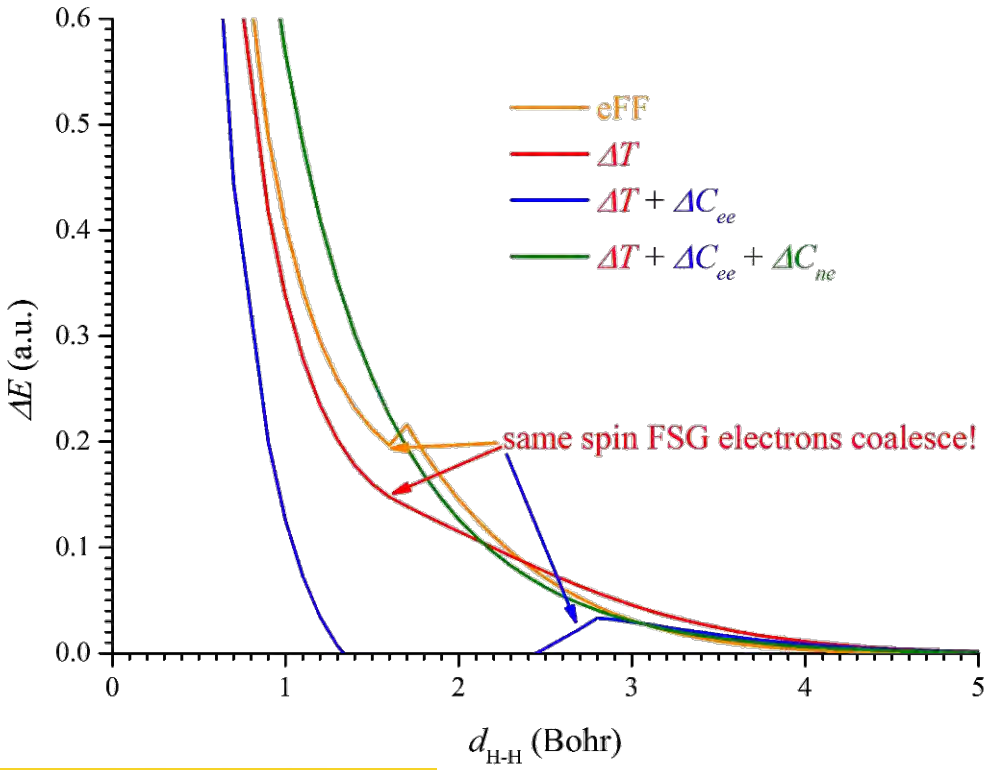
Xiao, Dong, Jaramillo-Botero, Goddard III, **2015**, *in preparation*

Coulomb interaction penalties between e-e and n-e

ΔT dominates; ΔC_{ee} stabilizes at intermediate d



ΔC_{ne} prevents unphysical same spin overlap



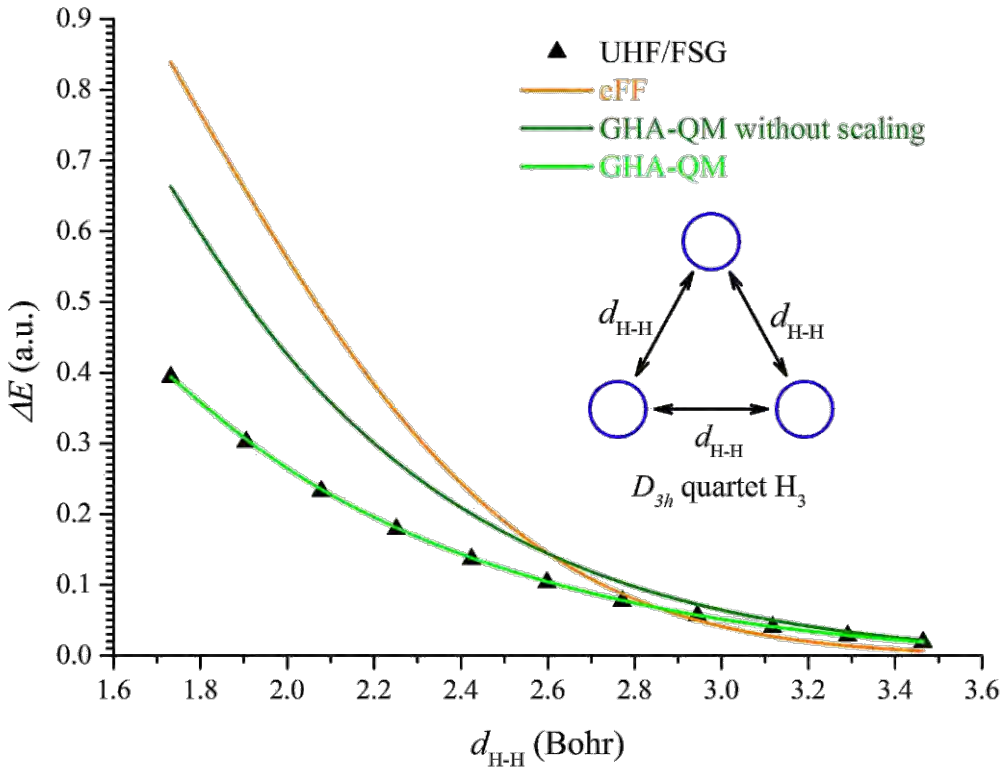
$$E^{\text{base}}_{\text{Pauli}}(\uparrow\uparrow) = \Delta T + \Delta C_{ee} + \Delta C_{ne}$$

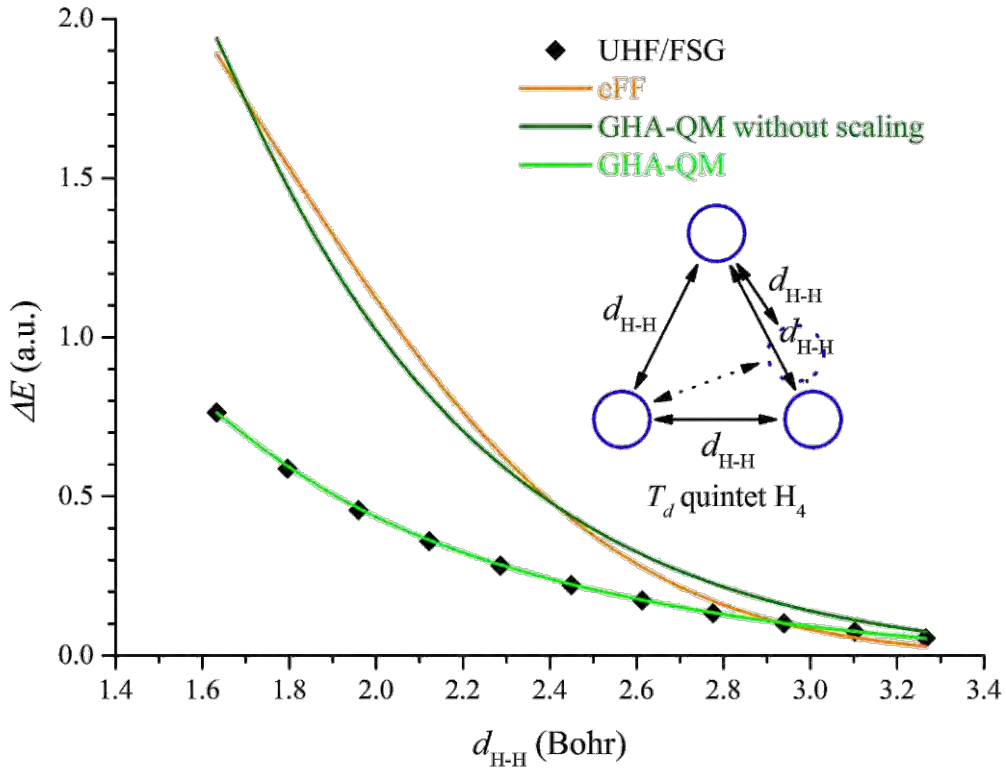
Same spin pair Pauli includes all interactions (T, C) and reproduces exact QM energy

Xiao, Dong, Jaramillo-Botero, Goddard III, **2015**, *in preparation*

Scaling factors are necessary for multiple electrons (symmetric and asymmetric)

Direct sum of local energies (eFF or GHA-QM without scaling) does not work properly





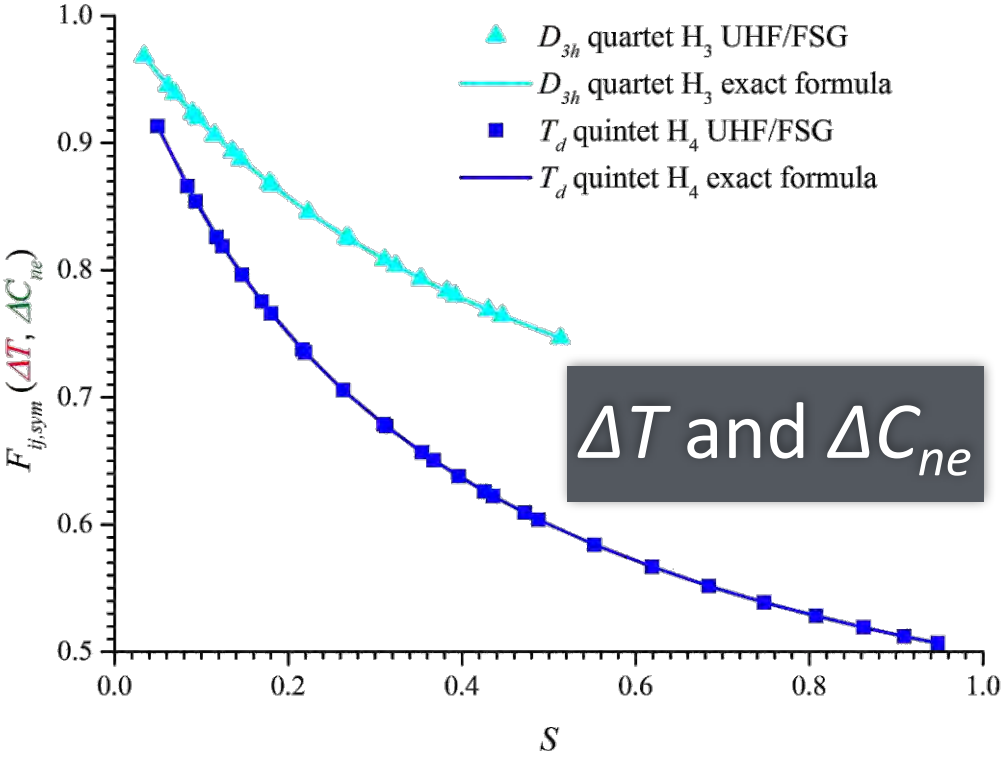
GHA-QM with scaling matches exact UHF energy for quartet and quintet states

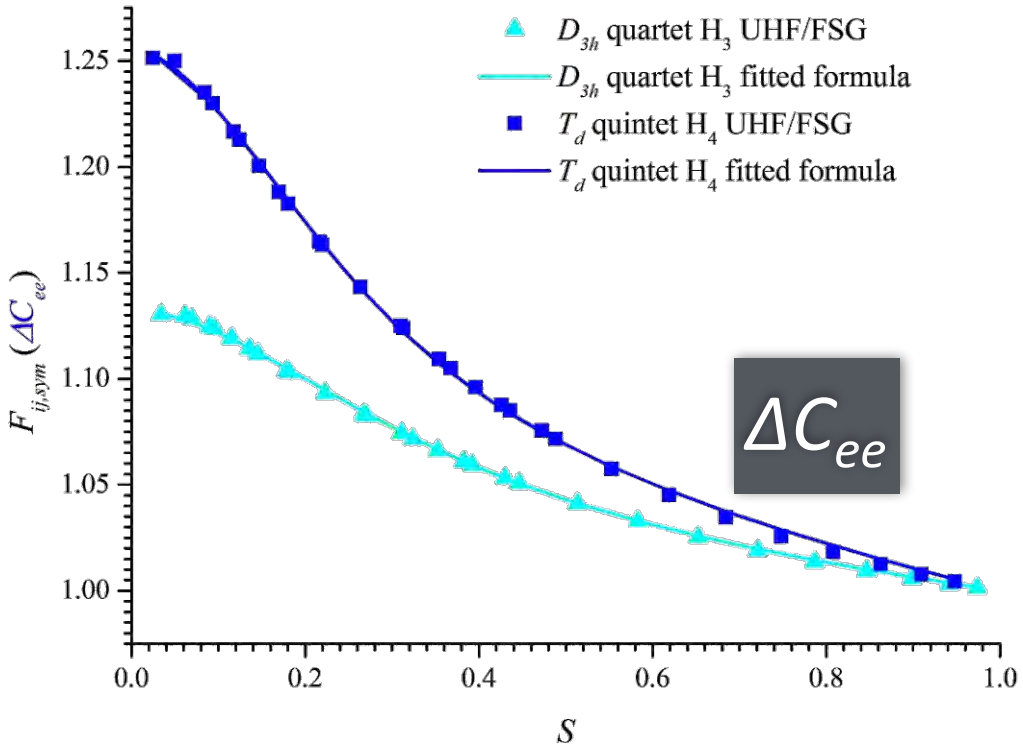
Xiao, Dong, Jaramillo-Botero, Goddard III, **2015**, *in preparation*

Symmetric scaling factors for same spin Pauli

$$F_{ij,sym}(\Delta T, \Delta C_{ne}) = \frac{1+S_{ij}}{1+\sum S}$$

$$F_{ij,sym}(\Delta C_{ee}) = f\left(\frac{a+S_{ij}}{a+\sum S}+\frac{\sum S - S_{ij}}{aS_{ij}+\sum S}\right)^{b} + (1-f)\left(\frac{c+S_{ij}^2}{c+\sum S^2}+\frac{\sum S^2 - S_{ij}^2}{cS_{ij}^2+\sum S^2}\right)^{d}$$





$$\sum S \equiv \frac{1}{2}\left(\sum_k S_{ik} + \sum_{k'} S_{jk'}\right) \qquad \sum S^2 \equiv \frac{1}{2}\left(\sum_k S_{ik}^2 + \sum_{k'} S_{jk'}^2\right)$$

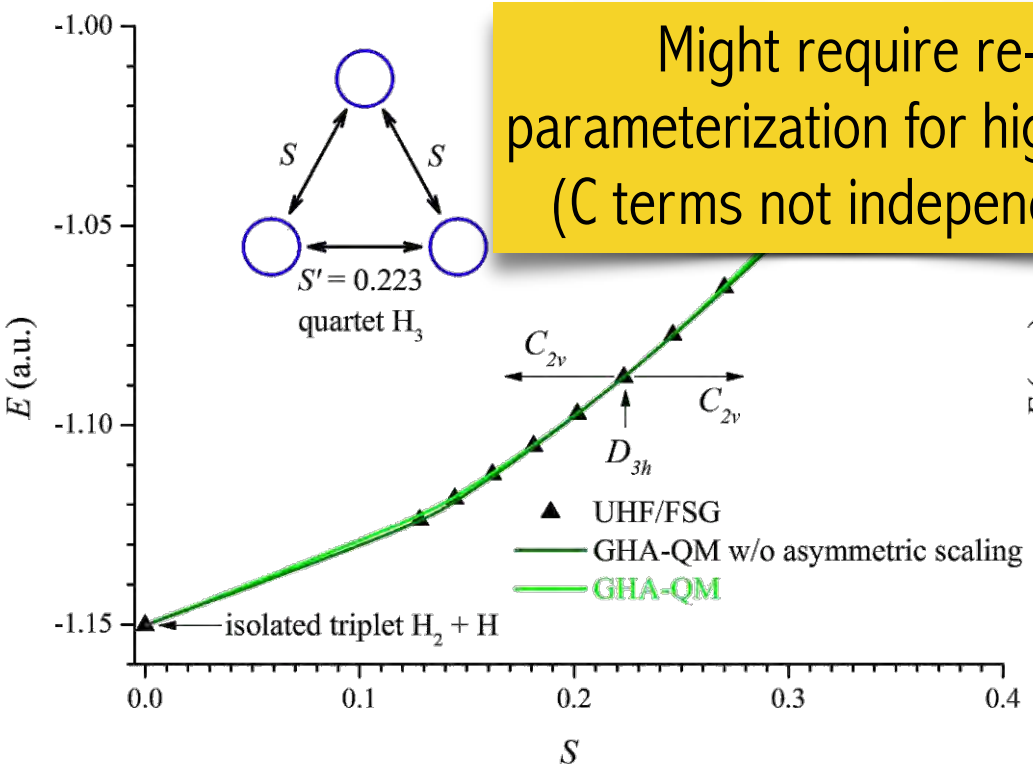
Exact for higher Z elements (Z is out of the integral)

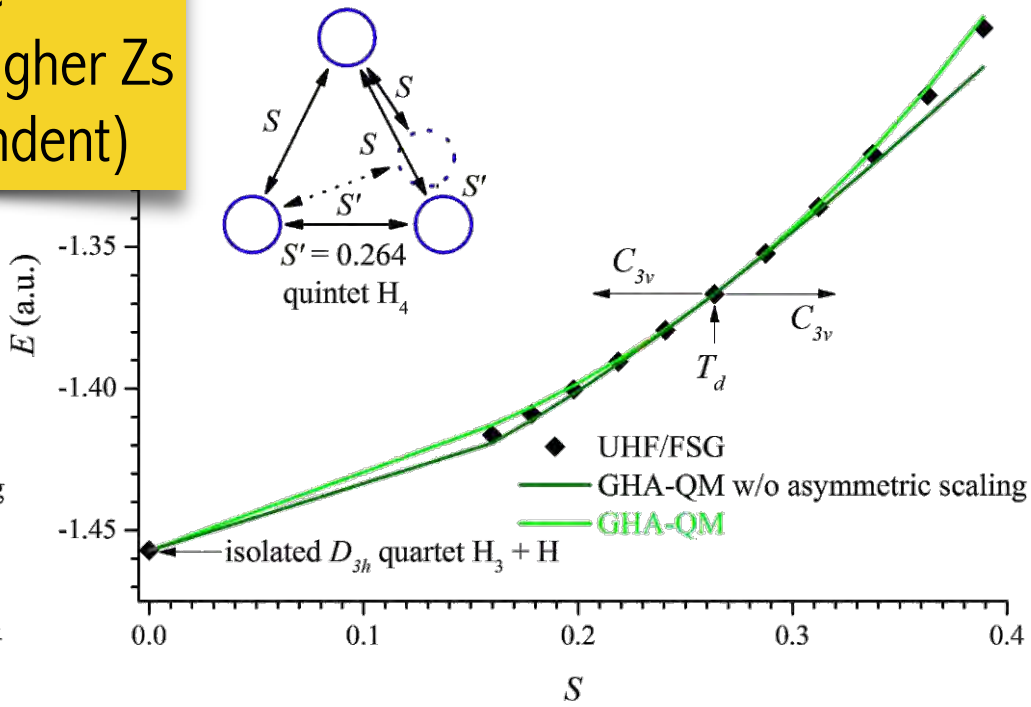
Xiao, Dong, Jaramillo-Botero, Goddard III, **2015**, *in preparation*

Asymmetric scaling factors for same spin Pauli

$$F_{ij,asym}\left(\Delta T, \Delta C_{ee}, \Delta C_{ne}\right) = 1 + a\left(S_{ij}\sum S - \sum S^2\right) + b\left(S_{ij}\sum S - \sum S^2\right)^2 + c\left(S_{ij}\sum S - \sum S^2\right)^3$$

Might require re-parameterization for higher Zs (C terms not independent)





The final same spin Pauli potential of GHA-QM is

$$E_{\text{Pauli}}\left(\uparrow\uparrow\right) = F_{asym}\left(\Delta T\right) F_{sym}\left(\Delta T\right) \Delta T + F_{asym}\left(\Delta C_{ee}\right) F_{sym}\left(\Delta C_{ee}\right) \Delta C_{ee} + F_{asym}\left(\Delta C_{ne}\right) F_{sym}\left(\Delta C_{ne}\right) \Delta C_{ne}$$

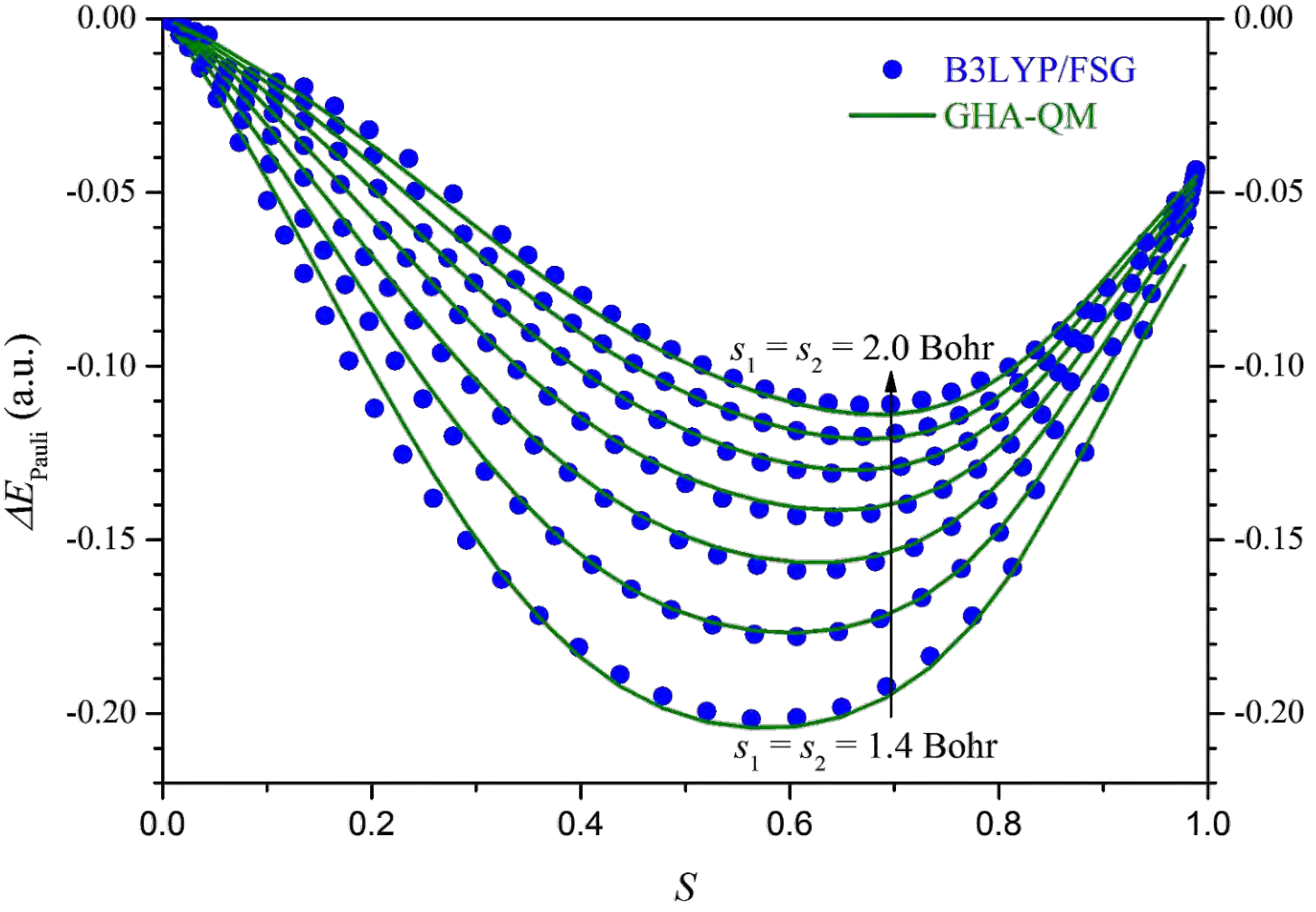
Xiao, Dong, Jaramillo-Botero, Goddard III, **2015**, *in preparation*

Opposite spin Pauli potential: correlation

Wave function consideration always fails, due to complete linear dependence for opposite spin electron pair overlap-coalesce (e.g. in He atom)

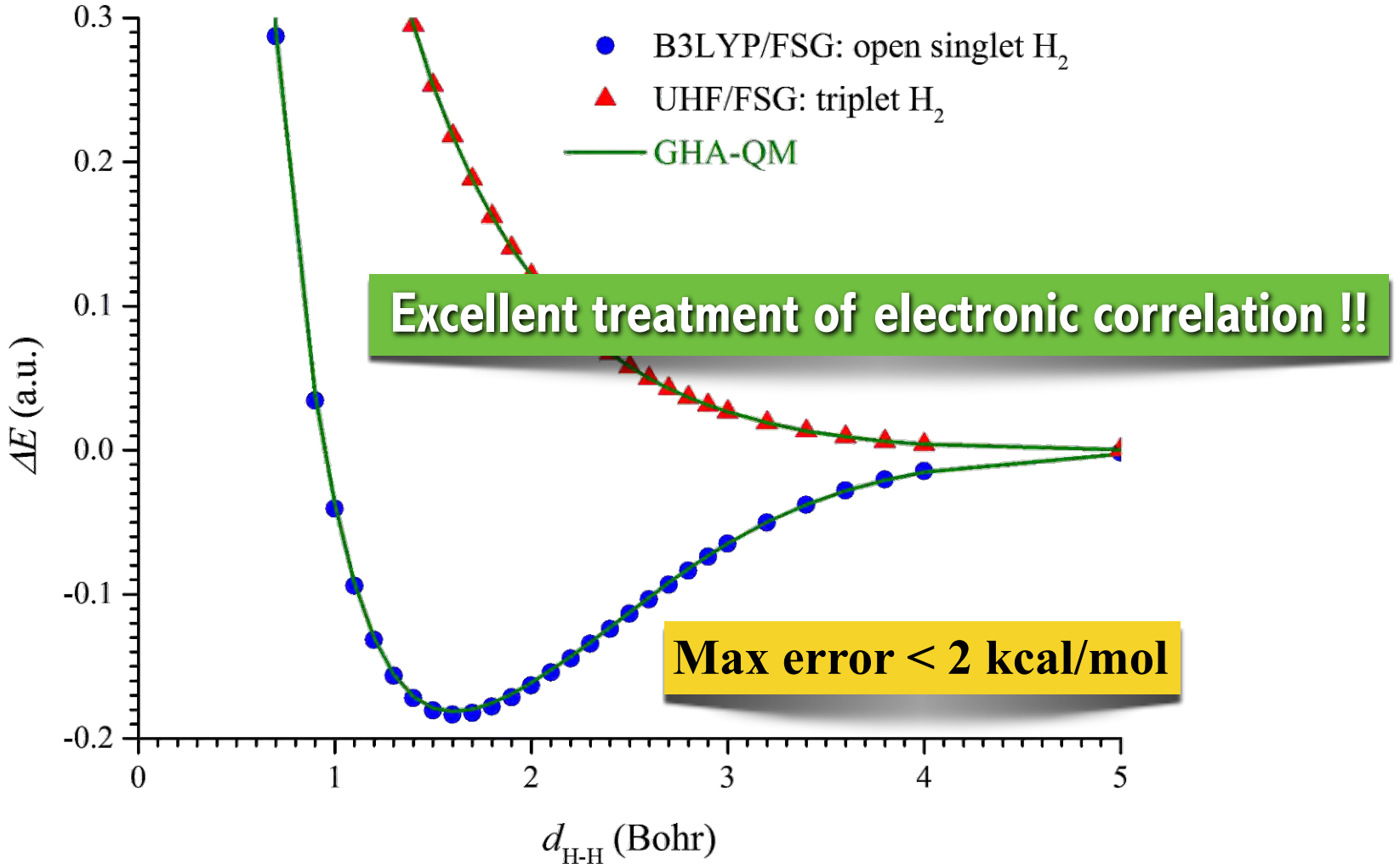
DFT-like: overlap density and average size (we relate electron size to electron density directly).

$$E_{\text{Pauli}}^{\text{base}}(\uparrow\downarrow) = -\frac{p_0 S^{p_1} + p_2 S^{p_3}\bar{s}^{p_4}}{1 + p_5 S^{p_6} + p_7 S^{p_8}\bar{s}^{p_9}} \qquad \bar{s} \equiv \frac{s_1 s_2}{\sqrt{s_1^2 + s_2^2}}$$



Xiao, Dong, Jaramillo-Botero, Goddard III, **2015**, *in preparation*

Accurate opposite spin pair description



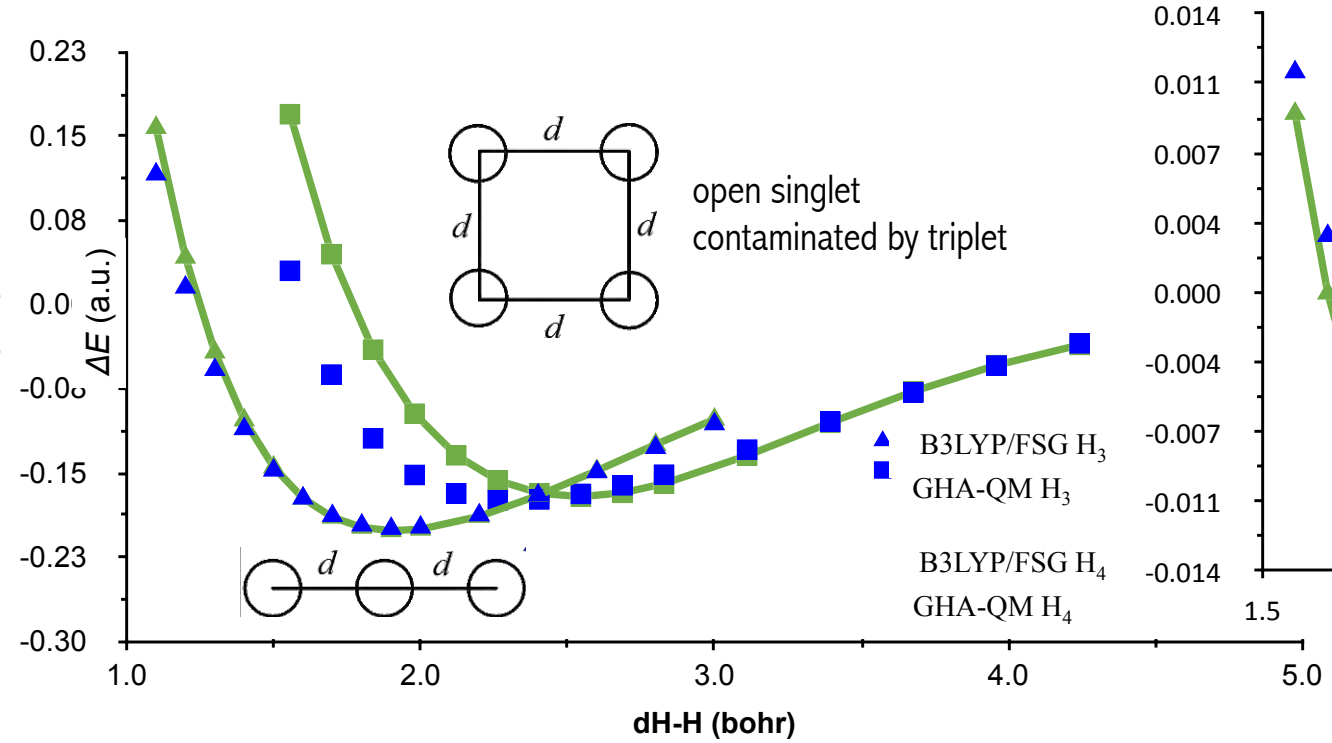
Xiao, Dong, Jaramillo-Botero, Goddard III, **2015**, *in preparation*

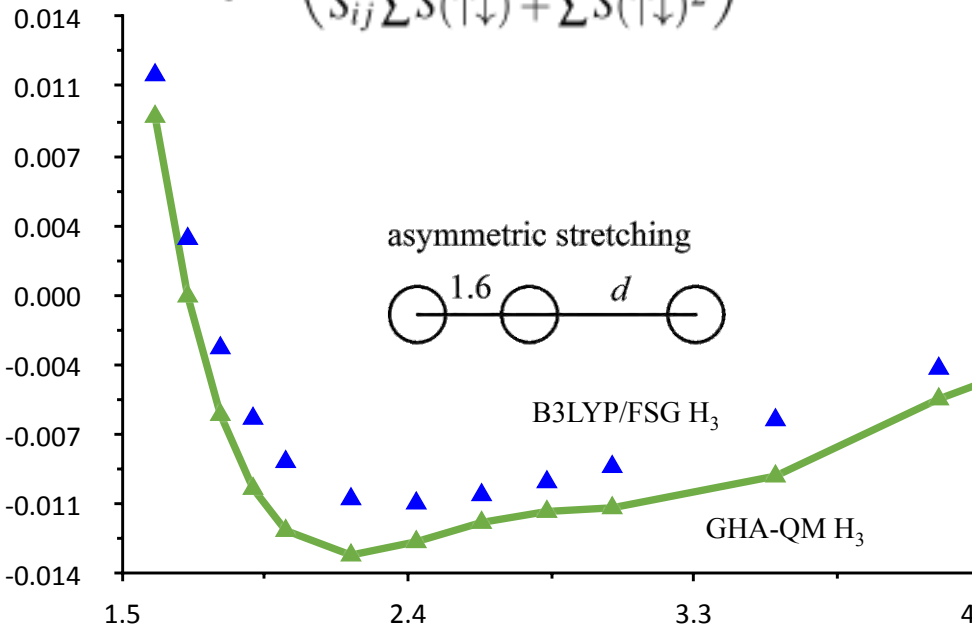
Symmetric and asymmetric scaling for opposite spin

$$F_{ij,sym}(\uparrow\downarrow) = \left(\frac{1 + p_2 S_{ij} + p_3 S_{ij}^2}{1 + p_2 \sum S + p_3 \sum S^2} \right)^{p_1}$$

$$F_{ij,asym}(\uparrow\downarrow) = p_{a1} D_{ij} + p_{a2} D_{ij}^2 + p_{a3} D_{ij}^3$$

$$D_{ij} = \left(\frac{S_{ij} \sum S(\uparrow\downarrow) - \sum S(\uparrow\downarrow)^2}{S_{ij} \sum S(\uparrow\downarrow) + \sum S(\uparrow\downarrow)^2} \right)$$





Errors < 2.2 kcal/mol

GHA-QM final opposite spin Pauli

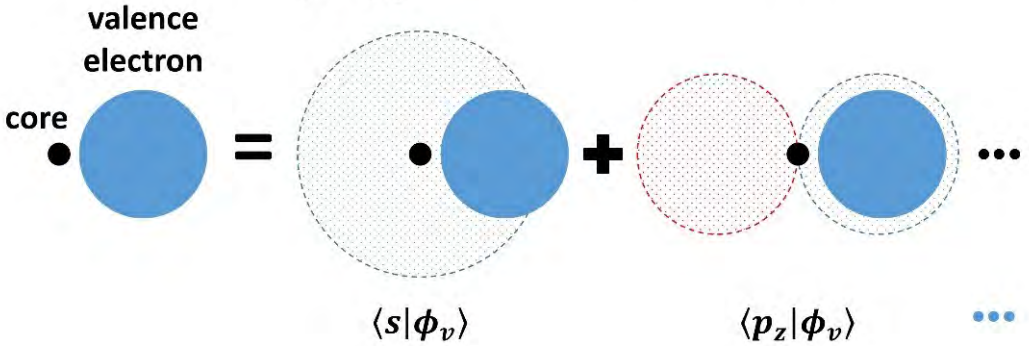
$$E_{Pauli}(\uparrow\downarrow) = [F_{asym}(\uparrow\downarrow) + F_{sym}(\uparrow\downarrow)] E_{Pauli}^{base}(\uparrow\downarrow)$$

Xiao, Dong, Jaramillo-Botero, Goddard III, **2015**, *in preparation*

Angular Momentum Projected Effective coRE (AMPERE) design

$$|\phi_v\rangle = \sum_{\{lm\}_c} |\{lm\}_c\rangle \langle\{lm\}_c | \phi_v\rangle$$

Xiao, Dong, Jaramillo-Botero, Goddard III, **2015**, *in preparation*



The floating nature of FSG provides the flexibility to describe orbitals with higher angular momenta

$$\hat{h}_v = -\frac{1}{2}\nabla^2 - \frac{Z_c}{|\vec{r}-\vec{R}_c|} + V(\vec{r}-\vec{R}_c)$$

$$V(\vec{r}-\vec{R}_c) \cong V_L(|\vec{r}-\vec{R}_c|) + \sum_{l=0}^{L-1}\sum_{m}\left(V_l(|\vec{r}-\vec{R}_c|) - V_L(|\vec{r}-\vec{R}_c|)\right)|lm\rangle\langle lm|$$

$$\equiv V_L(|\vec{r}-\vec{R}_c|) + \sum_{l=0}^{L-1}\sum_{m} V_{l-L}(|\vec{r}-\vec{R}_c|)\,|lm\rangle\langle lm|$$

$$E_{cv} = -\frac{Z_v}{r_{cv}}\,\mathrm{Erf}\left(\frac{\sqrt{2}r_{cv}}{s_v}\right) + \langle\phi_v\,|\,V(\vec{r}-\vec{r}_c)\,|\,\phi_v\rangle$$

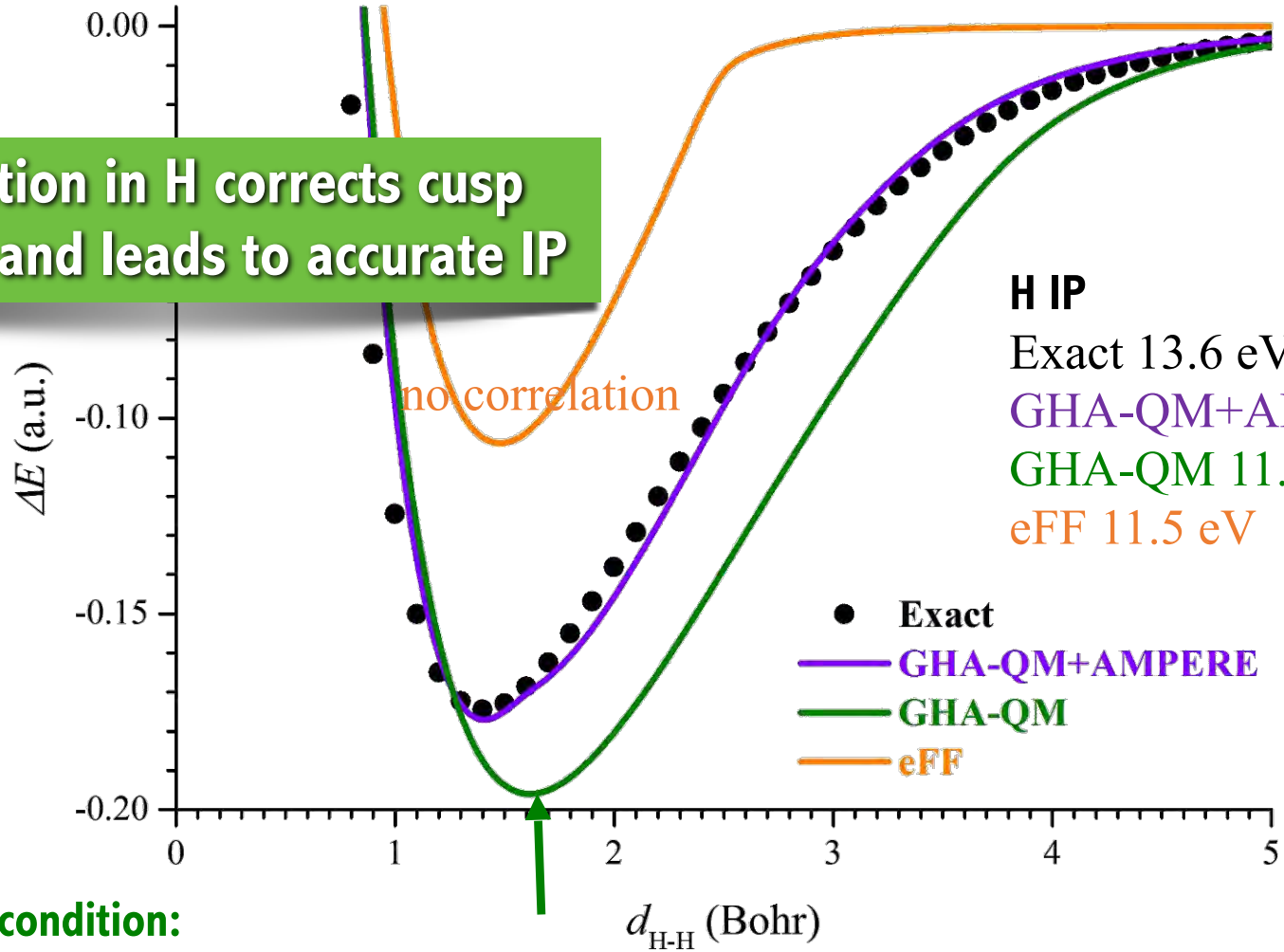
adapted to eFF framework

- *Embeds interactions associated with* ***cusp condition and explicit nodal structures.***
- ***Automatic hybridization*** *in valence e- wave function*

Compensating cusp condition in H with AMPERE

Xiao, Dong, Jaramillo-Botero, Goddard III, **2015**, *in preparation*

S projection in H corrects cusp condition and leads to accurate IP



H IP

Exact 13.6 eV

GHA-QM+AMPERE 13.8 eV

GHA-QM 11.5 eV

eFF 11.5 eV

Lack of cusp condition:

- weak binding to proton (low H energy)
- overestimated bonding

Low-T crystalline material's growth

1. Gas-phase reaction energy
2. Reactant flux to surface
3. Surface reaction energy
4. Surface species mobility
5. Byproduct removal

Our focus

Reactant flux:

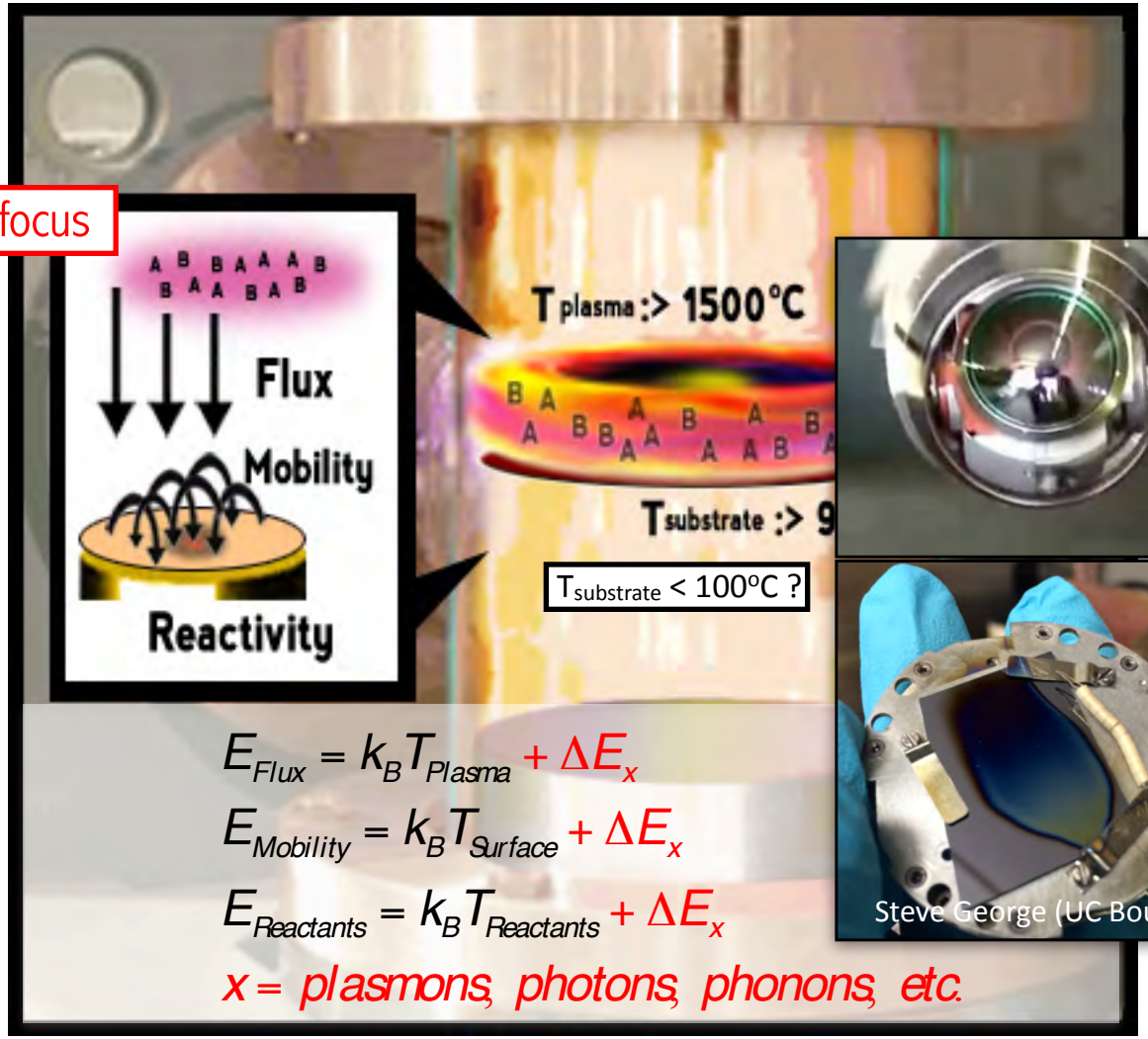
$$J_l = \frac{1}{4} n \sqrt{\frac{8 E_{flux}}{\pi m}}$$

Surface mobility:

$$D = D_0 e^{-E_{diff}/E_{mobility}}$$

Surface reactions:

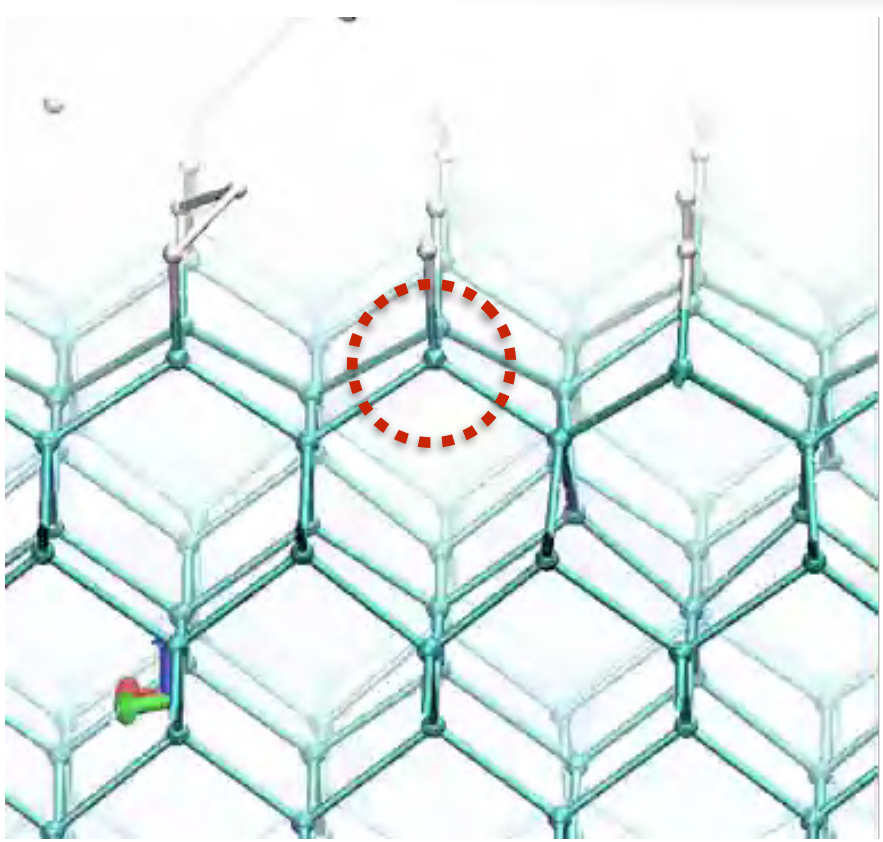
$$E_a = -E_{Reactants} \ln\left(k/A\right)$$

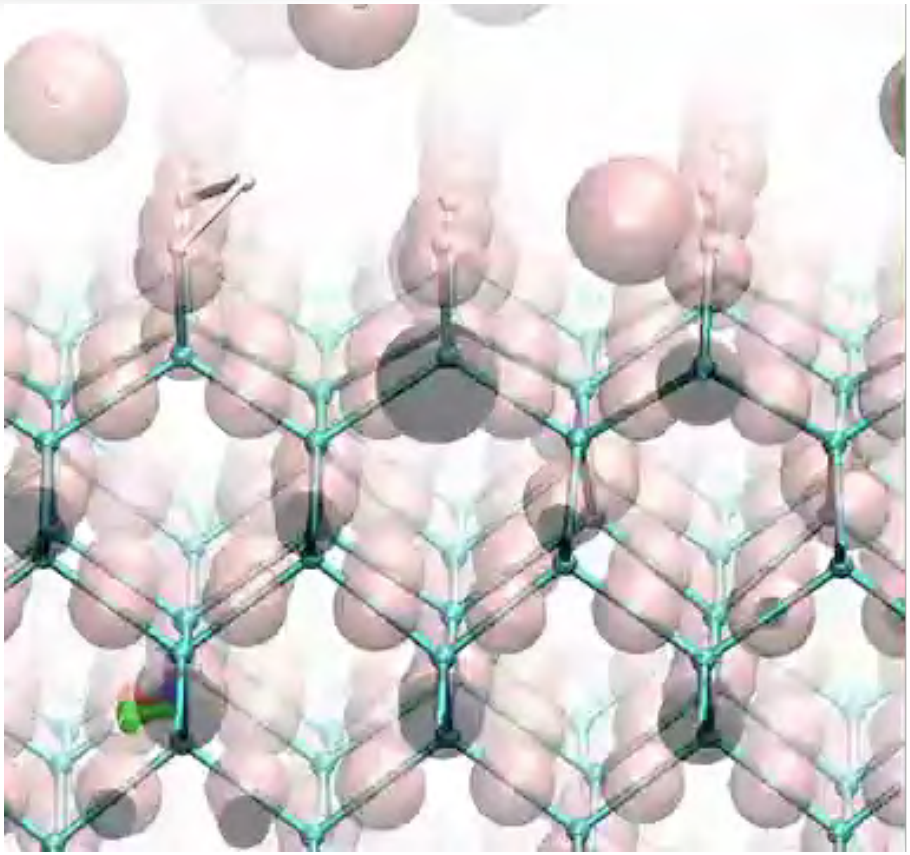


Explore diamond TF growth mechanisms to predict kinetic/thermodynamic requirements/opportunities

Enhanced surface H desorption from diamond (<5eV excitations)

H abstracted into H_2 by gas phase atomic H at 80/400 fs and 15,000K





Electrons not shown

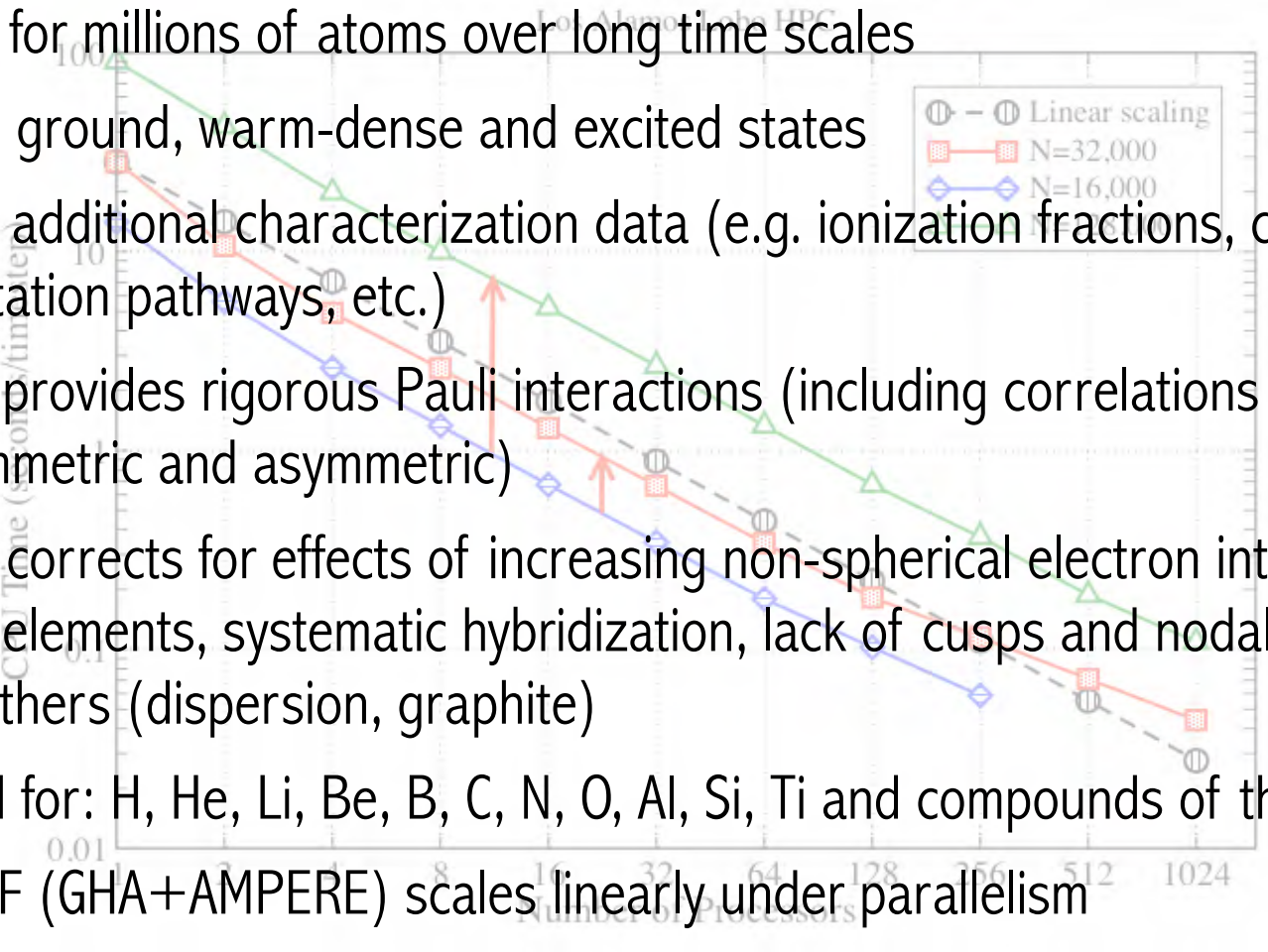
Electronic excitations enhanced H desorption

Jaramillo-Botero, IUTAM, Sevilla, 2014

No desorption event w/out e- excitation

GHA-QM+AMPERE non-adiabatic dynamics capabilities

- Practical for millions of atoms over long time scales
- Captures ground, warm-dense and excited states
- Provides additional characterization data (e.g. ionization fractions, conductivity, fragmentation pathways, etc.)
- GHA-QM provides rigorous Pauli interactions (including correlations for opposite spin, symmetric and asymmetric)
- AMPERE corrects for effects of increasing non-spherical electron interactions in higher Z elements, systematic hybridization, lack of cusps and nodal structures, among others (dispersion, graphite)
- Validated for: H, He, Li, Be, B, C, N, O, Al, Si, Ti and compounds of these
- USER-EFF (GHA+AMPERE) scales linearly under parallelism
- Current apps: Hugoniots (metallic H), LEE surface chemistry, dielec break, RTI …



Acknowledgements

- Thank you all for listening

- Steve Plimpton and Organizers
- Hai Xiao
- Sijia Dong
- William A. Goddard III

Funding:

- DOE-NNSA (Caltech-PSAAP), NASA-JPL, DARPA