SCIENCE & SOFTWARE for PREDICTIVE SIMULATIONS of CHEMO-MECHANICAL PHENOMENA IN REAL MATERIALS

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University of Illinois

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$ NSF, ITR, DMR $

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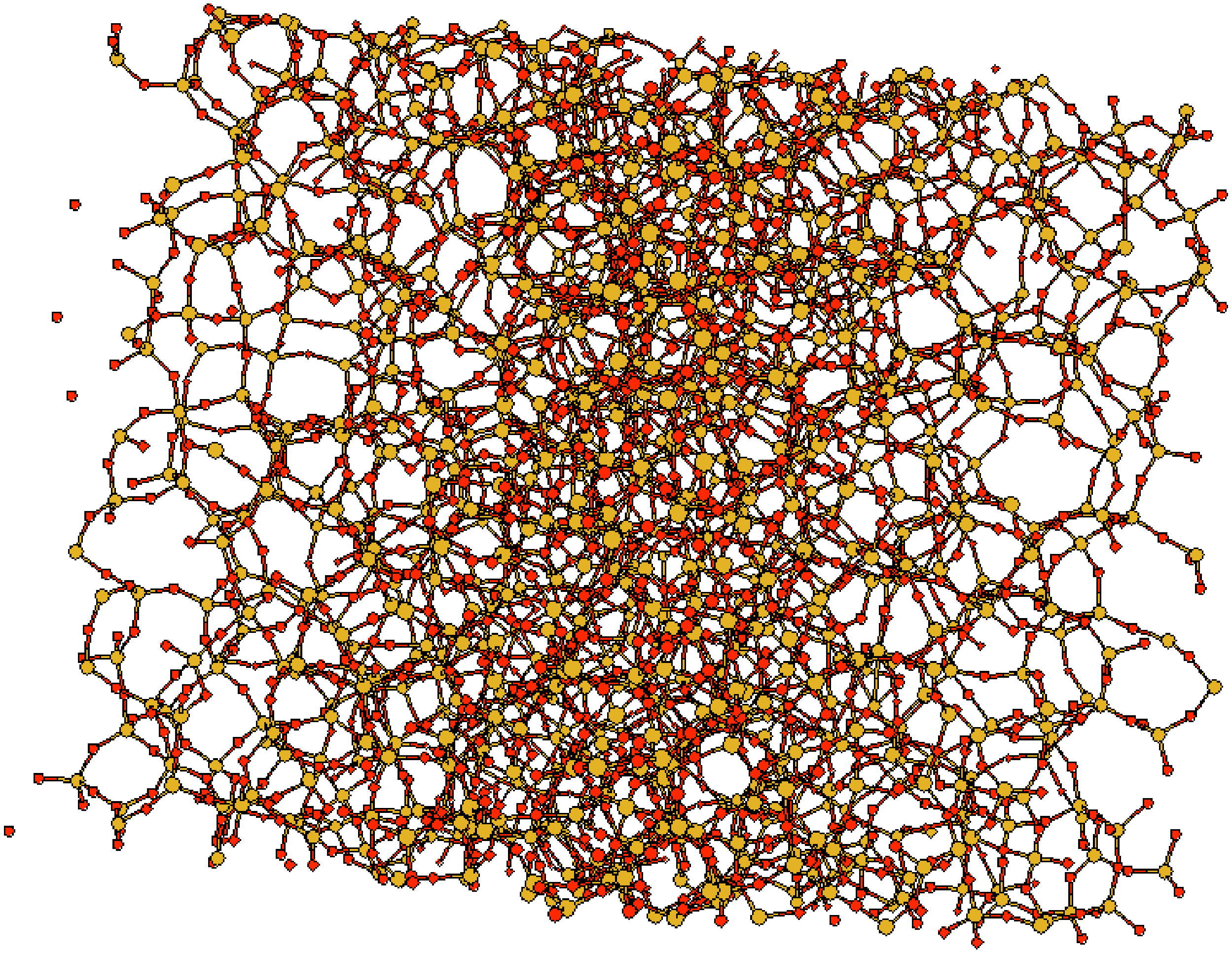
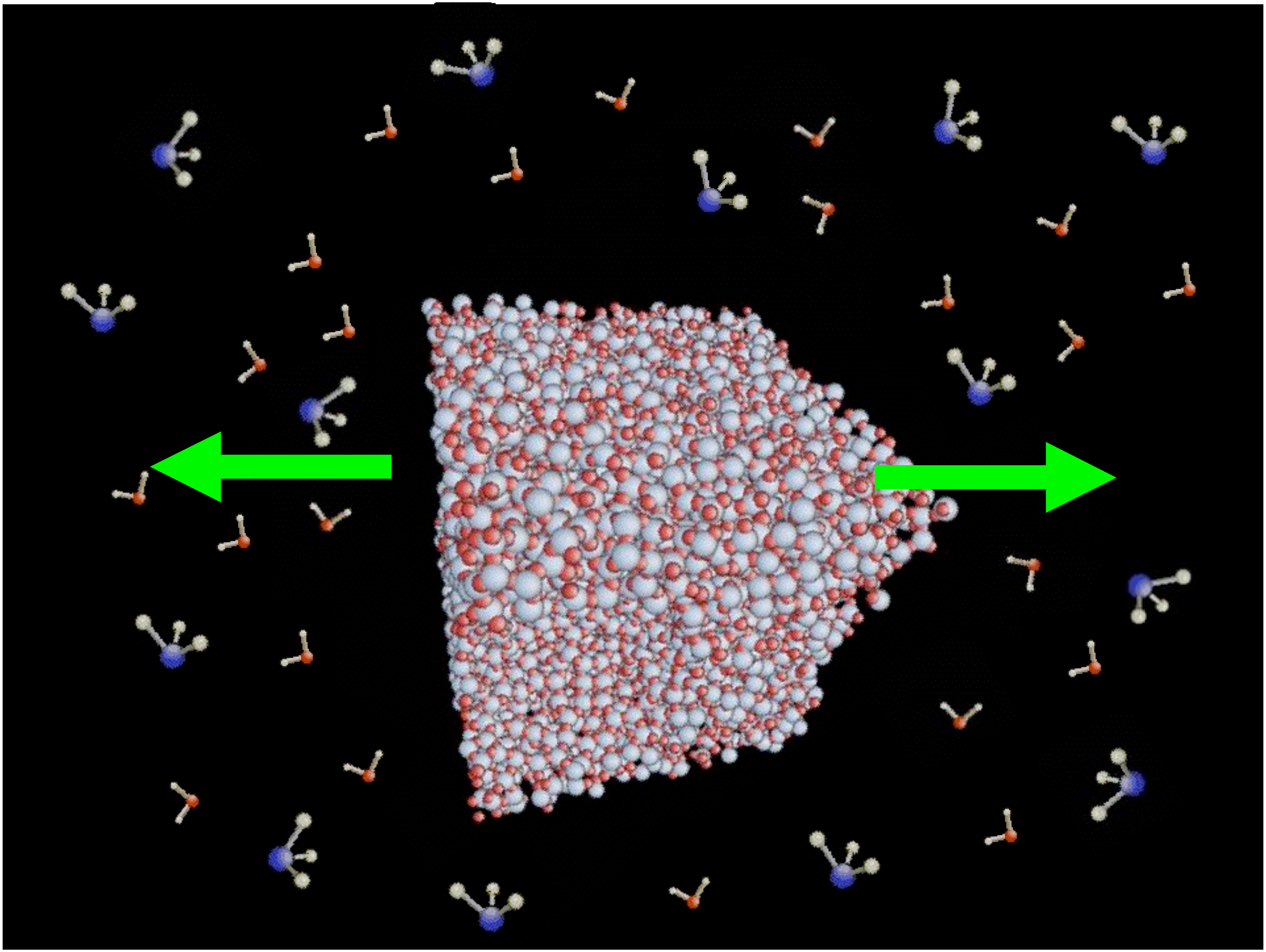
‘Predictive Theory’ for molecular systems, means that a computer model which implements that theory will provide reliable results in the absence of experiment, qualitatively or quantitatively.

Amorphous silica sample

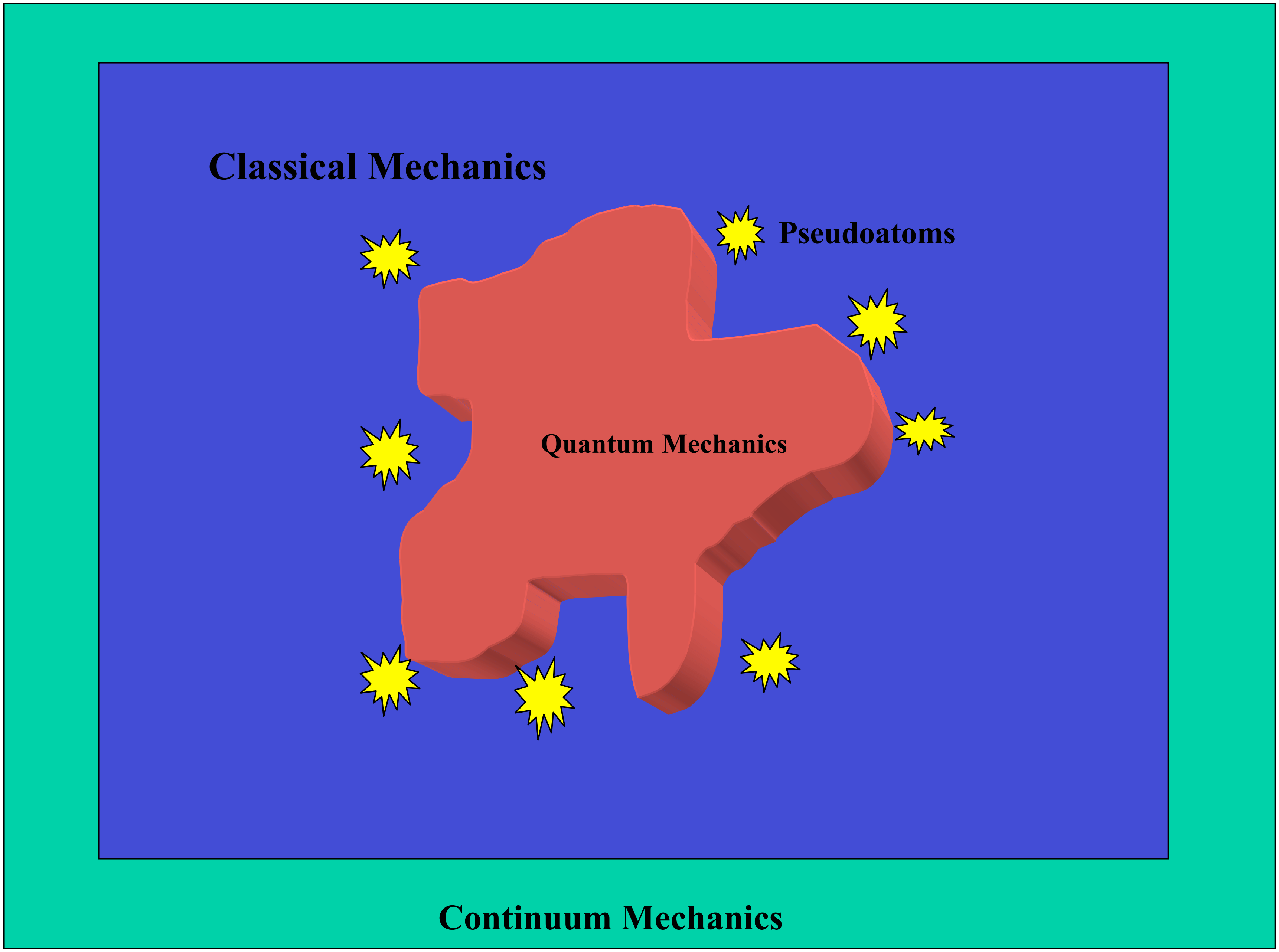




OBJECTIVE: ‘PREDICTIVE’ SIMULATIONS (FIRST PRINCIPLES)

PROBLEMS:

- Simulations can be no better than the forces of interaction, and those would preferably come from quantum mechanics.
- Required size of simulation places severe demands on the rapid generation of forces, making it difficult to use QM forces, exclusively.
- The description of optical properties requires a multi-state QM description.


Classical Mechanics
Pseudoatoms
Quantum Mechanics
Continuum Mechanics

OUTLINE
(Predictive Multi-scale Simulations)

IDENTIFICATION: Mixed potential/wavelet description to identify location of strain in material.

- INTERFACE: Achieving consistent forces between classical and quantum regions.

- HYDROLYTIC WEAKENING: Addition of water to silica to assess mechanisms, kinetics, and energetics.

REGION I: The quantum mechanical core.
"Transfer Hamiltonian" as a new route toward the QM part of predictive simulations. (Several other routes also under development.)

- ACCOMPLISHMENTS.

PLEASE CONSULT THE 6 POSTERS FOR MORE DETAILED INFORMATION!

DUAL POTENTIAL/WAVELET IDENTIFICATION OF WHERE FRACTURE WILL OCCUR

Kidong Oh
Krishna Muralidharan

Pierre Deymier
Materials Science and Engineering
Univ. Of Arizona

Dynamical multiscale approach to bridging classical and quantum interatomic potentials for the simulation of failure of amorphous SiO_2

Objectives:

1. Identify, on the fly, regions in a homogeneously strained glass that require more accurate treatment of intermolecular forces (e.g. quantum)
2. Develop a molecular dynamics-based seamless concurrent multiscale simulation method with different intermolecular potentials e.g. classical (potential 1) and quantum (potential 2).
3. Use dynamical multiscale mixed-potentials approach to simulate crack initiation and failure in homogeneously strained amorphous SiO_2 .

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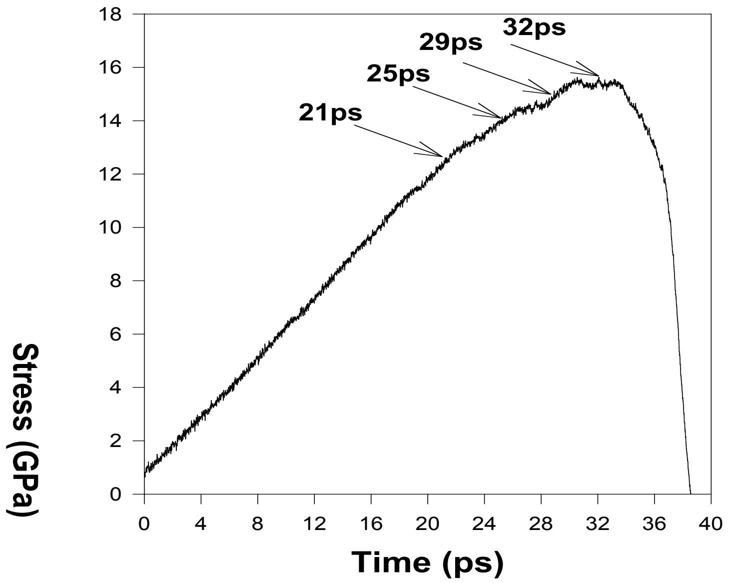
1-D wavelet-based method for identifying region that is most likely to fail (i.e. P)



- Optimum Haar's wavelet's order for filtering local stress/particle=2.
- Location of failure identified prior to actual failure

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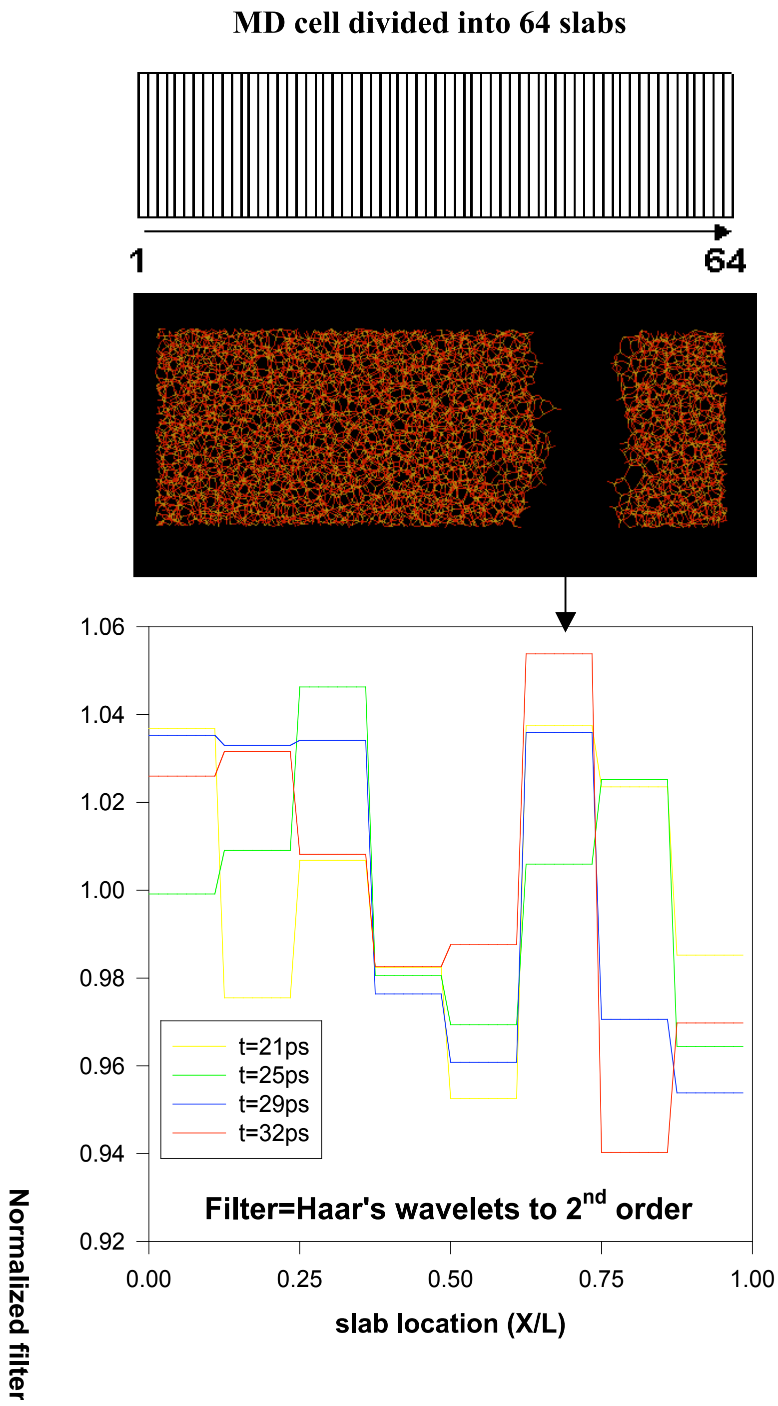
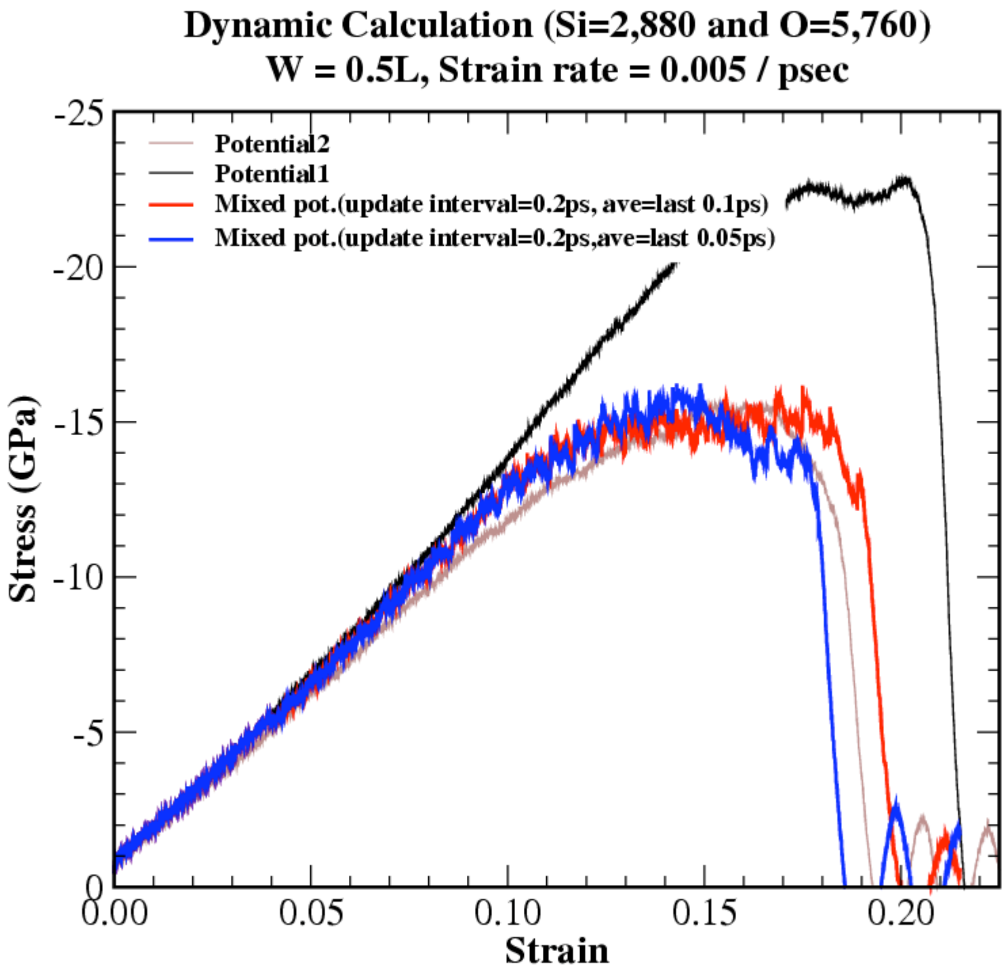


Predicted location of failure at t=32ps, failure occurs at t~34ps.

Dynamical multiscale mixed-potentials method



Dynamical multiscale mixed-potentials method (red and blue lines) reproduces satisfactorily the stress/strain relationship of an all-potential 2 system

Procedure:

- •MD cell divided into 64 slabs
- •Position of “potential 2” region updated every 0.2ps
- •Local stress/particle calculated at each slab at each time step
- •Local stress/particle averaged over last 0.1 (or 0.05)ps of updating interval
- •Averaged local stress versus slab position filtered with Haar’s wavelet (order 2)
- •“potential 2”region relocated (centered on the slab with highest wavelet-filtered stress).

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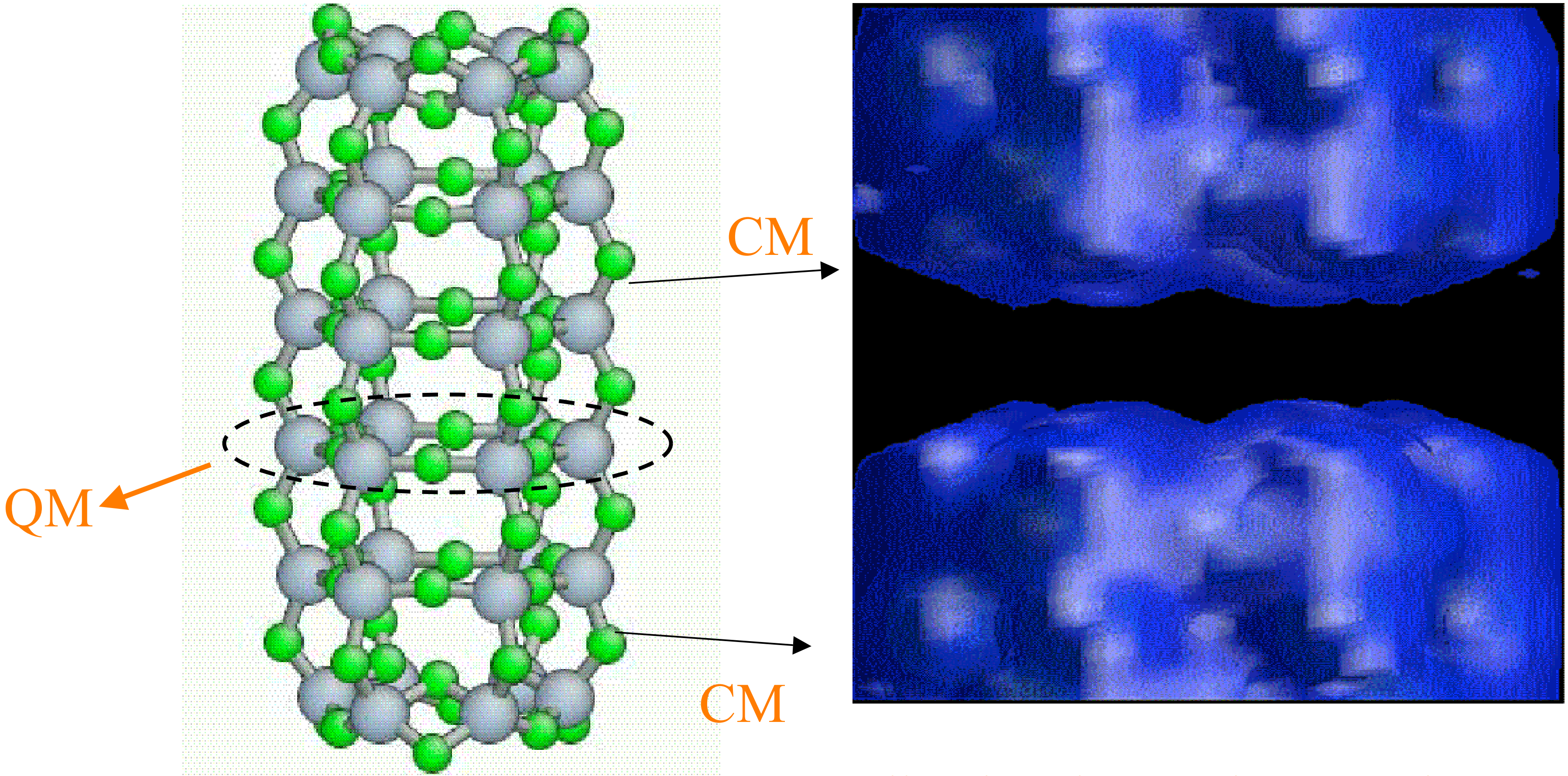
PRINCIPAL CONCLUSIONS

- Wavelet analysis identifies area of failure BEFORE fracture.
- Potential can be dynamically centered in identifed region.
- Analysis is applicable to dual potential description, as in QM + CM, and follows correct potential.

REGION II: CLASSICAL TO QUANTUM INTERFACE
FOR TRANFER HAMILTONIAN

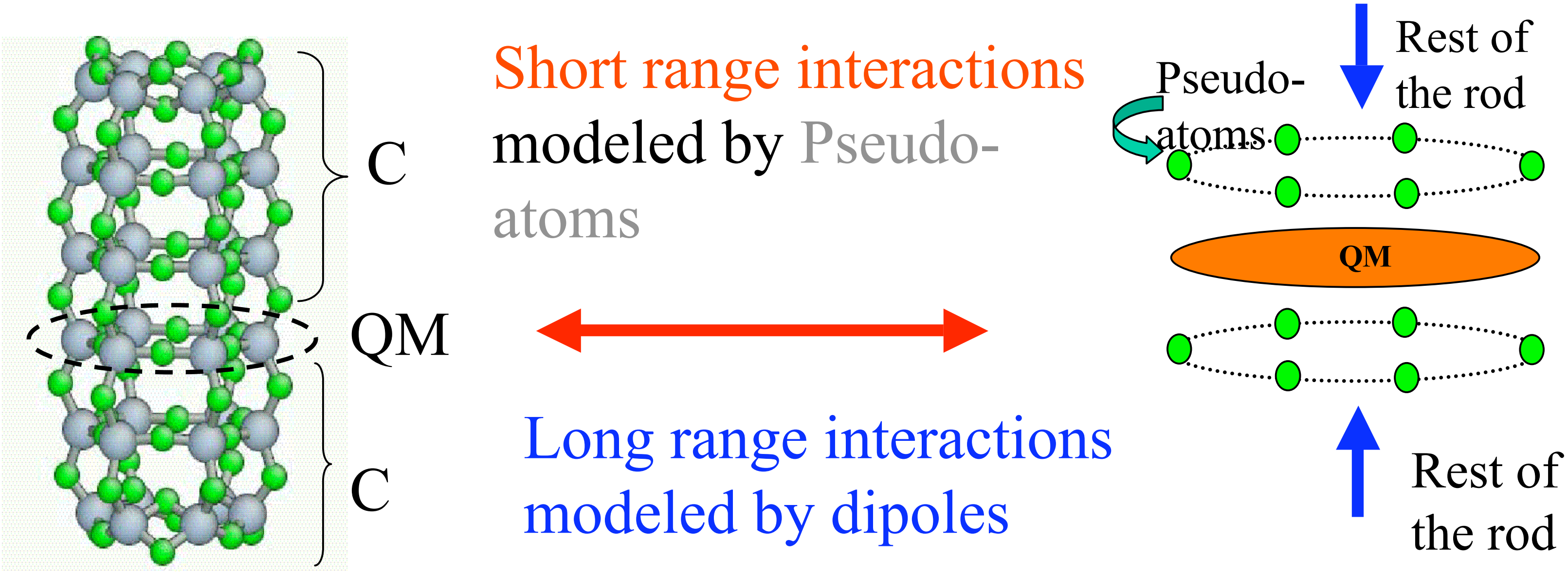
Aditi Mallik
DeCarlos Taylor
Keith Runge

Jim Dufty
Univ. Of Florida
Physics Department



Localized Valence electron charge density of CM ensures appropriateness of such partitioning

Partitioning of the nanorod



Short range interactions modeled by Pseudo-atoms

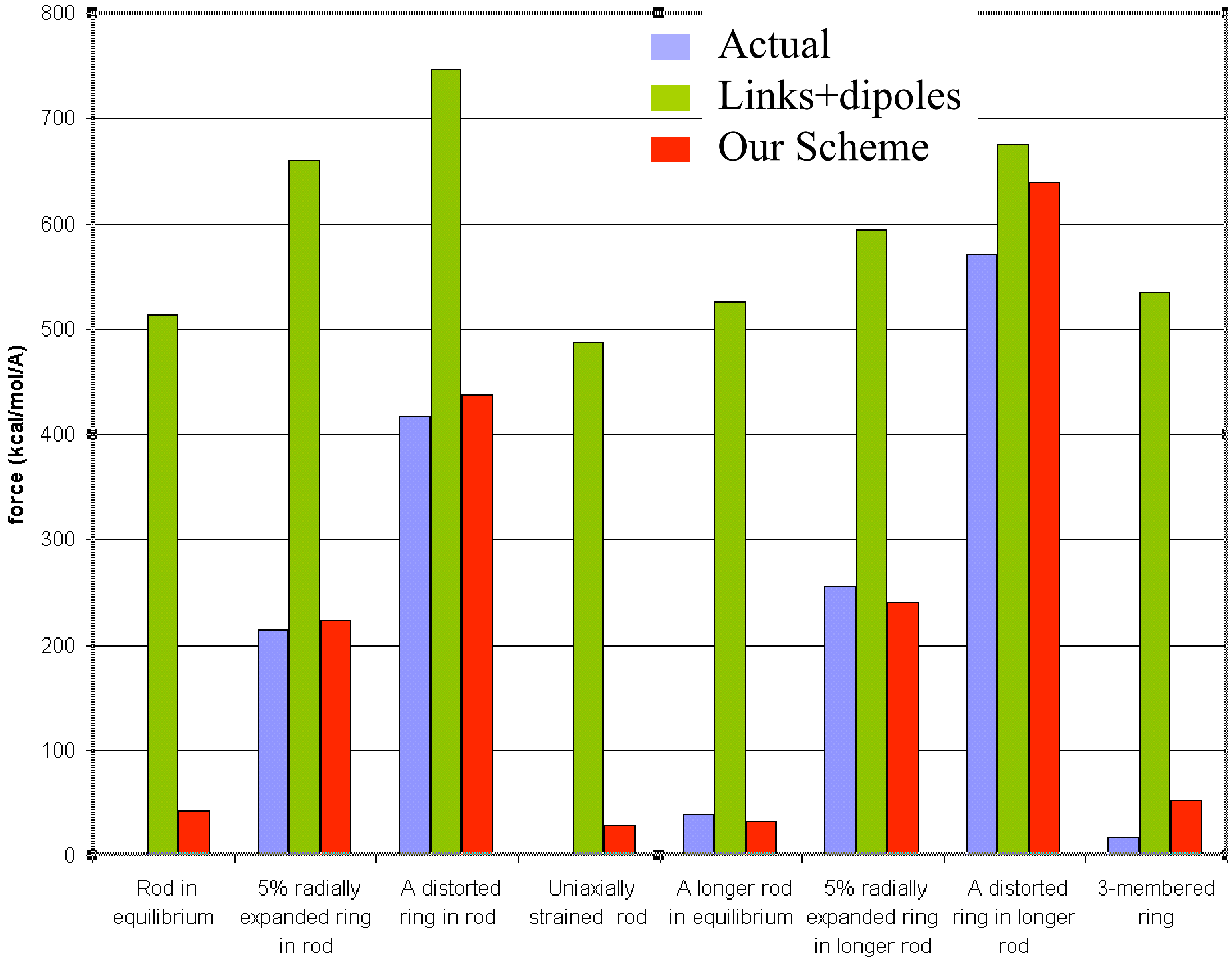
Long range interactions modeled by dipoles

This scheme gives charge density and forces in the QM domain same as those obtained from TH-NDDO on the entire system.

Generality of the proposed scheme extends to strained and longer rods as well.

For comparison we also study choice of link-atoms instead of Pseudo-atoms

Confirmation of Our Method in Various Cases for Values of Forces



Confirmation of Our Method for the Values of Charge Densities

Various Other Cases studied	% charge density difference with respect to bulk calculated with our method
I. For the rod with 6 rings	
a) Equilibrium	0.1
a) 5% radially expanded central ring	0.5
b) A distorted central ring	0.2
c) Uniaxially strained rod	0.7
II. For a longer rod with 10 rings	
a) In Equilibrium	0.1
b) 5% radially expanded central ring	0.7
c) A distorted ring	0.5
III. 3 -membered ring	0.8

PRINCIPAL CONCLUSIONS

- Localized charge density in silica nanorod, facilitated separating QM region from CM region using psuedo-atoms.
- Further represented CM part by first (dipole) term in multipole expansion.
- Inserting the dipole potential into the transfer Hamiltonian to obtain self-consistent solution, provided excellent forces and charge densities across CM/QM interface.

CLASSICAL TO QUANTUM INTERFACE AND ITS APPLICATION TO HYDROLYTIC WEAKENING

Mao-Hua Du
Yao He
Chao Cao

H-P Cheng

QTP, Univ. Florida

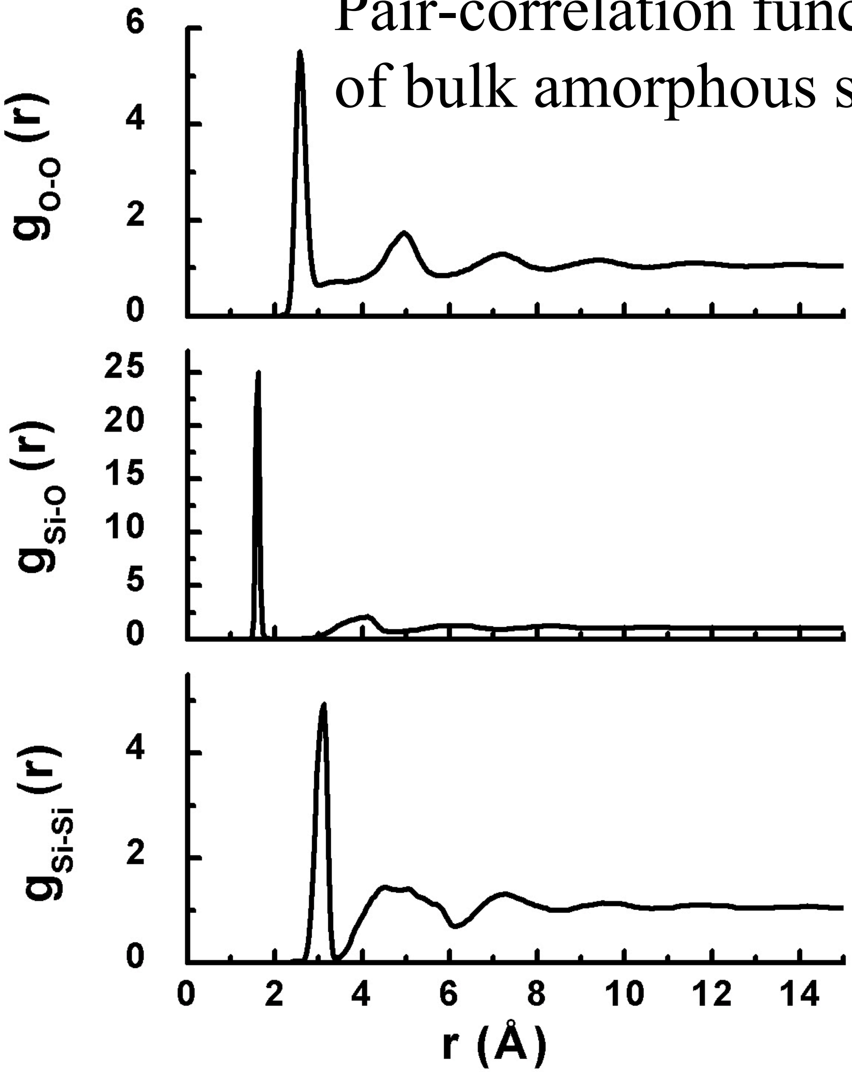
Amorphous silica surface (BKS)

- The amorphous silica surface is obtained by annealing of the liquid glass from 8000K to 300K.

Huff et al, J. Non-Cryst. Solids **253**, **133** (1999).

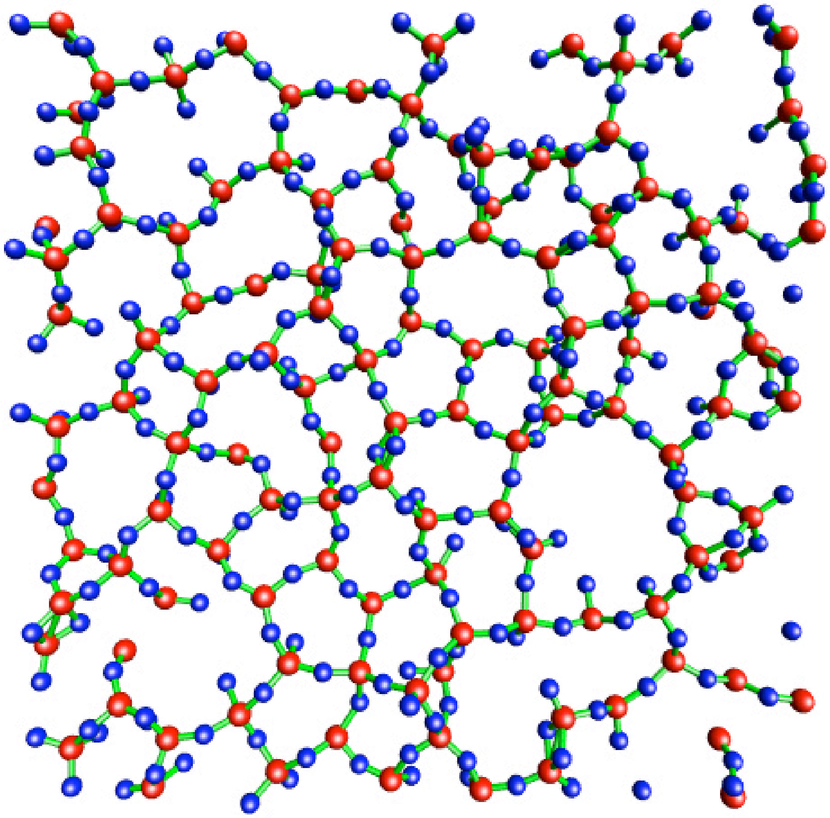
- A 12,000-atom slab is used to simulate the surface.
- Density, pair-correlation functions are in agreement with experimental data

Wright J. Non-Cryst. Solids, **179,** 84 (1994).



Pair-correlation functions of bulk amorphous silica

Properties of amorphous silica surfaces



Water destroys TMR, heating above 500 ^{o}C restores the TMR, surface dehydroxylation

λ In the absence of strain, the Si-O bonds are inert to H_2O and NH_3, etc.

λ Strained Si-O bonds greatly increase the reactivity by creating acidic and basic adsorption sites on silicon and oxygen.

λ Reactive sites (surface defects) play crucial roles in the surface corrosion

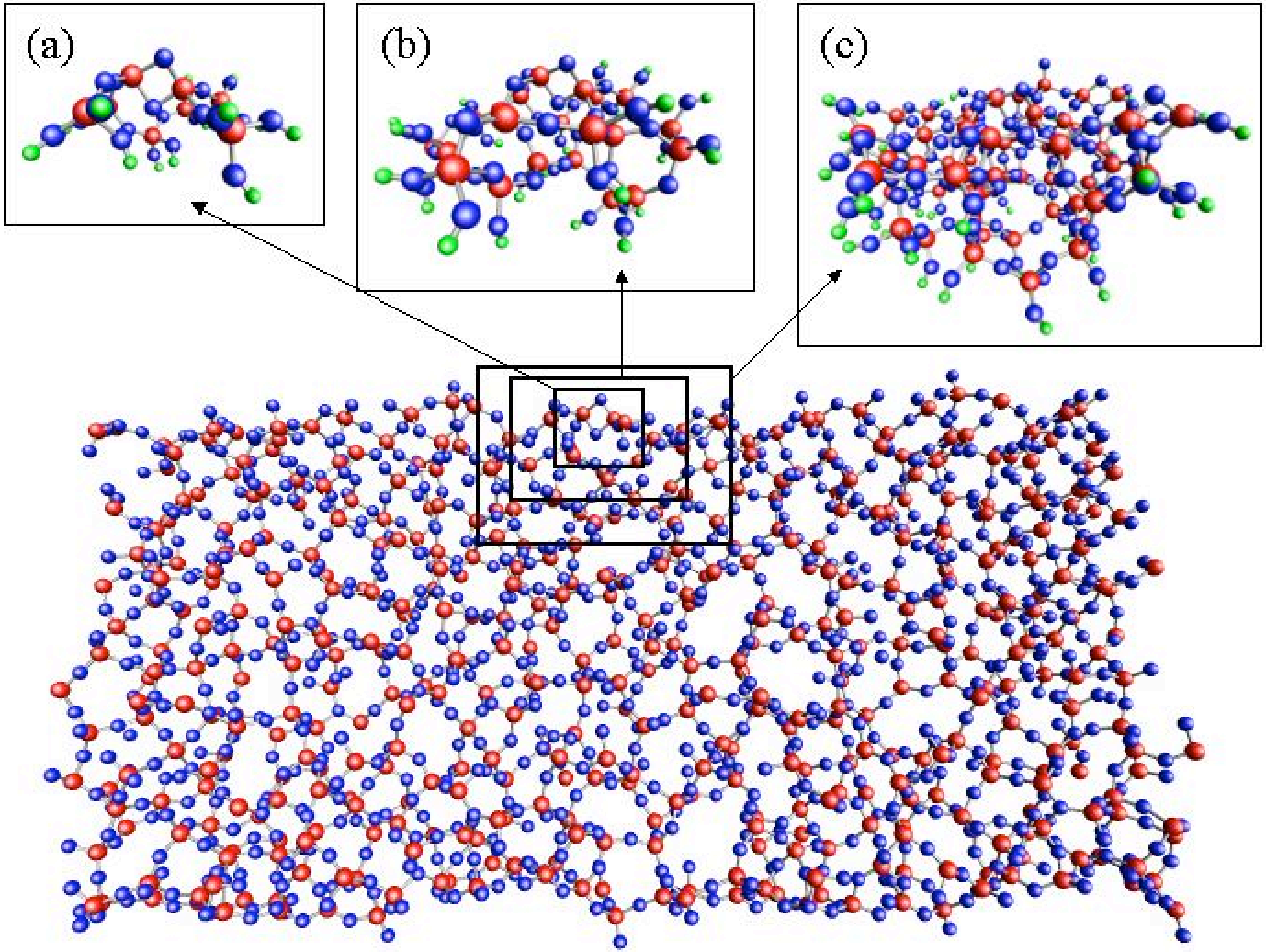
λ Two-membered-ring (TMR) is a surface defect with high abundance

Bunker et al, Surf. Sci. **222**, 95 (1989);
Bunker et al, Surf. Sci. **210**, 406 (1989).

………

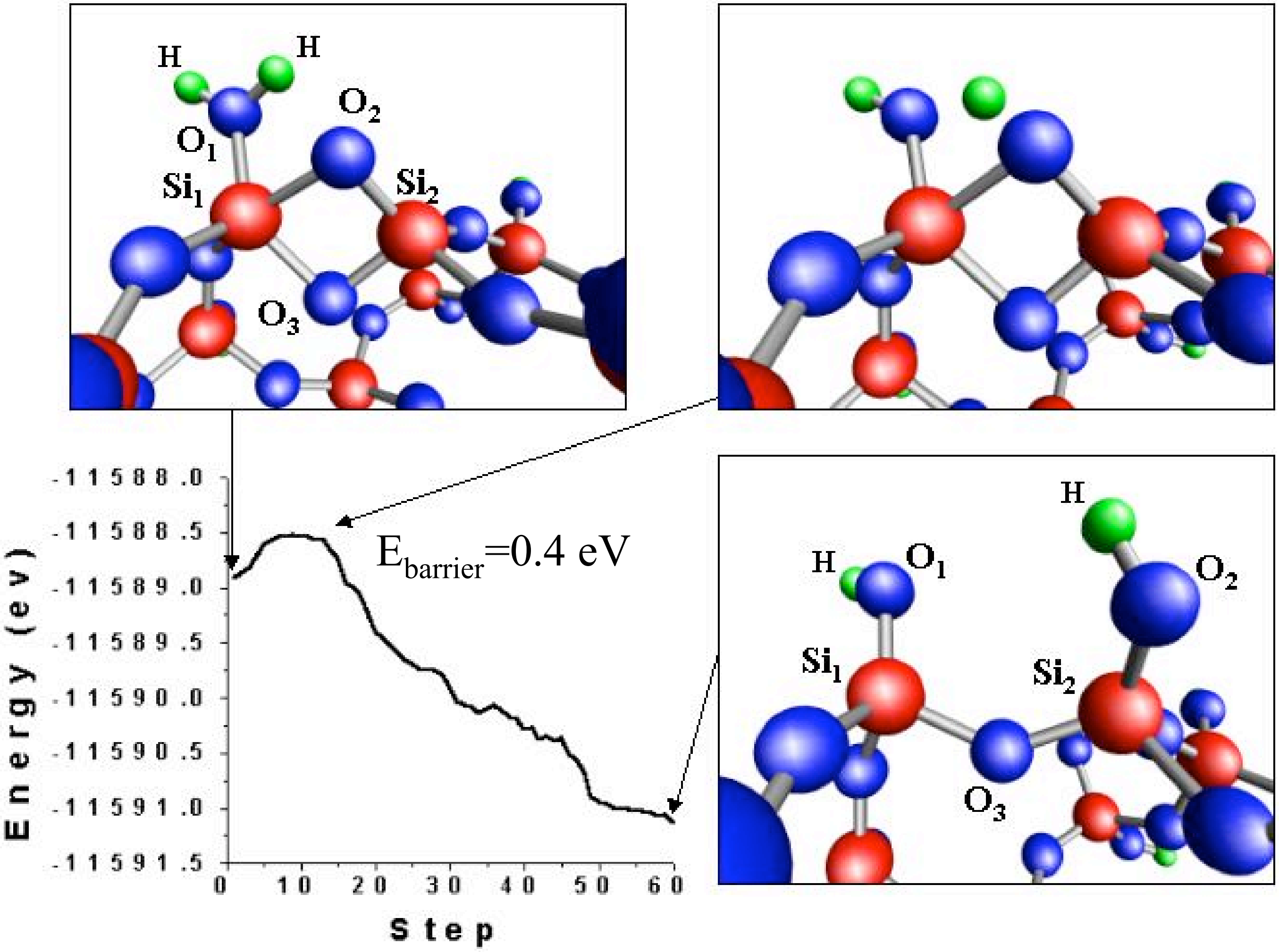
Walsh *et al*, JCP **113**,9191 (2000)
cluster model
S. Iarori *et al*, JPC B**105**, 8007 (2001)
β-cristobalite model

Two-membered-ring on silica surfaces



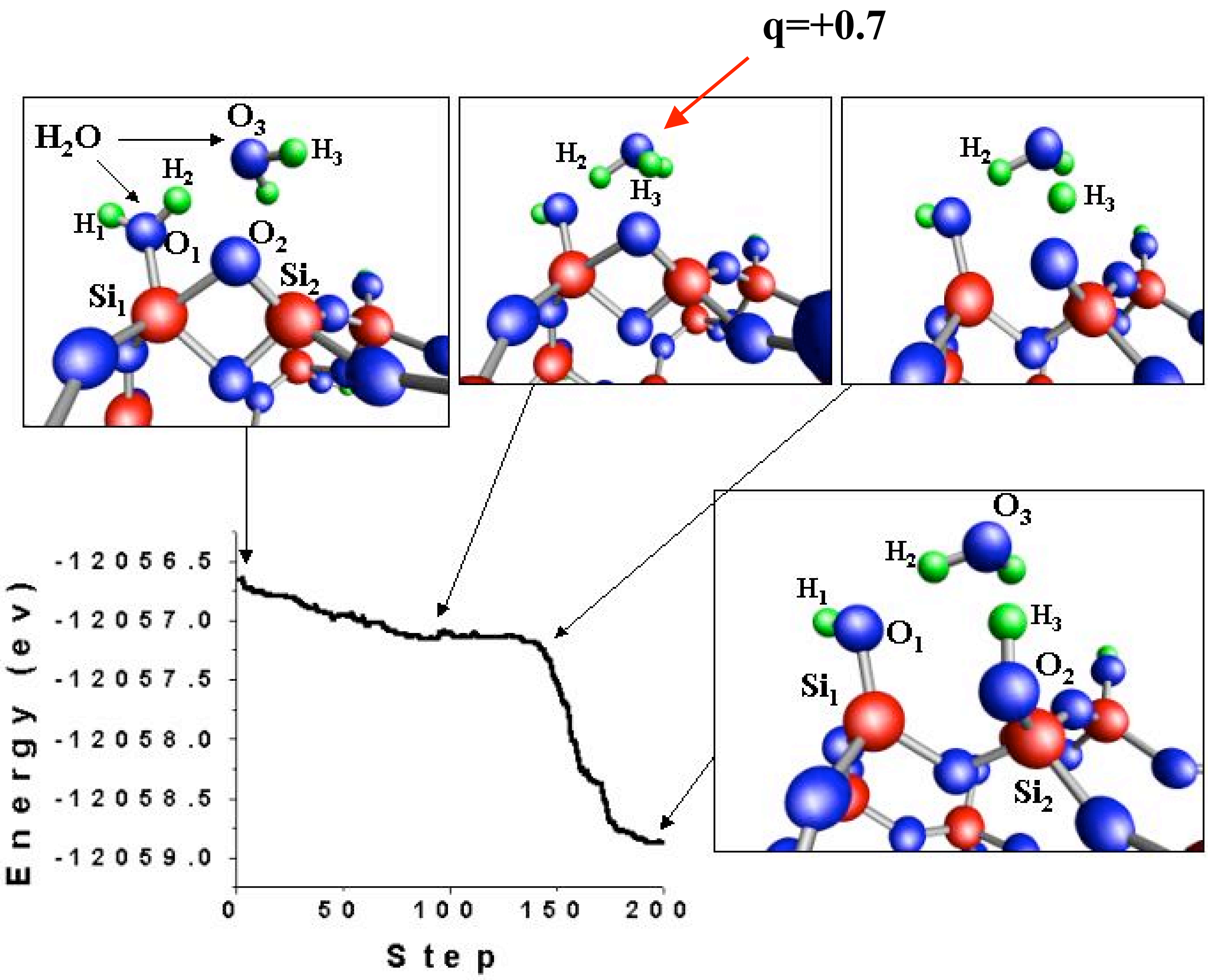
Du,Kolchin, Cheng, J. Chem.Phys. (in press)

Reaction path for 1-water dissociation



Walsh et al, JCP **113**,9191 (2000) cluster model --> $E_{barrire}$=0.7-1.1 eV

Reaction path for 2-water dissociation



PRINCIPAL CONCLUSIONS

- Built transparent CM/QM interface using link atoms.
- Large scale DFT based simulations emphasize the formation of strained Si_2O_2 rings in silica surface.
- Support water dimer mechanism suggested by (JDB, KR, RJB, Comp. Mat. Sci., 2003) as critical, as it has no barrier in reaction.

REGION I: QUANTUM MECHANICS

DeCarlos Taylor
Josh McClellan
Keith Runge
Norbert Flocke
Anatoli Korkin

Rod Bartlett

QTP, Univ. Florida

MATERIALS...

How can we hope to make simulations of materials ‘predictive’?

THEMES OF OUR WORK

- Predictive Simulations (If the forces are as accurate as those of coupled-cluster theory, any phenomena accessible to classical MD should be reliable.)
- Chemistry (Describe the interactions of a variety of different molecules routinely.)
- Quantum State Specific (Simulations should properly account for ions, radicals, and specific electronic states.)

QUANTUM REGION

HEIRARCHY

To get forces in quantum region...

I. Ab Initio Correlated Methods like Coupled-Cluster Theory.

II. Ab Initio dft, which unlike conventional DFT, has to converge to the right answer in the correlation and basis set limit.

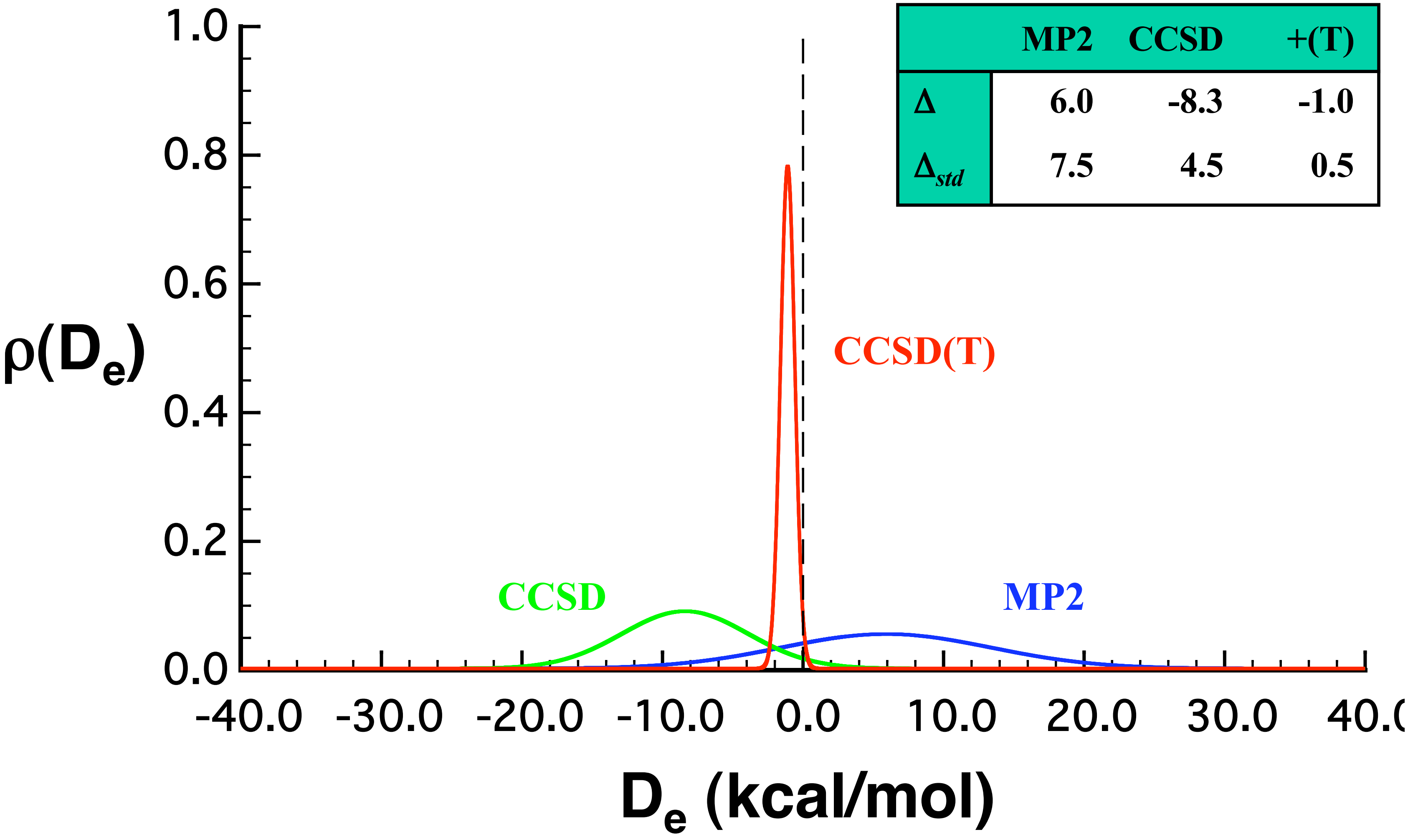
III. Conventional, local, GGA, hybrid DFT, plane wave or gaussian basis.

IV. Orbital independent DFT.

V. Semi-Empirical Quantum Methods or some version of Tight-Binding.

VI: Adaptive Potentials

Coupled Cluster Calculation of D_e's

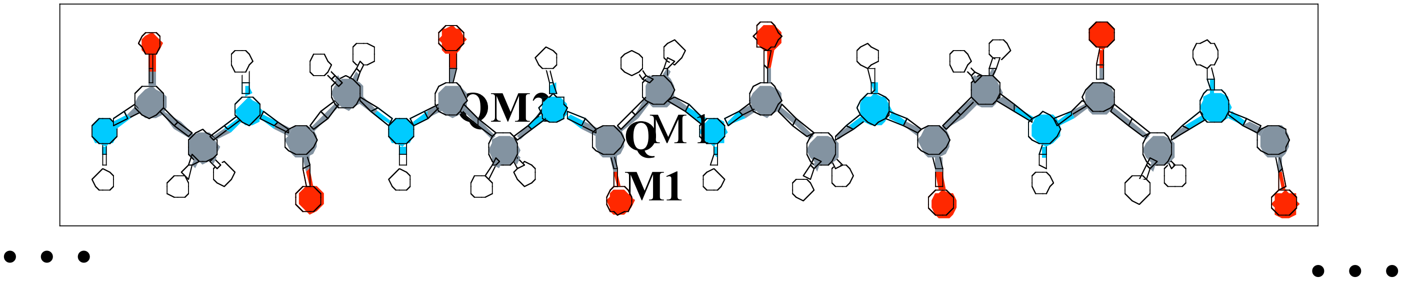


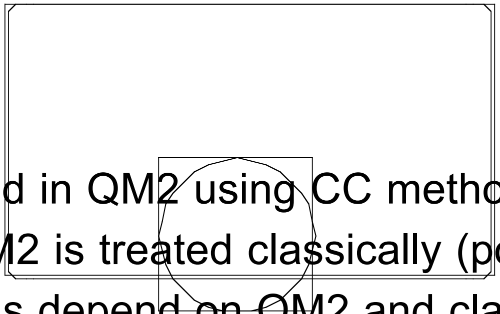
	MP2	CCSD	+(T)
Δ	6.0	-8.3	-1.0
Δ_{std}	7.5	4.5	0.5

From K. L. Bak et al., J. Chem. Phys. ***112****, 9229-9242 (2000)*

LINEAR SCALED COUPLED-CLUSTER

Forces, Energies and Properties of Extended Systems



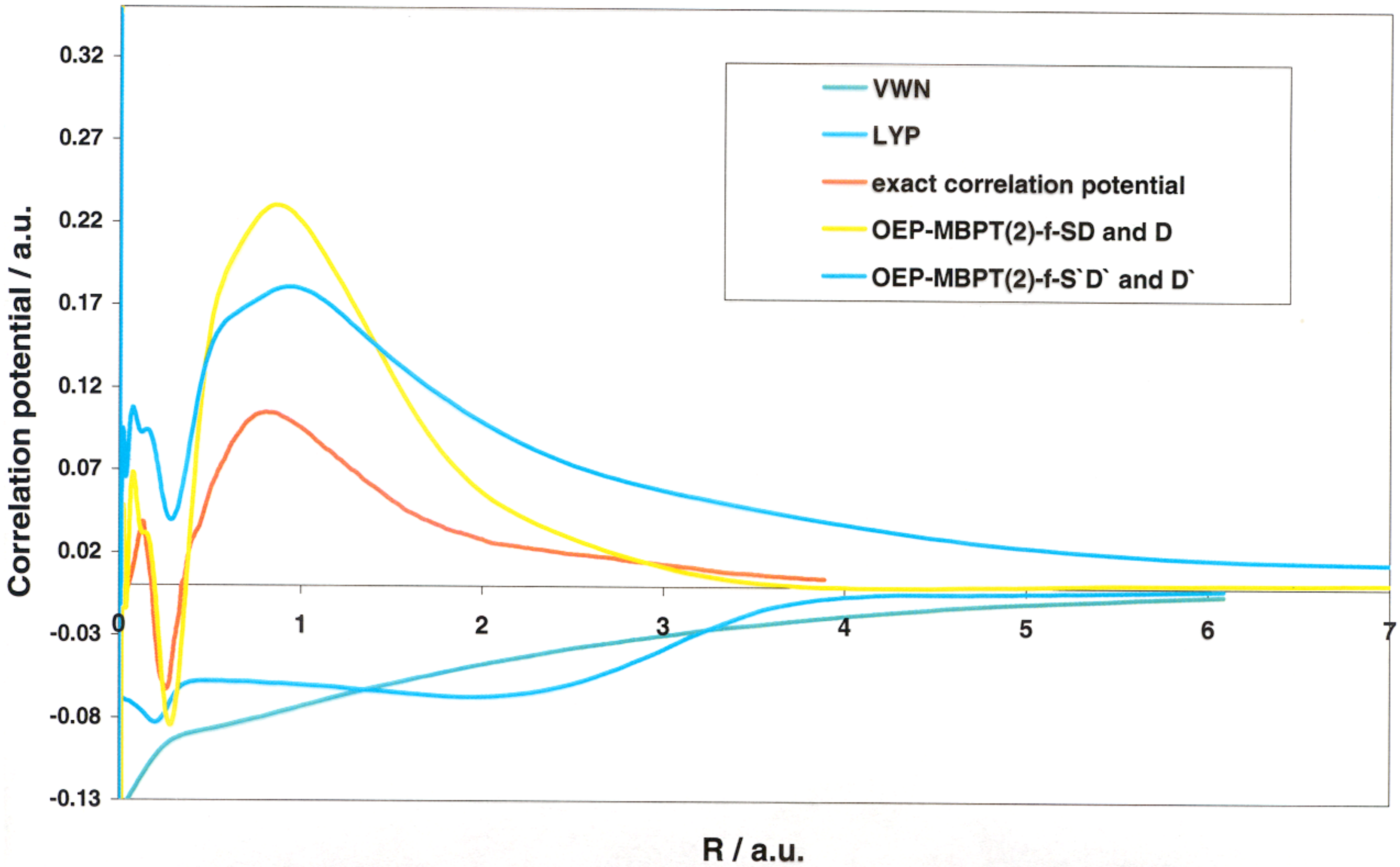


- Solve QM1 embedded in QM2 using CC methods with localized orbitals
- Region outside of QM2 is treated classically (point electron + nuclear charges).
- Forces on QM1 atoms depend on QM2 and classical part: $F_{QM1} = F_{QM2} + F_{classical}$
- Accuracy of QM1 values increase with increasing QM2 size.
- Natural linear scaling is achieved by moving QM1 over entire molecular systen
- Typically > 98% of exact property values are obtained already for fairly small QM
- Basis set size limitation to size of QM2 only => conventional CC programs suff

N. Flocke, RJB, JCP, in press

Ab Initio dft

Correlation potential of neon (Roos-ATZPU basis set) (2)

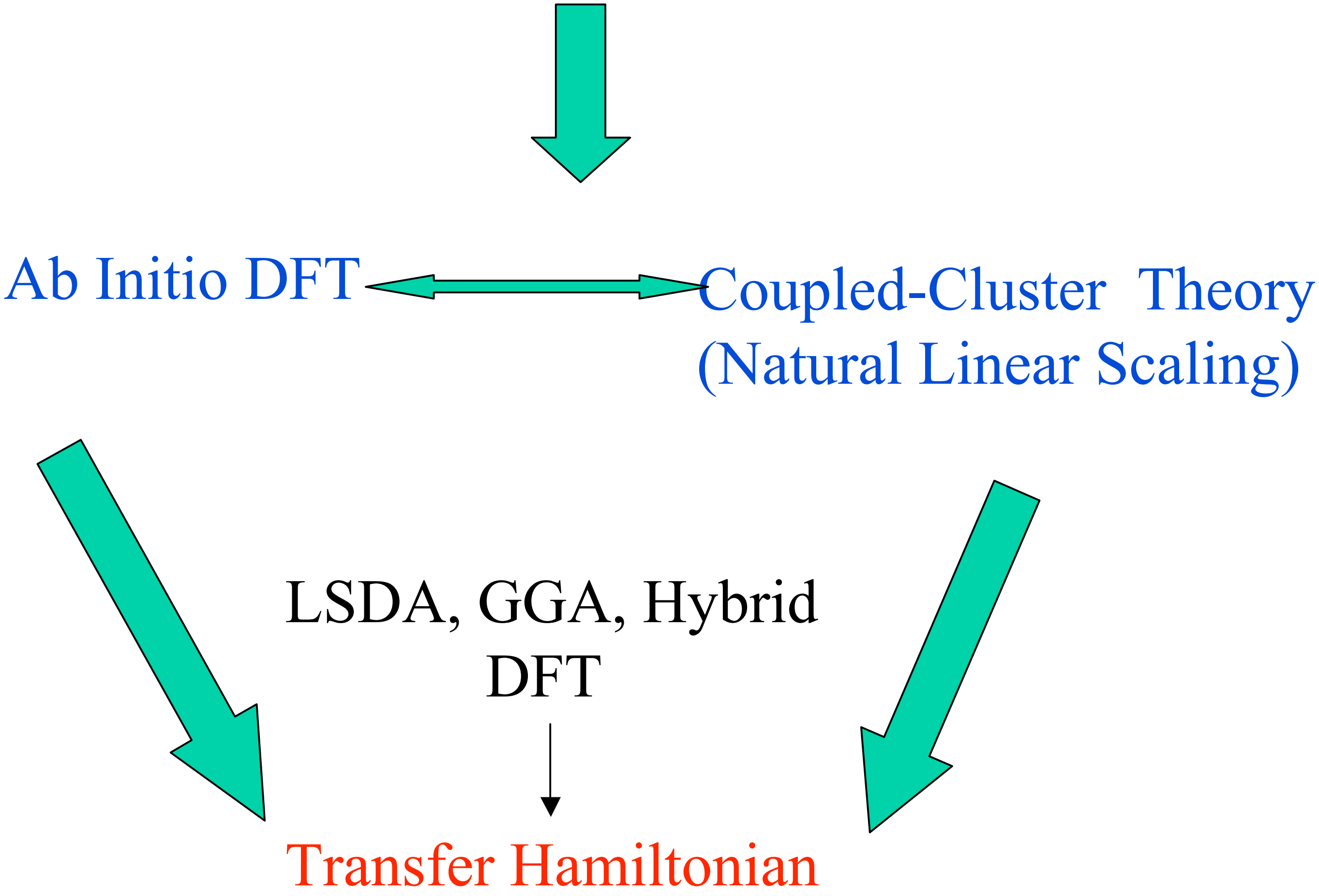


RJB, V. Lotrich, I Schweigert, JCP, Special Theme Issue on DFT, in press

COMPARISON OF DENSITY FUNCTIONAL METHODS

Property	GGA/Hybrid Methods	*Ab initio* dft
Convergence to Exact Answer	No	Yes
Correct Self-Interaction	No	Yes
Correct Behavior of Exchange	No	Yes
Correct Behavior of Correlation	No	Yes
Approximation for All Ionization Potentials	No	Yes
Rydberg Excitations	No	Yes
Potential Energy Curves to Dissociation	No	(?)
Weak Interactions	No	Yes

QUANTUM MECHANICAL CORE



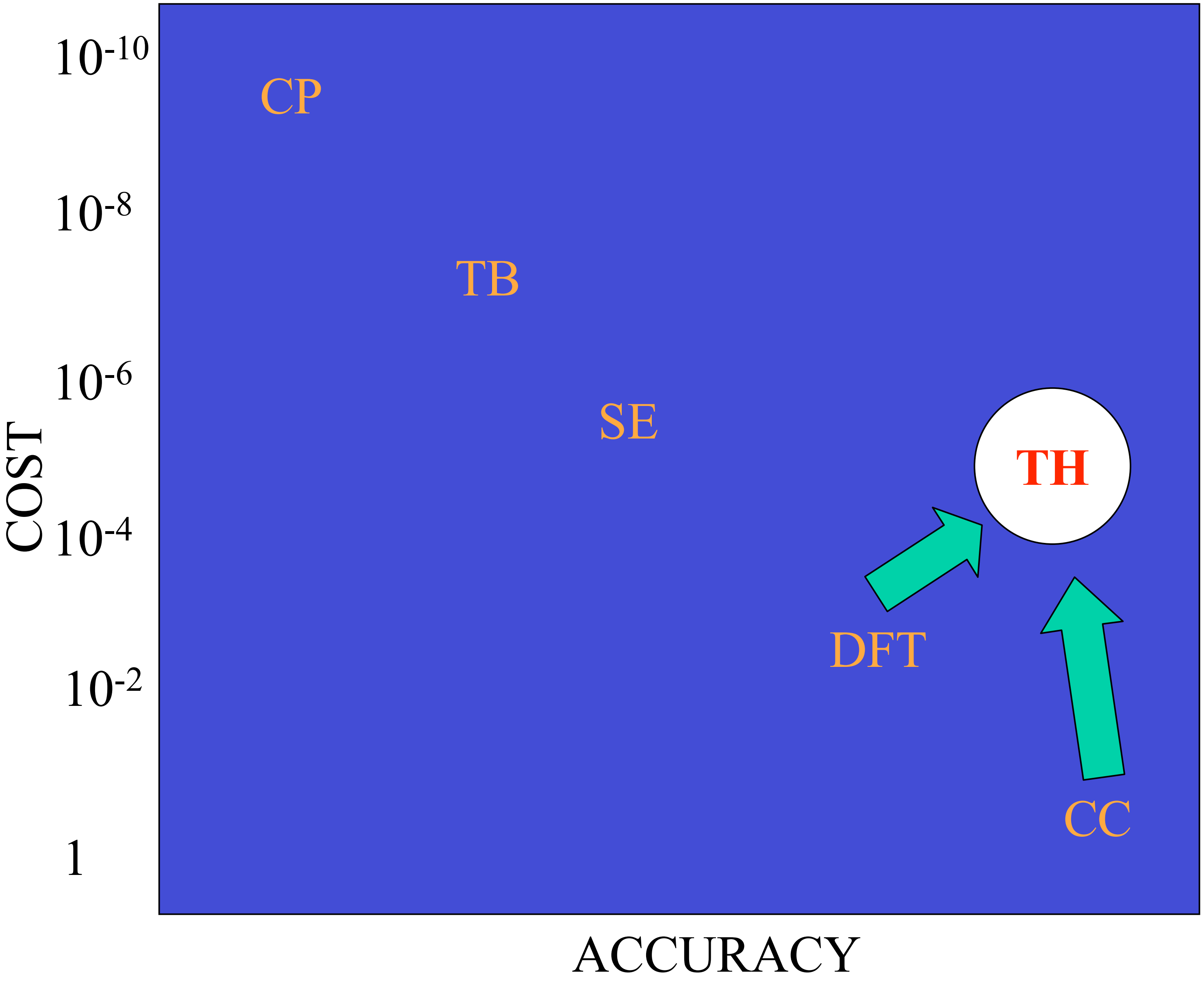
Ab Initio DFT

Coupled-Cluster Theory
(Natural Linear Scaling)

LSDA, GGA, Hybrid
DFT

Transfer Hamiltonian

COMPARATIVE APPLICABILITY OF METHODS



TRANSFER HAMILTONIAN

In CC theory we have the equations…

exp(-T) Hexp(T) = _

_|0⟩ = E|0⟩ Where E is the exact correlated energy

⟨m |_|0⟩ =0 Where ⟨m| is a single, double, triple, etc excitation which provides the equations for the coefficients in T, ie t_i^a, t_{ij}^{ab}, etc.

∇(**R**)E(**R**) = F(**R**) Provides the exact forces

ρ(x)= ⟨0| exp(-T) δ(x-x’)exp(T) |0⟩ gives the exact density

and ⟨m| _ |n⟩ ⇒ _ and _**R**$_k$ = ω_k**R**$_k$ Gives the excitation (ionization, electron attached) energies ω_k and eigenvectors **R**$_k$

TRANSITION FROM MANY-PARTICLE HAMILTONIAN TO EFFECTIVE ONE-PARTICLE HAMILTONIAN...

Wavefunction Approach

⟨0|{$i^{\dagger}$a}_|0⟩=0= ⟨a| _ |i⟩=0

_|i⟩=ε_i|i⟩ ∀i

Parameterize _ with a GA to satisfy E= ⟨0|_|0⟩,

∇E=F(R), ρ(r), ε(Fermi) = I

Density Functional Approach

_|i⟩=ε_i|i⟩ ∀i

where _ =t+δE/δρ(x)

and E[ρ]=E, ∇E=F(R),

ρ(r)=Σ |i⟩ ⟨i|, ε(Fermi) = I

Future? Remove orbital dependence
and/or self-consistency?

RELATIONSHIP BETWEEN COUPLED-CLUSTER/DFT HAMILTONIAN AND SIMPLIFIED THEORY

Second Quantized _

$$\_ = \sum g_{pq} \{p^{\dagger} q\} + \propto Z_A Z_B / R_{AB}$$

Transition from orbital based to atom based--

$$\approx \sum (h_{AA} + \gamma_{AA}) + \sum h_{AB}(R) + \sum \gamma_{AB}(R)$$

$$+ \sum Z'_A Z'_B / R_{AB} \{ \sum a_{kA} \exp[-b_{kA}(R_{AB} - c_{kA})^2] + \sum a_{kB} \exp[-b_{kB}(R_{AB} - c_{kB})^2] \}$$

$$h_{AB}(R) = \sum (\beta_{\mu} + \beta_{\nu}) K S_{\mu\nu}(R)$$

$$\gamma_{AB}(R) = [(R_{AB})^2 + 0.25(1/\gamma_{AA} + 1/\gamma_{BB})^2]^{-1/2}$$

SEMIEMPIRICAL METHODS HAVE MANY KNOWN FAILINGS

They...

- Approximate the Hartree-Fock equations
- Use a minimum basis set
- Parameterize to experimental values
- Cannot obtain structure and spectra with same set of parameters
- Attempt to describe all elements in one set of universal parameters

WHAT DO WE EXPECT FROM THE TRANSFER HAMILTONIAN?

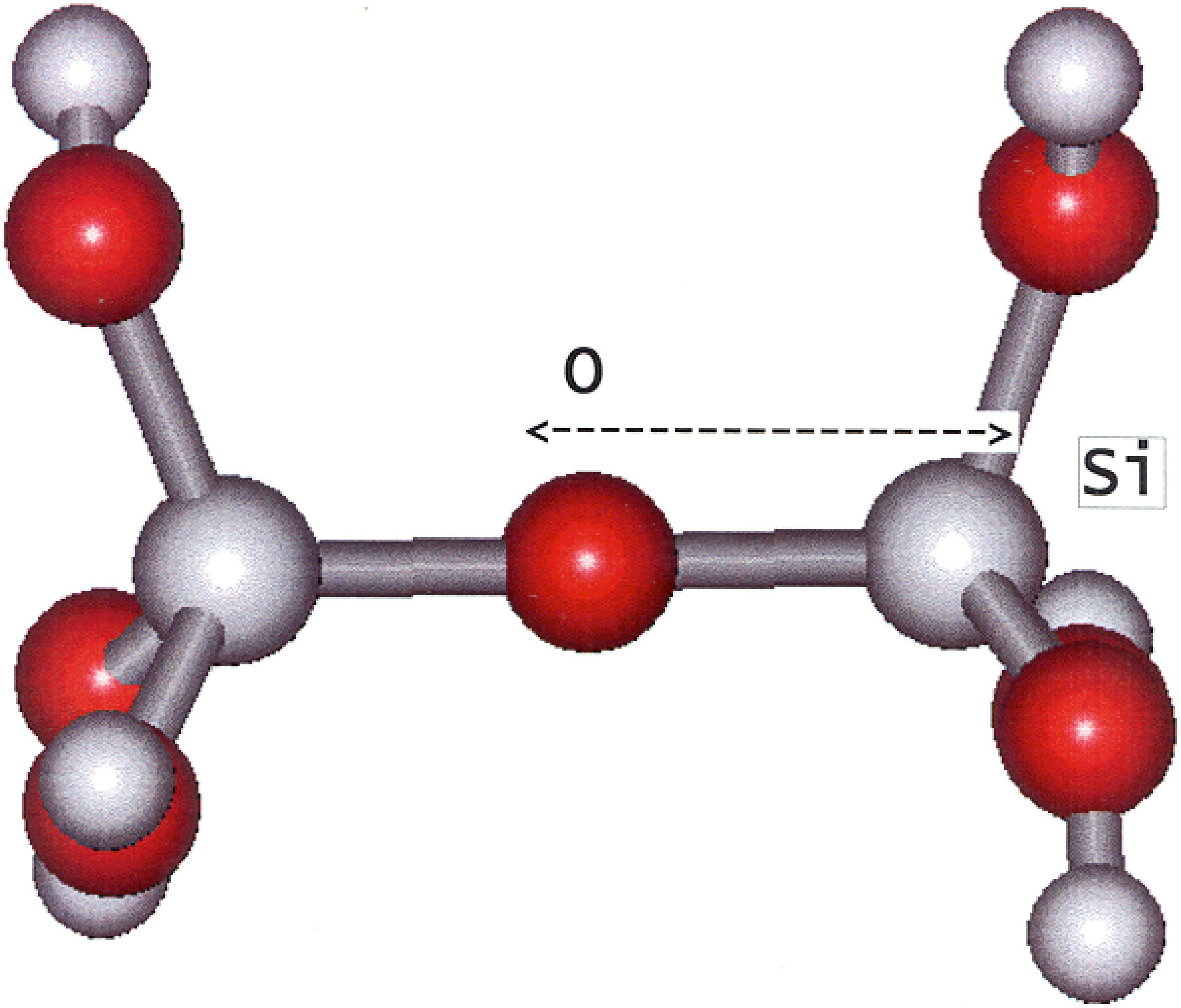
It should ...

- Reproduce *ab initio* forces as prototype molecules dissociate to fragments.
- Describe all relevant electronic states in the dissociation correctly, with one set of purely atomic parameters.
- Distinguish between cations, anions, and radicals.
- Provide the correct electronic density.
- Give the correct ionization potential and electron affinity, to ensure that EN=(I+A)/2 .
- Should be short-range (basically two-atom form) to saturate parameters for small clusters.
- No minimum basis and no universal parameterization, as applications limited to small number of different elements in a simulation.

INVERSE PROBLEM--

From a set of **targets** given by high-level ab initio quantum chemistry for representative clusters undegoing the phenomena of interest, create a one-particle (short-range) Hamiltonian, that can represent them. It should be composed of none or a few atomic parameters. Once the (second-quantized) Hamiltonian is known, in principle, everything about the potential energy surfaces, associated forces, density matrices, etc, would be rapidly obtainable from a simple, compact form. In this way, **NO FITTING of PES** are necessary, permitting direct dynamics applications to complex systems.

The remaining issue is how well can this be accomplished subject to the assumed form of the Hamiltonian, parameter sensitivity, and ability to describe both electronic properties and total energy properties (forces).


O
Si

SE PARAMETERIZATION OF THE TRANSFER HAMILTONIAN, TH

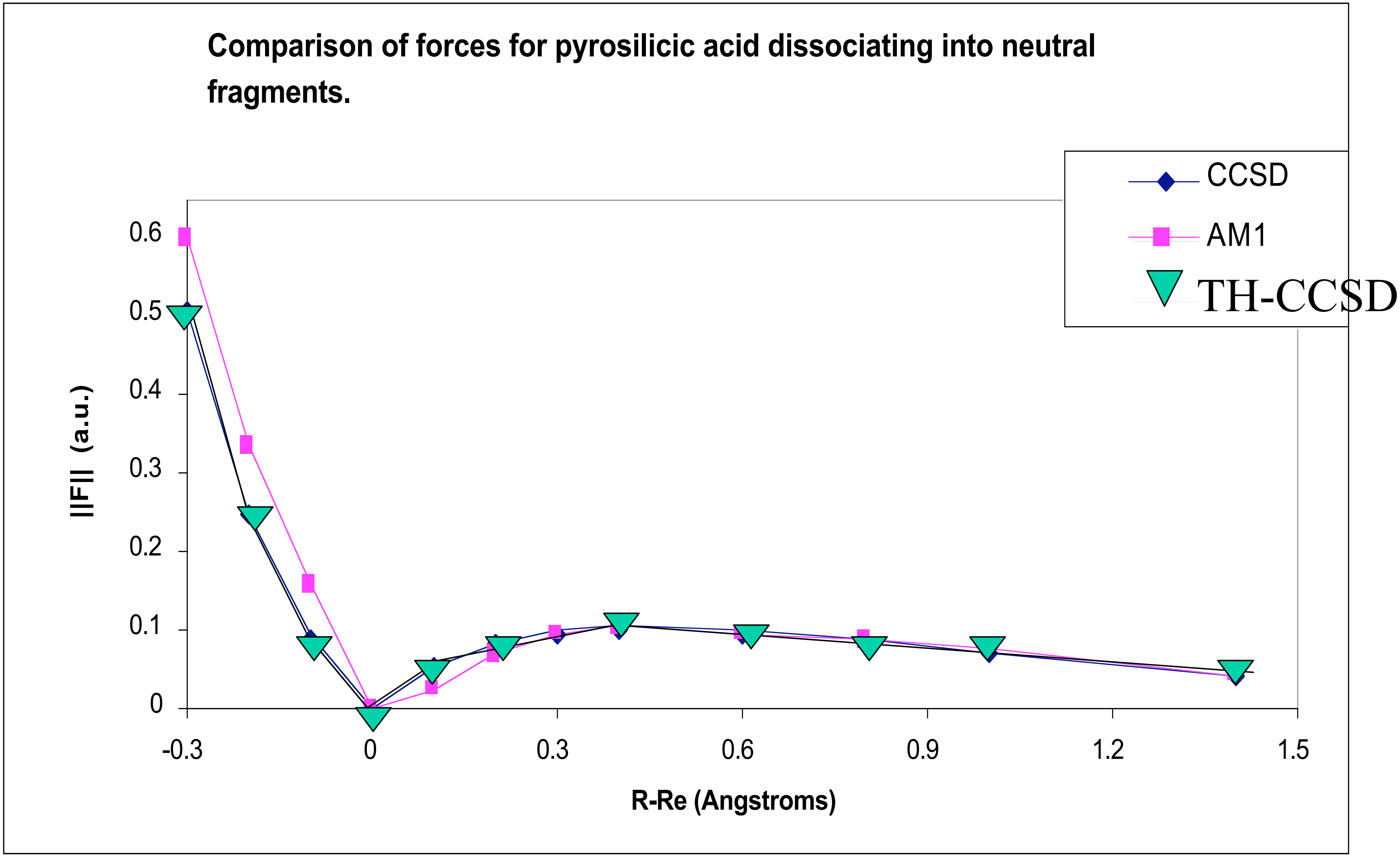
A Cost function

$$f = \sum_{i=1}^{NPTS} \left[\| F_i^{SE} \| - \| F_i^{CCSD} \| \right]^2$$

is minimized using a numerical optimization algorithm

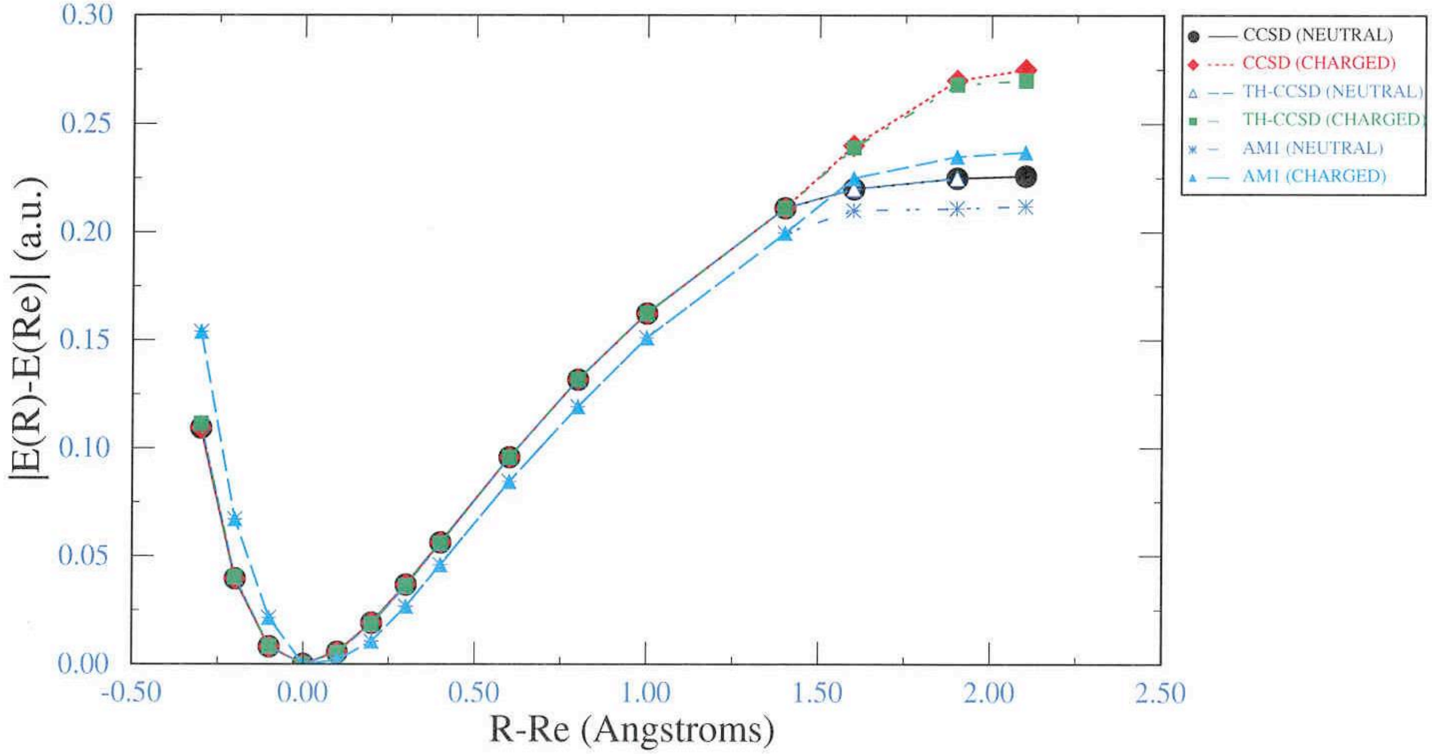
Only optimize parameters of the core repulsion (CR) term in the AM1 Hamiltonian for SiO_2 but also electronic terms for other systems

$$CR = Z'_A Z'_B \gamma_{AB} \{1 + \exp(-\alpha_A) + \exp(-\alpha_B) + \propto a_{kA} \exp[-b_{kA}(R_{AB} - c_{kA})^2] + \propto a_{kB} \exp[-b_{kB}(R_{AB} - c_{kB})^2]\}$$

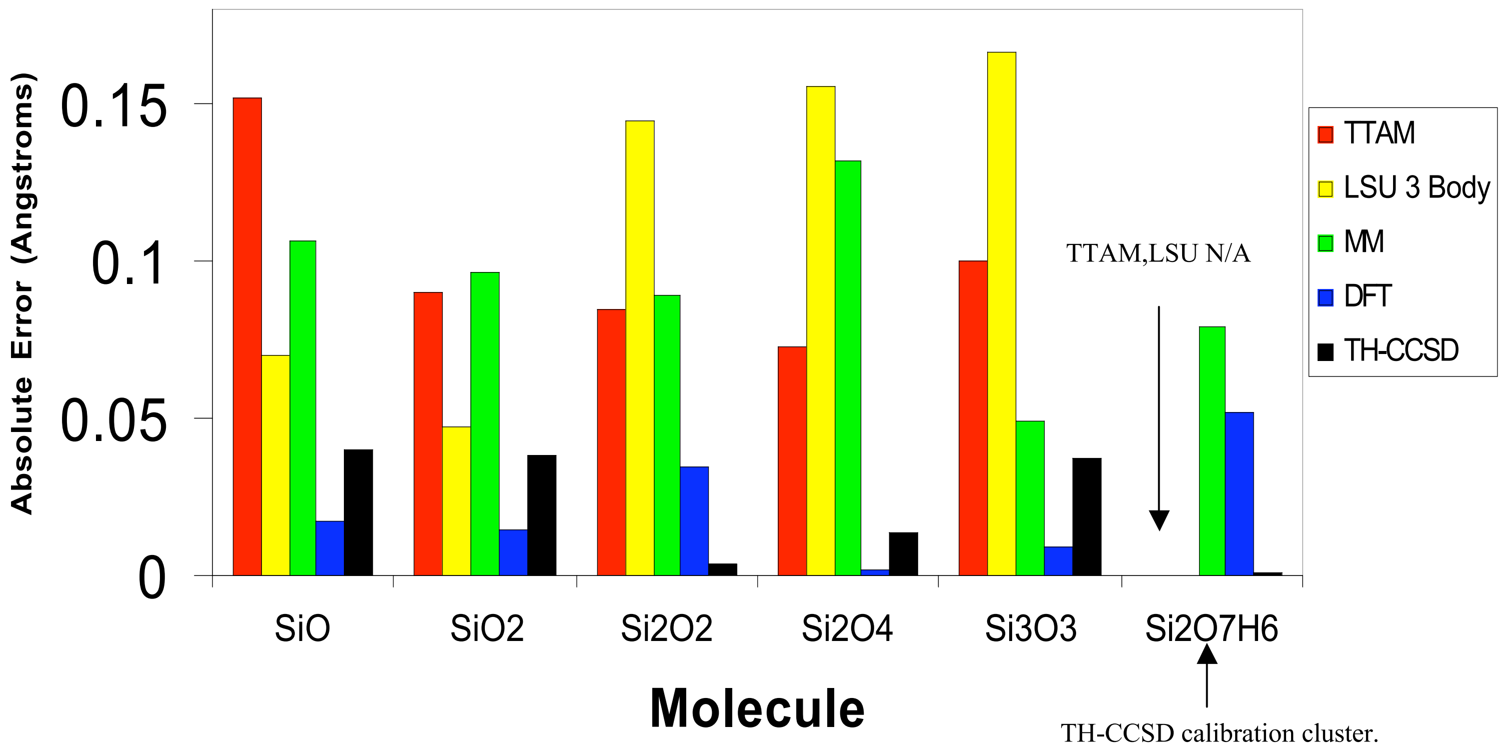


Comparison of forces for pyrosilicic acid dissociating into neutral fragments.

***Comparison of PES for pyrosilicic acid dissociating into charged and neutral fragments.



Comparison of Si-O Bond Lengths Relative to CCSD(T)



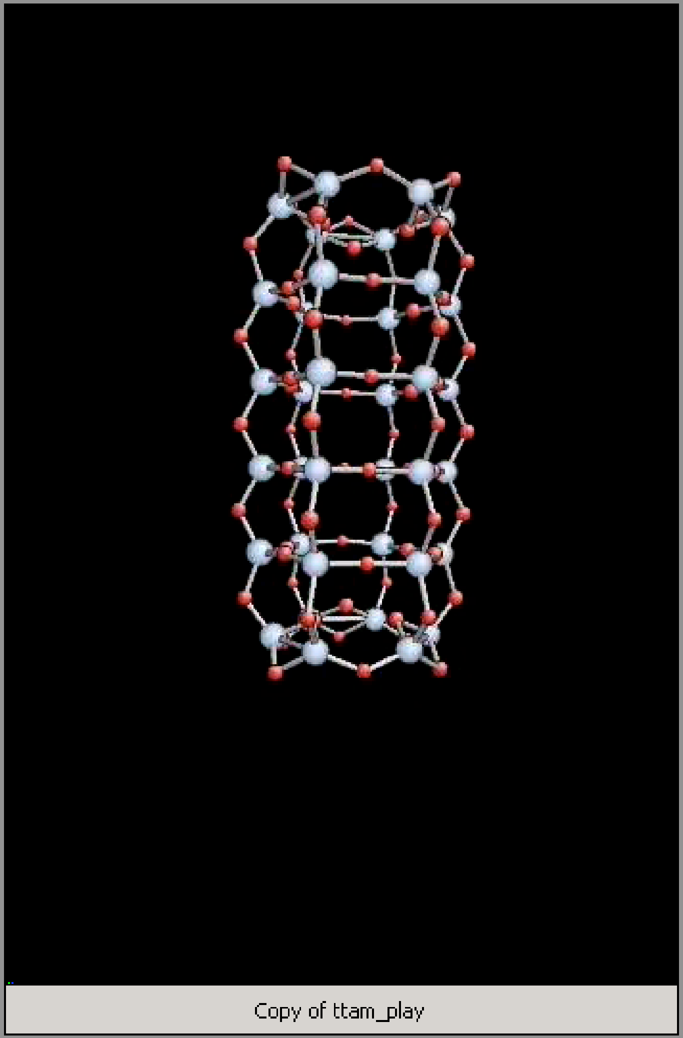
TTAM,LSU N/A

TH-CCSD calibration cluster.

CPU time required for one energy+gradient evaluation for pyrosilicic acid.

METHOD	CPU TIME (s)
CCSD	8656.1
DFT	375.4
TH-CCSD	0.17
BKS	.001

*All computations run on an IBM RS/6000


Copy of ttam_play

CPU time required for one energy+gradient evaluation for nanorod.

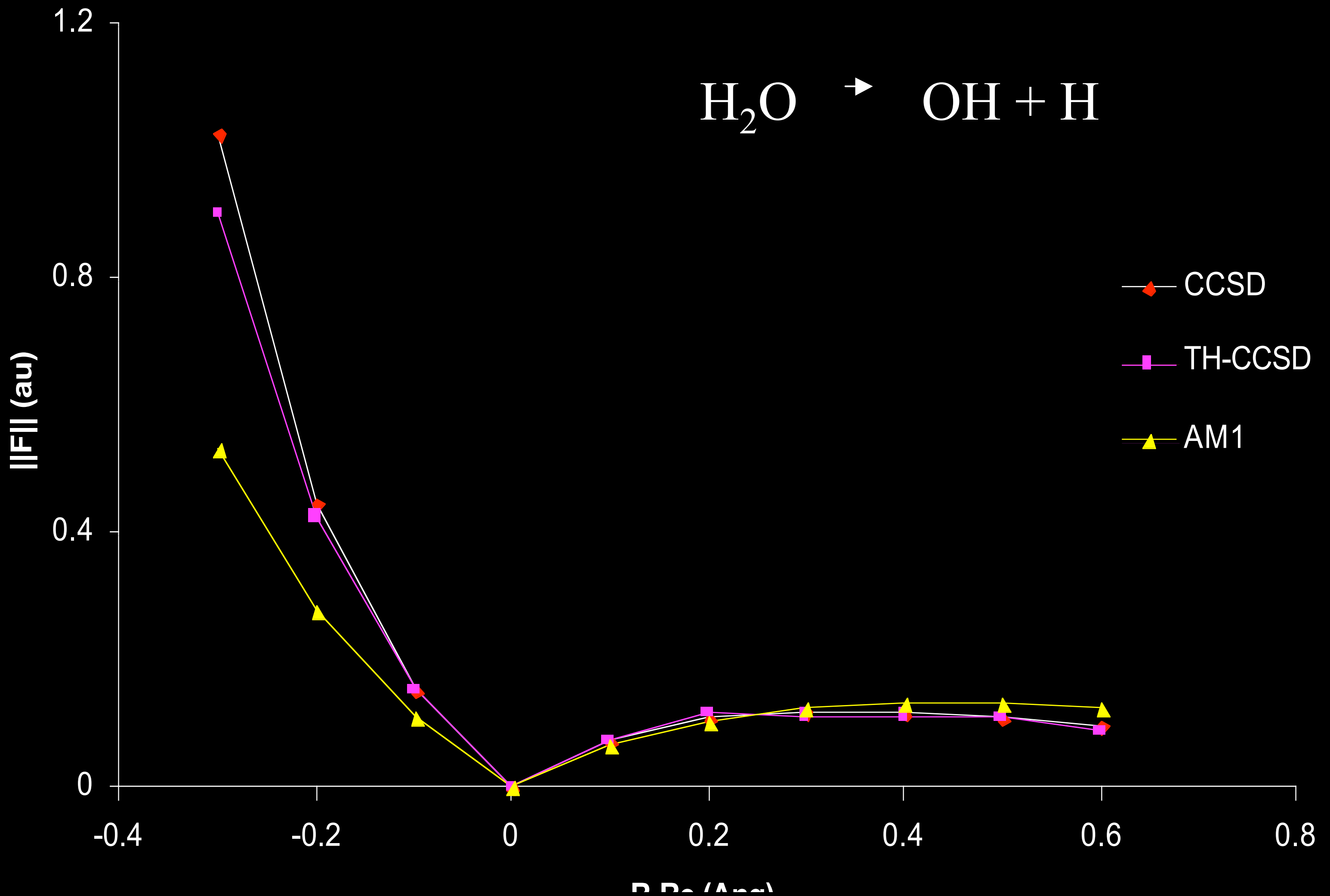
METHOD	CPU TIME (s)
CCSD	N/A
DFT	85,019
TH-CCSD	43.03
BKS	.02

*All computations run on an IBM RS/6000

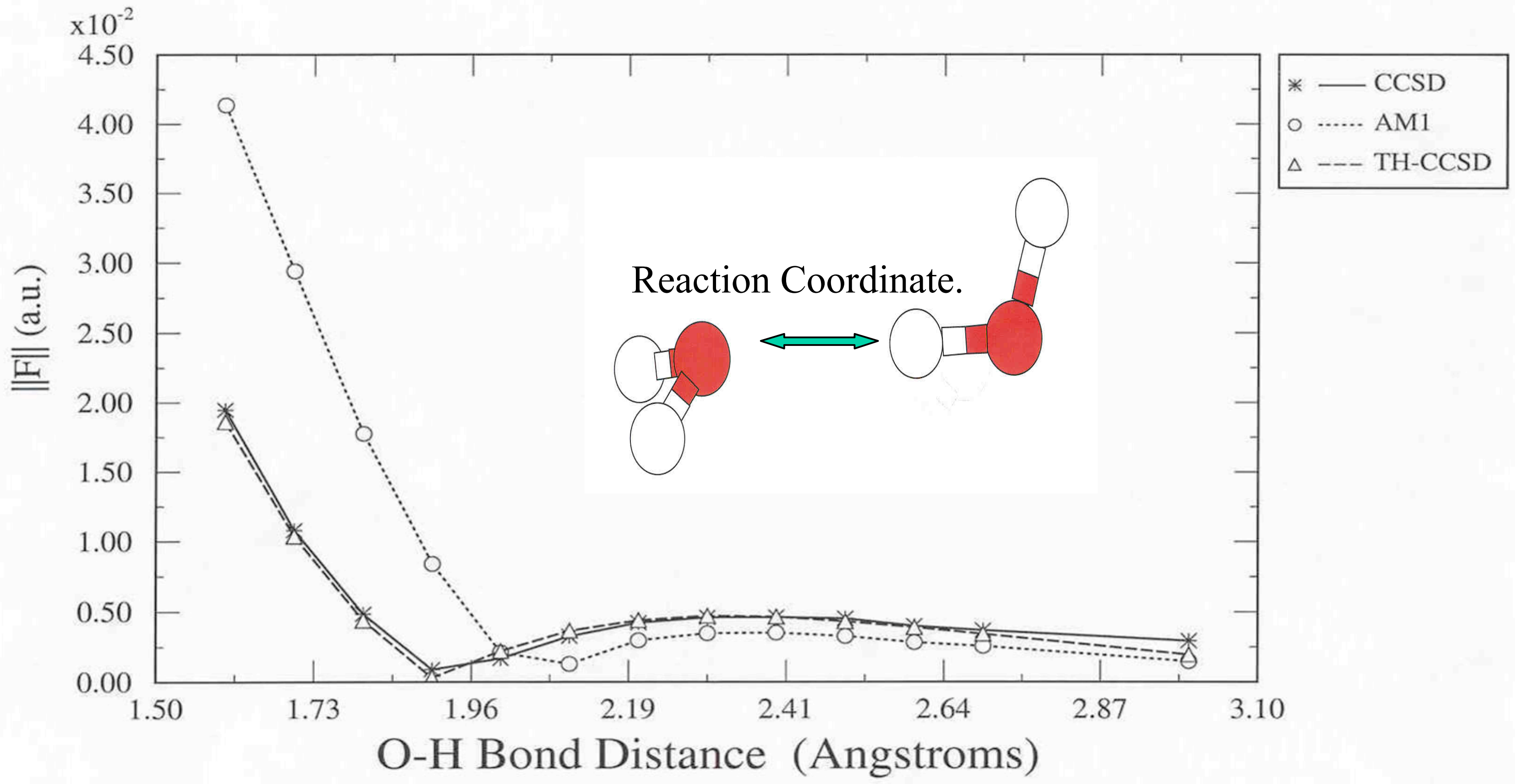
Water + Silica

- Very low concentrations of water are known to dramatically affect the strength of silica (hydrolytic weakening)
- To study this, we need:
  - Mechanism
  - Ab initio reference data to construct TH
    - water – water interaction
    - water – silica interaction
  - Simulations demonstrating the above mechanism and effect on stress-strain curve

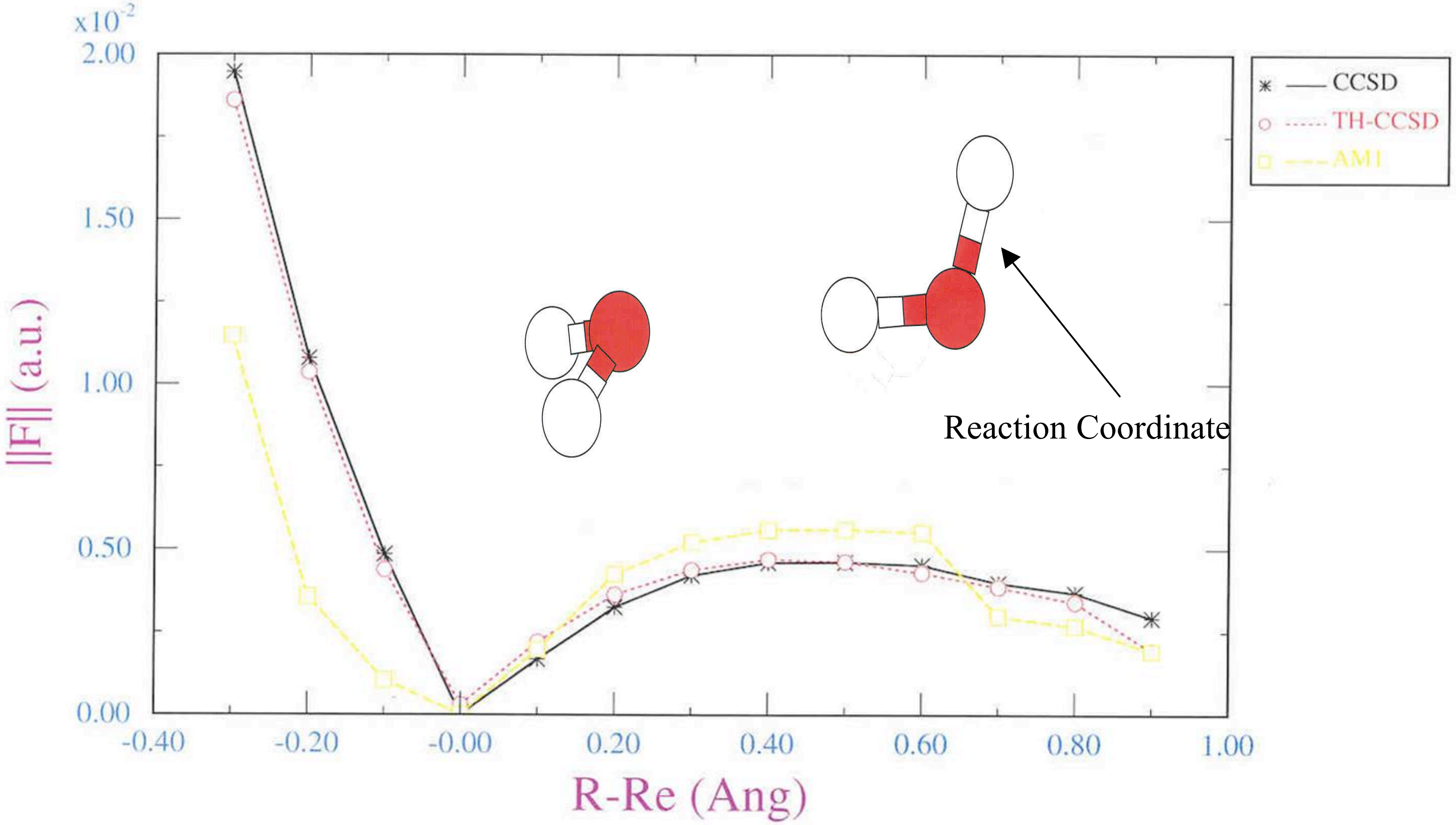
Water Monomer Force Curve



Comparison of computed forces along the donor-acceptor O-H bond in the water dimer using different Hamiltonians

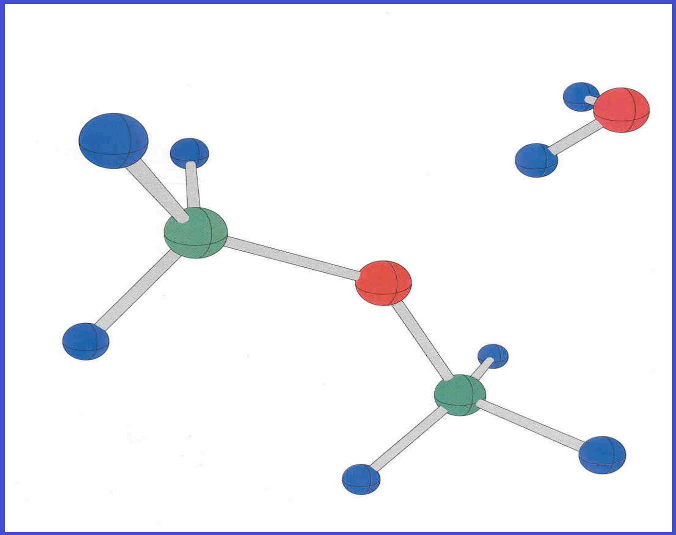


Comparison of forces for removal of a terminal proton in the water dimer

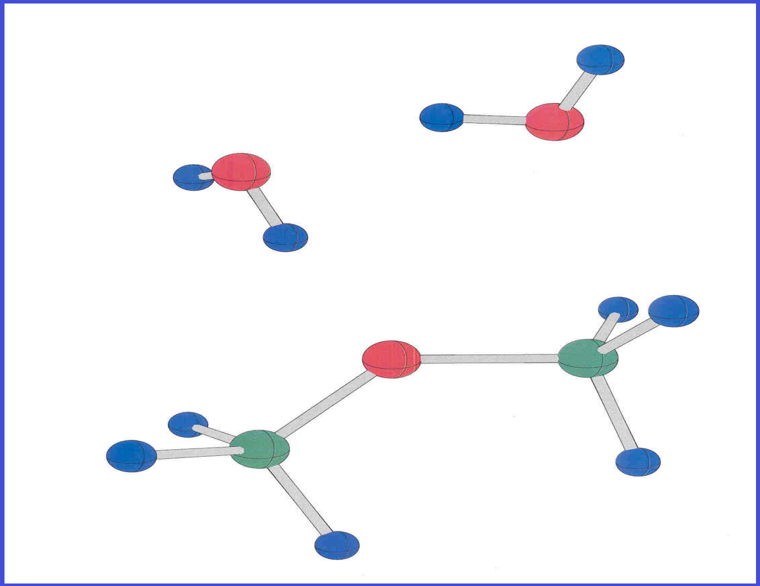


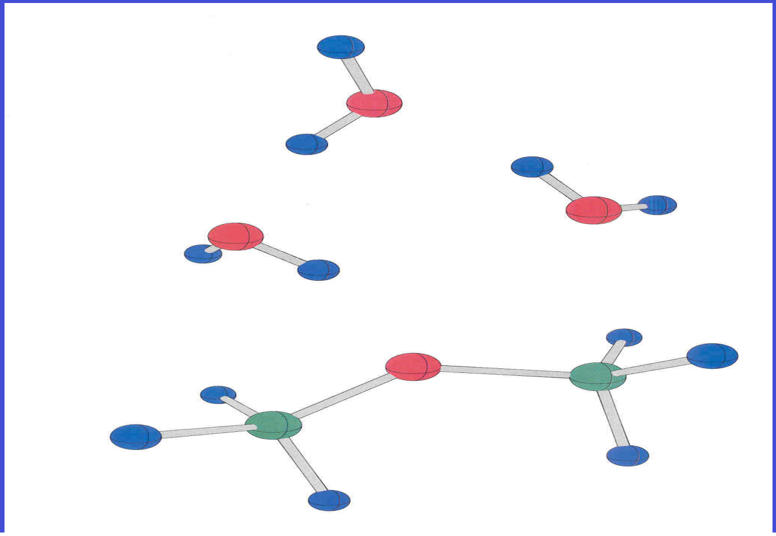
MECHANISM

Binding energy of $(H_2O)_n$ with $H_3SiOSiH_3$

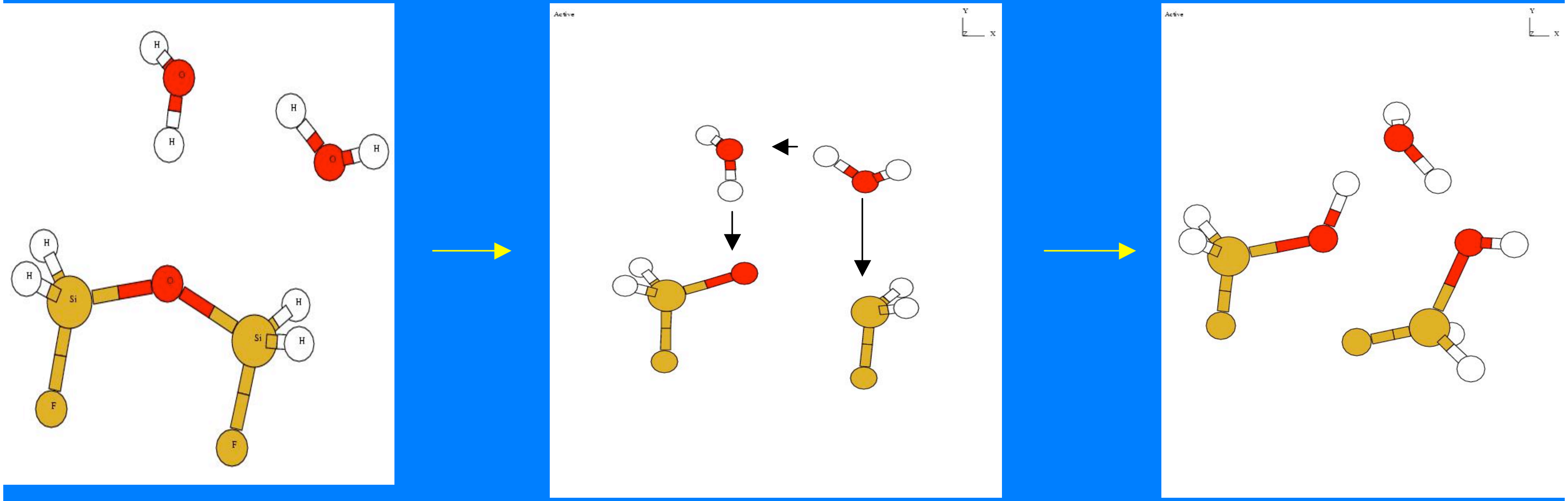


N	Delta E
1	-4.4
2	-6.4
3	-3.7

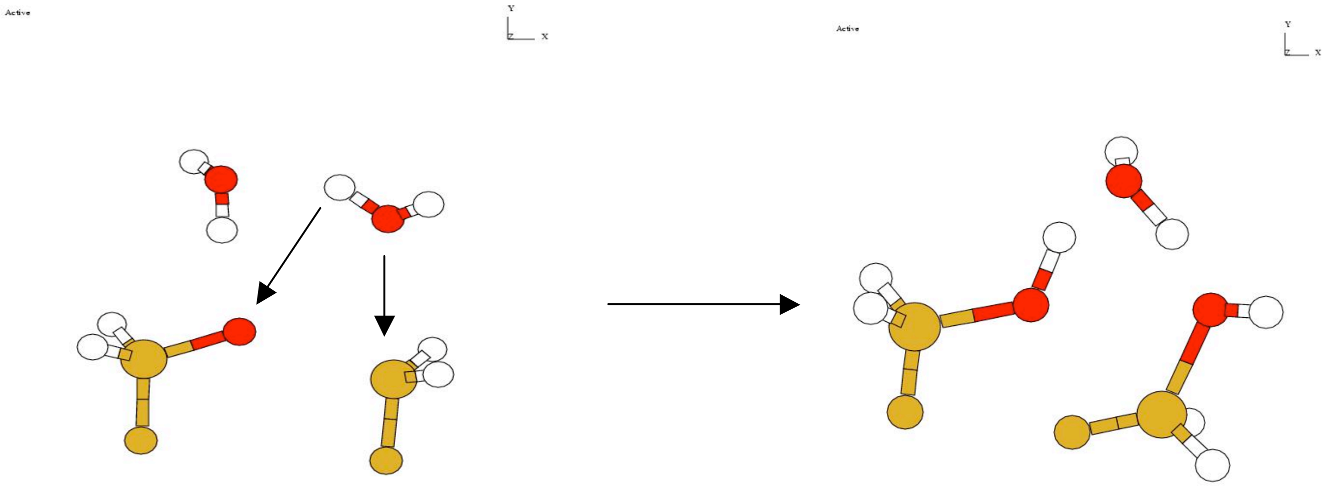




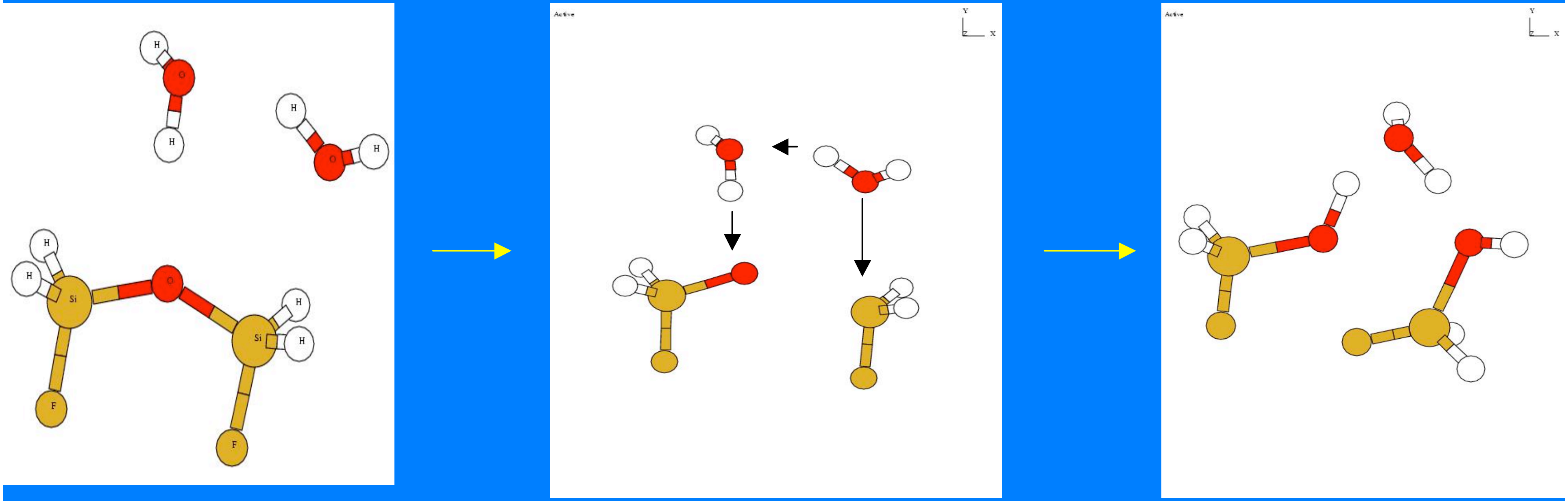
Water Assisted Rupture of Si-O bond (MBPT)



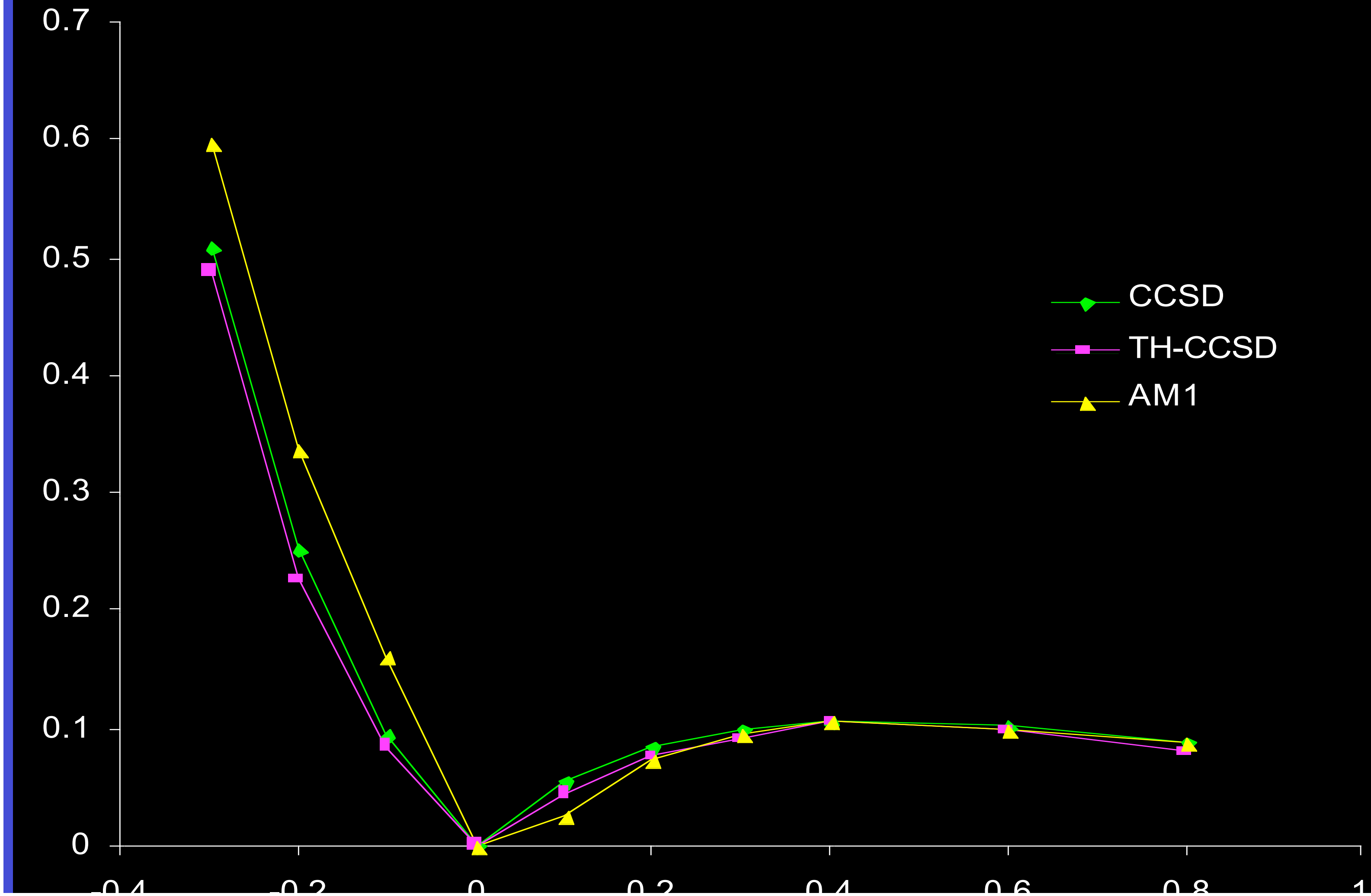
- None of the existing SE models reproduce the ab initio mechanism



Transfer Hamiltonian



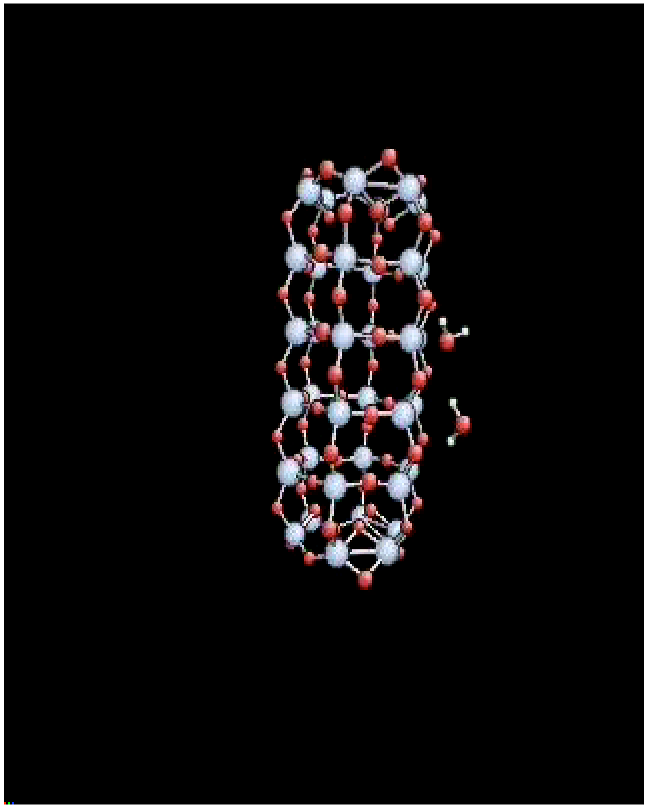
Force Curve for H_2O+Silica Model

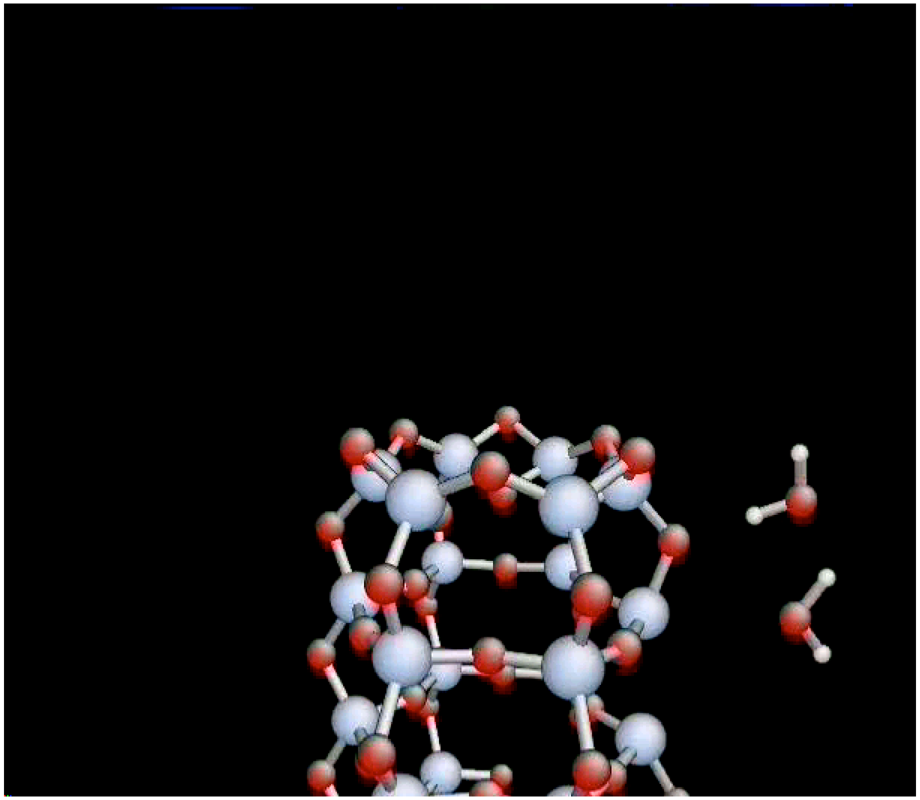


Nanorod + Water Dimer Simulation

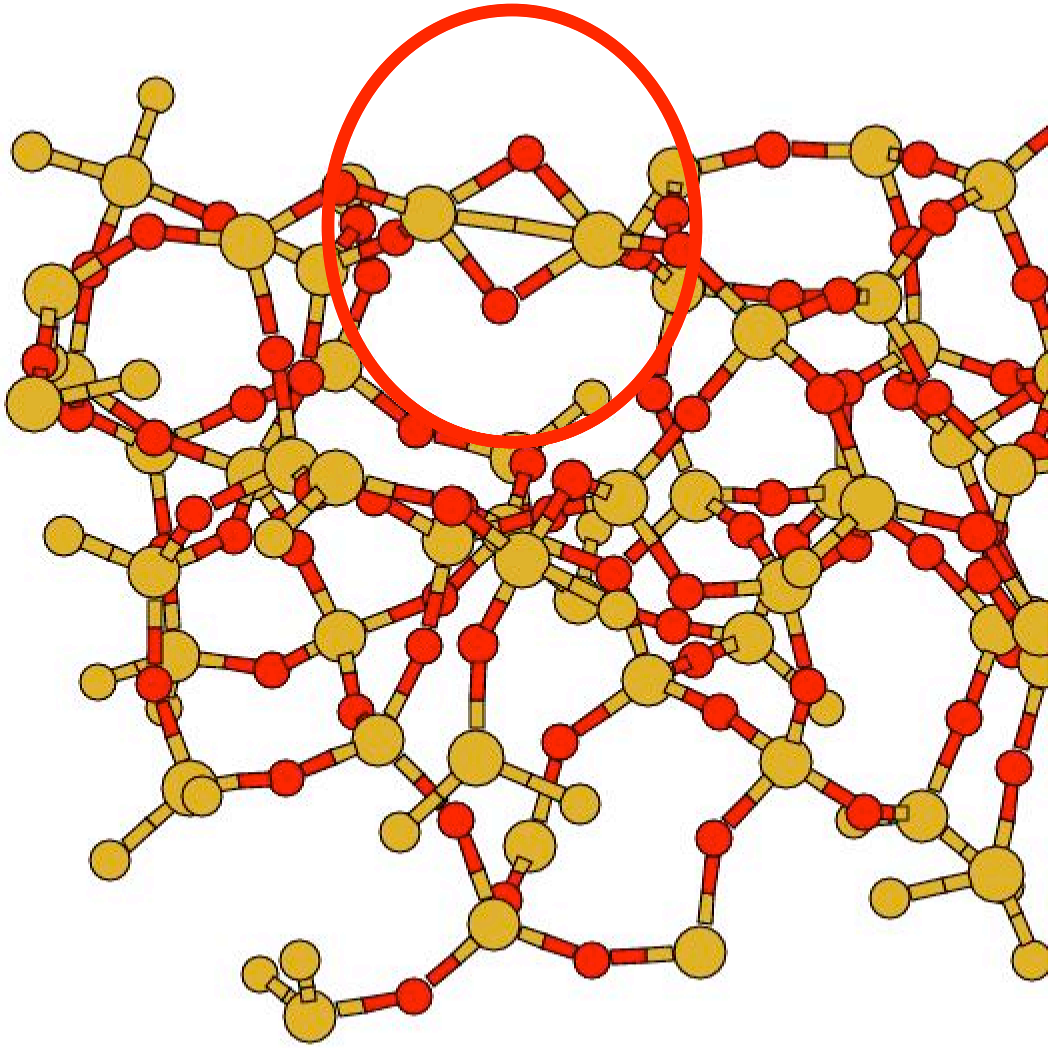
- Uniaxial Strain
  - Constant Strain Rate of 25 m/s
  - 2 ps simulation time
  - Predictor-Corrector algorithm with velocity scaling
- 113 QM atoms
  - spd heavy atoms / sp H (1000 functions total)
- Simulation required 6 days to complete
  - IBM RS600 SP

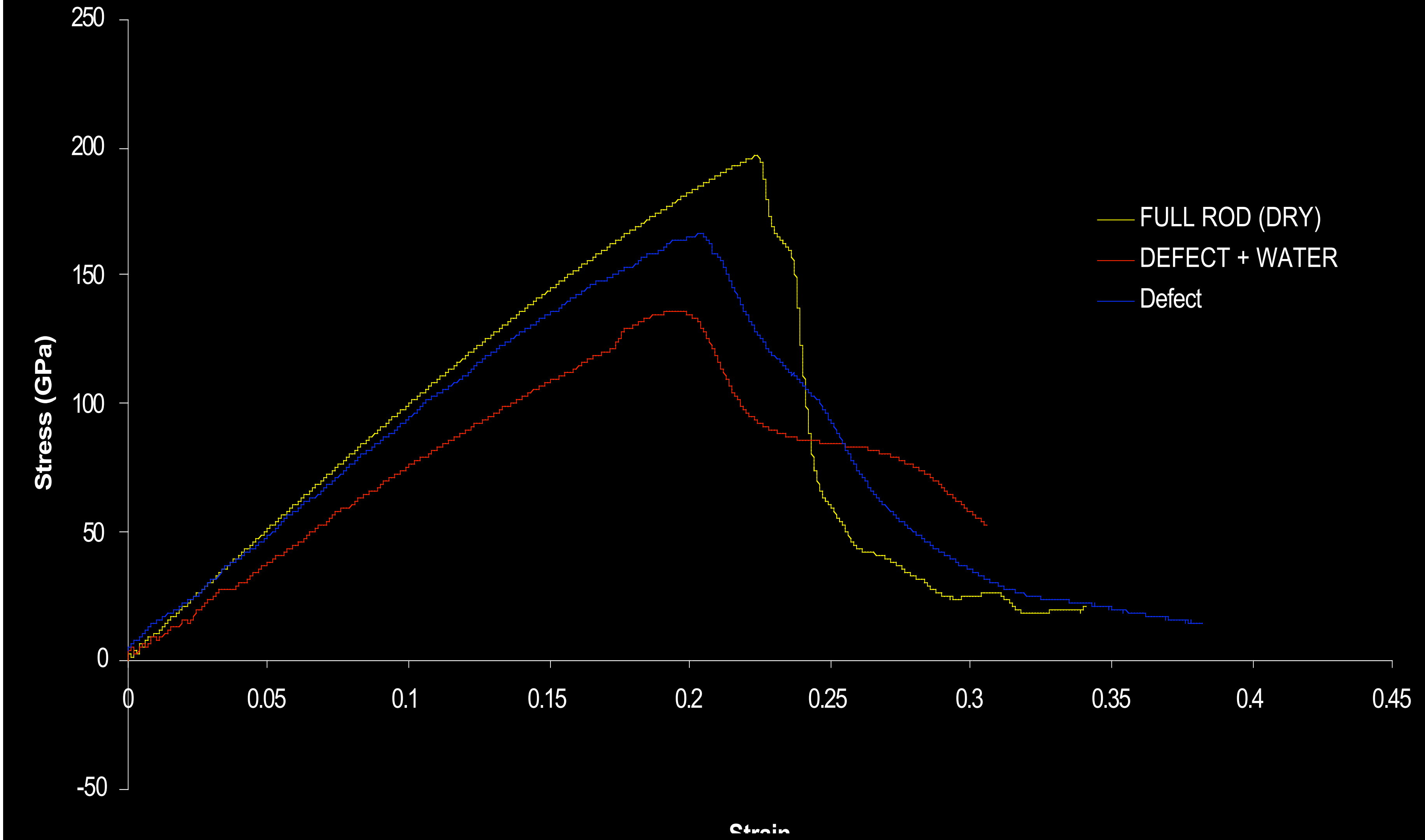
1002 Basis Functions
6 days to complete simulation





2 ring on surface of silica sample





Stress (GPa)
250
200
150
100
50
0
-50
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
Strain
FULL ROD (DRY)
DEFECT + WATER
Defect

CONCLUSIONS

- TH-CCSD takes three orders of magnitude less time per energy and gradient calculation than DFT.
- TH-CCSD can describe different electronic states with comparable accuracy from one set of parameters
- TH-CCSD readily allows for highly efficient hessian and gradient calculations
- A hybrid dynamics procedure that uses a QM iteration for every ~ten classical iterations results in the final QM results
- TH-CCSD’s can be generated for other molecules readily, helping to explore effects of chemistry together with strain.
- TH-CCSD provides a formal structure for state-specific and optical properties of materials
- Direct dynamics calculations with QM forces for ~500-1000 atoms possible.

SOFTWARE ISSUES

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Sam Trickey
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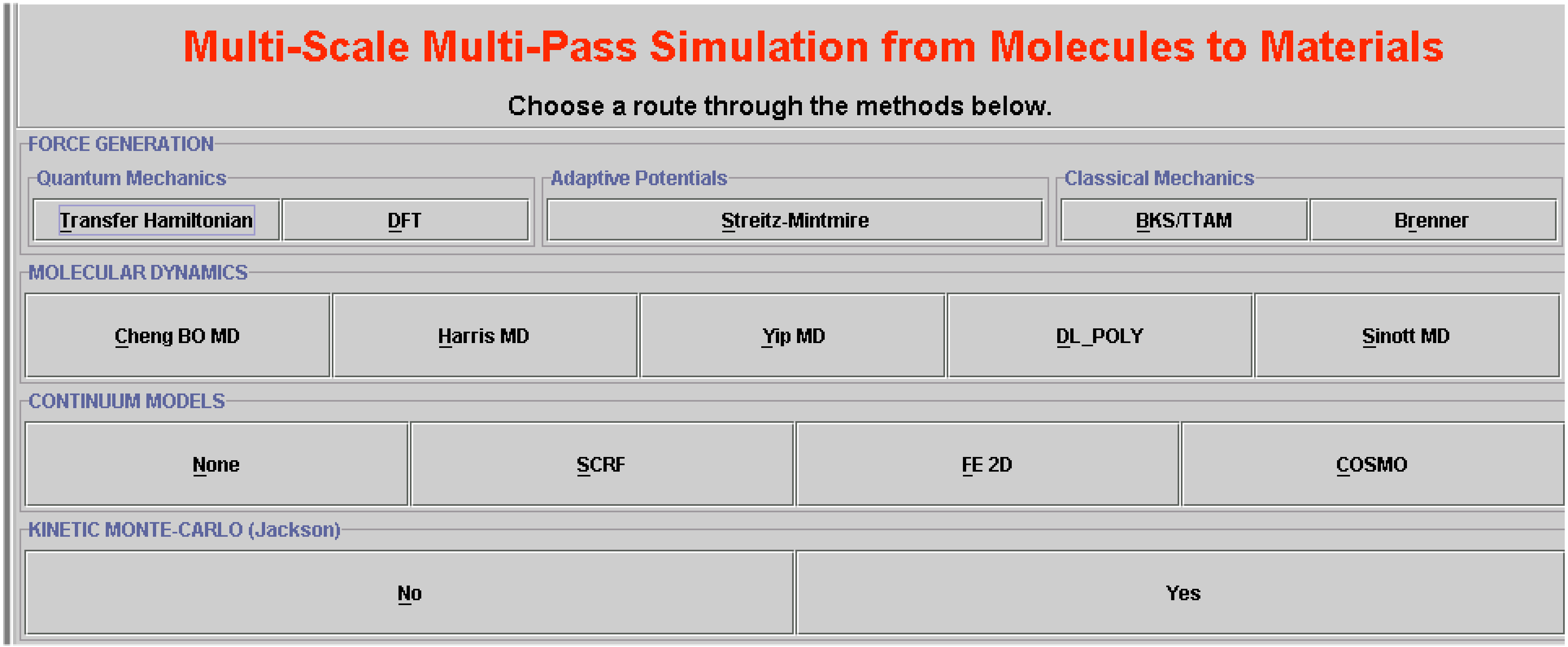
COMPUTER PROGRAMS



Multi-Scale Multi-Pass Simulation from Molecules to Materials

Choose a route through the methods below.

Choose forces, MD method, and Continuum Model

Common User Interface

Strategy

- Hide the data structures and codes
- Advantages – relatively quick to implement, does not require rework of codes
- Disadvantages – inflexible choices for users, delays the inevitable need to modernize “spaghetti code”; has high risk of internal data incompatibilities.

Partial Restructuring Approach

Strategy

- Harmonize the inter-code data structures, document the implicit validity and quality limitations of inter-code data, simplify the interfaces to large working codes to make them “object-like” at least at the Python script level. Support with a Graphical Interface also

Partial Restructuring Approach

Strategy (cont)

- Advantages – Requires “cleansing” and vetting of codes to make them as much as possible into autonomous objects, supports user flexibility for innovation, does not require rework of codes
- Disadvantages – lots of tedious analysis, fixing, and testing

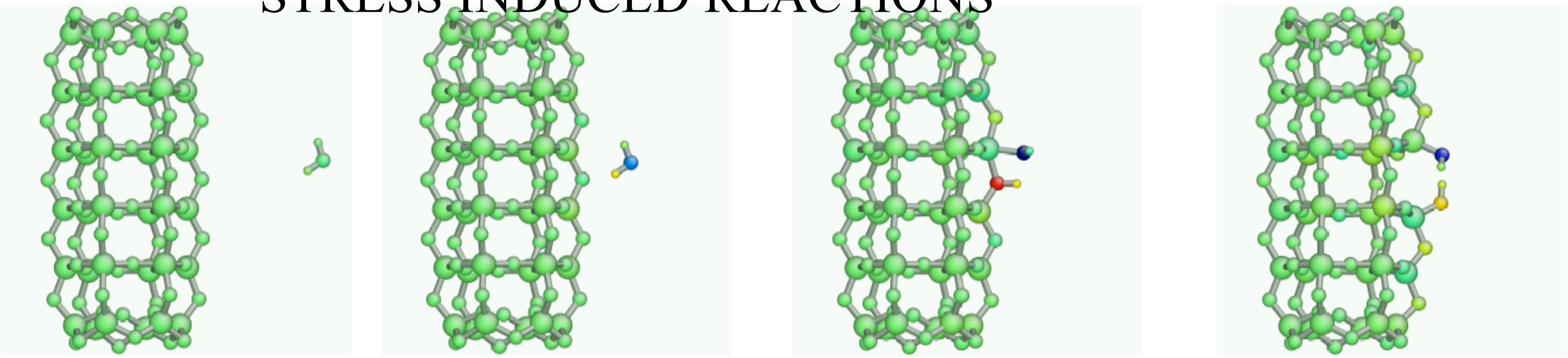
REGION III: CONTINUUM TO CLASSICAL TO QUANTUM INTERFACE

Ting Zhu

Sid Yip

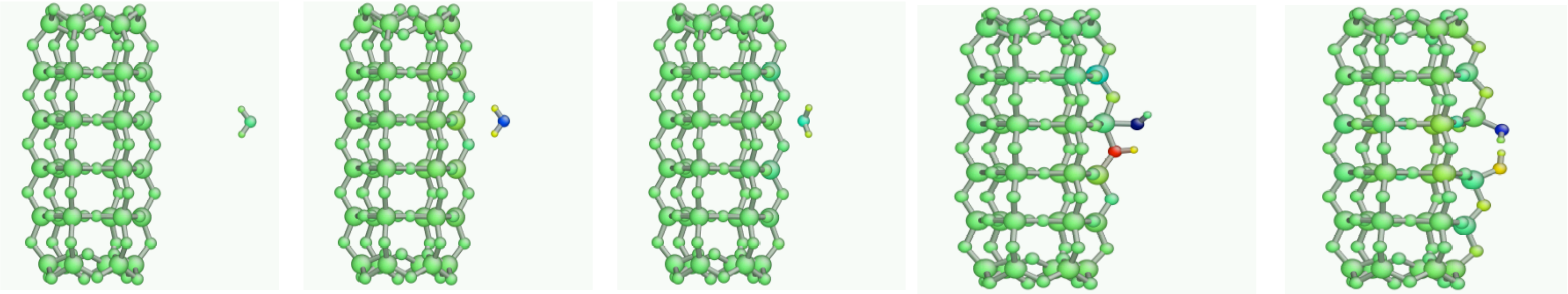
MIT

STRESS INDUCED REACTIONS



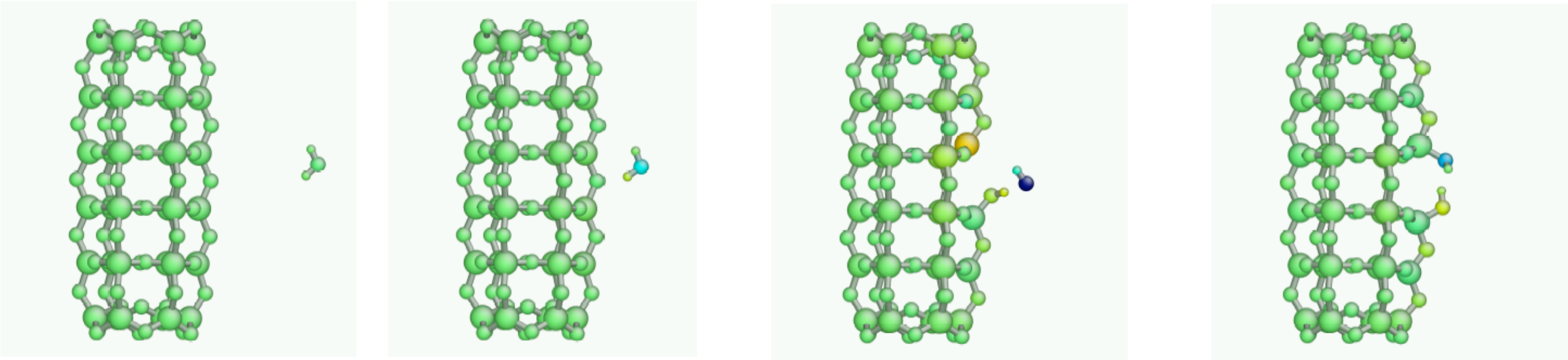
(a) (b) (c) (d)

MECH I: Water dissociation



(a) (b) (c) (e) (f)

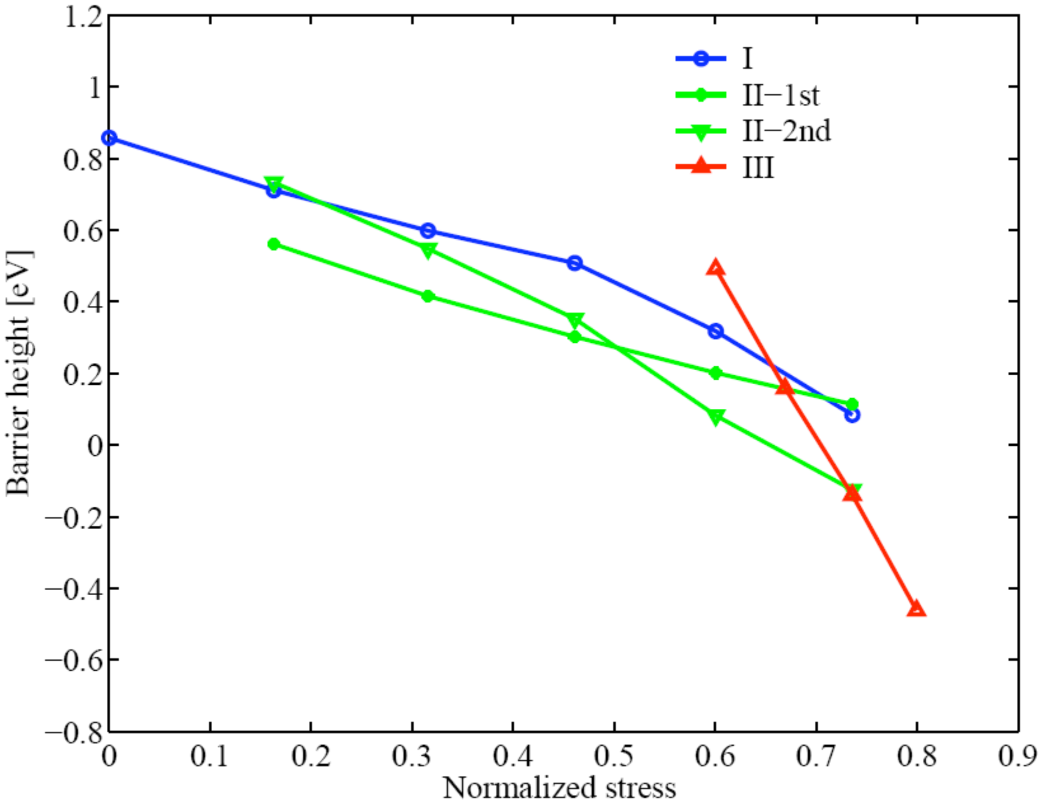
MECH II. Metastable chemisorption



(a) (b) (c) (d)

MECH III. Siloxane bond breaking

STRESS DEPENDENT ACTIVATION BARRIERS



ACCOMPLISHMENTS TO DATE

•Established that an exact one-particle theory can be obtained from WFT, to complement DFT. Ab Initio dft provides the link.

•Demonstrated that such a theory can be approximated adequately to describe CC quality forces for representative clusters, ie the ‘transfer hamiltonian,’ which represents a potential energy surface in an easily manipulated form that is suitable for direct dynamics.

•Showed that the results of quantum based simulations are qualitatively different from those using classical potentials.

•Proposed a water dimer based mechanism for the critical step in hydrolytic weakening of silica.

•Obtained same results from TH based simulations and DFT simulations, though done independently, with very different methodology.

ACCOMPLISHMENTS (cont)

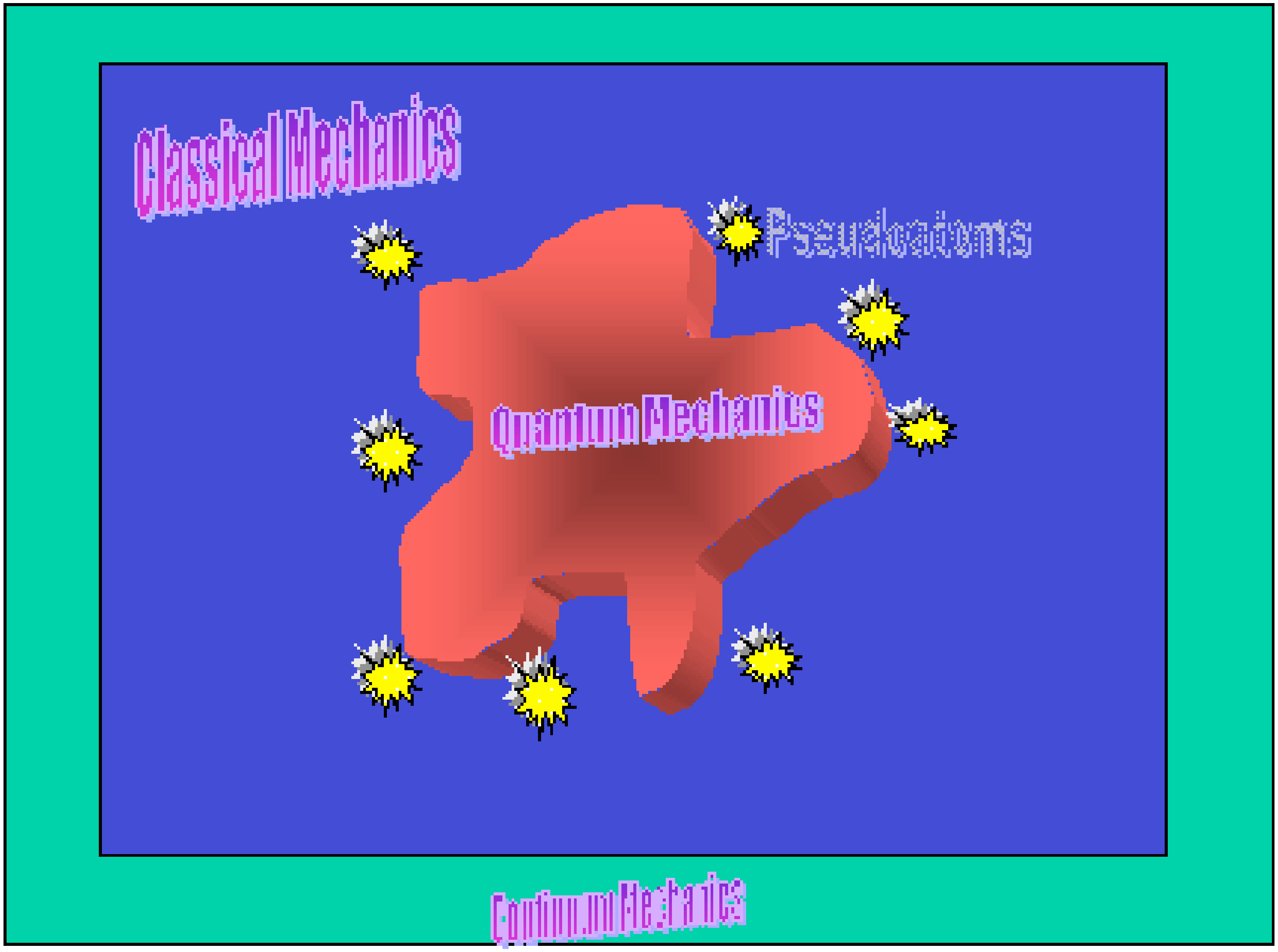
- Invented a wavelet method to identify area of fracture prior to failure, to locate quantum region unambiguously.

- Created alternative link atom-psuedo atom approaches to accurately describe the forces and charge distributions between the classical and quantum regions.

- Started to build easily applied software that incorporates our new methods to enable simulationsto be made with quantum potentials from dft, CC, and the transfer Hamiltonian.

- Identified the weakest link in current multi-scale simulations to be the classical potentials, which are still a necessity for most of the atoms in a realistic simulation.

- Studied stress dependent activation barriers for water silica reactions.


Classical Mechanics
Pseudoatoms
Quantum Mechanics
Continuum Mechanics

SIMULATION OF WATER + SILICA WITH TH FOR QUANTUM REGION, REPARAMETERIZED TTAM FOR CLASSICAL, RPRESENTED BY POINT DIPOLES AND CONNECTED BY PSUEDO-ATOMS. WATER CONTINUUM ADDED VIA COSMO.

WHOLE TEAM!