

Theoretical and Computational Nanoscience

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and

Center for Nanophase Materials Sciences
Oak Ridge National Laboratory

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Montgomery Bell State Park, Burns, TN
September 7-10, 2008



Outline of Talk

□ Introduction

- *Theory, Modeling and Simulation in Nanoscience*
- *ORNL Center for Nanophase Materials Science and Nanomaterials Theory Institute*

□ Molecular electronics

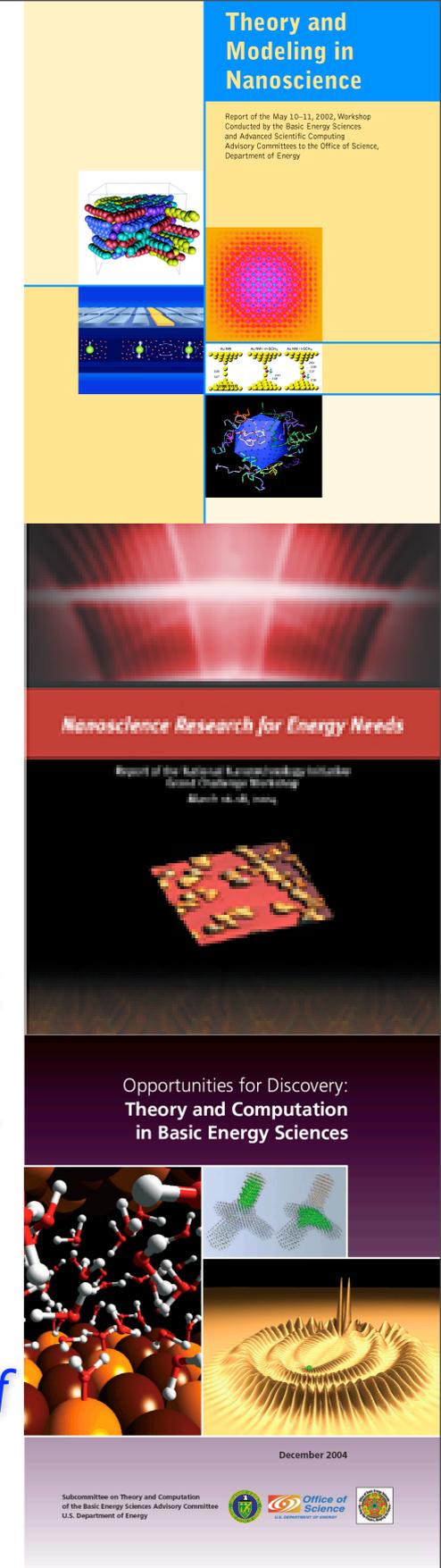
- *Electron transport in self-assembled nano-bridges*

□ Conclusions

Introduction

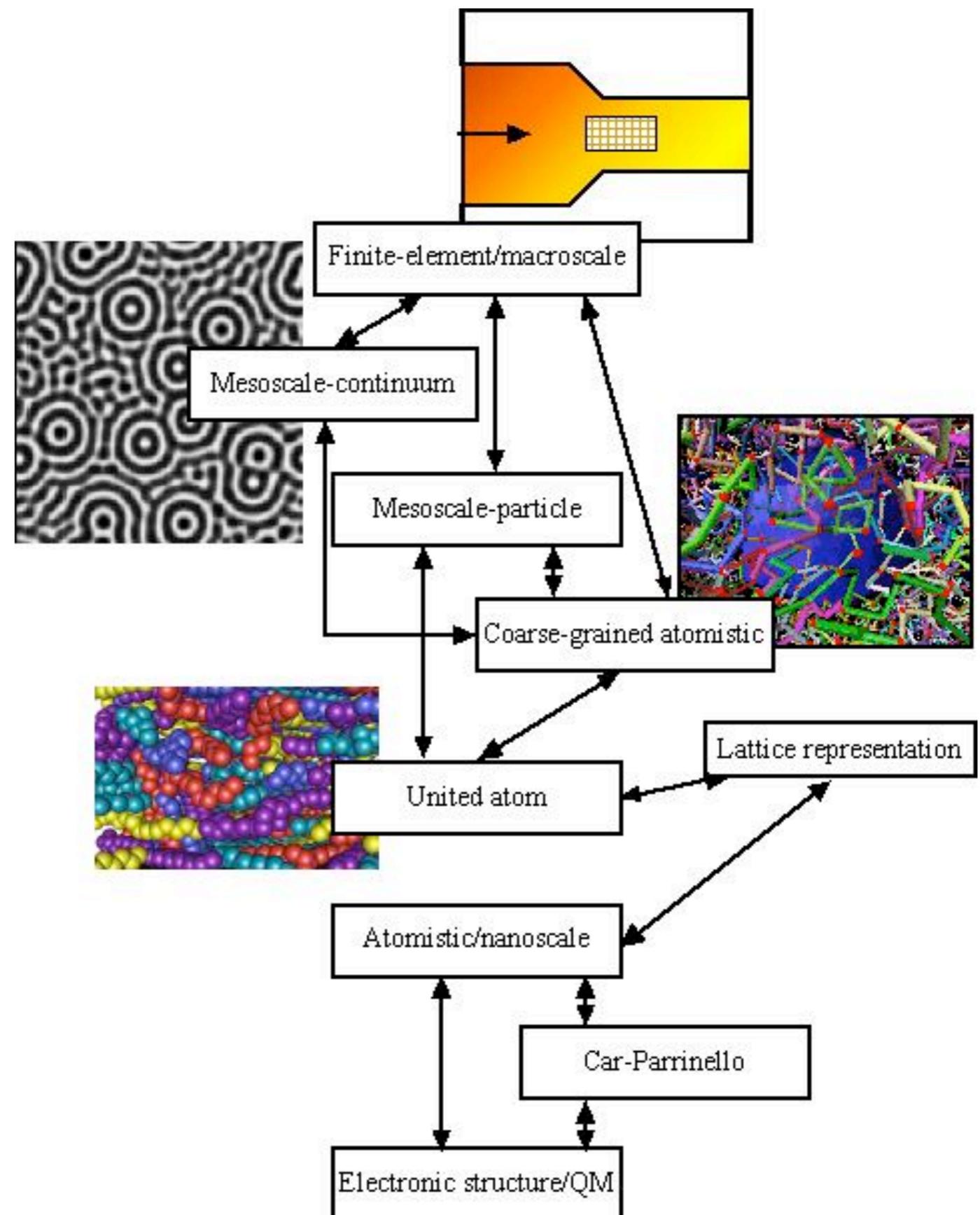
□ Theory, modeling and simulation (TMS)

- *Expected to play key role in nanoscale science and technology*
 - “Nanotechnology Research Directions: IWGN Workshop Report. Vision for Nanotechnology Research and Development in the Next Decade,” edited by M.C. Roco, S. Williams, P. Alivisatos, Kluwer Academic Publisher, 2000
 - Also available on-line at <http://www.wtec.org/loyola/nano/IWGN.Research.Directions/>
 - Chapter 2, *Investigative Tools: Theory, Modeling, and Simulation*, by D. Dixon, P.T. Cummings, and K. Hess
 - Discusses issues and examples
 - McCurdy, et al. "Theory and Modeling in Nanoscience: Report of the May 10-11, 2002, Workshop Conducted by the Basic Energy Sciences and Advanced Scientific Computing Advisory Committees of the Office of Science, Department of Energy
 - Published by DOE
 - Also available on the web at http://www.er.doe.gov/bes/reports/files/TMN_rpt.pdf
 - Alivisatos, et al., “Nanoscience Research for Energy Needs: Report of the March 2004 National Nanotechnology Initiative Grand Challenge Workshop
 - Published by DOE and NNI
 - Also available on the web at http://www.er.doe.gov/bes/reports/files/NREN_rpt.pdf
 - BESAC, “Opportunities for Discovery: Theory and Computation in Basic Energy”
 - Published by DOE
 - Also available on the web at http://www.er.doe.gov/bes/reports/files/OD_rpt.pdf



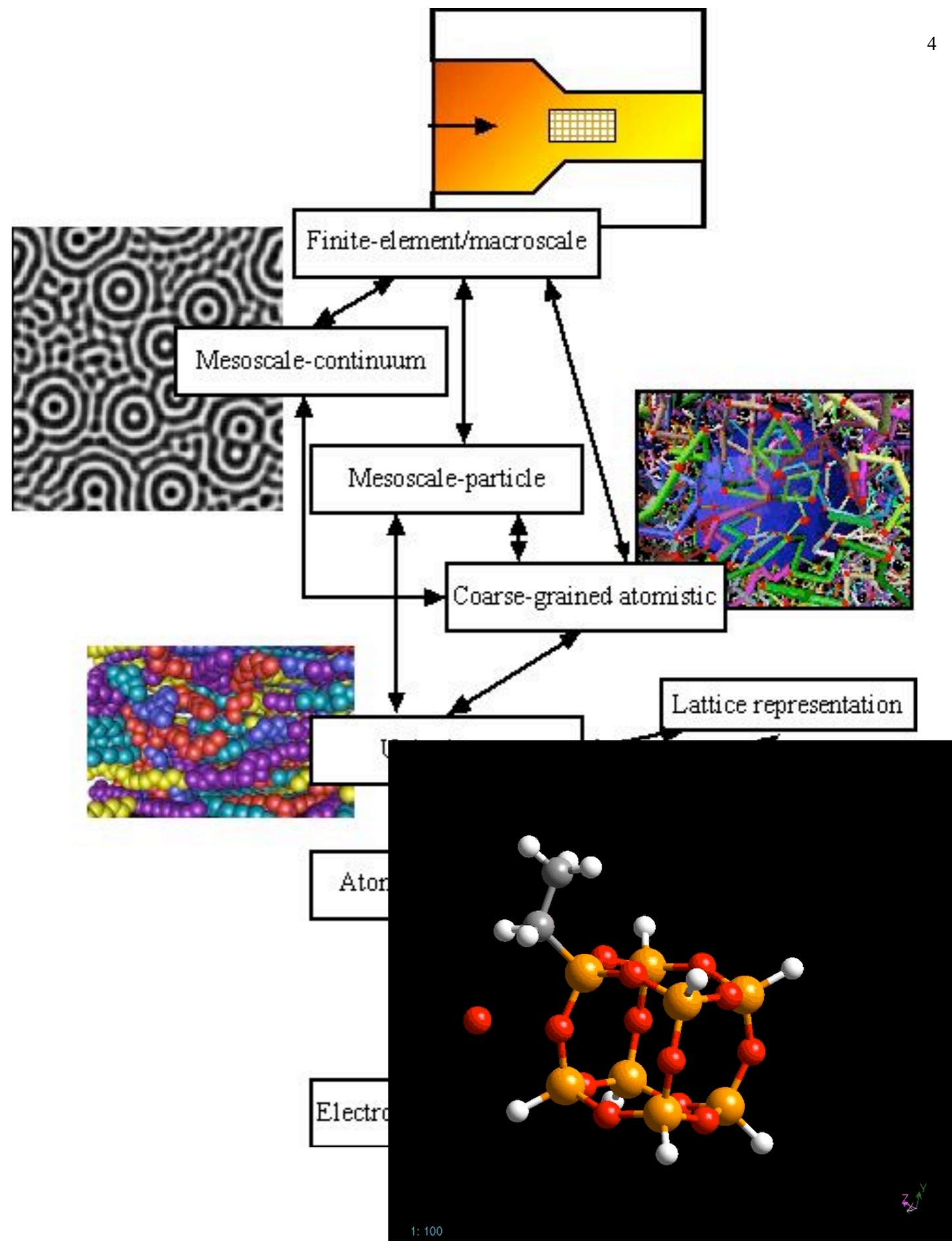
Introduction

- Hierarchy of methods relevant to nanoscale science and technology
 - *Connection to macroscale*
 - *Unlike bulk systems, large-scale manufacturability of nanoscale systems will require deep theoretical understanding*
 - *Inherent strong dependence on spatial dimensions*



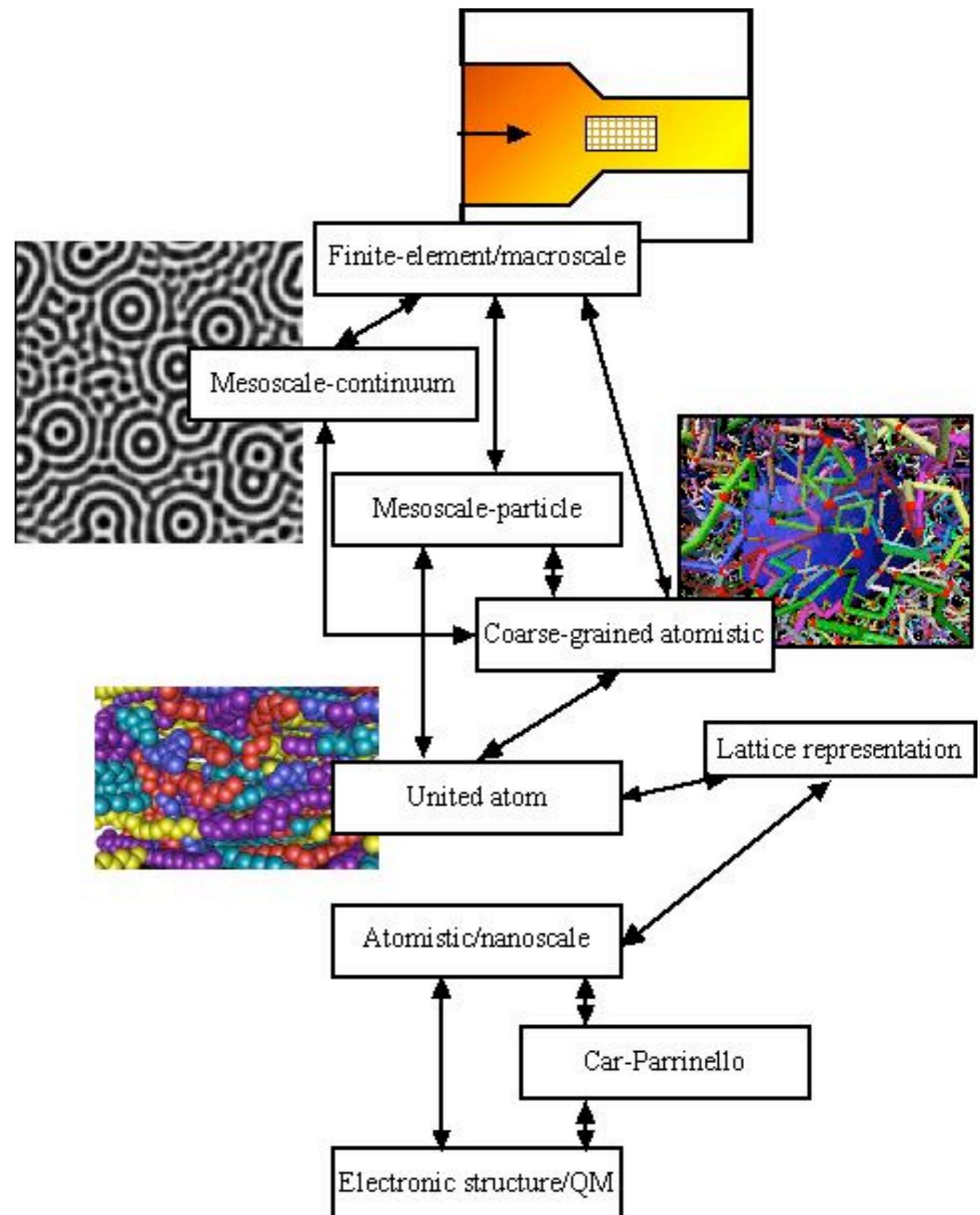
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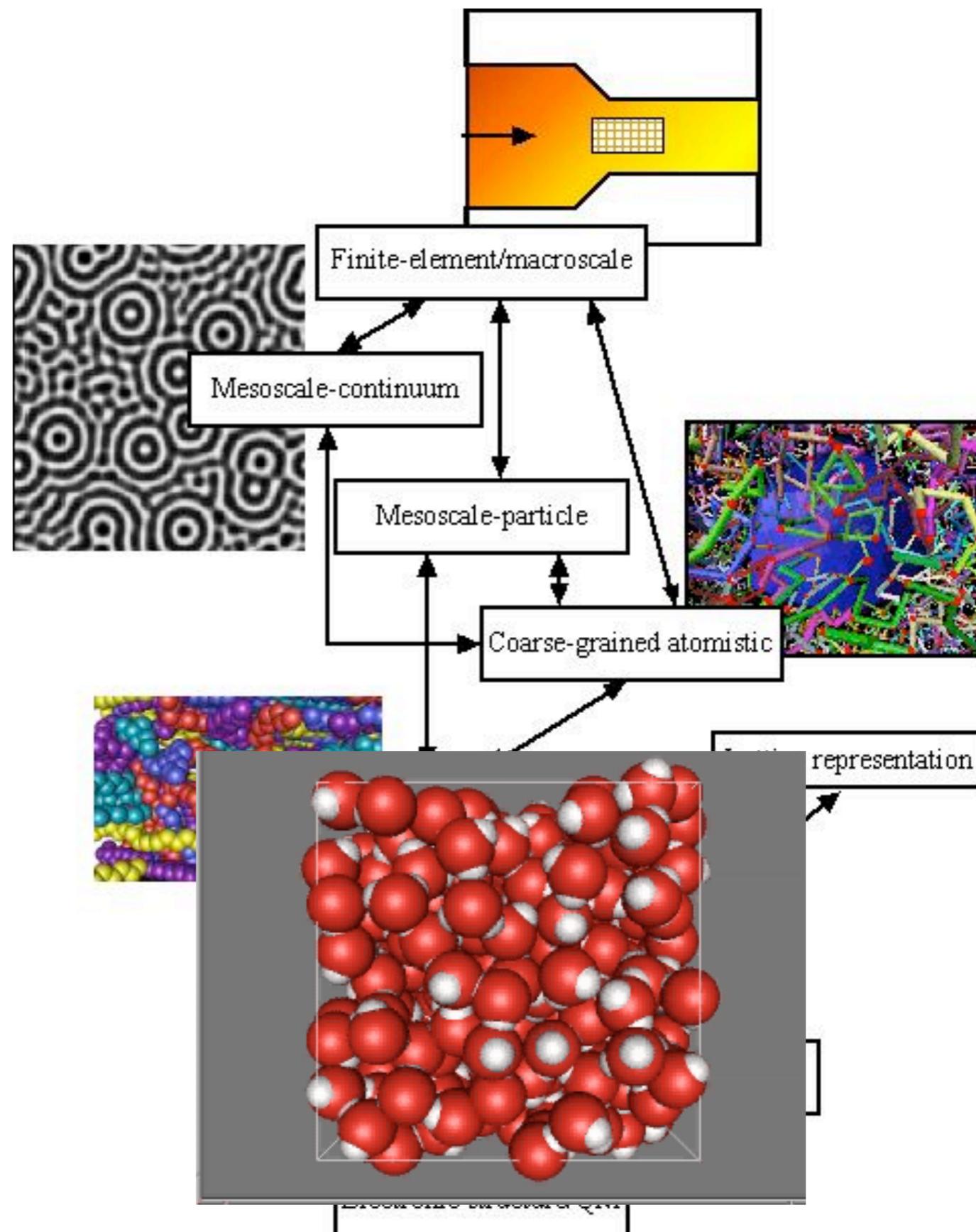
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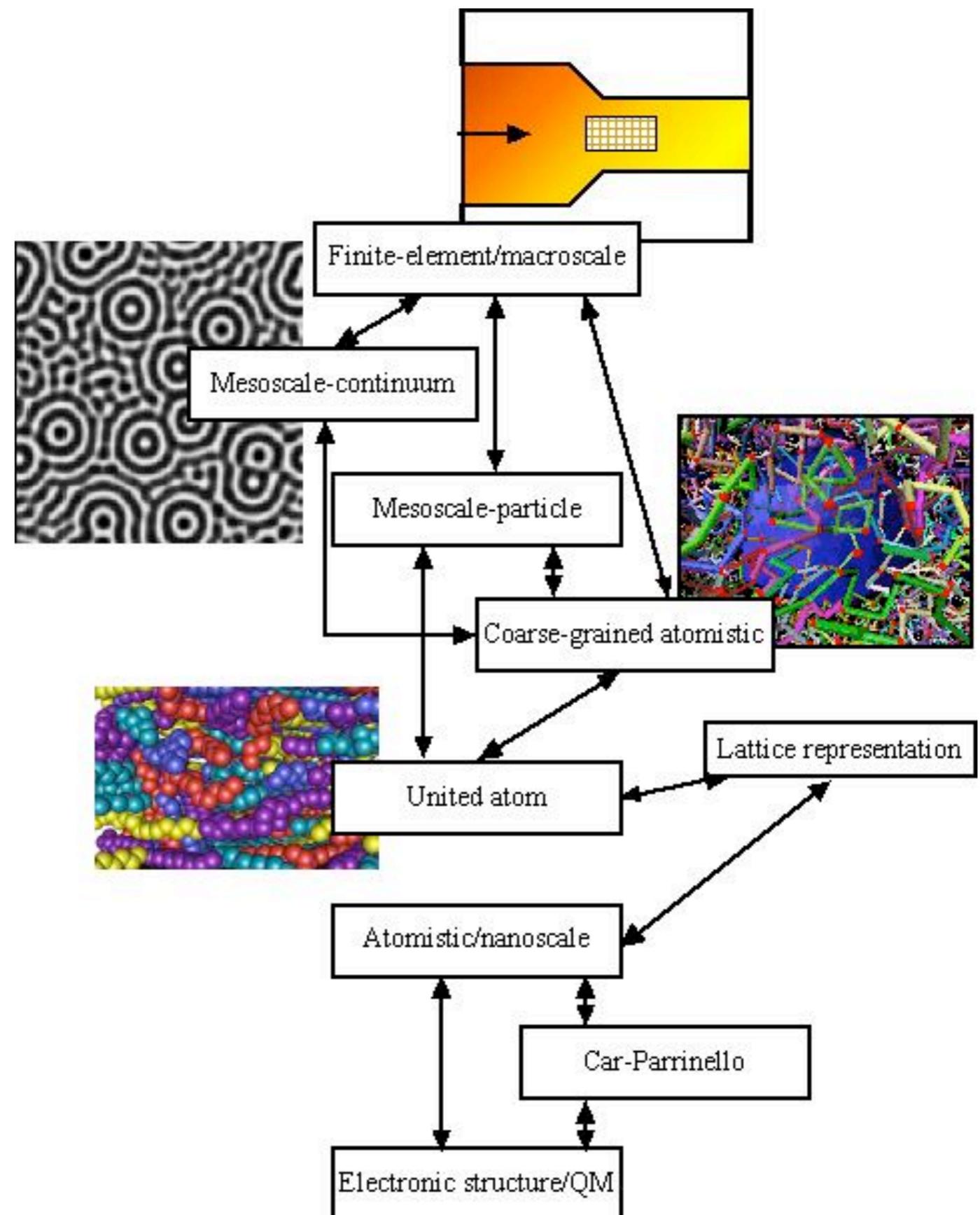
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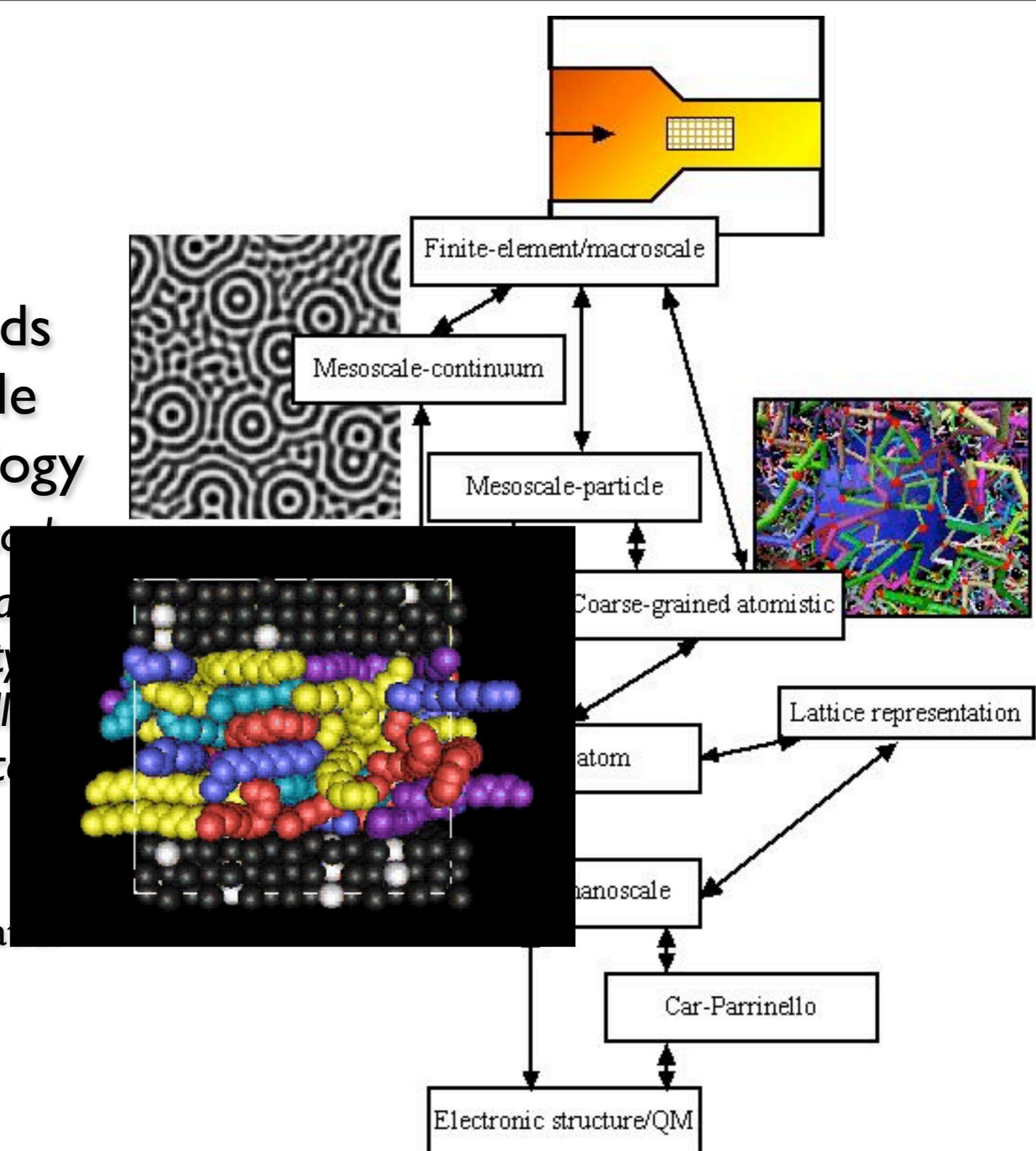
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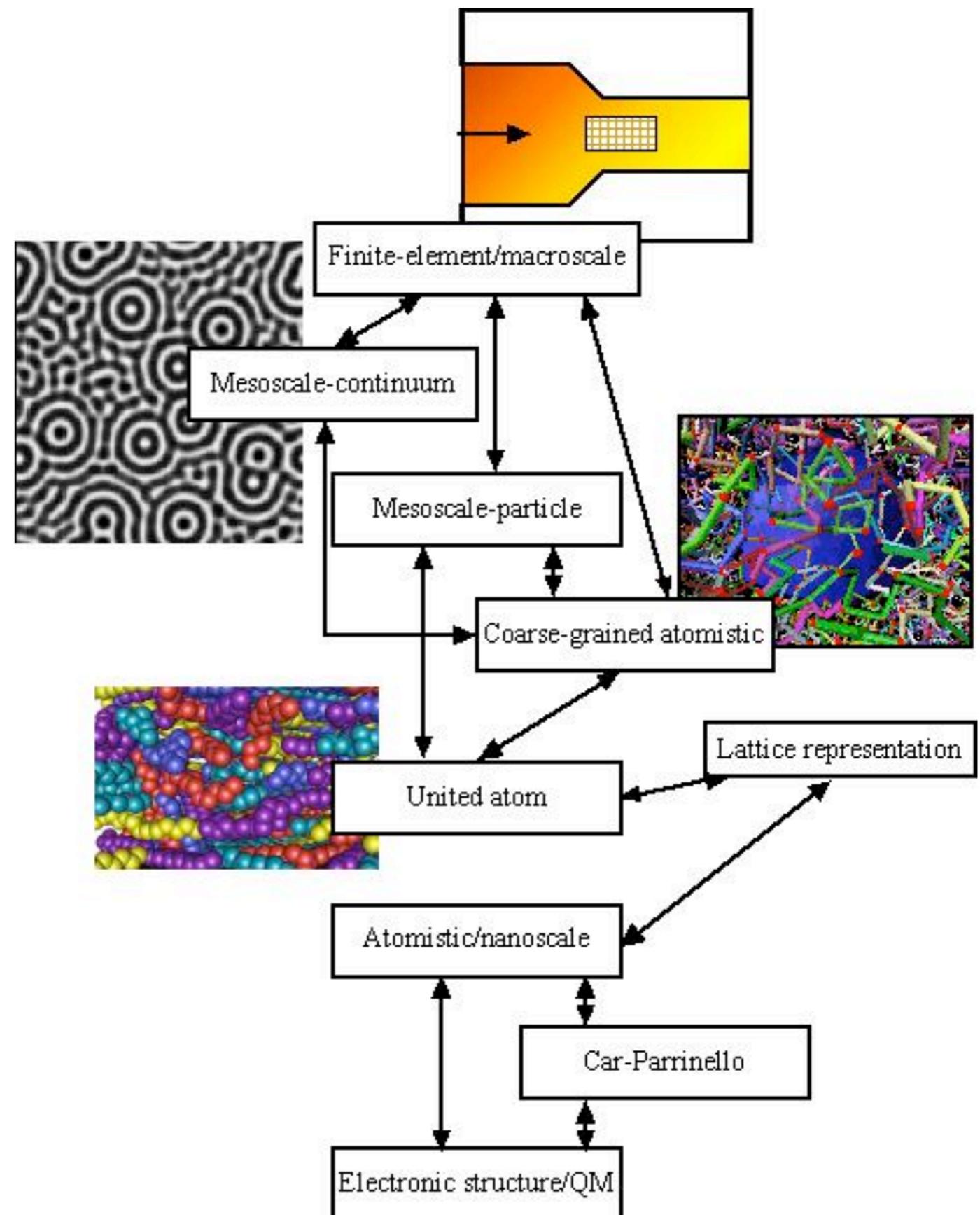
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- *Connection to macroscopic world*
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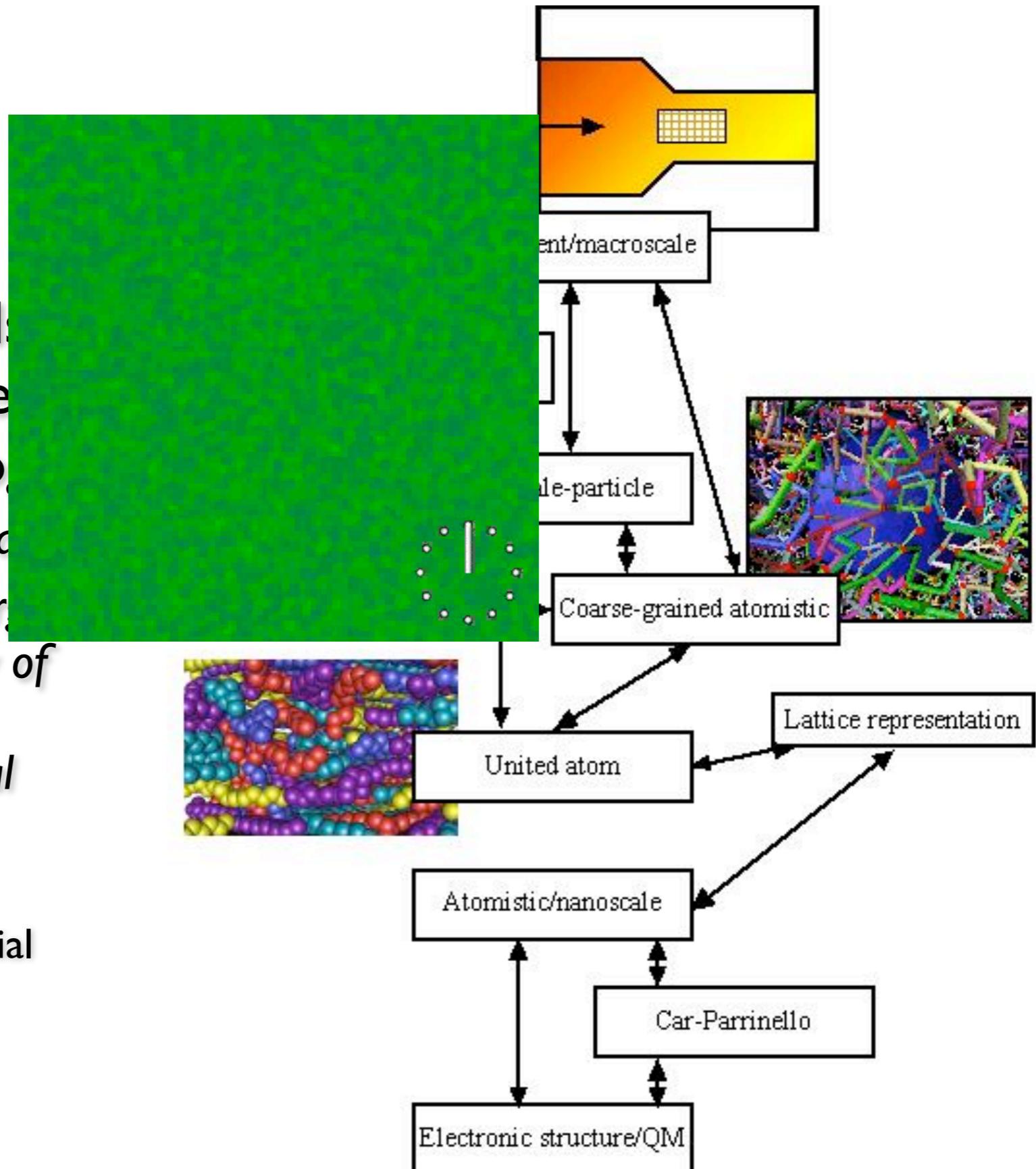
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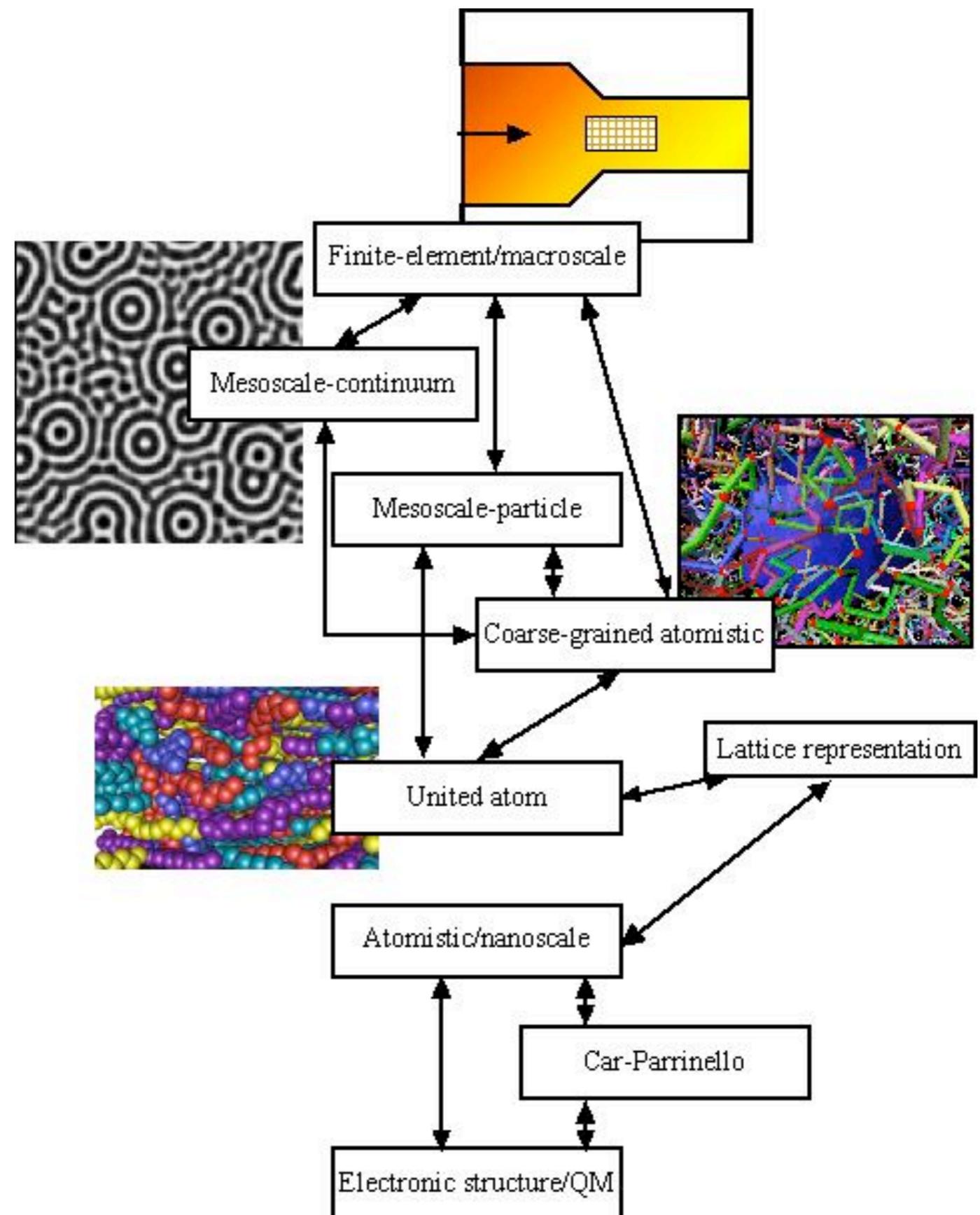
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Specializing in neutron science, synthesis science, and theory/modeling/simulation



- **Neutron Science**
 - Opportunity to use unique neutron scattering capabilities to understand nanoscale materials and processes
- **Synthesis Science**
 - Science-driven synthesis will be the enabler of new generations of advanced materials
- **Theory/Modeling/Simulation**
 - The Nanomaterials Theory Institute
- **Three scientific thrust areas, capabilities in eight major areas**
- **Access to other major ORNL facilities**
 - Spallation Neutron Source (SNS)
 - High-Flux Isotope Reactor (HFIR)
 - Center for Computational Sciences (CCS)
 - National Leadership Supercomputing Facility (NLCF)
- **Began Sept, 2003; completed May, 2005**
 - \$65M for building and equipment; \$18.5M/yr ongoing



SNS Central Lab and Office Building



CNMS 4-story lab and office complex

CNMS Cleanroom for Nanofabrication

Center for Nanophase Materials Sciences web site
<http://cnms.ornl.gov>

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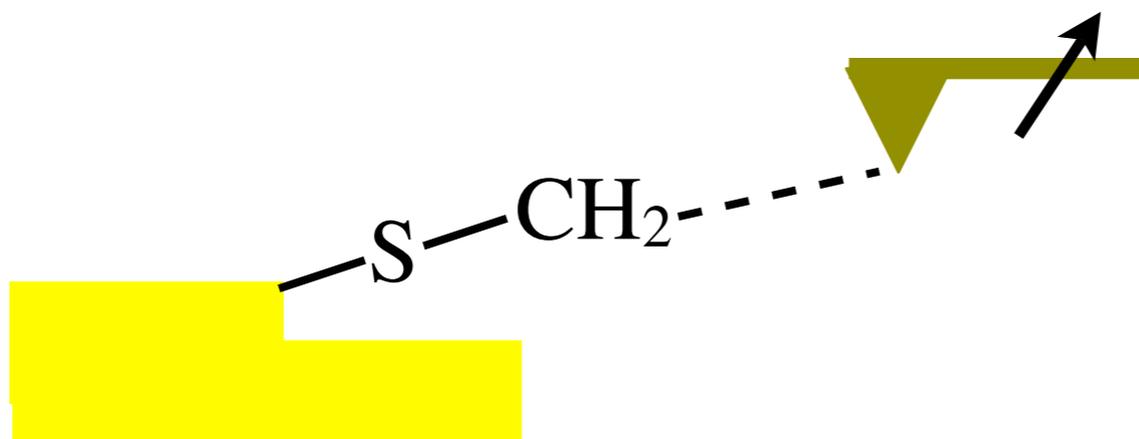
Role of Theory, Modeling and Simulation (TMS) in Nanoscience

- Interpretation of experiment

Developments in TMS - Examples

□ Interpretation of AFM experiment

- *Many experiments at the nanoscale require TMS to understand what is being measured*



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VOLUME 89, NUMBER 18

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28 OCTOBER 2002

Pulling Monatomic Gold Wires with Single Molecules: An *Ab Initio* Simulation

Daniel Krüger,¹ Harald Fuchs,¹ Roger Rousseau,² Dominik Marx,² and Michele Parrinello³

¹*Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm Klemm-Strasse 10, 48149 Münster, Germany*

²*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany*

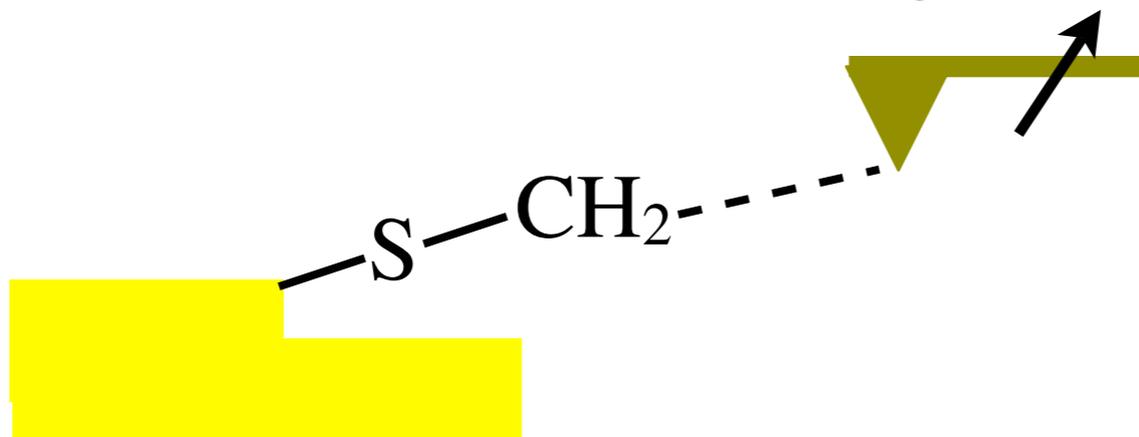
³*Swiss Center for Scientific Computing/ETH Zurich, Via Cantonale, Galleria 2, 6928 Manno (TI), Switzerland*

(Received 30 April 2002; published 10 October 2002)

Car-Parrinello molecular dynamics simulations demonstrate that pulling a single thiolate molecule anchored on a stepped gold surface does not preferentially break the sulfur-gold chemical bond. Instead, it is found that this process leads to the formation of a monoatomic gold nanowire, followed by breaking a gold-gold bond with a rupture force of about 1.2 nN. The simulations also indicate that previous single-molecule thiolate-gold and gold-gold rupture experiments both probe the same phenomenon, namely, the breaking of a gold-gold bond within a gold nanowire.

DOI: 10.1103/PhysRevLett.89.186402

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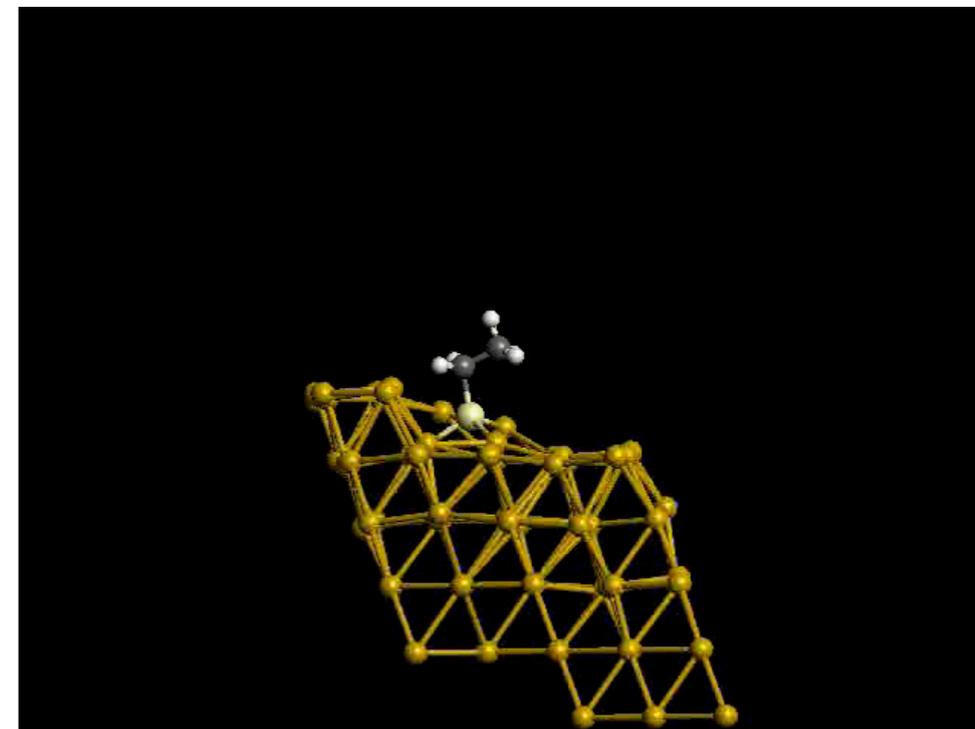
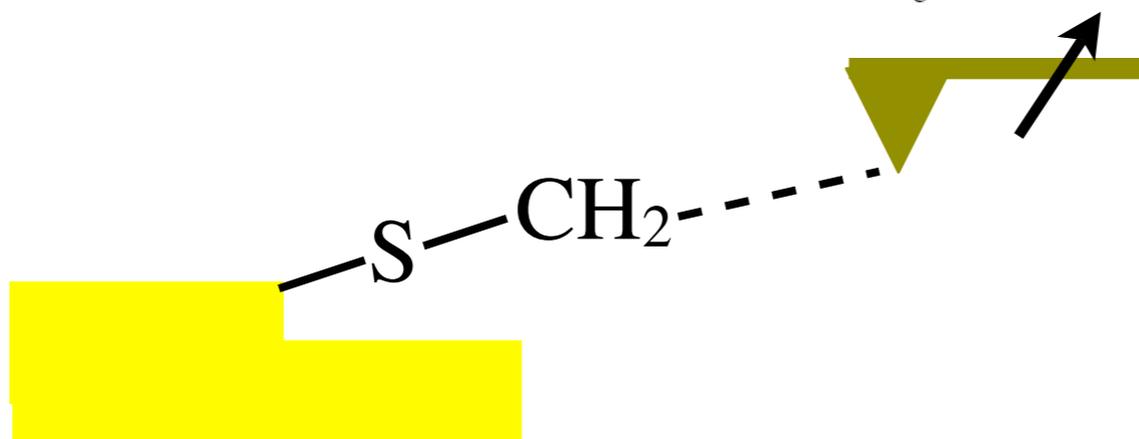
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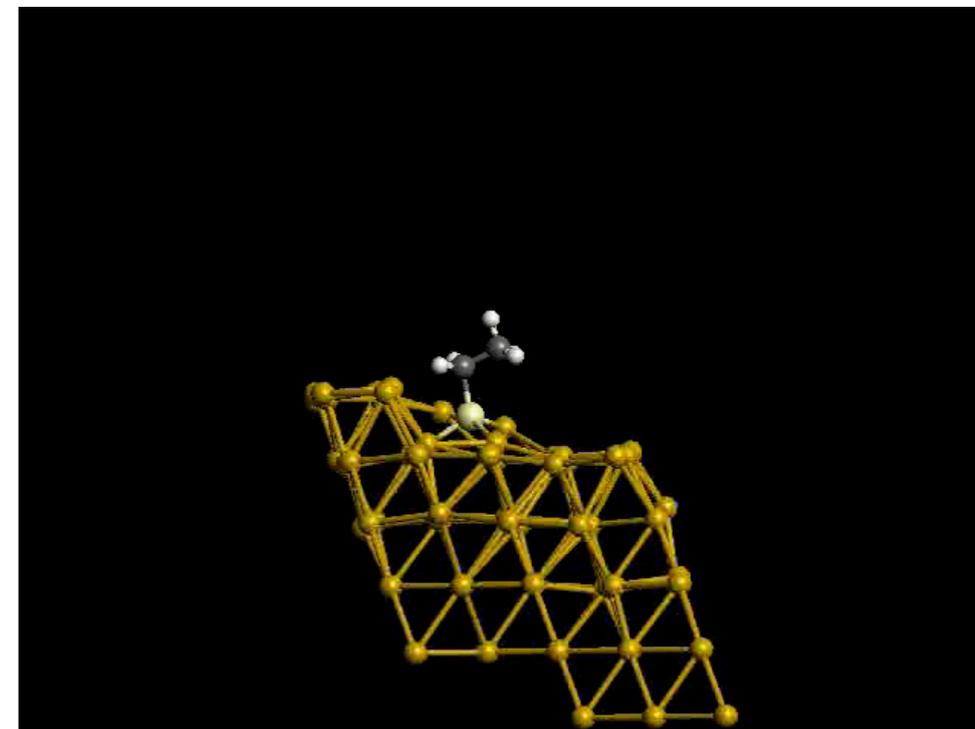
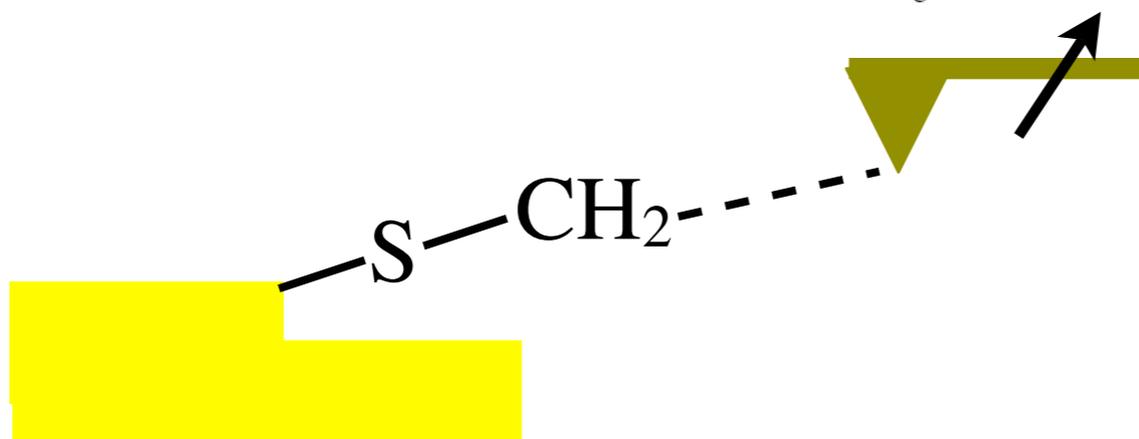
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Unifies two prior experimental results:

- Au-Au bond in nanowire - Rubio-Bollinger et al., *Phys. Rev. Letts.* **87** (2001) 026101
- Au-S “bond” measured at Au surface - Grandbois, *Science* **283** (1999) 1727-1730

Understanding STM Measurements of Catalytically Active Sites on Defective TiO_2 Surfaces

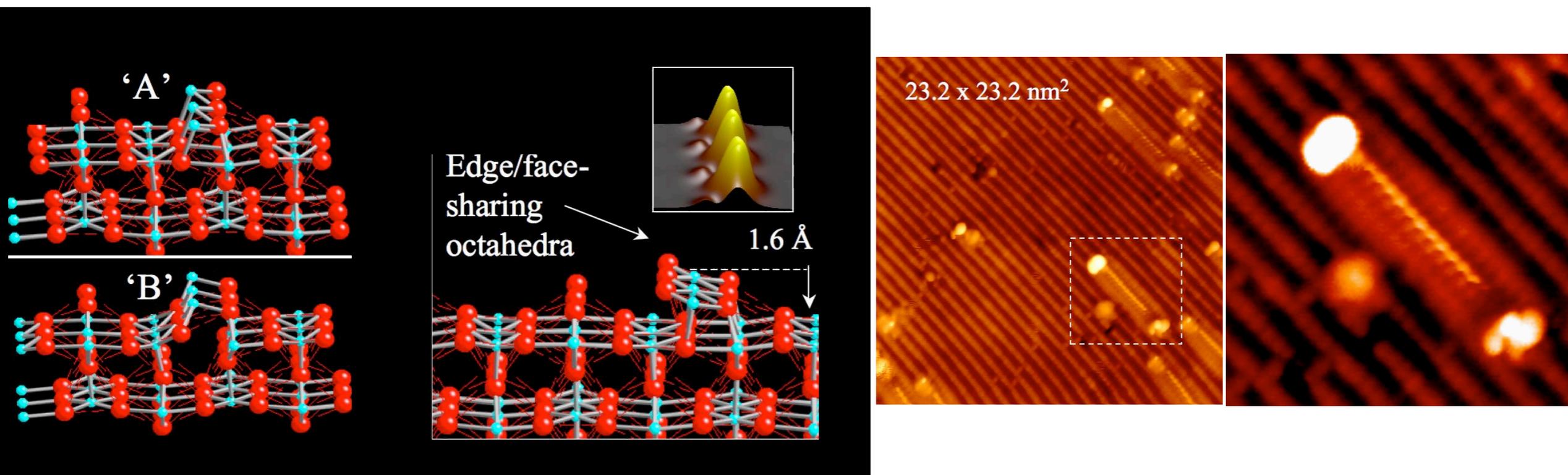
PHYSICAL REVIEW LETTERS **PRL 96, 226105 (2006)**

Surface Reconstructions of $\text{TiO}_2(110)$ Driven by Suboxides

K. T. Park,^{1,2} M. H. Pan,^{3,4} V. Meunier,^{5,3} and E. W. Plummer^{2,4,3}

(Received 9 March 2006)

Scanning tunneling microscopy and density functional theory are used to develop a new structural model for surface reconstructions driven by Ti interstitials on $\text{TiO}_2(110)$. Ti interstitials form the edge- or face-sharing octahedra that serve as building blocks for (1×1) reconstruction. Thus, contrary to conventional wisdom, the 1×1 periodicity is insufficient to establish the correct surface stoichiometry. Furthermore, in our structural and compositional model the reversible oxidation or reduction between (1×1) and (1×2) is entirely achieved by transfer of the added rows.



Park et al., Reoxidation of $\text{TiO}_2(110)$ via Ti interstitials and line defects, *Phys. Rev. B* **75** (2007) 245415

Role of TMS in Nanoscience

- ❑ Interpretation of experiment
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Tunable Spin-Hall Effect

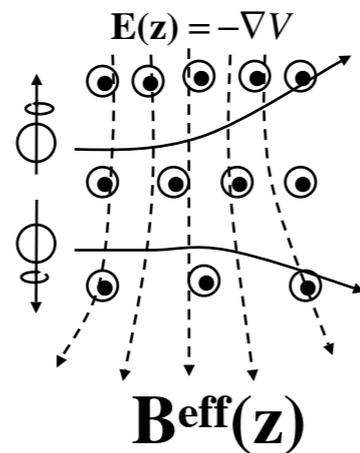
Lu, J., Zhang, X. G. and Pantelides, S., "Tunable spin Hall effect by Stern-Gerlach diffraction," *Phys. Rev. B* **74**, Art. No. 245319 (2006)

Tunable Spin-Hall Effect

Stern-Gerlach

Real-space inhomogeneity

Spin-dependent force

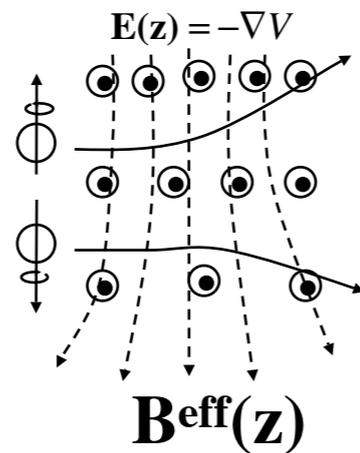


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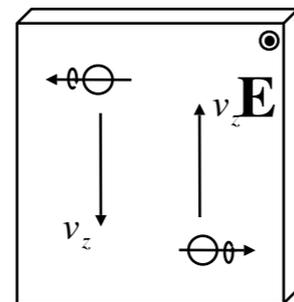
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Intrinsic SHE

Reciprocal-space inhomogeneity

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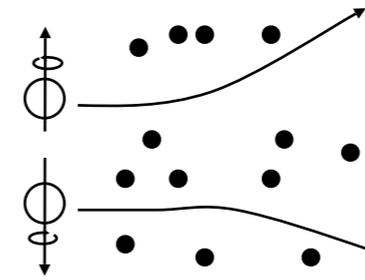
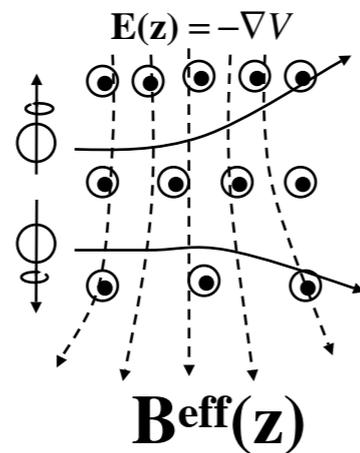


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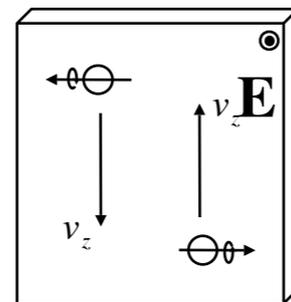
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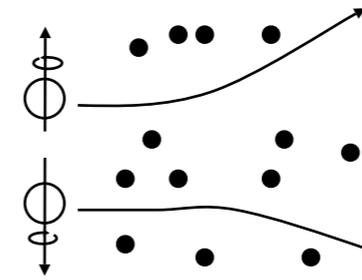
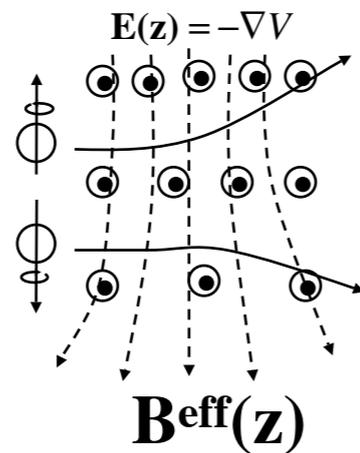
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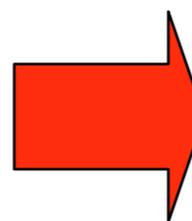
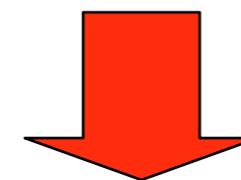
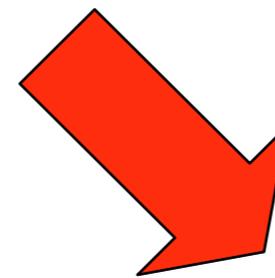
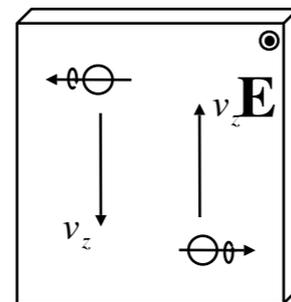
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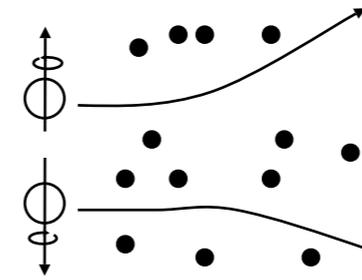
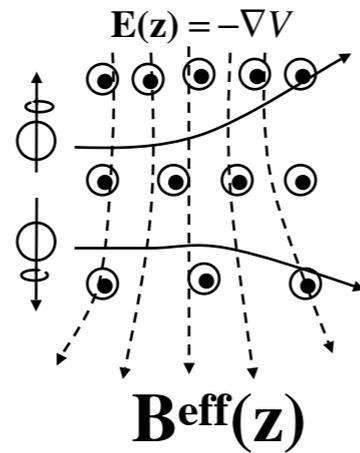
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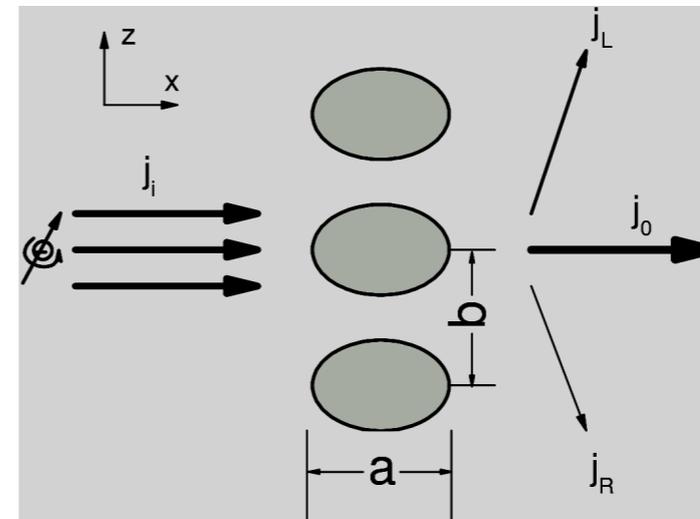
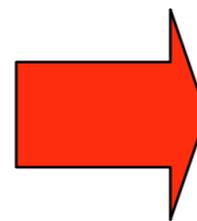
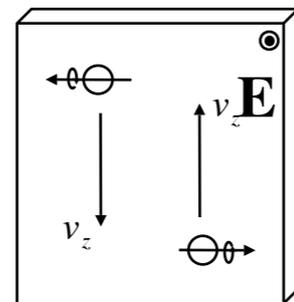
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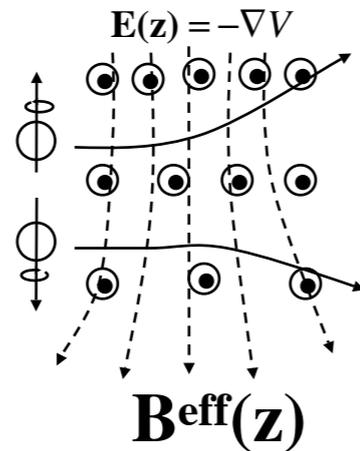
Spin-orbit coupling
+ **diffraction**

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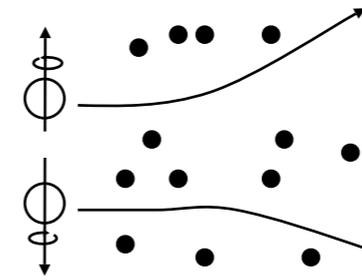
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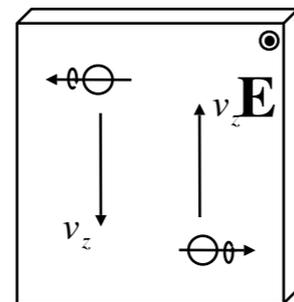
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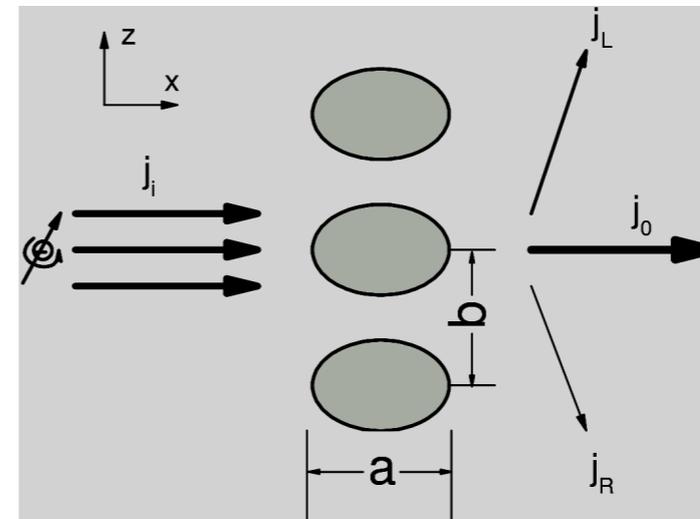
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This new device is being fabricated and tested at CNMS

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Role of TMS in Nanoscience

- ❑ Interpretation of experiment
- ❑ Design of new nanostructured materials and systems based on nanoscale phenomena
- ❑ Fundamental insight into nanoscale phenomena
 - *Crucial to design manufacturing processes for nanostructured materials*
 - *Example - fluctuation theorems*

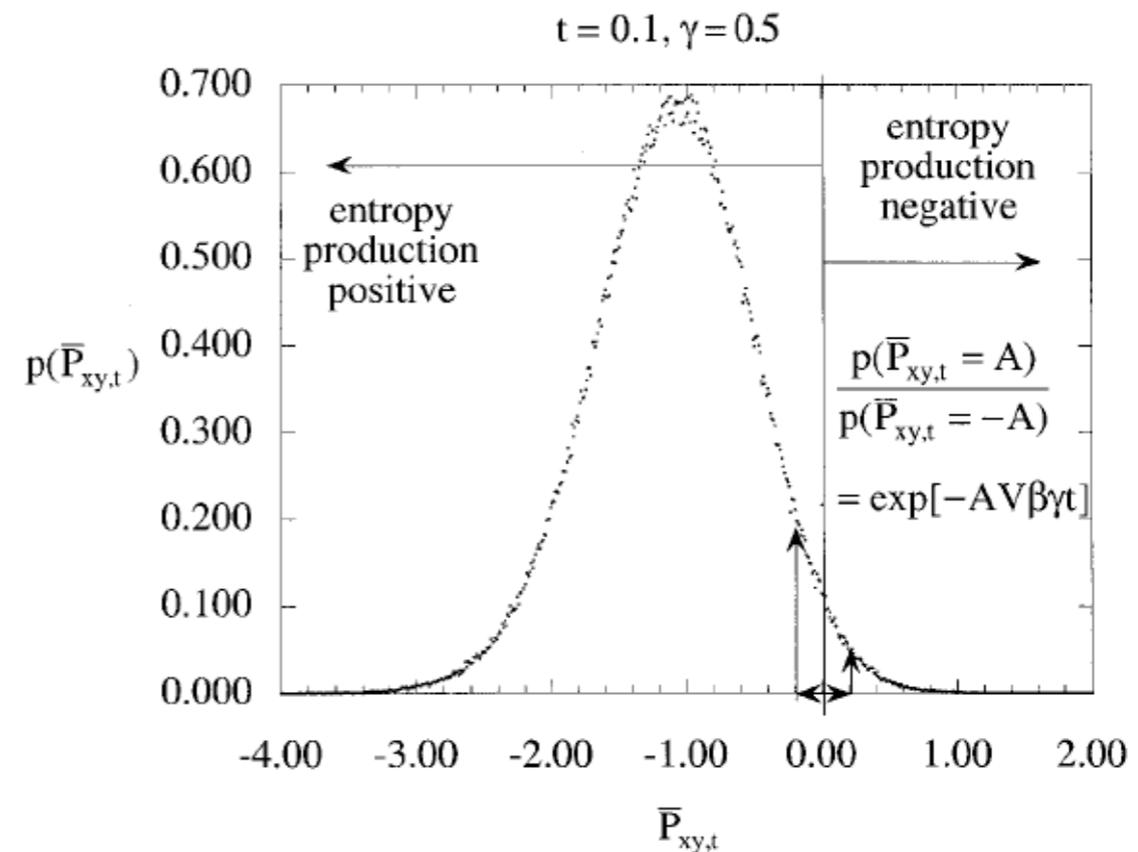
Theoretical Limits to Nanoscale Manipulation

Recent theoretical development

- *Evans's fluctuation theorem*
 - Quantifies the probability that a system will exhibit negative entropy production - NEP ("violate second law")
- *Application to nanomachines*
 - There will be random (but with a defined mathematical frequency and length distribution) periods of NEP
 - E.g., a nanomotor running backwards or manipulation resulting in atom moving in opposite direction of applied force

$$\frac{p(\bar{\Sigma}_t > 0)}{p(\bar{\Sigma}_t < 0)} = \langle \exp(-\bar{\Sigma}_t t) \rangle_{\bar{\Sigma}_t < 0} = \langle \exp(-\bar{\Sigma}_t t) \rangle_{\bar{\Sigma}_t > 0}^{-1}$$

$\bar{\Sigma}_t$ = time - averaged entropy production



ADVANCES IN PHYSICS, 2002, VOL. 51, NO. 7, 1529–1585



The Fluctuation Theorem

DENIS J. EVANS*

Research School of Chemistry, Australian National University, Canberra,
ACT 0200 Australia

and DEBRA J. SEARLES

School of Science, Griffith University, Brisbane, Qld 4111 Australia



Experimental Verification

- *Phys. Rev. Lett.*, **89**, 050601 (2002); **92**, 140601 (2004)
 - *Manipulation of a colloidal particle by optical tweezers*

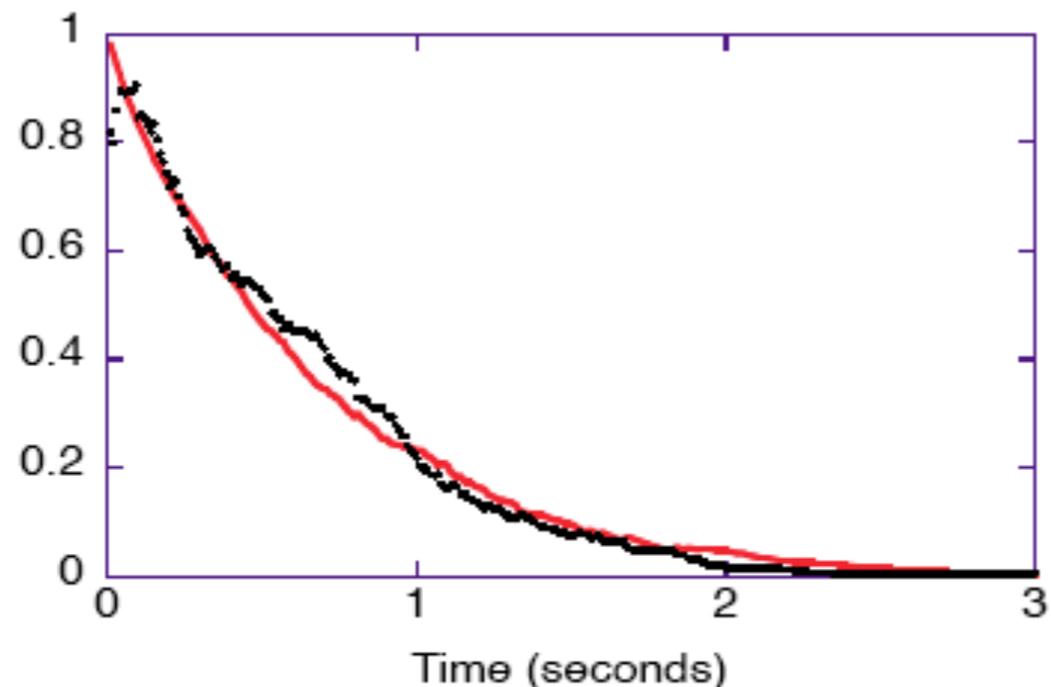


FIG. 2: The number ratio of entropy-consuming ($\Sigma_t < 0$) to entropy-producing ($\Sigma_t > 0$) trajectories (data points) and the entropy production averaged over entropy-producing trajectories, $\langle \exp -\Sigma_t \rangle_{\Sigma_t > 0}$ (grey line) versus duration, t , of 540 experimental trajectory, t . In accord with the IFT, both experimentally determined measures agree over time.

- *Additional verification: response of an electrical circuit to thermal noise*
 - Garnier and Ciliberto, *Phys Rev. E*, **71**, 060101 (2005)

Current and Recent Nanoscience Projects

- ❑ Nanoconfined fluid rheology and structure
 - *Rheology of nanoconfined alkanes and water (NSF)*
- ❑ Classical simulations of carbon nanotubes
 - *Sliding behavior of multiwall nanotubes (NSF/DOE/Mexican CoNaCyT)*
- ❑ Nanoscale complexity in electrical double layer
 - *Molecular simulations and XRSW experiments (3 universities, 3 labs - DOE)*
- ❑ Molecular electronics
 - *Multiscale modeling (6 universities, ORNL - DOE)*
- ❑ Development of high-throughput/low-cost genomic screening device
 - *Classical simulations and ab initio calculations (ORNL - NIH)*
- ❑ Molecular Simulation of metal oxide nanoparticles
 - *Structure and formation (4 universities - NSF NIRT)*
- ❑ Molecular modeling of nanostructured materials based on polyhedral oligomeric silsesquioxane
 - *Ab initio, classical, and mesoscale simulations (3 universities - NSF NIRT)*
- ❑ Computational nanotoxicology - binding of buckyballs to DNA
 - *Classical molecular dynamics simulations (ORNL/VU - DOE)*

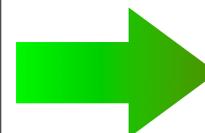
Typical Approach to Nanoscale Systems

- Need to access length ($\sim 1-10$ nm) and time (up to $\sim 100+$ ns)
 - *E.g., to connect to quasi-elastic neutron scattering results for water structure 1-2 nm from metal oxide surface*
 - Requires classical molecular dynamics (CMD)
 - Even on petascale computers, first principles calculations are limited to times of order 10-100 ps
 - *Forcefields for CMD do not exist for nanoscale systems*
 - CMD forcefields fitted to bulk behavior
 - Interfaces crucially important at nanoscale
 - *Different forcefields at surface*
 - Forcefields for nanoscopic systems obtained from *ab initio* calculations
 - *Final properties of interest may require first principles calculations*
 - E.g., electron transport
 - *Recipe: $ab\ initio \rightarrow forcefields \rightarrow CMD \rightarrow structure(s), dynamics$*
 - *Peta/ultrascale can eliminate forcefield/CMD step for some problems*

Outline of Talk

□ Introduction

- *Theory, Modeling and Simulation in Nanoscience*
- *ORNL Center for Nanophase Materials Science and Nanomaterials Theory Institute*



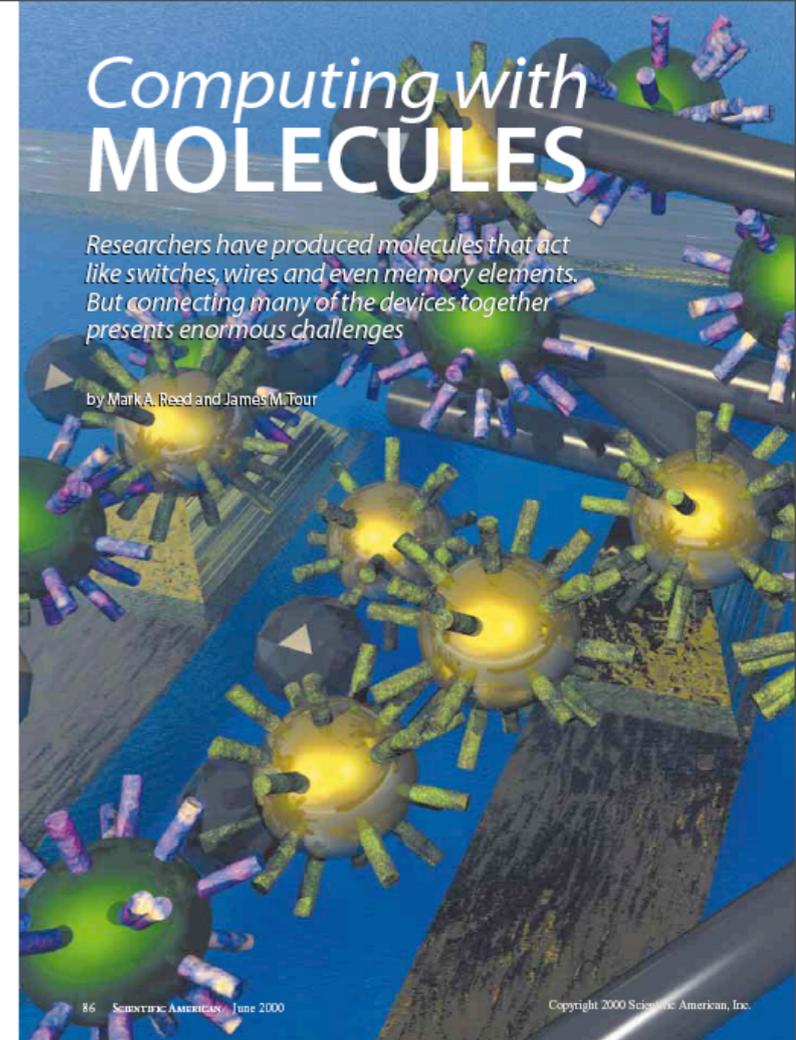
□ Molecular electronics

- *Electron transport in self-assembled nano-bridges*

□ Conclusions

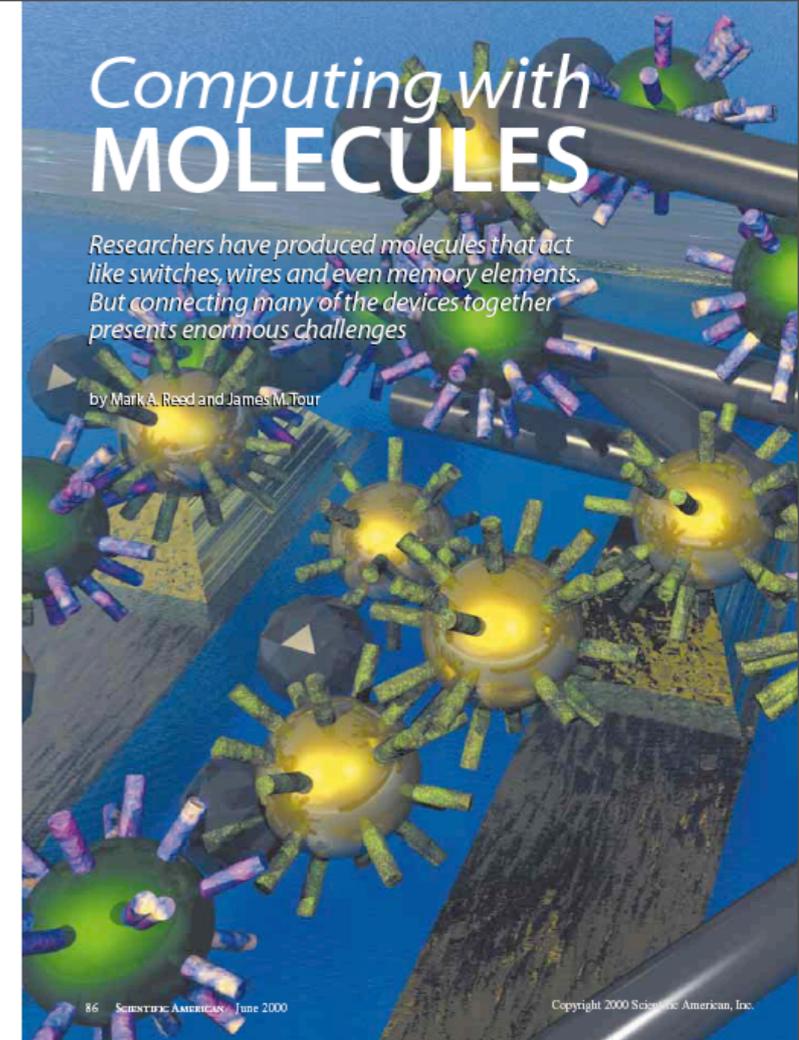
Molecular Electronics

Molecular Electronics



Molecular Electronics

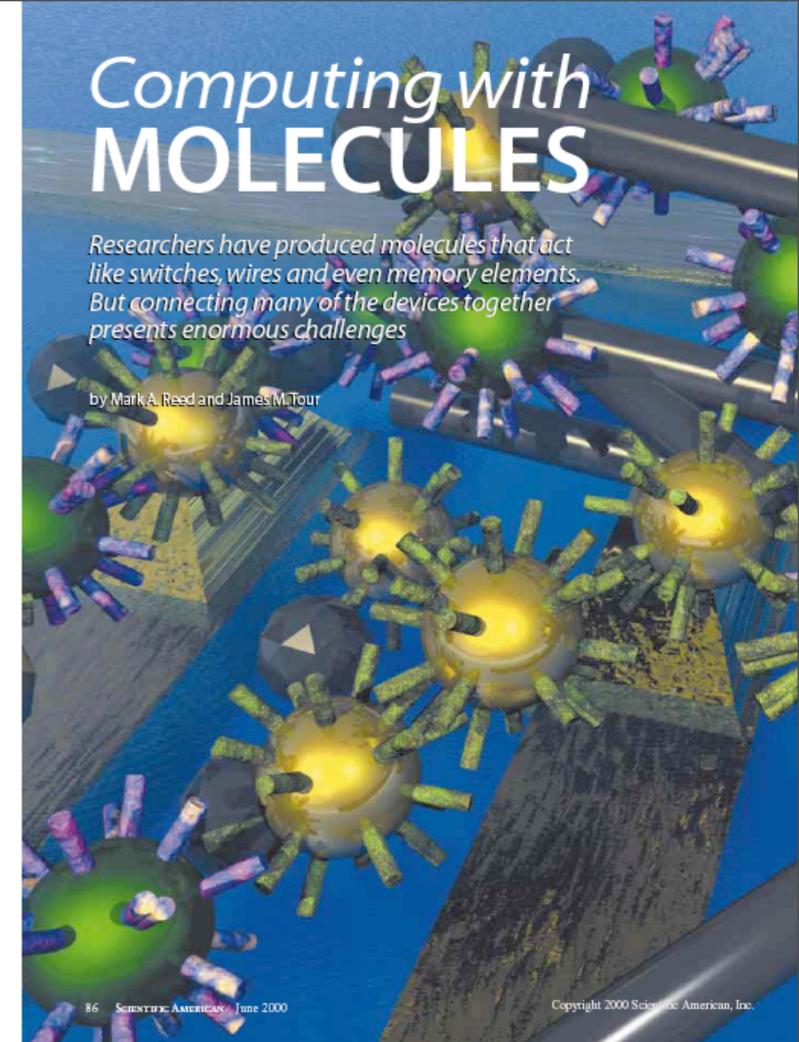
□ Motivation



Molecular Electronics

□ Motivation

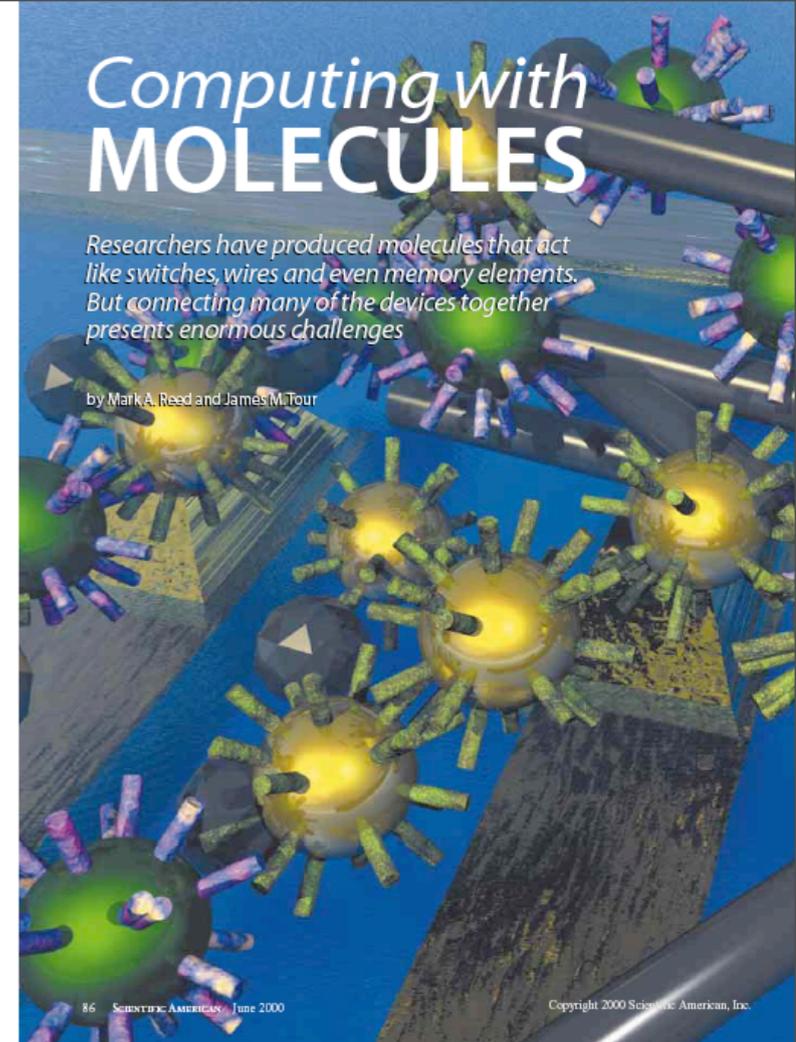
- *Lithographic fabrication of solid-state silicon-based electronic devices that obey Moore's law is reaching fundamental and physical limitations and becoming extremely expensive*



Molecular Electronics

□ Motivation

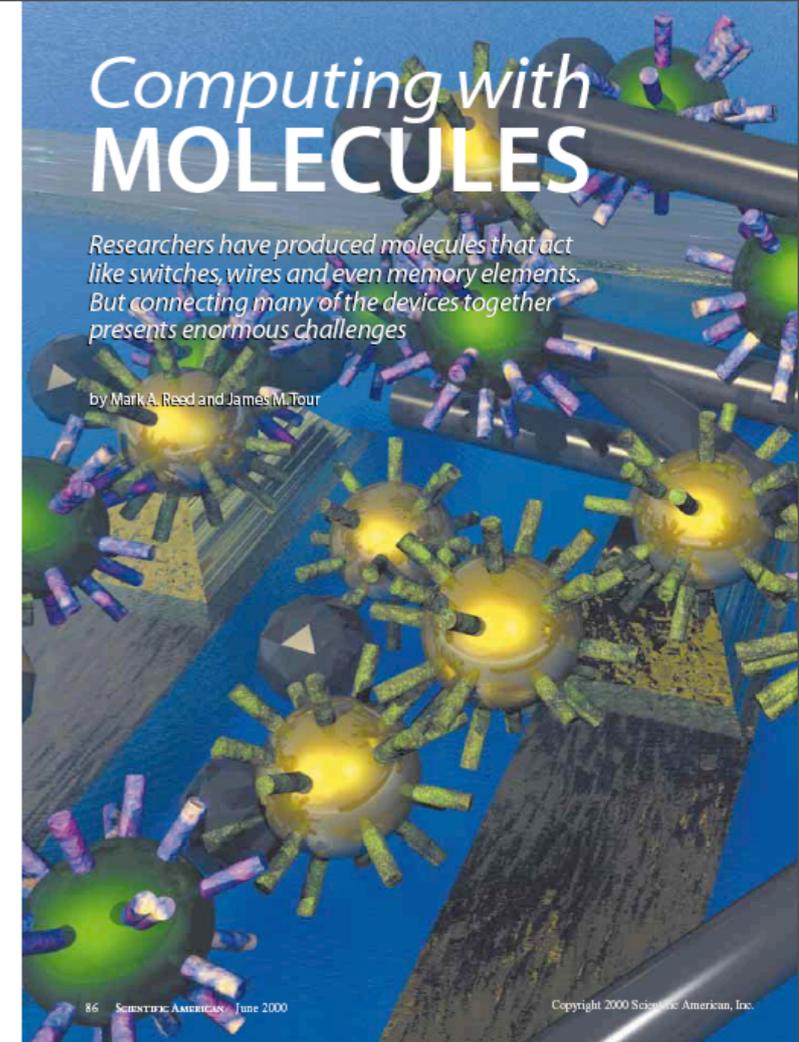
- *Lithographic fabrication of solid-state silicon-based electronic devices that obey Moore's law is reaching fundamental and physical limitations and becoming extremely expensive*
- *Self-assembled molecular-based electronic systems composed of many single-molecule devices may provide a way to construct future computers with ultra dense, ultra fast molecular-sized components*



Molecular Electronics

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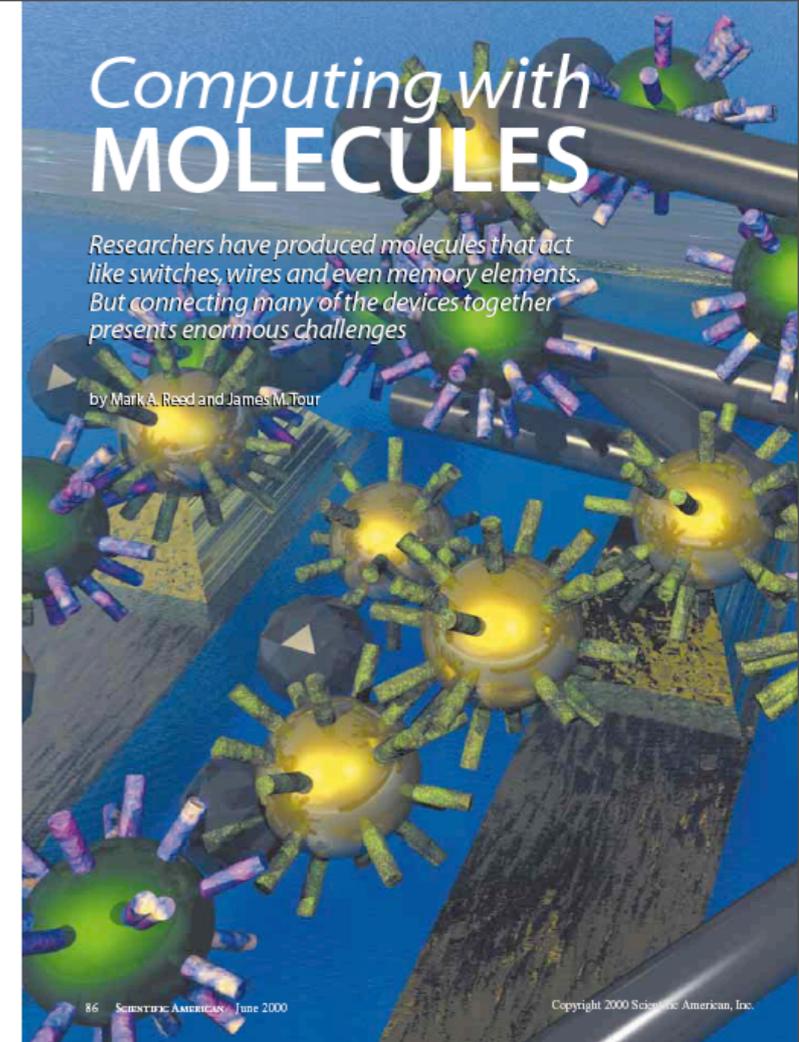
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- *Possibility of fabricating single-molecule devices proposed theoretically by Ratner*



Molecular Electronics

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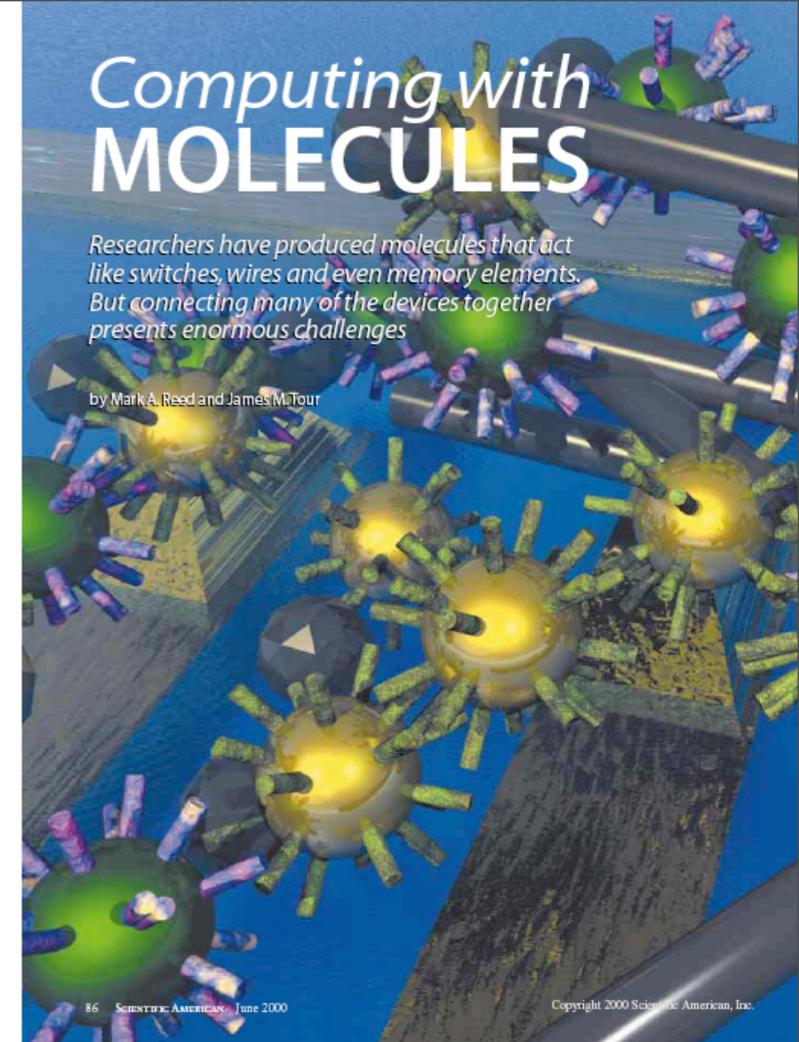
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 - Aviram and Ratner, "Molecular rectifiers," *Chem. Phys. Letts.*, **29** (1974) 283



Molecular Electronics

□ Motivation

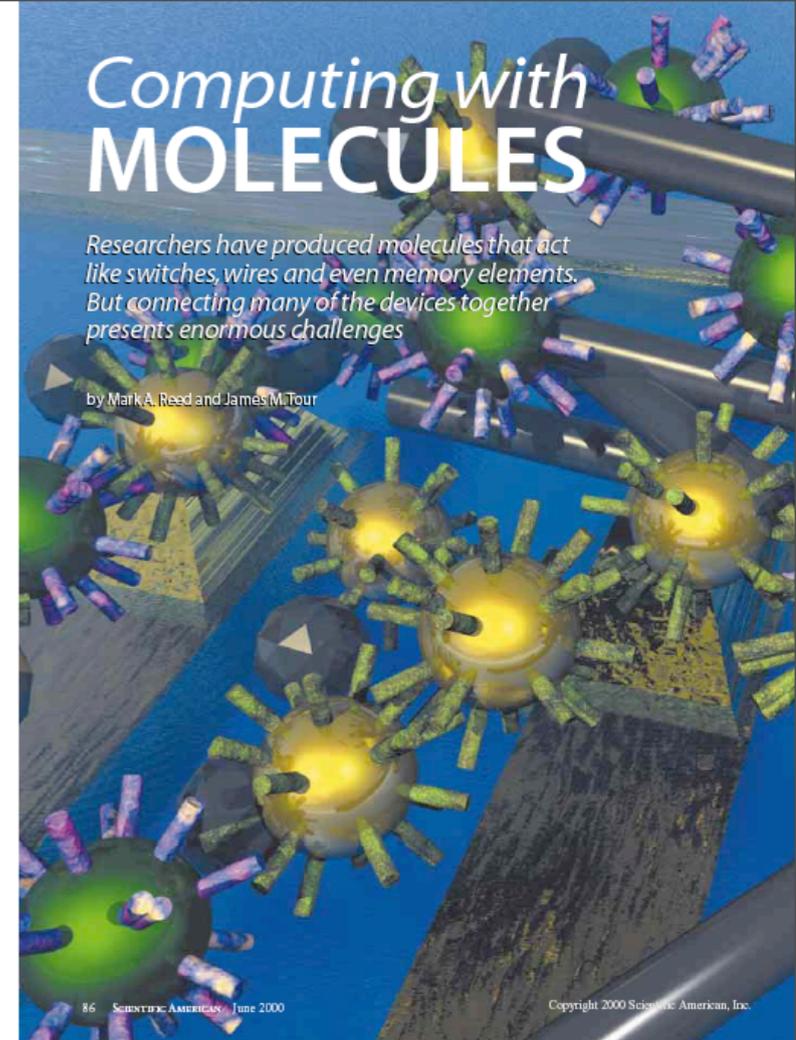
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 - Aviram and Ratner, "Molecular rectifiers," *Chem. Phys. Letts.*, **29** (1974) 283
- *Landmark experiment*



Molecular Electronics

□ Motivation

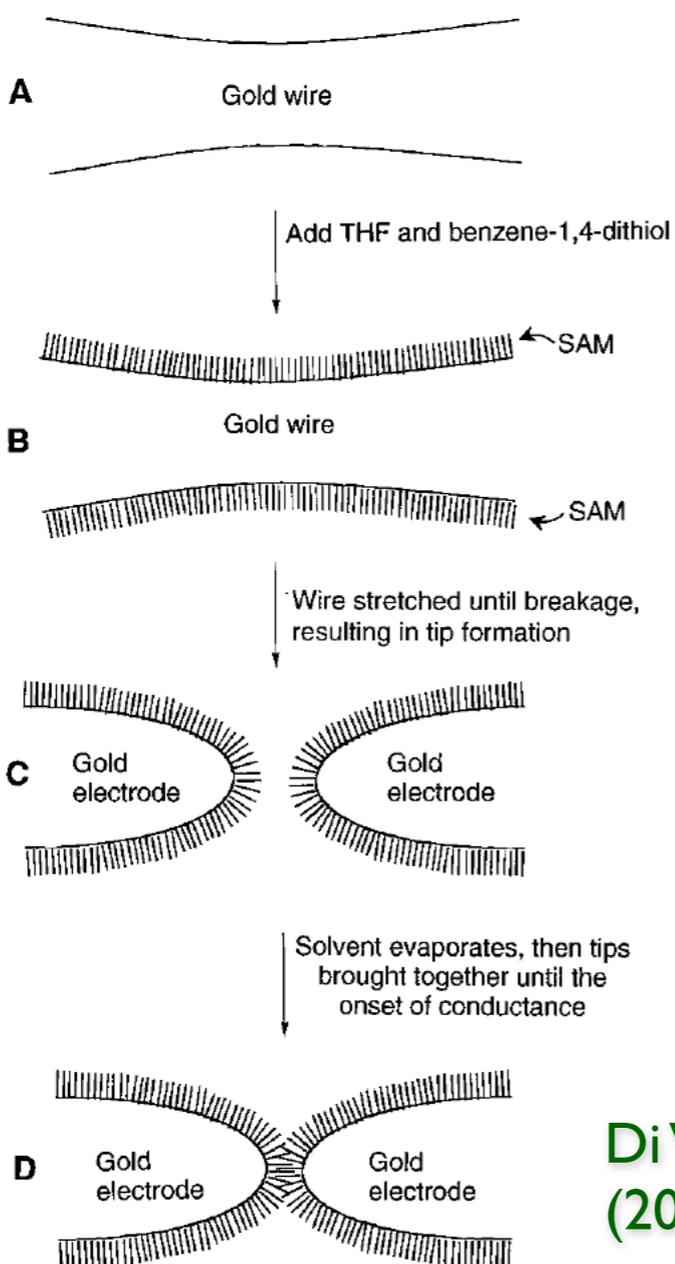
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- *Possibility of fabricating single-molecule devices proposed theoretically by Ratner*
 - Aviram and Ratner, "Molecular rectifiers," *Chem. Phys. Letts.*, **29** (1974) 283
- *Landmark experiment*
 - Experimental measurement of conductance of 1,4-benzenedithiol between Au contacts: Reed et al., "Conductance of a Molecular Junction," *Science*, **278** (1997) 252-254



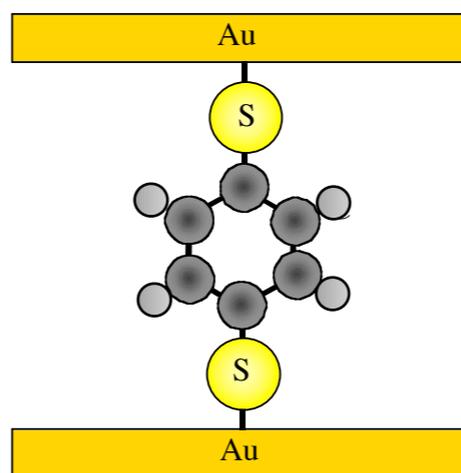
Molecular Electronics

□ Experiment vs. theory

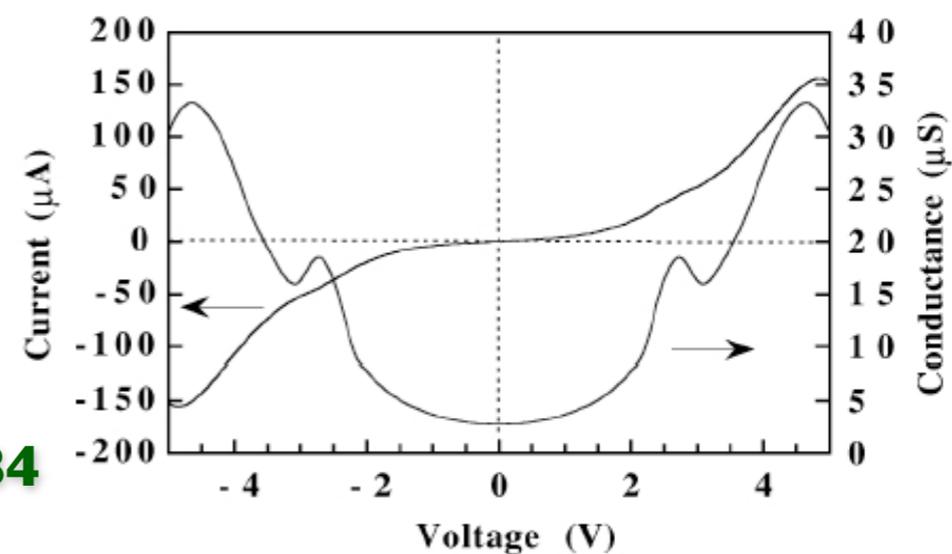
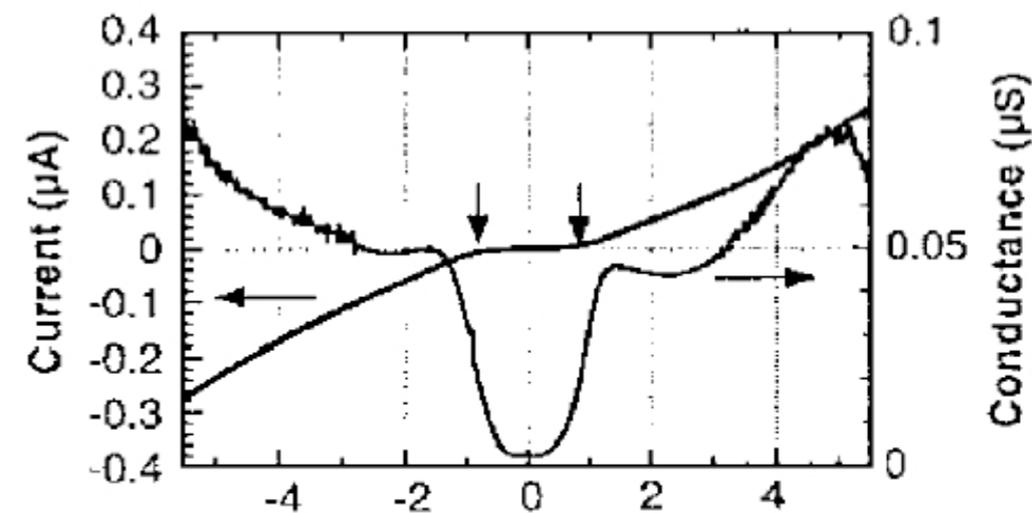
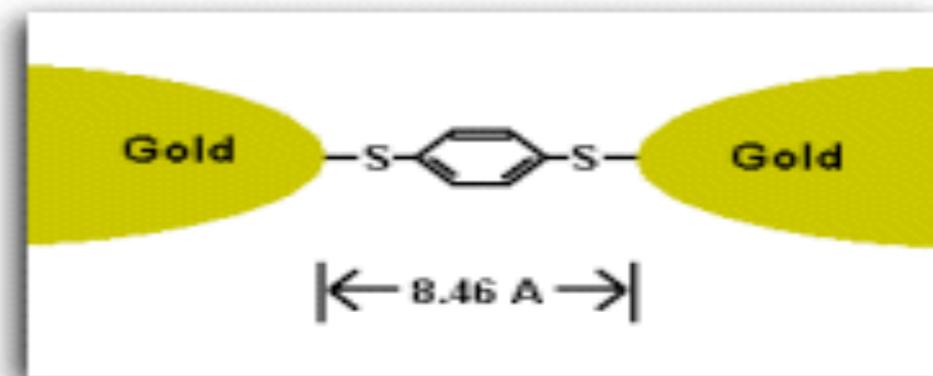
- 3 orders of magnitude difference



Reed et al., *Science*, **278**
(1997) 252-254



Di Ventra, et al., *Phys. Rev. Letts.*, **84**
(2000) 979-982



Molecular Electronics

□ Closing the gap

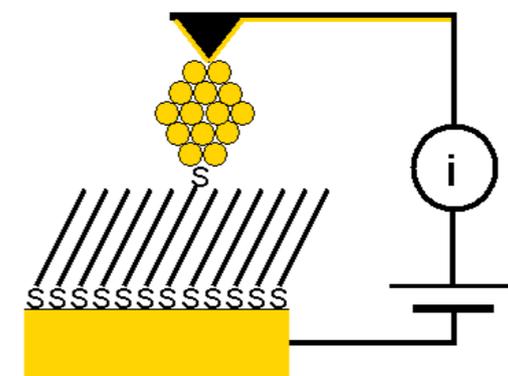
- *Cui et al. experiment*
 - Ensures bonded contact at each end of octanethiol molecule
 - Conductance measured in integer increments corresponding to 1-5 contacts
 - *Single-molecule conductance inferred*
 - *Reduces difference between theory and experiment to less than one order of magnitude*

Reproducible Measurement of Single-Molecule Conductivity

X. D. Cui,¹ A. Primak,^{2,3} X. Zarate,² J. Tomfohr,¹ O. F. Sankey,¹ A. L. Moore,² T. A. Moore,² D. Gust,² G. Harris,³ S. M. Lindsay¹

A reliable method has been developed for making through-bond electrical contacts to molecules. Current-voltage curves are quantized as integer multiples of one fundamental curve, an observation used to identify single-molecule contacts. The resistance of a single octanedithiol molecule was 900 ± 50 megohms, based on measurements on more than 1000 single molecules. In contrast, nonbonded contacts to octanethiol monolayers were at least four orders of magnitude more resistive, less reproducible, and had a different voltage dependence, demonstrating that the measurement of intrinsic molecular properties requires chemically bonded contacts.

Cui, *et al.*, *Science*, **294** (2001) 571-574



PERSPECTIVES: MOLECULAR ELECTRONICS

It's All About Contacts

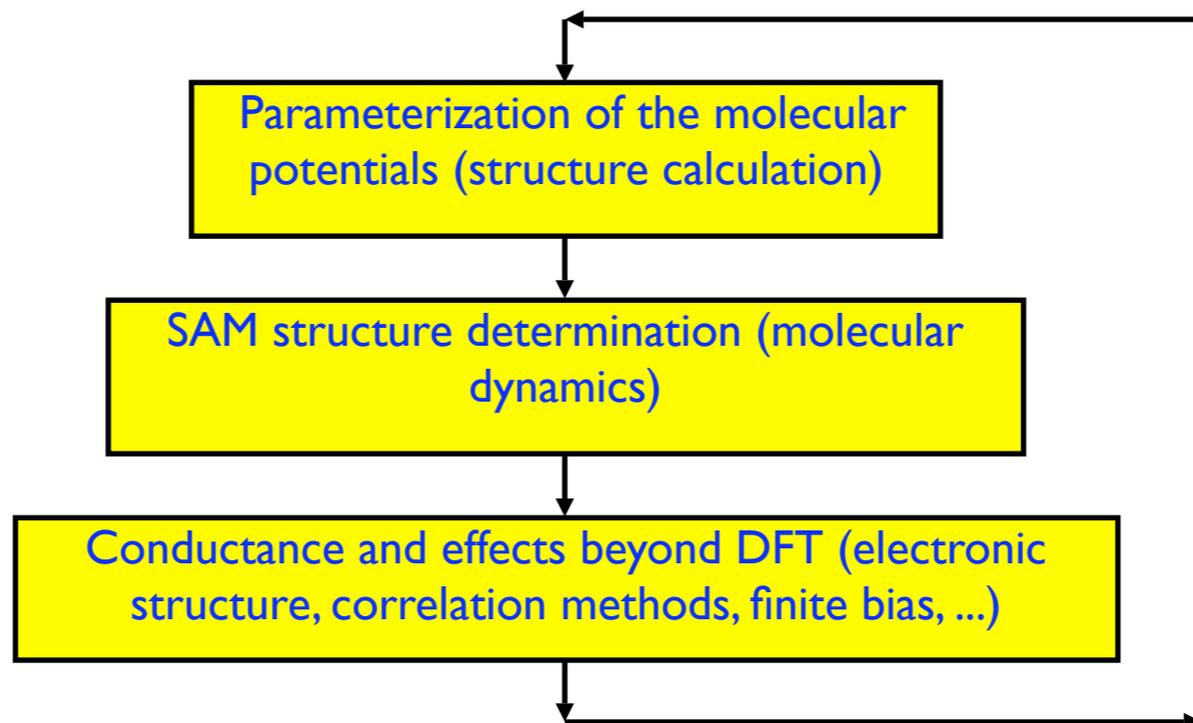
K. W. Hipps

Kipps, *Science*, **294** (2001) 536-537

Molecular Electronics

□ Multi-level approach

- *Ab initio* calculations to characterize gold-BDT interaction
- Structure of self-assembled monolayer (SAM) of BDT on Au(111) surface
- *Ab initio* calculation of conductance using structure within SAM



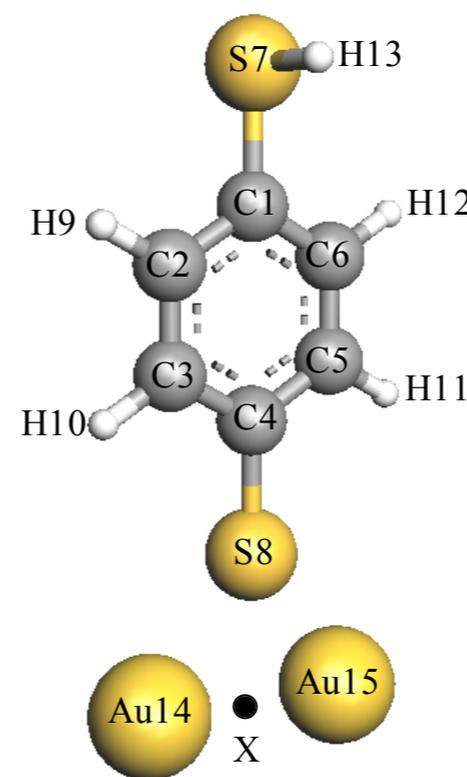
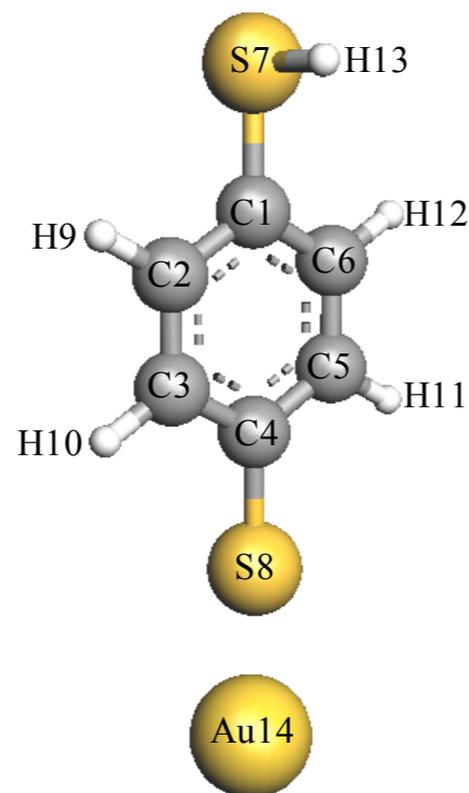
□ DoE computational nanoscience project

- *Six universities and Oak Ridge National Laboratory*
 - Vanderbilt, NCSU, Colorado, Princeton, Tennessee, Michigan

Forcefield Development

□ Goal in forcefield development

- Use DFT to develop classical potentials representing local bonding behavior of benzenedithiolate (BDT) molecule on Au (111) surface
 - Experimental and ab initio calculations show that bonding takes place at bridge or top sites, not in fcc hollows



Forcefield Development

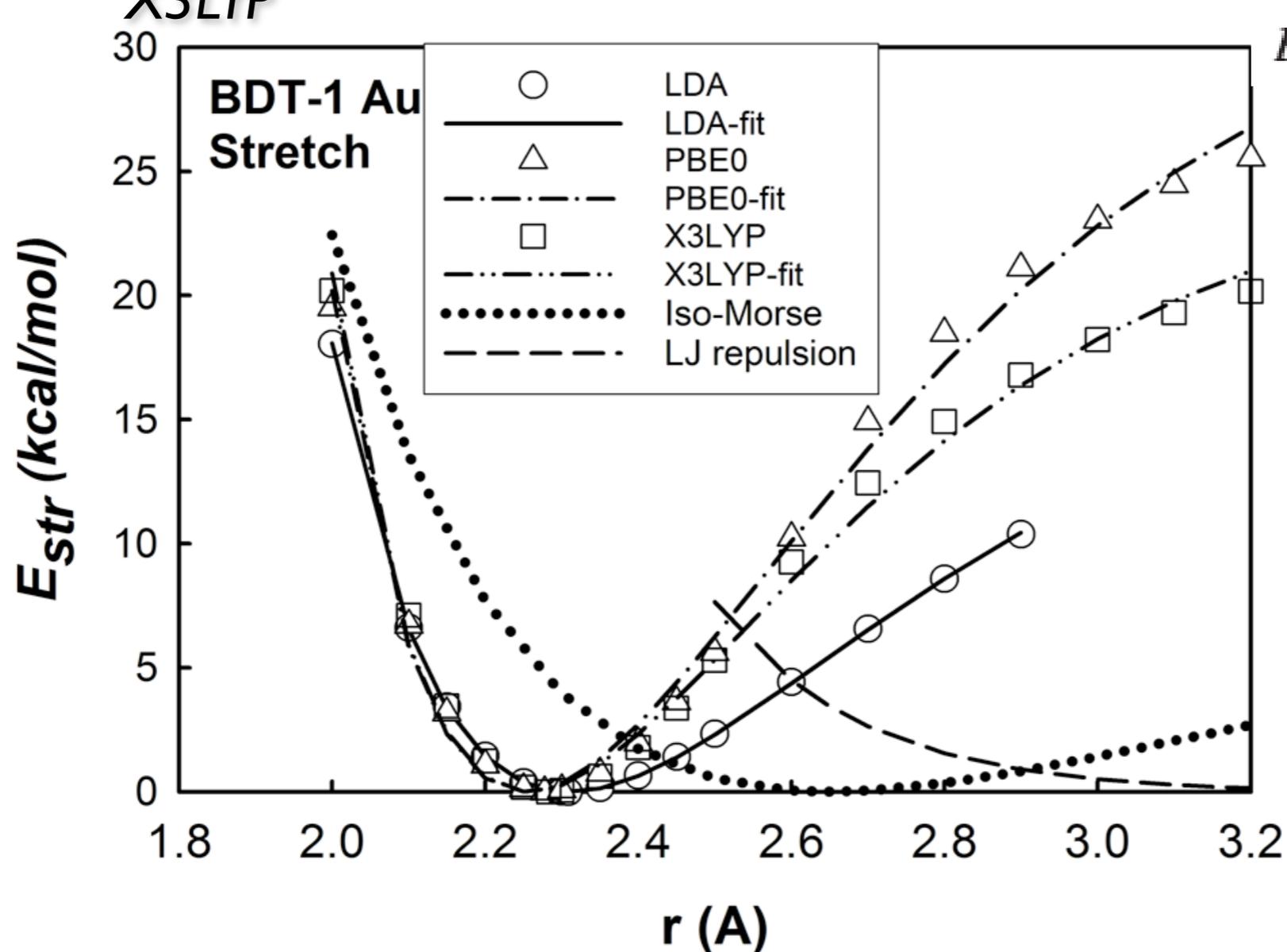
- All DFT calculations performed using NWCHEM package
 - Gaussian valence triple zeta basis set 6-311G used for S, C, and H in BDT molecule
 - Effective core potential CRENL-ECP and associated basis set used for Au
- Three DFT functionals used
 - Standard local-density approximation (LDA) with Slater exchange and Vosko–Wilk–Nusair VWN-V correlation
 - PBE0 (often used for transition metals) hybrid
 - X3LYP (often used for hydrocarbons)
 - Compare predictions from all functionals as test for consistency

Krstić *et al.*, “Computational Chemistry for Molecular Electronics,” *Comp. Mat. Res.* **28** (2003) 321-341; Leng *et al.*, “Structure and dynamics of benzenedithiol monolayer on Au (111) surface,” *J. Phys. Chem. B*, **107** (2003) 11940-11950; Leng *et al.*, “Interaction between benzenedithiolate and gold: Classical force field for chemical bonding,” *J. Chem. Phys.* **122** (2005) Art. No. 244721

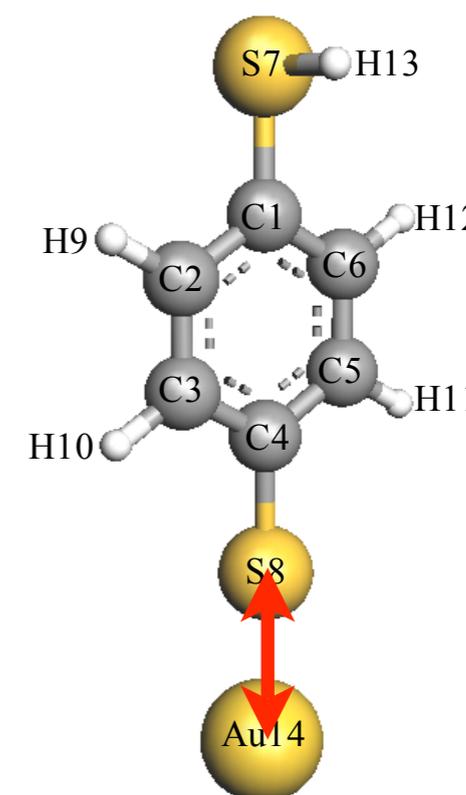
Forcefield Development

□ S-Au bond stretch - BDT on top site

- *LDA shows a slower increase in bonding energy compared with PBE0 and X3LYP*



$$E_{\text{str}} = E_0 e^{-\alpha(r-r_0)} [e^{-\alpha(r-r_0)} - 2] + E_0$$

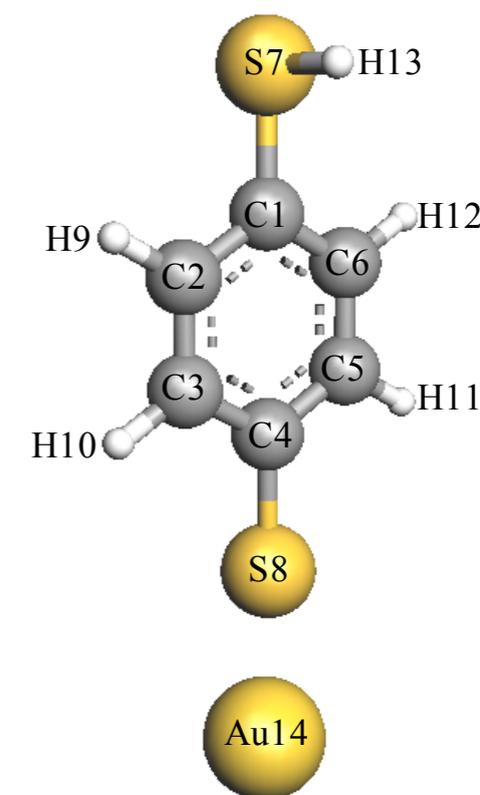
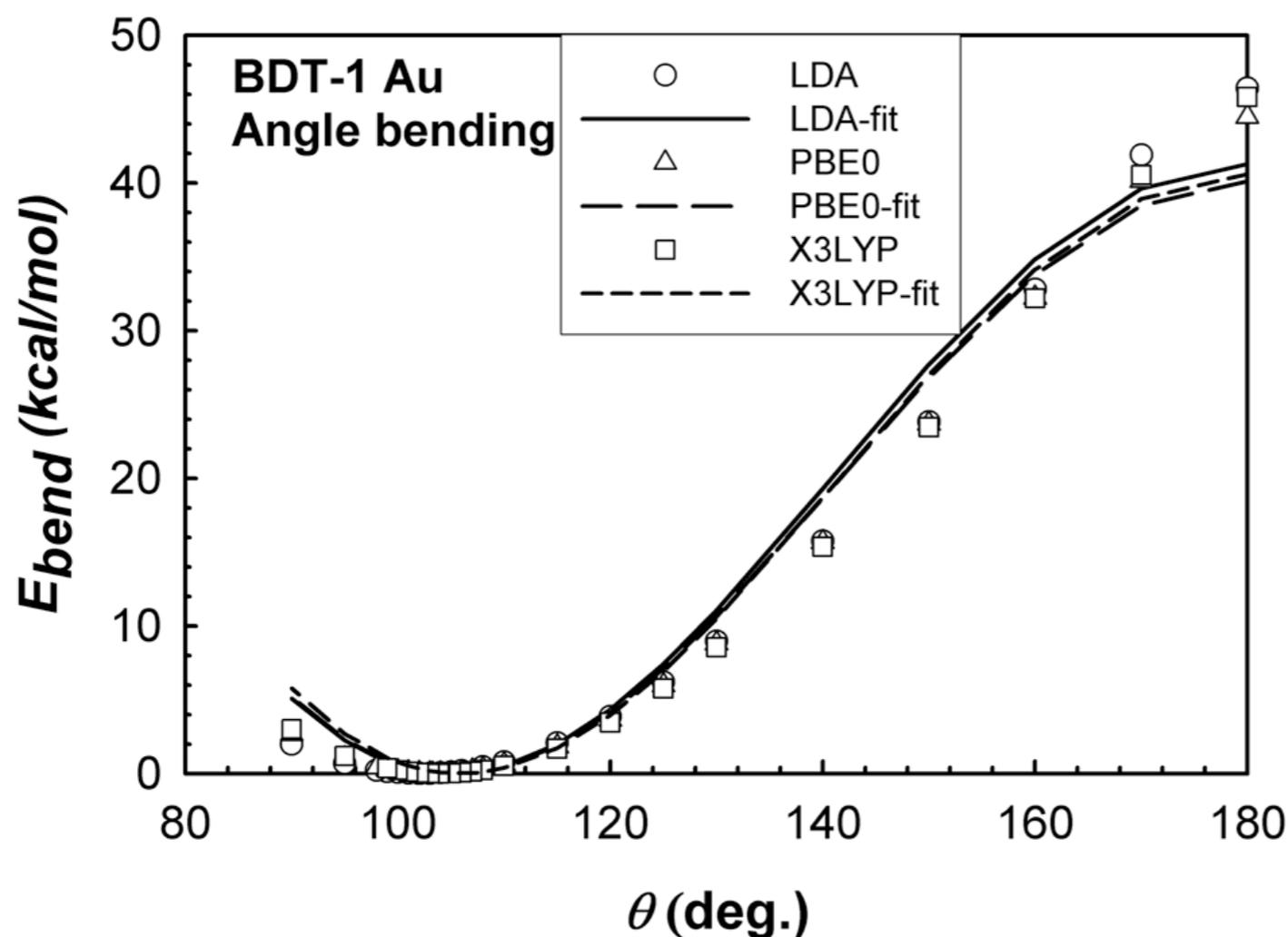
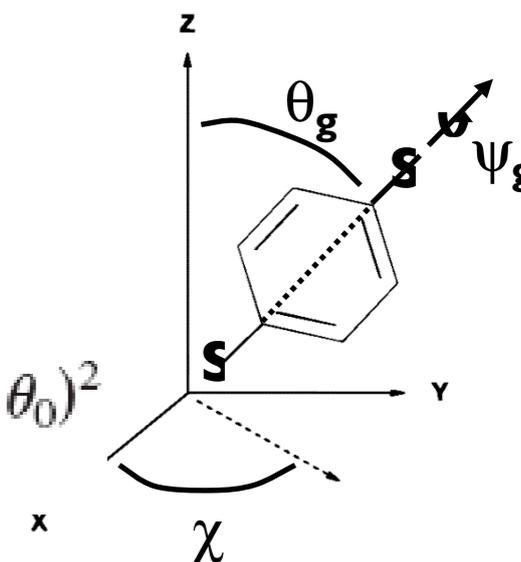


Leng, Krstic, Wells, Cummings, Dean, "Interaction between benzenedithiolate and gold: Classical force field for chemical bonding," *J. Chem. Phys.*, **122** (2005) Art. No. 244721

Forcefield Development

□ Au-S-C bond-angle bending - BDT on top site

$$E_{\text{bend}} = \frac{k_{\theta}}{2 \sin^2 \theta_0} (\cos \theta - \cos \theta_0)^2$$



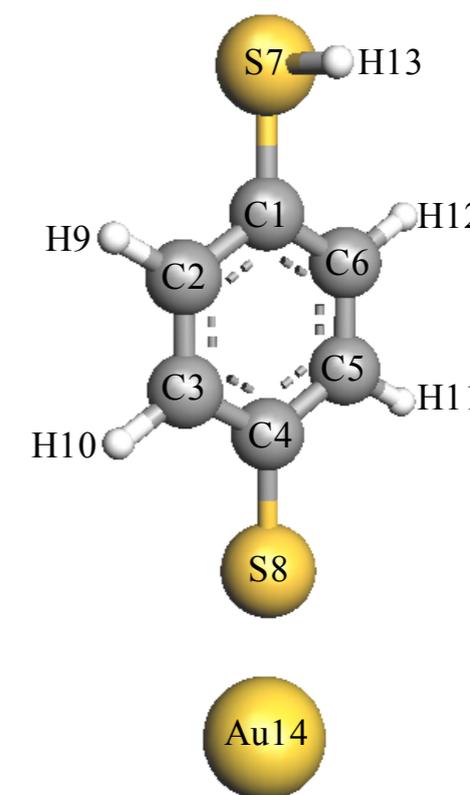
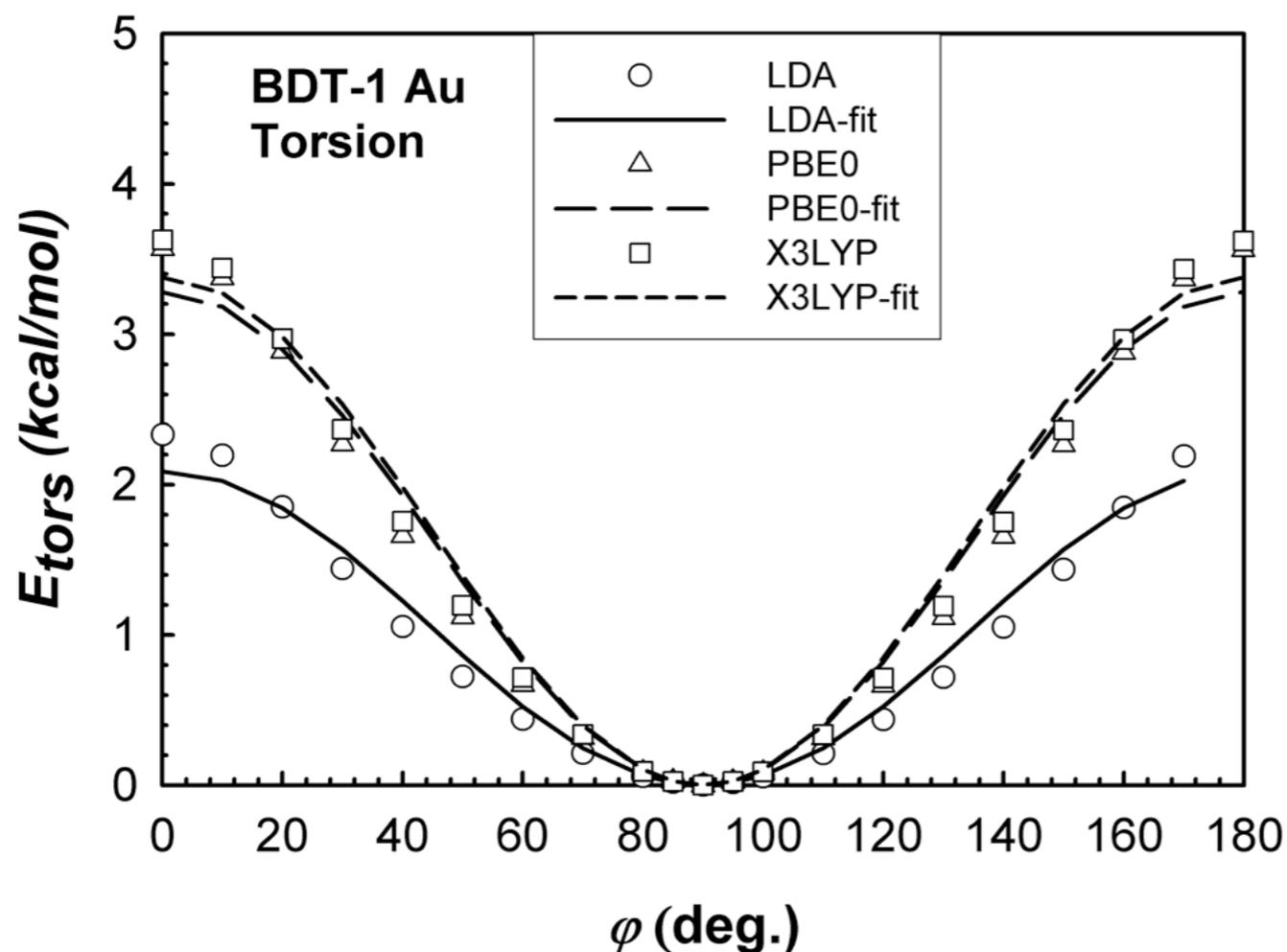
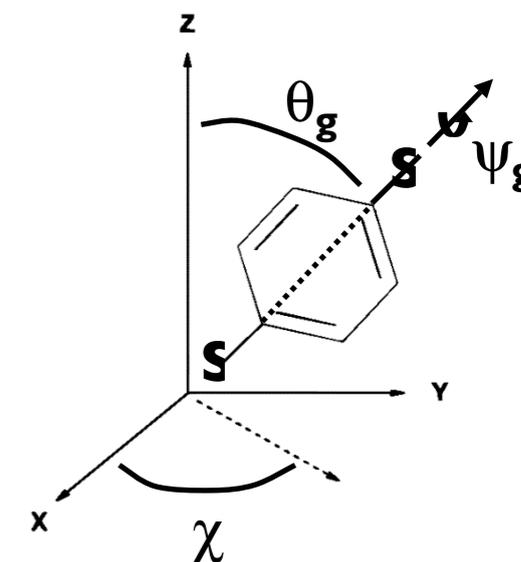
Leng, Krstic, Wells, Cummings, Dean, "Interaction between benzenedithiolate and gold: Classical force field for chemical bonding," *J. Chem. Phys.*, **122** (2005) Art. No. 244721

Forcefield Development

□ Torsion bending - BDT on top site

- *Au-S at equilibrium distance, Au-S-C at equilibrium angle*
- *Rotate around S-S axis*

$$E_{\text{tors}} = 1/2E_{\varphi}(1 - \cos 2\varphi_0 \cos 2\varphi)$$



Leng, Krstic, Wells, Cummings, Dean, "Interaction between benzenedithiolate and gold: Classical force field for chemical bonding," *J. Chem. Phys.*, **122** (2005) Art. No. 244721

Forcefield Development

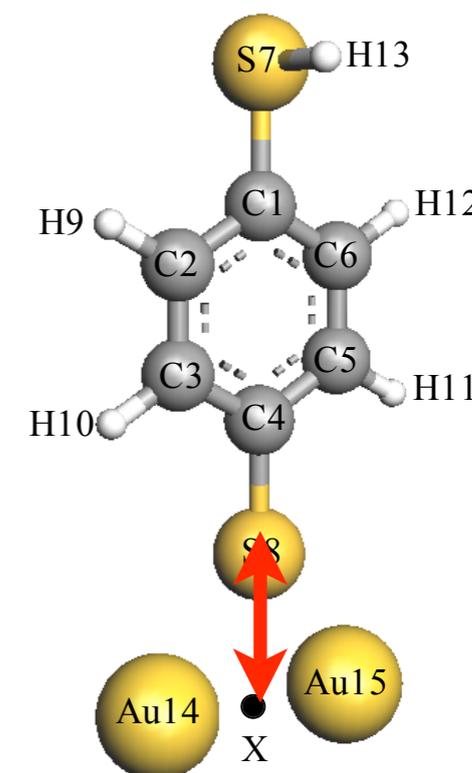
□ Similar calculations for bridge site

- *Site at center of Au-Au pair*
 - Distinction in direction for bond bending

□ Partial charges

- *Dependent on DFT*
- *Averaged over configurations*
- *Table: BDT-Au₁ / BDT-Au₂*

Atoms	LDA	PBE0	X3LYP
C3 (C5)	-0.08/-0.11	-0.08/-0.10	-0.08/-0.10
C4	-0.43/-0.35	-0.40/-0.32	-0.39/-0.32
S8	0.10/0.20	0.04/0.10	0.05/0.11
Au	0.04/(-0.04) × 2	0.15/0.02 × 2	0.12/0.01 × 2

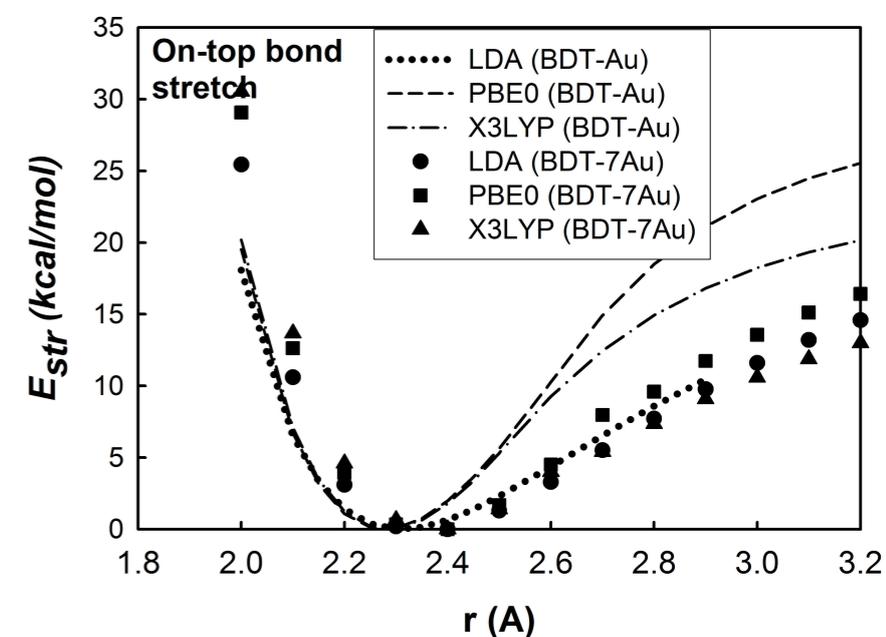
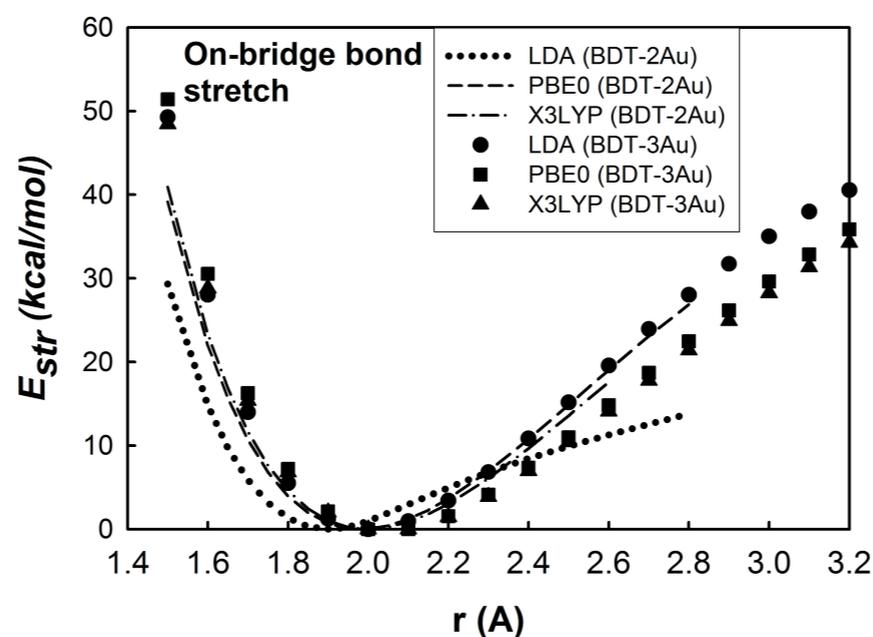
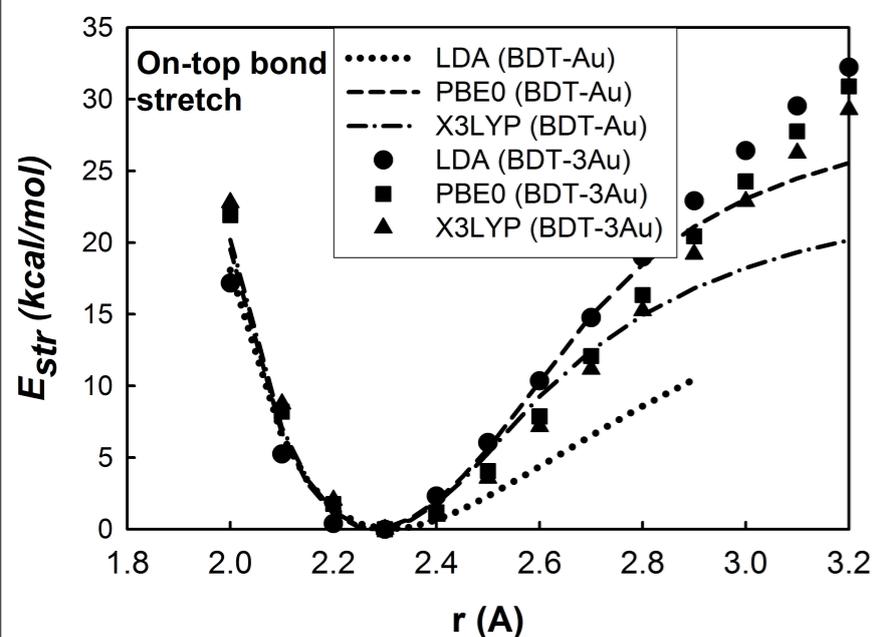
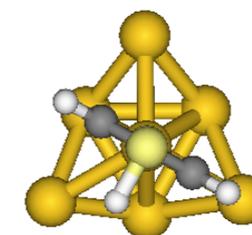
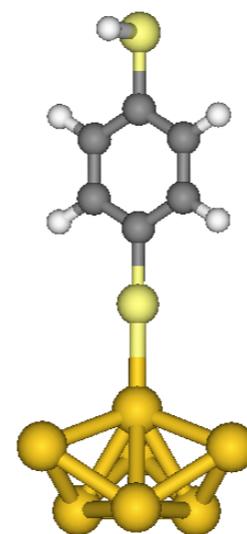
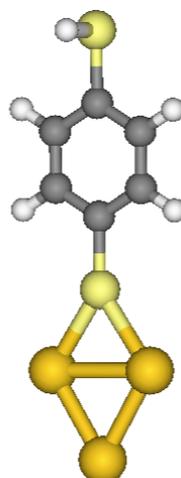
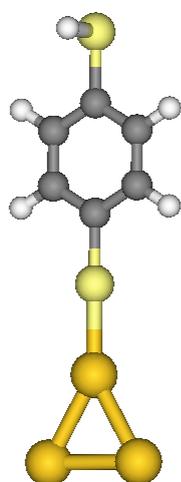


Leng, Krstic, Wells, Cummings, Dean, "Interaction between benzenedithiolate and gold: Classical force field for chemical bonding," *J. Chem. Phys.*, **122** (2005) Art. No. 244721

Forcefield Development

□ Similar calculations for other BDT-Au_n clusters

- *More consistent results for bond stretching from different DFT functionals*



Leng, Y. S., Dyer, P. J., Krstic, P. S., Harrison, R. J. and Cummings, P. T., "Calibration of chemical bonding between benzenedithiolate and gold: the effects of geometry and size of gold clusters," *Molecular Physics*, **105** (2007) 293-300

Molecular Simulation

□ Molecular dynamics simulations of fully-occupied surfaces

- *Double RESPA algorithm (in-house code) [Tuckerman et al., J. Chem. Phys. **97** (1990) 1992]*
- *Long-range electrostatic interactions computed by three-dimensional 3D Ewald summation with correction term (EW3DC) for 2D rhombic slab geometry [Yeh and Berkowitz, J. Chem. Phys. **111** (1999) 3155]*
- *UFF forcefield for BDT-BDT interactions*

*Krstić, Dean, Zhang, Keffer, Leng, Cummings and Wells, Computational Materials Science, **28** (2003) 321-341; Leng, Keffer and Cummings, J. Phys. Chem. B, **107** (2003) 11940-11950; Leng, Krstic, Wells, Cummings, Dean, J. Chem. Phys., **122** (2005) Art. No. 244721*

□ Grand Canonical Monte Carlo (GCMC) simulations of mono-layer formation

*Zhao, Leng and Cummings, Langmuir, **22** (2006) 4116-4124*

□ Molecular dynamics simulations of stretching Au nanowires

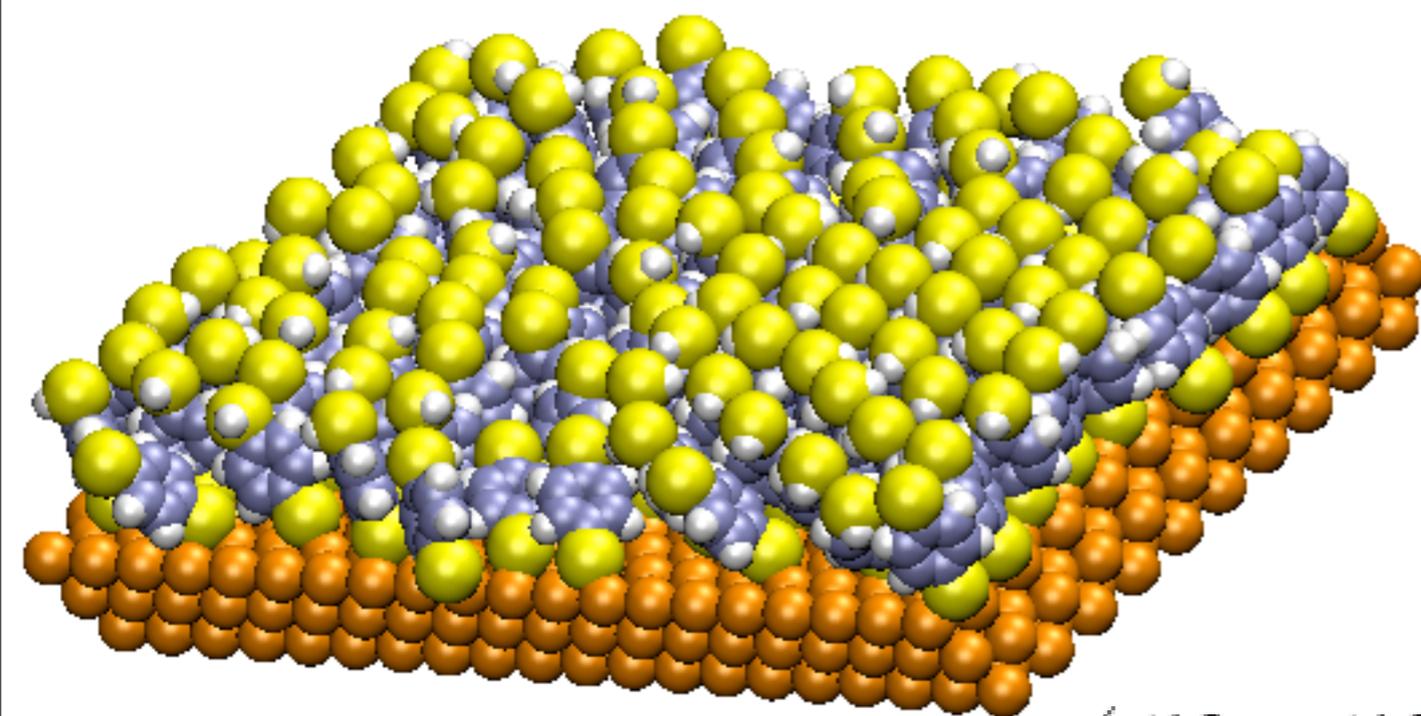
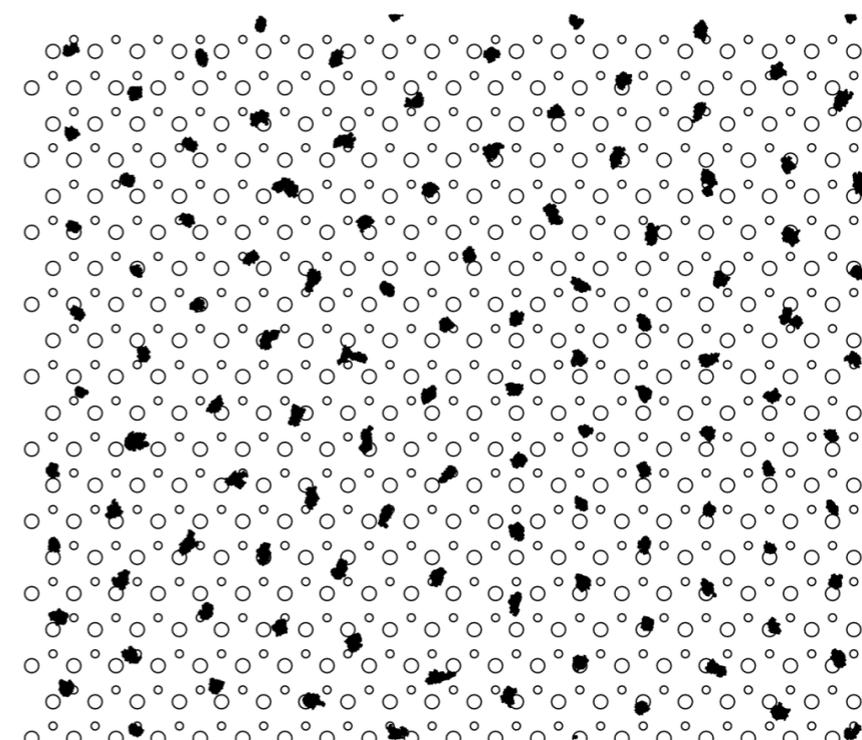
- *In vacuum Pu, Leng, Tsetseris, Park, Pantelides and Cummings, J. Chem. Phys. **126** (2007) 144707*
- *In inert solvent Pu, Leng, Zhao, Cummings, Nanotechnology **18** (2007) 424007*

□ Combined molecular dynamics/Monte Carlo simulations of BDT chemisorption onto stretching Au nanowire

Molecular Simulation

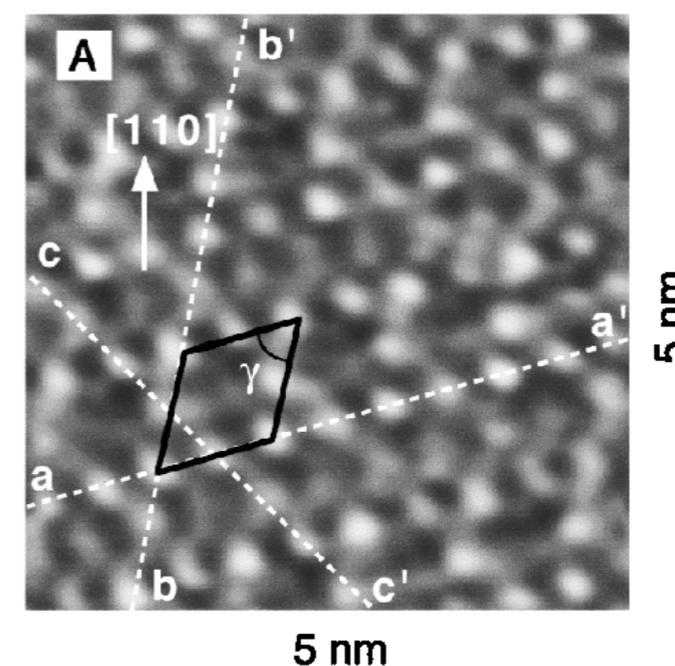
□ GCMC high-coverage state

- Structure predicted same as experimental



$(\sqrt{13} \times \sqrt{13}) R13.9^\circ$

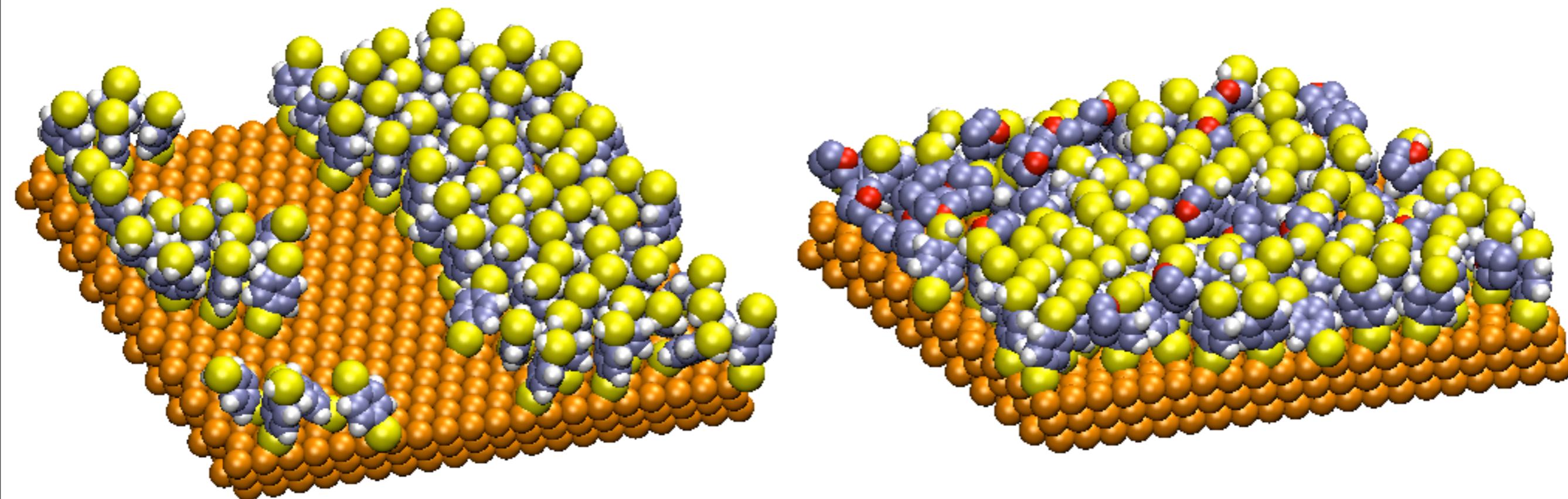
High-resolution STM image of ordered structure of benzenethiol SAM. From Wan *et al.*, *J. Phys. Chem. B* **104** (2000) 3563-3569



X. Zhao, Y.-S. Leng, P.T. Cummings, *Langmuir*, **22** (2006) 4116-4124

Molecular Simulation

- GCMC - mid-coverage and mixture simulations



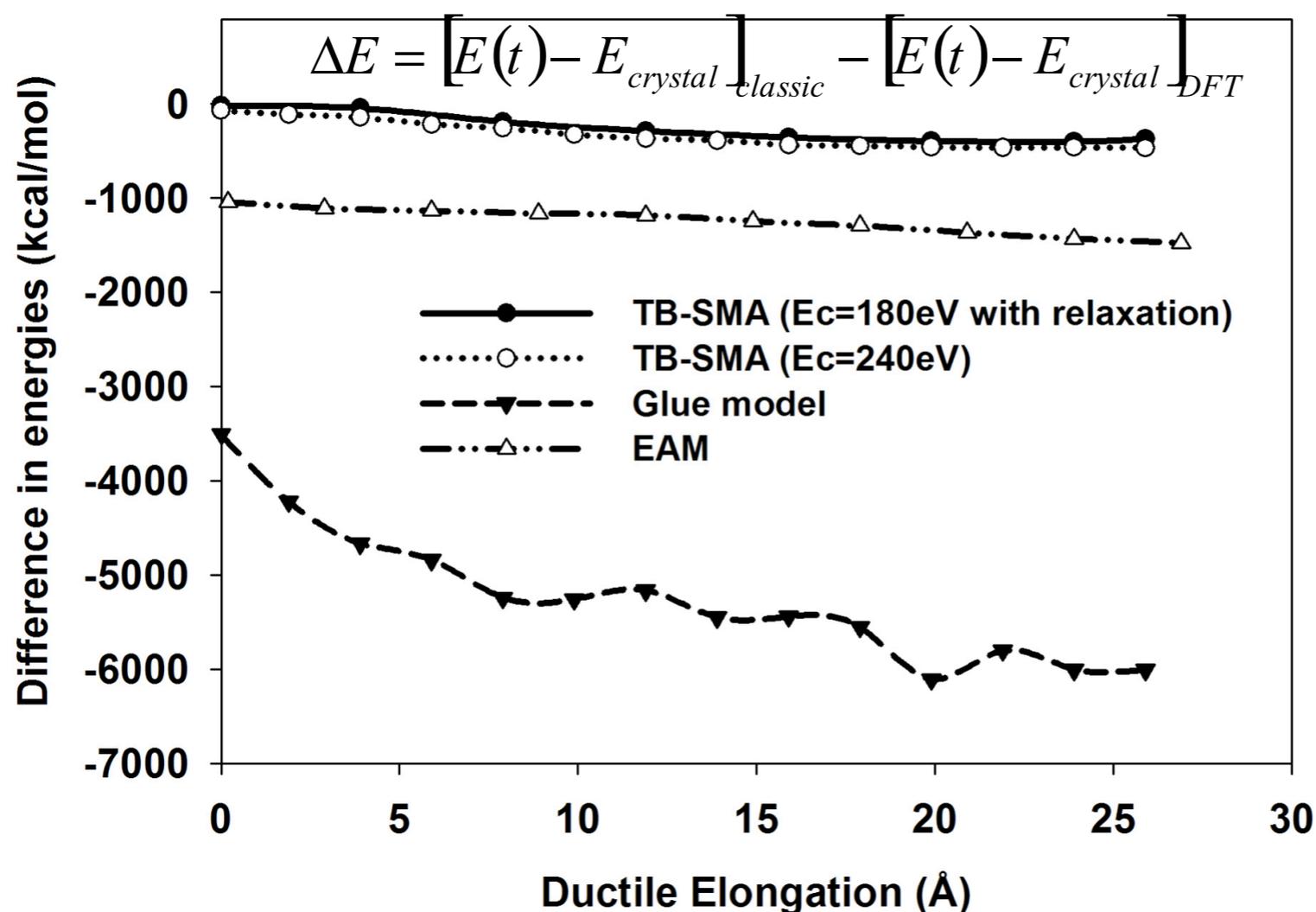
X. Zhao, Y.-S. Leng, P.T. Cummings, *Langmuir*, **22** (2006) 4116-4124

Molecular Simulation

□ Molecular dynamics simulations of stretching Au nanowires

■ Goals

- Determine optimal forcefield for Au
- Understand dynamics of stretching and breakage
- Evaluate impact of solvent for nanowire stretched and broken in solvent

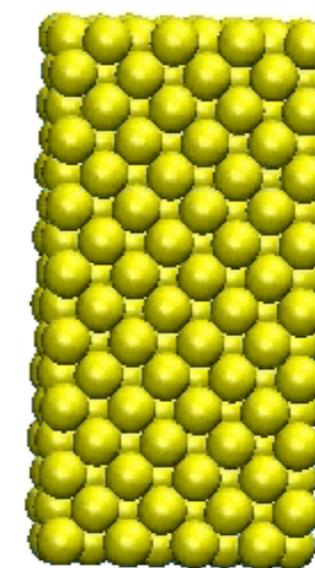
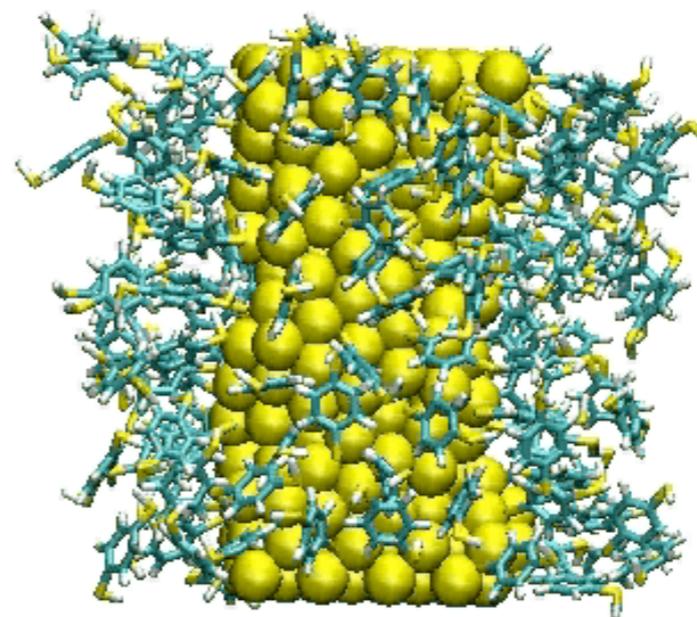


TB-SMA: second-moment approximation of the tight-binding scheme
 EAM: embedded-atom method

Pu, Leng, Tsetseris, Park, Pantelides, Cummings, "Molecular dynamics simulations of stretched gold nanowires: The relative utility of different semiempirical potentials," *J. Chem. Phys.* **126** (2007) Art. No. 144707

Molecular Simulation

- Elongation of Au nanowires in BDT solvent
 - *GCMC to chemisorb/adsorb BDT onto Au nanowire*
 - *MD simulation of stretching*
 - Simulation time ~6 ns
 - Elongation rate 0.05Å/ps
- Next steps
 - *Combined GCMC/MD*
 - *Creation of multiple dual-contact configurations*
 - *I-V calculations*

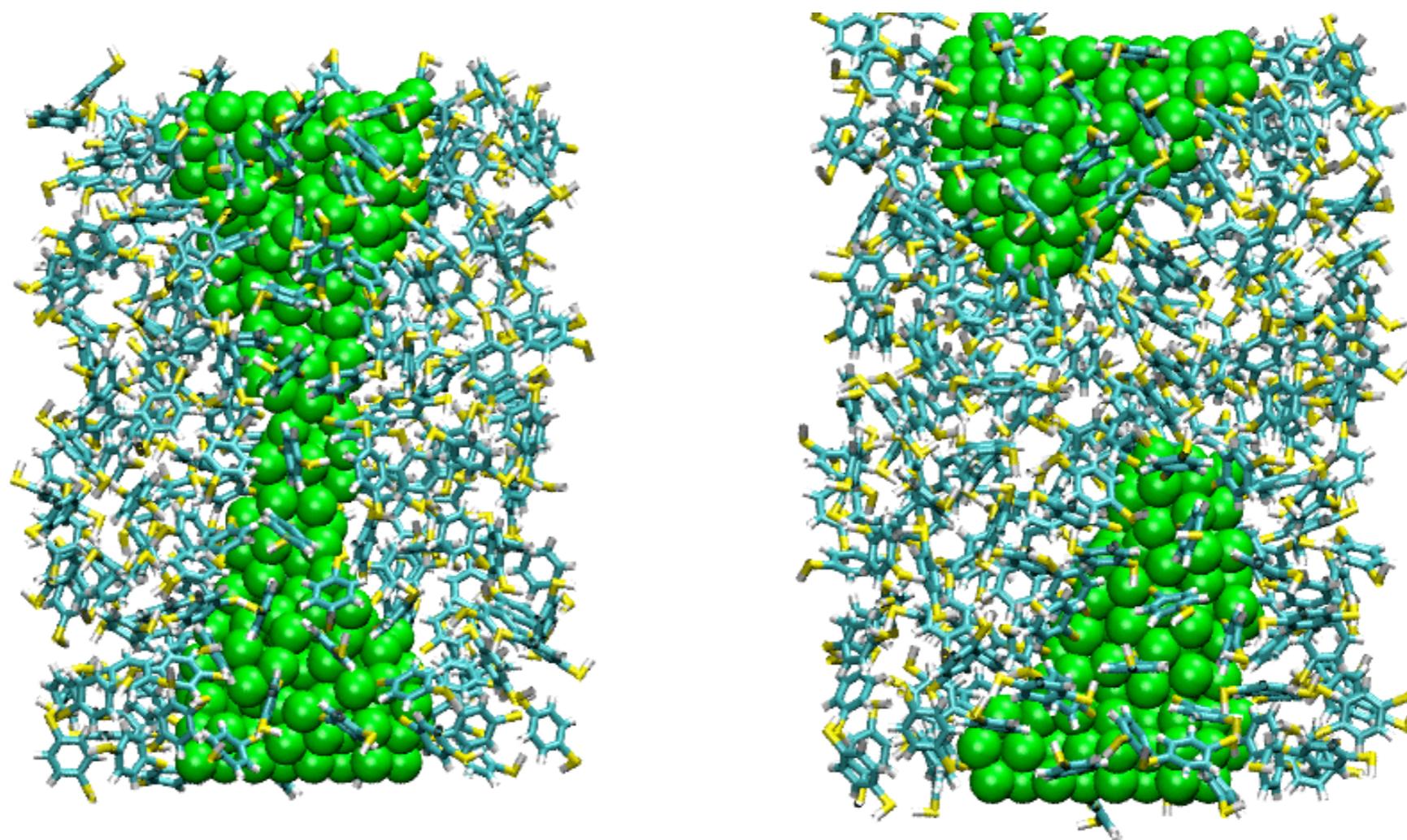


Combined GCMC-MD

- Breakage and moving back together

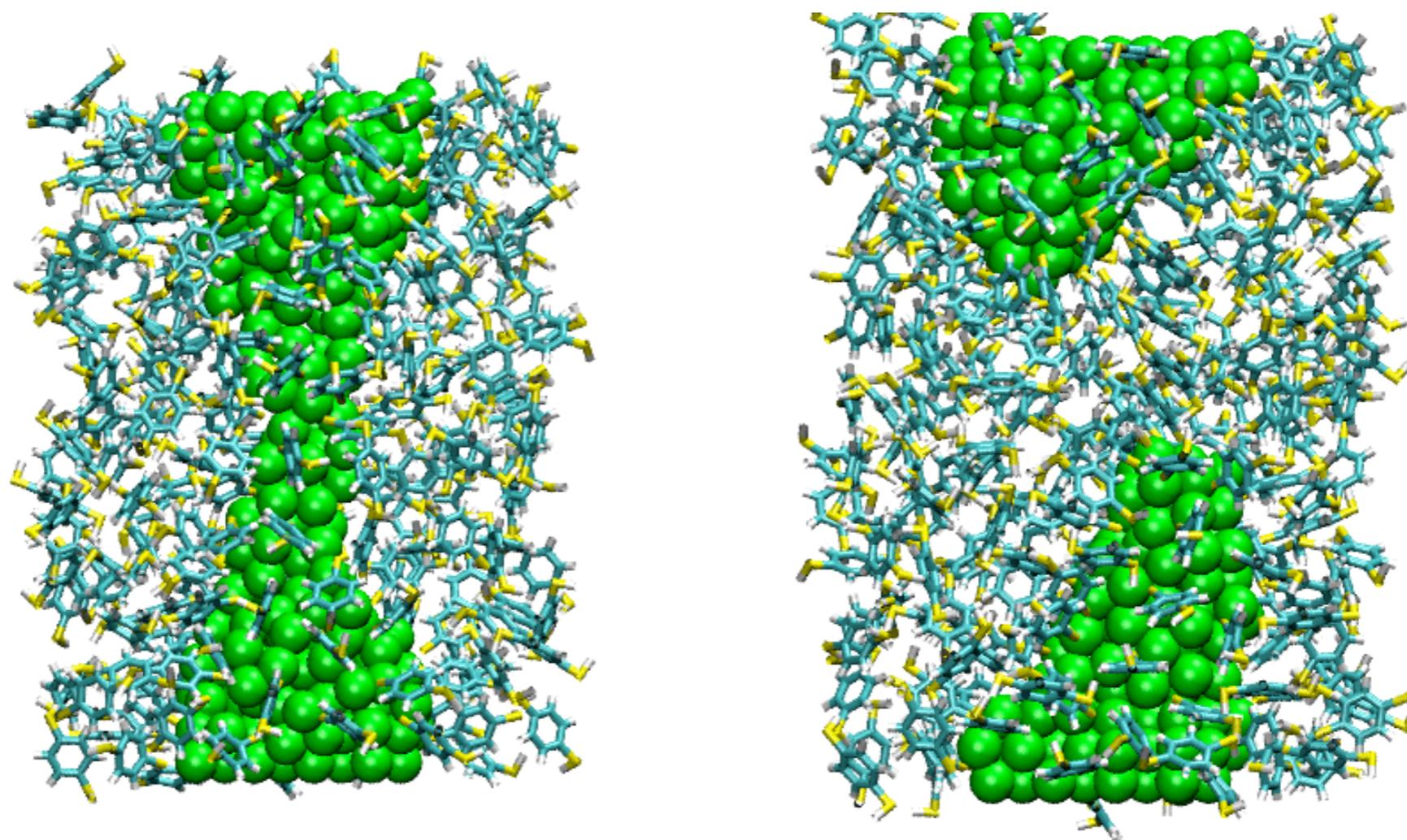
Combined GCMC-MD

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Combined GCMC-MD

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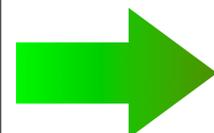
Outline of Talk

□ Introduction

- *Theory, Modeling and Simulation in Nanoscience*
- *ORNL Center for Nanophase Materials Science and Nanomaterials Theory Institute*

□ Molecular electronics

- *Electron transport in self-assembled nano-bridges*



□ Conclusions

Conclusions

□ Petascale and ultrascale computers

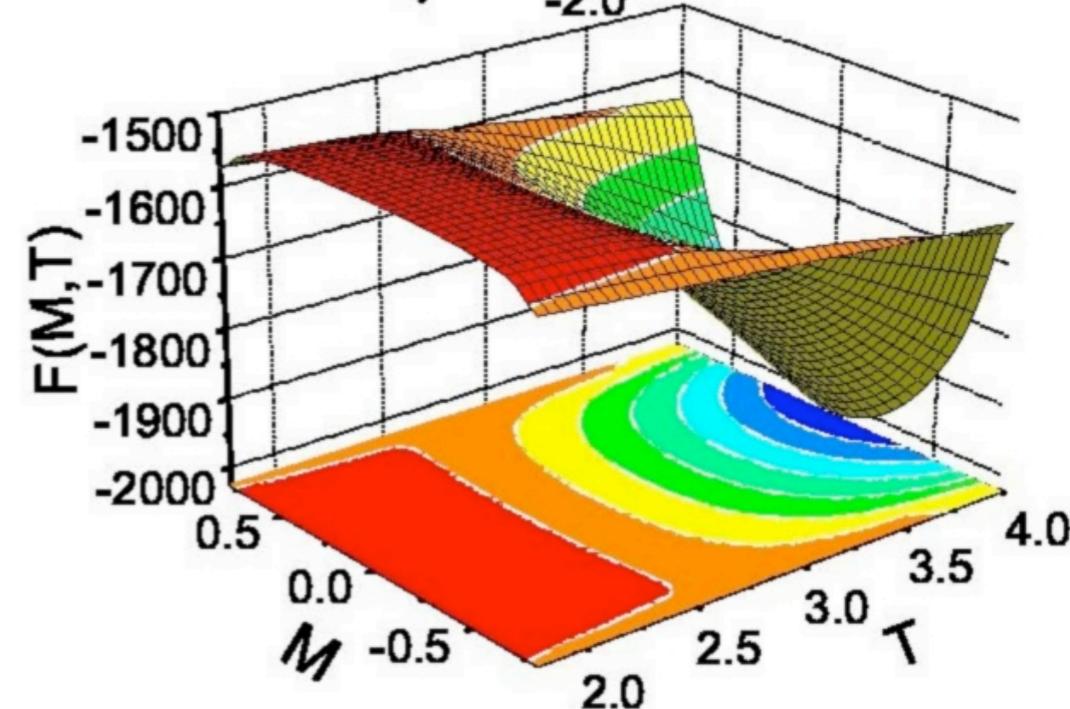
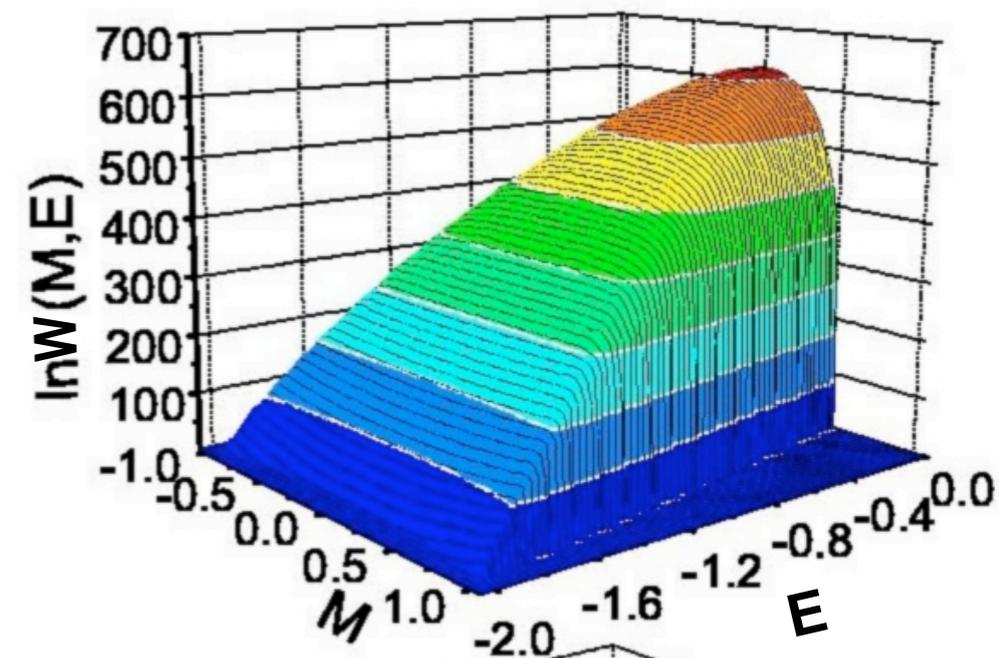
- *Cause us to re-think how to solve problems*
 - What are the best algorithms for massively parallel architectures
- *E.g., explicit atomistic dynamics vs. dynamics on a free energy surface*
 - Calculation of free energy surfaces can be more efficient on large machines
 - *Wang-Landau method to determine free energy surface as function of key variables*
 - *Constraint dynamics to determine free energy profile along “reaction” coordinate*

Conclusions

□ Petascale and ultrascale computers

- *Cause us to re-think how to solve problems*
 - What are the best algorithms for mass
- *E.g., explicit atomistic dynamics vs. dynamical density functional theory*
 - Calculation of free energy surfaces can
 - Wang-Landau method to determine free energy
 - Constraint dynamics to determine free energy

From Zhou, Schulthess, Torbrügge, and Landau, *Phys. Rev. Lett.* **96** (2006) 120201



Conclusions

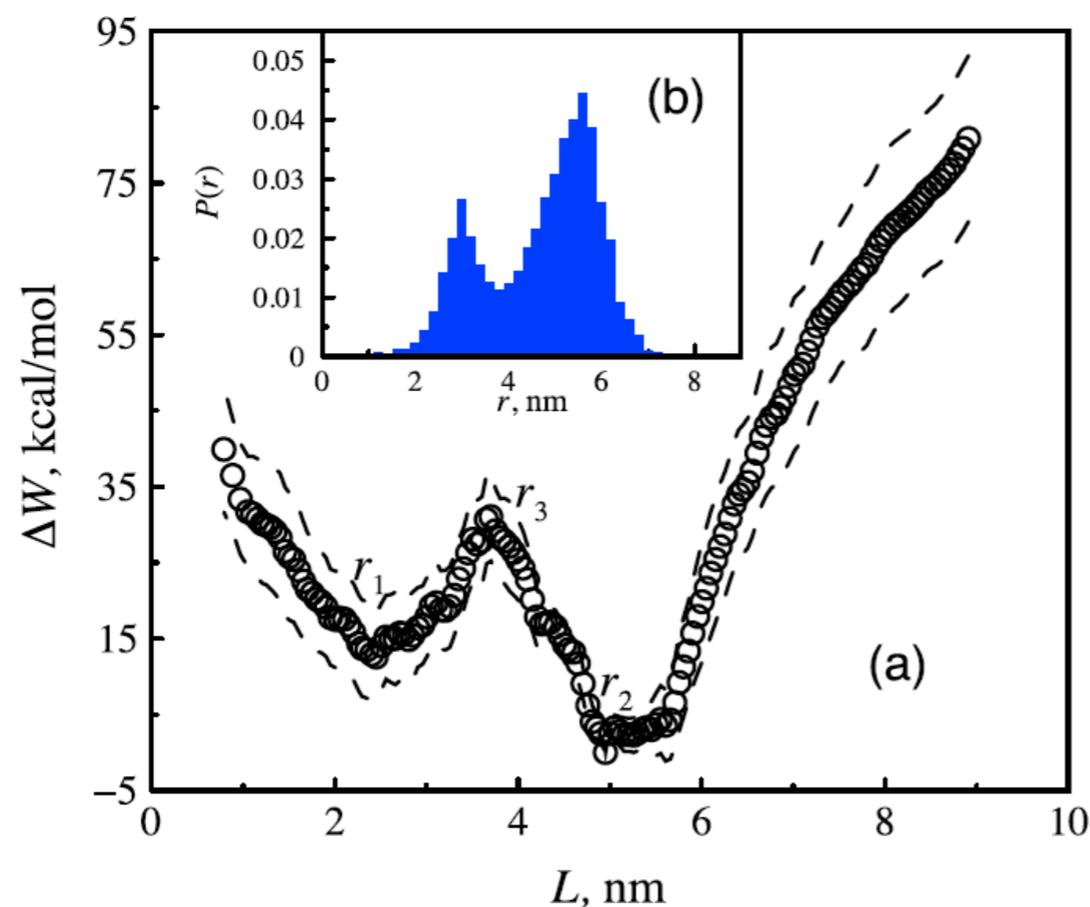
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Zhao, McCabe et al., “Molecular simulation evidence for processive motion of *Trichoderma reesei* Cel7A during cellulose depolymerization,” *Chem. Phys. Letts* **460** (2008) 284–288

160 independent constraint dynamics simulations, each covering 200 ps of phase-space trajectory, with 10 replicates (1600 simulations total, for total simulated time of 320 ns)

Conclusions

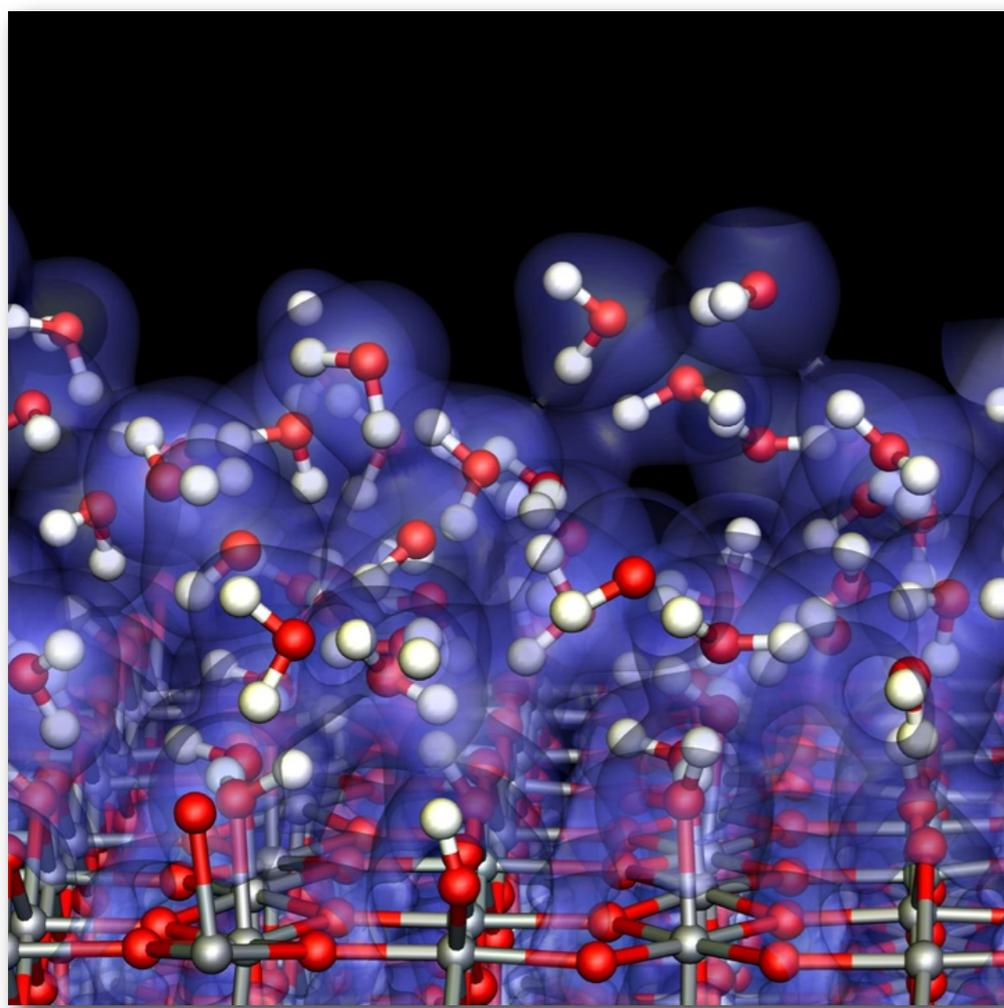
□ Petascale and ultrascale computers

▪ Large first-principles calculations

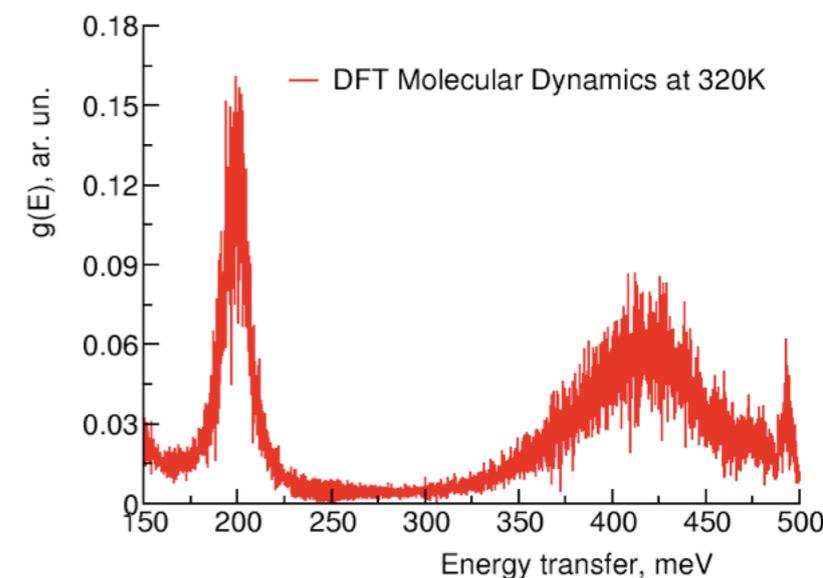
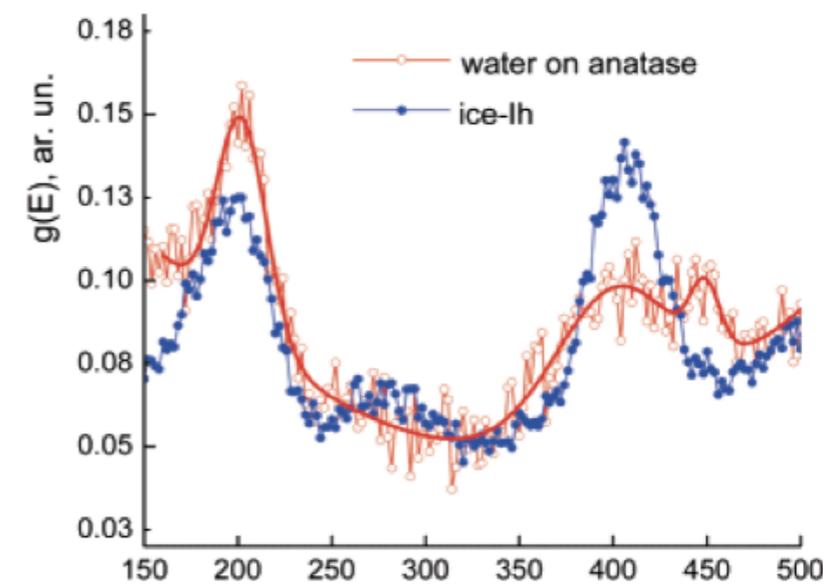
➤ Particularly relevant for reactions

➤ Paul Kent's efficient parallel implementation of VASP

– Most popular code on NERSC's franklin: 26796 invocations over the last 5 months



- ~700 atom cell,
>20000 MD steps,
2048 processors,
average ~1 min/step
including all real-world
overhead



Conclusions

- Theory, modeling and simulation (TMS) play vital role in nanoscale science and engineering
 - *Interpretation of experiments*
 - *Design of experiments*
 - *Characterization and design of nanostructured materials*
 - *Design and control of manufacture*
- TMS in nanoscale science and engineering
 - *Typically requires many different techniques*
 - *Future advances in field will result from development of additional methods*
 - *Multiscale methods, electron transport dynamics, optical properties, self-validating forcefields,...*

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