

*Many-body Methods in Nanoscience:
Application to Passivated Metal Clusters and
Molecular Electronics**

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INT Workshop

**“Advanced Computational Methods for the
Nuclear Many-Body Problem”**

14 March, 2002

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Advanced Computational Methods for Solving the Nuclear Many-Body Problem

The primary goal of the workshop is to bring together the nuclear-structure theory community with many-body theorists from other sub-fields of physics and experts in computational methods and computer technology to exchange ideas and develop new methods for the nuclear many-body problem.

Four Workshop Goals:

1. Identify the physics applications where new computational techniques will be beneficial..
2. Interaction with atomic and condensed matter theorists for the purpose of exchanging ideas on techniques.
3. Discussion on emerging supercomputer technologies and trends.
4. Focus on new algorithms and methods designed to exploit the architecture of modern supercomputers.

Talk Outline

- Density Functional Theory (Brief)
- Applications in Nanoscale Electronics
 - Passivated Metal Clusters
 - Molecular Electronics
- Hardware Trends in Supercomputing.
- Trends in Scientific Software for HPC.

DFT (Kohn, et al.)

$$E_{tot}(\Psi) = E_k + E_{ext} + E_H + E_{xc} + E_i \quad n_e(\mathbf{r}) = \sum_i f_i |\Psi_i(\mathbf{r})|^2$$

- Kinetic Energy $E_k = -\frac{1}{2} \sum_i f_i \langle \Psi_i | \nabla^2 | \Psi_i \rangle$
- External interaction $E_{ext} = \int V_{ext}(\mathbf{r}) n_e(\mathbf{r}) d\mathbf{r}$
- Hartree $E_H = \frac{1}{2} \iint \frac{n_e(\mathbf{r}_1) n_e(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$
- Exchange-correlation $E_{xc} = \int \varepsilon_{xc}(n_e(\mathbf{r}), \nabla n_e(\mathbf{r})) n_e(\mathbf{r}) d\mathbf{r}$
- Ion-ion interaction $E_i = \sum_{I < J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$

Kohn-Sham Equations

$$H_{KS}(\Psi)\Psi = \Psi\Lambda$$

$$H_{KS}(\Psi) = -\frac{1}{2}\nabla^2 + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + V_{ext}(\mathbf{r})$$

- Hartree Potential

$$V_H(\mathbf{r}) = \int \frac{n_e(\mathbf{r}_1)n_e(\mathbf{r})}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1$$

- Exchange-correlation Potential

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}(n_e(\mathbf{r}))}{\delta n_e(\mathbf{r})}$$

Exchange-Correlation Functional: Approximations must be used!

$$E_{xc} = \int \varepsilon_{xc} (n_e(\mathbf{r}), \nabla n_e(\mathbf{r})) n_e(\mathbf{r}) d\mathbf{r}, \quad \varepsilon_{xc} = \varepsilon_x + \varepsilon_c$$

- Local Density Approximation (LDA). $\varepsilon_{xc} = \varepsilon_{xc}(n_e(\mathbf{r}))$

$$\varepsilon_x(n_e) \approx -C_x n_e^{1/3} = -\frac{0.4582}{r_s}; \quad \frac{4}{3} \pi r_s^3 \equiv \frac{1}{n_e}$$

$$\varepsilon_c(n_e) \approx \gamma_i / \left(1 + \beta_1 \sqrt{r_s} + \beta_2 r_s\right); \quad r_s > 1 \quad \text{Ceperley \& Adler (1980)}$$

- Various gradient correction approaches:

- BP (Beck exchange + Perdew correlation).

$$\varepsilon_{xc} = \varepsilon_{xc}(n_e(\mathbf{r}), \nabla n_e(\mathbf{r}))$$

- BLYP (Beck exchange + Lee/Yang/Parr correlation).

- PBE (Perdew-Burke-Ernzerhof, Hybrid Approach).

- Spin-polarized functional used for open shell systems (LSDA).

- Strong similarities with effective interactions in Nuclear Physics (Skyrme Interactions).

Computational Methods

- Basis set expansions
 - GTO's (Localized Orbitals, Long-term standard in Comp. Chem),
 - Plane waves (FFT's, No Pulay correction terms).
- Minimization of the total DFT energy
 - Conjugate gradients,
 - Direct inversion of the iterative subspace (DIIS),
 - Simulated Annealing, CP Molecular Dynamics.
- Examples of Scalable Parallel Codes:
 - CPMD (CPMD Consortium, www.cpmd.org)
 - Pseudopotential, Plane Wave DFT-MD,
 - CPMD.
 - NWChem (PNNL, www.emsl.pnl.gov:2080/docs/nwchem/nwchem.html)
 - Complete Comp. Chem. Suite (SCF, MP-2, CI, CC-SD(T)),
 - Pseudopotential, Plane Wave DFT-MD, CPMD.
- Computing performed at ORNL's CCS
 - IBM-SP3 (Eagle)
 - Compaq SP (Falcon)

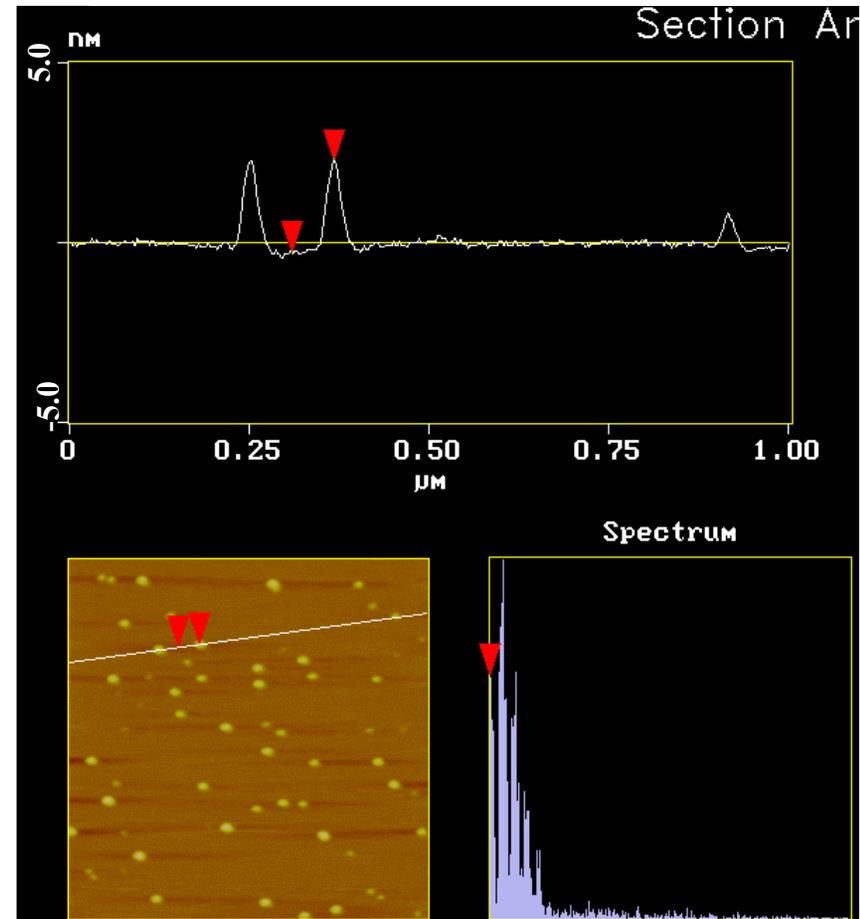
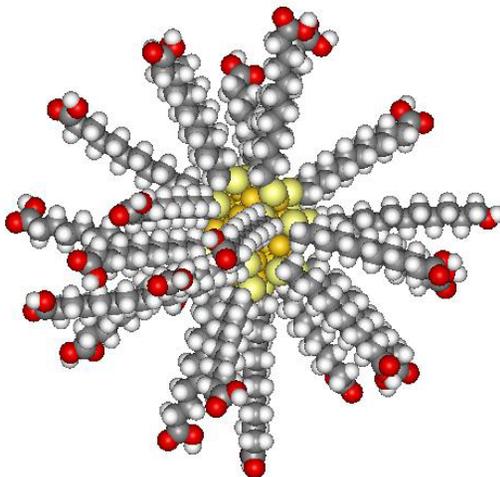
Nanoscale Metal Clusters

- Novel *size-dependent* properties (1-3 nm, < 200 atoms).
 - Electronic and optical properties, (Quantum size effects, Biological markers).
 - Novel catalytic materials.
 - Understanding and enabling nanoscale material synthesis.
 - One-dimensional nanocrystals (e.g., nanotubes and wires).
 - Chemical links for assembly of conjugate organic/inorganic materials.
- Specific interests:
 - Engineered quantum-dot arrays for novel electronic devices/sensors.
 - Catalytic nucleation and growth of carbon nanotubes.
 - Electron transport in molecule/nanoscale systems.
- Interpretation of experiment requires high-fidelity descriptions of metal nanoclusters.
- Techniques for size-selective synthesis enable quantitative comparisons between experiment and theory.

Synthesis of Gold Nanoparticles

- Produced metal (Au) clusters ~ 2 nm in diameter.
 - Room-temperature operation requires
Charging energy = $e^2/C \gg k_B T$, C =capacitance.

- Passivation plays a dual role.
 - Provides a barrier for cluster growth,
 - Provides chemical functionality for attachment to DNA template.



Programmed Materials Synthesis via DNA

- Synthesis of ~1nm gold clusters (QD) passivated by alkanethiolates.

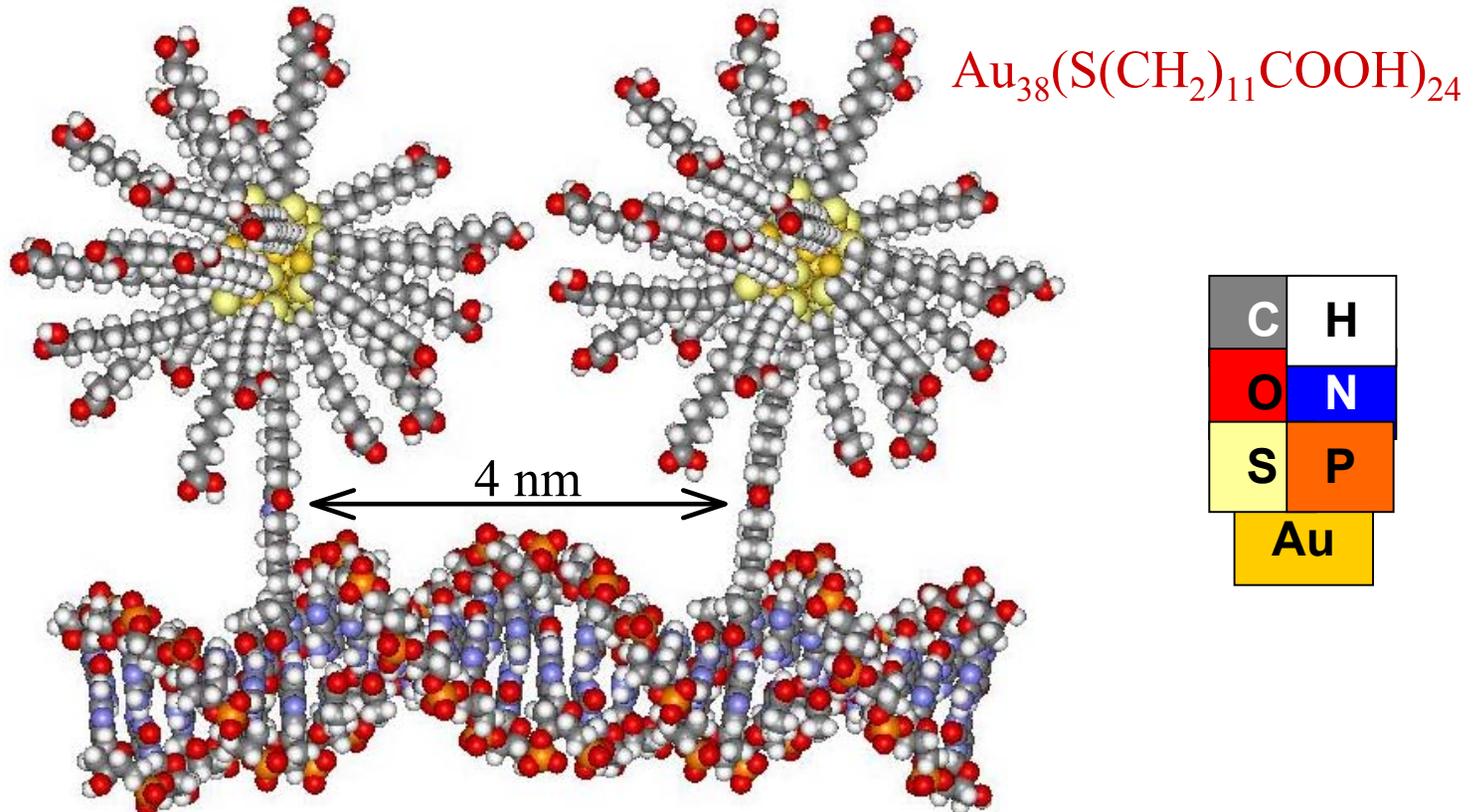
—E.g., functionalized with carboxylic-acid groups.

\$\$ DOE/BES/DMSE

- Construction of Linear QD Arrays via DNA templates.

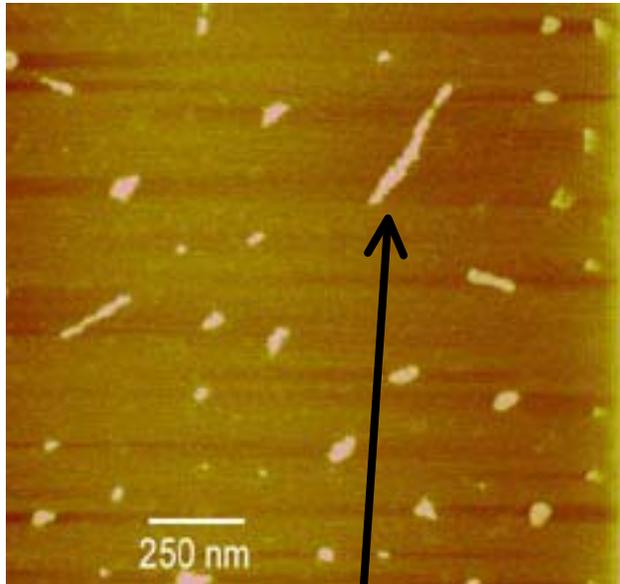
—DNA modified with amine (NH_2) groups as binding sites.

—Attachment of nanoparticle via peptide bonds.

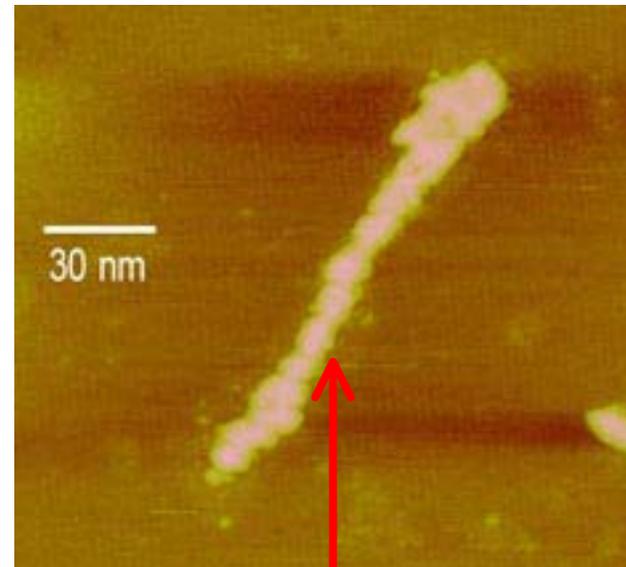


Programmed Materials Synthesis via DNA

- Method to covalently bond inorganic nanoparticles to duplex DNA in a programmable fashion.
- Fabrication of nanostructures with nanoscale periodicity.



Gold nanoparticles bound to DNA strand with 10 nm spacing.

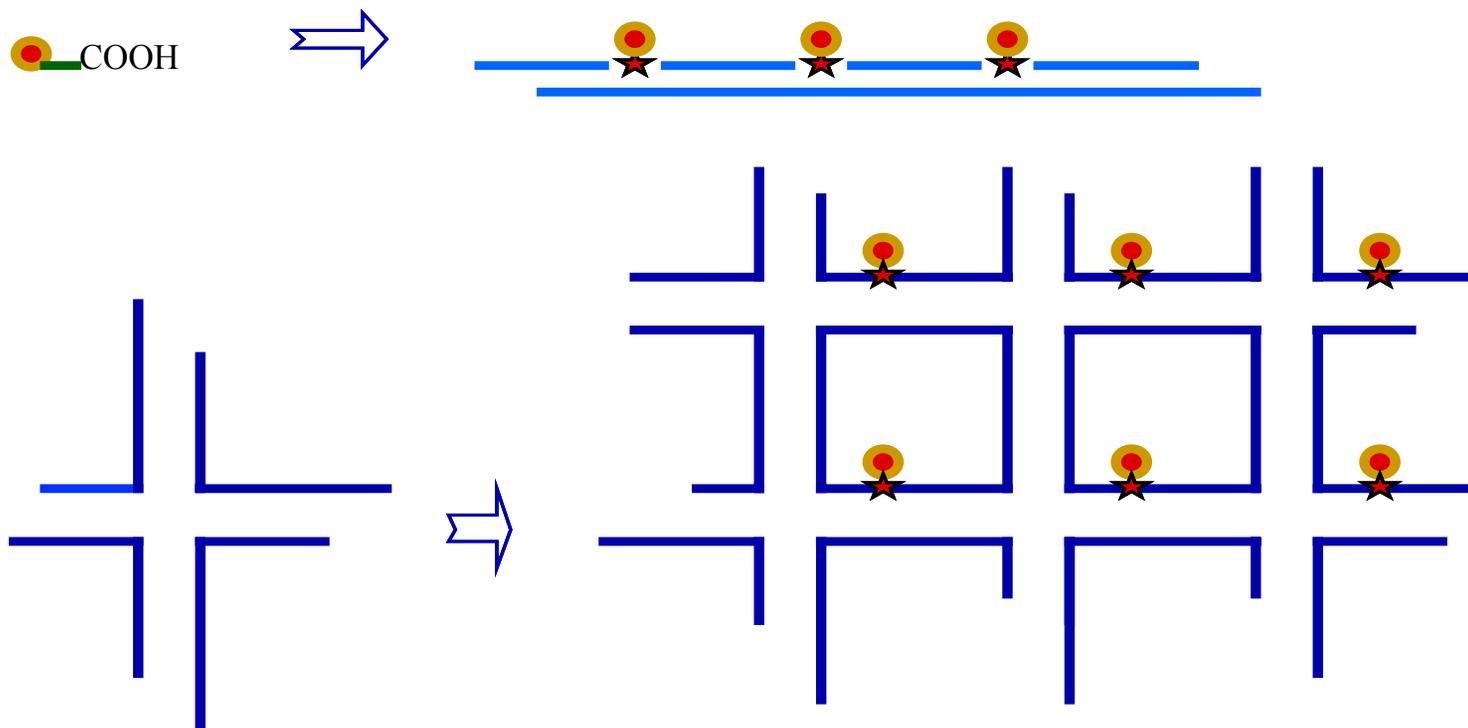


Small, periodic structures

“Covalent Attachment of Gold Nanoparticles to DNA Templates”

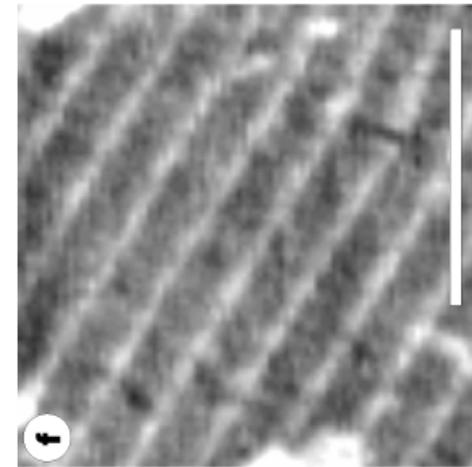
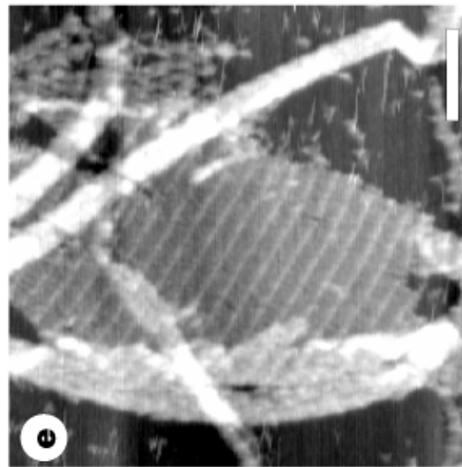
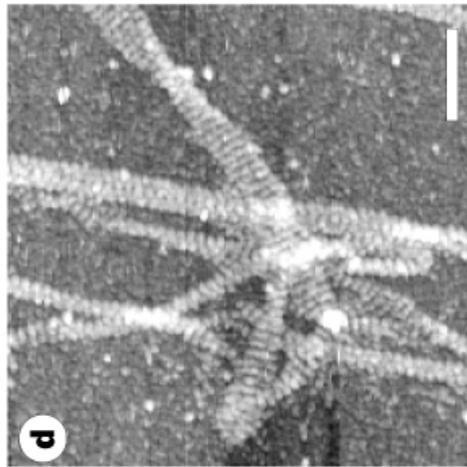
K.A. Stevenson, *et al.*, (submitted).

Construction of 2D Arrays

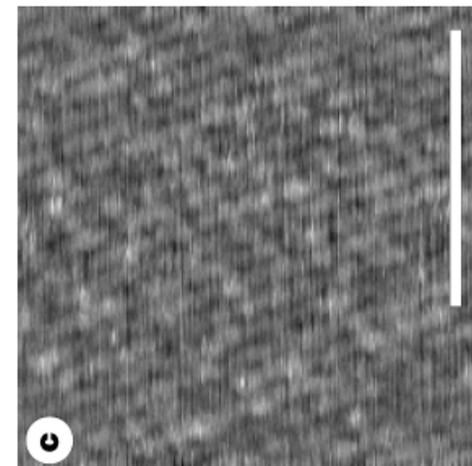
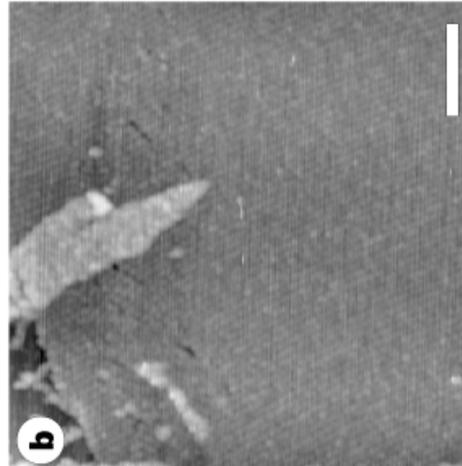
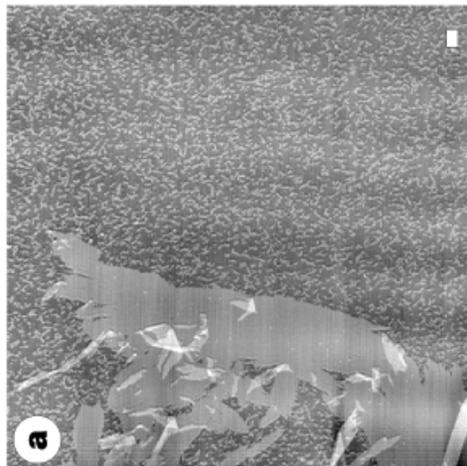


2D Lattices from DNA Crosslinked Structures

- Seeman and coworkers have produced DNA in regular 2D geometries
 - N.C. Seeman, *J. Vac. Sci. Technol A* 12, 1895 (1993);
 - E. Winfree, *et al.*, *Nature* 394, 539 (1998).



300 nm



SEEMAN'S DNA CONSTRUCTS

- **DNA CUBE**



- **DNA TRUNCATED OCTAHEDRON**



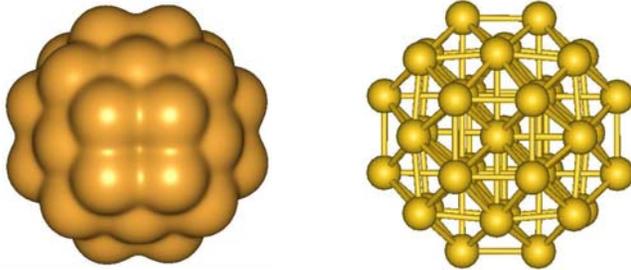
<http://seemanlab4.chem.nyu.edu/homepage.html>

Ab Initio Computations of Metal Nanocluster Arrays

- Perform microscopic simulations of gold nanoclusters.
 - DFT-MD: Plane Wave, Pseudopotential Approach
 - CPMD Consortium (www.cpmd.org): CPMD V3.0h
 - Copyright IBM Corp 1990-2001, MPI fuer Festkoerperforschung Stuttgart 1997-2001.
 - High-performance parallel computing (ORNL/CCS IBM-SP3).
 - Collaborators: W. Andreoni and A. Curioni, IBM-ZRL.
- Some details:
 - Exchange-correlation functionals including gradient corrections.
 - Norm-conserving, scalar relativistic, l -dependent pseudopotentials describe the core-valence electron interaction for Au, S, and C.
 - E.g., for Au, 11 valence electrons (4s and 5d).
 - Real-space, plane-wave representation
 - ⇒Basis independent of atomic positions!
- Performance issues:
 - Compute-intensive task: 3D FFT's;
 - Efficient implementation on cluster-based parallel computers.
 - Overhead dominated by matrix transposition (MPI “All-to-All” communication).

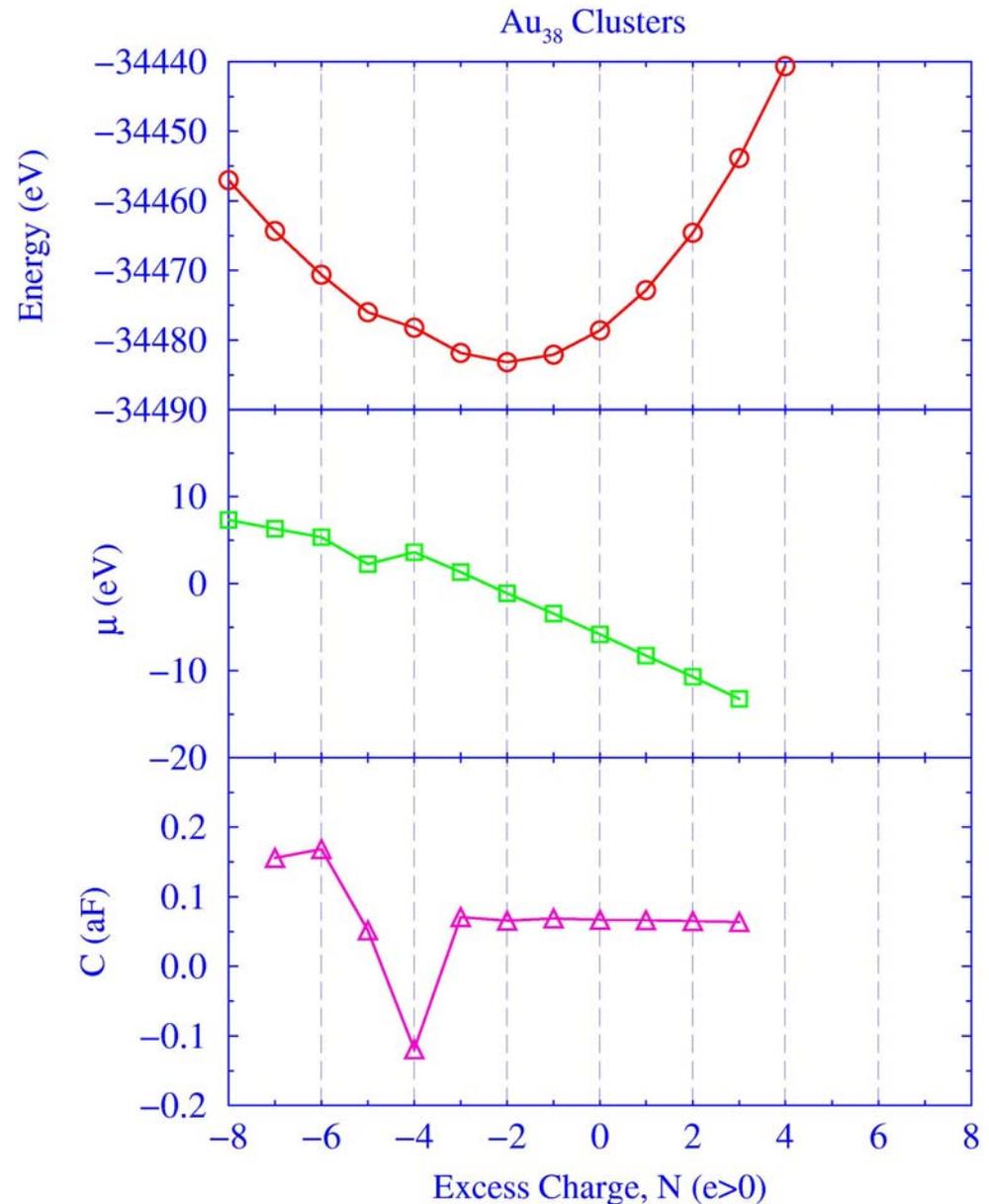
Ab Initio Structure Calculations of Au Nanoclusters

- Charging Characteristics:
 - “Bare” Au₃₈.
- Predictions:
 - Ordered cluster configuration (truncated octahedron).
 - Charge -2 is the lowest energy configuration.
 - Capacitance is constant over broad range of useful charge states.

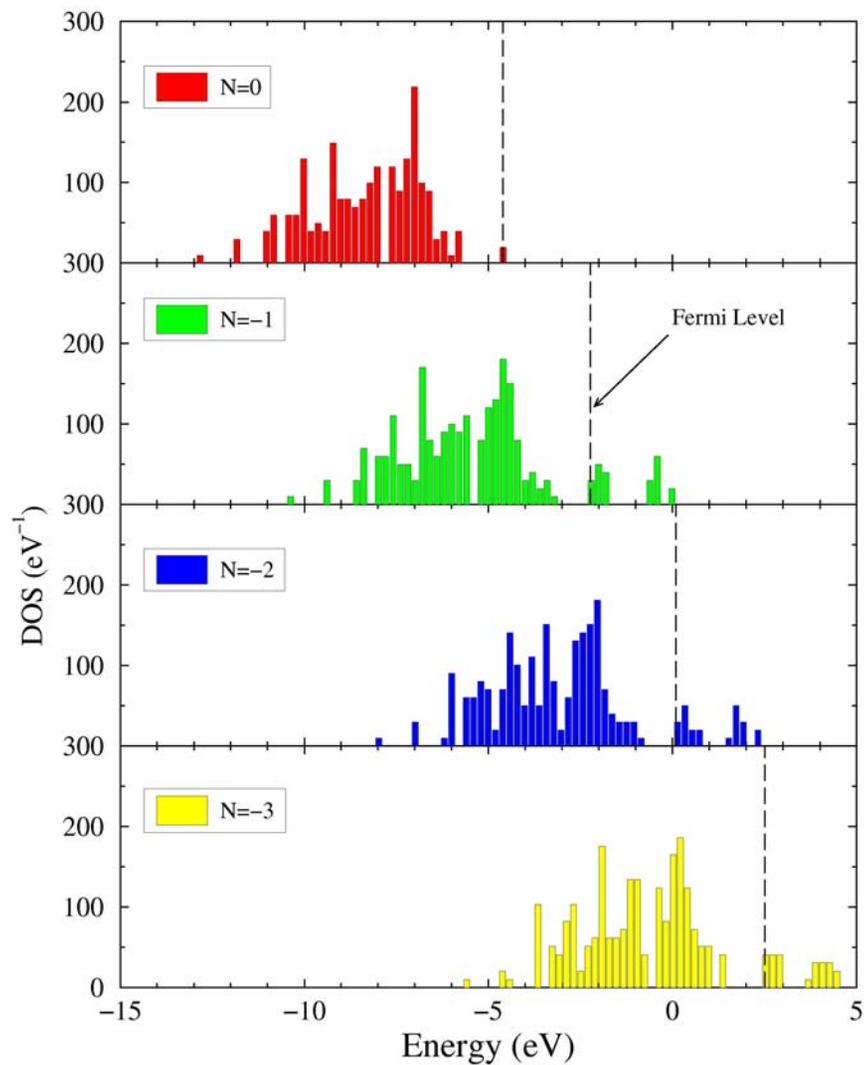
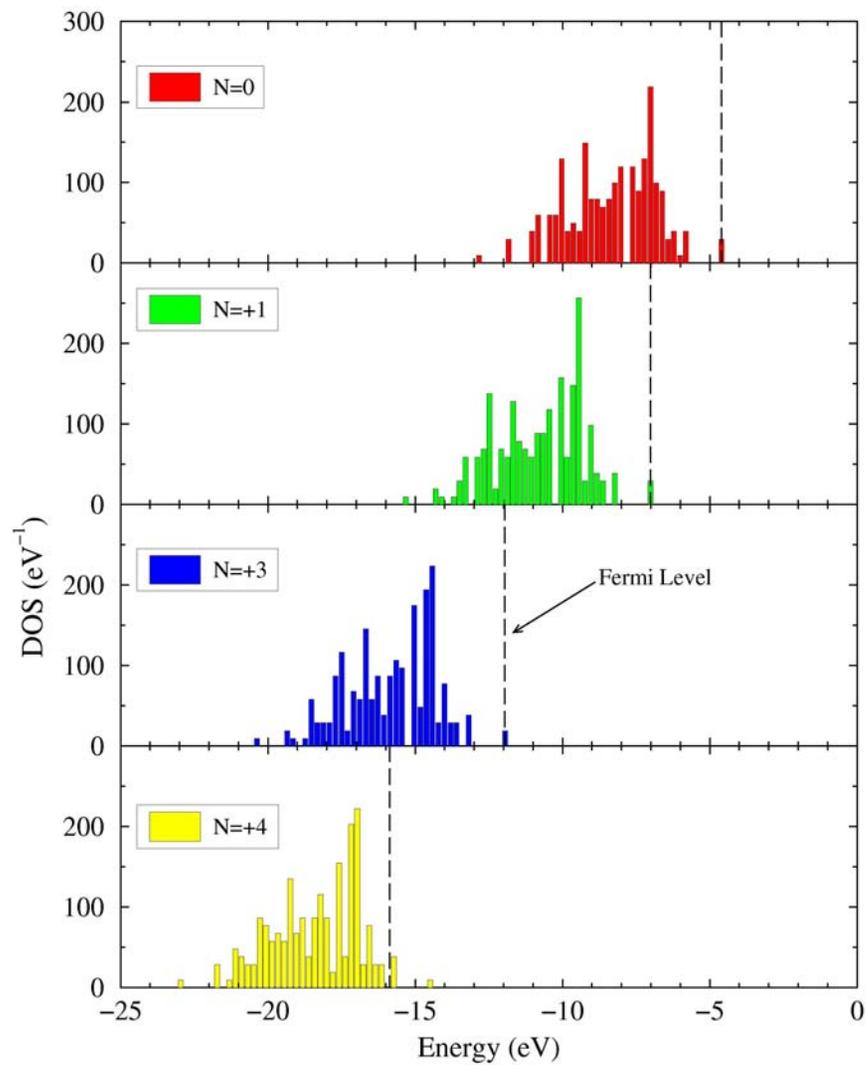


- Computational “Load”
 - 38 Au \Rightarrow 418 electrons
 - 30 “Winterhawk-II” nodes

Wells, Curioni, Andreoni (in preparation).

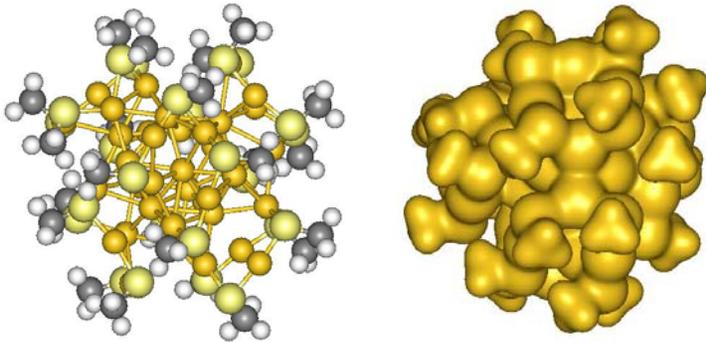


Electron Density of States: Charging Au_{38}



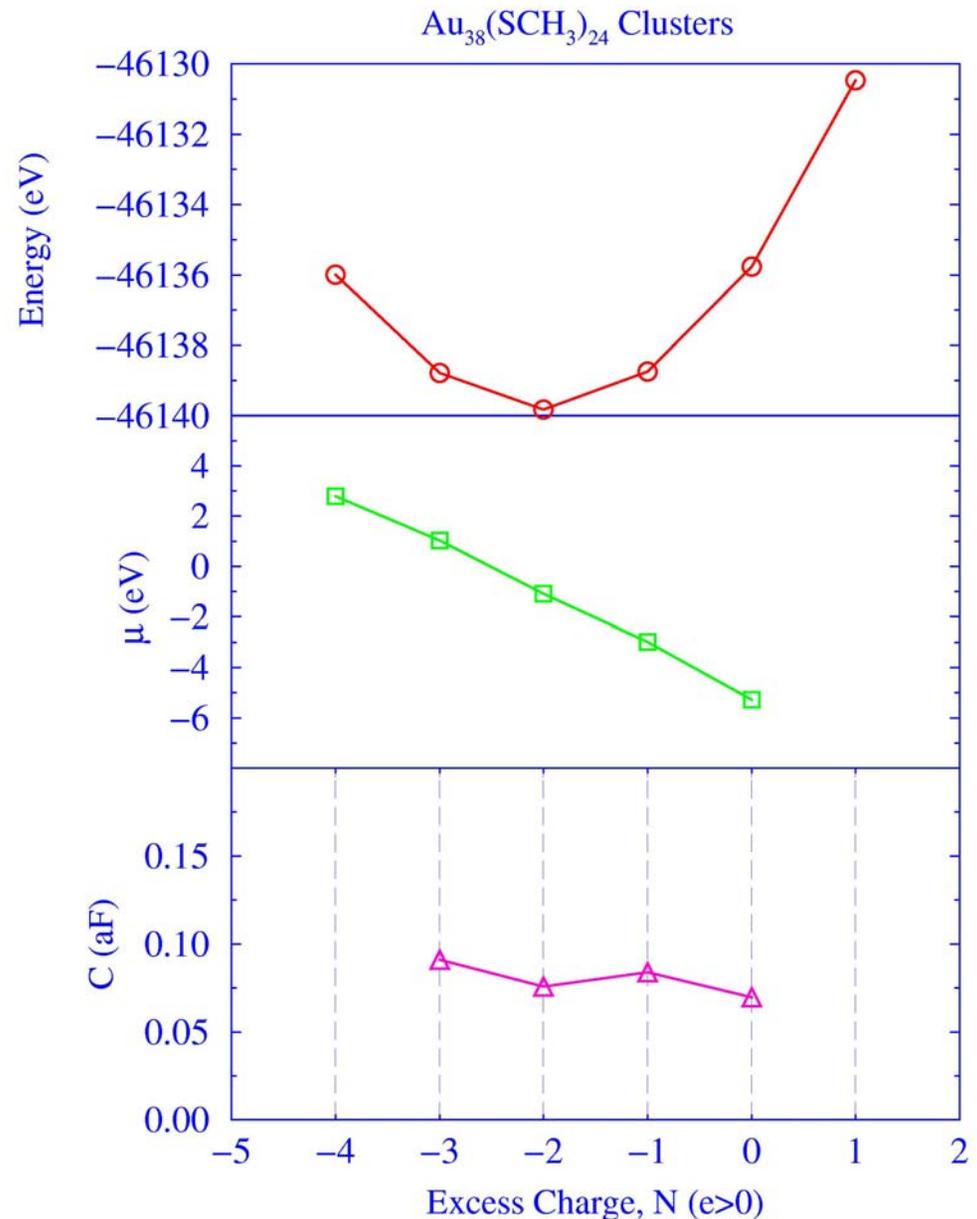
Ab Initio Structure Calculations of Passivated Au Nanoclusters

- Charging Characteristics:
 - “Passivated” $\text{Au}_{38}(\text{SCH}_3)_{24}$.
- Predictions:
 - Disordered Configuration.
 - Charge -2 state is the lowest energy configuration.
 - Capacitance is constant over range of useful charge states.



- Computational “Load”
 - 158 atoms \Rightarrow 730 electrons
 - 60 “Winterhawk-II” nodes

Wells, Curioni, Andreoni (in preparation).



Current and Future Research

Study of structure and electronic properties of passivated metal clusters, to investigate electronic transport and stability issues of specific cluster arrays.

- Compute the electronic structure and configuration of passivated gold clusters, including isolated clusters, clusters interacting with insulating substrates, and adjacent cluster-cluster interactions.
- Basic structure information, (i.e., the spectrum of eigenenergies ε_i and values ψ_i of the eigenfunctions at the tunnel barrier surfaces of QDs, we will compute the capacities C_i , the single-particle energies, E_i , and the tunneling rates, $\Gamma_{i,k} \propto |\psi_i^* \psi_k|$, for the QD arrays.
- Mixed quantum-classical descriptions (QM/MM) for hybrid materials.

Electronics on the Molecular Level

Predrag Krstic and D.J. Dean, ORNL/Physics

Xiaoguang Zhang and J.C. Wells, ORNL/CS & Math

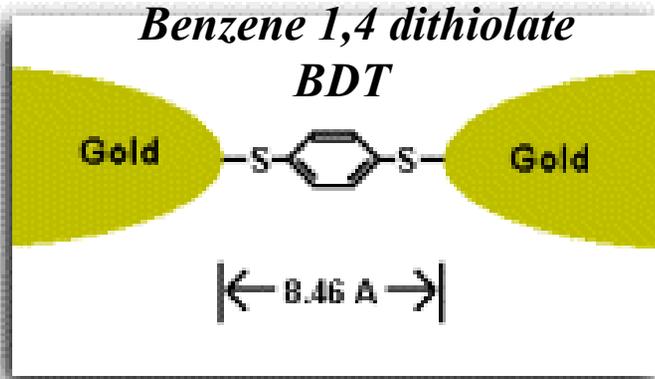
P.T. Cummings and D. Keffer, ORNL/Chemistry and UTK

W.H. Butler, University of Alabama and ORNL/M&C

\$\$: ORNL/LDRD

Present Status in the Field

Conductance through a molecule



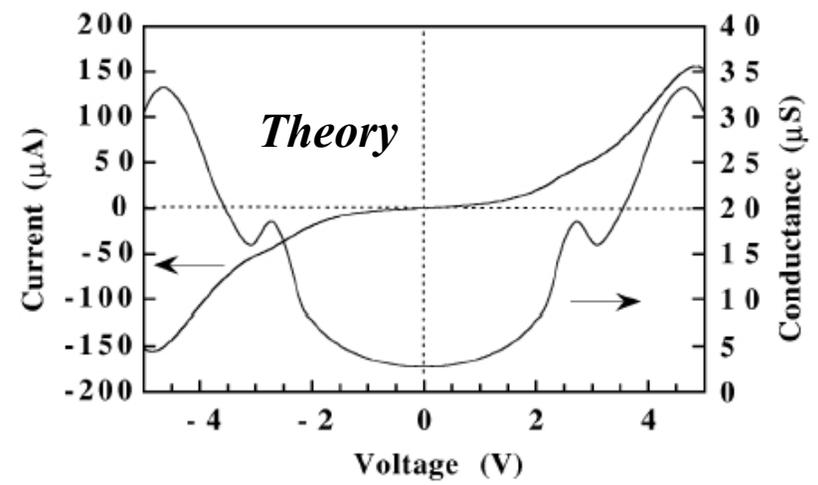
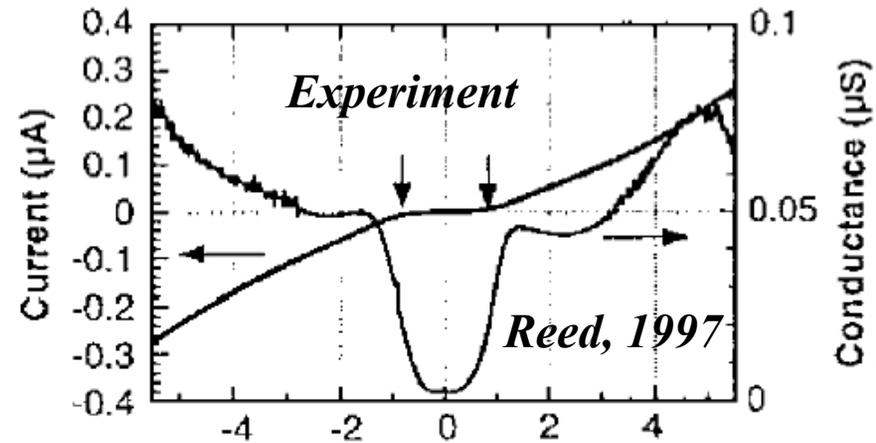
Reed & Tour, *Sc. Am.* (June, 2000)

Open Questions:

• Why is theoretical result orders of magnitude larger than the experimental one?

?? Because of:

- Surface-molecule interface?
- Correlations beyond DFT?
- Neighboring molecular strands?
- External electric bias?
- Temperature?

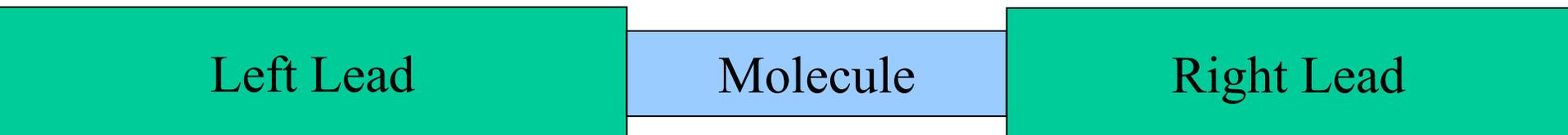


Di Ventra et al., *PRL* 84, 979 (2000)
Jellium model for leads

Electron transport through a molecular device - Conductance

Connection molecule-lead is crucial!

Tunneling of electron between lead and molecule mostly defines “molecular” conductance!



Left Lead

Molecule

Right Lead

$$\sigma = \frac{e^2}{h} T$$

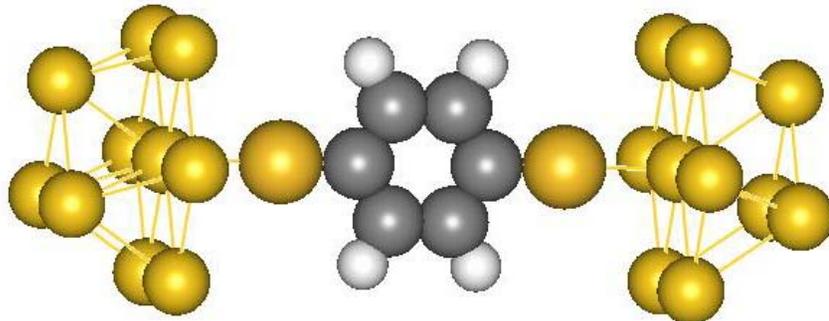
Landauer formula for conductance:

T is transmission probability from L to R

$$T = \text{Tr}(\Gamma_{\text{left}} G_{\text{mol}}^r \Gamma_{\text{right}} G_{\text{mol}}^a) \quad \text{Caroli formula}$$

Structure for Transport

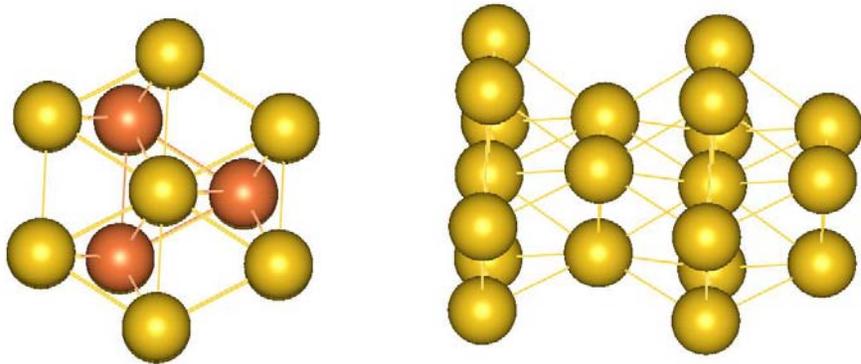
Structure calculations provide input for electron transport (conductance) calculations: Hamilton matrices (H), Overlap matrices (S).



BDT with gold leads

332 GTO basis functions

*BDT-leads couplings,
BDT Hamiltonian
(for BDT Green's function
and self-energies)*



Au (111), 10-atom -layer

*Layer-layer coupling+
a layer Hamiltonian*

View from the top

*For description of characteristics
of infinite and semi-infinite
nanowire (using first-principles
Tight-Binding Model (TBM))*

G is Green's function of the molecule (in presence of the leads)

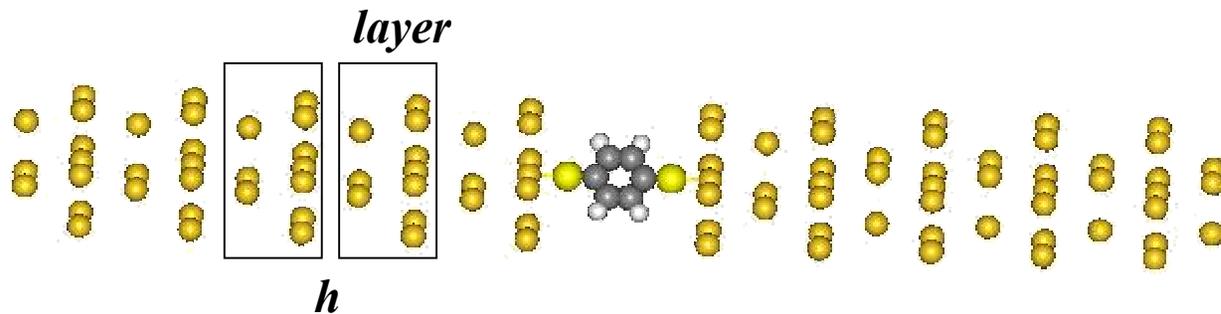
$$\Gamma_{left} = i(\Sigma_{left}^r - \Sigma_{left}^a)$$

$$\Gamma_{right} = i(\Sigma_{right}^r - \Sigma_{right}^a)$$

Γ_{left} and Γ_{right} *characterize self-energy of the molecule due to coupling with the leads*



Apply Tight Binding Model (TBM)

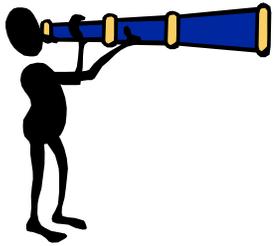


Only adjacent layers coupled (by h)

Several numerical, iterative methods exists to solve the problem.



We developed an exact, analytical and stable solution to calculate electron transmission through a molecule in the presence of any configuration of the leads-molecule.



This enables deeper insight into physics of the process



Example: Allows analytic decomposition of the transmission into Bloch channels and evanescent states.

Consequence: Transmission of an ideal, infinite lead is an integer (= number of Bloch channels).

Some detail:

For *semi-infinite* leads we find



left: $g_L = \alpha h^{-1}$

$$\Sigma_L^{LEAD} = h \beta$$

right: $g_R = \beta (h^T)^{-1}$

$$\Sigma_R^{LEAD} = h^T \alpha$$

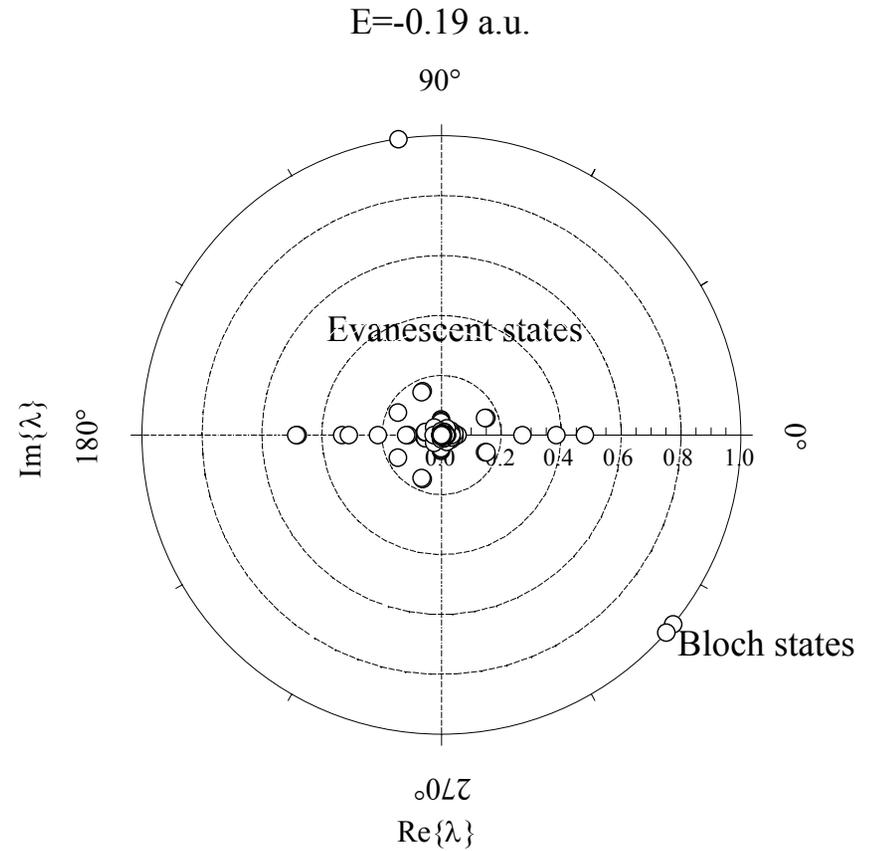
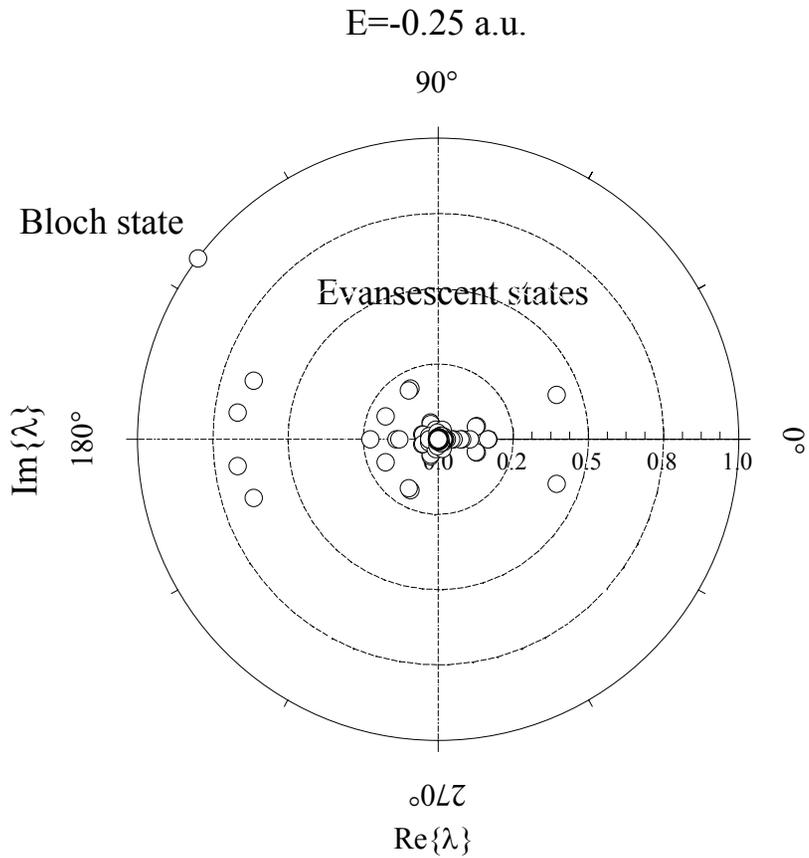
α, β in terms of eigenvalues and eigenmatrices of quadratic, complex, generalized eigenvalue problem in $z = \exp(ikd)$

$$Mz - h - h^T z^2 = 0$$

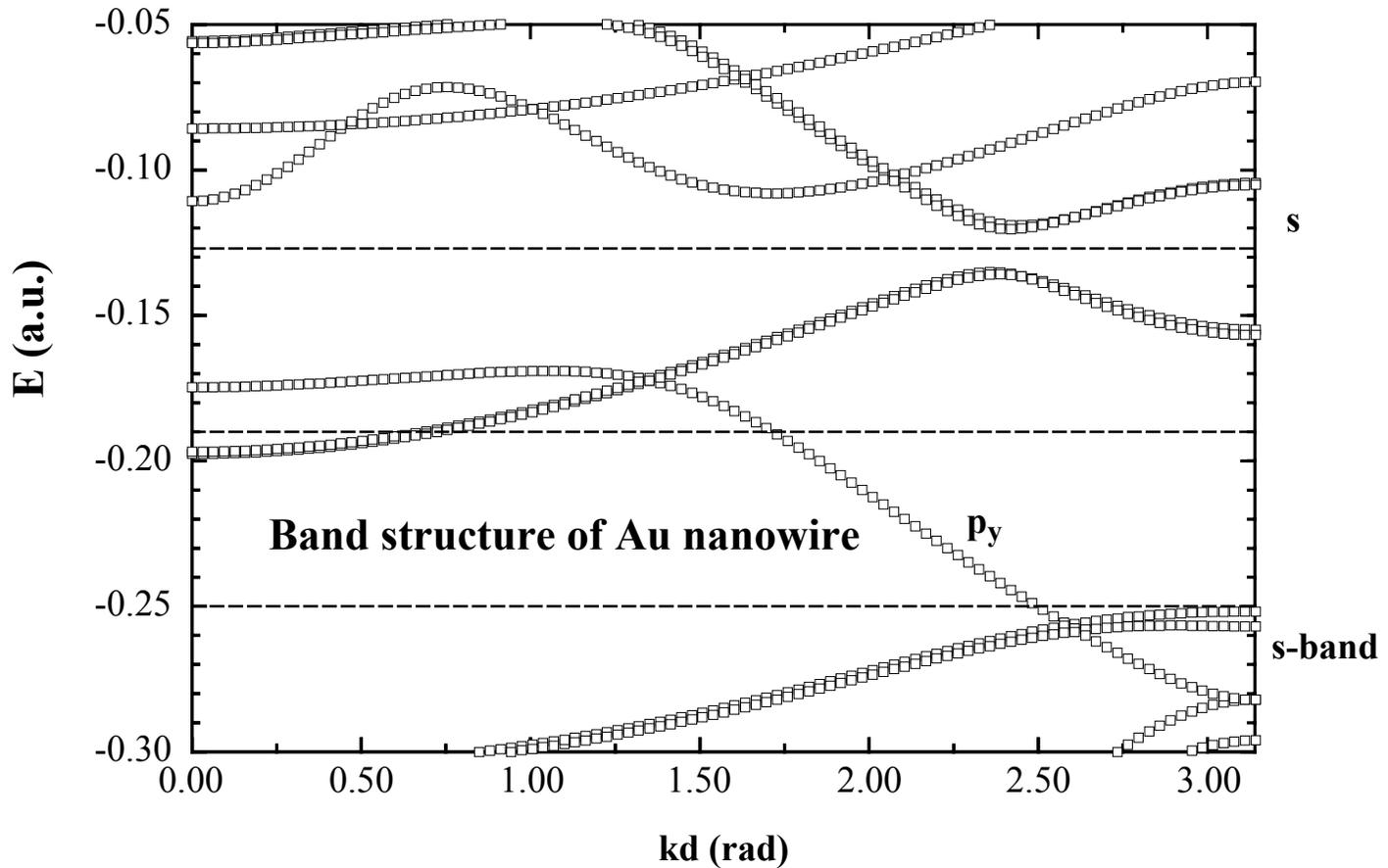
$$M = ES_{00} - H_{00}$$



Analytical structure of the evanescent and Bloch eigenvalues

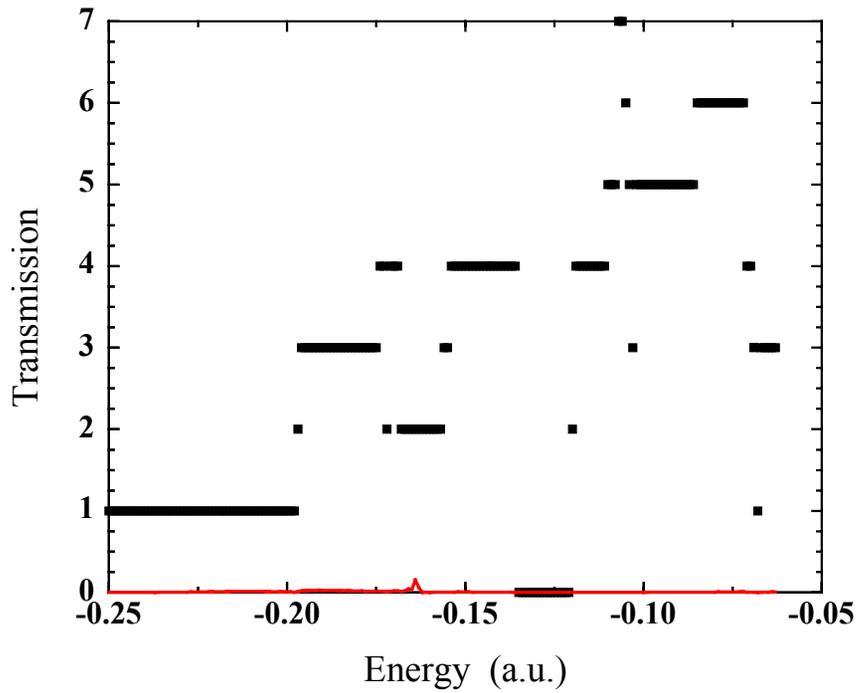


Au lead

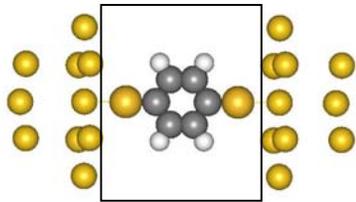
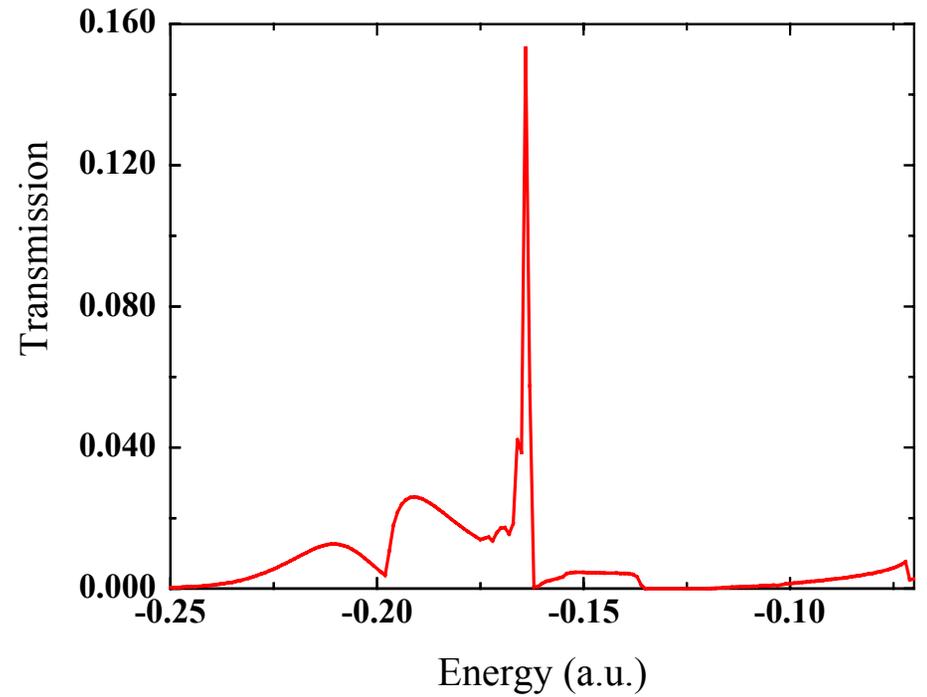


Can obtain an infinite-lead transmission looking into band structure

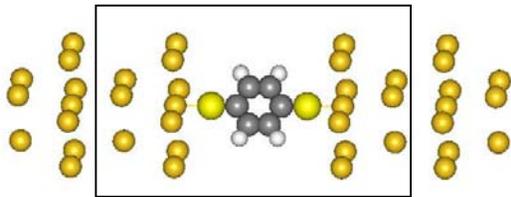
Comparison of infinite lead and BDT transmission



Total transmission through BDT with gold leads



“molecule” 1



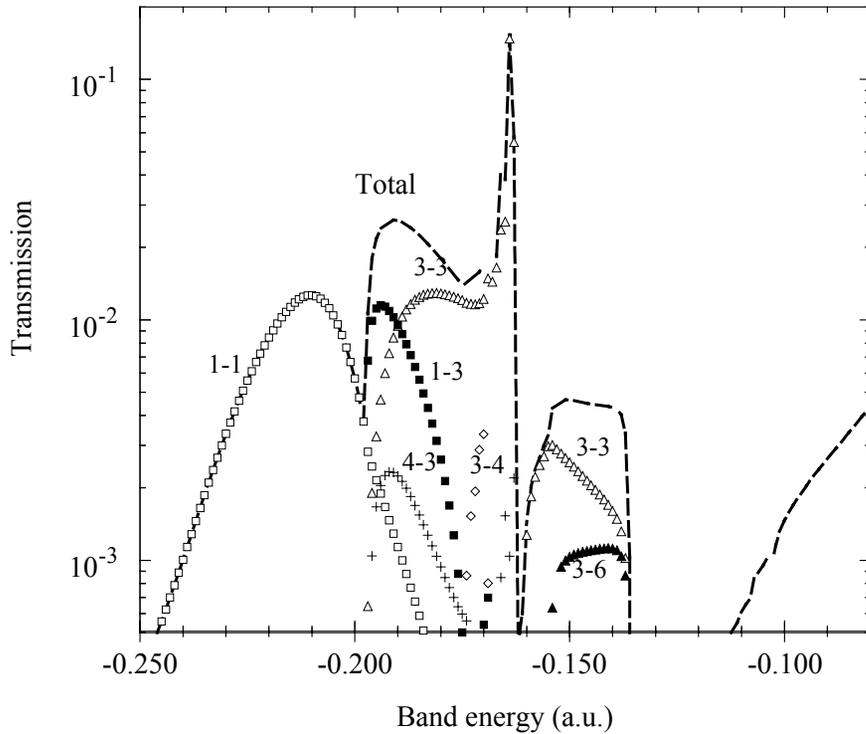
“molecule” 2

The total transmission invariant to a number of the lead-layer pairs included in the “molecule”.

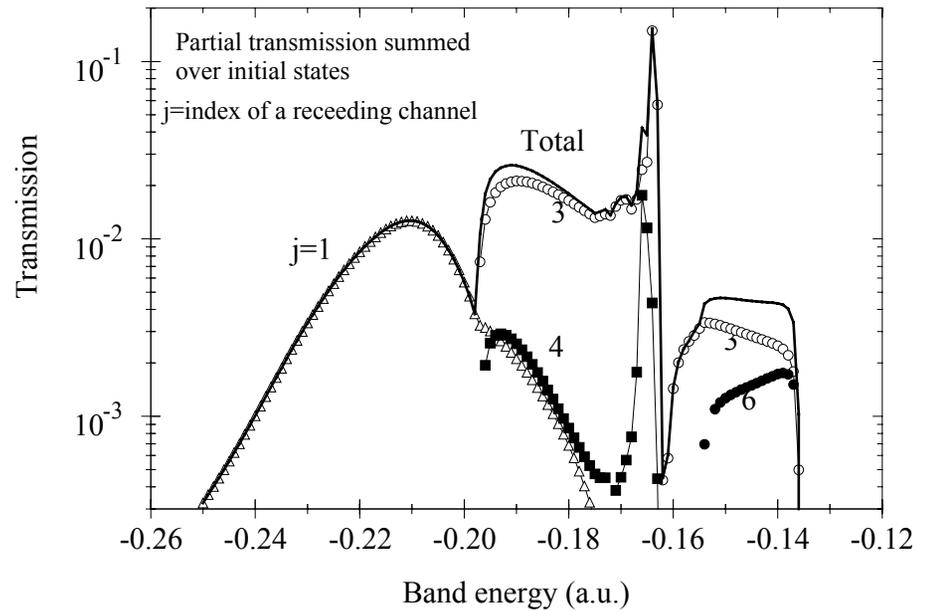


Consider partial contributions of Bloch states
Asymptotically no contribution of evanescent states

Partial transmissions between various Bloch states



Partial transmissions summed over initial states



Summary

- *Significant advances in theory of electron transport through leads and molecule*
- *Tools for ab-initio structure calculations of large metal-organic systems*

Future Work

- *Finite electric bias transport theory- conductance*
- *Numerical experimentation for a fast, practically realizable molecular switch*
- *Further parameterization of potentials for MD of SAMs, conductance of SAMs*

Examples of Currently Available HPC's

•IBM-SP3 (Production machines)

–LBNL/NERSC Seaborg:

- 184 Winterhawk-II nodes, 16 P3-II/node, 3000 proc, 32GB/node,
- 5 Tflops.

–ORNL/CCS Eagle:

- 184 Winterhawk-II nodes, 4 P3-II/node, 736 proc, 2GB/node,
- 1 Tflops.

•IBM-SP4 (Currently Testing)

–ORNL's Cheetah:

- 24 Regatta nodes, 32 P4/node, 768 proc., 1 TB/machine,
- 4 Tflops.

Developments: IBM's Blue Gene Project

November 9, 2001 -- IBM today announced a partnership with the Department of Energy's National Nuclear Security Agency to expand IBM's Blue Gene research project. IBM and NNSA's Lawrence Livermore National Laboratory will jointly design a new supercomputer in the Blue Gene family. Called *Blue Gene/L*, the machine will be at least 15 times faster, 15 times more power efficient and consume about 50 times less space per computation than today's fastest supercomputers.

~200 TFlops

<http://www.research.ibm.com/bluegene/>

The Blue Gene Project

- In December 1999, IBM Research announced a 5 year, \$100M US, effort to build a petaflop scale supercomputer to attack problems such as protein folding.
- The Blue Gene project has two primary goals:
 - ▶ Advance the state of the art of biomolecular simulation.
 - ▶ Advance the state of the art in computer design and software for extremely large scale systems.
- In November 2001, a partnership with Lawrence Livermore National Laboratory was announced.



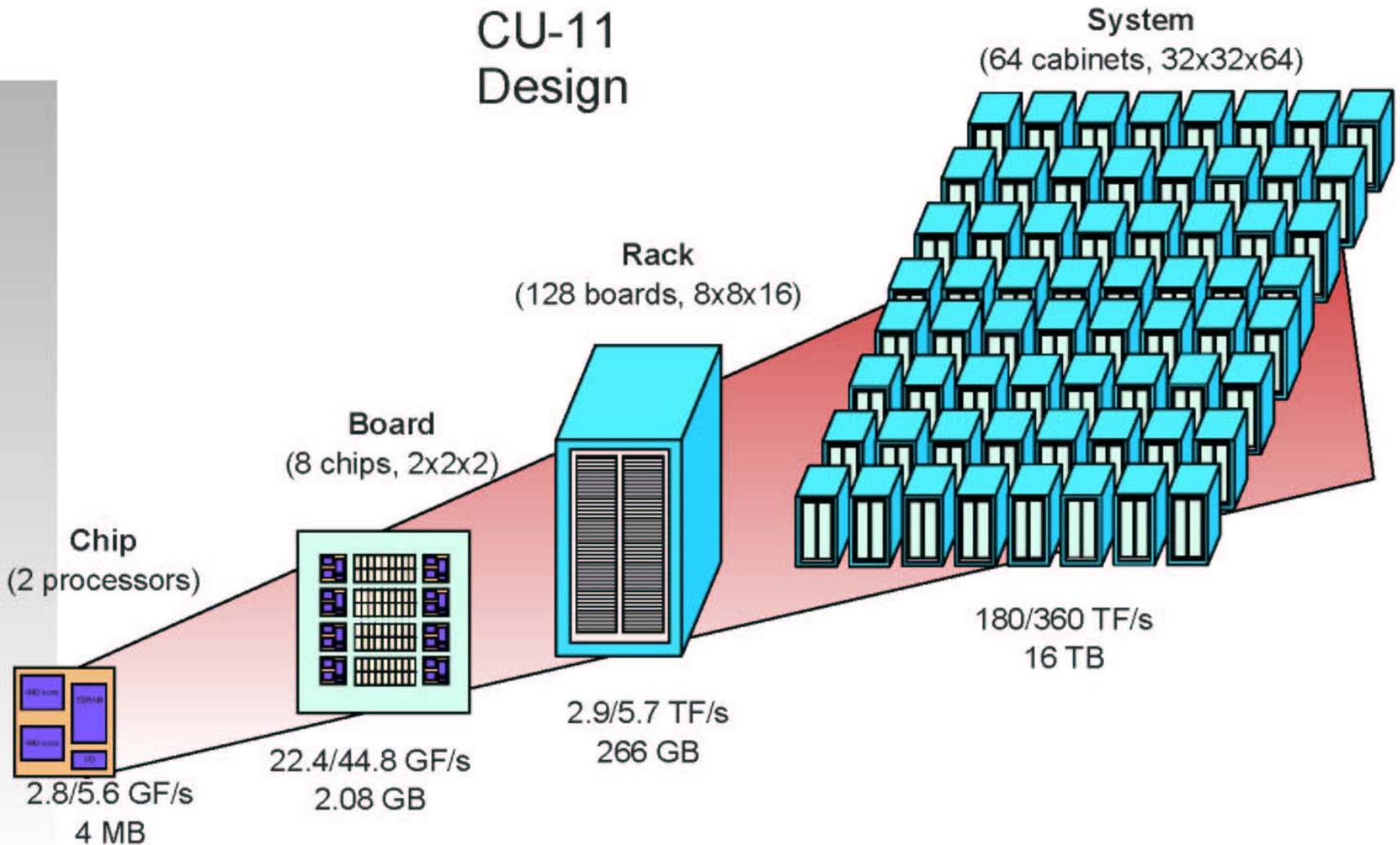
Blue Gene/L

- Massively parallel architecture applicable to a wide class of problems.
- Third generation of low power - high performance super computer
 - ▶ QCDSF (600GF based on Texas Instruments DSP C31)
 - Gordon Bell Prize for Most Cost Effective Supercomputer in '98
 - ▶ QCDOC (20TF based on IBM System-on-a-Chip)
 - Collaboration between Columbia University and IBM Research
 - ▶ Blue Gene/L (180/360 TF)
 - Processor architecture included in the optimization
- Outstanding price performance
- Partnership between IBM, ASCI-Trilab and Universities
- Initial focus on numerically intensive scientific problems



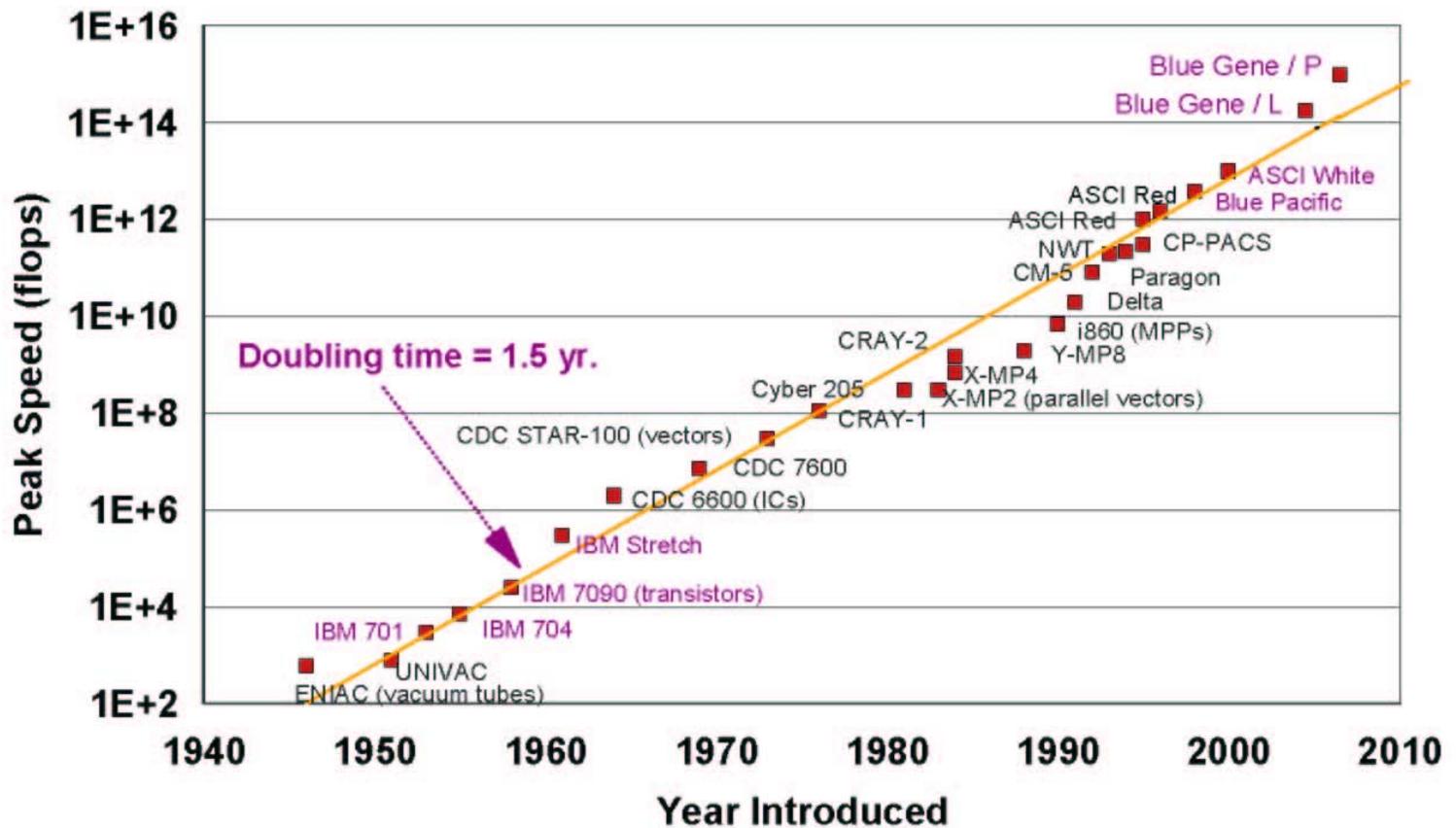
Blue Gene/L

CU-11 Design





Supercomputer Peak Performance



Summary

- The Future is Bright!
 - HPC capacity continues to rapidly increase.
 - Look forward to ~ 200 Tflops machines.
- ... But also challenging! We need
 - Effectively utilize these resources to increase the rate of scientific discovery.
 - Methods and codes that scale to 10^5 processors!

Current Status

- Understanding of nanoscale phenomena and devices requires
 - Simulation over a large range of length and time scale,
 - Wide range of approaches are required.
- Computational nanoscience (and Mat. Sci. in general) is increasingly evolving toward large-scale problems.
 - Required expertise not found in individual researcher.
- Current Scientific Software Development:
 - Individuals/small groups for own purposes, interests, use.
 - Monolithic approach/code to solve a problem at a single scale.
 - Codes live much longer than HPCs.
 - Cottage Industry Approach.

Opportunity

- Multiscale/Multiphysics Simulations call for a different approach to scientific HPC software design.
 - Old model does not possess flexibility, ease of use, or reuse.
- Community Software Development/Community Codes:
 - Open source code repository:
 - Open source software tool set:
 - Encapsulates basic elements,
 - Basis for future community code development.
 - Common Problem Solving Environment and Pre/Post processing SW.
 - Interdisciplinary teams to develop new methods/approaches.
- Advantages:
 - Reduce redundancy in development and maintenance
 - Maximize efficiency of user community.
 - Complementary apps evolve to be software compatible.
 - Community \$\$ support for community software.

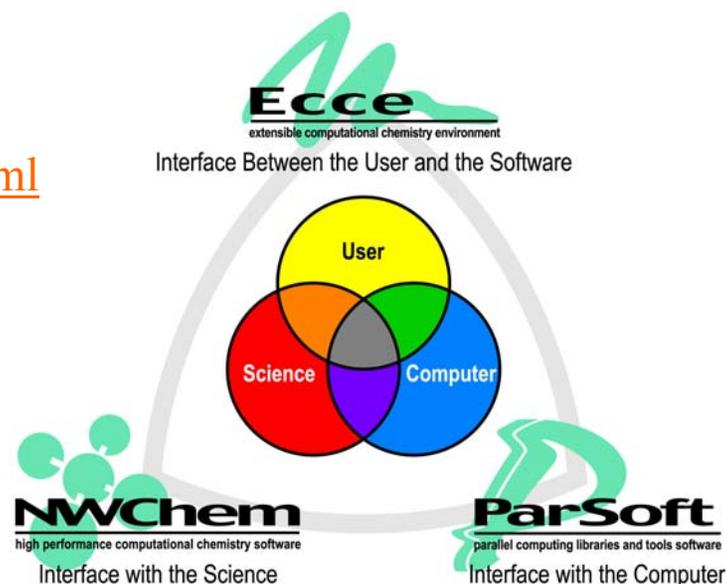
Examples Exist For Community Codes

- PNNL's Environmental Molecular Science Laboratory
 - NWChem, Ecce', ParSoft

www.emsl.pnl.gov:2080/docs/mssg/index.html

www.emsl.pnl.gov:2080/docs/nwchem/nwchem.html

- Columbia-BNL-Riken QCD Center



- At ORNL's CCS, we are working to develop such ideas into a Computational Materials Research Facility.