

AMES LABORATORY

COMPUTATIONAL CHEMISTRY

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www.msg.ameslab.gov

PARTICIPANTS



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- **Mark Gordon, Mike Schmidt, Klaus Ruedenberg**
 - Electronic structure theory
 - Highly correlated wavefunctions
 - Highly scalable codes: GAMESS
- **James Evans:**
 - Non-equilibrium statistical mechanics
 - Kinetic MC studies of surface phenomena

COLLABORATIONS



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- **Piotr Piecuch (Michigan State)**
 - Coupled cluster methods
- **Don Truhlar (Minnesota)**
 - GAMESS-RATE, GAMESS-SOL
- **Scalable Computing Lab: Ames Lab**
 - Scalable Systems Software project (Bode)
 - Programming Models project (Kendall)
- **PNNL**
 - GAMESS <-> NWChem collaborations

OBJECTIVES #1



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- **Highly Accurate Quantum Chemistry Codes**
 - **Full Configuration Interaction (Full CI)**
 - **Exact wavefunction for a given atomic basis**
 - **Serves as benchmark for approximate correlated methods:**
 - truncated CI
 - coupled cluster (CC - see Piecuch poster)
 - Many body perturbation theory (MBPT)

OBJECTIVES # 2



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- **Highly Accurate Quantum Chemistry Codes**
 - **Full Configuration Interaction (Full CI)**
 - **Currently limited to modest basis sets, atoms, very small molecules**
 - **Need scalable code to apply Full CI more broadly**
 - **Replicated data algorithm: limited molecular size**
 - **Distributed data algorithm: communication issues**
 - **Programming Models interface: Data compression (Kendall)**

OBJECTIVES # 3



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- **Highly Accurate Quantum Chemistry Codes**
 - **Scalable General CI**
 - Full CI limited in scope
 - Most truncated CI based on “full space” *ansatz*
 - All single excitations (SCI, “Tamm-Dancoff”)
 - All single & double excitations (CISD), ...
 - Quickly runs out of steam
 - Extend scope of CI by eliminating “deadwood”: only include important configurations
 - Ivancic & Ruedenberg, TCA, 106, 339 (2001)

OBJECTIVES # 4



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- **Highly Accurate Quantum Chemistry Codes**
 - Scalable MCSCF
 - Frequently require orbitals optimized in CI space
 - Diradical species
 - Transition states
 - Electronic excited states
 - Unsaturated transition metals
 - Unusual structure & bonding
 - More demanding than CI
 - Optimize *both* orbital & CI coefficients
 - MCSCF CI space usually smaller than in CI calculation
 - CI or perturbation theory adds “dynamic correlation”

OBJECTIVES # 5



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- **Highly Accurate Quantum Chemistry Codes**
 - Scalable MCSCF
 - Most common MCSCF implementation: FORS/CAS
 - Active space defined “chemically”
 - All configurations obtained by distributing m electrons in n orbitals: CASSCF(m,n)
 - Replicated data algorithm in place (Theresa Windus)
 - Distributed data algorithm in progress (Graham Fletcher, Yuri Alexeev)
 - Limitation: ~ CASSCF(14,14) + dynamic correlation

OBJECTIVES # 6



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- **Highly Accurate Quantum Chemistry Codes**
 - **Expand Accessible MCSCF Active Space**
 - **MCSCF based on General CI: eliminating deadwood**
 - Increases active space by eliminating un-needed configurations
 - **Q-CAS based on localized orbitals**
 - Subdivides active space into sub-spaces defined by localized orbitals
 - **Efficient Scalable Coupled Cluster Methods: Piecuch**
 - **Open Shell Perturbation Theory Gradients**

OBJECTIVES # 7



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- **Spanning Multiple Time and Length Scales**
 - Scalable Kinetic Monte Carlo Codes with Focus on Surface Phenomena
 - Develop New Integrated Atomistic & Mesoscale Descriptions of Surface Phenomena
 - Pattern formation in catalytic surface reactions
 - Nanostructure evolution during surface processes
 - Chemical vapor deposition (CVD)
 - Etching of semiconductor surfaces
 - Heterogeneous catalysis
 - Interface with continuum mesoscale modeling

Multi-scale Modeling of Etching & CVD Growth on Semiconductor Surfaces [especially Si(100)2x1]



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QUANTUM CHEM (Surface-Integrated **MO/MM**) → REACTION ENERGETICS

- * *ab-initio* (Molecular Orbital) treatment of key (local) surface reaction region
- * lower level (Molecular Mechanics) treatment of extended surrounding region



KINETIC MONTE CARLO SIMULATION OF ATOMISTIC MODELS:

- * Input key atomistic rates based on SIMOMM energetics (activation barriers)
- * Challenges: - need extensive catalogue of (local) environment-dependent rates
- large spread time-scales/rates (treated by n-fold algorithms)
- * Capabilities: describes kinetics & morphology on correct time & length scales



COARSE-GRAINED CONTINUUM MODELS (...*MUST BE DERIVED*):

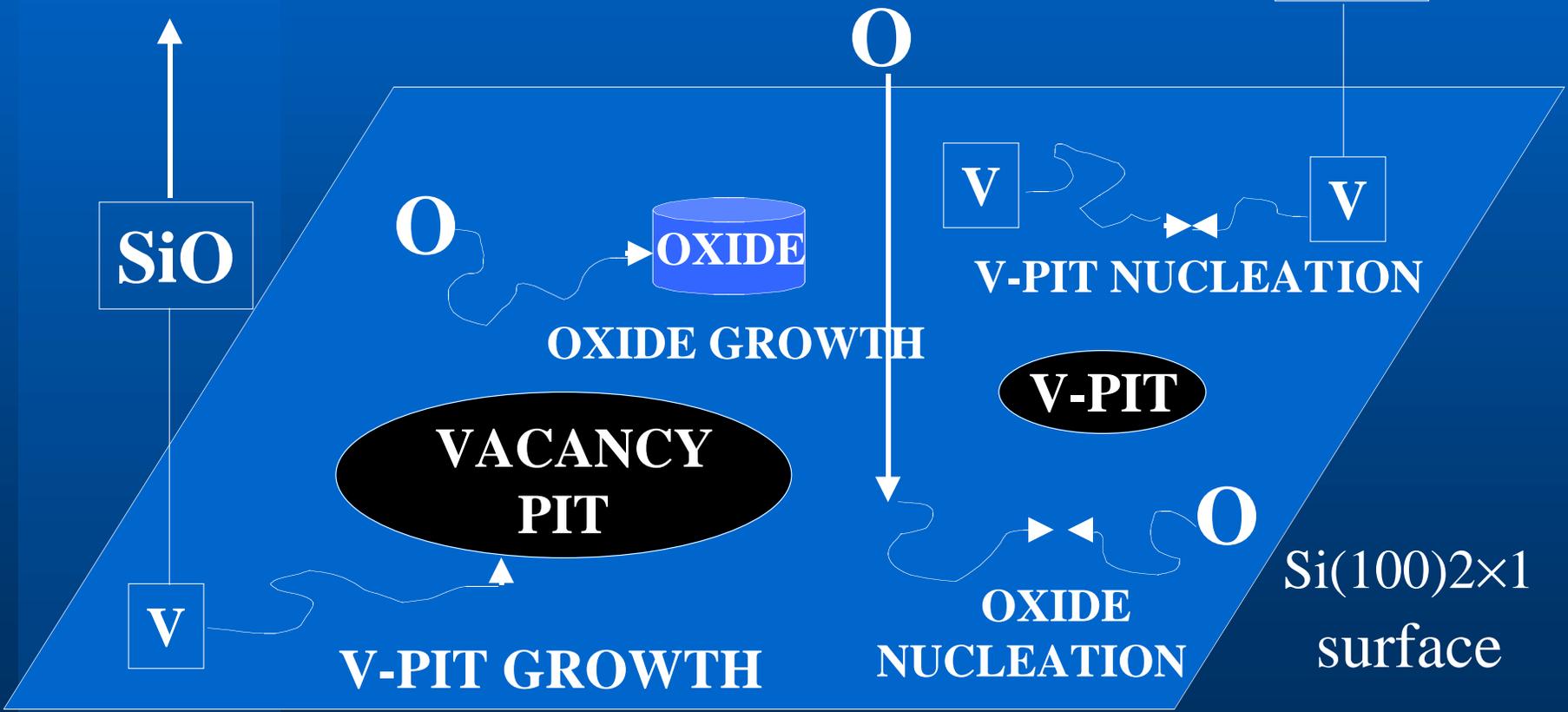
- * Mesoscale parameters describing kinetics & morphology from atomistic model
- * Need efficient algorithms for interface propagation (e.g., level set methods)
- * Computational challenges (numerical PDE's) may relate to Applied Math ISIC's

SCHEMATIC of MODEL being developed for ETCHING [VACANCY PIT FORMATION] and SURFACE OXIDE FORMATION upon exposure of Si(100)2×1 to oxygen (O)



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SiO



Nb. V = vacancy (i.e., a missing Si in the surface layer resulting from etching via SiO desorption)

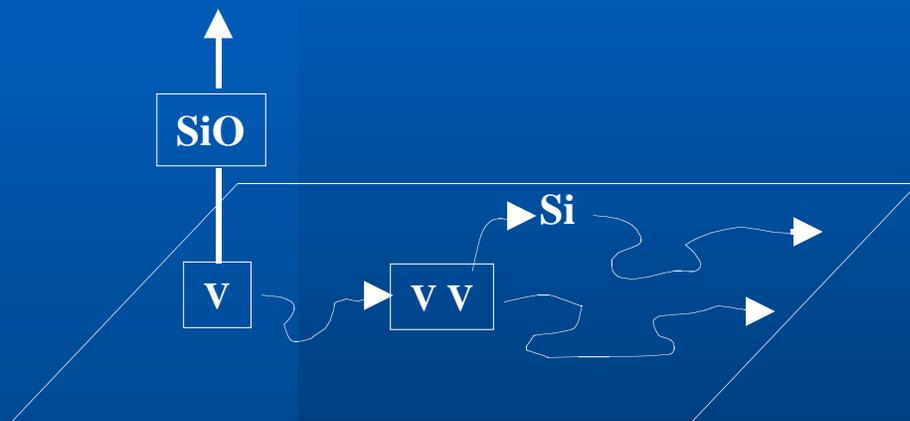
KEY PARAMETERS IN ATOMISTIC MODEL:

O(gas) adsorption rate, P_O (from experiment)

SiO desorption rate/barrier, d (from SIMOMM)

O(ads) diffusion rate, h_O (from SIMOMM)

Single vacancy* diffusion rate, D_{SV} , on Si(100) - expt./theory



*A single vacancy (SV) quickly converts to a divacancy (DV) plus an Si-atom; our simplest model with only SV's sets $D_{SV}=D_{DV}$

Note: diffusion of all species is anisotropic.

FACTORS IN CONTINUUM MODELING:

Stochastic nucleation & deterministic growth of oxide islands and vacancy pits determined from O and V diffusion fields.

Island/pit growth algorithms? Cooperative SiO desorption?

A LONG-TERM GOAL:

- *Develop versatile KMC simulation software for atomistic models of a *selected class* of etching and growth processes on Si(100) 2×1
- *Integrate with QChem codes (e.g., SIMOMM) for input parameters

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EXAMPLES OF ETCHING /GROWTH PROCESSES:

- *Homoepitaxy (MBE) of Si on Si(100) and H-Si(100)
- *Reaction of Si(100) with O, O₂, and H₂O (etching & oxidation)
- *Etching of Si(100) with halogens
- *Chemical Vapor Deposition (CVD) on Si(100) with silane/disilane

COMMON INGREDIENTS:

- *Coupling of deposition/reaction/etching kinetics with evolution of film morphology (also connects with PDE's/interface propagation)
- *Many common adsorbed species in above processes (Si, O, H,...) exploited in code structure (allows switching on/off various processes)

SIMPLE LMO E_{CORR} SCHEME

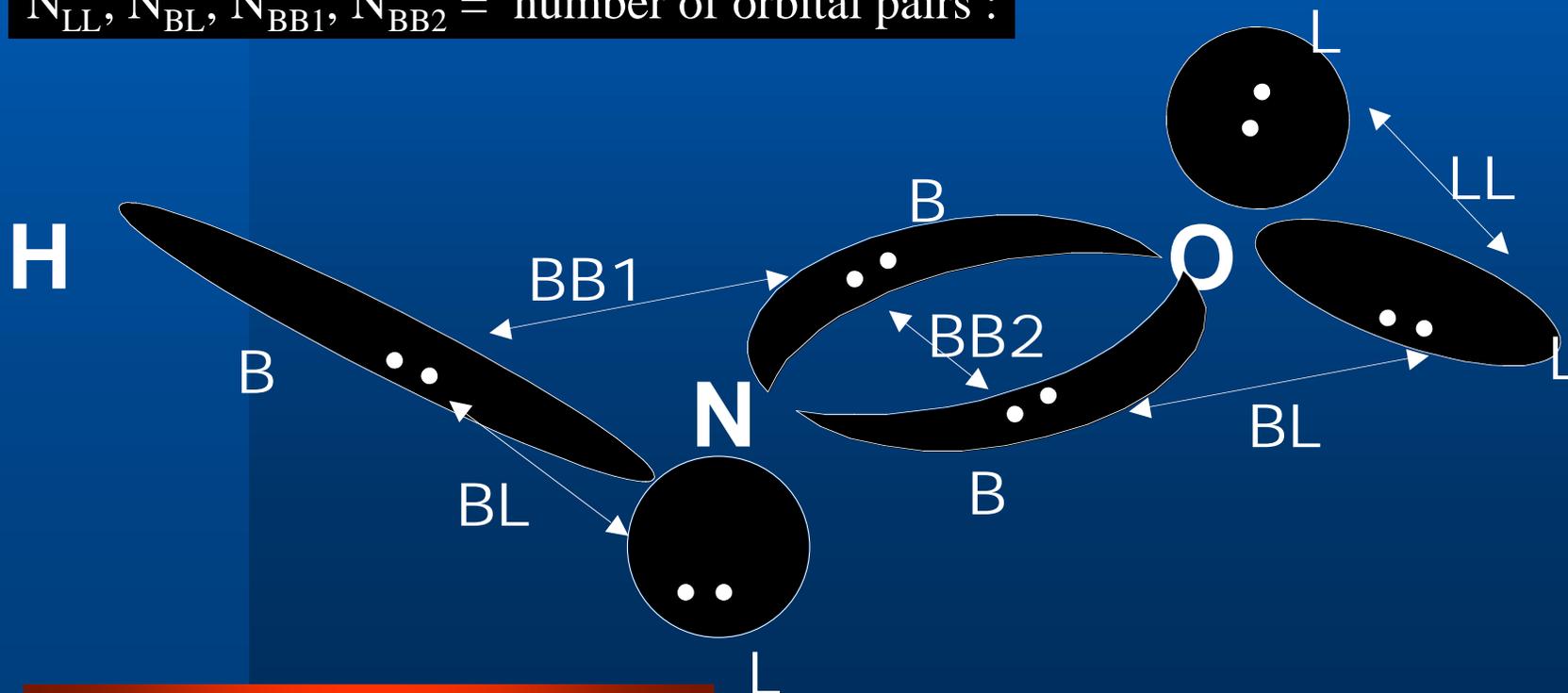


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$$E_{\text{corr}}(\text{mh}) \sim 29.0 N_L + 34.0 N_B + 26.1 N_{LL} + 26.7 N_{BL} + 26.2 N_{BB2} + 14.7 N_{BB1}$$

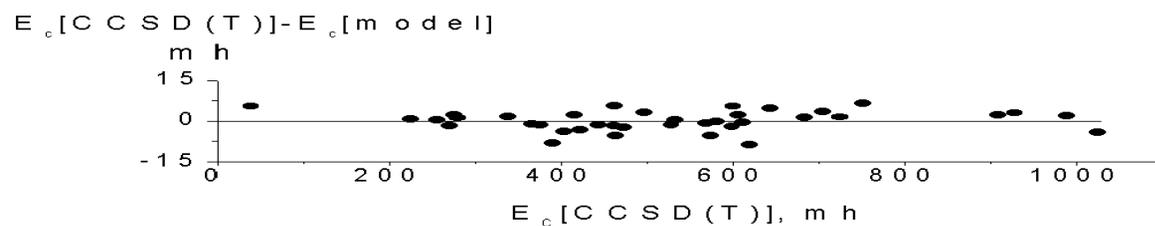
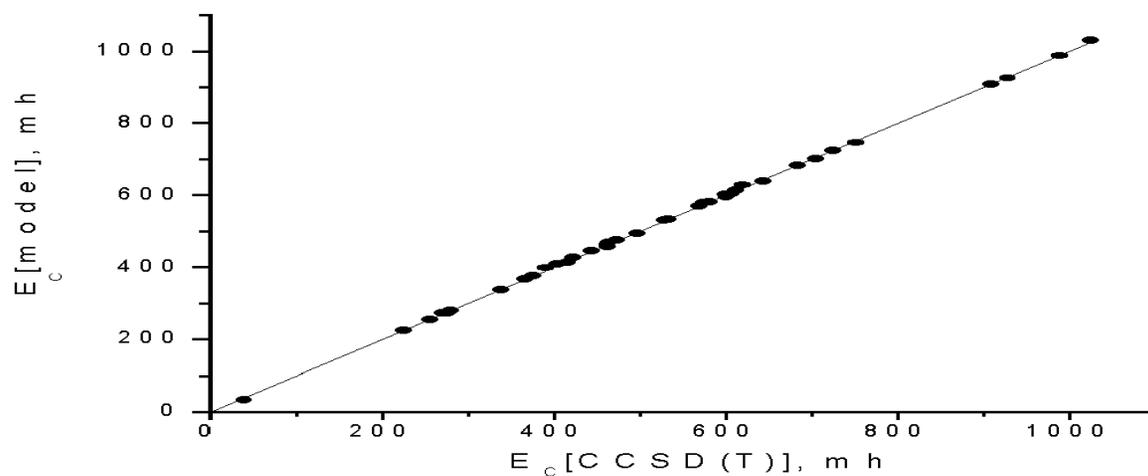
N_L, N_B = number of lone-pair and bonding orbitals

$N_{LL}, N_{BL}, N_{BB1}, N_{BB2}$ = number of orbital pairs :





Model versus CCSD(T) correlation energies
for 38 molecules from H_2 to C_6H_6
(Mean absolute deviation = 2.85 m h)



INTERIM CONCLUSIONS



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- **Localized orbitals are key to eliminating deadwood**
 - Example: only 25,000 determinants are “live” in the full valence space of 160,000,000 determinants for CO₂
- **In the LMO representation, correlation effects are very short range, resulting in a nearly linear increase in E_{corr} with # of valence electrons**
- **Tools are developed in terms of *local* building blocks: ideal for scalability**
- **Next steps:**
 - Addition of *local* single & double excitations
 - Implementation of energy derivatives

FCI Algorithmic Limitations



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- **Why is FCI important?**
 - Most accurate method available.
 - A Measuring Stick for all other correlated methods.
- **How can we expand the applicability of FCI?**
 - What are the limitations to the method?
 - Cost of producing the matrix-vector product.
 - Available cycles
 - Factorial based scaling based on the number of orbitals (e.g., basis functions) and electrons.
 - Size of the matrix-vector product.
 - Local or aggregate Memory
 - A proper data compression scheme can better utilize the available storage space.

FCI and the Compression Library



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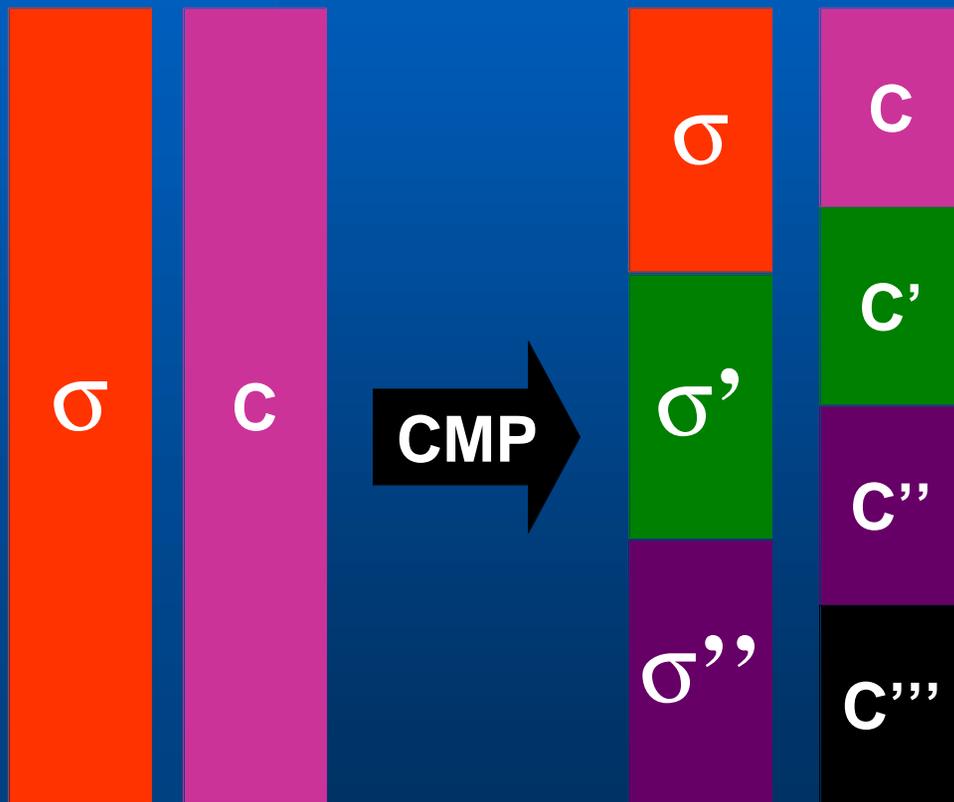
- **The Compression Library**

- developed for general use; targeted at FCI.
 - Standard tradeoff of cycles (free) for storage (expensive).
- Provides put, get, accumulate, BLAS operations on compressed vectors.
- Mixed compression level operations allowed.
 - Matrix-Vector Product may be stored more accurately than the guess vectors.
- Uses multiple standard compression algorithms with a user defined compression level and zero threshold.
- Expandable API to meet application needs.

FCI and the Compression Library



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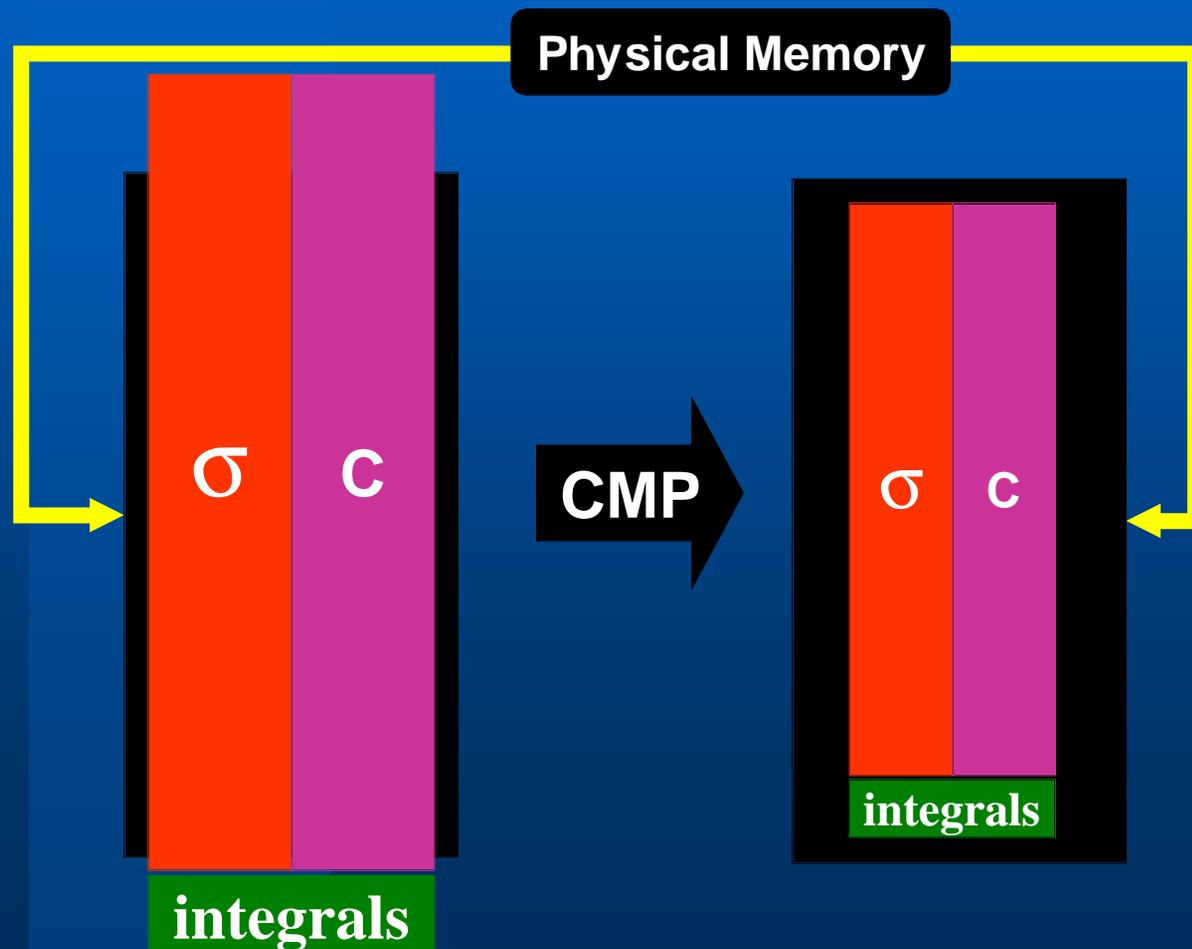


More operations can take place in memory before required access to secondary storage.

FCI and the Compression Library



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**Enable
computations
that were not
previously
possible on a
fixed
computational
resource.**

Parallel implementation of FCI in GAMESS

Objective of parallel implementation

- ❖ Efficient parallel FCI algorithm for clusters
- ❖ A cooperative effort on parallel CASSCF code in GAMESS

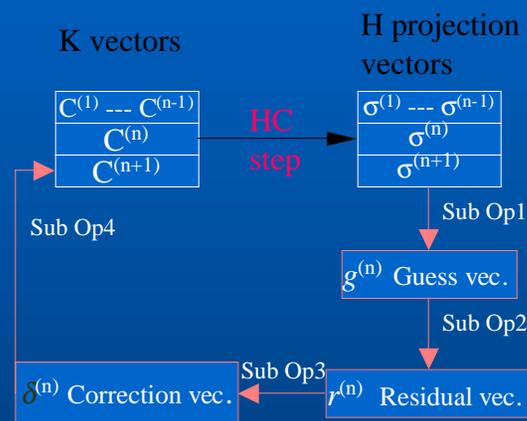
Description of FCI in GAMESS

- ❖ FCI program solves the Schrödinger equation by expanding the wavefunction as a linear combination of basis functions.

$$\hat{H}\Psi = E\Psi \quad \Psi = \sum_k C_k \Phi_k \quad \longrightarrow \quad HC = EC$$

- ❖ GAMESS FCI code uses determinants as basis functions for efficient computing of Hamiltonian matrix elements.
- ❖ Davidson-Liu Diagonalization method is employed to obtain one or several lowest eigen vectors

Outline of Davidson iteration



Sub Op1. Diagonalization of K space

Sub Op2. $r^{(n)} = Hg^{(n)} - Eg^{(n)}$

Sub Op3. Relaxation step

Sub Op4. Orthogonalization and normalization

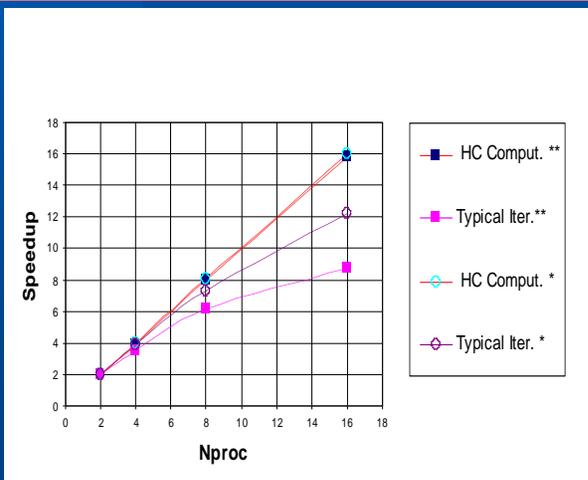
- ❖ The most computational demanding part is HC step, i.e, to compute the Hamiltonian projection for each k-space vector.

Parallel performance and analysis on PC clusters.

- Reasonable speedup achieved with our parallel FCI code running on PC cluster up to 16 nodes.
- The HC computational part scales almost perfectly, illustrating the effectiveness of DLB.

Parallel FCI performance on PC clusters

(PII 400MHz, 100Mbps Fast Ethernet, 16 Nodes)



*Ex. 1 H₃CSiH₂ doublet: 10,306,296 Dets generated by distributing 13 electrons among 14 active orbitals.

** Ex. 2 H₃COH singlet: 11,778,624 Dets generated by distributing 14 electrons among 14 active orbitals

- Ratio of communication to computation has a significant effect on overall speedup. The very large ratio of example2 indicates the poor performance of collective operation on PC clusters is the bottleneck for replicated data implementation.

Timing analysis of one typical FCI iteration on 16 nodes.

	Example 1	Example 2 ***
Dim.	10,306,296	11,778,624
Spdup	12.2	8.7
Ratio	0.34	0.91
T_subop	0.3%	0.5%
T_commu	25.4%	47.4%
T_compu	74.4%	52.1%

*** For singlet calculation (Example2) the computational effort can be halved by applying the relationship $\sigma(a,b)=(-1)^S \sigma(b,a)$

Conclusions



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- ◆ We have implemented a parallel, mostly replicated data, FCI code. Example calculations show that it is possible to run parallel FCI calculations effectively on PC clusters.
- ◆ Distributed data approach is used in the code to store k-space vectors. This benefits both memory saving and the parallel performance of subspace operations.
- ◆ The replicated data approach for HC step has both advantages and disadvantages.
 - Upside:
 1. No communication inside HC computation. This part can be parallelized very efficiently with our dynamic load balancing scheme.
 2. The replicated data model is applicable for most CASSCF calculations, especially running on clusters with large memory/ node.
 - Downside:
 1. Memory bottle neck for very large FCI calculation. It cannot use the aggregate memory on MPP effectively.
 2. The inefficient collective operations is the major performance bottleneck.
- ◆ A fully distributed parallel FCI code is being developed.