

Advanced Methods for Electronic Structure

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MICS SAP

BES
SciDAC

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Outline

- Challenges in computational chemistry – BES SciDAC
- Multiresolution quantum chemistry
 - Practical computation in higher dimensions
 - Accuracy, timing and scaling
- The Tensor Contraction Engine
 - Automated synthesis of high-performance programs from the many-body equations
 - DOE SciDAC + NSF/ITR collaboration
- Full Configuration Interaction on the ORNL Cray X1
 - New benchmark calculations possible on emerging ORNL ultrascale computing resources. Gan (previously with Gordon) has developed a new parallel-vector algorithm.

Theoretical Challenges

- Basis sets – one electron, two electron
- Linear-scaling methods with accurate correlation
- Rigorous development of density functional theory
- Open-shell problem
- Heavy elements – all of the above + relativity
- Physically relevant models and questions
- Dynamics, excited states, scattering, response
- Long time dynamics
- QM – nano – micro – macro

Molecular electronic Schrödinger equation

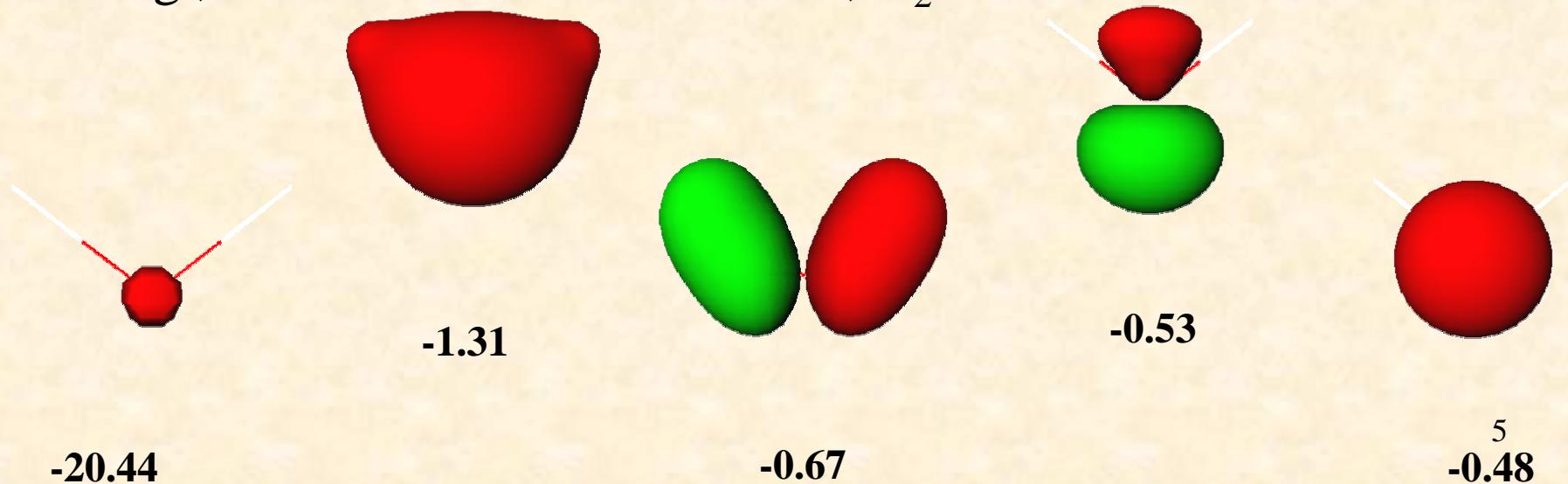
- A 3-N dimensional, non-separable, second-order differential equation

$$H\Psi(r_1, r_2, \dots, r_n) = E\Psi(r_1, r_2, \dots, r_n)$$

$$H = -\frac{1}{2} \sum_{i=1,m} \nabla_i^2 - \sum_{\substack{i=1,n \\ \mu=1,N}} \frac{Z_\mu}{|r_i - r_\mu|} + \sum_{\substack{i=1,n \\ j=1,i-1}} \frac{1}{|r_i - r_j|}$$

“Independent” particle models

- Atomic and molecular orbitals
 - Each electron feels the *mean field* of all other electrons (self-consistent field, Hartree-Fock)
 - Replaces linear 3N-D Schrödinger w. non-linear 3-D eigen-problem
 - Provides the structure of the periodic table and the chemical bond
 - Linear combination of atomic orbitals - LCAO
 - E.g., molecular orbitals for water, H₂O



The Full-CI wavefunction

- Within a given one-particle basis, the exact solution is formed by a linear combination of all possible excitations from the occupied (i,j,k,\dots) to the virtual orbitals (a,b,c,\dots)
 - In a complete basis, it is called complete-CI and it is the *exact solution* to the BO-Schrödinger eqn.
 - Only full-CI is invariant to mixing occupied with virtual orbitals.

$$\Psi = c_0 |0\rangle + \sum_i c_i^a \left| \begin{smallmatrix} a \\ i \end{smallmatrix} \right\rangle + \sum_{\substack{i>j \\ a>b}} c_{ij}^{ab} \left| \begin{smallmatrix} ab \\ ij \end{smallmatrix} \right\rangle + \sum_{\substack{i>j>k \\ a>b>c}} c_{ijk}^{abc} \left| \begin{smallmatrix} abc \\ ijk \end{smallmatrix} \right\rangle + \dots$$

singles doubles triples

- On Cray X1 at ORNL 20 billion determinants now routine; with new S/W and expected H/W upgrades are planning for 2-500 B
- Community effort (ORNL, Gordon, Sherrill, Taylor, NIST, ...)

Many-body Coupled Cluster Methods

- If the energy is additively separable the wavefunction must be multiplicatively separable

$$(H_A + H_B) \Psi = (E_A + E_B) \Psi$$

$$\Rightarrow \Psi = \Psi_A \Psi_B$$

- CI is a linear expansion ... CC is non-linear

$$\Psi_{CI} = \hat{C} |0\rangle = |0\rangle + \sum_i \sum_a c_i^a \begin{vmatrix} a \\ i \end{vmatrix} + \sum_{i>j} \sum_{a>b} c_{ij}^{ab} \begin{vmatrix} ab \\ ij \end{vmatrix} + \dots$$

$$\Psi_{CC} = e^{\hat{T}} |0\rangle = \left(1 + \hat{T} + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \dots \right) |0\rangle$$

- T is an excitation operator from occupied to unoccupied (virtual)
- Even if T only includes double excitations, the CC wavefunction includes quadruple, hextuple, ...

Many-electron correlation problem - I

- Exact wavefunction has a cusp as two electrons coalesce
 - E.g., simplest form of helium atom wave function that satisfies the nuclear and electronic cusp conditions

$$\psi(r_1, r_2, r_{12}) = \left(1 + \frac{1}{2} r_{12}\right) e^{-2(r_1+r_2)}$$

- Such wave functions have historically been impracticable except for very small systems (Hylleraas, Morgan)
 - Inclusion of r_{12} (Kutzelnigg, Klopper, Noga, Taylor, Schaefer, Valeev)
 - Instead represent the two-electron wavefunction as products of one-electron wavefunctions

$$\psi(\underline{r}_1, \underline{r}_2) = \sum_{ab} [\phi_a(\underline{r}_1)\phi_b(\underline{r}_2) + \phi_b(\underline{r}_1)\phi_a(\underline{r}_2)]$$

Many-electron correlation problem - II

- Convergence of atomic correlation energy (Hill, Reed)
 - Saturate basis up to angular momentum L

$$E_L^{corr} = E_\infty^{corr} + c(L+1)^{-3}$$

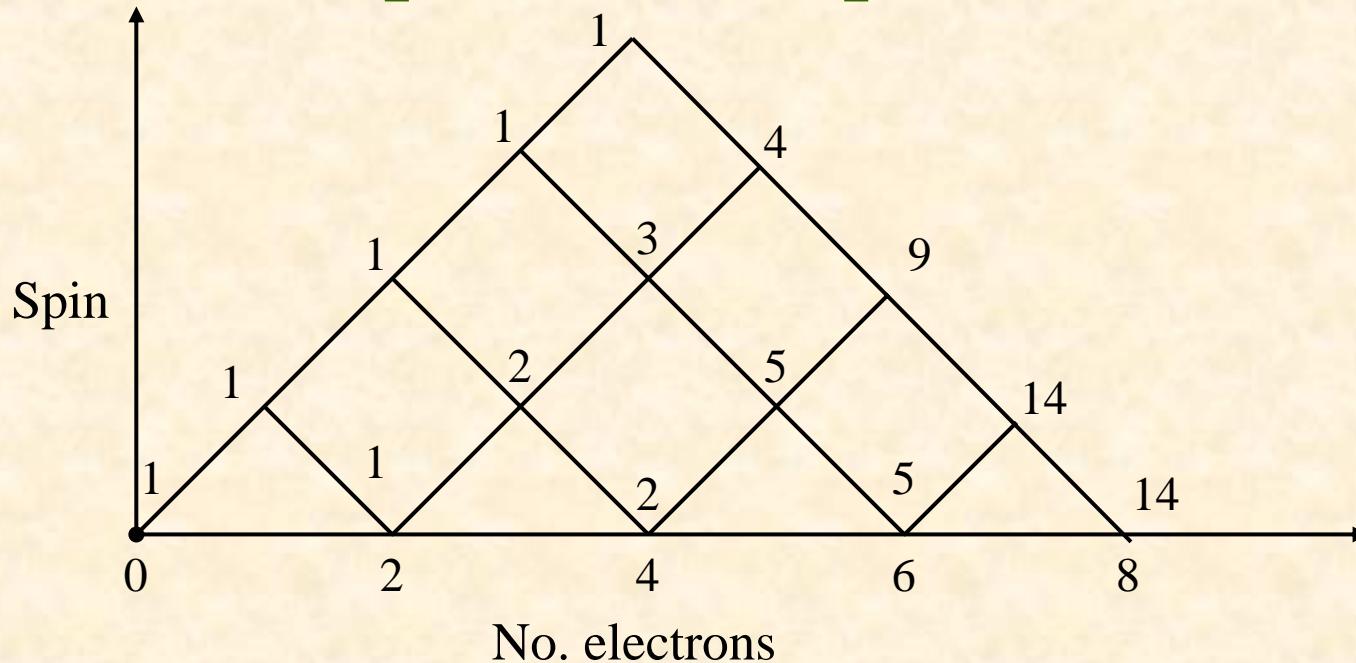
L	d (2)	f (3)	g (4)	h (5)
(L+1) ⁻³	0.04	0.016	0.008	0.0046

- Correlation-consistent basis sets (Dunning)
 - cc-pVXZ (X=2,3,...) - designed to converge smoothly
 - $\varepsilon = O(X^{-1/3})$
 - No. of functions in set is $N = (X+1)(X+3/2)(X+2)/3 = O(\varepsilon^1)$
 - Calculation cost is at least $O(X^4)$, thus ...

$$\text{Cost} \propto \varepsilon^{-4}$$

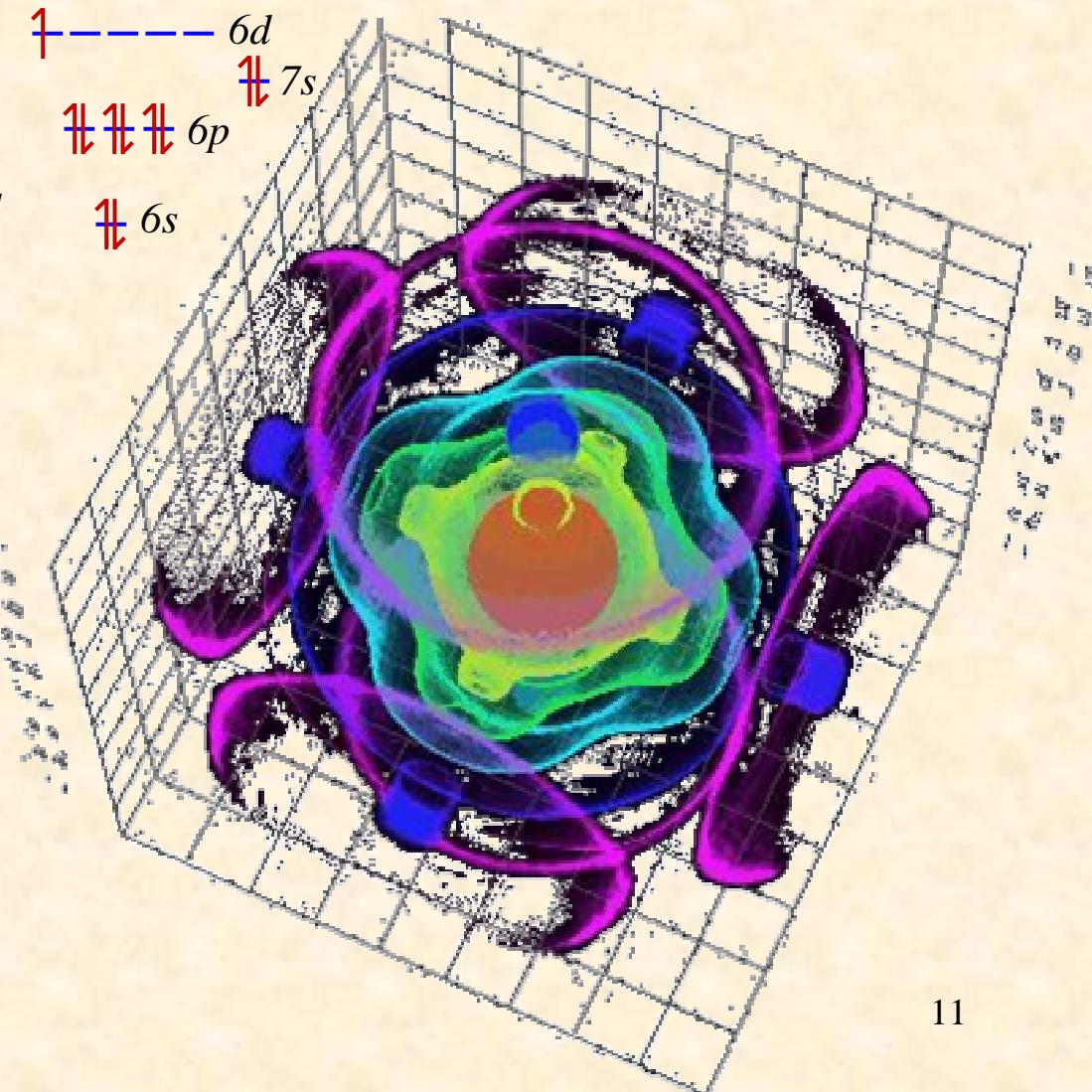
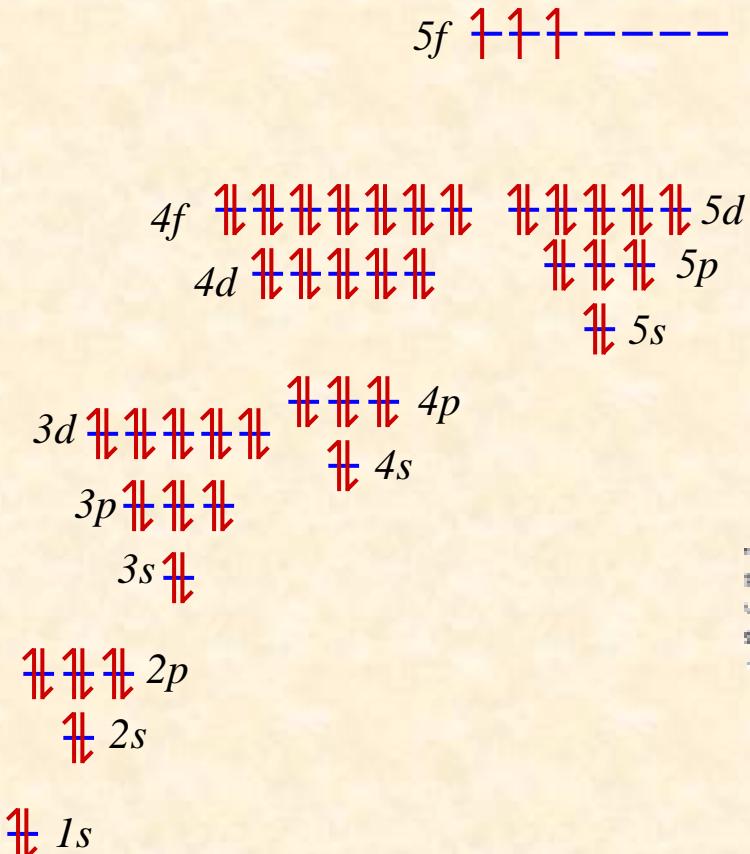
- r_{12} methods at best $O(\varepsilon^{2.4})$
- Target for multiresolution approach is $O(-\log \varepsilon)$ 9

Open-shell problem



- Unpaired electrons give rise to many spin-states
 - Bond-breaking, excited states, metals
- Problems
 - Grows nearly factorially
 - Must still incorporate dynamic correlation
 - Intruder state problems in perturbation theories

The electronic configuration of *uranium* – the high-nuclear charge and the partially occupied f-orbitals require relativistically correct methods which are expensive for even modest precision.



Dirac Equation

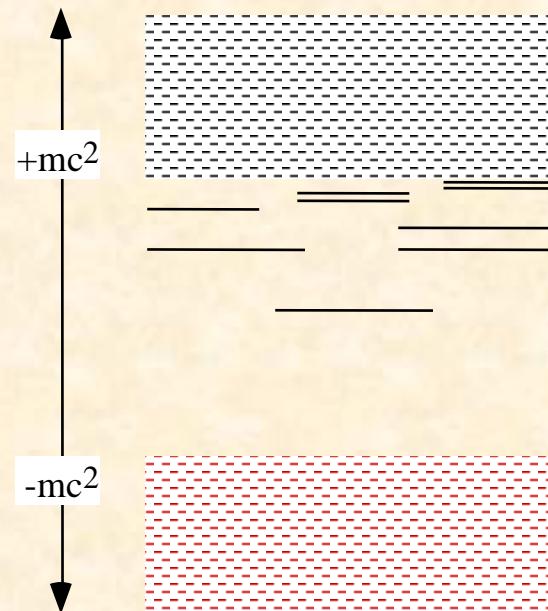
$$\underbrace{\begin{pmatrix} V + mc^2 & c\sigma \bullet p \\ c\sigma \bullet p & V - mc^2 \end{pmatrix}}_{h_i^D} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = \epsilon \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix}$$

One-electron Dirac equation

Many-electron Dirac equation

$$\hat{H} \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} = E \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix}$$

$$\hat{H} = \sum_i^N h_i^D + \frac{1}{2} \sum_{i \neq j}^N \left(\frac{1}{r_{ij}} - \frac{(\alpha_i \bullet \alpha_j)}{r_{ij}} \right)$$



Electronlike continuum

Electronlike Bound states

Positronlike continuum

MADNESS



*Multiresolution
Adaptive
Numerical
Scientific
Simulation*

Multiresolution chemistry objectives

- Complete elimination of the basis error
 - One-electron models (e.g., HF, DFT)
 - Pair models (e.g., MP2, CCSD, ...)
- Correct scaling of cost with system size
- General approach
 - Readily accessible by students and researchers
 - Higher level of composition
 - No two-electron integrals – replaced by fast application of integral operators
- New computational approaches
- *Fast algorithms with guaranteed precision*¹⁴

References

- The (multi)wavelet methods in this work are primarily based upon
 - Alpert, Beylkin, Grimes, Vozovoi (J. Comp. Phys., 2002)
 - B. Alpert (SIAM Journal on Mathematical Analysis 24, 246-262, 1993).
 - Beylkin, Coifman, Rokhlin (Communications on Pure and Applied Mathematics, 44, 141-183, 1991.)
 - Beylkin and Mohlenkamp, (Proc. Nat. Acad. 2002)
- The following are useful further reading
 - Daubechies, “*Ten lectures on wavelets*”
 - Walnut, “*An introduction to wavelets*”
 - Meyer, “*Wavelets, algorithms and applications*”
 - Burrus et al, “*Wavelets and Wavelet transforms*”

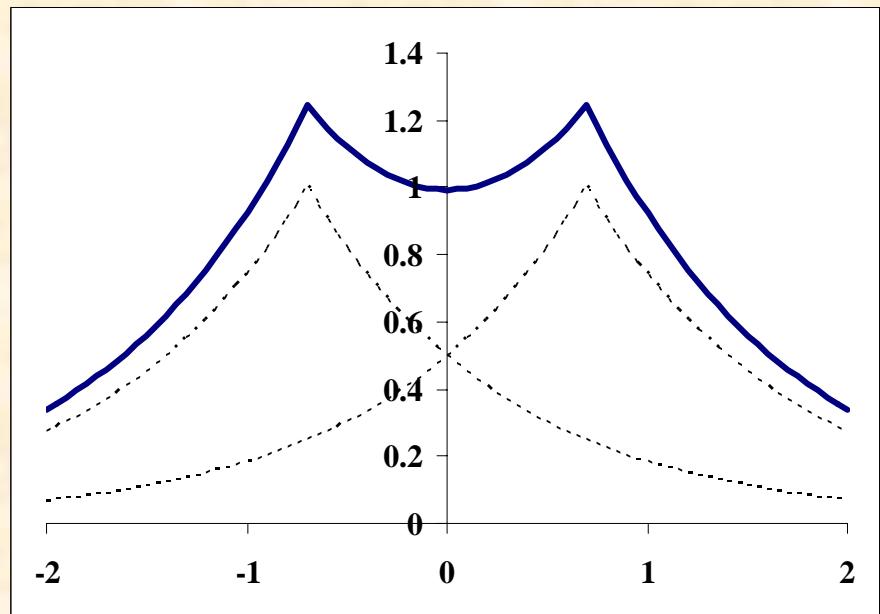
Linear Combination of Atomic Orbitals (LCAO)

- Molecules are composed of (weakly) perturbed atoms
 - Use finite set of atomic wave functions as the basis
 - Hydrogen-like wave functions are exponentials
- E.g., hydrogen molecule (H_2)

$$1s(r) = e^{-|r|}$$

$$\phi(r) = e^{-|r-a|} + e^{-|r-b|}$$

- Smooth function of molecular geometry
- MOs: cusp at nucleus with exponential decay



LCAO

- A fantastic success, but ...
- Basis functions have extended support
 - causes great inefficiency in high accuracy calculations
 - origin of non-physical density matrix
- Basis set superposition error (BSSE)
 - incomplete basis on each center leads to over-binding as atoms are brought together
- Linear dependence problems
 - accurate calculations require balanced approach to a complete basis on every atom
- Must extrapolate to complete basis limit
 - unsatisfactory and not feasible for large systems

How to “think” multiresolution

- Consider a ladder of function spaces

$$V_0 \subset V_1 \subset V_2 \subset \cdots \subset V_n$$

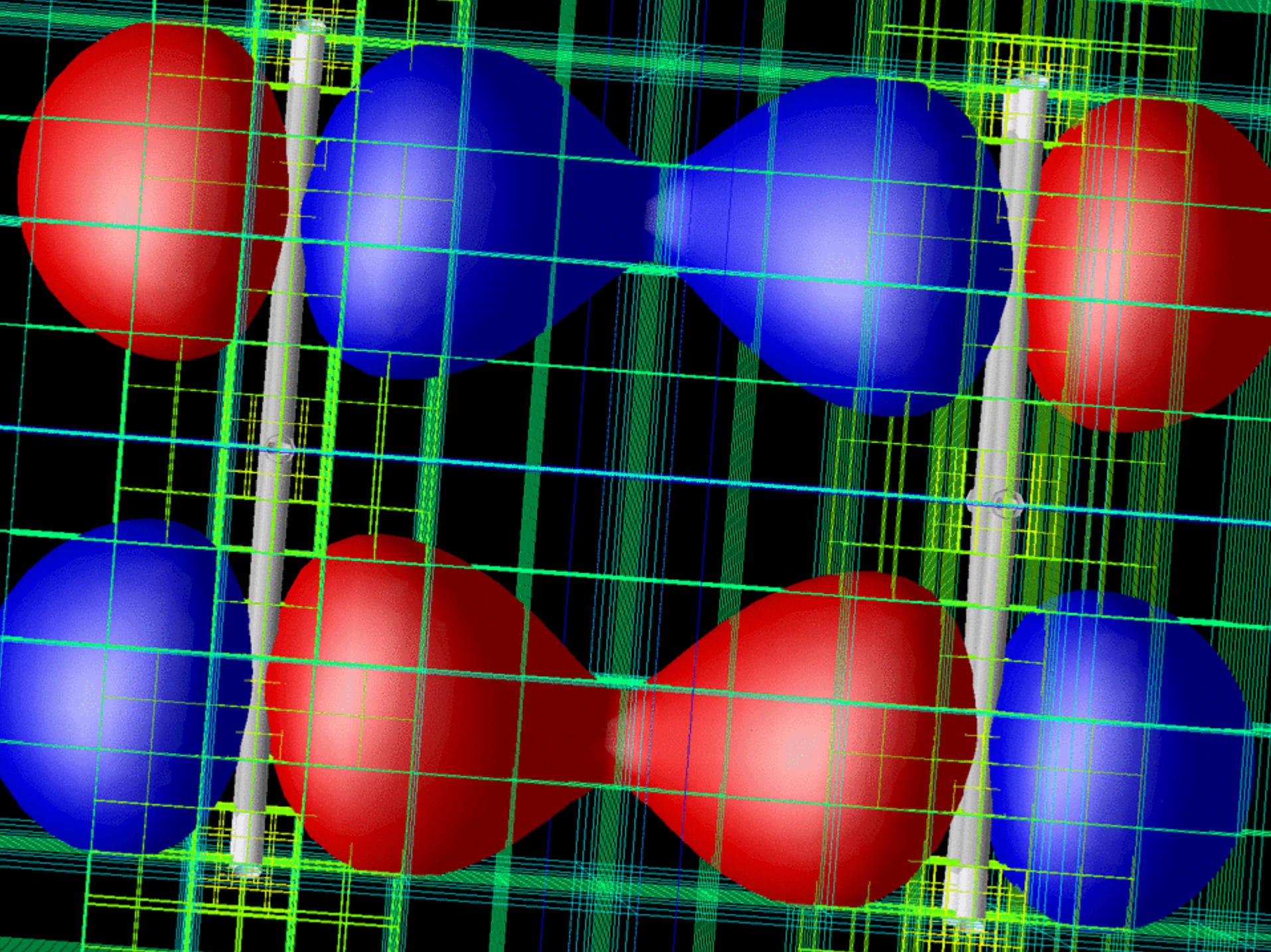
- E.g., increasing quality atomic basis sets, or finer resolution grids, ...

- Telescoping series

$$V_n = V_0 + (V_1 - V_0) + (V_2 - V_1) + \cdots + (V_n - V_{n-1})$$

- Instead of using the most accurate representation, use the difference between successive approximations
 - Representation on V_0 small/dense; differences sparse
 - Computationally efficient; possible insights

- Slice thru grid used to represent the nuclear potential for H_2 using $k=7$ to a precision of 10^{-5} .
- Automatically adapts – it does not know a priori where the nuclei are.
- Nuclei at dyadic points on level 5 – refinement stops at level 8
- If were at non-dyadic points refinement continues (to level ??) but the precision is still guaranteed.
- In future will unevenly subdivide boxes to force nuclei to dyadic points.



Density functional theory (DFT)

- Hohenberg-Kohn theorem
 - The energy is a functional of the density (3D)
- Kohn-Sham
 - Practical approach to DFT, parameterizing the density with orbitals (easier treatment of kinetic energy)
 - Very similar computationally to Hartree-Fock, but potentially exact

$$\left(-\frac{1}{2} \nabla^2 + V_{coul}(r; \rho) + V_{xc}(r; \rho) + V_{ext}(r) \right) \phi_i(r) = \varepsilon_i \phi_i(r)$$

$$\rho(r) = \sum_i \phi_i^2(r)$$

Integral Formulation

- Solving the integral equation
 - Eliminates the derivative operator and related “issues”
 - Converges as fixed point iteration *with no preconditioner*

$$\left(-\frac{1}{2}\nabla^2 + V\right)\Psi = E\Psi$$

$$\Psi = -2\left(-\nabla^2 - 2E\right)^{-1}V\Psi$$

$$= -2G * (V\Psi)$$

$$(G * f)(r) = \int ds \frac{e^{-k|r-s|}}{4\pi|r-s|} f(s) \text{ in 3D ; } k^2 = -2E$$

Separated form for integral operators

$$T * f = \int ds K(r - s) f(s)$$

- Approach in current prototype code
 - Represent the kernel over a finite range as a sum of Gaussians

$$r_{ii', jj', kk'}^{nl} = \sum_i \omega_i X_{ii'}^{nl_x} Y_{ii'}^{nl_y} Z_{ii'}^{nl_z} \quad \text{in 3D}$$

$$K(r) = \sum_i \omega_i e^{-t_i r^2} + O(\varepsilon)$$

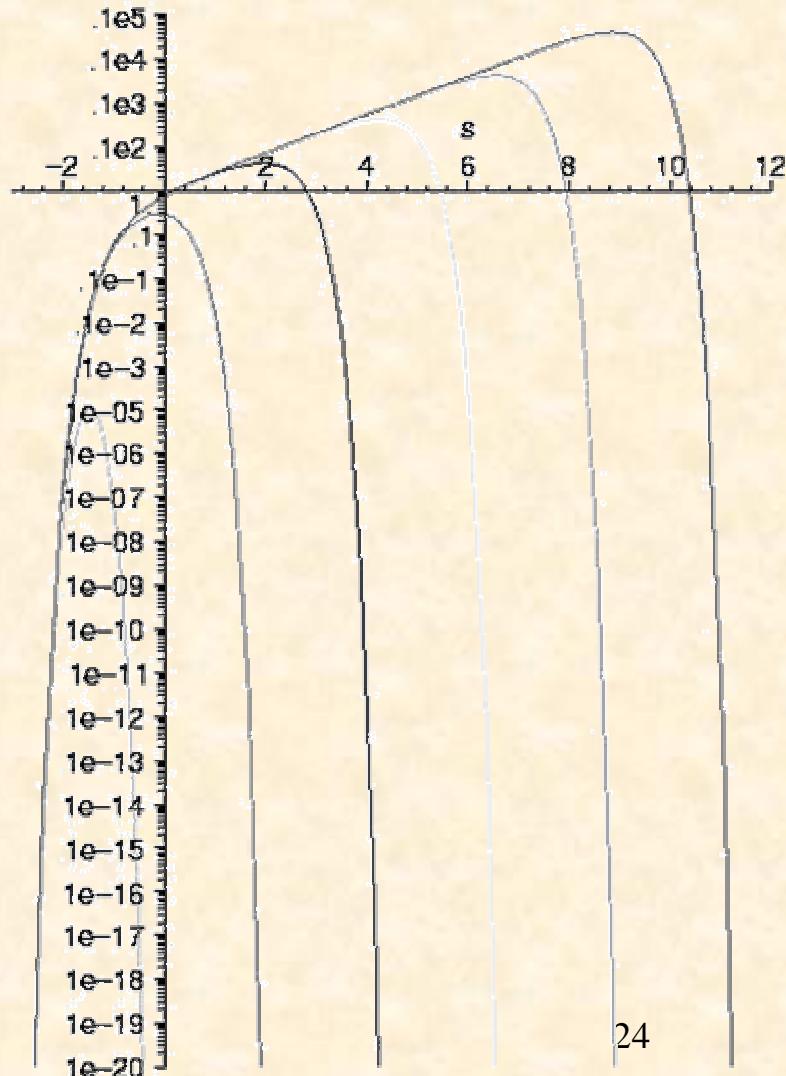
- Only need compute 1D transition matrices (X,Y,Z)
- SVD the 1-D operators (low rank away from singularity)
- Apply most efficient choice of low/full rank 1-D operator
- Even better algorithms not yet implemented

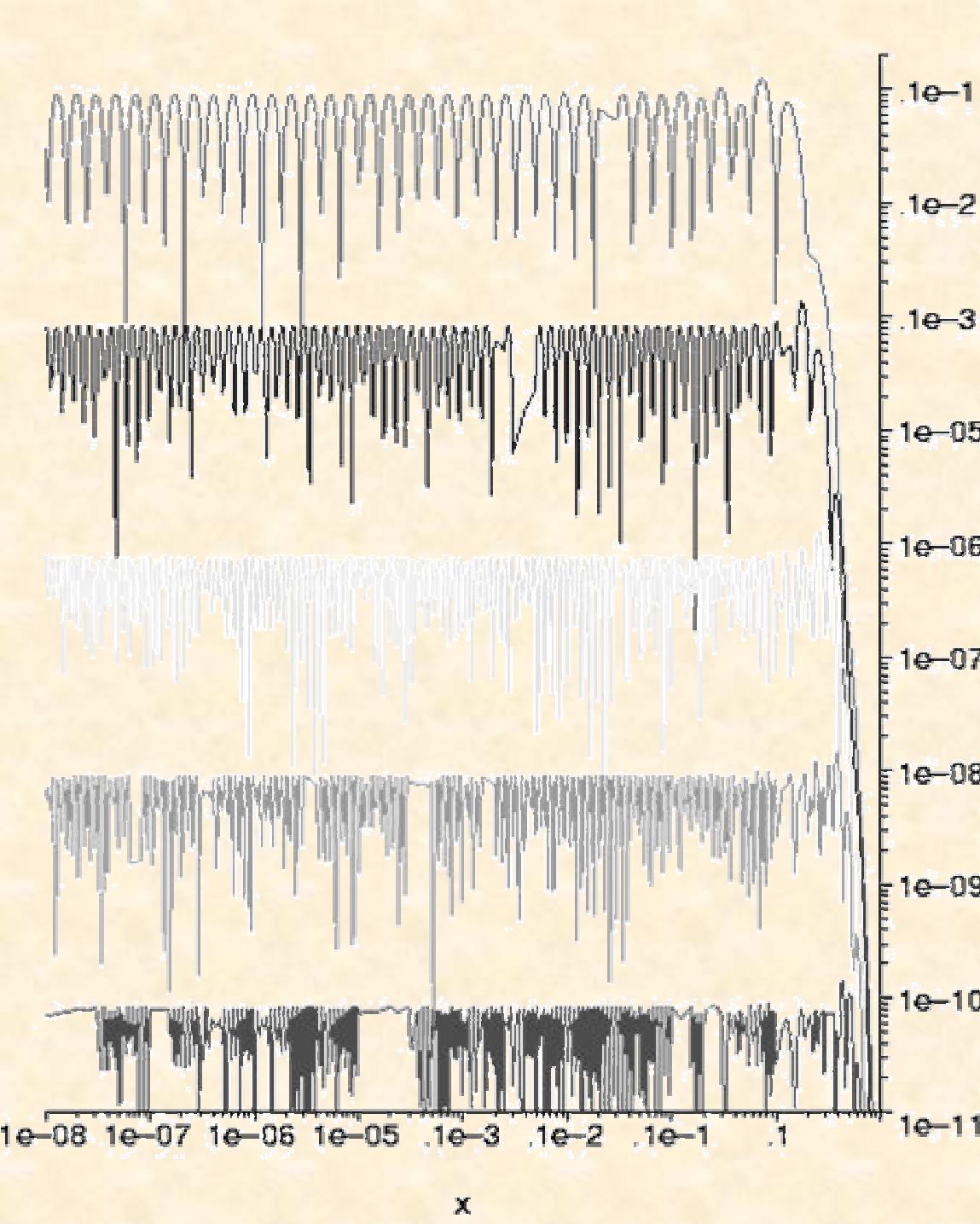
Accurate Quadratures

$$\frac{e^{-\mu r}}{r} = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-x^2 t^2 - \mu^2 / 4t^2} dt$$
$$= \frac{2}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-x^2 e^{2s} - \mu^2 e^{-2s} / 4 + s} ds$$

- Trapezoidal quadrature
 - Geometric precision for periodic functions with sufficient smoothness.

The kernel for $x=1e-4, 1e-3, 1e-2, 1e-, 1e0$.
The curve for $x=1e-4$ is the rightmost





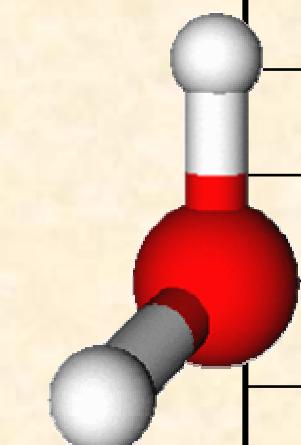
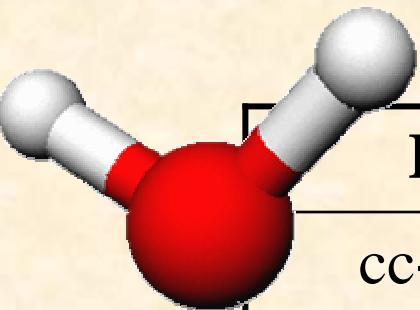
Automatically generated representations of $\exp(-30r)/r$ accurate to 1e-10, 1e-8, 1e-6, 1e-4, 1e-2 (relative error) for r in [1e-8,1] (92, 74, 57, 39 and 21 terms, respectively).

Low-energy scattering states also possible (but stronger dependence on range)

Periodic systems (cubic subgroups) straightforward.

Water dimer LDA

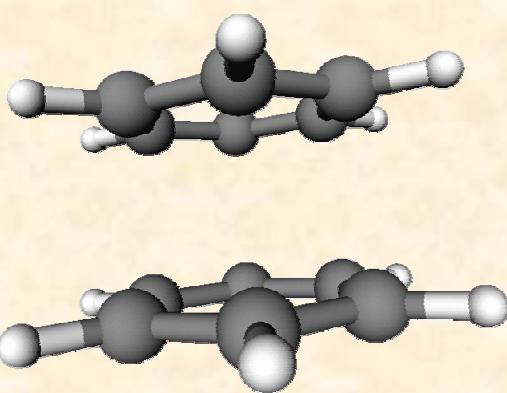
aug-cc-pVTZ geometry, kcal/mol.



Basis	Uncorrected	BSSE	Corrected
cc-pVDZ	-11.733	-3.958	-7.775
cc-pVTZ	-9.464	-1.654	-7.810
cc-pVQZ	-8.708	-0.821	-7.888
aug-cc-pVDZ	-8.187	-0.382	-7.805
aug-cc-pVTZ	-7.992	-0.086	-7.906
aug-cc-pVQZ	-7.995	-0.054	-7.941
$\epsilon=10^{-3}$	-6.483		
$\epsilon=10^{-5}$	-7.932		
$\epsilon=10^{-7}$	-7.943		

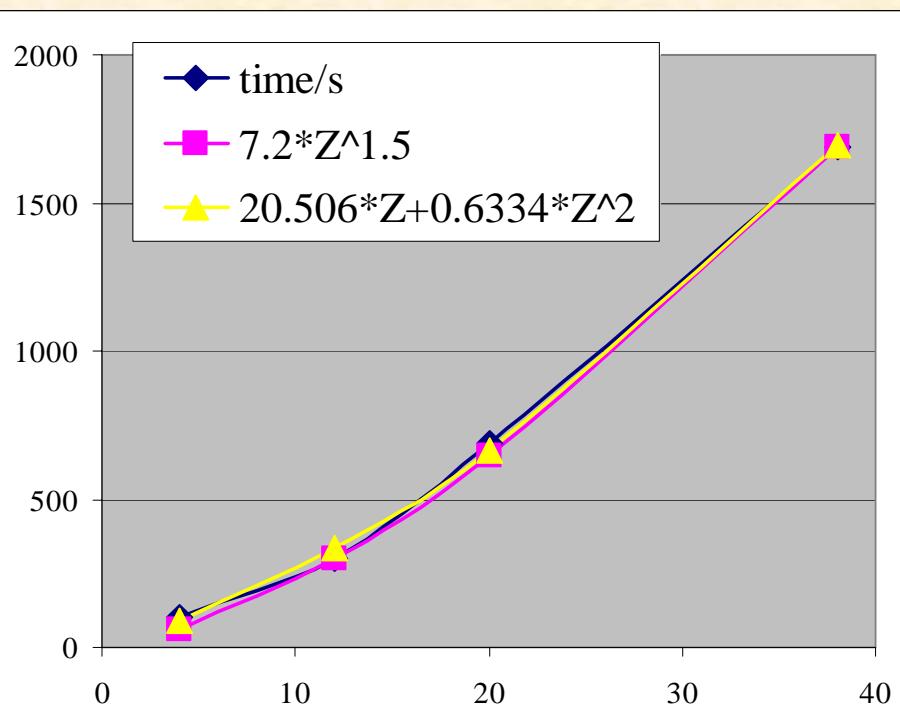
Benzene dimer LDA

aug-cc-pVDZ geometry, kcal/mol.



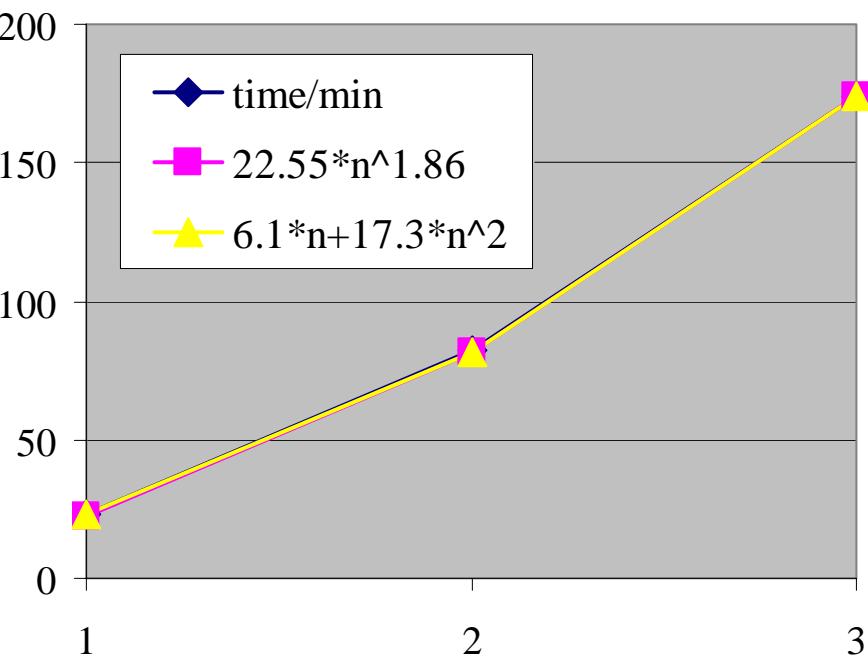
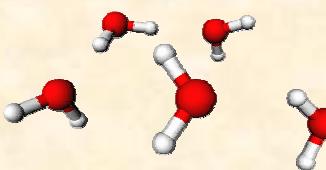
Basis	Uncorrected	BSSE	Corrected
cc-pVDZ	-1.506	-1.035	-0.471
cc-pVTZ	-1.271	-0.387	-0.884
cc-pVQZ	-1.074	-0.193	-0.881
aug-cc-pVDZ	-1.722	-0.698	-1.024
aug-cc-pVTZ	-1.159	-0.193	-0.966
$\varepsilon=10^{-5}$	-0.872		
$\varepsilon=10^{-7}$	-0.956		
$\varepsilon=10^{-9}$	-0.956		

LDA scaling with Z and system size (energy $\varepsilon=10^{-5}$)

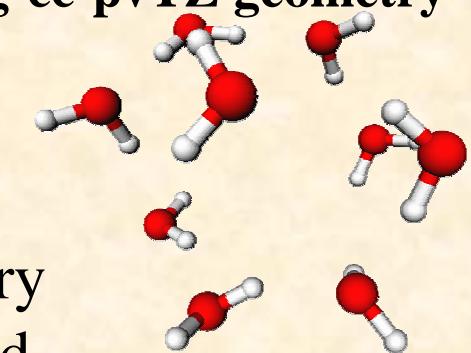


Rare earth atoms $Z=4,12,20,38$

$(H_2O)_n$ $n=5,9 \dots t = O(n^{1.1})$



$(C_6H_6)_n$ MP2 aug-cc-pvTZ geometry



Stacked benzene – MOs are delocalized by symmetry

Water cluster – MOs are asymptotically localized

(long tail is smooth so is inexpensively treated)²⁸

Current Capabilities

- Open/closed shell Hartree-Fock and DFT
 - Wide range of GGAs, hybrid ($O(N)$ HF exchange), and AC functionals
 - Energies and analytic derivatives
 - Full TDDFT and RPA for excitation energies
 - Abelian point groups
 - Parallel execution on shared memory computers (e.g., ORNL 256 processor SGI Altix)
 - Interfaces to NWChem and GAMESS-US
- Several prototypes for computing in 6D
 - Density matrix, Green's function, 2-e wave function⁹

Low Separation Rank Representation

$$f(x_1, \dots, x_d) = \sum_{l=1}^M \sigma_l \prod_{i=1}^d f_i^{(l)}(x_i) + O(\varepsilon)$$

$$\left\| f_i^{(l)} \right\|_2 = 1 \quad \sigma_l > 0$$

- Different from low operator rank
 - Identity has full operator rank, but unit separation rank
- Beylkin & Mohlenkamp Proc. Nat. Acad. 2002
 - Many functions and operators have low sep. rank
 - E.g., Poisson GF; the many-electron Schrödinger Hamiltonian
- We are combining adaptive multires. & separated representations to compute in 6D

High-level composition using functions and operators

- Conventional quant. chem. uses explicitly indexed sparse arrays of matrix elements
 - Complex, tedious and error prone

- Python classes for Function and Operator

- in 1,2,3,6 and general dimensions

$$H\varphi = -\frac{1}{2}\nabla^2\varphi + V\varphi$$

- wide range of operations

$$J(r) = G * \rho$$

Hpsi = -0.5*Delsq*psi + V*psi

J = Coulomb.apply(rho)

$$= \int \frac{\rho(s)}{|r-s|} ds$$

- All with guaranteed speed and precision

Synthesis of High Performance Algorithms for Electronic Structure Calculations

<http://www.cis.ohio-state.edu/~gb/TCE>

- Collaboration between DOE/SciDAC, NSF/ITR and ORNL/LDRD
- Objective: *develop a high level programming tool that translates many-body quantum theory into efficient massively parallel codes. This is anticipated to revolutionize the rate of progress in this field by eliminating man-years of programming effort.*
- NSF Project:
 - Sadayappan (PI), Baumgartner, Cociorva, Pitzer (OSU)
 - Bernholdt, Harrison (unfunded) (ORNL)
 - Ramanujam (LSU)
 - Nooijen (Waterloo)
- DOE SciDAC: Harrison (PI), Hirata (PNNL)
- DOE ORNL/LDRD: Bernholdt (PI, 2002-3)
- Other SciDAC projects adopting this tool: Piecuch, Gordon

CCSD Doubles Equation

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hbar[a,b,i,j] == sum[f[b,c]*t[i,j,a,c],{c}] -sum[f[k,c]*t[k,b]*t[i,j,a,c],{k,c}] +sum[f[a,c]*t[i,j,c,b],{c}] -
sum[f[k,c]*t[k,a]*t[i,j,c,b],{k,c}] -sum[f[k,j]*t[i,k,a,b],{k}] -sum[f[k,c]*t[j,c]*t[i,k,a,b],{k,c}] -sum[f[k,i]*t[j,k,b,a],{k}] -
sum[f[k,c]*t[i,c]*t[j,k,b,a],{k,c}] +sum[t[i,c]*t[j,d]*v[a,b,c,d],{c,d}] +sum[t[i,j,c,d]*v[a,b,c,d],{c,d}] +sum[t[j,c]*v[a,b,i,c],{c}] -
sum[t[k,b]*v[a,k,i,j],{k}] +sum[t[i,c]*v[b,a,j,c],{c}] -sum[t[k,a]*v[b,k,j,i],{k}] -sum[t[k,d]*t[i,j,c,b]*v[k,a,c,d],{k,c,d}] -
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+sum[t[i,c]*t[j,d]*t[k,a]*t[l,b]*v[k,l,c,d],{k,l,c,d}] -2*sum[t[k,b]*t[l,d]*t[i,j,a,c]*v[k,l,c,d],{k,l,c,d}] -
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+sum[t[j,d]*t[l,b]*t[i,k,c,a]*v[k,l,c,d],{k,l,c,d}] -2*sum[t[i,c]*t[l,d]*t[j,k,b,a]*v[k,l,c,d],{k,l,c,d}] -
+sum[t[i,c]*t[l,a]*t[j,k,b,d]*v[k,l,c,d],{k,l,c,d}] +sum[t[i,c]*t[l,b]*t[j,k,d,a]*v[k,l,c,d],{k,l,c,d}] -
+sum[t[i,k,c,d]*t[j,l,b,a]*v[k,l,c,d],{k,l,c,d}] +4*sum[t[i,k,a,c]*t[j,l,b,d]*v[k,l,c,d],{k,l,c,d}] -
2*sum[t[i,k,c,a]*t[j,l,b,d]*v[k,l,c,d],{k,l,c,d}] -2*sum[t[i,k,a,b]*t[j,l,c,d]*v[k,l,c,d],{k,l,c,d}] -
2*sum[t[i,k,a,c]*t[j,l,d,b]*v[k,l,c,d],{k,l,c,d}] +sum[t[i,k,c,a]*t[j,l,d,b]*v[k,l,c,d],{k,l,c,d}] -
+sum[t[i,c]*t[j,d]*t[k,l,a,b]*v[k,l,c,d],{k,l,c,d}] +sum[t[i,j,c,d]*t[k,l,a,b]*v[k,l,c,d],{k,l,c,d}] -
2*sum[t[i,j,c,b]*t[k,l,a,d]*v[k,l,c,d],{k,l,c,d}] -2*sum[t[i,j,a,c]*t[k,l,b,d]*v[k,l,c,d],{k,l,c,d}] -
+sum[t[j,c]*t[k,b]*t[l,a]*v[k,l,c,i],{k,l,c}] +sum[t[l,c]*t[j,k,b,a]*v[k,l,c,i],{k,l,c}] -2*sum[t[l,a]*t[j,k,b,c]*v[k,l,c,i],{k,l,c}] -
+sum[t[l,a]*t[j,k,c,b]*v[k,l,c,i],{k,l,c}] -2*sum[t[k,c]*t[j,l,b,a]*v[k,l,c,i],{k,l,c}] +sum[t[k,a]*t[j,l,b,c]*v[k,l,c,i],{k,l,c}] -
+sum[t[k,b]*t[j,l,c,a]*v[k,l,c,i],{k,l,c}] +sum[t[j,c]*t[l,k,a,b]*v[k,l,c,i],{k,l,c}] +sum[t[i,c]*t[k,a]*t[l,b]*v[k,l,c,j],{k,l,c}] -
+sum[t[l,c]*t[i,k,a,b]*v[k,l,c,j],{k,l,c}] -2*sum[t[l,b]*t[i,k,a,c]*v[k,l,c,j],{k,l,c}] +sum[t[l,b]*t[i,k,c,a]*v[k,l,c,j],{k,l,c}] -
+sum[t[i,c]*t[k,l,a,b]*v[k,l,c,j],{k,l,c}] +sum[t[j,c]*t[l,d]*t[i,k,a,b]*v[k,l,d,c],{k,l,c,d}] -
+sum[t[j,d]*t[l,b]*t[i,k,a,c]*v[k,l,d,c],{k,l,c,d}] +sum[t[j,d]*t[l,a]*t[i,k,c,b]*v[k,l,d,c],{k,l,c,d}] -
2*sum[t[i,k,c,d]*t[j,l,b,a]*v[k,l,d,c],{k,l,c,d}] -2*sum[t[i,k,a,c]*t[j,l,b,d]*v[k,l,d,c],{k,l,c,d}] -
+sum[t[i,k,c,a]*t[j,l,b,d]*v[k,l,d,c],{k,l,c,d}] +sum[t[i,k,a,b]*t[j,l,c,d]*v[k,l,d,c],{k,l,c,d}] -
+sum[t[i,k,c,b]*t[j,l,d,a]*v[k,l,d,c],{k,l,c,d}] +sum[t[i,k,a,c]*t[j,l,d,b]*v[k,l,d,c],{k,l,c,d}] +sum[t[k,a]*t[l,b]*v[k,l,i,j],{k,l}] -
+sum[t[k,l,a,b]*v[k,l,i,j],{k,l}] +sum[t[k,b]*t[l,d]*t[i,j,a,c]*v[l,k,c,d],{k,l,c,d}] +sum[t[k,a]*t[l,d]*t[i,j,c,b]*v[l,k,c,d],{k,l,c,d}] -
+sum[t[i,c]*t[l,d]*t[j,k,b,a]*v[l,k,c,d],{k,l,c,d}] -2*sum[t[i,c]*t[l,a]*t[j,k,b,d]*v[l,k,c,d],{k,l,c,d}] -
+sum[t[i,c]*t[l,a]*t[j,k,d,b]*v[l,k,c,d],{k,l,c,d}] +sum[t[i,j,c,b]*t[k,l,a,d]*v[l,k,c,d],{k,l,c,d}] -
+sum[t[i,j,a,c]*t[k,l,b,d]*v[l,k,c,d],{k,l,c,d}] -2*sum[t[l,c]*t[i,k,a,b]*v[l,k,c,j],{k,l,c}] +sum[t[l,b]*t[i,k,a,c]*v[l,k,c,j],{k,l,c}] -
+sum[t[l,a]*t[i,k,c,b]*v[l,k,c,j],{k,l,c}] +v[a,b,i,j]

```

Tensor Contraction Engine

Definition of a many-electron theory

$$E = \langle \Phi_0 | \left[e^{-T_1 - T_2} H e^{T_1 + T_2} \right]_C | \Phi_0 \rangle$$

$$0 = \langle \Phi_i^a | \left[e^{-T_1 - T_2} H e^{T_1 + T_2} \right]_C | \Phi_0 \rangle$$

$$0 = \langle \Phi_{ij}^{ab} | \left[e^{-T_1 - T_2} H e^{T_1 + T_2} \right]_C | \Phi_0 \rangle$$

Mathematical expressions

$$(\Xi_1)_{h_1 p_9}^{h_7 h_{10}} = +t_{h_1}^{p_5} v_{p_5 p_9}^{h_7 h_{10}}$$

$$(\Xi_2)_{h_1 h_2}^{h_{10} h_{11}} = -\frac{1}{2} t_{h_1 h_2}^{p_7 p_8} v_{p_7 p_8}^{h_{10} h_{11}}$$

$$(\Xi_3)_{h_1 p_5}^{h_{10} p_3} = -\frac{1}{2} t_{h_1}^{p_6} v_{p_5 p_6}^{h_{10} p_3}$$

$$(\Xi_4)_{p_5}^{h_{10}} = -t_{h_7}^{p_6} v_{p_5 p_6}^{h_7 h_{10}}$$

$$(\xi_{222})_{h_1 p_5}^{h_{10} h_{11}} = +v_{h_1 p_5}^{h_{10} h_{11}} + \frac{1}{2} (\Xi_1)_{h_1 p_5}^{h_{10} h_{11}}$$

$$(\xi_{22})_{h_1 h_2}^{h_{10} h_{11}} = -v_{h_1 h_2}^{h_{10} h_{11}} + P_2 t_{h_1}^{p_5} (\xi_{222})_{h_2 p_5}^{h_{10} h_{11}} + (\Xi_2)_{h_1 h_2}^{h_{10} h_{11}}$$

$$(\xi_{23})_{h_1 p_5}^{h_{10} p_3} = +v_{h_1 p_5}^{h_{10} p_3} + (\Xi_3)_{h_1 p_5}^{h_{10} p_3}$$

$$(\xi_{24})_{p_5}^{h_{10}} = +f_{p_5}^{h_{10}} + (\Xi_4)_{p_5}^{h_{10}}$$

$$(\xi_{25})_{h_1 p_9}^{h_7 h_{10}} = +v_{h_1 p_9}^{h_7 h_{10}} + (\Xi_1)_{h_1 p_9}^{h_7 h_{10}}$$

$$(\xi_2)_{h_1 h_2}^{h_{10} p_3} = +v_{h_1 h_2}^{h_{10} p_3} + \frac{1}{2} t_{h_1}^{p_3} (\xi_{22})_{h_1 h_2}^{h_{10} h_{11}} - P_2 t_{h_1}^{p_5} (\xi_{23})_{h_2 p_5}^{h_{10} p_3}$$

$$-t_{h_1 h_2}^{p_3 p_5} (\xi_{24})_{p_5}^{h_{10}} + P_2 t_{h_1 h_7}^{p_3 p_9} (\xi_{25})_{h_2 p_9}^{h_7 h_{10}} + \frac{1}{2} t_{h_1 h_2}^{p_5 p_6} v_{p_5 p_6}^{h_{10} p_3}$$

$$(\xi_3)_{h_1 p_5}^{p_3 p_4} = +v_{h_1 p_5}^{p_3 p_4} - \frac{1}{2} t_{h_1}^{p_6} v_{p_5 p_6}^{p_3 p_4}$$

$$(\xi_{42})_{p_8}^{h_9} = +f_{p_8}^{h_9} + (\Xi_4)_{p_8}^{h_9}$$

$$(\xi_4)_{h_1}^{h_9} = +f_{h_1}^{h_9} + t_{h_1}^{p_8} (\xi_{42})_{p_8}^{h_9} - t_{h_7}^{p_6} v_{h_1 p_6}^{h_7 h_9} - \frac{1}{2} t_{h_1 h_8}^{p_6 p_7} v_{p_6 p_7}^{h_8 h_9}$$

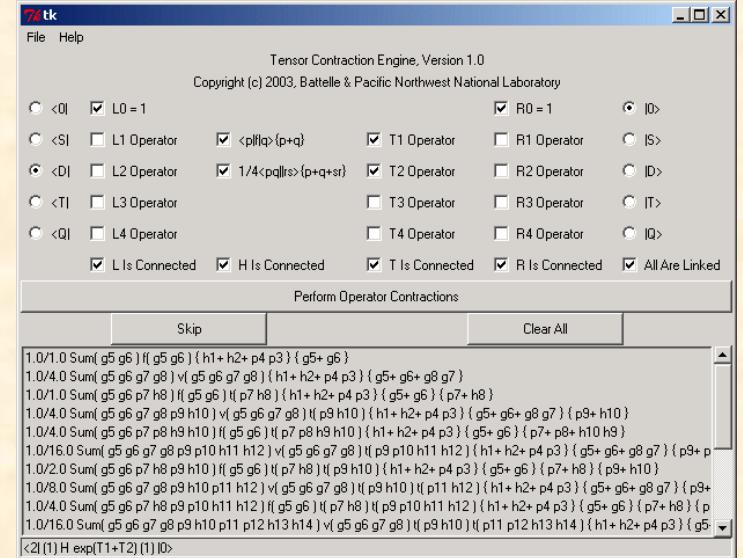
$$(\xi_5)_{p_5}^{p_3} = +f_{p_5}^{p_3} - t_{h_7}^{p_6} v_{p_5 p_6}^{h_7 p_3} - \frac{1}{2} t_{h_7 h_8}^{p_3 p_6} v_{p_5 p_6}^{h_7 h_8}$$

$$(\xi_{62})_{h_1 p_8}^{h_9 h_{11}} = +v_{h_1 p_8}^{h_9 h_{11}} + \frac{1}{2} (\Xi_1)_{h_1 p_8}^{h_9 h_{11}}$$

$$(\xi_6)_{h_1 h_2}^{h_9 h_{11}} = -v_{h_1 h_2}^{h_9 h_{11}} + P_2 t_{h_1}^{p_8} (\xi_{62})_{h_2 p_8}^{h_9 h_{11}} + (\Xi_2)_{h_1 h_2}^{h_9 h_{11}}$$

$$(\xi_7)_{h_1 p_5}^{h_6 p_3} = +v_{h_1 p_5}^{h_6 p_3} + 2 (\Xi_3)_{h_1 p_5}^{h_6 p_3} - \frac{1}{2} t_{h_1 h_8}^{p_3 p_7} v_{p_5 p_7}^{h_6 h_8}$$

Hirata, PNNL



A parallel computer program

```

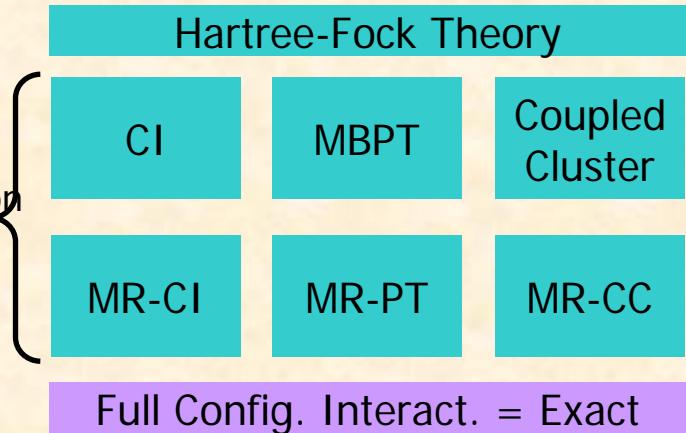
nprocs = GA_NNODES()
count = 0
next = NXTEVAL(nprocs)
DO p3b = noab+1,noab+nvab
DO h6b = 1,noab
DO h1b = 1,noab
DO p5b = noab+1,noab+nvab
IF (next.eq.count) THEN
IF ((.not.restricted).or.(int_mb(k_spin+p3b-1)+int_mb(k_spin+h6b-1)
&+int_mb(k_spin+h1b-1)+int_mb(k_spin+p5b-1).ne.8)) THEN
IF (int_mb(k_spin+p3b-1)+int_mb(k_spin+h6b-1) .eq. int_mb(k_spin+h
&1b-1)+int_mb(k_spin+p5b-1)) THEN
IF (ieor(int_mb(k_sym+p3b-1),ieor(int_mb(k_sym+h6b-1),ieor(int_mb(
&k_sym+h1b-1),int_mb(k_sym+p5b-1)))) .eq. ieor(irrep_v,irrep_t)) TH
&EN
DO p7b = noab+1,noab+nvab
DO h8b = 1,noab
IF (int_mb(k_spin+p3b-1)+int_mb(k_spin+p7b-1) .eq. int_mb(k_spin+h
&1b-1)+int_mb(k_spin+h8b-1)) THEN
IF (ieor(int_mb(k_sym+p3b-1),ieor(int_mb(k_sym+p7b-1),ieor(int_mb(
&k_sym+h1b-1),int_mb(k_sym+h8b-1)))) .eq. irrep_t) THEN
IF ((restricted).and.(int_mb(k_spin+p3b-1)+int_mb(k_spin+p7b-1)+in
&t_mb(k_spin+h1b-1)+int_mb(k_spin+h8b-1).eq.8)) THEN

```

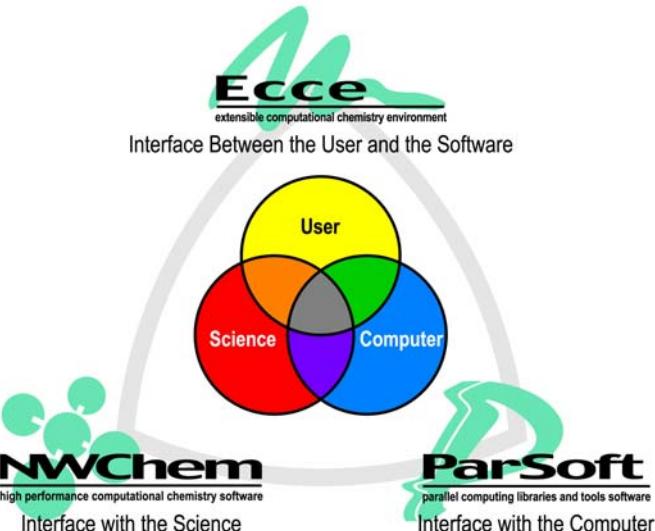
Complex many-electron theories are now implemented in hours!

LCCD, CCD, LCCSD, CCSD,
QCISD, CCSQT, CCSDTQ,
CISD, CISDT, CISDTQ,
MBPT(2), MBPT(3),
MBPT(4), CCSD(T), CCSD[T]
CCSD- λ , CCSQT- λ , CCSDTQ- λ ,
CCSD- p_1 , CCSQT- p_1 ,
CCSDTQ- p_1 , EOM-CCSD,
EOM-CCSDT, EOM-CCSQTQ,
Relativistic CC, CI, MBPT.

100% of derivation
99% of implementation
can be automated!



Hirata, PNNL

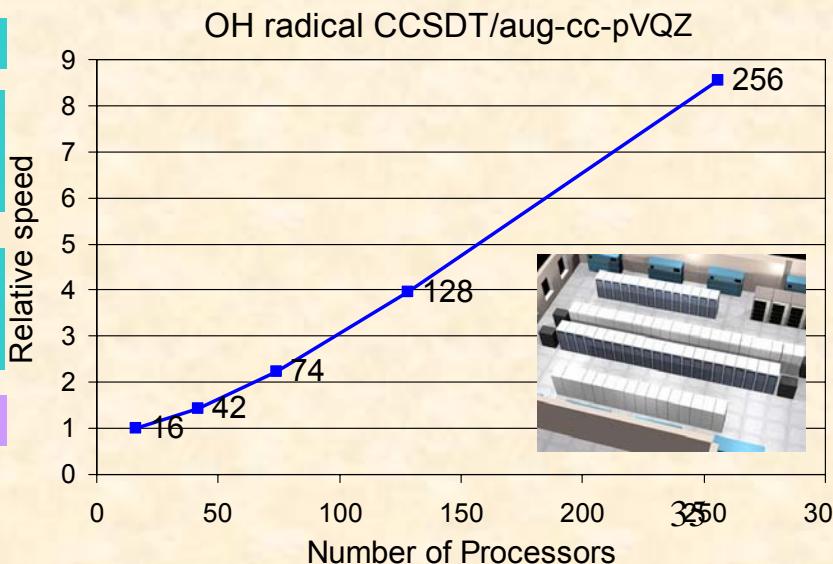


Equilibrium bond length

InH 1.841 (theory) vs. 1.838 (exp)
SnH 1.771 (theory) vs. 1.770 (exp)
SbH 1.712 (theory) vs. 1.711 (exp)
TeH 1.656 (theory) vs. 1.656 (exp)
IH 1.609 (theory) vs. 1.609 (exp)

Vibrational frequency

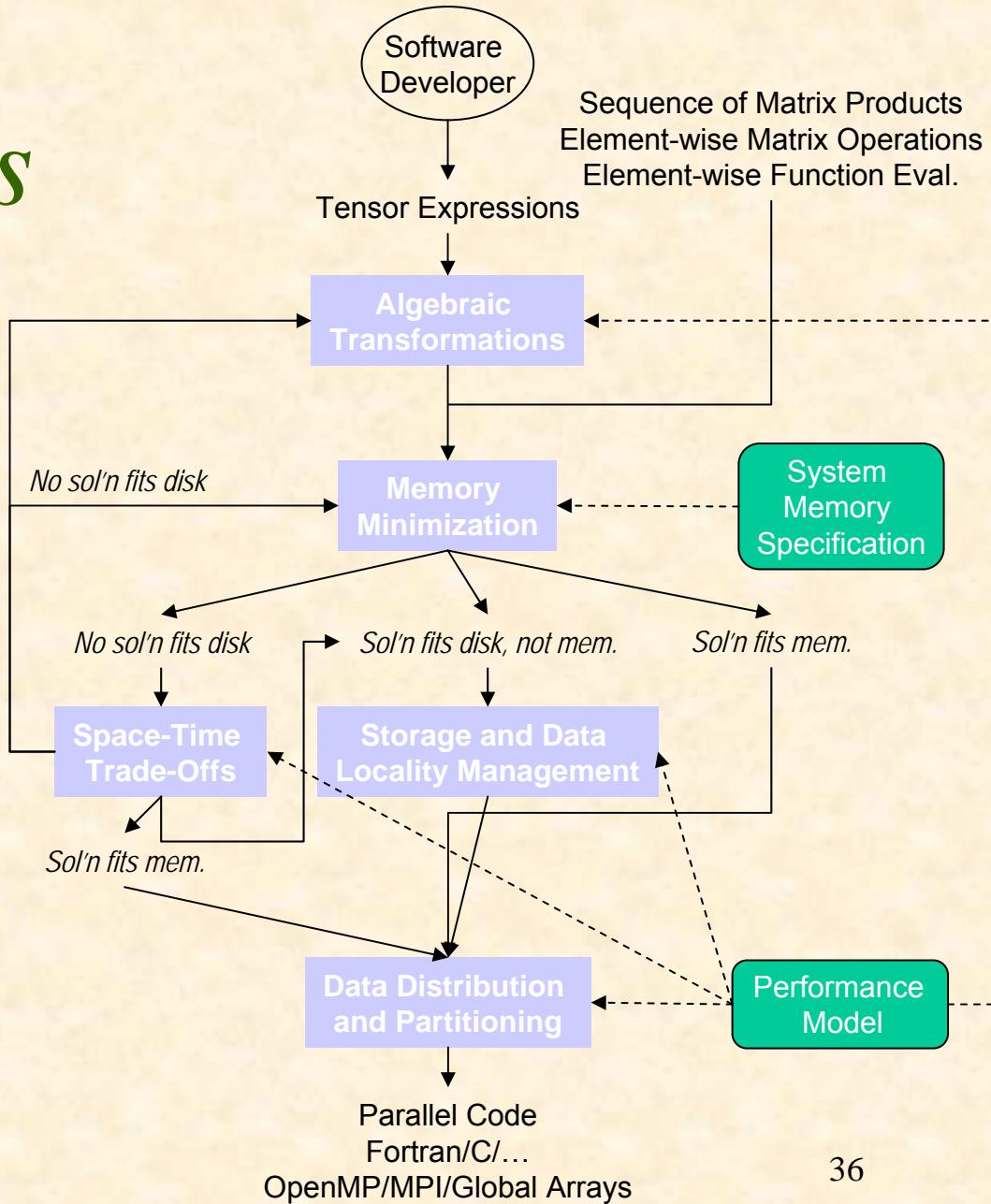
InH 1467 (theory) vs. 1476 (exp)
SnH 1711 (theory) vs. 1715 (exp)
SbH 1918 (theory) vs. 1923 (exp)
TeH 2144 (theory) vs. 2137 (exp)
IH 2328 (theory) vs. 2309 (exp)



TCE

Components

- Algebraic Transformations
 - Minimize operation count
- Memory Minimization
 - Reduce intermediate storage
- Space-Time Transformation
 - Trade storage for recomputation
- Storage Management and Data Locality Optimization
 - Optimize use of storage hierarchy
- Data Distribution and Partitioning
 - Optimize parallel layout



Current TCE Capabilities

Capability	Prototype TCE	Optimizing TCE
Basic sequential code generation for CC-based methods	Yes	Yes
QC Packages Interfaced: <ul style="list-style-type: none">• File based• General (file, memory, direct)	NWChem, UTChem, GAMESS	NWChem Under development
Symmetry Support: <ul style="list-style-type: none">• Spin• Spatial• Permutational	Spin orbitals Abelian Fermions	General, in progress Abelian, in progress General, in progress
Optimizations: <ul style="list-style-type: none">• Operation Minimization• Memory Minimization• Space-Time Transformation• Data Locality	Partial Partial No Partial	Yes Yes Yes Yes
Parallel code generation	Limited general	³⁷ General, in progress

Summary

- The gulf that separates science from its computational realization is growing rapidly
 - Semantic gap between math and comp. lang. (Phil Colella)
 - Complexity of S/W and H/W environment
- Tensor Contraction Engine
 - Promises to eliminate man-years from development projects
 - Use new theories in hours/days with production quality code
- Multiresolution analysis provides a general framework for computational chemistry
 - Accurate and efficient with high-level composition
 - Multiwavelets provide high-order convergence and readily accommodate singularities and boundary conditions
 - Real impact will be application to many-body models
- Separated form for operators and functions
 - Critical for efficient computation in higher dimension