MADNESS

Multiresolution
Adaptive
Numerical
Scientific
Simulation

Multiresolution Approach in Computational Chemistry

George I. Fann[1], Zhengting Gan[1], Robert J. Harrison[1,2], Takeshi Yanai[1]

[1]Oak Ridge National Laboratory

[2]University of Tennessee, Knoxville

In collaboration with

Gregory Beylkin[4], Fernando Perez[4], Lucas Monzon[4], Martin Mohlenkamp[5] and others

[4]University of Colorado

[5]Ohio University

harrisonrj@ornl.gov

SciDAC
Scientific Discovery through Advanced Computing

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SciDAC

Scientific Discovery through Advanced Computing

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*

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"*

Essential techniques for fast computation

- Multiresolution

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

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

- Low-separation rank

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

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

- Low-operator rank

$$A = \sum_{\mu=1}^{r} \underline{u}_\mu \sigma_\mu \underline{v}_\mu^T + O(\varepsilon)$$

$$\sigma_\mu > 0 \qquad \underline{v}_\mu^T . \underline{v}_\lambda = \underline{u}_\mu^T . \underline{u}_\lambda = \delta_{\mu\lambda}$$

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

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

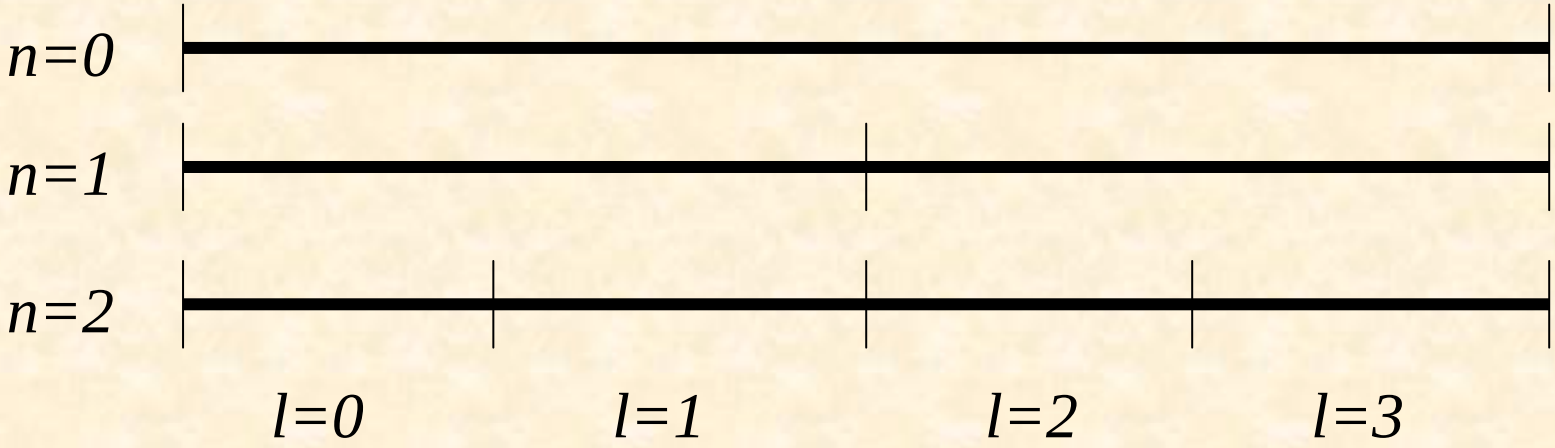
  – Instead of using the most accurate representation, use the difference between successive approximations

  – Representation on V_0 small/dense; differences sparse

  – Computationally efficient; possible insights

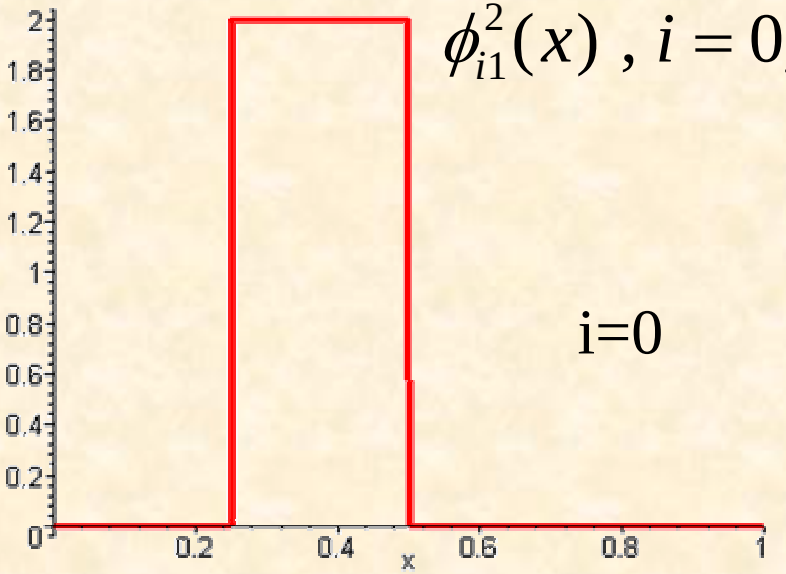
Scaling Function Basis

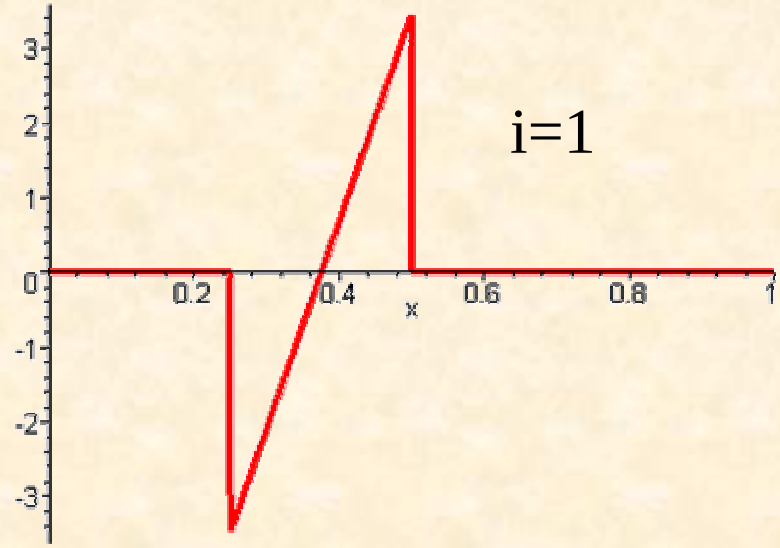
- Divide domain into 2^n pieces (level n)
  - Adaptive sub-division (local refinement)
  - l^{th} sub-interval $[l*2^{-n},(l+1)*2^{-n}]$ $l=0,\ldots,n-1$
- In each sub-interval define a polynomial basis
  - First k Legendre polynomials $\phi_i(x) = \sqrt{2i+1}P_i(2x-1)$
  - Orthonormal, disjoint support $\phi_{il}^n(x) = 2^{n/2}\phi_i(2^n x - l)$

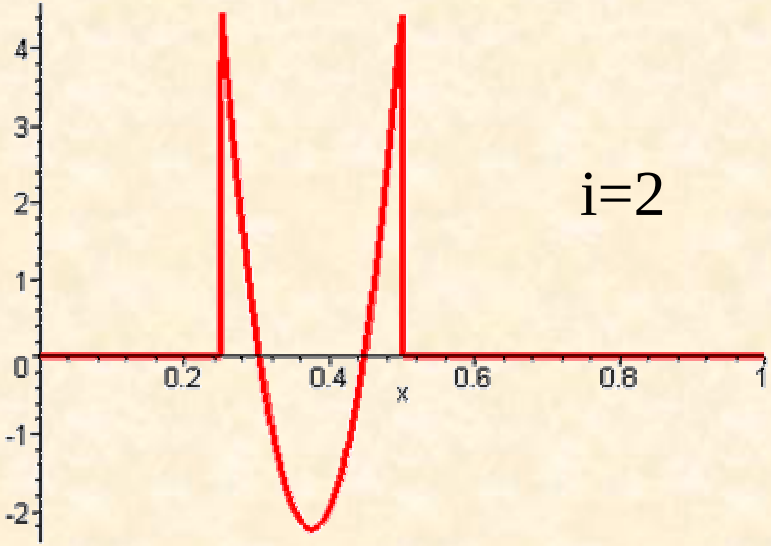


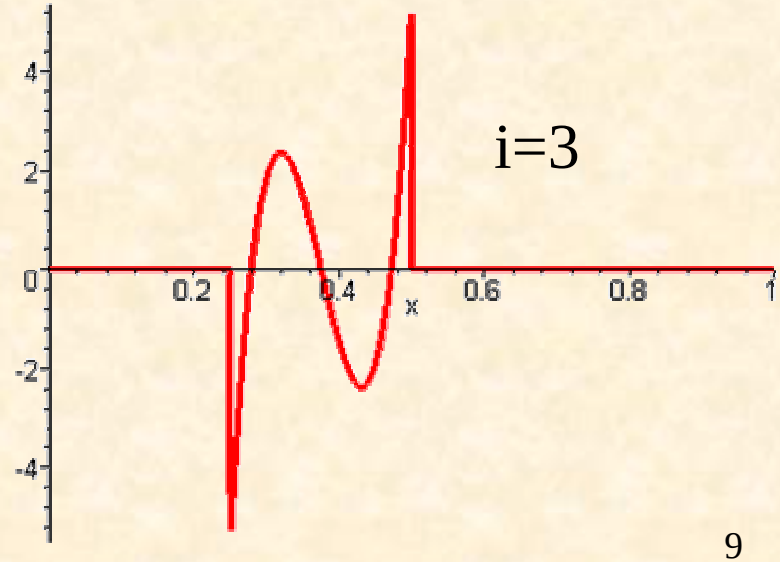
Scaling Function Basis - III

$$\phi_{i1}^{2}(x)\ ,\ i = 0,\ldots,3$$



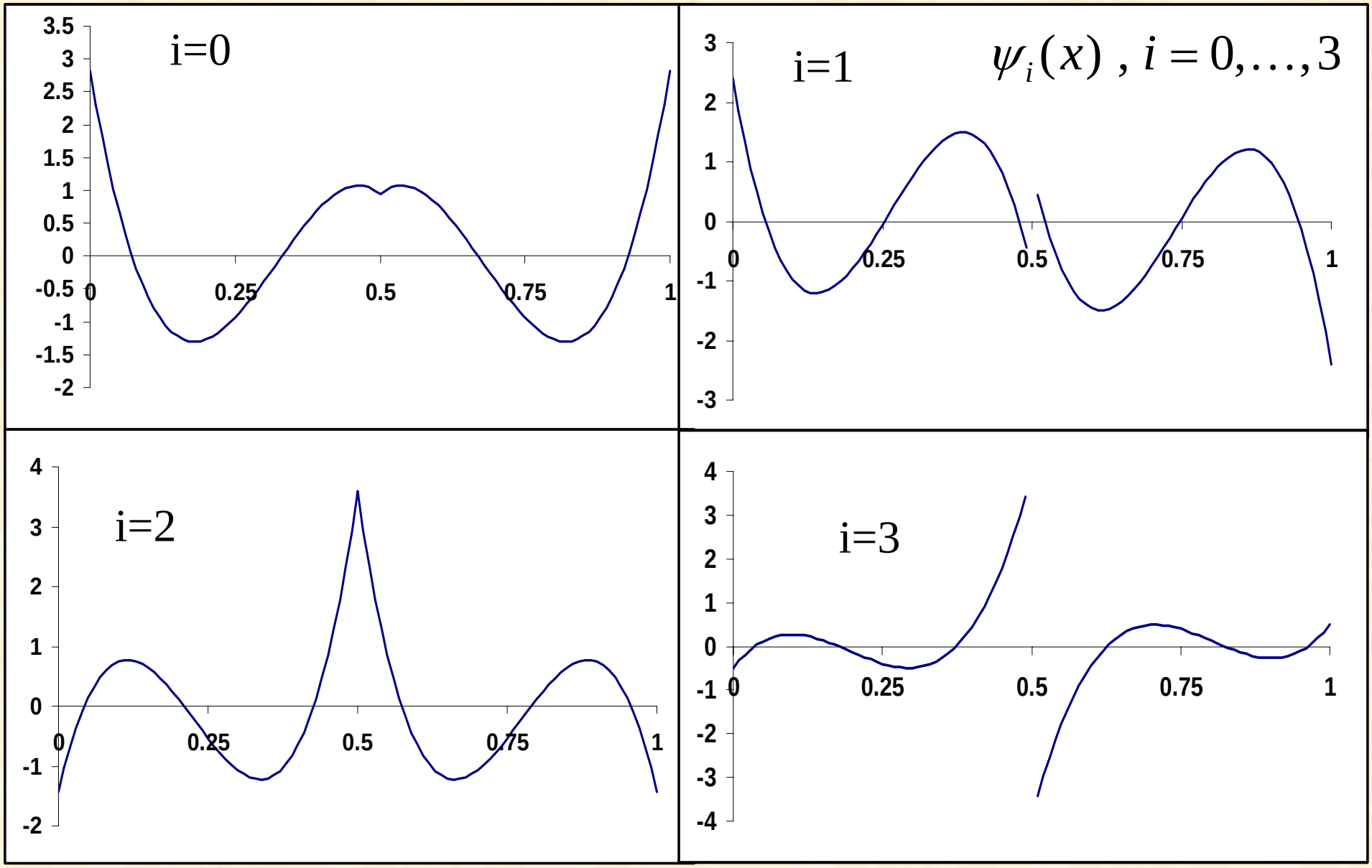






Multiwavelet Basis - III

$k=4$



Multiwavelet Basis

- An orthonormal basis to span $W_{n-1} = V_n - V_{n-1}$

Haar (piecewise constant basis)

$$\phi_l^{n-1} = 2^{-1/2}\left(\phi_{2l}^n + \phi_{2l}^n\right) \quad \text{sum}$$

$$\psi_l^{n-1} = 2^{-1/2}\left(\phi_{2l}^n - \phi_{2l}^n\right) \quad \text{difference}$$

$$\phi_{il}^{n-1}(x) = \sum_{j=0}^{k-1}\left(h_{ij}^{(0)}\phi_{j2l}^n(x) + h_{ij}^{(1)}\phi_{j2l+1}^n(x)\right)$$

$$\psi_{il}^{n-1}(x) = \sum_{j=0}^{k-1}\left(g_{ij}^{(0)}\phi_{j2l}^n(x) + g_{ij}^{(1)}\phi_{j2l+1}^n(x)\right)$$

Vanishing moments

- Critically important property
  - Since W_n is orthogonal to V_n the first k moments of functions in W_n vanish, i.e.,

$$\int x^j \psi_i(x)dx = 0,\ j = 0,\ldots,k-1$$

- Compact representation of smooth functions
  - Consider Taylor series … the first k terms vanish and smooth implies higher order terms are small
- Compact representation of integral operators
  - E.g., 1/|r-s| … interaction decays as r^{-2k-1}
- Derivatives vanish at origin in Fourier space
  - Diminishes effect of singularities at that point

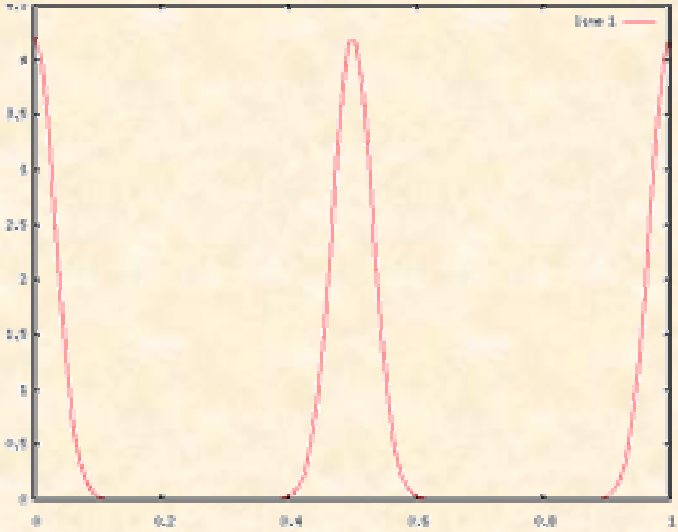
Truncation Error

- To satisfy the global error condition $$\left\| f - f^{n} \right\|_2 \le \varepsilon \left\| f \right\|_2$$
- Truncate according to $$\left\| d_l^n \right\|_2 \le 2^{-n/2} \varepsilon \left\| f \right\|_2$$
- Above is rather conservative – often use $$\left\| d_l^n \right\|_2 \le \varepsilon$$
- For accurate function & derivative $$\left\| d_l^n \right\|_2 \le 2^{-n} \varepsilon$$

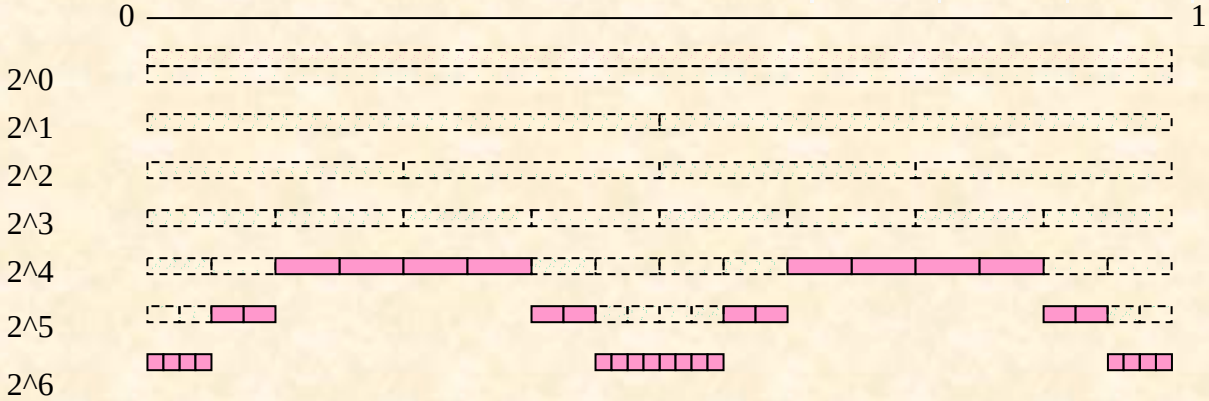
1-D example

$$f(x) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-a(x-1)^2} + \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-a(x-0.5)^2} + \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-a(x)^2}$$

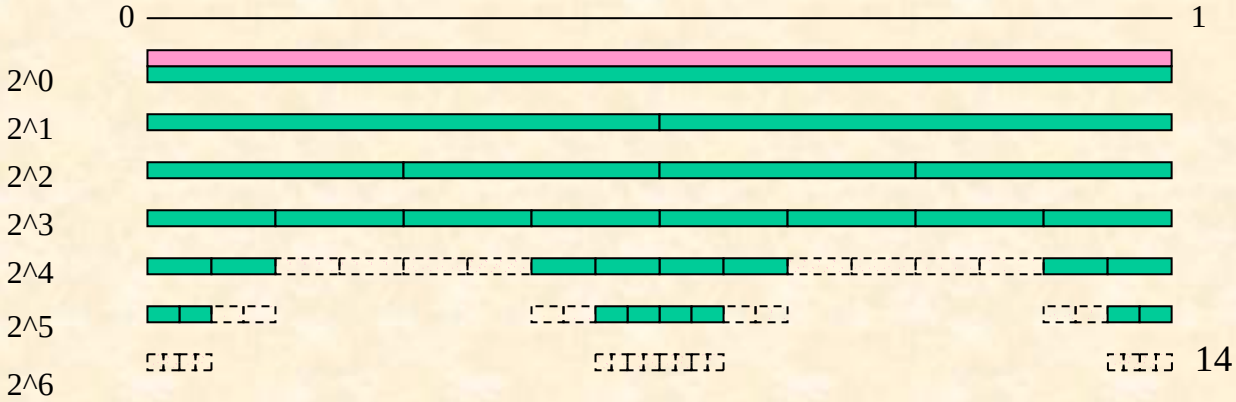
with k = 6 (#basis fn) and accuracy threshold = 1e-4

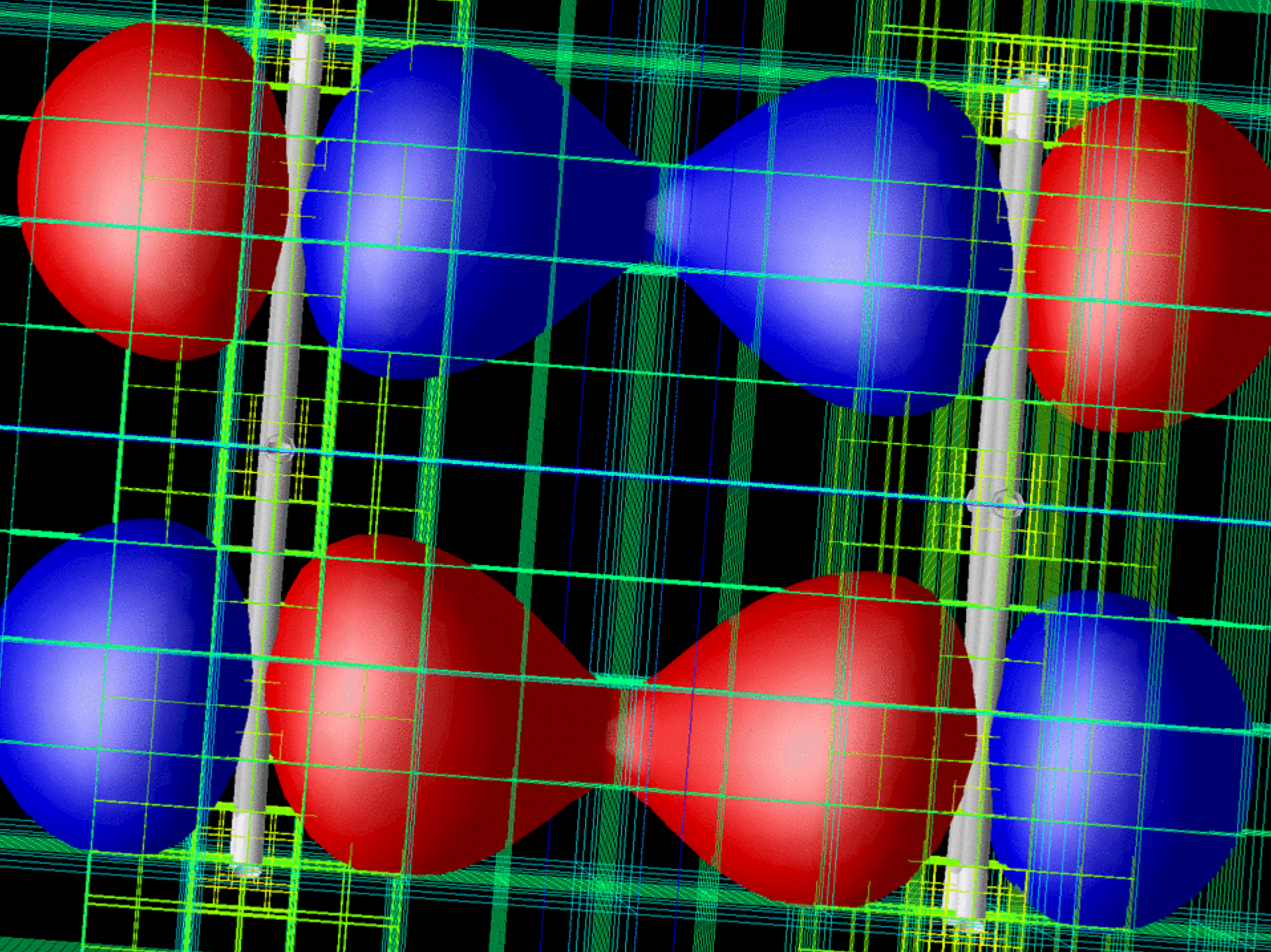


Refinement tree in the *scaling function basis*



Refinement tree in the *multi-wavelet basis*





Integral Formulation

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

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

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

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

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

Separated form for integral operators

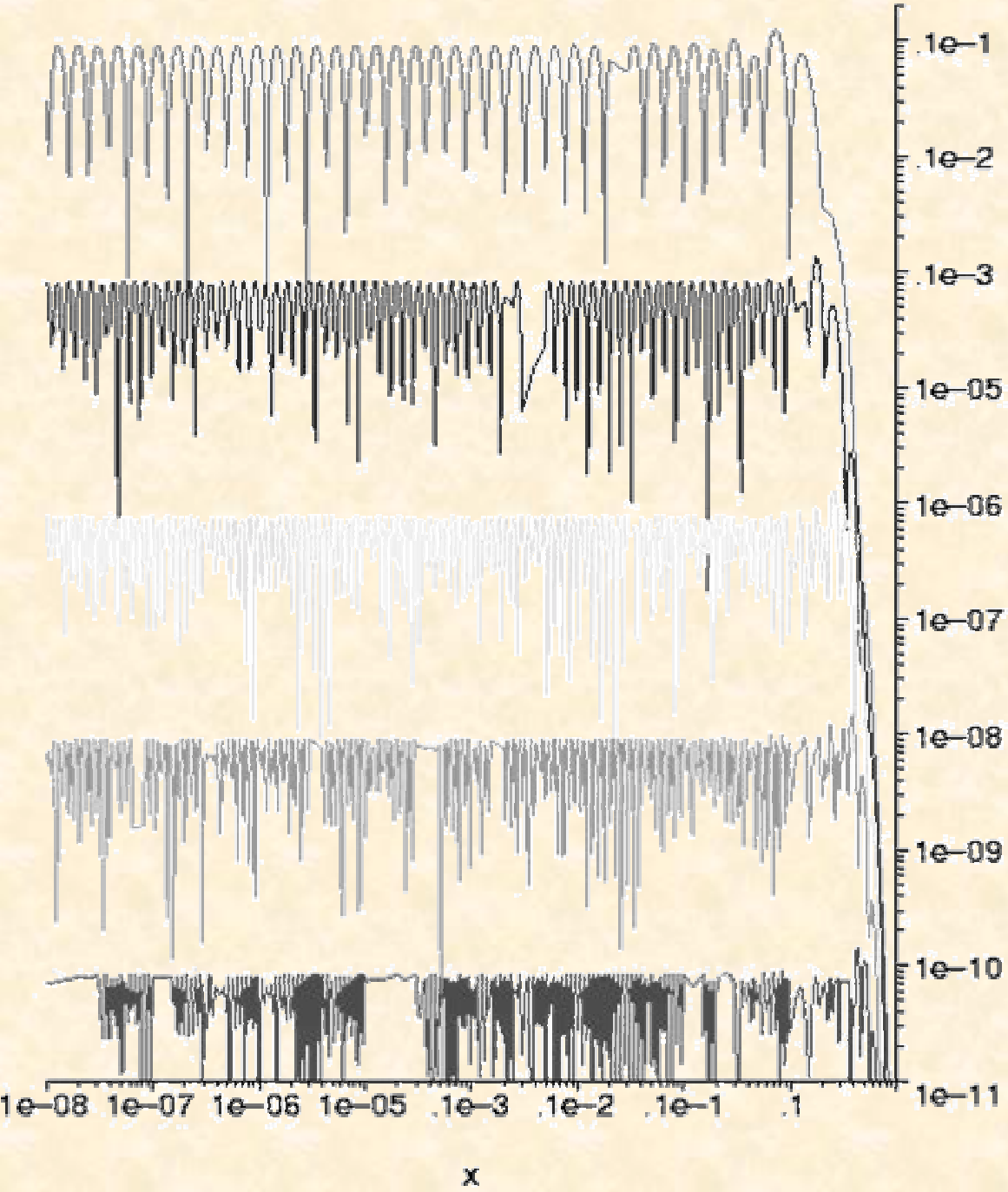
$$T * f = \int ds K(r-s) f(s)$$

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

$$r^{nl}_{ii',jj',kk'} = \sum_i \omega_i X^{nl_x}_{ii'} Y^{nl_y}_{ii'} Z^{nl_z}_{ii'} + O(\varepsilon) \quad \text{in 3D}$$

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

  - 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



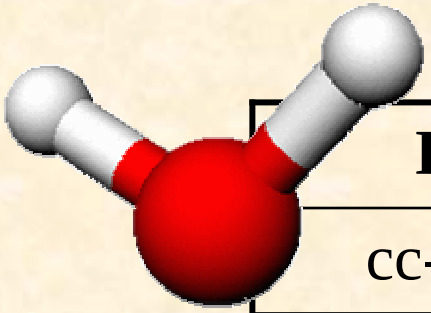
Automatically generated representations of *exp(-30r)/r* accurate to 1e-10, 1e-8, 1e-6, 1e-4, 1e-2 (relative error) for *r* in [1e-8,1] (92, 74, 57, 39 and 21 terms, respectively).

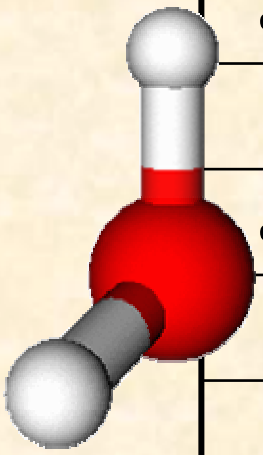
Low-energy *scattering* states also possible (but stronger dependence on range)

Periodic systems (cubic subgroups) straightforward.

Water dimer LDA

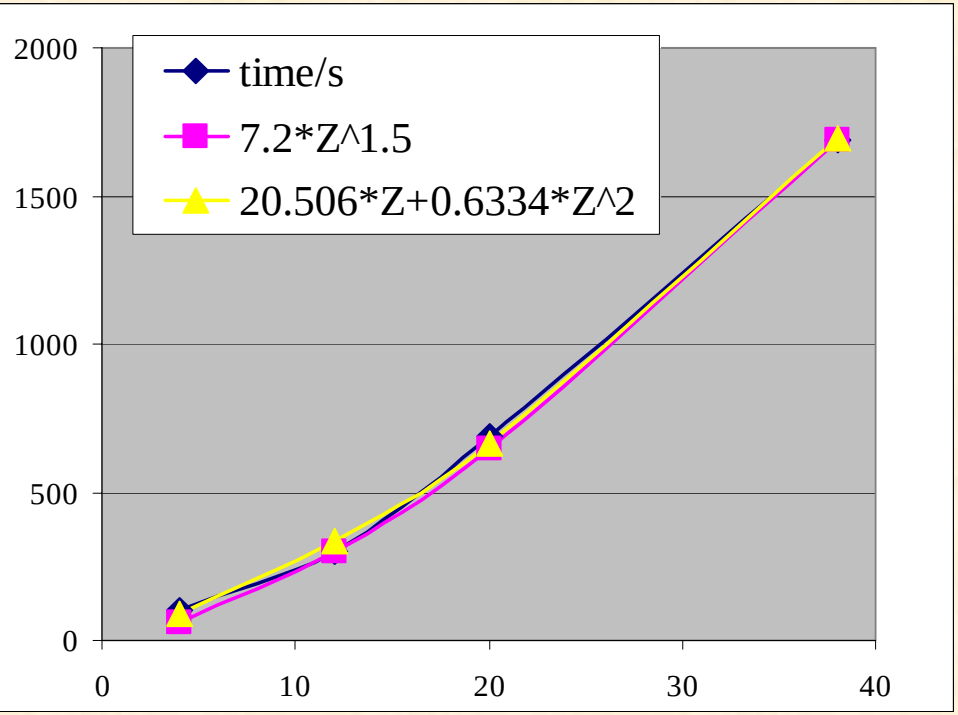
aug-cc-pVTZ geometry, kcal/mol.



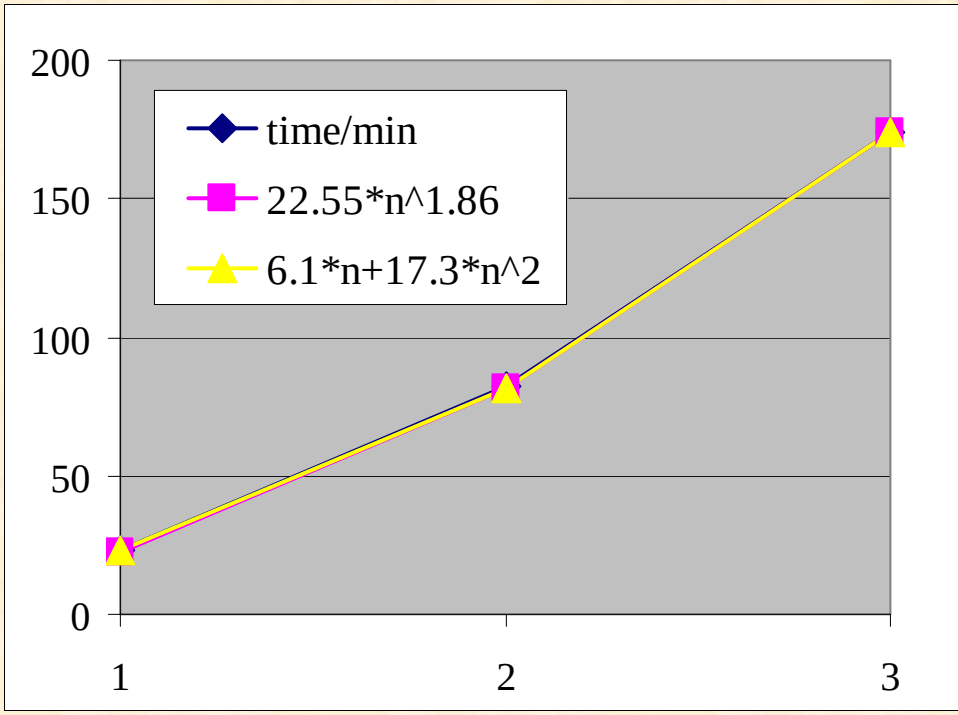


Basis	Uncorrected	BSSE	Corrected
cc-pVDZ	-11.733	-3.958	-7.775
cc-pVTZ	-9.464	-1.654	-7.810
cc-pVQZ	-8.708	-0.821	-7.888
aug-cc-pVDZ	-8.187	-0.382	-7.805
aug-cc-pVTZ	-7.992	-0.086	-7.906
aug-cc-pVQZ	-7.995	-0.054	-7.941
$\varepsilon=10^{-3}$	-6.483		
$\varepsilon=10^{-5}$	-7.932		
$\varepsilon=10^{-7}$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

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

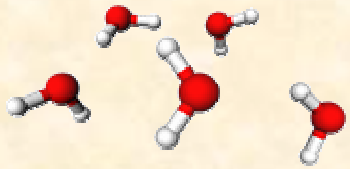


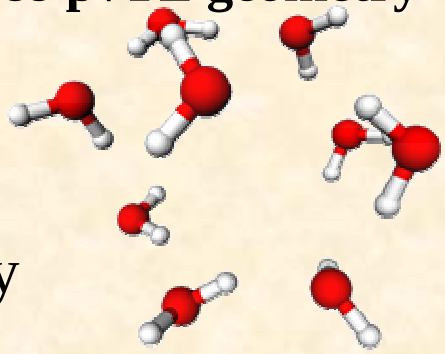
Rare earth atoms Z=4,12,20,38



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

$(H_2O)_n$ n=5,9 … t = $O(n^{1.1})$





Stacked benzene – MOs are delocalized by symmetry

Water cluster – MOs are asymptotically localized

(long tail is smooth so is inexpensively treated)

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
  - Interfaces to NWChem and GAMESS-US
- Several prototypes for computing 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
  - wide range of operations

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

$$J(r) = G * \rho = \int \frac{\rho(s)}{|r-s|}\,ds$$

```
Hpsi = -0.5*Delsq*psi+ V*psi
J = Coulomb.apply(rho)
```

- All with guaranteed speed and precision

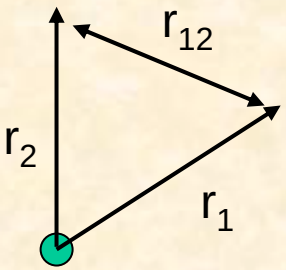
New solver being developed

- Working with localized orbitals
  - O(1) application of operators to one orbital
  - O(N) computation of Coulomb potential (already)
  - O(N) computation of Fock-like matrices
  - More robust convergence
    - Current code suffers from convergence problem due to poorly defined resolution of nearly degenerate orbitals
- Near total rewrite in C++
  - Two-levels of parallelism targeting massively parallel computer using multi-processor nodes

Electron correlation

- All defects in the mean-field model are ascribed to electron correlation
- Consideration of singularities in the Hamiltonian imply that for a two-electron singlet atom (e.g., He)

$$\Psi(r_1, r_2, r_{12}) = 1 + \tfrac{1}{2} r_{12} + O(r_{12}^2) \quad \text{as} \quad r_{12} \to 0$$



- Include the inter-electron distance in the wavefunction
  - E.g., Hylleraas 1938 wavefunction for He

$$\Psi(r_1, r_2, r_{12}) = e^{-\varsigma(r_1 + r_2)}(1 + a r_{12} + \cdots)$$

  - Potentially very accurate, but not systematically improvable, and (until recently) not computationally feasible for many-electron systems

Conventional approach

- The two-electron wave function is expanded as a product of one-particle functions (orbitals)

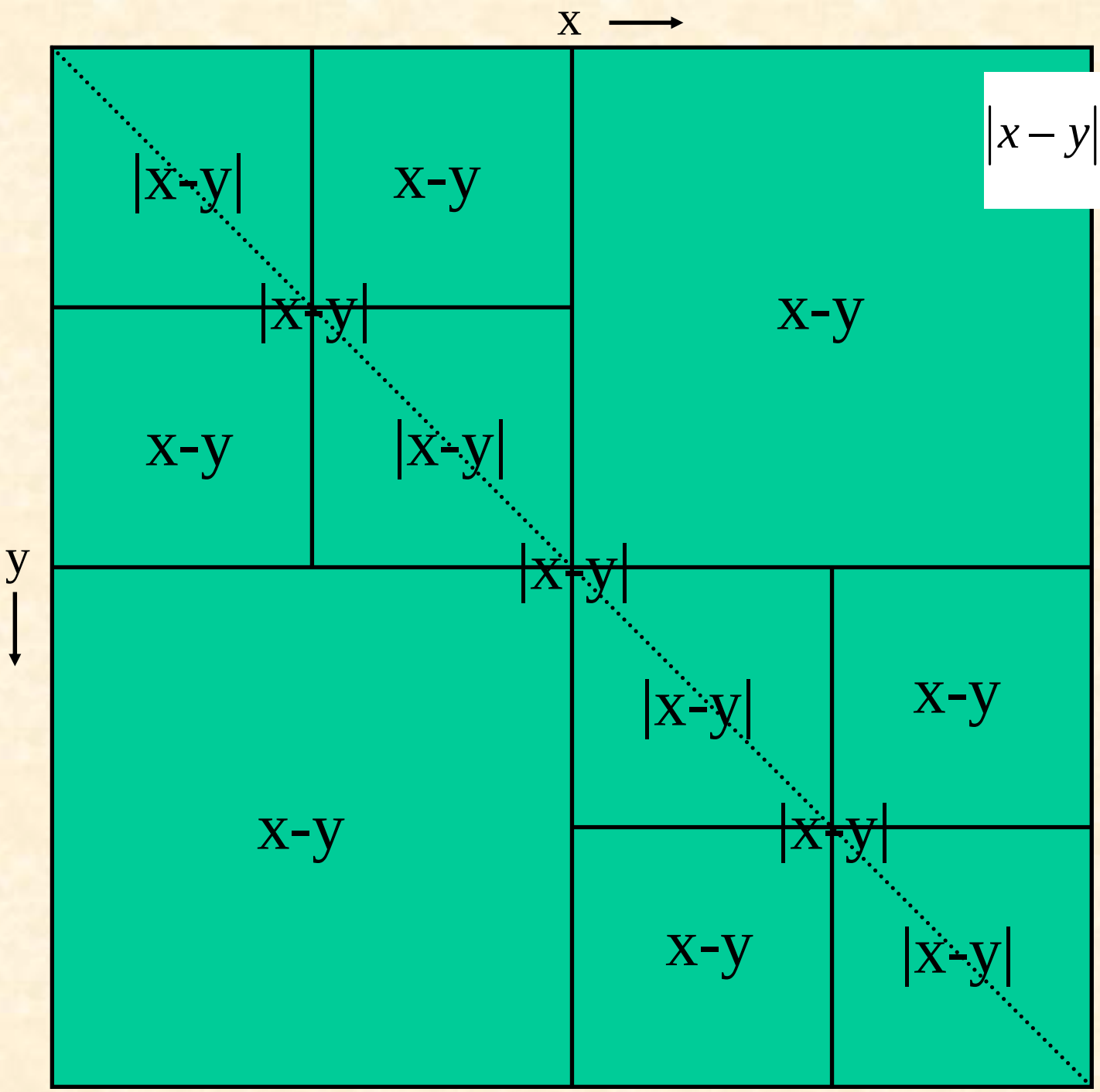
$$\Psi(r_1, r_2) = \sum_{ij} c_{ij} \phi_i(r_1) \phi_j(r_2)$$

- Can prove for atoms, that if saturate the atomic basis up to some angular momentum L, then

$$\Delta E_{corr} \propto (L+1)^{-3}$$

L	d	f	g	h
$(L+1)^{-3}$	0.04	0.016	0.008	0.0046

- Correlation consistent basis sets (Dunning) are currently the best choice – cost is $O(\varepsilon^{-4})$
- Explicitly correlated wave functions yields $O(\varepsilon^{-2.4})$
- Fully numerical promises $O(\log \varepsilon^{-1})$



$$|x-y| = \sum_{\mu=1}^{r} f_\mu(x) g_\mu(y)$$

r = separation rank

In 3D, ideally must be one box removed from the diagonal

Diagonal box has full rank

Boxes touching diagonal (face, edge, or corner) have increasingly low rank

Away from diagonal $r = O(-\log \varepsilon)$

Multiresolution solver of two-electron Schrödinger equation

- Wavefunction in 6-D multiresolution representation
- Solve integral equation
  - The 6D GF nominally has 12 indices! Separated representation of operator accurate and efficient
- Partly or fully use SVD to represent 6-D tensor coefficient sets
  - Blocks separated from the diagonal have low rank (1 or 2, the full rank being k^3)
  - Directly analogous to linear CI expansion but not global
- Can compute directly in this form, but other refinements make it much more practical

Analytic removal of cusp(s)

- Two-electron Hamiltonian

$$H = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + V(r_1, r_2) + \frac{1}{|r_1 - r_2|}$$

- Two-electron wavefunction

$$\Psi(r_1, r_2) = e^{u(|r_1 - r_2|)}\phi(r_1, r_2)$$

- Transformed problem

$$e^{-u}He^{u}\phi = -\frac{1}{2}\Delta_1\phi - \frac{1}{2}\Delta_2\phi - u'\frac{r_1 - r_2}{|r_1 - r_2|}\bullet\left(\nabla_1\phi - \nabla_2\phi\right)$$

$$+\left(V - \left((u')^2 + u''\right) + \frac{1}{|r_1 - r_2|}(1 - 2u')\right)\phi$$

- Choose u to eliminate singularity at $r_{12}=0$

Smoothed potential and wave function

- Similarity-transformed Hamiltonian with correlation factor (cf. transcorrelated Hamiltonian)
  - The effective wavefuntion Φ as well as the transformed Hamiltonian is smoothed at r_{12}=0

$$\bar{H} = e^{-u(r_{12})}\hat{H}e^{u(r_{12})}$$

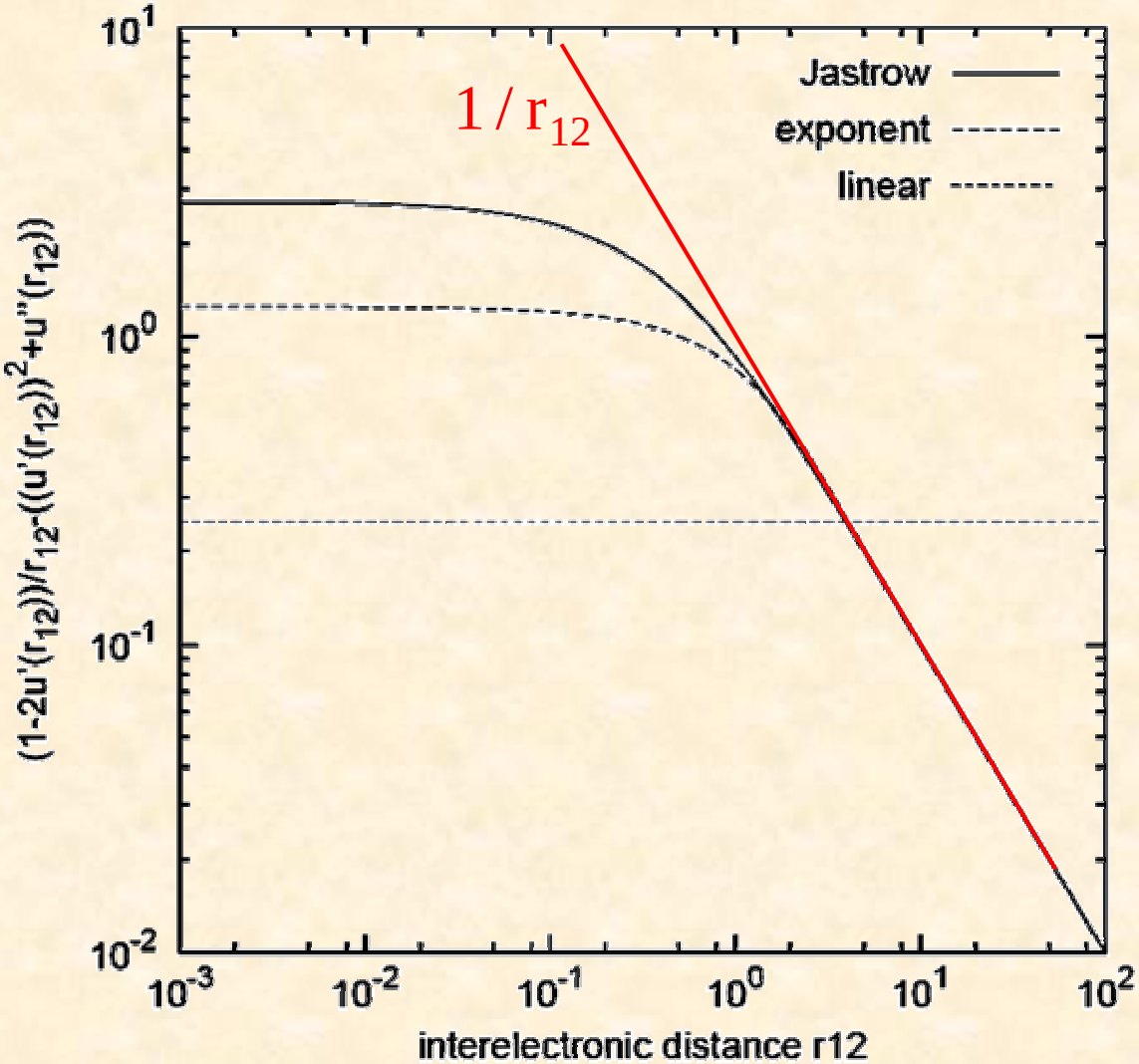
$$\Psi(r_1, r_2) = e^{u(r_{12})}\Phi(r_1, r_2)$$

Correlation factor: $u(r_{12})$

  - Electron-electron repulsion is smoothed

$$\frac{1}{r_{12}} \rightarrow \begin{array}{l} \frac{1}{r_{12}}\left(1-2u'(r_{12})\right)-u'(r_{12})^2-u''(r_{12}) \\ -u'(r_{12})\frac{\mathbf{r}_1-\mathbf{r}_2}{r_{12}}\cdot(\nabla_1-\nabla_2) \end{array}$$

Smoothed interelectron potential



- Correlation factor
  - Jastrow

$$u(r_{12}) = \frac{ar_{12}}{1+br_{12}}$$

  - Exponential

$$u(r_{12}) = a\left(1-e^{-br_{12}}\right)$$

  - Linear

$$u(r_{12}) = \frac{1}{2}r_{12}$$

Solve for the correlation correction to the HF wavefunction

- The smoothed wavefunction is separated into Hartree-Fock wavefunction and its perturbation.
  - The perturbative wavefunction is numerically smaller than Hartree-Fock wavefunction.

$$\Phi\left(r_1, r_2\right) = \Phi^{HF}\left(r_1, r_2\right) + \underline{\delta\Phi\left(r_1, r_2\right)}$$

$$\begin{cases} \left\|\Phi^{HF}\left(r_1, r_2\right)\right\|_2 = 1.0 \\ \left\|\underline{\delta\Phi\left(r_1, r_2\right)}\right\|_2 \approx 0.1 \end{cases}$$

For He atom

Preliminary results for He atom

	Variational E	ΔE	residual
HF	-2.861 61		
Iter. 0	-2.871 08		0.414 73
1	-2.894 92	-0.023 84	0.017 28
2	-2.900 43	-0.005 51	0.007 94
3	-2.902 18	-0.001 75	0.003 84
4	-2.902 88	-0.000 70	0.002 02
5	-2.903 20	-0.000 32	0.001 25
6	-2.903 39	-0.000 20	0.000 91
…	…	…	…
12	-2.903 73	-0.000 04	0.000 36
13	-2.903 73	+0.000 004	0.000 32
14	-2.903 77	-0.000 04	0.000 28

exact	-2.903 74 (E(HF)=-2.861 68)
Hylleraas (6 terms)	-2.903 24
Löwdin and Redei	-2.895 4
cc-pV6Z	-2.903 48 (FCI) (E(HF)= -2.861 67)

Computational details:

- 5-th order multiwavelets
- Wavelet threshold: 2×10^{-5}
- SVD threshold: 2×10^{-6}
- Exponential correlation factor

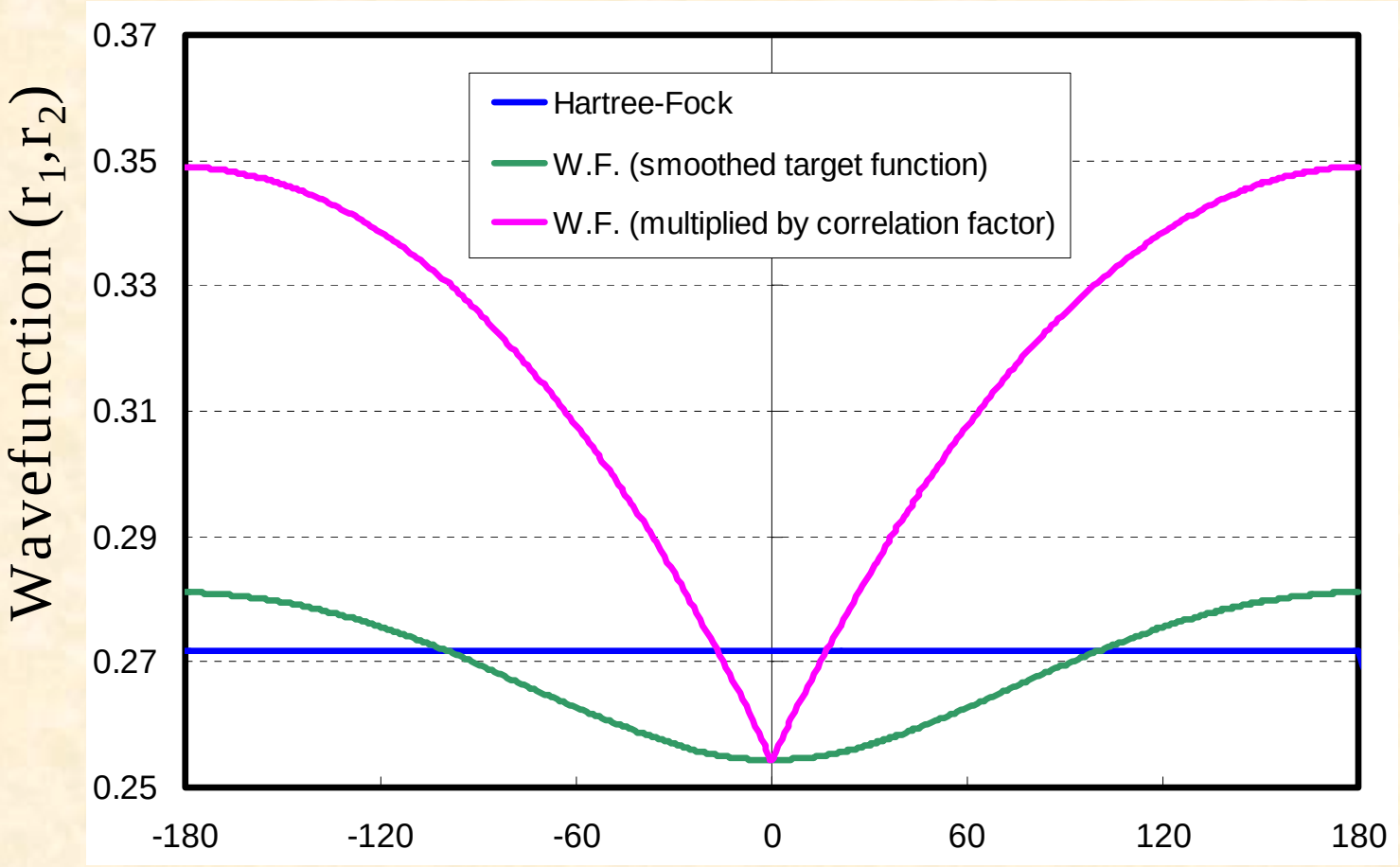
Perturbative wavefunction:

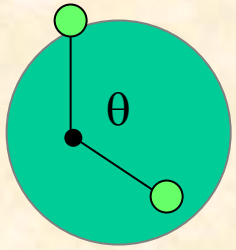
- Maximum refinement: n=4

-Memory: 132M in full SVD form

-Energy is variational (small non-variational is just truncation err)

Coulomb hole (He)





$r_1=r_2=0.5a_0$

Summary

- 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/boundary conditions
  - General framework readily accessible to researchers
  - Real impact will be application to many-body models
- Separated form for operators and functions
  - Critical for efficient computation in higher dimension
- Precision is guaranteed
  - Excited states, non-linear response, …