A multiresolution approach to quantum chemistry in multiwavelet bases

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The mathematicians …

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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
  - Much smaller computer code than Gaussians
  - No two-electron integrals - replaced by fast application of integral operators

Distinguishing Features

- Multiwavelet bases
  - Disjoint support maintains high-order convergence up to singularities and complex boundary conditions
- Non-standard form of operators and functions
  - Fully adaptive local representation
  - Operators are easy to compute and fast to apply
- Integral operator formulation
  - Avoids problems inherent to differential operators of high norm
  - O(N) and with rapid convergence

Many electron basis problem

- Scaling of cost of CCSD(T)
  - $O(o^3V^4)$ (o=occupied, V=virtual)
  - Error in correlation energy is $\varepsilon=O(L^{-3})$ where L is the maximum angular momentum
  - $O(o^3\varepsilon^{-4})$ in Dunning cc-pVnZ
  - $O(o^3\varepsilon^{-2.5})$ if exactly include linear r_{12} for atoms
  - An appropriate basis should give near $O(o^3 \log \varepsilon)$ and linear methods should enable $O(o \log \varepsilon)$
  - An appropriate basis must fully account for the singularities in the pair function (e-e, n-e).

Overview

- An introduction to multiresolution analysis in multiwavelet bases
  - Multiwavelets on *disjoint* intervals
  - Two-scale relations
  - Standard and non-standard representation of functions and operators
  - Integral operators
- Density Functional Theory
- Initial applications

References

- The (multi)wavelet methods in this work are primarily based upon
  - Alpert, Beylkin, Grimes, Vozovoi (to be published)
  - B. Alpert (SIAM Journal on Mathematical Analysis 24, 246-262, 1993).
  - Beylkin, Coifman, Rokhlin (Communications on Pure and Applied Mathematics, 44, 141-183, 1991.)

- 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"*

Why “think” multiresolution?

- It is everywhere in nature/chemistry/physics
  - Core/valence; high/low frequency; short/long range; smooth/non-smooth; atomic/nano/micro/macro scale
- Common to separate just two scales
  - E.g., core orbital heavily contracted, valence flexible
  - More efficient, compact, and numerically stable
- Multiresolution
  - Recursively separate all length/time scales
  - Computationally efficient and numerically stable
  - Coarse-scale models that capture fine-scale detail

How to "think" multiresolution - I

- 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

How to "think" multiresolution - II

- Homogenization (Beylkin, Brewster/Athan)
  - Coarse scale equations that capture fine-scale detail
  - E.g., Schur complement for linear equations

$$\begin{bmatrix} T & C \\ B & A \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} s \\ d \end{bmatrix} \quad s, x \text{ in } V_{n-1} \; y, d \text{ in } V_n - V_{n-1}$$

$$Bx + Ay = d$$

$$\Rightarrow y = A^{-1}\left(d - Bx\right)$$

$$Tx + Cy = s$$

$$\Rightarrow \left(T - CA^{-1}B\right)x = s - A^{-1}d$$

A coarse-scale-only equation that exactly includes fine-scale contributions

Another Key Component

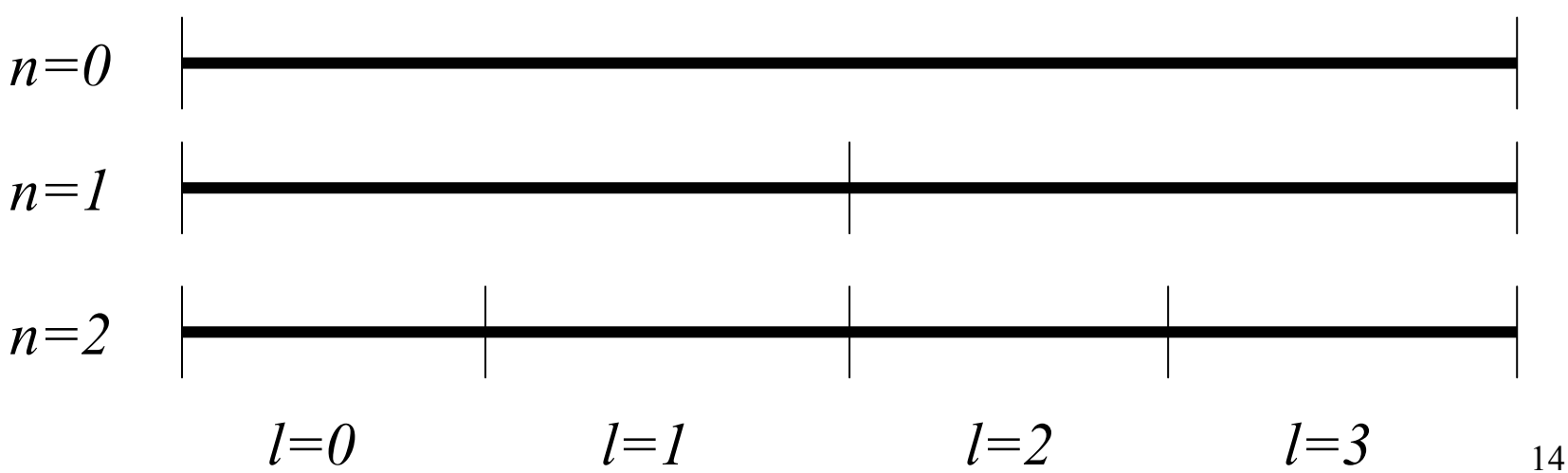
- Trade precision for speed – everywhere
  - Don't do anything exactly
  - Perform everything to $O(\varepsilon)$
  - Require
    - Robustness
    - Speed, and
    - Guaranteed, arbitrary, *finite* precision

Problem Setup

- In 1-D solve on [0,1]
- Tensor product in n-D
- Periodic and infinite domains also feasible

Scaling Function Basis - I

- Divide domain into 2^n pieces
  - Referred to as level n
  - Adaptive sub-division – local refinement
  - Non-uniform division important (not yet done)
  - l^{th} sub-interval $[l*2^{-n},(l+1)*2^{-n}]$ $l=0,\ldots,n-1$



Scaling Function Basis - II

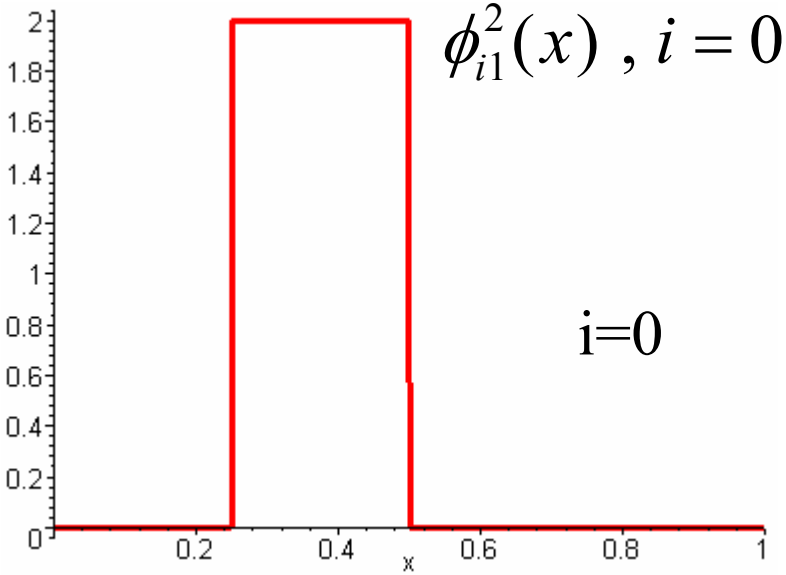
- In each sub-interval define a polynomial basis
  - Currently use the first *k* Legendre polynomials
  - Other bases interesting (e.g, interpolating polynomials, non-polynomial functions)
  - Zero outside of the sub-interval

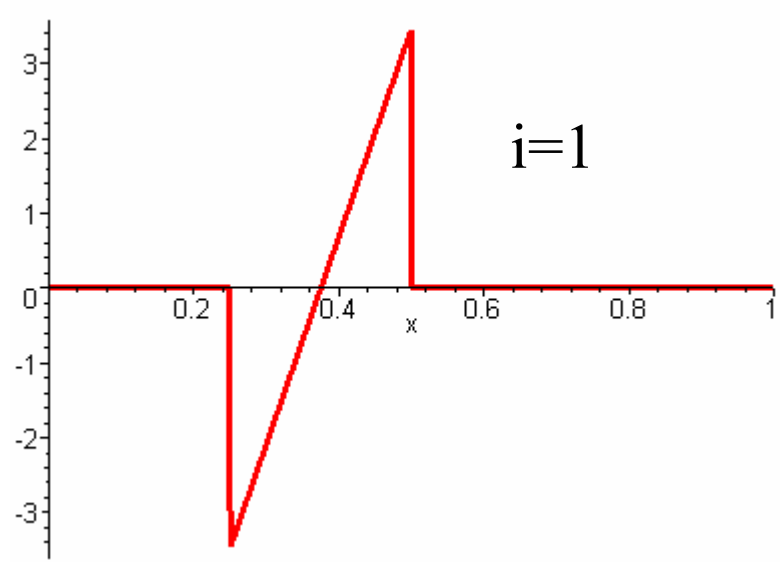
$$\phi_i(x) = \begin{cases} \sqrt{2i+1}P_i(2x-1) & 0 \le x \le 1 \\ 0 & \text{otherwise} \end{cases}$$

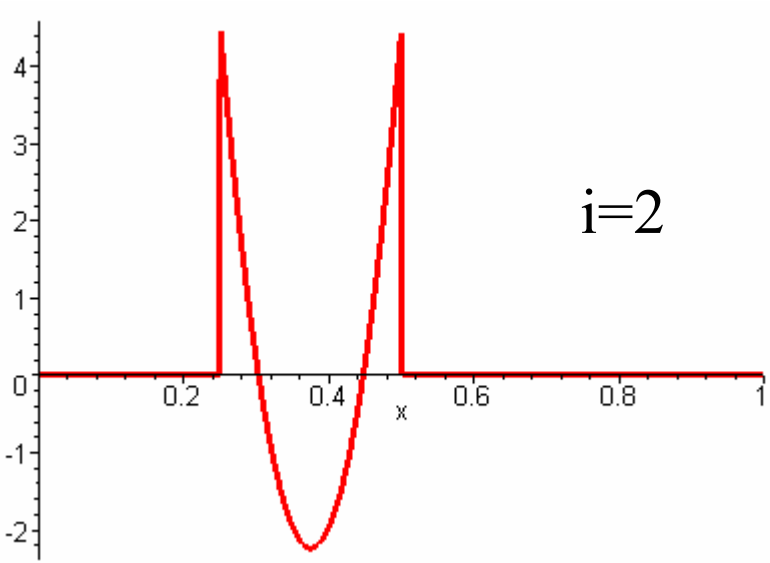
$$\phi_{il}^n(x) = 2^{n/2}\phi_i(2^n x - l)$$

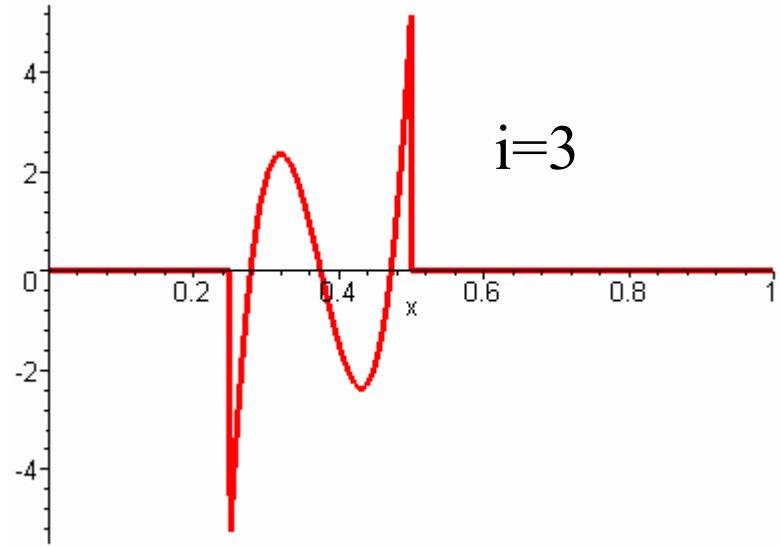
Scaling Function Basis - III

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









Scaling Function Basis - IV

- Translation and dilation

$$\phi_{il}^{n}(x) = 2^{n/2}\phi_i(2^n x - l)$$

- Orthonormal

$$\int_{-\infty}^{\infty} \phi_{il}^{n}(x)\phi_{jm}^{n}(x) = \delta_{lm}\delta_{ij}$$

- Ladder of spaces

$$V_n = \left\{\phi_{il}^{n}(x)\right\}$$

$$i = 0,\ldots,k-1; l = 0,\ldots,2^n - 1$$

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

- Complete basis for L_2 [0,1] in limit of *either* large *k* or large *n*.

Two-scale relationship

- $V_0 \subset V_1$ – can represent coarse scale basis exactly in the fine scale basis

$$\phi_i(x) = \sqrt{2}\sum_{j=0}^{k-1}\left(h_{ij}^{(0)}\phi_j(2x) + h_{ij}^{(1)}\phi_j(2x-1)\right)$$

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

- The filter coefficients (H) may be computed analytically or numerically.

Expansion of a function

- Projection of a function into V_n

$$f^n(x) = \sum_{l=0}^{2^n-1} \sum_{i=0}^{k-1} s_{il}^n \phi_{il}^n(x)$$

$$s_{il}^n = \int dx f(x) \phi_{il}^n(x)$$

- Local error is $O(f^{(k)}(\xi)2^{-nk})$ – high-order convergence
- If a function is expanded in V_n, what is the error from truncating to V_{n-1}?
- The error is contained in $W_{n-1}=V_n - V_{n-1}$

Multiwavelet Basis - I

- An orthonormal basis to span $W_{n-1} = V_n - V_{n-1}$
- Also demand
  - Disjoint support (important!)
  - Dilation/translation of wavelets at level 0
- Expand in V_n

$$\psi_i(x) = \sqrt{2}\sum_{j=0}^{k-1}\left(g_{ij}^{(0)}\phi_j(2x) + g_{ij}^{(1)}\phi_j(2x-1)\right)$$

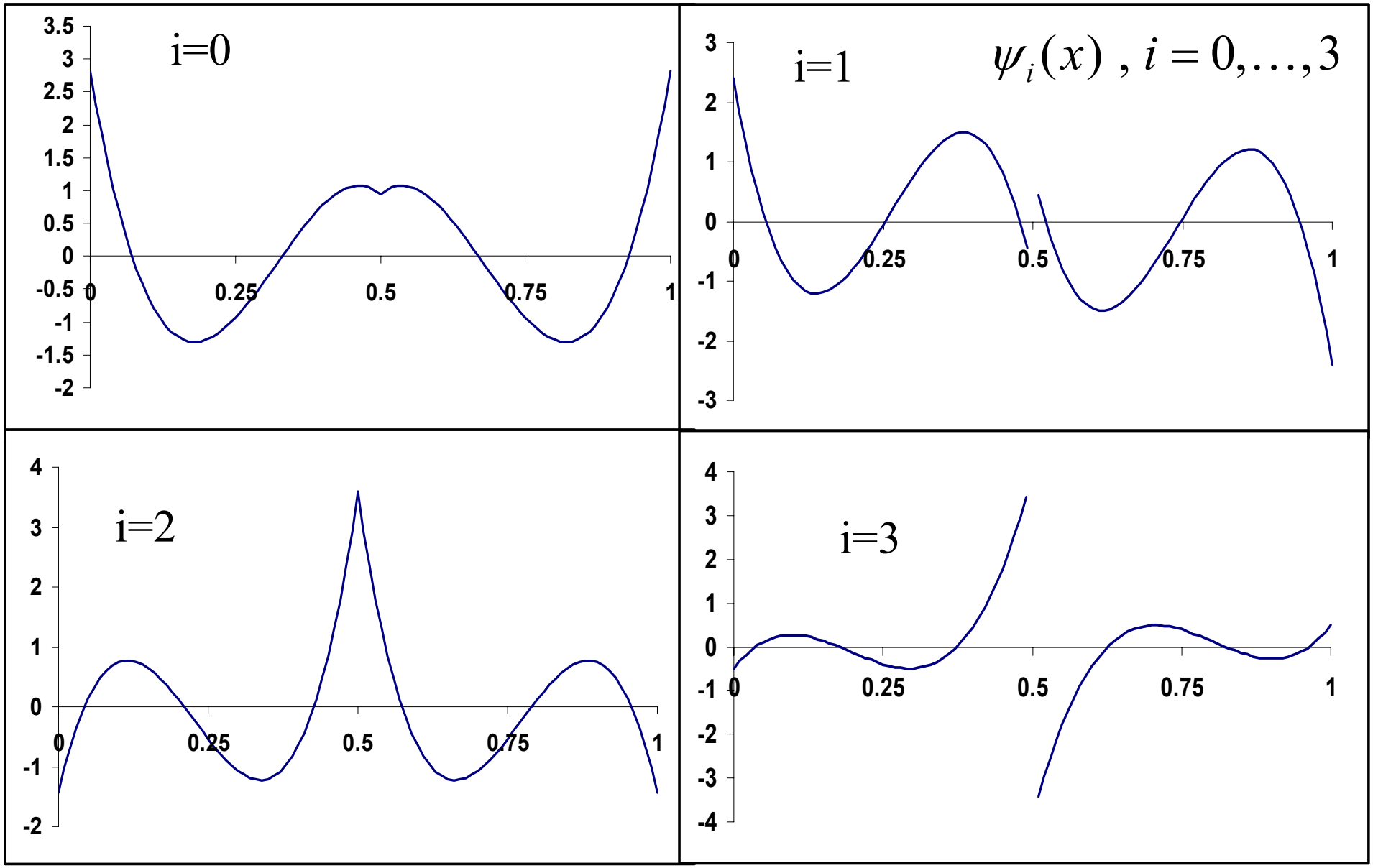
$$\psi_{il}^{n-1}(x) = \sum_{j=0}^{k-1}\left(g_{ij}^{(0)}\phi_{j2l}^{n}(x) + g_{ij}^{(1)}\phi_{j2l+1}^{n}(x)\right)$$

Multiwavelet Basis - II

- Basis not yet completely specified
  - Currently use Alpert's basis (which imposes additional constraints … more about this later)
- The coefficients (G) may be evaluated analytically or numerically
  - Numerical evaluation requires extended precision arithmetic (e.g., 208 bits used for k=22).
- Constructive approach
  - From scaling function make the wavelets
  - Often the reverse (e.g., Daubechies wavelets)

Multiwavelet Basis - III

$k=4$



Multiwavelet Basis - IV

- Translation and dilation $$\psi_{li}^{n}(x) = 2^{n/2}\psi_i(2^n x - l)$$
- Orthonormal $$\int_{-\infty}^{\infty} \psi_{li}^{n}(x)\psi_{mj}^{n'}(x) = \delta_{nn'}\delta_{lm}\delta_{ij}$$
- Direct sum of sub-spaces $$V_n = V_0 \oplus W_0 \oplus W_1 \oplus \cdots \oplus W_{n-1}$$
- Complete basis for L_2 [0,1] in limit of *either* large *k* or large *n*.

Multiwavelet Basis - V

- 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.,

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

- In Alpert's basis, additional moments of some of the multiwavelet components also vanish

Some Consequences of Vanishing Moments

- 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., $1/|r-s|$
  - Consider double Taylor series or multipole expansion
  - Interaction between wavelets decays as r^{-2k-1}
- Derivatives at origin vanish in Fourier space
  - Diminishes effect of singularities at that point

Two-scale relationship - I

$$\begin{pmatrix} \phi(x) \\ \psi(x) \end{pmatrix} = \sqrt{2} \begin{pmatrix} H^{(0)} & H^{(1)} \\ G^{(0)} & G^{(1)} \end{pmatrix} \begin{pmatrix} \phi(2x) \\ \phi(2x-1) \end{pmatrix}$$

Two-scale relationship II

$$f^n(x) = \sum_{l=0}^{2^n-1} \sum_{i=0}^{k-1} s_{il}^n \phi_{il}^n(x)$$

- May be rewritten without approximation as

$$f^n(x) = \sum_{l=0}^{2^{n-1}-1} \sum_{i=0}^{k-1} \left(s_{il}^{n-1} \phi_{il}^{n-1}(x) + d_{il}^{n-1} \psi_{il}^{n-1}(x) \right)$$

- Where

$$\begin{pmatrix} s_{il}^{n-1} \\ d_{il}^{n-1} \end{pmatrix} = \begin{pmatrix} H^{(0)} & H^{(1)} \\ G^{(0)} & G^{(1)} \end{pmatrix} \begin{pmatrix} s_{i2l}^{n} \\ s_{i2l+1}^{n} \end{pmatrix}$$

Compression of a function

$$V_n = V_0 \oplus W_0 \oplus W_1 \oplus \cdots \oplus W_{n-1}$$

- Recursively apply the two-scale relation
- The basis is the scaling functions at level 0 and the multiwavelets at all levels

$$f^n(x) = \sum_{i=0}^{k-1} s_{i0}^0 \phi_{i0}^0(x) + \sum_{n'=0}^{n-1} \sum_{l=0}^{2^{n'}-1} \sum_{i=0}^{k-1} d_{il}^{n'} \psi_{il}^{n'}(x)$$

- Haar basis (*k=1*) gives rise to calling coefficients of the scaling functions and wavelets as sums and differences respectively (hence notation *s* and *d*)
- Compression & reconstruction are *O(N)* operations

Two equivalent representations

- Scaling function basis (reconstructed)

$$f^n(x) = \sum_{l=0}^{2^n-1} \sum_{i=0}^{k-1} s_{il}^n \phi_{il}^n(x)$$

- Multi-wavelet basis (compressed)

$$f^n(x) = \sum_{i=0}^{k-1} s_{i0}^0 \phi_{i0}^0(x) + \sum_{n'=0}^{n-1} \sum_{l=0}^{2^{n'}-1} \sum_{i=0}^{k-1} d_{il}^{n'} \psi_{il}^{n'}(x)$$

- Rapid compression/reconstruction
  - Asymptotically faster than the FFT
  - Use most appropriate basis for a given operation

A Third Equivalent Representation

- The function tabulated at the Gauss-Legendre quadrature points in each of the adaptively refined boxes
  - Enables rapid multiplication of functions and application of local functions (e.g., V_{xc})
  - Diagonal transformation from interpolating polynomials

Truncation Error

- To satisfy the global error condition

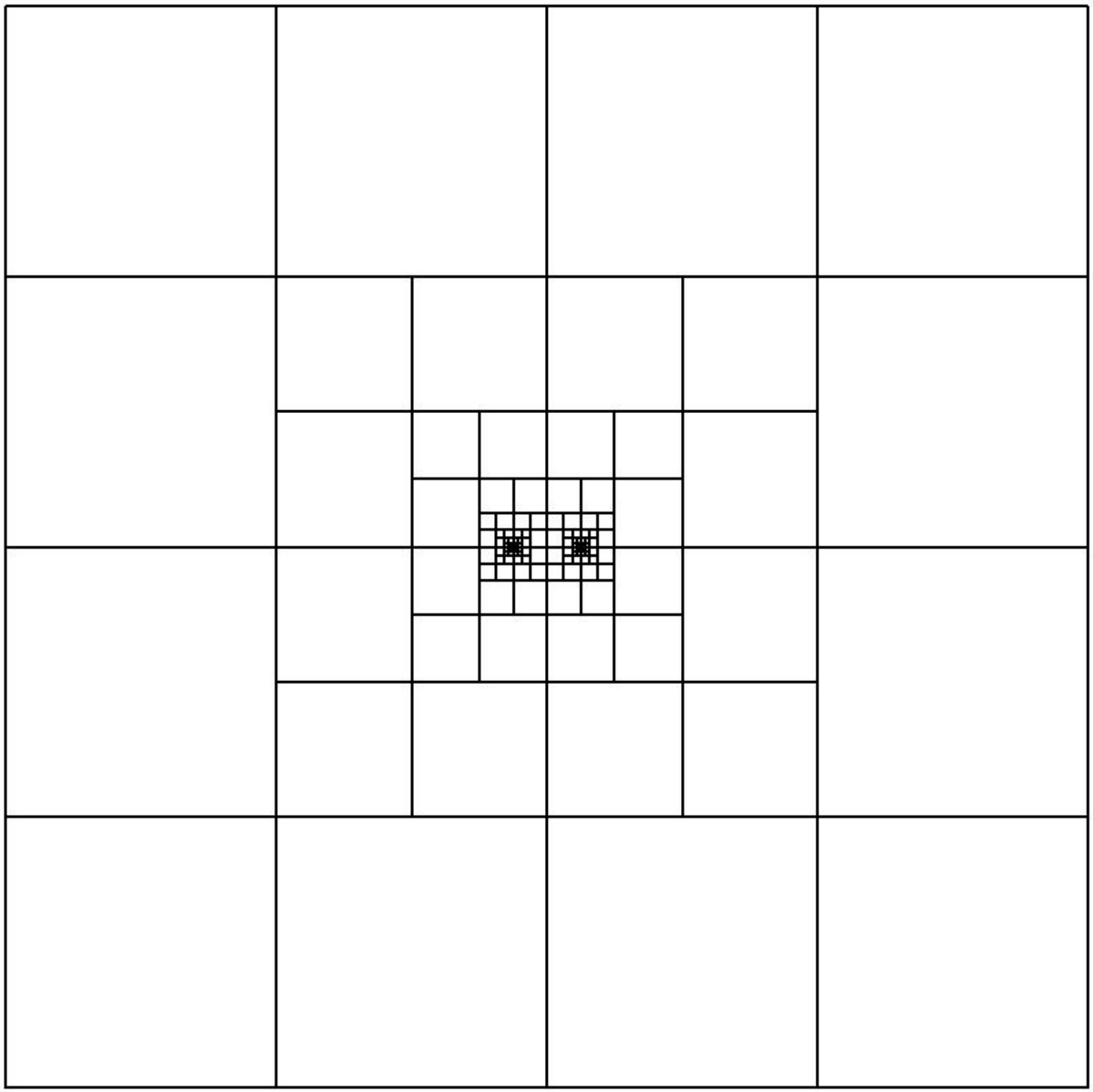
$$\left\| f - f^n \right\|_2 \le \varepsilon \left\| f \right\|_2$$

- Truncate according to

$$\left\| d_l^n \right\|_2 \le 2^{-n/2} \varepsilon \left\| f \right\|_2$$

- This is rather conservative – usually use

$$\left\| d_l^n \right\|_2 \le \varepsilon$$



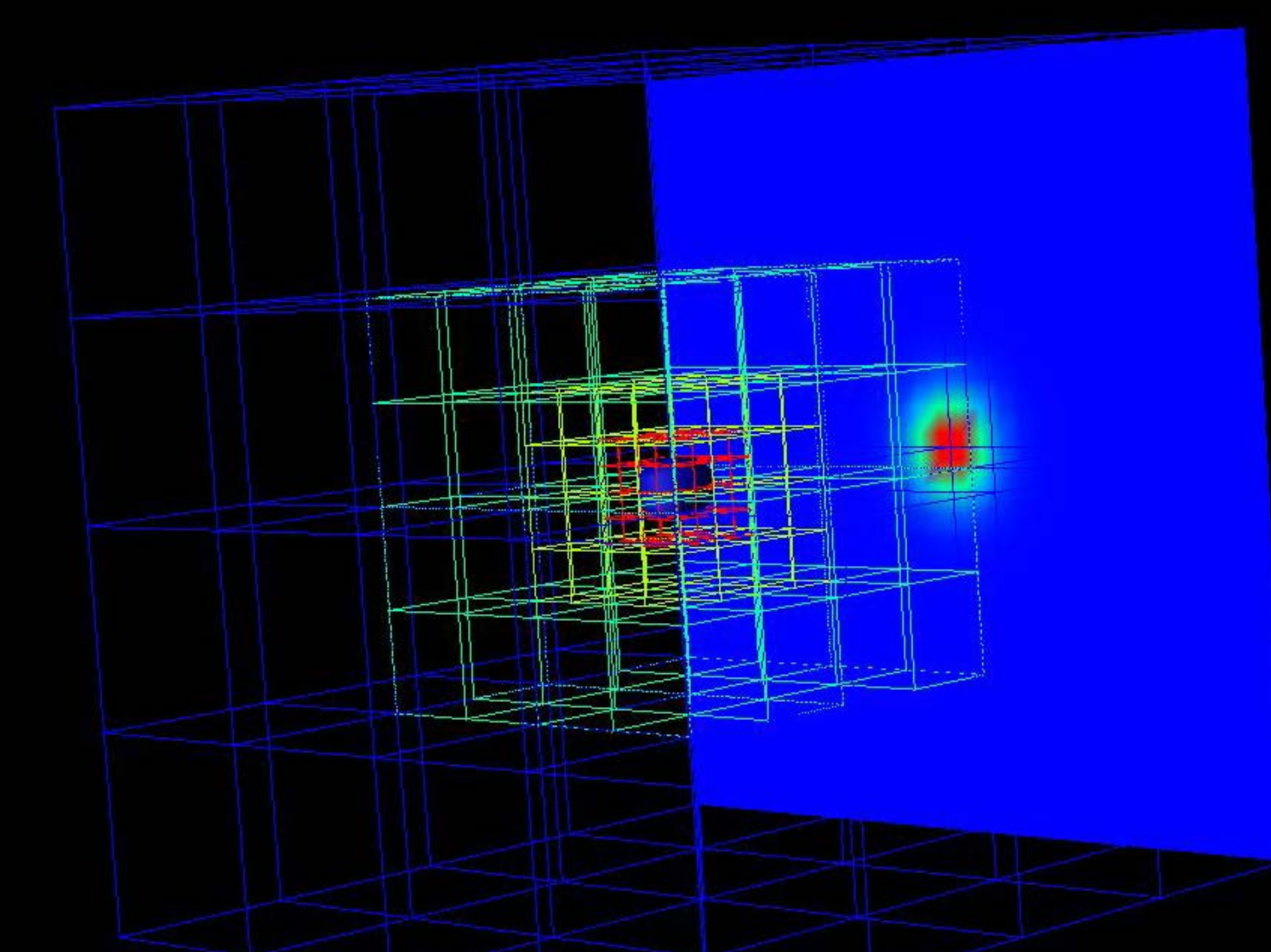
- Slice thru grid used to represent the nuclear potential for H_2 using k=7 to a precision of 10^{-5}.

- 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.



Summary so far

- Scaling functions
  - Easy to manipulate, evaluate, integrate, …
- Multi-resolution analysis
  - Separates behavior on different length scales
  - Local truncation while preserving global error bound
  - Vanishing moments
- Multi-wavelets
  - High-order convergence with adaptive representation
  - Disjoint support – efficient description of singularities if locacated at faces/edges/corners (more efficient than smooth wavelets since they do not have disjoint support)
- Fast compression and reconstruction
  - Orthogonal transformations – numerically stable

Compression of a Matrix

- Compression is just a linear transformation
  - Apply separately to each dimension

$$\tilde{A} = QAQ^T$$

  - Result is said to be in "standard form"

Extension to higher dimensions

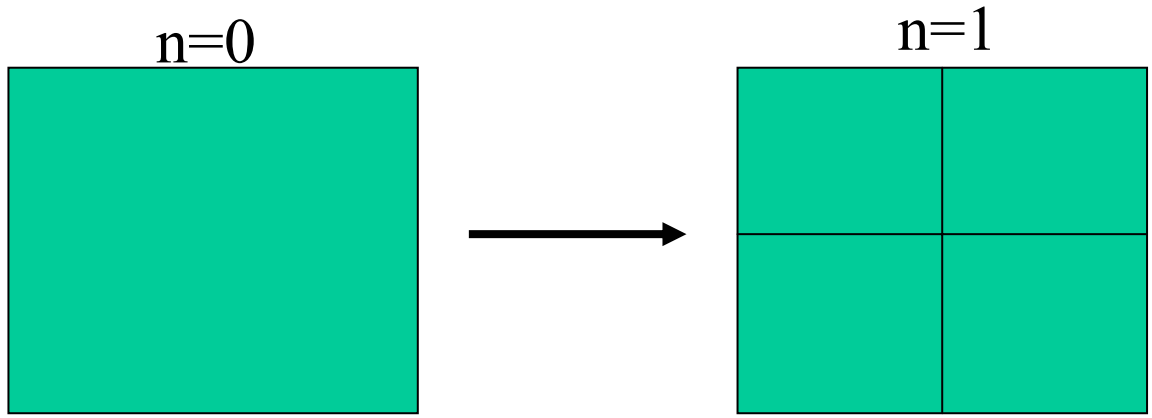
- Scaling function basis is tensor product

$$\phi^n_{ii'll'}(x,y) = \phi^n_{il}(x)\phi^n_{i'l'}(y)$$

- Wavelet basis – tensor product is one choice
  - Standard form – compress each dimension just as for a matrix
  - But cannot refine strictly locally since length scales are mixed between dimensions
- To refine locally need the non-standard form

Non-standard form of functions

- Construct local basis for $W_{n-1}=V_n - V_{n-1}$



$$V_0 = \phi(x)\phi(y)$$

$$V_1 = \sqrt{2}\left\{\begin{array}{l}\phi(2x)\phi(2y), \phi(2x)\phi(2y-1), \phi(2x-1)\phi(2y), \\ \phi(2x-1)\phi(2y-1)\end{array}\right\}$$

$$= \{\phi(x)\phi(y), \phi(x)\psi(y), \psi(x)\phi(y), \psi(x)\psi(y)\}$$

$$W_0 = V_1 - V_0 = \{\phi(x)\psi(y), \psi(x)\phi(y), \psi(x)\psi(y)\}$$

Non-standard form of operators - I

- Standard form
  - Matrix elements between different length scales
  - Not very efficient on modern computers with deep memory hierarchies
  - Potentially *O(Nlog N)* non-zero terms
- Non-standard form
  - No matrix elements between lengths scales
  - *O(N)* terms
  - Act on (modified) non-standard form of functions
  - Derivation is instructive

Non-standard form of operators - II

- P_n an orthogonal projection into V_n
- Q_n an orthogonal projection into $W_n = V_{n+1} - V_n$

$$P_n + Q_n = P_{n+1}$$

- Consider the projection of an operator T

$$\begin{aligned}
T_n &= P_n T P_n \\
&= \left(P_{n-1} + Q_{n-1}\right) T \left(P_{n-1} + Q_{n-1}\right) \\
&= P_{n-1} T P_{n-1} + Q_{n-1} T Q_{n-1} + Q_{n-1} T P_{n-1} + P_{n-1} T Q_{n-1} \\
&= T_{n-1} + A_{n-1} + B_{n-1} + C_{n-1} \\
&= T_0 + \sum_{\eta=0}^{n-1} A_\eta + B_\eta + C_\eta
\end{aligned}$$

NS Form of Operators III

- Matrix elements in the scaling function basis

$$\left[r_{lm}^{n} \right]_{ij} = \int \phi_{il}^{n}(x) \left(T \phi_{jm}^{n}(x) \right) dx$$

- Matrix elements of the NS form

$$\begin{pmatrix} r_{l,m}^{n-1} & \gamma_{l,m}^{n-1} \\ \beta_{l,m}^{n-1} & \alpha_{l,m}^{n-1} \end{pmatrix} = \begin{pmatrix} H^{(0)} & H^{(1)} \\ G^{(0)} & G^{(1)} \end{pmatrix} \begin{pmatrix} r_{2l,2m}^{n} & r_{2l,2m+1}^{n} \\ r_{2l+1,2m}^{n} & r_{2l+1,2m+1}^{n} \end{pmatrix} \begin{pmatrix} H^{(0)} & H^{(1)} \\ G^{(0)} & G^{(1)} \end{pmatrix}^{T}$$

Integral operators - I

- Consider $Tf(x) = \mathrm{pv}\int dyK(x-y)f(y)$

$$\left[r_{lm}^{n}\right]_{ij} = \int dx\int dyK(x-y)\phi_{il}^{n}(x)\phi_{jm}^{n}(y)$$

$$= 2^{-n}\int dx\int dyK(2^{-n}\left(x-y+l-m\right))\phi_i(x)\phi_j(y)$$

$$= 2^{-n}\int dzK(2^{-n}\left(z+l-m\right))\Phi_{ij}(z)$$

$$\Phi_{ij}(z) = \int dx\phi_i(x)\phi_j(x-z)$$

$$= \sum_{p=0}^{2k-1}\left(c_{ijp}^{(-)}\phi_p(z+1) + c_{ijp}^{(+)}\phi_p(z)\right)$$

$$\left[r_l^n\right]_p = 2^{-n}\int dzK(2^{-n}\left(z+l\right))\phi_p(z)$$

Integral operators - II

- Matrix elements easy to evaluate from compressed form of kernel $K(x)$
- Application in 1-d is fairly efficient
  - $O(k^2)$ operations
- In 3-d seems to need $O(N_{box}k^6)$ operations
  - Prohibitively expensive
- More intelligent approach
  - $O(N_{box}k^4)$ operations for many "physical" kernels
  - Even better is known to be possible

Vanishing Moments

- Sparse integral operators
  - If the derivatives decay rapidly (i.e., the kernel becomes smoother at long range)
  - See this by Taylor expansion (multipole series)
- Consider NS form of Poisson kernel (*1/r*)

$$\left[\alpha_{lm}^{n}\right]_{ij} = \psi_{il}^{n}(x) \leftrightarrow \psi_{jm}^{n}(y) = O\left(\left|l-m\right|^{-2k-1}\right)$$

$$\left[\beta_{lm}^{n}\right]_{ij} = \psi_{il}^{n}(x) \leftrightarrow \phi_{jm}^{n}(y) = O\left(\left|l-m\right|^{-k-1}\right)$$

$$\left[\gamma_{lm}^{n}\right]_{ij} = \phi_{il}^{n}(x) \leftrightarrow \psi_{jm}^{n}(y) = O\left(\left|l-m\right|^{-k-1}\right)$$

Relationship to the FMM

- Greengard, Rokhlin
- Separate the behavior on different length scales
- Exploit low-rank form of off-diagonal blocks
- Approaches each kernel as a special case
- Highly-optimized, but complex
  - E.g., latest FMM uses seven different representations
- MRA approach is immediately general
  - Simpler than FMM since don't need to traverse up/down tree
  - Not as fast unless use kernel-specific separated forms
  - Perhaps more straightforward to parallelize

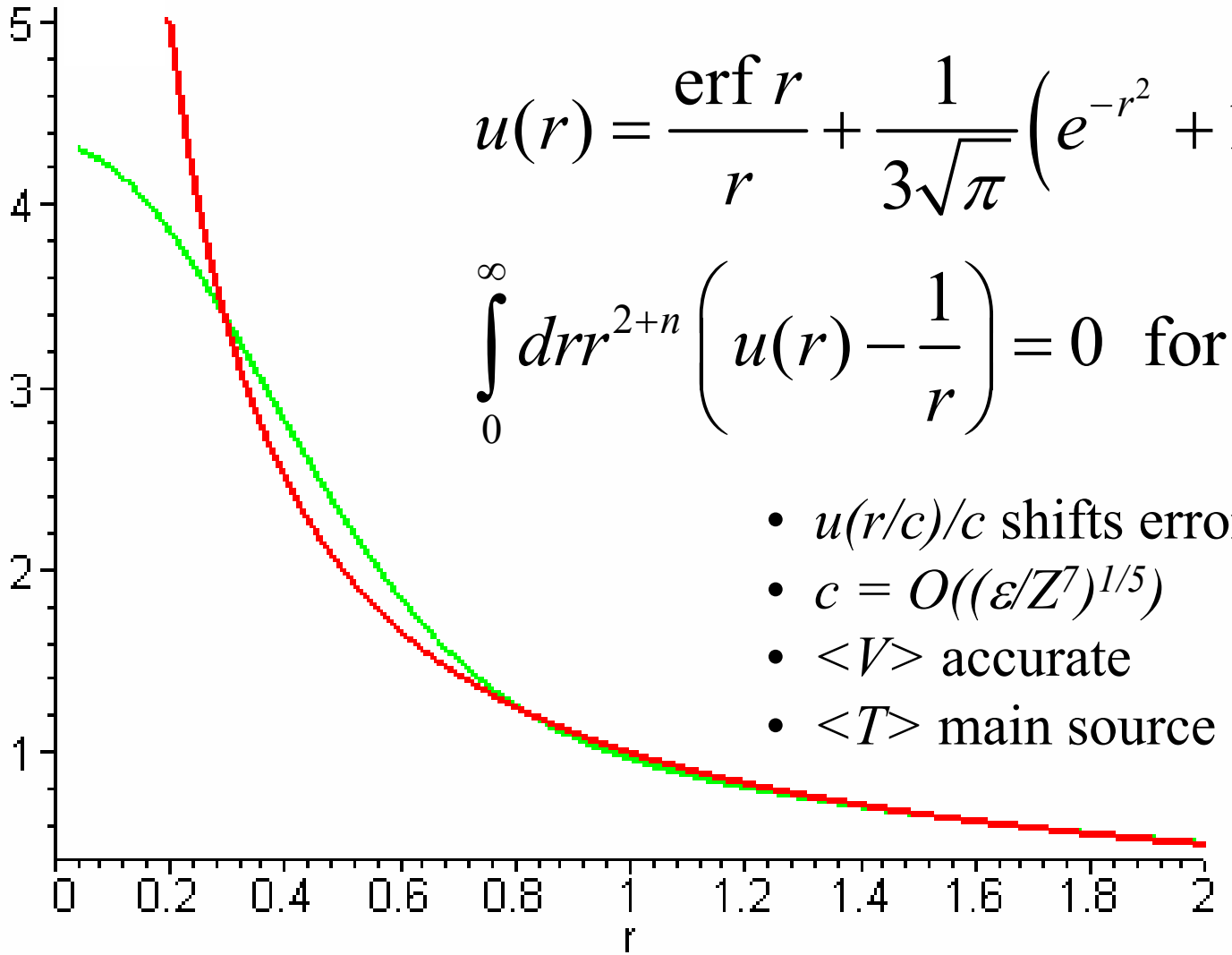
Summary so far

- Standard and non-standard form of functions and operators
  - Non-standard form facilitates local refinement of functions
  - Non-standard operators easy to compute/apply
- Integral convolution operators
  - Importance of vanishing moments
  - *O(N)* to any finite precision

Regularized Nuclear Potential - I

- Compression of singular functions
  - Do-able (if L_2 integrable) but not efficient (logarithmic convergence)
- Regularization
  - Smooth the singularity retaining accurate information for the length scales of interest
  - Beylkin, Cramer, Fann – algebraic/numerical regularization can handle any (hyper-) singular kernel even if not integrable.
  - Here use simpler analytic regularization

Regularized Nuclear Potential - II



$$u(r) = \frac{\operatorname{erf} r}{r} + \frac{1}{3\sqrt{\pi}}\left(e^{-r^2} + 16e^{-4r^2}\right)$$

$$\int_0^\infty dr r^{2+n}\left(u(r) - \frac{1}{r}\right) = 0 \quad \text{for} \quad n = 0,1,2$$

- $u(r/c)/c$ shifts error to $r<c$
- $c = O((\varepsilon/Z^7)^{1/5})$
- $\langle V \rangle$ accurate
- $\langle T \rangle$ main source of error

Analytic Derivatives

- Hellman-Feynman theorem applies

$$\frac{\partial E}{\partial x} = \left\langle \frac{\partial V}{\partial x} \right\rangle + O(\varepsilon)$$

Integral Formulation - I

- Kalos, 1962

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

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

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

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

- No derivative operator; fixed point iteration
- Accelerate with (Davidson-like) sub-space
- Not efficient for scattering states

Integral Formulation - II

- Extension to multiple roots via deflation

Q projects onto lower eigen vectors

$$\tilde{H} = (1-Q)H(1-Q) + \Delta Q \quad \text{shift low roots to } \Delta$$

$$= H - QH - HQ + QHQ + \Delta Q$$

$$= T + \tilde{V}$$

- Apply integral equation with this potential specific to individual excited state

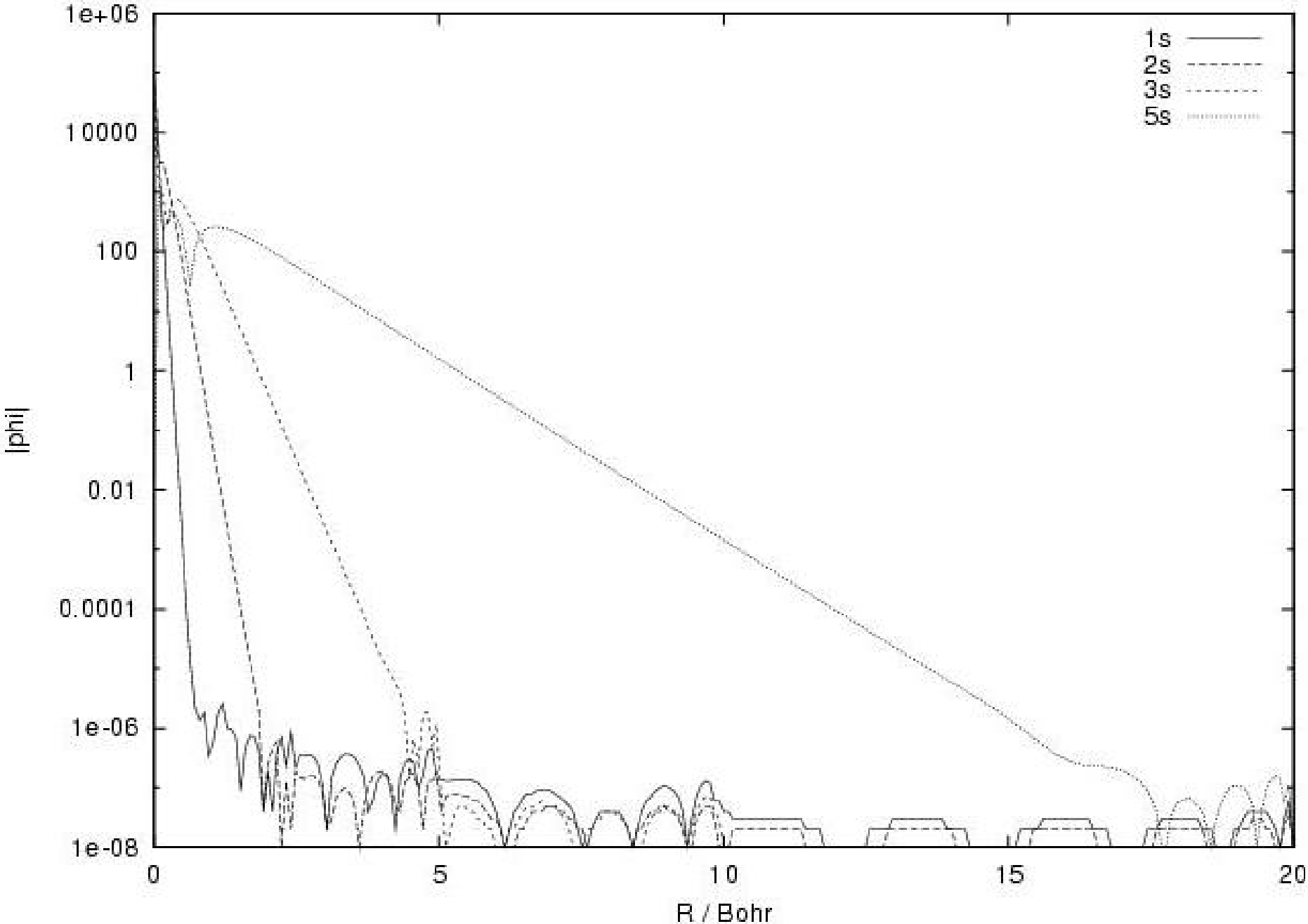
$$\tilde{V}(1-Q)\Psi = (V - QH)(1-Q)\Psi$$

Solution scheme

- For given precision ε
  - Choose smallest odd k such that $10^{2-k} < \varepsilon$
  - Empirically the most efficient choice
  - Regularize nuclear potential as described above
- Currently (still being refined)
  - Initial guess from STO-3G NWChem calculation
  - Solve with thresholds $\varepsilon = 10^{-3}, 10^{-5}, 10^{-7}, 10^{-9}$
  - Converge until residual norm $< max(10^{-4}, \varepsilon * 10)$
  - Project solution between bases
  - Enable automatic refinement intermittently

Test atomic calculations

- Hartree-Fock
  - He iso-electronic sequence
  - Comparison with results of Thakkar to 7dp
- LDA
  - Be (4), Mg (12), Ca (20), Sr (38)
  - Comparison to NIST results to 6 dp


1e+06
10000
100
1
0.01
0.0001
1e-06
1e-08
|phi|
0
5
10
15
20
R / Bohr
1s
2s
3s
5s

H_2^+

- R=2.0 L=64 a.u.

ε	Energy
10^{-3}	(?)
10^{-5}	-1.10262
10^{-7}	-1.1026342
10^{-9}	-1.102634203

- David Bates (1953) 1.10263
- Uncontracted cc-pv6z 1.102632

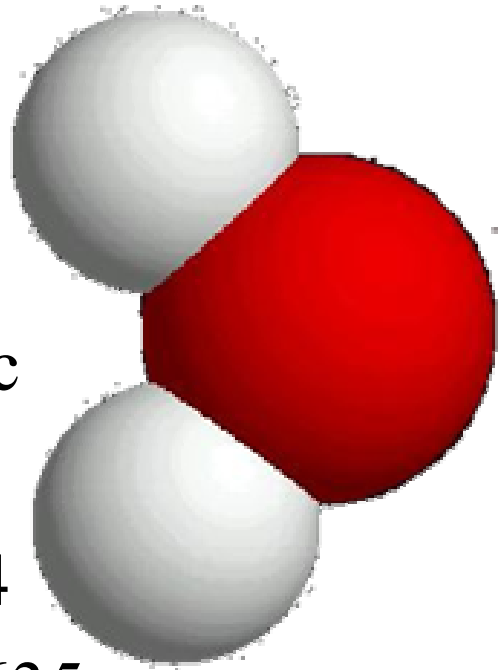
Hartree-Fock H_2

- R=1.4 L=44.8 a.u.

ε	Energy	Gradient
10^{-3}	-1.1334	0.0057
10^{-5}	-1.133628	0.005396
10^{-7}	-1.13362957	0.00538804
10^{-9}	-1.133629565	
23s9p4d4f2g1h	-1.133629366	
Mitin	-1.133629571463	

Mitin – best literature value PRA 62 10501
– extrapolation from distributed Gaussian bases

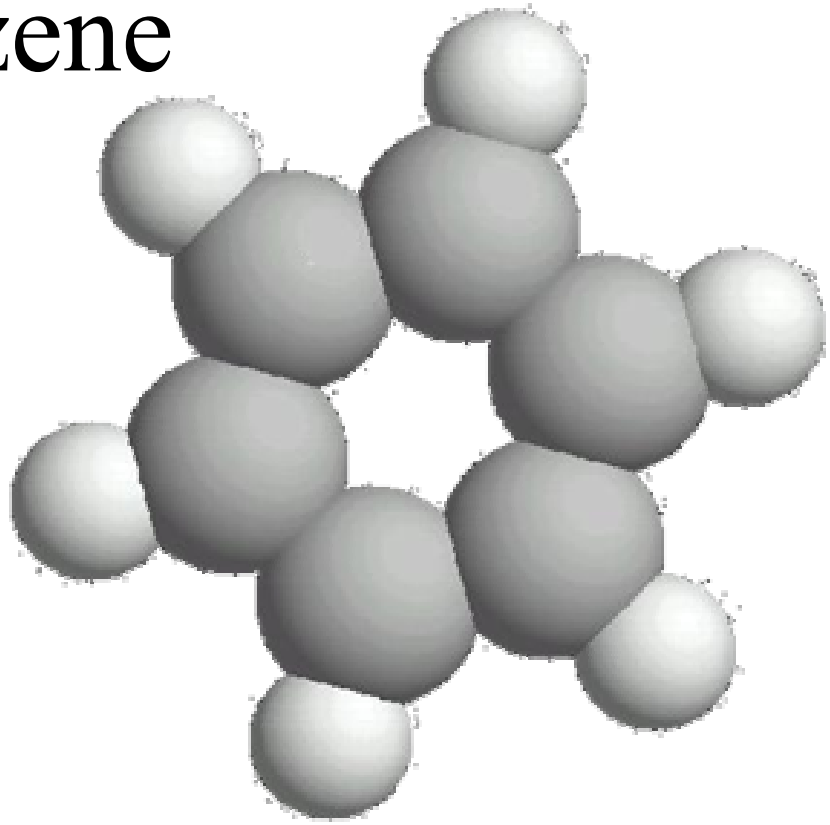
Water LDA



	Dyadic	Non-dyadic
10^{-3}	-75.9139	-75.9139
10^{-5}	-75.913564	-75.913564
10^{-7}	-75.91355634	-75.91355635

- Uncontracted aug-cc-pVQZ –75.913002
- Solving with e=1e-3, 1e-5, 1e-7 (k=7,9,11)
- Demonstrates translation invariance and that forcing to dyadic points is only an optimization and does not change the obtained precision.
- Average orbital sizes 1.6Mb, 8Mb, 56Mb

Benzene

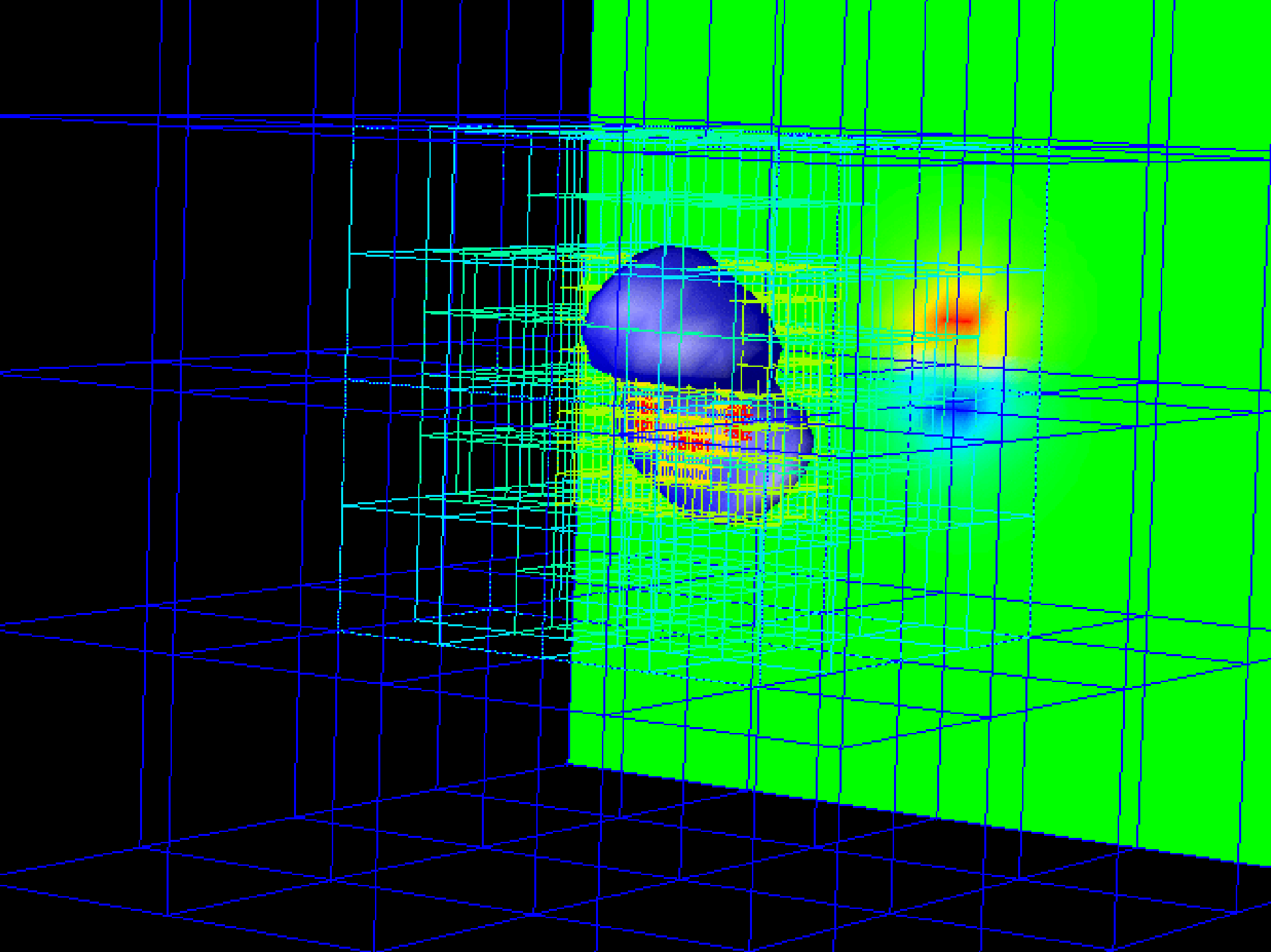


10^{-3} -230.194

10^{-5} -230.19838

10^{-7} -230.198345

- No symmetry used
- Partridge-3 prim + aug-cc-pvTZ pol. -230.158382
- Average orbital sizes 4 Mb, 16 Mb, 64 Mb



Also working

- Takeshi Yanai
  - Analytic derivatives
  - Fast Hartree-Fock exchange
  - TDDFT within Tamm-Damcoff approximation

- Thanks to
  - So Hirata for guidance with TDDFT
  - Edo Apra for insights into DFT

Two-electron Functions

- Currently exploring feasibility and approaches
- E.g., He 3- and 6-term Hylleraas functions
  - Straightforward 6-D compression in Cartesians
  - $\varepsilon=10^{-3}$ k=5 have $1.3*10^{8}$ variables
  - $\varepsilon=10^{-4}$ k=6 have $3.8*10^{8}$ variables
- Need to exploit known behavior at large r_{12}
  - Reduces volume with high dimension
  - Non-standard v.s. standard form?
- $\underline{R}=\underline{r}_1+\underline{r}_2$ and $\underline{r}_{12}=\underline{r}_1-\underline{r}_2$
  - Moves e-e singularity to origin but smears out nuclear singularities and many operators are harder to apply
- Variational models (e.g., MP2) require low precision

Summary

- Multi-wavelets provide a general framework for computational chemistry
  - Accurate and efficient with a very small code
  - Higher-order convergence and accommodates singularities, discontinuities and complicated boundary conditions
- Readily accessible by students and researchers
  - Familiar orthonormal basis (Legendre polynomials)
  - Compression and reconstruction (c.f., FFT)
  - Fast integral operators
- Expect speed competitive to Gaussians in near future
  - Optimal separated forms for kernels, multi-scale non-linear solver, low-rank form for operators

SciDAC: Advanced Methods for Electronic Structure

- Robert J. Harrison (PI) with Fann (PNNL), Beylkin (U. Colorado)
- Objectives:
  - Elimination of basis set error
  - Correct scaling with system size
  - One- (DFT/HF) and two-electron (MP2) models
- Distinguishing features
  - Multiresolution in multiwavelet bases
  - Near-spectral precision
  - Integral formulation of quantum theory (efficient, avoids iterative solution of linear equation and problems with differential operators)
  - Separated representation of integral operators