Advanced Methods for Electronic Structure

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- Objectives:
  - Eliminate basis set error
  - Correct scaling with system size
  - One- (DFT/HF) and two-electron (MP2) models

- Funded by DOE/OBES/Chem. Sci. SciDAC

Distinguishing features

- Multiresolution in multiwavelet bases
- Near-spectral precision
- Integral formulation of quantum theory
  - efficient, avoids iterative solution of linear equations and problems with differential operators
- Separated representation of integral operators
  - computation in higher dimensions
- Non-standard form of operators

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 <u>all</u> length/time scales
  - Computationally efficient and numerically stable in an orthogonal basis
  - Coarse-scale models that capture fine-scale detail

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 (V_n), use the difference between successive approximations
  - Representation on V_0 small/dense; differences sparse
  - Computationally efficient; possible insights (e.g., homogenization, regularization)

Key Components - I

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

Key Components - II

- 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

$$K(r) = \sum_{i=1}^{M} \omega_i e^{-t_t r^2} + O(\varepsilon)$$

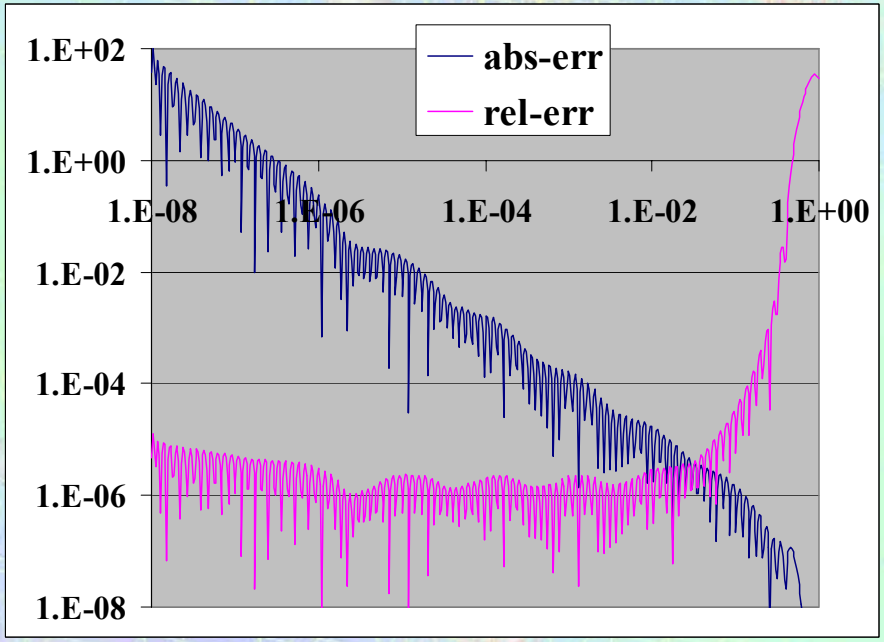
$$r^{nl}_{ii',jj',kk'} = \sum_{i=1}^{M} \omega_i X^{nl_x}_{ii'} Y^{nl_y}_{ii'} Z^{nl_z}_{ii'}$$

  - Only need 1D transition matrices (X,Y,Z) which are also low rank away from singularity – asymptotic cost of $O(N_{box}k^3M) = O(NM)$

Key Components – II cont'd

- E.g., bound-state Helmholtz Green Function

$$\left(-\nabla^2+\mu^2\right)^{-1} f(r) = \int ds \frac{e^{-\mu|r-s|}}{4\pi|r-s|} f(s) \quad \text{in 3D}$$



50-term expansion μ=30

Key components - III

- Multiwavelet basis
  - Adaptively refine space into boxes
  - In each box use an orthogonal tensor-product basis (currently Legendre polynomials of order *k*)
  - High-order convergence (10^{-k}) in smooth regions
  - Disjoint support
    - Maintains high-order convergence even in presence of singularities (e.g., nuclei) and boundary conditions
    - Provides analogs of forward/backward differences
  - Wavelets span difference space V_n-V_{n-1}
  - Efficient computation within box (good cache locality)
  - Orthogonality - deep refinement without precision loss

Three 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)

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

- Function value at Gauss-Legendre quadrature points in each adaptively refined box
  - Enables fast multiplication and local function eval.
- Fast wavelet transform – *O(N)*

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

Prototype implementation

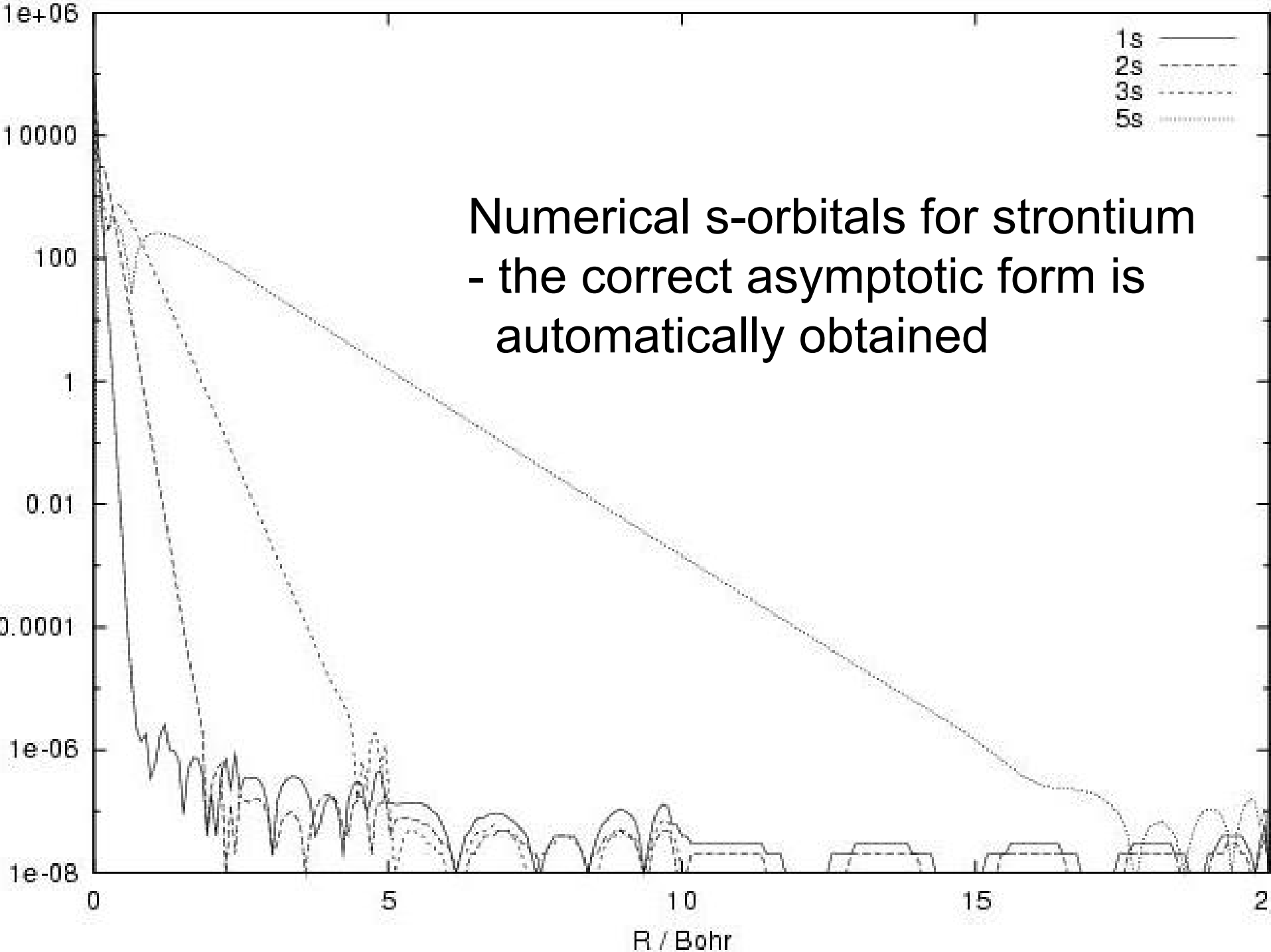
- Python with C and Fortran extensions
  - High level composition – very rapid development
  - Custom tensor/matrix/vector classes for efficient computation and easy extension (via SWIG)
- Adaptively refined functions
  - Store blocks of coefficients in directory/hash table
  - Not tied to specific algorithm/data structure
- Polymorphism – code looks (a little) like math

```
-0.5*(Delsq*psi) + V*psi
```

$$-1/2\nabla^2\psi + V\psi$$

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



Numerical s-orbitals for strontium
- the correct asymptotic form is automatically obtained

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

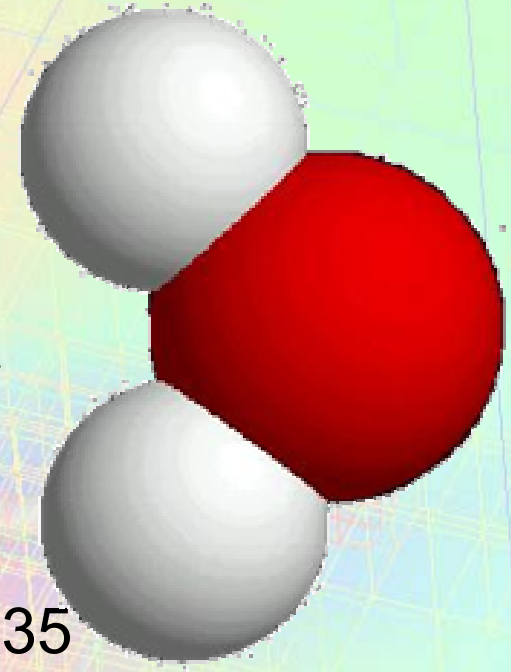
- R=1.4 L=44.8 a.u.

ε	Energy	Gradient
10^{-3}	-1.13356	0.0057
10^{-5}	-1.1336287	0.005396
10^{-7}	-1.133629566	0.00538804
10^{-9}	-1.1336295737	
23s9p4d4f2g1h	-1.133629366	
Mitin	-1.133629571463	

Mitin – best literature value PRA 62 10501

– extrapolation from distributed Gaussian bases

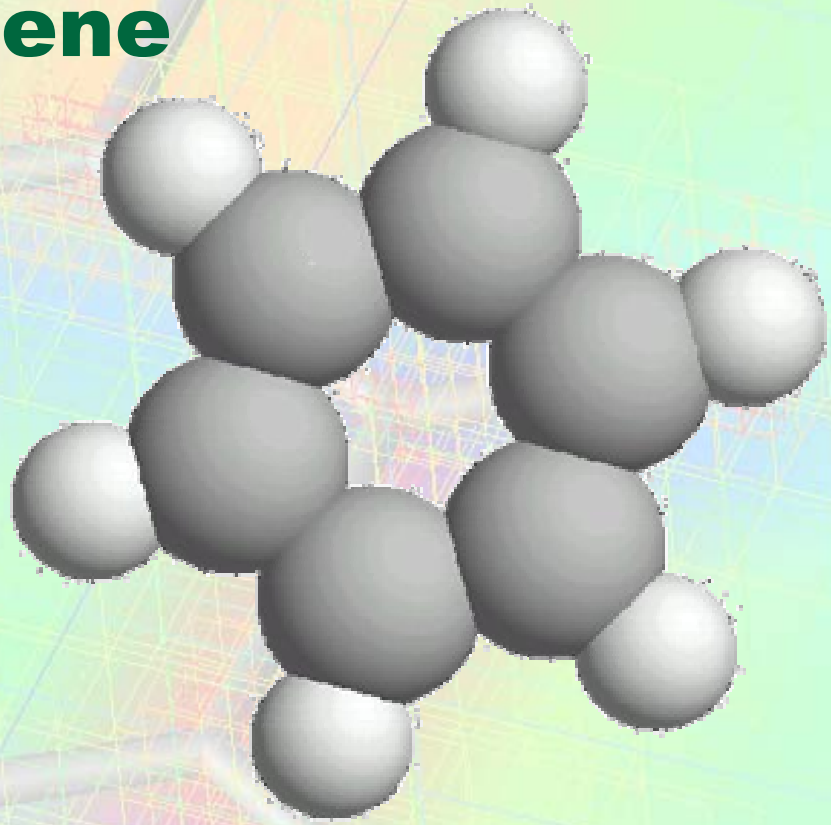
Water LDA



	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; does not change the result.
- 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 (postdoc)
  - Analytic derivatives
  - Fast Hartree-Fock exchange
  - TDDFT within Tamm-Damcoff approximation
  - Abelian point group symmetry (D_{2h} and subgroups)
- Thanks also to
  - So Hirata for guidance with TDDFT
  - Edo Apra for insights into DFT

Summary

- Multiresolution provides a general framework for computational chemistry
  - Accurate and efficient with a very small code
  - Multiwavelets provide high-order convergence and accommodate singularities
- Readily accessible by students and researchers
  - Familiar orthonormal basis (Legendre polynomials)
  - Compression and reconstruction (c.f., FFT)
  - Fast integral operators (c.f., FMM)
- Expect speed competitive to Gaussians in near future
  - Optimal separated forms for kernels, multi-scale non-linear solver, better implementation