Fast methods with guaranteed precision

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MADNESS

Multiresolution
Adaptive
Numerical
Scientific
Simulation

The funding

- This work is funded by the U.S. Department of Energy, the division of Basic Energy Science, Office of Science, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory. This research was performed in part using
  - the Molecular Science Computing Facility in the Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory under contract DE-AC06-76RLO 1830 with Battelle Memorial Institute,
  - resources of the National Energy Scientific Computing Center which is supported by the Office of Energy Research of the U.S. Department of Energy under contract DE-AC03-76SF0098,
  - and the Center for Computational Sciences at Oak Ridge National Laboratory under contract DE-AC05-00OR22725 .

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, …

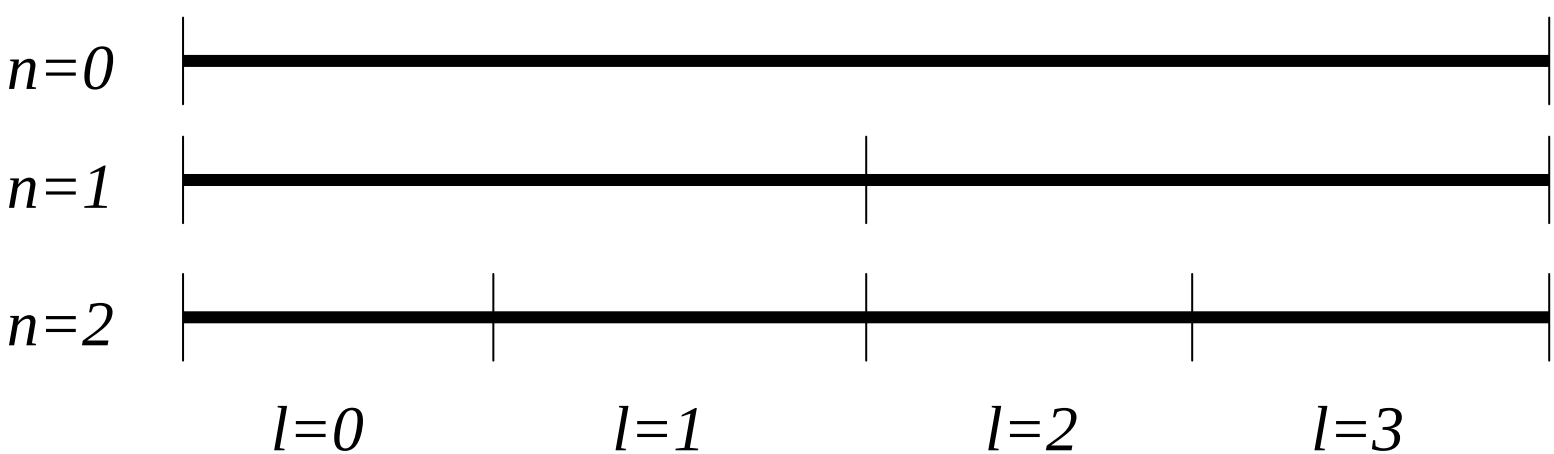
- Telescoping series

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

  – 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

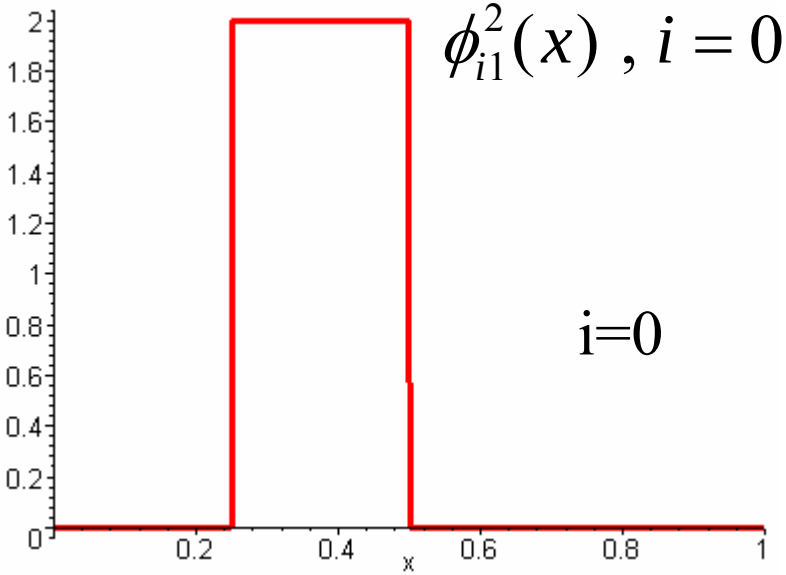
Scaling Function Basis

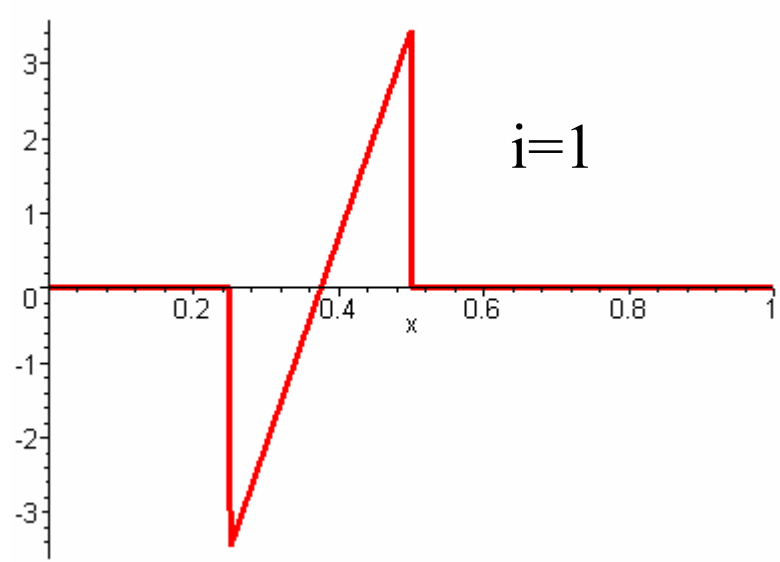
- Divide domain into 2^n pieces (level n)
  - Adaptive sub-division (local refinement)
  - l^{th} sub-interval $[l*2^{-n},(l+1)*2^{-n}]$ $l=0,\ldots,n-1$
- In each sub-interval define a polynomial basis
  - First k Legendre polynomials $\phi_i(x) = \sqrt{2i+1}P_i(2x-1)$
  - Orthonormal, disjoint support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

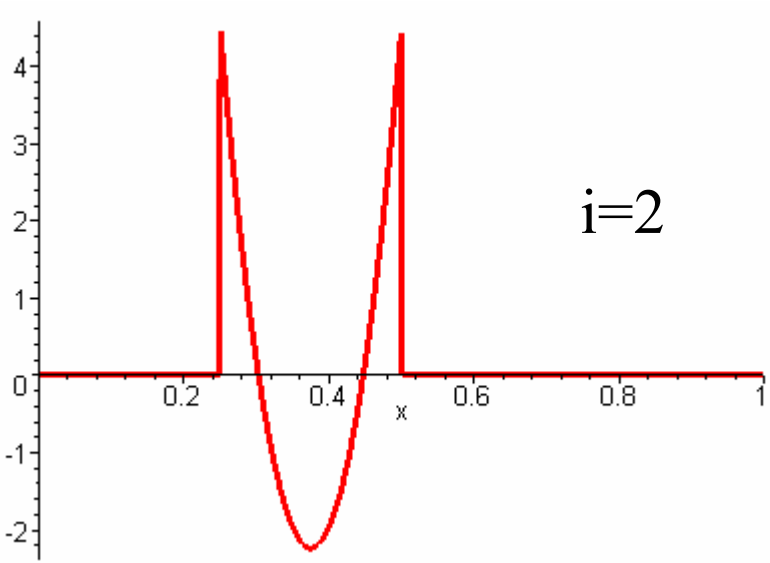


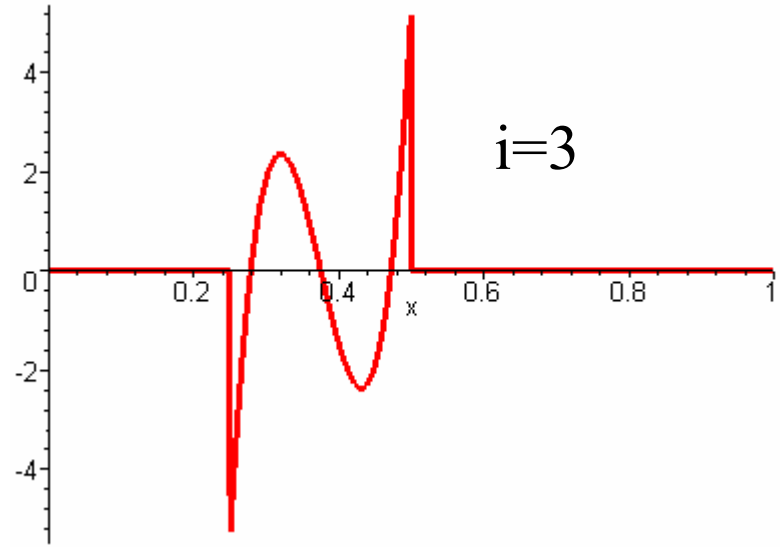
Scaling Function Basis - III

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









Multiwavelet Basis

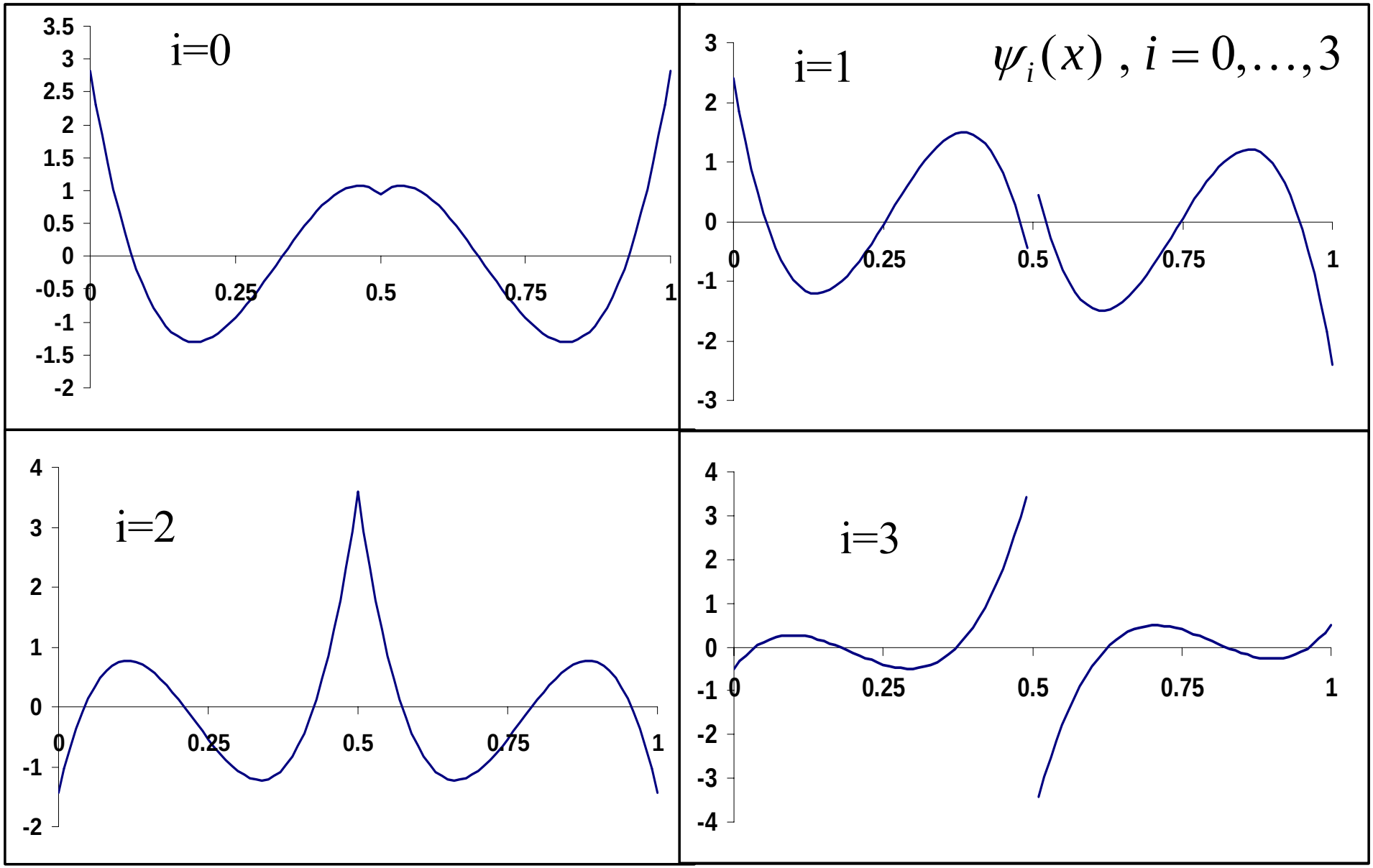
- Space of polynomials on level n is V_n
- Wavelets - an orthonormal basis to span $W_n = V_{n+1} - V_n$
- Currently use Alpert's basis
- Vanishing moments
  - Critically important property
  - Since W_n is orthogonal to V_n the first k moments of functions in W_n vanish, i.e.,

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

- Sparse representations of many physically important kernels

Multiwavelet Basis - III

$k=4$



Adaptive Refinement

- To satisfy the global error condition

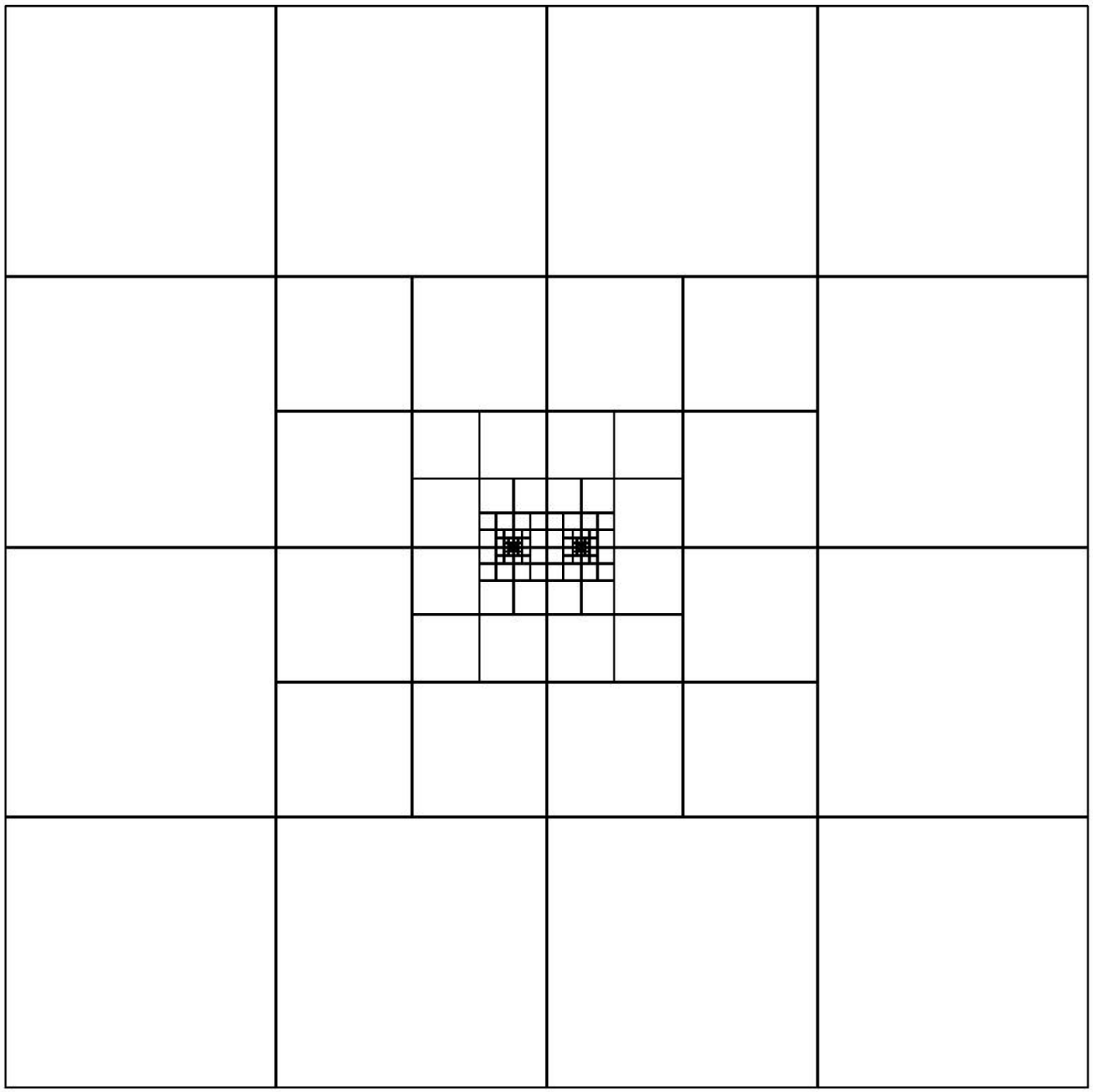
$$\left\| f - f^{n} \right\|_2 \le \varepsilon \left\| f \right\|_2$$

- Truncate according to

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

- This is rather conservative – usually use

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



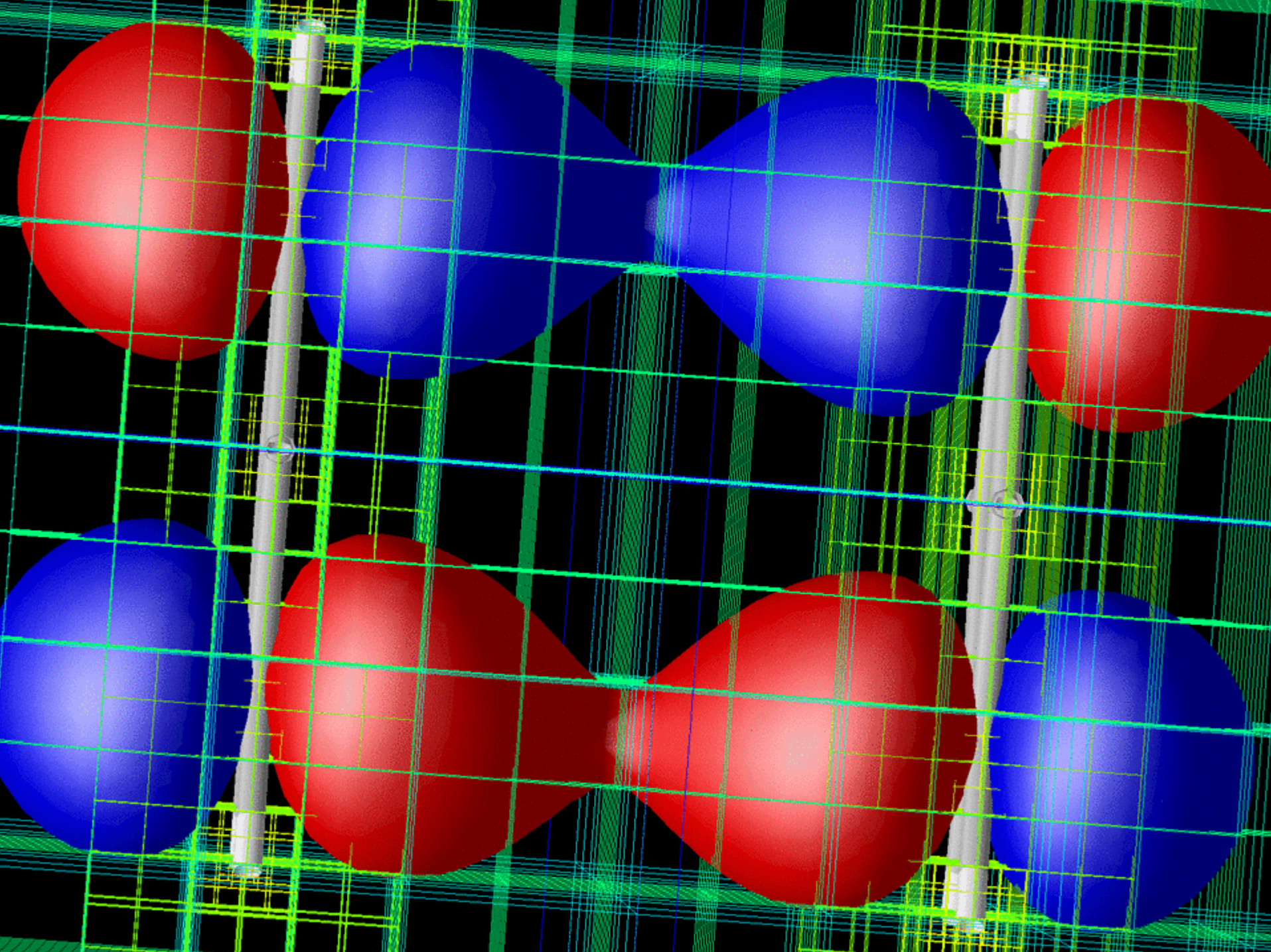
- Slice thru grid used to represent the nuclear potential for H_2 using k=7 to a precision of 10^{-5}.

- 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.



Integral Formulation

- E.g., used by Kalos, 1962

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

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

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

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

Converges as a fixed-point iteration without preconditioning for the lowest eigen function.

Integral operators in 3D

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

- Non-standard-form matrix elements easy to evaluate from compressed form of kernel *K(x)*
- Application in 1-d is fairly efficient
  - $O(N_{box}k^2)$ operations
- In 3-d seems to need $O(N_{box}k^6)$ operations
  - Prohibitively expensive
- Separated form
  - Beylkin, Cramer, Mohlenkamp, Monzon
  - $O(N_{box}k^4)$ or even $O(N_{box}k^3)$ in 3D

$$r_{ii'}^{nl}$$

$$r_{ii',jj',kk'}^{n\underline{l}}$$

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

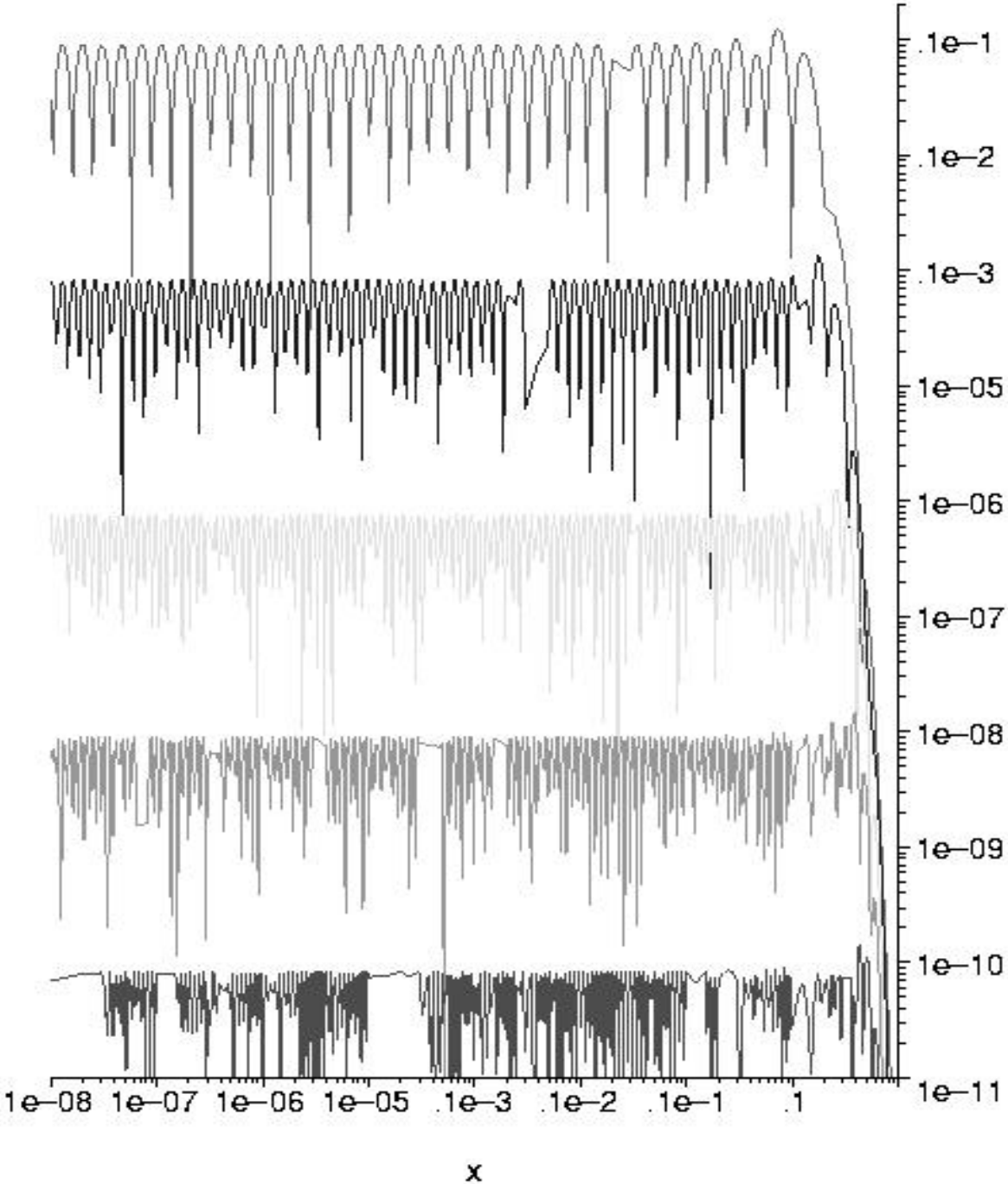
Separated form for integral operators

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

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

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

  - 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

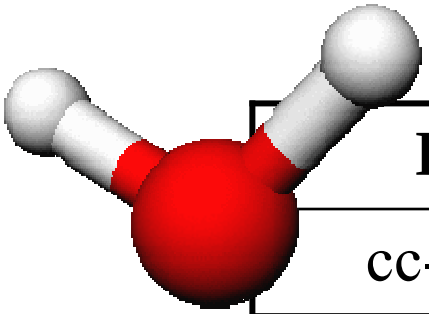


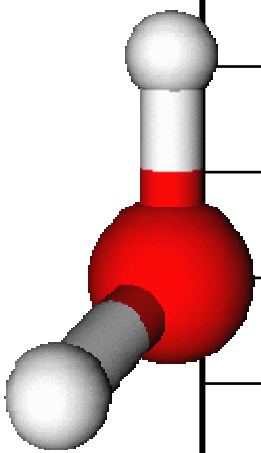
Automatically generated representations of *exp(-30r)/r* accurate to 1e-10, 1e-8, 1e-6, 1e-4, and 1e-2 (measured by the weighted error *r(exp(-30r)/r - fit(r))*) for *r* in [1e-8,1] were formed with 92, 74, 57, 39 and 21 terms, respectively.

Note logarithmic dependence upon precision.

Water dimer LDA

aug-cc-pVTZ geometry, kcal/mol.

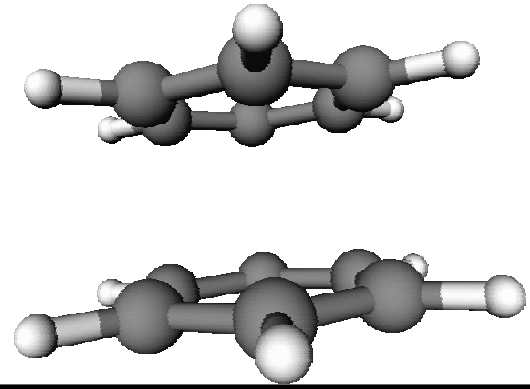




Basis	Uncorrected	BSSE	Corrected
cc-pVDZ	-11.733	-3.958	-7.775
cc-pVTZ	-9.464	-1.654	-7.810
cc-pVQZ	-8.708	-0.821	-7.888
aug-cc-pVDZ	-8.187	-0.382	-7.805
aug-cc-pVTZ	-7.992	-0.086	-7.906
aug-cc-pVQZ	-7.995	-0.054	-7.941
$\varepsilon=10^{-3}$	-6.483		
$\varepsilon=10^{-5}$	-7.932		
$\varepsilon=10^{-7}$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

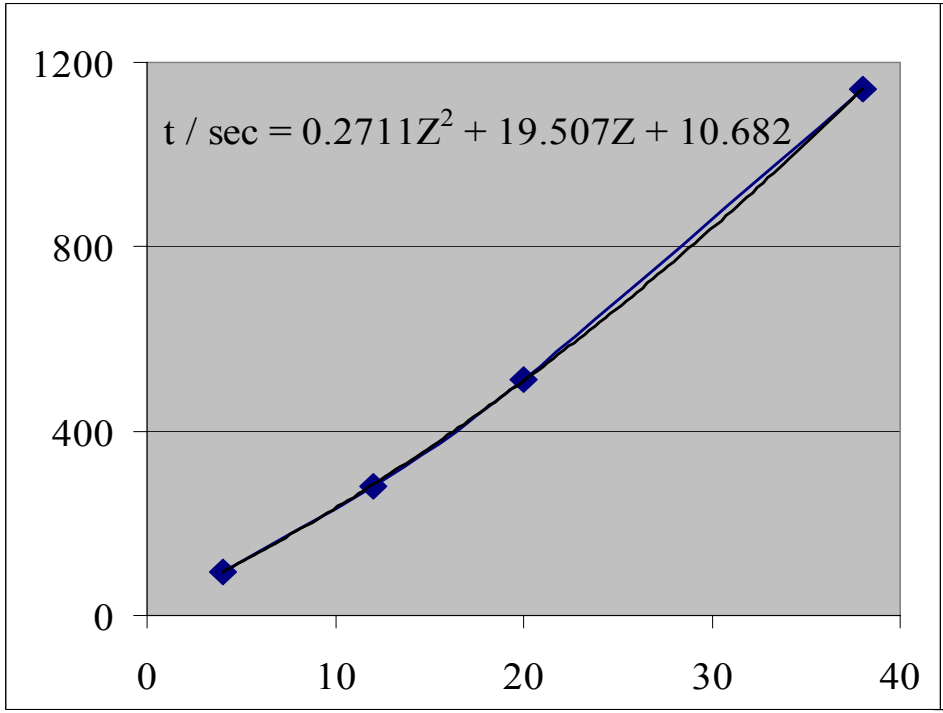
Benzene dimer LDA

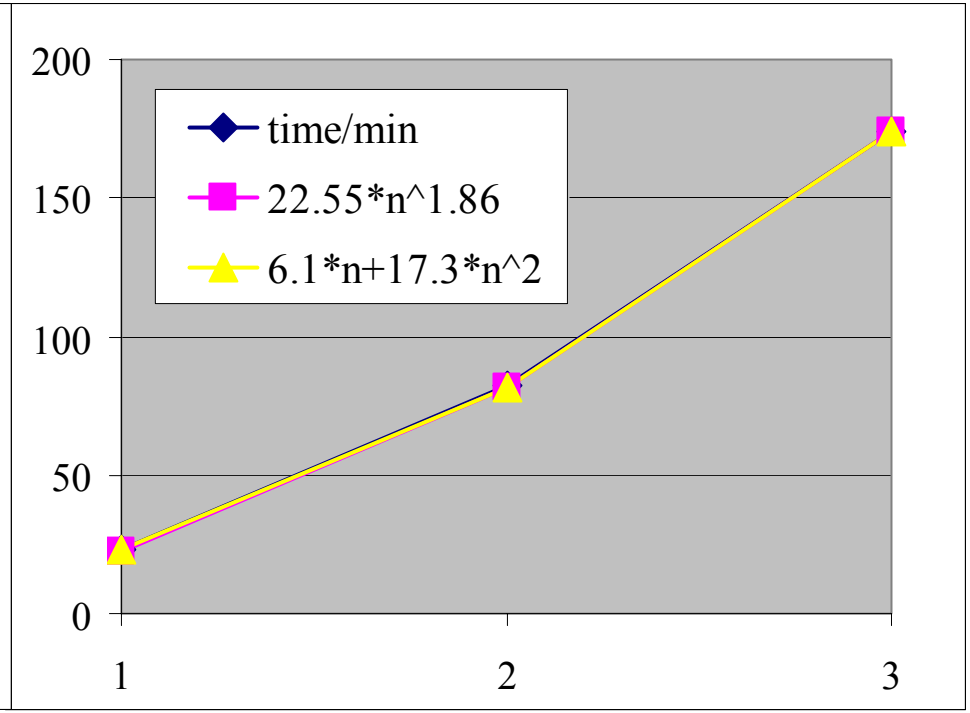
aug-cc-pVDZ geometry, kcal/mol.



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 $\varepsilon=10^{-5}$)

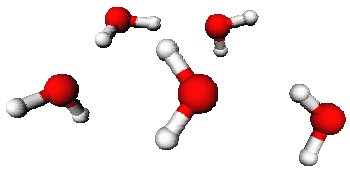


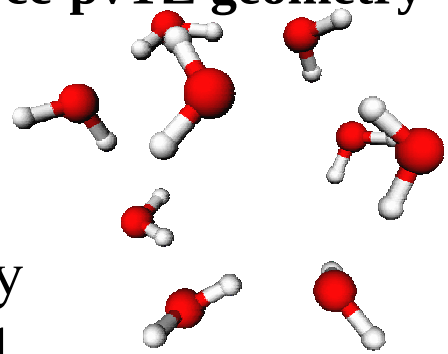


Alkali earth atoms Z=4,12,20,38

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

$(H_2O)_n$ n=5,9 … t = O($n^{1.1}$)





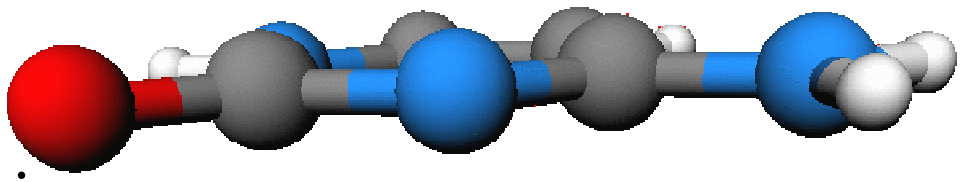
Stacked benzene – MOs are delocalized by symmetry

Water cluster – MOs are asymptotically localized

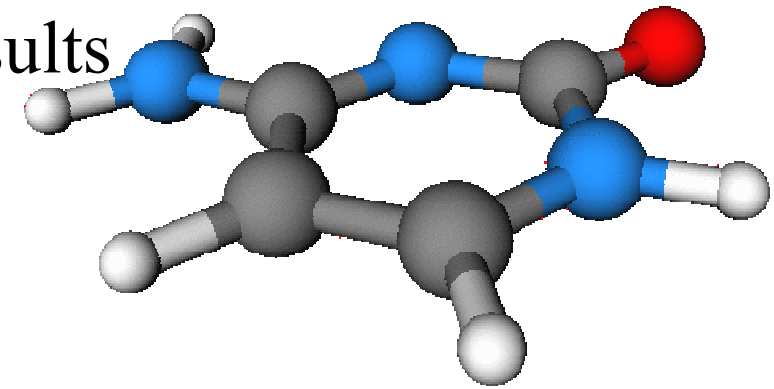
(long tail is smooth so is inexpensively treated)

Cytosine Dimer

- Sekino, Kurita and Inoue



- Definitive value of the stacking energy of bases to resolve apparent discrepancy between Slater and Gaussian basis results



- DFT, PW91 potential
- Advantage of STOs was illusory

Analytic Derivatives

- Hellman-Feynman theorem applies

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

Computation of the gradient

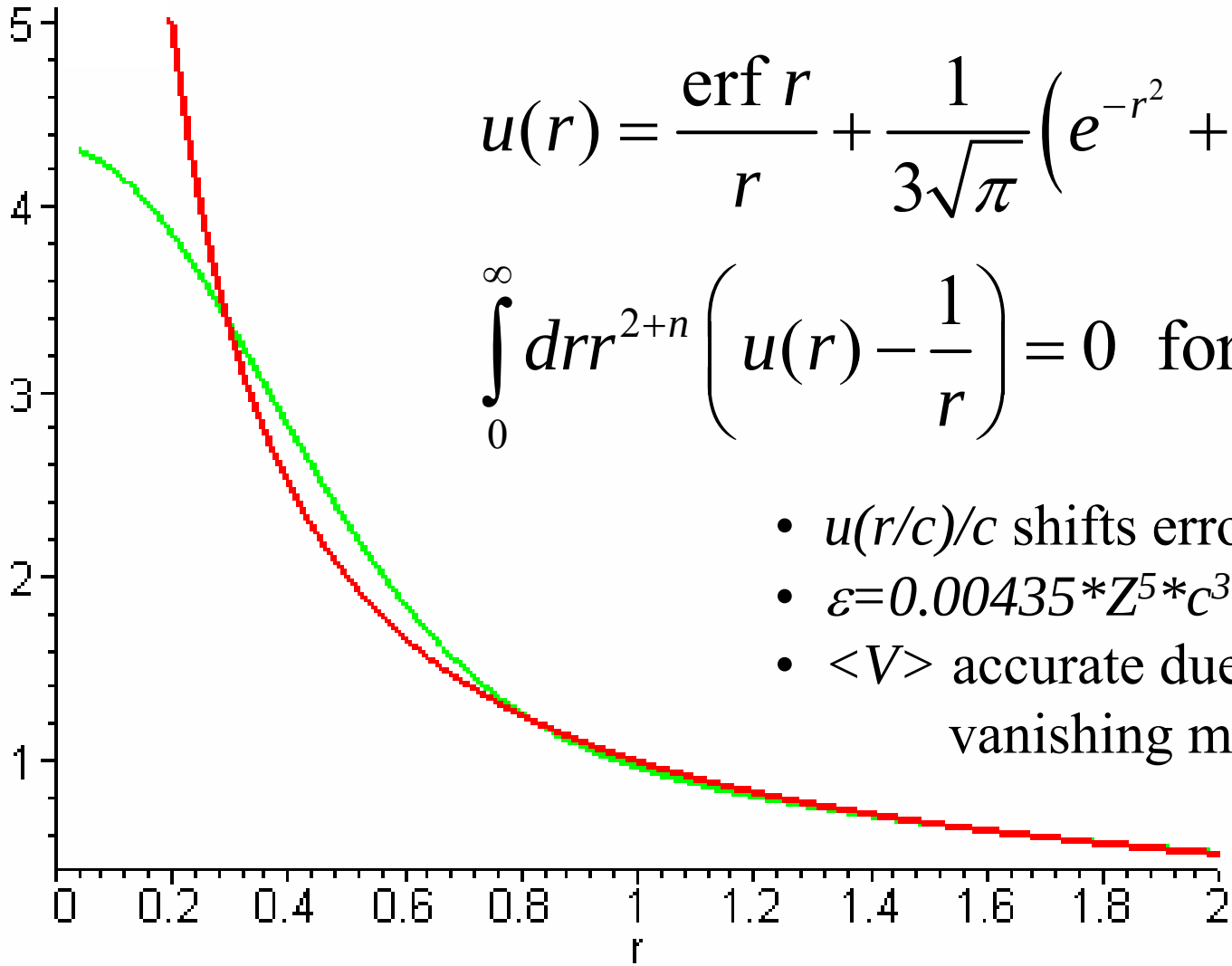
$$\rho(\underline{r}) = \sum_{\underline{i}=0}^{k-1} s_{\underline{i}\,0}^{0} \phi_{\underline{i}\,0}^{0}(\underline{r}) + \sum_{n'=0}^{n-1} \sum_{\underline{l}}^{2^{n'}-1} \sum_{\underline{i}=0}^{k-1} d_{\underline{i}\,\underline{l}}^{n'} \psi_{\underline{i}\,\underline{l}}^{n'}(\underline{r})$$

$$\frac{\partial V}{\partial q}(\underline{r}) = \sum_{\underline{i}=0}^{k-1} r_{\underline{i}\,0}^{0} \phi_{\underline{i}\,0}^{0}(\underline{r}) + \sum_{n'=0}^{n-1} \sum_{\underline{l}}^{2^{n'}-1} \sum_{\underline{i}=0}^{k-1} c_{\underline{i}\,\underline{l}}^{n'} \psi_{\underline{i}\,\underline{l}}^{n'}(\underline{r})$$

$$\int \frac{\partial V(\underline{r})}{\partial q} \rho(\underline{r}) d\underline{r} = \sum_{\underline{i}=0}^{k-1} r_{\underline{i}\,0}^{0} s_{\underline{i}\,0}^{0} + \sum_{n'=0}^{n-1} \sum_{\underline{l}}^{2^{n'}-1} \sum_{\underline{i}=0}^{k-1} c_{\underline{i}\,\underline{l}}^{n'} d_{\underline{i}\,\underline{l}}^{n'}$$

Since the basis is orthonormal, the integral is a simple inner product

Smoothed Nuclear Potential

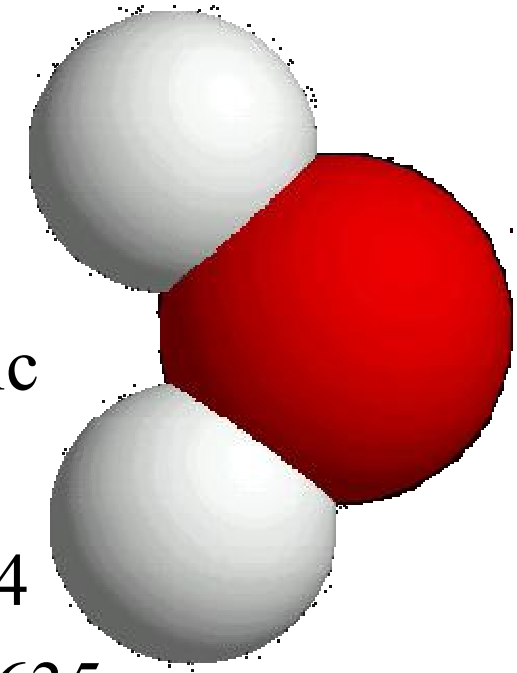


$$u(r) = \frac{\operatorname{erf} r}{r} + \frac{1}{3\sqrt{\pi}}\left(e^{-r^2} + 16e^{-4r^2}\right)$$

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

- $u(r/c)/c$ shifts error to $r<c$
- $\varepsilon = 0.00435 * Z^5 * c^3$
- $\langle V \rangle$ accurate due to vanishing moments

Translational Invariance

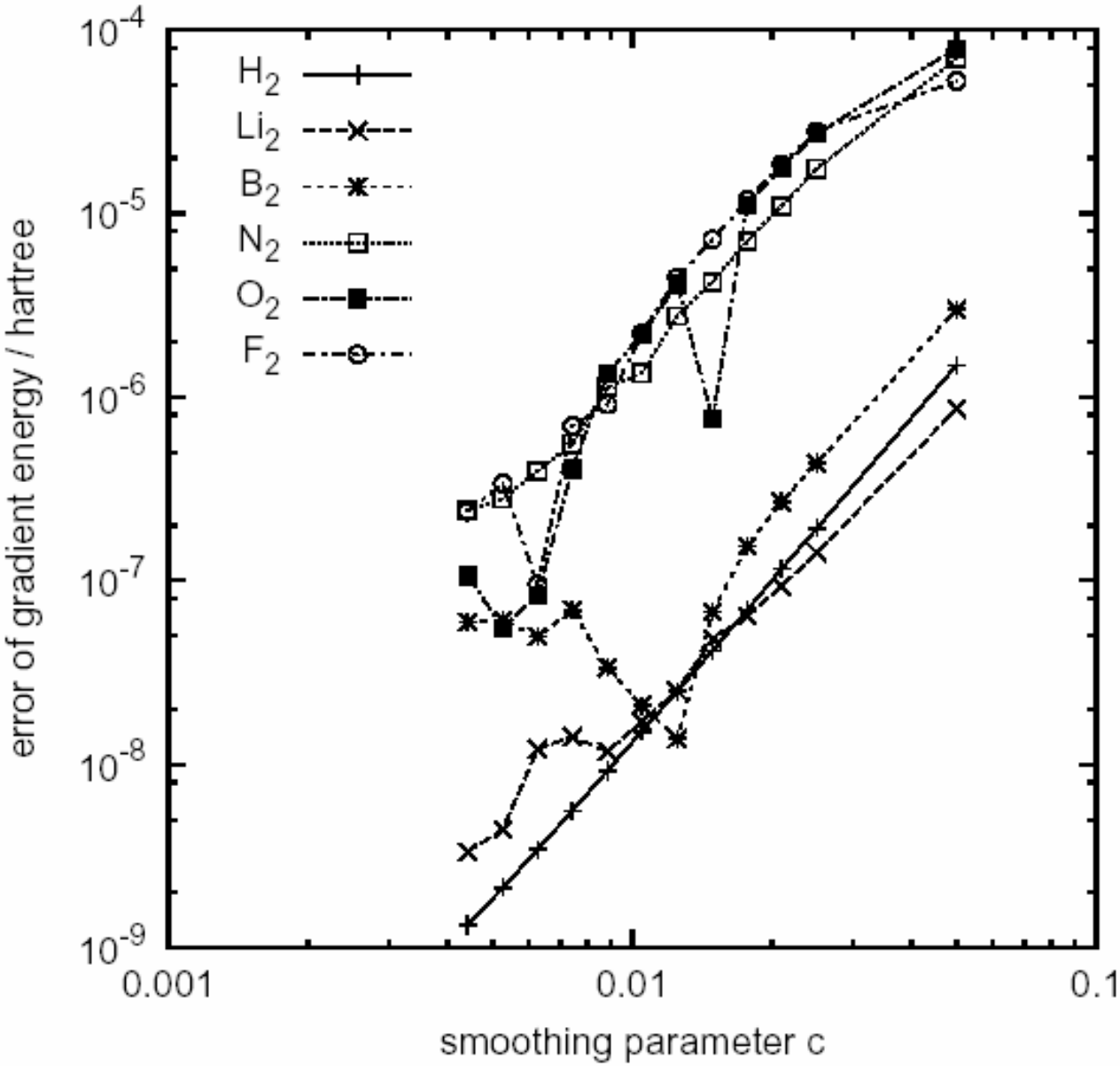


	Dyadic	Non-dyadic
10^{-3}	-75.9139	-75.9139
10^{-5}	-75.913564	-75.913564
10^{-7}	-75.91355634	-75.91355635

- 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

Sources of error in the gradient

- Partially converged orbitals
  - Same as for "conventional" methods
- Smoothed potential
- Numerical errors in the density/potential
  - Higher-order convergence except where the functions are not sufficiently smooth
    - Inadequate refinement (clearly adequate for the energy, but not necessarily for other properties)
    - Exacerbated by nuclei at non-dyadic points
    - Gradient measures loss of spherical symmetry around the nucleus … the large value of the derivative potential amplifies small errors

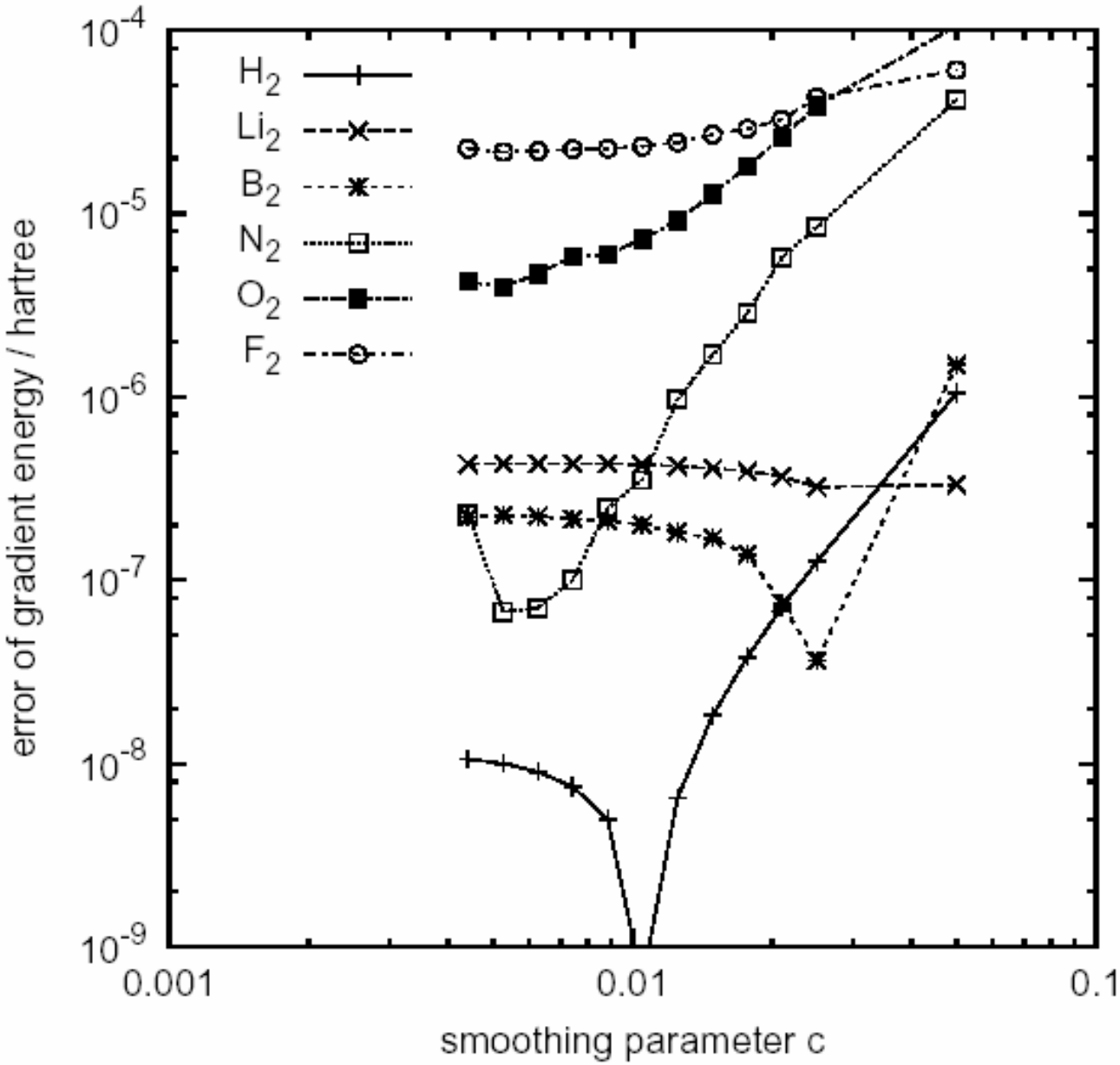


Dependence on potential smoothing parameter (c)

Absolute errors of derivatives for diatomics with the nuclei at *dyadic* points.

For *energy* accuracy of 1e-6

H	0.039
Li	0.0062
B	0.0026
N	0.0015
O	0.0012
F	0.00099_{28}



Dependence on potential smoothing parameter (c)

Absolute errors of derivatives for diatomics with the nuclei at *non-dyadic* points.

For *energy* accuracy of 1e-6

H	0.039
Li	0.0062
B	0.0026
N	0.0015
O	0.0012
F	0.00099

N_2 Hartree-Fock R=2.0 a.u.

Basis	Grad.Err.	EnergyErr.
cc-pVDZ	5e-2	4e-2
aug-cc-pVDZ	5e-2	4e-2
cc-pVTZ	7e-3	1e-2
aug-cc-pVTZ	6e-3	9e-3
cc-pVQZ	8e-4	2e-3
aug-cc-pVQZ	9e-4	2e-3
cc-pV5Z	1e-4	4e-4
aug-cc-pV5Z	2e-5	2e-4
k=5	6e-3	1e-2
k=7	4e-5	2e-5
k=9	3e-7	-2e-7
k=11	0.0	0.0
	0.026839623	-108.9964232

Comparison with NUMOL and aug-cc-pVTZ

- H_2, Li_2, LiH, CO, N_2, Be_2, HF, BH, F_2, P_2, BH_3, CH_2, CH_4, C_2H_2, C_2H_4, C_2H_6, NH_3, H_2O, CO_2, H_2CO, SiH_4, SiO, PH_3, HCP
- NUMOL, Dickson & Becke JCP 99 (1993) 3898
- Dyadic points (0.001a.u.) + Newton correction
- Agrees with NUMOL to available precision
  - LDA (k=7,0.002; k=9, 0.0006)
- k=9 vs. aug-cc-pVTZ rms error
  - Hartree-Fock 0.004 a.u. (0.019 SiO)
  - LDA 0.003 a.u. (0.018 SiO)

Asymptotic Scaling

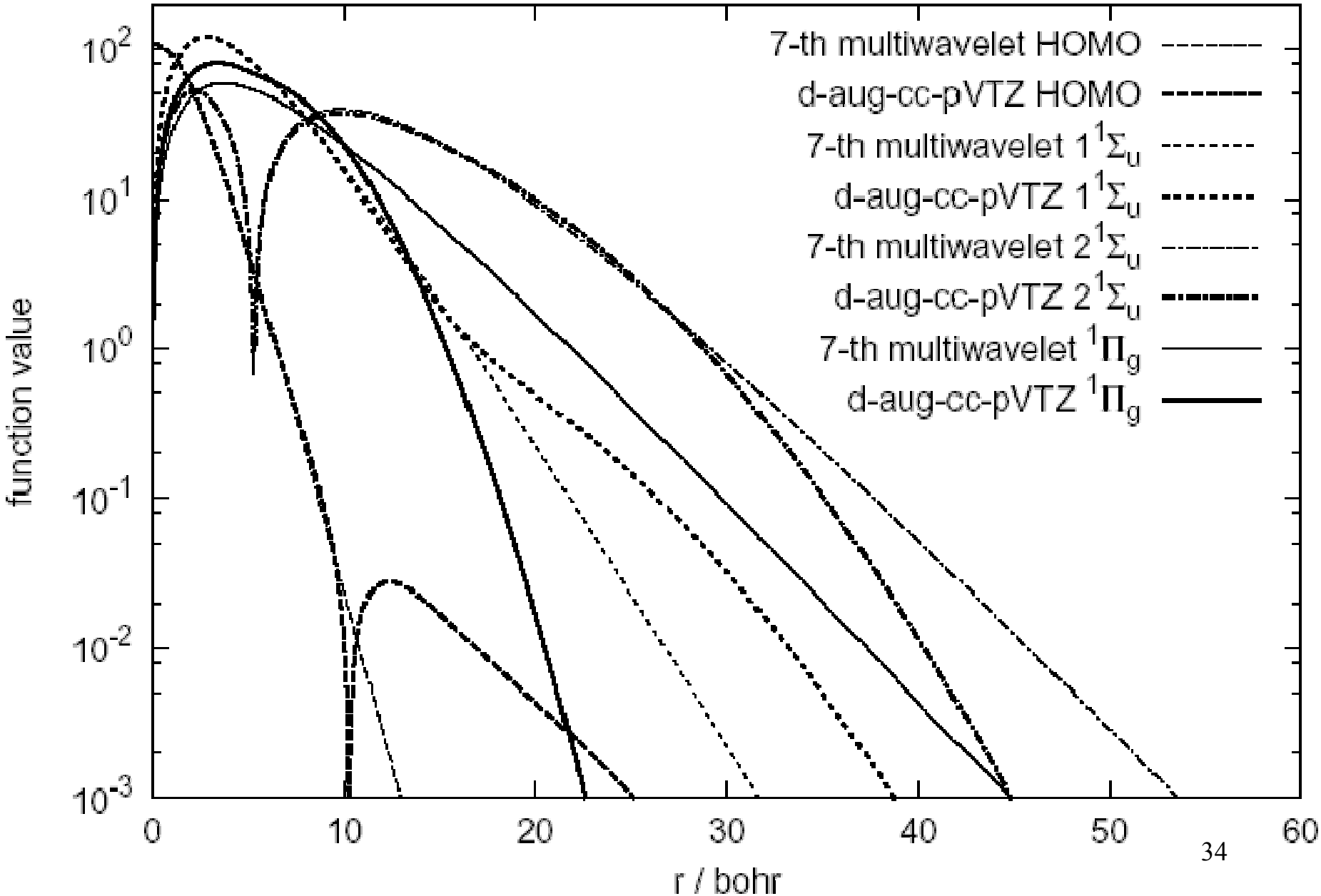
- Current implementation
  - Based upon canonical orbitals – $O(N^{1\text{-}2})$
- Density matrix/spectral projector
  - Well established – $O(N_{atom} log^m(\varepsilon))$ to any finite precision (Goedecker, Beylkin, …)
  - This is *not* possible with conventional AO Gaussians
  - Need separated representation for efficiency
- Gradient
  - each dV/dx requires $O(-log(\varepsilon)log(vol.))$ terms
  - All gradients evaluated in $O(-N_{atom} log(\varepsilon)log(vol.))$

High-precision Hartree-Fock geometry for water

- Pahl and Handy Mol. Phys. 100 (2002) 3199
  - Plane waves + polynomials for the core
  - Finite box (L=18) requires extrapolation
  - Estimated error 3μH, 1e-5 Angstrom
- k=11, conv.tol=1e-8, ε=1e-9, L=40
  - Max. gradient = 3e-8, RMS step=5e-8
  - Difference to Pahl 10μH, 4e-6 Angstrom, 0.0012

Basis	**OH**	**HOH**	**Energy**
k=11	0.939594	106.3375	-76.06818006
Pahl	0.939598	106.3387	-76.068170
cc-pVQZ	0.93980	106.329	-76.066676

H_2 HOMO and CIS excited states



		$1^3\Sigma_u$	$1^3\Sigma g$	$^3\Pi_u$	$2^3\Sigma_u$	$2^3\Sigma_g$	$^3\Pi_g$
HF	**aug-cc-pVTZ**	**9.5520**	**11.958**	**12.81**	**14.36**	**16.98**	**17.74**
	aug-cc-pVQZ	**9.5529**	**11.961**	**12.59**	**14.29**	**16.32**	**16.79**
	d-aug-cc-pVQZ	**9.5523**	**11.959**	**12.26**	**14.15**	**14.49**	**14.81**
	k=7, r< $3*10^{-4}$	**9.55178**	**11.95491**	**12.26**	**14.11**	**14.48**	**14.66**
	k=9, r< $3*10^{-6}$	**9.55176**	**11.95490**	**12.26**	**14.11**	**14.48**	**14.66**
LSDA	**aug-cc-pVTZ**	**9.94**	**10.65**	**12.46**	**12.40**	**15.76**	**16.37**
	aug-cc-pVQZ	**9.95**	**10.61**	**12.07**	**12.10**	**14.85**	**15.22**
	d-aug-cc-pVQZ	**9.93**	**10.31**	**10.94**	**10.72**	**11.19**	**11.98**
LSDA(AC)	**k=7, r< $3*10^{-4}$**	**10.53**	**12.26**	**12.35**	**14.11**	**14.45**	**14.53**
HCTH	**aug-cc-pVTZ**	**10.19**	**10.79**	**12.74**	**12.71**	**15.85**	**16.30**
	aug-cc-pVQZ	**10.19**	**10.76**	**12.28**	**12.42**	**14.89**	**15.14**
	d-aug-cc-pVQZ	**10.18**	**10.52**	**11.12**	**10.95**	**11.36**	**12.23**
HCTH(AC)	**k=7, r< $3*10^{-4}$**	**10.87**	**12.40**	**12.50**	**14.10**	**14.44**	**14.50**

H_2 low-lying triplet excitation energies in eV

Table 6: The total, HOMO (ϵ_h) energies, and ionization potential (I) (in Hartree) of C_2H_4.

	k=7, r(MO)$< 3 \times 10^{-5}$ a)				Tozer et al. b)
	LSDA	HCTH	CAM-B3LYP	PBE0	HCTH
Total energy	-77.863 098	-78.603 861	-78.575 697	-78.519 234	-78.578 26
ϵ_h	-0.255 545	-0.246 448	-0.340 295	-0.289 974	...
I	0.404 218	0.388 123	0.387 648	0.385 352	0.390
Total energy (AC)	-77.862 891	-78.603 593	-78.575 653	-78.519 176	-78.578 18
ϵ_h (AC)	-0.400 493	-0.384 269	-0.385 994	-0.383 516	...

a) The asymptotic correction uses $X = 3.0, Y = 4.0$ for eq. (16).

b) Ref. [6]. The basis: augmented Sadlej basis sets.

	k=7, r(MO)$< 3 \times 10^{-5}$ a) b)				Tozer et al.[c]		
	LSDA	HCTH	CAM-B3LYP	PBE0	HCTH	CASPT2[d]	Exptl.[d]
$^1B_{1u}$	9.686	9.288	9.343	9.278	9.32	9.31	9.33
$^1B_{2u}$	9.287	8.937	8.946	8.898	9.04	9.18	9.05
$^1B_{3u}$	9.270	9.057	9.107	9.038	8.95	9.03	8.90
$^1B_{3u}$	8.949	8.691	8.688	8.661	8.70	8.66	8.62
$^3B_{3u}$	8.895	8.583	8.639	8.586	8.64	8.57	8.57
^1A_g	8.737	8.393	8.384	8.338	8.33	8.40	8.28
^3A_g	8.487	8.071	8.128	8.035	8.15	8.26	8.15
$^1B_{1u}$	8.404	8.322	8.262	8.289	7.61	8.40	8.0
$^1B_{2g}$	8.161	7.907	7.926	7.903	7.77	7.95	7.90
$^1B_{1g}$	8.117	7.890	7.831	7.838	7.78	7.85	7.80
$^3B_{1g}$	8.072	7.812	7.790	7.802	7.76	7.80	7.79
$^1B_{3u}$	7.429	7.280	7.198	7.217	7.16	7.17	7.11
$^3B_{3u}$	7.332	7.190	7.101	7.081	7.10	7.05	6.98
$^3B_{1u}$	4.807	4.468	4.103	4.064	4.33	4.39	4.36
Error	0.34	0.11	0.10	0.10	0.07	0.09	
Max	0.46	0.32	0.26	0.30	0.39	0.40	

C_2H_4 excitation energies with asymptotically corrected potentials[37]

Table 9: The excitation energies (in eV) of benzene.

	k=7, r(MO)< 3×10^{-5} a) b)			Handy et al. / HCTH c)		
	LSDA	HCTH	CAM-B3LYP	6-31G*	TZ2P	Exptl./CASPT2* d)
Valence excitations						
1^3B_{1u}	4.408	4.019	3.595	4.11	4.02	3.94
1^3E_{1u}	4.757	4.651	4.781	4.78	4.66	4.76
1^1B_{2u}	5.276	5.283	5.489	5.44	5.28	4.90
1^3B_{2u}	5.006	4.977	5.088	5.15	4.98	5.60
1^1B_{1u}	6.045	6.006	6.158	6.24	6.02	6.20
1^1E_{1u}	6.895	6.912	7.012	7.00	6.94	6.94
Rydberg excitations						
1^1E_{1g}	6.529	6.404	6.504	6.15	6.24	6.334
1^1A_{2u}	6.885	6.992	7.221	6.81	6.92	6.932
1^1E_{2u}	6.980	6.980	7.109	6.79	6.90	6.953
1^1A_{1u}	7.004	6.990	7.014	6.81	6.91	6.99*
2^1E_{1u}	7.426	7.360	7.297	7.34	7.24	7.41
1^1B_{1g}	7.783	7.546	7.702	7.39	7.50	7.460
1^1B_{2g}	7.811	7.561	7.715	7.41	7.52	7.460
2^1E_{1g}	7.614	7.451	7.539	7.41	7.52	7.535
1^1E_{2g}	8.071	7.729	7.874	7.66	7.76	7.81
2^1A_{1g}	8.085	7.747	7.924	7.63	7.80	7.81
1^1A_{2g}	8.079	7.746	7.877	7.63	7.78	7.81

Mean absolute deviations						
Valence	0.27	0.24	0.26	0.21	0.22	
Rydberg	0.17	0.06	0.14	0.13	0.06	
total	0.21	0.12	0.18	0.16	0.12	
Maximum absolute deviation						
Valence	0.59	0.62	0.59	0.54	0.62	
Rydberg	0.35	0.10	0.29	0.18	0.17	
total	0.59	0.62	0.59	0.54	0.62	

a) The computed energies are converged within 10^{-3} eV.

b) The asymptotic correction uses $X = 3.0$ and $Y = 4.0$ for eq. (16).

c) The asymptotic correction uses $X = 3.5$ and $Y = 4.7$ for eq. (16). The basis sets are augmented with the double spd (0,01, 0.04) set.

d) Ref. [26].

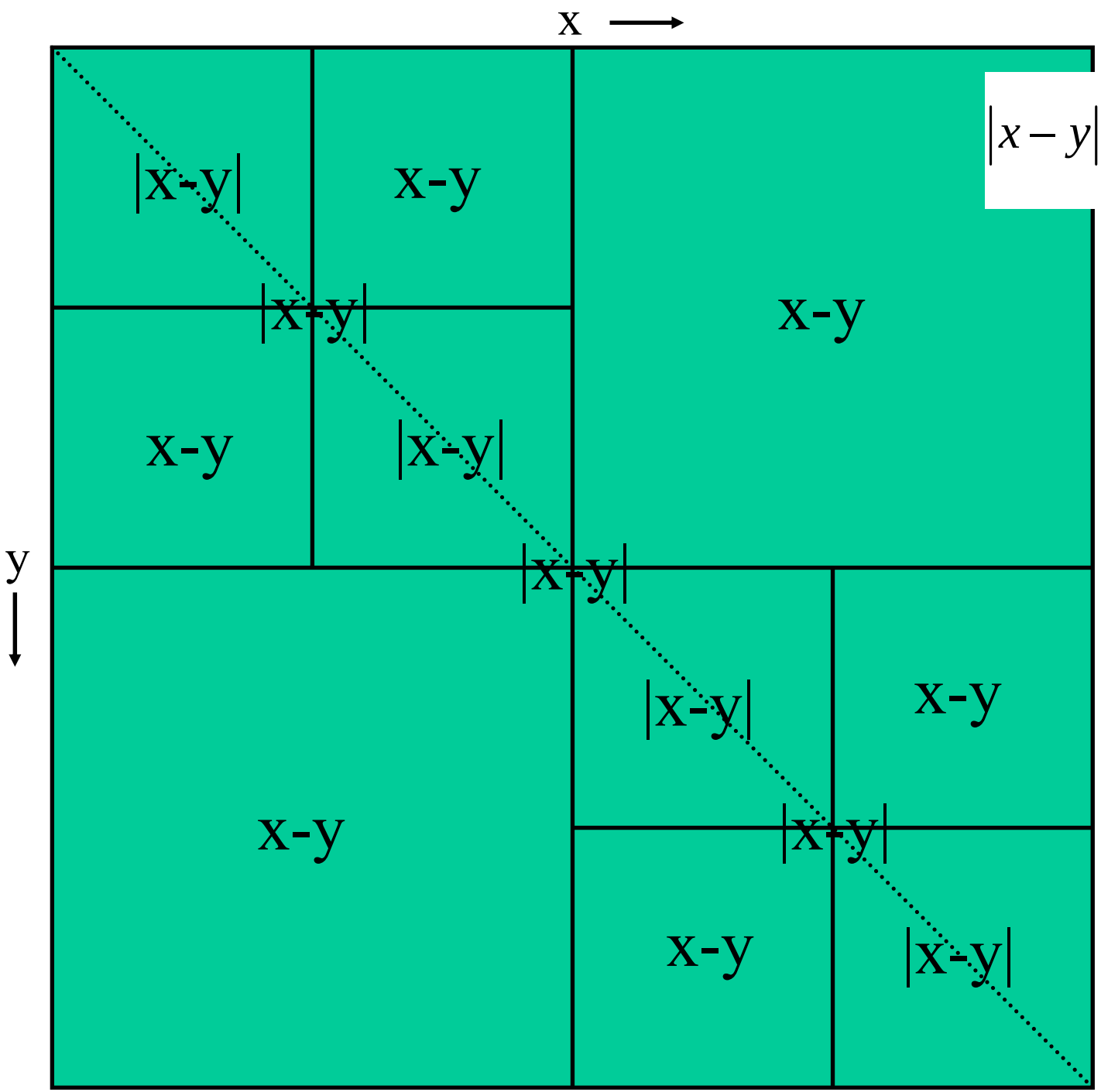
Mean abs. error of Gaussian results relative to MRA

- augmented 6-31g* 0.14 eV
- augmented TZ2P 0.05 eV
- augmented TZ2P 0.01 eV (valence only)

Fast Multipole Method

3 equivalent perspectives

- Multipole expansion of long-range interactions
- Increasing smoothness of kernel at long range
- Blocks of operator well-separated from the diagonal have low operator rank
- [Also need fast translation operator]



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

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 $r = O(-\log \varepsilon)$

He atom (results from yesterday)

- Compute expectation value of the total Hamiltonian for He atom with a trial wavefunction in 6-D multiresolution
  - 5-th order multiwavelet bases
  - truncation threshold: 1e-3

$$\Psi(r_1, r_2) = (1 + c\, r_{12})\, e^{-\xi(r_1 + r_2)}$$

		$\langle\Psi\|H\|\Psi\rangle$	$\langle\Psi\|V_{nuc}\|\Psi\rangle$	$\langle\Psi\|1/r_{12}\|\Psi\rangle$
c=0.50, ξ=2.0	6D MRA	–2.873 37	– 7.189 83	1.022 19
	Analytic	–2.876 58	– 7.189 87	1.022 15
c=0.00, ξ=2.0	6D MRA	–2.748 40	– 7.999 86	1.250 04
	Analytic	–2.750 00	– 8.000 00	1.250 00

Kinetic energy is currently a problem for the prototype – will be resolved with better refinement criterion

- in 3D there is no problem; in 6D should get identical result at C=0

Timings and sizes

- Wavefunction (k=4, ε=1e-3, deepest n=5)
  - (c=0.5) 0.9GB
  - (c=0.0) 42MB
- R12*Wavefunction
  - (c=0.5) 1.8GB memory + 0.5h CPU
- Kinetic*Wavefuction
  - (c=0.5) 0.8h CPU
  - (c=0.0) 50s CPU
- Vnuc*Wavefunction
  - (c=0.5) 0.5h CPU
  - (c=0.0) 133s CPU

Anticipate 10+x speedup possible with better implementation and algorithms.

But, more general systems will require deeper refinement and higher-order wavelets.

Also looking at fast algorithms for Gaussian geminal form

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, GAMESS-US and UTChem
- Several prototypes for computing in 6D
  - Density matrix, Green's function, 2-e wave function

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

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)
- Separated form for operators and functions
  - Critical for efficient computation in higher dimension
- Expect speed competitive to Gaussians in near future
  - Optimal separated forms for kernels, multi-scale non-linear solver, better implementation