Chemistry in Many Dimensions

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MADNESS

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Multiresolution
Adaptive
Numerical
Scientific
Simulation

The funding

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Molecular electronic Schrödinger equation

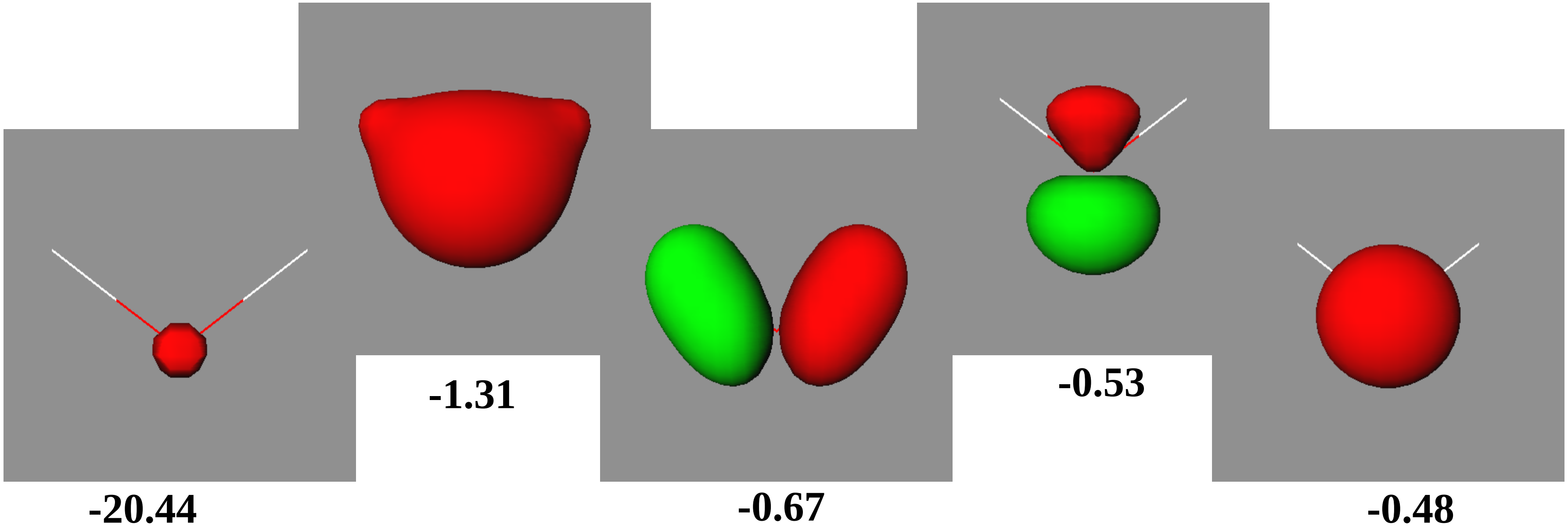
- A 3-N dimensional, non-separable, second-order differential equation

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

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

Hartree-Fock $\Psi_{HF} = A\left[\phi_1(r_1)\phi_2(r_2)\ldots\phi_n(r_n)\right]$

- Reduces the *3N*-dimension linear Schrödinger equation to *N* *3*-dimension non-linear equations
  - Vary orbitals to minimize the energy
  - Each electron feels the average field of all other electrons.
  - Predicts (most of) the structure of the periodic table, the chemical bond, language of spectroscopy
  - E.g., spatial molecular orbitals for water, H_2O



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 (but we don't know V_{xc})

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

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

Ab Initio Hierarchies of Theories

- Configuration interaction – a linear expansion

$$\left|\Psi\right\rangle = \left(1 + \sum_{ia} c_i^a \left(i \to a\right) + \sum_{ijab} c_{ij}^{ab} \left(ij \to ab\right) + \cdots\right)\left|0\right\rangle$$

  - i,j,… occupied; a,b,… unoccupied; orthonormal MO basis

- Coupled cluster (many-body) non-linear expansion

$$\left|\Psi\right\rangle = \exp\left(1 + \sum_{ia} t_i^a \left(i \to a\right) + \sum_{ijab} t_{ij}^{ab} \left(ij \to ab\right) + \cdots\right)\left|0\right\rangle$$

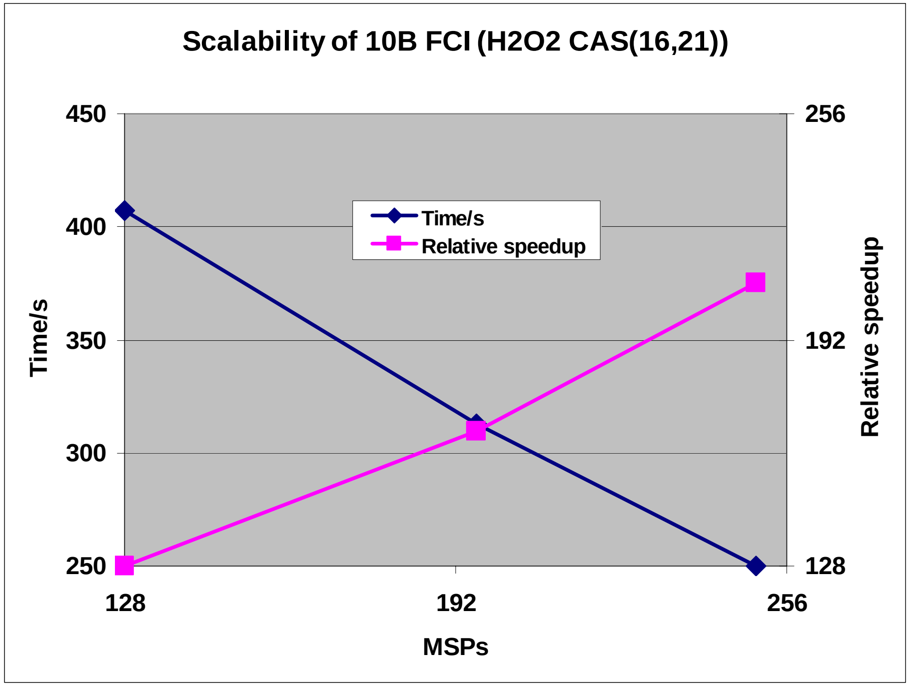
- Size extensivity – consider non-interacting subsystems
  - Energy is additively separable – $E = E_1+E_2+\ldots$
  - Wave function is multiplicatively separable – $\Psi = \Psi_1\Psi_2\ldots$
  - Coupled cluster is size extensive; truncated CI is not.

Cray-X1 – definitive electronic structure calculations at 2.3 TFLOP/s on 256 MSP (Gan & Harrison CCSG/CSMD/ORNL)

- **Full-configuration interaction *exactly* solves the N-electron problem in a given 1-electron basis**
- **It provides a critical benchmark for understanding and calibrating many-body calculations**
- **Several new parallel-vector algorithms have been developed each of which is optimal for certain parameter values – the new code automatically selects the optimal algorithm**
- **Optimal algorithms for the Cray differ sharply from those for IBM Power4**
- **The new code already enables computations 40x larger and 100+x faster than previous work**

Benchmark calculations of Oxygen anion with different Full-CI algorithms

$\alpha-\alpha$ **Algorithm**	**Time/s**
SAXPY Kernel-1	2240
SAXPY Kernel-2	355
Indexed SAXPY	485
DGEMM Kernel	55
$\alpha-\beta$ **Algorithm**	**Time/s**
SAXPY Kernel-2	1250
DGEMM Kernel	125



* FCI (7,79) calculation of Oxygen anion using aug-cc-pvdz basis. 1s electrons are frozen. The FCI involves 14,851,999,576 determinants in D2h symmetry. Timings are measured for one Davidson iteration on 256 MSPs, Cray-X1.

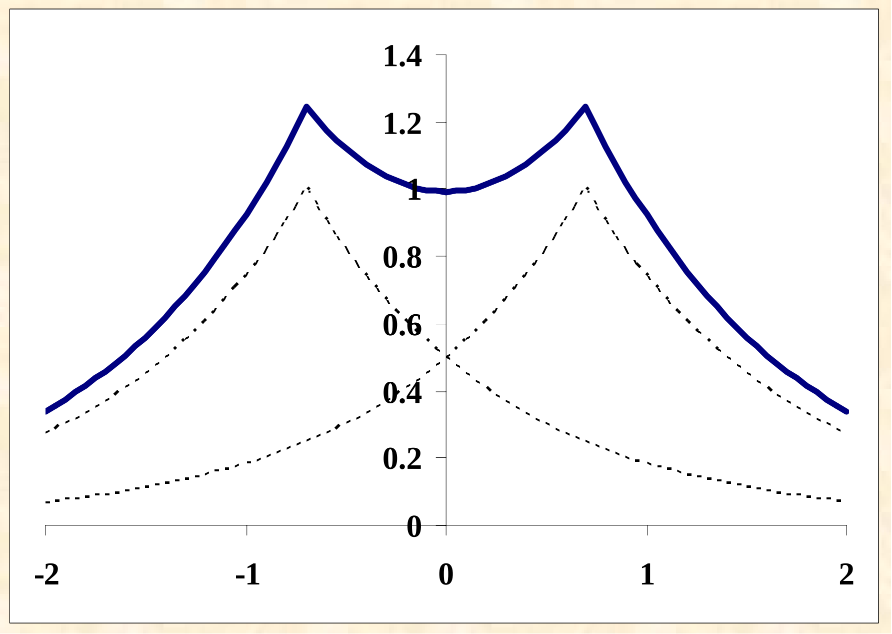
* The DGEMM-based algorithm runs at 9.5GFlops for alpha-beta piece and 8Gflops for alpha-alpha and beta-beta piece *per MSP*. It takes about 180 seconds (3 minutes) per iteration. The total calculation requires 18 iterations to converge to the required threshold of residual norm 1.D-04.

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)

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

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



- 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

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*

Advantages of multiresolution & multiwavelet approach

- A complete framework for computation
  - Integral and differential operators
  - High-order convergence
  - Ready accommodation of boundary conditions
  - Explicit sparse representation of many operators
  - Automatic adaptive refinement
  - Fast algorithms with guaranteed precision
- Need separated representations for efficiency

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)
  - Harrison, Yanai, Gan, Fann, Beylkin, (J. Chem. Phys, 2004)

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

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

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

Adaptive Refinement

- To satisfy the global error condition

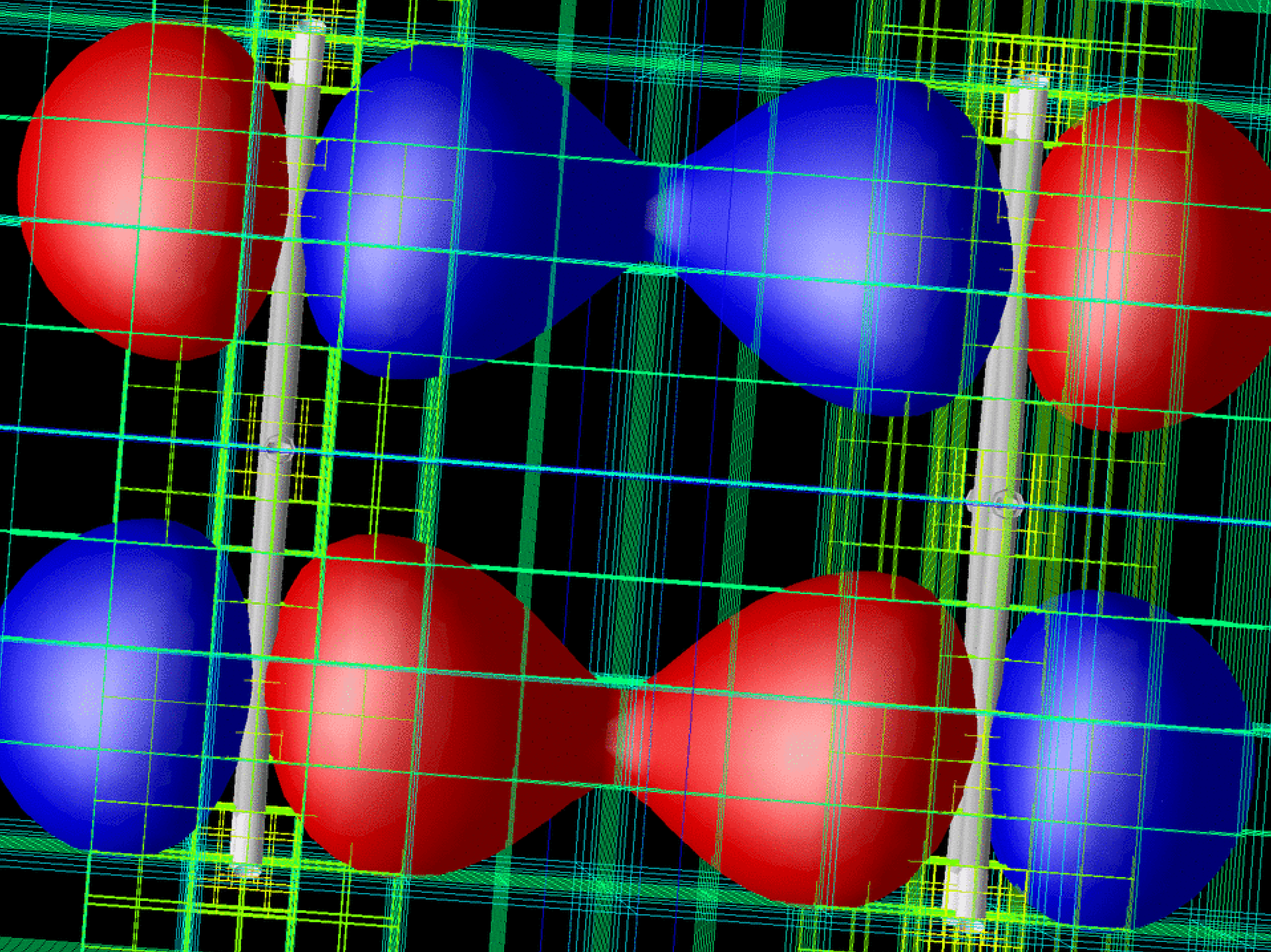
$$\left\| f - f^{n} \right\|_2 \leq \varepsilon \left\| f \right\|_2$$

- Truncate according to

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

- This is rather conservative – usually use

$$\left\| d_l^{n} \right\|_2 \leq \varepsilon$$



Integral Formulation

- Lippmann-Schwinger form
  - E.g., used by Kalos, 1962, in nuclear physics QMC

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

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

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

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

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

$$r^{nl}_{ii'}$$

- In 3-d seems to need $O(N_{box}k^6)$ operations
  - Prohibitively expensive

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

- Separated form
  - Beylkin, Cramer, Mohlenkamp, Monzon
  - $O(N_{box}k^4)$ or even $O(N_{box}k^3)$ in 3D

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

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

$$K(r) = \sum_i \omega_i e^{-t_i r^2} + O(\varepsilon) \text{ for } r \in [r_{lo}, r_{hi}]$$

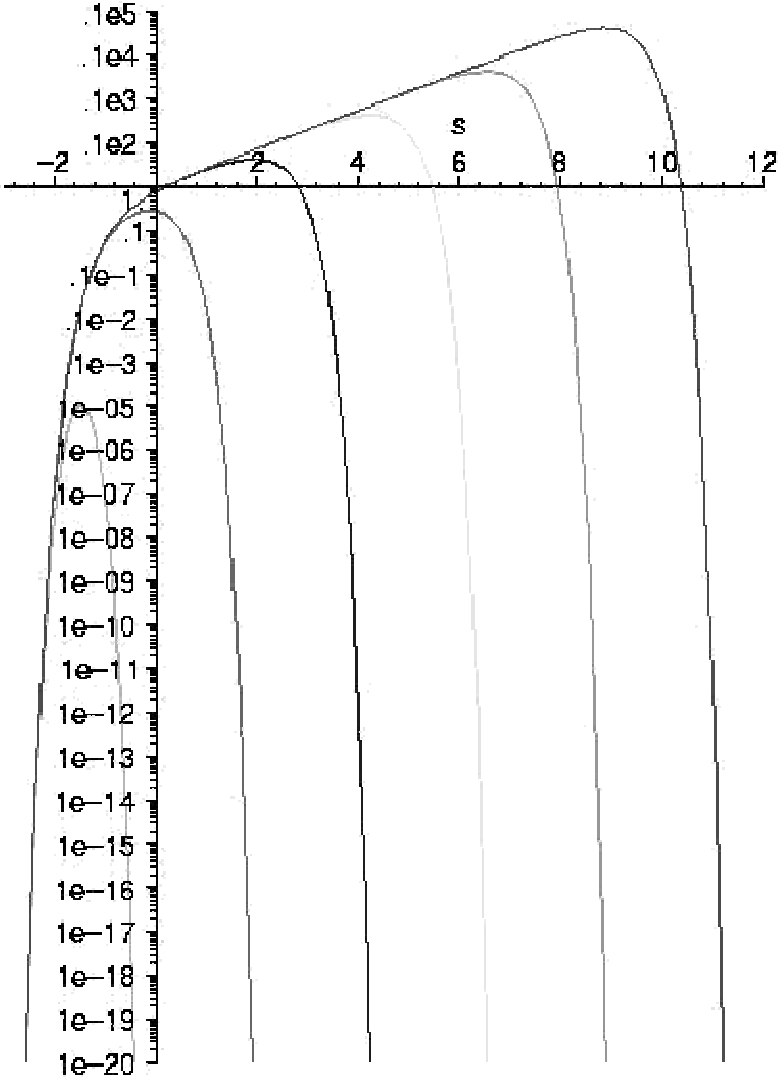
  - Only need compute 1D transition matrices (X,Y,Z)
  - SVD the 1-D operators (low rank away from singularity)
  - Apply most efficient choice of low/full rank 1-D operator
  - Even better algorithms not yet implemented
    - Multiscale expansion of kernel

Accurate Quadratures

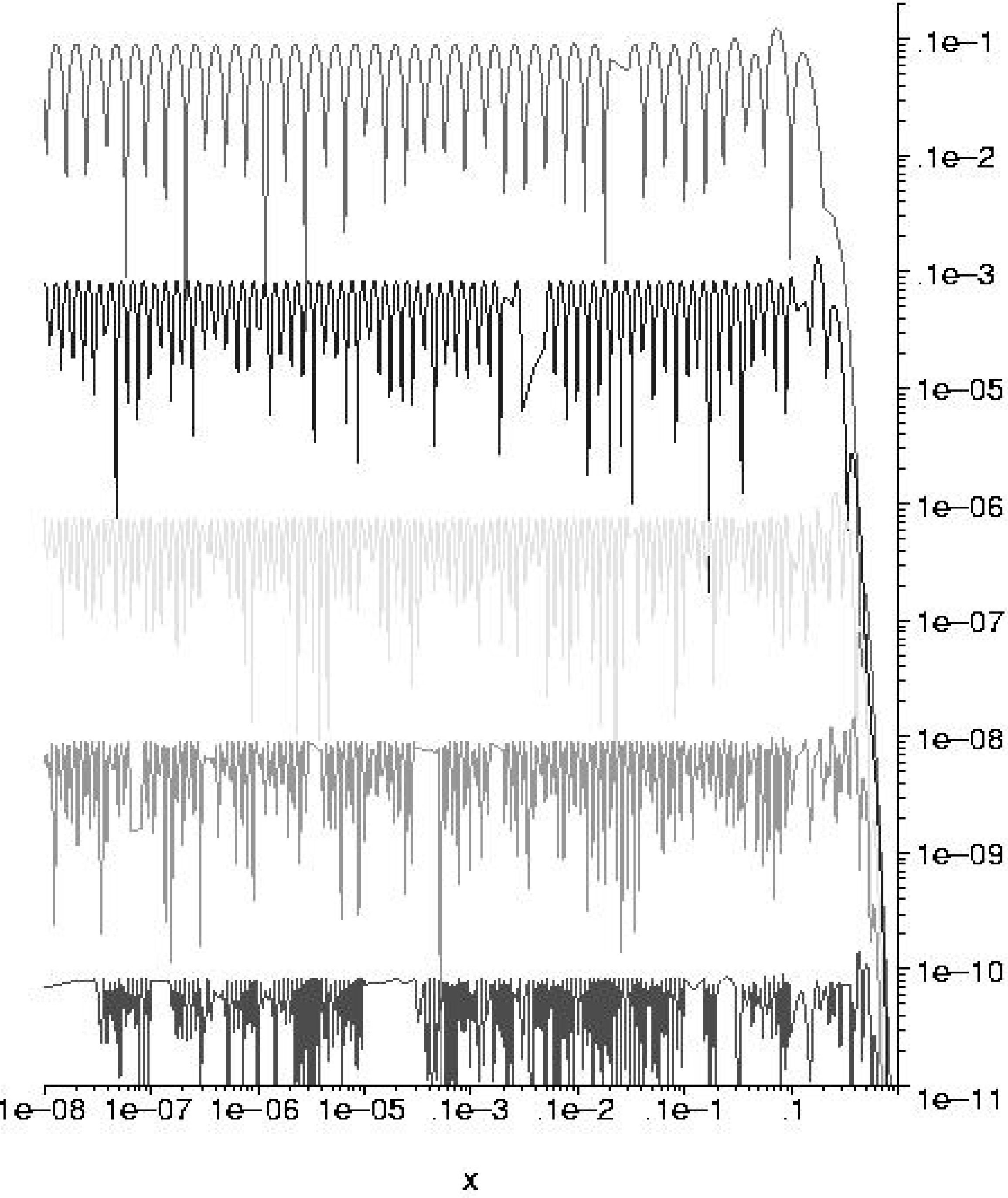
$$\frac{e^{-\mu r}}{r} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-x^2 t^2 - \mu^2/4t^2}\, dt$$

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

- Trapezoidal quadrature
  - Geometric precision for periodic functions with sufficient smoothness
- Beylkin & Monzon
  - Further reductions, but not yet automated



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



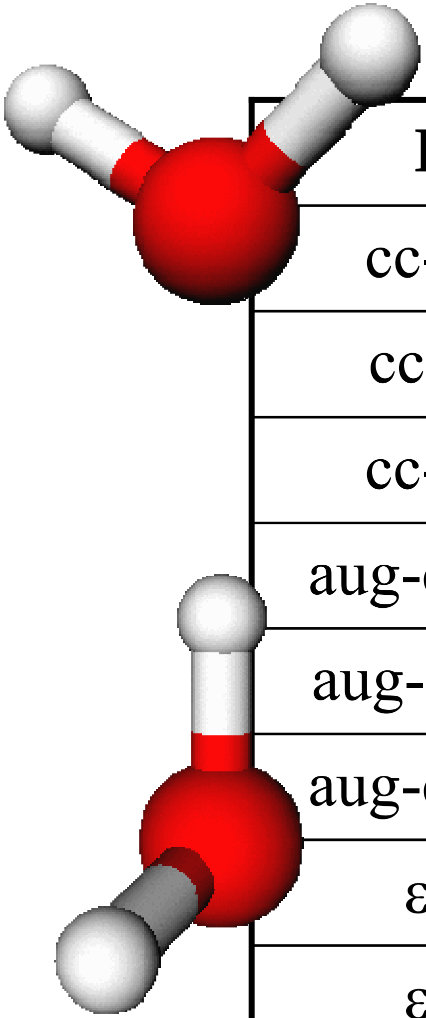
The error in automatically generated Gaussian expansions of *exp(-30r)/r* accurate to 1e-10, 1e-8, 1e-6, 1e-4, and 1e-2 (measured by the weighted error *r(exp(-30r)/r* - *fit(r)))* for *r* in [1e-8,1].

The number of terms are 92, 74, 57, 39 and 21.

Note logarithmic dependence upon precision.

Water dimer LDA

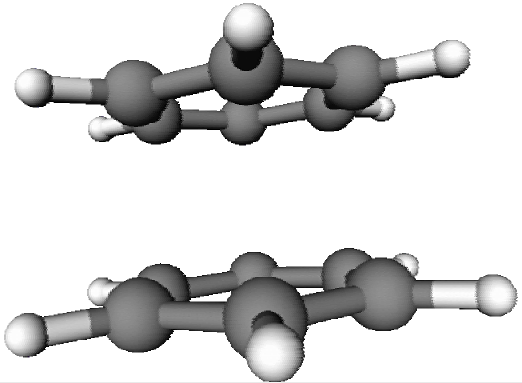
aug-cc-pVTZ geometry, kcal/mol.



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		

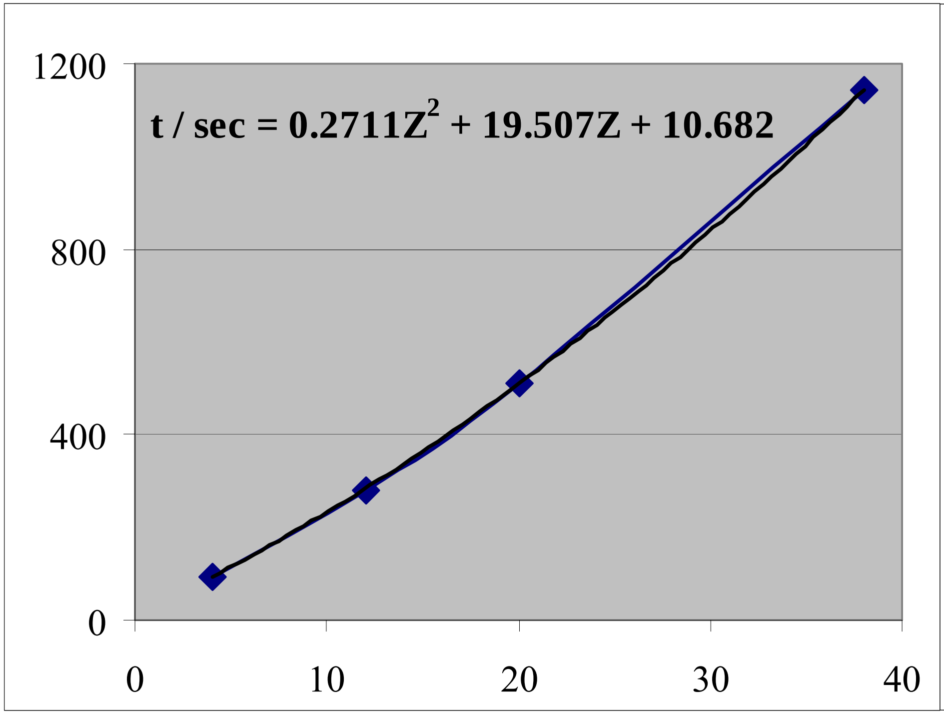
Benzene dimer LDA

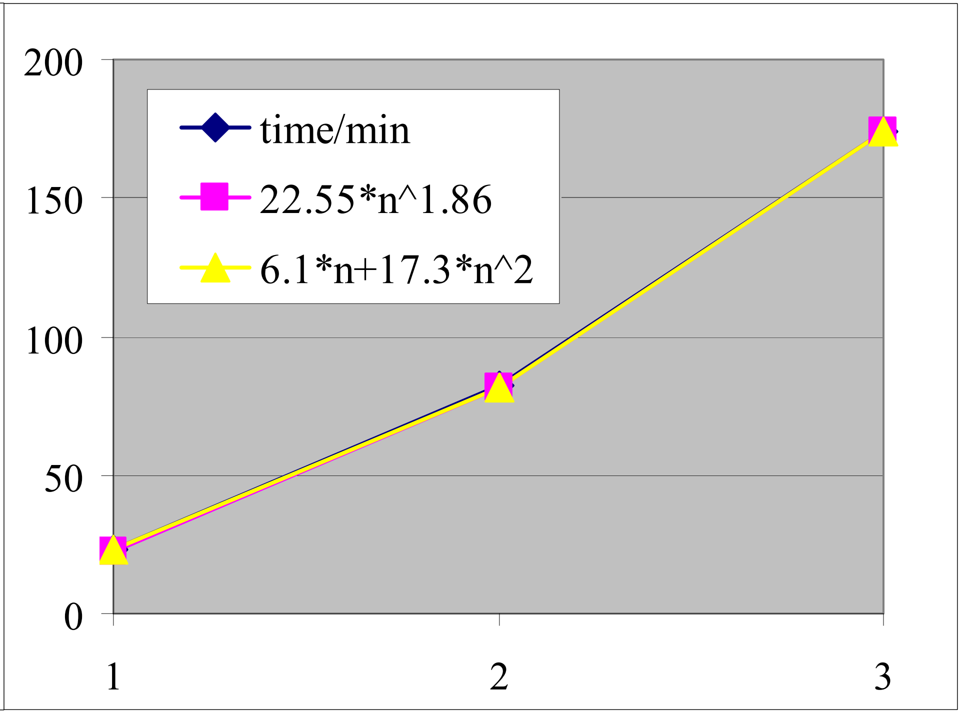
aug-cc-pVDZ geometry, kcal/mol.



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

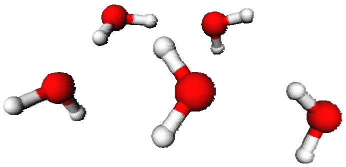


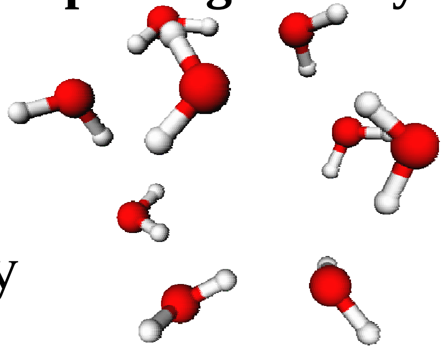


Alkali earth atoms Z=4,12,20,38

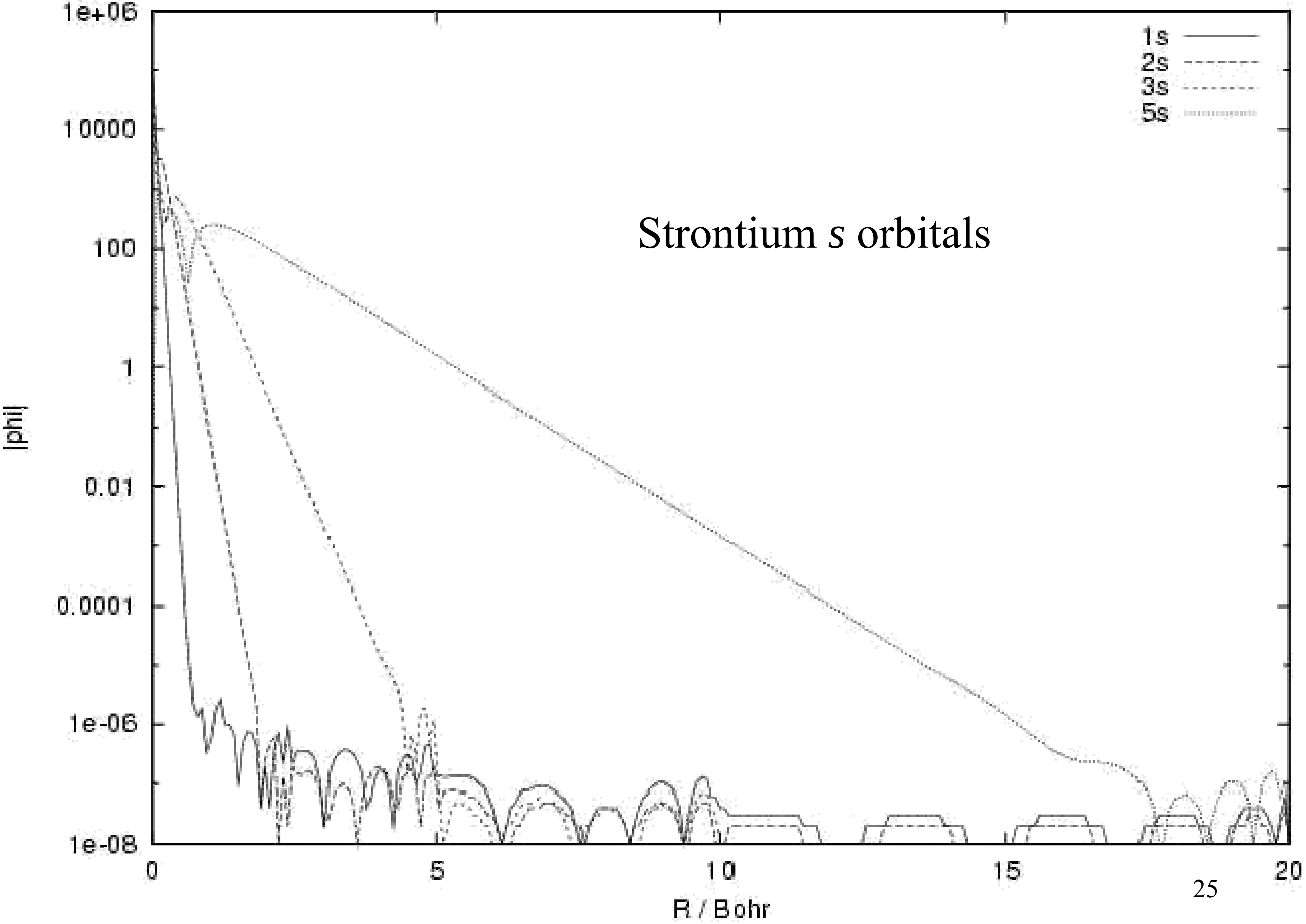
$(C_6H_6)_n$ MP2 aug-cc-pvTZ geometry

$(H_2O)_n$ 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)


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

Analytic Derivatives

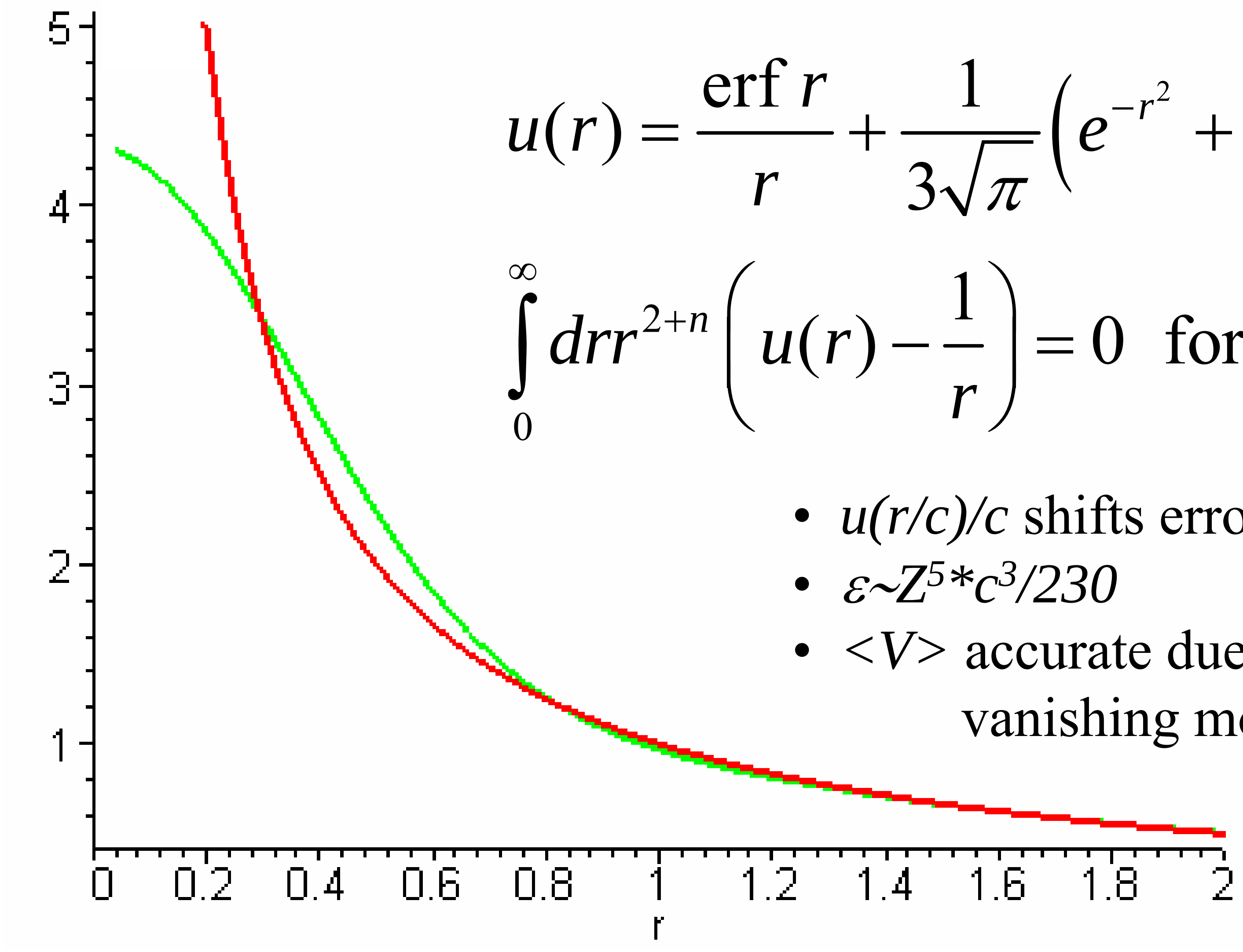
- Derivative of the energy w.r.t. atomic coordinates
  - Essential for geometry optimization, dynamics, …
- Hellmann-Feynman theorem applies

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

$$= \int \rho(r) \frac{\partial V(r)}{\partial q} dr^3 + O(\varepsilon)$$

- In an atom-centered basis this is much harder
  - the incomplete basis moves with the atoms, so you must also differentiate the basis functions.

Smoothed Nuclear Potential

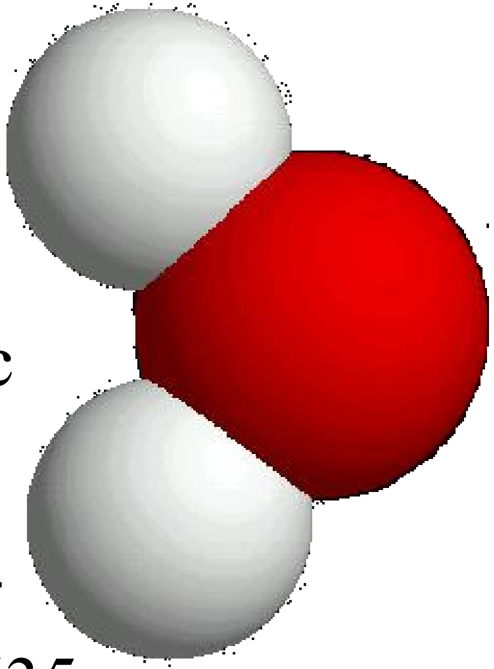


$$u(r) = \frac{\operatorname{erf} r}{r} + \frac{1}{3\sqrt{\pi}}\left(e^{-r^2} + 16e^{-4r^2}\right)$$

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

- $u(r/c)/c$ shifts error to $r<c$
- $\varepsilon \sim Z^5 * c^3/230$
- $\langle V \rangle$ accurate due to vanishing moments

Translational Invariance

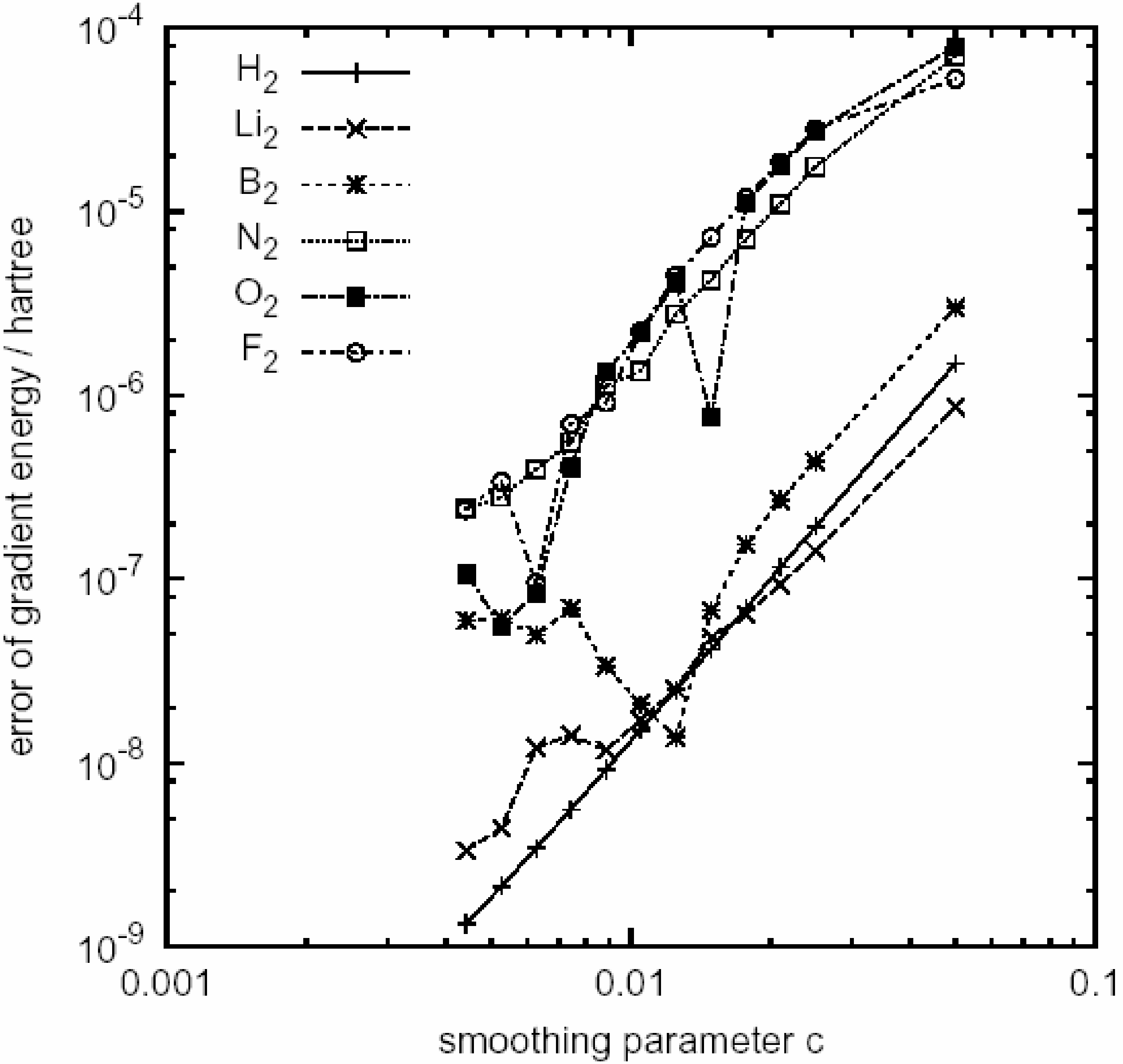


	Dyadic	Non-dyadic
10^{-3}	-75.9139	-75.9139
10^{-5}	-75.913564	-75.913564
10^{-7}	-75.91355634	-75.91355635

- 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

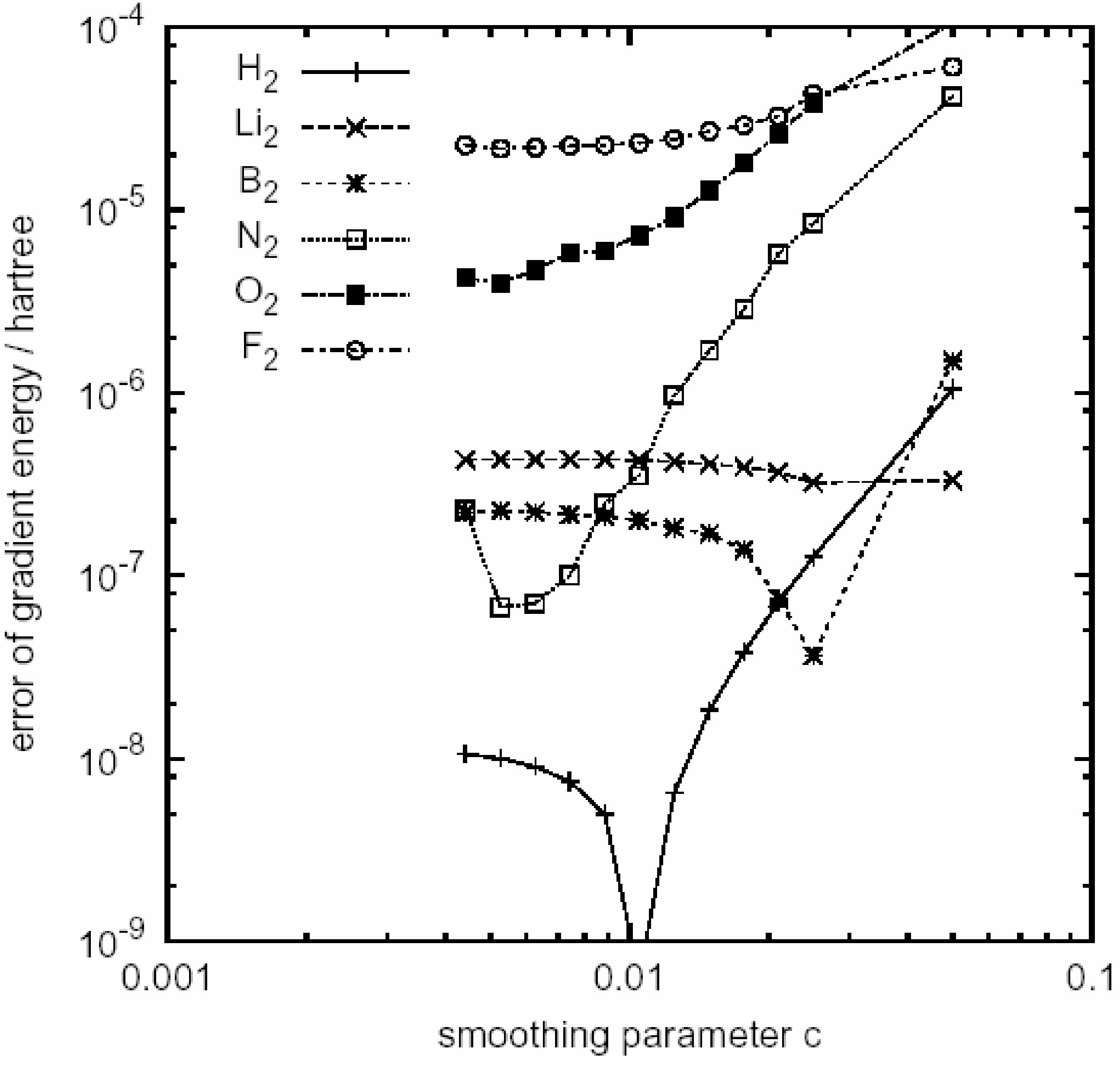


Dependence on potential smoothing parameter (c)

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



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
  - $O(N_{atom} log^m(\varepsilon))$ to any finite precision (Goedecker, Beylkin, …)
  - This is *not* possible with conventional atomic orbitals
- Gradient
  - Each dV/dx requires $O(log(\varepsilon^{-1})log(vol.))$ 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

“Time-dependent” DFT

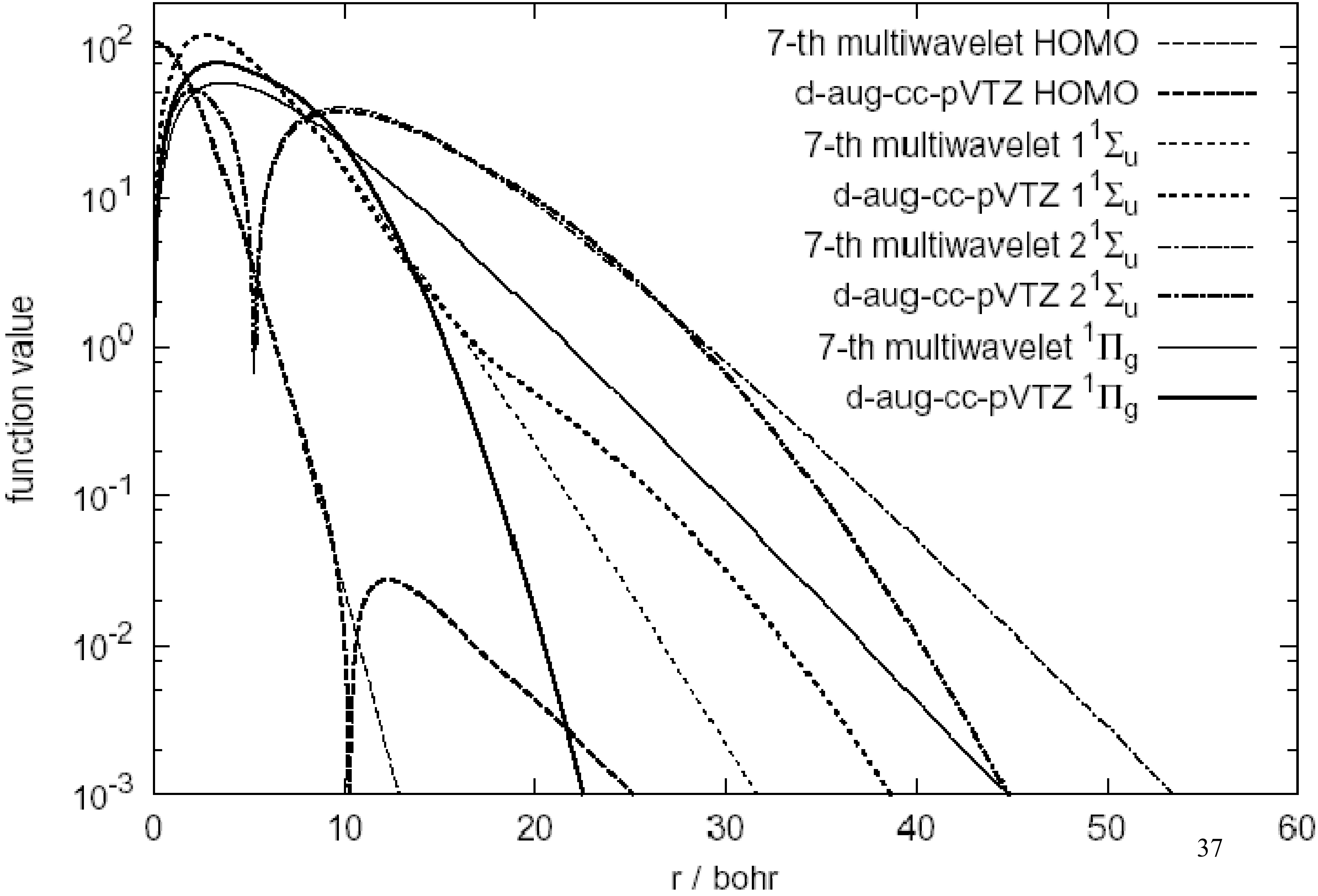
- Linear response to frequency dependent perturbation
  - Eigenvalues yield excitation energies

Transition density for one excited state

$$\left(1-\hat{\rho}^{0}\right)\left[\left(\hat{F}^{0}-\varepsilon_{i}^{0}\right)x_{i}(r)+\frac{\partial V_{coul}}{\partial\rho}*\left(\sum_{j}^{occ}x_{j}(r)\phi_{j}^{\dagger}(r')\right)\phi_{i}(r)\right]=\omega x_{i}(r)$$

  - Actually solve corresponding integral equation

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

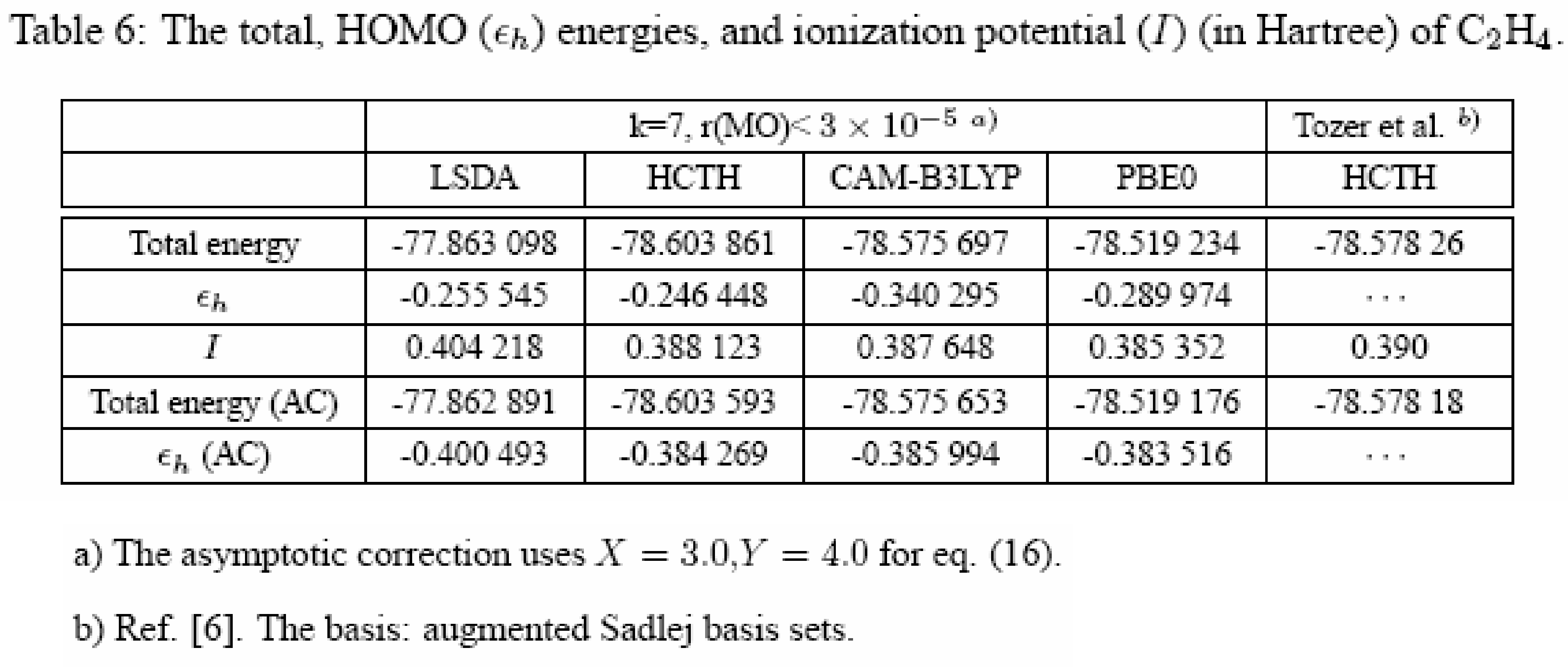
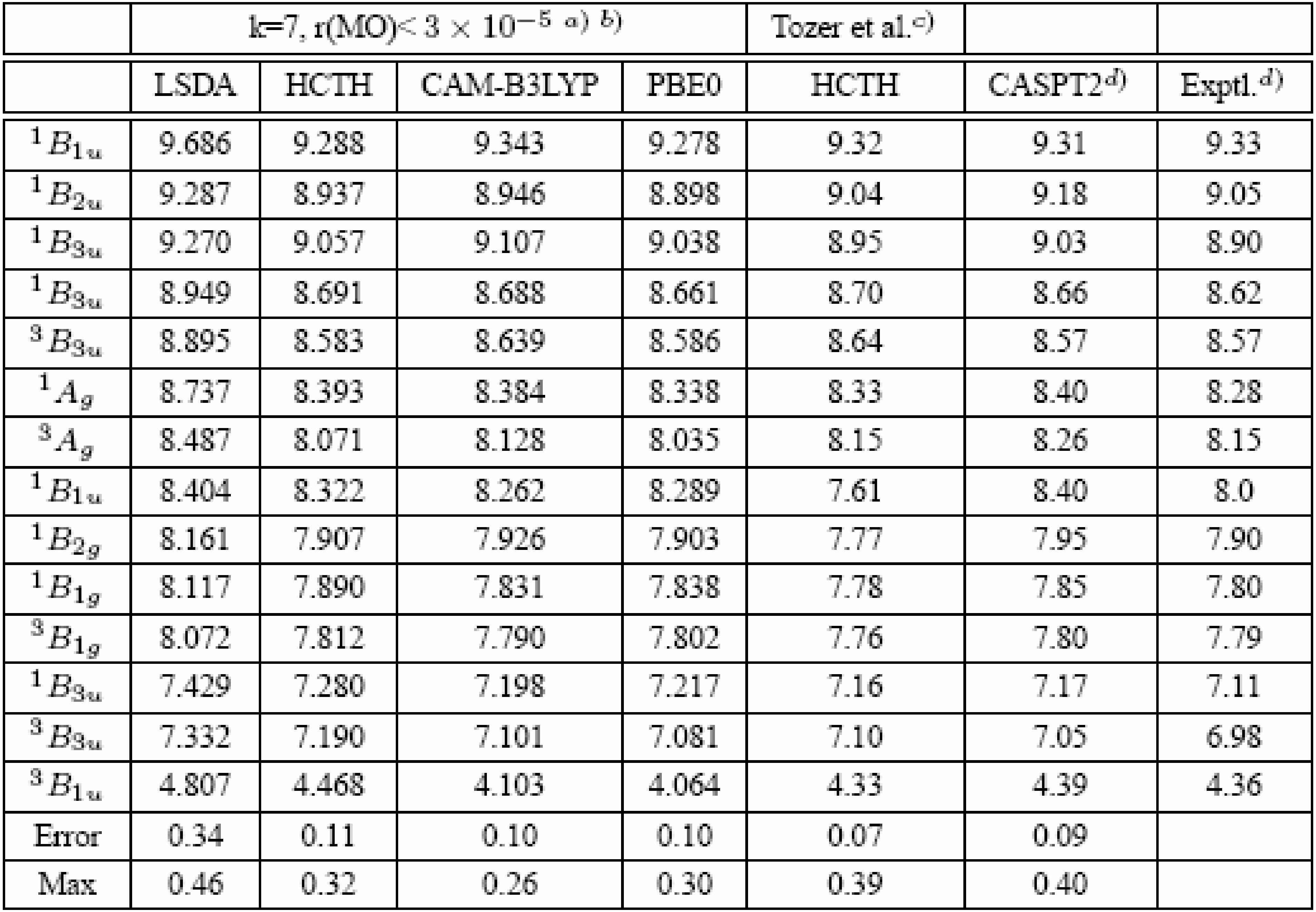


Table 6: The total, HOMO (ϵ_h) energies, and ionization potential (I) (in Hartree) of C_2H_4.

	k=7, r(MO)< 3×10^{-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	$\cdots$
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	$\cdots$

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

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

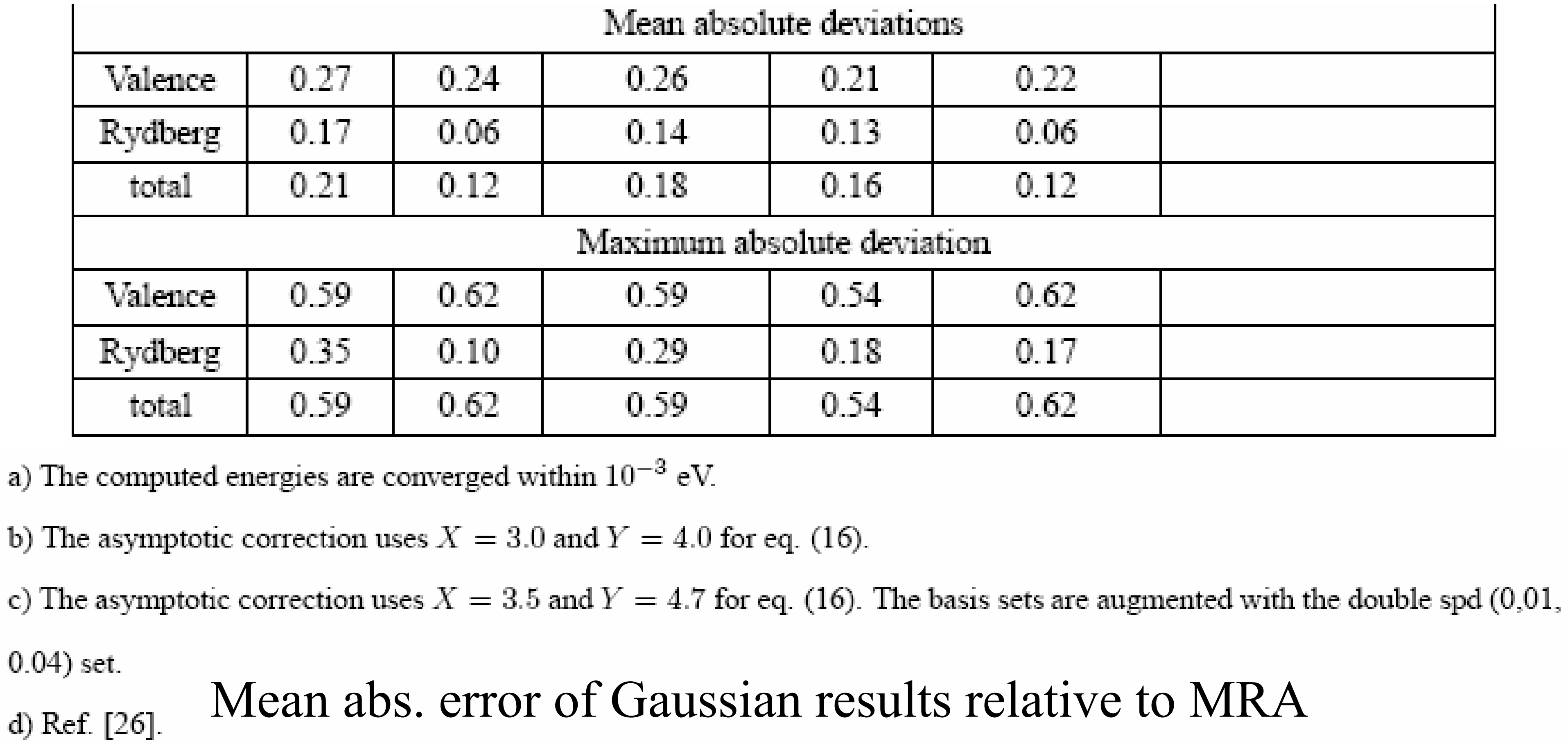


	k=7, r(MO)$< 3 \times 10^{-5}$ a) b)				Tozer et al.c)		
	LSDA	HCTH	CAM-B3LYP	PBE0	HCTH	CASPT2d)	Exptl.d)
$^1B_{1u}$	9.686	9.288	9.343	9.278	9.32	9.31	9.33
$^1B_{2u}$	9.287	8.937	8.946	8.898	9.04	9.18	9.05
$^1B_{3u}$	9.270	9.057	9.107	9.038	8.95	9.03	8.90
$^1B_{3u}$	8.949	8.691	8.688	8.661	8.70	8.66	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[40]

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)
- augmented 6-31g*   0.13 eV (Rydgberg only) 0.25 eV max
- augmented TZ2P   0.07 eV (Rydberg only) 0.16 eV max

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

Compute energy of H atom

$$H = -\frac{1}{2}\Delta - \frac{1}{r}$$

$$\psi(r) = e^{-r}$$

$$E = <\psi \mid H \mid \psi> / <\psi \mid \psi>$$

```
from mra import *
Function.k, Function.thresh = 7,1e-5

L = 32.0

def psi(x,y,z):
   x, y, z = (x-0.5)*L, (y-0.5)*L, (z-0.5)*L
   return 100.0*exp(-sqrt(x*x+y*y+z*z))

def V(x,y,z):
   x, y, z = (x-0.5)*L, (y-0.5)*L, (z-0.5)*L
   return -1.0/sqrt(x*x+y*y+z*z)

psi = Function(function=psi)
V   = Function(function=V)
```

```
Hpsi = -0.5*Delsq*psi + V*psi
err = Hpsi + 0.5*psi
print err.norm2()


px, py, pz = Del*psi


S  = psi.norm2()**2
VE = (V*psi).inner(psi)/S
TE = 0.5*(px.inner(px) + py.inner(py) +
      pz.inner(pz))/L**
print " S=%.8f T=%.8f V=%.8f E=%.8f" %
      (S, TE, VE, TE+VE)



#  S=0.95873799 T=0.50000034
     V=-1.00000014 E=-0.49999980
```

Solve Hartree-Fock for H_2 - I

```
from mra import *
import autoswig, clda, sepop
Function.k, Function.thresh = k, thresh = 5, 1e-3
thresh1 = thresh*0.1

R = 1.4    # bond length
L = 32.0*R # box size
```

Solve Hartree-Fock for H_2 - II

```
C = autoswig.autoswig('''
static double L = 32.0;
static double guess(double x,double y,double z) {
   x =(x-0.5)*L; y=(y-0.5)*L; z=(z-0.5)*L;
   return 100.0*(exp(-sqrt(x*x+y*y+(z-0.7)*(z-0.7)))+
                 exp(-sqrt(x*x+y*y+(z+0.7)*(z+0.7))));
}
void *Cguess = (void *) guess;
```

Guess orbital

$$\phi(r) = e^{-|r-r_a|} + e^{-|r-r_b|}$$

```
double V(double x, double y, double z) {
   x =(x-0.5)*L; y=(y-0.5)*L; z=(z-0.5)*L;
   return -1.0/sqrt(x*x+y*y+(z-0.7)*(z-0.7))+
          -1.0/sqrt(x*x+y*y+(z+0.7)*(z+0.7));
}
void *CV = (void *) V;
''')
```

Potential

$$V(r) = -\frac{1}{|r-r_a|} - \frac{1}{|r-r_b|}$$

Solve Hartree-Fock for H_2 - III

```
def iterate(V,psi,eps):
    Vpsi = (V*psi).scale(-2.0*L*L).truncate(thresh1)
    op = sepop.BSH(Vpsi.k,L*sqrt(-2*eps),0.001/L)
    tmp = op.apply(Vpsi).truncate(thresh1)
    tmp = (tmp*mask).truncate(thresh1)
    norm = tmp.norm2()
    r = tmp-psi
    rnorm = r.norm2()
    eps_new = eps + Vpsi.inner(r) / (-2.0*L*L) / norm**2
    psi_new = tmp.scale(1.0/norm)
    print "norm=%.5f eps=%.5f err(psi)=%.5f err(eps)=%.5f " % \
          (norm, eps_new, rnorm, eps_new-eps)

    return psi_new, eps_new
```

$$\mathrm{tmp} = G(\varepsilon) * V\phi$$

$$\varepsilon \leftarrow \varepsilon + \langle \phi - G * V\phi | V\phi \rangle / \| G * V\phi \|^2$$

$$\phi \leftarrow G * V\phi / \| G * V\phi \|$$

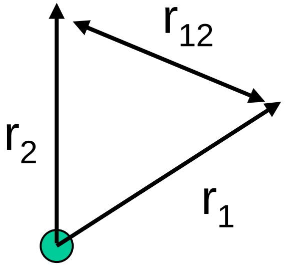
Solve Hartree-Fock for H_2 - IV

```
Vnuc = Function(cfunction=C.cvar.CV,thresh=thresh/L).truncate(thresh1/L)
mask = Function(cfunction=clda.cvar.Cmask,initial_level=4,refine=0,compress=0)
psi  = Function(cfunction=C.cvar.Cguess).truncate(thresh1)
psi = (psi*mask).truncate(thresh1)
psi = psi.scale(1.0/psi.norm2())

eps = -1.25
for iter in range(10):
    psi,eps = iterate(Vnuc,psi,eps)

px, py, pz = Del*psi

S  = psi.norm2();  VE = (V*psi).inner(psi)/S
TE = 0.5*(px.inner(px) + py.inner(py) + pz.inner(pz))/L**2/S
print "    norm",S, "  kinetic",TE, "potential",VE,” energy“,(TE+VE)
```

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)

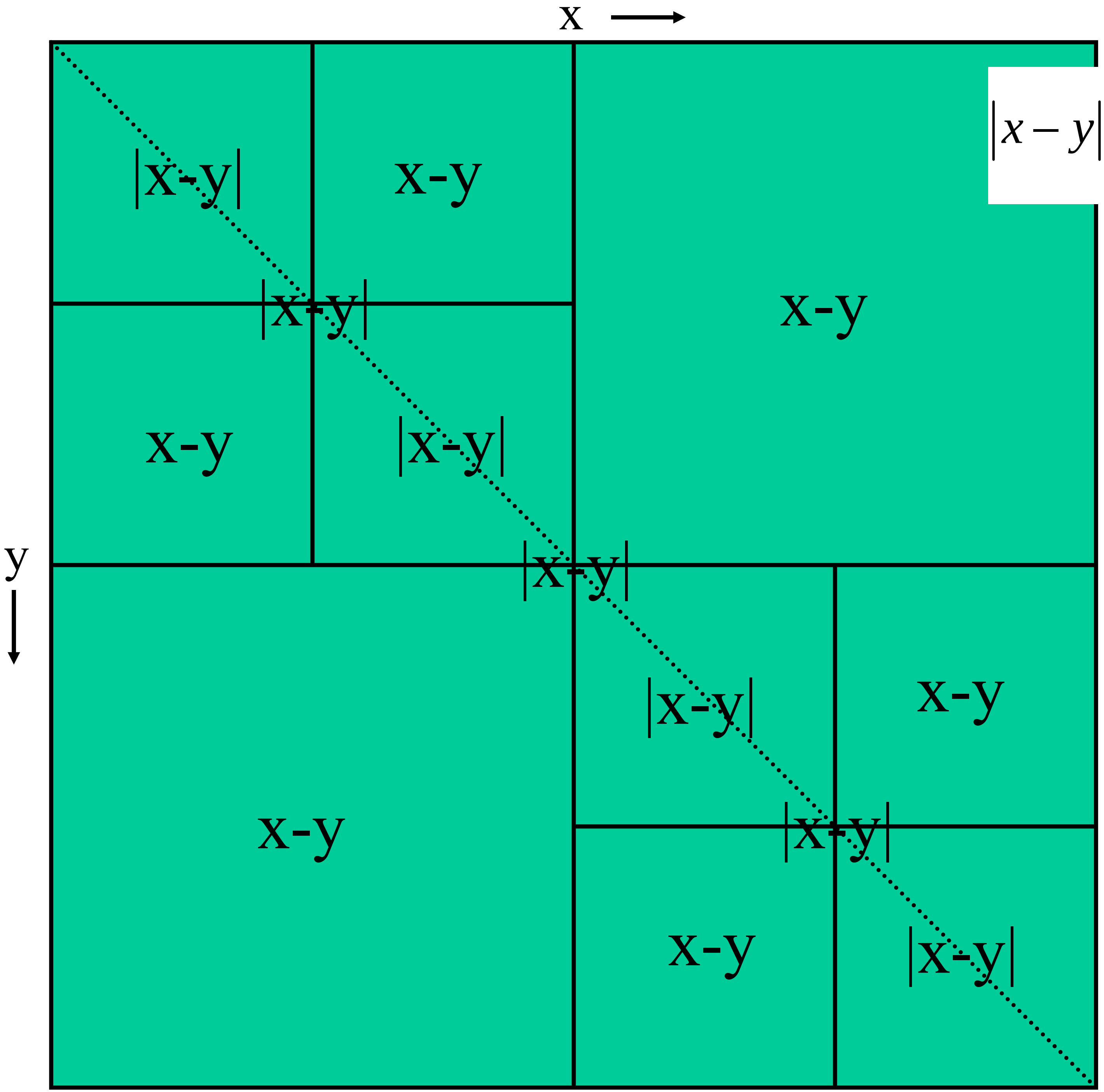
$$\Psi(r_1, r_2) = \sum_{ij} c_{ij} \phi_i(r_1) \phi_j(r_2)$$

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

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

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

Preliminary results

- k=5 ε=1e-3
- Iterating Lippman-Schwinger equation in 6d for helium atom

iter	energy	residual
0	-2.861 52	(HF wavefunction)
1	-2.890 60	0.051
2	-2.902 91	0.020
3	-2.905 80	0.010
4	-2.906 67	0.005
Exact	-2.903 74	

Timings and sizes

- Wavefunction (k=5, ε=1e-3, deepest n=5)
  - (c=0.5) 0.1GB (partitioned SVD form)
- R12*Wavefunction
  - (c=0.5) 1.8GB memory + 2m CPU
- BSH
  - (c=0.5) 2.5 hours!

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

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

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
$$e^{-u}He^{u}\phi=-\frac{1}{2}\Delta_1\phi-\frac{1}{2}\Delta_2\phi-u'\frac{r_1-r_2}{|r_1-r_2|}\bullet(\nabla_1\phi-\nabla_2\phi)$$
$$+\left(V-\left((u')^2+u''\right)+\frac{1}{|r_1-r_2|}(1-2u')\right)\phi$$
- Choose *u* to eliminate singularity at $r_{12}=0$
- Quantum Monte Carlo calculations
  - Best to eliminate all $r_1=0$, $r_2=0$, $r_{12}=0$, $r_1=r_2=r_{12}=0$

Chemical Energy Differences

- Why do chemists compute at such high precision?
  - Chemical energies formed as differences of total energies
  - $\Delta E(AB \rightarrow A+B) = E(A) + E(B) - E(AB)$
  - Total energy is unavoidably at least *O(N)* computation
  - Cannot tolerate size dependent error unless cancels in differences (i.e., intra-atomic)
- Direct computation of energy differences
  - Multiresolution view accords with physical intuition
    - Potential from distant fine-scale structure decays rapidly due to vanishing moments
    - Only need coarse scale information from distant parts (but, …)
  - Need non-linear response of the system
- Sub-linear scaling ↔ multiscale approach

Basic idea

$$E(1) - E(0) = \int_0^1 \frac{dE}{d\lambda} d\lambda$$

- E.g., λ=occupation number in DFT $\frac{dE}{d\lambda} = \varepsilon_{HOMO}$

Ionization energies	**Water**		**Calcium**	
	k=7		**k=5**	**k=7**
npt	**Trapezoid**	**Gauss**	**Gauss**	**Gauss**
1	**-**	**-13.07**	**-6.20**	**-6.21**
2	**-13.24**	**-13.12**	**-**	**-**
3	**-13.15**	**-**	**-**	**-**
4	**-13.14**	**-**	**-**	**-**
6	**-13.12**	**-**	**-**	**-**
E(1)	**-75.913533**		**-675.696606**	**-675.742199**
E(0)	**-75.431268**		**-675.469054**	**-675.513952**
E(1)-E(0) eV	**-13.12**		**-6.19**	**-6.21**

Chemical energy differences

- Assign orbitals to fragments A and B and partition density

$$\rho = \rho_A + \rho_B \qquad \rho_A(r) = \sum_{i \in A} \phi_i^2 \qquad \rho_B(r) = \sum_{i \in B} \phi_i^2$$

- Partitioning of potential immediately follows (except exchange correlation)

$$V_A(\lambda) = V_A^{ext}(\lambda) + V_A^{coul}(\lambda) + V_A^{xc}(\lambda)$$

$$V_A^{ext}(\lambda) = v_A(r) + \lambda v_B(r)$$

$$V_A^{coul}(\lambda) = \int \frac{\rho_A(s) + \lambda \rho_B(s)}{|r - s|} ds$$

$$V_A^{xc}(\lambda) = V_{xc}\left(\rho_A + \lambda \rho_B\right) + \lambda \rho_B \left(\left. \frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} \right|_{\rho = \rho_B + \lambda \rho_A} - \left. \frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} \right|_{\rho = \rho_A + \lambda \rho_B} \right)$$

- Total energy

$$E(\lambda) = T(\lambda) + E_{ext}(\lambda) + J(\lambda) + E_{xc}(\lambda) + E_{nuc}(\lambda)$$

$$T(\lambda) = -\frac{1}{2}\sum_{i\in(A+B)} \left\langle \phi_i \middle| \nabla^2 \middle| \phi_i \right\rangle$$

$$E_{ext}(\lambda) = \int \rho_A(r)v_A(r)dr + \int \rho_B(r)v_B(r)dr + \lambda\left(\int \rho_A(r)v_B(r)dr + \int \rho_B(r)v_A(r)dr\right)$$

$$J(\lambda) = \tfrac{1}{2}\int \frac{\rho_A(r)\rho_A(s)}{|r-s|}drds + \tfrac{1}{2}\int \frac{\rho_B(r)\rho_B(s)}{|r-s|}drds + \lambda\int \frac{\rho_A(r)\rho_B(s)}{|r-s|}drds$$

$$E_{xc}(\lambda) = \int \rho_A\varepsilon_{xc}\left(\rho_A + \lambda\rho_B\right)dr + \int \rho_B\varepsilon_{xc}\left(\rho_B + \lambda\rho_A\right)dr$$

$$E_{nuc}(\lambda) = \sum_{(I<J)\in A}\frac{Z_I Z_J}{|r_I - r_J|} + \sum_{(I<J)\in B}\frac{Z_I Z_J}{|r_I - r_J|} + \lambda\sum_{\substack{I\in A\\ J\in B}}\frac{Z_I Z_J}{|r_I - r_J|}$$

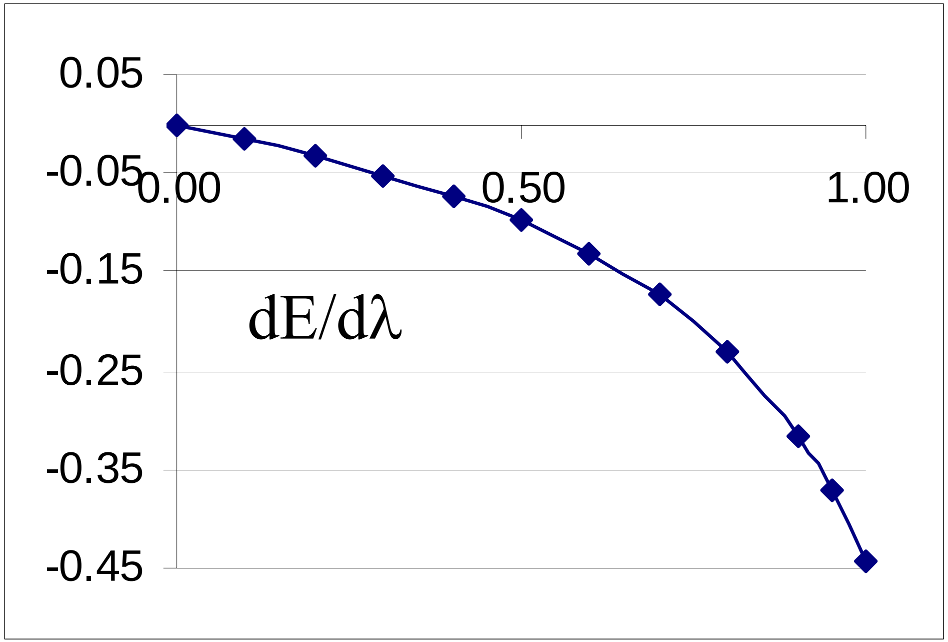
- Orthogonality $\langle \phi_A | \phi_B \rangle \le 1 - \lambda$

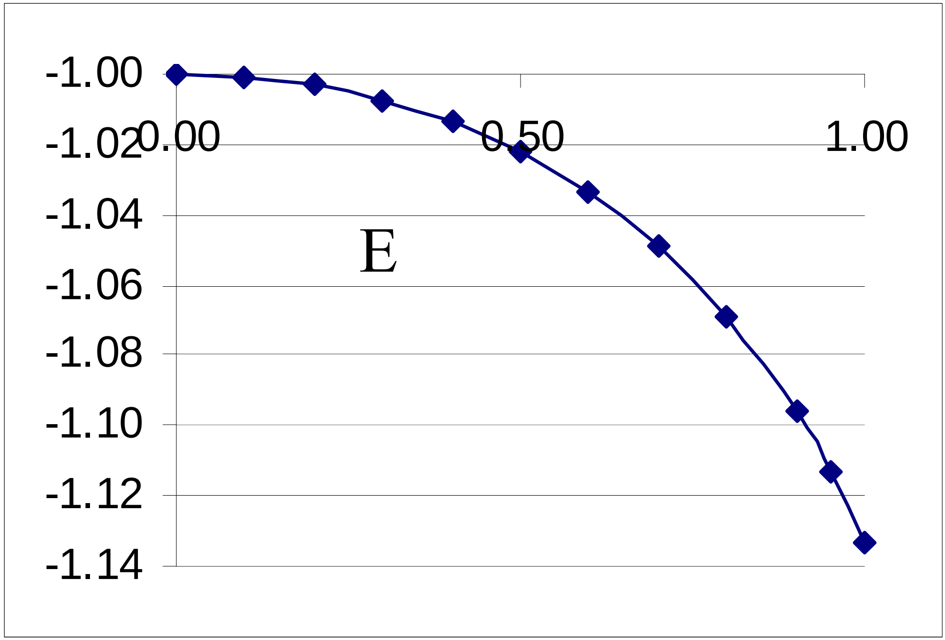
- Lagrangian

$$W = E\left[\rho_A, \rho_B\right] - \sum_{i \in A} \varepsilon_i^A \left(\left\langle \phi_i^A \middle| \phi_i^A \right\rangle - 1 \right) - \sum_{i \in B} \varepsilon_i^B \left(\left\langle \phi_i^B \middle| \phi_i^B \right\rangle - 1 \right)$$

$$-2 \sum_{\substack{i \in A \\ j \in B}} \varepsilon_{ij}^{AB} \left(\left\langle \phi_i^A \middle| \phi_j^B \right\rangle + \left(s_{ij}^{AB} \right)^2 - \lambda \right)$$

E.g., H_2





Trapezoidal		**Gauss-Legendre**	
#points	**ΔE/kcal/mol**	**#points**	**ΔE/kcal/mol**
2	**-139.8**	**1**	**-62.1**
3	**-101.0**	**2**	**-81.3**
5	**-88.5**	**3**	**-83.8**
6	**-86.9**		
E(1)-E(0)	**-83.8**		

Highly non-linear response.

Second energy differences?

Practical?

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
- Electron correlation is *the* nut to crack
- Multiscale computation of chemical energy differences
  - Second-differences most attractive