Q-Chem Program: Best Available Fundamental Methods

Jing Kong (孔静)
Q-Chem Inc.
Pittsburgh, PA

DFT in Q-Chem

- All types of functionals – B3LYP, BMK, M06
- Linear scaling
- Dual basis
- Special methods: Constrained-DFT, spin-flip DFT

DFT in Q-Chem

HF and DFT have three components:

- Coulomb O(N^2): $F_{\mu\nu} \leftarrow \sum_{\lambda\sigma} (\mu\nu \left| r_{12}^{-1} \right| \lambda\sigma) P_{\lambda\sigma}$
- Exchange O(N^2): $F_{\mu\nu} \leftarrow \sum_{\lambda\sigma} (\mu\lambda \left| r_{12}^{-1} \right| \nu\sigma) P_{\lambda\sigma}$
- DFT Exchange&Correlation O(N):

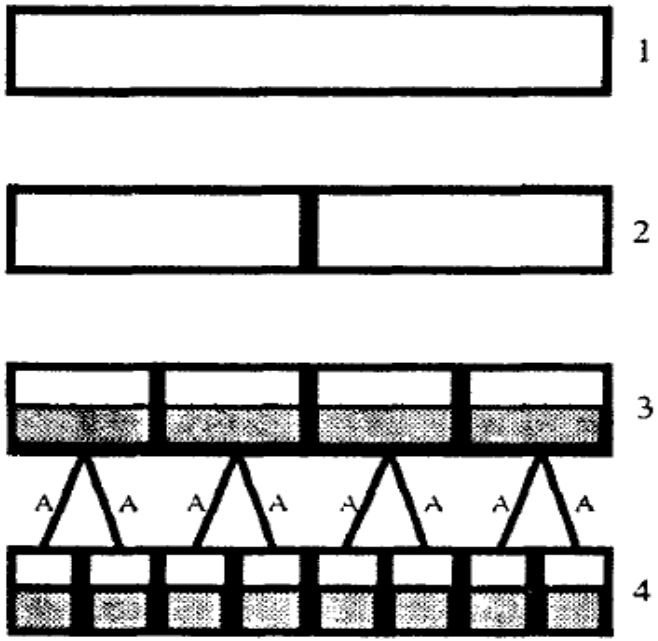
$$F_{\mu\nu} \leftarrow \sum_{Atom} \sum_{i} f'_{\rho,i} \phi_{\mu,i} \phi_{\nu,i}$$

Coulomb: Fast Multipole Method

Developers: *White, Head-Gordon @ Berkeley*

- Invented by Greenard at MIT for point charges in 1987
- Q-Chem the first in the implementation to quantum chemistry for continuous charge in 1996
- First realization of linear-scaling DFT molecules

Continuous Fast Multipole Method



Coulomb: J Engine

Developers: *Shao, Head-Gordon*

- Reduce the number of intermediates
- Faster coulomb energy and force

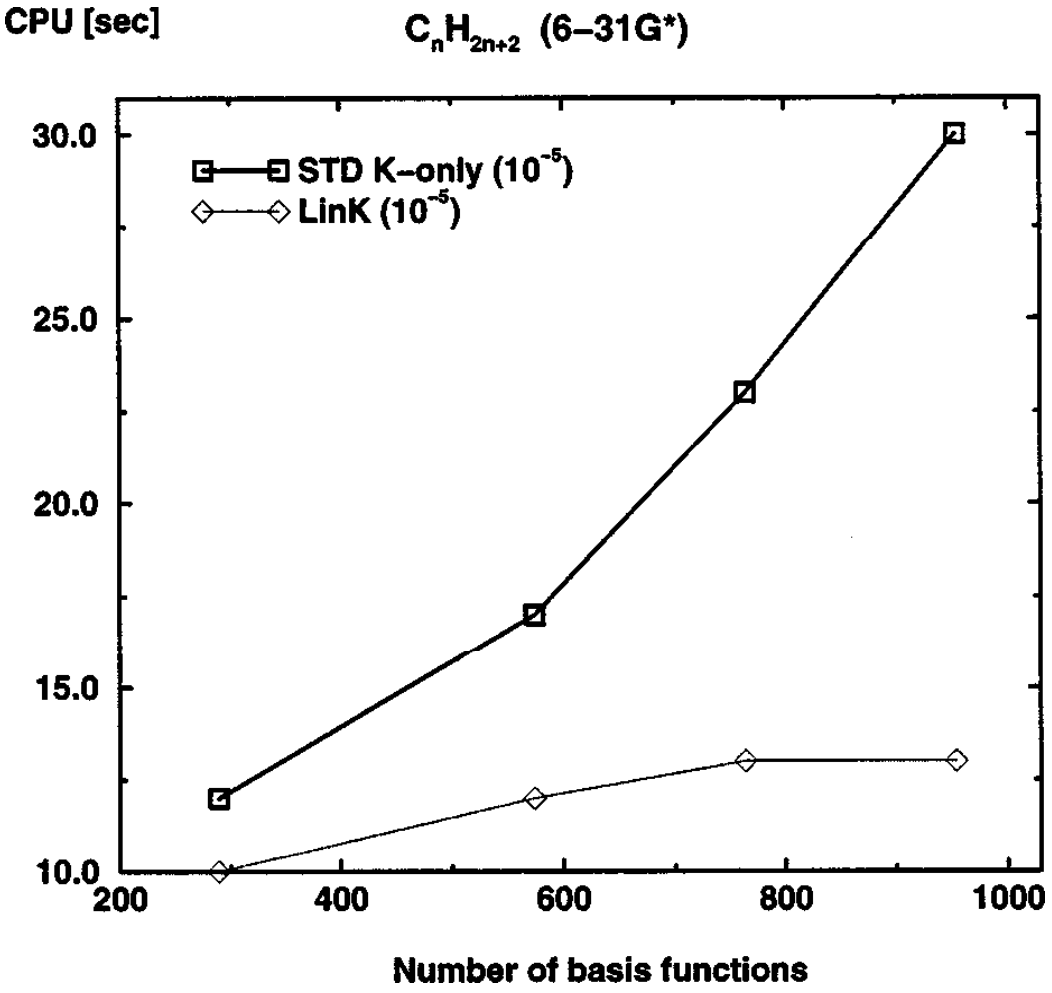
	J-engine	***integrals***	***speed-up***
(pp|pp)	28.1	160.2	5.7
(dd|dd)	69.3	792.3	11.4
(ff|ff)	141.4	2630.3	18.6

HF Exchange: Linear Scaling

Ochsenfeld, Head-Gordon @berkeley

Using the sparsity of density matrix:

$$\sum_{\lambda\sigma}(\mu\lambda\left|r_{12}^{-1}\right|\nu\sigma)P_{\lambda\sigma}$$

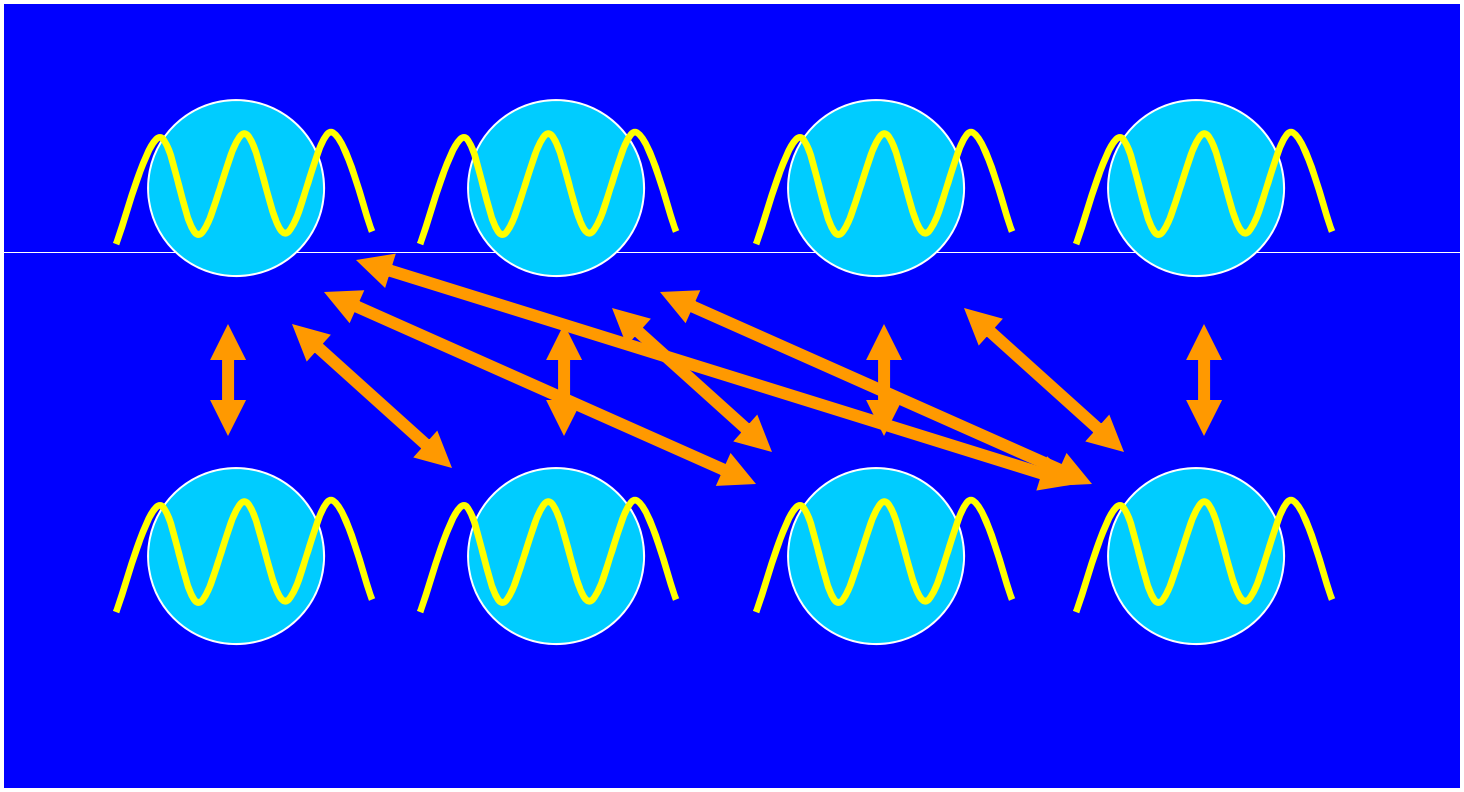


Latest: Fourier Transform Coulomb

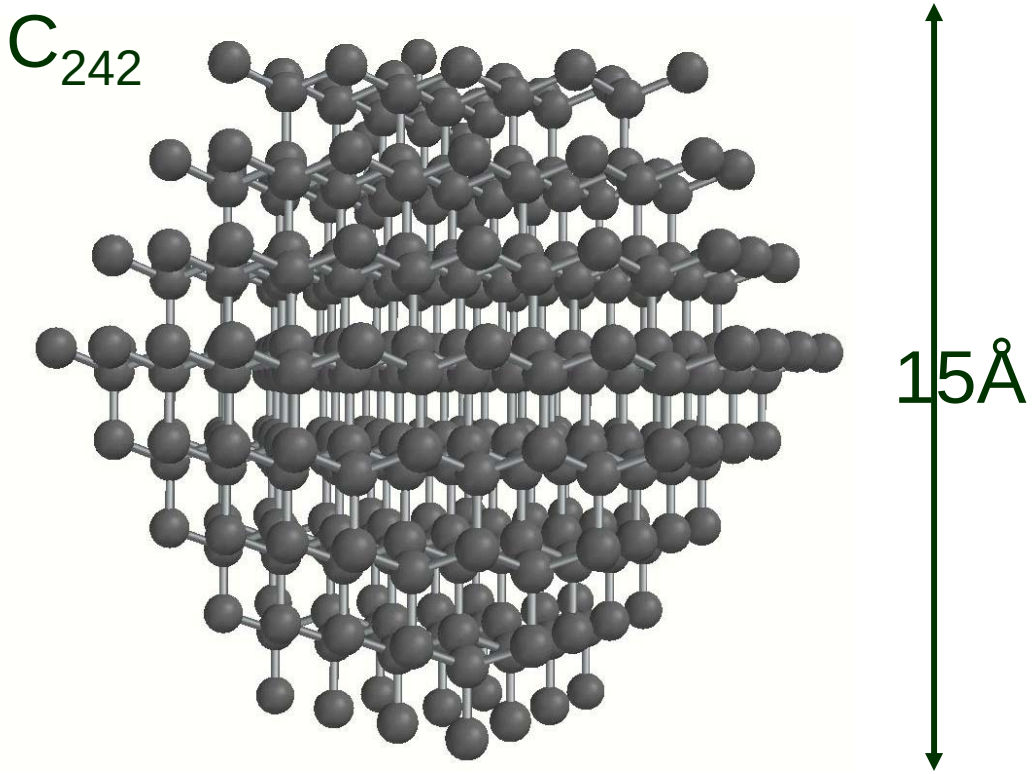
Fusti-Molnar, Kong

- Uses planewaves as auxilary basis
- Fusti-Molnar and Peter Pulay's operator (JCP, Vol 116, 2002)
- Calculates the integrals with diffuse functions
- $O(N^2)$ in basis set size versus $O(N^4)$
- O(N) in system size with a small crossover
- No loss of accuracy

Mechanism of FTC

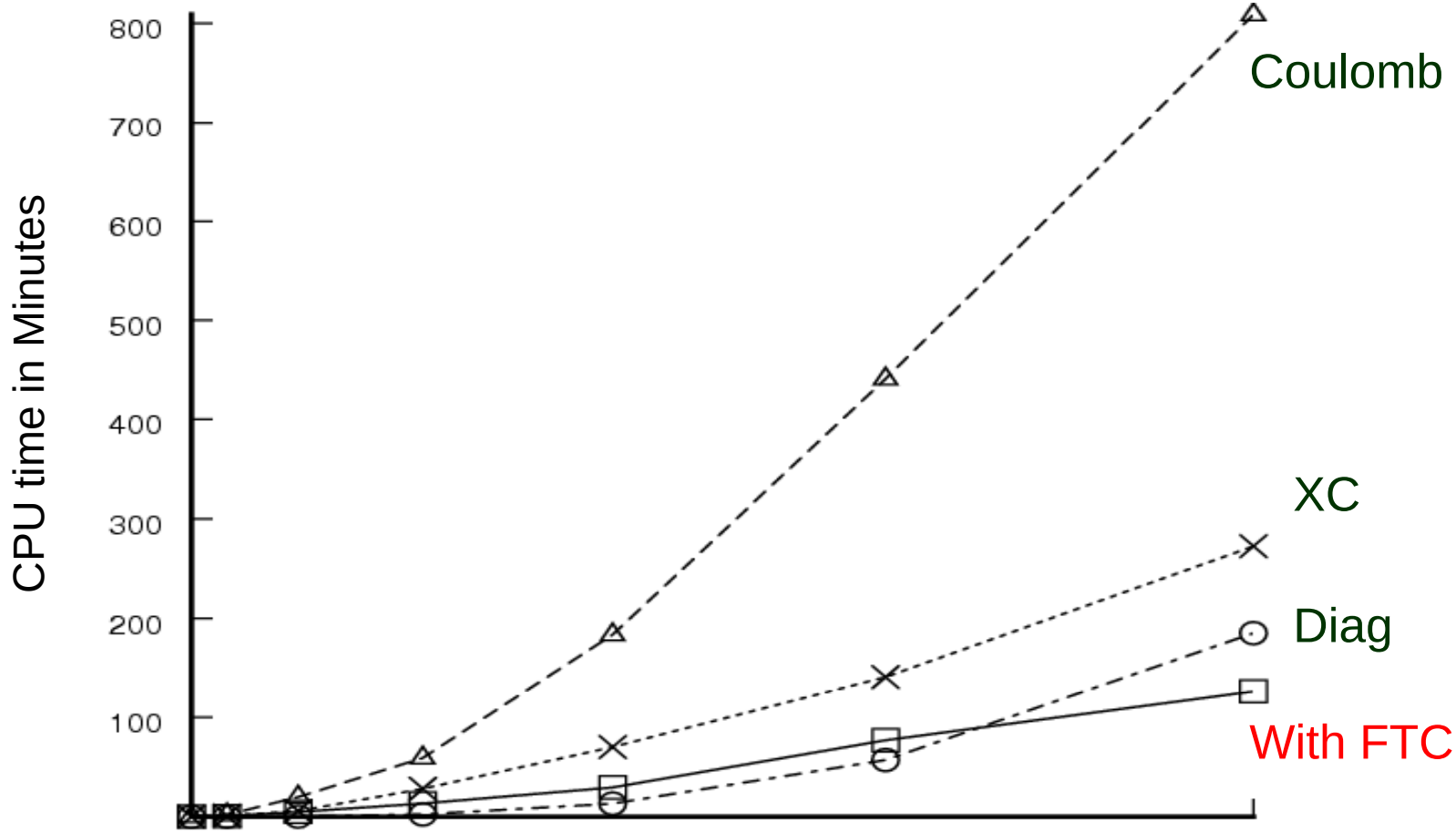


Coulomb: FTC



6-311G(d), 6-311G(df), IBM Pwr4, 1 CPU

Coulomb: FTC



Atoms	8	20	44	86	150	242	366
6-311G(df)	200	500	1100	2150	3750	6050	9150

Efficient Large Basis Method

Liang, Steele, Head-Gordon @berkeley.edu

Large Basis Calculation
at the Cost of Small Basis

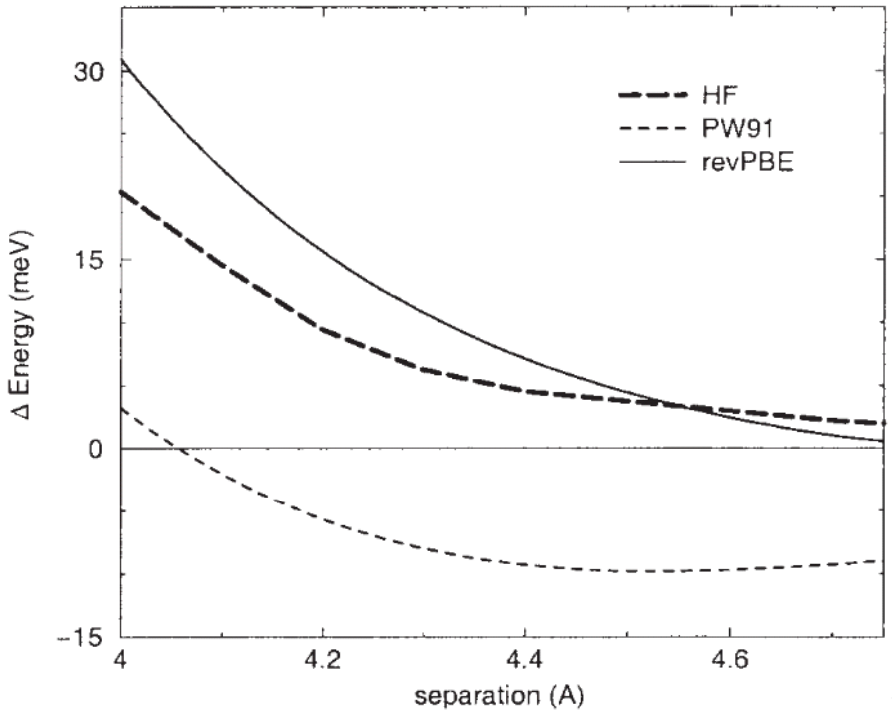
- Basis extrapolation
- 10 times faster for SCF

DFT: Dual Basis

G2 database Calculations with B3LYP in kcal/mol.
Target basis is always 6-311++G(3df,3pd).

Small basis	single basis	dual basis
6-311G	MAD = 24.3	MAD = 4.0
6-311G*	MAD = 7.0	MAD = 2.2
6-311G**	MAD = 4.9	MAD = 2.2
6-311++G(3df,3pd)	MAD = 2.2	MAD = 2.2

DFT Long Range Correction



More accurate DFT

Chai, Head-Gordon @berkeley.edu

$$\frac{1}{r_{12}} = \frac{\mathrm{erf}(\omega r_{12})}{r_{12}} + \frac{\mathrm{erfc}(\omega r_{12})}{r_{12}}$$

- Several versions
- ωB97X-D
- Much better than B3LYP-D:

  Mean Absolute Error: 1.93 vs 2.77

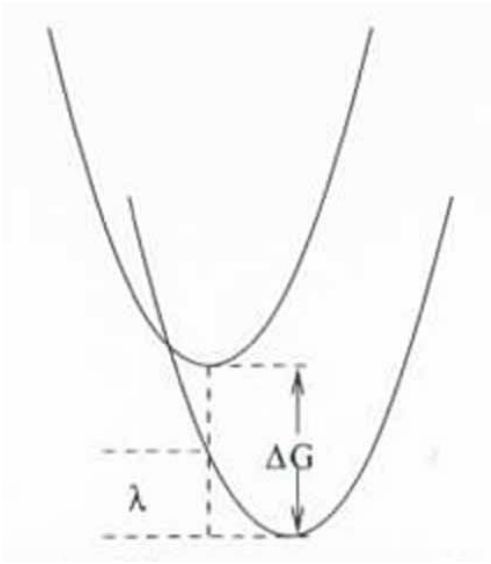
Charge Transfer with DFT

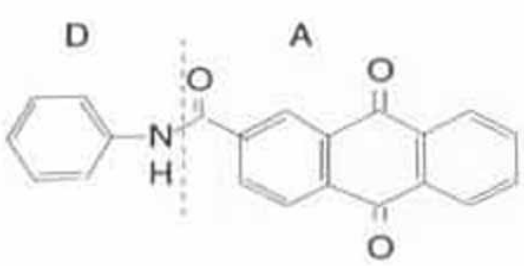
Wu, van Hoorhis @mit.edu

Constrained DFT

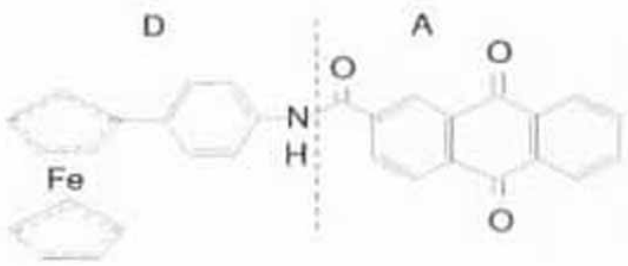
- DFT calculation with predefined charge separation
- Used for Marcus Theory for CT reactions

Charge Transfer with DFT





FA-AQ



Fc-FA-AQ

TABLE 2: Calculated Driving Force and Inner-Sphere Reorganization Energy for the Charge Recombination Reaction of FA-AQ and Fc-FA-AQ[a]

		$-\Delta G_{CR}$ (exptl)	$-\Delta G_{CR}$ (calcd)		
	τ_{CR}		gas phase	in DMSO	λ_i
FA-AQ	>900 μs	2.24	3.25	2.31	0.26
Fc-FA-AQ	20 ps	1.16	2.29	1.02	0.21

Parallel DFT

Dachsel, Korambath, Brown, Fusti-Molnar, Kong

- Up to 2nd derivatives for HF and DFT
- Including linear scaling J-engine, CFMM and FTC
- Distributed memory for frequency calc
- Available on all the platforms

Parallel DFT

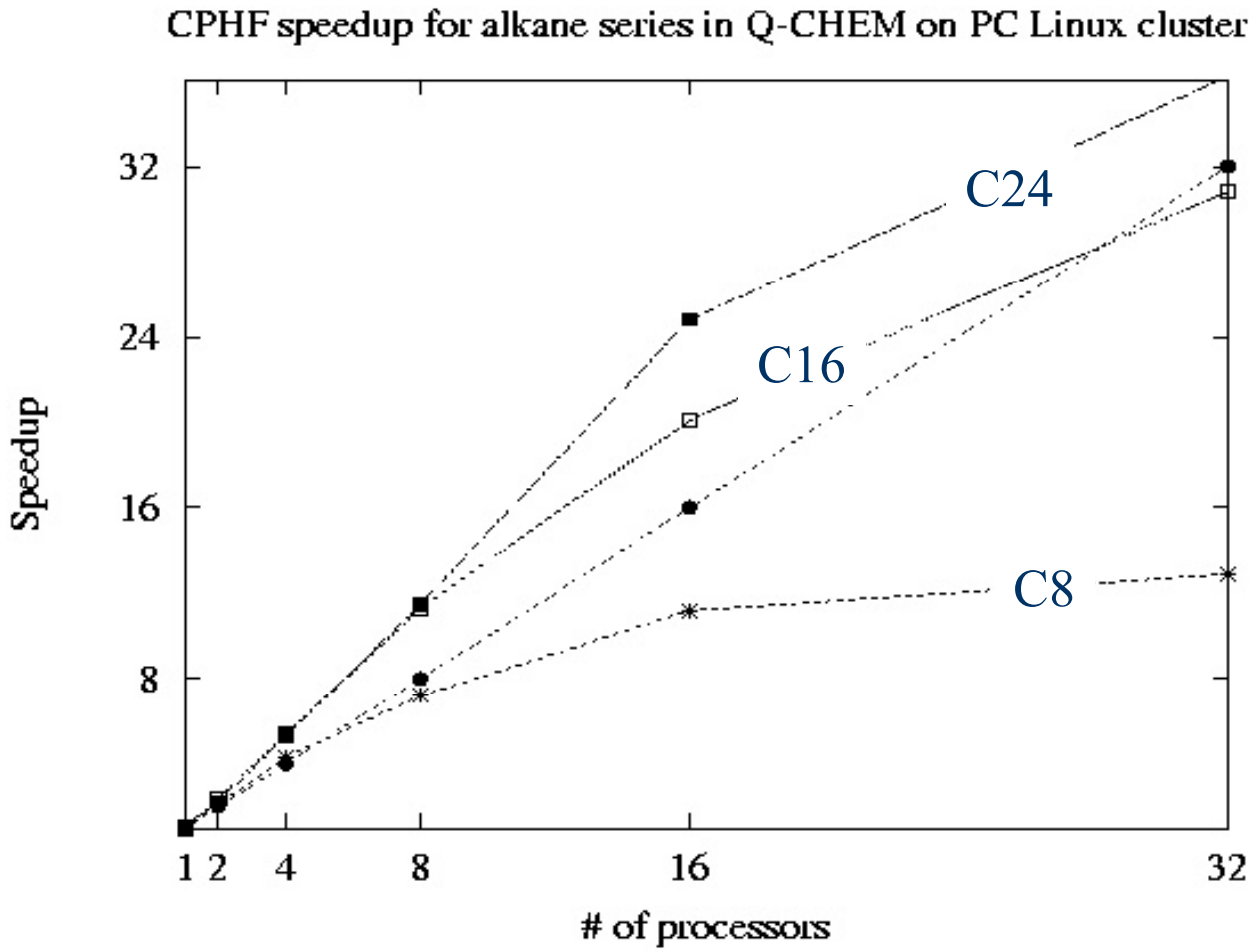
CPSCF: $(1 - \mathrm{A})\mathbf{B}^x = \mathbf{B}_0^x$

Parallelization Strategy:

Distribute the Nuclear Perturbations *x*

- All steps in parallel except (2)
- Scalable
  - the larger the system, the higher the speed-up
- Virtually no communication
- Memory usage distributed

Parallel: Frequency



MP2 in Q-Chem

- Very efficient semidirect MP2
- Local MP2
- RI-MP2
- Scaled modified-spin models
- Dual basis

Q-CHEM
A Quantum Leap Into the Future of Chemistry

Faster DFT, MP2

Jung, Lochan, Dutoi, Head-Gordon @berkeley.edu

MP2 at HF Speed

RI approximation

$$\langle\mu\nu|\lambda\sigma\rangle \rightarrow \langle ij|kl\rangle$$

$$|\mu\nu\rangle \approx \sum_{K,L} |L\rangle V_{KL}^{-1} \langle K|\mu\nu\rangle$$

$$\langle\mu\nu|\lambda\sigma\rangle \rightarrow \sum_{K,L} \langle\mu\nu|K\rangle V_{KL}^{-1} \langle L|\lambda\sigma\rangle$$

Faster DFT, MP2

MP2 at HF Speed

Jung, Lochan, Dutoi, Head-Gordon @berkeley.edu

- Speed-up: 7X – 10X
- Errors are chemically insignificant:

Atomization energies of
148 neutral molecules (G2 set)

RMS = 0.10 kcal/mol

Max = 0.27 kcal/mol

Better MP2

Jung, Lochan, Dutoi, Head-Gordon @berkeley.edu

Empirical MP2 Models

How MP2 can be faster and more accurate?

$$E_{\text{SCS-MP2}} = c_{\text{OS}} E^{\text{OS}}_{\text{MP2}} + c_{\text{SS}} E^{\text{SS}}_{\text{MP2}}$$

- SOS (scaled opposite-spin)
- Faster: O(N^4) vs O(N^5)
- Can be more accurate
- Wrong aymptotic behavior!

Better MP2

MOS – Modified Opposite Spin

- Scaling factor that depends on the distance:

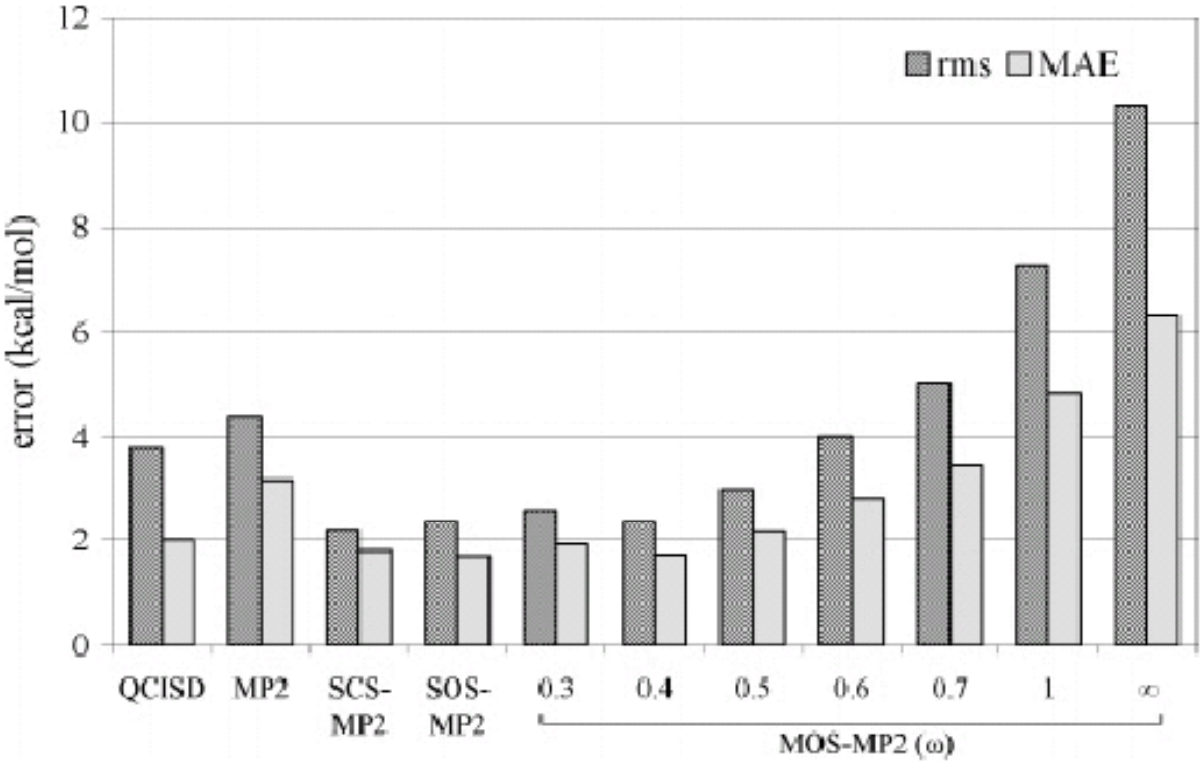
$$\frac{1}{r} + c_{\mathrm{MOS}} \frac{erf(\omega r)}{r}$$

$$c_{\mathrm{MOS}} = \sqrt{2} - 1$$

$$E_{\mathrm{MP2}}^{\mathrm{MOS}} \to 2E_{\mathrm{MP2}}^{\mathrm{OS}}, \qquad r \to \infty$$

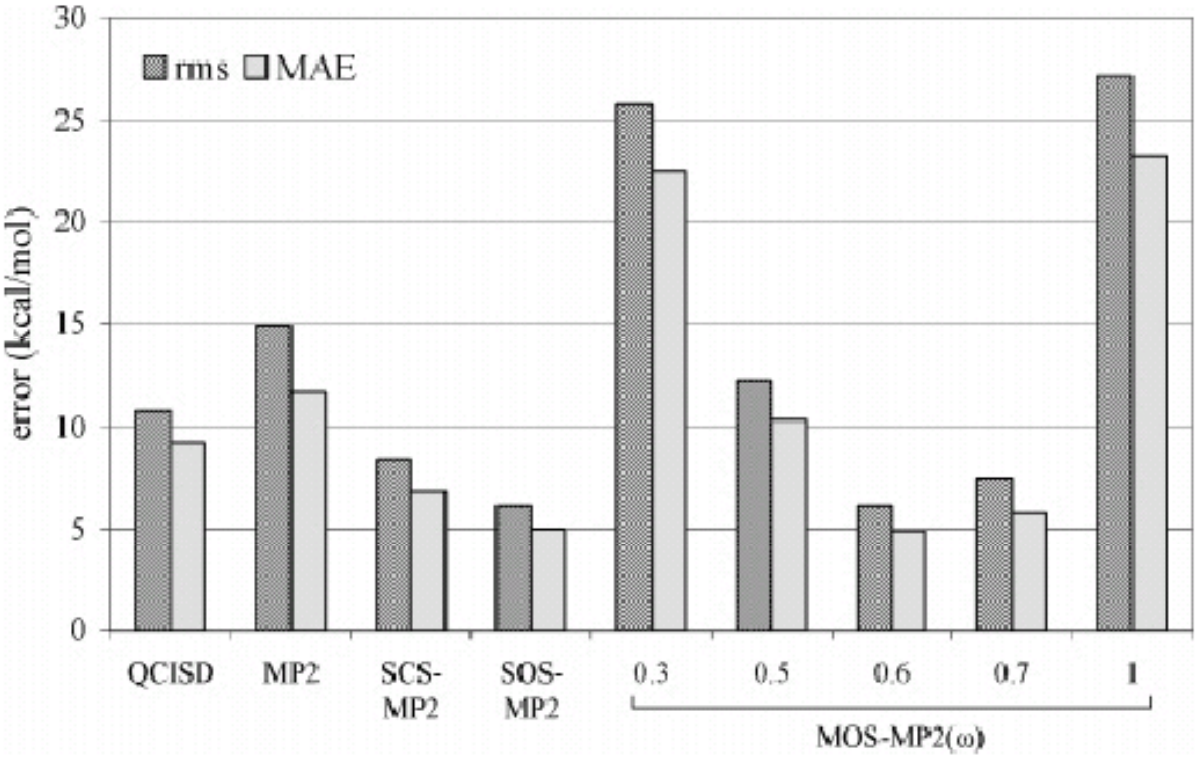
MOS-MP2

Reaction energies



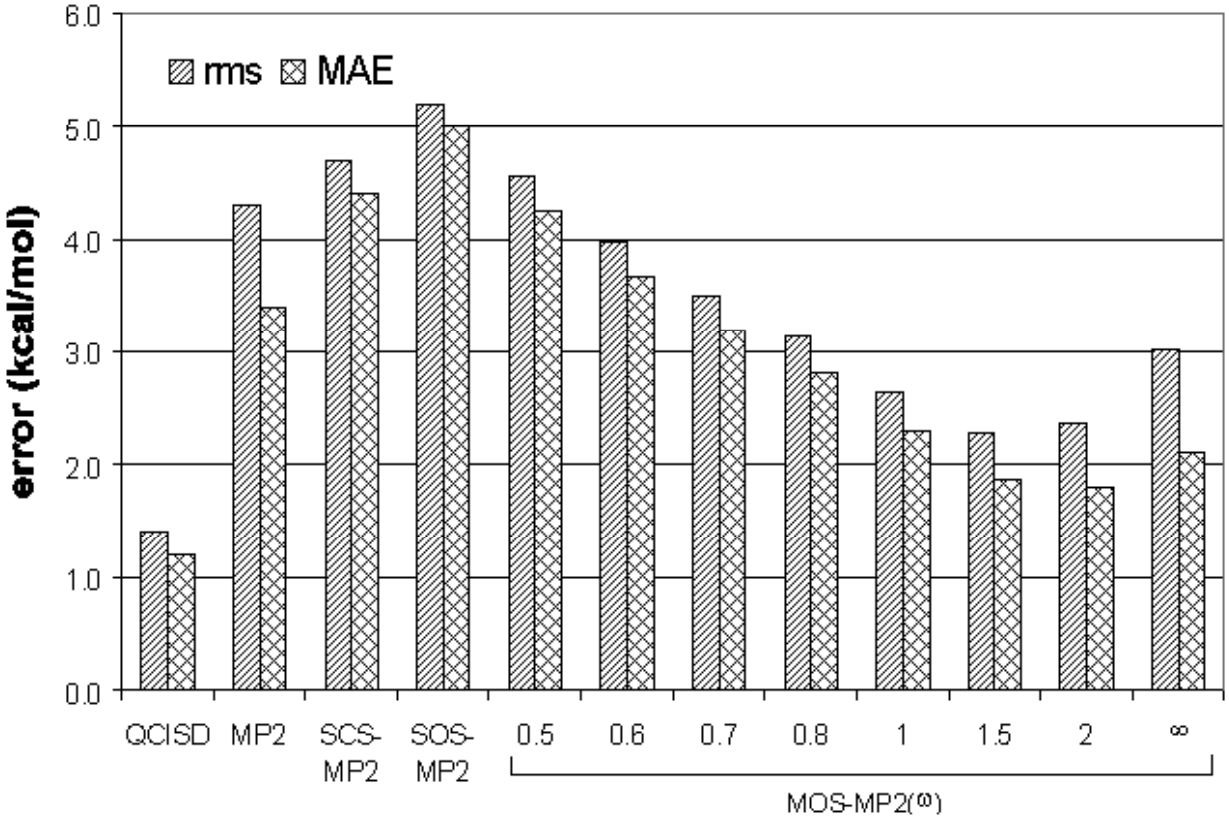
MOS-MP2

Atomization Energies



MOS-MP2

Reaction Barriers



Efficient Large Basis Method

Dual-Basis MP2

- Avoid SCF convergence problem with diffuse basis functions

谢谢！