CHM 673
Lecture 14: Summary of correlated methods

Suggested reading:

Chapter 4.13, 12.1-12.6 from Jensen

Summary of correlated models

method	variational	iterative
HF		
CISD		
MP2		
CCSD		
CCSD(T)		
CCSDT		

Computational cost and accuracy of correlated models

Scaling	CI methods	MP methods	CC methods
N^5	CIS, CIS(D)	MP2	CC2
N^6	CISD	MP3	CCSD
N^7	QCISD(T)	MP4	CCSD(T)
N^8	CISDT	MP5	CCSDT
N^9		MP6	
N^{10}	CISDTQ	MP7	CCSDTQ

Accuracy (when HF provides a "good" reference, i.e. no significant non-dynamical correlation):
HF << MP2 < CISD < CCSD ~ MP4 < CCSD(T) < CCSDT

However, when HF reference is not too good, CC methods perform better than MP
(recall diverging denominator in MP energy expressions!)

Accuracy of correlated methods: molecular geometries

Error in computed distances:

$$\Delta_i = R_i^{calc} - R_i^{exp}.$$

TABLE I. The 19 molecules, on which the statistical analysis is based.

HF, H_2O, NH_3, CH_4, N_2, CH_2, CO, HCN, CO_2, HNC, C_2H_2, CH_2O, HNO, N_2H_2, O_3, C_2H_4, F_2, HOF, H_2O_2

Statistical measures:

$$\bar{\Delta} = \frac{1}{n} \sum_{i=1}^{n} \Delta_i,$$

The mean error

$$\Delta_{std} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (\Delta_i - \bar{\Delta})^2},$$

Standard deviation of the error

$$\bar{\Delta}_{abs} = \frac{1}{n} \sum_{i=1}^{n} |\Delta_i|,$$

The mean absolute error

$$\Delta_{max} = \max_i |\Delta_i|.$$

The maximum error

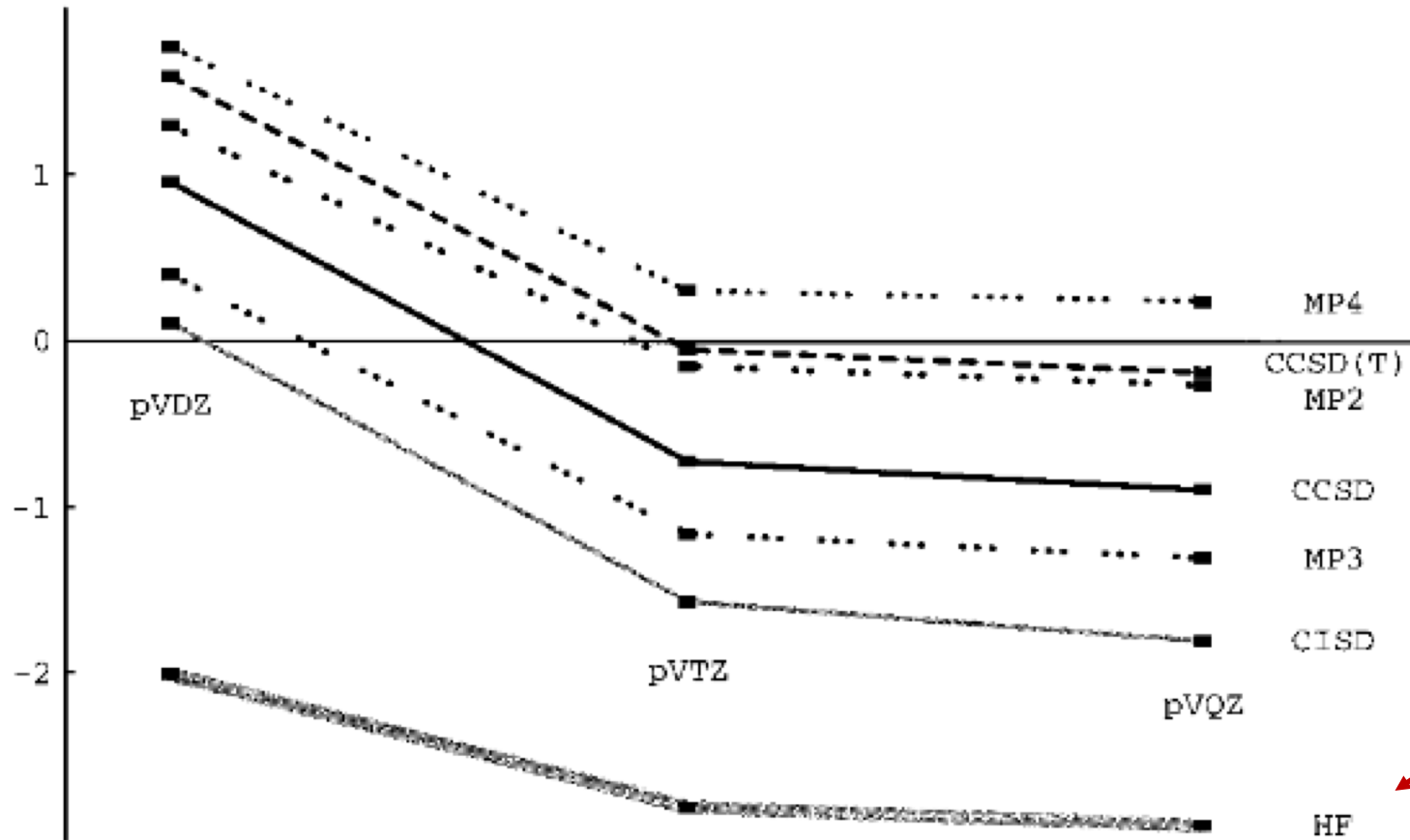# Accuracy of correlated methods: molecular geometries

FIG. 1. Mean errors $\bar{\Delta}$ relative to experiment in the calculated bond distances (pm).

Bonds are shorter in larger bases: this is due to better description of density in the bonding region (~further from nuclei) in larger bases

All correlated methods produce longer bonds than HF: dynamical correlation elongates bonds / corrects HF ionic bond character

Hartree-Fock:
bonds are always too short (recall ionic components in wave function!)
accuracy becomes worse in larger basis set!

Accuracy of correlated methods: molecular geometries
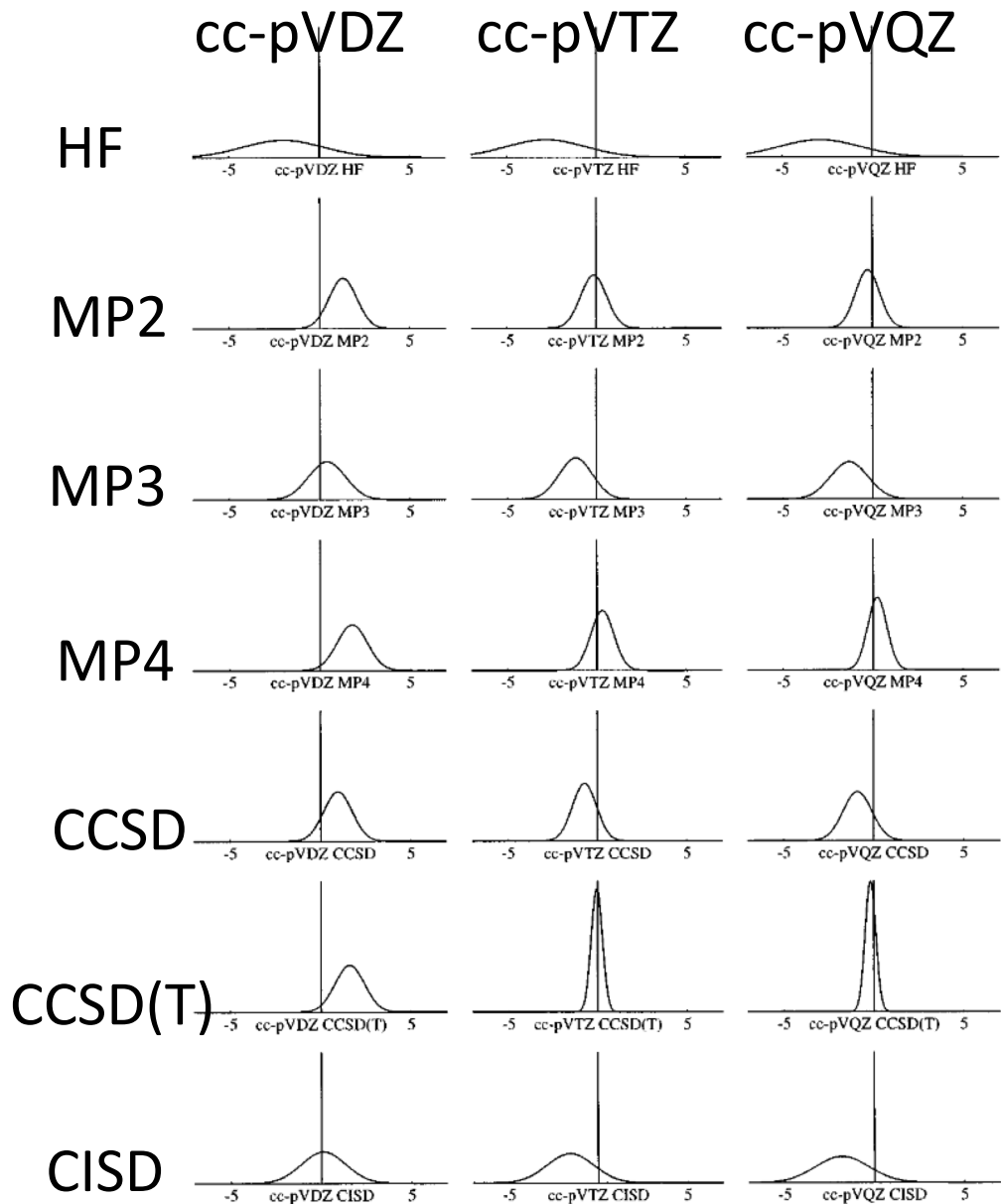
	cc-pVDZ	cc-pVTZ	cc-pVQZ
HF				poor; HF/cc-pVDZ as a last resort
MP2				MP2/cc-pVTZ is great!
MP3				do not use; MP2 is better
MP4				do not use; MP2 produces almost the same quality
CCSD				do not use; MP2 is better
CCSD(T)				CCSD(T)/cc-pVTZ is great! Rarely need CCSD(T)/cc-pVQZ
CISD				☹

Computational cost and accuracy of correlated models

Hartree-Fock: model calculations, frequencies are ~10% off
CCSD(T)/large_basis: ~1 kcal/mol accuracy in thermochemistry → chemical accuracy

Nowadays, we can (routinely) do the following calculations:
HF ~ 5000 b.f.
MP2 ~ 1000 b.f.
CCSD(T) ~ 300 b.f.

Computer speed (of a single processor) increase twice in 18 months →
a factor of 10 in 5 years → 1.4-1.7 increase in the system size in 5 years ☹

But performance of electronic structure calculations increases faster than that, because of:
- Parallelization of computer codes, also using GPUs
- Algorithm development
- Linear scaling techniques
- Divide and conquer (fragmentation) techniques
- DFT models