

The *a priori* calculation of molecular properties to chemical accuracy

T. Helgaker, Department of Chemistry, University of Oslo, Norway

T. Ruden, University of Oslo, Norway

W. Klopper, University of Karlsruhe, Germany

A. Halkier, K. Bak, P. Jørgensen, J. Olsen, F. Pawlowksi, University of Aarhus, Denmark

J. Gauss, University of Mainz, Germany

J. Stanton, University of Austin, USA

Overview

- one- and N -electron hierarchies of quantum chemistry
 - basis-set convergence and extrapolation
 - atomization energies and reaction enthalpies
 - bond distances and frequencies

Ab initio hierarchies

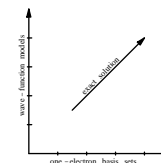
- The quality of *ab initio* calculations is determined by the description of
 1. the one-electron space (basis set);
 2. the N -electron space (wave-function model).
- In each space, there is a hierarchy of levels of increasing complexity:

1. one-electron hierarchy:
correlation-consistent basis sets

SZ, cc-pVDZ, cc-pVTZ, cc-pVQZ, ...

2. N -electron hierarchy:
coupled-cluster excitation levels

HF, CCSD, CCSDT, CCSDTQ, ...



- The quality is systematically improved by going up in the hierarchies.
- “Two-Dimensional Chart of Quantum Chemistry”, Pople (1965)

Convergence of the coupled-cluster hierarchy

- Example: the atomization energy (AE) of CO (exp. 1071.8 kJ/mol)

	E_C	+	E_O	−	E_{CO}	=	D_{CO}	err.
HF	−98964.9	−	196437.1	+	296132.2	=	730.1	−341.7
SD	−388.4	−	639.6	+	1350.2	=	322.1	−19.6
(T)	−7.7	−	11.9	+	54.2	=	34.6	15.0
vib.	0.0	+	0.0	−	12.9	=	−12.9	2.1
rel.	−40.1	−	139.0	+	177.1	=	−2.0	−0.1
tot.	−99401.1	−	197227.6	+	297700.8	=	1071.9	

- The AE constitutes less than 1% of the total energy.

- Bonds are broken—correlation is important:

	HF	SD	(T)
% of E	99.5	0.5	0.01
% of AE	67	30	3

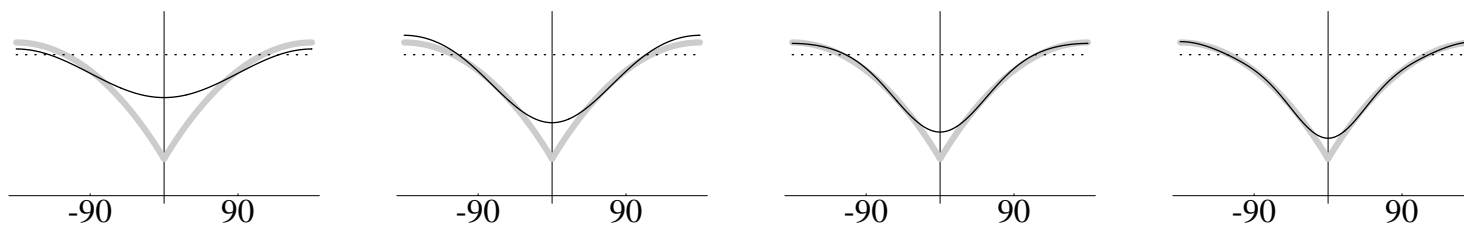
- Nevertheless, the coupled-cluster convergence is rapid:
the error is reduced by an order of magnitude with each new level.
- The zero-point vibrational energy is of the same order of magnitude as the triples energy but in the opposite direction.
- The CCSD(T) model appears to be adequate, but what about the quadruples?

Basis-set convergence

- Convergence of the contributions to the AE of CO (kJ/mol):

	N_{bas}	HF		SD		(T)		CCSD(T)	Error
cc-pCVDZ	36	710.2	+	277.4	+	24.5	=	1012.1	-74.8
cc-pCVTZ	86	727.1	+	297.3	+	32.6	=	1057.0	-29.9
cc-pCVQZ	168	730.3	+	311.0	+	33.8	=	1075.1	-11.8
cc-pCV5Z	290	730.1	+	316.4	+	34.2	=	1080.7	-6.2
cc-pcV6Z	460	730.1	+	318.8	+	34.4	=	1083.3	-3.6
limit	∞	730.1	+	322.1	+	34.6	=	1086.9	0.0

- The **doubles** converge very slowly—chemical accuracy requires 460 AOs (6Z)!
- The **Hartree–Fock** and **triples** contributions are less of a problem.
- The slow convergence arises from a poor description of short-range (dynamical) correlation in the orbital approximation:



- For an accurate and compact description of Coulomb holes, we must use the interelectronic distances r_{ij} as variables.

Explicitly correlated methods

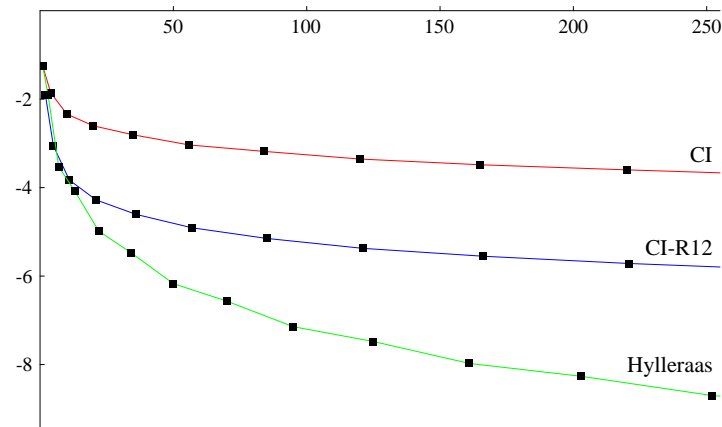
- To improve basis-set convergence, we may use *explicitly correlated wave functions* (Hylleraas, 1928).
- In such wave functions, the interelectronic distances r_{ij} are used as variables.
- In its simplest manifestation, only terms linear in r_{ij} occur: the R12 method

$$\Psi_{\text{R12}} = \sum_K C_K \Phi_K + C_{R12} r_{12} \Phi_0$$

← Kutzelnigg (1985)

Klopper and Kutzelnigg (1987)

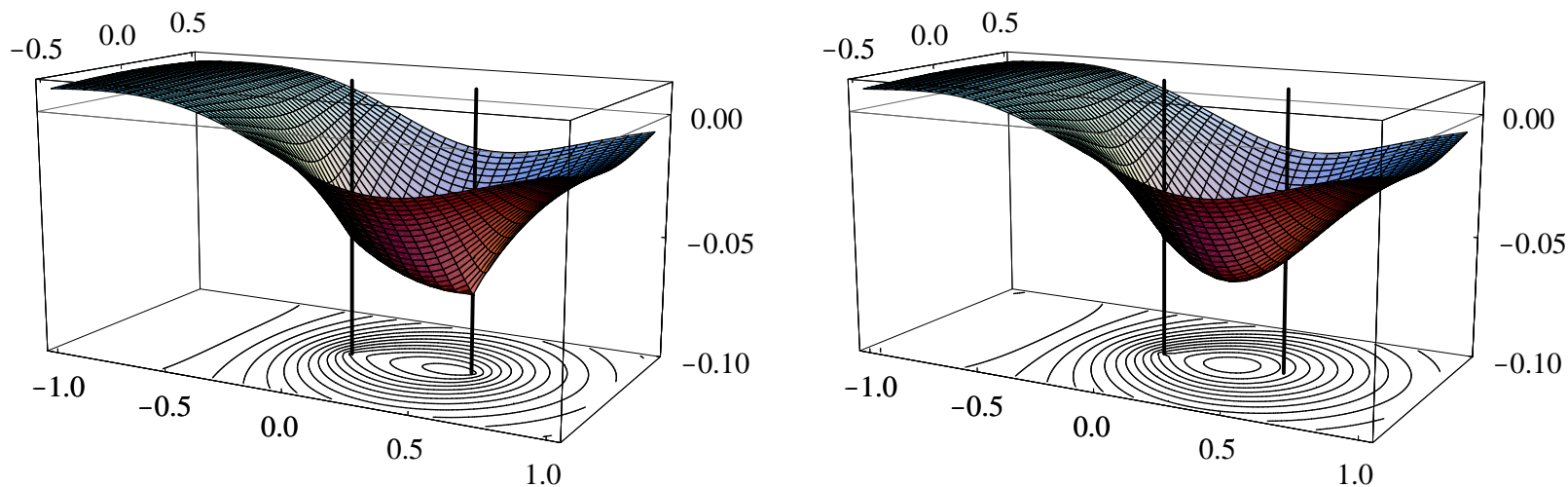
- Helium-atom convergence of
 - the standard CI expansion
 - the CI-R12 expansion
 - the Hylleraas expansionon a logarithmic energy scale:



- In the following, we shall investigate the convergence of traditional, orbital-based wave functions as parametrized in *coupled-cluster theory*.
- However, we shall often use R12 calculations as benchmarks.

The Coulomb hole

- Consider the Coulomb hole in the **ground-state helium atom**, with the nucleus at the origin and one electron fixed in space $0.5a_0$ away from the nucleus.
- The exact wave function minus the HF wave function is depicted to the left; to the right, we have made similar plot for the FCI/cc-pV5Z wave function.



- Even the FCI/cc-pV5Z wave function gives a poor description of the Coulomb hole.
- To make the most of standard wave functions, we must choose our orbitals carefully.
- This leads us to the concept of the **principal expansion**.

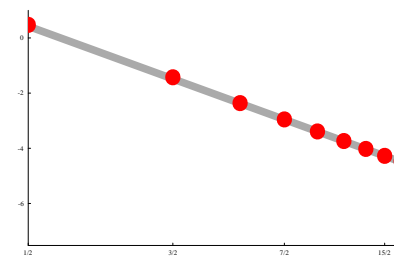
The principal expansion and correlation-consistent basis sets

- The energy contribution from each AO in large CI calculations on helium:

$$\varepsilon_{nlm} \approx n^{-6} \quad \leftarrow \text{Carroll } et \text{ al. (1979)}$$

- The principal expansion:** include all AOs belonging to the same shell simultaneously, in order of increasing principal quantum number n :

$$\varepsilon_n \approx n^2 n^{-6} = n^{-4}$$



- Practical realization: the correlation-consistent basis sets **cc-pVXZ** (Dunning, 1989)
- Energy-optimized AOs are added one shell at a time:

SZ	cc-pVDZ	cc-pVTZ	cc-pVQZ	number of AOs
$2s1p$	$3s2p1d$	$4s3p2d1f$	$5s4p3d2f1g$	$\frac{1}{3}(X+1)(X+\frac{3}{2})(X+2) \propto X^3$
	$+3s3p3d$	$+4s4p4d4f$	$+5s5p5d5f5g$	$(X+1)^2 \propto X^2$

- The error in the energy is equal to the contributions from all omitted shells:

$$\Delta E_X \approx \sum_{n=X+1}^{\infty} n^{-4} \approx X^{-3}$$

Some observations

- The dependence of the error in the correlation energy on the number of AOs N :

$$\left. \begin{array}{l} \Delta\varepsilon_N \propto X^{-3} \\ N \propto X^3 \end{array} \right\} \Rightarrow \Delta\varepsilon_N \propto N^{-1}$$

- The dependence of the error in the correlation energy on the CPU time:

$$\left. \begin{array}{l} \Delta\varepsilon_N \propto N^{-1} \\ T \propto N^4 \end{array} \right\} \Rightarrow \Delta\varepsilon_n \propto T^{-1/4}$$

- Each new digit in the energy therefore costs 10000 times more CPU time!

$$1 \text{ minute} \rightarrow 1 \text{ week} \rightarrow 200 \text{ years}$$

- The convergence is exceedingly **slow**!
- Clearly, a brute-force extension of the basis set until convergence (to some target accuracy) may not always be possible.
- Fortunately, the convergence is very **smooth**.
- Careful analysis of the convergence of the partial-wave expansion: **Schwartz (1962)**

Extrapolations

- From two separate calculations with basis sets E_X and E_Y

$$E_\infty = E_X + AX^{-3}$$

$$E_\infty = E_Y + AY^{-3}$$

we eliminate A to obtain the following **two-point extrapolation formula**:

$$E_\infty = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3} \leftarrow \begin{array}{l} \text{Helgaker } et \text{ al. (1997)} \\ \text{Halkier } et \text{ al. (1998)} \end{array}$$

- Mean absolute error in the electronic energy of CH₂, H₂O, HF, N₂, CO, Ne, and F₂:

mE_h	DZ	TZ	QZ	5Z	6Z	R12
plain	194.8	62.2	23.1	10.6	6.6	1.4
extr.		21.4	1.4	0.4	0.5	

- For the error in the AE of CO relative to R12, we now obtain:

kJ/mol	DZ	TZ	QZ	5Z	6Z
plain	-73.5	-28.3	-11.4	-6.0	-3.5
extr.		-18.5	-0.7	0.0	0.0

- Chemical accuracy is now achieved with just 168 AOs (QZ), at a fraction of the cost.

Extrapolation of the total electronic energy

	D	T	Q	5	6	Exptl. ^b
CH ₂ (¹ A ₁)	-39.060	-39.111	-39.126	-39.130	-39.131	-39.133
H ₂ O	-76.282	-76.390	-76.421	-76.431	-76.434	-76.439
HF	-100.270	-100.400	-100.438	-100.450	-100.454	-100.460
N ₂	-109.355	-109.482	-109.520	-109.532	-109.535	-109.543
CO	-113.134	-113.264	-113.303	-113.315	-113.319	-113.326
Ne	-128.722	-128.868	-128.912	-128.927	-128.932	-128.938
F ₂	-199.182	-199.419	-199.488	-199.511	-199.519	-199.531
$\bar{\Delta}_{\text{abs}}$	0.1948	0.0622	0.0231	0.0106	0.0066	

^b Obtained from experimental dissociation energies and estimated total atomic energies, see text.

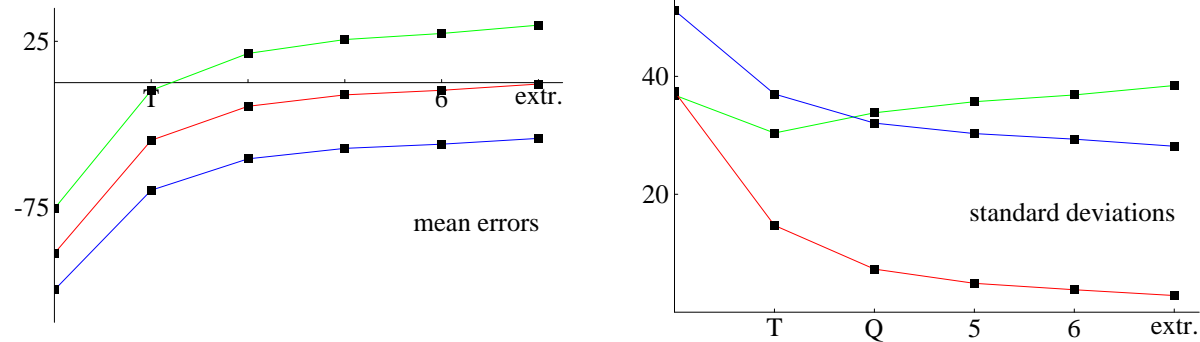
Changes upon basis-set extension

- When the basis-set increases, the energy is lowered most for systems of low electronic energy—that is, differences increase upon basis-set extension.
- This observation helps us predict changes in calculated properties upon basis-set extension:
 1. AEs increase since molecular energies are lower than atomic energies.
 2. Exothermic reactions become more exothermic.
 3. Polarizabilities increase since the energy is lower in the field.
 4. Bond distances shorten since shorter bonds give lower electronic energy.
- Equipped with a knowledge of convergence rate and direction, we shall now consider the convergence of a number of molecular properties:
 1. Atomization energies
 2. Reaction enthalpies
 3. Molecular bond distances
 4. Vibrational frequencies
 5. Two-electron Darwin term

Statistical analysis: atomization energies and reaction enthalpies

- We begin our survey of convergence by considering two properties directly related to the total electronic energy:
 - atomization energies (AEs): $D_e = \sum_A E^A ({}^{2S+1}L) - E(R_e)$
 - reaction enthalpies (REs): $\Delta_r H_e^\circ (0K) = \sum_P E^P (R_e) - \sum_R E^R (R_e)$
- Comparisons with experiment (corrected for vibrations and relativity)
- 20 closed-shell organic molecules and 15 exothermic isogyric reactions among these molecules
- N -electron models: HF, MP2, CCSD, CCSD(T), CCSDT, CCSDTQ
- geometries: all-electron CCSD(T)/cc-pCVQZ
- Much work done by Martin and coworkers and by Feller, Peterson and coworkers.

Atomization energies



- Difficult property: electron pairs are broken; HF underestimates AEs by typically 40%.
- AEs increase with cardinal number.
- AEs increase with excitation level in the coupled-cluster hierarchy:

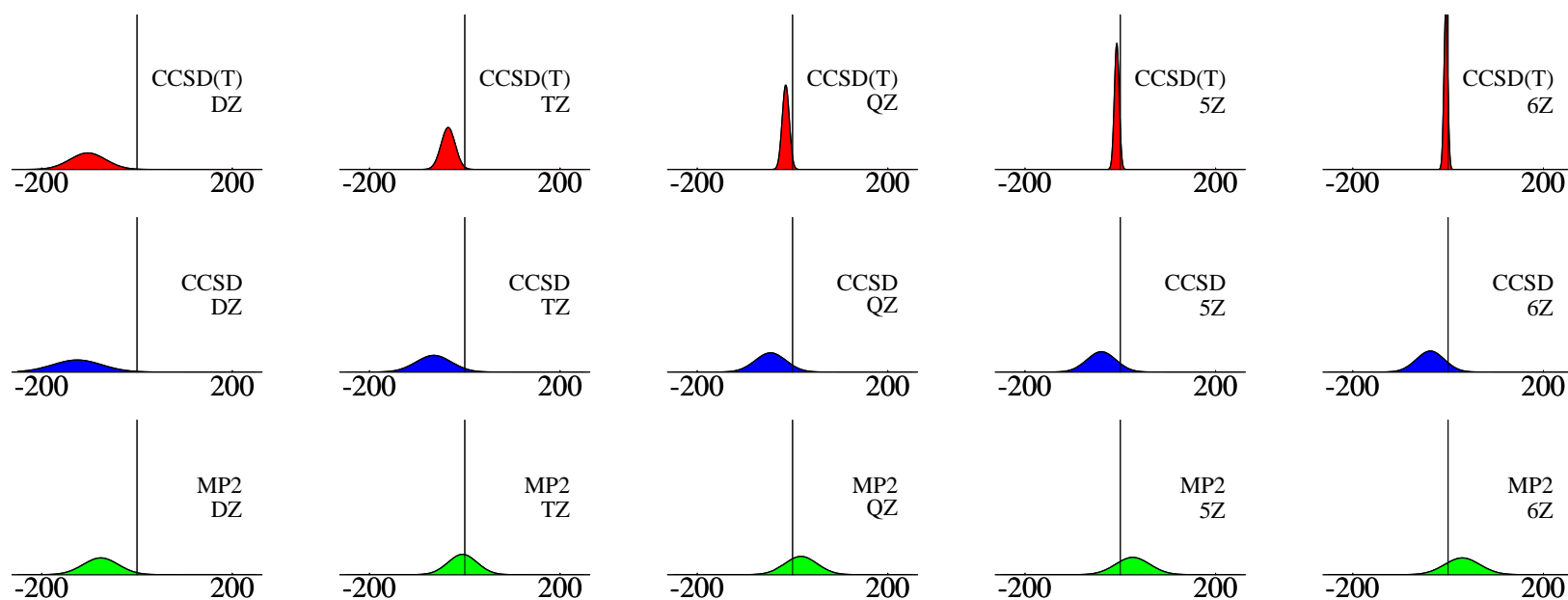


- MP2 overestimates AEs—but note error cancellation at TZ!
- Mean abs. cc-pcV6Z err. (kJ/mol): 423 (HF), 37 (MP2), 30 (CCSD), 4 (CCSD(T))
- Only CCSD(T) is capable of chemical accuracy, but DZ and TZ are inadequate (kJ/mol):

DZ	TZ	QZ	5Z	6Z
-103.3	-34.9	-14.3	-7.4	-4.7

Normal distributions of errors in atomization energies

- A useful way to visualize the performance of the different methods is to plot the normal distribution of the errors.
- For MP2, CCSD, and CCSD(T) in the cc-pCVXZ basis sets, we obtain (kJ/mol):



- Except for benchmarking and extrapolation, CCSD(T)/DZ calculations are meaningless.
- To take full advantage of CCSD(T), basis sets of at least QZ quality should be used.

AEs calculated by two-point extrapolation

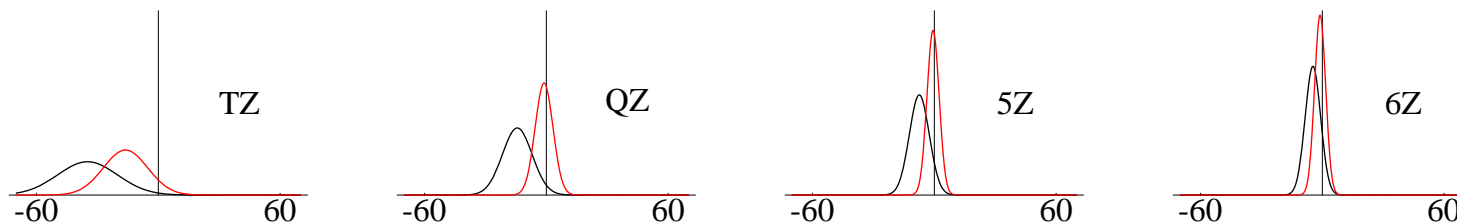
- To accelerate convergence, let us apply the two-point extrapolation formula

$$E_{\infty} = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3}$$

- The mean errors in the AEs (kJ/mol) relative to experiment are now:

DZ	TZ	QZ	5Z	6Z
-103.3	-34.9	-14.3	-7.4	-4.7
	-16.2	-1.1	-0.6	-0.9

- Chemical accuracy achieved with QZ basis!
- Normal distributions:



Comparison of CCSD(T) and experimental AEs

	cc-pCVQZ		cc-pCV(TQ)Z		cc-pCV6Z		exp
F ₂	153.4	-9.9	159.5	-3.9	161.1	-2.2	163.4(06)
H ₂	456.6	-1.5	458.4	0.4	458.1	0.1	458.0(00)
HF	586.1	-7.0	592.8	-0.3	593.3	0.1	593.2(09)
O ₃	583.6	-32.6	600.8	-15.4	605.5	-10.7	616.2(17)
HOF	649.5	-25.4	661.7	-13.2	662.9	-12.0	674.9(42)
CH ₂	751.3	-5.7	758.7	1.6	757.9	0.9	757.1(22)
HNO	842.7	-18.8	858.5	-3.0	860.4	-1.1	861.5(03)
N ₂	936.3	-19.9	952.3	-4.0	954.9	-1.3	956.3(02)
H ₂ O	963.5	-11.8	974.7	-0.5	975.5	0.2	975.3(01)
CO	1075.5	-11.2	1086.6	-0.1	1086.9	0.2	1086.7(05)
H ₂ O ₂	1108.0	-18.6	1125.5	-1.1	1126.1	-0.5	1126.6
NH ₃	1232.7	-15.1	1247.3	-0.6	1247.4	-0.5	1247.9(04)
HCN	1294.1	-18.6	1311.3	-1.4	1311.0	-1.7	1312.8(26)
CH ₂ O	1552.4	-14.2	1568.3	1.7	1568.0	1.4	1566.6(07)
CO ₂	1612.3	-20.1	1633.3	0.8	1633.2	0.7	1632.5(05)
C ₂ H ₂	1681.0	-16.8	1698.8	1.0	1697.1	-0.8	1697.8(10)
CH ₄	1749.9	-9.4	1762.0	2.7	1759.4	0.1	1759.3(06)
C ₂ H ₄	2343.6	-16.2	2363.2	3.4	2360.8	1.0	2359.8(10)

- Only O₃ and HOF have an error larger than 2.2 kJ/mol.
- Without extrapolation: cc-p(c)V6Z needed; with extrapolation: cc-pCV(TQ)Z sufficient
- Core correlation important: F₂ - 0.1 kJ/mol; CO - 4.8 kJ/mol; C₂H₂ - 10.8 kJ/mol

The (in)adequacy of CCSD(T)

	CCSD(T)		CCSDT		CCSDTQ		experiment	
	cc-pCV(56)Z		cc-pCV(Q5)Z		cc-pVTZ		D_e	D_0
CH ₂	757.9	-0.9	758.9	0.1	759.3	0.5	758.8	714.8±1.8
H ₂ O	975.3	0.1	974.9	-0.3	975.7	0.5	975.2	917.8±0.2
HF	593.2	0.0	593.0	-0.2	593.6	0.4	593.2	566.2±0.7
N ₂	954.7	-1.6	951.3	-5.0	955.2	-1.1	956.3	941.6±0.2
F ₂	161.0	-2.4	159.6	-3.8	162.9	-0.5	163.4	154.6±0.6
CO	1086.7	0.0	1084.4	-2.3	1086.7	0.0	1086.7	1071.8±0.5

- The excellent performance of CCSD(T) for AEs relies on error cancellation:
 - relaxation of triples from CCSD(T) to CCSDT **reduces** the AEs;
 - inclusion of quadruples from CCSDT to CCSDTQ **increases** the AEs.
- The error incurred by treating the connected triples perturbatively is quite large (about 10% of the full triples contribution) but cancelled by the neglect of quadruples.
- The rigorous calculation of AEs to chemical accuracy requires **CCSDTQ/cc-pCV6Z!**

Reaction enthalpies

- Closed-shell, isogyric exothermic reactions
- Convergence faster than for AEs but still governed by short-range correlation:

		CCSD(T)	DZ	TZ	QZ	5Z	6Z
REs	plain		36.9	12.0	2.7	-0.3	-0.7
	extr.			-2.0	-2.1	-1.7	-1.2
AEs	plain		-103.3	-34.9	-14.3	-7.4	-4.7
	extr.			-16.2	-1.1	-0.6	-0.9

- Errors relative to experimental results corrected for vibrations and relativity:

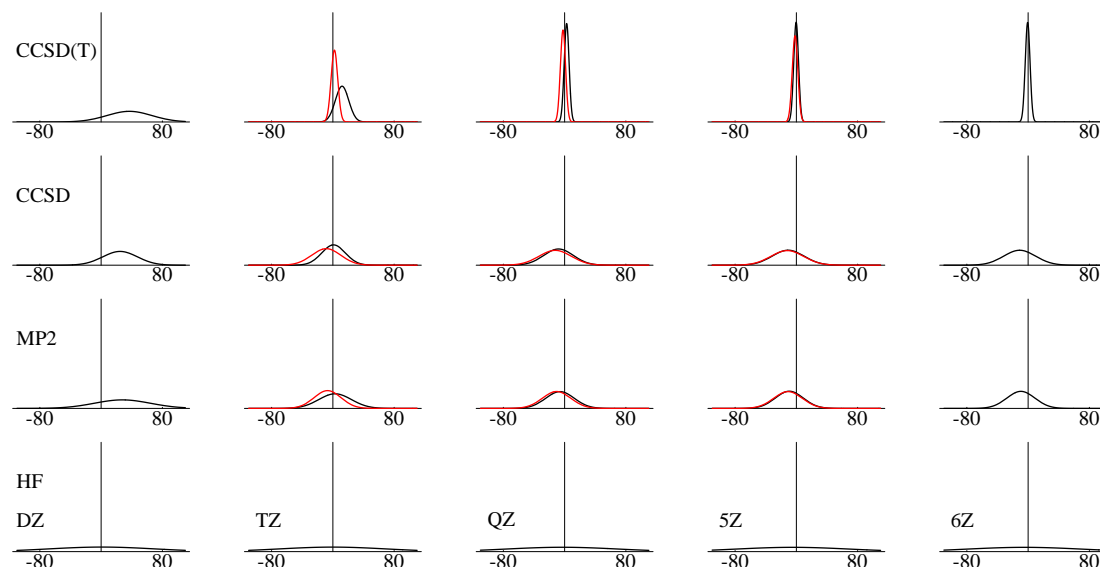
Mean absolute errors:

CCSD(T): 1.8 kJ/mol

CCSD: 14.5 kJ/mol

MP2: 13.5 kJ/mol

HF: 43.0 kJ/mol



Enthalpies of some reactions (kJ/mol)

	exp.	R12	CBS	G2	B3LYP	(56)
CH ₂ + H ₂ → CH ₄	-544(2)	-542	-544	-534	-543	-543
C ₂ H ₂ + H ₂ → C ₂ H ₄	-203(2)	-204	-207	-202	-208	-206
C ₂ H ₂ + 3H ₂ → 2CH ₄	-446(2)	-447	-450	-440	-450	-447
N ₂ H ₂ → N ₂ + H ₂		-174	-174	-177	-162	-173
CO + H ₂ → CH ₂ O	-21(1)	-22	-22	-17	-34	-23
N ₂ + 3H ₂ → 2NH ₃	-164(1)	-162	-161	-147	-166	-165
F ₂ + H ₂ → 2HF	-563(1)	-562	-558	-564	-540	-564
O ₃ + 3H ₂ → 3H ₂ O	-933(2)	-943	-928	-912	-909	-946
CH ₂ O + 2H ₂ → CH ₄ + H ₂ O	-251(1)	-250	-248	-235	-234	-250
H ₂ O ₂ + H ₂ → 2H ₂ O	-365(2)	-365	-362	-360	-346	-362
CO + 3H ₂ → CH ₄ + H ₂ O	-272(1)	-272	-270	-251	-268	-273
HCN + 3H ₂ → CH ₄ + NH ₃	-320(3)	-320	-321	-305	-320	-321
HNO + 2H ₂ → H ₂ O + NH ₃	-444(1)	-445	-440	-426	-429	-446
HNC → HCN		-64	-62	-63	-58	-63
H ₂ O + F ₂ → HOF + HF	-129(4)	-118	-117	-123	-119	-118
CO ₂ + 4H ₂ → CH ₄ + 2H ₂ O	-244(1)	-242	-238	-216	-211	-244
2CH ₂ → C ₂ H ₄	-844(3)	-842	-844	-829	-845	-845
mean error		0	2	12	8	-1
standard deviation		4	4	8	13	5
mean absolute error		2	4	12	11	3
maximum absolute error		11	12	28	33	13

Comparison of different methods for REs (kJ/mol)

	$\bar{\Delta}$	Δ_{std}	$ \bar{\Delta} $	$ \Delta _{\text{max}}$
HF	-5.0	72.8	43.0	207.2
CCSD	-11.0	20.9	14.5	73.6
CCSD(T)	-1.2	3.2	1.7	11.1
DT	2.0	4.3	3.7	10.8
TQ	-2.1	3.4	2.3	12.7
G2	14.0	9.1	14.0	29.3
DFT	7.6	14.5	11.0	34.3

two-electron Darwin term

$$V^{2D} = -\frac{1}{2}\alpha^2\pi \sum_{i \neq j} \delta(r_{ij})$$

- contributes to the first-order relativistic correction
- measures the bottom of the Coulomb hole
- converges very slowly (Salomonsen and Öster, 1989)
- principal expansion:

$$D_X^{2D} = D_\infty^{2D} + CX^{-1}$$

- convergence with and without two-point extrapolation (μE_h):

	DZ	TZ	QZ	5Z	6Z	limit
He	-7.1	-9.8	-11.0	-11.7	-12.1	-14.1
		-15.1	-14.7	-14.5	-14.3	
H ₂	-2.8	-3.5	-3.7	-3.9	-4.0	-4.4
		-4.9	-4.5	-4.5	-4.5	
HF	-28.2	-38.1	-48.3	-53.7	-57.3	-74.8
		-57.9	-78.9	-75.5	-75.3	

Hydrogen-bonded systems

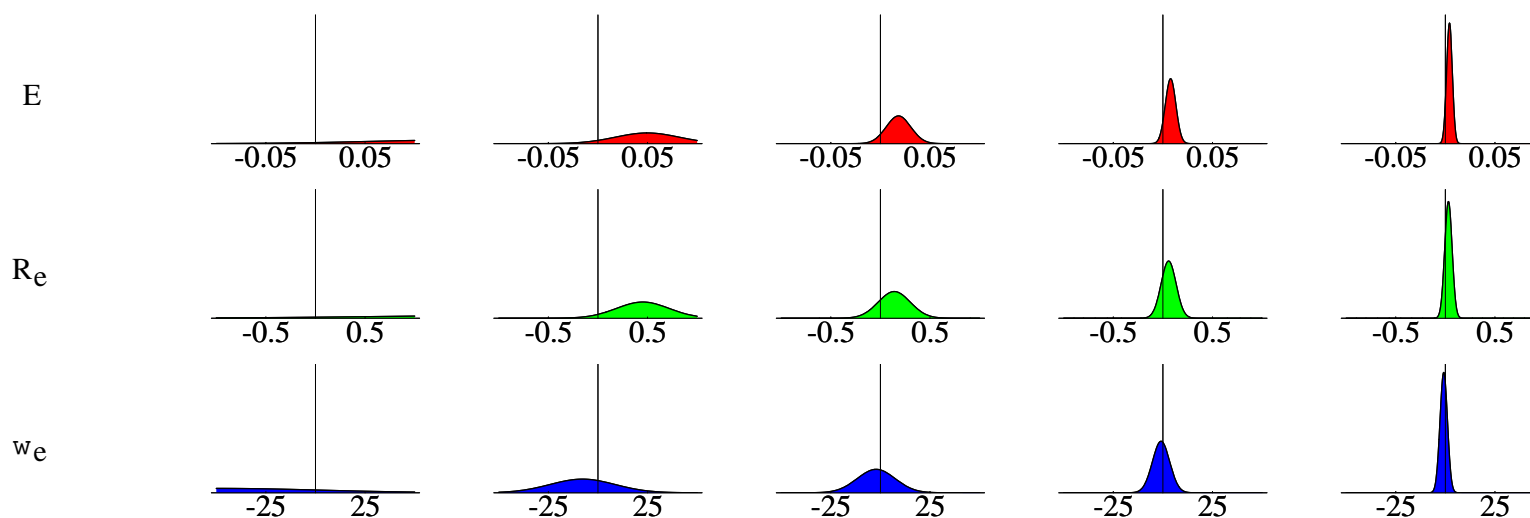
- statistics for the following systems
 - $(\text{H}_2\text{O})_2$, $(\text{HF})_2$, $(\text{HCl})_2$, $\text{HF}\cdot\text{H}_2\text{O}$, $\text{HF}\cdot\text{HCN}$at the CCSD(T)/aug-cc-pVTZ geometry (exp. geometry for monomers)
- basis sets: aug-cc-pVTZ
- mean errors (μE_h) for plain and counterpoise-corrected energies:

	DZ	TZ	QZ	5Z
plain	-26	-247	-222	-160
		-340	-263	-95
CP	988	420	188	104
		181	19	15

- The CP correction makes convergence smoother but increases the error for low X .
- Extrapolation reduces the error significantly (by an order of magnitude at the QZ level) but works only for the CP-corrected energies.

Basis-set convergence of molecular properties

- The basis-set convergence of molecular properties is no faster than that of the energy.
- At the CCSD/cc-pVXZ level, comparison with R12 gives the following results for the **energy** (E_h), **bond distances** (pm), and **frequencies** (cm^{-1}):



- Clearly, must be as much concerned with basis-set convergence for structure and vibrational frequencies as for energies and energy differences:
 - What basis set is necessary to achieve chemical accuracy?
 - Is basis-set extrapolation a useful strategy?

Extrapolation of properties

- Most properties can be related to derivatives of the electronic energy.
- Neglecting higher-order terms, we would expect properties to behave in the same manner as the energy:

$$E_\infty = E_X + AX^{-3} \Rightarrow P_\infty = P_X + BX^{-3}$$

- This is indeed the case for dipole moments, whose convergence is nicely accelerated by two-point extrapolation.
- For properties related to nuclear displacements (forces, force constants, structure, vibrational frequencies), convergence is less well described by the simple X^{-3} formula.
- The problem arises since, as we increase X , we also change the geometry (i.e., the Hamiltonian), making additional changes to the electronic energy.
- Truhlar and coworkers (1998) has used a modified two-point extrapolation for geometry optimizations.
- Reduction in the CCSD error relative to R12 achieved by two-point extrapolation:

	DT	TQ	Q5	56
E	0.45	0.09	0.12	0.10
ω_e	0.47	0.67	0.18	0.44

Dipole moments

- Differentiating the energy expression

$$E_{\infty} = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3}$$

with respect to the electric field, we obtain for the dipole moment

$$\mu_{\infty} = \frac{X^3 \mu_X - Y^3 \mu_Y}{X^3 - Y^3}$$

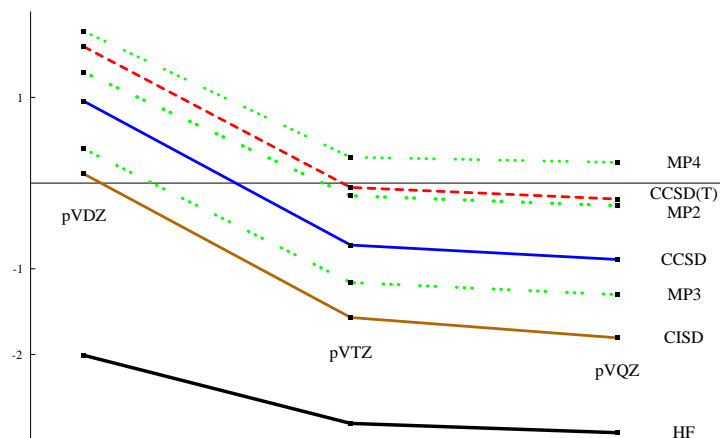
- Mean errors (mea_0) at the MP2, CCSD, and CCSD(T) levels of theory relative to R12 for BH and HF:

	DZ	TZ	QZ	5Z	6Z
cc-p(C)VXZ	-14.7	-6.2	-2.3	-1.0	-0.8
		-2.7	0.6	0.4	-0.5
aug-cc-p(C)VXZ	-15.8	-6.5	-2.7	-1.5	-0.9
		-2.7	0.1	-0.1	0.1

- Extrapolation works as well as for energies, but diffuse (augmented) basis sets are needed.
- The two-point extrapolation scheme can easily be extended to any molecular property.

Bond distances I

- Mean and mean absolute errors for 28 distances at the all-electron cc-pVXZ level (pm):



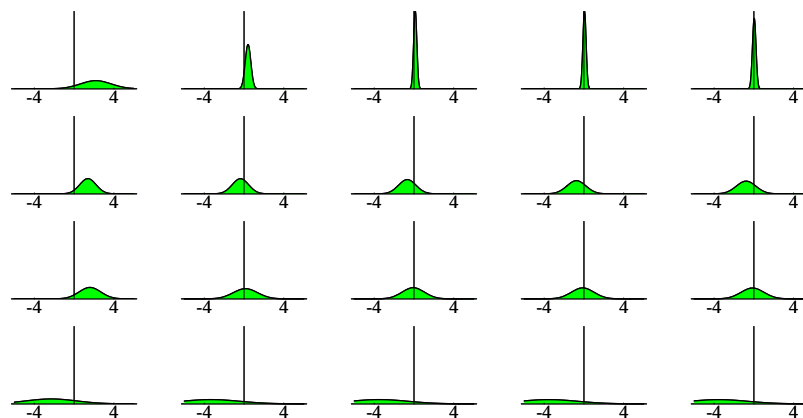
$ \bar{\Delta} $	DZ	TZ	QZ
HF	1.94	2.63	2.74
MP2	1.35	0.56	0.51
CCSD	1.19	0.64	0.80
CCSD(T)	1.68	0.20	0.16

- Bonds shorten with increasing basis:
 - HF: DZ \rightarrow TZ 0.8 pm; TZ \rightarrow QZ 0.1 pm
 - corr.: DZ \rightarrow TZ 1.6 pm; TZ \rightarrow QZ 0.1–0.2 pm
- Bonds lengthen with improvements in the N -electron model:
 - singles < doubles < triples < ...
- There is considerable scope for error cancellation: CISD/DZ, MP3/DZ

	DZ	TZ & QZ
• DZ/TZ inversion:		
best	CISD & MP3	CCSD(T) & MP4
worst	CCSD(T) & MP4	CISD & MP3

Bond distances II

- Normal distributions of errors in bond distances relative to experiment for HF, MP2, CCSD, and CCSD(T) at the valence-electron cc-pVXZ level (pm):



- CCSD(T) bond distances compared with experiment (pm):

	DZ	TZ	QZ
$\overline{\Delta}$	1.68	0.01	-0.12
$ \overline{\Delta} $	1.68	0.20	0.16

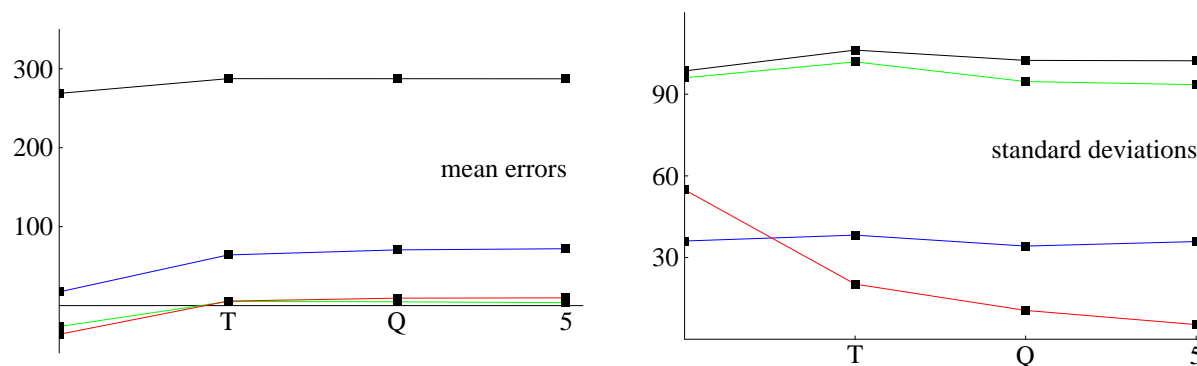
- However, the high accuracy arises partly because of error cancellation.
- Bond distances are further reduced by
 - basis-set extension QZ \rightarrow 6Z: ≈ -0.10 pm
 - triples relaxation CCSD(T) \rightarrow CCSDT: ≈ -0.02 pm
- Intrinsic error of the CCSDT model: ≈ -0.2 pm

Bond distances III

		HF	MP2	CCSD	CCSD(T)	emp.	exp.
H ₂	R_{HH}	73.4	73.6	74.2	74.2	74.1	74.1
HF	R_{FH}	89.7	91.7	91.3	91.6	91.7	91.7
H ₂ O	R_{OH}	94.0	95.7	95.4	95.7	95.8	95.7
HOF	R_{OH}	94.5	96.6	96.2	96.6	96.9	96.6
HNC	R_{NH}	98.2	99.5	99.3	99.5	99.5	99.4
NH ₃	R_{NH}	99.8	100.8	100.9	101.1	101.1	101.1
N ₂ H ₂	R_{NH}	101.1	102.6	102.5	102.8	102.9	102.9
C ₂ H ₂	R_{CH}	105.4	106.0	106.0	106.2	106.2	106.2
HCN	R_{CH}	105.7	106.3	106.3	106.6	106.5	106.5
C ₂ H ₄	R_{CH}	107.4	107.8	107.9	108.1	108.1	108.1
CH ₄	R_{CH}	108.2	108.3	108.5	108.6	108.6	108.6
N ₂	R_{NN}	106.6	110.8	109.1	109.8	109.8	109.8
CH ₂ O	R_{CH}	109.3	109.8	109.9	110.1	110.1	110.1
CH ₂	R_{CH}	109.5	110.1	110.5	110.7	110.6	110.7
CO	R_{CO}	110.2	113.2	112.2	112.9	112.8	112.8
HCN	R_{CN}	112.3	116.0	114.6	115.4	115.3	115.3
CO ₂	R_{CO}	113.4	116.4	115.3	116.0	116.0	116.0
HNC	R_{CN}	114.4	117.0	116.2	116.9	116.9	116.9
C ₂ H ₂	R_{CC}	117.9	120.5	119.7	120.4	120.4	120.3
CH ₂ O	R_{CO}	117.6	120.6	119.7	120.4	120.5	120.3
N ₂ H ₂	R_{NN}	120.8	124.9	123.6	124.7	124.6	124.7
C ₂ H ₄	R_{CC}	131.3	132.6	132.5	133.1	133.1	133.1
F ₂	R_{FF}	132.7	139.5	138.8	141.1	141.3	141.2
HOF	R_{OF}	136.2	142.0	141.2	143.3	143.4	143.4

Harmonic frequencies

- Errors in the harmonic frequency of BH, HF, CO, N₂, and F₂ at optimized geometry (cm⁻¹):



- Mean absolute errors quite large—in particular, for HF, MP2, and CCSD:

$ \overline{\Delta} $	HF	MP2	CCSD	CCSD(T)
opt.	287	71	72	10

- Connected triples are important for vibrational frequencies (bonds stretching).
- CCSD(T) error is quite small at the TZ level (17 cm⁻¹) but error cancellation often occurs:

		DZ	TZ	QZ	5Z	6Z
$\overline{\Delta}$	val.	-38	-0.4	2.6	2.6	2.2
	all	-36	5.7	9.4	9.8	
$ \overline{\Delta} $	val.	43	17	8.8	7.0	6.4
	all	42	14	9.4	9.8	

Harmonic frequencies of diatoms (cm^{-1})

- Basis-set convergence for all-electron CCSD(T)

	CVDZ	CVTZ	CVQZ	CV5Z
BH	2342	2357	2369	2370
HF	4152	4178	4166	4155
CO	2147	2163	2174	2175
N ₂	2341	2355	2366	2370
F ₂	786	925	922	928

- Wave-function convergence

	HF	MP2	CCSD	CCSD(T)	exp.
BH	2489	2448	2382	2370	2367
HF	4474	4151	4203	4155	4138
CO	2427	2139	2247	2175	2170
N ₂	2731	2222	2452	2370	2358
F ₂	1267	1010	1026	928	917

Anharmonicities of diatoms (cm^{-1})

- Basis-set convergence for all-electron CCSD(T)

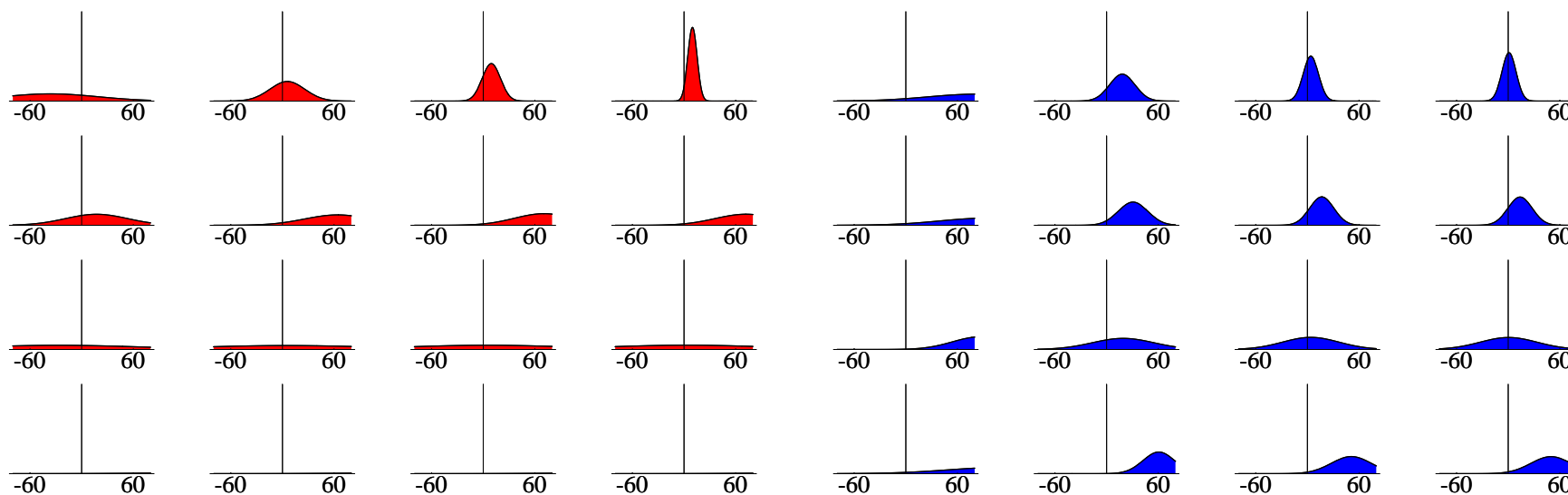
	CVDZ	CVTZ	CVQZ	CV5Z
BH	49	49	49	49
HF	93	89	90	90
CO	13	13	13	13
N ₂	15	14	14	14
F ₂	12	12	12	12

- Wave-function convergence

	HF	MP2	CCSD	CCSD(T)	exp.
BH	43	44	48	49	49
HF	85	87	88	90	90
CO	11	13	12	13	14
N ₂	11	19	13	14	14
F ₂	7	9	9	12	11

Harmonic frequencies at experimental geometry

- Harmonic frequencies are significantly improved by carrying out the calculations at the experimental geometry.
- Pulay *et al.* (1983), Allen and Császár (1993)
- This approach is equivalent to the addition of an empirical linear term to the force field.



- It is particularly useful for simple models such as HF and MP2.

Conclusions

- We have considered the convergence of the **one- and N -electron hierarchies** of quantum chemistry.
- In the N -electron hierarchy (coupled-cluster theory), convergence is rapid:
 - the error is reduced by several factors with each new excitation level;
 - most properties (such as geometries and AEs) are converged at the CCSD(T) level;
 - to some extent, CCSD(T) works well because of error cancellation.
- In the one-electron hierarchy (correlation-consistent basis sets), convergence is slow:
 - the error is proportional to X^{-3} ;
 - for some properties such as AEs, 6Z basis sets are needed for chemical accuracy; other properties are well represented in the QZ or TZ basis sets;
 - convergence can often be accelerated by basis-set extrapolation.
- **Fortuitous error cancellation** is ubiquitous in quantum chemistry—at all levels of theory!