

The Accurate Calculation of Harmonic and Fundamental Vibrational Frequencies

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Software

- Dalton (<http://www.kjemi.uio.no/software/dalton>)
 - LUCIA (J. Olsen)
- ACES II (J. Gauss, J. Stanton, R. Bartlett)

Ab initio hierarchies

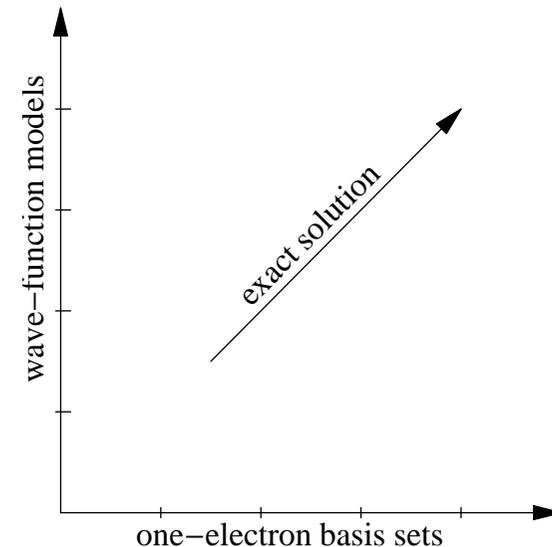
- The quality of *ab initio* calculations is determined by the description of
 1. the N -electron space (wave-function model);
 2. the one-electron space (basis set).
- In each space, there is a hierarchy of levels of increasing complexity:

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

HF, CCSD, CCSDT, CCSDTQ, ... FCI

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

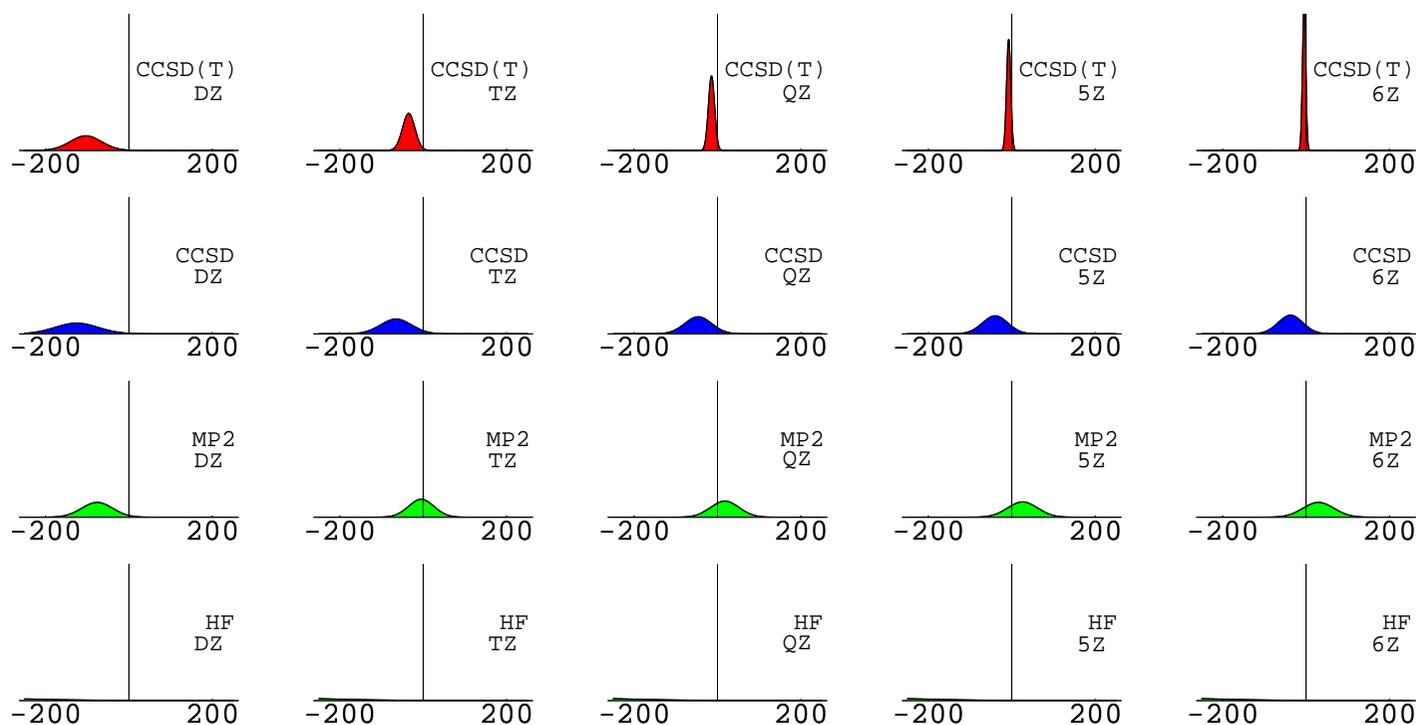
DZ, TZ, QZ, 5Z, 6Z, ...



- The quality is systematically improved upon by going up in the hierarchies.

Example of an *ab initio* hierarchy: atomization energies

- Normal distribution of errors (kJ/mol) for RHF, MP2, CCSD, and CCSD(T) in the cc-pCVXZ basis sets:



- The *ab initio* hierarchy of wave-function theory enables it to approach the exact solution in an orderly, controlled manner.
- In this aspect, it distinguishes itself from density-functional theory.

Studies of convergence

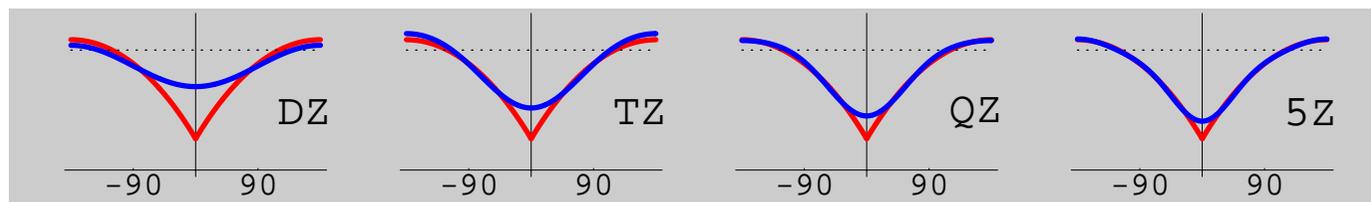
- For the *ab initio* hierarchy to be truly useful, it must be mapped out in detail.
- In particular, we must establish, for each property:
 - the direction of change along each axis,
 - the rate of change along each axis.
- Only in this manner will we be able to answer important questions such as:
 - how reliable are the results of a given calculation?
 - what resources are needed for a given accuracy?
 - will we be able to refute or verify a given observation?
- Of special interest here:
 - what is needed to calculate frequencies **rigorously** to within 1 cm^{-1} , bond distances to **0.1 pm** and atomization energies to **1 kJ/mol**?
- We shall here consider such questions, with emphasis on molecular vibrational constants.
 - we shall draw on previous results for atomization energies and bond distances
- We begin by considering some general aspects of convergence.
 - we shall pay particular attention to basis-set convergence
 - we assume that that the coupled-cluster wave-function hierarchy is well-known

Basis-set convergence and two-electron interactions

- Consider the valence contribution to the harmonic vibrational frequency of N_2 (cm^{-1}):

basis	N_{bas}	HF	SD	(T)	CCSD(T)
cc-pVDZ	28	2758	-350	-70	2339
cc-pVTZ	60	2732	-308	-78	2346
cc-pVQZ	110	2730	-294	-79	2356
cc-pV5Z	182	2730	-291	-80	2360
cc-pV6Z	280	2731	-289	-80	2361
limit	∞	2731	-287	-80	2363

- The **doubles** contribution converges slowly—we are still off by 2 cm^{-1} with 280 AOs.
- The **Hartree–Fock** and **triples** contributions are less of a problem (a general observation)
- The slow convergence arises from a poor description of short-range (dynamical) correlation in the orbital approximation (since r_{ij} is not present in the wave function):



- To make the most of standard wave functions, we must choose our orbitals carefully.

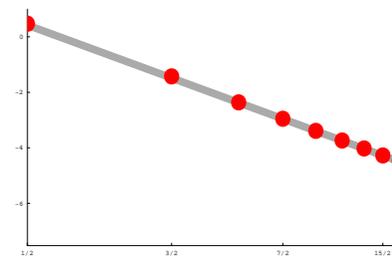
The principal expansion and correlation-consistent basis sets

- 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:

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

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

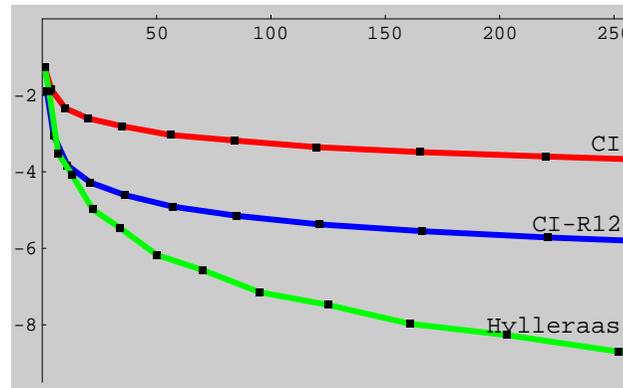
1 minute → 1 week → 200 years

Solutions to slow basis-set convergence

1. Use explicitly correlated methods!

- Include **interelectronic distances** r_{ij} in the wave function (Hylleraas 1928):

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



- We use CCSD-R12 (Klopper and Kutzelnigg, 1987) for benchmarking

2. Use basis-set extrapolation!

- Exploit the smooth convergence $E_\infty = E_X + AX^{-3}$ to extrapolate to basis-set limit

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

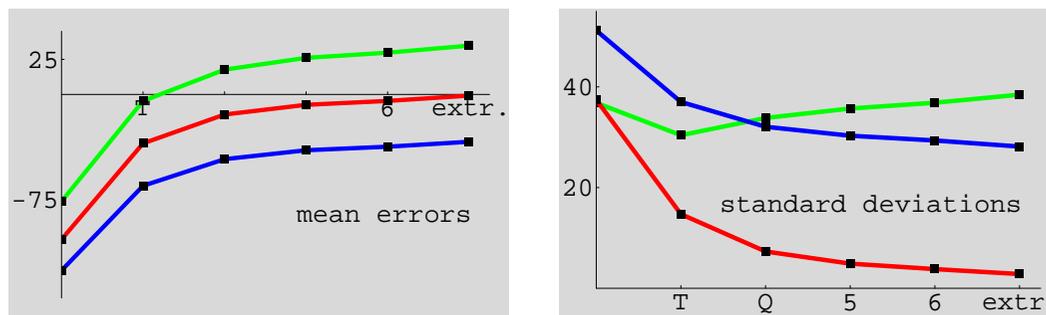
mE_h	DZ	TZ	QZ	5Z	6Z	R12
plain	194.8	62.2	23.1	10.6	6.6	1.4
extr.		21.4	1.4	0.4	0.5	

- The formula is linear and contains no parameters; applicable to many properties

3. Use density-functional theory!

Atomization energies (AEs)

- Let us consider the situation for an important molecular property: AEs
- Statistics based on 20 closed-shell organic molecules (kJ/mol)



- AEs increase with excitation level in the coupled-cluster hierarchy:

$$\text{HF} < \text{CCSD} < \text{CCSD(T)} < \text{MP2}$$

- Mean abs. cc-pcV6Z err. (kJ/mol): 423 (HF), 37 (MP2), 30 (CCSD), 4 (CCSD(T))
- AEs increase with cardinal number.
- CCSD(T) performs excellently, but DZ and TZ are inadequate:

kJ/mol	DZ	TZ	QZ	5Z	6Z
raw	103.1	34.0	13.5	6.6	4.1
extrapolated		14.5	1.7	0.9	0.8

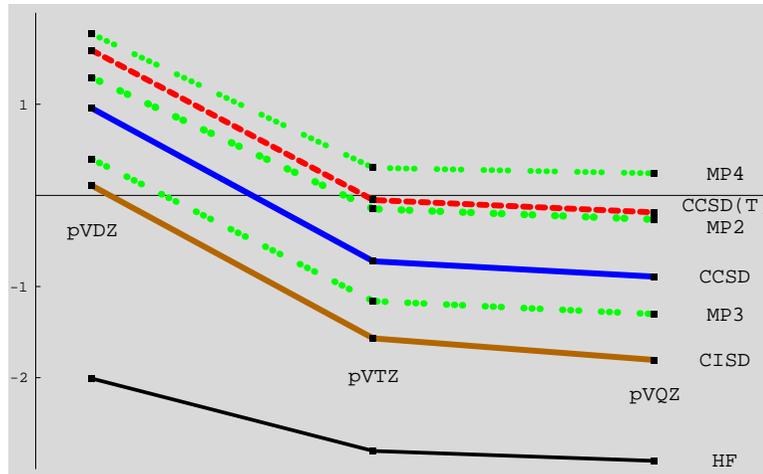
The (in)adequacy of CCSD(T)

	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 canceled by the neglect of quadruples.
- The rigorous calculation of AEs to chemical accuracy requires **CCSDTQ/cc-pCV6Z!**

Bond distances

- Statistics based on 28 bond distances at the all-electron cc-pVXZ level (pm):



- Bonds shorten with increasing basis:
DZ > TZ > QZ
- Bonds lengthen with increasing excitations:
HF < CCSD < MP2 < CCSD(T)
- Considerable scope for error cancellation:
CISD/DZ, MP3/DZ

- CCSD(T) distances compared with experiment:

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

- The high accuracy of CCSD(T) 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: ≈ -0.04 pm
- Intrinsic error of the CCSDT model: ≈ -0.2 pm
- Connected quadruples increase bond lengths by about 0.1–0.2 pm

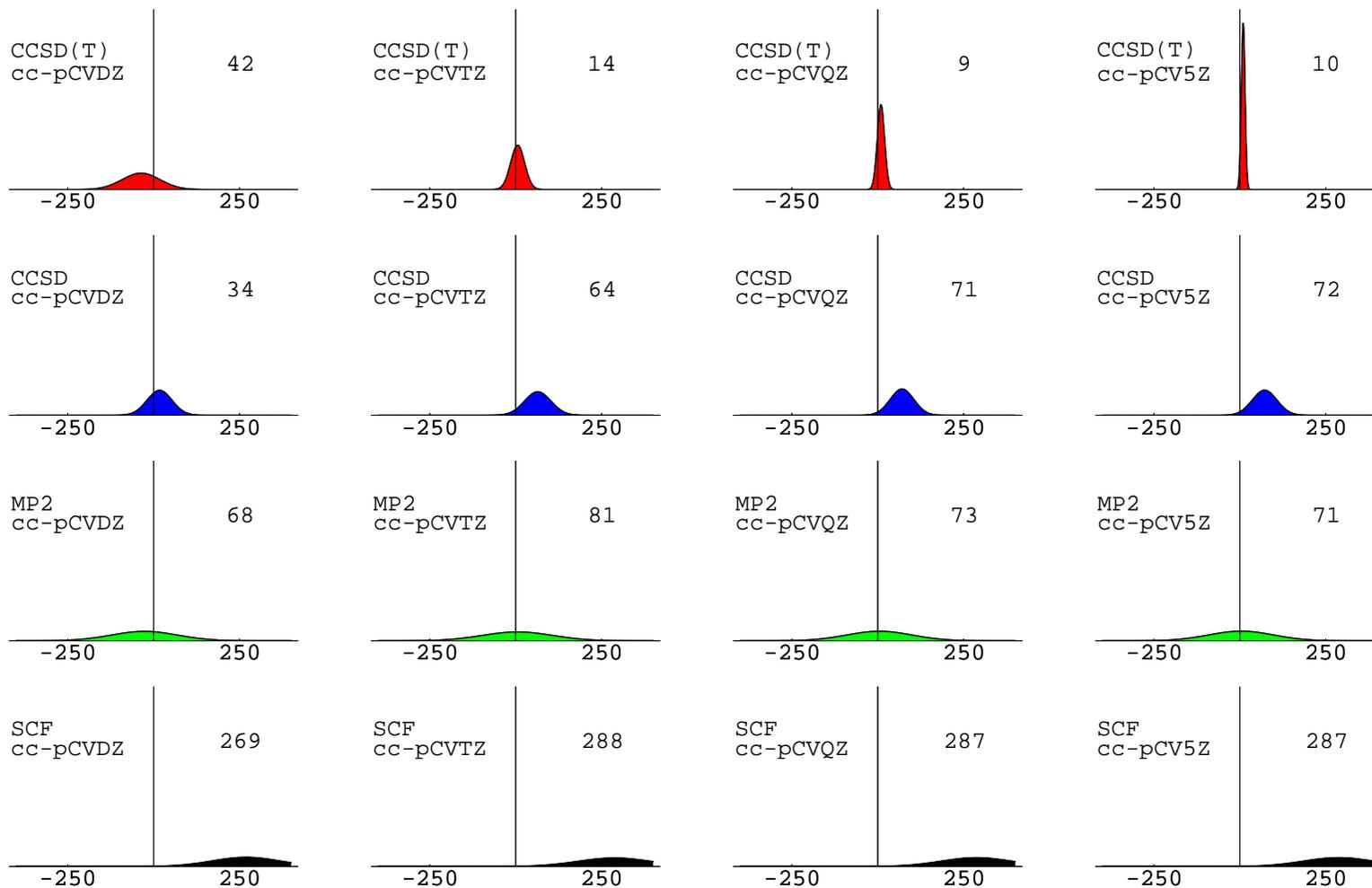
Vibrational frequencies of diatoms

- The frequency of a diatomic fundamental transition is given by

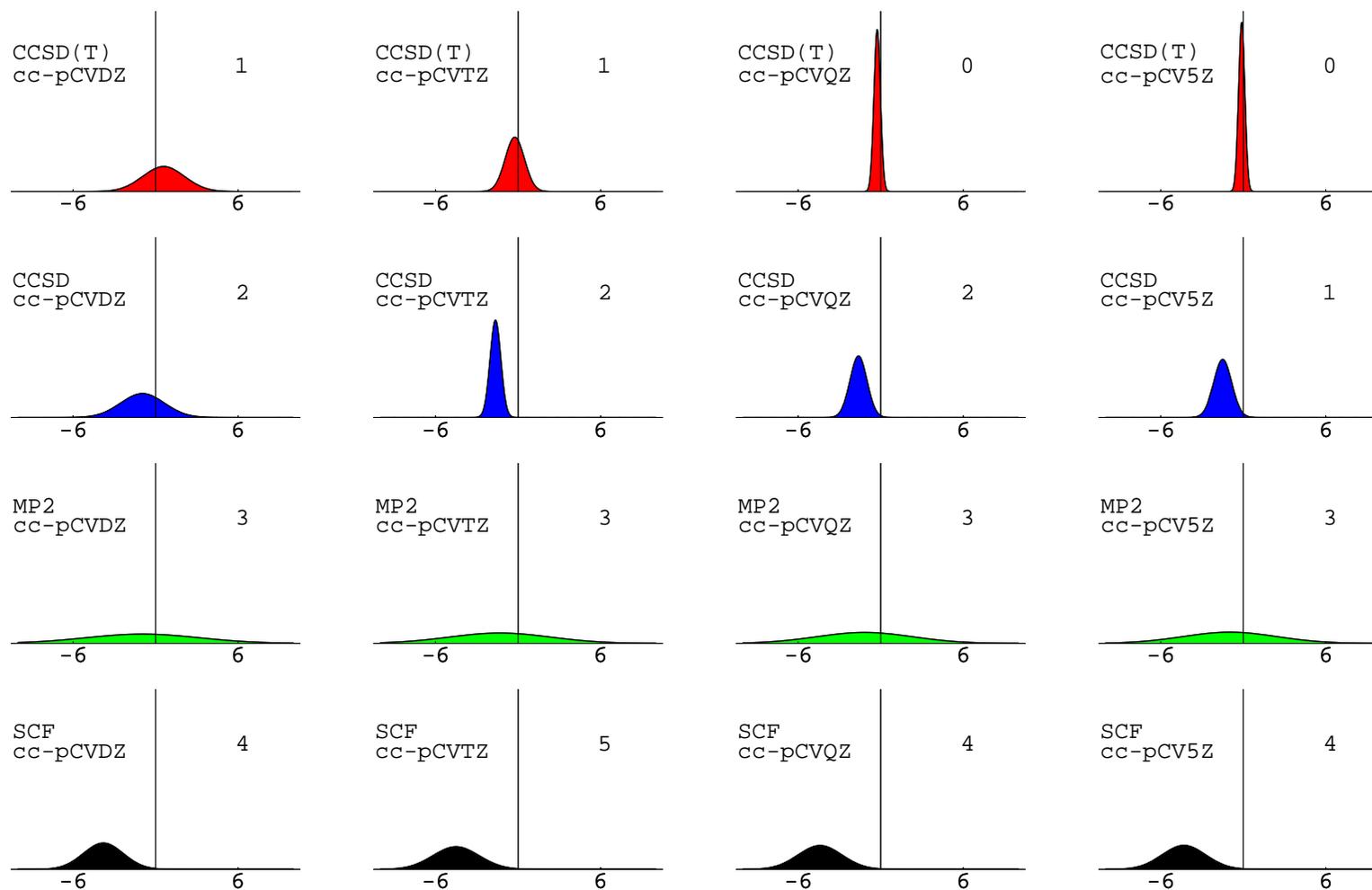
$$\nu = \omega_e - 2\omega_e x_e$$

- the harmonic constant ω_e requires 2nd derivatives of PES
- the anharmonic constant $\omega_e x_e$ requires 4th derivatives of PES
- With the advent of CCSD(T) in the 1990s, it was soon realized that this model is capable of highly accurate vibrational constants (to within a few wavenumbers at the TZ level)
- However, with the development of codes capable of handling very large basis sets and high excitation levels, it has slowly transpired that things are perhaps not so simple
- We have carried out accurate benchmark calculations for BH, HF, CO, N₂, and F₂
 - basis sets up to aug-cc-pV6Z and aug-cc-pCV5Z
 - CCSD, CCSD(T), CCSDT, CCSDTQ, and CCSDTQ5
- Important work carried out by:
Allen, Bartlett, Császár, Feller, Lee, Martin, Schaefer, Taylor, and others
- We shall first consider the harmonic constants, next the anharmonic ones

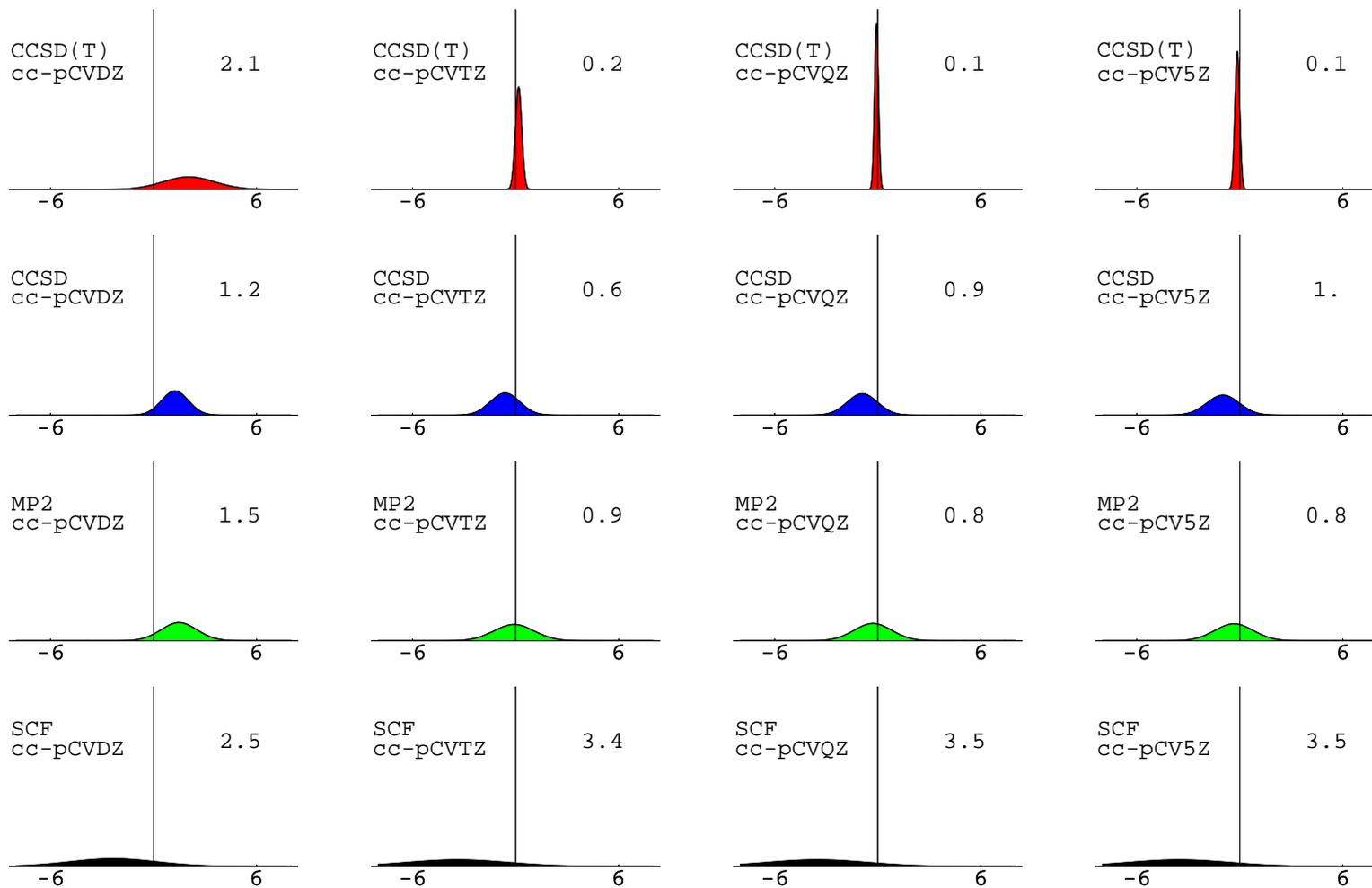
Harmonic constants ω_e of BH, CO, N₂, HF, and F₂ (cm⁻¹)



Anharmonic constants $\omega_e x_e$ of BH, CO, N₂, HF, and F₂ (cm⁻¹)



Bond distances R_e of BH, CO, N₂, HF, and F₂ (cm⁻¹)



Difficulties with harmonic constants

$ \overline{\Delta} $ (cm ⁻¹)	RHF	MP2	CCSD	CCSD(T)	judgment
ω_e	287	71	72	10	DIFFICULT!
$\omega_e x_e$	4	3	1	0	EASY!

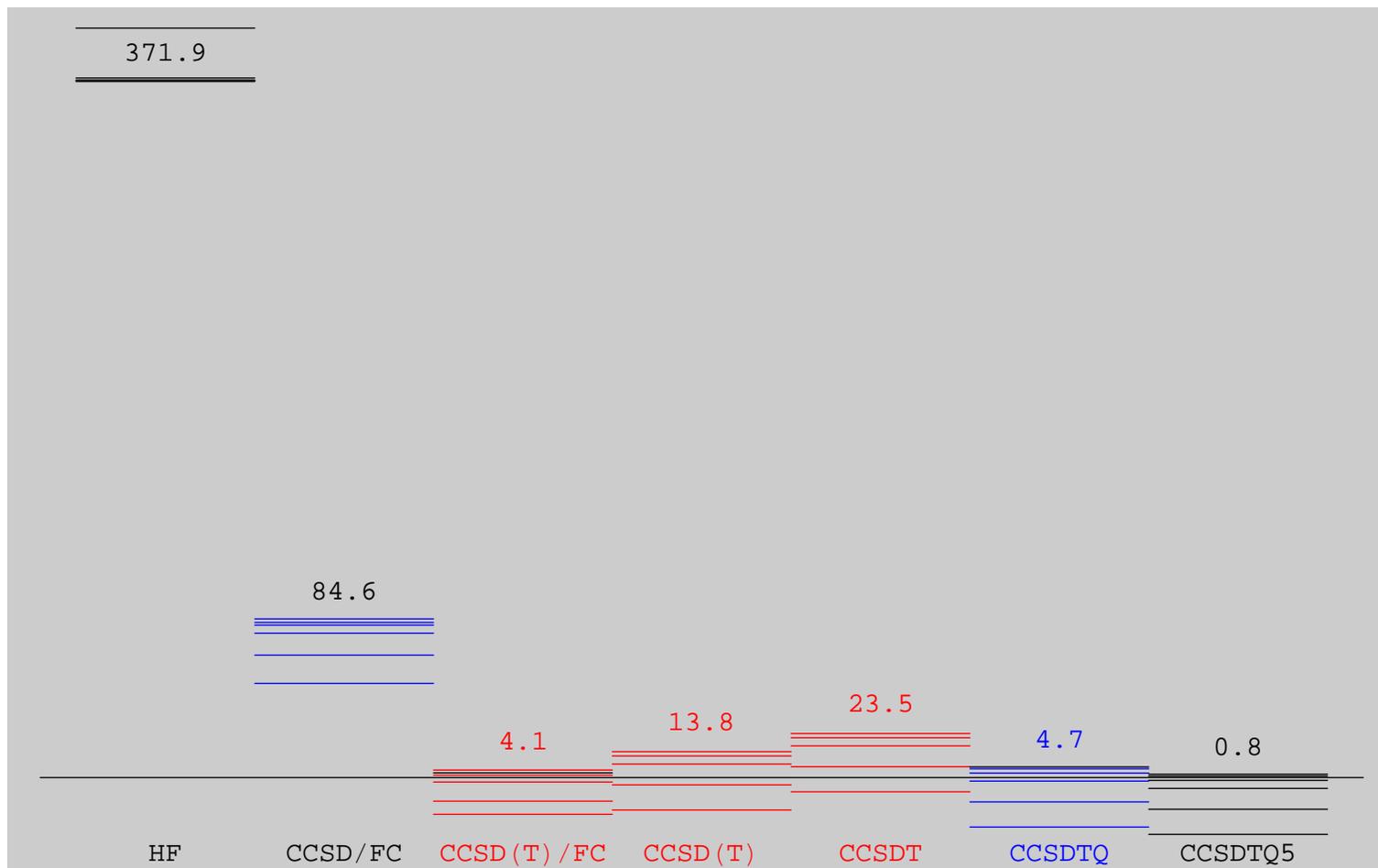
- There are two main problems with harmonic constants:
 - basis-set incompleteness
 - lack of high-order connected excitations
- Basis-set incompleteness can be treated by extrapolation or explicitly correlated methods
 - valence-electron CCSD/cc-pVXZ calculations on N₂:

cm ⁻¹	D	T	Q	5	6	R12
raw	2408.8	2423.9	2435.6	2439.9	2441.3	2443.2
extrapolated		2440.2	2445.6	2443.9	2443.1	

- extrapolation does improve results but not as consistently as for AEs
- we have relied more on the R12 results
- Higher excitations requires special CC code (or another approach)

Higher-order connected contributions to ω_e in N_2

- There are substantial higher-order corrections:



- connected triples relaxation contributes 9.7 cm^{-1} (total triples -70.5 cm^{-1})
- connected quadruples contribute -18.8 cm^{-1}
- connected quintuples contribute -3.9 cm^{-1}

Harmonic frequencies of HF, N₂, F₂, and CO

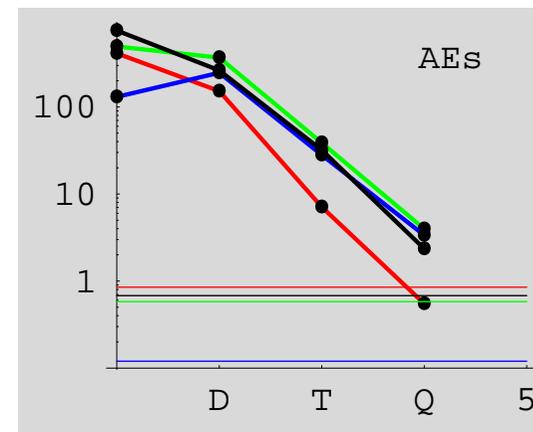
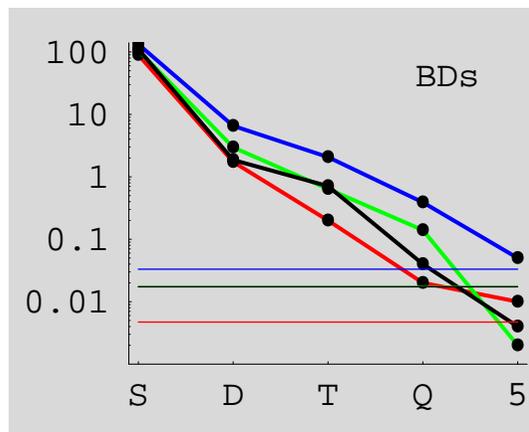
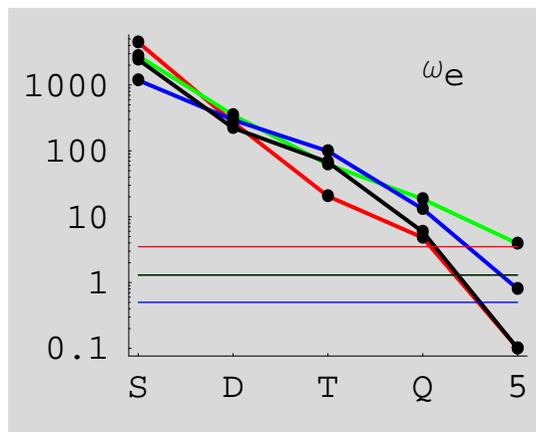
- Harmonic frequencies were obtained in the following manner:

		HF	N ₂	F ₂	CO
CCSD-R12		4191.0	2443.2	1026.5	2238.5
CCSD(T)–CCSD	aug-cc-pV6Z/FC	–48.4	–80.6	–95.7	–71.5
CCSDTQ–CCSD(T)	cc-pVTZ/FC	–4.5	–9.1	–12.2	–6.5
CCSDTQ5–CCSDTQ	cc-pVDZ/FC	–0.1	–3.9	–0.8	0.0
CCSD(T) core correlation	aug-cc-pCV5Z	4.0	9.8	1.6	9.9
relativistic correction		–3.5	–1.4	–0.5	–1.3
adiabatic correction		0.4	0.0	0.0	0.0
theory		4138.9	2358.0	918.9	2169.1
experiment		4138.3	2358.6	916.6	2169.8
error		0.1	–0.6	2.3	0.7

- it does not seem possible yet to obtain harmonic frequencies to within 1 cm^{–1}
- error in F₂ may be explained by a too short bond distance (141.19 vs. 141.27 pm)

Excitation-level convergence

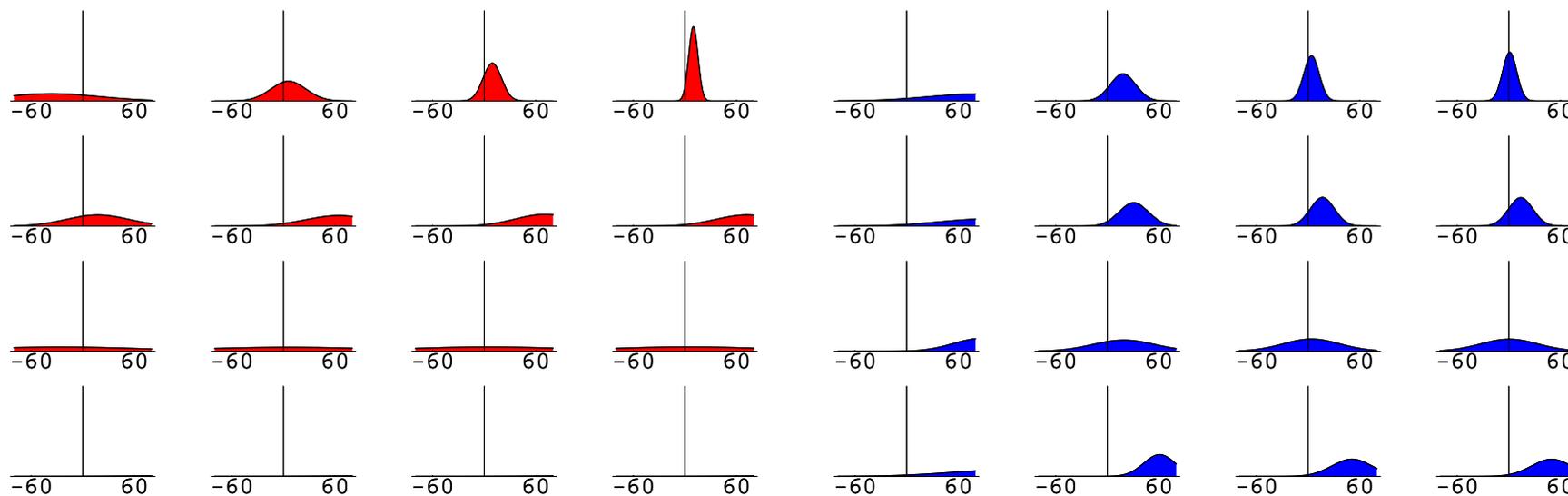
- Log plots of contributions to harmonic frequencies, bond lengths, and atomization energies:



- color code: HF (red), N₂ (green), F₂ (blue), and CO (black)
- straight lines indicate first-order relativistic corrections
- Excitation-level convergence is approximately linear
- Relativity becomes important beyond connected quadruples
- Basis-set convergence is much slower: X^{-3}

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;
 - harmonic frequencies are in error by 10 cm^{-1} at the CCSD(T) level; the CCSDTQ5 model is needed to be within about 1 cm^{-1}
 - relativistic corrections are of same size as connected quintuples contributions
- 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;
 - 6Z gives errors gives frequencies in error by a few cm^{-1} ; extrapolation or R12 is needed for errors of about 1 cm^{-1}
 - convergence can often be accelerated by basis-set extrapolation.
- **Fortuitous error cancellation** is ubiquitous in quantum chemistry—at all levels of theory!