The right result for the ~~wrong~~ RIGHT reason!

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Software

- Dalton (http://www.kjemi.uio.no/software/dalton)

- LUCIA (J. Olsen)

- ACES II (J. Gauss, J. Stanton, R. Bartlett)

High-precision quantum-chemical calculations

- The last decade has seen a dramatic improvement in our ability to treat molecular electronic systems accurately
  - development of techniques for systematic convergence towards the exact solution
  - extensive benchmarking on small and light molecular systems
- In many cases, we can now confidently confirm or reject experimental observations
- Many black-box methods have been developed
  - well-defined levels of theory
- Still, the exact solution can be approached in infinitely many ways
  - at many (incomplete) levels of theory, agreement with experiment may be obtained
  - such agreement always arises by error cancellation
  - error cancellation is treacherous: the right answer for the wrong reason
- For a reliable application of quantum-chemistry methods, one must be wary of the pitfalls of error cancellation
- We shall here review high-precision quantum chemistry, paying special attention to the problem of error cancellation

The Hartree–Fock model

- All information about the electronic system is contained in the wave function, obtained by solving the Schrödinger equation (or the corresponding relativistic equation).

  - Molecular electronic systems represent a difficult many-body problem that cannot be treated exactly—even on modern computers.

  - We are thus forced to make approximations, setting up simplified descriptions that incorporate the most important features of the system.

- This should preferably be done in an orderly fashion, so that the exact solution can be approached in a systematic manner: hierarchy of approximations

- The Hartree–Fock model—the fundamental approximation of wave-function theory

  - each electron moves in the mean field of all other electrons

  - provides an uncorrelated description: average rather than instantaneous interactions

  - gives rise to the concept of molecular orbitals

  - typical errors: 0.5% in the energy; 1% in bond distances, 5%–10% in other properties

  - forms the basis for more accurate treatments
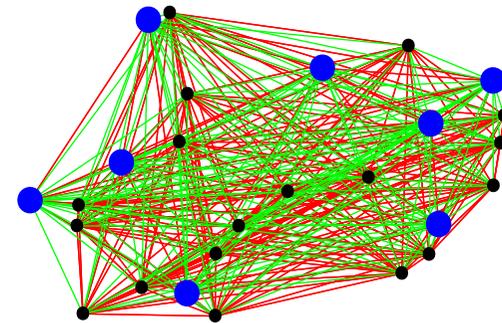
Electron correlation and virtual excitations

- electron correlation:

  – to improve upon the HF model, we must take into account the instantaneous interactions among the electrons

  – in real space, the electrons are constantly being scattered by collisions

  – in the orbital picture, these collisions manifest themselves as excitations from occupied to virtual (unoccupied) spin orbitals

- double excitations:

  – the most important events are collisions between two electrons

  – in the orbital picture, such an event corresponds to an excitation from two occupied to two virtual spin orbitals, known as pair excitations or double excitations

  – with each such excitation, we associate an amplitude, representing its probability

  – our description is then said to be correlated

- coupled-cluster theory:

  – by allowing all possible single and double excitations to happen in all possible combinations, we arrive at the coupled-cluster singles-and-doubles (CCSD) model

  – in the CCSD model, the HF error is typically reduced by a factor of three or four

  – for higher accuracy, we must also include triple excitations (CCSDT), and so on

Basis sets of Gaussian functions

- In our calculations, we expand the molecular orbitals in one-electron Gaussian-type functions (GTOs):

$$G_{ijk}(\mathrm{r}_A, \alpha) = x_A^i y_A^j z_A^k \exp\left(-\alpha r_A^2\right)$$

- Basis sets of increasing size:

  - minimal or single-zeta (SZ) basis sets:
    * one set of GTOs for each occupied atomic shell $(2s1p)$
    * gives a rudimentary description of electron structure

  - double-zeta (DZ) basis sets:
    * two sets of GTOs for each occupied atomic shell $(3s2p1d)$
    * sufficient for a qualitative description of the electron system

  - triple-zeta (TZ), quadruple-zeta (QZ) and larger basis sets:
    * needed for a quantitative description of the electronic system

- The number of GTOs per atom increases rapidly:

SZ	DZ	TZ	QZ	5Z	6Z
5	14	30	55	91	140

- Large basis sets are needed to generate a flexible virtual space!

- The quality of nonrelativistic molecular electronic-structure 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. the N-electron hierarchy:
     coupled-cluster excitation levels

     HF, CCSD, CCSDT, CCSDTQ, ...

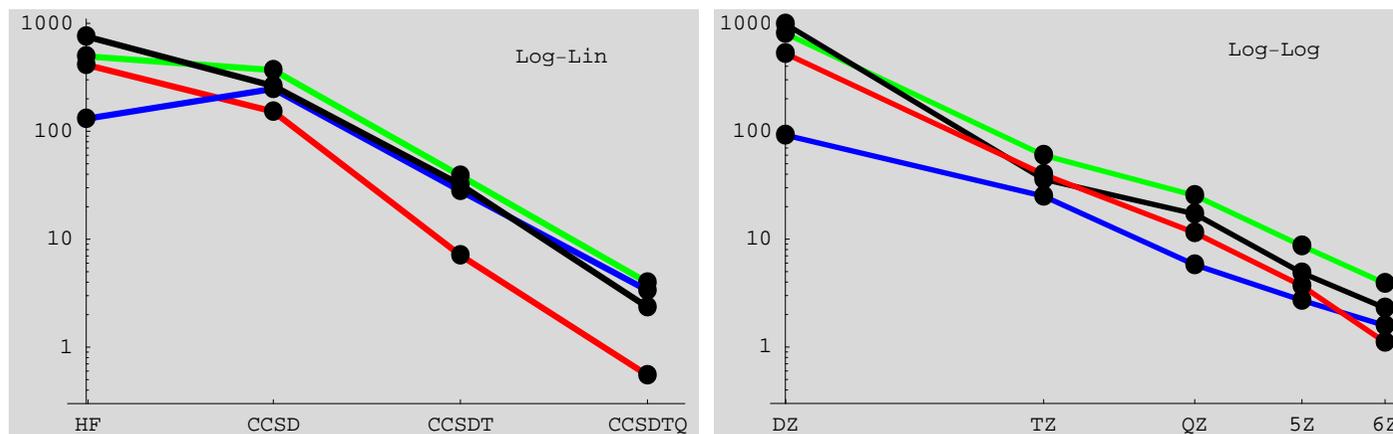 2. the one-electron hierarchy:
     correlation-consistent basis sets

     DZ, TZ, QZ, 5Z, 6Z, ...
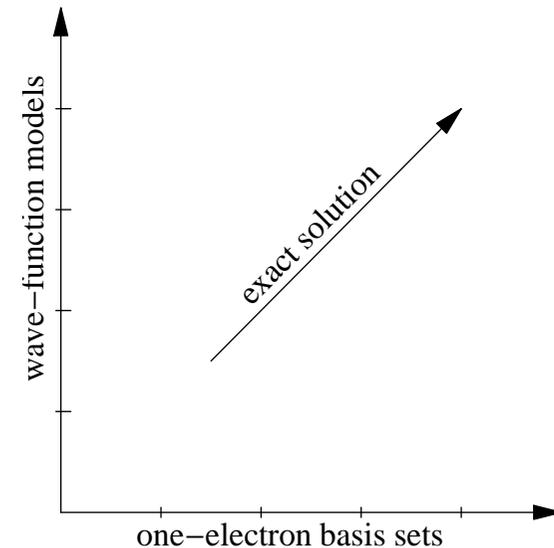
- The quality is systematically improved upon by going up in the hierarchies.

Energy contributions to atomization energies (kJ/mol)

- Contributions of each CC excitation level (left) and AO basis-set shell (right)

  - color code: HF , N$_2$, F$_2$, and CO

- The excitation-level convergence is approximately linear (log–linear plot)

  - each new excitation level reduces the error by about an order of magnitude

  - the contributions from quintuples are negligible (about 0.1 kJ/mol)

- The basis-set convergence is much slower (log–log plot)

  - each shell contributes an energy proportional to X^{-4} where X is the cardinal number

  - a similarly small error (0.1 kJ/mol) requires $X > 10$

  - clearly, we must choose our orbitals in the best possible manner

Contributions to atomization energies (kJ/mol)

	RHF	SD	T	Q	rel.	vib.	total	experiment	error
CH_2	531.1	218.3	9.5	0.4	−0.7	−43.2	715.4	714.8±1.8	0.6
H_2O	652.3	305.3	17.3	0.8	−2.1	−55.4	918.2	917.8±0.2	0.4
HF	405.7	178.2	9.1	0.6	−2.5	−24.5	566.7	566.2±0.7	0.5
N_2	482.9	426.0	42.4	3.9	−0.6	−14.1	940.6	941.6±0.2	−1.1
F_2	−155.3	283.3	31.6	3.3	−3.3	−5.5	154.1	154.6±0.6	−0.5
CO	730.1	322.2	32.1	2.3	−2.0	−12.9	1071.8	1071.8±0.5	−0.0

- agreement with experiment in all cases except for N_2

- all purely electronic contributions are positive (except Hartree–Fock for F_2)

  – very large correlation contributions

  – the neglected quintuples contribute a few tenths of 1 kJ/mol

- relativistic corrections are small ($\approx 0.5\%$) but needed for agreement with experiment

  – nearly cancel quadruples contributions

- vibrational corrections are substantial

  – similar to triples contributions but oppositely directed

Contributions to bond distances (pm)

	RHF	SD	T	Q	5	rel.	theory	exp.	err.
HF	89.70	1.67	0.29	0.02	0.00	0.01	91.69	91.69	0.00
N_2	106.54	2.40	0.67	0.14	0.03	0.00	109.78	109.77	0.01
F_2	132.64	6.04	2.02	0.44	0.03	0.05	141.22	141.27	-0.05
CO	110.18	1.87	0.75	0.04	0.00	0.00	112.84	112.84	0.00

- agreement with experiment to within 0.01 pm except for F_2

- Hartree–Fock theory underestimates bond distances by up to 8.6 pm (for F_2)

- all correlation contributions are positive
  - approximate linear convergence, slowest for F_2
  - triples contribute up to 2.0 pm, quadruples up to 0.4 pm, and quintuples 0.03 pm
  - sextuples are needed for convergence to within 0.01 pm

- relativistic corrections are small except for F_2 (0.05 pm)
  - of the same magnitude and direction as the quintuples

Contributions to harmonic frequencies ω_e (cm^{-1})

	RHF	SD	T	Q	5	rel.	theory	exp.	err.
HF	4473.8	−277.4	−50.2	−4.1	−0.1	−3.5	4138.5	4138.3	0.2
N$_2$	2730.3	−275.8	−72.4	−18.8	−3.9	−1.4	2358.0	2358.6	−0.6
F$_2$	1266.9	−236.1	−95.3	−15.3	−0.8	−0.5	918.9	916.6	2.3
CO	2426.7	−177.4	−71.7	−7.2	0.0	−1.3	2169.1	2169.8	0.7

- agreement with experiment to within 1 cm^{-1} except for F$_2$

- Hartree–Fock theory overestimates harmonic frequencies by up to 38% (in F$_2$).

- all correlation contributions are large and negative
  - triples contribute up to 95 cm^{-1}, quadruples 20 cm^{-1}, and quintuples 4 cm^{-1}
  - sextuples are sometimes needed for convergence to within 1 cm^{-1}

- relativistic corrections are of the order of 1 cm^{-1}
  - of the same magnitude and direction as the quadruples or quintuples
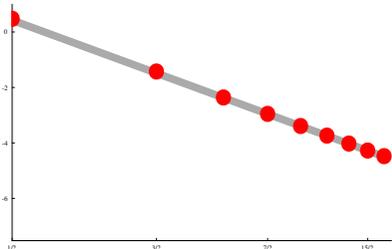
The principal expansion and correlation-consistent basis sets

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

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

- 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
	$+3s3p3d$	$+4s4p4d4f$	$+5s5p5d5f5g$	$\propto X^2$
$2s1p$	$3s2p1d$	$4s3p2d1f$	$5s4p3d2f1g$	$\propto X^3$

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

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

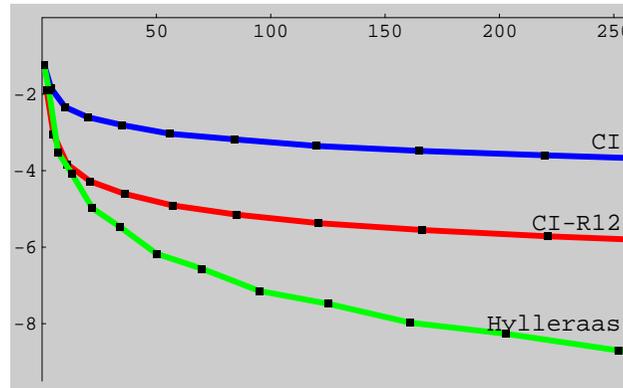- Each new digit in the energy therefore costs 10000 times more CPU time!

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

Solutions to slow basis-set convergence

1. **Use explicitly correlated methods!**

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

   $$\Psi_{\mathrm{R12}} = \sum_K C_K \Phi_K + C_R r_{12} \Phi_0$$

   - We use CCSD-R12 (Noga, Kutzelnigg, and Klopper, 1992) for benchmarking
   - Note: basis-set convergence mainly a problem for double excitations

2. **Use basis-set extrapolation!**

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

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

 | $\mathrm{m}E_\mathrm{h}$ | 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

Practical levels of theory: error cancellation

- We have seen how the "exact" result can be approached systematically.

- In practice, we cannot carry out such studies in chemical applications
  - only relatively low excitation levels can be reached
  - only relatively small basis sets can be used

- To reduce cost, additional (simplified) levels are introduced
  - typically based on perturbation theory: MP2, CCSD(T)
  - introduces additional sources of error cancellations

- We shall now examine the convergence more carefully
  - emphasis on the interplay between excitation-level and basis-set convergence

- We shall do this for the three properties considered about:
  - atomization energies
  - bond distances
  - vibrational frequencies

## Many-body perturbation theory: approximate coupled-cluster theory

- Coupled-cluster amplitudes may be estimated by perturbation theory

- Caveat: the resulting perturbation series is frequently divergent, even in simple cases

- Here are some examples for the HF molecule (10 electrons):
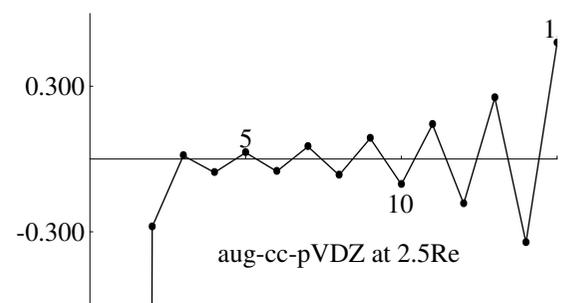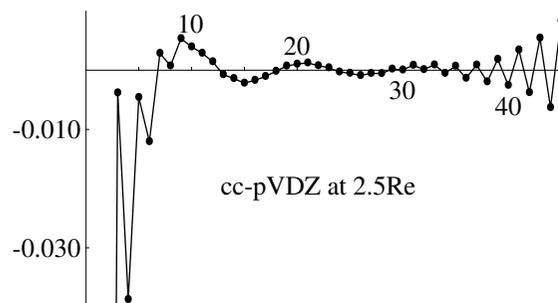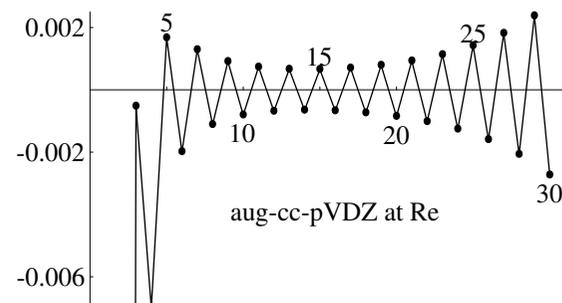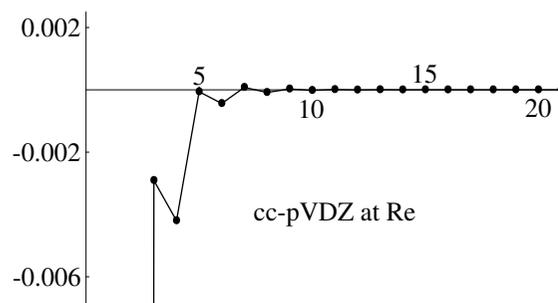
- However, to lowest order, perturbational corrections are very useful and popular
  - MP2 (approximate CCSD) and CCSD(T) (approximate CCSDT)

Atomization energies (AEs)

- Let us consider the situation for an important molecular property: AEs

- Statistics based 20 closed-shell organic molecules (kJ/mol)
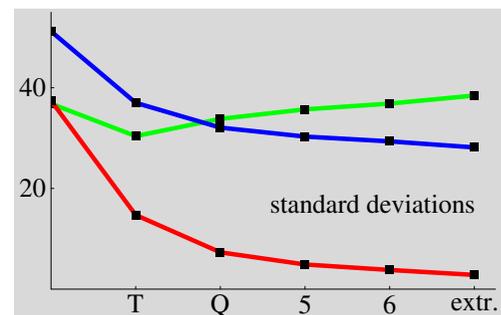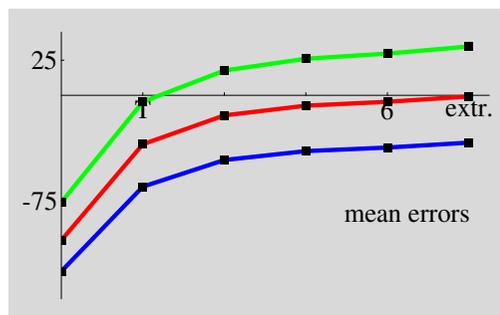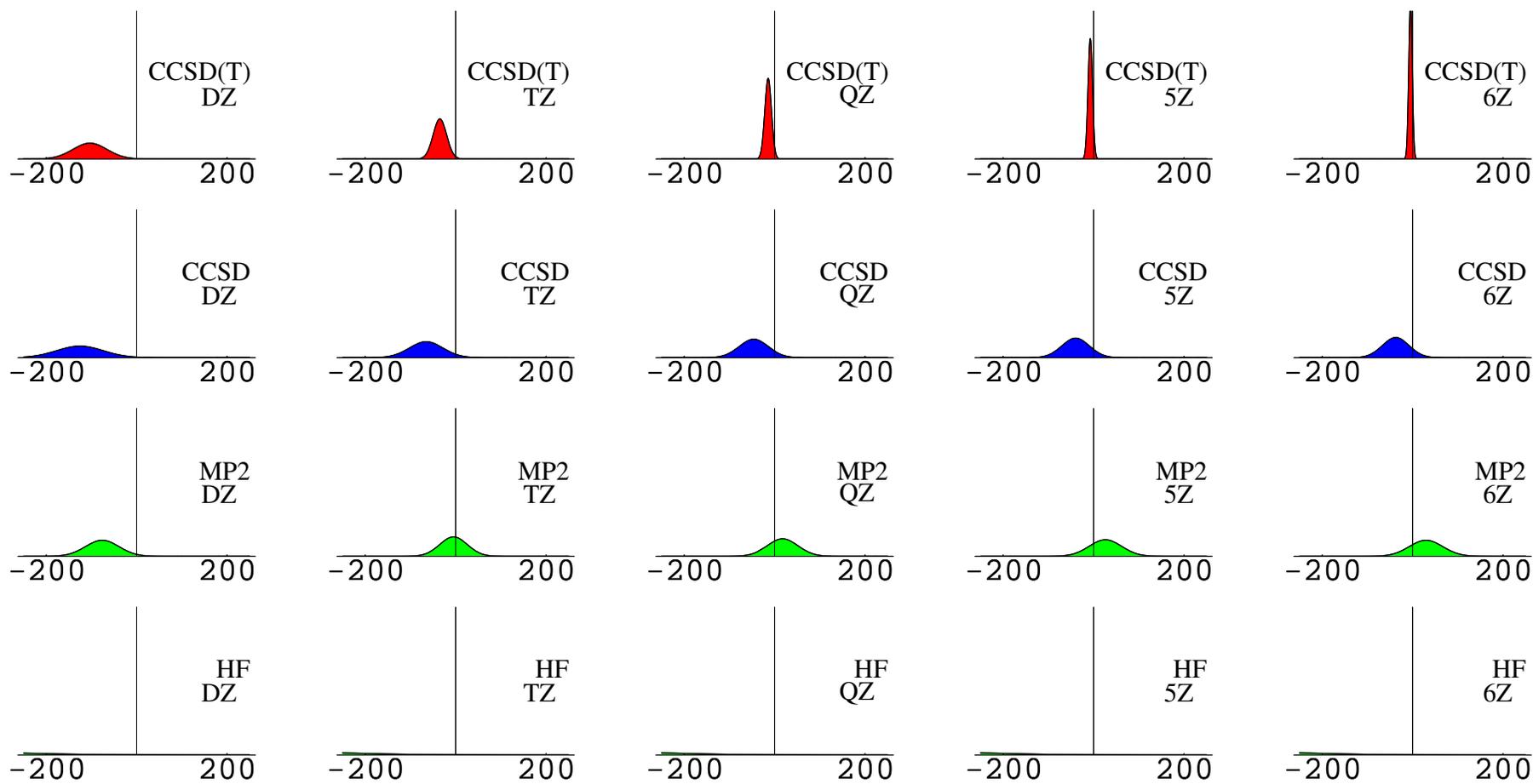

- AEs increase with excitation level in the coupled-cluster hierarchy:

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

- 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

Atomization energies (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$\pm$1.8
H_2O	975.3	0.1	974.9	-0.3	975.7	0.5	975.2	917.8$\pm$0.2
HF	593.2	0.0	593.0	-0.2	593.6	0.4	593.2	566.2$\pm$0.7
N_2	954.7	-1.6	951.3	-5.0	955.2	-1.1	956.3	941.6$\pm$0.2
F_2	161.0	-2.4	159.6	-3.8	162.9	-0.5	163.4	154.6$\pm$0.6
CO	1086.7	0.0	1084.4	-2.3	1086.7	0.0	1086.7	1071.8$\pm$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

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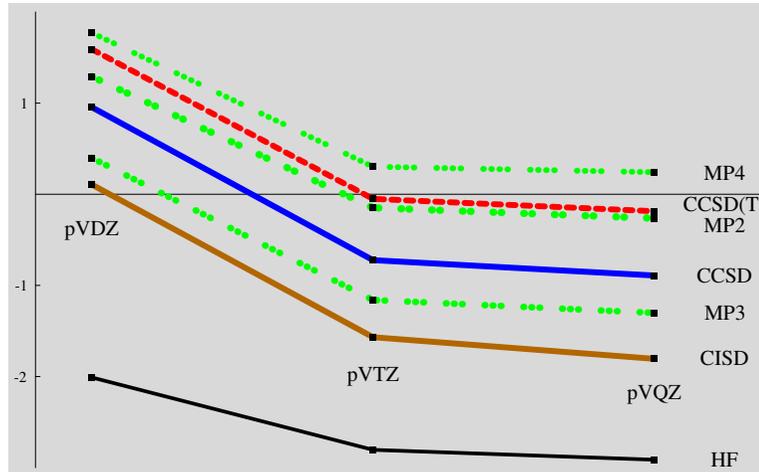

- Bonds shorten with increasing basis:
  DZ > TZ > QZ

- 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 → 6Z: ≈ -0.10 pm
  - triples relaxation CCSD(T) → CCSDT: ≈ -0.04 pm

- Intrinsic error of the CCSDT model: ≈ -0.2 pm

- Connected quadruples increase bond lenghts by about 0.1–0.2 pm

Bond distances R_e of BH, CO, N$_2$, HF, and F$_2$ (cm^{-1})
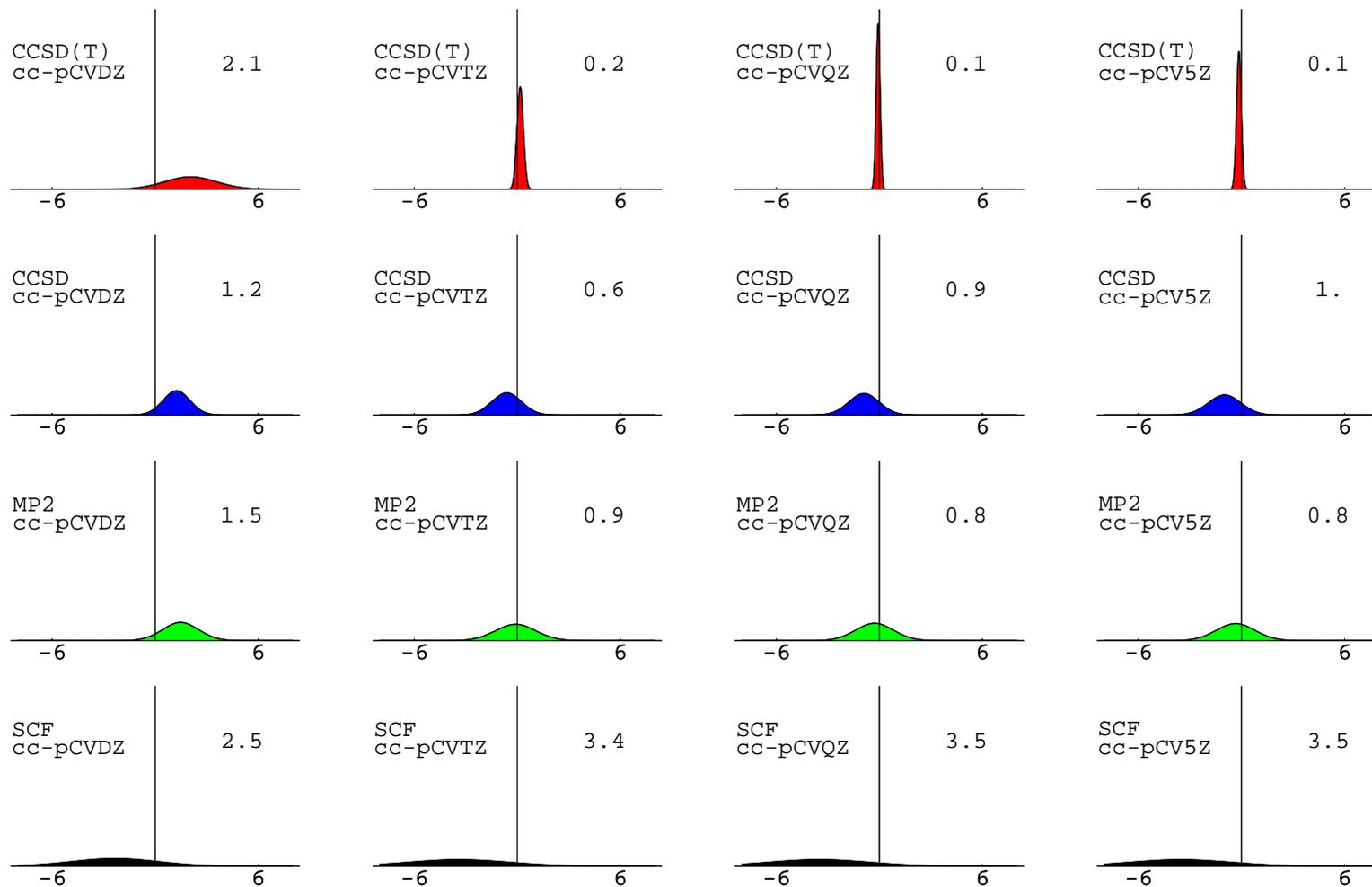
Error cancellation: some general considerations

- In an infinite basis, the CC hierarchy is related to experiment as follows:
  - HF < CCSD < CCSDT < CCSDTQ < $\cdots$ < FCI = exp (BDs and AEs)
  - no error cancellation may occur (ignoring relativity and adiabatic corrections)

- In a finite basis, results are shifted and cancellation occurs for BDs but not for AEs:
  - HF < CCSD $\approx$ exp < CCSDT < CCSDTQ < $\cdots$ < FCI (BDs shifted up)
  - HF < CCSD < CCSDT < CCSDTQ < $\cdots$ < FCI < exp (AEs shifted down)

- Perturbative treatments of connected excitations tend to overestimate their effect:
  - HF < CCSD < MP2 $\leftarrow$ (over)compensates for lack of triples
  - CCSD < CCSDT < CCSD(T) $\leftarrow$ compensates for lack of quadruples
  - a new source of error cancellation

- For BDs and AEs, we now observe
  - HF < CCSD < MP2 $\approx$ CCSD(T) $\approx$ exp (BDs)
  - HF < CCSD < CCSD(T) $\approx$ exp < MP2 (AEs)
  - error cancellation may now occur also for AEs

- We shall see that vibrational frequencies behave in much the same manner as BDs since basis-set extension and increased excitation levels work in opposite directions

Vibrational frequencies of diatoms

- The frequency of a diatomic fundamental transition is given by

$$\nu = \omega_\mathrm{e} - 2\omega_\mathrm{e}x_\mathrm{e}$$

  – the harmonic constant ω_e requires 2nd derivatives of PES

  – the anharmonic constant $\omega_\mathrm{e}x_\mathrm{e}$ 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

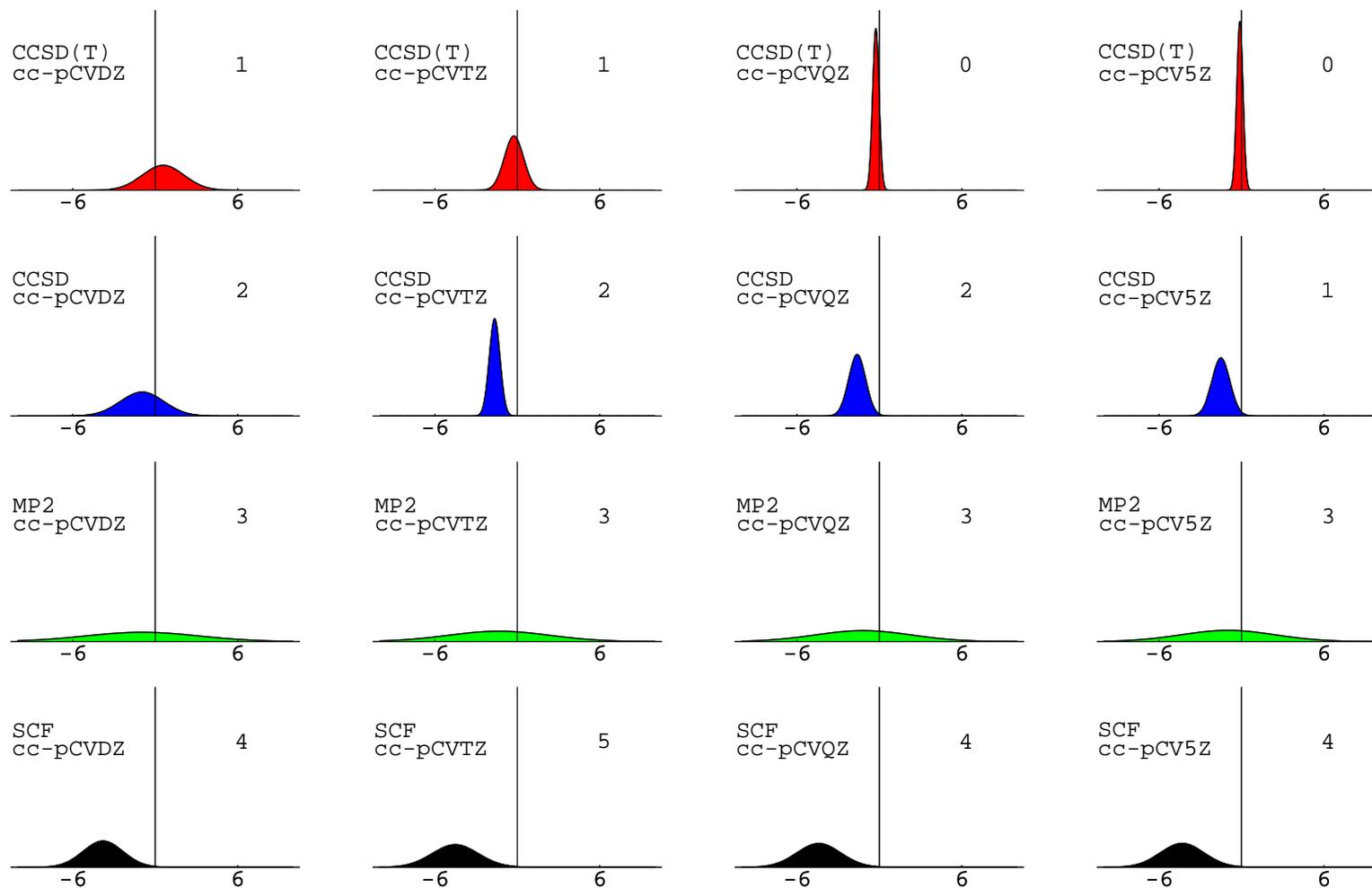- It is easier to converge harmonic than anharmonic constants:

$\overline{|\Delta|}$ (cm^{-1})	RHF	MP2	CCSD	CCSD(T)	judgment
ω_e	287	71	72	10	DIFFICULT!
$\omega_\mathrm{e}x_\mathrm{e}$	4	3	1	0	EASY!

- There are two main problems with harmonic constants:

  – basis-set incompleteness
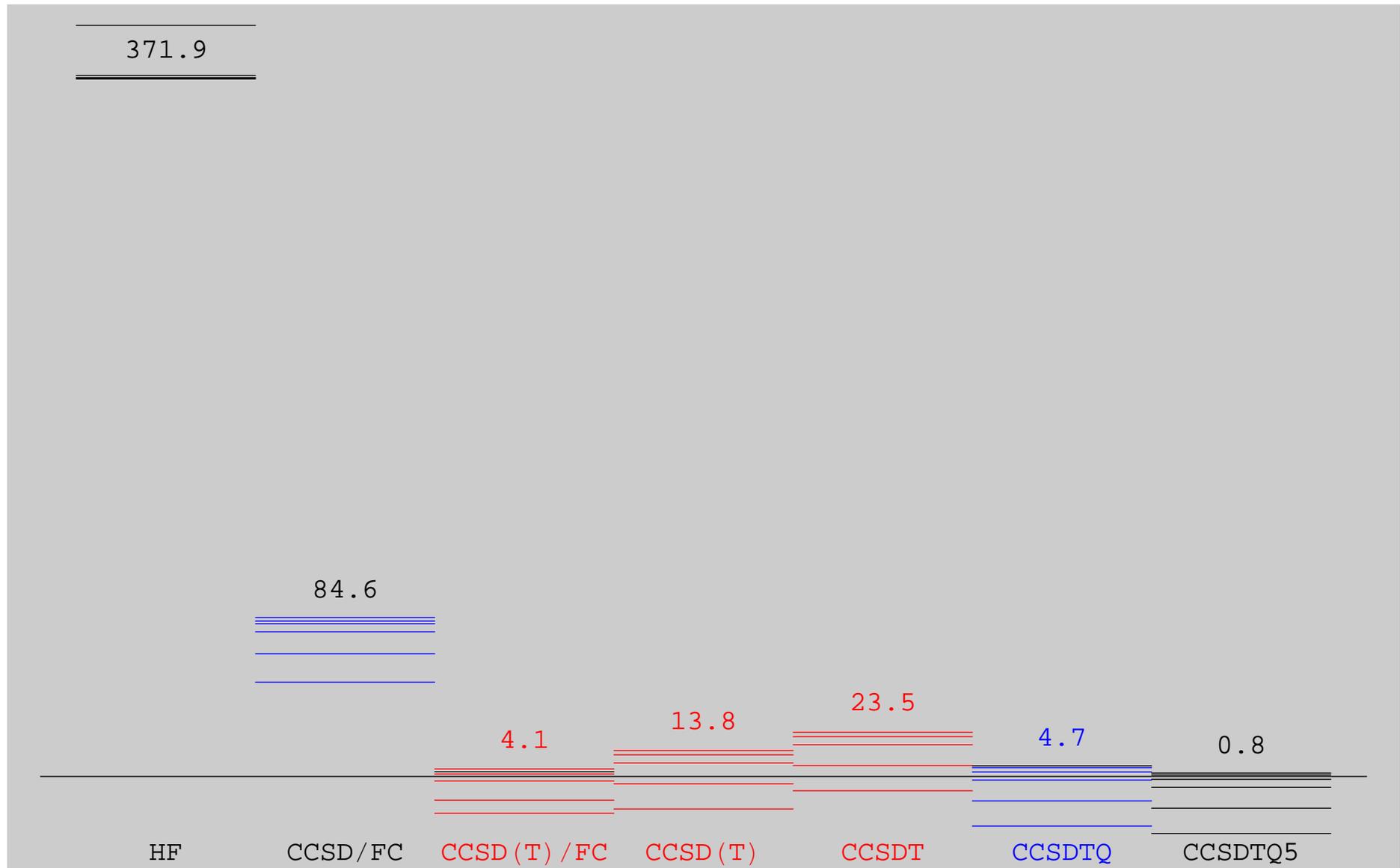
  – lack of high-order connected excitations

Harmonic constants ω_e of BH, CO, N$_2$, HF, and F$_2$ (cm^{-1})
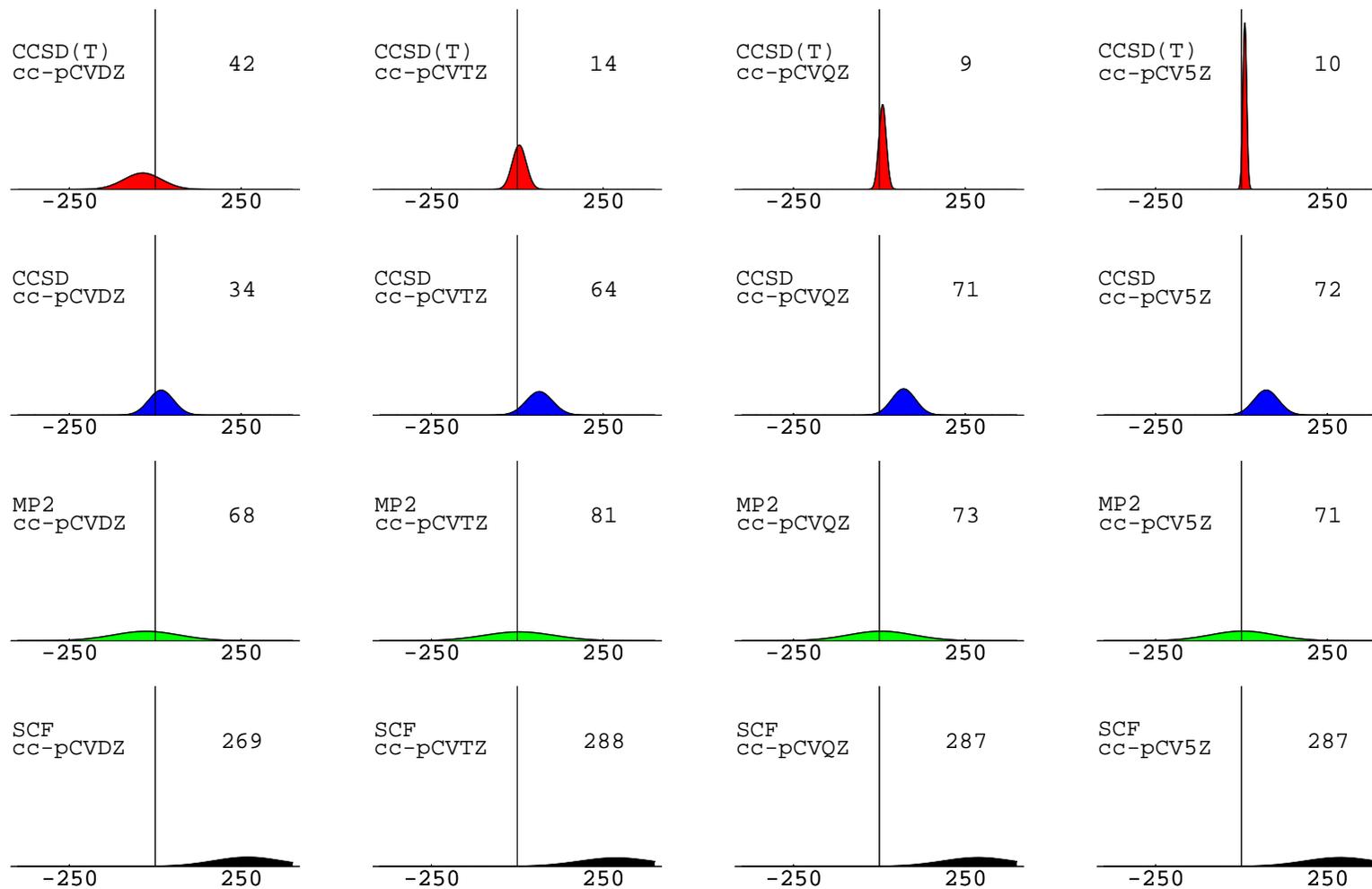
Anharmonic constants $\omega_{\mathrm{e}}x_{\mathrm{e}}$ of BH, CO, N$_2$, HF, and F$_2$ (cm^{-1})

Higher-order connected contributions to ω_e in N_2

371.9

84.6

4.1   13.8   23.5   4.7   0.8

HF   CCSD/FC   CCSD(T)/FC   CCSD(T)   CCSDT   CCSDTQ   CCSDTQ5

Conclusions

- Quantum chemistry provides a set of well-defined levels of approximation
  - excitation-level expansion
  - basis-set expansion

- The "exact" result can be approached in a systematic manner

- In practice, we have to be content with low levels of theory
  - low excitation levels, approximated by perturbation theory
  - small basis sets

- Sometimes complicated interplay between different approximations
  - useful and reliable (balanced) levels of theory have been implemented in codes
  - can be usefully applied without deep knowledge of quantum chemistry

- Still, some knowledge of these methods, their errors and the interplay of these errors, will make the application of these methods more reliable

- Discipline is always needed!