

The exhaustion of the Schrödinger equation:
the accurate calculation of molecular properties for light systems

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Quantum Chemistry Applied: From H₃ to Biocatalysis

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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
 - heightened awareness of pitfalls related to error cancellation
- In many cases, we can now confidently confirm or reject experimental observations
- As a result, it has become increasingly important to account for many “small” effects:
 - vibrational corrections to molecular properties
 - adiabatic and nonadiabatic corrections
 - relativistic corrections for light molecular systems
- In this talk, we shall consider such relativistic corrections, in three parts:
 - first, we review the techniques for highly accurate nonrelativistic calculations
 - next, we consider the calculation and magnitude of relativistic corrections
 - finally, we investigate how and when such corrections need to be included
- Central question: **When have we exhausted the Schrödinger equation?**

The two-dimensional chart of nonrelativistic quantum chemistry

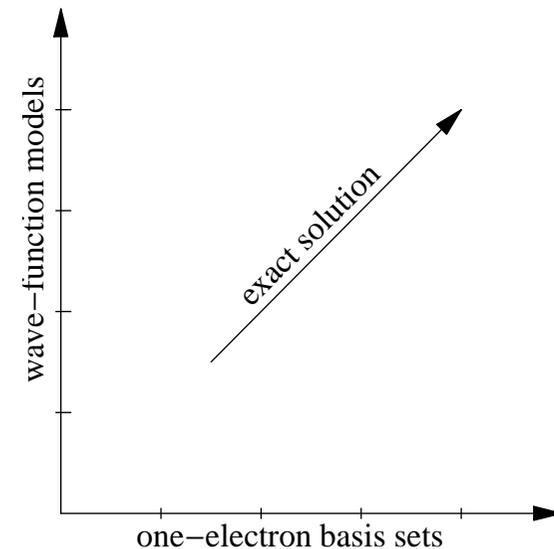
- The quality of nonrelativistic molecular electronic-structure calculations is determined by the description of
 1. the N -electron space (wave-function model),
 2. the one-electron space (basis set).
- In each space, there is a hierarchy of levels of increasing complexity:

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

HF, CCSD, CCSDT, CCSDTQ, ...

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

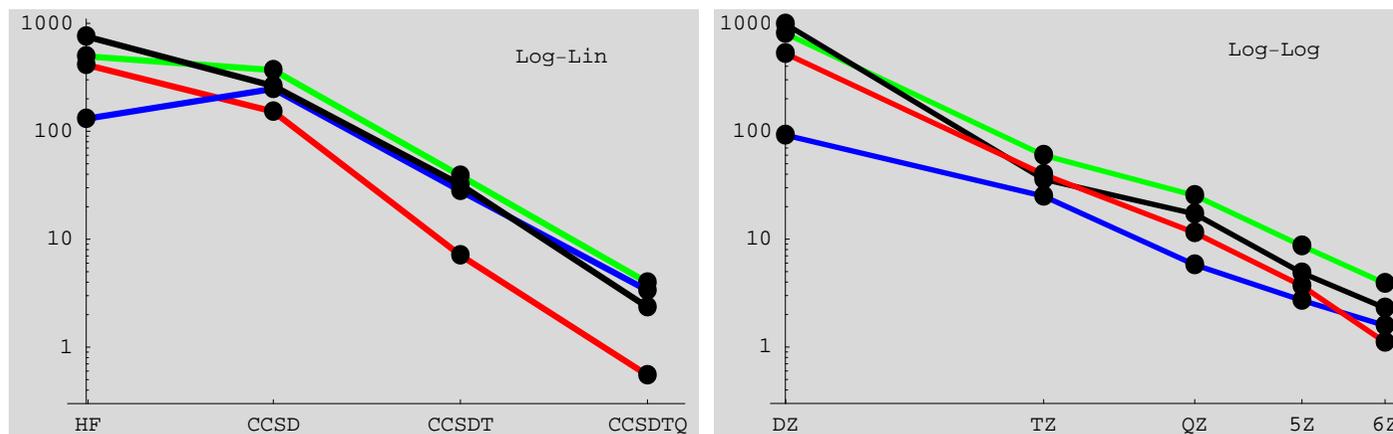
DZ, TZ, QZ, 5Z, 6Z, ...



- 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**, **N₂**, **F₂**, 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

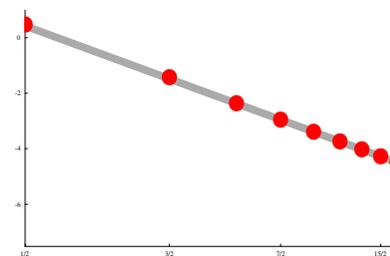
The principal expansion and correlation-consistent basis sets

- 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
	+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!

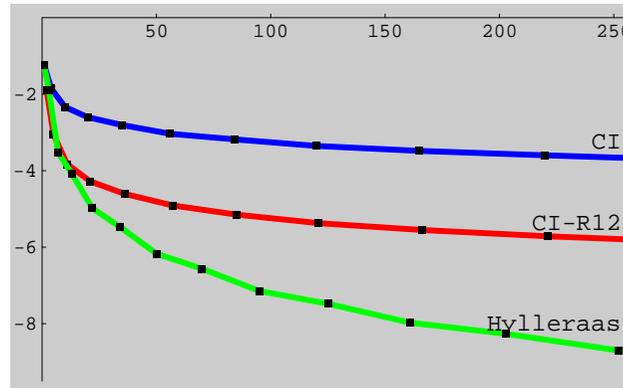
$$1 \text{ minute} \quad \rightarrow \quad 1 \text{ week} \quad \rightarrow \quad 200 \text{ years}$$

Solutions to slow basis-set convergence

1. Use explicitly correlated methods!

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

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



- 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!

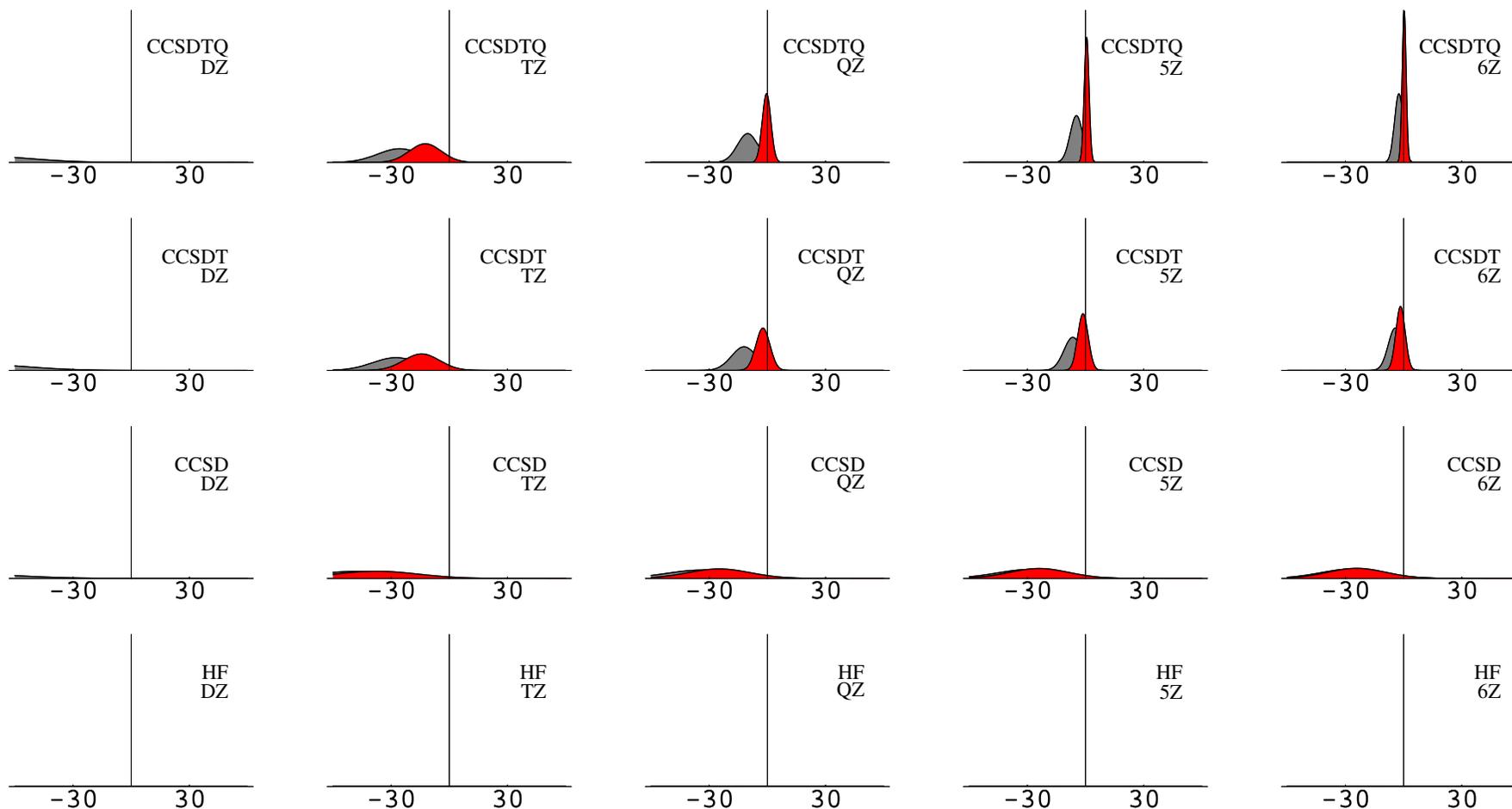
- Exploit the smooth convergence $E_\infty = E_X + AX^{-3}$ to extrapolate to basis-set limit

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

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

Example of an *ab initio* hierarchy: atomization energies (kJ/mol)



Relativistic corrections for light molecular systems

- We have seen how it is possible to approach the **nonrelativistic infinite-basis FCI limit**
 - the coupled-cluster hierarchy (string-based methods, Olsen, Kállay, Hirata)
 - correlation-consistent basis sets, extrapolation, explicitly correlated methods
- For many purposes, the nonrelativistic infinite-basis FCI limit is not sufficient and we must include the **effects of relativity**:
 - for **heavy** molecular systems, relativity plays a **central role**
 - for **light** molecular systems, it comes into play in **high-precision work**
- The important questions are then:
 - how do we calculate relativistic corrections?
 - when do we need to calculate relativistic corrections?
- We shall answer each question in turn:
 - the Coulomb–Pauli and Breit–Pauli operators
 - atomization energies, vibrational frequencies, and bond lengths
- Tarczay, Császár, Klopper, and Quiney: *Mol. Phys.* **21**, 1769–1794 (2001):
“Anatomy of relativistic energy corrections in light molecular systems”

Relativistic calculations

- In a fully relativistic (four-component) treatment of molecular electronic systems, the Dirac–Coulomb operator is frequently used

$$\hat{H}^{\text{DC}} = \sum_i (c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + V_i + \beta_i c^2) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \quad \text{Dirac–Coulomb}$$

- Typical relativistic contributions for light molecular systems:

	HF	corr.	rel.
total electronic energies	99.5%	0.5%	0.05%
atomization energies	65%	35%	0.3%

- Clearly, for light systems, a perturbation treatment is called for
 - to first order in perturbation theory, the relativistic correction scales as $Z^4\alpha^2$
 - the fine-structure constant $\alpha \approx 1/137$
 - a first-order treatment is usually sufficient (Davidson *et al.* 1981)
- The four-component \hat{H}^{DC} cannot be used directly with nonrelativistic wave functions:
 - a standard approach is to reduce \hat{H}^{DC} to a two-component Pauli-type operator
 - direct perturbation theory (DPT) of Rutkowski, Kutzelnigg and coworkers

The Coulomb–Pauli Hamiltonian

- Reduction of the Dirac–Coulomb operator yields the Coulomb–Pauli Hamiltonian

$$\hat{H}^{\text{DC}} \rightarrow \hat{H}^{\text{CP}} = \hat{H}^{\text{NR}} + \hat{H}^{\text{MV}} + \hat{H}^{\text{D}} + \hat{H}^{\text{SO}}$$

- The **mass-velocity operator** corrects the kinetic energy for relativistic mass variation:

$$\hat{H}^{\text{MV}} = -\frac{\alpha^2}{8} \sum_i p_i^4 \quad \text{singlet scalar}$$

– responsible for the main first-order (negative) relativistic energy correction

- The **Darwin operator** corrects the potential energy for electron charge smearing:

$$\hat{H}^{\text{D}} = \frac{\pi\alpha^2}{2} \sum_{i,K} Z_K \delta(r_{iK}) - \frac{\pi\alpha^2}{2} \sum_{i \neq j} \delta(r_{ij}) \quad \text{singlet scalar}$$

– reduces all Coulomb interactions, partly cancelling the MV correction

- The **spin–orbit operator** couples the spin of an electron to its orbital motion in the presence of the nuclei and other electrons:

$$\hat{H}^{\text{SO}} = \frac{\alpha^2}{4} \sum_{i,K} \boldsymbol{\sigma}_i \cdot \frac{Z_K \mathbf{r}_{iK}}{r_{iK}^3} \times \mathbf{p}_i - \frac{\alpha^2}{4} \sum_{i \neq j} \boldsymbol{\sigma}_i \cdot \frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_i \quad \text{triplet nonscalar}$$

– to first order, it contributes only to open-shell systems

Example: Coulomb–Pauli corrections to the electronic energies of H₂O and H₂S (mE_h)

	H ₂ O		H ₂ S	
	RHF	CCSD(T)	RHF	CCSD(T)
mass–velocity (MV)	–251.5	–251.9	–4549.0	–4550.9
+ one-electron Darwin (D1)	199.9	199.9	3473.6	3473.6
= Cowan–Griffin (MVD1)	–51.6	–52.0	–1075.4	–1077.3
+ two-electron Darwin (D2)	–3.4	–3.1	–34.1	–33.0
= Coulomb–Pauli	–55.0	–55.1	–1109.5	–1110.3

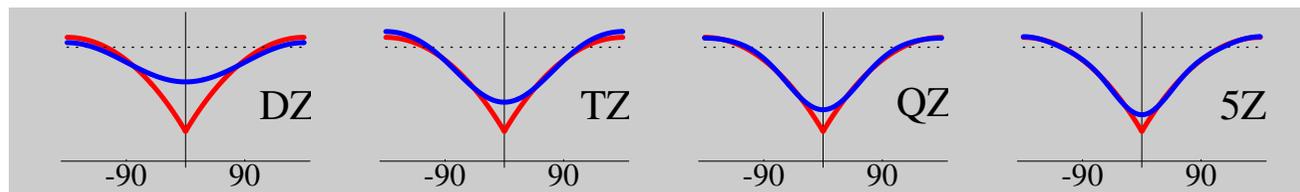
- The first-order energy is dominated by the **MVD1 correction** (Cowan & Griffin, 1976)
 - a dominant negative mass-velocity correction
 - a slightly smaller, positive one-electron Darwin correction
- The MVD1 term appears to **underestimate** the relativistic correction (by 6% and 3%)
 - the **two-electron Darwin correction** is an order of magnitude smaller
 - the one- and two-electron contributions scale as $Z^4\alpha^2$ and $Z^3\alpha^2$, respectively
- **Electron correlation** increases the CP correction by 0.2% in H₂O and 0.1% in H₂S.

Coulomb–Pauli basis-set convergence

- The two-electron Darwin operator contributes only when two electron coincide:

$$\hat{H}^{\text{D2}} = -\frac{\pi\alpha^2}{2} \sum_{i \neq j} \delta(r_{ij})$$

- its expectation value converges slowly (Salomonsen and Öster, 1989)



- in the principal expansion, the error is inversely proportional to the cardinal number:

$$\langle \infty | \hat{H}^{\text{D2}} | \infty \rangle = \langle X | \hat{H}^{\text{D2}} | X \rangle + AX^{-1}$$

- convergence of correlation contribution in H_2 with and without extrapolation (μE_h):

RHF	corr.	total	DZ	TZ	QZ	5Z	6Z
-7.8	4.4	-2.8	2.8	3.5	3.7	3.9	4.0
				4.9	4.5	4.5	4.5

- The MV energy converges in the same manner but with a small correlation contribution.
- The one-electron Darwin operator presents few problems with respect to convergence.

The Breit–Pauli Hamiltonian

- At least a formal problem with the CP approach is that \hat{H}^{DC} is **not Lorentz invariant**
 - a lowest-order correction to the Coulomb interaction operator yields

$$\hat{H}^{\text{DB}} = \hat{H}^{\text{DC}} - \frac{1}{4} \sum_{i \neq j} \frac{r_{ij}^2 \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot \boldsymbol{\alpha}_j}{r_{ij}^3} \quad \text{Dirac–Breit}$$

- Reduction of the Dirac–Breit Hamiltonian now yields the **Breit–Pauli (BP) operator**

$$\hat{H}^{\text{BP}} = \hat{H}^{\text{CP}} + \hat{H}^{\text{SoO}} + \hat{H}^{\text{OO}} + \hat{H}^{\text{SS}}$$

with the following new α^2 two-electron terms added to the CP operator:

$$\hat{H}^{\text{SoO}} = \frac{\alpha^2}{2} \sum_{i \neq j} \frac{\boldsymbol{\sigma}_i \cdot \mathbf{r}_{ij} \times \mathbf{p}_j}{r_{ij}^3} \quad \text{spin–other–orbit}$$

$$\hat{H}^{\text{SS}} = \frac{\alpha^2}{8} \sum_{i \neq j} \left[\frac{r_{ij}^2 \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j - 3 \boldsymbol{\sigma}_i \cdot \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot \boldsymbol{\sigma}_j}{r_{ij}^5} - \frac{8\pi}{3} \delta(r_{ij}) \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \right] \quad \text{spin–spin}$$

$$\hat{H}^{\text{OO}} = -\frac{\alpha^2}{4} \sum_{i \neq j} \frac{r_{ij}^2 \mathbf{p}_i \cdot \mathbf{p}_j + \mathbf{p}_i \cdot \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot \mathbf{p}_j}{r_{ij}^3} \quad \text{orbit–orbit}$$

- Unlike the CP operator, the BP operator is complete to order α^2 in perturbation theory.

Example: Breit–Pauli corrections to the electronic energies of H₂O and H₂S (mE_h)

- Do we need to worry about the Breit corrections?

	CCSD(T)	H ₂ O	H ₂ S
	MVD1	−52.0	−1077.3
+	D2	−3.1	−33.0
+	spin–spin	6.3	66.0
+	orbit–orbit	0.5	17.8
=	Breit–Pauli	−48.3	−1026.5

- The Breit terms reverse the sign of the two-electron relativistic correction:
 - the **spin–spin** correction is easy since $\langle cs | \hat{H}^{SS} | cs \rangle = -2 \langle cs | \hat{H}^{D2} | cs \rangle$
 - the **orbit–orbit** correction is smaller and more difficult
 - the **spin–orbit** correction vanishes for closed shells
- The **MVD1** correction now **overestimates** the correction by 8% in H₂O and 5% in H₂S.
- The **Lamb shift** contributes to order $Z^4 \alpha^3$ (Pyykkö *et al.* 2001)
 - comparable with the BP two-electron terms, which scale as $Z^2 \alpha^2$

Overview

- We have examined the **convergence of nonrelativistic calculations**:
 - excitation-level convergence is linear
 - basis-set convergence is slow, with an error X^{-3}
- We have examined the **first-order relativistic corrections**:
 - the two-electron interactions contribute less than 10%
 - electron correlation contributes less than 1%
- We shall now **compare the nonrelativistic and relativistic contributions**:
 - when do we need to include relativistic corrections?
 - at what level must these corrections be calculated?
- We shall consider **the following properties**:
 - atomization energies
 - harmonic frequencies
 - bond distances

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 ₂ O	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

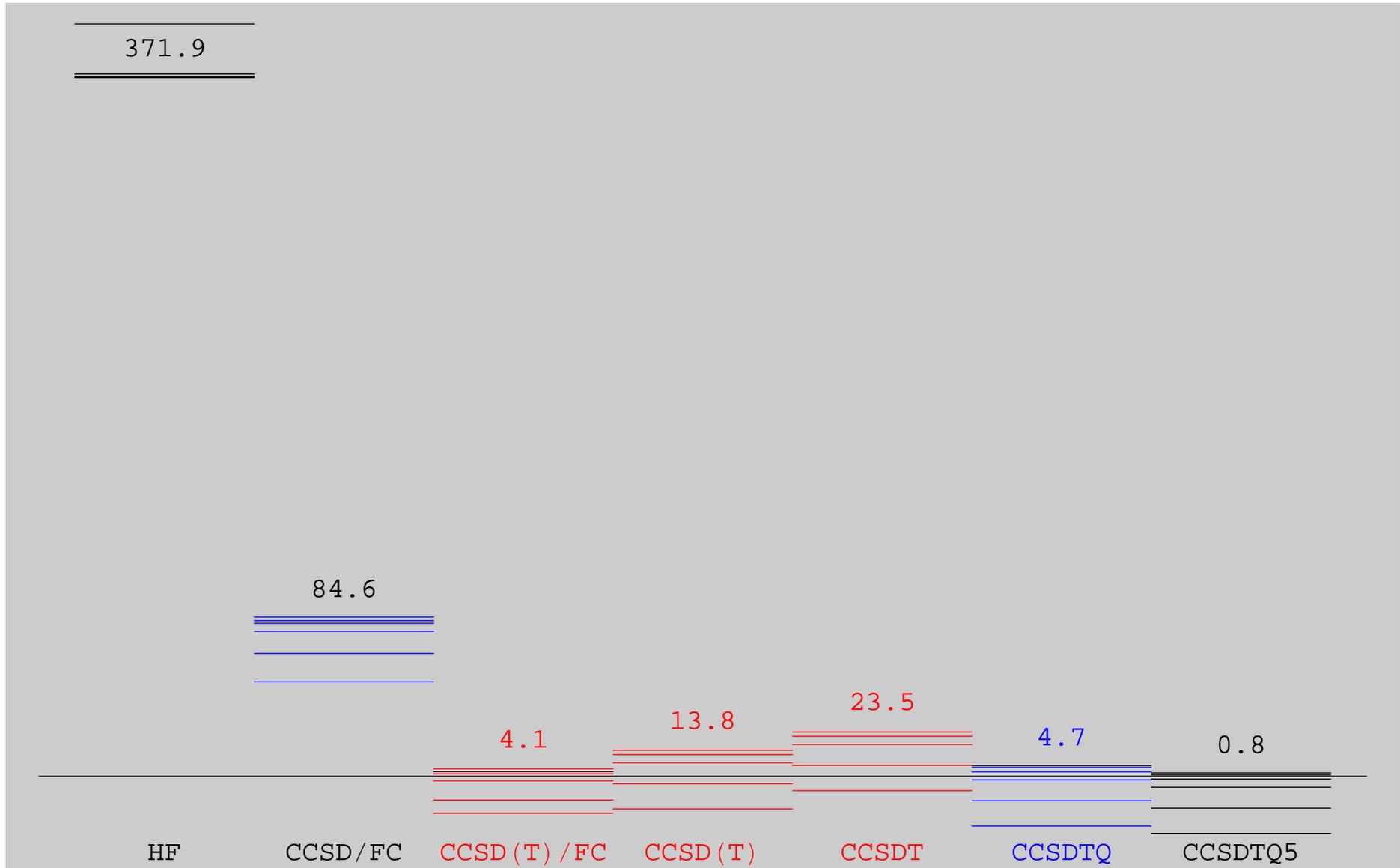
- agreement with experiment in all cases except for N₂
- all purely electronic contributions are positive (except Hartree–Fock for F₂)
 - very large correlation contributions
 - the neglected quintuples contribute a few tenths of 1 kJ/mol
- relativistic corrections are small ($\approx 0.5\%$) but needed for agreement with experiment
 - nearly cancel quadruples contributions
 - MVD1 is sufficient at the CCSDTQ level of theory
- vibrational corrections are substantial
 - similar to triples contributions but oppositely directed

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

	RHF	SD	T	Q	5	rel.	adia.	theory	exp.	err.
HF	4473.8	-277.4	-50.2	-4.1	-0.1	-3.5	0.4	4138.9	4138.3	0.1
N ₂	2730.3	-275.8	-72.4	-18.8	-3.9	-1.4	0.0	2358.0	2358.6	-0.6
F ₂	1266.9	-236.1	-95.3	-15.3	-0.8	-0.5	0.0	918.9	916.6	2.3
CO	2426.7	-177.4	-71.7	-7.2	0.0	-1.3	0.0	2169.1	2169.8	0.7

- agreement with experiment to within 1 cm^{-1} except for F₂
- Hartree–Fock theory overestimates harmonic frequencies by up to 38% (in F₂).
- 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
 - two-electron terms may be needed for CCSDTQ5 wave functions

Higher-order connected contributions to ω_e in N_2



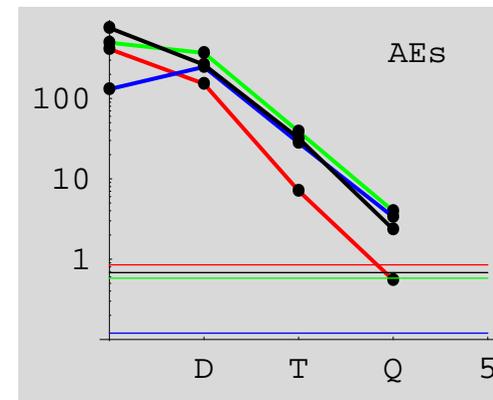
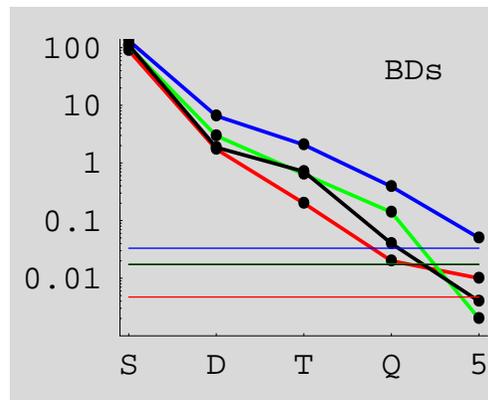
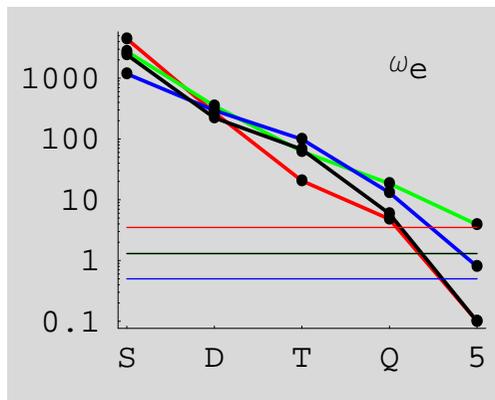
Contributions to equilibrium bond distances (pm)

	RHF	SD	T	Q	5	rel.	adia.	theory	exp.	err.
HF	89.70	1.67	0.29	0.02	0.00	0.01	0.0	91.69	91.69	0.00
N ₂	106.54	2.40	0.67	0.14	0.03	0.00	0.0	109.78	109.77	0.01
F ₂	132.64	6.04	2.02	0.44	0.03	0.05	0.0	141.22	141.27	-0.05
CO	110.18	1.87	0.75	0.04	0.00	0.00	0.0	112.84	112.84	0.00

- agreement with experiment to within 0.01 pm except for F₂
- Hartree–Fock theory underestimates bond distances by up to 8.6 pm (for F₂)
- all correlation contributions are positive
 - approximate linear convergence, slowest for F₂
 - 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 F₂ (0.05 pm)
 - of the same magnitude and direction as the quintuples
 - MVD1 sufficient at the CCSDTQ5 level

Conclusions

- Excitation-level convergence is approximately linear:
 - errors are reduced by several factors at each new excitation level
- Basis-set convergence is much slower:
 - the basis-set error is proportional to X^{-3} or N^{-1}
 - basis-set extrapolation or explicitly correlated methods are necessary
- Inclusion of relativistic corrections is necessary in high-precision work:
 - the Schrödinger equation is exhausted beyond connected quadruples
 - for light systems, the uncorrelated MVD1 correction is usually sufficient
 - two-electron terms may be needed beyond CCSDTQ
- Log plots of contributions to frequencies, bond lengths, and atomization energies:



- HF (red), N₂ (green), F₂ (blue), and CO (black); relativity straight lines