

Relativistic corrections in highly accurate calculations  
on small molecular systems

T. Helgaker

Centre for Theoretical and Computational Chemistry,  
Department of Chemistry, University of Oslo, Norway

A. C. Hennum and T. Ruden, University of Oslo, Norway

S. Coriani, University of Trieste, Italy

W. Klopper, University of Karlsruhe, Germany

P. Jørgensen and J. Olsen, University of Aarhus, Denmark

Relativistic Effects in Heavy Elements (REHE) 2007

Domaine Saint-Jacques, Ottrott, France

March 21–25, 2007

Software

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

## Highly accurate 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

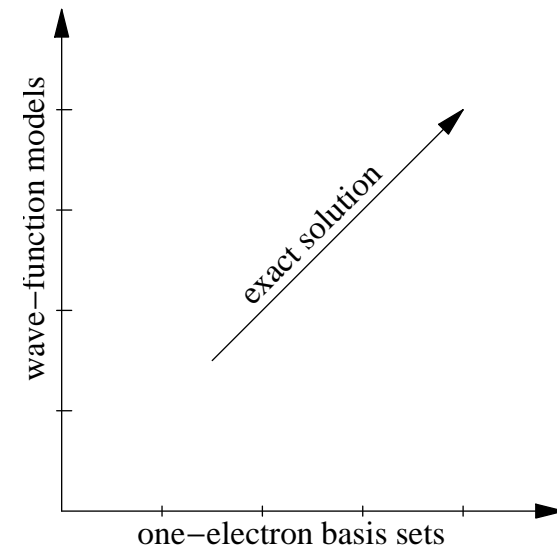
- The quality of nonrelativistic molecular electronic-structure calculations is determined by the description of
  1. the  $N$ -electron space (wave-function model),
  2. the one-electron space (basis set).
- In each space, there is a hierarchy of levels of increasing complexity:

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

HF, CCSD, CCSDT, CCSDTQ, ...

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

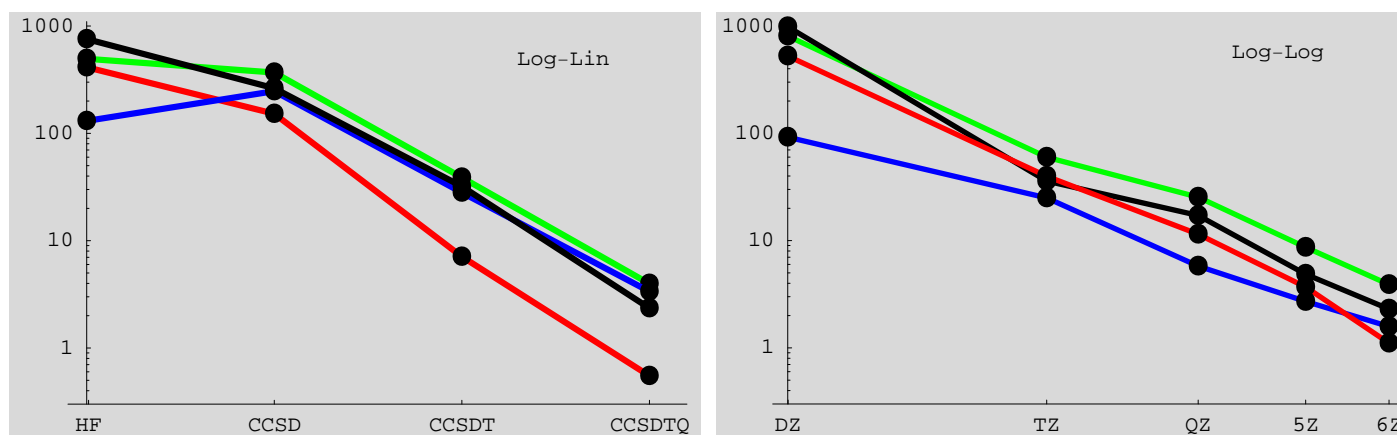
DZ, TZ, QZ, 5Z, 6Z, ...



- 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**, **N<sub>2</sub>**, **F<sub>2</sub>**, 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 basis-set extrapolation

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

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

- **the principal expansion**: include all  $n^2$  AOs of the same shell simultaneously

- We may now estimate the exact energy from a calculation truncated at  $n = X$ :

$$E_\infty = E_X + A \sum_{n=X+1}^{\infty} n^2 n^{-6} \approx E_X + AX^{-3}$$

- to eliminate  $A$ , carry out a smaller calculation truncated at  $Y = X - 1$ :

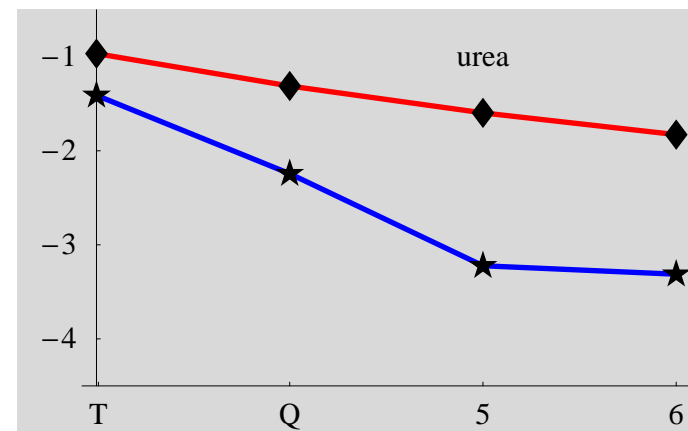
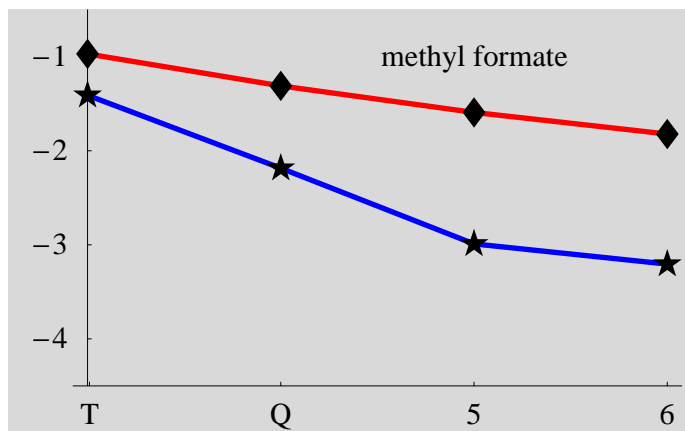
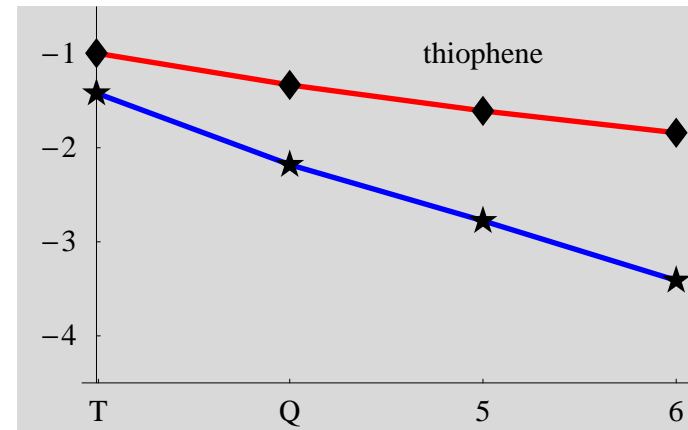
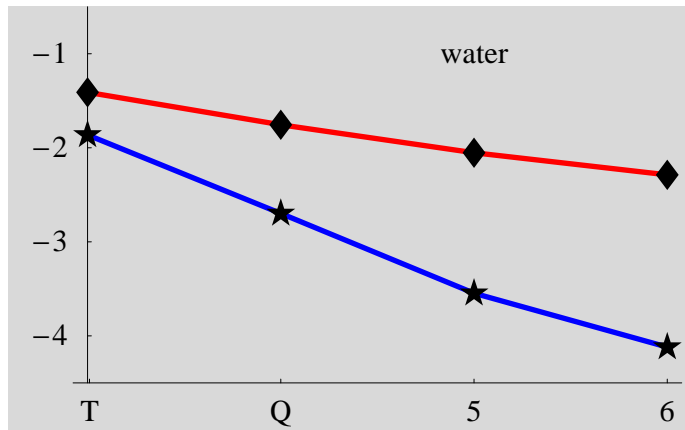
$$E_\infty = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3} \quad \leftarrow \text{two-point (Richardson) extrapolation}$$

- Finally, we identify  $X$  with the cardinal number of Dunning's cc-pVXZ basis sets
  - mean absolute errors of the CH<sub>2</sub>, H<sub>2</sub>O, HF, N<sub>2</sub>, CO, Ne, and F<sub>2</sub> energies:

$mE_h$	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	

## Extrapolation

- Logarithmic errors in **plain** and **extrapolated** energies relative to explicit correlation



– from Klopper, Manby, Ten-no and Valeev, *Int. Rev. Phys. Chem.* **25**, 427 (2006)

## Explicitly correlated methods

- Basis-set convergence improved by including  $r_{12}$  in the wave function
  - pair function of second-order Møller–Plesset (MP2) theory:

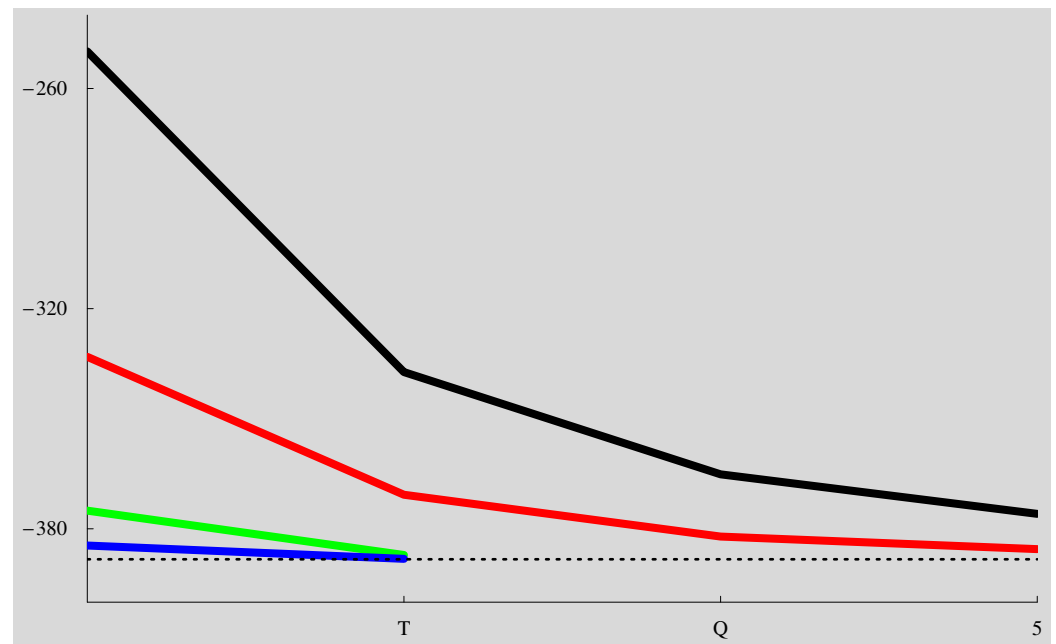
$$u_{ij}(1,2) = \sum_{ab} c_{ij}^{ab} \underbrace{\det |\phi_a(1)\phi_b(2)|}_{\text{orbital part}} + \sum_{pq} \sum_v c_{ij}^{pq,v} \underbrace{\exp(-\gamma_v r_{12}^2) \det |\phi_p(1)\phi_q(2)|}_{\text{geminal part}}$$

- Convergence of the neon atom in the aug-cc-CVXZ basis sets

– four sets of MP2 calculations:

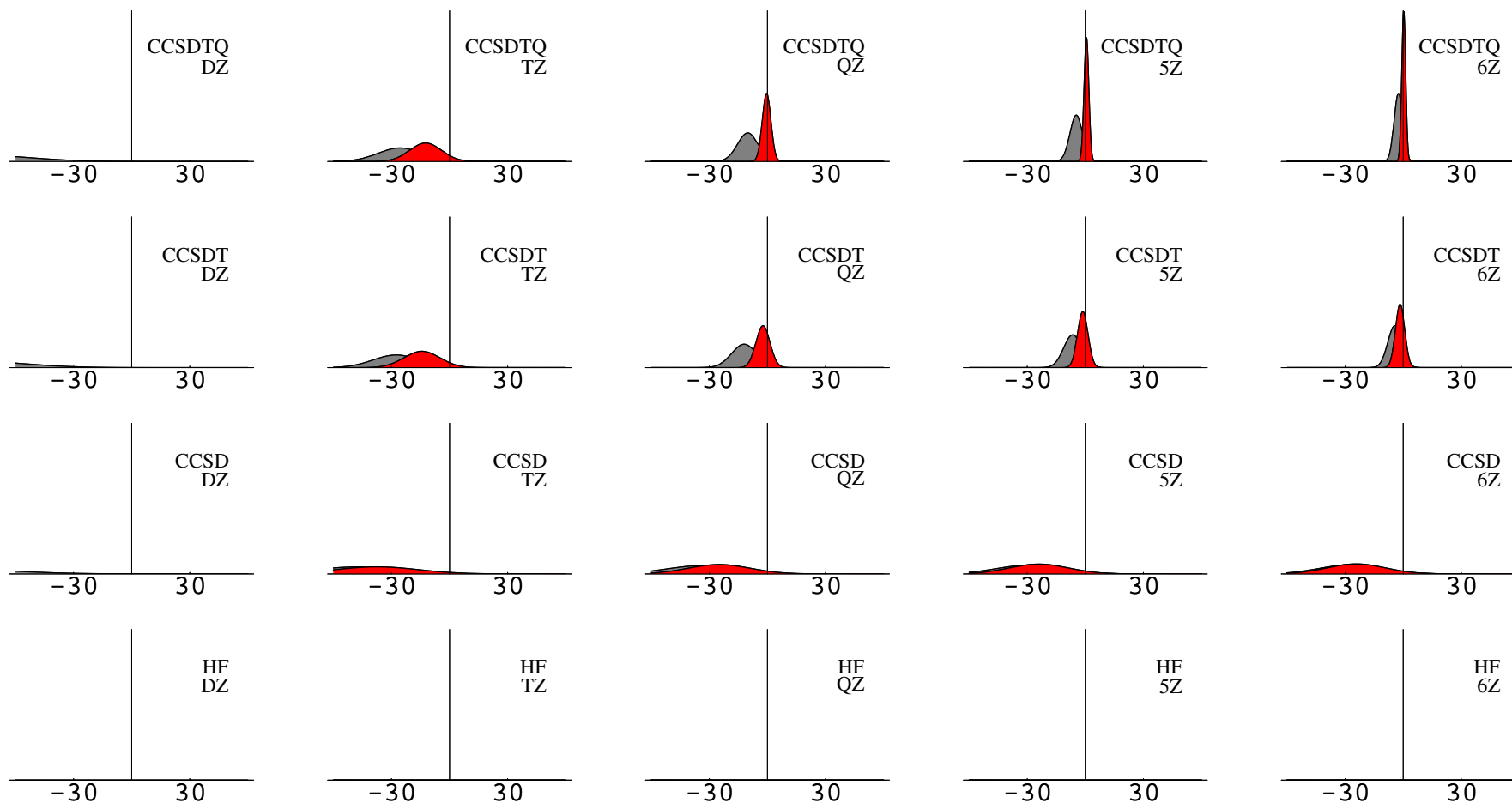
- \* no geminals
- \* **only doubly-occupied geminals**
- \* **also singly-excited geminals**
- \* **also doubly-excited geminals**

– normally, only doubly-occupied geminals are used



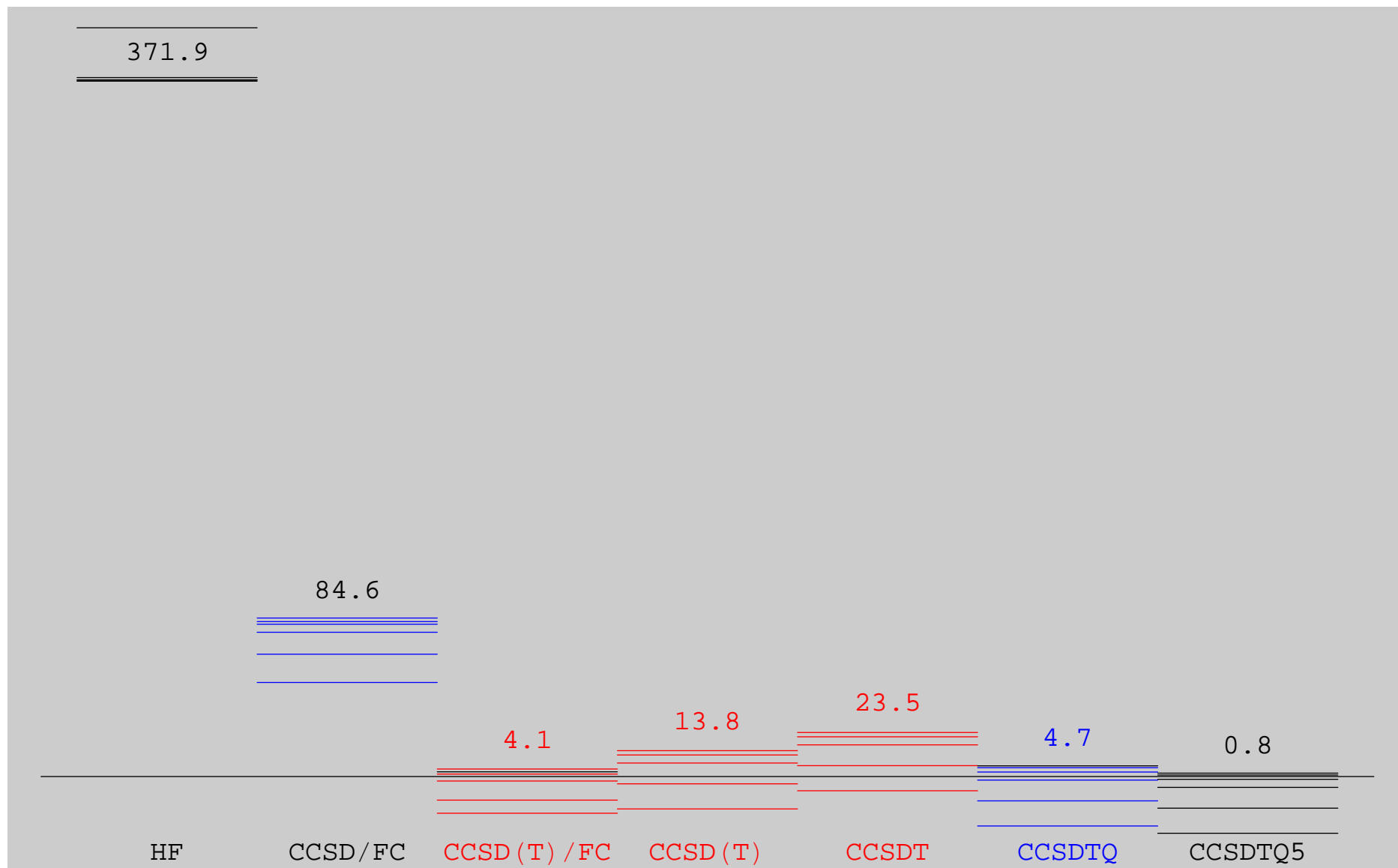
- We use CCSD-R12 (Noga, Kutzelnigg, and Klopper, 1992) for benchmarking

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





# Convergence to $\omega_e$ in $N_2$



## 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-accuracy 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  $Z^4\alpha^2$
  - a first-order treatment is usually sufficient (Davidson *et al.* 1981)
- The four-component  $\hat{H}^{\text{DC}}$  cannot be used directly with nonrelativistic wave functions:
  - a standard approach is to reduce  $\hat{H}^{\text{DC}}$  to a two-component Pauli-type operator
  - direct perturbation theory (DPT) of Rutkowski, Kutzelnigg and coworkers
  - Helgaker, Hennum and Klopper, JCP **125**, 024102 (2006)

## 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 canceling 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 H<sub>2</sub>O and H<sub>2</sub>S ( $mE_h$ )

	H <sub>2</sub> O		H <sub>2</sub> 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
= <b>Cowan–Griffin (MVD1)</b>	–51.6	–52.0	–1075.4	–1077.3
+ two-electron Darwin (D2)	–3.4	–3.1	–34.1	–33.0
= <b>Coulomb–Pauli</b>	–55.0	–55.1	–1109.5	–1110.3

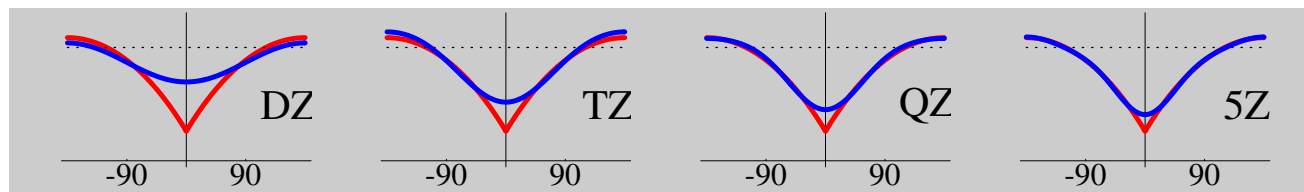
- The first-order energy is dominated by the **MVD1 correction** (Cowan & Griffin, 1976)
  - a dominant negative mass-velocity correction
  - a slightly smaller, positive one-electron Darwin correction
- The MVD1 term appears to **underestimate** the relativistic correction (by 6% and 3%)
  - the **two-electron 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 H<sub>2</sub>O and 0.1% in H<sub>2</sub>S.

## 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  $\text{H}_2$  with and without extrapolation ( $\mu E_h$ ):

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  $\hat{H}^{\text{DC}}$  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  $\alpha^2$  two-electron terms added to the CP operator:

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

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

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

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

Example: Breit–Pauli corrections to the electronic energies of H<sub>2</sub>O and H<sub>2</sub>S (mE<sub>h</sub>)

- Do we need to worry about the Breit corrections?

CCSD(T)		H <sub>2</sub> O	H <sub>2</sub> 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 to evaluate
  - the **spin–orbit** correction vanishes for closed shells
- The **MVD1** correction now **overestimates** the correction by 8% in H<sub>2</sub>O and 5% in H<sub>2</sub>S.
- The **Lamb shift** contributes to order  $Z^4 \alpha^3$  (Pyykkö *et al.* 2001)
  - comparable with the BP two-electron terms, which scale as  $Z^3 \alpha^2$



## Overview

- We have examined the **convergence of nonrelativistic calculations**:
  - excitation-level convergence is linear
  - basis-set convergence is slow, with a truncation error  $X^{-3}$
- We have examined the **first order relativistic corrections** to light systems:
  - about 0.05% of the total energy, about one tenth of the correlation energy
  - the relativistic corrections are dominated by one-electron interactions
    - \* 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
  - bond distances
  - bond distances

## Contributions to atomization energies (kJ/mol)

	RHF	SD	T	Q	rel.	vib.	total	experiment	error
CH <sub>2</sub>	531.1	218.3	9.5	0.4	-0.7	-43.2	715.4	714.8±1.8	0.6
H <sub>2</sub> 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 <sub>2</sub>	482.9	426.0	42.4	3.9	-0.6	-14.1	940.6	941.6±0.2	-1.1
F <sub>2</sub>	-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

- We have agreement with experiment in all cases except for N<sub>2</sub>
- All purely electronic contributions are positive (except Hartree–Fock for F<sub>2</sub>)
  - 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 $\omega_e$ ( $\text{cm}^{-1}$ )

	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 <sub>2</sub>	2730.3	-275.8	-72.4	-18.8	-3.9	-1.4	0.0	2358.0	2358.6	-0.6
F <sub>2</sub>	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

- We agree with experiment to within  $1 \text{ cm}^{-1}$  except for F<sub>2</sub>
- Hartree–Fock theory overestimates harmonic frequencies by up to 38% (in F<sub>2</sub>).
- All correlation contributions are large and negative
  - triples contribute up to  $95 \text{ cm}^{-1}$ , quadruples  $20 \text{ cm}^{-1}$ , and quintuples  $4 \text{ cm}^{-1}$
  - sextuples are sometimes needed for convergence to within  $1 \text{ cm}^{-1}$
- Relativistic corrections are of the order of  $1 \text{ cm}^{-1}$ 
  - of the same magnitude and direction as the quadruples or quintuples
  - two-electron terms may be needed for CCSDTQ5 wave functions

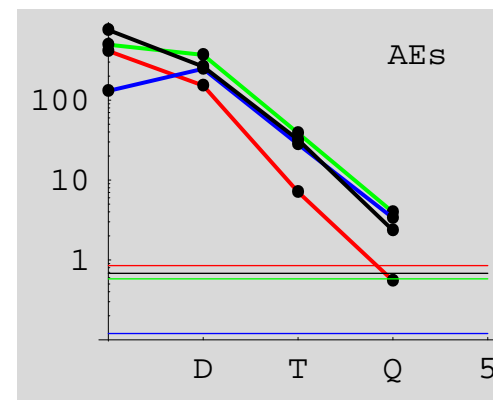
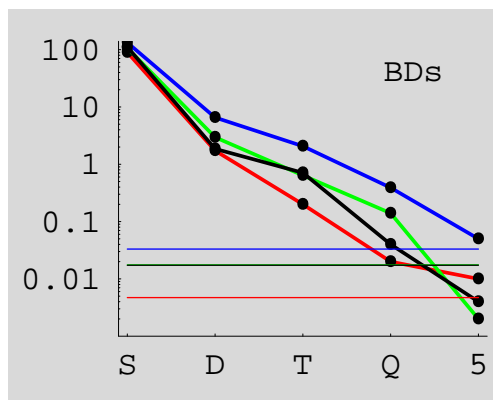
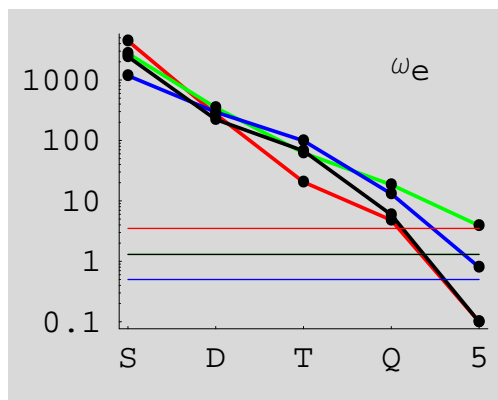
## Contributions to equilibrium bond distances (pm)

	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 <sub>2</sub>	106.54	2.40	0.67	0.14	0.03	0.00	0.0	109.78	109.77	0.01
F <sub>2</sub>	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

- The agreement with experiment is very good (to within 0.01 pm except for F<sub>2</sub>)
- Hartree–Fock theory underestimates bond distances by up to 8.6 pm (for F<sub>2</sub>)
- All correlation contributions are positive
  - approximate linear convergence, slowest for F<sub>2</sub>
  - 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<sub>2</sub> (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-accuracy 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), N<sub>2</sub> (green), F<sub>2</sub> (blue), and CO (black); relativity straight lines