

The Rigorous Calculation of Molecular Properties to Chemical Accuracy

T. Helgaker, 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

Software

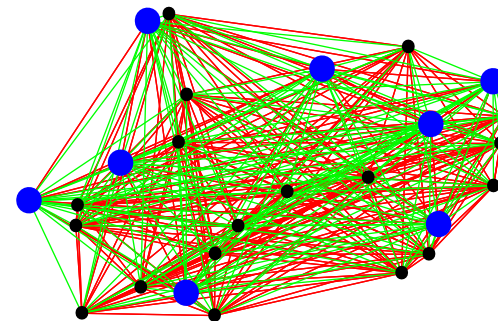
- Dalton (<http://www.kjemi.uio.no/software/dalton>)
 - LUCIA (J. Olsen)
 - ACES II (J. Gauss, J. Stanton, R. Bartlett)

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 four parts:
 1. a preamble on wave-function–based electronic-structure theory
 2. a review of the techniques for highly accurate nonrelativistic calculations
 3. a discussion of the calculation and magnitude of relativistic corrections
 4. a presentation of results: properties calculated with relativistic corrections
- Central question: **When have we exhausted the Schrödinger equation?**

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

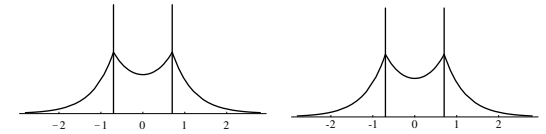
- **electron correlation:**
 - to improve upon the HF model, we must take into account the instantaneous interactions among the electrons
 - in real space, the electrons are constantly being scattered by **collisions**
 - in the orbital picture, these collisions manifest themselves as **excitations** 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

Example: Electron Correlation in H₂

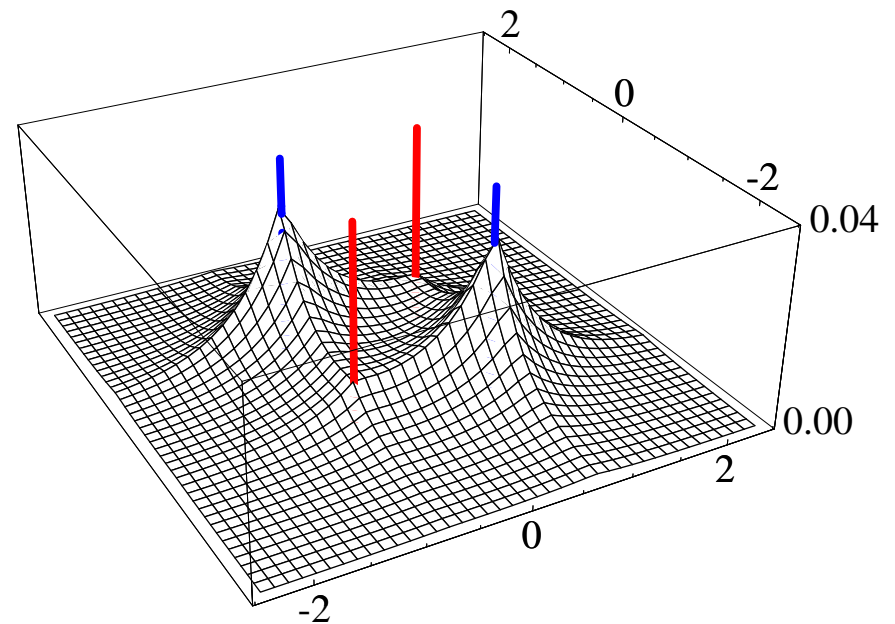
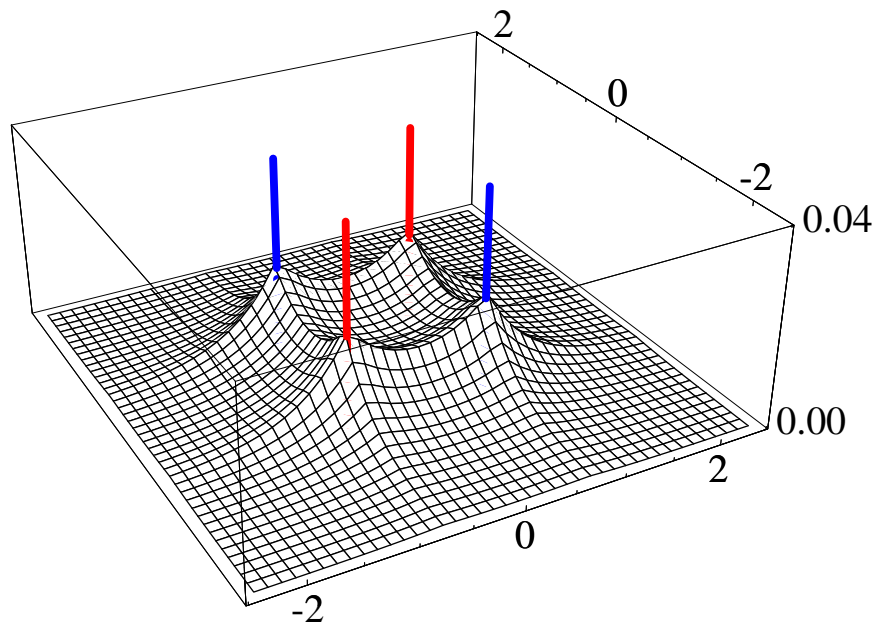
- Consider the effect of a double excitation in H₂:

$$|1\sigma_g^2\rangle \rightarrow (1 + \hat{X}_{gg}^{uu})|1\sigma_g^2\rangle = |1\sigma_g^2\rangle - 0.11|1\sigma_u^2\rangle$$

- The one-electron density $\rho(z)$ is hardly affected:

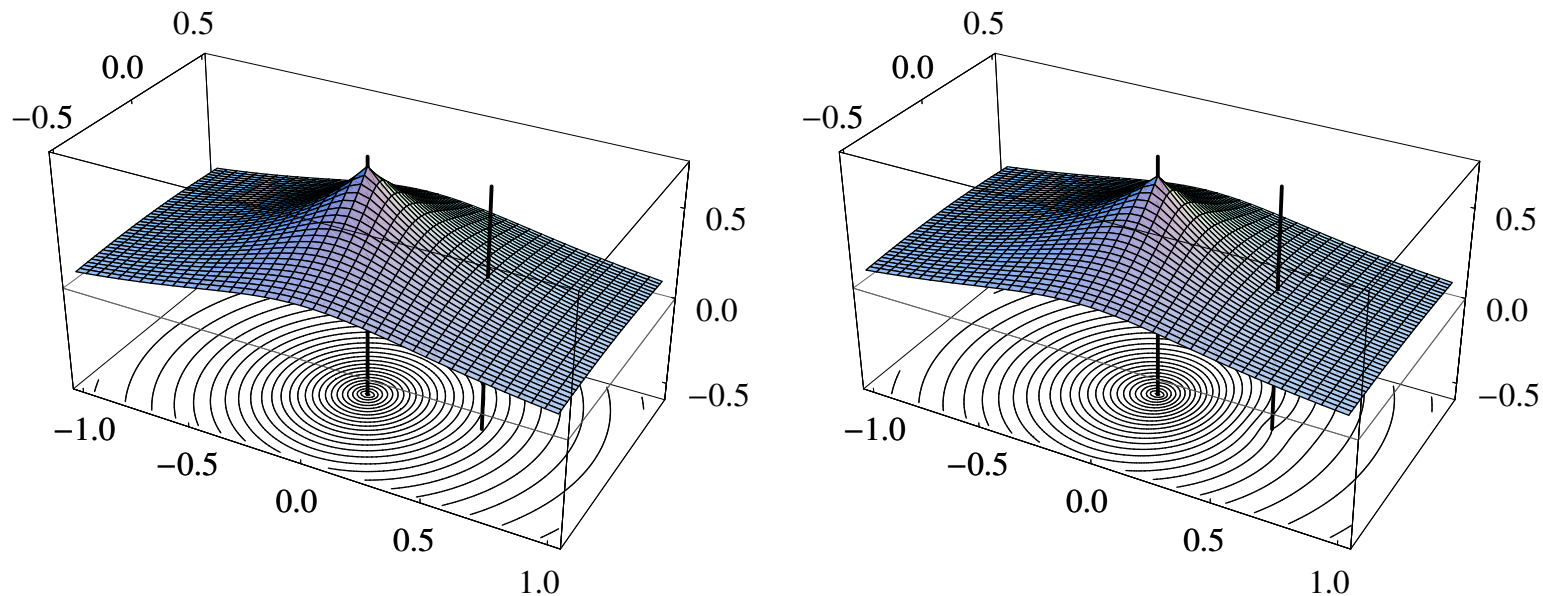


- The two-electron density $\rho(z_1, z_2)$ changes dramatically:



The helium atom

- Consider the wave function of 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 Hartree–Fock wave function is depicted to the left; to the right, we have made similar plot for the exact wave function.



- In the Hartree–Fock model, the contour lines are concentric, reflecting an uncorrelated description.
- In the exact wave function, the electrons see each other and the contour lines are distorted around the second electron.

Basis sets of Gaussian functions

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

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

- 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 two-dimensional chart of nonrelativistic quantum chemistry

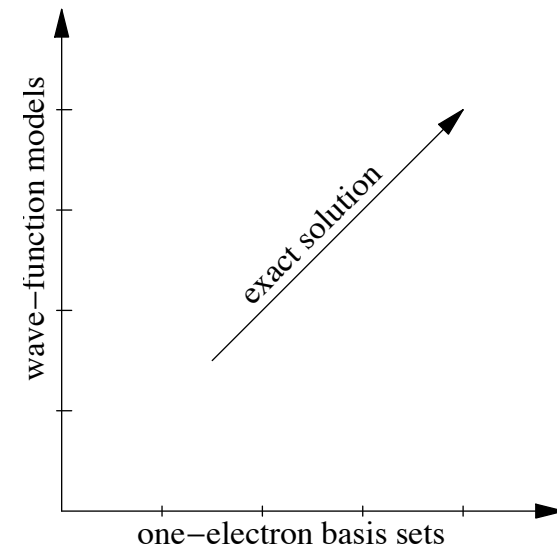
- The quality of nonrelativistic molecular electronic-structure calculations is determined by the description of
 1. the N -electron space (wave-function model),
 2. the one-electron space (basis set).
- In each space, there is a hierarchy of levels of increasing complexity:

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

HF, CCSD, CCSDT, CCSDTQ, ...

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

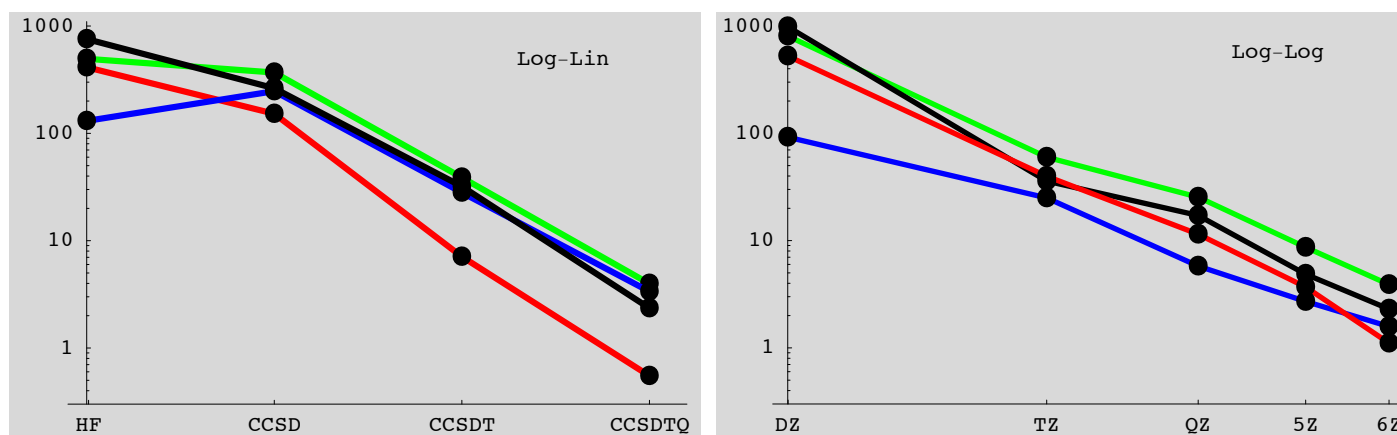
DZ, TZ, QZ, 5Z, 6Z, ...



- 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

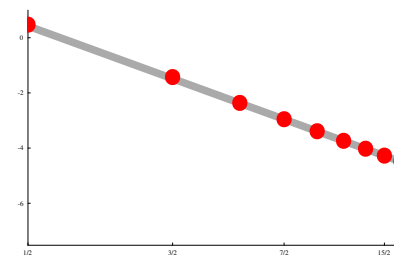
The principal expansion and correlation-consistent basis sets

- 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!

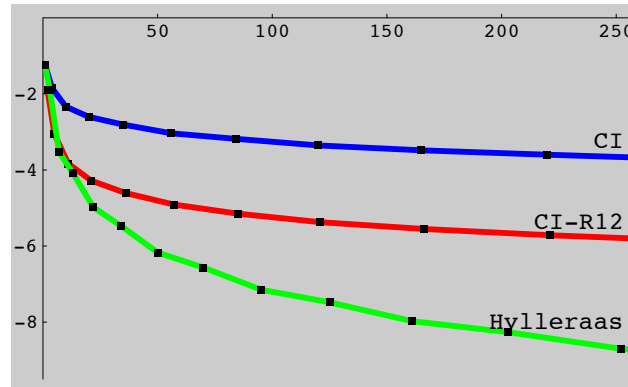
$$1 \text{ minute} \quad \rightarrow \quad 1 \text{ week} \quad \rightarrow \quad 200 \text{ years}$$

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!

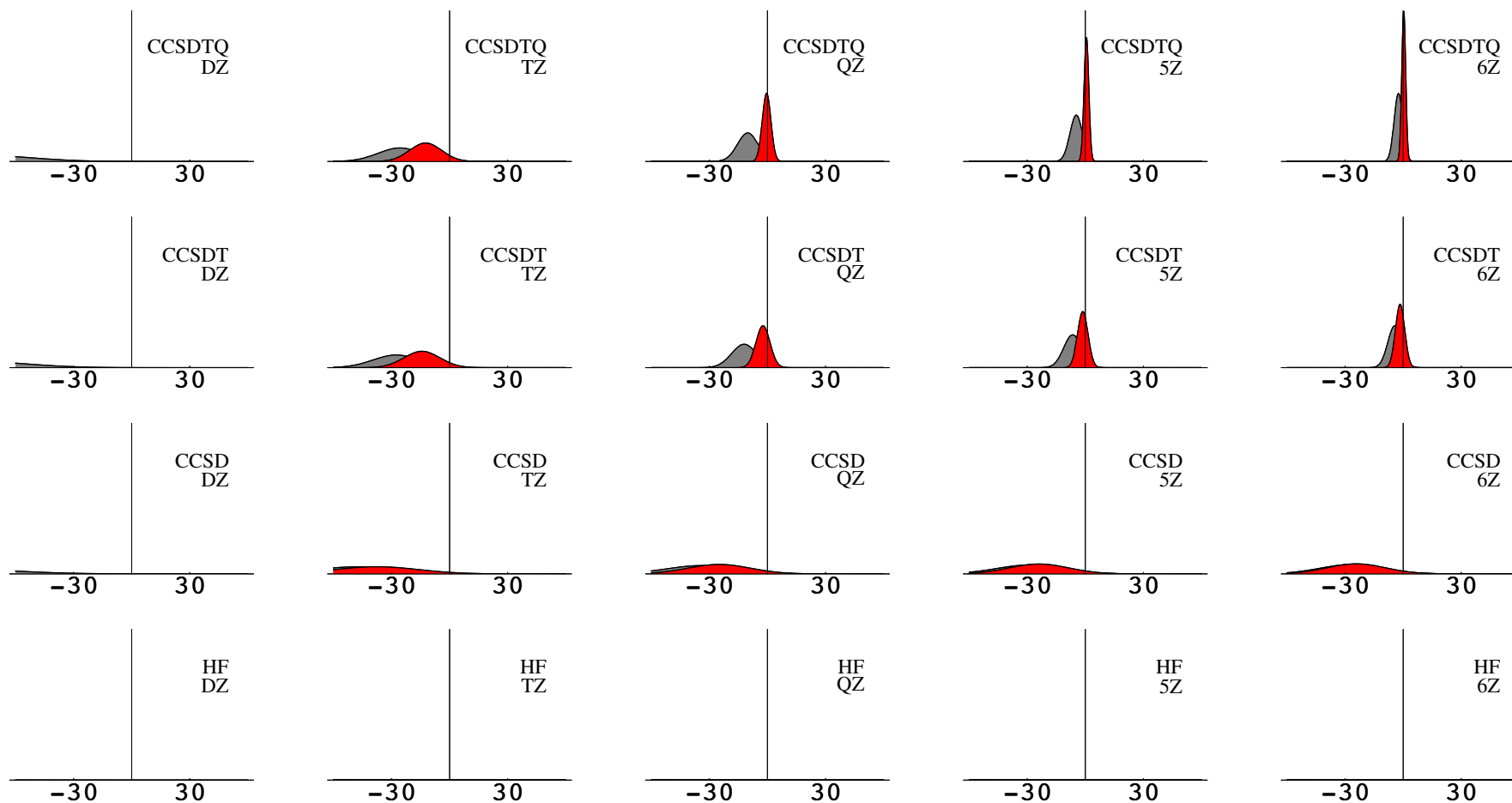
- Exploit the smooth convergence $E_\infty = E_X + AX^{-3}$ to extrapolate to basis-set limit

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

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

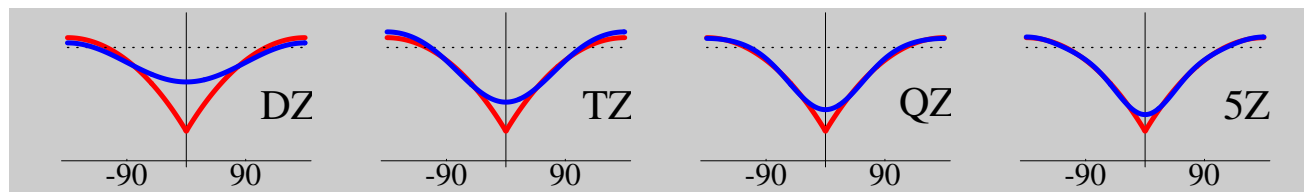
- The first-order energy is dominated by the **MVD1 correction** (Cowan & Griffin, 1976)
 - a dominant negative mass-velocity correction
 - a slightly smaller, positive one-electron Darwin correction
- The MVD1 term appears to **underestimate** the relativistic correction (by 6% and 3%)
 - the **two-electron 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:

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

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

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

- 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

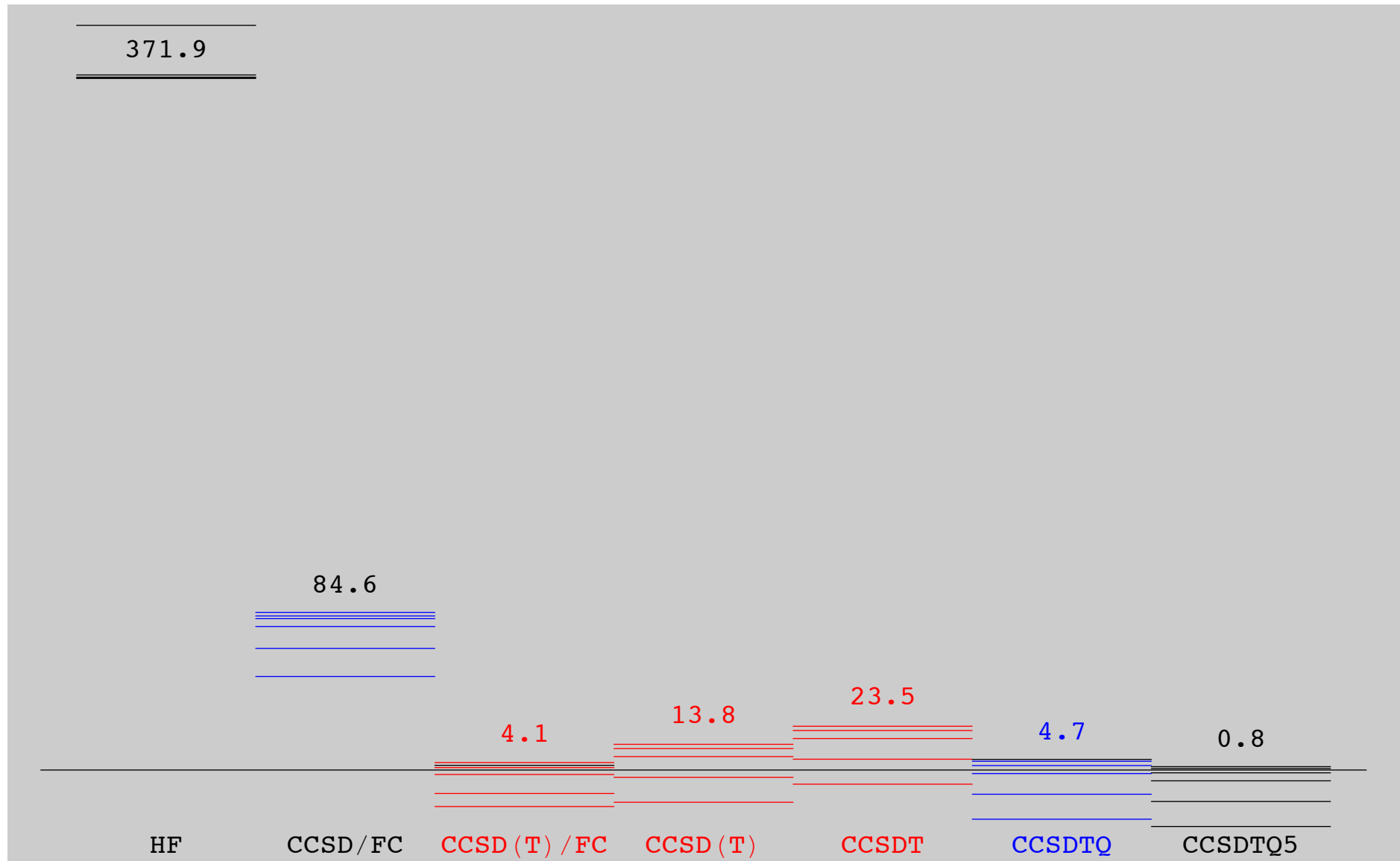
- agreement with experiment in all cases except for N₂
- all purely electronic contributions are positive (except Hartree–Fock for F₂)
 - very large correlation contributions
 - the neglected quintuples contribute a few tenths of 1 kJ/mol
- relativistic corrections are small ($\approx 0.5\%$) but needed 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



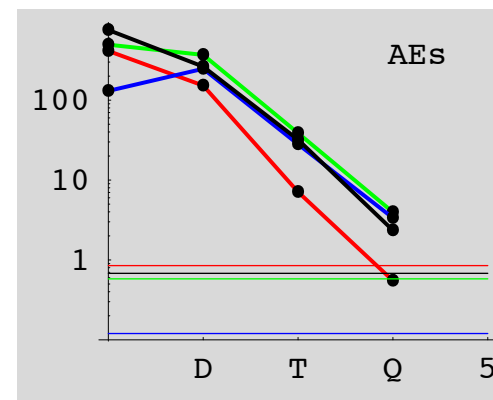
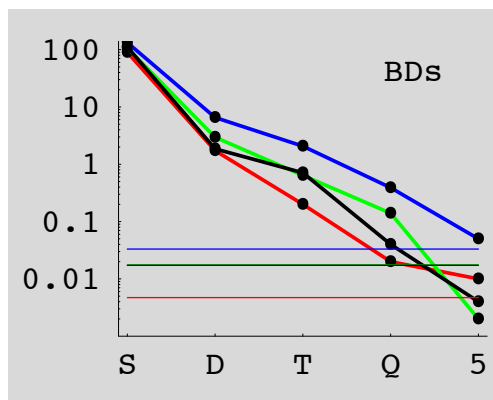
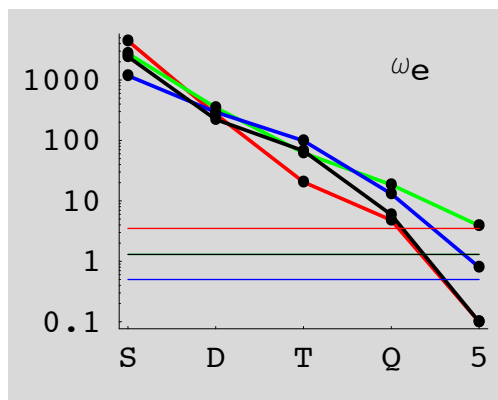
Contributions to equilibrium bond distances (pm)

	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