The Accurate Calculation of Molecular Energies and Properties: A Tour of High-Accuracy Quantum-Chemical Methods

T. Helgaker

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

T. Ruden, University of Oslo, Norway

W. Klopper, University of Karlsruhe, Germany

A. Halkier, K. Bak, P. Jørgensen, J. Olsen, F. Pawlowksi, University of Aarhus, Denmark

School of Chemistry, University of Bristol

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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
  - relatively easy to use by the nonspecialist
- 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
Overview

• The many-electron problem
  – Hartree–Fock theory
  – electron correlation and virtual excitations
  – coupled-cluster theory
  – convergence to the “exact” solution

• Orbital expansions and basis sets
  – electron cusp and the Coulomb hole
  – basis-set convergence
  – basis-set extrapolation
  – explicit correlation

• Practical calculations and error cancellation
  – atomization energies
  – bond distances
  – vibrational frequencies
North Cape: the northernmost point in Europe (71°N 25°E)
North Cape: the sun over the north pole
The many-body problem of quantum chemistry

- All information about the electronic system is contained in the wave function, obtained by solving the Schrödinger equation.

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

P. A. M. Dirac, 1929

- We are thus forced to make approximations—that is, set 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.

- In this manner, we establish hierarchies of approximations—that is, a system of ever more accurate and expensive computational models.
The Hartree–Fock approximation

- 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

- The Hartree–Fock and exact wave functions in helium:

  - concentric Hartree–Fock contours, reflecting an uncorrelated description
  - in reality, the electrons see each other and the contours becomes distorted
Electron correlation and virtual excitations

- **electron correlation:**
  - to improve upon the Hartree–Fock 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
  - Consider the following double-excitation operator:
    \[
    \hat{X}_{ij}^{ab} = t_{ij}^{ab} a_b^\dagger a_a^\dagger a_i a_j
    \]
    - the amplitude \( t_{ij}^{ab} \) represents the probability that the electrons in \( \phi_i \) and \( \phi_j \) will interact and be excited to \( \phi_a \) and \( \phi_b \)
    - by applying \( 1 + \hat{X}_{ij}^{ab} \) to the Hartree–Fock state, we obtain an improved, correlated description of the electrons:
    \[
    |\text{HF}\rangle \rightarrow (1 + \hat{X}_{ij}^{ab})|\text{HF}\rangle
    \]
Example: electron correlation in H\textsubscript{2}

- Consider the effect of a double excitation in H\textsubscript{2}:

\[ |1\sigma^2_g\rangle \rightarrow (1 + \hat{X}^{uu}_{gg})|1\sigma^2_g\rangle = |1\sigma^2_g\rangle - 0.11|1\sigma^2_u\rangle \]

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

- The two-electron density \( \rho(z_1, z_2) \) changes dramatically:
**Coupled-cluster theory**

- In coupled-cluster (CC) theory, we generate the correlated state from the HF reference state by applying all possible excitation operators

\[ |CC\rangle = \left( 1 + \hat{X}_i^a \right) \cdots \left( 1 + \hat{X}_{ij}^{ab} \right) \cdots \left( 1 + \hat{X}_{ijk}^{abc} \right) \cdots \left( 1 + \hat{X}_{ijkl}^{abcd} \right) \cdots |HF\rangle \]

  - singles
  - doubles
  - triples
  - quadruples

- with each excitation, there is an associated probability amplitude \( t_{ij...}^{abc...} \)

- single excitations represent orbital adjustments rather than interactions

- double excitations are particularly important, arising from pair interactions

- higher excitations should become progressively less important

- This classification provides a hierarchy of ‘truncated’ CC wave functions:

  - CCS, CCSD, CCSDT, CCSDTQ, CCSDTQ5, ...

  - errors are typically reduced by a factor of three to four at each new level

- Lower-order excitations work in tandem to produce higher-order excited configurations

\[ \left( 1 + \hat{X}_{ij}^{ab} \right) \left( 1 + \hat{X}_{kl}^{cd} \right) |HF\rangle = |HF\rangle + \hat{X}_{ij}^{ab} |HF\rangle + \hat{X}_{kl}^{cd} |HF\rangle + \hat{X}_{ij}^{ab} \hat{X}_{kl}^{cd} |HF\rangle \]

  - the important thing is to parameterize the excitations rather than the resulting states
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:

<table>
<thead>
<tr>
<th></th>
<th>SZ</th>
<th>DZ</th>
<th>TZ</th>
<th>QZ</th>
<th>5Z</th>
<th>6Z</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>14</td>
<td>30</td>
<td>55</td>
<td>91</td>
<td>140</td>
</tr>
</tbody>
</table>

• 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
     \[
     \text{HF, CCSD, CCSDT, CCSDTQ, ...}
     \]
  2. the one-electron hierarchy:
     correlation-consistent basis sets
     \[
     \text{DZ, TZ, QZ, 5Z, 6Z, ...}
     \]
- The quality is systematically improved upon by going up in the hierarchies.
Coupled-cluster (CC) vs. basis-set (AO) convergence

- Atomization energies of HF, N₂, F₂, and CO
  - contributions of each CC excitation level (left) and AO basis-set shell (right)

- The excitation-level convergence is approximately linear (log–linear plot)
  - each new excitation level reduces the error by about an order of magnitude

- 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

- Convergence is smooth in both directions!
  - we shall consider the CC convergence first, the AO convergence next
## CC convergence: atomization energies (kJ/mol)

<table>
<thead>
<tr>
<th></th>
<th>RHF</th>
<th>SD</th>
<th>T</th>
<th>Q</th>
<th>rel.</th>
<th>vib.</th>
<th>total</th>
<th>experiment</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂</td>
<td>531.1</td>
<td>218.3</td>
<td>9.5</td>
<td>0.4</td>
<td>-0.7</td>
<td>-43.2</td>
<td>715.4</td>
<td>714.8±1.8</td>
<td>0.6</td>
</tr>
<tr>
<td>H₂O</td>
<td>652.3</td>
<td>305.3</td>
<td>17.3</td>
<td>0.8</td>
<td>-2.1</td>
<td>-55.4</td>
<td>918.2</td>
<td>917.8±0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>HF</td>
<td>405.7</td>
<td>178.2</td>
<td>9.1</td>
<td>0.6</td>
<td>-2.5</td>
<td>-24.5</td>
<td>566.7</td>
<td>566.2±0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>N₂</td>
<td>482.9</td>
<td>426.0</td>
<td>42.4</td>
<td>3.9</td>
<td>-0.6</td>
<td>-14.1</td>
<td>940.6</td>
<td>941.6±0.2</td>
<td>-1.1</td>
</tr>
<tr>
<td>F₂</td>
<td>-155.3</td>
<td>283.3</td>
<td>31.6</td>
<td>3.3</td>
<td>-3.3</td>
<td>-5.5</td>
<td>154.1</td>
<td>154.6±0.6</td>
<td>-0.5</td>
</tr>
<tr>
<td>CO</td>
<td>730.1</td>
<td>322.2</td>
<td>32.1</td>
<td>2.3</td>
<td>-2.0</td>
<td>-12.9</td>
<td>1071.8</td>
<td>1071.8±0.5</td>
<td>-0.0</td>
</tr>
</tbody>
</table>

- agreement with experiment in all cases except for N₂
- all purely electronic contributions are positive (except Hartree–Fock for F₂)
  - very large correlation contributions
- relativistic corrections are small (≈ 0.5%) but needed for agreement with experiment
  - nearly cancel quadruples contributions (error cancellation possible)
- vibrational corrections are substantial
  - similar to triples contributions but oppositely directed (error cancellation)
## CC convergence: bond distances (pm)

<table>
<thead>
<tr>
<th></th>
<th>RHF</th>
<th>SD</th>
<th>T</th>
<th>Q</th>
<th>5</th>
<th>rel.</th>
<th>theory</th>
<th>exp.</th>
<th>err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>89.70</td>
<td>1.67</td>
<td>0.29</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
<td>91.69</td>
<td>91.69</td>
<td>0.00</td>
</tr>
<tr>
<td>N₂</td>
<td>106.54</td>
<td>2.40</td>
<td>0.67</td>
<td>0.14</td>
<td>0.03</td>
<td>0.00</td>
<td>109.78</td>
<td>109.77</td>
<td>0.01</td>
</tr>
<tr>
<td>F₂</td>
<td>132.64</td>
<td>6.04</td>
<td>2.02</td>
<td>0.44</td>
<td>0.03</td>
<td>0.05</td>
<td>141.22</td>
<td>141.27</td>
<td>−0.05</td>
</tr>
<tr>
<td>CO</td>
<td>110.18</td>
<td>1.87</td>
<td>0.75</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>112.84</td>
<td>112.84</td>
<td>0.00</td>
</tr>
</tbody>
</table>

- 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
- relativistic corrections are small except for F₂ (0.05 pm)
  - of the same magnitude and direction as the quintuples
  - no sources of error cancellation (in a complete AO basis)
### CC convergence: harmonic constants $\omega_e$ (cm$^{-1}$)

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

- 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.
- No sources of error cancellation in a complete AO basis.
Tromsø in June (69°N 19°E), looking north
Tromsø, looking west
Tromsø at noon in winter
Basis-set convergence

• In all examples up to now, we have worked in a complete AO basis

• However, the overall quality is determined by the description of one/electron basis sets

  1. the wave-function model
  2. the AO basis set

• We shall now consider basis-set convergence
  – new sources of errors
  – new opportunities for error cancellation

• We begin by investigating convergence in the helium atom
The helium atom contains only two electrons
  - ideal system to study basis-set convergence
  - pair interactions dominate also molecules

Historical interest: the first many-body system treated with quantum mechanics
  - experimental ionization potential of helium: 24.59 eV

Unsöld 1927: 20.41 eV
  - first-order perturbation theory—not much better than Bohr theory

Hylleraas 1928: 24.47 eV
  - expansion in antisymmetric orbital products
  - excruciatingly slow AO convergence

Hylleraas 1929: 24.58 eV
  - introduced the interelectronic coordinate $r_{12}$ to arbitrary powers
  - the discrepancy of 0.01 eV due to relativistic corrections
  - full agreement between experiment and quantum mechanics

Hylleraas discovered both the slow CI convergence and the efficacy of introducing $r_{12}$
  - the question of CI expansions vs. explicit correlation is still with us today
The local kinetic energy

- Consider the local energy of the helium atom
  \[ E_{\text{loc}} = (H\Psi)/\Psi \quad \leftarrow \text{constant for exact wave function} \]

- The electronic Hamiltonian has singularities at points of coalescence
  \[ H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \]
  - the infinite potential terms must be canceled by infinite kinetic terms at coalescence

- Local kinetic energy in the helium atom
  - positive around the nucleus
  - negative around the second electron

- Negative kinetic energy counterintuitive
  - classical forbidden region
  - internal “tunneling”
  - w. f. decays towards the singularity
  - the Coulomb hole

- The difficulty Hylleraas ran into was the description of the Coulomb hole!
The Coulomb hole: the forbidden region

- Each electron is surrounded by a classically forbidden region: the Coulomb hole
  - without a good description of this region, our results will be inaccurate
The electron cusp and the Coulomb hole

- The behaviour of the wave function at coalescence was established by Slater (1928)
  - nuclear and electronic cusp conditions

\[
\left( \frac{\partial \Psi}{\partial r_i} \right)_{r_i=0,\text{ave}} = -Z \Psi (r_i = 0)
\]

\[
\left( \frac{\partial \Psi}{\partial r_{12}} \right)_{r_{12}=0,\text{ave}} = \frac{1}{2} \Psi (r_{12} = 0)
\]

- The electronic cusp condition implies the existence of a Coulomb hole
  - the helium atom, with one electron fixed at a distance of 0.5a₀ from the nucleus
Basis-set convergence

- Convergence of the contributions to the atomization energy of CO (kJ/mol):

<table>
<thead>
<tr>
<th>$N_{bas}$</th>
<th>HF ($n^4$)</th>
<th>SD ($n^6$)</th>
<th>(T)($n^7$)</th>
<th>CCSD(T)</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>cc-pCVDZ</td>
<td>36</td>
<td>710.2</td>
<td>+</td>
<td>24.5</td>
<td>=</td>
</tr>
<tr>
<td>cc-pCVTZ</td>
<td>86</td>
<td>727.1</td>
<td>+</td>
<td>32.6</td>
<td>=</td>
</tr>
<tr>
<td>cc-pCVQZ</td>
<td>168</td>
<td>730.3</td>
<td>+</td>
<td>33.8</td>
<td>=</td>
</tr>
<tr>
<td>cc-pCV5Z</td>
<td>290</td>
<td>730.1</td>
<td>+</td>
<td>34.2</td>
<td>=</td>
</tr>
<tr>
<td>cc-pcV6Z</td>
<td>460</td>
<td>730.1</td>
<td>+</td>
<td>34.4</td>
<td>=</td>
</tr>
<tr>
<td>limit</td>
<td>$\infty$</td>
<td>730.1</td>
<td>+</td>
<td>34.6</td>
<td>=</td>
</tr>
</tbody>
</table>

- the doubles converge very slowly—chemical accuracy requires 460 AOs (6Z)!
- the Hartree–Fock and triples contributions are less of a problem.

- 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):
The principal expansion and correlation-consistent basis sets

- The energy contribution from each AO in large CI calculations on helium:
  \[ \varepsilon_{nlm} \approx n^{-6} \quad \leftarrow \text{Carroll et al. (1979)} \]

- 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 \( \text{cc-pVXZ} \) (Dunning, 1989)

- Energy-optimized AOs are added one shell at a time:
  
<table>
<thead>
<tr>
<th>SZ</th>
<th>cc-pVDZ</th>
<th>cc-pVTZ</th>
<th>cc-pVQZ</th>
<th>number of AOs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+3s3p3d</td>
<td>+4s4p4d4f</td>
<td>+5s5p5d5f5g</td>
<td>( \propto X^2 )</td>
</tr>
<tr>
<td>2s1p</td>
<td>3s2p1d</td>
<td>4s3p2d1f</td>
<td>5s4p3d2f1g</td>
<td>( \propto X^3 )</td>
</tr>
</tbody>
</table>

- 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 \( \rightarrow \) 1 week \( \rightarrow \) 200 years
Solutions to slow basis-set convergence

1. Use explicitly correlated methods!
   - Include interelectronic distances $r_{ij}$ in the wave function:
     \[
     \Psi_{R12} = \sum_K C_K \Phi_K + C_R r_{12} \Phi_0
     \]

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
For some purposes, extrapolation is competitive with explicit correlation

- logarithmic errors in **plain** and **extrapolated** energies relative to R12
Neon: explicit correlation and extrapolation

aug–cc–pCVXZ
Oslo (60°N 10°E): skiing and NUFC
Oslo looking south
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

\[ D_e = \sum_A E^A (2S+1 L) - E_{\text{mol}} (R_e) \]

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

- AEs increase with cardinal number
- AEs increase with excitation level in the coupled-cluster hierarchy:
  \[ \text{HF} < \text{CCSD} < \text{CCSD}(T) < \text{MP2} \]

- MP2 overestimates the doubles contribution
  - benefits from error cancellation at the MP2/TZ level

- CCSD(T) performs excellently in large basis sets
  - DZ and TZ basis are inadequate for CCSD(T)
Atomization energies (kJ/mol)
## The (in)adequacy of CCSD(T)

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!

<table>
<thead>
<tr>
<th></th>
<th>CCSD(T)</th>
<th>CCSDT</th>
<th>CCSDTQ</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cc-pCV(56)Z</td>
<td>cc-pCV(Q5)Z</td>
<td>cc-pVTZ</td>
<td>$D_e$</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>757.9 ± 0.9</td>
<td>758.9 ± 0.1</td>
<td>759.3 ± 0.5</td>
<td>758.8 ± 1.8</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>975.3 ± 0.1</td>
<td>974.9 ± 0.3</td>
<td>975.7 ± 0.5</td>
<td>975.2 ± 0.2</td>
</tr>
<tr>
<td>HF</td>
<td>593.2 ± 0.0</td>
<td>593.0 ± 0.2</td>
<td>593.6 ± 0.4</td>
<td>593.2 ± 0.7</td>
</tr>
<tr>
<td>N$_2$</td>
<td>954.7 ± 1.6</td>
<td>951.3 ± 5.0</td>
<td>955.2 ± 1.1</td>
<td>956.3 ± 0.2</td>
</tr>
<tr>
<td>F$_2$</td>
<td>161.0 ± 2.4</td>
<td>159.6 ± 3.8</td>
<td>162.9 ± 0.5</td>
<td>163.4 ± 0.6</td>
</tr>
<tr>
<td>CO</td>
<td>1086.7 ± 0.0</td>
<td>1084.4 ± 2.3</td>
<td>1086.7 ± 0.0</td>
<td>1086.7 ± 0.5</td>
</tr>
</tbody>
</table>
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) mean errors: DZ: 1.68 pm; TZ: 0.01 pm; QZ: −0.12 pm
Bond distances $R_e$ of BH, CO, N$_2$, HF, and F$_2$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Method</th>
<th>Re (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD(T) cc-pCVDZ</td>
<td>2.1</td>
</tr>
<tr>
<td>CCSD(T) cc-pCVTZ</td>
<td>0.2</td>
</tr>
<tr>
<td>CCSD(T) cc-pCVQZ</td>
<td>0.1</td>
</tr>
<tr>
<td>CCSD(T) cc-pCV5Z</td>
<td>0.1</td>
</tr>
<tr>
<td>CCSD cc-pCVDZ</td>
<td>1.2</td>
</tr>
<tr>
<td>CCSD cc-pCVTZ</td>
<td>0.6</td>
</tr>
<tr>
<td>CCSD cc-pCVQZ</td>
<td>0.9</td>
</tr>
<tr>
<td>CCSD cc-pCV5Z</td>
<td>1.0</td>
</tr>
<tr>
<td>MP2 cc-pCVDZ</td>
<td>1.5</td>
</tr>
<tr>
<td>MP2 cc-pCVTZ</td>
<td>0.9</td>
</tr>
<tr>
<td>MP2 cc-pCVQZ</td>
<td>0.8</td>
</tr>
<tr>
<td>MP2 cc-pCV5Z</td>
<td>0.8</td>
</tr>
<tr>
<td>SCF cc-pCVDZ</td>
<td>2.5</td>
</tr>
<tr>
<td>SCF cc-pCVTZ</td>
<td>3.4</td>
</tr>
<tr>
<td>SCF cc-pCVQZ</td>
<td>3.5</td>
</tr>
<tr>
<td>SCF cc-pCV5Z</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Vibrational frequencies of diatoms

- The frequency of a diatomic fundamental transition is given by
  \[ \nu = \omega_e - 2\omega_xe \]

  - the harmonic constant \( \omega_e \) requires 2nd derivatives of PES
  - the anharmonic constant \( \omega_xe \) 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:

| \(|\Delta|\) (cm\(^{-1}\)) | RHF | MP2 | CCSD | CCSD(T) | judgment |
|-------------------------------|-----|-----|------|---------|---------|
| \(\omega_e\)                 | 287 | 71  | 72   | 10      | DIFFICULT! |
| \(\omega_xe\)                | 4   | 3   | 1    | 0       | EASY!    |
Harmonic constants $\omega_e$ of BH, CO, N$_2$, HF, and F$_2$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Method</th>
<th>cc-pCVDZ</th>
<th>cc-pCVTZ</th>
<th>cc-pCVQZ</th>
<th>cc-pCV5Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF</td>
<td>269</td>
<td>288</td>
<td>287</td>
<td>287</td>
</tr>
<tr>
<td>CCSD (T)</td>
<td>42</td>
<td>14</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>MP2</td>
<td>68</td>
<td>81</td>
<td>73</td>
<td>71</td>
</tr>
<tr>
<td>CCSD</td>
<td>34</td>
<td>64</td>
<td>71</td>
<td>72</td>
</tr>
</tbody>
</table>

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Anharmonic constants $\omega_e x_e$ of BH, CO, N$_2$, HF, and F$_2$ (cm$^{-1}$)
Calculations of $\omega_e$ in N$_2$

<table>
<thead>
<tr>
<th>Method</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>84.6</td>
</tr>
<tr>
<td>CCSD/FC</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)/FC</td>
<td>4.1</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>13.8</td>
</tr>
<tr>
<td>CCSDT</td>
<td>23.5</td>
</tr>
<tr>
<td>CCSDTQ</td>
<td>4.7</td>
</tr>
<tr>
<td>CCSDTQ5</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Kristiansand (58°N 8°E): Southern Norway
Seaton Sluice (53°N 2°W): Northumberland
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!