Convergence properties of the coupled-cluster method: 
the accurate calculation of molecular properties for light 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

CMA–CTCC workshop on computational quantum mechanics
Department of Chemistry, University of Oslo, Norway
June 18–19, 2010

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 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.
Energy contributions to atomization energies (kJ/mol)

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

  - color code: HF, N\textsubscript{2}, F\textsubscript{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
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:

\[ \hat{X}_{ij}^{ab} = t_{ij}^{ab} a^\dagger_b a^\dagger_a a_i a_j \]

- 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$_2$

- Consider the effect of a double excitation in H$_2$:

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

- 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

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

- with each excitation, there is an associated probability amplitude \(t_{i,j,k,\ldots}^{abc,\ldots}\)
- single excitations represent orbital readjustments rather than direct 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

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

- the important thing is to parameterize the excitations rather than the resulting states
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 \( \text{cc-pV}XZ \) (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>2s1p</td>
<td>+3s3p3d</td>
<td>+4s4p4d4f</td>
<td>+5s5p5d5f5g</td>
<td>( \propto X^2 )</td>
</tr>
<tr>
<td></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:
  \[ \Delta E_X \approx \sum_{n=1}^{\infty} n^{-4} \approx X^{-3} \approx N^{-1} \approx T^{-1/4} \]

- Each new digit in the energy therefore costs 10000 times more CPU time!
  
  \[ 1 \text{ minute} \rightarrow 1 \text{ week} \rightarrow 200 \text{ years} \]
1. Use explicitly correlated methods!
   - Include interelectronic distances \( r_{ij} \) in the wave function (Hylleraas 1928):
     \[
     \Psi_{R12} = \sum_{K} C_K \Phi_K + C_{Rr_{12}} \Phi_0
     \]
     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
     \[
     E_\infty = \frac{X^3E_X - Y^3E_Y}{X^3 - Y^3}
     \]
     The formula is linear and contains no parameters; applicable to many properties

<table>
<thead>
<tr>
<th>( mE_h )</th>
<th>DZ</th>
<th>TZ</th>
<th>QZ</th>
<th>5Z</th>
<th>6Z</th>
<th>R12</th>
</tr>
</thead>
<tbody>
<tr>
<td>plain</td>
<td>194.8</td>
<td>62.2</td>
<td>23.1</td>
<td>10.6</td>
<td>6.6</td>
<td>1.4</td>
</tr>
<tr>
<td>extr.</td>
<td>21.4</td>
<td>1.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>
Extrapolation

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

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

  \begin{itemize}
  \item cc-pVDZ at Re:
    \begin{itemize}
    \item -0.030
    \item -0.010
    \item 0.000
    \end{itemize}
  \item aug-cc-pVDZ at Re:
    \begin{itemize}
    \item -0.300
    \item 0.000
    \item 0.300
    \end{itemize}
  \end{itemize}

- However, to lowest order, perturbational corrections are very useful and popular:
  - MP2 (approximate CCSD) and CCSD(T) (approximate CCSDT)
    - Correlation effects are typically overestimated, leading to fortuitously good results.
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

  “Anatomy of relativistic energy corrections in light molecular systems”
In a fully relativistic (four-component) treatment of molecular electronic systems, the Dirac–Coulomb operator is frequently used

\[ \hat{H}^{DC} = \sum_i (c\alpha_i \cdot p_i + V_i + \beta_i c^2) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \]

Typical relativistic contributions for light molecular systems:

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>corr.</th>
<th>rel.</th>
</tr>
</thead>
<tbody>
<tr>
<td>total electronic energies</td>
<td>99.5%</td>
<td>0.5%</td>
<td>0.05%</td>
</tr>
<tr>
<td>atomization energies</td>
<td>65%</td>
<td>35%</td>
<td>0.3%</td>
</tr>
</tbody>
</table>

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 \(\hat{H}^{DC}\) 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

\[ \hat{H}^{DC} \rightarrow \hat{H}^{CP} = \hat{H}^{NR} + \hat{H}^{MV} + \hat{H}^{D} + \hat{H}^{SO} \]

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

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

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

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

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

  - 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:

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

  - to first order, it contributes only to open-shell systems
Example: Coulomb–Pauli corrections to the electronic energies of $\text{H}_2\text{O}$ and $\text{H}_2\text{S}$ ($mE_h$)

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{H}_2\text{S}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RHF</td>
<td>CCSD(T)</td>
</tr>
<tr>
<td>mass–velocity (MV)</td>
<td>$-251.5$</td>
<td>$-251.9$</td>
</tr>
<tr>
<td>+ one-electron Darwin (D1)</td>
<td>199.9</td>
<td>199.9</td>
</tr>
<tr>
<td>= Cowan–Griffin (MVD1)</td>
<td>$-51.6$</td>
<td>$-52.0$</td>
</tr>
<tr>
<td>+ two-electron Darwin (D2)</td>
<td>$-3.4$</td>
<td>$-3.1$</td>
</tr>
<tr>
<td>= Coulomb–Pauli</td>
<td>$-55.0$</td>
<td>$-55.1$</td>
</tr>
</tbody>
</table>

- 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 $\text{H}_2\text{O}$ and 0.1% in $\text{H}_2\text{S}$. 
The two-electron Darwin operator contributes only when two electron coincide:

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

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

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

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

- convergence of correlation contribution in H\(_2\) with and without extrapolation (\(\mu E_h\)):

<table>
<thead>
<tr>
<th></th>
<th>RHF</th>
<th>corr.</th>
<th>total</th>
<th>DZ</th>
<th>TZ</th>
<th>QZ</th>
<th>5Z</th>
<th>6Z</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-7.8</td>
<td>4.4</td>
<td>-2.8</td>
<td>2.8</td>
<td>3.5</td>
<td>3.7</td>
<td>3.9</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.9</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

- 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.
• 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
\[ \hat{H}^{\text{DB}} = \hat{H}^{\text{DC}} - \frac{1}{4} \sum_{i \neq j} \frac{r_{ij}^2 \alpha_i \cdot \alpha_j + \alpha_i \cdot r_{ij} r_{ij} \cdot \alpha_j}{r_{ij}^3} \]

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:
\[ \hat{H}^{\text{SoO}} = \frac{\alpha^2}{2} \sum_{i \neq j} \frac{\sigma_i \cdot r_{ij} \times p_j}{r_{ij}^3} \]

spin-other-orbit
\[ \hat{H}^{\text{SS}} = \frac{\alpha^2}{8} \sum_{i \neq j} \left[ \frac{\sigma_i \cdot r_{ij}^2 \sigma_j - 3 \sigma_i \cdot r_{ij} r_{ij} \cdot \sigma_j}{r_{ij}^5} - \frac{8\pi}{3} \delta(r_{ij}) \sigma_i \cdot \sigma_j \right] \]

spin–spin
\[ \hat{H}^{\text{OO}} = -\frac{\alpha^2}{4} \sum_{i \neq j} \frac{p_i \cdot r_{ij}^2 p_j + p_i \cdot r_{ij} r_{ij} \cdot p_j}{r_{ij}^3} \]

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\textsubscript{2}O and H\textsubscript{2}S (m\(E_h\))

- Do we need to worry about the Breit corrections?

<table>
<thead>
<tr>
<th></th>
<th>H\textsubscript{2}O</th>
<th>H\textsubscript{2}S</th>
</tr>
</thead>
<tbody>
<tr>
<td>MVD1</td>
<td>−52.0</td>
<td>−1077.3</td>
</tr>
<tr>
<td>+ D2</td>
<td>−3.1</td>
<td>−33.0</td>
</tr>
<tr>
<td>+ spin–spin</td>
<td>6.3</td>
<td>66.0</td>
</tr>
<tr>
<td>+ orbit–orbit</td>
<td>0.5</td>
<td>17.8</td>
</tr>
<tr>
<td>= Breit–Pauli</td>
<td>−48.3</td>
<td>−1026.5</td>
</tr>
</tbody>
</table>

- The Breit terms reverse the sign of the two-electron relativistic correction:
  - the spin–spin correction is easy since \(\langle \text{cs} | \hat{H}^{SS} | \text{cs} \rangle = -2\langle \text{cs} | \hat{H}^{D2} | \text{cs} \rangle\)
  - 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\textsubscript{2}O and 5% in H\textsubscript{2}S.

- The Lamb shift contributes to order \(Z^4\alpha^3\) (Pyykkö \textit{et al.} 2001)
  - comparable with the BP two-electron terms, which scale as \(Z^3\alpha^2\)
• 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)

<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>

- We have 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 (≈ 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 $\omega_e$ (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>adia.</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>0.4</td>
<td>4138.9</td>
<td>4138.3</td>
<td>0.1</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>0.0</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>0.0</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>0.0</td>
<td>2169.1</td>
<td>2169.8</td>
<td>0.7</td>
</tr>
</tbody>
</table>

- We agree 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
  - two-electron terms may be needed for CCSDTQ5 wave functions
Contributions to equilibrium 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>adia.</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>0.0</td>
<td>91.69</td>
<td>91.69</td>
<td>0.00</td>
</tr>
<tr>
<td>N\textsubscript{2}</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>0.0</td>
<td>109.78</td>
<td>109.77</td>
<td>0.01</td>
</tr>
<tr>
<td>F\textsubscript{2}</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>0.0</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>0.0</td>
<td>112.84</td>
<td>112.84</td>
<td>0.00</td>
</tr>
</tbody>
</table>

- The agreement with experiment is very good (to within 0.01 pm except for F\textsubscript{2})
- Hartree–Fock theory underestimates bond distances by up to 8.6 pm (for F\textsubscript{2})
- All correlation contributions are positive
  - approximate linear convergence, slowest for F\textsubscript{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\textsubscript{2} (0.05 pm)
  - of the same magnitude and direction as the quintuples
  - MVD1 sufficient at the CCSDTQ\textsubscript{5} level
Atomization energies (AEs)

- 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)
Convergence to $\omega_e$ in N$_2$

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>371.9</td>
</tr>
<tr>
<td>CCSD/FC</td>
<td>84.6</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>
Bond distances

- Statistics based on 28 bond distances at the all-electron cc-pV\(X\)Z 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
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$_2$ (green), F$_2$ (blue), and CO (black); relativity straight lines