Quantum-chemical calculations using
Gaussian-type orbital
and
Gaussian-type geminal
basis sets

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CI expansions and explicit correlation

- Experimental ionization potential of helium: 24.59 eV
  - Unsöld 1927: 20.41 eV (first-order perturbation theory)
  - Hylleraas 1928: 24.47 eV (CI expansion: slow convergence!)
  - Hylleraas 1929: 24.58 eV (explicit correlation: fast convergence!)
  - full agreement between experiment and quantum mechanics
  - the question of CI expansions vs. explicit correlation is still with us today

Overview

- We shall consider
  - cusp conditions and Coulomb hole
  - energy convergence and extrapolation
  - explicit correlation at the MP2 level of theory
  - Gaussian-type geminal (GTG) methods: GTG-$n$ models
  - comparison with R12 and F12 theories as well as with extrapolation
  - some conclusions and recommendations
The electron cusp

• Consider the local energy of the helium atom

\[ E_{\text{loc}} = \frac{(H\Psi)}{\Psi} \]

- for the exact solution to the Schrödinger equation, the local energy must be constant
- 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
- the first derivatives must be discontinuous at the singularities

• Nuclear and electronic cusp conditions (Slater 1928)

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

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

• The electronic cusp condition implies the existence of a Coulomb hole
The Coulomb hole

- For high accuracy in the energy, we need a good description of the Coulomb hole
  - calculations where we include one shell at a time: 1s, 2s2p, 3s3p3d, ...

\[ \Psi^\text{CI}_N \rightarrow \Psi^\text{CI}_N + c_{12} r_{12} \Psi_{1s^2} \]

- CI wave functions \( \Psi^\text{CI}_N \) can only indirectly describe the Coulomb hole
- the inclusion of a single term linear in \( r_{12} \) vastly improves the description
- the cusp condition is satisfied

- Energetically, what matters is not the cusp but the hole
  - correlation functions \( f(r_{12}) \) different from \( r_{12} \) may in fact more easily create a hole

\[
\begin{align*}
  f(r_{12}) &= r_{12} & \text{linear} \\
  f(r_{12}) &= 1 - \exp(-\gamma r_{12}) & \text{exponential} \\
  f(r_{12}) &= 1 - \exp(-\gamma r_{12}^2) & \text{Gaussian}
\end{align*}
\]
Basis-set convergence

• Calculations on the helium atom using single-zeta Slater functions
  – standard CI expansion, CI-R12 expansion, the Hylleraas expansion

  - Left: log–lin plots of the error in the energy against the number of terms
  - Right: log–log plots of energy contributions against the principal quantum number $n$

• The standard CI expansion converges slowly but smoothly
  – the inclusion of a single R12 term reduces the error dramatically
  – each new shell contributes $n^{-4}$ energy for CI and $n^{-5}$ for CI-R12
The principal expansion and basis-set extrapolation

- The energy contribution from each AO in large CI calculations on helium:
  \[ \varepsilon_{nlm} \approx An^{-6} \leftarrow \text{Carroll et al. (1979)} \]
  - 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 \( n = X \):
  \[ E_\infty = E_X + A \sum_{n=X+1}^{\infty} n^2n^{-6} \approx E_X + AX^{-3} \]
  - to eliminate \( A \), carry out a smaller calculation truncated at \( Y = X - 1 \):
    \[ E_\infty = \frac{X^3E_X - Y^3E_Y}{X^3 - Y^3} \leftarrow \text{two-point extrapolation formula} \]

- Finally, we identify \( X \) with the cardinal number of Dunning’s cc-pV\( \text{X} \)Z basis sets
  - mean absolute errors of the CH\(_2\), H\(_2\)O, HF, N\(_2\), CO, Ne, and F\(_2\) energies:

<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>
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<tr>
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<td>23.1</td>
<td>10.6</td>
<td>6.6</td>
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<tr>
<td>extr.</td>
<td>21.4</td>
<td>1.4</td>
<td>0.4</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Extrapolation vs. explicit correlation

- For some purposes, extrapolation is competitive with explicit correlation
  - logarithmic errors in plain and extrapolated energies relative to R12

  - recent review on explicitly correlated methods
We have seen how standard methods converge slowly
- orbital products cannot easily model the Coulomb hole
- error proportional to $X^{-3}$, extrapolation is possible

A more fundamental solution is the use of explicitly correlated methods
- insert $f(r_{12})$ explicitly into the wave function
- accurate total energies obtainable without extrapolation

We shall now consider several such explicitly correlated methods
- the GTG method of Szalewicz, Jezierski, Monkhorst and Zabolitzky (1982)
- a mixed GTO–GTG method GTG-$n$ explored by us

We shall consider small systems, asking the question
- what error reduction can be expected from these methods?

It is sufficient to consider Møller–Plesset theory
- the doubles contributions converge more slowly than higher excitations
Møller–Plesset theory

- Zero-order system represented by the Fock operator and the Hartree–Fock wave function

\[
H_0 = \sum_i F_i, \quad H_0 |\text{HF}\rangle = (\sum_i \varepsilon_i) |\text{HF}\rangle, \quad F_1 \phi_i(1) = \varepsilon_i \phi_i(1)
\]

- To first order in perturbation theory, electrons are correlated pairwise:

\[
\phi_{ij}(1, 2) = \phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2) \rightarrow \phi_{ij}(1, 2) + Q_{12} u_{ij}(1, 2)
\]

  - the first-order pair function \( u_{ij} \) may or may not depend on \( r_{12} \)
  - the strong-orthogonality (SO) operator \( Q_{12} \) ensures orthogonality to occupied pairs

\[
Q_{12} = [1 - P_{\text{occ}}(1)] [1 - P_{\text{occ}}(2)], \quad P_{\text{occ}} = \sum_i |\phi_i\rangle \langle \phi_i|
\]

- The first-order corrections are obtained by minimizing the Hylleraas functional

\[
J[u_{ij}] = 2 \left\langle u_{ij} \left| Q_{12} r_{12}^{-1} \right| \phi_{ij} \right\rangle + \left\langle u_{ij} \left| Q_{12} \left( F_1 + F_2 - \varepsilon_i - \varepsilon_j \right) Q_{12} \right| u_{ij} \right\rangle
\]

  - 3-electron integrals
  - 5(4)-electron integrals

  - this is Sinanoglu’s SO functional
  - the MP2 correlation energy can be written as the sum of pair energies

\[
E_{\text{corr}} = \sum_{ij} \varepsilon_{ij}, \quad \varepsilon_{ij} = \left\langle u_{ij} \left| Q_{12} r_{12}^{-1} \right| \phi_{ij} \right\rangle
\]
In Møller–Plesset theory, we minimize the SO functional for each orbital pair

\[
J[u_{ij}] = 2 \langle u_{ij} | Q_{12} r_{12}^{-1} | \phi_{ij} \rangle + \langle u_{ij} | Q_{12} (F_1 + F_2 - \varepsilon_i - \varepsilon_j) Q_{12} | u_{ij} \rangle
\]

3-electron integrals

4-electron integrals

In standard orbital-based theory, we use a CI-type expansion of each pair function:

\[
u_{ij} = \sum_{ab} C_{ij}^{ab} \phi_{ab}, \quad \langle \phi_{ij} | \phi_{ab} \rangle = 0
\]

- the pair functions are automatically orthogonal to \( \phi_{ij} \) and \( Q_{12} \) is not needed
- the Fock operator is diagonal in the occupied and virtual MOs

This leads to great simplifications in the SO functional:

\[
J_{\text{orb}}[u_{ij}] = 2C_{ij}^{ab} \langle \phi_{ab} | r_{12}^{-1} | \phi_{ij} \rangle + (C_{ij}^{ab})^2 (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)
\]

- only two-electron integrals needed

\[
C_{ij}^{ab} = -\frac{\langle \phi_{ab} | r_{12}^{-1} | \phi_{ij} \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}
\]

A simple scheme but slow convergence!

- for more general first-order pair functions \( u_{ij} \), things become more difficult...
Gaussian-type geminal (GTG) theory

- In GTG theory, the pair functions are expanded in Gaussian-type geminals
  \[ u_{ij} = A_{\text{anti}} \sum_v c_v \exp \left( -\alpha_v (r_1 - P_v)^2 - \beta_v (r_2 - Q_v)^2 - \gamma_v r_{12}^2 \right) \sigma_1 \sigma_2 \]
  - all exponents \( \alpha_v, \beta_v, \gamma_v \) and centers \( P_v, Q_v \) variationally optimized
  - a difficult nonlinear optimization of pair energies

- To avoid four-electron integrals for these \( u_{ij} \), Szalewicz et al. [CPL 91, 169 (1982)] modified Sinanoglu’s SO functional
  \[
  W[u_{ij}] = 2 \langle u_{ij} | Q_{12} r_{12}^{-1} | \phi_{ij} \rangle + \langle u_{ij} | \times (\tilde{F}_1 + \tilde{F}_2 - \epsilon_i - \epsilon_j) Q_{12} | u_{ij} \rangle
  \]
  where the shifted Fock operators are given by
  \[
  \tilde{F} = F + \eta_{ij} P_{\text{occ}}, \quad \eta_{ij} = \frac{1}{2} (\epsilon_i + \epsilon_j) - \epsilon_1 + \eta, \quad \eta > 0
  \]

- This weak-orthogonality (WO) functional is an upper bound to the SO functional:
  \[
  W[u_{ij}] \geq J[u_{ij}] \geq \epsilon_{ij}
  \]
  - equality for the exact first-order pair function
  - orthogonality controlled by a penalty function
  - only two- and three-electron integrals now remain
The linear GTG-\textit{n} model

- A mixed Gaussian-type-orbital (GTO) and Gaussian-type-geminal (GTG) expansion:

\[
\begin{align*}
\psi_{ij} &= \sum_{ab} C_{ij}^{ab} \phi_{ab} + \sum_{pq} \sum_{v} c_{ij}^{pq,v} \exp(-\gamma v r_{12}^2) \phi_{pq} \\
& \text{GTO part} + \text{GTG part}
\end{align*}
\]

- there are three levels of theory, depending on what geminals are included:

  - **GTG-0**: include only “doubly-occupied” geminals \( \exp(-\gamma v r_{12}^2) \phi_{ij} \)
  - **GTG-1**: include also “singly-excited” geminals \( \exp(-\gamma v r_{12}^2) \phi_{ai} \)
  - **GTG-2**: include also “doubly-excited” geminals \( \exp(-\gamma v r_{12}^2) \phi_{ab} \)

- We avoid nonlinear optimizations by using
  - standard atom-fixed GTOs
  - fixed GTO and GTG exponents

- The coefficients \( C_{ij}^{ab} \) and \( c_{ij}^{pq,v} \) are determined by minimizing the WO functional:
  - the solution of a linear set of equations for each orbital pair \( ij \)
  - all three-electron integrals are evaluated explicitly (expensive!)

- GREMLIN code written by Pål Dahle (DALTON module)
We use nine even-tempered GTG exponents ($\gamma_v = 1/9, 1/3, 1, 3, 9, 27, 81, 243, 729$)

- all-electron GTG-0, GTG-1, GTG-2 aug-cc-pCVTZ(spd) neon calculations

- for GTG-0, only GTGs with $\gamma \geq 1$ are important
- the three steepest GTGs improve mainly the $1s^2$ energy
- the diffuse GTGs are important for excited GTGs
- with all nine GTGs included, the energy is converged to within 0.1 mH
Level shifting and strong orthogonality

- The weak orthogonality functional depends on the level-shift parameter $\eta > 0$
  - large $\eta$ improves orthogonality but pushes energy up

- Error in energy (mH) and nonorthogonal proportion of $u_{ij}$ (right) as functions of $\eta$ (left)
  - all-electron aug-cc-pCVTZ(spd) neon calculations
  - GTG-0, GTG-1, GTG-2,

- We have used the level shift $\eta = 0.1$ in all calculations
  - orthogonality increases with $n$ in GTG-$n$
Helium and beryllium

- A comparison of the GTG-\(n\) models with standard MP2 theory
  - standard MP2, GTG-0, GTG-1, GTG-2,

- aug-cc-pVXZ for helium; 14s to 14s9p4d3f for beryllium

- As expected the use of GTG improves convergence considerably
  - errors reduced by several factors at the GTG-0 level of theory
  - errors reduced by an order of magnitude at the GTG-1 and GTG-2 levels of theory

- Our results are very close to nonlinear GTG, with variationally optimized exponents
  - helium: \(-37.3773\) mH; Patkowski et al.: \(-37.3775\) mH
  - beryllium: \(-76.355\) mH; Bukowski et al.: \(-76.358\) mH
Neon

- A similar behavior is observed for the neon atom:

- our best neon energy: $-388.19 \text{ mH}$ (best variationally bounded)
- Lindgren and Salomonsen: $-388.31 \text{ mH}$
- Klopper and Samson: $-388.24 \text{ mH}$
- Wind, Klopper and Helgaker: $-388.29 \text{ mH}$

- GTG-0 reduces correlation error by a factor of three of four
  - for better results in a small basis, GTGs must be introduced into excited MO pairs
  - R12 theory introduces correlation factors only in doubly-occupied MO pairs
In R12 theory, the pair function is taken to have the form

\[ u_{ij} = \sum_{ab} C_{ij}^{ab} \phi_{ab} + Q_{12} \sum_{kl} c_{ij}^{kl} f(r_{12}) \phi_{kl} \]

- explicit correlation only for doubly occupied pairs

To avoid three- and four-electron integrals, resolution of identity (RI) is invoked
- this dramatically improves performance
- application to large molecules possible—a hugely successful theory

A variety of correlation functions have been tried
- \( f(r_{12}) = r_{12} \): original R12 method of Kutzelnigg and Klopper
- \( f(r_{12}) = 1 - \exp(-\gamma r_{12}) \): Ten-no and others, F12 theory
- \( f(r_{12}) = 1 - \sum v c_v \exp(-\gamma_v r_{12}^2) \): May and Manby

In addition, various flavors of R12 theories exist, depending on:
- the form of the projector \( Q_{12} \) (against occupied or all MOs)
- the (non)neglect of certain exchange commutators (A and B)
- (no) use of the extended Brillouin theorem (EBT): \( F\phi_a = \varepsilon_a \phi_a \)

Unlike GTG-\( n \) theory, R12 theory is not variationally bounded
Neon: comparison of explicitly correlated methods I

  - Ansatz 1: all MO pairs projected out; Ansatz 2: occupied MO pairs projected out
  - Ansatz A: exchange commutator \([K, r_{12}]\) neglected; Ansatz B: \([K, r_{12}]\) included

  - GTGs fitted to \(\exp(-\zeta r_{12})\), numerical quadrature, \([K, r_{12}]\) neglected, EBC assumed

- The R12/2A’, R12/2B and MP2-geminal model (but we are lower than GTG-0)
  - MP2-geminal close to GTG-1! WO penalty? error cancellation?
• No diffuse functions—higher energies for low cardinal numbers

• R12-SO is similar to Ansatz 2 but with explicit 3-electron integration
  – follows GTG-0 curve closely (indicating that WO penalty is small)

• Excellent behavior of Ten-no’s MP2-geminal model (follows GTG-1 again)

• May et al. [PCCP 7, 2710 (2005)] suggested a problem with the correlation factor
  – advocated the use of linear combinations of Gaussian geminals rather than $r_{12}$
Small molecules

- The molecular correlation energies show the same performance

- We obtained the lowest ever energies for H$_2$ and HF
  - H$_2$: $-34.252$ mH with GTG-2/aug-cc-pVTZ
  - LiH: $-72.877$ mH with GTG-1/(14s9p4d3f/8s4p3d) [72.890 mH by Bukowski et al.]
  - HF: $-384.41$ mH with GTG-2/aug-cc-pCVTZ(spd,spd)

- Basis sets
  - H$_2$: aug-cc-pVXZ
  - LiH: uncontracted ANO (14s, 8s), (14s9p, 8s4p), (14s9p4d3f, 8s4p3d)
  - HF: aug-cc-pCVTZ subspaces (sp, s), (sdp, sp) (sdf, spd)
### MP2 correlation energy (%) recovered

- All-electron correlation energies of Ne, HF, and H$_2$O in aug-cc-pCVXZ basis sets

<table>
<thead>
<tr>
<th></th>
<th>std</th>
<th>ext</th>
<th>GTG-0</th>
<th>GTG-1</th>
<th>GTG-2</th>
<th>2A’</th>
<th>2B</th>
<th>Ten-no</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ</td>
<td>68.2</td>
<td></td>
<td>87.8</td>
<td>97.2</td>
<td><strong>99.2</strong></td>
<td>96.2</td>
<td>91.1</td>
<td>96.9</td>
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<tr>
<td>TZ</td>
<td>88.3</td>
<td>96.8</td>
<td>96.3</td>
<td><strong>99.8</strong></td>
<td><strong>100.0</strong></td>
<td>99.1</td>
<td>98.0</td>
<td>99.1</td>
</tr>
<tr>
<td>QZ</td>
<td>94.8</td>
<td><strong>99.6</strong></td>
<td>98.5</td>
<td></td>
<td></td>
<td><strong>99.8</strong></td>
<td>99.4</td>
<td><strong>99.7</strong></td>
</tr>
</tbody>
</table>

- blue: more than 99% correlation energy for all systems

- Extrapolation works well, recovering more than 99% at the aug-cc-pCV[TQ]Z level

- The variational GTG-$n$ sequence behaves in a very systematic manner
  - GTG-2 recovers 99% correlation energy in DZ basis and 100% in TZ basis

- The F12 methods appear to perform better than GTG-0
  - we believe that the WO penalty is small, indicating F12 error cancellation
  - the more rigorous R12/2B method is slightly better than GTG-0
  - the less rigorous R12/2A’ works well by error cancellation (overshoots H$_2$O in DZ)
  - Ten-no’s MP2-geminal is similar to R12/2A’ (also neglects exchange commutator)
  - QZ basis is necessary to recover consistently more than 99% correlation energy
## MP2 correlation energies of small molecules (mH)

<table>
<thead>
<tr>
<th>system</th>
<th>this work(^a)</th>
<th>current best</th>
<th>energy recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>37.37729</td>
<td>37.37747(^b)</td>
<td>99.9995%</td>
</tr>
<tr>
<td>Be</td>
<td>76.355</td>
<td>76.358(^c)</td>
<td>99.996%</td>
</tr>
<tr>
<td>Ne</td>
<td>388.19</td>
<td>388.19</td>
<td>100%</td>
</tr>
<tr>
<td>H(_2)</td>
<td>34.252</td>
<td>34.252</td>
<td>100%</td>
</tr>
<tr>
<td>LiH</td>
<td>72.877</td>
<td>72.890(^c)</td>
<td>99.98%</td>
</tr>
<tr>
<td>HF</td>
<td>384.41</td>
<td>384.41</td>
<td>100%</td>
</tr>
</tbody>
</table>

\(^a\) GTG-2/TZ calculations except GTG-1/TZ for LiH  
\(^b\) Patkowski, Bukowski, Jeziorski and Szalewicz, personal communication  
\(^c\) Bukowski, Jeziorski and Rutkowski, JCP 110, 4165 (1999)
Conclusions

• There are two solutions to the basis-set problem of orbital-based quantum chemistry
  – extrapolation techniques
  – explicitly correlated methods
  – both can deliver an error reduction by an order of magnitude or more

• The modern development of explicit correlation began with GTG methods
  – high accurate but applicable only to small systems (nonlinear optimization)

• With R12 theory, explicitly correlated methods became (almost) routine
  – many-electron integrals avoided by RI, applicable too large systems

• The GTG-\( n \) approach combines elements of both these approaches
  – WO functional (variationally bounded), explicit three-electron integration

• The GTG-0 model typically recovers less correlation energy than does F12 theory
  – this could be a WO penalty but we note agreement with R12-SO theory
  – this could arise from error cancellation in F12 theory
  – it could be a combination

• To recover consistently more than 99% correlation energy, QZ basis is needed
  – DZ calculations give about 90% correlation energy