

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

$$E_{\text{loc}} = (H\Psi)/\Psi$$

- for the exact solution to the Schrödinger equation, the local energy must be constant
- the electronic Hamiltonian has singularities at points of coalescence

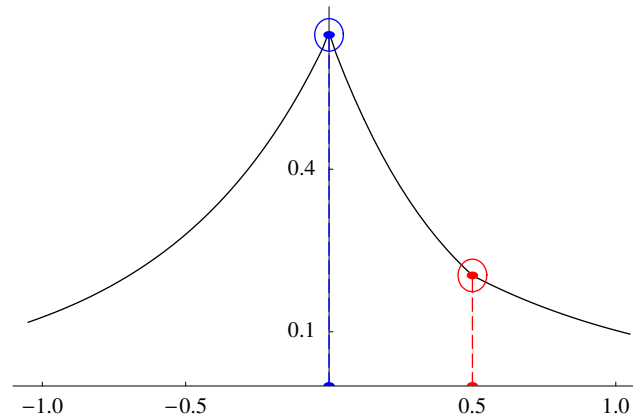
$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

- 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)

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

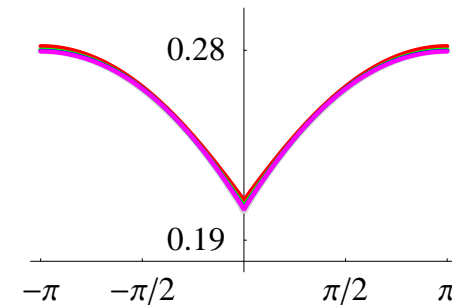
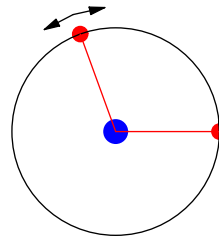
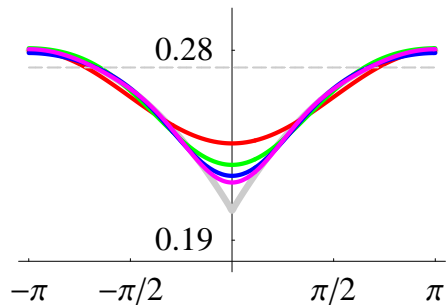
$$\left(\frac{\partial\Psi}{\partial r_{12}}\right)_{r_{12}=0,\text{ave}} = \frac{1}{2}\Psi(r_{12}=0)$$



- 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: $1s, 2s2p, 3s3p3d, \dots$



$$\Psi_N^{\text{CI}} \rightarrow \Psi_N^{\text{CI}} + c_{12} r_{12} \Psi_{1s^2}$$

- CI wave functions Ψ_N^{CI} 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

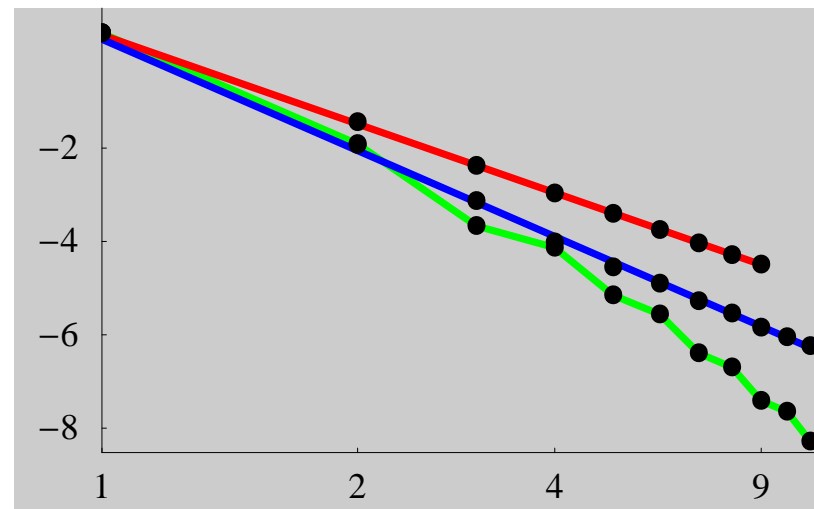
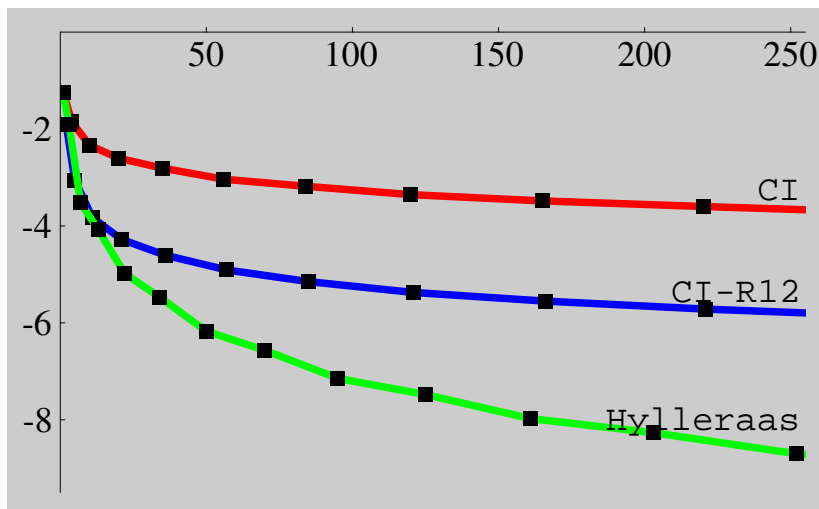
$$f(r_{12}) = r_{12} \quad \text{linear}$$

$$f(r_{12}) = 1 - \exp(-\gamma r_{12}) \quad \text{exponential}$$

$$f(r_{12}) = 1 - \exp(-\gamma r_{12}^2) \quad \text{Gaussian}$$

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:

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

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

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

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

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

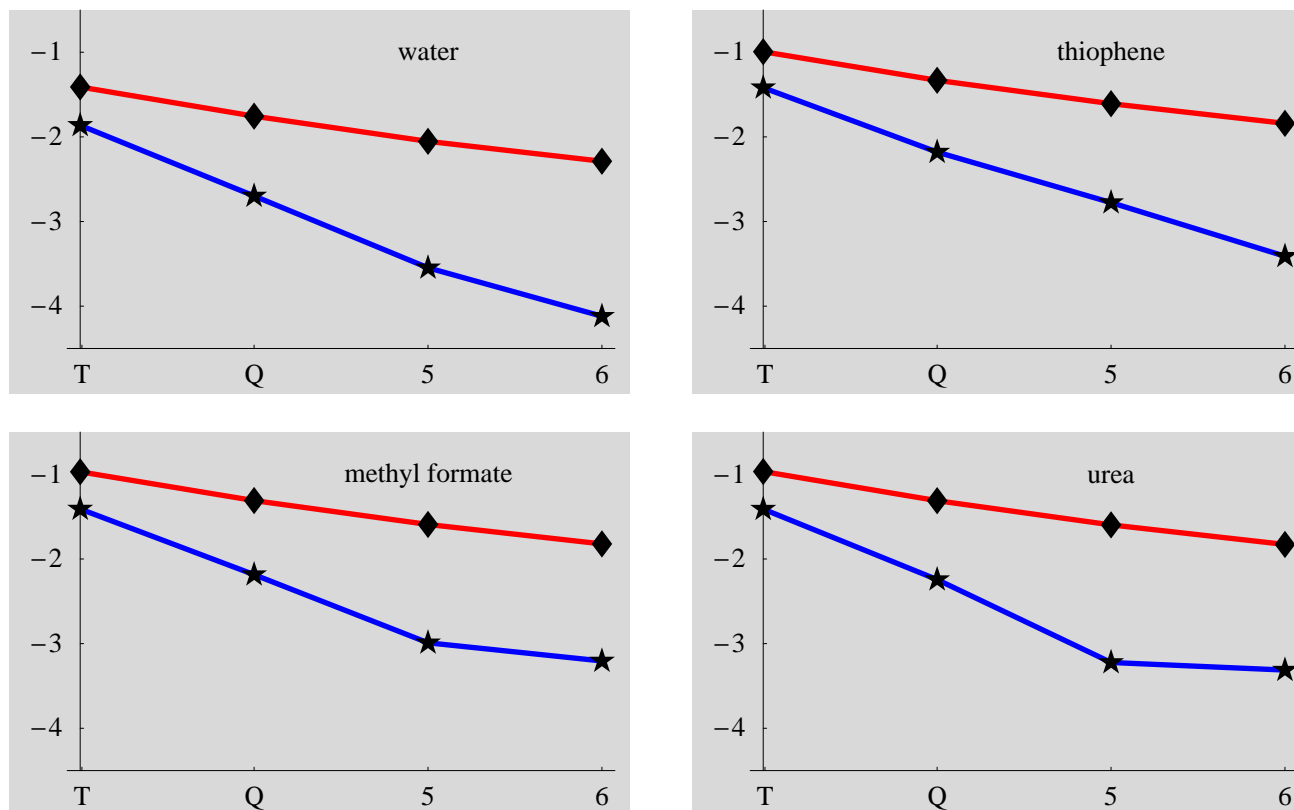
$$E_\infty = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3} \quad \leftarrow \text{two-point extrapolation formula}$$

- Finally, we identify X with the cardinal number of Dunning's cc-pVXZ basis sets
 - mean absolute errors of the CH₂, H₂O, HF, N₂, CO, Ne, and F₂ energies:

mE_h	DZ	TZ	QZ	5Z	6Z	R12
plain	194.8	62.2	23.1	10.6	6.6	1.4
extr.		21.4	1.4	0.4	0.5	

Extrapolation vs. explicit correlation

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



- from: Klopper, Manby, Ten-no and Valeev, *Int. Rev. Phys. Chem.* **25**, 427 (2006)
 - recent review on explicitly correlated methods

Review and preview

- 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, Jeziorski, Monkhorst and Zabolitzky (1982)
 - a mixed GTO–GTG method GTG- n explored by us
 - the R12 method of Kutzelnigg and Klopper (1985, 1986)
- 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:

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

- 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

$$J[u_{ij}] = 2 \underbrace{\langle u_{ij} | Q_{12} r_{12}^{-1} | \phi_{ij} \rangle}_{\text{3-electron integrals}} + \underbrace{\langle u_{ij} | Q_{12} (F_1 + F_2 - \varepsilon_i - \varepsilon_j) Q_{12} | u_{ij} \rangle}_{\text{5(4)-electron integrals}}$$

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

$$E_{\text{corr}} = \sum_{ij} \varepsilon_{ij}, \quad \varepsilon_{ij} = \langle \tilde{u}_{ij} | Q_{12} r_{12}^{-1} | \phi_{ij} \rangle$$

Standard Møller–Plesset theory

- In Møller–Plesset theory, we minimize the SO functional for each orbital pair

$$J[u_{ij}] = 2 \underbrace{\langle u_{ij} | Q_{12} r_{12}^{-1} | \phi_{ij} \rangle}_{\text{3-electron integrals}} + \underbrace{\langle u_{ij} | Q_{12} (F_1 + F_2 - \varepsilon_i - \varepsilon_j) Q_{12} | u_{ij} \rangle}_{\text{4-electron integrals}}$$

- 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 ϕ_{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

$$u_{ij} = \mathcal{A}_{\text{anti}} \sum_v c_v \exp \left[-\alpha_v (\mathbf{r}_1 - \mathbf{P}_v)^2 - \beta_v (\mathbf{r}_2 - \mathbf{Q}_v)^2 - \gamma_v r_{12}^2 \right] \sigma_1 \sigma_2$$

- all exponents α_v , β_v , γ_v and centers \mathbf{P}_v , \mathbf{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

$$W[u_{ij}] = 2 \left\langle u_{ij} \left| Q_{12} r_{12}^{-1} \right| \phi_{ij} \right\rangle + \left\langle u_{ij} \left| \cancel{Q_{12}} \left(\tilde{F}_1 + \tilde{F}_2 - \varepsilon_i - \varepsilon_j \right) \cancel{Q_{12}} \right| u_{ij} \right\rangle$$

where the shifted Fock operators are given by

$$\tilde{F} = F + \eta_{ij} P_{\text{occ}}, \quad \eta_{ij} = \frac{1}{2} (\varepsilon_i + \varepsilon_j) - \varepsilon_1 + \eta, \quad \eta > 0$$

- This **weak-orthogonality (WO) functional** is an upper bound to the SO functional:

$$W[u_{ij}] \geq J[u_{ij}] \geq \varepsilon_{ij}$$

- 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- n model

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

$$u_{ij} = \underbrace{\sum_{ab} C_{ij}^{ab} \phi_{ab}}_{\text{GTO part}} + \underbrace{\sum_{pq} \sum_v c_{ij}^{pq,v} \exp(-\gamma_v r_{12}^2) \phi_{pq}}_{\text{GTG part}}$$

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

GTG-0: include only “doubly-occupied” geminals $\exp(-\gamma_v r_{12}^2) \phi_{ij}$

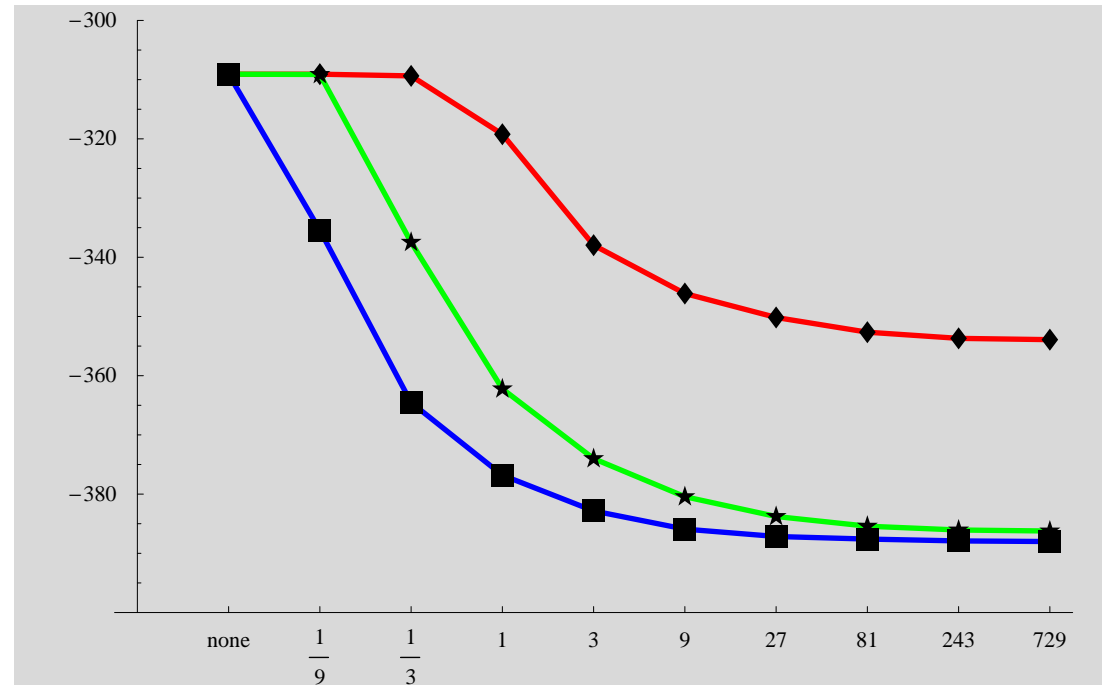
GTG-1: include also “singly-excited” geminals $\exp(-\gamma_v r_{12}^2) \phi_{ai}$

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)

GTG exponents

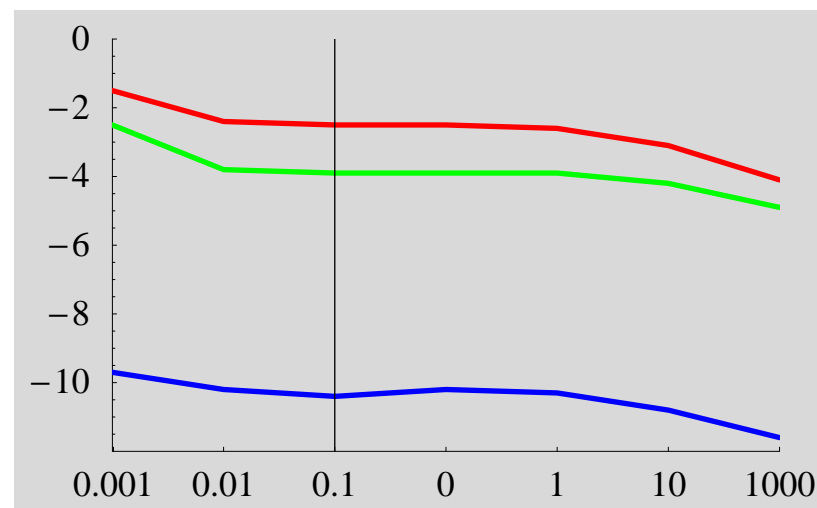
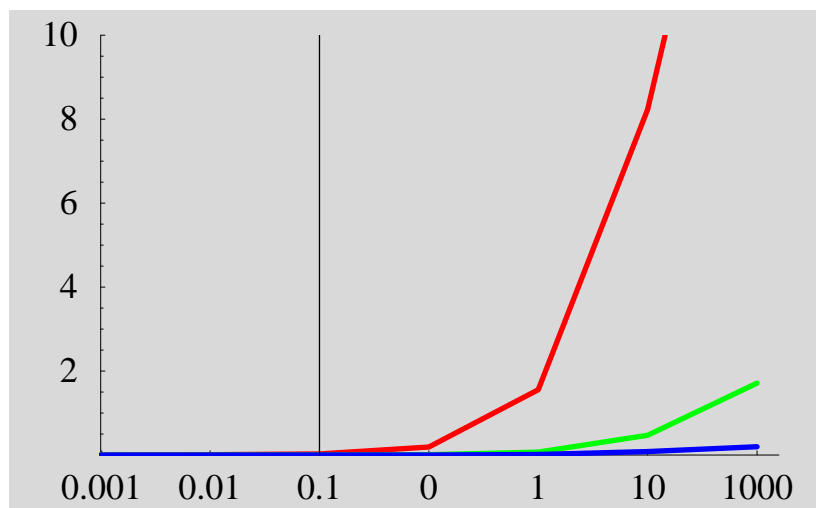
- We use nine even-tempered GTG exponents ($\gamma_v = 1/9, 1/3, 1, 3, 9, 27, 81, 243, 729$)
 - all-electron **GTG-0**, **GTG-1**, **GTG-2** aug-cc-pCVTZ(sp) neon calculations



- 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

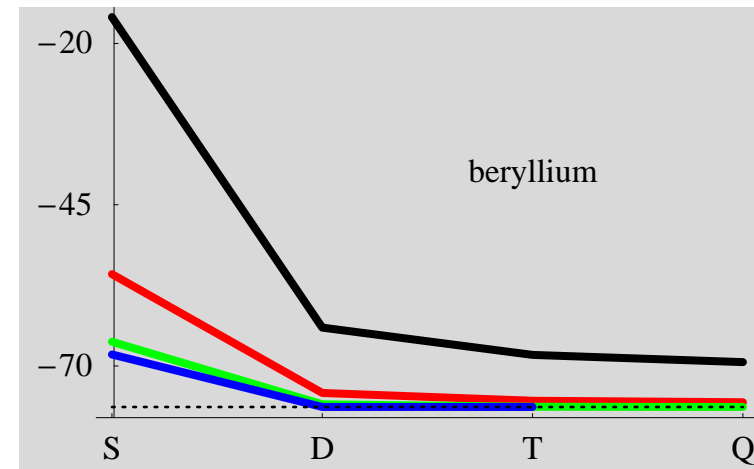
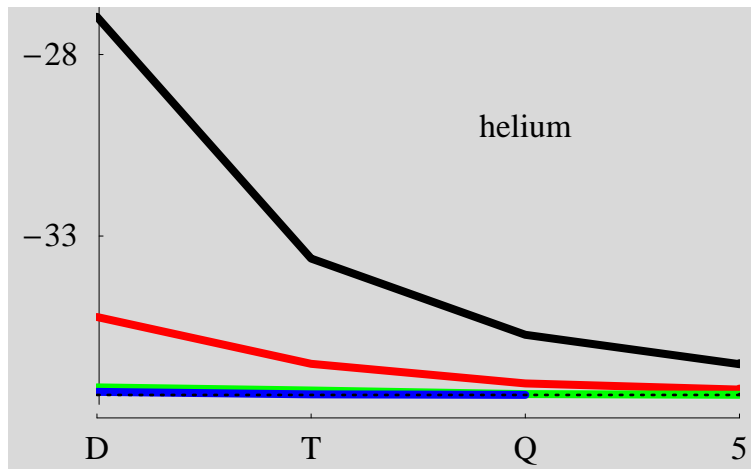
- The weak orthogonality functional depends on the level-shift parameter $\eta > 0$
 - large η improves orthogonality but pushes energy up
- Error in energy (mH) and nonorthogonal proportion of u_{ij} (right) as functions of η (left)
 - all-electron aug-cc-pCVTZ(sp) neon calculations
 - GTG-0, GTG-1, GTG-2,



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

Helium and beryllium

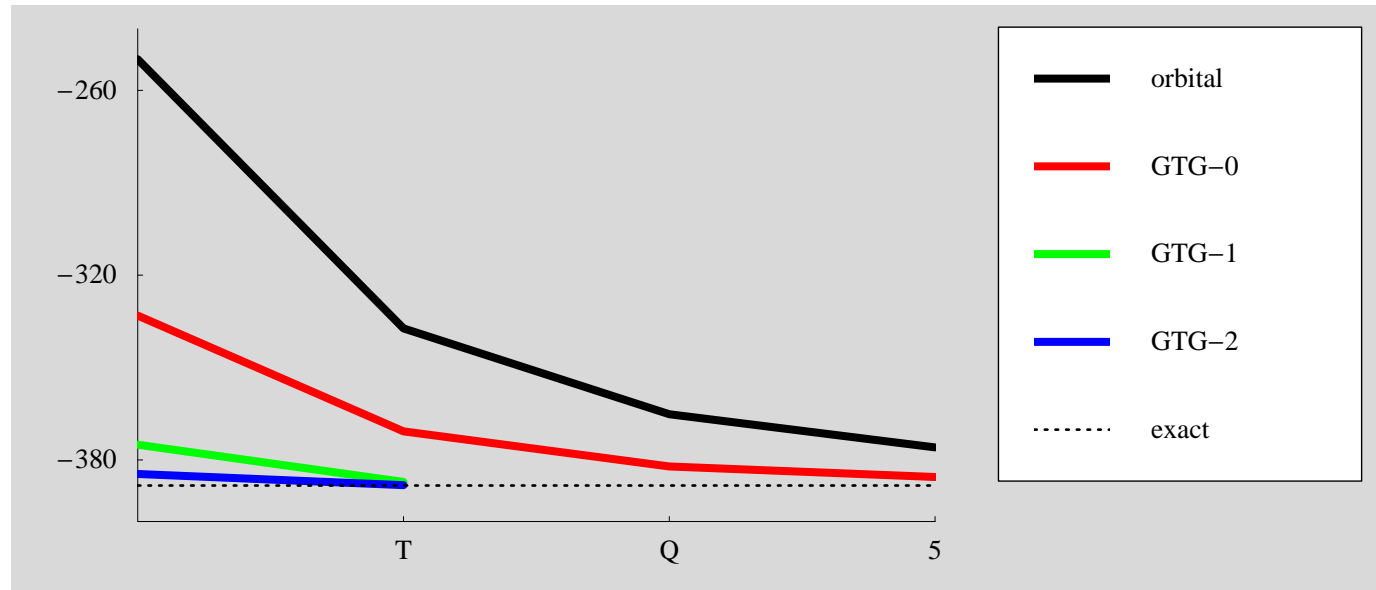
- A comparison of the GTG- n models with standard MP2 theory
 - standard MP2, GTG-0, GTG-1, GTG-2,



- 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 mH (best variationally bounded)
- Lindgren and Salomonsen: -388.31 mH
- Klopper and Samson: -388.24 mH
- Wind, Klopper and Helgaker: -388.29 mH
- GTG-0 reduces correlation error by a factor of three or 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

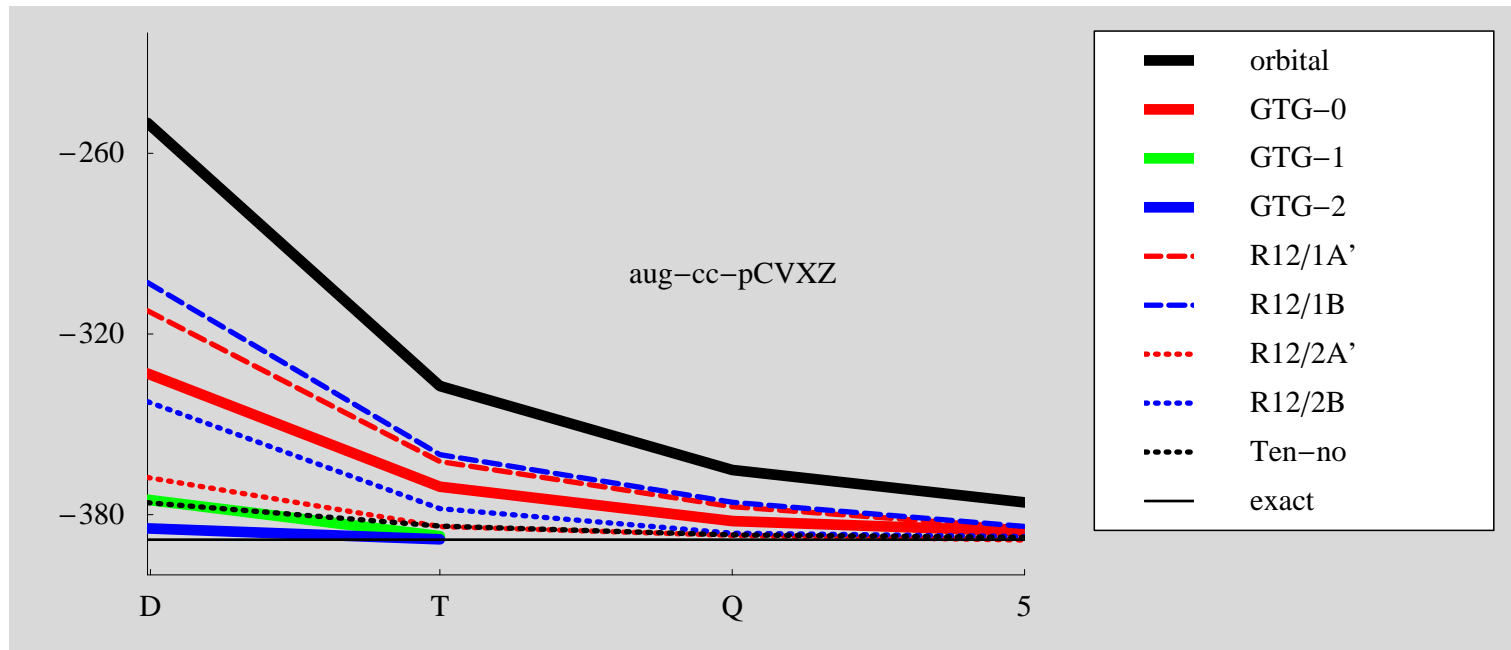
R12 theory

- In R12 theory, the pair function is taken to have the form

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

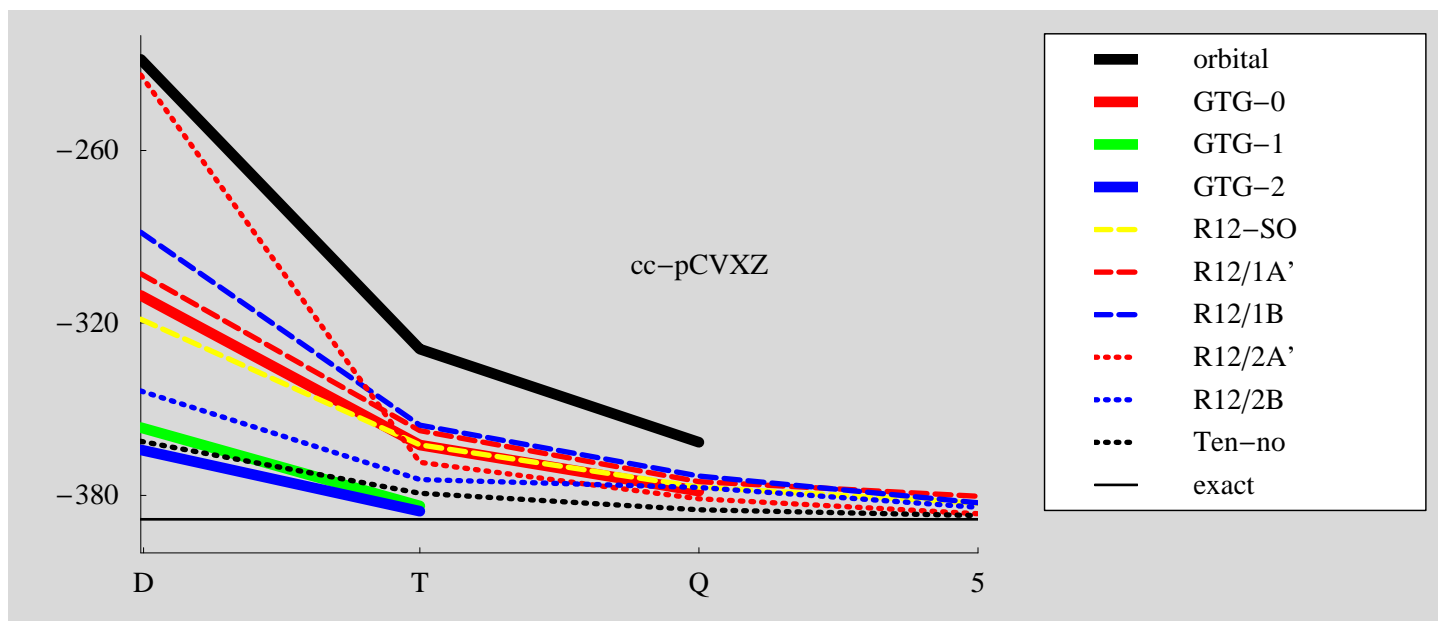
- explicit correlation only for doubly occupied pairs
- To avoid three- and four-electron integrals, resolution of identity (RI) is invoked
 - this dramatically improves performance
 - application to large molecules possible—a hugely successful theory
- A variety of correlation functions have been tried
 - $f(r_{12}) = r_{12}$: 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



- R12 calculations: Klopper and Samson, JCP **116**, 6397 (2002)
 - 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
- MP2-geminal calculations: Ten-no, JCP **121**, 117 (2004)
 - 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?

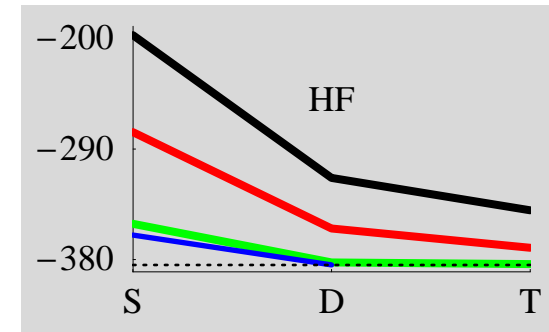
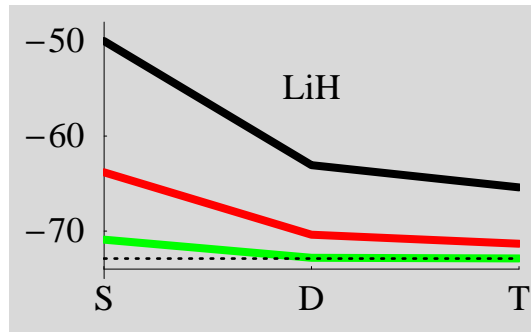
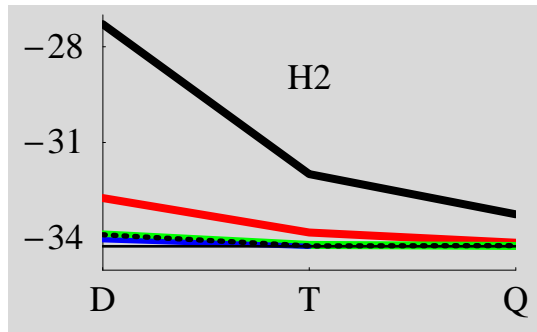
Neon: comparison of explicitly correlated methods II



- 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 H₂ and HF
 - H₂: -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(sp,spd)
- Basis sets
 - H₂: 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 H₂O in aug-cc-pCVXZ basis sets

	std	ext	GTG-0	GTG-1	GTG-2	2A'	2B	Ten-no
DZ	68.2		87.8	97.2	99.2	96.2	91.1	96.9
TZ	88.3	96.8	96.3	99.8	100.0	99.1	98.0	99.1
QZ	94.8	99.6	98.5			99.8	99.4	99.7

- 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 H₂O 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)

system	this work ^a	current best	energy recovered
He	37.37729	37.37747 ^b	99.9995%
Be	76.355	76.358 ^c	99.996%
Ne	388.19	388.19	100%
H ₂	34.252	34.252	100%
LiH	72.877	72.890 ^c	99.98%
HF	384.41	384.41	100%

^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