

Quantum-chemical calculations with  
Gaussian-type orbital and 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
  - 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

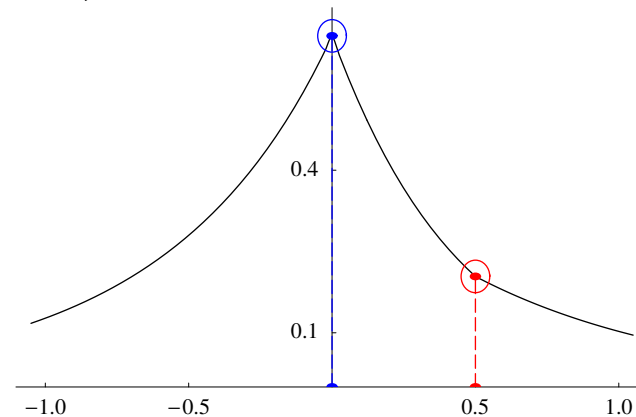
$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

- 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)

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

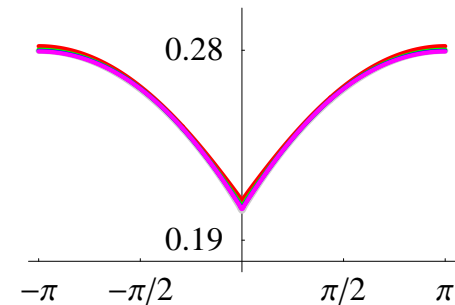
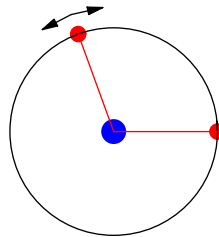
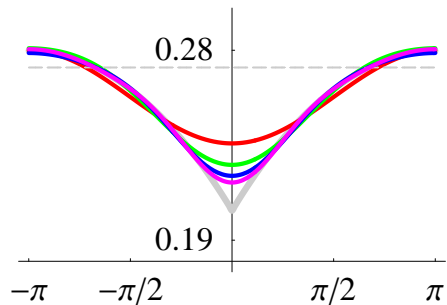
$$\left(\frac{\partial\Psi}{\partial r_{12}}\right)_{r_{12}=0,\text{ave}} = \frac{1}{2}\Psi(r_{12}=0)$$



- 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  $\Psi_N^{\text{CI}}$  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

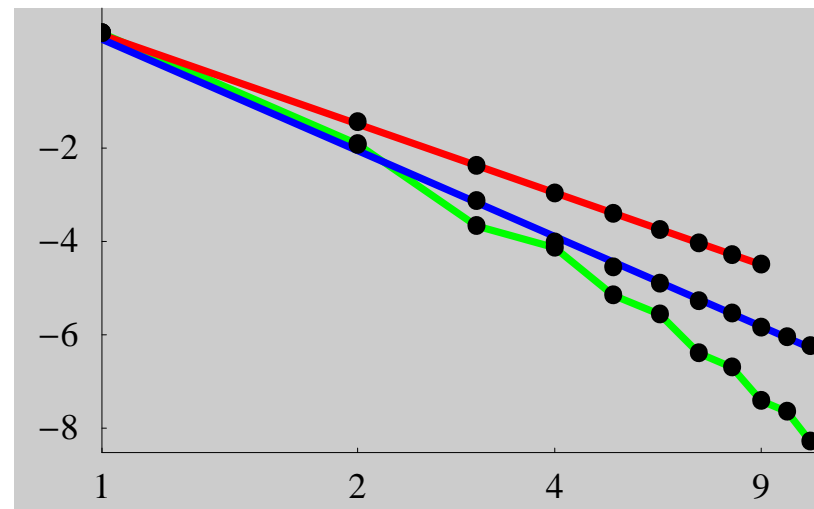
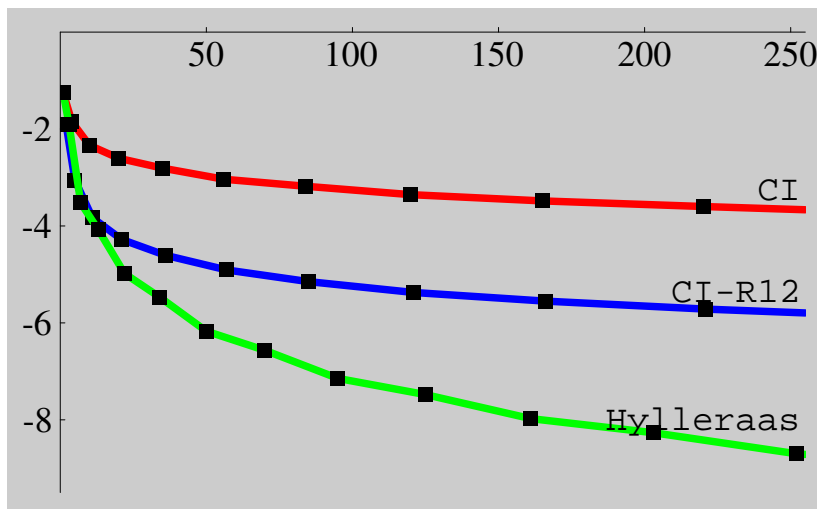
$$f(r_{12}) = r_{12} \quad \text{linear}$$

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

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

## 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  $Y = X - 1$ :

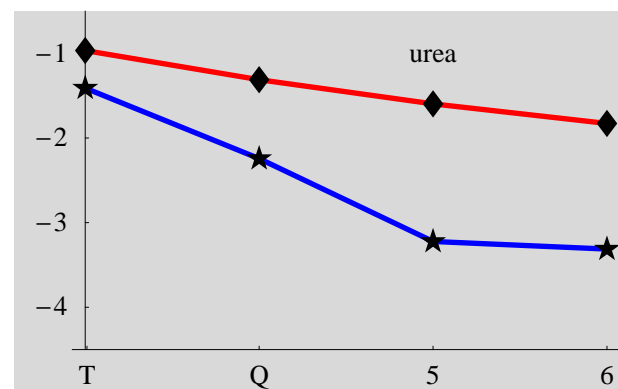
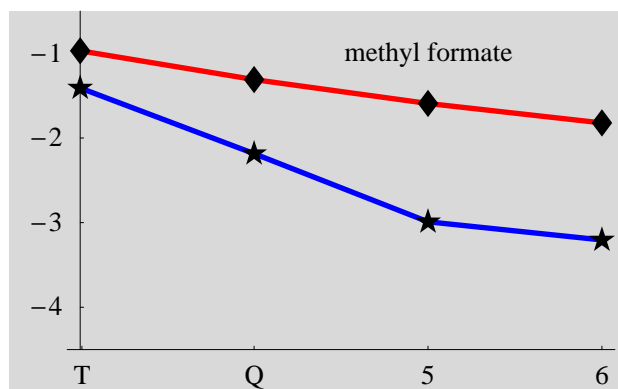
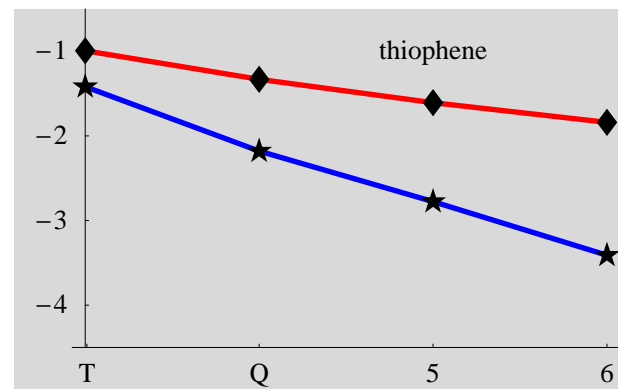
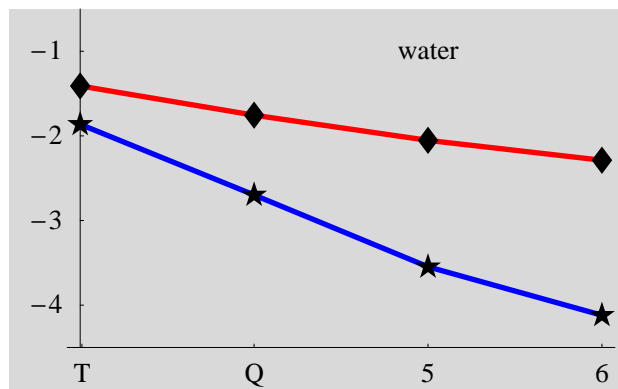
$$E_\infty = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3} \quad \leftarrow \text{two-point extrapolation formula}$$

- Finally, we identify  $X$  with the cardinal number of Dunning's cc-pVXZ basis sets
  - mean absolute errors of the CH<sub>2</sub>, H<sub>2</sub>O, HF, N<sub>2</sub>, CO, Ne, and F<sub>2</sub> energies:

mE <sub>h</sub>	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)
  - the GG*n* model (a mixed GTO–GTG model) 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 second-order Møller–Plesset (MP2) 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

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

- 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  $\phi_{ij}$  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 and the coefficients become

$$C_{ij}^{ab} = - \frac{\langle \phi_{ab} | r_{12}^{-1} | \phi_{ij} \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \leftarrow \text{only two-electron integrals needed}$$

- 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  $\alpha_v$ ,  $\beta_v$ ,  $\gamma_v$  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

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

- only two- and three-electron integrals now remain
- 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

## The GG*n* model: a mixed GTO–GTG pair-function expansion

- 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:

**GG0:** include only “ground-state” geminals  $\exp(-\gamma_v r_{12}^2) \phi_{ij}$

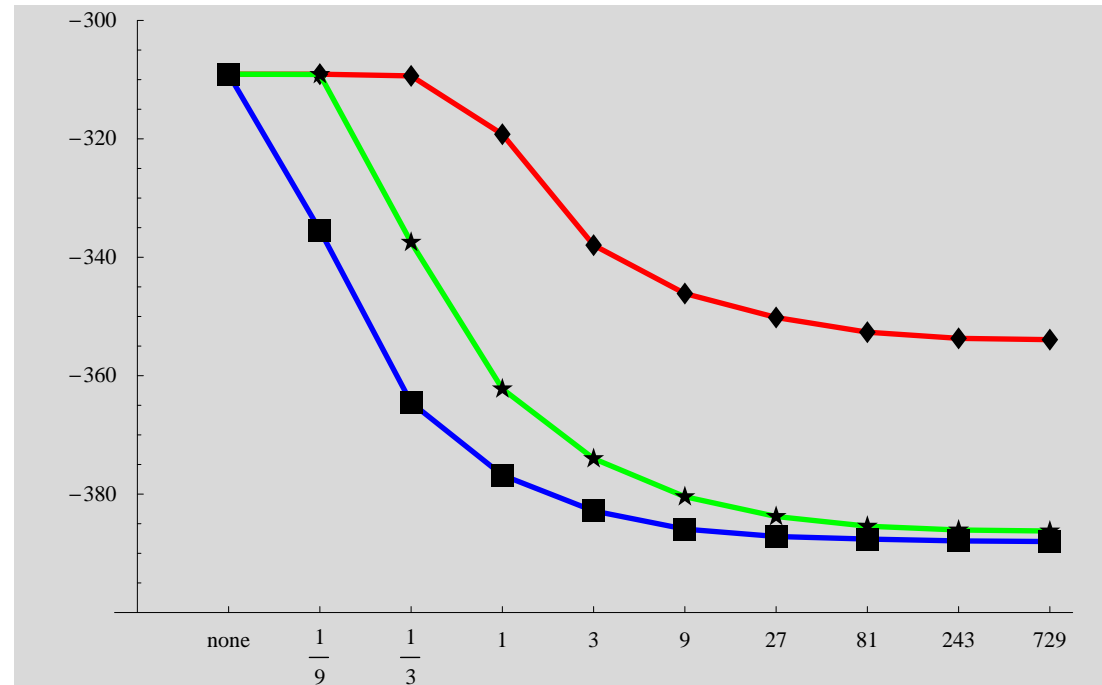
**GG1:** include also “singly-excited” geminals  $\exp(-\gamma_v r_{12}^2) \phi_{ai}$

**GG2:** 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

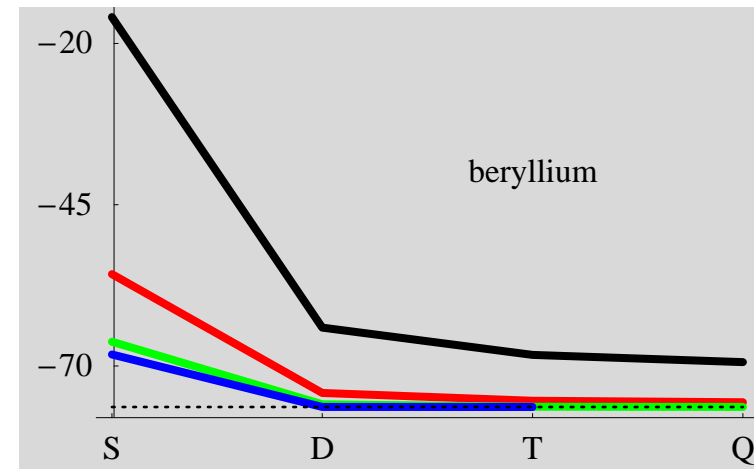
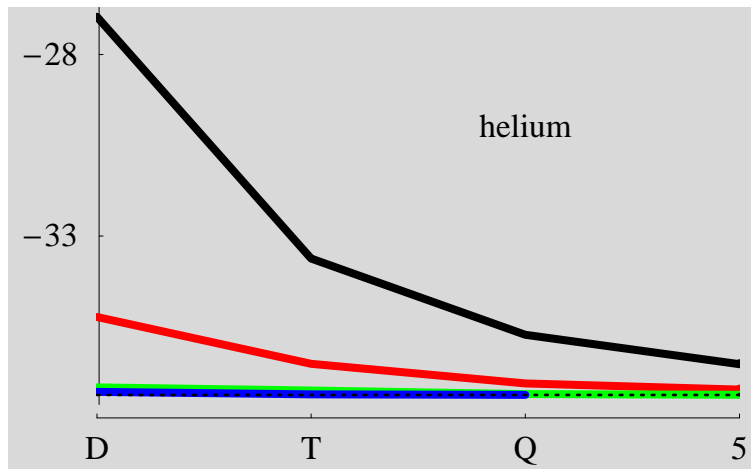
- We use nine even-tempered GTG exponents ( $\gamma_v = 1/9, 1/3, 1, 3, 9, 27, 81, 243, 729$ )
  - all-electron **GG0**, **GG1**, **GG2** aug-cc-pCVTZ(sp) neon calculations



- for GG0, only GTGs with  $\gamma \geq 1$  are important
- diffuse GTGs are important for excited GTGs (for GG1 and GG2)
- the three steepest GTGs improve mainly the  $1s^2$  energy
- with all nine GTGs included, the energy is converged to within 0.1 mH

## Helium and beryllium

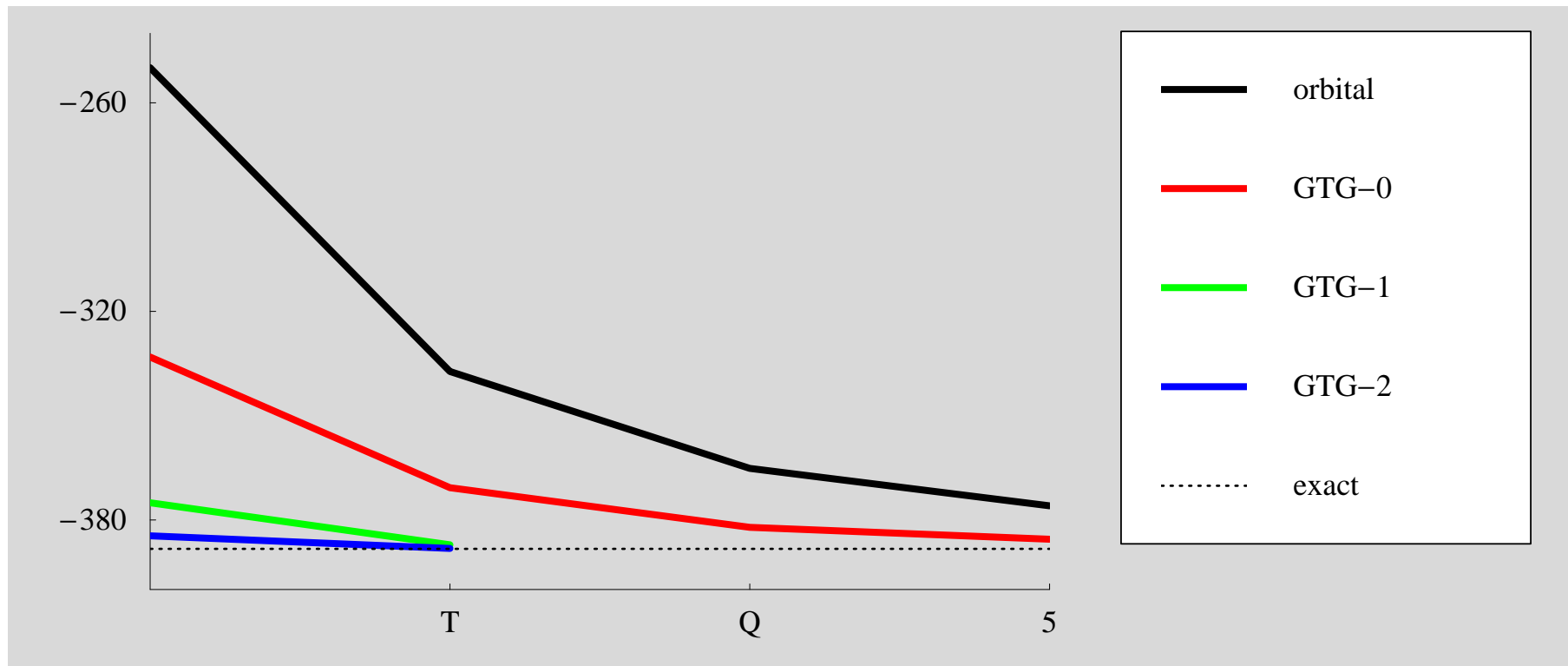
- A comparison of the MP2-GG $n$  models with standard MP2 theory
  - standard MP2, MP2-GG0, MP2-GG1, MP2-GG2



- aug-cc-pVXZ for helium; 14s to 14s9p4d3f for beryllium
- As expected, the use of geminals improves convergence considerably
  - errors reduced by several factors at the GG0 level of theory
  - errors reduced by an order of magnitude at the GG1 and GG2 levels of theory
- Our results are very close to GTG theory, 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 behaviour is observed for the neon atom:



- our best energy of  $-388.19$  mH is the lowest variationally bounded literature value
- GG0 theory reduces error by a factor of three or four relative to standard MP2 theory
  - 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

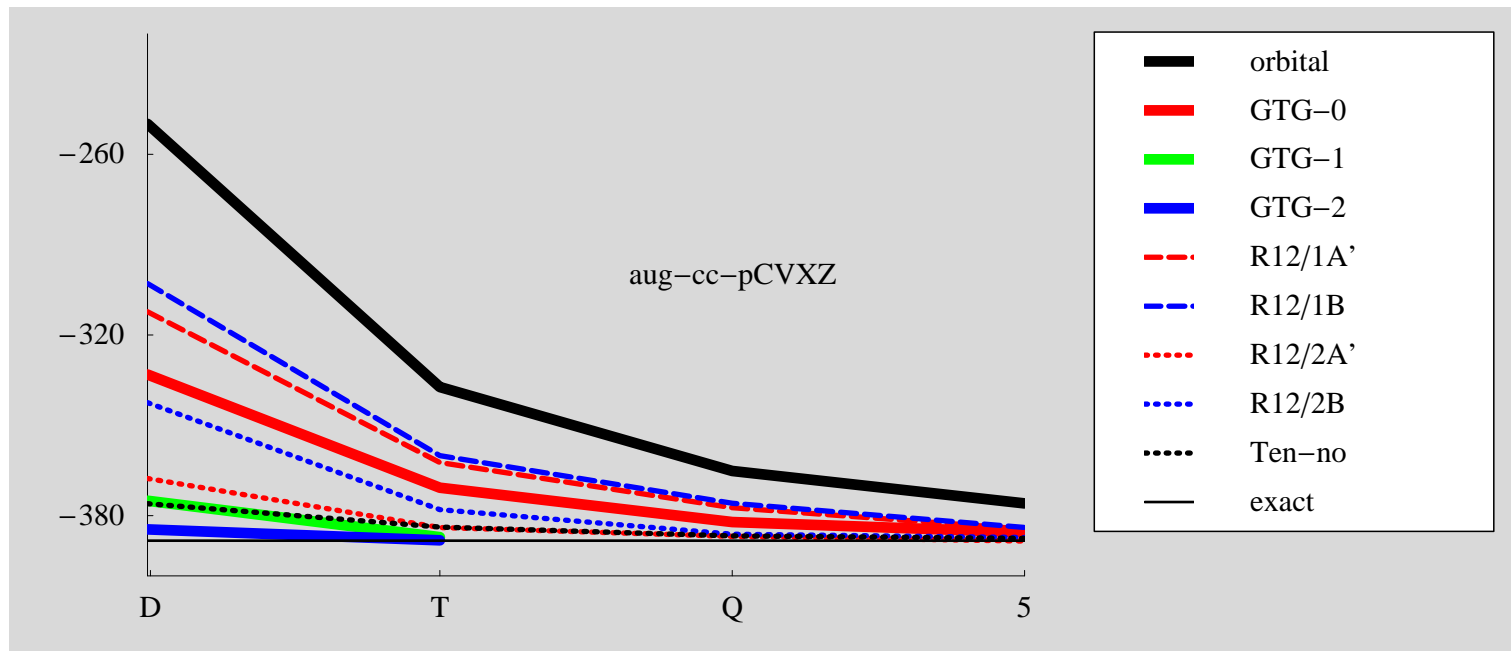
- In R12 theory, the pair function is taken to have the form

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

- explicit correlation only for doubly occupied pairs
- To avoid three- and four-electron integrals, resolution of identity (RI) is invoked
  - this dramatically improves performance—applicable to large molecules
- 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
- 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 MP2-GGn theory, MP2-R12 theory is not variationally bounded

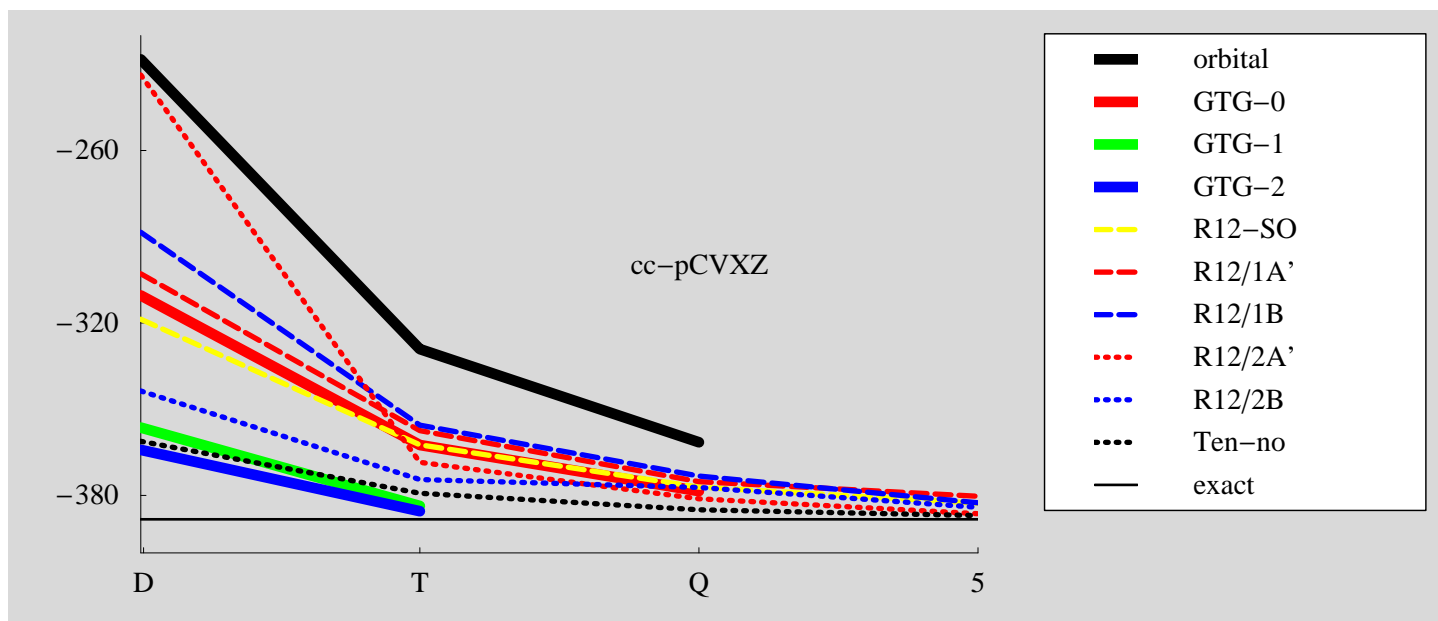


## Neon: comparison of explicitly correlated methods I



- 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 energies are lower than the GG0 energy
  - MP2-geminal close to MP2-GG1! WO penalty? error cancellation?

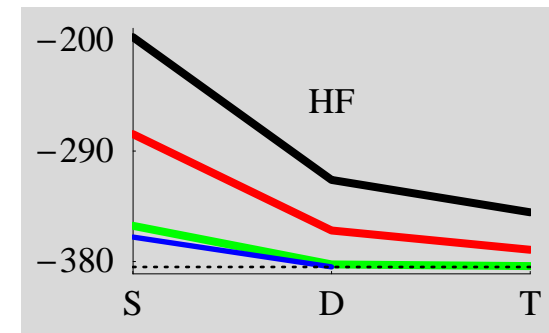
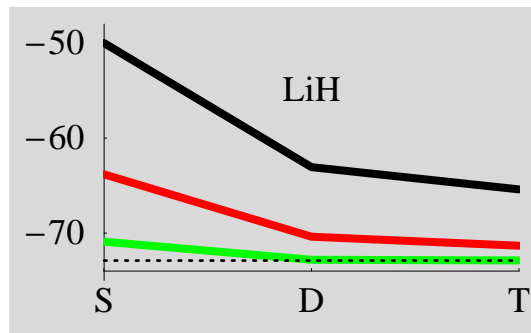
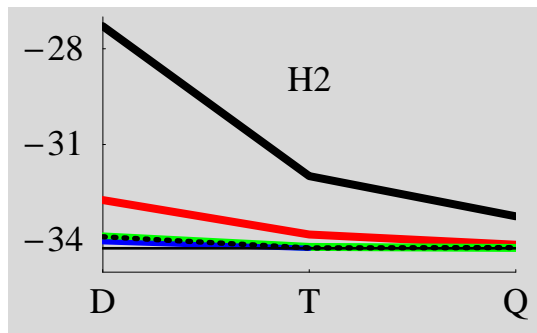
## Neon: comparison of explicitly correlated methods II



- No diffuse functions—higher energies for low cardinal numbers
- R12-SO is similar to Ansatz 2 but with explicit 3-electron integration
  - follows the GG0 curve closely (indicating that WO penalty is small)
- Excellent behavior of Ten-no's MP2-geminal model (follows GG1 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<sub>2</sub> and HF
  - H<sub>2</sub>: -34.252 mH with GG2/aug-cc-pVTZ
  - LiH: -72.877 mH with GG1/(14s9p4d3f/8s4p3d) [72.890 mH by Bukowski *et al.*]
  - HF: -384.41 mH with GG2/aug-cc-pCVTZ(sp,sp)
- Basis sets
  - H<sub>2</sub>: 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<sub>2</sub>O in aug-cc-pCVXZ basis sets

	std	ext	GG0	GG1	GG2	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% of the correlation energy has been recovered for all systems
- Extrapolation works well, recovering more than 99% at the aug-cc-pCV[TQ]Z level
- The variationally bounded MP2-GG $n$  sequence behaves in a very systematic manner
  - GG2 recovers 99% correlation energy in DZ basis and 100% in TZ basis
- The F12 methods appear to perform better than GG0
  - we believe that the WO penalty is small, indicating F12 error cancellation
  - the more rigorous R12/2B method is slightly better than GG0
  - the less rigorous R12/2A' works well by error cancellation (overshoots H<sub>2</sub>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)

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

<sup>a</sup> GG2/TZ calculations except GG1/TZ for LiH

<sup>b</sup> Patkowski, Bukowski, Jeziorski and Szalewicz, personal communication

<sup>c</sup> 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 GG*n* approach combines elements of both these approaches
  - WO functional (variationally bounded), explicit three-electron integration
- The GG0 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