Explicit electron correlation by a combined use of Gaussian-type orbitals and Gaussian-type geminals

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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!)
  - the question of CI expansions vs. explicit correlation is still with us today

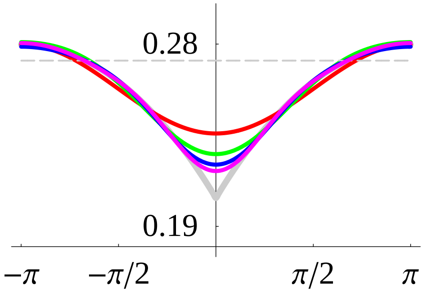
Overview

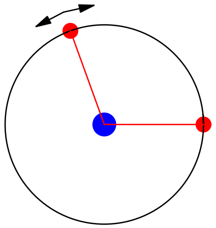
- We shall consider
  - Coulomb hole and energy convergence
  - extrapolation and explicit correlation
  - comparison of explicitly correlated methods (GTG, R12, GGn) and extrapolation
  - some conclusions
- Dahle, Helgaker, Jonsson and Taylor, PCCP **9**, 3112 (2007)

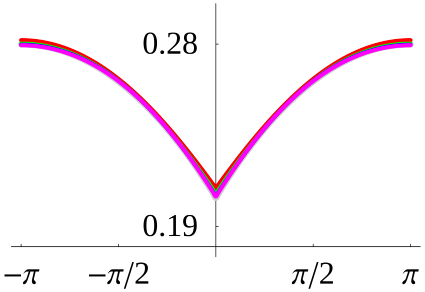
The Coulomb hole

- When electrons approach one another, the wave function behaves in special manner
  - large (infinite) repulsion is canceled by large (infinite) negative kinetic energy
  - for singlet pairs, a Coulomb hole is created, with a cusp at the point of coalescence
- Below we have plotted the Coulomb hole in helium for two classes of wave functions
  - CI wave functions with one shell included at a time: $1s$, $2s2p$, $3s3p3d$, $\ldots$
  - the same wave functions with a single term linear in r_{12} added (CI-R12)

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



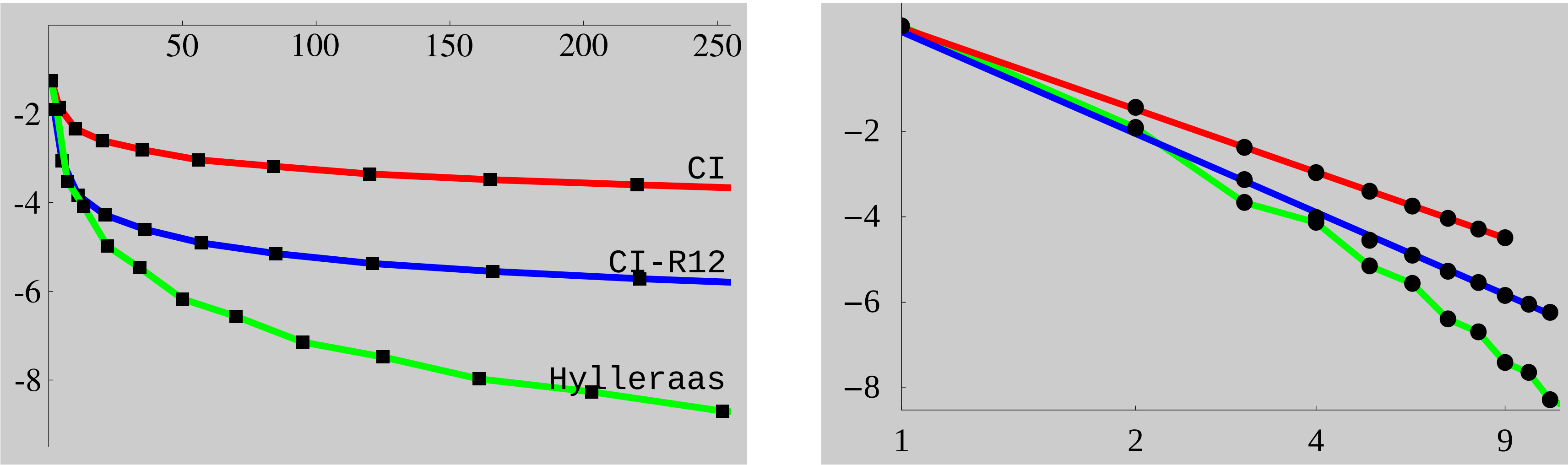




  - the CI wfs. can only indirectly describe the Coulomb hole and converge slowly
  - the CI-R12 wfs. contain a cusp by construction and model the Coulomb hole well
- For high accuracy in the energy, we need a good description of the Coulomb hole

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
  - each new shell contributes n^{-4} energy for CI
  - convergence is very smooth
- The inclusion of a single R12 term reduces the energy error dramatically

The principal expansion and basis-set extrapolation

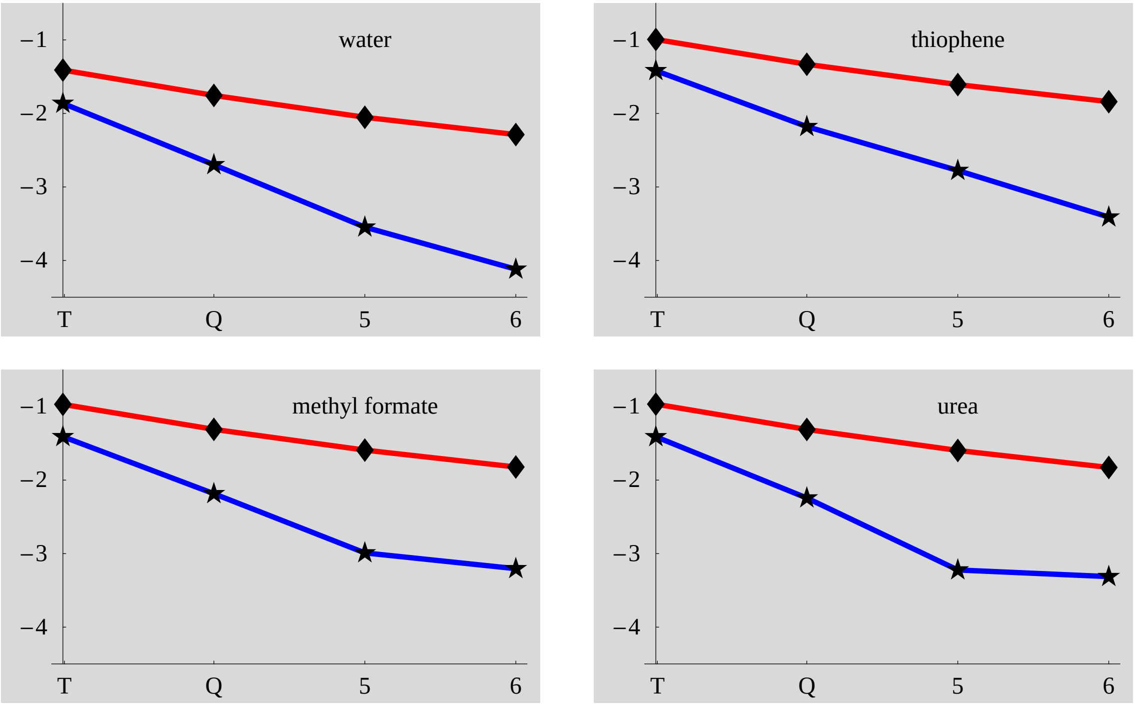
- The principal expansion: include orbitals in full shells of principal quantum number n
  - we can now easily estimate the omitted contributions and hence the basis-set limit

$$E_\infty = E_X + A \sum_{n=X+1}^{\infty} n^{-4} \approx E_X + AX^{-3}$$

  - the unknown constant A is eliminated by carrying out two separate calculations

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

  - practical realization: cc-pVXZ
  - logarithmic errors in plain and extrapolated energies relative to R12
  - from: Klopper, Manby, Ten-no and Valeev, *Int. Rev. Phys. Chem.* **25**, 427 (2006)



Explicit correlation

- Extrapolation improves our description significantly
  - it is very simple and does not require new coding
- 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 R12 method of Kutzelnigg and Klopper (1985, 1986)
  - the GGn model (a mixed GTO–GTG model) explored by us
- We shall consider small systems, asking the questions
  - what error reduction can be expected from these methods?
  - how does it compare with basis-set extrapolation?
- It is sufficient to consider second-order Møller–Plesset (MP2) theory
  - the doubles contributions converge more slowly than higher excitations

Møller–Plesset theory

- The zero-order system is represented by the Fock operator

$$F_1\phi_i(1) = \varepsilon_i\phi_i(1) \qquad \leftarrow \text{spin orbitals and energies}$$

  - the zero-order wave function is a determinant

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

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

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

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

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

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

  - this is Sinanoglu's SO functional

- The MP2 correlation energy may be written as the sum of pair energies

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

Møller–Plesset theory—choice of pair function

- In standard orbital-based MP2 theory, we use a CI-type expansion of each pair function:

$$u_{ij} = \sum_{ab} C_{ij}^{ab} \phi_{ab}, \quad Q_{12} u_{ij} = u_{ij}$$

  - strong orthogonality is ensured and only two-electron integrals arise
  - slow convergence

- In explicitly-correlated MP2 theory, the pair functions depend explicitly on r_{12}:

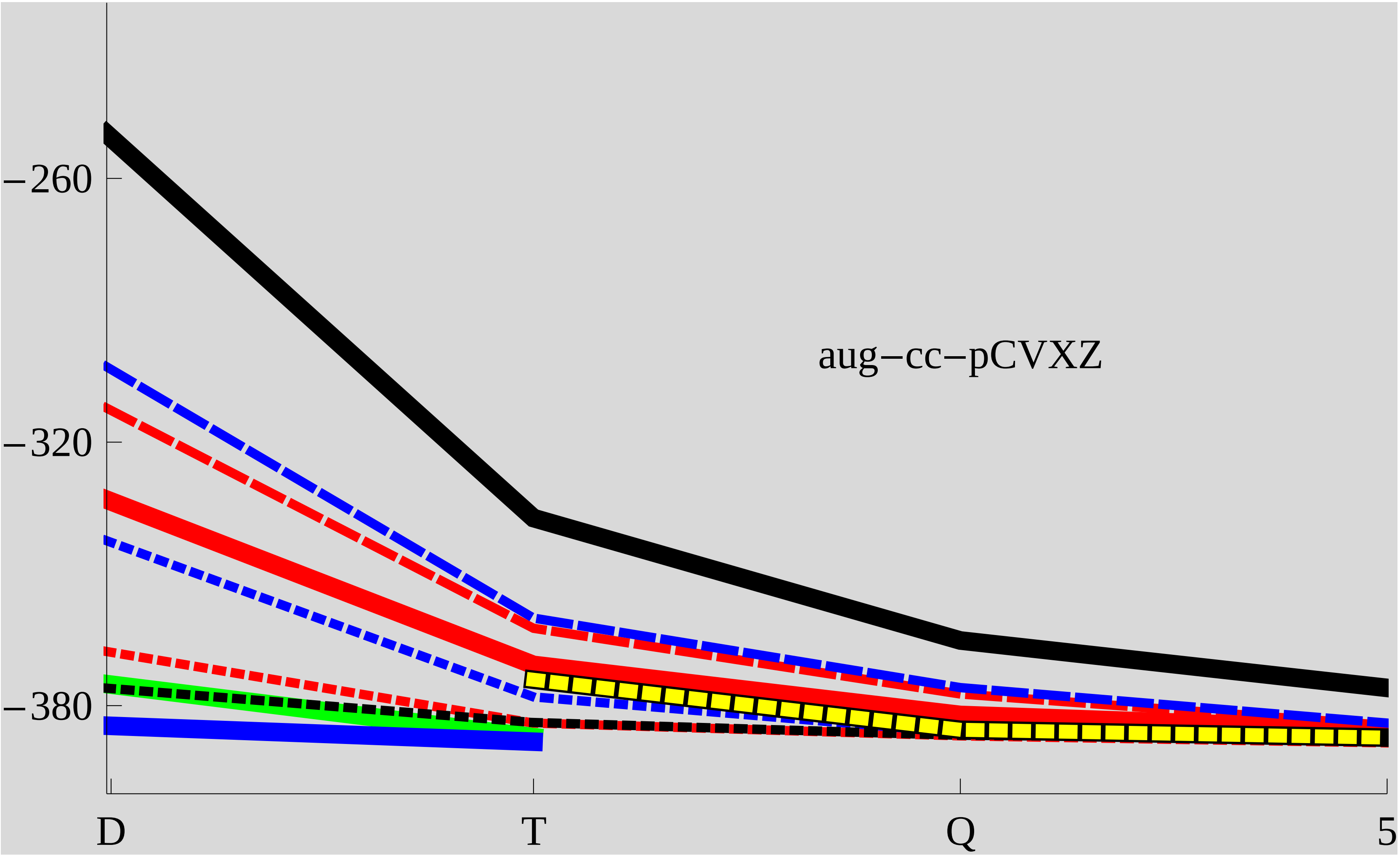
$$u_{ij} = u_{ij}(r_{12}), \quad Q_{12} u_{ij} \neq u_{ij}$$

  - strong orthogonality is not ensured and many-electron integrals arise
  - faster convergence

- A variety of explicitly correlated methods have been developed, depending on
  - the choice of correlation function $u_{ij}(r_{12})$
    - linear correlation function: $r_{12}\phi_{ab}$
    - Gaussian Gaussian function: $\exp\left(-\gamma_v r_{12}^2\right) \phi_{ab}$
  - the treatment of strong orthogonality Q_{12}
    - operators that project out more than Q_{12}
    - operators that project out less than Q_{12} (compensated for by penalty functions)

- The models have been dictated not only by physics but also by difficulties in integration

Explicit correlation—a plethora of methods (neon atom)



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 such u_{ij}, Szalewicz *et al.* [CPL **91**, 169 (1982)] modified Sinanoglu's SO functional

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

where the shifted Fock operators introduce a penalty and are given by

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

  - 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 only
  - orthogonality controlled by a penalty function—requires a flexible pair function

R12 theory

- In Kutzelnigg's and Klopper's R12 theory, the pair function is taken to have the form

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

  - a combined conventional and explicitly correlated expansion
  - only parameters (expansion coefficients) are optimized (conventional GTOs are used)
- To avoid three- and four-electron integrals, resolution of identity (RI) is invoked
  - this dramatically improves performance—applicable to large molecules
- Recently, more general correlation factors have been explored (F12 theory)
  - $f(r_{12}) = 1 - \exp(-\gamma r_{12})$ (Ten-no, 1994)
  - $f(r_{12}) = 1 - \sum_v c_v \exp\left(-\gamma_v r_{12}^2\right)$ (May and Manby, 1994)
- Various flavors (Ansätze) of R12/F12 theories exist, depending on:
  - Q_{12} projection against all MOs or only the occupied MOs (Ansätze 1 and 2)
  - the omission or inclusion of certain exchange commutators (Ansätze A and B)
  - the (non)assumption of the extended Brillouin theorem (EBT): $F\phi_a = \varepsilon_a \phi_a$

The GGn model: a mixed GTO–GTG pair-function expansion

- We have investigated a method that combines elements of GTG and R12 theories

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

- In common with GTG theory:
  - we use the WO functional, avoiding 4-electron integrals but not 3-electron integrals
  - we use Gaussian geminals for explicit correlation
- In common with R12 theory:
  - we combine explicit correlation with a traditional GTO expansion
  - we avoid nonlinear optimization (fixed exponents and positions)
- There are three levels of GGn theory, depending on what geminals are included:

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

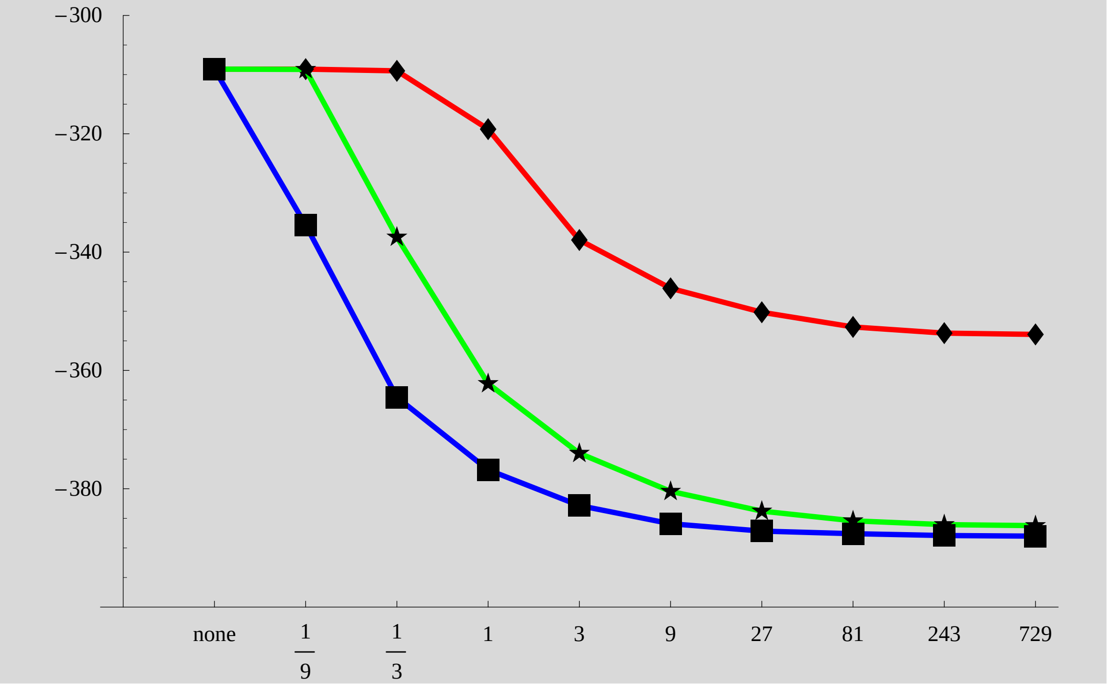
GG1: include also “singly-excited” geminals $\exp(-\gamma_v r_{12}^2)\phi_{ai}$

GG2: include also “doubly-excited” geminals $\exp(-\gamma_v r_{12}^2)\phi_{ab}$

- GREMLIN code written by Pål Dahle (DALTON module)

GTG exponents

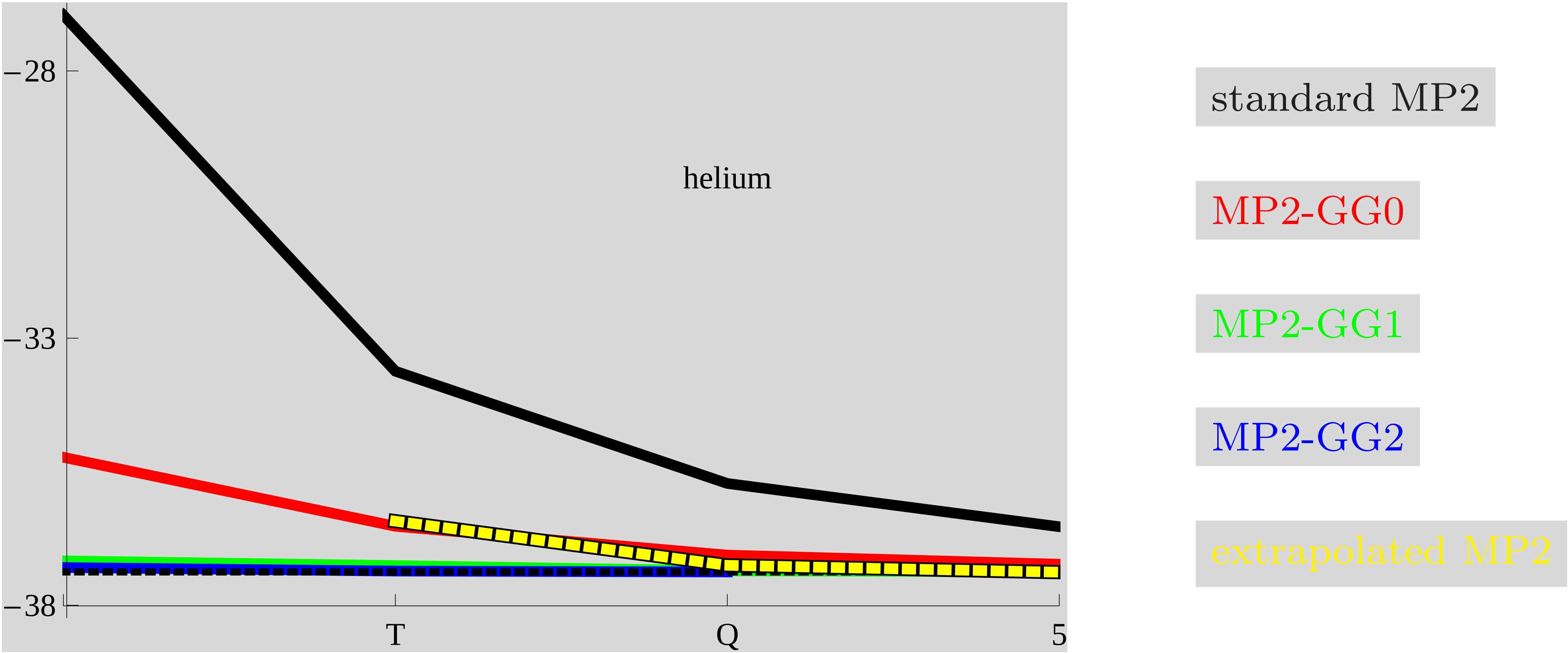
- We use nine even-tempered GTG exponents ($\gamma_v = 1/9,\ 1/3,\ 1,\ 3,\ 9,\ 27,\ 81,\ 243,\ 729$)
  - all-electron GG0, GG1, GG2 aug-cc-pCVTZ(spd) neon calculations



  - 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

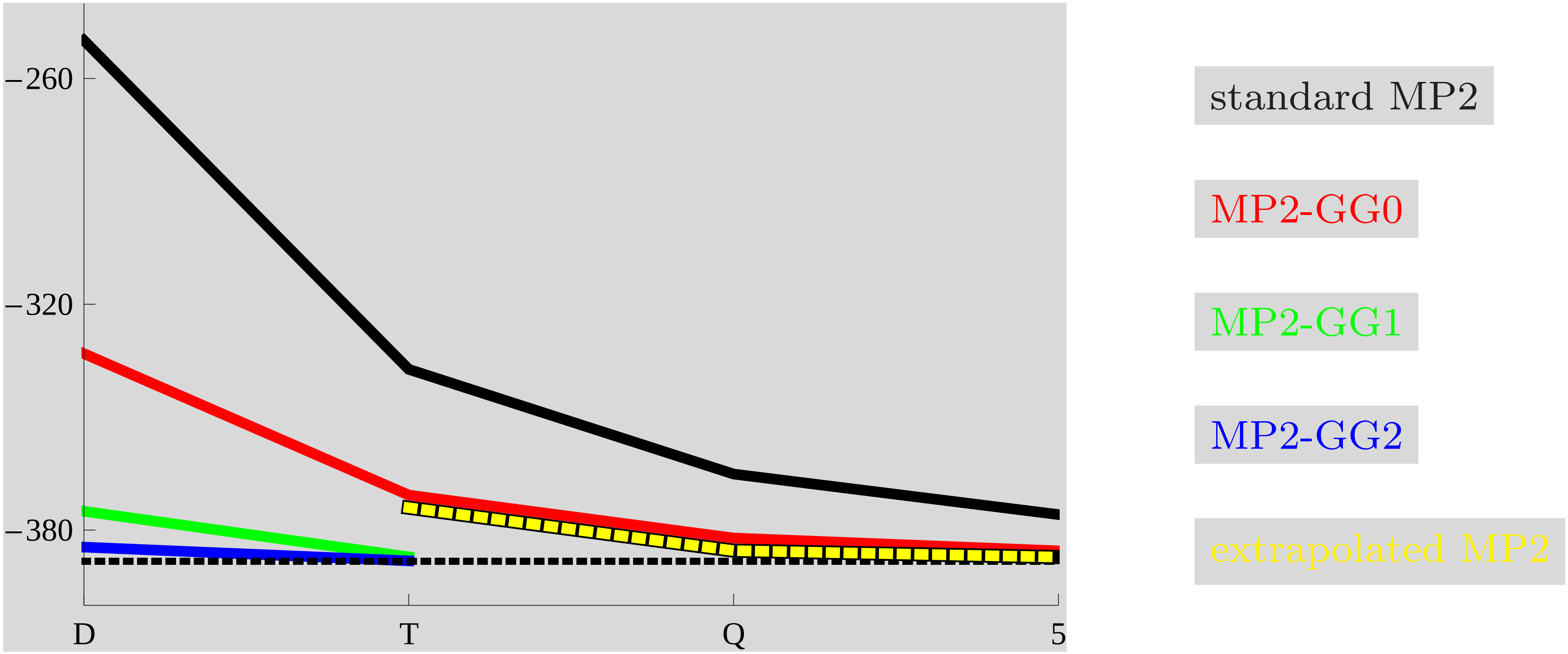
- A comparison of MP2-GGn/aug-cc-pVXZ with standard and extrapolated MP2 theory



- As expected, the use of geminals improves convergence considerably
  - errors reduced by an order of magnitude at the GG1 and GG2 levels of theory
  - note: the GG0 error reduction is no better than extrapolation!
- Our results are very close to the nonlinear GTG theory:
  - GG2: −37.3773 mH; Patkowski *et al.*: −37.3775 mH; extrapolation: −37.36 mH

Neon

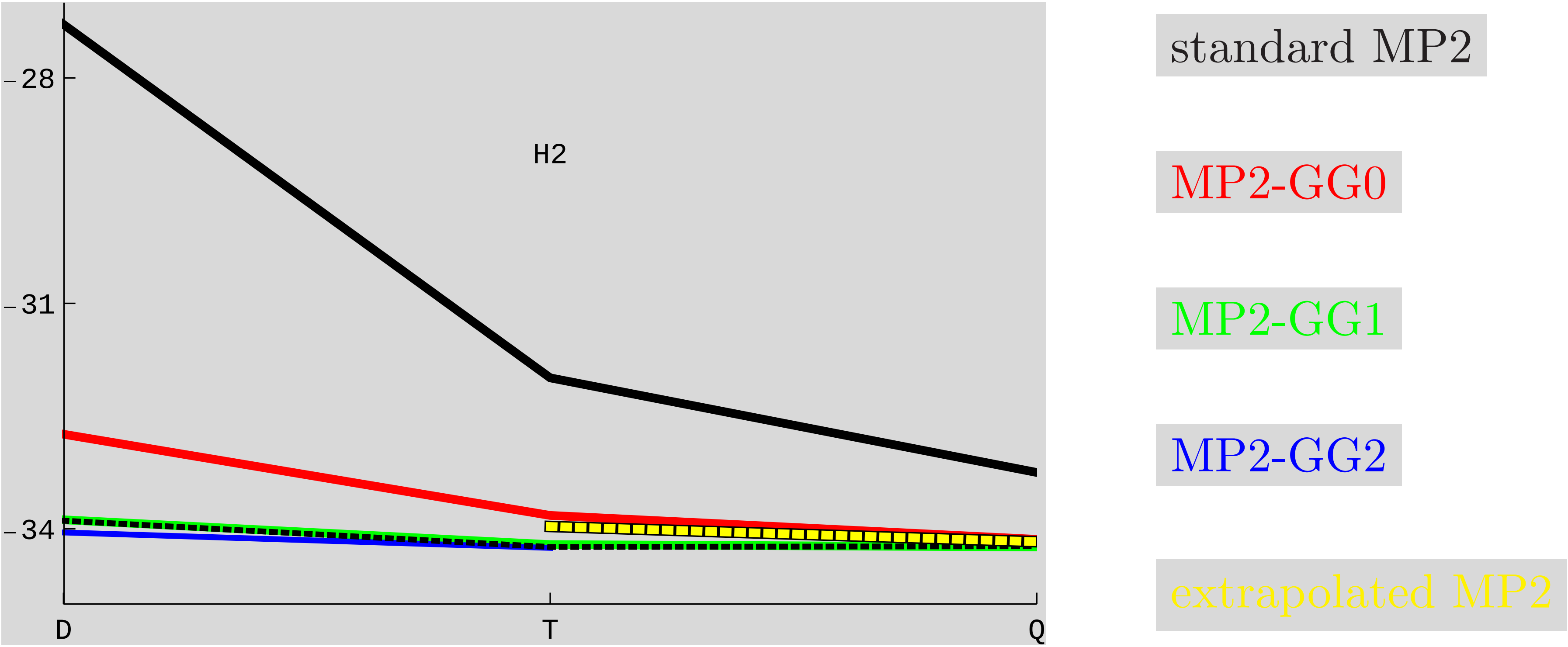
- A similar behaviour is observed for the neon atom in the aug-cc-pCVXZ basis:



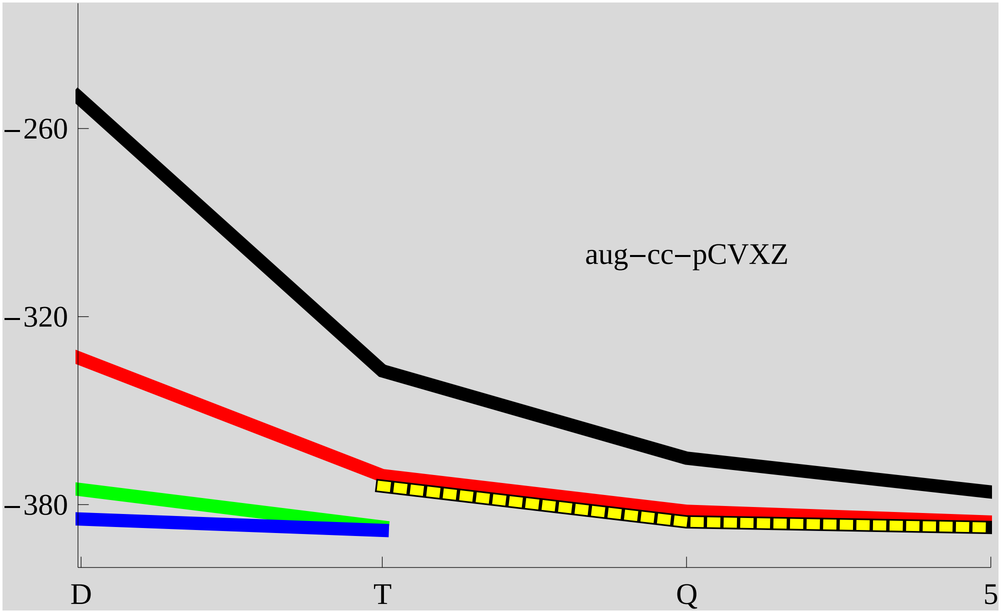
- GG0 theory reduces error by a factor of three or four relative to standard MP2 theory
  - but basis-set extrapolation gives similar results
- The GG2/aug-cc-pCVTZ value is −388.19 mH
  - this is the lowest variationally bounded literature value
  - 0.25% (1 mH) below the best extrapolated value

Hydrogen molecule

- The same pattern is observed for other systems
  - H_2 in aug-pVXZ basis



Neon: a comparison with R12/F12 methods



- 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?

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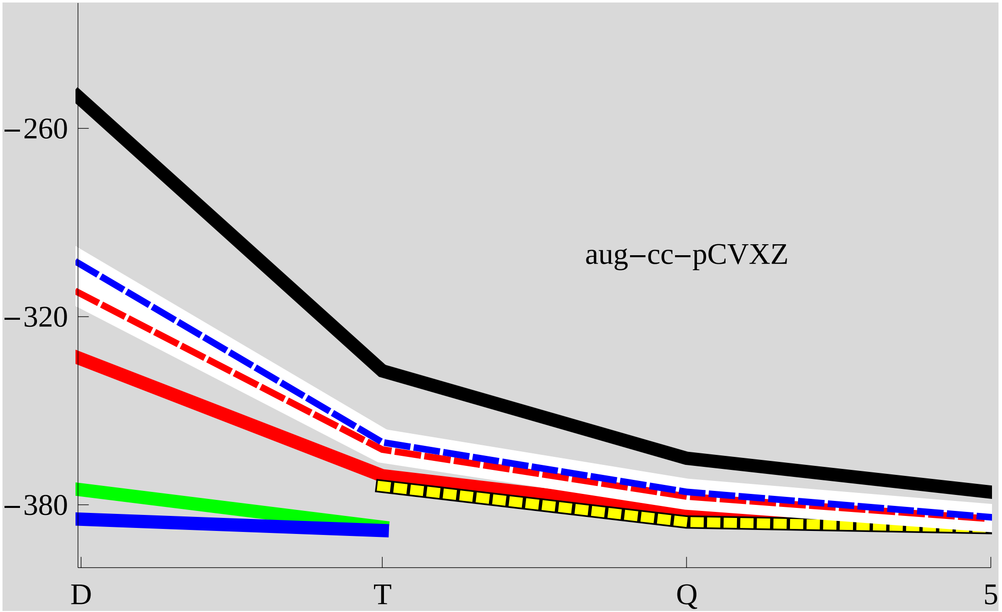

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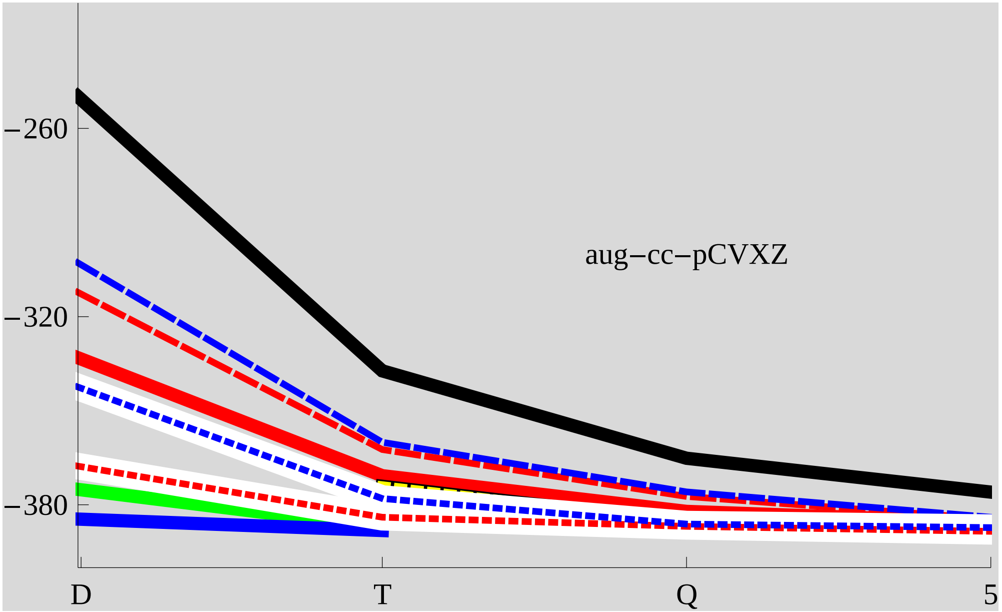

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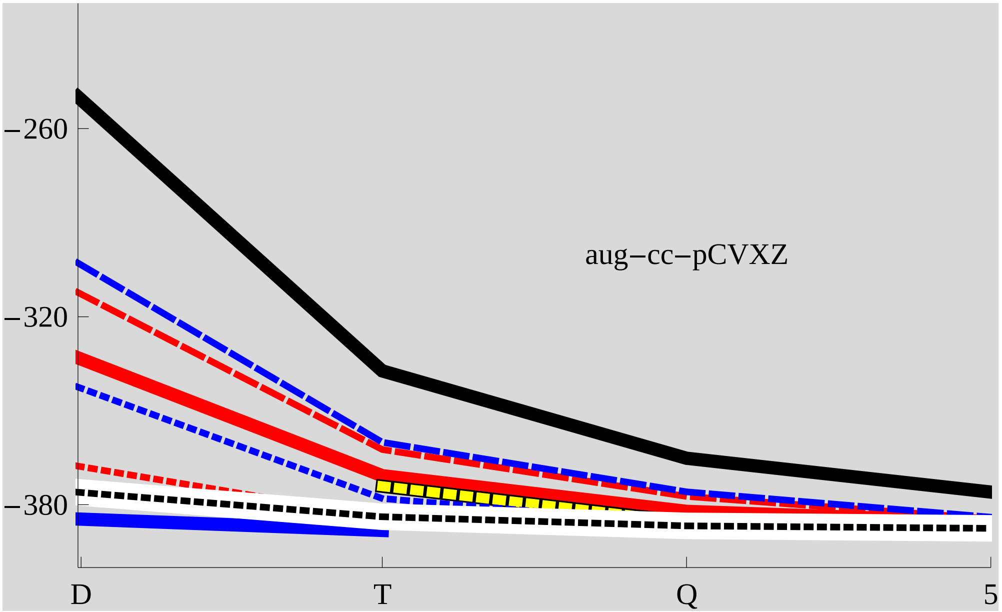

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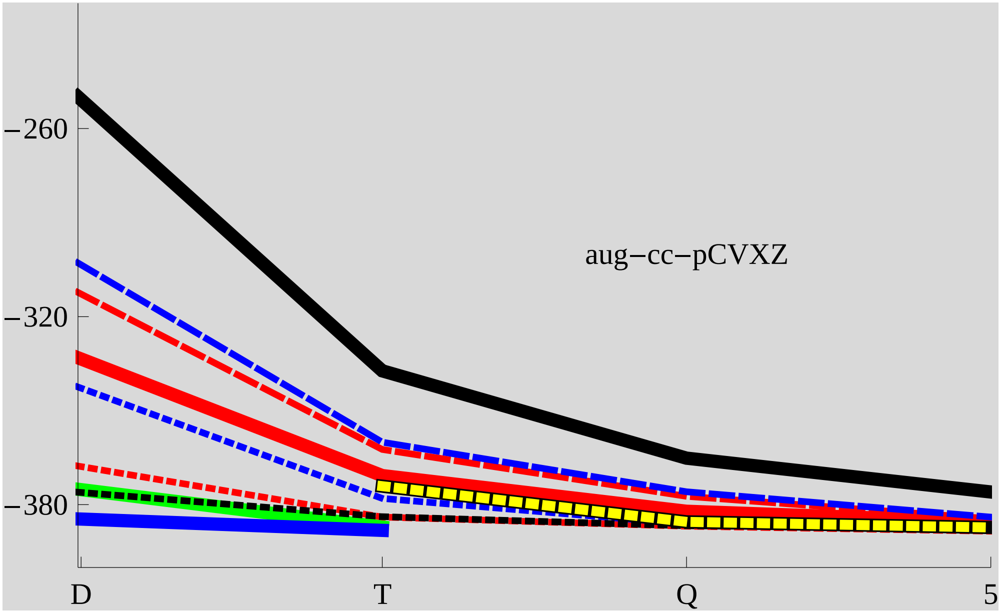

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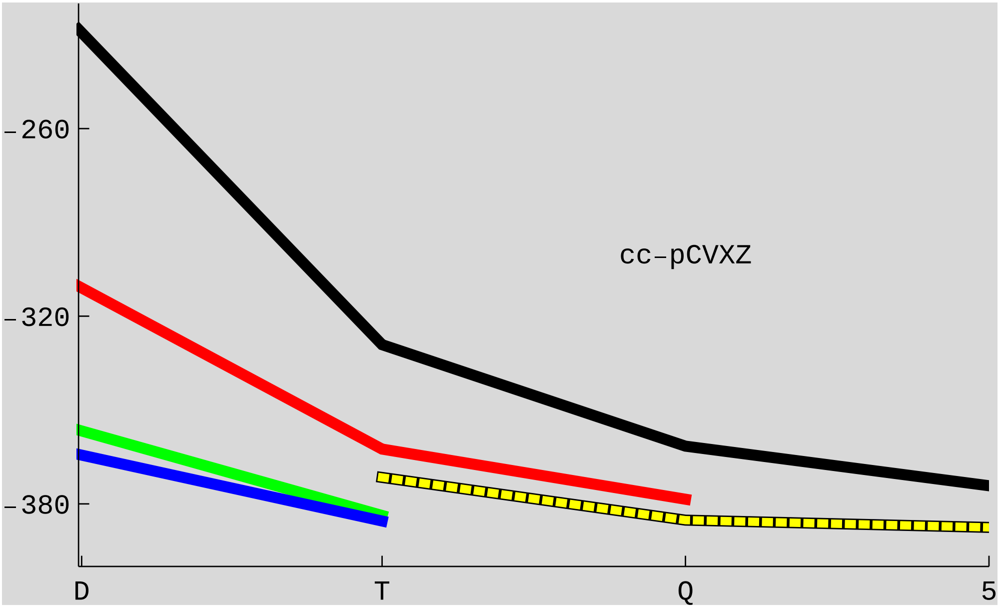
Neon: sorting out the models



- GG0 converges slowly, slightly poorer than extrapolation
  - Gaussian correlation factor and WO functional
- R12-SO converges no faster than GG0
  - linear correlation factor and SO functional
- Ten-no's MP2-geminal model converges much faster—as fast as GG1
  - Gaussian correlation function and SO functional
- Conclusion: the WO functional and R12 factor are both poor in small basis sets

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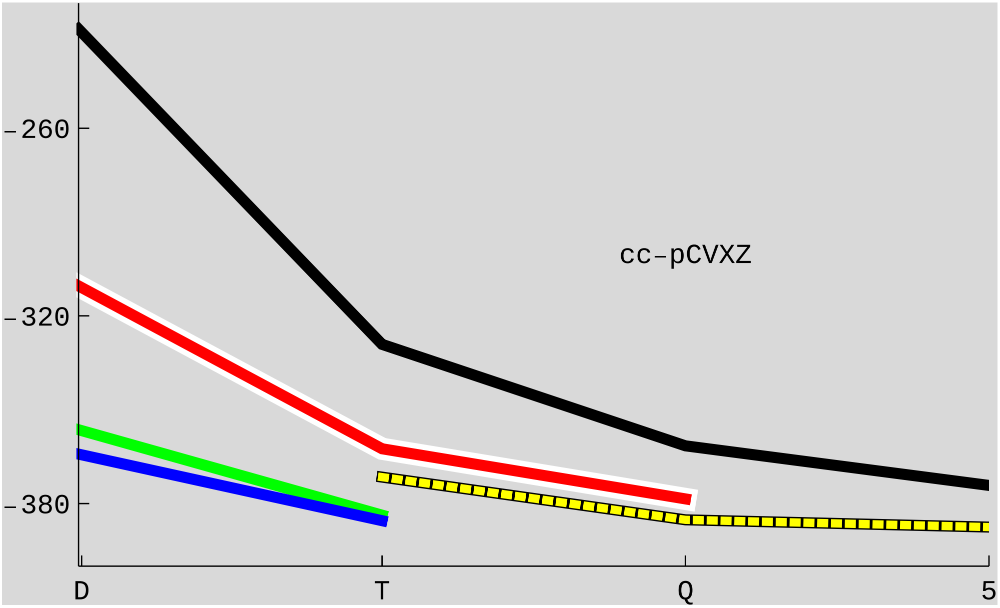

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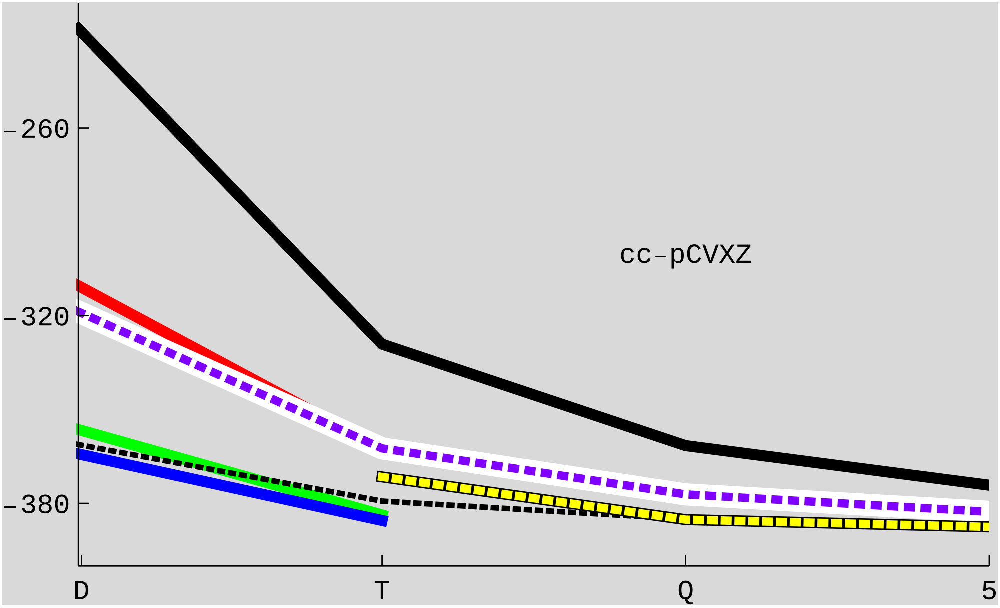

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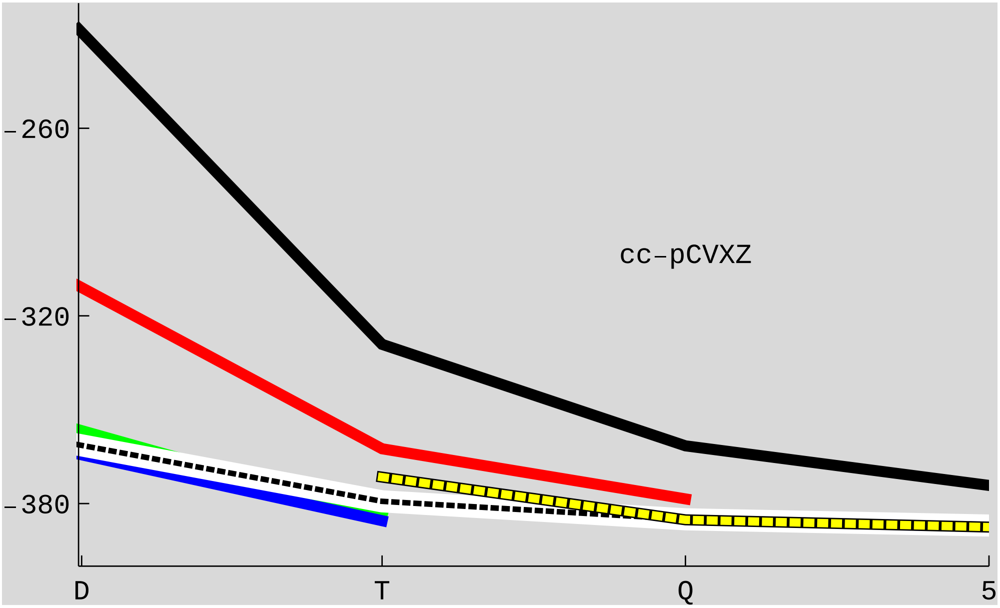

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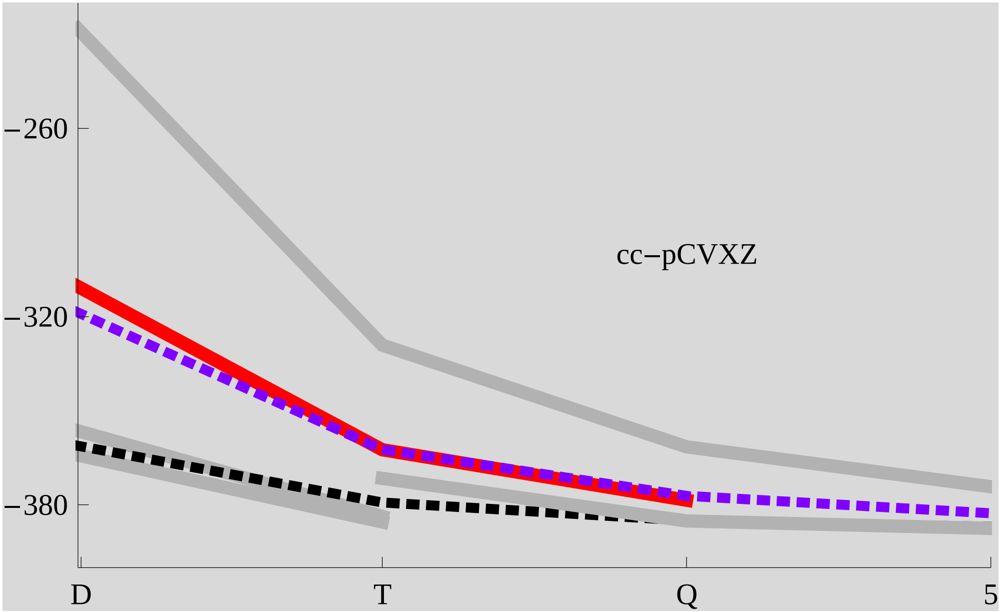

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Some conclusions

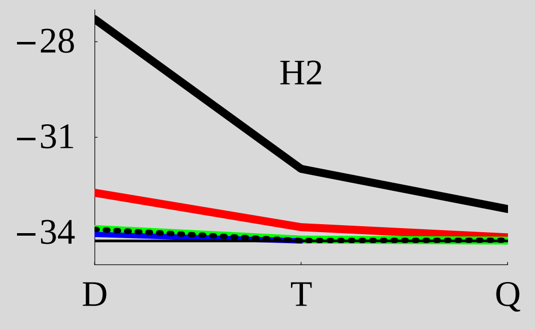
- Indeed, May *et al.* [PCCP **7**, 2710 (2005)] suggested a problem with the r_{12} factor
  - advocated the use of linear combinations of Gaussian geminals rather than r_{12}
- Very recent Tew, Klopper and Manby studied the WO penalty
  - large penalty for GG0 only—GG1, GG2 and GTG can model orthogonality
- One should probably avoid both linear r_{12} and WO with small basis sets
- All-electron correlation energies of Ne, HF, and H_2O in aug-cc-pCVXZ basis sets

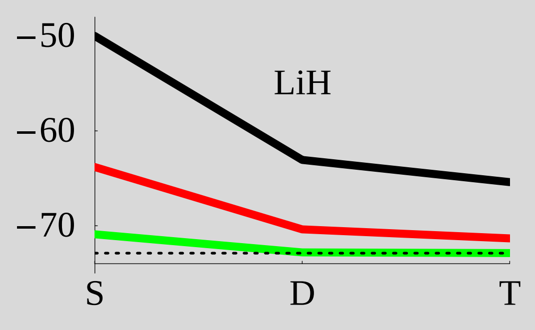
	std	ext	GG0	GG1	GG2	2A'	2B	Ten-no
DZ	68.2		87.8	97.2	99.2	96.2	91.1	96.9
TZ	88.3	96.8	96.3	99.8	100.0	99.1	98.0	99.1
QZ	94.8	99.6	98.5			99.8	99.4	99.7

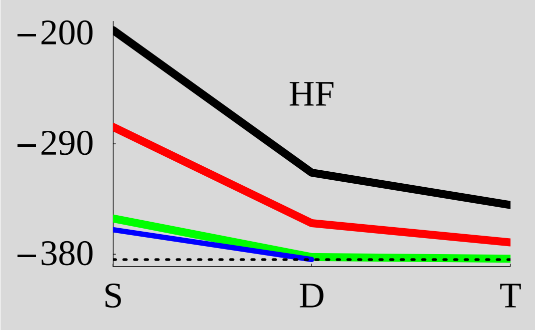
  - blue: more than 99% of the correlation energy has been recovered for all systems
- Extrapolation works well, recovering more than 99% at the aug-cc-pCV[TQ]Z level
  - the F12 methods outperform GG0—in particular, in a small basis
  - GG2 recovers 99% correlation energy in DZ basis and 100% in TZ basis
  - QZ basis needed to recover consistently more than 99% correlation energy

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 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(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 energies of small systems (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] GG2/TZ calculations except GG1/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 GGn approach combines elements of both these approaches
  - WO functional (variationally bounded), explicit three-electron integration
  - the GG0 model recovers less correlation energy than does F12 theory
  - the GG1 and GG2 models recover more than 99% correlation energy in a TZ basis
  - in general QZ basis is needed for such an accuracy