- **Introduction to coupled-cluster theory: Energies, cluster equations and derivatives**
- **Performance assessment and basis sets**
- **Explicitly correlated coupled-cluster response theory**

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Part I

Introduction to coupled-cluster theory: Energies, cluster equations and derivatives

(Tuesday 15.02.)

The Coupled-Cluster Wavefunction Ansatz

Wavefunction ansatz for single-reference coupled-cluster methods:

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{Ref}\rangle \quad \text{with} \quad \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots$$

where

$$\hat{T}_1 = \sum_{ai} t_a^i \, a_a^\dagger a_i$$

$$\hat{T}_2 = \sum_{\substack{a>b \\ i>j}} t_{ab}^{ij} \, a_a^\dagger a_i \, a_b^\dagger a_j$$

$$\hat{T}_3 = \sum_{\substack{a>b>c \\ i>j>k}} t_{abc}^{ijk} \, a_a^\dagger a_i \, a_b^\dagger a_j \, a_c^\dagger a_k$$

short: $\hat{T} = \sum_\mu t_\mu \hat{\tau}_\mu$

$|\mathrm{Ref}\rangle$ is a Slater determinant

(usually $|\mathrm{Ref}\rangle = |\mathrm{HF}\rangle$)

$i, j, k, \ldots$ occupied orbitals

$a, b, c, \ldots$ virtual orbitals

intermediate normalization:

$$\langle \mathrm{Ref}|\mathrm{CC}\rangle = 1$$

The Coupled-Cluster Wavefunction

For to non-interacting subsystems with

$$\hat{H}_A \exp(\hat{T}_A)|\mathrm{Ref_A}\rangle = E_A \exp(\hat{T}_A)|\mathrm{Ref_A}\rangle$$
$$\hat{H}_B \exp(\hat{T}_B)|\mathrm{Ref_B}\rangle = E_B \exp(\hat{T}_B)|\mathrm{Ref_B}\rangle$$

we get

$$(\hat{H}_A + \hat{H}_B) \exp(\hat{T}_A + \hat{T}_B)|\mathrm{Ref_A Ref_B}\rangle =$$
$$(E_A + E_B) \exp(\hat{T}_A + \hat{T}_B)|\mathrm{Ref_A Ref_B}\rangle$$

- Product separability allows to set up size-extensive approximations

The Coupled-Cluster Energy

Computation and variational optimization of the expectation value

$$\frac{\langle \mathrm{HF}| \exp(\hat{T})^\dagger \hat{H} \exp(\hat{T}) |\mathrm{HF}\rangle}{\langle \mathrm{HF}| \exp(\hat{T})^\dagger \exp(\hat{T}) |\mathrm{HF}\rangle}$$

is difficult...

The Coupled-Cluster Energy

Computation and variational optimization of the expectation value

$$\frac{\langle \mathrm{HF}|\exp(\hat{T})^\dagger \hat{H} \exp(\hat{T})|\mathrm{HF}\rangle}{\langle \mathrm{HF}|\exp(\hat{T})^\dagger \exp(\hat{T})|\mathrm{HF}\rangle}$$

is difficult...

Standard CC models use instead a projected Schrödinger equation.

Two variants:

unlinked: $\langle\mu| \left(\hat{H}-E\right)\exp(\hat{T})|\mathrm{HF}\rangle = 0$

linked: $\langle\mu|\exp(-\hat{T})\left(\hat{H}-E\right)\exp(\hat{T})|\mathrm{HF}\rangle = 0$

where $\langle\mu| \in \left\{\langle \mathrm{HF}|, \langle \mathrm{HF}|\hat{\tau}_\mu^\dagger\right\}$ with same set of $\hat{\tau}_\mu$ as included in $\hat{T}$

The Unlinked CC Equations

Unlinked formulation:

$$E = \langle \mathrm{HF} | \hat{H} \exp(\hat{T}) | \mathrm{HF} \rangle$$
$$0 = \langle \mu | \hat{H} \exp(\hat{T}) | \mathrm{HF} \rangle$$

after expansion of $\exp(\hat{T})$

$$E = \langle \mathrm{HF} | \hat{H} \left(1 + \hat{T}_1 + \tfrac{1}{2}\hat{T}_1 + \hat{T}_2\right) | \mathrm{HF} \rangle$$
$$0 = \langle \mu | \hat{H} \left(1 + \hat{T} + \tfrac{1}{2}\hat{T}^2 + \ldots\right) | \mathrm{HF} \rangle$$

- keeps similarity to CI and CEPA equations

The Linked CC Equations

Linked formulation:

$$E = \langle \mathrm{HF} | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | \mathrm{HF} \rangle$$

$$0 = \langle \mu | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | \mathrm{HF} \rangle$$

BCH expansion leads to:

$$E = \langle \mathrm{HF} | \hat{H} + [\hat{H}, \hat{T}_1 + \hat{T}_2] + \tfrac{1}{2}[[\hat{H}, \hat{T}_1], \hat{T}_1] | \mathrm{HF} \rangle$$

$$0 = \langle \mu | \hat{H} + [\hat{H}, \hat{T}] + \tfrac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \tfrac{1}{3!}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \tfrac{1}{4!}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}] | \mathrm{HF} \rangle$$

- requires second quantization techniques
- term-wise size-consistent

Linked vs. Unlinked Form

Linked and unlinked form of CC equations equivalent if:

- the only approximation made is a truncation of the excitation manifold

- and the excitation manifold is closed under deexcitation:

  $\hat{\tau}_\mu$ & $\hat{\tau}_\nu$ included $\Rightarrow$ also $\hat{\tau}_\mu^\dagger \hat{\tau}_\nu$ included unless $\hat{\tau}_\mu^\dagger \hat{\tau}_\nu |\mathrm{HF}\rangle = 0$

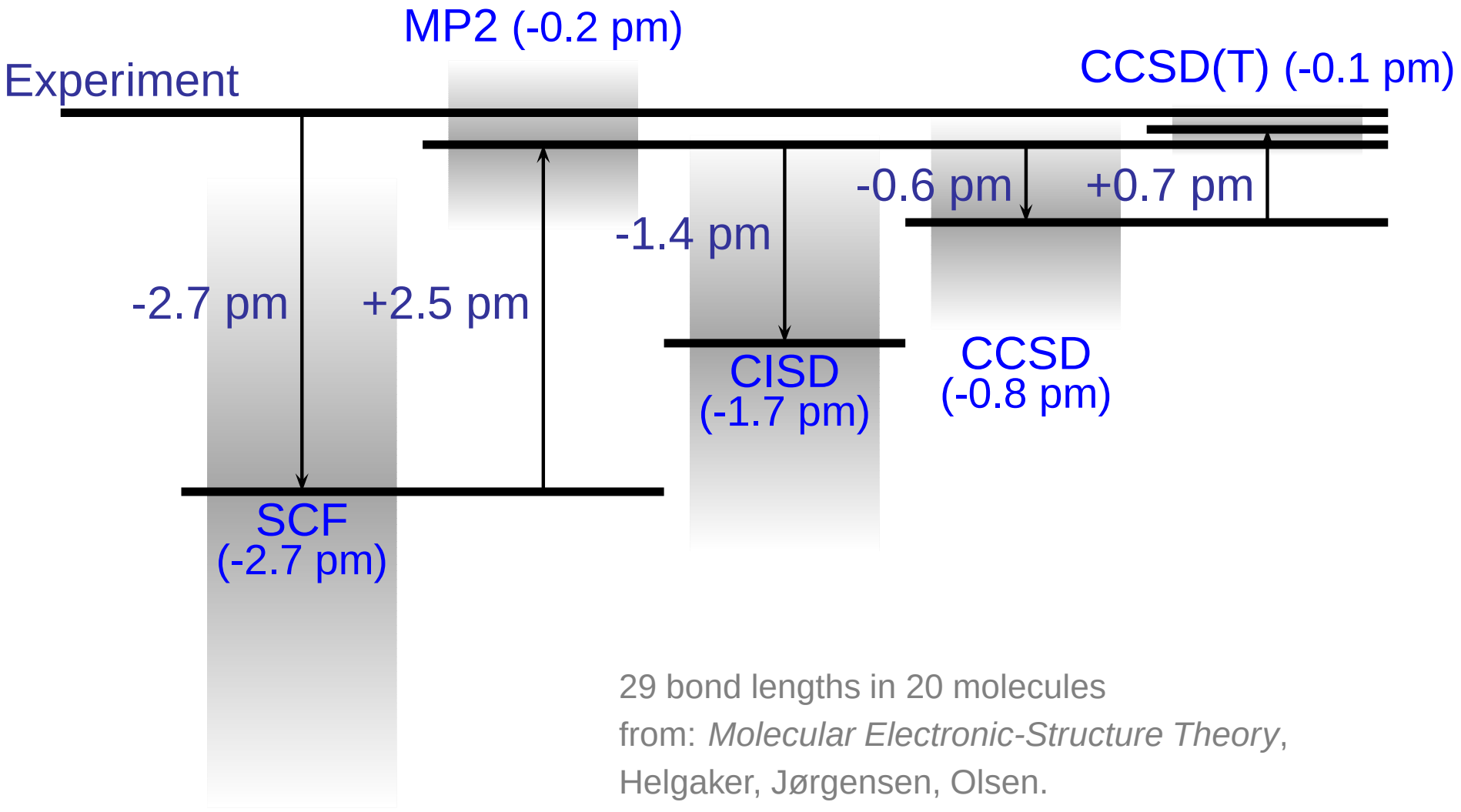
  e.g. $a_a^\dagger a_i a_b^\dagger a_j$ & $a_a^\dagger a_j$ included $\Rightarrow$ also $a_b^\dagger a_i$ included

Hierarchy of Standard CC Models

CC Model	$\hat{T}$	costs	order PT	CI Model	order PT
CCS	$\hat{T}_1$	$\mathcal{O}(N^4)$	1	CIS	1
CCSD	$\hat{T}_1 + \hat{T}_2$	$\mathcal{O}(O^2N^{2+2})$	3	CISD	3
CCSDT	$\hat{T}_1 + \hat{T}_2 + \hat{T}_3$	$\mathcal{O}(O^3N^{3+2})$	4	CISDT	3
CCSDTQ	$\hat{T}_1 + \cdots + \hat{T}_4$	$\mathcal{O}(O^4N^{4+2})$	6	CISDTQ	5
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
CCn	$\hat{T}_1 + \cdots + \hat{T}_n$	$\mathcal{O}(O^nN^{n+2})$	[3n/2]	CIn	2[n/2]+1

- enhanced convergence with excitation level compared to CI
- size-consistent

Convergence of bond lenghts



29 bond lengths in 20 molecules
from: *Molecular Electronic-Structure Theory*,
Helgaker, Jørgensen, Olsen.

Combination with F12

Extension of the excitation and projection manifolds with the explicitly correlated double excitations:

excitations: $\hat{T}_{2'} = \sum_{\substack{x>y \\ i>j}} c_{xy}^{ij} \hat{\tau}_{xiyi}$ projections: $\langle {}_{xy}^{ij} | = \langle \mathrm{HF} | \tau_{xiyi}^{\dagger}$

where

$$\hat{\tau}_{xiyi} = \sum_{\alpha>\beta} w_{\alpha\beta}^{xy} a_\alpha^\dagger a_i a_\beta^\dagger a_j \quad \text{and} \quad w_{\alpha\beta}^{xy} = \langle \alpha\beta | \hat{Q}_{12} \hat{S}_{xy} f_{12}(r_{12}) | xy \rangle$$

where $\hat{S}_{xy} = \frac{1}{8}\left(3 - \delta_{\sigma_x\sigma_y} + (1 - 3\delta_{\sigma_x\sigma_y})\hat{P}_{xy}\right)$

ansatz 1: $\hat{Q}_{12} = (1 - \hat{P}_1)(1 - \hat{P}_2)$

ansatz 2: $\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2)(1 - \hat{V}_1\hat{V}_2)$

$\hat{O}$ occupied MO space $\hat{V}$ virtual MO space $\hat{P} = \hat{O} + \hat{V}$

Combination with F12 (cont.)

$$\hat{\tau}_{xiyi} = \sum_{\alpha>\beta} w^{xy}_{\alpha\beta} a^\dagger_\alpha a_i a^\dagger_\beta a_j \quad \text{and} \quad w^{xy}_{\alpha\beta} = \langle \alpha\beta | \hat{Q}_{12} \hat{S}_{xy} f_{12}(r_{12}) | xy \rangle$$

ansatz 1: $\hat{Q}_{12} = (1 - \hat{P}_1)(1 - \hat{P}_2)$

ansatz 2: $\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2)(1 - \hat{V}_1 \hat{V}_2)$

Single excitations leading to $(a^\dagger_i a_a)\hat{\tau}_{xiyi}|\mathrm{HF}\rangle$ are not included

ansatz 1: $(a^\dagger_i a_a)\hat{\tau}_{xiyi}|\mathrm{HF}\rangle = 0$

ansatz 2: $(a^\dagger_i a_a)\hat{\tau}_{xiyi}|\mathrm{HF}\rangle \neq 0$

- with ansatz 2 not closed under de-excitations

  $\rightsquigarrow$ use linked form of CC equations or

  eliminate non-size consistent contributions (if present)

Energy derivatives

Consider a Hamiltonian partitioned as:

$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \hat{V}$$

We restrict us here to orbital-unrelaxed derivatives:

$$|\mathrm{CC}(\lambda)\rangle = \exp\left(\hat{T}(\lambda)\right)|\mathrm{HF}\rangle,$$

i.e. use $|\mathrm{HF}\rangle$ of the unperturbed system, as needed for

- reponse theory (more on Thursday)
- coupled-cluster perturbation theory
  - alternative formulation of Møller-Plesset PT
  - analysis of approx. methods & perturbative corrections

The Coupled-Cluster Lagrange Function

We include the cluster equation as constraints in a Lagrange function:

$$L = \underbrace{\langle \mathrm{HF}|\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle}_{E_{\mathrm{CC}}} + \sum_{\mu} \bar{t}_{\mu} \underbrace{\langle \mu|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle}_{\text{residual of eqs.}}$$

Often written as

$$L = \langle \Lambda|\hat{H}|\mathrm{CC}\rangle \qquad \text{with} \qquad \langle \Lambda| = \langle \mathrm{HF}| + \sum_{\mu} \bar{t}_{\mu}\langle \mu|\exp(-\hat{T})$$

We will also use the shorthand notations $\langle \bar{t}| = \sum_{\mu} \bar{t}_{\mu}\langle \mu|$

or with excitation level i: $\langle \bar{t}_i| = \sum_{\mu_i} \bar{t}_{\mu_i}\langle \mu_i|$

The Coupled-Cluster Lagrange Function

$$E^{(n)} = \left(\frac{d^n E}{d\lambda^n}\right)_{\lambda=0} = \left(\frac{d^n L}{d\lambda^n}\right)_{\lambda=0}$$

evaluation of the derivatives of L to order n requires only

$$t_\mu^{(m)} = \left(\frac{d^n t_\mu}{d\lambda^n}\right)_{\lambda=0} \quad \text{with} \quad m < \left[\frac{n}{2}\right]$$

$$\bar{t}_\mu^{(m)} = \left(\frac{d^n \bar{t}_\mu}{d\lambda^n}\right)_{\lambda=0} \quad \text{with} \quad m < \left[\frac{n-1}{2}\right]$$

$t_\mu^{(m)}$ and $\bar{t}_\mu^{(m)}$ determined by the variational conditions

$$\left(\frac{d^m}{d\lambda^m}\frac{dL}{d\bar{t}_\mu}\right)_{\lambda=0} = 0 \qquad \text{and} \qquad \left(\frac{d^m}{d\lambda^m}\frac{dL}{dt_\mu}\right)_{\lambda=0} = 0$$

Coupled-Cluster Perturbation Theory

$$\hat{H}(\lambda) = \hat{F}_D + \lambda \underbrace{\left(\hat{F}_{OD} + \hat{\Phi}\right)}_{=\hat{V}}$$

- $\hat{F}_D$ diagonal occ/occ and vir/vir blocks of Fock matrix
- $\hat{F}_{OD}$ off-diagonal occ/vir and vir/occ blocks of Fock matrix
  (vanishes if Brillouin condition fulfilled, but not e.g. for ROHF)
- $\hat{\Phi} = \hat{H} - \hat{F}$ electron fluctuation potential

n.th order Møller-Plesset PT energies:

$$E_{\mathrm{MP}n} = \frac{1}{n!} \left(\frac{d^n L}{d\lambda^n} \right)_{\lambda=0}$$

Coupled-Cluster Perturbation Theory (cont.)

Zeroth-order amplitudes and multipliers vanish:

$$0 = \langle\mu|\left[\hat{F}_D, \hat{T}^{(0)}\right]|\mathrm{HF}\rangle, \quad 0 = \langle\bar{t}^{(0)}|\left[\hat{F}_D, \hat{\tau}_\nu\right]|\mathrm{HF}\rangle \quad \rightsquigarrow \quad t_\mu^{(0)} = \bar{t}_\mu^{(0)} = 0$$

Equations for first-order amplitudes and multipliers:

$$0 = \langle\mu|\left[\hat{F}_D, \hat{T}^{(1)}\right] + \hat{V}|\mathrm{HF}\rangle \quad \rightsquigarrow \quad t_\mu^{(1)} = -\epsilon_\mu^{-1}\langle\mu|\hat{V}|\mathrm{HF}\rangle$$

$$0 = \langle\mathrm{HF}|\left[\hat{V}, \hat{\tau}_\nu\right]|\mathrm{HF}\rangle + \langle\bar{t}^{(1)}|\left[\hat{F}_D, \hat{\tau}_\nu\right]|\mathrm{HF}\rangle \rightsquigarrow \quad \bar{t}_\mu^{(1)} = -\epsilon_\mu^{-1}\langle\mathrm{HF}|\hat{V}|\nu\rangle$$

with $\epsilon_\mu = \langle\mu|\left[\hat{F}_D, \hat{\tau}_\mu\right]|\mathrm{HF}\rangle$

- up to first order $\bar{t}_\mu = t_\mu$ (we assume real orbitals)
- only singles and doubles contribute

  (singles disappear if Brillouin condition fulfilled)

Coupled-Cluster Perturbation Theory (cont.)

Second order energy correction:

$$E_{\mathrm{MP2}} = \langle \mathrm{HF} | \left[\hat{V}, \hat{T}^{(1)} \right] | \mathrm{HF} \rangle + \sum_{\mu} \bar{t}_{\mu}^{(1)} \underbrace{\langle \mu | \left[\hat{F}_D, \hat{T}^{(1)} \right] + \hat{V} | \mathrm{HF} \rangle}_{=0 \text{ if eqs. for } t_{\mu}^{(1)} \text{ solved}}$$

Third order energy correction:

$$E_{\mathrm{MP3}} = \underbrace{\langle \mathrm{HF} | \left[\hat{V}, \hat{T}^{(2)} \right] | \mathrm{HF} \rangle + \sum_{\mu} \bar{t}_{\mu}^{(1)} \langle \mu | \left[\hat{F}_D, \hat{T}^{(2)} \right] + \hat{V} | \mathrm{HF} \rangle}_{=0 \text{ if eqs. for } \bar{t}_{\mu}^{(1)} \text{ solved}}$$

$$+ \sum_{\mu} \bar{t}_{\mu}^{(1)} \langle \mu | \left[\hat{V}, \hat{T}^{(1)} \right] | \mathrm{HF} \rangle + \sum_{\mu} \bar{t}_{\mu}^{(2)} \underbrace{\langle \mu | \left[\hat{F}_D, \hat{T}^{(1)} \right] + \hat{V} | \mathrm{HF} \rangle}_{=0 \text{ if eqs. for } t_{\mu}^{(1)} \text{ solved}}$$

$$= \langle \bar{t}^{(1)} | \left[\hat{V}, \hat{T}^{(1)} \right] | \mathrm{HF} \rangle = \langle t^{(1)} | \left[\hat{V}, \hat{T}^{(1)} \right] | \mathrm{HF} \rangle$$

Perturbative Triples Corrections to CCSD

Further analysis shows that CCSD includes all terms up to MP4 apart from those of the 2. order triples amplitudes:

$$E_{4,T3} = \langle \bar{t}_1^{(1)} | [\hat{V}, \hat{T}_3^{(2)}] | \mathrm{HF} \rangle + \langle \bar{t}_2^{(1)} | [\hat{V}, \hat{T}_3^{(2)}] | \mathrm{HF} \rangle$$

with $\quad t_{\mu_3}^{(2)} = -\epsilon_{\mu_3}^{-1} \langle \mu_3 | [\hat{V}, \hat{T}_2^{(1)}] | \mathrm{HF} \rangle$

CCSD(T):

$$E_{\mathrm{CCSD(T)}} = E_{\mathrm{CCSD}} + \langle t_1^{\mathrm{CCSD}} | [\hat{V}, \hat{T}_3] | \mathrm{HF} \rangle + \langle t_2^{\mathrm{CCSD}} | [\hat{V}, \hat{T}_3] | \mathrm{HF} \rangle$$

with $\quad t_{\mu_3} = -\epsilon_{\mu_3}^{-1} \langle \mu_3 | [\hat{V}, \hat{T}^{\mathrm{CCSD}}] | \mathrm{HF} \rangle$

CCSD[T]:

$$E_{\mathrm{CCSD[T]}} = E_{\mathrm{CCSD}} + \langle \bar{t}_2^{\mathrm{CCSD}} | [\hat{\Phi}, \hat{T}_3] | \mathrm{HF} \rangle$$

Stability w.r.t. Errors in Amplitudes

Consider incomplete solution of CC equations: $\tilde{t}_\mu = t_\mu + \delta t_\mu$

Evaluation of the approx. Lagrange functions gives:

$$L(\tilde{t},\tilde{t}) = \langle \mathrm{HF}|\hat{H}e^{\hat{T}+\delta\hat{T}}|\mathrm{HF}\rangle + \sum_\mu (t_\mu + \delta t_\mu)\langle\mu|e^{-\hat{T}-\delta\hat{T}}\hat{H}e^{\hat{T}+\delta\hat{T}}|\mathrm{HF}\rangle$$

$$= E_{\mathrm{CC}} + \sum_\nu \delta t_\nu \underbrace{\left(\langle \mathrm{HF}|[\hat{H},\tau_\nu]|\mathrm{CC}\rangle + \textstyle\sum_\mu t_\mu \langle\mu|e^{-\hat{T}}[\hat{H},\tau_\nu]|\mathrm{CC}\rangle\right)}_{\approx 0 \quad \text{(up to 1. order MPPT)}} + \mathcal{O}(\delta t^2)$$

Errors linear in δt_μ cancel approximately out.

- during CC iterations used to estimate convergence error
- used to calculate energy in CCSD-F12 models with approximate $\hat{T}_{2'}$

Energy derivatives / Response Theory

Slightly different situation:

$$\hat{H}(\boldsymbol{\epsilon}) = \hat{H}^{(0)} + \sum_X \epsilon_X \hat{X}$$

- $\hat{H}^{(0)}$ full Hamiltonian of the unperturbed system
- $\hat{X}$ perturbation operators
- $\boldsymbol{\epsilon}$ perturbation strengths

We discuss here only the static case ($\boldsymbol{\epsilon}$ time-/freq.-independent)

(more on response theory on friday)

Expectation Values (First-Order Properties)

Equations for zeroth-order Lagrange multipliers:

$$\underbrace{\langle \mathrm{HF}|[\hat{H}^{(0)},\hat{\tau}_\nu]e^{\hat{T}^{(0)}}|\mathrm{HF}\rangle}_{=\left(\frac{\partial L}{\partial t_\nu}\right)_{\boldsymbol{\epsilon}=0}=\eta_\nu^{(0)}} + \sum_\mu \bar{t}_\mu^{(0)} \underbrace{\langle \mu|e^{-\hat{T}^{(0)}}[\hat{H}^{(0)},\hat{\tau}_\nu]e^{\hat{T}^{(0)}}|\mathrm{HF}\rangle}_{=\left(\frac{\partial^2 L}{\partial \bar{t}_\mu \partial t_\nu}\right)_{\boldsymbol{\epsilon}=0}=A_{\mu\nu}} = 0$$

Jacobi matrix

$\rightsquigarrow$ linear equation system: $\quad \bar{\mathbf{t}}^{(0)}\mathbf{A} = -\boldsymbol{\eta}^{(0)}$

Expectation valudes (first-order properties):

$$\left(\frac{dE}{d\epsilon_X}\right)_{\boldsymbol{\epsilon}=0} = \langle \Lambda^{(0)}|\hat{X}|\mathrm{CC}^{(0)}\rangle = \bar{\mathbf{t}}^{(0)}\boldsymbol{\xi}^X \quad \text{with} \quad \xi_\mu^X = \left(\frac{\partial^2 L}{\partial \bar{t}_\mu \partial \epsilon_X}\right)_{\boldsymbol{\epsilon}=0}$$

$$= D_{pq}^{(0)} X_{pq} \quad \text{with} \quad D_{pq}^{(0)} = \langle \Lambda^{(0)}|a_p^\dagger a_q|\mathrm{CC}^{(0)}\rangle$$

First-order Equations

Equations for first-order amplitudes:

$$\sum_\nu \underbrace{\langle\mu|e^{-\hat{T}^{(0)}}[\hat{H}^{(0)},\hat{\tau}_\nu]e^{\hat{T}^{(0)}}|\mathrm{HF}\rangle}_{=\ A_{\mu\nu}\ \text{Jacobi matrix}} t_\nu^X + \underbrace{\langle\mu|e^{-\hat{T}^{(0)}}\hat{X}e^{\hat{T}^{(0)}}|\mathrm{HF}\rangle}_{\xi_\mu^X} = 0$$

Equations for first-order multipliers:

$$\sum_\mu \bar{t}_\mu^X \underbrace{\langle\mu|e^{-\hat{T}^{(0)}}[\hat{H}^{(0)},\hat{\tau}_\nu]e^{\hat{T}^{(0)}}|\mathrm{HF}\rangle}_{=\ A_{\mu\nu}\ \text{Jacobi matrix}} +$$

$$\sum_\mu \underbrace{\langle\Lambda^{(0)}|[[\hat{H}^{(0)},\hat{\tau}_\mu],\hat{\tau}_\nu]|\mathrm{CC}^{(0)}\rangle}_{=+\left(\frac{\partial^2 L}{\partial t_\mu \partial t_\nu}\right)_{\epsilon=0}=F_{\mu\nu}} t_\mu^X + \underbrace{\langle\Lambda^{(0)}|[\hat{X},\hat{\tau}_\nu]|\mathrm{CC}^{(0)}\rangle}_{=\left(\frac{\partial^2 L}{\partial t_\nu \partial \epsilon_X}\right)_{\epsilon=0}=\eta_\nu^X} = 0$$

Second Derivatives

Two different possible routes:

1. “symmetric” form:

$$\left(\frac{d^2E}{d\epsilon_X d\epsilon_Y}\right)_{\boldsymbol{\epsilon}=0} = \sum_{\mu\nu} F_{\mu\nu} t_\mu^X t_\nu^Y + \sum_\mu \eta_\mu^X t_\mu^Y + \sum_\mu \eta_\mu^Y t_\mu^X$$

   - requires only first derivatives of t_μ
   - most efficient if for set of operators all 2. derivatives needed

2. “asymmetric” form:

$$\left(\frac{d^2E}{d\epsilon_X d\epsilon_Y}\right)_{\boldsymbol{\epsilon}=0} = \sum_\mu \eta_\mu^Y t_\mu^X + \sum_\mu \xi_\mu^Y \bar{t}_\mu^X = \sum_{pq} D_{pq}^X Y_{pq}$$

   - requires only derivatives of t_μ, $\bar{t}_\mu$ w.r.t. X
   - most efficient for a small set of X operators combined with a large set of Y operators

Summary

- linked and unlinked CC equations equivalent if projection manifold closed under deexcitation

  (not exactly fulfilled for CCSD-F12 with ansatz 2)

- linked formulation also term-wise size-extensive

  (useful for approximations)

- derivatives based on the CC Lagrange function provide a useful framework for
  - perturbation theory
  - energy correction for approximate models
  - response theory
  - analytic derivatives

Part II

Performance assessment and basis sets

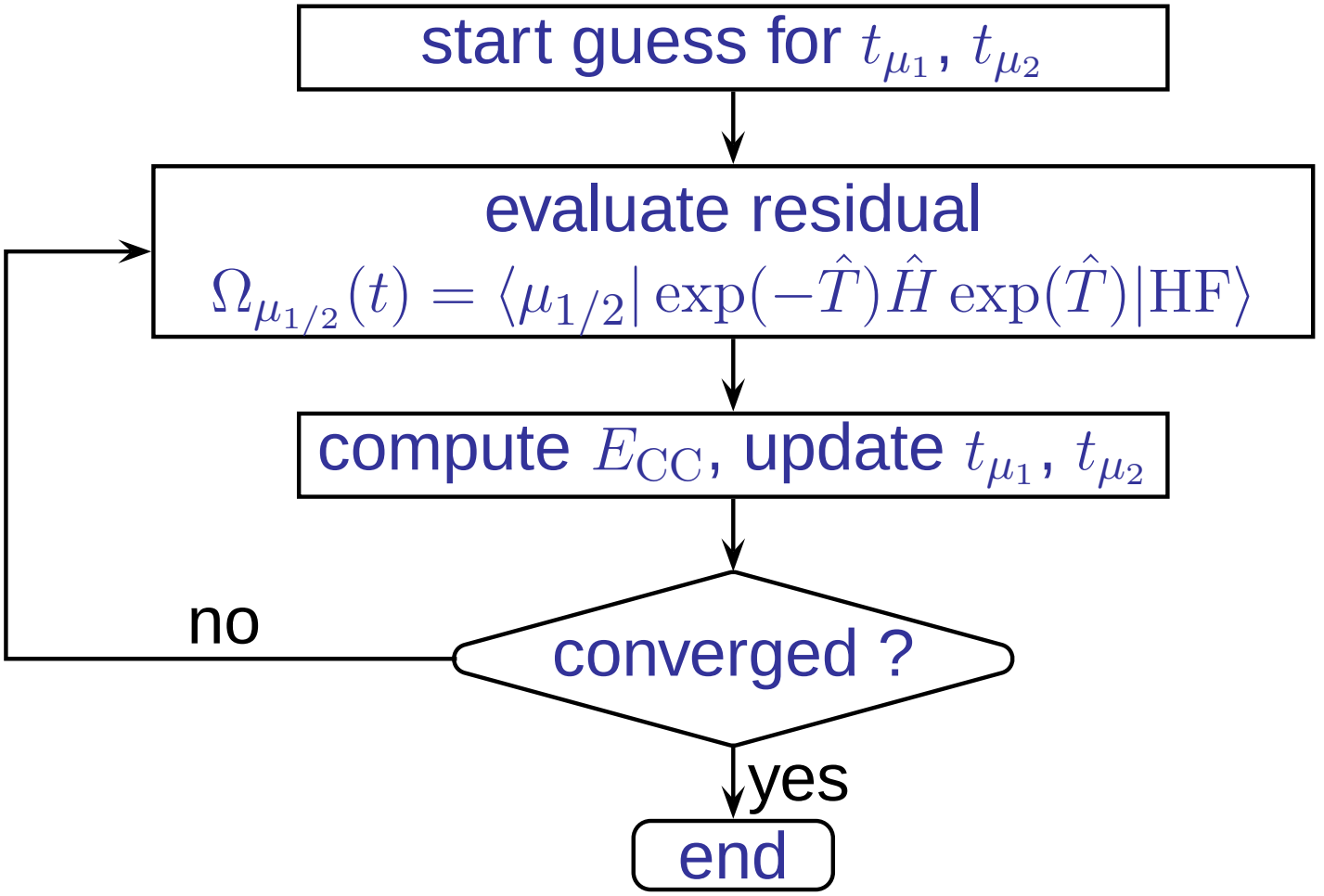
(Wednesday 16.02.)

Questions addressed...

- What determines the computational costs of CCSD-like calculations?

- How should the orbital and auxiliary basis sets be chosen?

Solution of CCSD Equations



- Rate-determining step for CCSD: evaluation of doubles residual Ω_{μ_2} during iterative solution of the equations

Evaluation of Doubles Residual

Doubles residual (ignoring $\hat{T}_1$):

$$ {}^{\mathrm{CCD}}\Omega_{ij}^{ab} = \left\langle {}^{ab}_{ij} \middle| \hat{H} + [\hat{H}, \hat{T}_2] + \tfrac{1}{2}[[\hat{H}, \hat{T}_2], \hat{T}_2] \middle| \mathrm{HF} \right\rangle $$

Most costly contributions:

$$ \begin{aligned} {}^{\mathrm{A}}\Omega_{ij}^{ab} &= \frac{1}{2} \sum_{cd} t_{ij}^{cd} \langle ab|cd\rangle \\ {}^{\mathrm{B}}\Omega_{ij}^{ab} &= \frac{1}{2} \sum_{kl} t_{kl}^{ab} \left(\langle kl|ij\rangle + \frac{1}{2} \sum_{cd} t_{ij}^{cd} \langle kl|cd\rangle \right) \\ {}^{\mathrm{C}}\Omega_{ij}^{ab} &= \sum_{ck} t_{ik}^{ac} \left(\langle kb\|cj\rangle - \frac{1}{2} \sum_{dl} t_{jl}^{db} \langle kl\|cd\rangle \right) \end{aligned} $$

$i, j, k, l, \ldots$ occ. orbitals; $a, b, c, d, \ldots$ vir. orbitals

Evaluation of Doubles Residual

$$ {}^{\mathrm{A}}\Omega_{ij}^{ab} = \frac{1}{2} \sum_{cd} t_{ij}^{cd} \langle ab|cd \rangle $$

- formal scaling with O^2V^4

  $\rightsquigarrow$ rate-determining step if no screening applied

Evaluation of Doubles Residual

$$ {}^{\mathrm{A}}\Omega_{ij}^{ab} = \tfrac{1}{2} \sum_{cd} t_{ij}^{cd} \langle ab|cd\rangle = \sum_{\mu\nu} C_{\mu a}\, C_{\nu b}\, \Omega_{ij}^{\mu\nu} $$

with $\Omega_{ij}^{\mu\nu} = \tfrac{1}{2} \sum_{\kappa\lambda} \langle \mu\nu|\kappa\lambda\rangle\, M_{ij}^{\kappa\lambda}$ and $M_{ij}^{\kappa\lambda} = \sum_{cd} t_{ij}^{cd}\, C_{\kappa c}\, C_{\lambda d}$

- formal scaling with O^2V^4
  - $\rightsquigarrow$ rate-determining step if no screening applied

    today typically done AO integral-direct

    with Schwarz screening asymptotic scaling $\mathcal{O}(O^2\mathcal{N}^2)$

Evaluation of Doubles Residual

$$ {}^{\mathrm{A}}\Omega_{ij}^{ab} = \tfrac{1}{2} \sum_{cd} t_{ij}^{cd} \langle ab|cd\rangle = \sum_{\mu\nu} C_{\mu a}\, C_{\nu b}\, \Omega_{ij}^{\mu\nu} $$

with $\Omega_{ij}^{\mu\nu} = \tfrac{1}{2} \sum_{\kappa\lambda} \langle \mu\nu|\kappa\lambda\rangle\, M_{ij}^{\kappa\lambda}$ and $M_{ij}^{\kappa\lambda} = \sum_{cd} t_{ij}^{cd}\, C_{\kappa c}\, C_{\lambda d}$

- formal scaling with O^2V^4
  - $\rightsquigarrow$ rate-determining step if no screening applied
    today typically done AO integral-direct
    with Schwarz screening asymptotic scaling $\mathcal{O}(O^2\mathcal{N}^2)$
- contribution beyond MP2 with slowest basis set convergence and steepest cost increase $\mathcal{O}(\mathcal{M}^4)$ with atomic basis set size
  - $\rightsquigarrow$ term beyond MP2 where F12 contribution is most important!

Evaluation of Doubles Residual

$$ {}^{\mathrm{B}}\Omega_{ij}^{ab} = \tfrac{1}{2} \sum_{kl} t_{kl}^{ab} \Big(\langle kl|ij\rangle + \tfrac{1}{2} \sum_{cd} t_{ij}^{cd} \langle kl|cd\rangle \Big) $$

- second term (contraction over cd) also slowly convergent, but its energy contributions are smaller (MP4 and beyond)
- formal scaling with O^4V^2

  $\rightsquigarrow$ not rate-determining

Evaluation of Doubles Residual

$$ {}^{\mathrm{B}}\Omega_{ij}^{ab} = \tfrac{1}{2} \sum_{kl} t_{kl}^{ab} \Big(\langle kl|ij\rangle + \tfrac{1}{2} \sum_{cd} t_{ij}^{cd} \langle kl|cd\rangle \Big) $$

- second term (contraction over cd) also slowly convergent, but its energy contributions are smaller (MP4 and beyond)
- formal scaling with O^4V^2

  $\rightsquigarrow$ not rate-determining
- in AO integral-direct codes partially as byproduct of ${}^{\mathrm{A}}\Omega_{ij}^{ab}$:

$$ {}^{\mathrm{B}}\Omega_{ij}^{ab} = \tfrac{1}{2} \sum_{kl} t_{kl}^{ab} \Big(\langle kl|ij\rangle + \sum_{\mu} \big(\sum_{\nu} \Omega_{ij}^{\mu\nu} C_{\nu l} \big) C_{\mu k} \Big) $$

Evaluation of Doubles Residual

$$ {}^{\mathrm{C}}\Omega_{ij}^{ab} = \sum_{ck} t_{ik}^{ac} \left(\langle kb \| cj \rangle - \frac{1}{2} \sum_{dl} t_{jl}^{db} \langle kl \| cd \rangle \right) $$

- formal scaling with O^3V^3
  - $\rightsquigarrow$ but use of Schwarz screening difficult and
    due to antisym. integrals larger prefactor/higher complexity
    $\Longrightarrow$ together with ${}^{\mathrm{A}}\Omega_{ij}^{ab}$ rate-determining

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    due to antisym. integrals larger prefactor/higher complexity
    $\Longrightarrow$ together with ${}^{\mathrm{A}}\Omega_{ij}^{ab}$ rate-determining
- faster with basis set convergence than ${}^{\mathrm{A}}\Omega_{ij}^{ab}$, ${}^{\mathrm{B}}\Omega_{ij}^{ab}$
  - $\rightsquigarrow$ F12 contributions less important

Contributions from Singles Amplitudes

Different strategies:

- similarity-transformed integrals:

$$e^{-\hat{T}_1}\,\hat{H}\,e^{\hat{T}_1} = \sum_{pq}\tilde{h}_{pq}\,a_p^\dagger\,a_q + \tfrac{1}{2}\sum_{pqrs}\tilde{g}_{pqrs}\,a_p^\dagger\,a_q\,a_r^\dagger\,a_s$$

$$\tilde{h}_{pq} = \sum_{\mu\nu} X_{\mu p}\,Y_{\nu q}\,h_{\mu\nu} \qquad \mathbf{X} = \mathbf{C}(\mathbf{1}-\mathbf{t}_1)^T$$

$$\tilde{g}_{pqrs} = \sum_{\mu\nu\kappa\lambda} X_{\mu p}\,Y_{\nu q}\,X_{\kappa r}\,Y_{\lambda s}\,g_{\mu\nu\kappa\lambda} \qquad \mathbf{Y} = \mathbf{C}(\mathbf{1}+\mathbf{t}_1)$$

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- absorption in doubles amplitudes, f.x.:

$$\tilde{t}_{ij}^{ab} = \tfrac{1}{m}t_{ij}^{ab} + \tfrac{1}{n}\left(t_i^a t_j^b - s t_i^b t_j^a\right) \qquad (m, n, s \text{ term-dependent})$$

$\rightsquigarrow$ less transformations, but “absorbs” not all contrib. from $\hat{T}_1$

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  $\rightsquigarrow$ less transformations, but “absorbs” not all contrib. from $\hat{T}_1$

- $\hat{T}_1$ can be included with $\mathcal{O}(O^2V^3)$ costs, not rate-determining

Explicitly-Correlated Contributions

Doubles residual (ignoring $\hat{T}_1$):

$$ {}^{\mathrm{CCD(F12)}}\Omega_{ij}^{ab} = {}^{\mathrm{CCD}}\Omega_{ij}^{ab} + \left\langle {}^{ab}_{ij} \middle| [\hat{H}, \hat{T}_{2'}] + [[\hat{H}, \hat{T}_{2'}], \hat{T}_2] \middle| \mathrm{HF} \right\rangle $$

$$ \hat{T}_{2'} = \sum_{i>j;\alpha>\beta} \Big(\sum_{x>y} c_{ij}^{xy} w_{xy}^{\alpha\beta} \Big) a_\alpha^\dagger a_i a_\beta^\dagger a_j = \sum_{i>j;\alpha>\beta} t_{ij}^{\alpha\beta} a_\alpha^\dagger a_i a_\beta^\dagger a_j $$

Most costly contributions:

$$ \begin{aligned} {}^{\mathrm{A'}}\Omega_{ij}^{ab} &= \frac{1}{2} \sum_{\gamma\delta} t_{ij}^{\gamma\delta} \langle ab|\gamma\delta\rangle \\ {}^{\mathrm{B'}}\Omega_{ij}^{ab} &= \frac{1}{2} \sum_{kl} t_{kl}^{ab} \Big(\frac{1}{2} \sum_{\gamma\delta} t_{ij}^{\gamma\delta} \langle kl|\gamma\delta\rangle \Big) \\ {}^{\mathrm{C}}\Omega_{ij}^{ab} &= \sum_{\gamma k} t_{ik}^{a\gamma} \Big(\langle kb\|\gamma j\rangle - \sum_{dl} t_{jl}^{db} \langle kl\|\gamma d\rangle \Big) \end{aligned} $$

i, j, k, l, occupied orbitals; a, b, c, d, virtual orbitals;

x, y geminal indices; $\alpha, \beta, \gamma, \delta$ orbitals from complete virtual basis

Explicitly-Correlated Ladder Terms

For contractions over virtual pairs one uses (as for MP2-F12):

$$\sum_{\gamma\beta} t_{ij}^{\gamma\delta} \langle pq|\gamma\delta\rangle = \sum_{x>y} c_{ij}^{xy} \langle pq|\frac{1}{r_{12}} \sum_{\gamma\delta} |\gamma\delta\rangle\langle\gamma\delta| \hat{Q}_{12} f_{12}|xy\rangle = \sum_{x>y} c_{ij}^{xy} V_{xy}^{pq}$$

- V_{xy}^{pq} evaluated with $\hat{Q}_{12} \approx 1 - \hat{P}_1\hat{P}_2 - \hat{O}_1\hat{P}_2' - \hat{P}_1'\hat{O}_2$:

$$V_{xy}^{pq} = \langle pq|\frac{f_{12}}{r_{12}}|xy\rangle - \sum_{rs} \langle pq|rs\rangle\langle rs|f_{12}|xy\rangle - \hat{P}_{xy}^{pq} \sum_{ic'} \langle pq|ic'\rangle\langle ic'|f_{12}|xy\rangle$$

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- costs scale with $\mathcal{O}(ON^4 + ON^3N_{CABS}) + O^2N^4 + O^3N^2N_{CABS}$
  $\rightsquigarrow$ comparable to costs for one CCSD iteration

- but needs to be done only once (V_{xy}^{pq} independent of t_μ and c_{ij}^{xy})

Explicitly-Correlated Ladder Terms (cont.)

For contractions over virtual pairs one uses (as for MP2-F12):

$$\sum_{\gamma\beta} t_{ij}^{\gamma\delta} \langle pq|\gamma\delta\rangle = \sum_{x>y} c_{ij}^{xy} \langle pq|\frac{1}{r_{12}}\hat{Q}_{12} f_{12}|xy\rangle = \sum_{x>y} c_{ij}^{xy} V_{xy}^{pq}$$

Ladder-type contributions:

$$^{\mathrm{A}'}\Omega_{ij}^{ab} = \frac{1}{2}\sum_{xy} c_{ij}^{xy} V_{xy}^{ab} \qquad \mathcal{O}(O^4V^2)$$

$$^{\mathrm{B}'}\Omega_{ij}^{ab} = \frac{1}{2}\sum_{kl} t_{kl}^{ab}\left(\frac{1}{2}\sum_{xy} c_{ij}^{xy} V_{xy}^{kl}\right) \qquad \mathcal{O}(O^6)$$

In an AO integral-direct code combined with conv. terms:

$$^{\mathrm{CCD(F12)}}\Omega_{ij}^{\mu\nu} = {}^{\mathrm{CCD}}\Omega_{ij}^{\mu\nu} + \frac{1}{2}\sum_{xy} c_{ij}^{xy} V_{xy}^{\mu\nu} \qquad \mathcal{O}(O^4N^2)$$

- not rate-determining

Explicitly-Correlated Ring Terms

Contractions over occupied/virtual pairs:

$$\sum_{\gamma k} t_{ik}^{a\gamma} \langle kp \| \gamma q \rangle = \sum_{k\gamma} \langle kp \| \gamma q \rangle \sum_{x>y} \langle a\gamma | \hat{Q}_{12} f_{12} | xy \rangle c_{ik}^{xy}$$

- evaluated with $\hat{Q}_{12} \approx \hat{P}'_1 \hat{P}'_2 + \hat{V}_1 \hat{P}'_2 + \hat{P}'_1 \hat{V}_2$:

$$^{\mathrm{C}}\Omega_{ij}^{ab} = \sum_{c'k} t_{ik}^{ac'} \Big(\langle kb \| c'j \rangle - t_{jl}^{db} \langle kl \| c'd \rangle \Big)$$

with $\quad t_{ik}^{ac'} = \sum_{x>y} \langle ac' | \hat{Q}_{12} f_{12} | xy \rangle c_{ik}^{xy}$

- costs scale with $O^3V^2N_{CABS}$

  $\rightsquigarrow$ one of the rate-determining steps in CCSD(F12)

Evaluation of Geminal Residual

Geminal residual for CCD(F12):

$$ {}^{\mathrm{CCD(F12)}}\Omega_{ij}^{xy} = \left\langle {}^{xy}_{ij} \middle| [\hat{F}, \hat{T}_{2'}] + \hat{H} + [\hat{H}, \hat{T}_2] \middle| \mathrm{HF} \right\rangle $$

Most costly contributions:

$$ {}^{\mathrm{Ladder}}\Omega_{ij}^{ab} = \sum_{\alpha\beta} w_{\alpha\beta}^{xy} \left(\frac{1}{2} \sum_{cd} t_{ij}^{cd} \langle \alpha\beta | cd \rangle \right) \approx \frac{1}{2} \sum_{cd} t_{ij}^{cd} V_{xy}^{cd} $$

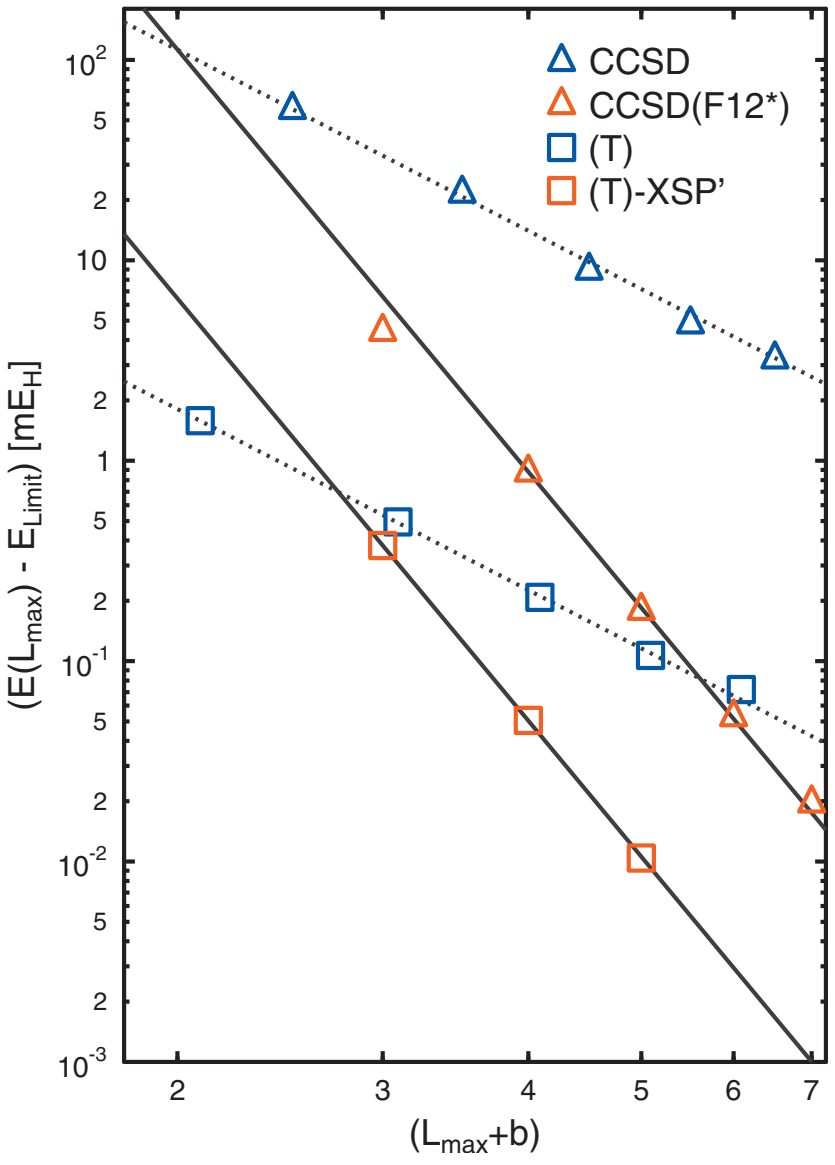
$$ {}^{\mathrm{Ring}}\Omega_{ij}^{xy} = \sum_{a\beta} w_{a\beta}^{xy} \left(\sum_{ck} t_{ik}^{ac} \langle k\beta \| cj \rangle \right) \approx \sum_{ab'} w_{ab'}^{xy} \left(\sum_{ck} t_{ik}^{ac} \langle kb' \| cj \rangle \right) $$

- costs scale as O^4V^2 (Ladder terms) and $O^3V^2N_{CABS}$ (Ring terms)
- inclusion of $\hat{T}_1$ increases number of $O^3V^2N_{CABS}$-scaling steps

Costs for CCSD(F12) – Summary

approx.	$\hat{T}_{2'}$	$O^2V^4 + O^3V^3$	MP2-F12	$O^3V^2N_{CABS}$
CCSD(F12)	opt.	$\surd$	$\surd$	iter.
CCSD(F12)	fixed	$\surd$	$\surd$	iter.
CCSD(F12*)	fixed	$\surd$	$\surd$	non-iter.
CCSD(2)$_{\overline{\mathrm{F12}}}$	fixed	$\surd$	$\surd$	non-iter.
CCSD-F12a	fixed	$\surd$	$\surd$	–
CCSD-F12b	fixed	$\surd$	$\surd$	–
CCSD	–	$\surd$	–	–

Convergence With The Basis Set

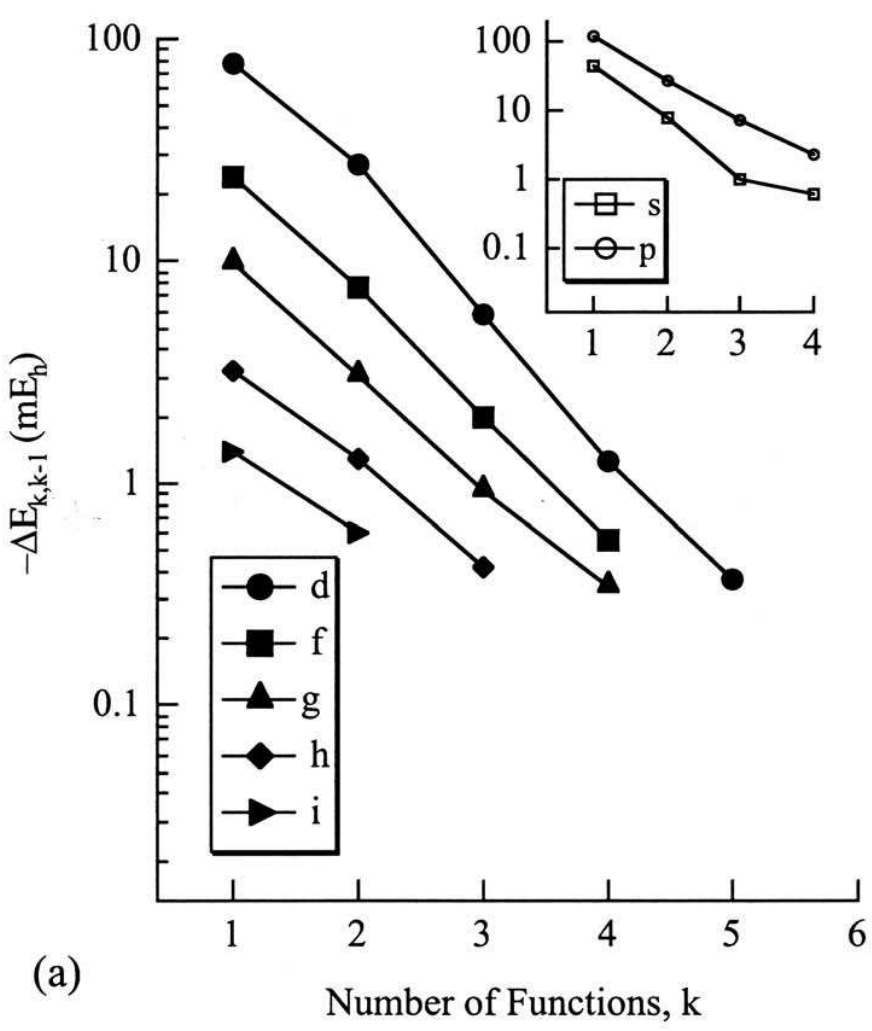


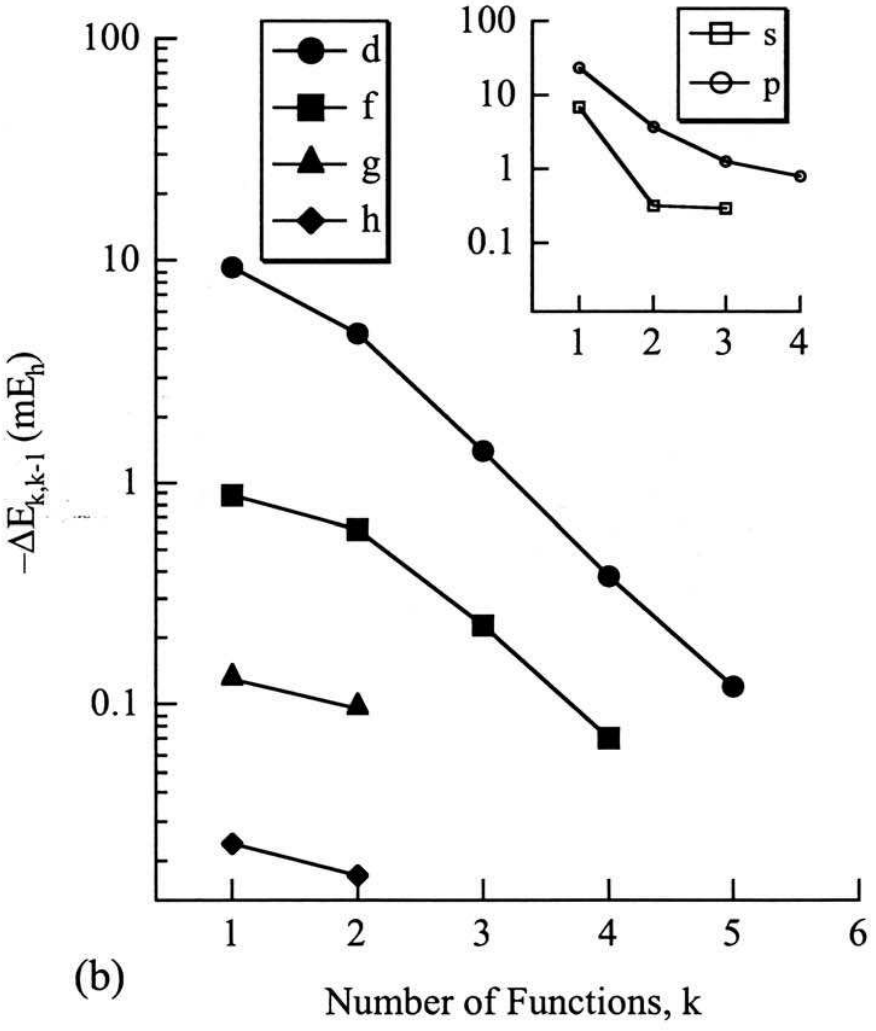
A. Köhn, JCP 133, 174118 (2010)

- CCSD and other correlated wavefunction methods converge for atoms with $(L_{max} + b)^{-3}$ to the basis set limit
- CCSD-F12 and carefully constructed approximations to it the convergence is enhanced to $(L_{max} + b)^{-7}$
- But what does this mean for basis sets meant for routine calculations (i.e. not constructed this way)?

Convergence With The Basis Set

K.A. Peterson, T.B. Adler, H.-J. Werner, JCP 128, 084102 (2008)



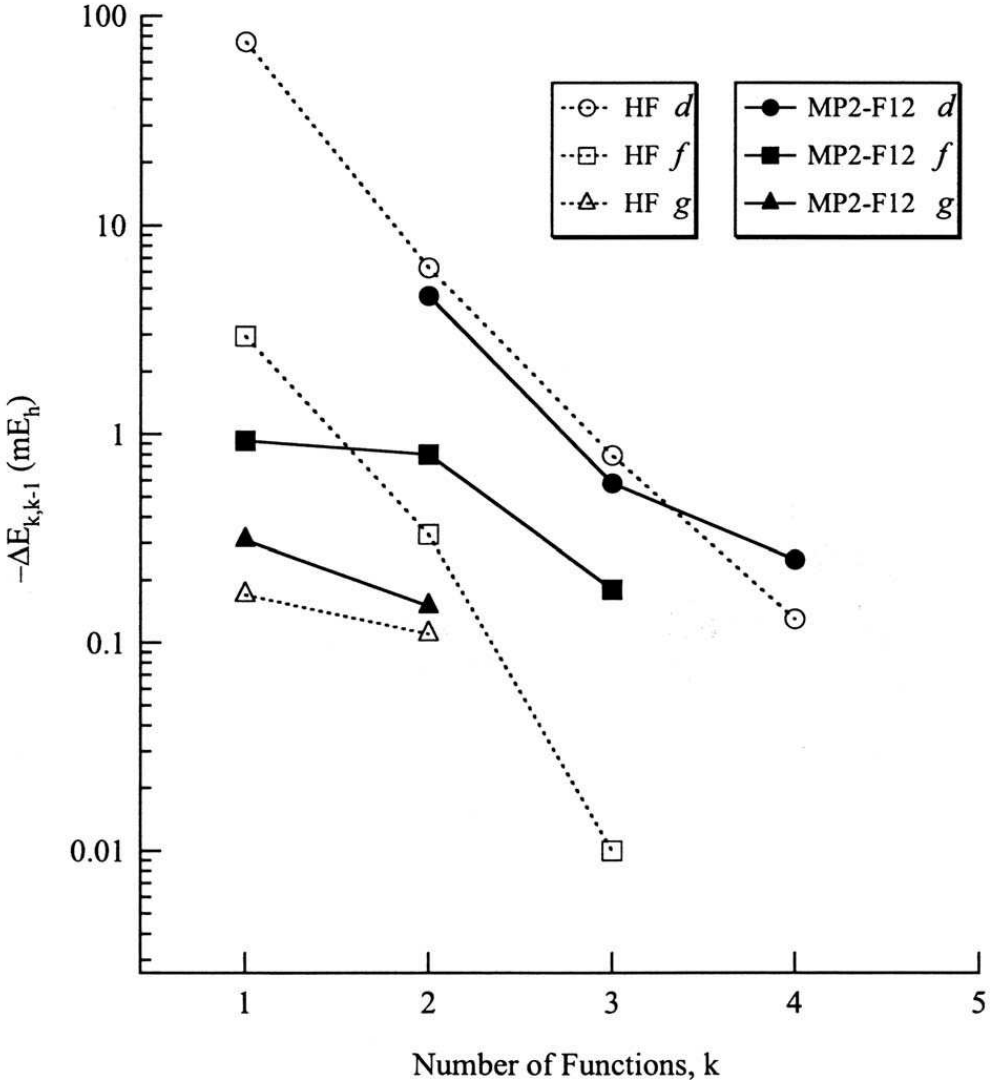


Increments for MP2
valence correlation energy for Ne

increments for MP2-F12/3C
valence correlation energy for Ne

Convergence With The Basis Set

K.A. Peterson, T.B. Adler, H.-J. Werner, JCP 128, 084102 (2008)



Increments for HF & MP2-F12/3C total energies for Ne

- fast convergence with highest angular momentum
- convergence with number of functions for a given angular momentum not accelerated
- first functions for a given angular momentum will be compromises between Hartree-Fock and correlation contributions

Basis Set Extrapolation

J.G. Hill, K.A. Peterson, G. Knizia, H.-J. Werner, JCP 131, 194105 (2009)

Fit of conventional MP2 results to:

$$E_X^{corr} \approx E_{CBS}^{corr} + AX^{-p} \quad \Rightarrow \quad E_{CBS}^{corr} \approx \left(E_Y^{corr} - E_X^{corr}\right) \frac{Y^p}{Y^p - X^p}$$

Basis sets	Exponent p
AVDZ/AVTZ	2.14
AVTZ/AVQZ	2.53
AVQZ/AV5Z	2.74
AV5Z/AV6Z	2.83

- follows approximately idealized law $E_X^{corr} = E_{CBS}^{corr} + AX^{-3}$

Basis Set Extrapolation with F12 Methods

J.G. Hill, K.A. Peterson, G. Knizia, H.-J. Werner, JCP 131, 194105 (2009)

Fit of MP2-F12 results to:

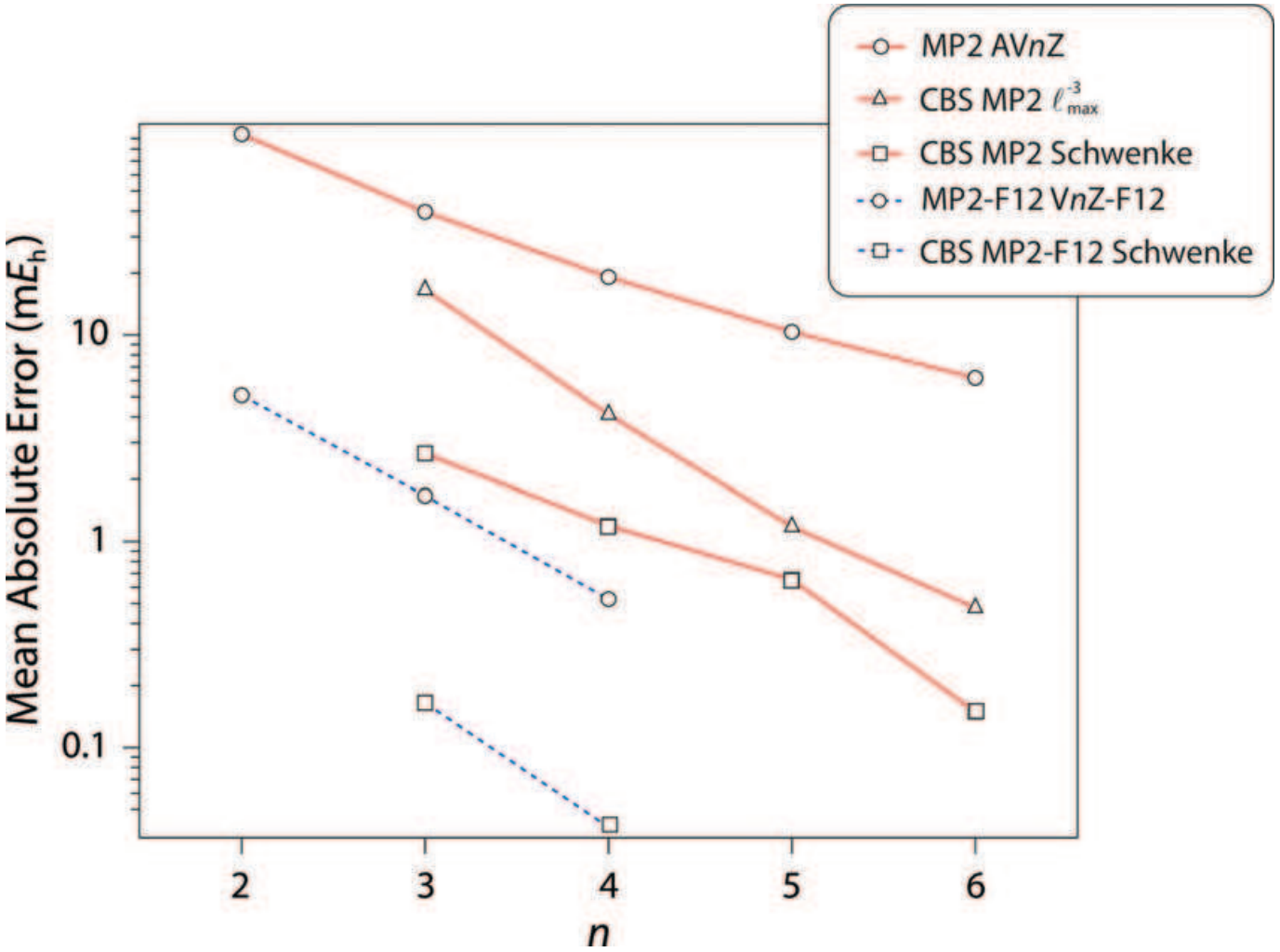
$$E_X^{corr} \approx E_{CBS}^{corr} + AX^{-p} \quad \Rightarrow \quad E_{CBS}^{corr} \approx \left(E_Y^{corr} - E_X^{corr}\right) \frac{Y^p}{Y^p - X^p}$$

Basis sets	Exponent p	
	MP2-F12/3C	MP2-F12/3C(FIX)
VDZ-F12/VTZ-F12	2.75	3.09
VTZ-F12/VQZ-F12	4.07	4.35
AVDZ/AVTZ	2.08	2.30
AVTZ/AVQZ	2.98	3.25
AVQZ/AV5Z	4.11	4.33

- for small X exponent p deviates strongly from the ideal value $p = 7$
  $\rightsquigarrow$ reliable extrapolation requires optimized p

Basis Set Extrapolation with F12 Methods

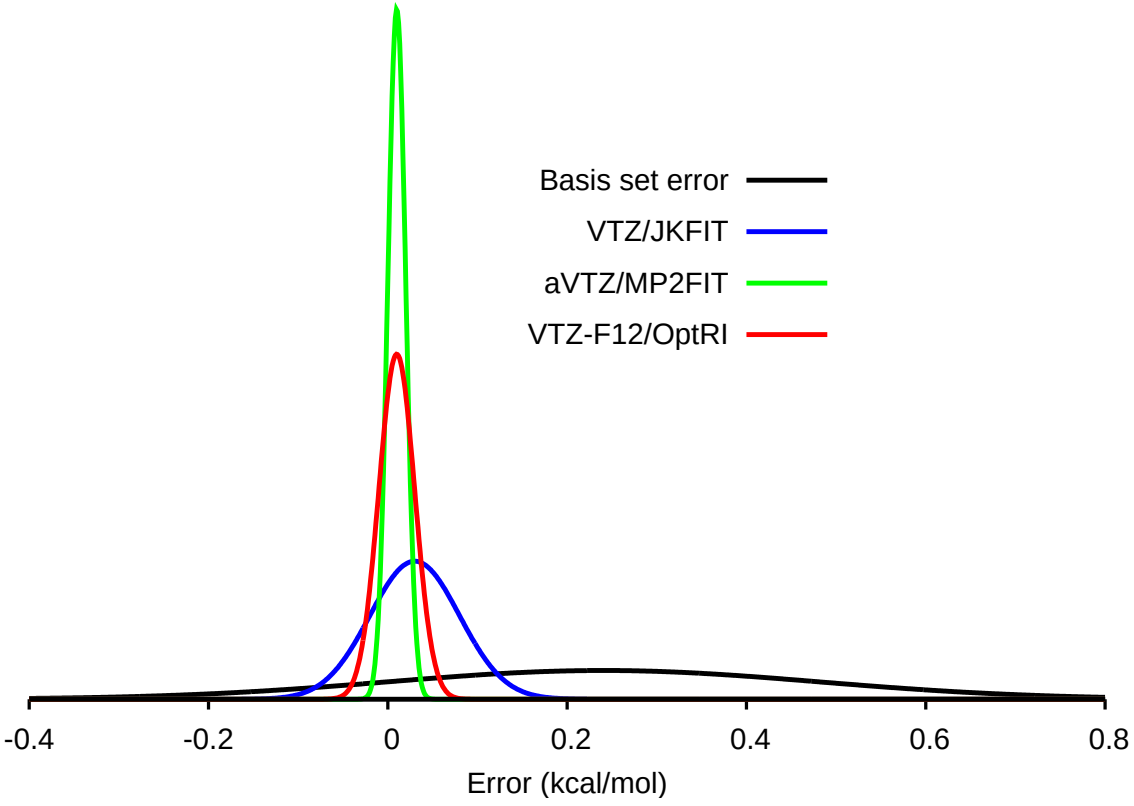
J.G. Hill, K.A. Peterson, G. Knizia, H.-J. Werner, JCP 131, 194105 (2009)



- with optimized coefficients significant improvement from extrapolation

The CABS/RI Basis Set

K.E. Yousaf, K.A. Peterson, JCP 129, 184108 (2008)



Error in atomization energies

for atoms formally

- ansatz 1: only $L_{RI} \leq 3L_{occ}$ contribute
- ansatz 2: no exact truncation

for practical calculations:

- $L_{RI} \leq \min(3L_{occ}, L_{max}) + 1$

- RI errors are about an order of magnitude smaller than basis set errors
  $\rightsquigarrow$ can be significant if results depend heavily on error compensation

Auxiliary Basis Sets for Density Fitting

- density-fitting usually applied to $(ip|\hat{o}|rs)$ and $(ip'|\hat{o}|rs)$ integrals with $\hat{o} = \frac{1}{r_{12}}, f(r_{12}), \frac{f(r_{12})}{r_{12}}, \ldots$
  (i occupied, p orbital basis, p' CA basis for RI)

- required angular momenta: $L_{DF} \leq L_{occ} + \max(L_{max}, L'_{max})$

- auxiliary basis sets for RI-MP2 constructed only for $(ia|jb)$, for RI-MP2-F12 calculations:
  - needs tighter functions for $(ij|rs)$ integrals
    $\rightsquigarrow$ use auxiliary sets aug-cc-pwCVXZ
  - higher angular momenta for $(ip'|rs)$ integrals
    $\rightsquigarrow$ use aug-cc-pwCVXZ for $X = L'$

- for Fock matrices use auxiliary cc-pVXZ for $X = L'$

Summary: Basis Set

Well tested combinations:

- cc-pVXZ-F12 basis sets in combination with
  - optimized complementary cc-pVTZ-F12 RI basis sets
  - aug-cc-pwCV(X+1)Z for DF in MP2 part
  - cc-pV(X+1)Z for Fock matrices

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  - optimized complementary aug-cc-pVTZ RI basis sets
  - aug-cc-pwCV(X+1)Z for DF in MP2 part
  - cc-pV(X+1)Z for Fock matrices

References: F12 & Basis sets

A few references on basis set & basis set convergence:

- K.A. Peterson, T.B. Adler, H.-J. Werner, JCP 128, 084102 (2008)
- J.G. Hill, K.A. Peterson, G. Knizia, H.-J. Werner, JCP 131, 194105 (2009)
- Y.E. Yousaf, K.A. Peterson, JCP 129, 184108 (2008)
- F.A. Bischoff, S. Wolfsegger, D.P. Tew, W. Klopper, MP 107, 963, (2009)

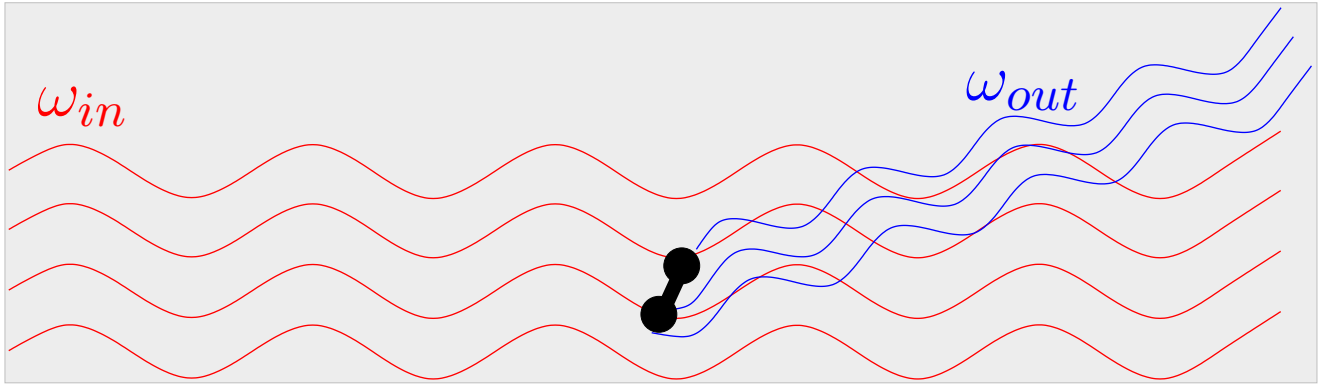
Part III

Explicitly correlated coupled-cluster response theory

(Thursday 17.02.)

Introduction: What is Response Theory?

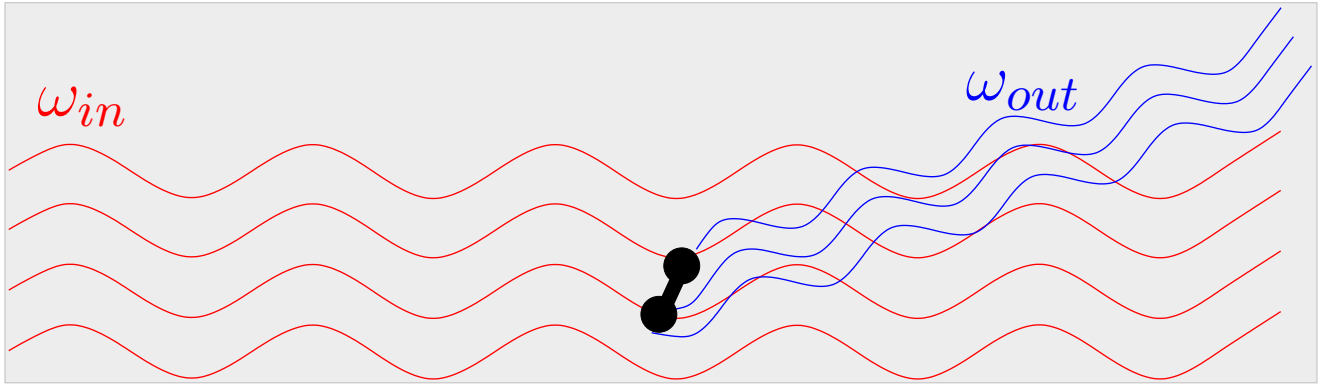
Consider a molecule in an electromagnetic field:



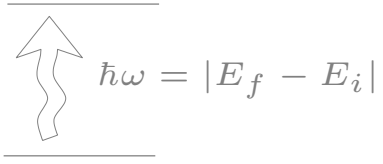
- Scattering — linear and nonlinear optical properties:
  - frequency-dependent (hyper-)polarizabilities
  - higher harmonic generation $(\omega_{out} = n \cdot \omega_{in})$
  - Faraday effect
  - ⋮

Introduction: What is Response Theory?

Consider a molecule in an electromagnetic field:



- Adsorption — spectroscopy:



  - UV/Vis, CD, NEXAFS, XPS, . . .
  - two-, three-, & multiphoton adsorption
  - structure & properties of excited states

⋮

What is Response Theory?

$$H(t) = H^{(0)} + \sum_j X_j \boxed{f_j(\omega_j) e^{-i\omega_j t}} \longrightarrow \textit{field strengths}$$

What is Response Theory?

$$H(t) = H^{(0)} + \sum_j X_j \boxed{f_j(\omega_j) e^{-i\omega_j t}}$$

field strengths

Study wavefunction, properties, etc. as function of frequency:

$$\Psi(t) = \boxed{\left[\Psi^{(0)} + \sum_j \Psi_j^{(1)}(\omega_j)\ f_j(\omega_j) e^{-i\omega_j t} + \ldots\right]}\ e^{-i\int_{t_0}^{t} dt' \left\langle \widetilde{\Psi} \middle| H(t') - i\frac{\partial}{\partial t'} \middle| \widetilde{\Psi} \right\rangle}$$

phase-isolated wavefunction $\widetilde{\Psi}$

Excitation energies are identified from singularities in e.g. $\Psi_j^{(1)}(\omega_j)$

What is Response Theory?

$$H(t) = H^{(0)} + \sum_j X_j \boxed{f_j(\omega_j) e^{-i\omega_j t}}$$

field strengths

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$$\Psi(t) = \boxed{\left[\Psi^{(0)} + \textstyle\sum_j \Psi_j^{(1)}(\omega_j)\ f_j(\omega_j) e^{-i\omega_j t} + \ldots\right]}\ e^{-i\int_{t_0}^{t} dt' \left\langle \widetilde{\Psi} \middle| H(t') - i\frac{\partial}{\partial t'} \middle| \widetilde{\Psi} \right\rangle}$$

phase-isolated wavefunction $\widetilde{\Psi}$

$$\langle \mu_i \rangle(t) = \langle \widetilde{\Psi}(t) | \mu_i | \widetilde{\Psi}(t) \rangle = \mu_i^{(0)} + \sum_j \boxed{\langle\langle \mu_i; X_j \rangle\rangle_{\omega_j}}\ f_j(\omega_j) e^{-i\omega_j t} + \ldots$$

response functions

Excitation energies are identified from singularities in e.g. $\Psi_j^{(1)}(\omega_j)$

Response Theory Methods

Two flavours of response theory methods:

- generalization of standard methods for time-dependent case in combination with derivative techniques
  $\rightsquigarrow$ TD-SCF, TD-DFT, CC response, etc.

- tailored approximations for excitation energies, response functions, etc. (typically defined such that results are correct up to a certain order of perturbation theory)
  $\rightsquigarrow$ propagator methods: SOPPA, ADC, etc.

In the following we consider only the first type of response methods, and restrict ourselfes to periodic perturbations.

Response Theory for Standard Methods

Periodic perturbations are similar to static case:

- Variation principle:

$$\delta E = 0 \quad \longrightarrow \quad \delta\left\{\langle\tilde{\Psi}|\hat{H} - i\frac{\partial}{\partial t}|\tilde{\Psi}\rangle\right\}_T = 0$$

time average

- Hellmann-Feynman theorem:

$$\langle\mu_i\rangle = \left(\frac{d\{\langle\tilde{\Psi}|\hat{H} - i\frac{\partial}{\partial t}|\tilde{\Psi}\rangle\}_T}{df_i}\right)_{f_i=0}$$

field strength

- higher-order properties (response functions):

$$\langle\langle V_i; V_j, V_k, \ldots\rangle\rangle_{\omega_j,\omega_k,\ldots} = \left(\frac{d^n\{\langle\tilde{\Psi}|\hat{H} - i\frac{\partial}{\partial t}|\tilde{\Psi}\rangle\}_T}{df_i(\omega_i)df_j(\omega_j)df_k(\omega_k)\ldots}\right)_{\vec{f}=0}$$

field strengths

Wavefunction requirements

$$\Psi(t) = \left[\Psi^{(0)} + \sum_j \Psi_j^{(1)}(\omega_j)\ f_j(\omega_j) e^{-i\omega_j t} + \dots\right] e^{-i\int_{t_0}^{t} dt' \left\langle \widetilde{\Psi} \middle| H(t') - i\frac{\partial}{\partial t'} \middle| \widetilde{\Psi} \right\rangle}$$

- for a physical consistent pole structure the freq.-dep. perturbation must be handled in a one-step procedure
  - not freq.-dep. SCF followed by freq.-dep. CI/CC
  - no perturbation theory
- requires relaxation of orbitals & correlation in one-step
  - DFT, MCSCF
  - in CC approx. orbital relaxation through $e^{\hat{T}_1}$

(with CI and unrelaxed orbitals poor convergence with excitation level)

Response Theory for CC Methods

Simple to generalize to non-variational CC methods:

- use a Lagrangian:

$$L = \mathrm{Re}\left\{ \left\langle \mathrm{HF} \middle| (\hat{H} - i\frac{\partial}{\partial t}) e^{\hat{T}} \middle| \mathrm{HF} \right\rangle + \sum_{\mu_i} \lambda_{\mu_i} \left\langle \mu_i \middle| e^{-\hat{T}} (\hat{H} - i\frac{\partial}{\partial t}) e^{\hat{T}} \middle| \mathrm{HF} \right\rangle \right\}$$

quasienergy — Lagrangian multiplier — cluster equations as constraints

Response Theory for CC Methods

Simple to generalize to non-variational CC methods:

- use a Lagrangian:

$$L = \mathrm{Re}\left\{ \left\langle \mathrm{HF} \middle| (\hat{H} - i\frac{\partial}{\partial t}) e^{\hat{T}} \middle| \mathrm{HF} \right\rangle + \sum_{\mu_i} \lambda_{\mu_i} \left\langle \mu_i \middle| e^{-\hat{T}} (\hat{H} - i\frac{\partial}{\partial t}) e^{\hat{T}} \middle| \mathrm{HF} \right\rangle \right\}$$

- use L instead of quasienergy in variational expressions

  $\Longrightarrow$ standard techniques for properties with CC methods

  $\Longrightarrow$ requires minor modifications in CC programs

Response Theory with CC-R12 Methods

- include additional double excitations

$$T = T_1 + T_2 + T_{2'} + \ldots \qquad \text{with} \quad T_{2'} = \frac{1}{2} \sum_{xiyj} c_{ij}^{xy} \hat{\tau}_{ij}^{xy}$$

into explicitly correlated pair functions:

$$\chi_{xy}(\vec{r}_1, \vec{r}_2) = \hat{Q}_{12}\ f(r_{12})\ \phi_x(\vec{r}_1)\, \phi_y(\vec{r}_2)$$

$\phi_x(\vec{r}_1)$, $\phi_y(\vec{r}_2)$ usually are the occupied valence orbitals

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- implemented in Dalton for

CC2-F12, CCSD(F12), CC3(F12)

and R12 variants

Excitation Energies in CC Response Theory

(IJCQ 68, 1-52, 1998; JCP 108, 8331-8354, 1998)

- equations for first derivatives of amplitudes:

$$\left[\mathbf{A}_{\mu_i\nu_j} - \omega_x \mathbf{S}_{\mu_i\nu_j}\right] t^x_{\nu_j}(\omega_x) = -\xi^x_{\mu_i}$$

Jacobi matrix

$$A_{\mu_i\nu_j} = \frac{d\Omega_{\mu_i}}{dt_{\nu_j}}$$

Overlap matrix

$$S_{\mu_i\nu_j} = i\frac{d\Omega_{\mu_i}}{dt_{\nu_j}} = \langle\mu_i|\nu_j\rangle$$

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$\rightsquigarrow$ poles (excitation energies) at eigenvalues of Jacobi matrix

- cmp. with exact wavefunctions:

$$\left[H^{(0)} - E_0 - i\frac{\partial}{\partial t}\right]\Psi^x = -V_x\Psi^{(0)}$$

$\rightsquigarrow$ Jacobi matrix model for $H^{(0)} - E_0$

Excitation Energies in Response Theory

correlated ground state wavefunction:

$$\left|\mathrm{CC}_{GS}\right\rangle = \exp(\hat{T}_1 + \hat{T}_2 + \ldots)\left|\mathrm{HF}\right\rangle$$

excited state wavefunction in CC response (contrib. $\perp$ to $\left|\mathrm{HF}\right\rangle$):

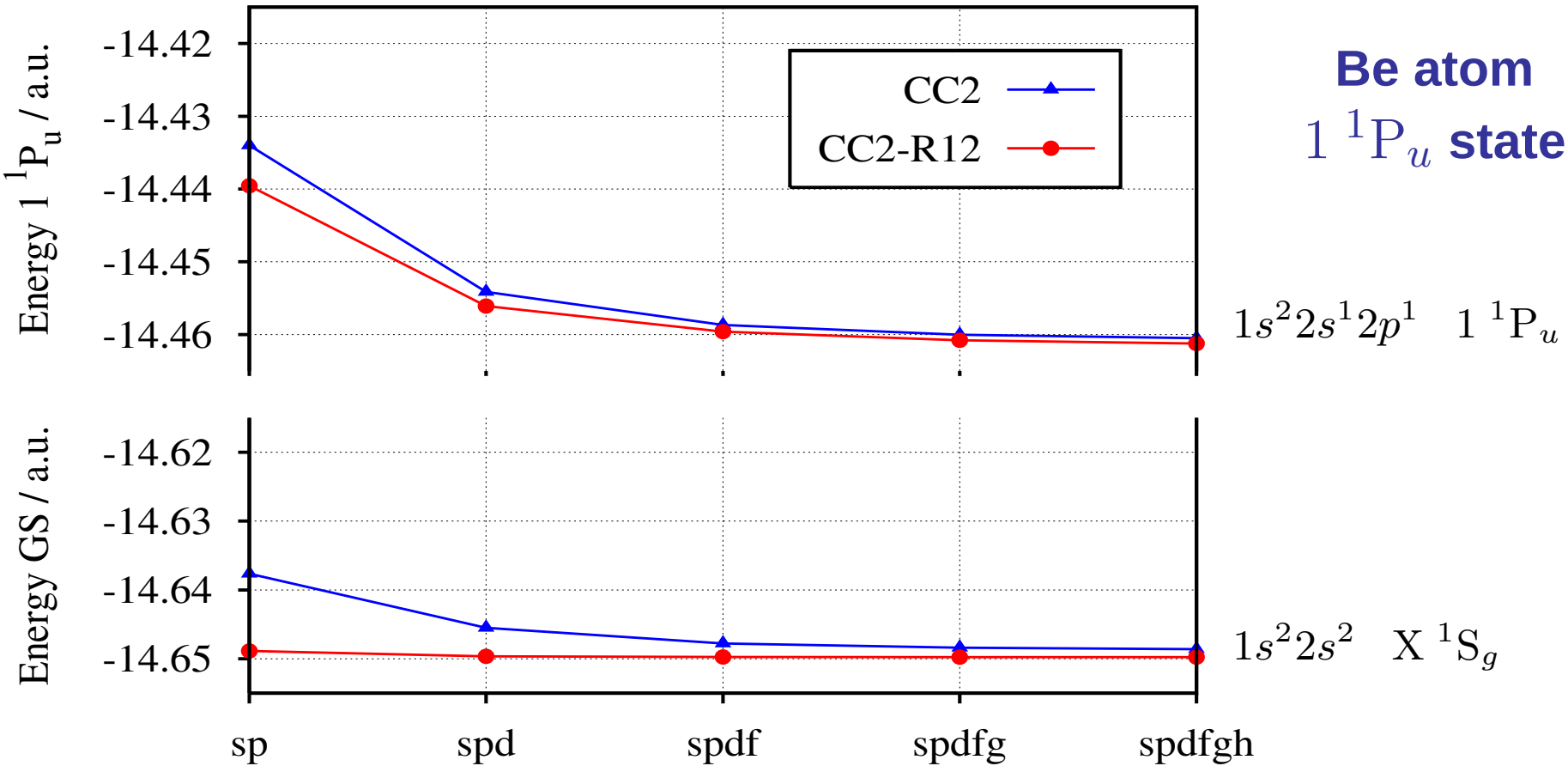
$$\left|\Psi_{ex}\right\rangle = \Big(\sum_{\mu_1} E_{\mu_1}\hat{\tau}_{\mu_1} + \sum_{\mu_2} E_{\mu_2}\hat{\tau}_{\mu_2} + \sum_{\mu_3} E_{\mu_3}\hat{\tau}_{\mu_3} + \ldots\Big)\left|\mathrm{CC}_{GS}\right\rangle$$

where E_{μ_i} is a solution of

$$\left[\mathbf{A}_{\mu_i\nu_j} - \omega\,\mathbf{S}_{\mu_i\nu_j}\right] E_{\nu_j} \;=\; 0$$

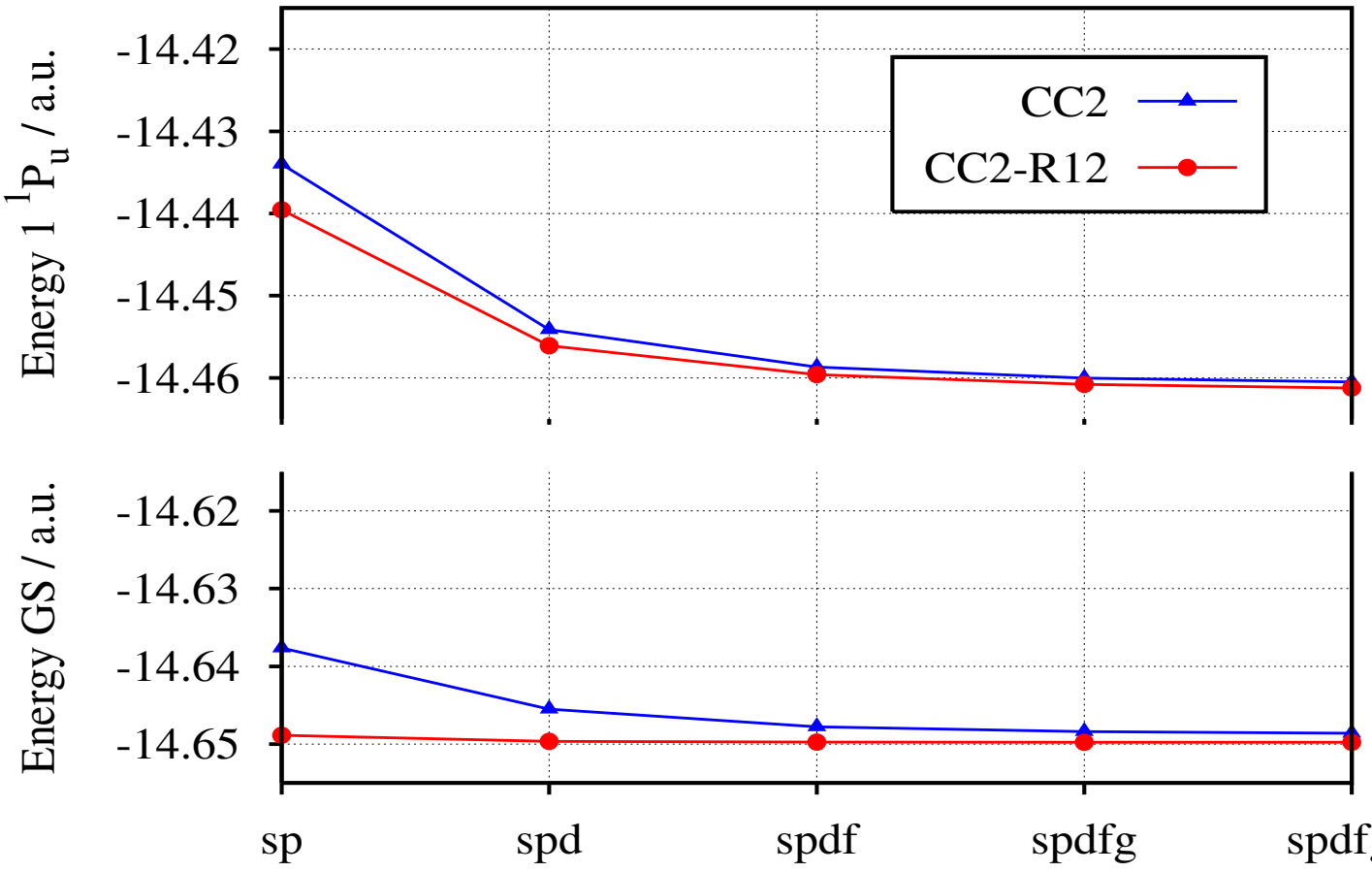
First results: $1\ ^1\mathrm{P}_u$ state of the Be atom

(H. Fliegl, C.H., W. Klopper, *JCP* 124 (2006) 044112)



First results: $1\ ^1\mathrm{P}_u$ state of the Be atom

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Be atom

$1\ ^1\mathrm{P}_u$ state

$1s^2 2s^1 2p^1 \quad 1\ ^1\mathrm{P}_u$

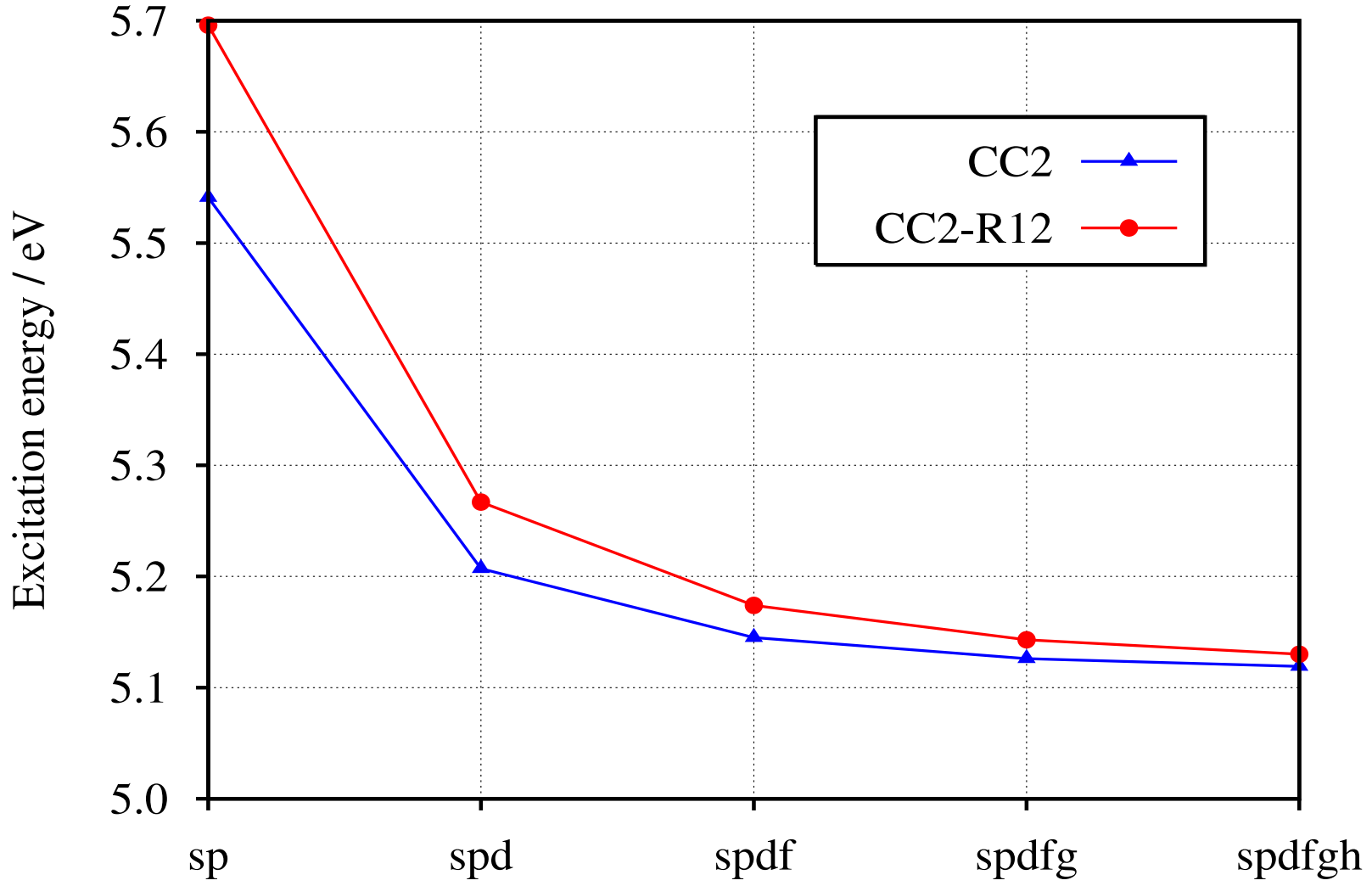
$1s^2 2s^2 \quad \mathrm{X}\ ^1\mathrm{S}_g$

pair functions: $\chi_{xy}(\vec{r}_1, \vec{r}_2) = \hat{Q}_{12}\ r_{12}\ \phi_x(\vec{r}_1)\ \phi_y(\vec{r}_2)$ (all of S_g symmetry)

occupied orbitals

First results: $1\ ^1\mathrm{P}_u$ state of the Be atom

(H. Fliegl, C.H., W. Klopper, *JCP* 124 (2006) 044112)



Be atom
$1\ ^1\mathrm{P}_u$ state

- unbalanced treatment of ground and excited state

Extension of R12 orbital/pair function space

- standard choice of pair functions for CC-R12

$$\chi_{kl}(\vec{r}_1, \vec{r}_2) = \hat{Q}_{12}\, r_{12}\, \phi_k(\vec{r}_1)\, \phi_l(\vec{r}_2)$$

  biased by restriction to orbitals occupied in $|\mathrm{HF}\rangle$

- extension of orbital set used for geminals

$$\chi_{xy}(\vec{r}_1, \vec{r}_2) = \hat{Q}_{12}\, r_{12}\, \phi_x(\vec{r}_1)\, \phi_y(\vec{r}_2)$$

  with $\phi_x, \phi_y \in \{\text{occ. orb.}\} \cup \{\text{most. important virt. orb.}\}$

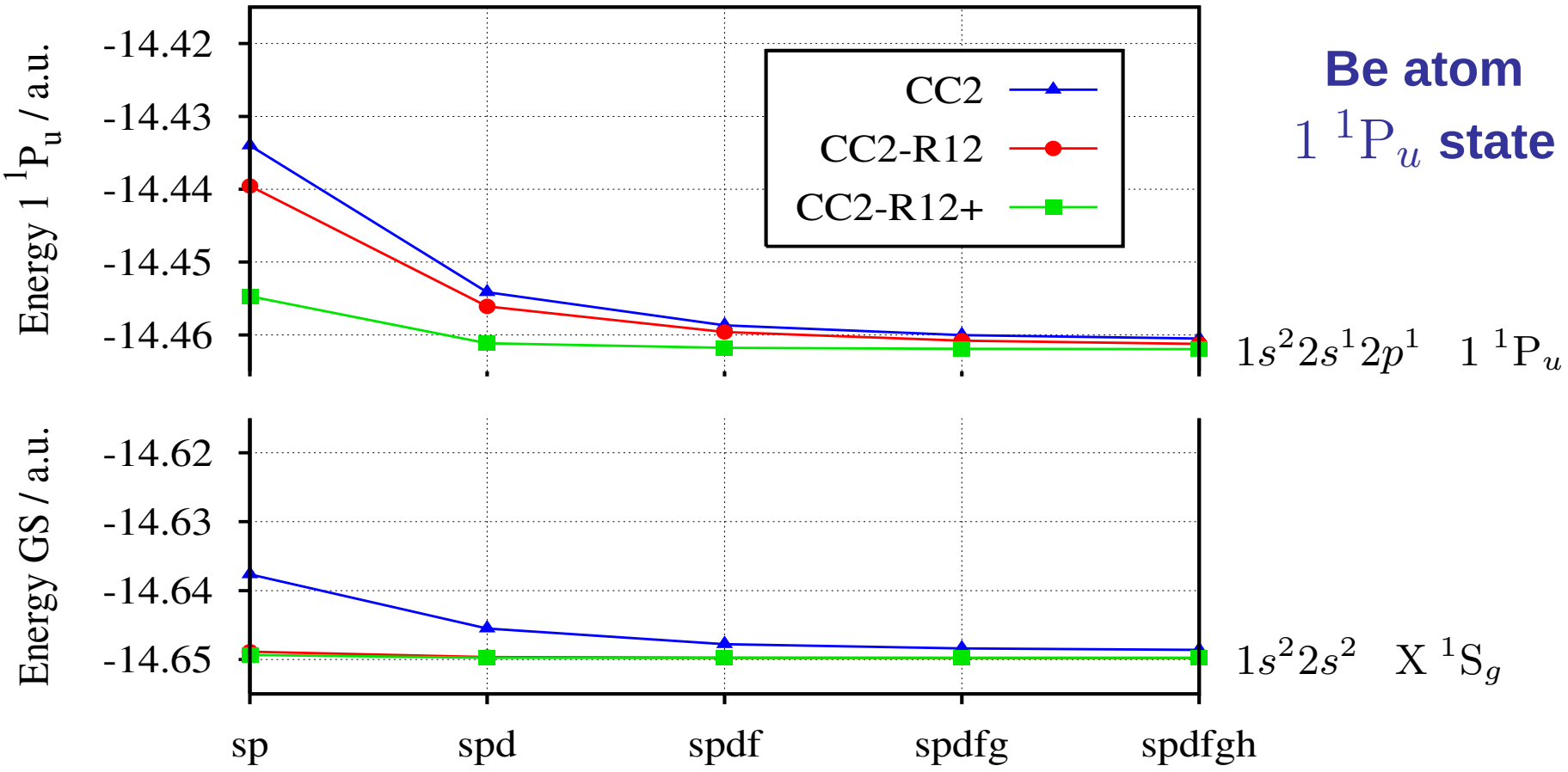
- choice for valence states:

  MP2 semi-natural orbitals with highest occupation numbers

  ↷ important unoccupied valence orbitals

$1\ ^1\mathrm{P}_u$ state of the Be atom

(C. Neiss, C.H., W. Klopper, JCP 125, 064111 (2006))



Be atom

$1\ ^1\mathrm{P}_u$ state

$1s^2 2s^1 2p^1 \quad 1\ ^1\mathrm{P}_u$

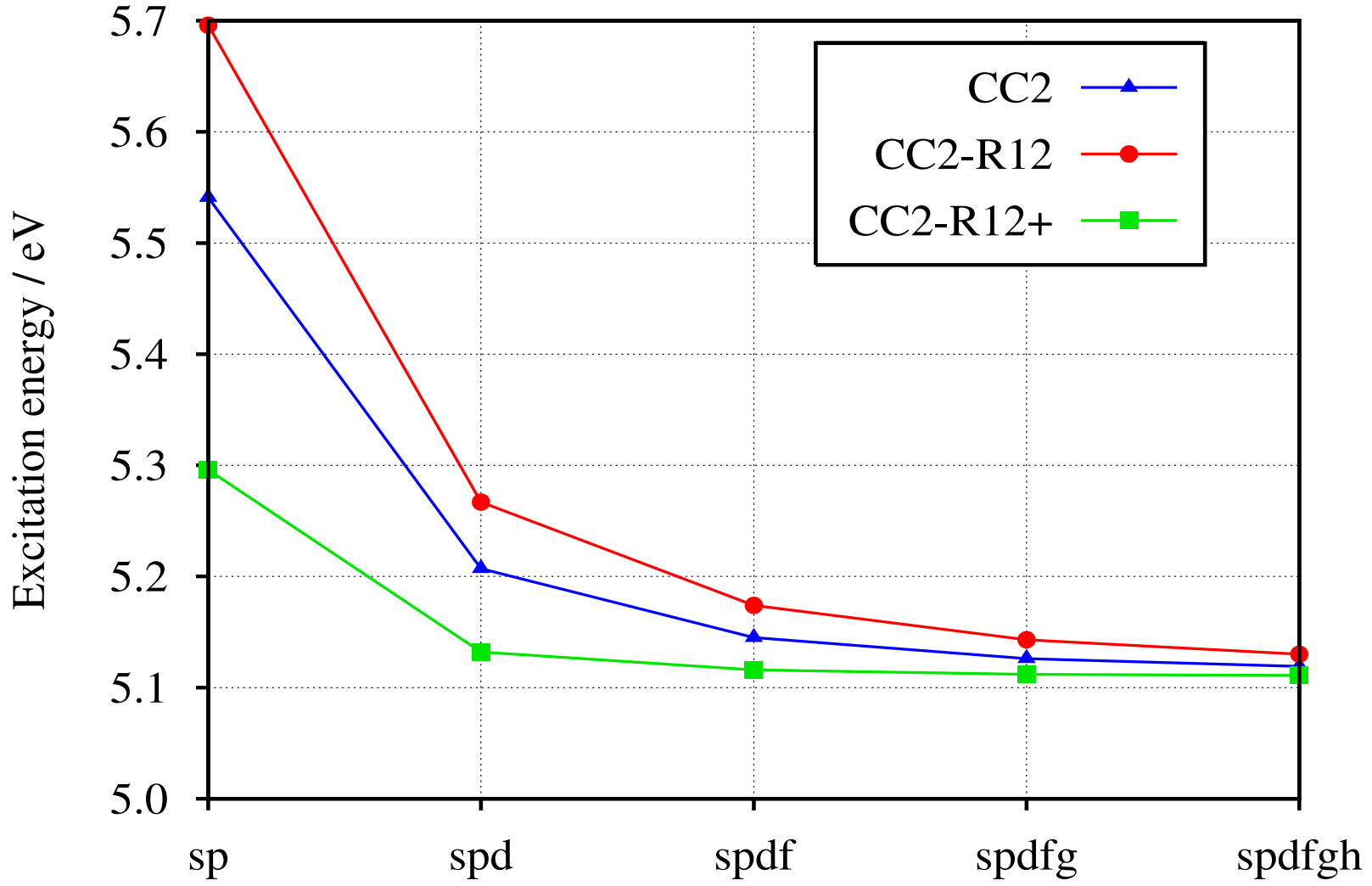
$1s^2 2s^2 \quad \mathrm{X}\ ^1\mathrm{S}_g$

pair functions: $\chi_{xy}(\vec{r}_1, \vec{r}_2) = \hat{Q}_{12}\ r_{12}\ \phi_x(\vec{r}_1)\ \phi_y(\vec{r}_2)$ (of S_g and P_g symmetry)

valence orbitals

$1\ ^1\mathrm{P}_u$ state of the Be atom

(C. Neiss, C.H., W. Klopper, JCP 125, 064111 (2006))



Be atom
$1\ ^1\mathrm{P}_u$ state

- re-establishes balance between ground and excited state

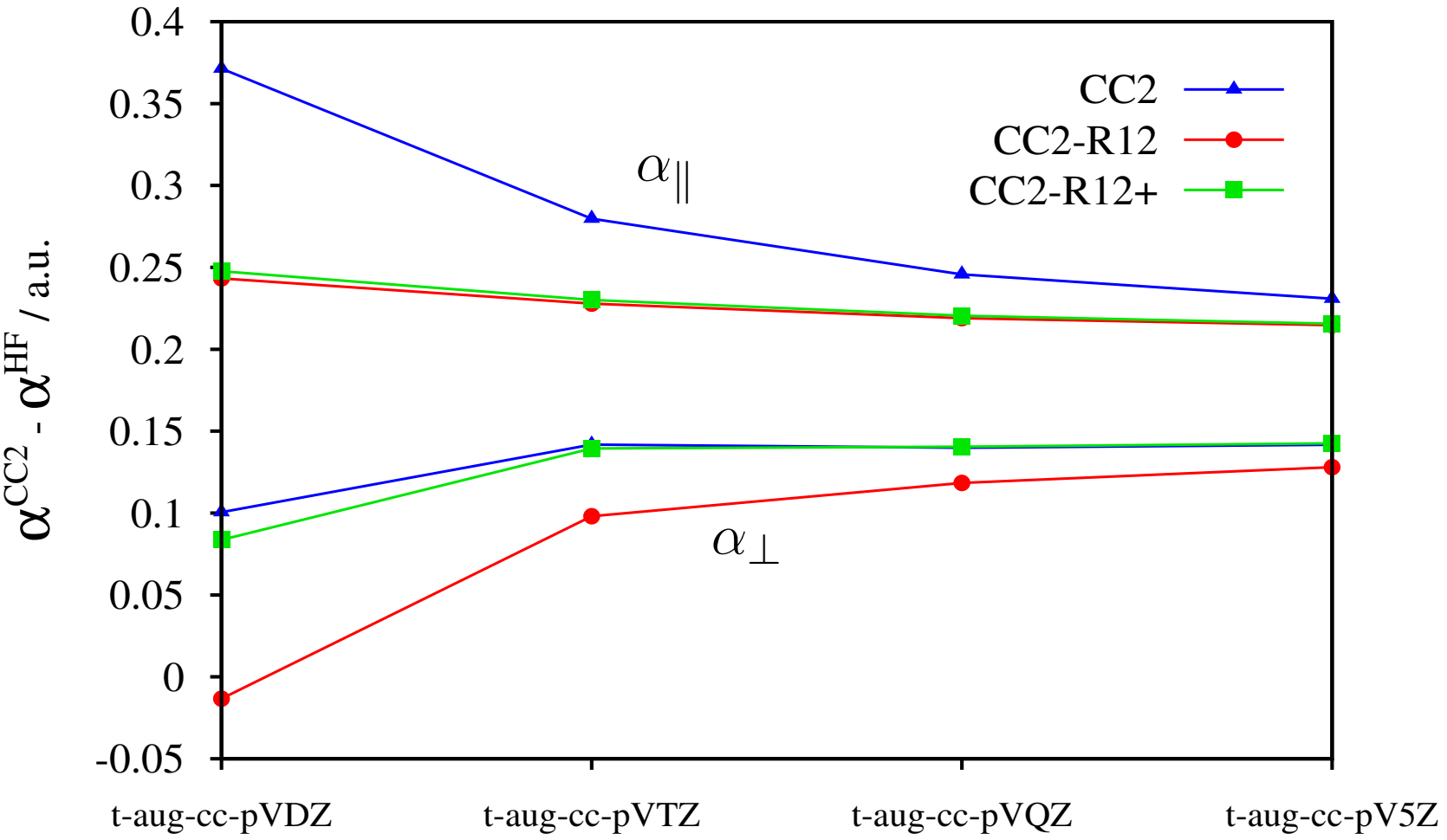
Harmonic Frequencies in Excited States

(Jun Yang, C. H., *JCP*, **130** (2009) 124101)

		CCSD		CCSD(R12)		CCSD(F12)		CCSD
		TZ	QZ	TZ	QZ	TZ	QZ	Limit
CO	$A^1\Pi$	1561	1581	1579	1589	1580	1589	1592
		(1566)		(1583)		(1584)		
	$B^1\Sigma^+$	2221	2244	2241	2252	2246	2253	2253
		(2230)		(2248)		(2254)		
	$C^1\Sigma^+$	2259	2281	2277	2289	2282	2289	2289
		(2267)		(2284)		(2289)		
BF	$A^1\Pi$	1258	1271	1271	1278	1275	1278	1279
		(1260)		(1273)		(1277)		
	$B^1\Sigma^+$	1704	1715	1714	1720	1717	1720	1720
		(1708)		(1717)		(1720)		
	$C^1\Sigma^+$	1620	1632	1630	1637	1633	1637	1637
		(1625)		(1635)		(1638)		

d-aug-cc-pVXZ basis sets; results in parentheses include correction for TD-SCF basis set error.

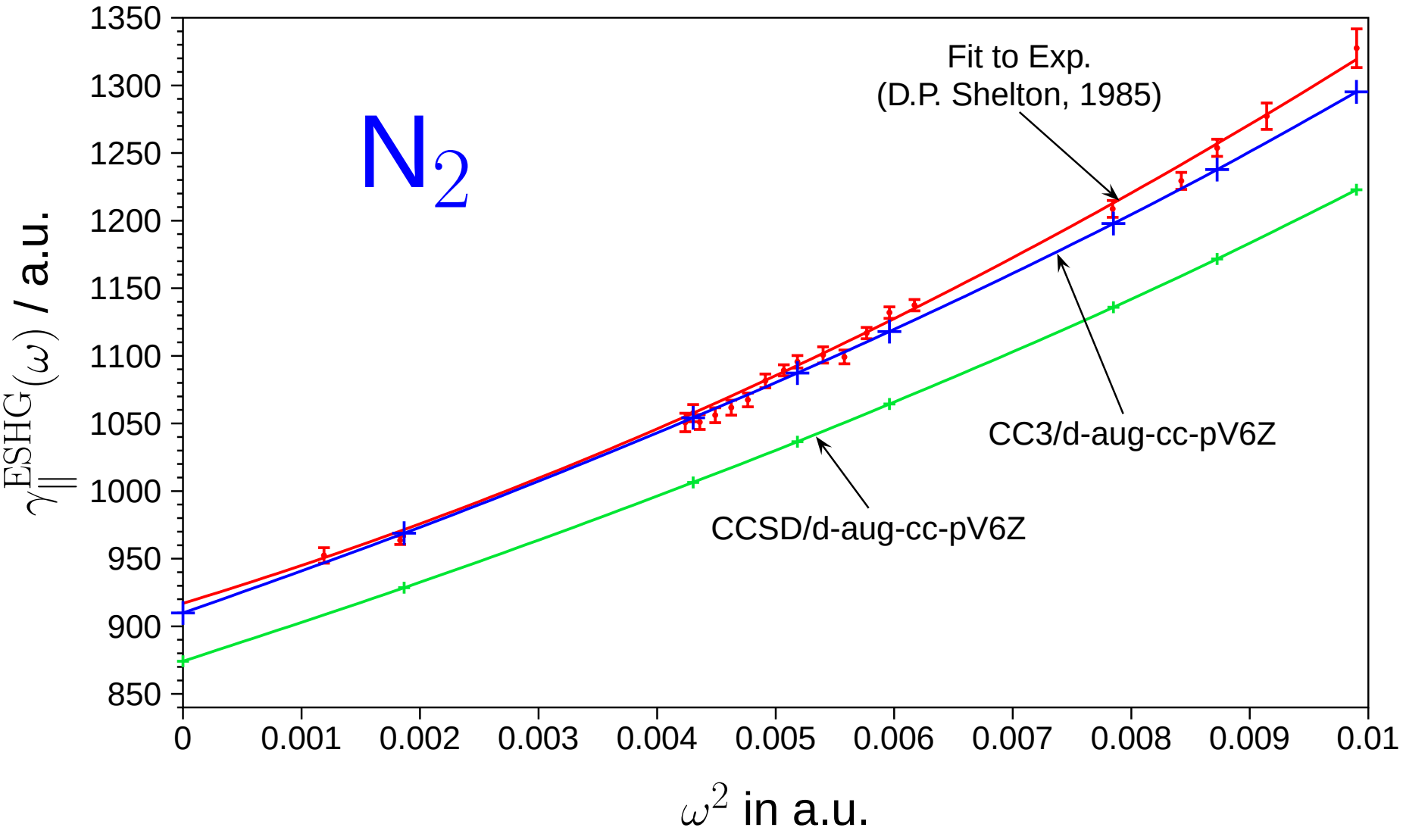
The dipole polarizability of CH^+



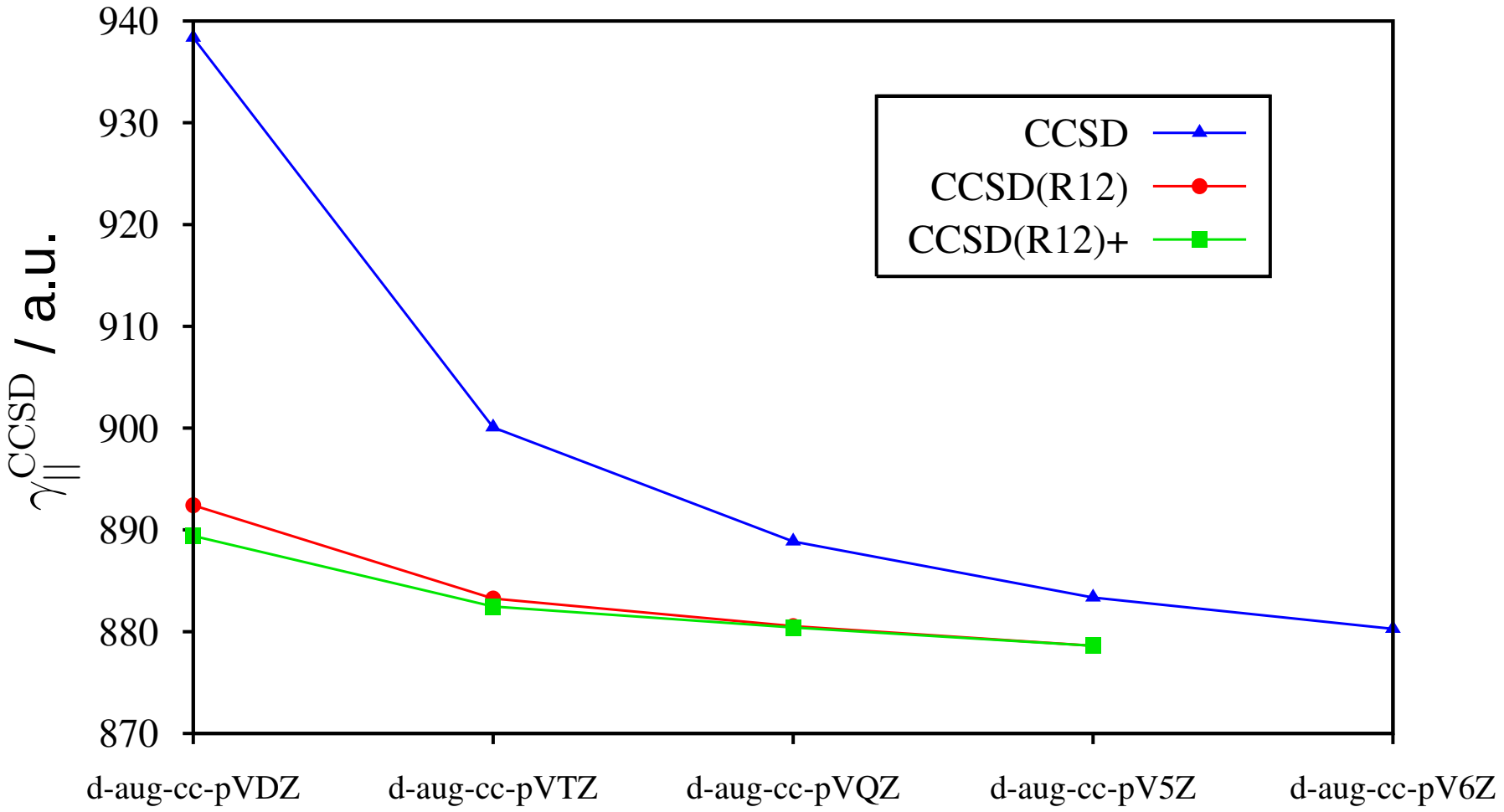
(R12 Ansatz 1A, ABS, t-aug-cc-pV(X+1)Z aux. basis)

ESHG Hyperpolarizability of Nitrogen (N_2)

(F. Pawlowski, P. Jørgensen, C. H., *CPL*, **413** (2005) 272)

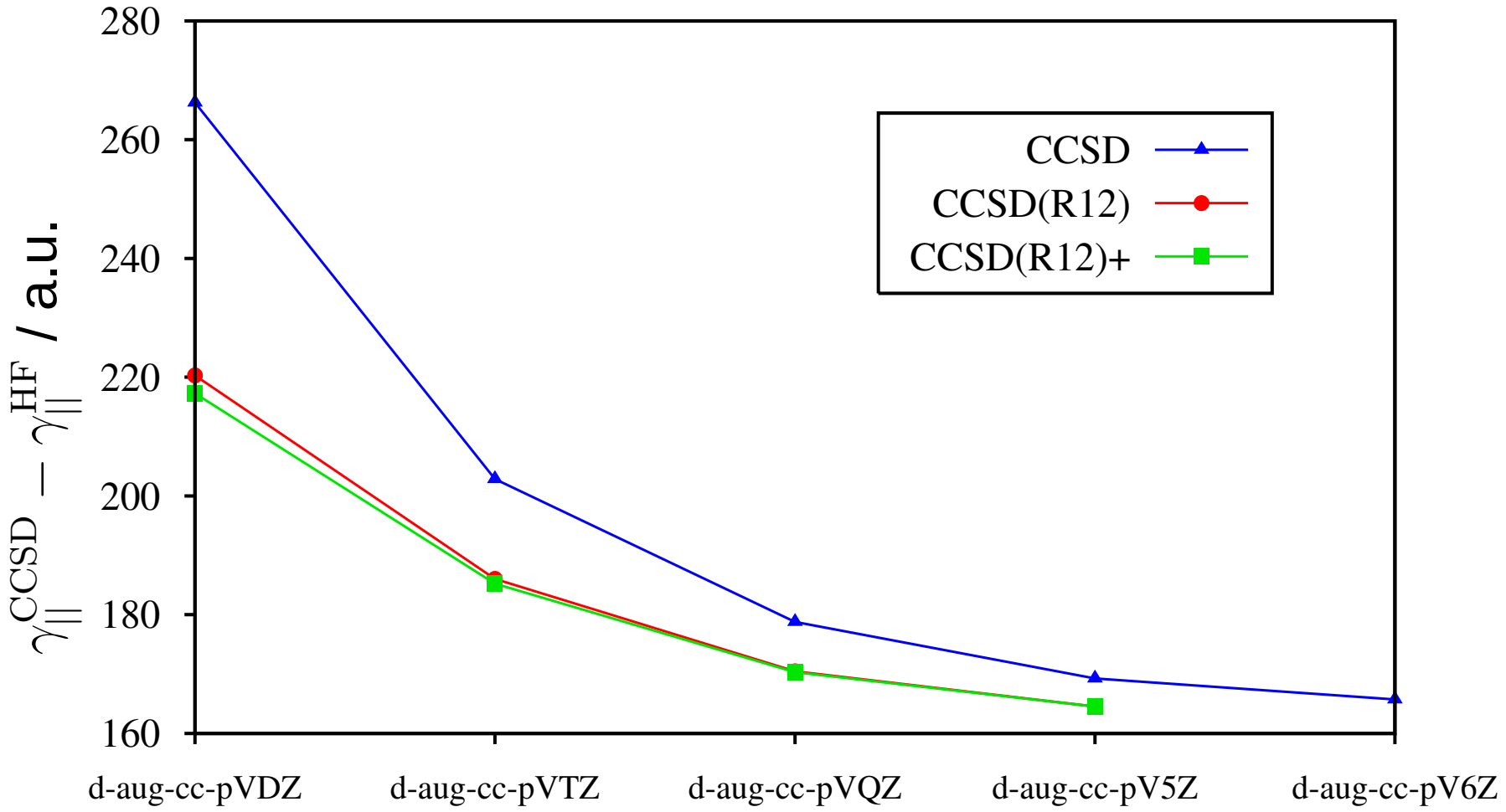


The dipole hyperpolarizability of N_2



(R12 Ansatz 1B, CABS, decontr. d-aug-cc-pV(X+1)Z aux. basis)

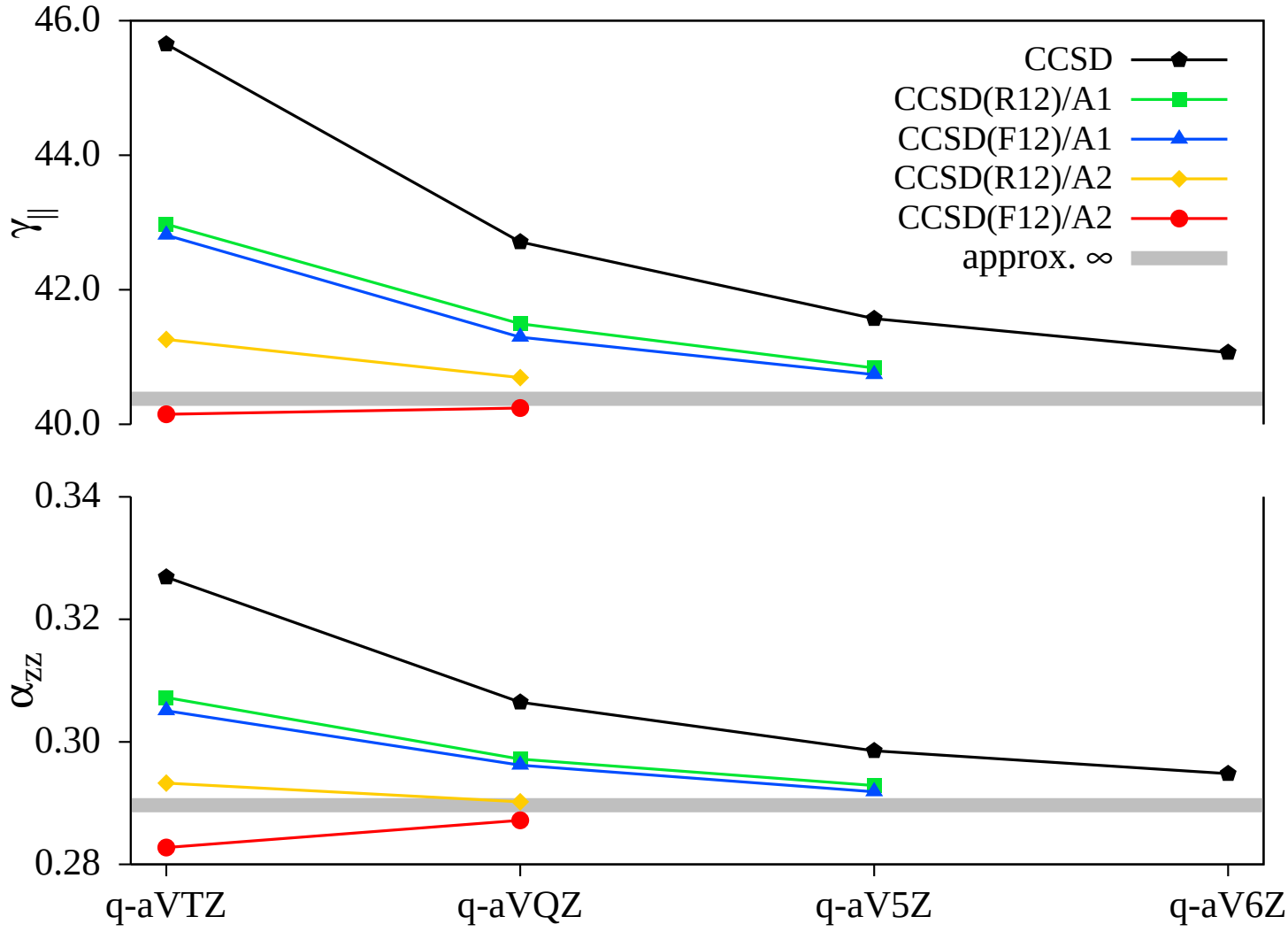
The dipole hyperpolarizability of N_2



(R12 Ansatz 1B, CABS, decontr. d-aug-cc-pV(X+1)Z aux. basis)

(Hyper-)polarizability of the Neon Atom

(Jun Yang, C. H., *JCP*, **131** (2009) 074102)



- similar improvements in correlation contribution as for energies but requires (still) many diffuse functions

Conclusions From First Results

- with optimized geminal amplitudes basis set convergence of response calculations is similarly enhanced as for ground state energies provided that:
  - geminal basis suitable to correlate response of $|\mathrm{CC}\rangle$
  - one-electron basis sufficient to converge response of $|T\rangle_1$
  - ansatz 2 is used

- but optimization of $\hat{T}_{2'}$ and its responses is computationally demanding...

  $\rightsquigarrow$an SP approach would reduce costs significantly

The SP Approach

Fulfilling the cusp conditions to first-order:

$$|\Psi\rangle \quad \longrightarrow \quad |\Psi\rangle + \frac{1}{4}\sum_{\substack{pq\\ \alpha\beta}} R^{pq}_{\alpha\beta} a^\dagger_\alpha a_p a^\dagger_\beta a_q |\Psi\rangle \quad = \quad (1+\hat{R})|\Psi\rangle$$

with $R^{\alpha\beta}_{pq} = \langle \alpha\beta | \hat{Q}_{12} \hat{S}_{pq} f(r_{12}) | pq \rangle$ integrals over correlation factor

$\hat{S}_{pq} = \frac{1}{8}\left(3 - \delta_{\sigma_p\sigma_q} + (1 - 3\delta_{\sigma_p\sigma_q})\hat{P}_{pq}\right)$ spin-dependent numerical factor

First-order correction for Hartree-Fock wavefunction:

$$|\mathrm{HF}\rangle \quad \longrightarrow \quad |\mathrm{HF}\rangle + \frac{1}{4}\sum_{\substack{ij\\ \alpha\beta}} R^{ij}_{\alpha\beta} a^\dagger_\alpha a_i a^\dagger_\beta a_j |\mathrm{HF}\rangle = (1+\hat{R}^{hh})|\mathrm{HF}\rangle$$

CCSD-F12-SP: choose $T_{2'}$ as $\hat{R}^{hh}$

$$|\mathrm{HF}\rangle \quad \longrightarrow \quad e^{\hat{R}^{hh}}|\mathrm{HF}\rangle \qquad \text{or} \qquad \hat{T} \quad \longrightarrow \quad \hat{T} + \hat{R}^{hh}$$

Extension of SP Approach to Response

Excited state wavefunction in CC response (contrib. $\perp$ to $\big|\mathrm{HF}\big\rangle$):

$$\big|\Psi_{ex}\big\rangle = \Big(\sum_{\mu_1} E_{\mu_1}\hat{\tau}_{\mu_1} + \sum_{\mu_2} E_{\mu_2}\hat{\tau}_{\mu_2} + \sum_{\mu_3} E_{\mu_3}\hat{\tau}_{\mu_3} + \dots\Big)\big|\mathrm{CC}_{GS}\big\rangle$$

Zeroth-order contribution if single-excitation dominated:

$$\big|\Psi_{ex}^{(0)}\big\rangle = \sum_{aj} E_a^j a_a^\dagger a_j \big|\mathrm{HF}\big\rangle = \hat{E}_1|\mathrm{HF}\rangle$$

Fulfilling the cusp conditions to first order requires

$$\big|\Psi_{ex}^{(0)}\big\rangle = \hat{E}_1|\mathrm{HF}\rangle \quad \longrightarrow \quad (1+\hat{R})\big|\Psi_{ex}^{(0)}\big\rangle = (1+\hat{R})\hat{E}_1|\mathrm{HF}\rangle$$

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Response with CCSD-F12-SP gives

$$\hat{E}_1(1+\hat{R})\big|\mathrm{HF}\big\rangle$$

Extension of SP Approach to Response

(A. Köhn, *JCP*, **130** (2009) 104104)

Fulfilling the first-order cusp conditions requires

$$\left|\Psi_{ex}^{(0)}\right\rangle = \hat{E}_1|\mathrm{HF}\rangle \quad \longrightarrow \quad (1+\hat{R})\left|\Psi_{ex}^{(0)}\right\rangle = (1+\hat{R})\hat{E}_1|\mathrm{HF}\rangle$$

Response with CCSD-F12-SP gives

$$\hat{E}_1(1+\hat{R})\left|\mathrm{HF}\right\rangle = (1+\hat{R})\hat{E}_1|\mathrm{HF}\rangle - [\hat{R},\hat{E}_1]|\mathrm{HF}\rangle$$

Extended SP approaches:

$$\hat{T} \quad \longrightarrow \quad \hat{T} + \hat{R}^{hh} + [\hat{R},\hat{T}_1]^{hh} \qquad \text{CCSD-F12-XSP}$$

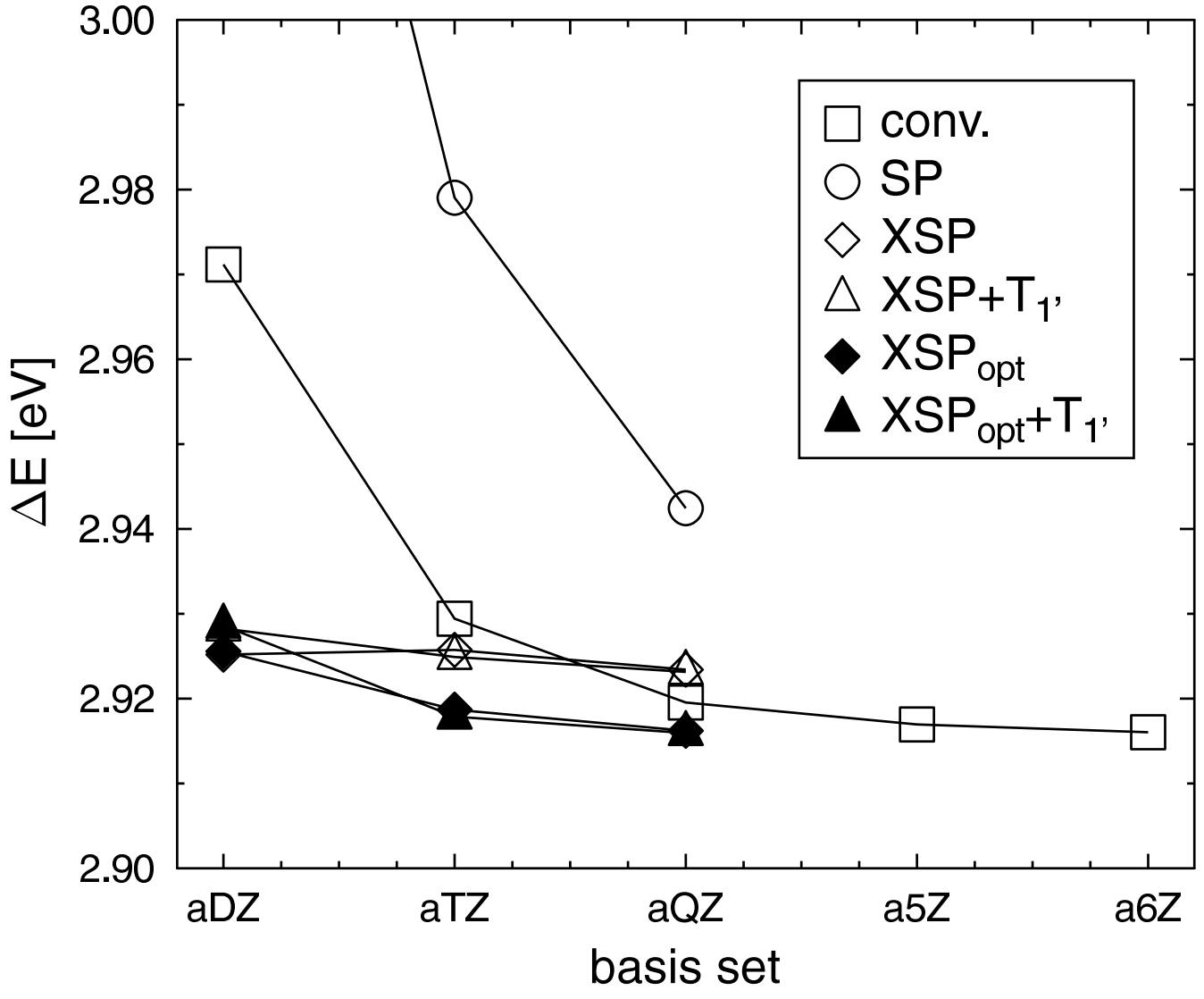
$$\hat{T} \quad \longrightarrow \quad \hat{T} + \hat{R}^{hh} + [\hat{R},\hat{\tilde{T}}_1]^{hh} \qquad \text{CCSD-F12-XSP}_{\mathrm{opt}}$$

CCSD-F12-XSP gives correct first-order contribution:

$$\left|\Psi_{ex}\right\rangle = (\hat{E}_1 + [\hat{R},\hat{E}_1]^{hh} + \ldots)(1+\hat{R}+\ldots)|\mathrm{HF}\rangle = (1+\hat{R})\hat{E}_1|\mathrm{HF}\rangle + \mathcal{O}(\hat{R}^2) + \ldots$$

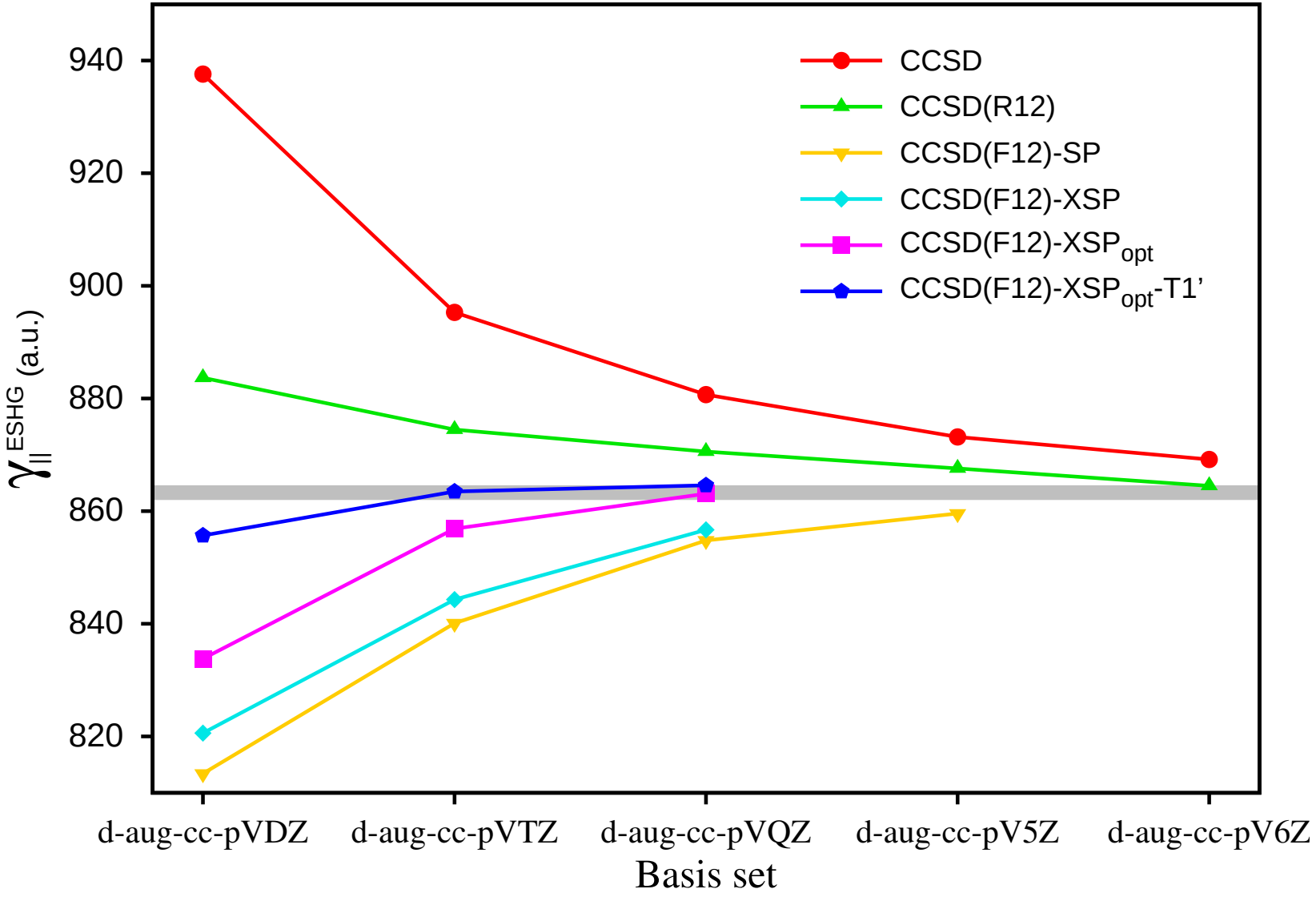
Excitation Energies with XSP Approach: BH

(A. Köhn, *JCP*, **130** (2009) 104104)



Hyperpolarizabilities with XSP Approach: N_2

(M. Hanauer, A. Köhn, *JCP*, **131** (2009) 124118)



Summary: CC-F12 Response Theory

- extending $\hat{T}$ with $[\hat{R}, \hat{T}_1]^{(hh)}$ in the XSP approaches allows to exploit cusp conditions also in response calculations
  $\rightsquigarrow$ will lead to approximations with comparable efficiency as present approx. CCSD-F12-SP variants for energies

- augmentation with $\hat{T}_{1'}$ will reduce demands for one-electron basis set error similar as CABS singles correction for ground state energies

- these methods are still under development and less standardized as F12 methods for ground state energies

References: CC & CC-F12 Response Theory

Some references for the presented topics:

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- Christiansen *et al.*, in: Non-Linear Optical Properties of Matter, 2006, Springer, Berlin, Germany.
- Fliegl, Hättig, Klopper, J. Chem. Phys. **124** 044112 (2006)
- Neiss, Hättig, Klopper, J. Chem. Phys. **125** 064111 (2006); Neiss, Hättig, J. Chem. Phys. **126** 154101 (2007)
- Yang, Hättig, J. Chem. Phys. **130** 124101 (2009); Yang, Hättig, J. Chem. Phys. **131** 074102 (2009); Yang, Hättig, Z. Phys. Chem. **225**, 695-708 (2010)
- Köhn, J. Chem. Phys. **130** 104104 (2009)
- Hanauer, Köhn, J. Chem. Phys. **131** 124118 (2009)