Overview on Explicitly Correlated Methods

Wim Klopper

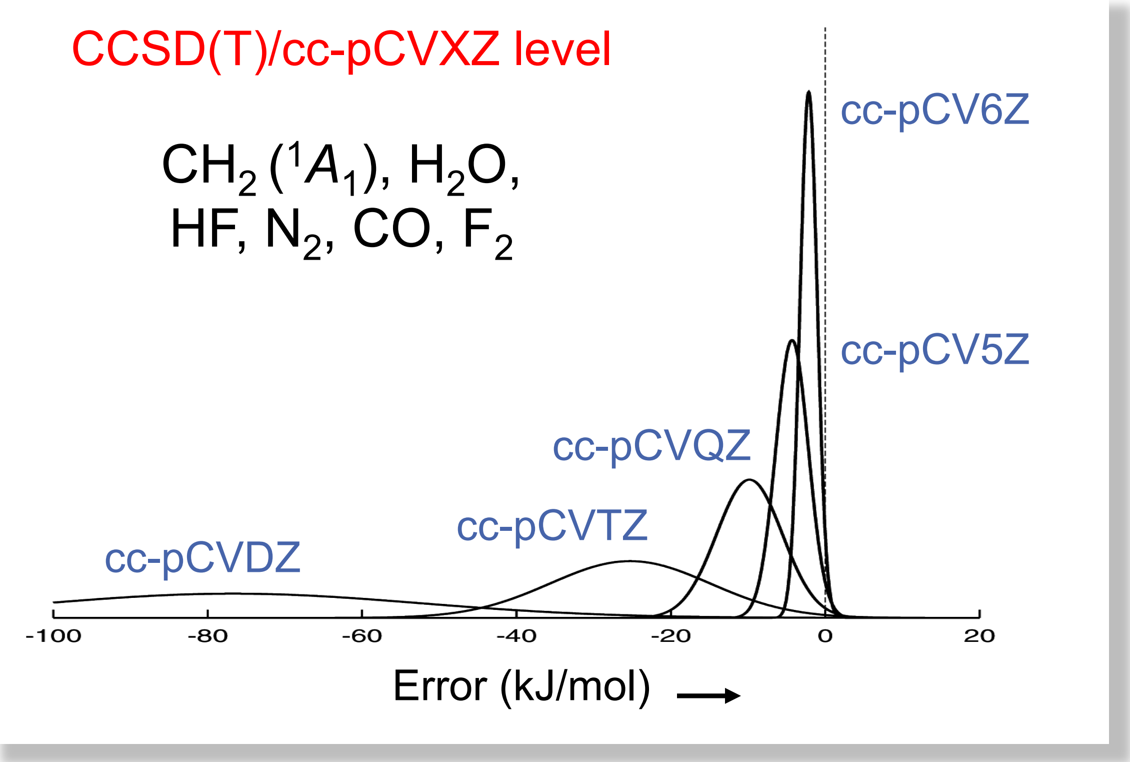
Contact: klopper@kit.edu

Institute of Physical Chemistry

Motivation

Why do we need explicitly correlated methods?

Normal distributions of error in atomization energies (AE)


CCSD(T)/cc-pCVXZ level

CH_2 ($^1A_1$), H_2O, HF, N_2, CO, F_2

- Convergence of the computed AE towards the CCSD(T) basis-set limit is very slow (only as X^{-3})

$$E_X = E_\infty + cX^{-3} + O\left(X^{-4}\right)$$

- Results (E_X) as function of X converge towards a limiting value E_∞ for $X \to \infty$
- This limiting value corresponds to the value that we would have obtained in a complete and infinitely large basis set
- We can improve our calculations systematically by increasing the cardinal number X of the basis set

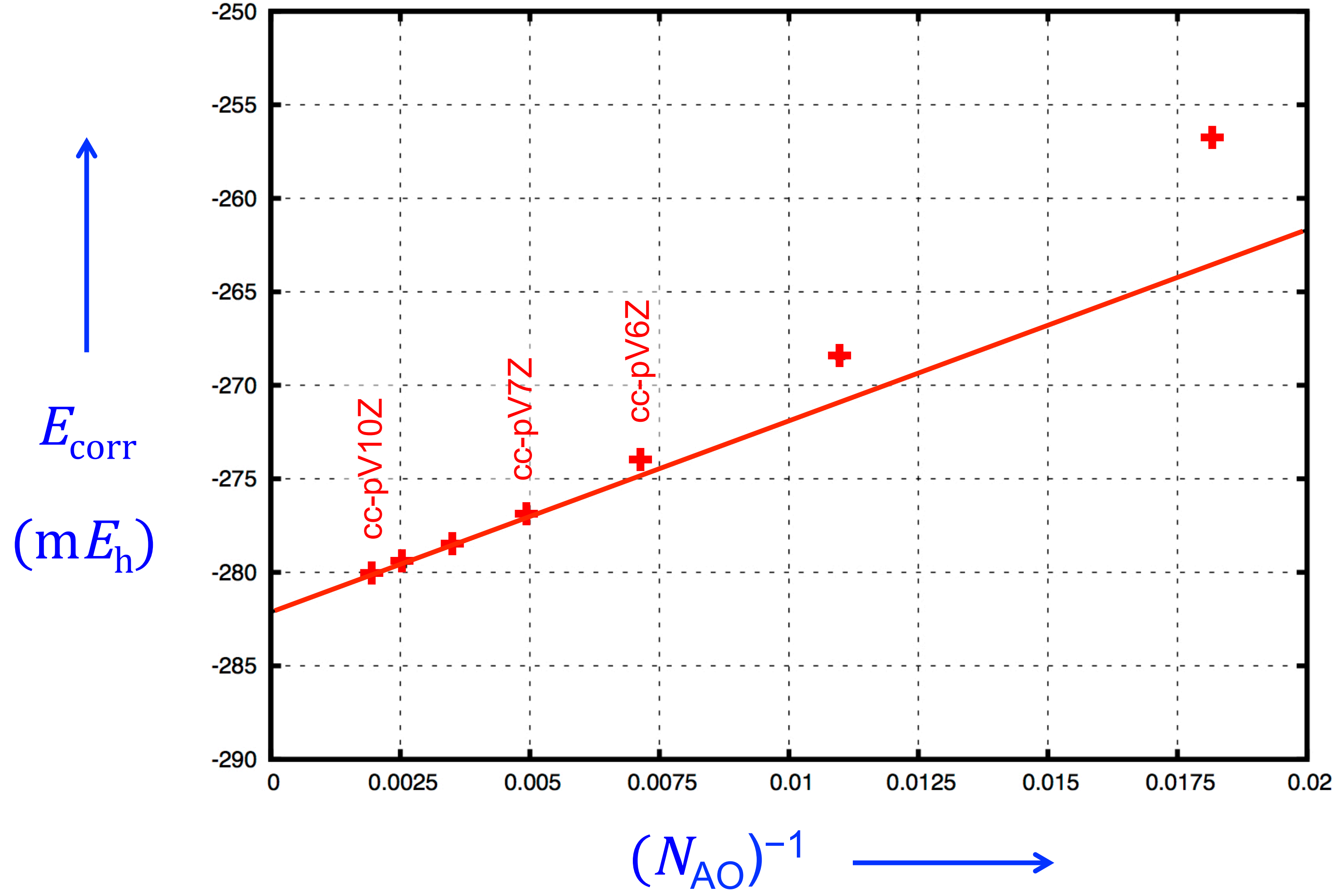
T. Helgaker, W. Klopper, H. Koch, and J. Noga,
J. Chem. Phys. **106**, 9639 (1997)

The number of basis functions grows very rapidly

Ne atom	cc-pVXZ basis	Number of AOs (N_{AO})
$X = 1$	2s1p	$2+3=5$
$X = 2$	3s2p1d	$3+6+5=14$
$X = 3$	4s3p2d1f	$4+9+10+7=30$
$X = 4$	5s4p3d2f1g	$5+12+15+14+9=55$
		$\frac{1}{3}(X+1)(X+\frac{3}{2})(X+2)$

$$N_{\mathrm{AO}} \propto X^3$$

Valence-shell MP2 energy of the Ne atom



Computed results convergence extremely slowly to the complete-basis-set limit

- Let N_{atoms} be the number of atoms in the molecule
- Let N_{AO} be the number of basis functions per atom
- The computation time is at least $t_{\text{CPU}} \propto N_{\text{atoms}}(N_{\text{AO}})^4$
- **Computation times grow as $(N_{\text{AO}})^4$**
- **The basis set errors vanish as $(N_{\text{AO}})^{-1}$**

- **Reducing the error by one order of magnitude requires 10,000 times more computation time**

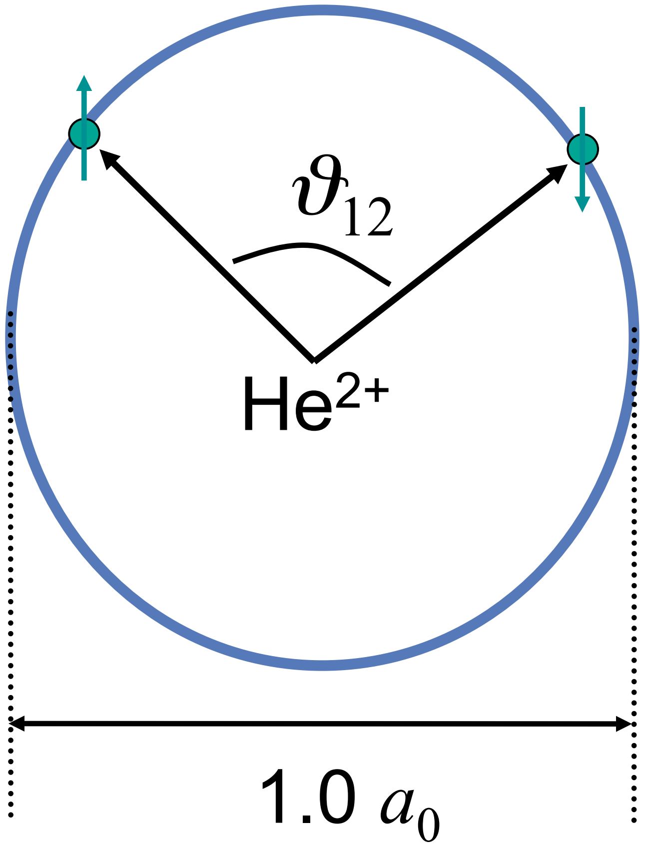
– Error = 10%	t_{CPU} = ca. 1 minute
– Error = 1%	t_{CPU} = ca. 1 week
– Error = 0.1%	t_{CPU} = ca. 200 years

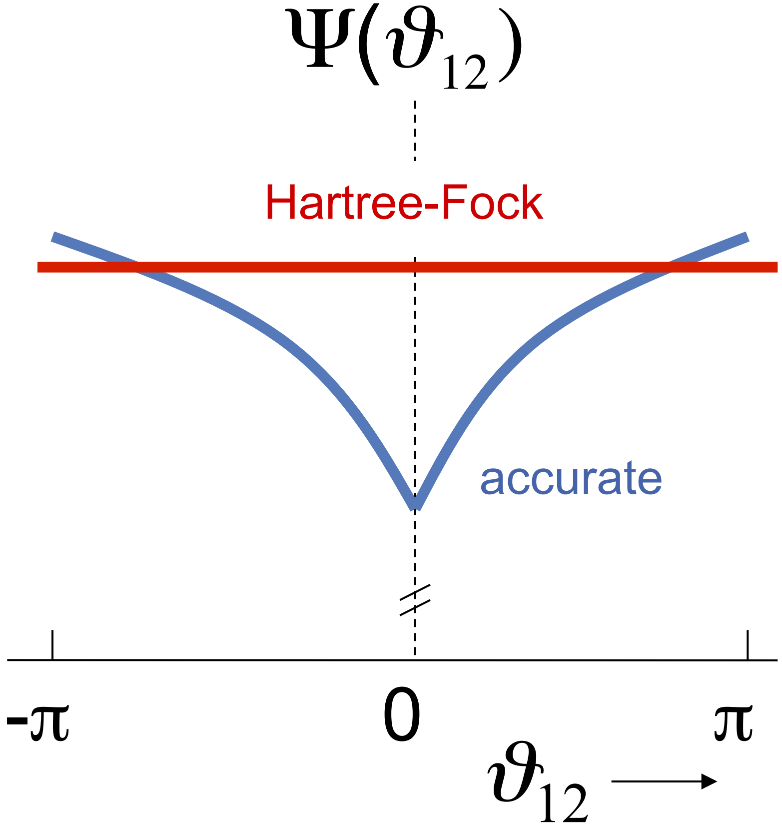
Outline

- Reason for slow basis-set convergence: The Coulomb hole
- Kutzelnigg's ansatz
- Other approaches

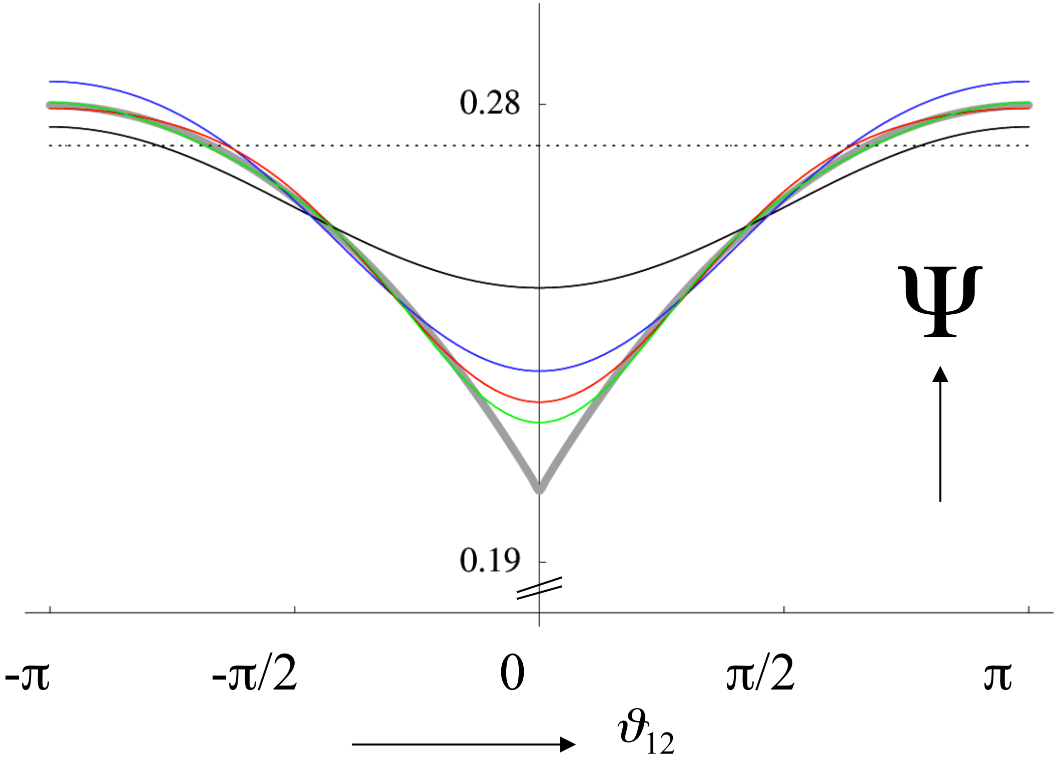
- Explicitly correlated wave function theory (WFT)
  - The CCSD(F12) approach
- Explicitly correlated density functional theory (DFT)
  - The RPA(F12) approach

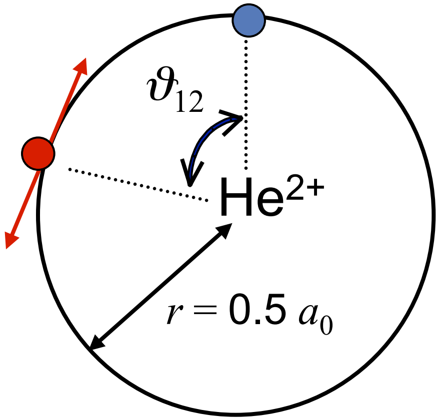
Coulomb hole of the He atom in its ground state



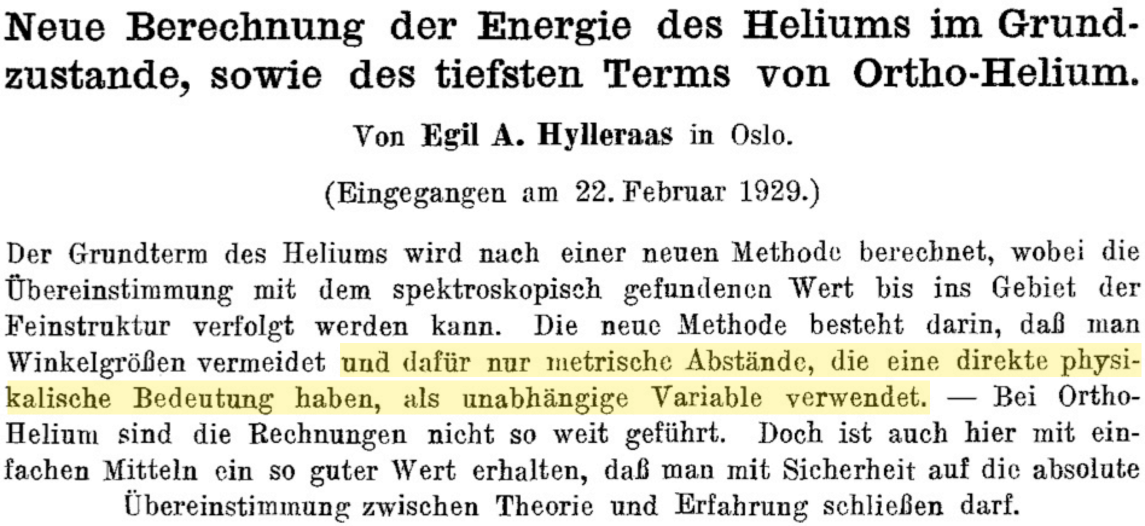


Hartree-Fock and CISD Coulomb holes of He in its ground state





Hylleraas' wave function for He (1929)



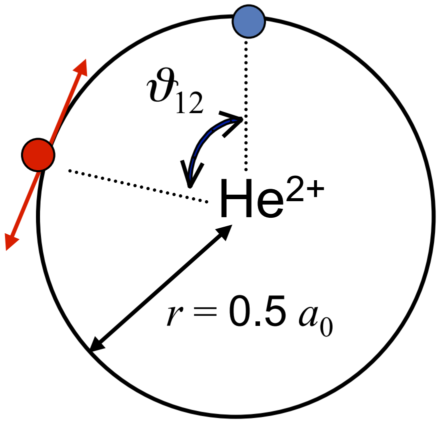
Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium.

Von **Egil A. Hylleraas** in Oslo.

(Eingegangen am 22. Februar 1929.)

Der Grundterm des Heliums wird nach einer neuen Methode berechnet, wobei die Übereinstimmung mit dem spektroskopisch gefundenen Wert bis ins Gebiet der Feinstruktur verfolgt werden kann. Die neue Methode besteht darin, daß man Winkelgrößen vermeidet und dafür nur metrische Abstände, die eine direkte physikalische Bedeutung haben, als unabhängige Variable verwendet. — Bei Ortho-Helium sind die Rechnungen nicht so weit geführt. Doch ist auch hier mit einfachen Mitteln ein so guter Wert erhalten, daß man mit Sicherheit auf die absolute Übereinstimmung zwischen Theorie und Erfahrung schließen darf.

Z. Phys. **54**, 347 (1929)



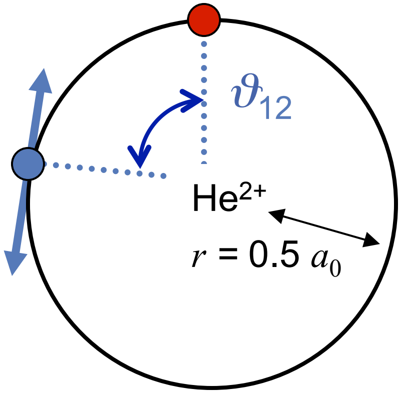
With $r_1 = r_2 = 0.5\ a_0$ Hylleraas' wave function for He takes the following form:

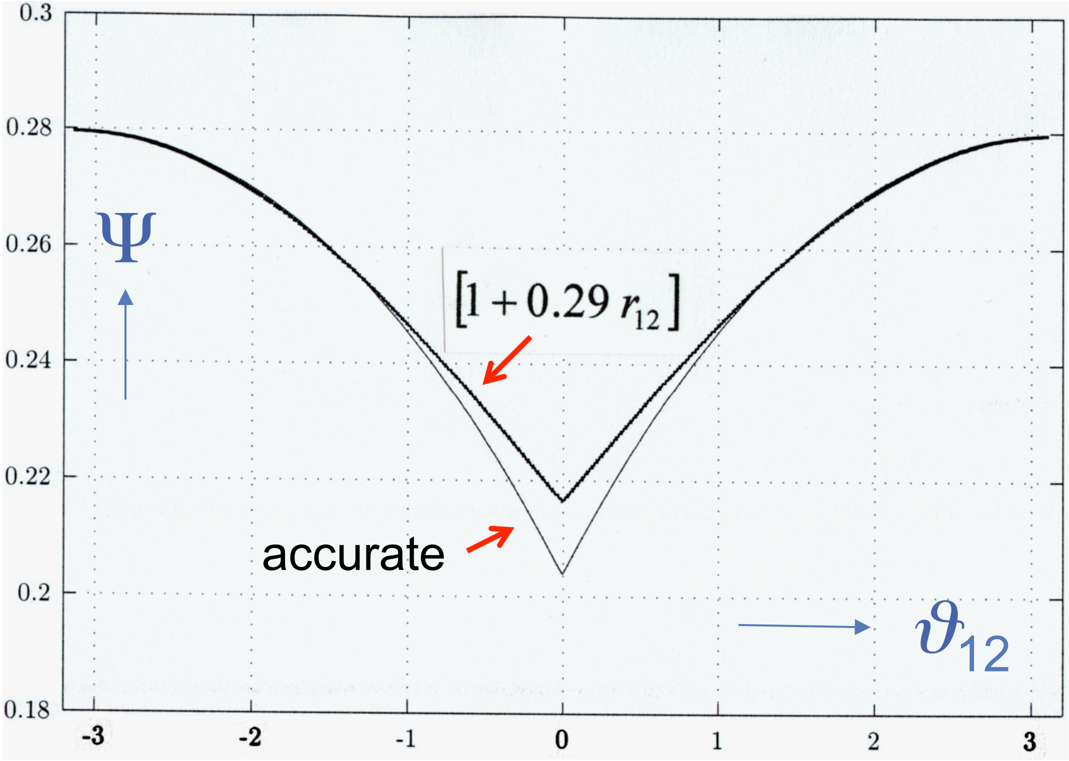
$$\Psi(\vartheta_{12}) = \text{constant} \times \left(1 + 0.29\ r_{12}\right)$$

Hylleraas' wave function for He (1929)

With $r_1 = r_2 = 0.5\ a_0$ Hylleraas' wave function for He takes the following form:

$$\Psi(\vartheta_{12}) \ = \ \text{constant} \times \left(1 + 0.29\ r_{12}\right)$$





30 years of R12/F12 methods

- r_{12} is the electron-electron distance:

$$r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$$

- The traditional methods of quantum chemistry use Slater determinants, that is, products of one-electron functions:

$$\phi_a(1)\phi_b(2)$$

- The R12 methods use also terms linear in r_{12}:

$$r_{12} \times \phi_x(1)\phi_y(2)$$

(Kutzelnigg, 1985)

- Or, more general (F12 methods):

$$f(r_{12}) \times \phi_x(1)\phi_y(2)$$

(Ten-no, 2004)

Kutzelnigg's ansatz for the He atom

$$\hat{H}_0 \Psi_0 = E_0 \Psi_0, \qquad \hat{H}_0 = \hat{T}_1 - \frac{2}{r_1} + \hat{T}_2 - \frac{2}{r_2}$$

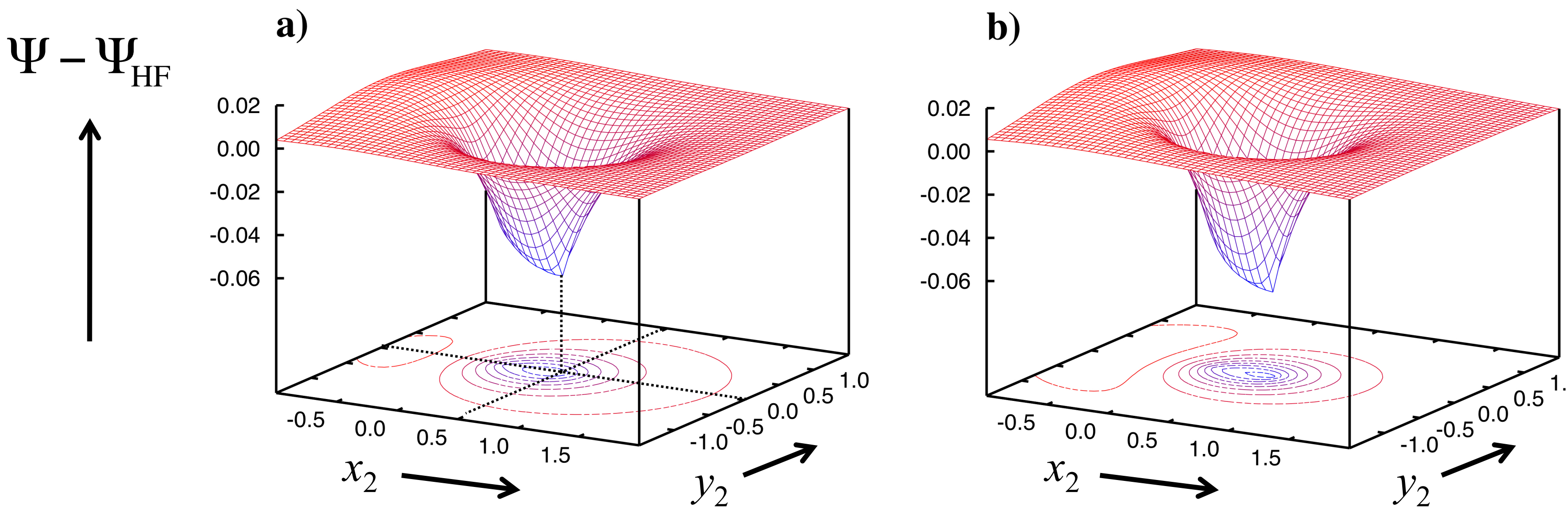
$$\Psi = (1 + \frac{1}{2} r_{12}) \Psi_0 + \sum_{p<q} c_{pq} \left| \phi_p \phi_q \right|$$

$$H_{00} = \left\langle (1 + \frac{1}{2} r_{12}) \Psi_0 \middle| \hat{H} \middle| (1 + \frac{1}{2} r_{12}) \Psi_0 \right\rangle = -2.876582 \ E_\mathrm{h}$$

Accurate ground-state energy $= -2.903724 \ E_\mathrm{h}$

W. Kutzelnigg, *Theor. Chim. Acta* **1985**, *68*, 445

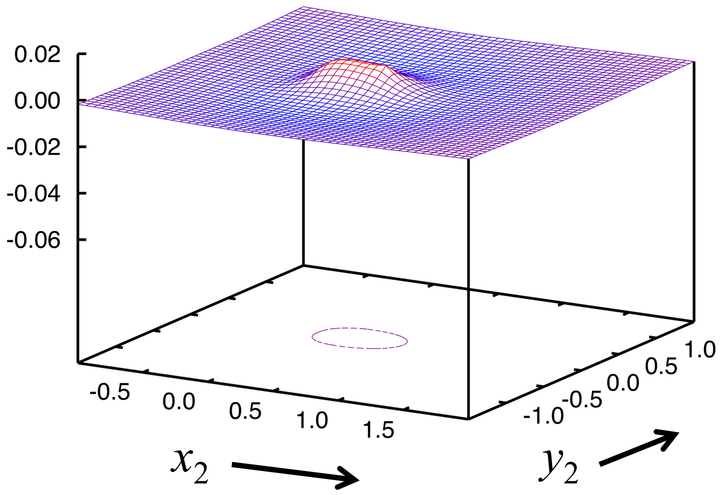
Coulomb hole of the He atom in its ground state



a) The accurate Coulomb hole of the He ground state plotted as a function of electron 2, with electron 1 positioned 0.5 bohr from the nucleus

b) The F12 basis function $-\frac{1}{2}\hat{Q}_{12}\exp(-r_{12})\,\Psi_{HF}$

Coulomb hole of the He atom in its ground state

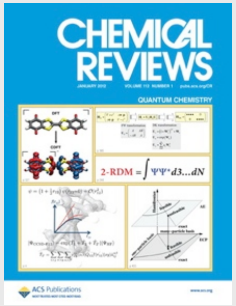


$$\Psi = -\frac{1}{2}\hat{Q}_{12}\exp(-r_{12})\,\Psi_{\mathrm{HF}} + \sum_{p<q} c_{pq}\left|\phi_p\phi_q\right|$$

- The figure shows the difference between the accurate Coulomb hole and F12 basis function
- Only this difference needs to be described by the conventional CI expansion in terms of orbital products

Other approaches

- r_{12}-dependent functions for He
  - Pekeris
- r_{12}-dependent functions for H_2
  - Kołos & Wolniewicz
- Transcorrelated methods
  - Handy
- Hylleraas-CI methods for atoms
  - Ruiz
- Gaussian geminals / GGn / exponentially correlated Gaussians (ECGs)
  - Jeziorski, Adamowicz, Komasa
- Jastrow factor in Quantum Monte Carlo (QMC) methods
  - See lecture by Cyrus Umrigar !

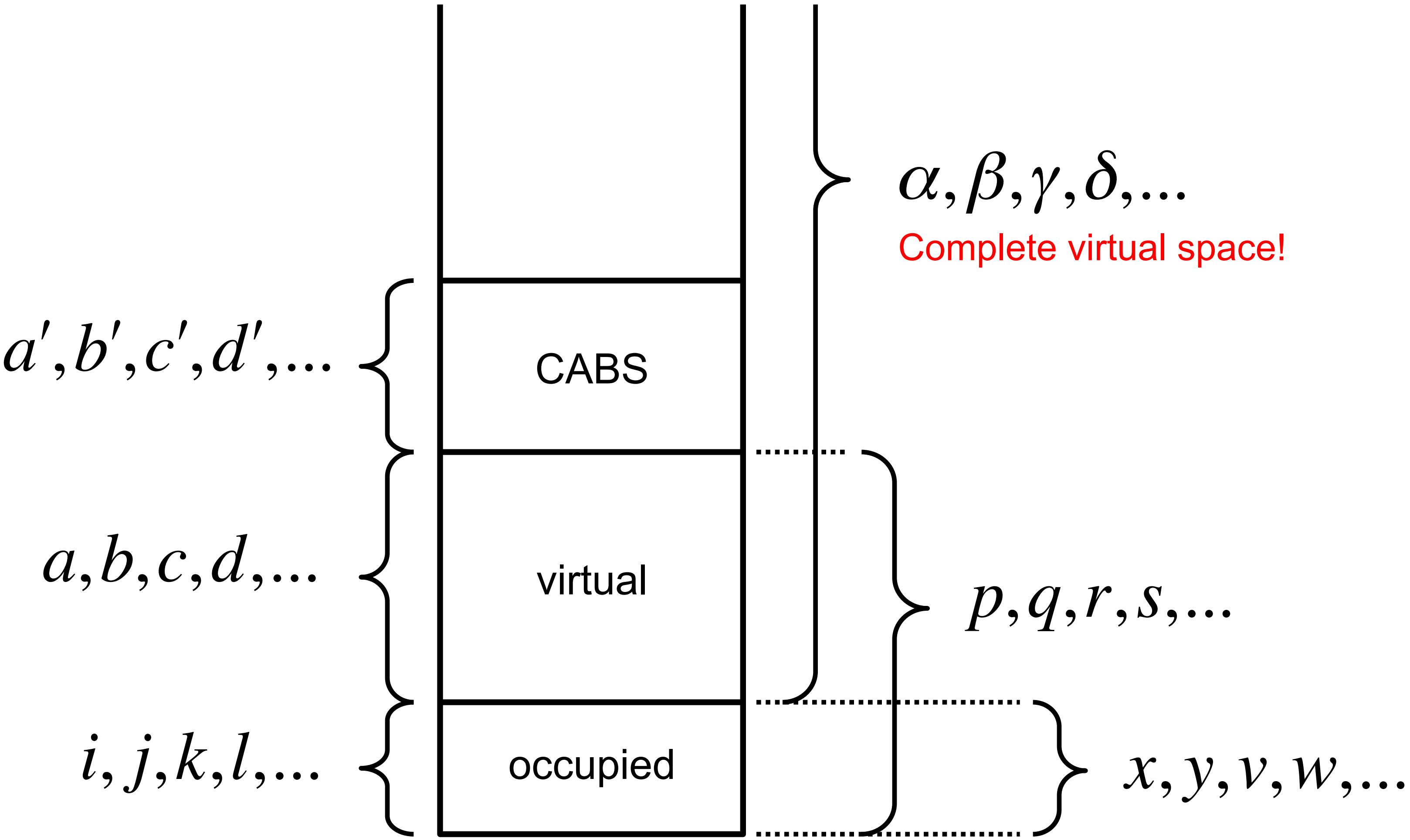


C. Hättig, W. Klopper,
A. Köhn, D.P. Tew,
Chem. Rev. **2012**, *112*, 4-74

Explicitly correlated wave function theory (WFT)

The CCSD(F12) approach

A complete orbital space



CABS = complementary auxiliary basis set

CCSD-F12 theory

$$\hat{T}_{2'} = \sum_{i<j} \sum_{\alpha<\beta} \sum_{x<y} c^{ij}_{xy} \, w^{xy}_{\alpha\beta} \, a^{+}_{\alpha} a_i a^{+}_{\beta} a_j$$

$$w^{xy}_{\alpha\beta} = \langle \alpha\beta | \, \hat{Q}_{12} \left(\tfrac{3}{8} + \tfrac{1}{8} \hat{S}_{xy} \right) f(r_{12}) \, | xy \rangle$$

$$f(r_{12}) = \gamma^{-1} (1 - e^{-\gamma \, r_{12}})$$

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

Generates doubles excitations that are not already contained in the conventional CCSD expansion

$$\hat{S}_{xy} \longleftarrow$$

Permutes the spatial components of spin orbitals x and y in the determinant $| xy >$

Contracted spin-flipped geminals

- The operator $\hat{S}_{xy}$

$$\left(\tfrac{3}{8}+\tfrac{1}{8}\hat{S}_{xy}\right)\left|\phi_x\phi_y\right| = \tfrac{3}{8}\left|\phi_x\phi_y\right| + \tfrac{1}{8}\left|\phi_y\phi_x\right| = \tfrac{3}{8}\left|\phi_x\phi_y\right| - \tfrac{1}{8}\left|\phi_x\phi_y\right| = \tfrac{1}{4}\left|\phi_x\phi_y\right| \qquad \alpha\alpha$$

$$\left(\tfrac{3}{8}+\tfrac{1}{8}\hat{S}_{xy}\right)\left|\overline{\phi}_x\overline{\phi}_y\right| = \tfrac{3}{8}\left|\overline{\phi}_x\overline{\phi}_y\right| + \tfrac{1}{8}\left|\overline{\phi}_y\overline{\phi}_x\right| = \tfrac{3}{8}\left|\overline{\phi}_x\overline{\phi}_y\right| - \tfrac{1}{8}\left|\overline{\phi}_x\overline{\phi}_y\right| = \tfrac{1}{4}\left|\overline{\phi}_x\overline{\phi}_y\right| \qquad \beta\beta$$

$$\left(\tfrac{3}{8}+\tfrac{1}{8}\hat{S}_{xy}\right)\left|\phi_x\overline{\phi}_y\right| = \tfrac{3}{8}\left|\phi_x\overline{\phi}_y\right| + \tfrac{1}{8}\left|\phi_y\overline{\phi}_x\right| \qquad \alpha\beta$$

Contracted spin-flipped geminals

- Applied to singlet and triplet pairs in closed-shell systems:

$$\left(\tfrac{3}{8}+\tfrac{1}{8}\hat{S}_{xy}\right)\left\{\left|\phi_x\overline{\phi}_y\right|+\left|\phi_y\overline{\phi}_x\right|\right\}=\tfrac{3}{8}\left|\phi_x\overline{\phi}_y\right|+\tfrac{1}{8}\left|\phi_y\overline{\phi}_x\right|+\tfrac{3}{8}\left|\phi_y\overline{\phi}_x\right|+\tfrac{1}{8}\left|\phi_x\overline{\phi}_y\right|$$

$$=\tfrac{1}{2}\left\{\left|\phi_x\overline{\phi}_y\right|+\left|\phi_y\overline{\phi}_x\right|\right\}$$

singlet pairs

$$\left(\tfrac{3}{8}+\tfrac{1}{8}\hat{S}_{xy}\right)\left\{\left|\phi_x\overline{\phi}_y\right|-\left|\phi_y\overline{\phi}_x\right|\right\}=\tfrac{3}{8}\left|\phi_x\overline{\phi}_y\right|+\tfrac{1}{8}\left|\phi_y\overline{\phi}_x\right|-\tfrac{3}{8}\left|\phi_y\overline{\phi}_x\right|-\tfrac{1}{8}\left|\phi_x\overline{\phi}_y\right|$$

$$=\tfrac{1}{4}\left\{\left|\phi_x\overline{\phi}_y\right|-\left|\phi_y\overline{\phi}_x\right|\right\}$$

triplet pairs

- The factors ½ and ¼ are in agreement with Kato's cusp conditions

CCSD-F12 theory

$$\hat{H}\left|\text{CCSD-F12}\right\rangle = E\left|\text{CCSD-F12}\right\rangle$$

$$\hat{H}\exp(\hat{T}_1+\hat{T}_2+\hat{T}_{2'})\left|\text{HF}\right\rangle = E\exp(\hat{T}_1+\hat{T}_2+\hat{T}_{2'})\left|\text{HF}\right\rangle$$

$$\exp(-\hat{T}_1-\hat{T}_2-\hat{T}_{2'})\hat{H}\exp(\hat{T}_1+\hat{T}_2+\hat{T}_{2'})\left|\text{HF}\right\rangle = E\left|\text{HF}\right\rangle$$

The explicitly correlated CCSD(F12) energy and equations are obtained by projecting this Schrödinger onto appropriate functions

CCSD-F12 theory

The Schrödinger equation is projected onto the following functions:

singles $$\left| \begin{matrix} a \\ i \end{matrix} \right\rangle = a_a^+ a_i \left| \mathrm{HF} \right\rangle$$

doubles $$\left| \begin{matrix} ab \\ ij \end{matrix} \right\rangle = a_a^+ a_i a_b^+ a_j \left| \mathrm{HF} \right\rangle$$

F12 doubles $$\left| \begin{matrix} xy \\ ij \end{matrix} \right\rangle = \sum_{\alpha<\beta} w_{\alpha\beta}^{xy} \, a_\alpha^+ a_i a_\beta^+ a_j \left| \mathrm{HF} \right\rangle$$

CCSD-F12 theory

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_{2'}$$

$$\hat{\tilde{H}} = \exp(-\hat{T}_1)\hat{H}\exp(\hat{T}_1)$$

$$E_{\text{CCSD–F12}} = \left\langle \text{HF} \right| \hat{\tilde{H}} + \left[\hat{H},\ \hat{T}_2 + \hat{T}_{2'}\right] \left| \text{HF} \right\rangle$$

$$0 = \Omega^{i}_{a} = \left\langle {}^{i}_{a} \right| \hat{\tilde{H}} + \left[\hat{\tilde{H}},\ \hat{T}_2 + \hat{T}_{2'}\right] \left| \text{HF} \right\rangle$$

$$0 = \Omega^{ij}_{ab} = \left\langle {}^{ij}_{ab} \right| \hat{\tilde{H}} + \left[\hat{\tilde{H}} + \tfrac{1}{2}\left[\hat{H},\ \hat{T}_2 + \hat{T}_{2'}\right],\ \hat{T}_2 + \hat{T}_{2'}\right] \left| \text{HF} \right\rangle$$

$$0 = \Omega^{ij}_{xy} = \left\langle {}^{ij}_{xy} \right| \hat{\tilde{H}} + \left[\hat{\tilde{H}},\ \hat{T}_2 + \hat{T}_{2'}\right] + \tfrac{1}{2}\left[\left[\hat{H},\ \hat{T}_2 + \hat{T}_{2'}\right],\ \hat{T}_2 + \hat{T}_{2'}\right] \left| \text{HF} \right\rangle$$

CCSD(F12) theory

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_{2'}$$

$$\hat{\tilde{H}} = \exp(-\hat{T}_1)\hat{H}\exp(\hat{T}_1)$$

Simplifications in the doubles equations

$$E_{\mathrm{CCSD(F12)}} = \langle \mathrm{HF} | \, \hat{\tilde{H}} + \left[\hat{H},\, \hat{T}_2 + \hat{T}_{2'}\right] | \mathrm{HF} \rangle$$

$$0 = \Omega^{i}_{a} = \left\langle {}^{i}_{a} \right| \, \hat{\tilde{H}} + \left[\hat{\tilde{H}},\, \hat{T}_2 + \hat{T}_{2'}\right] | \mathrm{HF} \rangle$$

$$0 = \Omega^{ij}_{ab} = \left\langle {}^{ij}_{ab} \right| \, \hat{\tilde{H}} + \left[\hat{\tilde{H}},\, \hat{T}_2 + \hat{T}_{2'}\right] + \tfrac{1}{2}\left[\left[\hat{H},\, \hat{T}_2 + 2\hat{T}_{2'}\right],\, \hat{T}_2\right] | \mathrm{HF} \rangle$$

$$0 = \Omega^{ij}_{xy} = \left\langle {}^{ij}_{xy} \right| \, \hat{\tilde{H}} + \left[\hat{F},\, \hat{T}_{2'}\right] + \left[\hat{\tilde{H}},\, \hat{T}_2\right] | \mathrm{HF} \rangle$$

The IP and EA (in eV) of the F atom

	IP		EA	
Experiment		**17.4228**		**3.4012**
CCSD/d-aug-cc-pwCV5Z		17.3353		3.2276
+ full triples/d-aug-cc-pwCVQZ	+0.0687	17.4040	+0.1714	3.3990
+ full quadruples/d-aug-cc-pwCVTZ	+0.0020	17.4060	+0.0093	3.4082
+ full quintuples/d-aug-cc-pwCVDZ	+0.0000	17.4060	−0.0013	3.4069
+ spin-orbit correction	−0.0041	17.4019	−0.0167	3.3902
+ scalar relativistic corr. (MV+D1+D2)	−0.0126	17.3892	−0.0098	3.3804
+ diagonal Born-Oppenheimer corr.	−0.0001	17.3891	+0.0001	3.3805
+ (scalar) Breit + QED (Lamb shift)	−0.0015	17.3877	+0.0001	3.3806
+ F12 correction	**+0.0349**	**17.4226**	**+0.0207**	**3.4013**

CCSD(F12)/d-aug-cc-pwCV5Z calculation performed with Turbomole

The IP and EA (in eV) of the atoms H–Ne

	IP		EA	
	Calc.	Expt.	Calc.	Expt.
H	13.59829	13.59843	0.75360	0.75419
He	24.58741	24.58739		
Li	5.39172	5.39172	0.61770	0.61805
Be	9.32284	9.32270		
B	8.29881	8.29802	0.28027	0.27972
C	11.26100	11.26030	1.26273	1.26212
N	14.53475	14.5341		
O	13.61776	13.61805	1.46104	1.46111
F	17.42255	17.4228	3.40127	3.40119
Ne	21.56401	21.56454		

Atomic IPs and EAs

- The F12 correction is the difference between a CCSD(F12) and a CCSD calculation in the d-aug-cc-pwCV5Z basis
- For all atoms H−Ne, we find …
  - … a mean absolute deviation of 0.35 meV for the IPs (max. error 0.79 meV)
  - … a mean absolute deviation of 0.36 meV for the EAs (max error 0.61 meV)

Phys. Rev. A **81**, 022503 (2010)

Note on accuracy

- Mean absolute deviation:
  - 0.35 meV
  - 2.8 cm^{-1}
  - 0.034 kJ/mol
  - 0.008 kcal/mol (<< 1 kcal/mol)

- Electron correlation contributes about 1.7–2.0 eV to the IPs and EAs of atoms such as O, F, and Ne
- As much as 99.98% of the electron-correlation contribution must be recovered to obtain an agreement to within 0.0004 eV
- This refers to full CI in a complete basis

Other approximations to CCSD-F12 theory

- CCSD-F12a and CCSD-F12b
  - T.B. Adler, G. Knizia, and H.-J. Werner,
    J. Chem. Phys. **127**, 221106 (2007)
  - CCSD-F12a and -F12b not more expensive than CCSD
- $\mathrm{CCSD(2)}_{\overline{\mathrm{F12}}}$ and $\mathrm{CCSD[2]}_{\mathrm{F12}}$
  - M. Torheyden and E.F. Valeev, J. Chem. Phys. **131**, 171103 (2009)
- CCSD(F12*), CCSD[F12], $\mathrm{CCSD(2^*)}_{\overline{\mathrm{F12}}}$
  - C. Hättig, D.P. Tew, and A. Köhn, J. Chem. Phys. **132**, 231102 (2010)
  - A. Köhn and D.P. Tew, J. Chem. Phys. **133**, 174117 (2010)
  - CCSD(F12*) iterations not more expensive than CCSD

Implementations

- **The methods have been implemented in various quantum chemistry programs:**
  - **Molpro**: by H.-J. Werner, F.R. Manby, *et al*.
  - **PSI3** & **MPQC**: by E.F. Valeev, S. Hirata, *et al*.
  - **Gellan**: by S. Ten-no, J. Noga, *et al*.
  - **GeCCo**: by A. Köhn *et al*.
  - **Dalton** & **Turbomole**: by D.P. Tew, C. Hättig, W. Klopper, *et al*.

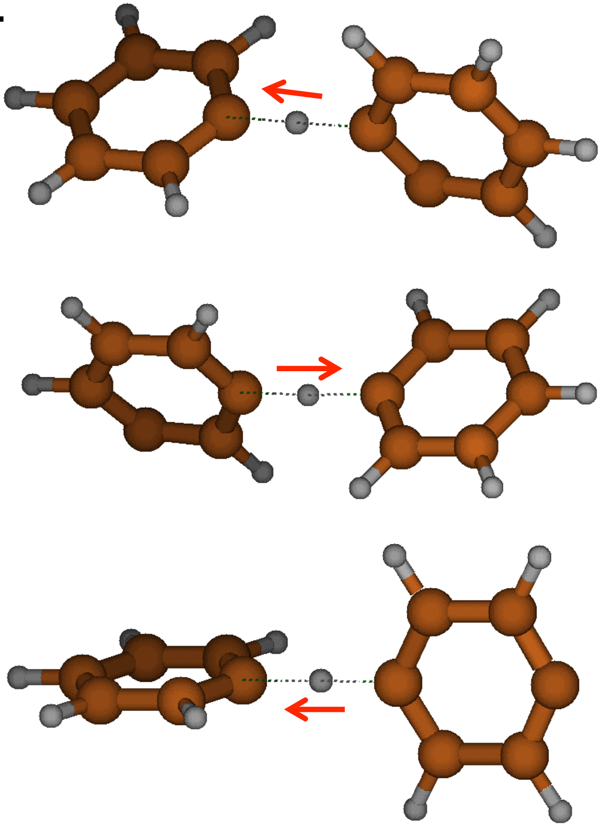
- **The Turbomole implementation includes:**
  - MP2-F12, CCSD(F12), and CCSD(T)(F12) energies
  - RHF, UHF, and ROHF references (spin-flipped geminals)
  - Optimized and fixed F12 amplitudes (*sp* ansatz)
  - MP2-F12 gradients

CCSD(F12) reaction barriers

- Ph + Ph →

  ↓

  Ph_2 (biphenyl)



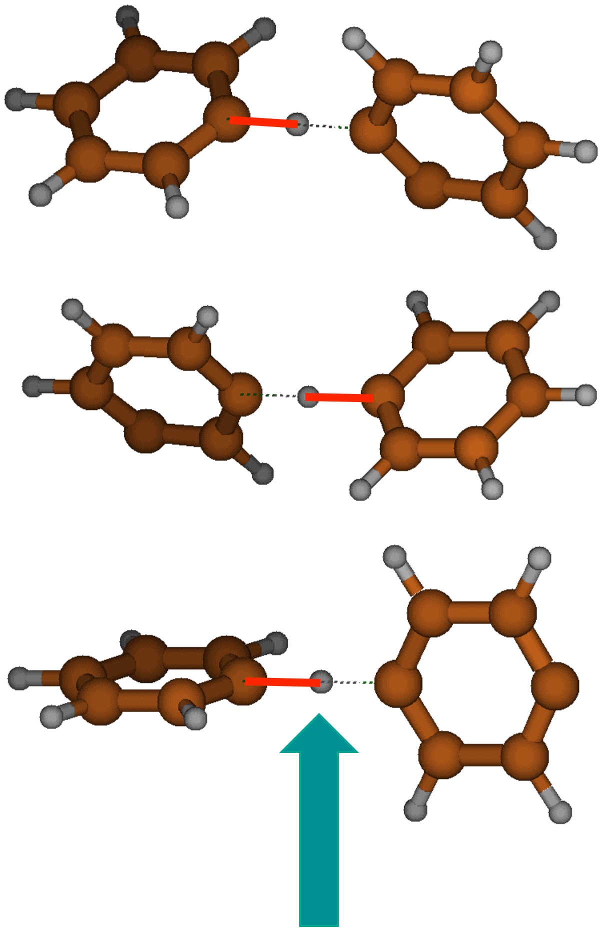
→ Bz + *o*-benzyne

→ *m*-benzyne + Bz

→ Bz + *p*-benzyne

Transition-state (TS) structures

CCSD(F12) reaction barriers

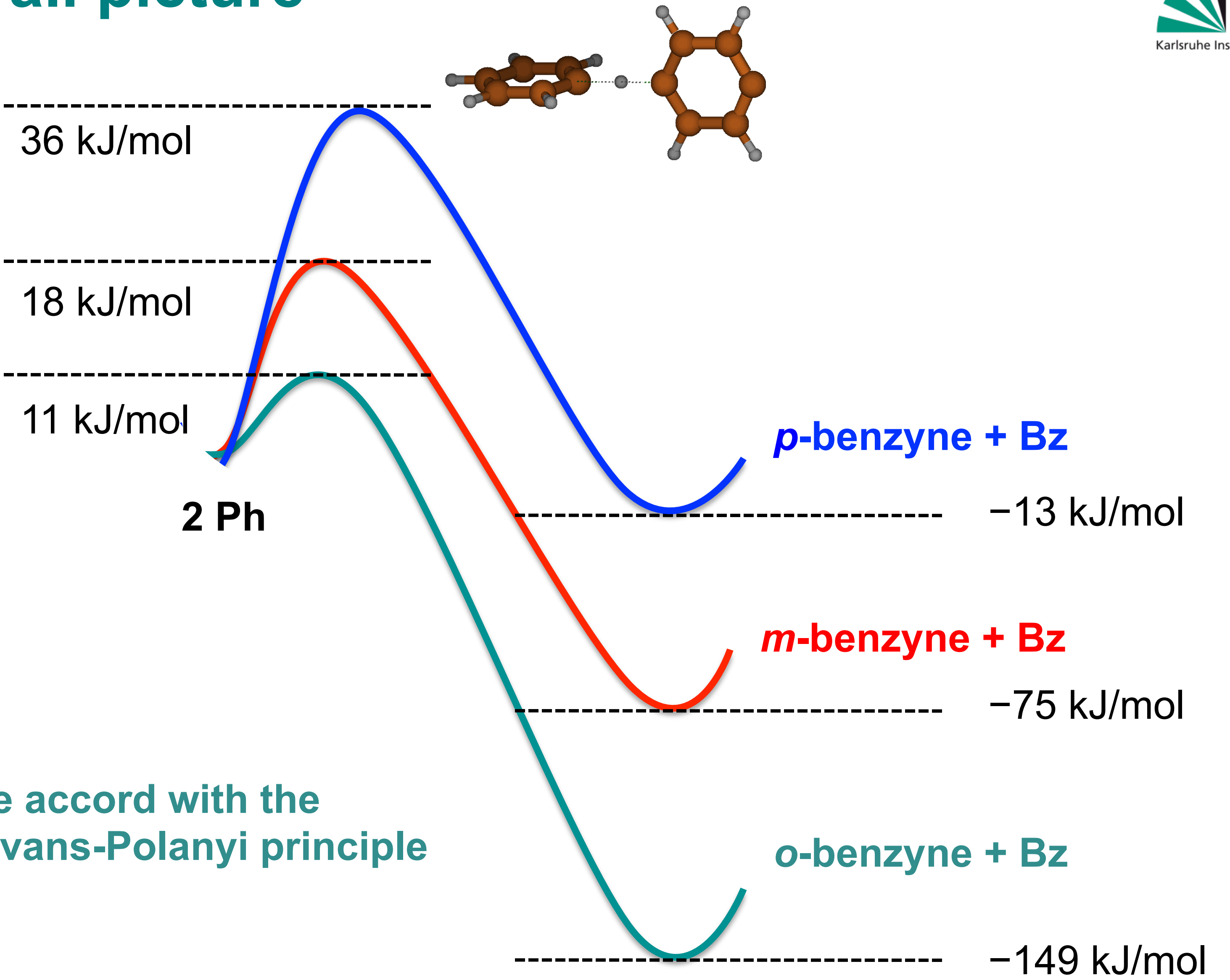


B3LYP/def2-TZVP optimized TS structures (distances in pm)

Product	Distance from C_6H_5 (product)	Distance from C_6H_4 (reactant)
o-benzyne	**155**	120
m-benzyne	**142**	126
p-benzyne	**134**	133

In nice accord with the Hammond-Leffler postulate

Overall picture



36 kJ/mol

18 kJ/mol

11 kJ/mol

2 Ph

***p*-benzyne + Bz**

−13 kJ/mol

***m*-benzyne + Bz**

−75 kJ/mol

***o*-benzyne + Bz**

−149 kJ/mol

In nice accord with the Bell-Evans-Polanyi principle

MP2-F12 theory

$$\hat{T} = \hat{T}_2 + \hat{T}_{2'}$$

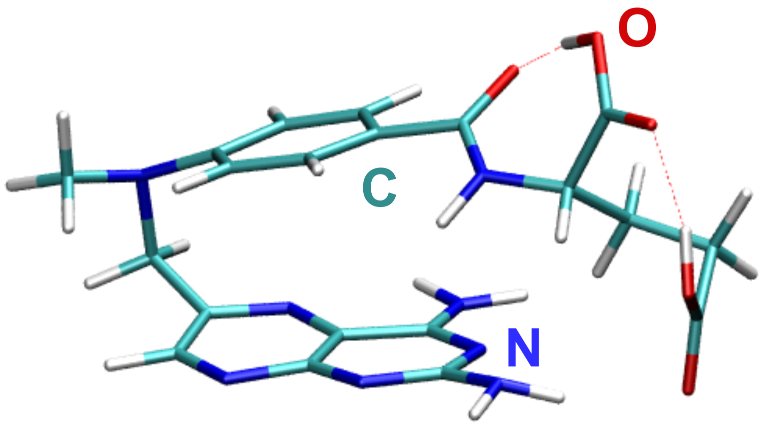
No single excitations

$$E_{\mathrm{MP2-F12}} = \left\langle \mathrm{HF} \right| \hat{H} + \left[\hat{H},\ \hat{T}_2 + \hat{T}_{2'}\right] \left| \mathrm{HF} \right\rangle$$

$$0 = \Omega^{ij}_{ab} = \left\langle {}^{ij}_{ab} \right| \hat{H} + \left[\hat{F},\ \hat{T}_2 + \hat{T}_{2'}\right] \left| \mathrm{HF} \right\rangle$$

$$0 = \Omega^{ij}_{xy} = \left\langle {}^{ij}_{xy} \right| \hat{H} + \left[\hat{F},\ \hat{T}_2 + \hat{T}_{2'}\right] \left| \mathrm{HF} \right\rangle$$

MP2-F12 theory: Correlation energy (in E_h) methotrexate (MTX)



Optimized MP2/aug-cc-pVTZ equilibrium geometry

Limit: −6.755(9) E_h

Basis	Size	ΔE_{MP2}	%	$\Delta E_{MP2\text{-}F12}$	%
aug-cc-pVDZ	957	−5.157	76.4	−6.644	98.4
aug-cc-pVTZ	2024	−6.142	90.9	−6.718	99.5
aug-cc-pVQZ	3652	−6.480	95.9	−6.745	99.9
aug-cc-pV5Z	5951	−6.611	97.9		
cc-pVDZ-F12	1188	−5.604	83.0	−6.690	99.0
cc-pVTZ-F12	2145	−6.257	92.6	−6.741	99.8
cc-pVQZ-F12	3619	−6.510	96.4	−6.755	100.0

Explicitly correlated density functional theory (DFT)

The RPA(F12) approach

RPA theory (random phase approximation)

$$\hat{H}^{\lambda} = \hat{T} + \hat{V}^{\lambda}\left[\rho\right] + \lambda \hat{V}_{ee}$$

Adiabatic connection

$$\hat{H}^{\lambda}\left|\Psi_0^{\lambda}\right\rangle = E_0^{\lambda}\left|\Psi_0^{\lambda}\right\rangle; \qquad \forall\ \lambda : \ \left|\Psi_0^{\lambda}\right\rangle \to \rho$$

$$E_0^{1} = \left\langle \Psi_0^{0}\right|\hat{H}^{1}\left|\Psi_0^{0}\right\rangle + \int_0^1 W^{\mathrm{C}}\left(\lambda\right)\,\mathrm{d}\lambda$$

Coupling strength integration

$$W^{\mathrm{C}}\left(\lambda\right) = \left\langle \Psi_0^{\lambda}\right|\hat{V}_{ee}\left|\Psi_0^{\lambda}\right\rangle - \left\langle \Psi_0^{0}\right|\hat{V}_{ee}\left|\Psi_0^{0}\right\rangle$$

RPA theory: Use of second quantization

Second quantization:

$$\hat{V}_{ee} = \frac{1}{2}\sum_{pqrs}(pq|rs)a_p^+ a_r^+ a_s a_q = \frac{1}{2}\sum_{pqrs}(pq|rs)[a_p^+ a_q a_r^+ a_s - \delta_{qr} a_p^+ a_s]$$

The term with the Dirac δ-function does not contribute:

$$W^C(\lambda) = \frac{1}{2}\sum_{pqrs}(pq|rs)\left\{\left\langle\Psi_0^\lambda\middle|a_p^+ a_q a_r^+ a_s\middle|\Psi_0^\lambda\right\rangle - \left\langle\Psi_0^0\middle|a_p^+ a_q a_r^+ a_s\middle|\Psi_0^0\right\rangle\right\}$$

We then insert an exact resolution of the identity:

$$\left\langle\Psi_0^\lambda\middle|a_p^+ a_q a_r^+ a_s\middle|\Psi_0^\lambda\right\rangle = \sum_n \left\langle\Psi_0^\lambda\middle|a_p^+ a_q\middle|\Psi_n^\lambda\right\rangle\left\langle\Psi_n^\lambda\middle|a_r^+ a_s\middle|\Psi_0^\lambda\right\rangle$$

RPA theory

After inserting a resolution of the identity in terms of all excited states *n*, the correlation energy can be computed from the Coulombic self-repulsion E_C of the transition densities

$$W^\mathrm{C}(\lambda) = \sum_n \left(E_\mathrm{C}(\rho_{0n}^{\lambda}) - E_\mathrm{C}(\rho_{0n}^{0}) \right)$$

$$\rho_{0n}^{\lambda}(\mathbf{r}) = \sum_{pq} \varphi_p(\mathbf{r})\, \varphi_q(\mathbf{r}) \sum_{n\neq 0} \left\langle \Psi_0^{\lambda} \middle| a_p^{+} a_q \middle| \Psi_n^{\lambda} \right\rangle$$

$$E_\mathrm{C}(\rho_{0n}^{\lambda}) = \int\!\!\int \frac{\rho_{0n}^{\lambda}(\mathbf{r})\rho_{0n}^{\lambda}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$

RPA theory: TDDFT transition densities

We now switch to DFT and compute the transition densities using time-dependent density-functional theory (TDDFT)

$$\boxed{\rho_{0n}^{\lambda}(\mathbf{r}) = \sum_{ia} \varphi_i(\mathbf{r})\varphi_a(\mathbf{r})\left(\mathbf{X}^{\lambda} + \mathbf{Y}^{\lambda}\right)_{ia}}$$

$$\begin{pmatrix} \mathbf{A}^{\lambda} & \mathbf{B}^{\lambda} \\ -\mathbf{B}^{\lambda} & -\mathbf{A}^{\lambda} \end{pmatrix}\begin{pmatrix} \mathbf{X}^{\lambda} & \mathbf{Y}^{\lambda} \\ \mathbf{Y}^{\lambda} & \mathbf{X}^{\lambda} \end{pmatrix} = \begin{pmatrix} \mathbf{X}^{\lambda} & \mathbf{Y}^{\lambda} \\ \mathbf{Y}^{\lambda} & \mathbf{X}^{\lambda} \end{pmatrix}\begin{pmatrix} \mathbf{w}^{\lambda} & \mathbf{0} \\ \mathbf{0} & -\mathbf{w}^{\lambda} \end{pmatrix}$$

$$A_{ia,jb}^{\lambda} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \lambda(ia\,|\,jb) \qquad B_{ia,jb}^{\lambda} = \lambda(ia\,|\,jb)$$

RPA theory: What remains to be computed

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix}\begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix} = \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix}\begin{pmatrix} \mathbf{w} & \mathbf{0} \\ \mathbf{0} & -\mathbf{w} \end{pmatrix}$$

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia \mid jb)$$

$$B_{ia,jb} = (ia \mid jb)$$

$$E_{\mathrm{RPA}}^{\mathrm{C}} = \frac{1}{2}\mathrm{tr}\left(\mathbf{w} - \mathbf{A}\right) \longleftarrow$$

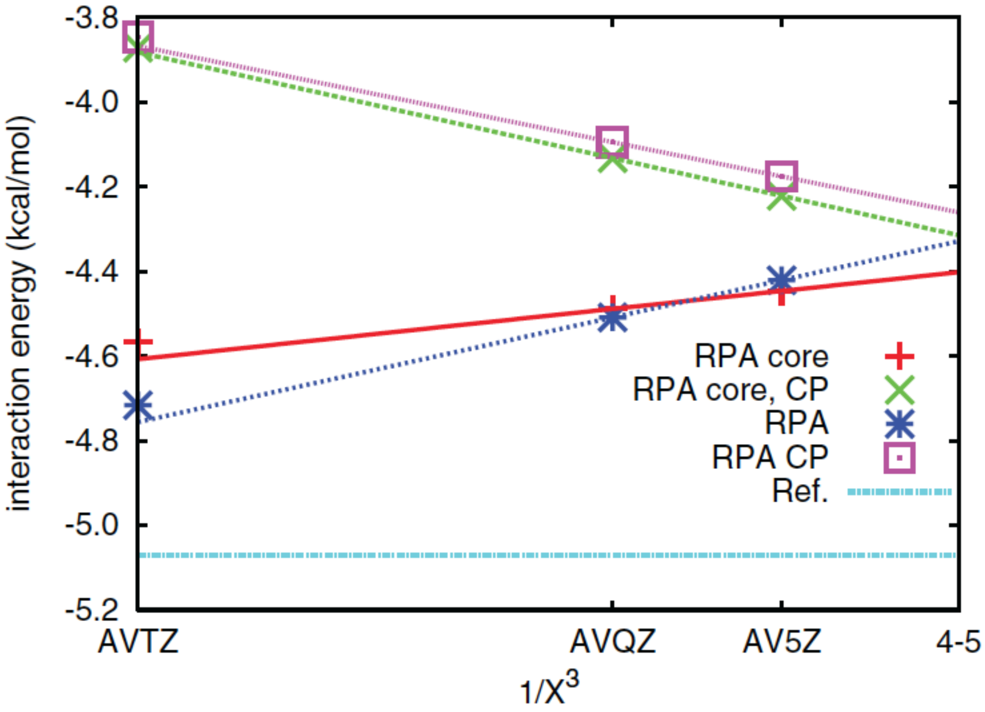
Bare or direct RPA (dRPA),
i.e., <u>without exchange</u>

$$E_{\mathrm{RPA}}^{\mathrm{Total}} = \left\langle \mathrm{KS} \middle| \hat{H} \middle| \mathrm{KS} \right\rangle + E_{\mathrm{RPA}}^{\mathrm{C}} \longleftarrow$$

Added to the expectation value
of the Kohn-Sham determinant

RPA+F12 theory: The water dimer

Counterpoise (CP) corrected and uncorrected RPA interaction energies (kcal/mol) for the water dimer (fixed geometry from the S22 test set), with and without inclusion of core excitations



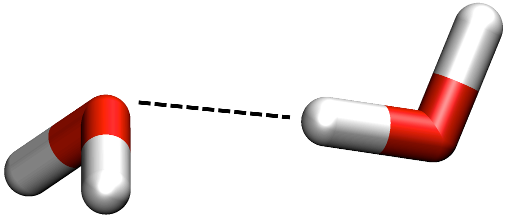


Figure taken from: H. Eshuis and F. Furche, *Basis set convergence of molecular correlation energy differences within the random phase approximation*, *J. Chem. Phys*. **2012**, *136*, 084105.

RPA theory

$$E_{\mathrm{RPA}}^{\mathrm{C}} = \frac{1}{2}\mathrm{tr}\left(\mathbf{w} - \mathbf{A}\right) = \frac{1}{2}\mathrm{tr}\left(\mathbf{BT}\right)$$

$$\mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT} = \mathbf{0}$$

← „direct ring“ coupled-cluster-doubles equation (drCCD)

↓ To first order in **B**

$$\mathbf{B} + \mathbf{A}^{(0)}\mathbf{T}^{(1)} + \mathbf{T}^{(1)}\mathbf{A}^{(0)} = \mathbf{0}, \qquad A_{ia,jb}^{(0)} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}$$

$$E_{\mathrm{dMP2}} = \frac{1}{2}\mathrm{tr}\left(\mathbf{BT}^{(1)}\right)$$

← Computed with Kohn-Sham orbitals and orbital energies

RPA+F12 theory

$$E^{\mathrm{C}}_{\mathrm{RPA+F12}} = E^{\mathrm{C}}_{\mathrm{RPA}} - E^{\mathrm{C}}_{\mathrm{dMP2}} + E^{\mathrm{C}}_{\mathrm{dMP2\text{-}F12}}$$

- To second-order in the energy, the RPA correlation energy is equal to the direct MP2 correlation energy [dMP2]
- This dMP2 contribution is replaced by the dMP2-F12 correlation energy, computed with F12 basis functions

- **dMP2 theory**
  - Equal to JMP2 („Coulomb-only" MP2) of Scuseria
  - Equal to Head-Gordon's SOS-MP2 for closed-shell systems

RPA+F12 theory: The oxygen atom

Valence-shell RPA and RPA+F12 correlation energies in mE_h

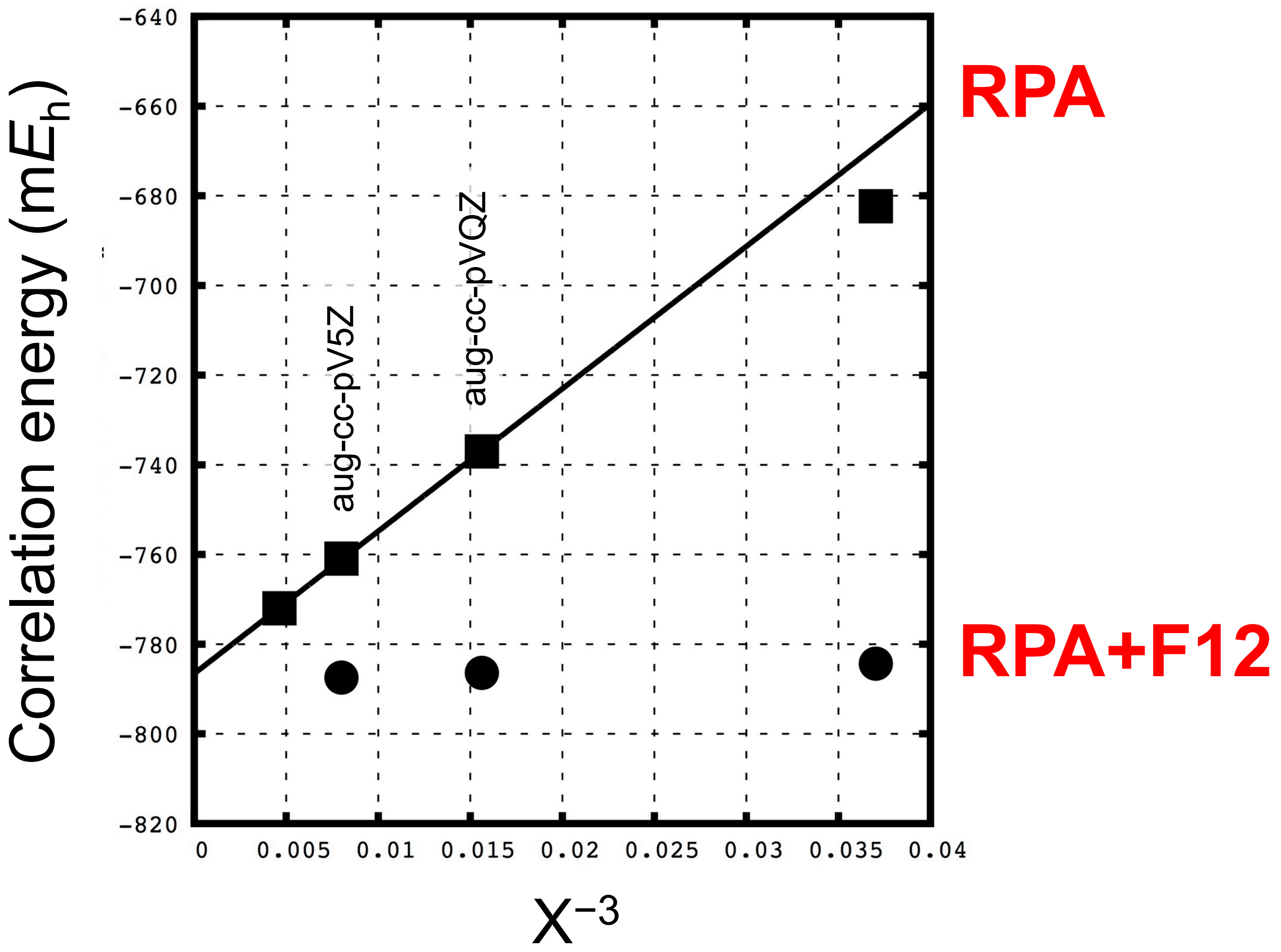
Basis	<KS|H|KS>	$E^\mathrm{C}_\mathrm{RPA}$	$E^\mathrm{C}_\mathrm{RPA+F12}$
AVDZ	−74 792.0	−209.9	**−330.2**
AVTZ	−74 806.2	−274.0	**−322.3**
AVQZ	−74 810.4	−299.8	**−323.4**
AV5Z	−74 811.0	−311.3	**−324.0**
AV6Z	−74 810.9	−316.6	
AV(56)Z		**−323.9**	

AVXZ = aug-cc-pVXZ

PBE self-consistent orbitals

F12 computation with ansatz 2*A [T+V] using OptRI auxiliary basis (CABS)

RPA+F12 theory: The oxygen molecule



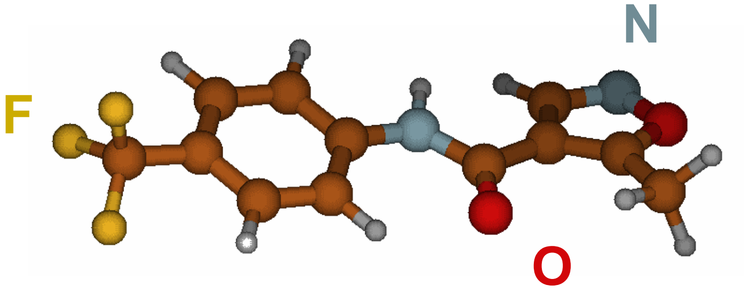
RPA+F12 theory: The oxygen molecule

Valence-shell RPA and RPA+F12 correlation-energy contributions to the dissociation energy in kJ/mol

Basis	<KS|H|KS>	E^{C}_{RPA}	$E^{C}_{\mathrm{RPA+F12}}$
AVDZ	97.1	325.9	**362.6**
AVTZ	105.0	352.8	**367.1**
AVQZ	107.4	360.9	**366.6**
AV5Z	107.9	363.0	**366.4**
AV6Z	108.0	364.2	
AV(56)Z		**365.9**	

AVXZ = aug-cc-pVXZ
PBE self-consistent orbitals
F12 computation with ansatz 2*A [T+V] using OptRI auxiliary basis (CABS)

RPA+F12 theory: Correlation energy (in E_h) of leflunomide



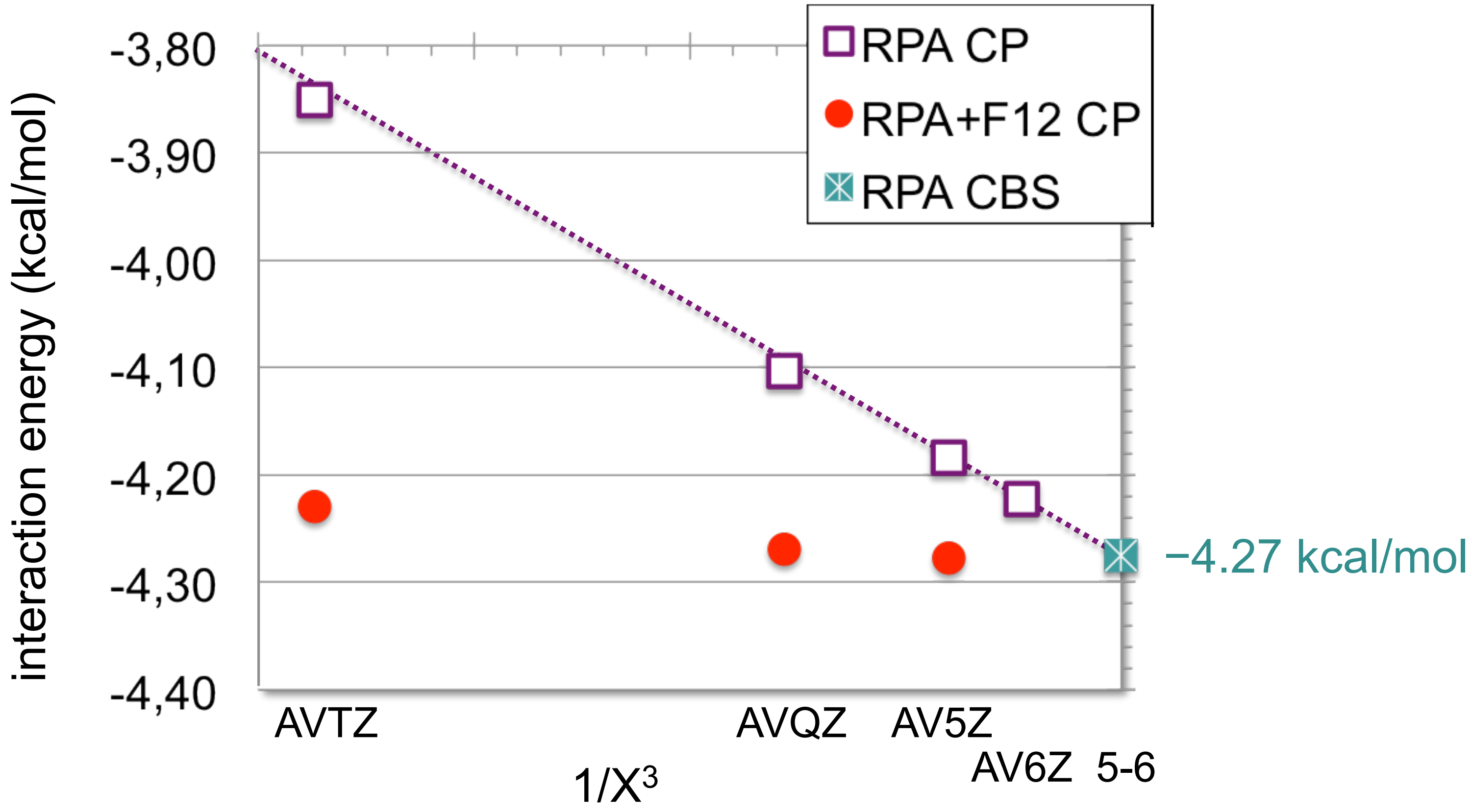
MP2/aug-cc-pVTZ optimized equilibrium geometry

Limit: −6.21(1) E_h

Basis	Size	E^C_{RPA}	%	$E^C_{\text{RPA+F12}}$	%
aug-cc-pVDZ	518	−4.426	71.3	−6.228	100.3
aug-cc-pVTZ	1081	−5.466	88.0	−6.186	99.6
aug-cc-pVQZ	1934	−5.858	94.3	−6.197	99.8
aug-cc-pV5Z	3133	−6.020	96.9	−6.202	99.9

RPA+F12 theory: The water dimer

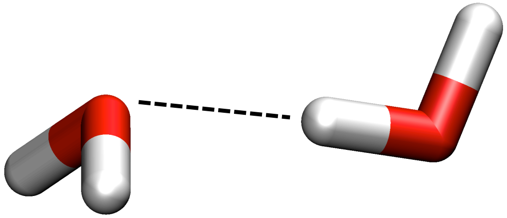
Counterpoise (CP) corrected RPA and **RPA+F12** interaction energies (kcal/mol) for the water dimer (fixed geometry from the S22 test set)



RPA+F12 theory: The water dimer

Counterpoise (CP) corrected RPA and **RPA+F12** interaction energies (kcal/mol) for the water dimer (fixed geometry from the S22 test set)

Basis	<KS|H|KS>	E^{C}_{RPA}	$E^{C}_{\mathrm{RPA+F12}}$
AVTZ	−2.60	−1.25	**−1.63**
AVQZ	−2.64	−1.46	**−1.63**
AV5Z	−2.64	−1.54	**−1.64**
AV6Z	−2.64	−1.58	
AV(56)Z		**−1.63**	



CABS singles correction in MP2 theory

- Singles amplitudes equation when an auxiliary basis is present:

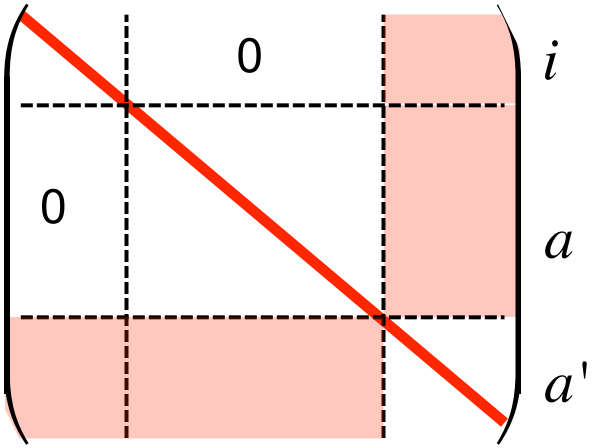
$$f_a^i + f_a^{b'} t_{b'}^i + \left(\varepsilon_a - \varepsilon_i\right) t_a^i = 0 \qquad \{a''\} = \{a\} \cup \{a'\}$$

$$f_{a'}^i + f_{a'}^{b'} t_{b'}^i + \left(\varepsilon_{a'} - \varepsilon_i\right) t_{a'}^i = 0$$

- The CABS singles correction is obtained from:

$$E_{\mathrm{CABS}} = f_i^a t_a^i + f_i^{a'} t_{a'}^i$$

Hartree−Fock matrix



CABS singles correction in RPA theory

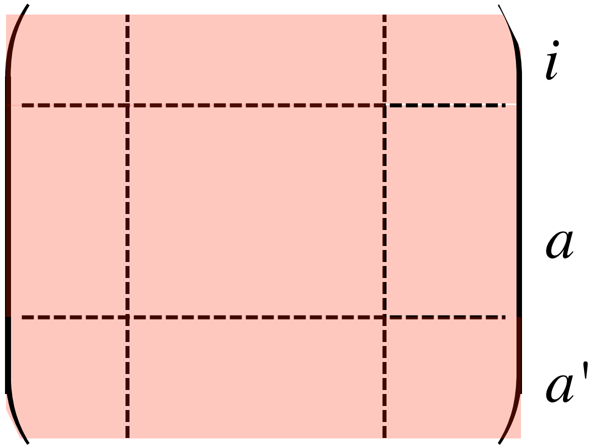
- Singles amplitudes equation when an auxiliary basis is present:

$$f_a^i + f_a^{b'} t_{b'}^i + \left(\varepsilon_a - \varepsilon_i\right) t_a^i = 0 \qquad \{a''\} = \{a\} \cup \{a'\}$$

$$f_{a'}^i + f_{a'}^{b'} t_{b'}^i + \left(\varepsilon_{a'} - \varepsilon_i\right) t_{a'}^i = 0$$

↑ **Kohn−Sham elements**

Hartree−Fock matrix



- The CABS singles correction is obtained from:

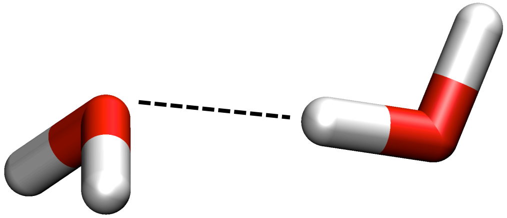
$$E_{\mathrm{CABS}} = f_i^a t_a^i + f_i^{a'} t_{a'}^i$$

RPA+F12 theory: The water dimer

Counterpoise (CP) corrected RPA and **RPA+F12** interaction energies (kcal/mol) for the water dimer (fixed geometry from the S22 test set)

Including a CABS singles correction to the expectation value

Basis	**<KS|H|KS> + CABS**	E^{C}_{RPA}	$E^{C}_{\mathrm{RPA+F12}}$
AVTZ	**−2.63**	−1.25	**−1.63**
AVQZ	**−2.64**	−1.46	**−1.63**
AV5Z	**−2.64**	−1.54	**−1.64**
AV6Z	−2.64	−1.58	
AV(56)Z		**−1.63**	



The RPA(F12) method

- A more sophisticated approach is obtained if we start from the CCSD(F12) equations

CCSD(F12)

↓ No single excitations

CCD(F12)

↓ Ring diagrams only

rCCD(F12)

↓ No exchange terms

drCCD(F12) = RPA(F12)

A.-S. Hehn, D.P. Tew, W. Klopper,
Explicitly correlated ring-coupled -cluster-doubles theory,
J. Chem. Phys. **2015**, *142*, 194106

The RPA(F12) method

- The equation for the **conventional doubles amplitudes** becomes:

$$g_{ij}^{ab} + f_c^a t_{ij}^{cb} + f_c^b t_{ij}^{ac} - \left(\varepsilon_i + \varepsilon_j\right) t_{ij}^{ab} + g_{ic}^{ak} t_{kj}^{cb} + t_{ik}^{ac} g_{cj}^{kb} + t_{il}^{ad} g_{dc}^{lk} t_{kj}^{cb} +$$

$$C_{xy}^{ab} c_{ij}^{xy} \boxed{+ g_{ic'}^{ak} f_{xy}^{c'b} c_{kj}^{xy} + c_{ik}^{xy} f_{xy}^{ac'} g_{c'j}^{kb}} \boxed{+ t_{il}^{ad} g_{dc'}^{lk} f_{xy}^{c'b} c_{kj}^{xy} + c_{il}^{xy} f_{xy}^{ad'} g_{d'c}^{lk} t_{kj}^{cb}} = 0$$

- The equation for the **F12 amplitudes** is:

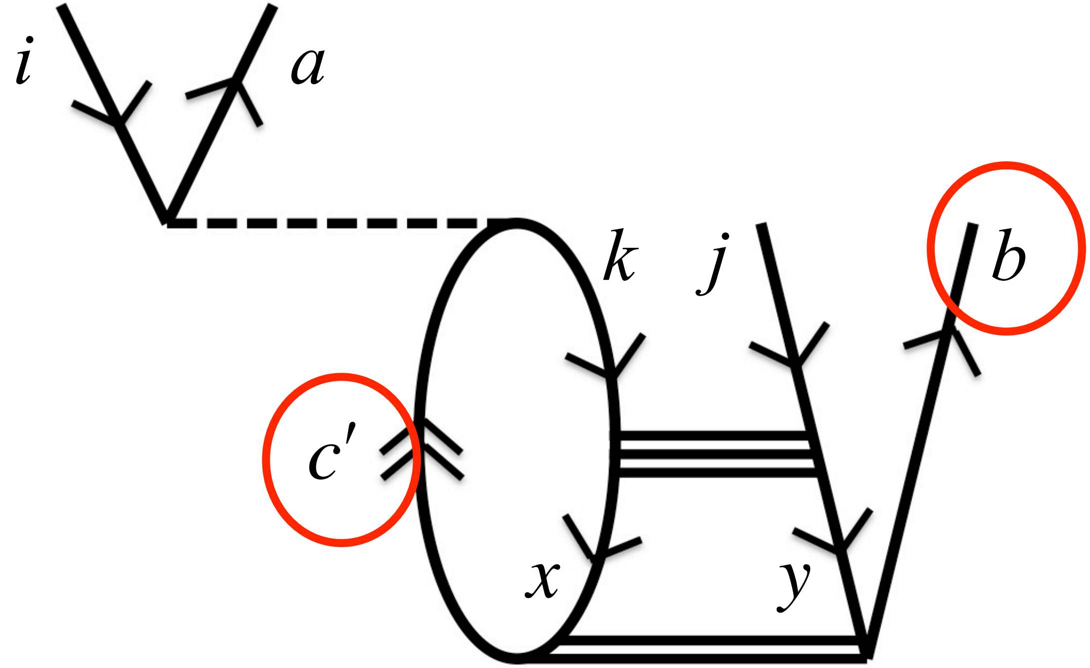
$$V_{ij}^{xy} + B_{vw}^{xy}(ij) c_{ij}^{vw} + C_{ab}^{xy} t_{ij}^{ab} \boxed{+ f_{a'b}^{xy} g_{ic}^{a'k} t_{kj}^{cb} + t_{ik}^{ac} g_{cj}^{kb'} f_{ab'}^{xy}} = 0$$

$$g_{pq}^{rs} = \left\langle rs \middle| r_{12}^{-1} \middle| pq \right\rangle; \quad f_{pq}^{rs} = \left\langle rs \middle| f(r_{12}) \middle| pq \right\rangle$$

Diagrammatic RPA(F12) theory

- 1st F12 diagram added to the **conventional doubles amplitudes**:

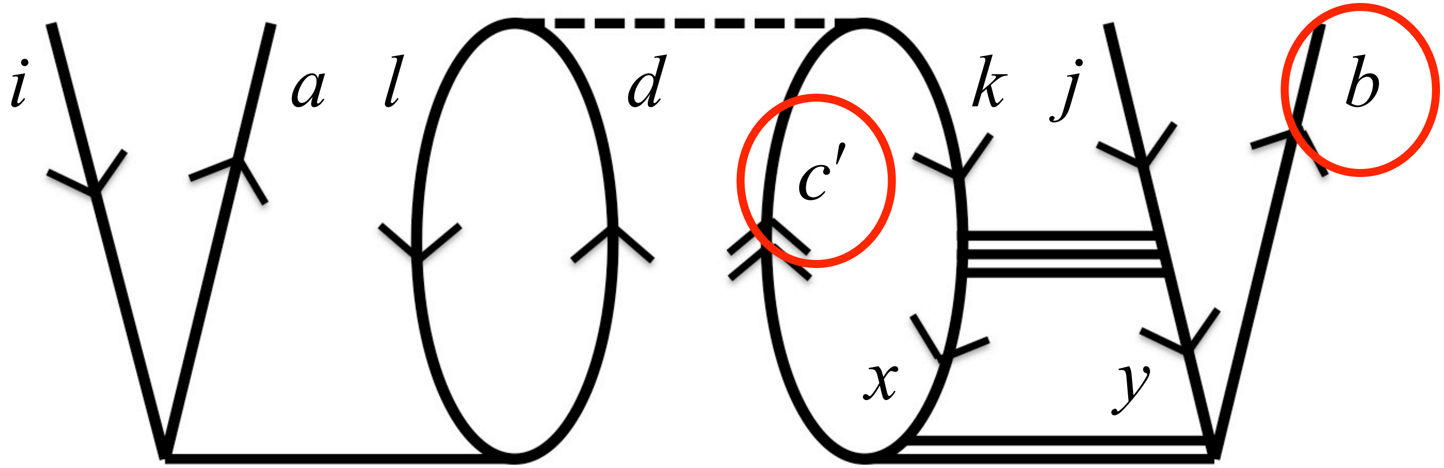
$$g_{ic'}^{ak} f_{xy}^{c'b} c_{kj}^{xy}$$



(diagram d4.8 in J. Noga and W. Kutzelnigg, *J. Chem. Phys*. **1994**, *101*, 7738−7762)

Diagrammatic RPA(F12) theory

- 2nd F12 diagram added to the **conventional doubles amplitudes**:

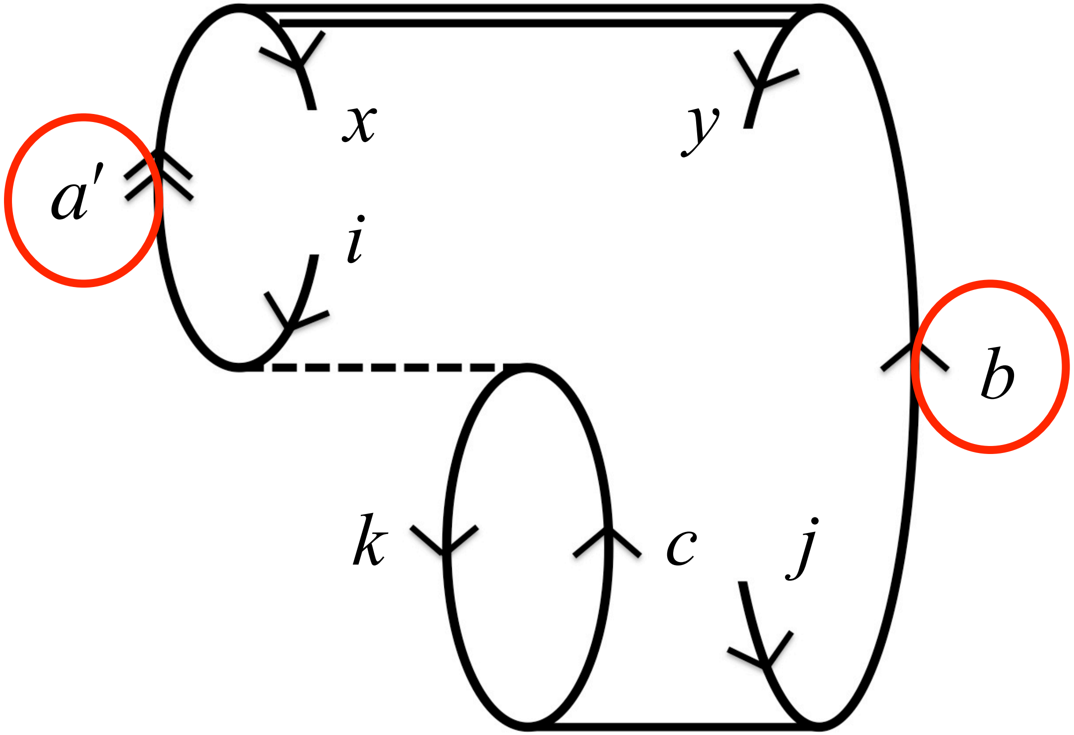


$$t_{il}^{ad}\, g_{dc'}^{lk}\, f_{xy}^{c'b}\, c_{kj}^{xy}$$

(diagram d4.12 in J. Noga and W. Kutzelnigg, *J. Chem. Phys*. **1994**, *101*, 7738−7762)

Diagrammatic RPA(F12) theory

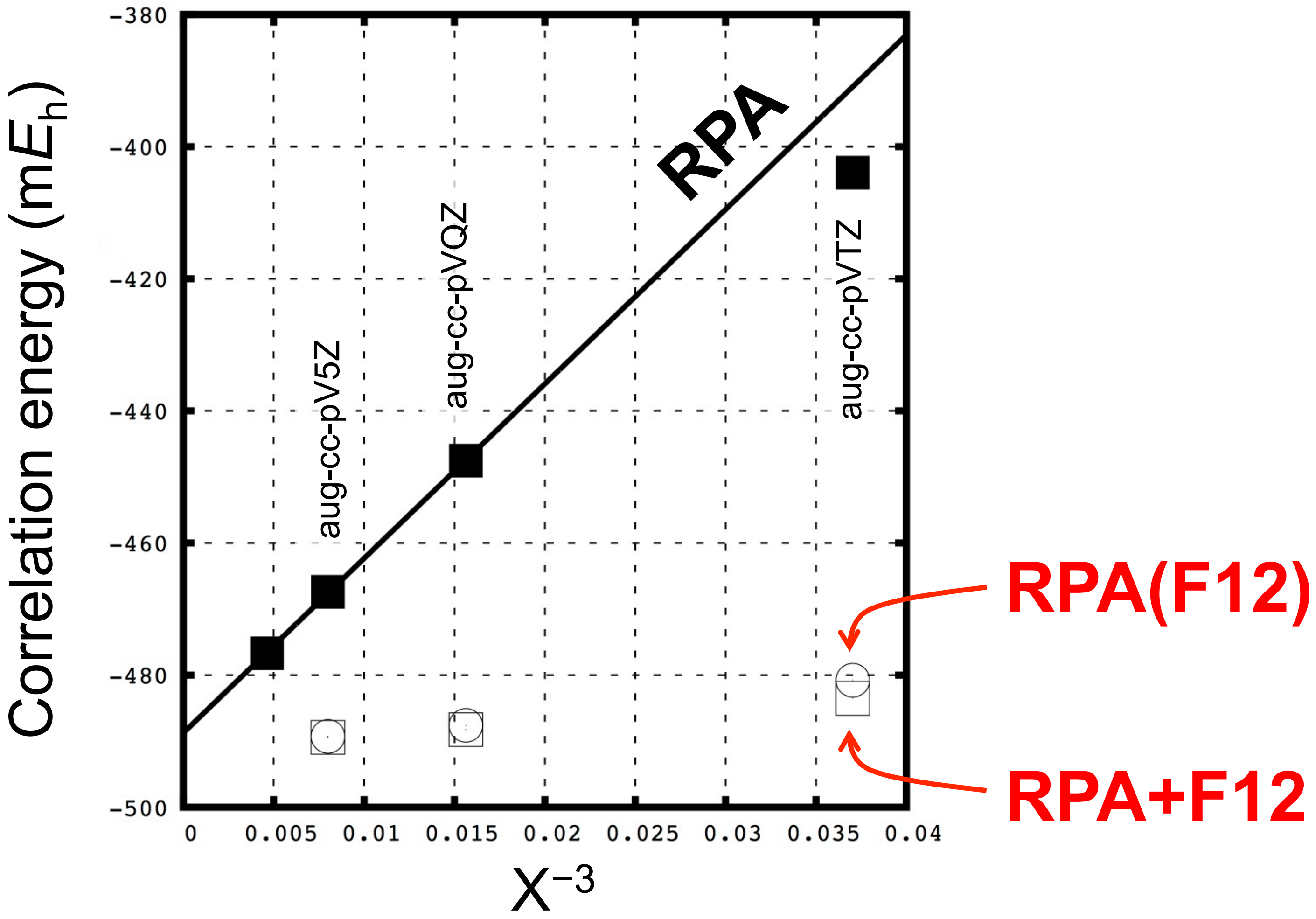
- Diagram added to the **F12 amplitudes**:



$$f_{a'b}^{xy} g_{ic}^{a'k} t_{kj}^{cb}$$

(diagram d6.23 in J. Noga and W. Kutzelnigg, *J. Chem. Phys*. **1994**, *101*, 7738−7762)

RPA(F12) theory: The neon atom

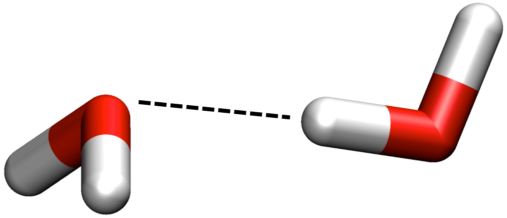


RPA(F12) theory: The water dimer

Counterpoise (CP) corrected RPA and **RPA(F12)** interaction energies (kcal/mol) for the water dimer (fixed geometry from the S22 test set)

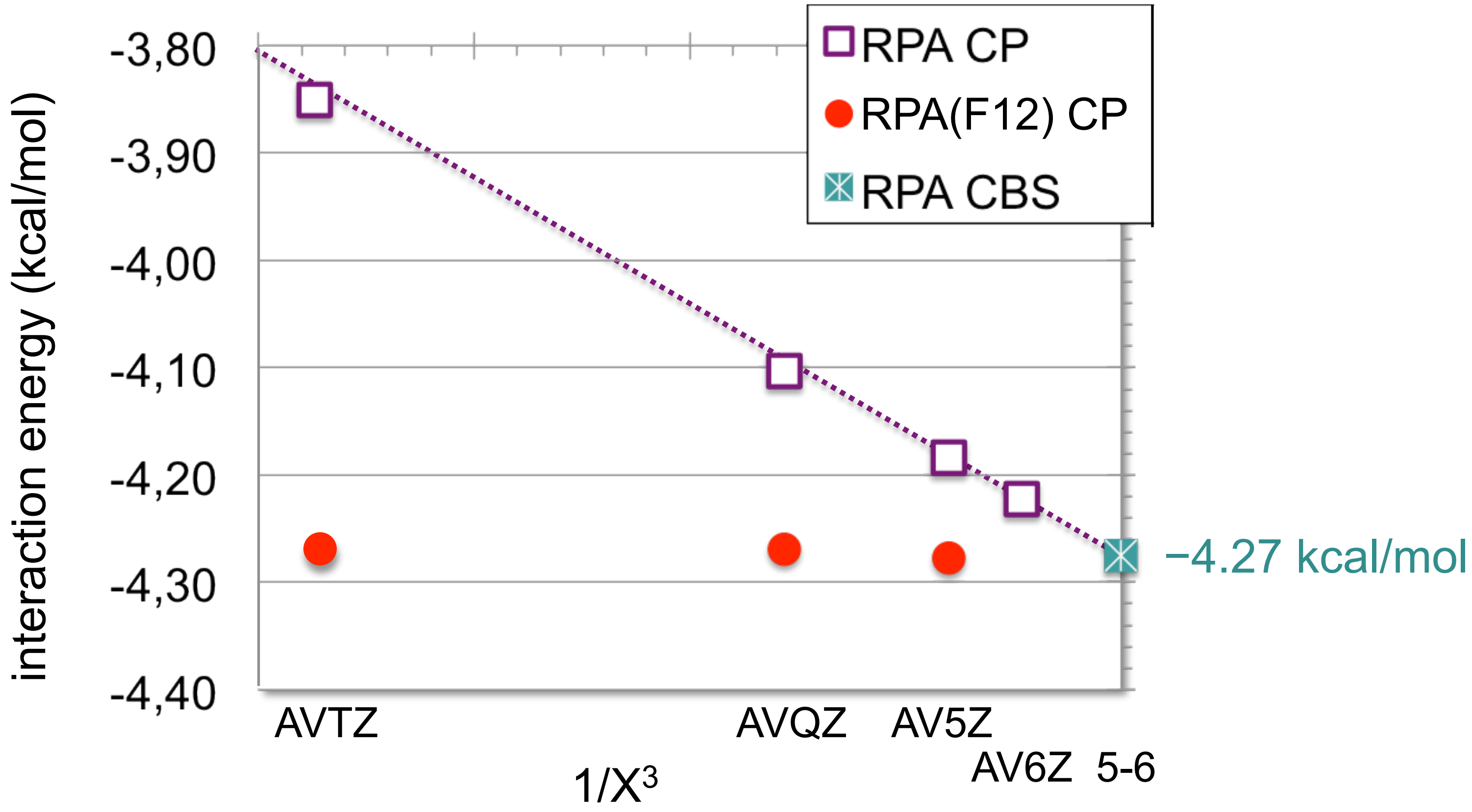
Including a CABS singles correction to the expectation value

Basis	**<KS|H|KS> + CABS**	E^{C}_{RPA}	$E^{C}_{\mathrm{RPA+F12}}$	$E^{C}_{\mathrm{RPA(F12)}}$
AVTZ	**−2.63**	−1.25	**−1.63**	**−1.62**
AVQZ	**−2.64**	−1.46	**−1.63**	**−1.63**
AV5Z	**−2.64**	−1.54	**−1.64**	**−1.64**
AV6Z	−2.64	−1.58		
AV(56)Z		**−1.63**		



RPA(F12) theory: The water dimer

Counterpoise (CP) corrected RPA and **RPA(F12)** interaction energies (kcal/mol) for the water dimer (fixed geometry from the S22 test set)



Outlook: Exchange RPA methods

- **rCCD(F12) theory** (in place of drCCD(F12) theory) can be used to improve the basis-set convergence of “exchange” RPA methods
  - SOSEX
  - RPAx
  - EXXRPA
  - AXK
- DFT with range separation?
- Self-consistent methods, orbital optimization?
- *GW* methods?
  - See lecture by Xavier Blase !

Literature

- **Review on F12 theory:**
  - C. Hättig, W. Klopper, A. Köhn, and D.P. Tew, *Chem. Rev.* **2012**, *112*, 4−74.
- **Implementation in TURBOMOLE:**
  - R. A. Bachorz, F. A. Bischoff, A. Glöß, C. Hättig, S. Höfener, W. Klopper, and D.P. Tew, *J. Comput. Chem.* **2011**, *32*, 2492−2513.
- **RPA+F12 theory:**
  - A.-S. Hehn and W. Klopper, *J. Chem. Phys.* **2013**, *138*, 181104.
- **RPA(F12) theory:**
  - A.-S. Hehn, D.P. Tew, and W. Klopper, *J. Chem. Phys.* **2015**, *142*, 194106.

Conclusions

- Explicitly-correlated approaches such as the MP2-F12, RPA(F12), CCSD(F12), and CCSD(T)(F12) methods have become useful tools for quantum chemistry
- The problem of slow basis-set convergence of double excitations in electron-correlation methods (*e.g.*, in MP2, CISD, or CCSD as well as RPA theory) may be regarded as solved

Acknowledgments

This research was supported by the Deutsche Forschungsgemeinschaft (DFG) through the Priority Programme (SPP) 1145 and through the Cluster of Excellence on Functional Nanostructures (CFN)