Coupled-cluster study of model systems: the nucleic acid bases and their dimers

Timo Fleig

Theoretical and Computational Chemistry
Heinrich Heine University Düsseldorf

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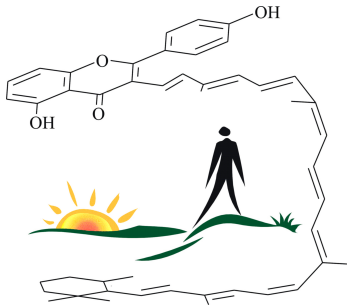

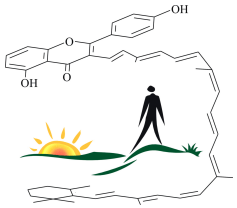

Outline

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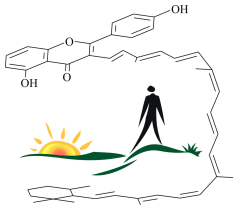
I. Introduction and Motivation

II. Results for nucleic acid bases

III. Accuracy of RI-CC2

One-particle basis sets
The CC hierarchy: correlation errors

IV. Results for nucleic acid base dimers



I. Introduction

Ab-initio Electronic-Structure Studies

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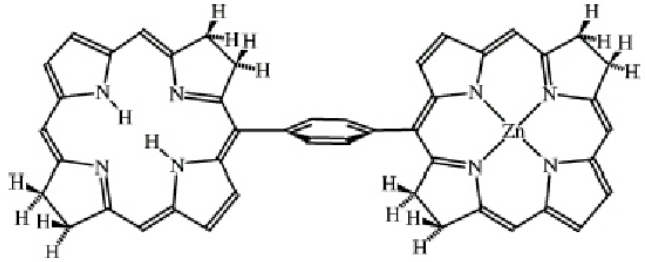
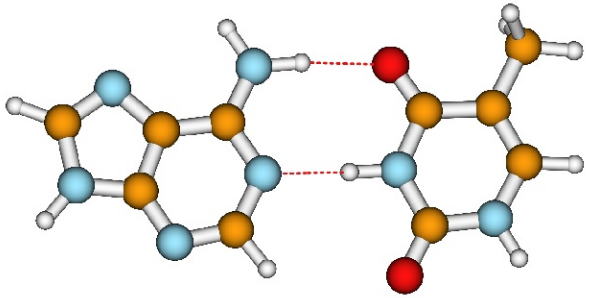




C3

Structure optimization

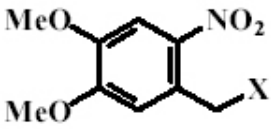
Vertical and adiabatic excitation energies

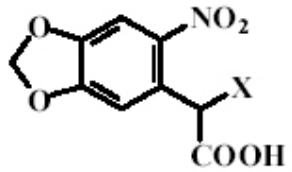
Charge−transfer states and processes

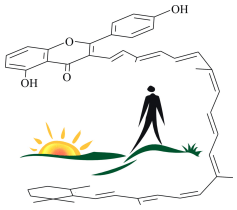
Methods:

Coupled Cluster

Configuration Interaction







Introduction

Overview of Current Activities

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- Rigorous study of monomer units (structures, excited states)

  T Fleig, S Knecht, C Hättig, *J. Phys. Chem. A* **2007**, accepted.

- Dimer studies at calibrated computational level

  Investigation of CT/proton transfer processes

- 1-Methylthymine: Simulation of solvation effects

  M Etinski, T Fleig, with K. Kleinermanns

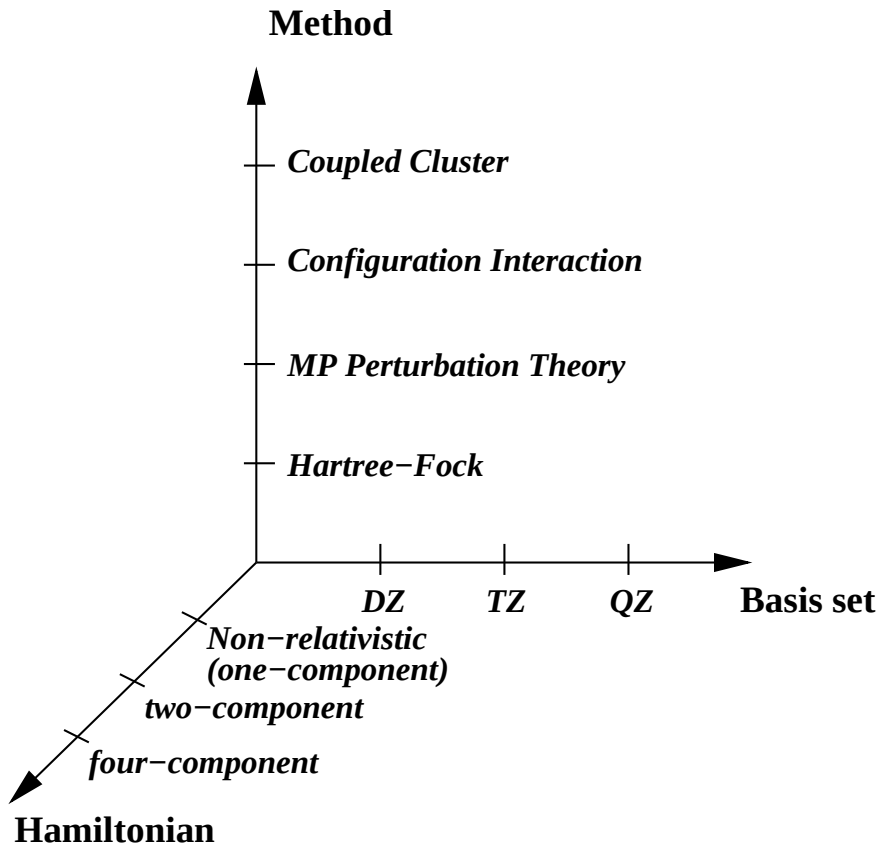
- Method development: Parallel large-scale MRCI

  S Knecht, T Fleig, *Chem. Phys. Lett.* **2007**, in preparation.

- Interfacing `LUCITA` to `TURBOMOLE` $\longrightarrow$ RI approximation

I. Introduction

The Accuracy of Quantum-Chemical Models



- **Electron Correlation:**
  Increasing rigor of treatment
  Hartree-Fock, MP2, CC2
  Coupled Cluster approaches
  Study of model hierarchies

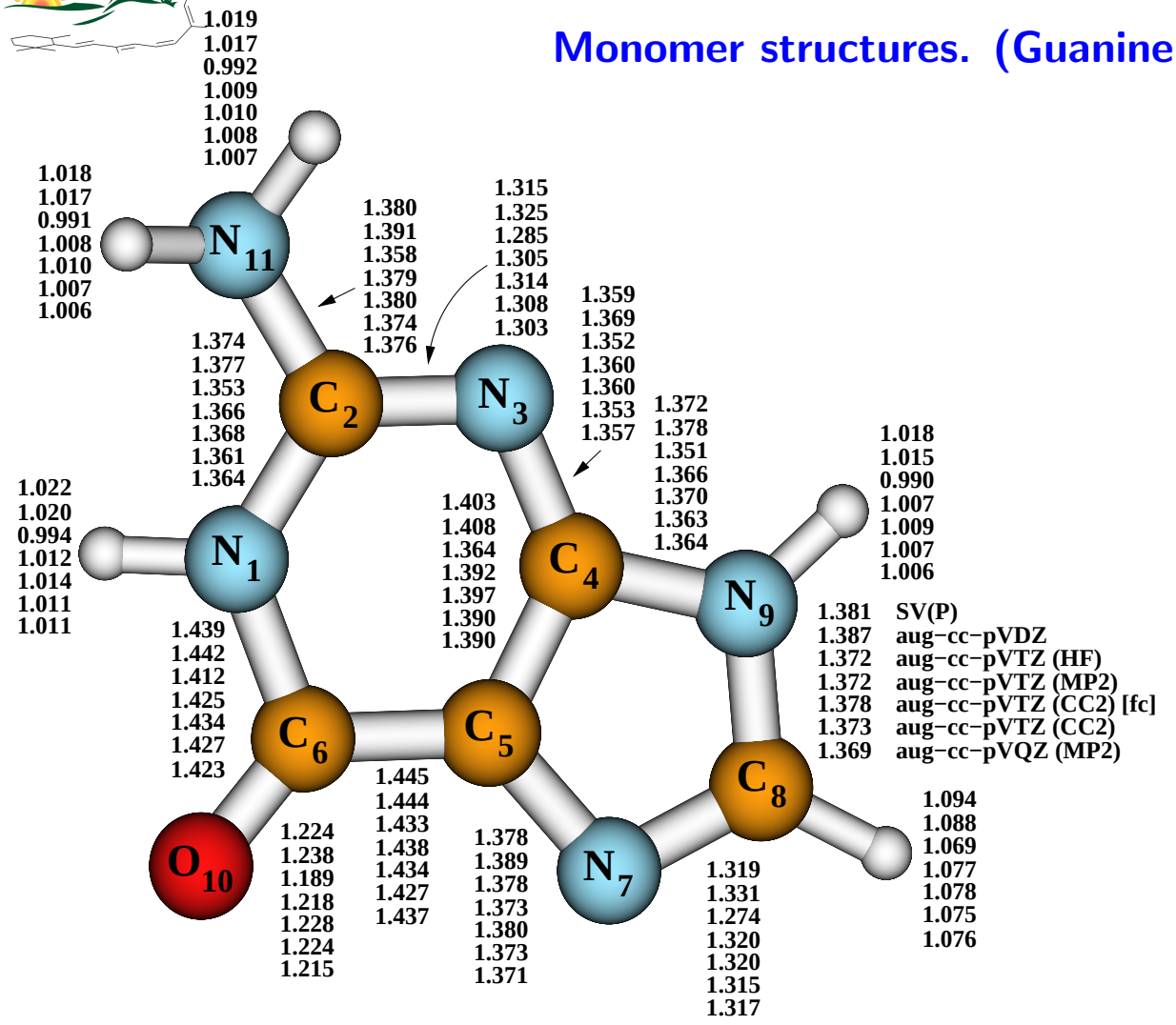
- **Basis set expansion:**
  Correlation-consistent
  one-particle basis sets
  SV(P), cc-pVTZ,
  aug-cc-pVXZ (X=D,T,Q)

- **Hamiltonian:**
  Non-relativistic Hamiltonian

$\longrightarrow$ Various approaches in direct comparison

II. Results

Monomer structures. (Guanine)



- Basis sets:

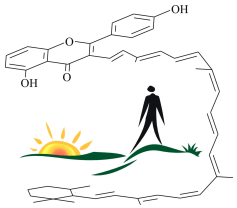
  aDZ $\rightarrow$ aTZ $\rightarrow$ aQZ
  Bond contraction ≈ -0.015 Å

  SV(P) error ≈ 0.02 Å

  XZ $\rightarrow$ aXZ $\approx +0.005$ Å

- Correlation:

  HF $\rightarrow$ MP2 $\approx$ CC2
  Bond stretching $\approx +0.004 \ldots + 0.04$ Å



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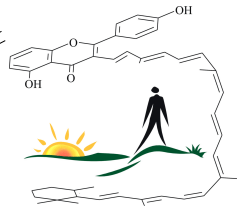
Excited states
(RI-CC2/aug-cc-pVTZ)



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Adenine			Cytosine			Guanine[b]			Thymine			Uracil		
$S_8(n\pi^*)$	6.14	0.001	$S_8(\pi[\sigma^*+Ryd])$	6.08	0.026	$S_8(n[\sigma^*+Ryd])$	6.13	0.011	$S_8(\pi[\pi^*+Ryd])$	6.53	0.178	$S_8(\pi\pi^*)$	6.70	0.167
$S_7(n\,Ryd])$	6.08	0.030	$S_7(n[\sigma^*+Ryd])$	5.95	0.031	$S_7(n[\pi^*+\sigma^*+Ryd])$	6.06	0.003	$S_7(\pi\,Ryd)$	6.49	0.000	$S_7(n\pi^*)$	6.54	0.001
$S_6(\pi[\,Ryd+\sigma^*])$	5.86	0.004	$S_6(n\pi^*)$	5.83	0.000	$S_6(\pi[\sigma^*+Ryd])$	5.99	0.003	$S_6(n\,Ryd])$	6.39	0.061	$S_6(n[Ryd+\sigma^*])$	6.41	0.040
$S_5(n[Ryd+\pi^*])$	5.75	0.003	$S_5(\pi\pi^*)$	5.61	0.138				$S_5(\pi\pi^*)$	6.27	0.037	$S_5(\pi\pi^*)$	6.25	0.032
$S_4(\pi[\,Ryd+\sigma^*])$	5.53	0.011	$S_4(\pi[\sigma^*+Ryd])$	5.53	0.005	$S_5(\pi[\sigma^*+Ryd])$	5.45	0.078	$S_4(n\pi^*)$	6.16	0.000	$S_4(n\pi^*)$	6.09	0.000
$S_{2/3}(\pi[\pi^*+Ryd])$[a]	5.25	0.302	$S_3(n\pi^*)$	5.26	0.002	$S_4(\pi[\pi^*+\sigma^*+Ryd])$	5.41	0.238				$S_3(\pi[\sigma^*+Ryd])$	6.02	0.003
$S_1(n\pi^*)$	5.12	0.007				$S_3(n\pi^*)$	5.35	0.003	$S_3(\pi\,Ryd)$	5.74	0.000			
			$S_2(n\pi^*)$	4.87	0.002	$S_2(\pi[\sigma^*+Ryd])$	5.07	0.014				$S_2(\pi\pi^*)$	5.34	0.182
			$S_1(\pi\pi^*)$	4.66	0.052	$S_1(\pi\pi^*)$	4.95	0.144	$S_2(\pi\pi^*)$	5.20	0.182			
									$S_1(n\pi^*)$	4.82	0.000	$S_1(n\pi^*)$	4.79	0.000

excitation energy [eV]

6.5 6 5.5 5 4.5

nucleic acid base

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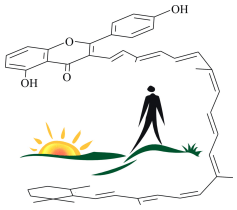

II. Results

Other methods and experiment

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9H-Adenine

Excitation	TD-DFT[1]	CASSCF/CASPT2[2]	DFT/MRCI[3]	RI-CC2	Exp.[4]	Exp.[5] E_{0-0}
$n - \pi^*$	5.04	6.15	5.01	5.12	*4.98*	4.40
$\pi - \pi^*$	5.09	5.13	4.90	5.25		4.48
$\pi - \pi^*$		5.20	5.04	5.25		

- TD-DFT/B3LYP performs well for monomer units
- CASSCF/CASPT2 suffers from limited active spaces
- Comparable (gas-phase) experiments are rare (vertical excitation)

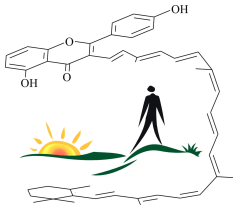
[1] A L Sobolewski, W Domcke, *Eur. Phys. J. D* **2002**, *20*, 369

[2] M P Fülscher, L Serrano-Andrés, B O Roos, *J. Am. Chem. Soc.* **1997**, *119*, 6168

[3] C M Marian, *J. Chem. Phys.* **2005**, *122*, 104314

[4] L B Clark, G G Peschel, J. I. Tinoco, *J. Phys. Chem.* **1965**, *69*, 3615

[5] N J Kim, G Jeong, Y S Kim, J Sung, S K Kim, Y D Park, *J. Chem. Phys.* **2000**, *113*, 10051



II. Results

Comparison with Experiment

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NA base	State (transition)	RI-CC2 T_v[eV]	Experimental
Adenine	$S_1\ (n-\pi^*)$	5.12	4.40[6]
	$S_2\ (\pi-\pi^*)$	5.25	4.48[6] 4.98[7]
Thymine	$S_1\ (n-\pi^*)$	4.82	
	$S_2\ (\pi-\pi^*)$	5.20	4.8[8] 4.7[9]
Guanine	$S_1\ (\pi-\pi^*)$	4.98	4.4 – 4.5[10]
Cytosine	$S_1\ (\pi-\pi^*)$	4.66	4.28[7]
Uracil	$S_1\ (n-\pi^*)$	4.80	
	$S_2\ (\pi-\pi^*)$	5.35	5.08[7]

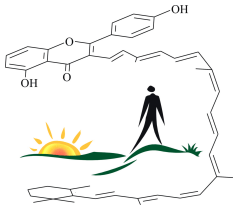
[6] E_{0-0}, vibration corrected; N J Kim, G Jeong, Y S Kim, J Sung, S K Kim, Y D Park, *J. Chem. Phys.* **2000**, *113*, 10051

[7] Vapor phase; L B Clark, G G Peschel, J. I. Tinoco, *J. Phys. Chem.* **1965**, *69*, 3615

[8] 1,3-Dimethyluracil; L B Clark, G G Peschel, J. I. Tinoco, *J. Phys. Chem.* **1965**, *69*, 3615

[9] In water and TMP; L B Clark, G G Peschel, J. I. Tinoco, *J. Phys. Chem.* **1965**, *69*, 3615

[10] In: M P Fülscher, L Serrano-Andrés, B O Roos, *J. Am. Chem. Soc.* **1997**, *119*, 6168



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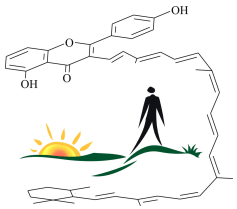
Excited states
(Uracil, Basis sets)



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excitation energy [eV]

7.5
7
6.5
6
5.5
5
4.5
0

SV(P)
$S_8(\pi\sigma^*)$ 7.42 0.000
$S_7(n\pi^*)$ 7.32 0.000
$S_6(\pi\pi^*)$ 7.26 0.180
$S_5(n\pi^*)$ 6.95 0.000
$S_4(\pi\pi^*)$ 6.63 0.050
$S_3(n\pi^*)$ 6.41 0.000
$S_2(\pi\pi^*)$ 5.67 0.199
$S_1(n\pi^*)$ 5.02 0.000

cc−pVTZ
$S_8(n\pi^*)$ 7.14 0.000
$S_7(\pi\pi^*)$ 7.01 0.174
$S_6(\pi\sigma^*)$ 7.00 0.000
$S_5(n\pi^*)$ 6.70 0.000
$S_4(\pi\pi^*)$ 6.41 0.044
$S_3(n\pi^*)$ 6.23 0.000
$S_2(\pi\pi^*)$ 5.48 0.187
$S_1(n\pi^*)$ 4.88 0.000

aug−cc−pVDZ
$S_8(\pi\pi^*)$ 6.57 0.154
$S_7(n\pi^*)$ 6.42 0.001
$S_6(n[\sigma^*+Ryd])$ 6.24 0.047
$S_5(\pi\pi^*)$ 6.11 0.027
$S_4(n\pi^*)$ 5.98 0.000
$S_3(\pi[\sigma^*+Ryd])$ 5.82 0.003
$S_2(\pi\pi^*)$ 5.23 0.180
$S_1(n\pi^*)$ 4.71 0.000

aug−cc−pVTZ
$S_8(\pi\pi^*)$ 6.70 0.161
$S_7(n\pi^*)$ 6.54 0.001
$S_6(n[\sigma^*+Ryd])$ 6.41 0.040
$S_5(\pi\pi^*)$ 6.25 0.032
$S_4(n\pi^*)$ 6.09 0.000
$S_3(\pi[\sigma^*+Ryd])$ 6.02 0.003
$S_2(\pi\pi^*)$ 5.34 0.182
$S_1(n\pi^*)$ 4.79 0.000

aug−cc−pVQZ
$S_8(\pi\pi^*)$ 6.70 0.166
$S_7(n\pi^*)$ 6.56 0.001
$S_6(n\,Ryd)$ 6.49 0.036
$S_5(\pi\pi^*)$ 6.26 0.036
$S_4(n\pi^*)$ 6.10 0.000
$S_3(\pi\,Ryd)$ 6.08 0.003
$S_2(\pi\pi^*)$ 5.35 0.182
$S_1(n\pi^*)$ 4.80 0.000

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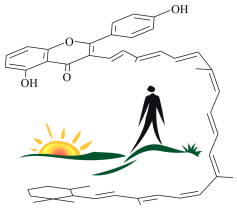

III. Analysis

Correlation-Consistent Basis Sets

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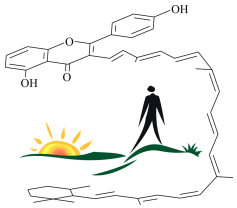
Some basic features:

- Generalized contraction for occupied orbitals
- Optimized primitives to maximize correlation contribution (CISD)
- cc-pVTZ: 2s 2p 2d 1f primitives
- Construction: Valence-correlated ground states of atoms !
- Excited states: Diffuse electron distributions
- aug-cc-pVTZ: + 1s 1p 1d 1f diffuse primitives
- cc-pVDZ sets do not have sufficient flexibility to describe excited states accurately



III. Analysis

Effect of augmenting functions

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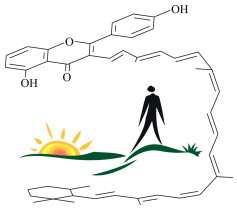
Uracil excited states, vertical RI-CC2/(aug-)cc-pVTZ

$$\Delta E_{T_v} = E_{T_v}^{cc-pVTZ} - E_{T_v}^{aug-cc-pVTZ}$$

State	ΔE_{T_v} [eV]
$n\pi^*$	-0.09
$\pi\pi^*$	-0.14
$n\pi^*$	-0.14
$\pi\pi^*$	-0.16
$n\pi^*$	-0.16
$\pi\pi^*$	-0.31

- Mean deviation of -0.17 eV
- Error increases with excitation energy
- Independent of character of state

- Explanation via orbitals involved in excitations
- Analysis of lowest $n\pi^*$ and highest $\pi\pi^*$ states



III. Analysis

Effect of augmenting functions

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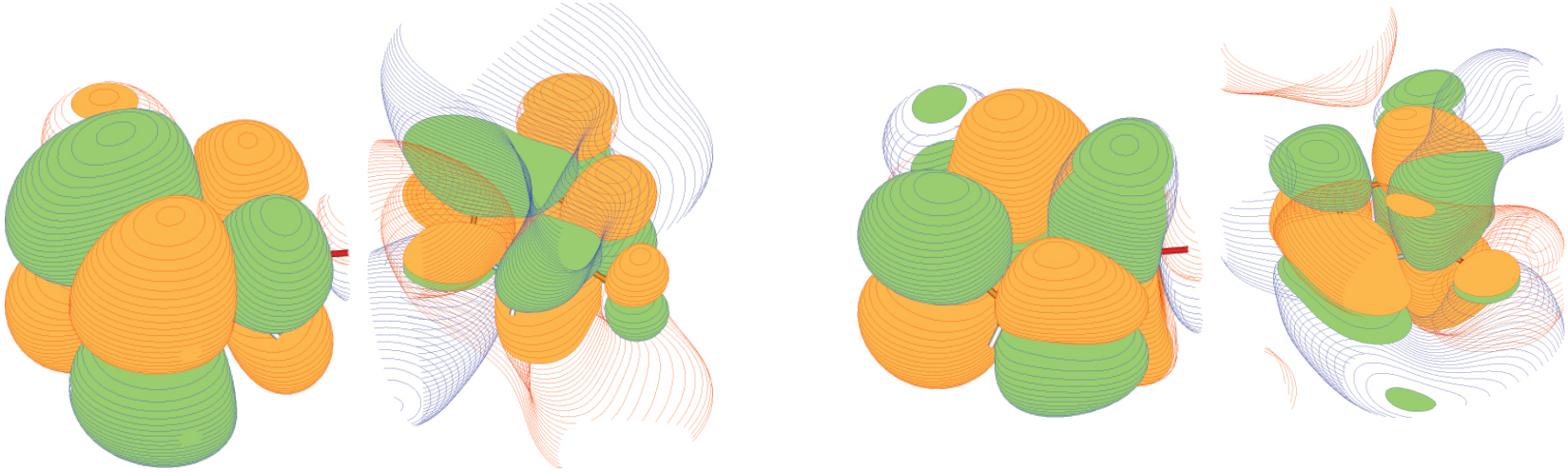
Electron density for involved π^* orbital (contour value 0.01):

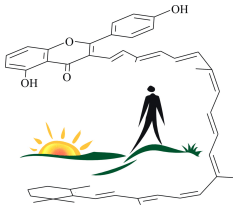
$\langle r^2 \rangle - \langle r \rangle^2 = 12.6$ $\quad$ 35.1 $\quad$ 13.7 $\quad$ 34.8



cc-pVTZ aug-cc-pVTZ cc-pVTZ aug-cc-pVTZ

S_1, ($n\pi^*$) S_7, ($\pi\pi^*$)

- Involved π^* are most compact virtual orbitals (aug-cc-pVTZ)
- Diffuse functions play significant role for excited states !



Some Conclusions on Basis Sets

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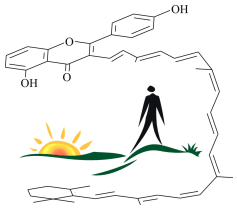
- SV(P) sets not suited for the description of excited states
- The cc-pVXZ series is significantly less accurate than series aug-cc-pVXZ
- aug-cc-pVXZ sets open for access to Rydberg states
- Wrong order of excited states using too small basis sets (guanine)
- Augmentation increases computational effort significantly.



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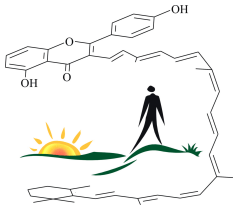
Excited states
(Uracil, Electron Correlation)



III. Accuracy: Electron Correlation

The CC Hierarchy

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O Christiansen, H Koch, P Jørgensen, *Chem. Phys. Lett.* **1995**, *243*, 409-418.

C Hättig, F Weigend, *J. Chem. Phys.* **2000**, *113*, 5154-5161.

$$\text{CC2} \qquad \left\langle \mu_2 \left| \hat{H} + \left[\hat{F}, \hat{T}_2 \right] \right| \text{Ref} \right\rangle = 0$$

$$\text{CCSD} \qquad \left\langle \mu_2 \left| \hat{H} + \left[\hat{H}, \hat{T}_2 \right] + \frac{1}{2} \left[\left[\hat{H}, \hat{T}_2 \right], \hat{T}_2 \right] \right| \text{Ref} \right\rangle = 0$$

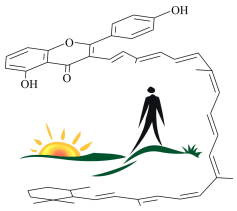
$$\text{CC3} \qquad \left\langle \mu_3 \left| \left[\hat{F}, \hat{T}_3 \right] + \left[\hat{H}, \hat{T}_2 \right] \right| \text{Ref} \right\rangle = 0$$

$$\text{CCSDT} \qquad \ldots$$

Scaling of the models with system size N:

CC2	CCSD	CC3	CCSDT
N^5	N^6	N^7	N^8

- Fock-operator approximation
  $\longrightarrow$ reduced cost
- $\hat{F} + \hat{V}^t$
  $\longrightarrow$ response theory for excited states
- Reduced scaling essential for large-scale applications
- Accuracy?



III. Accuracy: Electron Correlation

The Coupled Cluster Hierarchy

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H Koch, O Christiansen, P Jørgensen, J Olsen, *Chem. Phys. Lett.* **1995**, *244*, 75-82.

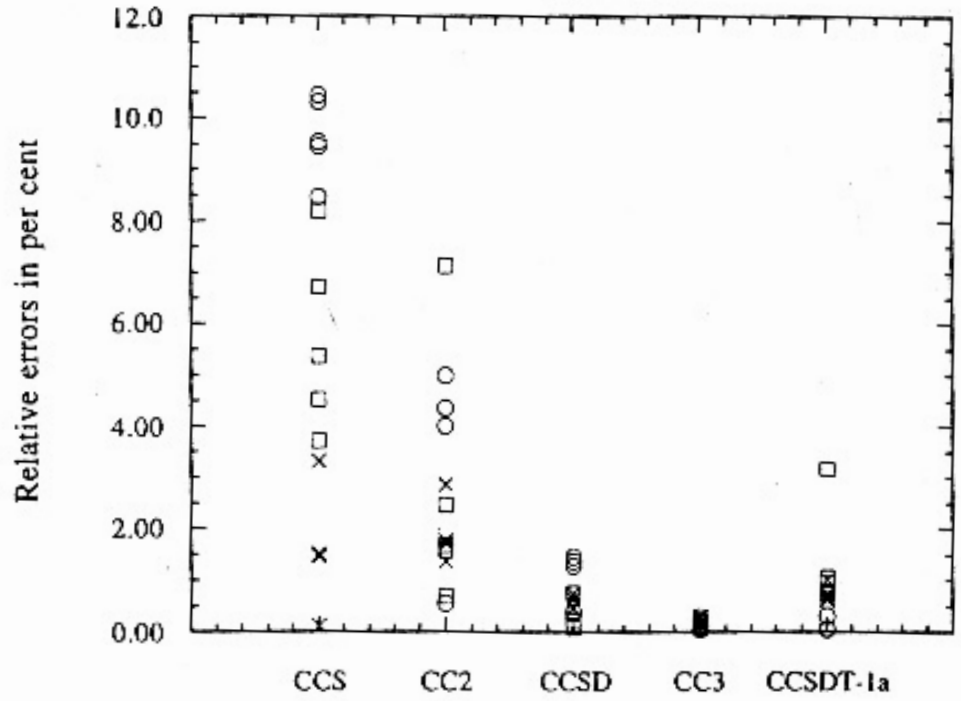


Fig. 1. The percent deviation from FCI excitation energies for the single replacement dominant excitation in Ne (○), BH (×) and CH_2 (□).

- Relative errors in small molecules
- (aug)-cc-pVDZ basis set
- Largest CC2 errors 0.04 eV
- CCSD consistently better than CC2
- CC3 close to exact values

III. Accuracy: Electron Correlation

The Coupled Cluster Hierarchy

O Christiansen, H Koch, P Jørgensen, J Olsen, *Chem. Phys. Lett.* **1996**, *256*, 185-194.

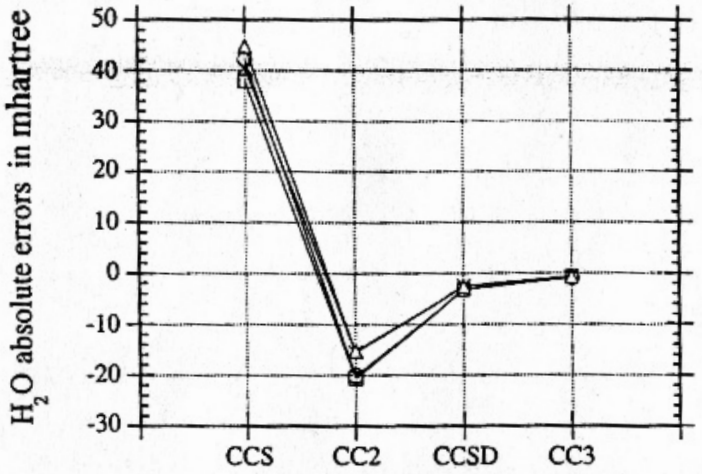


Fig. 1. The absolute deviation from the FCI excitation energies for H_2O: $2\,^1A_1$ (□), $1\,^1B_1$ (△), $1\,^1B_2$ (×), $1\,^1A_2$ (○).

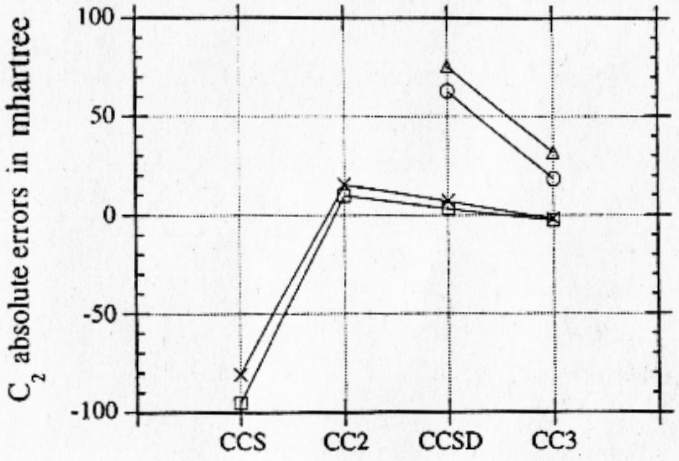
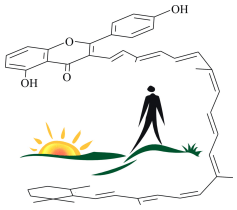


Fig. 3. The absolute deviation from the FCI excitation energies for C_2: $1\,^1\Pi_u$ (□), $1\,^1\Delta_g$ (△), $1\,^1\Sigma_u^+$ (×), $1\,^1\Pi_g$ (○).

- Errors decrease systematically (for correlated models)
- Errors may be positive or negative (different correlation cases)



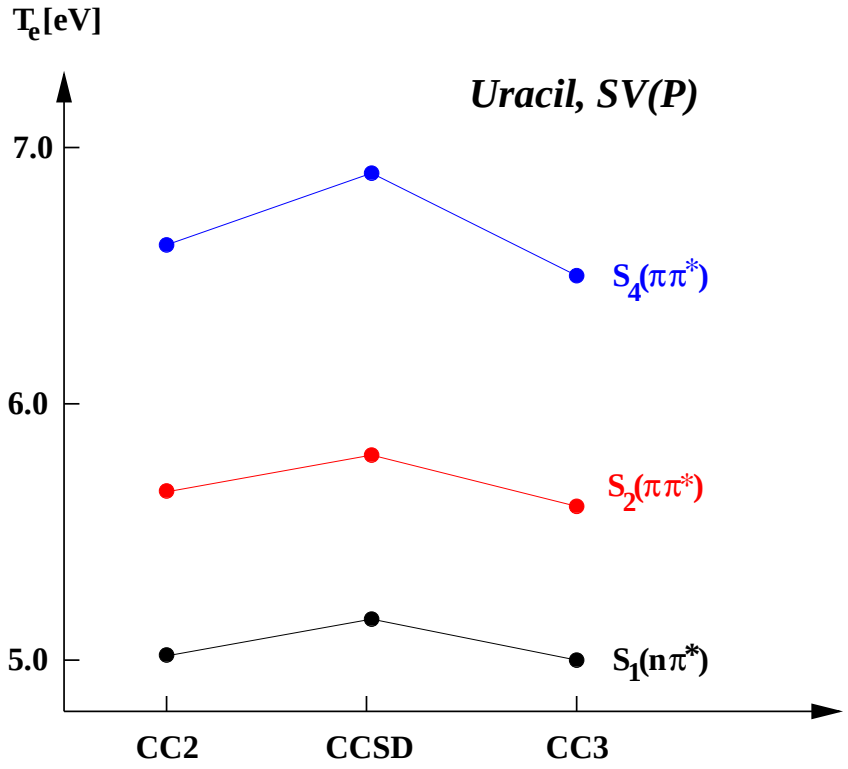
III. Accuracy: Electron Correlation

The NA Bases: Uracil

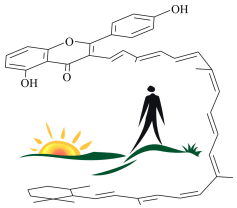
T Fleig, S Knecht, C Hättig, *J. Phys. Chem. A* **2007**, accepted.

State	RI-CC2	CC2	CCSD	CC3	t_1
S_2	5.67	5.67	5.81	5.61	91%
S_4	6.63	6.63	6.91	6.51	88%
S_1	5.02	5.01	5.17	5.00	92%

- RI is a valid approximation!
- CC2 values close to CC3
- CCSD does not necessarily give correct answer!
- Triple-excitation character increases in S_4 state



Is this fortuitous or systematic?



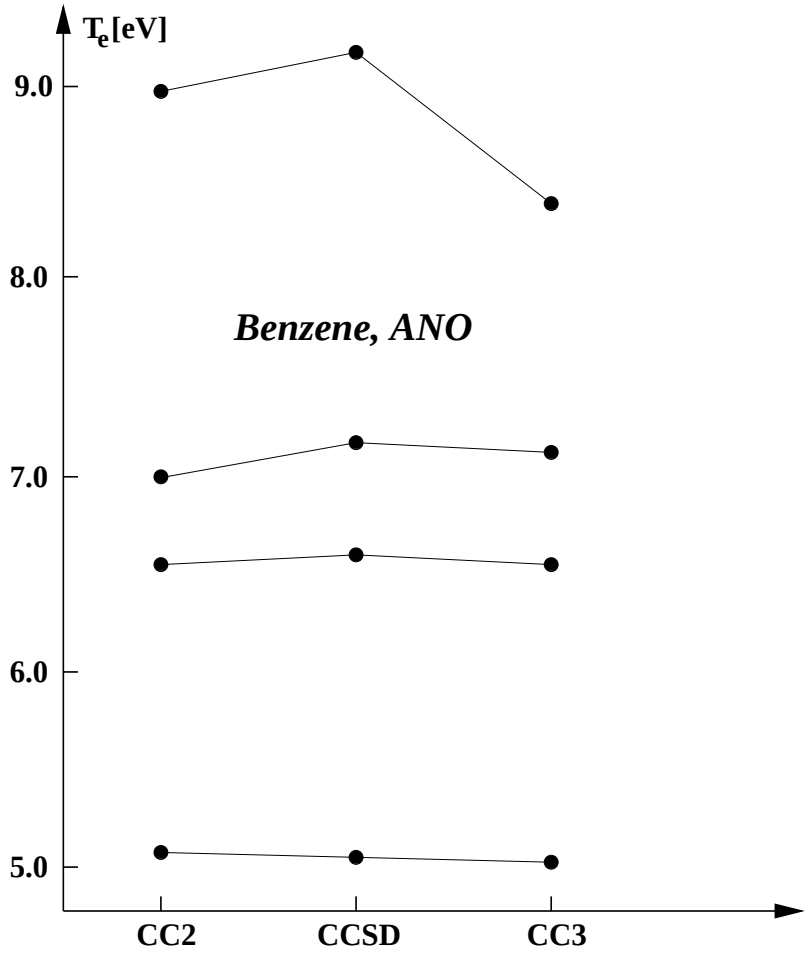
III. Accuracy: Electron Correlation

A comparison: Benzene

O Christiansen et al., *J. Chem. Phys.* **1996**, *105*, 6921-6939.

State	CC2	CCSD	CC3	t_1
1^1B_{2u} $(\pi\pi^*)$	5.27	5.19	5.08	86%
1^1B_{1u} $(\pi\pi^*)$	6.56	6.59	6.54	93%
1^1E_{1u} $(\pi\pi^*)$	7.01	7.17	7.13	93%
2^1E_{2g} $(\pi\pi^*)$	8.97	9.17	8.41	66%

- CC2 is accurate for singly-excited states
- Deviations between models are smaller
- Oscillatory behavior

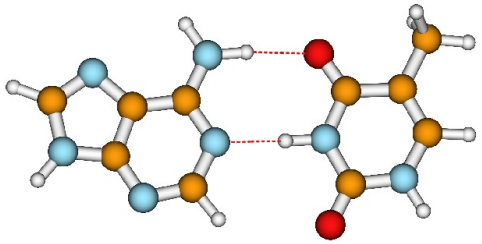


Similar trends in π systems

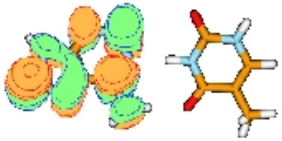
IV. Results

Nucleic acid base dimers

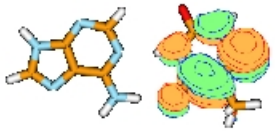
- Exploit knowledge from calbration studies
- Identify CT states in spectra
- Ground-state structures (C_1, frozen core); vertical excited-state calculations

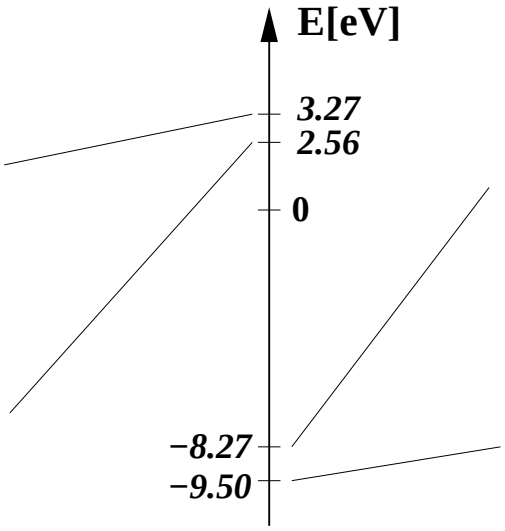


LUMO Adenine

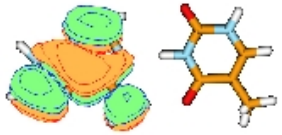


LUMO Thymine

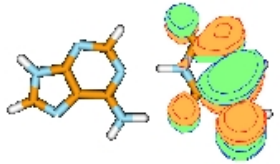


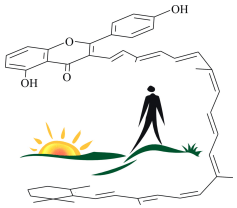


HOMO Adenine



HOMO Thymine





IV. Results

Test: DFT performance

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Adenine-Thymine (AT) base pair, Watson-Crick structure

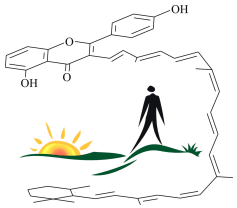
RI-TDDFT (SVWN), TZVP

State	System	Character	T_v [eV]
S_1	A→T	$\pi - \pi^*$	3.30
S_2	A→T	$n - \pi^*$	3.74
S_3	T→T	$n - \pi^*$	4.21
S_4	T→A	$\pi - \pi^*$	4.33
S_5	A→A	$n - \pi^*$	4.37
S_6	T→T(A)	$\pi - \pi^*$	4.52
S_7	A→A	$\pi - \pi^*$	4.53
S_8	AT→T	$n/\sigma - \pi^*$	4.59
S_9	A→T	$\pi - \pi^*$	4.61

RI-CC2, TZVP

State	System	Character	T_v [eV]
S_1	AT→T	$n - \pi^*$	5.12
S_2	A→A	$\pi - \pi^*$	5.26
S_3	A→A	$\pi - \pi^*$	5.31
S_4	A→A	$\pi - \pi^*$	5.41
	T→T	$\pi - \pi^*$	
S_5	A→A	$n - \pi^*$	5.46
S_6	A→A	$n - \pi^*$	5.96
S_7	A→T	$\pi - \pi^*$	6.17
S_8	AT→T	$n - \pi^*$	6.31
S_9	AT→A	$n - \pi^*$	6.51

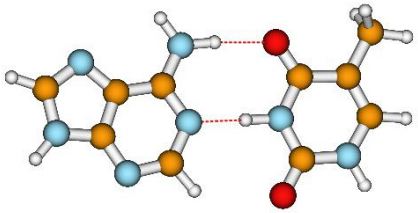
- DFT: Low-lying CT states, physically incorrect
- CC2: Spectrum corresponds to qualitative expectations

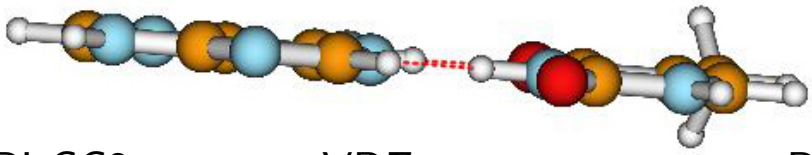


IV. Results

Adenine-Thymine: Structure and excited states

WC structure, opt. RI-CC2, aug-cc-pVDZ





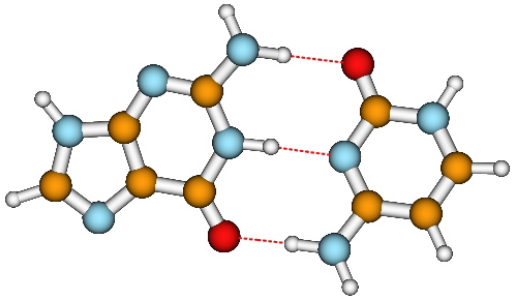
	RI-CC2, aug-cc-pVDZ			RI-CC2, cc-pVDZ[11]
State	Excitation Type	Character (CT)	T_v [eV]	T_v [eV]
S_1	T→T/A→T	$n-\pi^*$ (20 %)	4.81	5.13
S_2	T→T	$\pi-\pi^*$	4.94	5.37
S_3	A→A	$\pi-\pi^*$	5.05	5.25
S_4	A→A	$\pi-\pi^*$	5.05	5.45
S_5	A→A	$\pi-Ryd$	5.29	
S_6	A→A/A→T	$n-\pi^*$ (20 %)	5.31	5.51
S_7	T→T	$\pi-Ryd$	5.47	
S_8	A→A	$\pi-Ryd$	5.71	
S_9	A→A/A→T	$\pi-\pi^*$ (40 %)	5.71	6.26
...				
S_{12}	T→T/A→T	$\pi-\pi^*$ (45 %)	5.91	6.42
...				

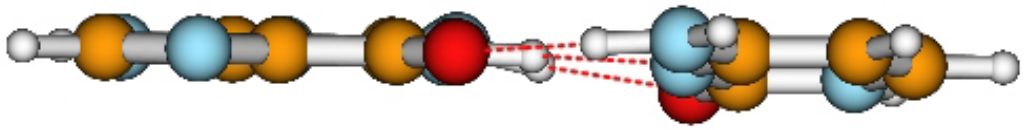
[11] S Perun, A L Sobolewski, W Domcke, *J. Phys. Chem. A* **2006**, *110*, 9031-9038

IV. Results

Guanine-Cytosine: Structure and excited states

WC structure, opt. RI-CC2, aug-cc-pVDZ





RI-CC2, aug-cc-pVDZ

State	Excitation Type	Character (CT contr.)	T_v [eV]
S_1	G→G/G→C	$\pi - \pi^*$ (35 %)	4.61
S_2	C→C	$\pi - \pi^*$	4.77
S_3	G→G	$\pi - Ryd$	4.77
S_4	G→G/G→C	$\pi - \pi^*$ (35 %)	5.03
S_5	G→G/G→C	$\pi - Ryd$ (40 %)	5.18
S_6	G→G	$\pi - \pi^*$	5.20
S_7	C→C	$\pi - \pi^*$	5.22
S_8	C→C/G→C	$n - \pi^*$ (20 %)	5.27
S_9	G→G/G→C	$\pi - Ryd$ (50 %)	5.41
...			

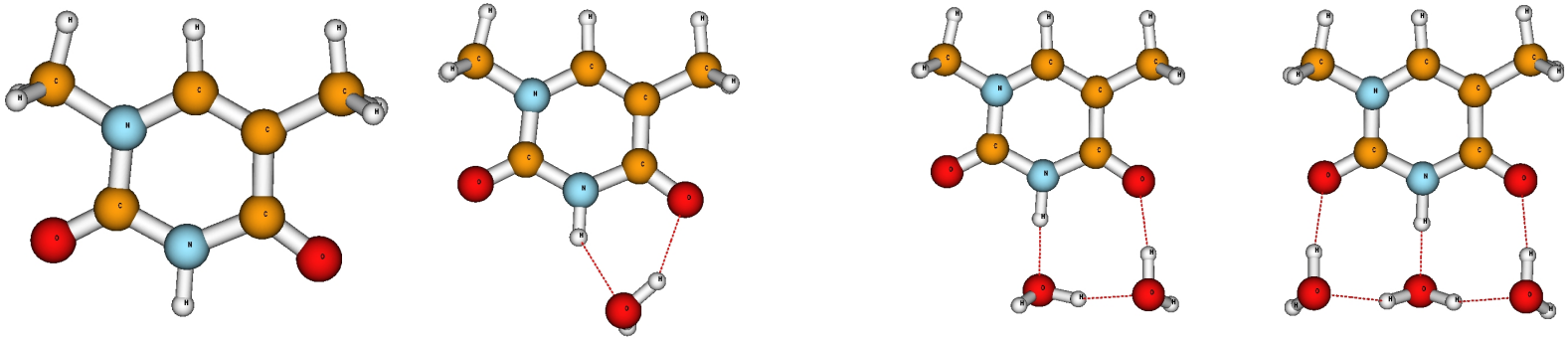
- Strong CT mixing
- Difficult designation

IV. Results

1-Methylthymine

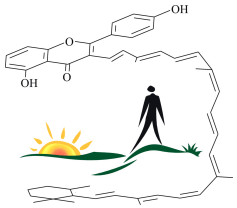
Investigation of an excited-state process.

RI-CC2/cc-pVDZ optimized structures:



- Trends by adding water molecules to form a solvation shell

→ **Poster** by **Mihajlo Etinski**



Final Conclusions

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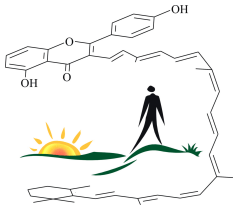
- CC2 correlation treatment appears to be very accurate
  Errors $<< 0.4$ eV

- CC2 applicable for larger molecules

- Description of excited states:
  Selection of basis set is a crucial issue
  (aug) leads to significant corrections

- In present case (NA bases and dimers):
  Favorable error cancellation
  Basis set: too low; Correlation: too high!

- Advocated model: RI-CC2/aug-cc-pVDZ



Thanks !

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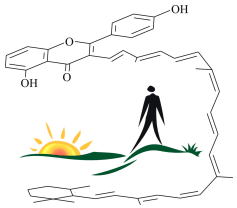
- Stefan Knecht (Düsseldorf)
- Christof Hättig (Bochum)
- Ove Christiansen (Aarhus)



I. Introduction and Motivation

Charge-Transfer Problem (in DFT)

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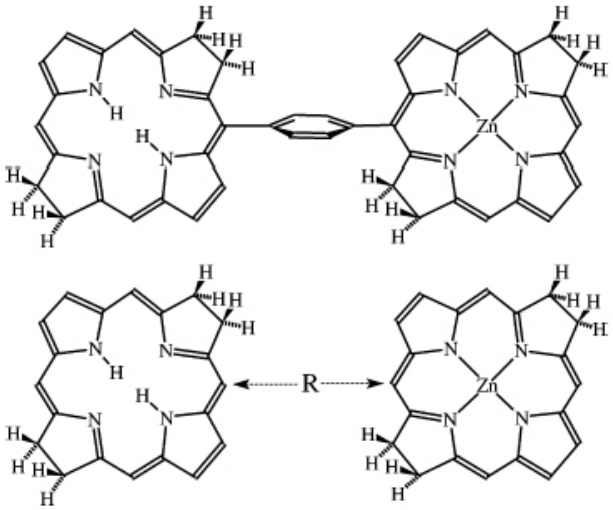
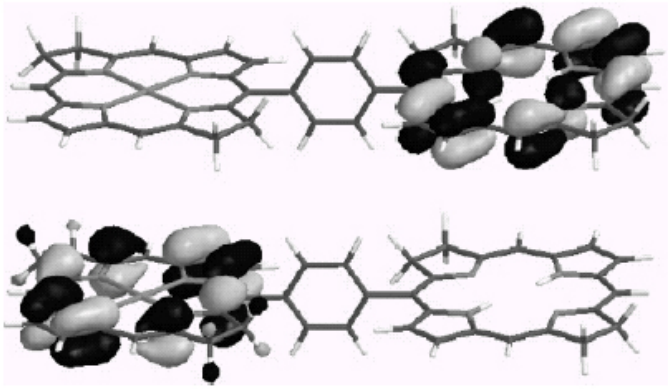
Zinc-Bacteriochlorin-Bacteriochlorin complex

A Dreuw, M Head-Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 4007-4016

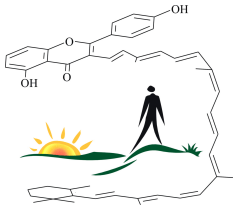




(TDDFT, BLYP functional, 6-31G*):

	Excitation energies [eV]				
	ZnBC-BC complex			Monomers	
State	Full	Model	Transition	Theory	Exp.
S_1	1.33	1.32	ZnBC → BC		
S_2	1.46	1.47	BC → ZnBC		
S_3	1.86	1.90	BC → ZnBC		
S_4	1.94	1.96	ZnBC → BC		
S_5	2.05	2.07	$\pi - \pi^*$ ZnBC	2.07	1.65
S_6	2.09	2.12	$\pi - \pi^*$ BC	2.10	1.6
S_7	2.38	2.40	$\pi - \pi^*$ BC	2.39	2.3
S_8	2.42	2.46	$\pi - \pi^*$ ZnBC	2.44	2.2
S_9	2.43	2.42	ZnBC → BC		

⇒ Spectrum ist qualitatively wrong !



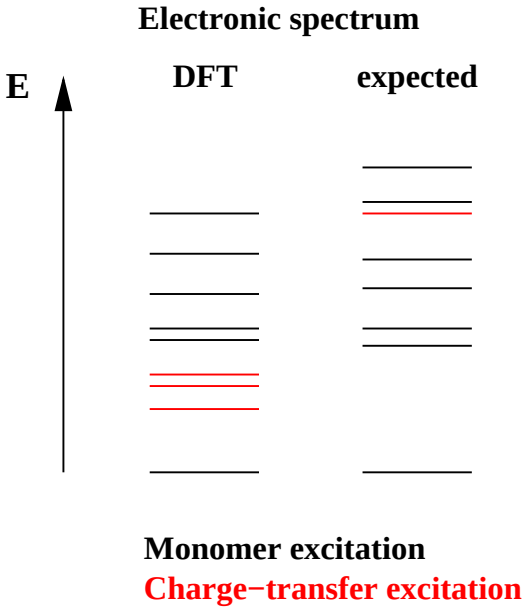
I. Introduction and Motivation

Charge-Transfer Problem (in DFT)

HEINRICH HEINE UNIVERSITÄT DÜSSELDORF

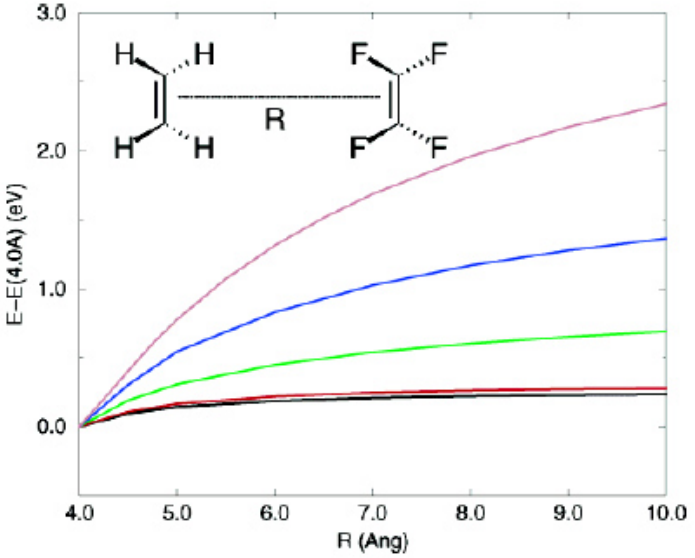
Problem 1:

CT excitation energies are considerably too small



Problem 2:

CT states exhibit wrong asymptotic behavior



CIS

half-and-half

B3LYP

LB94

SVWN

1. A Dreuw, M Head-Gordon, *Chem. Rev.* **2005**, *105*, 4009-4037
2. A Dreuw, M Head-Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 4007-4016
3. A Dreuw, J L Weisman, M Head-Gordon, *J. Chem. Phys.* **2003**, *119*, 2943-2946