

Equation-of-motion coupled cluster study of
the vertical excitation spectra of cytosine
adducts.

Tomasz Kus, Victor F. Lotrich and Rodney
J. Bartlett

Collaborators: Mark Ponton(Aces QC), Erik

Deumens(QTP), Norbert Flocke(QTP), Ajith Perera(QTP)

Introduction

- Equation-of-motion (EOM) theory
- Implementation: **ACESIII**
- Application: H and OH adducts of cytosine
- Performance

Coupled-cluster methods

- Standard tools used in highly accurate calculations of ground and **excited state** calculations.
- High scaling (CCSD: N^6) has previously limited the applicability of such calculations.
- Parallel computing has allowed these calculations to be performed, many problems can be reinvestigated now.

EOM-CCSD

- Direct method: A spectrum of electronic states obtained in a single calculation.
- Computationally 'simple' (at least conceptually!)
- Excited state wave functions generated from an RHF CC ground state are spin adapted.

Some fundamentals of the EOM-CCSD method.

$$|\Psi_x \rangle = \hat{R}|\Psi_g \rangle \quad (1)$$

where \hat{R} is a linear CI like excitation operator

$$\hat{R} = \hat{R}_1 + \hat{R}_2 + \dots \quad (2)$$

$$\hat{R}_n = \left(\frac{1}{n!}\right)^2 \sum r_{ijk\dots}^{abc\dots} a^\dagger i b^\dagger j c^\dagger k \dots \quad (3)$$

The ground state wavefunction (CC) is,

$$|\Psi_g \rangle = e^{\hat{T}}|\phi_0 \rangle \quad (4)$$

where $|\phi_0 \rangle$ is the single determinant reference wavefunction (SCF usually). Thus,

$$\hat{H}\hat{R}e^{\hat{T}}|\phi_0 \rangle = E\hat{R}e^{\hat{T}}|\phi_0 \rangle \quad (5)$$

leading to the eigenvalue problem,

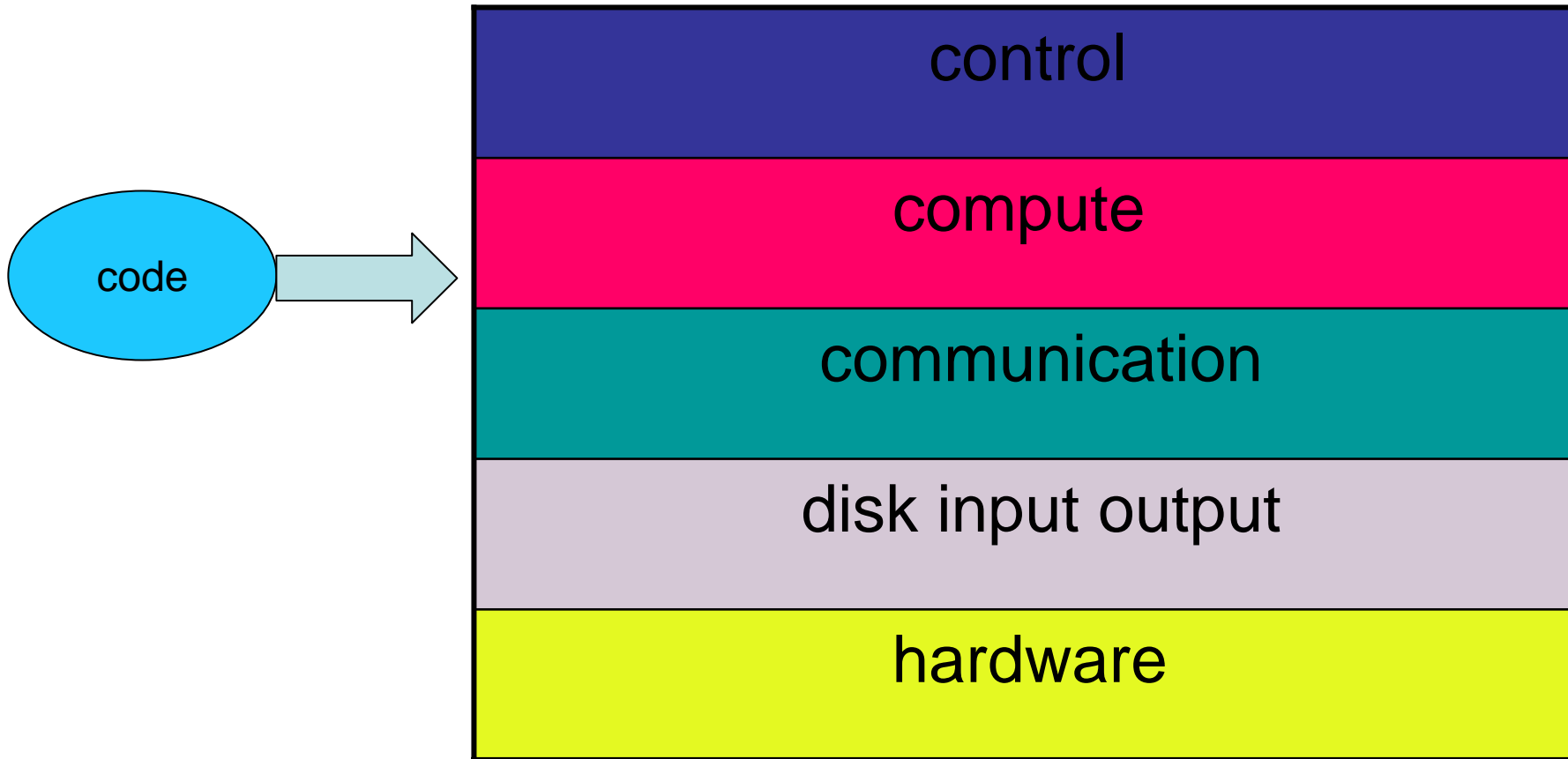
$$(\hat{\bar{H}} - E)\hat{R}|\phi_0 \rangle = 0 \quad (6)$$

where the effective Hamiltonian $\bar{H} = e^{-T}He^T$.

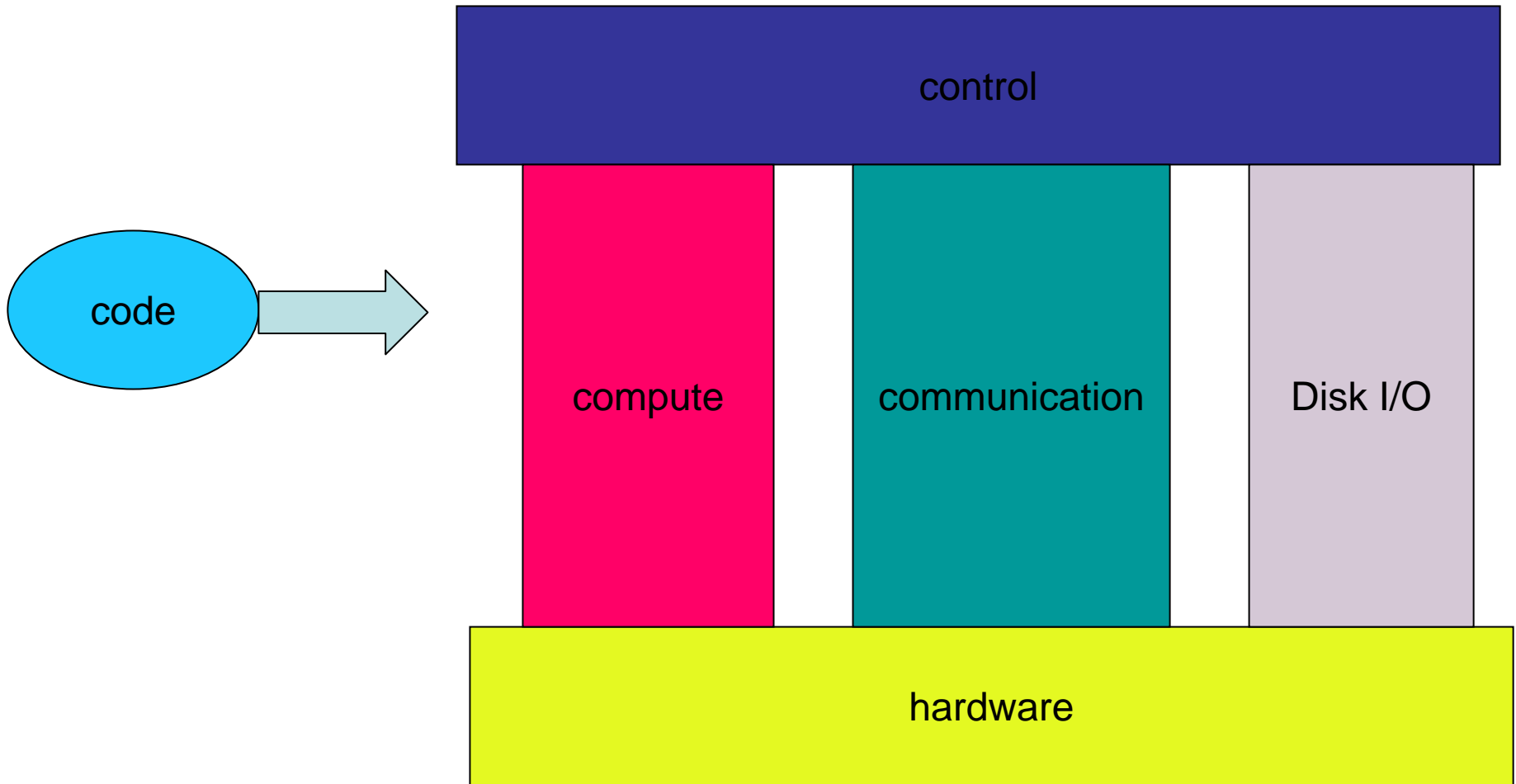
Steps required in EOM-CCSD

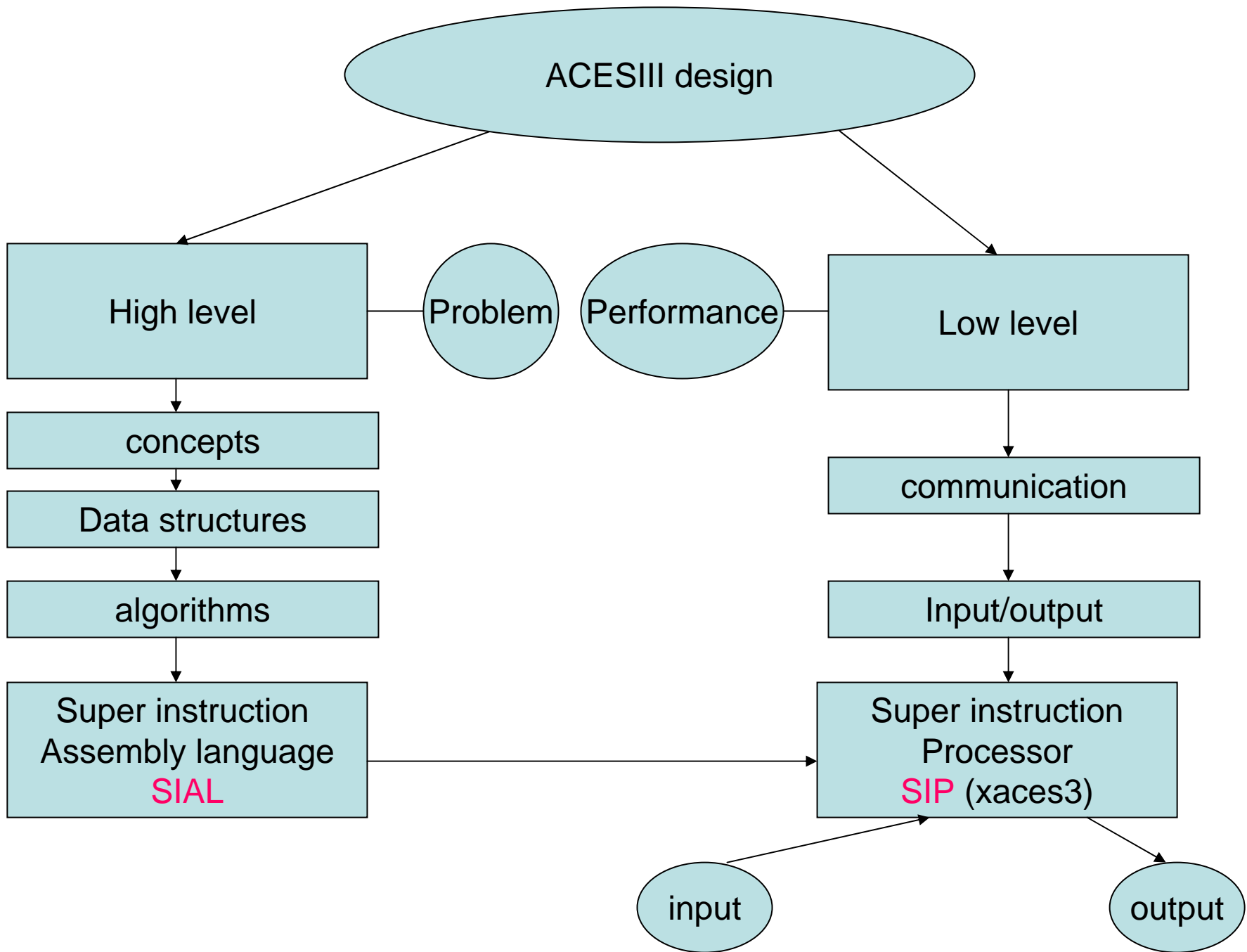
- SCF
- 2-electron integral transformation
- CCSD
- CI singles
- HBAR
- EOM
- Single determinant reference
- Transformed integrals
- Ground state wavefunction
- Initial excited state guess
- Effective Hamiltonian
- Excited states

Traditional Design



ACESIII Design





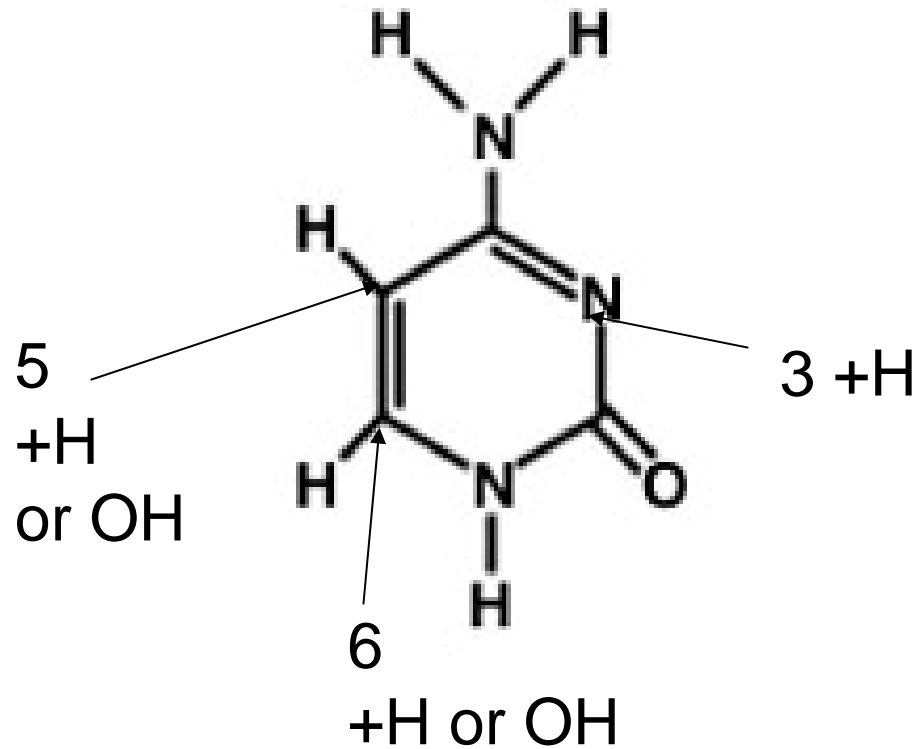
SIAL (Super Instruction Assembly Language)

- Key features
- Index segmentation
- Data blocking
- Task isolation
- Advantageous
- Flexibility
- Tune ability: Fast optimization
- New methods implemented in reduced time
- Portable

Cytosine

- One of five main nitrogenous bases used in storing and transporting information within a cell.
- Can be found as part of DNA, RNA, or as part of a nucleotide.
- Attacked by OH radicals(main species for DNA damage)
- Understanding the basic chemistry of OH radicals and DNA bases is an important step in characterizing the potential damage on DNA.

Geometry of cytosine



Some computational details

- Geometries were optimized at the MBPT(2) level using basis sets ranging from 6-31G to aug-cc-pvtz (PBS structures adequate).
- UHF reference functions were used in all calculations.
- Core electrons were not correlated.
- The C5-OH, C6-OH, C5-H, C6-H, and N3-H adducts were considered.

CCSD energies(Hartree) and energy differences(kJ/mol) for the adducts of cytosine. The MCSCF results are from M. Krauss and R. Osman, J. Phys. Chem. A, **101**, 33(1997).

Adduct	CCSD [Hartree]	Diff ₁ [kJ/mol]	Diff ₂ [kJ/mol]
C6-OH	-469.63198	-----	-----
C5-OH	-469.63175	0.61(19)	----
N3-H	-394.54380	----	----
C5-H	-394.53733	16.98(24)	----
C6-H	-394.53167	31.85(26)	14.86(2)

TABLE I: Vertical excitation energies[eV] for the H and OH radical adducts of cytosine. The MCSCF results are from M. Krauss and R. Osman, J. Phys. Chem. A, **101**, 33(1997).

Adduct	Method/BASIS	1	2	3	4	5
C6-OH	EOM/PBS	2.63	2.92	3.39	3.64	4.62
	EOM/aug-cc-pvtz	2.67	2.92	3.45	—	—
	MCSCF/DZd	2.92	2.97	—	3.51	4.52
	MCSCF/DZ	2.69	2.82	—	3.17	4.41
C5-OH	EOM/PBS	3.71	4.00	4.32	4.47	4.50
	MCSCF/DZ	3.64	3.93	—	—	—
C5-H	EOM/PBS	3.56	4.30	4.51	4.66	4.73
	MCSCF/DZ	3.92	4.14	—	—	—
C6-H	EOM/PBS	2.87	3.05	3.33	3.79	5.23
	MCSCF/DZ	2.69	2.89	3.13	4.04	—
N3-H	EOM/PBS	2.94	2.97	3.39	4.03	4.27
	EOM/aug-cc-pvtz	2.98	3.14	3.56	4.14	4.15
	MCSCF/DZ	3.17	—	—	—	—

The C6-OH adduct

- The lowest energy species among the OH radicals: 0.3kJ/mol lower in energy than the C5-OH radical and 21.3kJ/mol lower than the C4-OH radical. Yan Ju Ji et. al. Journal of Molecular Structure: Theochem 723 (2005) 123-129
- Consistent with our energy difference of 0.61kJ/mol.

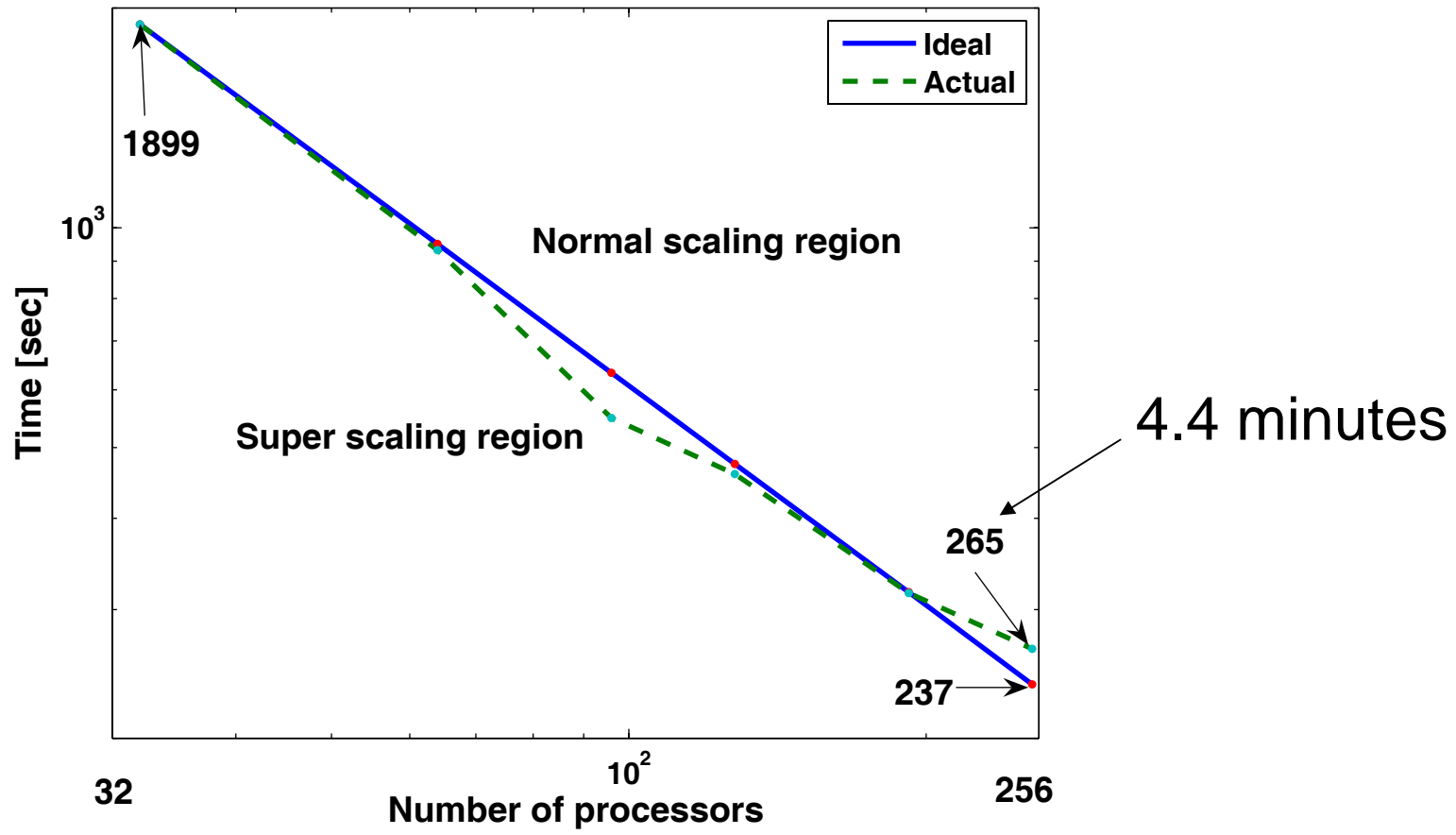
Vertical excitation energies[eV] for the C6-OH adduct of cytosine.

Method/ Basis	1	2	3	4	5
EOM/PBS	2.63	2.92	3.39	3.64	4.62
EOM/aug- cc-pvtz	2.67	2.92	3.45	-----	-----
MCSCF/D Zd	2.92	2.97	-----	3.51	4.52
MCSCF/D Z	2.69	2.82	-----	3.17	4.41

Performance: Scaling

- C5-OH adduct
- PBS basis (270 AO's)
- Number of alpha/beta correlated occupied orbitals: 34/33
- Reference: UHF
- Point group symmetry: C_1
- MO codes used in post HF calculations

Time for one CCSD-EOM iteration



Performance: Timings

- N3-H adduct
- Aug-cc-pvtz basis (506 AO's)
- 30/29 alpha/beta correlated occupied orbitals
- UHF reference
- C_1 point group symmetry
- 256 processors used (3/1 worker/server)

Time in minutes for calculation of the various modules required in the EOM-CCSD calculation

- SCF/iter
 - Transformation
 - CIS
 - Hbar
 - CCSD/iter
 - EOM/iter
 - Grand Total
- < 1 (42 iterations)
 - 12
 - 39
 - 88 (IO intense)
 - 11 (18 iterations)
 - 10.5 (146 iterations)
 - 1893