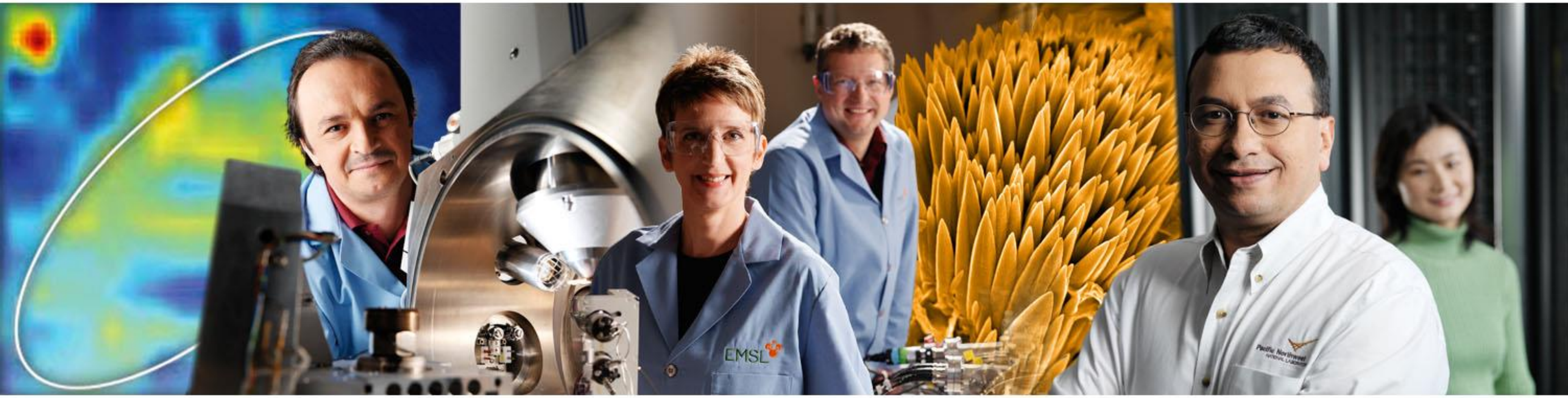
Critical Discussion of Recent NWChem Articles



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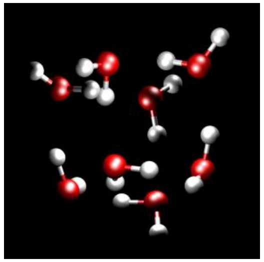
Approach in developing a force field for water

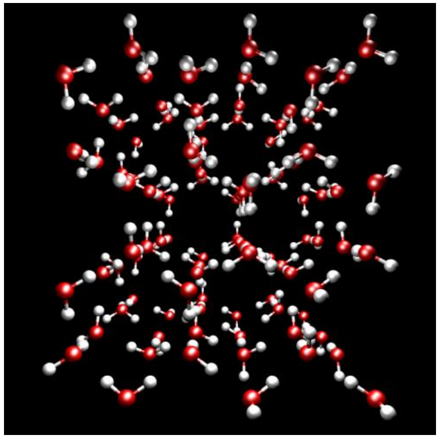
Fit to *ab-initio* cluster data → Perform Quantum MD Simulations → Compare with Experiment



Water octamer (D_{2d} isomer)

High level electronic structure calculations on water clusters: **quantifying the interactions at the molecular level**

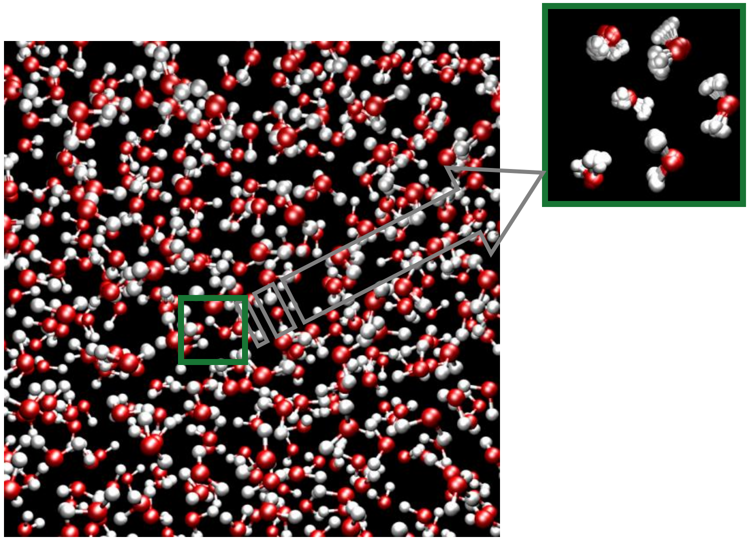
Development of the new generation of interaction potentials for water



$(H_2O)_{96}$ from an ice configuration

Electronic structure calculations and empirical potential dynamical simulations of chunks of ice and liquid water: **assessing the accuracy of the developed model**

Size effects on energetic properties and structural transitions



Liquid water

Fully quantum (Feynmann path integral) simulations of liquid water and ice with the developed interaction potential: **obtaining accurate energetics for condensed phases**

Macroscopic thermodynamic, structural and transport properties of liquid water and ice

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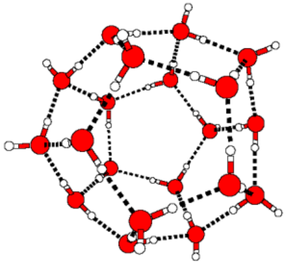
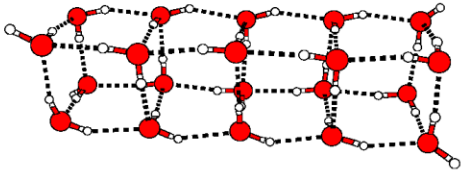
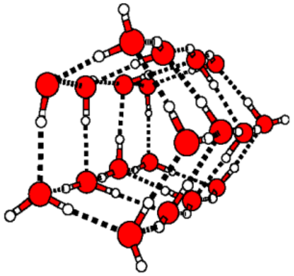
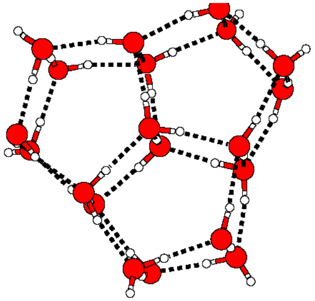
Energetics of $(H_2O)_{20}$

GS Fanourgakis, E Aprà and SS Xantheas, *JCP* **121**, 2655 (2004)

		TTM3-F	**MP2/CBS**	**$\lvert\Delta E/n\rvert$**	
"Dodecahedron"		-196.9	-200.1	0.16	
"Fused-cubes"		-2	-211.5	-212.6	0.06
"Face-sharing"			-210.4	-215.0	0.23
"Edge-sharing"			-212.3	-217.9	0.28

Convergence of the Enthalpy of Liquid Water

GS Fanourgakis, GK Schenter and SS Xantheas, *J. Chem. Phys.* **125**, 141102 (2006)

Enthalpy ΔH (= $-\Delta E + k_B T$)
(T = 298.15 K, ρ = 0.998 g/cm^3)

12.3 ± 0.02 kcal/mol (**Classical**)
11.2 ± 0.02 kcal/mol (**Quantum**)

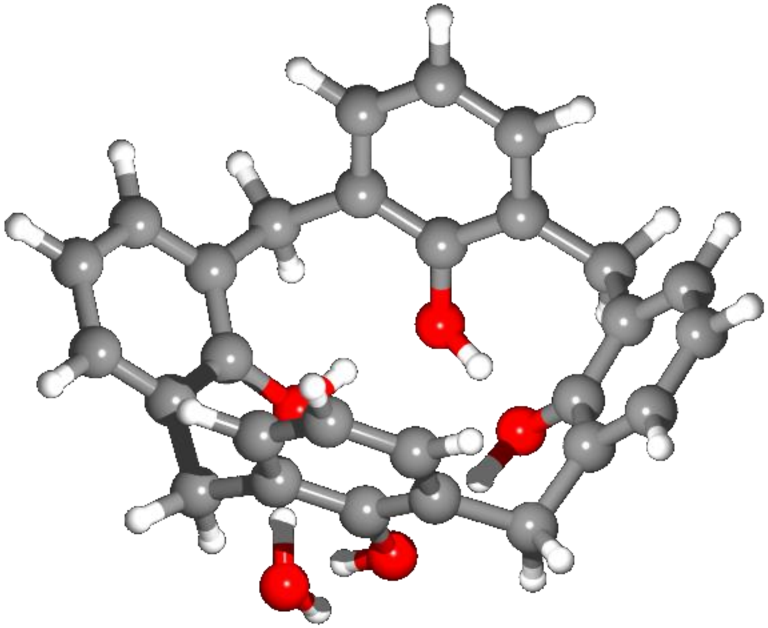
Best estimate: ΔH = 11.2 kcal/mol (exp. 10.51 kcal/mol)

Overestimated by ~ 6 % with respect to experiment

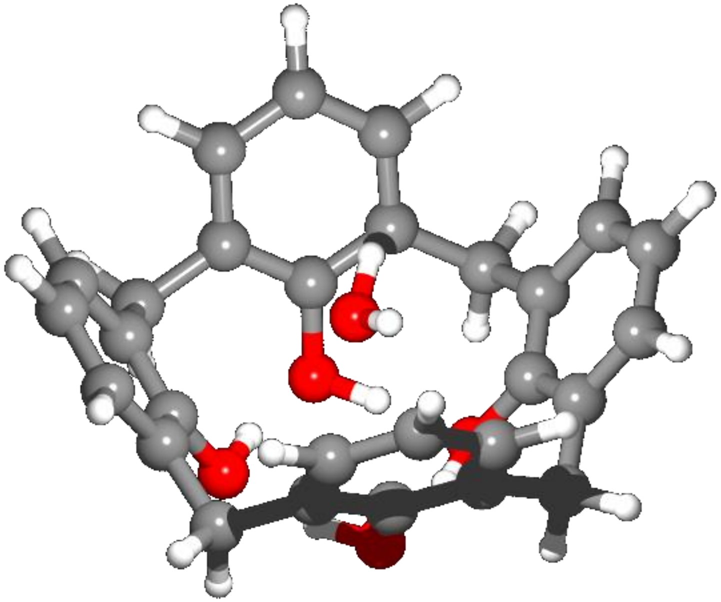
Fit to MP2 results which produce cluster binding energies that are 3-4% overestimated with respect to CCSD(T)
Remaining residual due to higher correlation effects (CCSDT, full triples)

New parametrization will be based on CCSD(T) cluster binding energies

Calix[4]arene: *endo*- *vs.* exo-complexes



Exo

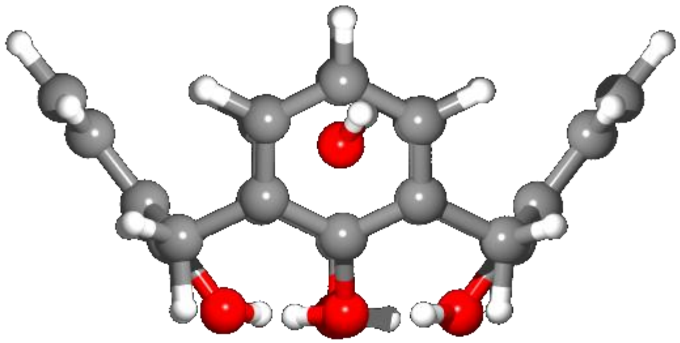


Endo

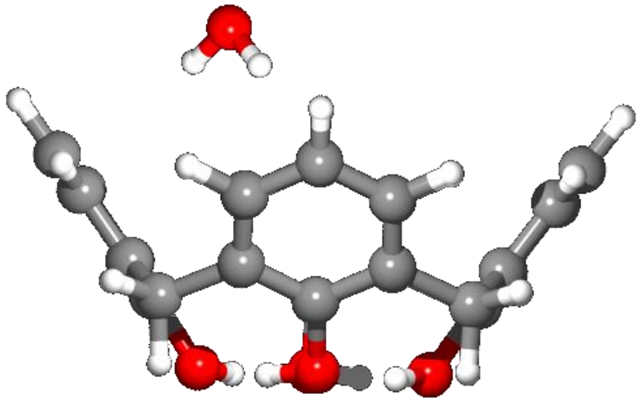
Relative stability of computed with

- •DFT
- •MP2 : endo more stable
- •CCSD(T): endo more stable

Calix[4]arene: DFT functionals



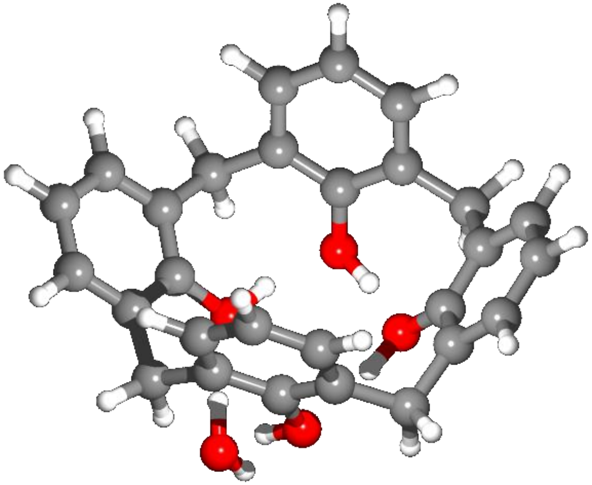
MP2



B3LYP

B3LYP: predicted exo- & looses water from cavity in exo-
M06-L, M06-2X predicted endo-
B97-D predicted endo-

Calix[4]arene: HW resources utilized



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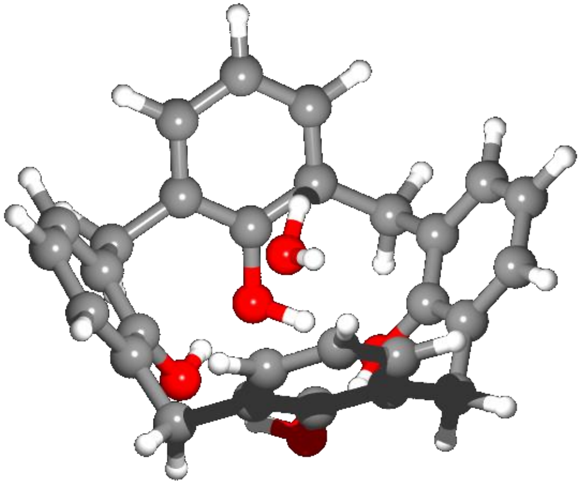
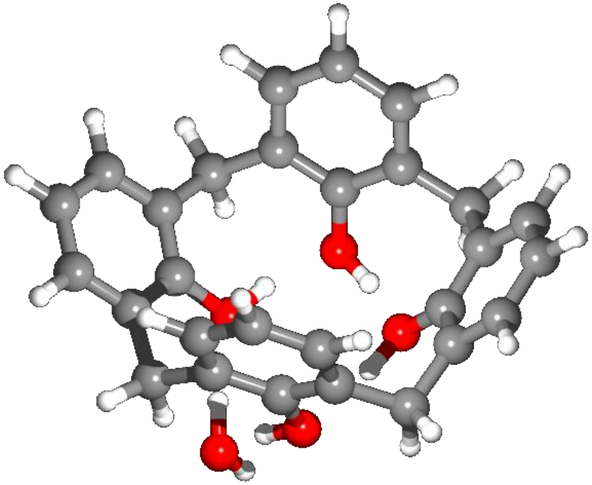


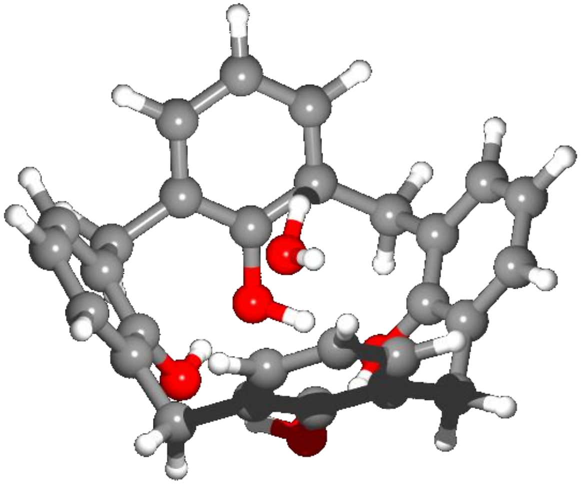
Endo

All the methods use I/O only for checkpoint/restart
DFT: # cores < 2400   numerical cost scales as N-N^2
MP2: # cores < 3000   numerical cost scales as N^5
CCSD(T) up to 144000 numerical cost scales as N^7

Calix[4]arene: MP2



Exo



Endo

Aug-cc-pv5z basis set
6271 basis functions
I/O algorithm “cheated” by caching I/O operations in memory
33K cores used out of 66K (memory requirements)
Wall-time: ~10 hours

Excited-state EOMCC calculations for π-conjugated chromophores

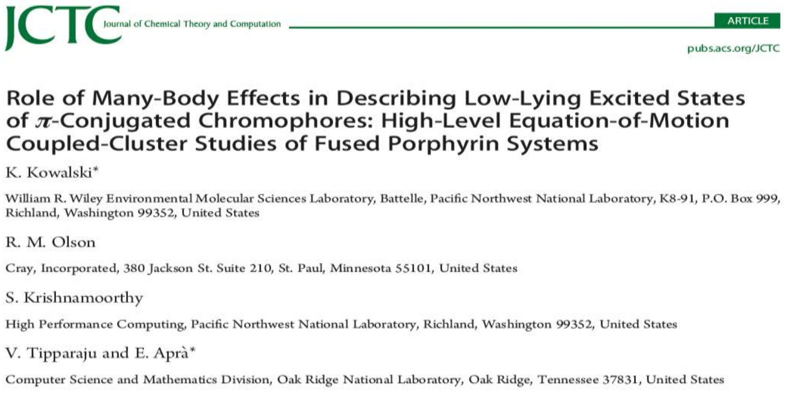
- **Goal:**

  Estimate of the role of particular correlation effects in description of the excitation energies in π-conjugated chromophores (light-harvesting systems & optical devices by design)

- **NWChem functionalities:** EOMCCSD and CR-EOMCCSD(T) implementations

- **Conclusions:**

  We demonstrated that for singly excited states for systems of interest the inclusion of triply excited configurations is crucial for attaining qualitative agreement with experiment.



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Role of Many-Body Effects in Describing Low-Lying Excited States of π-Conjugated Chromophores: High-Level Equation-of-Motion Coupled-Cluster Studies of Fused Porphyrin Systems

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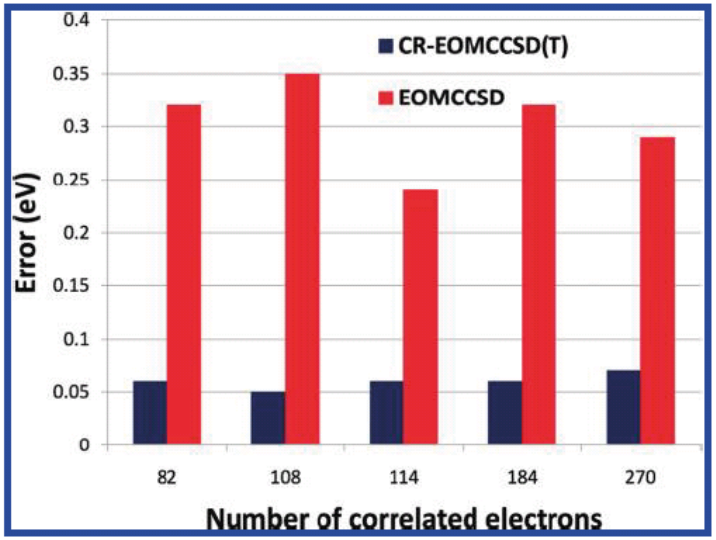


Excited states in acenes

- **Goal:**

  Description of the low-lying excited states in acenes

- **NWChem functionalities:**

  CAM-B3LYP; CR-EOMCCSD(T)

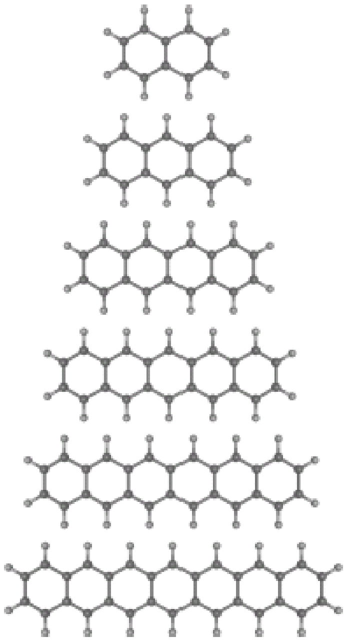
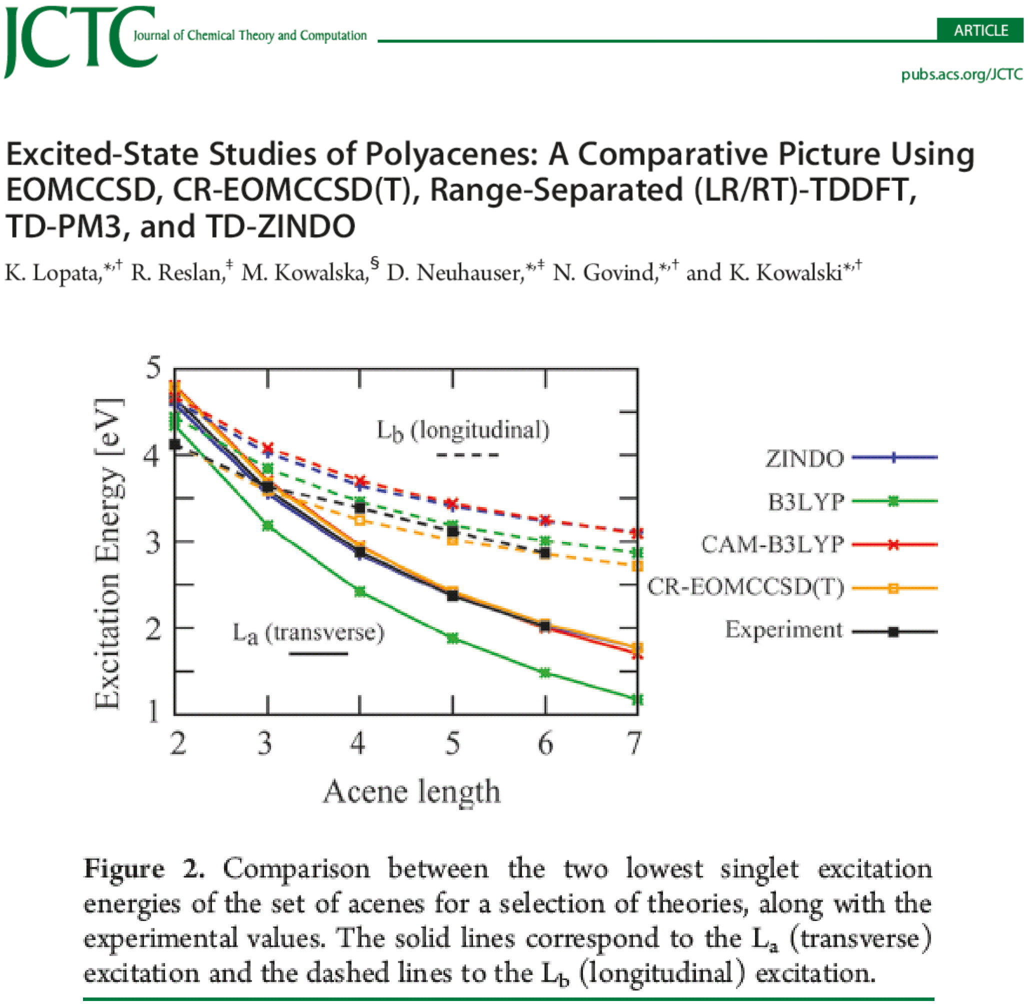


Figure 1. Structures of the acenes studied. From top to bottom: naphthalene ($N = 2$), anthracene ($N = 3$), tetracene ($N = 4$), pentacene ($N = 5$), hexacene ($N = 6$), heptacene ($N = 7$).



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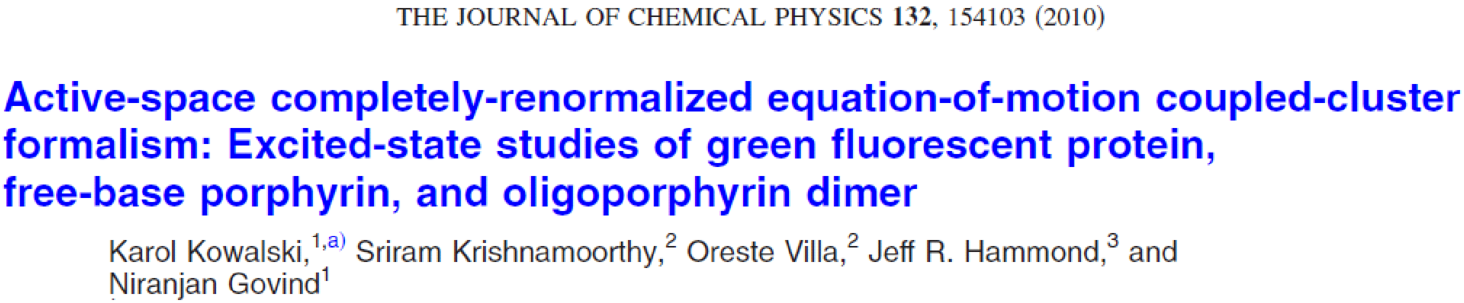
Excited-State Studies of Polyacenes: A Comparative Picture Using EOMCCSD, CR-EOMCCSD(T), Range-Separated (LR/RT)-TDDFT, TD-PM3, and TD-ZINDO

K. Lopata,[*,†] R. Reslan,[‡] M. Kowalska,[§] D. Neuhauser,[*,‡] N. Govind,[*,†] and K. Kowalski[*,†]

Figure 2. Comparison between the two lowest singlet excitation energies of the set of acenes for a selection of theories, along with the experimental values. The solid lines correspond to the L_a (transverse) excitation and the dashed lines to the L_b (longitudinal) excitation.

Active-space EOMCCSD(T) methods



THE JOURNAL OF CHEMICAL PHYSICS **132**, 154103 (2010)

Active-space completely-renormalized equation-of-motion coupled-cluster formalism: Excited-state studies of green fluorescent protein, free-base porphyrin, and oligoporphyrin dimer

Karol Kowalski,[1,a)] Sriram Krishnamoorthy,[2] Oreste Villa,[2] Jeff R. Hammond,[3] and Niranjan Govind[1]

- **Goal:**

  Test the novel reduced-scaling EOMCC methods
- **NWChem functionalities:** active-space CR-EOMCCSD(T) formulation
- **Conclusions:** see Table

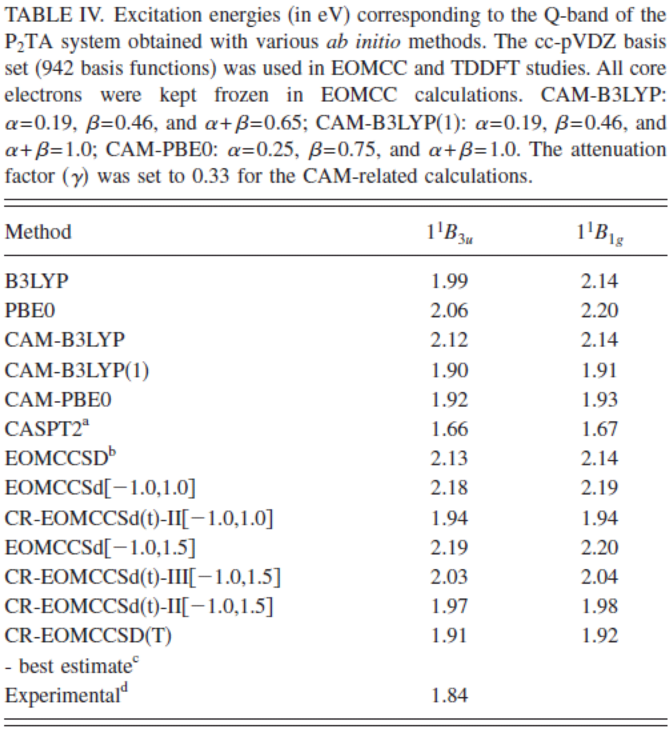
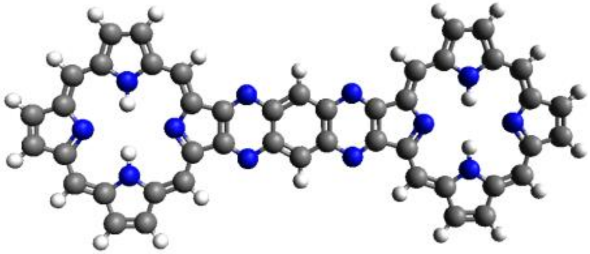


TABLE IV. Excitation energies (in eV) corresponding to the Q-band of the P_2TA system obtained with various *ab initio* methods. The cc-pVDZ basis set (942 basis functions) was used in EOMCC and TDDFT studies. All core electrons were kept frozen in EOMCC calculations. CAM-B3LYP: $\alpha=0.19$, $\beta=0.46$, and $\alpha+\beta=0.65$; CAM-B3LYP(1): $\alpha=0.19$, $\beta=0.46$, and $\alpha+\beta=1.0$; CAM-PBE0: $\alpha=0.25$, $\beta=0.75$, and $\alpha+\beta=1.0$. The attenuation factor (γ) was set to 0.33 for the CAM-related calculations.

Method	1^1B_{3u}	1^1B_{1g}
B3LYP	1.99	2.14
PBE0	2.06	2.20
CAM-B3LYP	2.12	2.14
CAM-B3LYP(1)	1.90	1.91
CAM-PBE0	1.92	1.93
CASPT2^a	1.66	1.67
EOMCCSD^b	2.13	2.14
EOMCCSd[−1.0,1.0]	2.18	2.19
CR-EOMCCSd(t)-II[−1.0,1.0]	1.94	1.94
EOMCCSd[−1.0,1.5]	2.19	2.20
CR-EOMCCSd(t)-III[−1.0,1.5]	2.03	2.04
CR-EOMCCSd(t)-II[−1.0,1.5]	1.97	1.98
CR-EOMCCSD(T) - best estimate^c	1.91	1.92
Experimental^d	1.84	



Studies of the effect of dopands on the excited states of the TiO_2

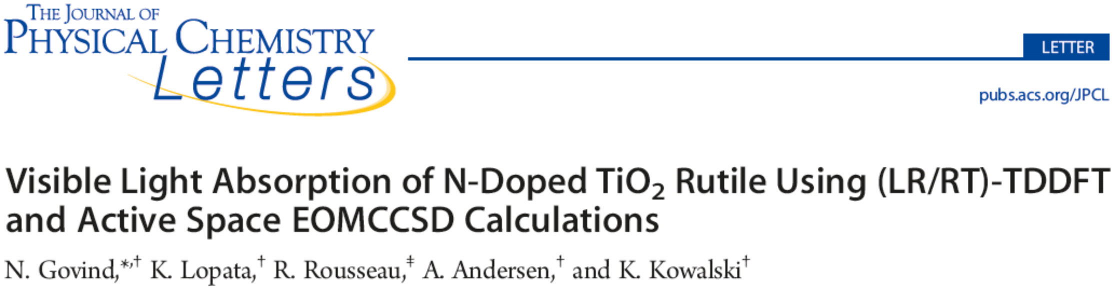
- **Goal:**

  Study the effect of dopands in TiO_2 rutile
- **NWChem functionalities:** (LR/RT)-TDDFT, active-space EOMCCSD & Embedded Cluster Model
- **Conclusions:**

Visible Light Photoresponse of pure and N-doped TiO_2 (active-space EOMCCSD calculations, 400 correlated electrons):

TiO_2 EOMCCSd ➔ 3.84 eV

N-doped TiO_2 EOMCCSd ➔ 2.79 eV



THE JOURNAL OF PHYSICAL CHEMISTRY Letters

LETTER

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Visible Light Absorption of N-Doped TiO_2 Rutile Using (LR/RT)-TDDFT and Active Space EOMCCSD Calculations

N. Govind,*,† K. Lopata,† R. Rousseau,‡ A. Andersen,† and K. Kowalski†

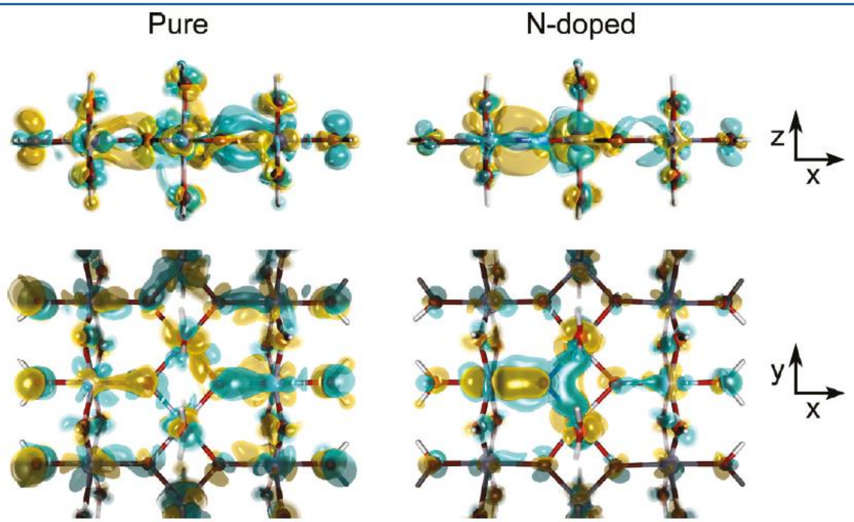


Figure 5. Side and top views of the excited-state charge density in the pure and N-doped clusters. The surfaces represent deviations of the charge density from the ground state (at an oscillation maximum), with cyan denoting charge accumulation and yellow depletion. The pure system was excited at 3.55 eV, which corresponds to the very bright absorption soon after the band edge, and the N-doped system was excited at the broad shoulder peak at 2.70 eV.

Studies of the effect of dopands on the excited states of the TiO_2 (cntd.)

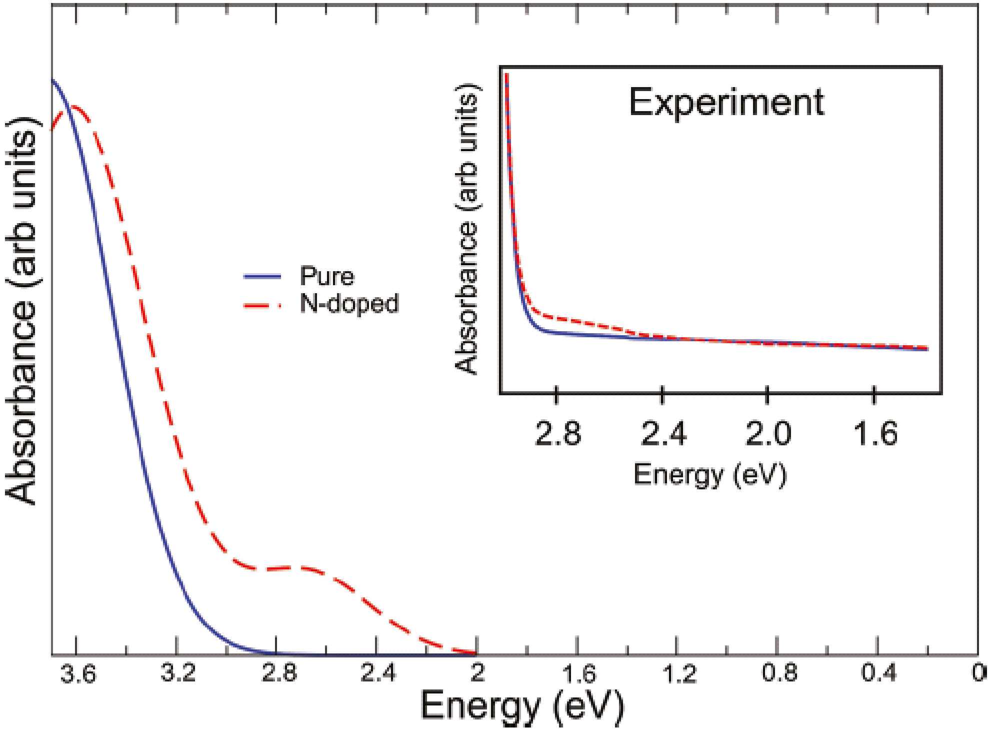


Figure 4. Optical spectra of pure (blue) and N-doped (red) TiO_2 rutile obtained using TDDFT (B3LYP) calculations. Spectra in the inset are from Chambers and co-workers[10] for pure (blue) and N-doped (red) TiO_2 rutile.

Excited states of acenes (cntd)

2.2. Real-Time TDDFT. In real-time time-dependent density functional theory (RT-TDDFT), the time-dependent Kohn–Sham (KS) equations are explicitly propagated in time:

$$i\frac{\partial\psi_i(\mathbf{r},t)}{\partial t} = \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}[\rho](\mathbf{r},t)\right]\psi_i(t) \qquad (5)$$

$$= \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r},t) + v_{\mathrm{H}}(\mathbf{r},t) + v_{\mathrm{XC}}[\rho](\mathbf{r},t)\right]\psi_i(t) \qquad (6)$$

where $\rho(\mathbf{r},t)$ is the charge density, $v_{\mathrm{ext}}(\mathbf{r},t)$ is the external potential describing the nuclear–electron and applied field contributions, $v_{\mathrm{H}}(\mathbf{r},t)$ is the electron–electron potential, and $v_{\mathrm{XC}}[\rho](\mathbf{r},t)$ is the exchange-correlation potential, which is henceforth assumed to depend only on the instantaneous density (adiabatic approximation). In a Gaussian-orbital basis, it is simpler to work with density matrices rather than KS orbitals, in which case the evolution of the electronic density is governed by the von Neumann equation:

$$i\frac{\partial\mathbf{P}'}{\partial t} = [\mathbf{F}'(t), \mathbf{P}'(t)] \qquad (7)$$

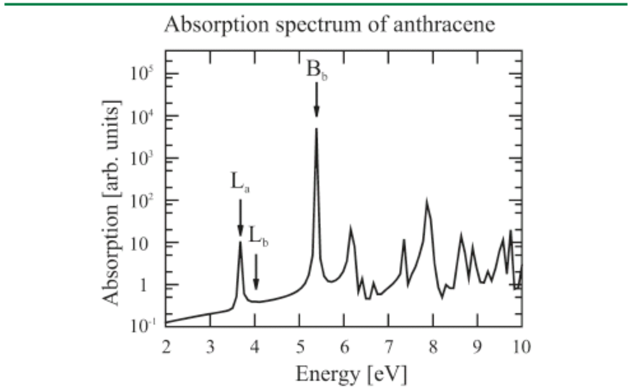
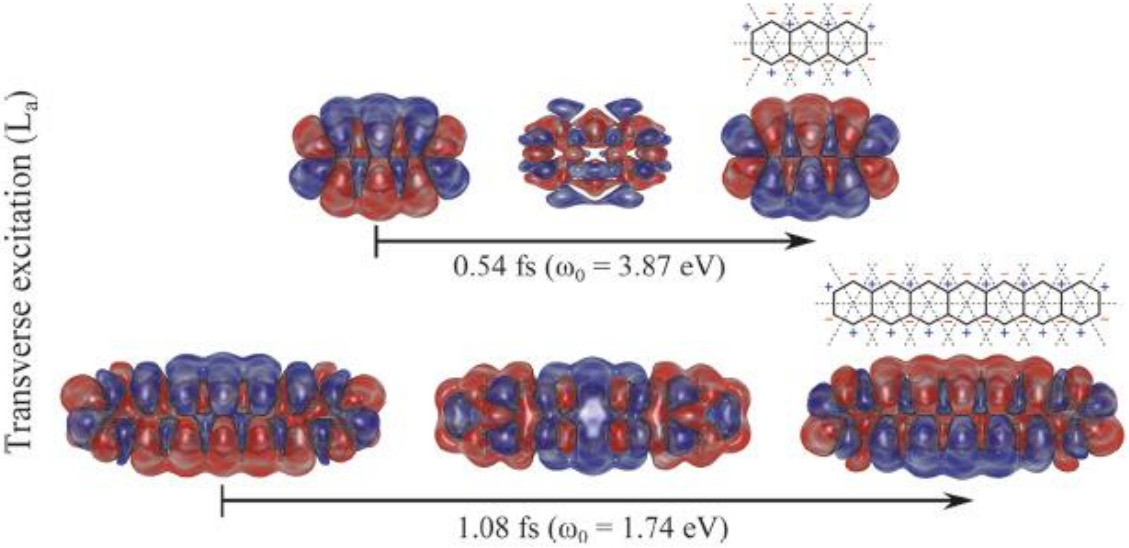


Figure 3. Absorption spectrum of anthracene ($N = 3$) obtained via RT-TDDFT (POL1/BNL). The bright L_a and dim L_b peaks correspond to transverse and longitudinal excitations, respectively. The intensely bright longitudinal UV B_b peak is visualized in Figure 4 but not compared in Table 1.



Excitons in ionic systems

TDDFT→ infty → 5.81 eV

EOMCCSD → infty → 6.38 eV

Surface Exciton Energy:
6.35 +/- 0.10 eV (expt)

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Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Excitons in potassium bromide: A study using embedded time-dependent density functional theory and equation-of-motion coupled cluster methods

N. Govind [a,*], P.V. Sushko [b,c], W.P. Hess [d], M. Valiev [a], K. Kowalski [a,*]

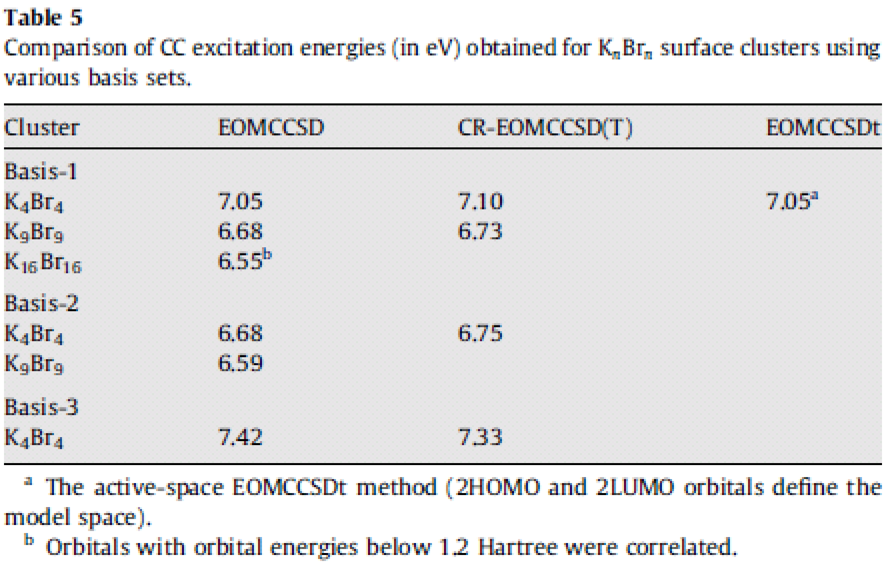


Table 5
Comparison of CC excitation energies (in eV) obtained for K_nBr_n surface clusters using various basis sets.

Cluster	EOMCCSD	CR-EOMCCSD(T)	EOMCCSDt
Basis-1			
K_4Br_4	7.05	7.10	7.05[a]
K_9Br_9	6.68	6.73	
$K_{16}Br_{16}$	6.55[b]		
Basis-2			
K_4Br_4	6.68	6.75	
K_9Br_9	6.59		
Basis-3			
K_4Br_4	7.42	7.33	

[a] The active-space EOMCCSDt method (2HOMO and 2LUMO orbitals define the model space).

[b] Orbitals with orbital energies below 1.2 Hartree were correlated.

$$E_{total}[\rho](Z,\mathbf{R},q,\tau) = E_{qm}[\rho](Z,\mathbf{R}) + E_{env}(q,\tau) + E_{int}[\rho](Z,\mathbf{R},q,\tau) \qquad (1)$$

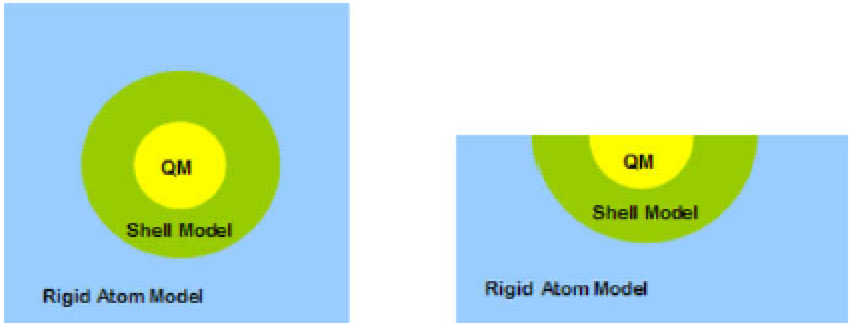


Fig. 1. Partitioning of the total system. The figure on the left shows the schematic of a bulk embedding and the figure on the right represents a surface embedding. The interactions between the various regions are defined in Eq. (2).

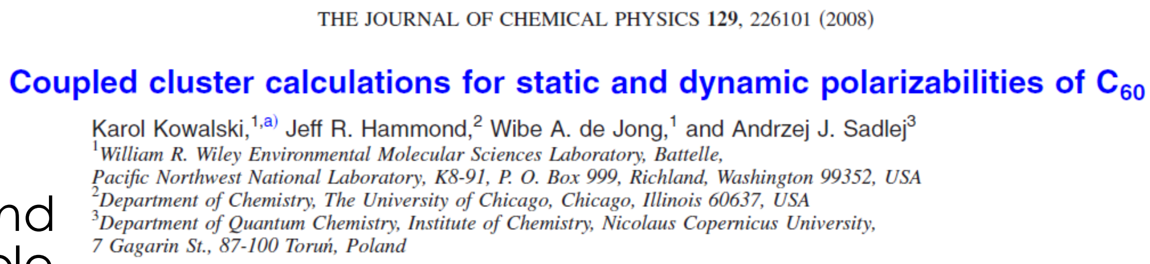
Calculations of the dipole polarizabilites for C_{60} using CCSD method

- **Goal:**

  Calculations for static and dynamic dipole polarizabilirties in C60
- **NWChem functionalities:**

  Linear response CCSD module
- **Conclusions:**

  Electron correlation effects are very important in describing static and frequency dependent properties in delocalized systems



THE JOURNAL OF CHEMICAL PHYSICS **129**, 226101 (2008)

Coupled cluster calculations for static and dynamic polarizabilities of C_{60}

Karol Kowalski,[1,a)] Jeff R. Hammond,[2] Wibe A. de Jong,[1] and Andrzej J. Sadlej[3]

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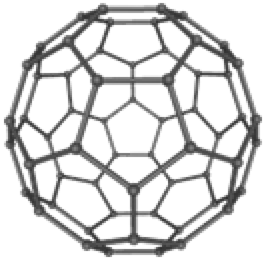
[2]Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, USA

[3]Department of Quantum Chemistry, Institute of Chemistry, Nicolaus Copernicus University, 7 Gagarin St., 87-100 Toruń, Poland



Static and frequency dependent polarizabilities of C_{60} in Å^3

Wavelength (nm)	CCSD	CC2	Expt.
∞	82.20	92.33	76.5±8
1064	83.62	94.77	79±4
532	88.62		

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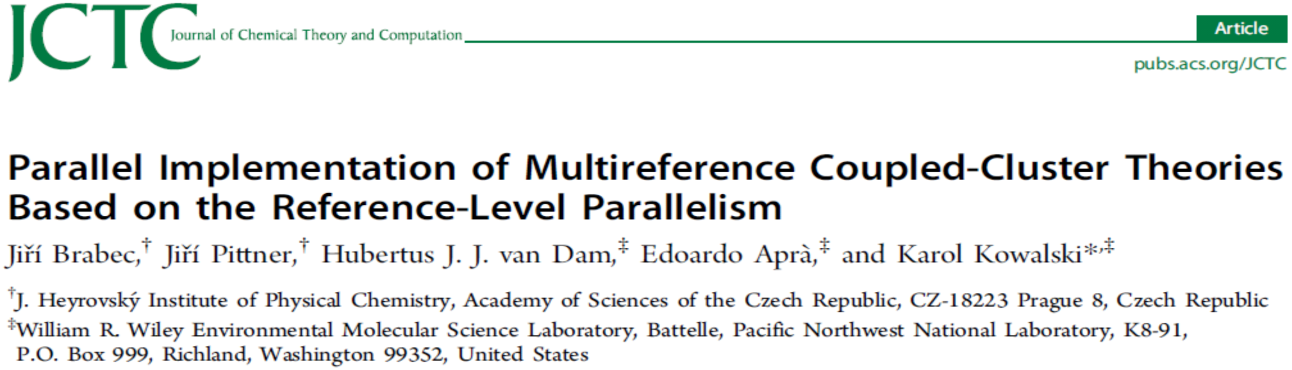
Development of Parallel Multireference CC implementations



JCTC Journal of Chemical Theory and Computation

Article

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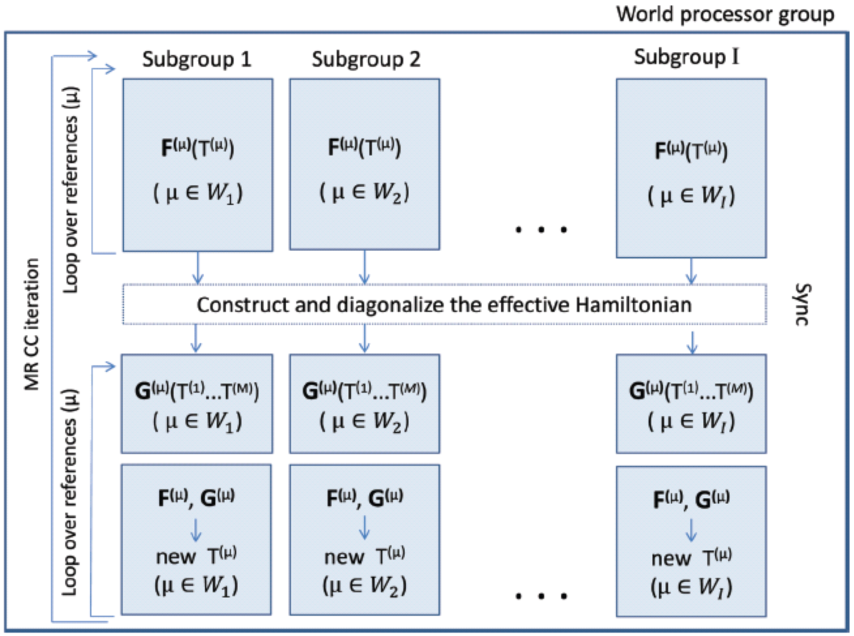
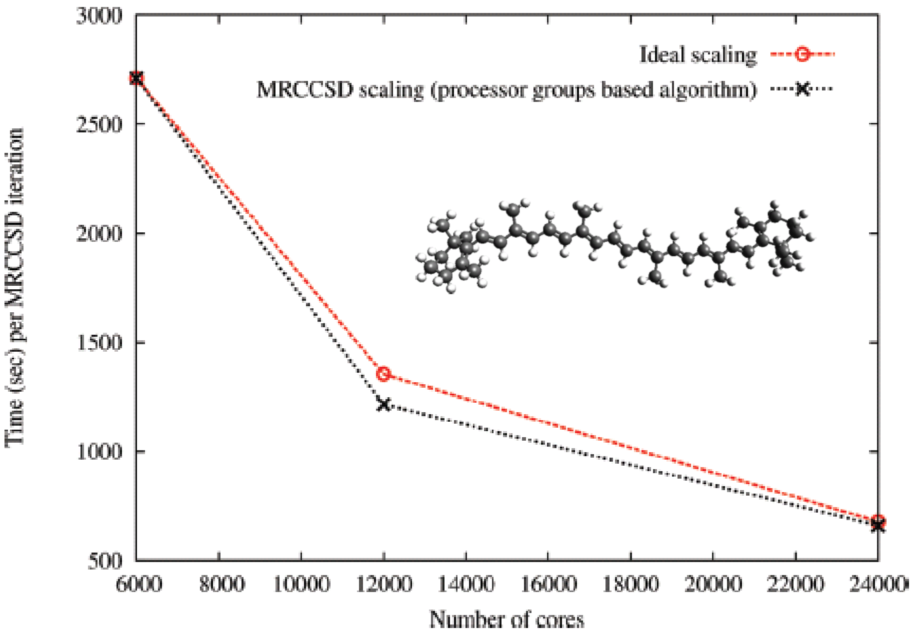
Parallel Implementation of Multireference Coupled-Cluster Theories Based on the Reference-Level Parallelism

Jiří Brabec,[†] Jiří Pittner,[†] Hubertus J. J. van Dam,[‡] Edoardo Aprà,[‡] and Karol Kowalski*[,‡]

[†]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, CZ-18223 Prague 8, Czech Republic
[‡]William R. Wiley Environmental Molecular Science Laboratory, Battelle, Pacific Northwest National Laboratory, K8-91, P.O. Box 999, Richland, Washington 99352, United States





Questions?