

# Computational Exploration of Non- Valence Anions from Biological Quinones

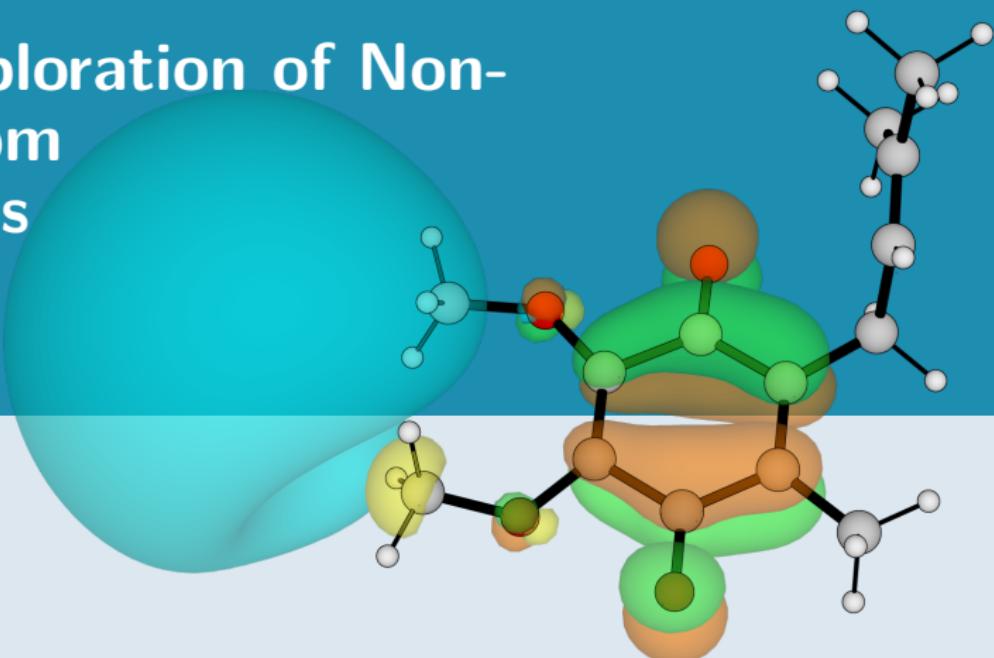
TCCM Thesis Defense

Mauro Gascón

Promotor: Prof. Thomas C. Jagau

Mentor: Robin E. Moorby

30th June 2025



# Overview

## ① Introduction

Non-valence anions  
Ubiquinone

## ② Theory

Second-Order Approximate Coupled Cluster  
Equation-of-Motion Electron-Attachment

## ③ Computational Methods

## ④ Results

Methoxy chains rotation

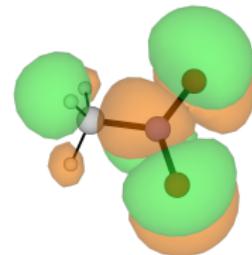
## ⑤ Conclusions

# Non-valence anions

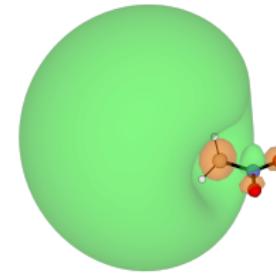
The excess electron is bound by long-range forces (e.g., dipole, quadrupole). The ‘extra’ electron density is located far from the molecule

Found in atmospheric, interstellar, and biological environments; they act as ‘doorway’ states for electron attachment

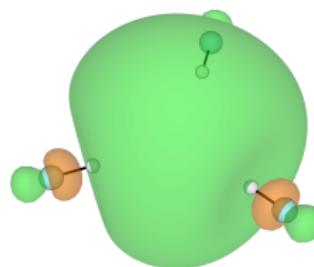
- Extremely diffuse electron clouds
- Sensitive to correlation and environmental effects
- Require huge basis sets and accurate correlation treatment



Valence-bound anion of  
nitromethane



Dipole-bound anion of nitromethane

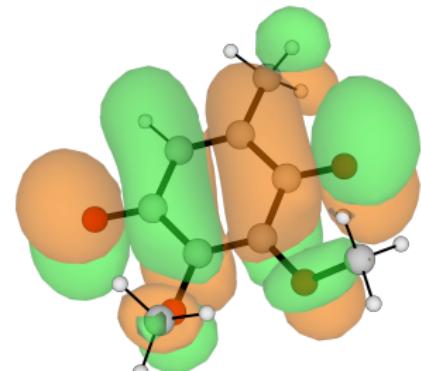
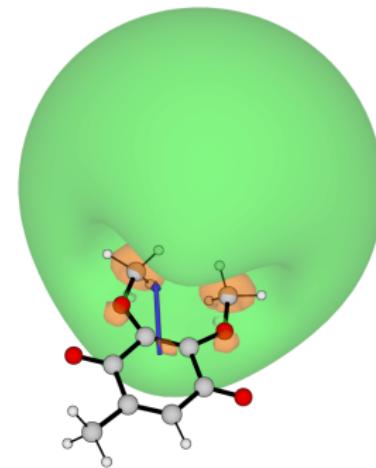
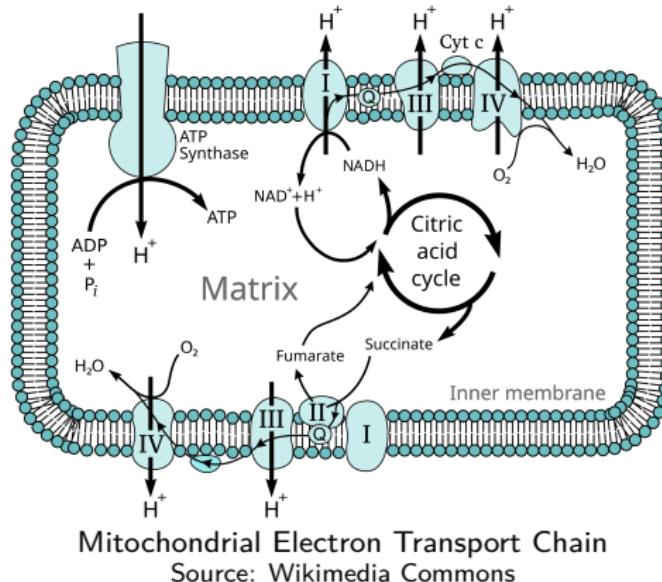


(HF)<sub>3</sub> solvated electron

# Biological Quinones: Ubiquinone (CoQ)

Quinones are essential electron carriers in biological processes

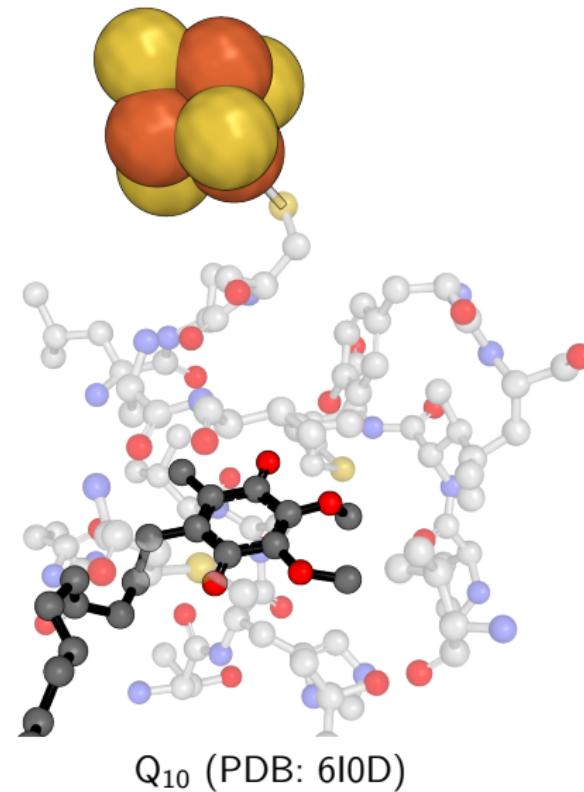
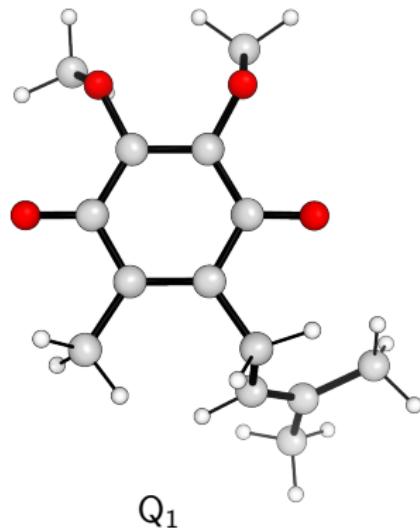
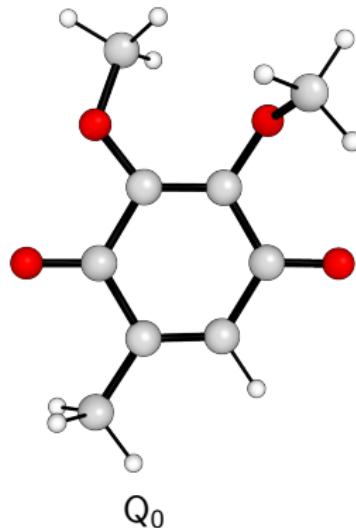
- Component of electron transport chains in bacterial photosynthesis and aerobic respiration
- Capable of both valence and dipole bound anion states



# Ubiquinone Structure

Each part of the molecule plays a distinct function:

- Quinone head involved in the electron transfer
- Isoprenoid tail responsible for the solubility in the membrane
- Methoxy chains determine the dipole moment



# CC2

Second-order approximate coupled-cluster singles and doubles (CC2) method is obtained from a perturbative analysis of the CCSD model

- Doubles amplitudes are identical to MP2, singles are treated exactly
- Lowers computational scaling from CCSD:  $O(N^5)$  vs.  $O(N^6)$
- Allows treatment of “big” molecules: > 25 heavy atoms

$$|\Psi_{\text{CC2}}\rangle = e^{\hat{T}_{\text{CC2}}} |\Psi_0\rangle$$

$$\hat{T}_{\text{CC2}} = 1 + \sum_{ai} t^a a_a^\dagger a_i + \frac{1}{2} \sum_{ab} \sum_{ij} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

$$t_{ij}^{ab} = \frac{1}{1 + \delta_{ij}\delta_{ab}} \frac{\langle \phi_a \phi_b || \phi_i \phi_j \rangle}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

Method	Scaling	Memory
CCSD	$O(N^6)$	$O(N^4)$
CC2	$O(N^5)$	$O(N^4)^*$

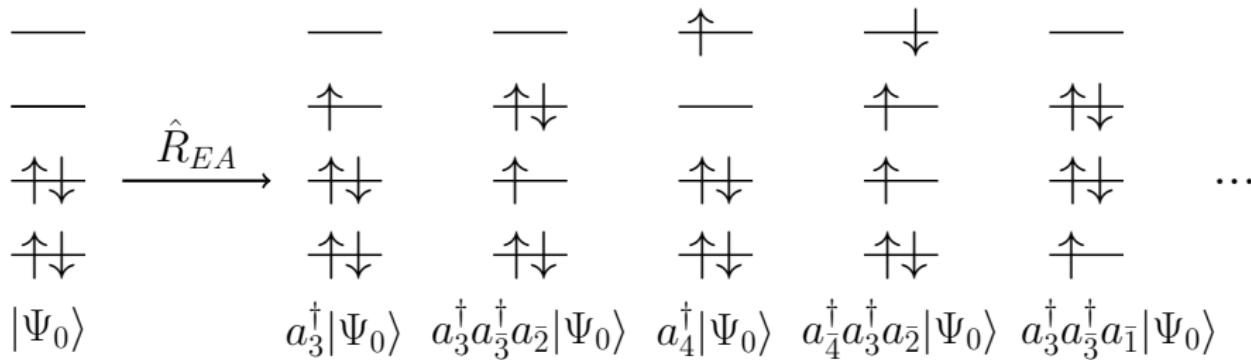
\*  $O(N^3)$  with RI approximation.

# EOM-EA

Equation-of-motion electron-attachment coupled-cluster (EOM-EA-CC) methods are particularly well suited to study non-valence anions. The description is based on the wave function of the parent neutral molecule

$$|\Psi_{\text{EA}}\rangle = \hat{R}_{\text{EA}} |\Psi_0\rangle$$

$$\hat{R}_{\text{EA}} = \sum_a r^a a_a^\dagger + \frac{1}{2} \sum_{ab} \sum_i r_i^{ab} a_a^\dagger a_i a_b^\dagger + \dots$$



# Computational methods

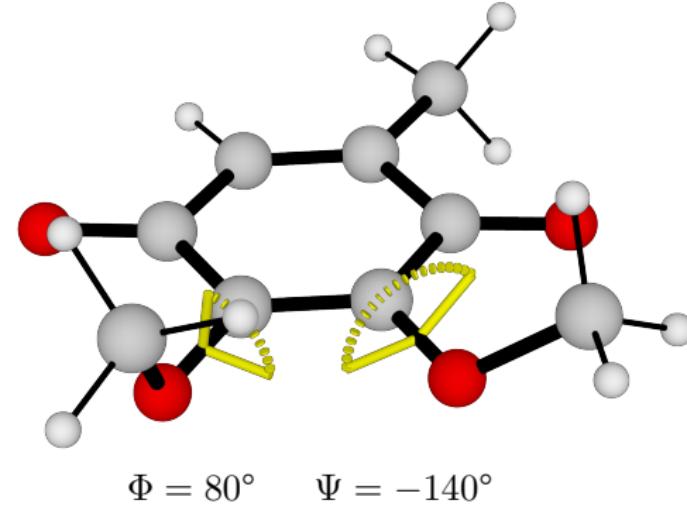
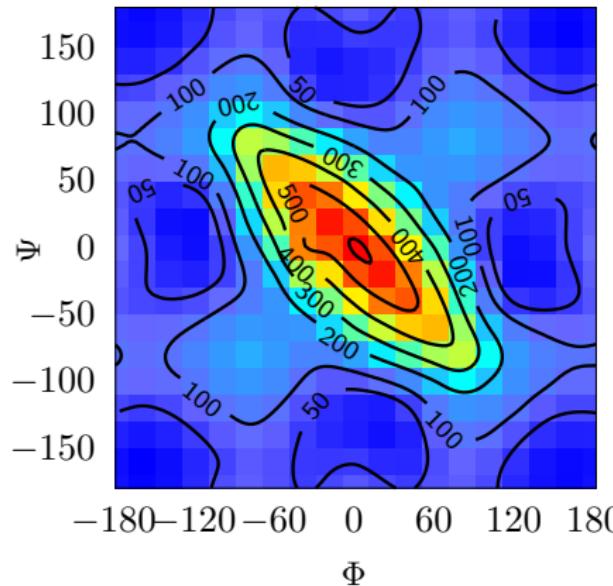
All calculations were performed using the *Q-Chem* software.

- Optimizations performed at TPSS+D3BJ/ma-def2-TZVP EA calculated at the RI-EOM-EA-CC2 using the neutral ground state as CC reference state
- aug-cc-pVDZ basis further augmented by 3 s-shells on hydrogen atoms and 6 s- and 3 p-shells on all non-hydrogen atoms
- Dyson orbitals calculated at the RI-EOM-EA-CC2 level (implemented in this thesis)

# Potential Energy Surface

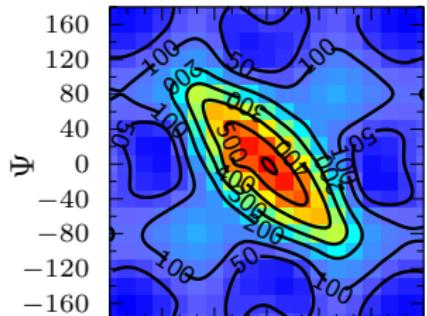
We can construct surfaces from the methoxy rotations ( $\Psi$  and  $\Phi$ ) of the Q0 model.

- PES is constructed by scanning the dihedral angles  $\Phi$  and  $\Psi$  and visualized as a 2D map
- Rest of the molecule, which is quite rigid, is optimized at each point

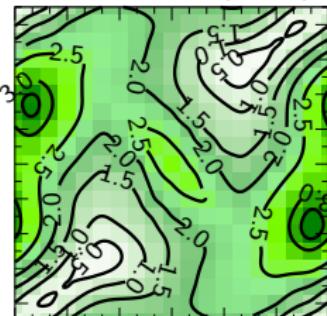


# Potential Energy Surfaces of Q0

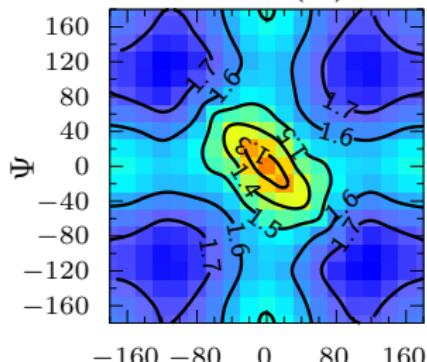
Conformational Energy (meV)



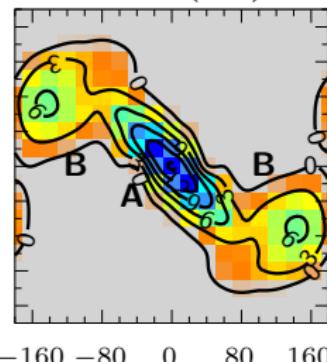
Dipole Strength (Debye)



VBA EA (eV)

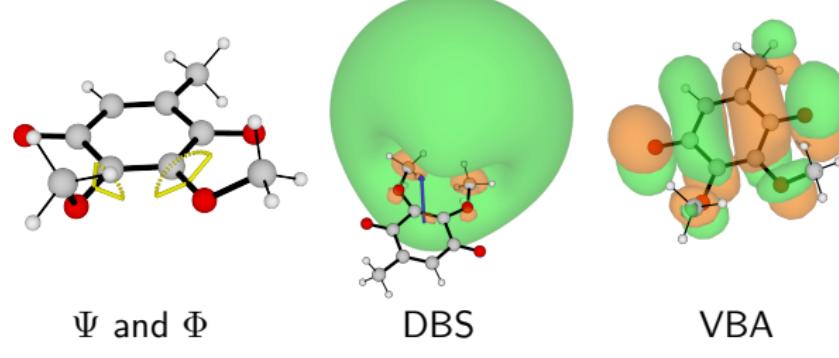


DBA EA (meV)

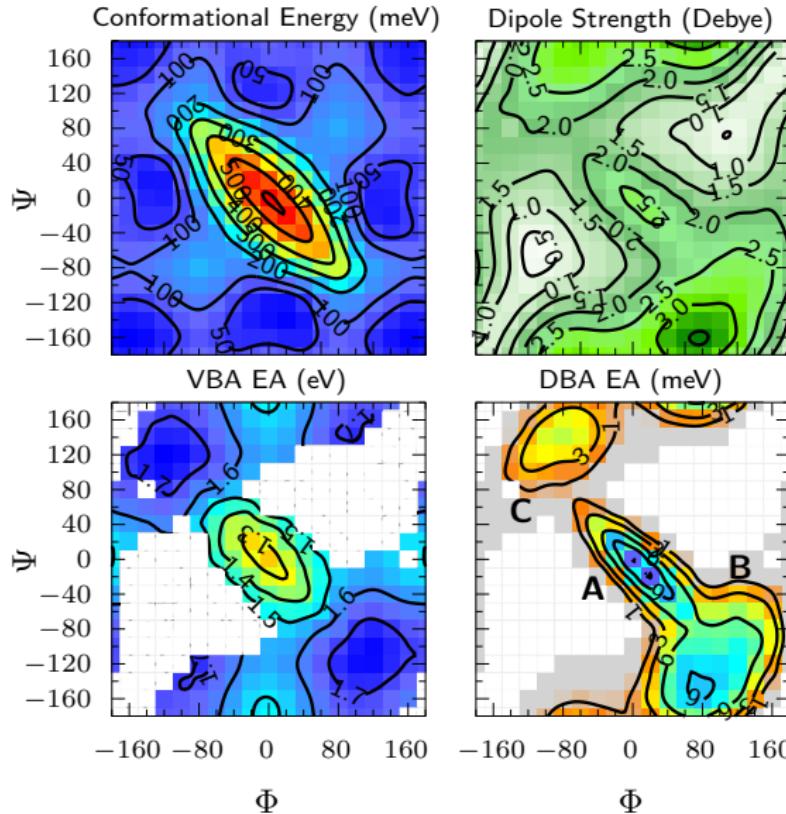


$C_2$  symmetry

- **PES:** Several minima
- **Dipole Moment:** Two strong dipole regions
- **VBS:** Dependent on electron donating or withdrawing character of the methoxy groups
- **DBS:** Follows dipole strength

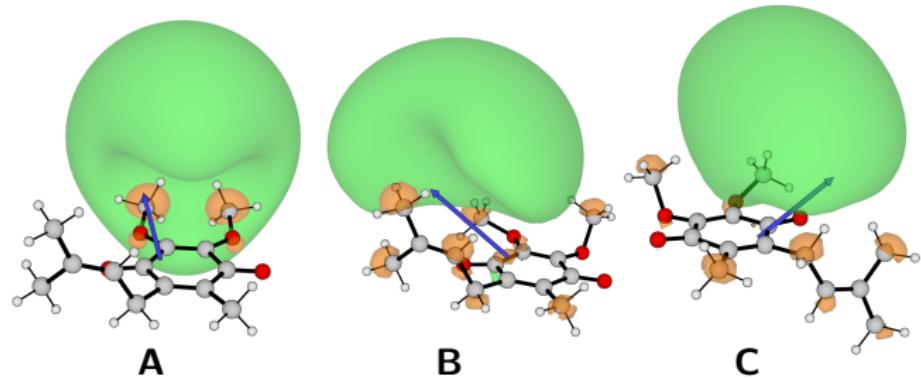


# Potential Energy Surfaces of Q1



Similar to Q0, though isoprene tail breaks the symmetry.

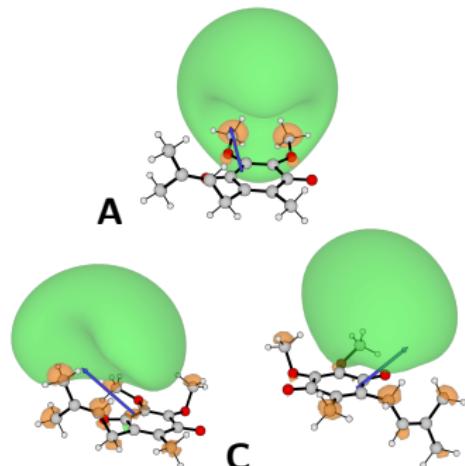
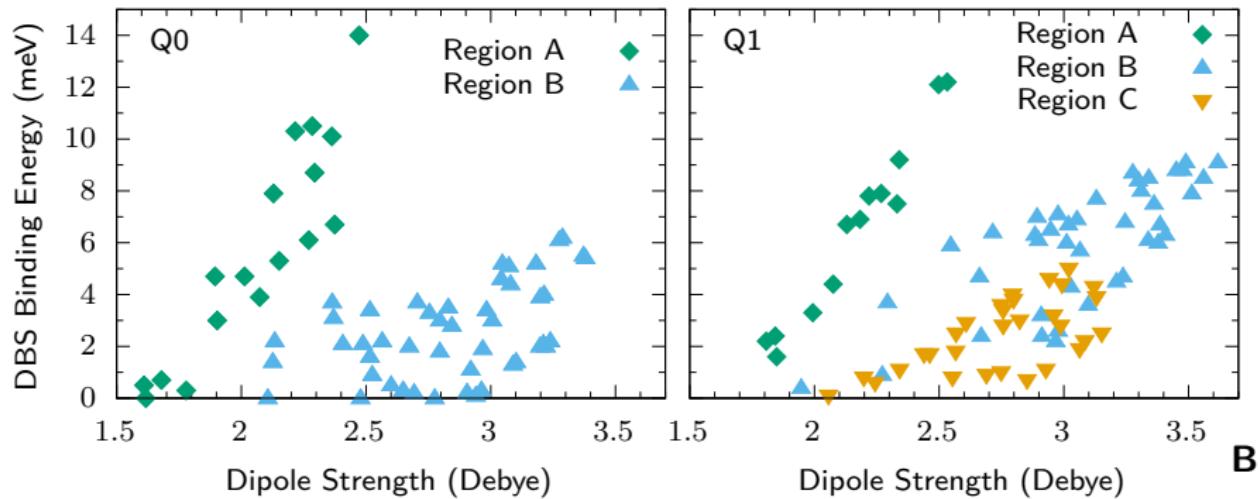
- **PES:** Isoprene tail distant, analogous to Q0.
- **Dipole Moment:** Isoprene adds fixed dipole.
- **VBS:** Isoprene tail has minor effect.
- **DBS:** Isoprene has a pronounced effect.



# DBS Populations

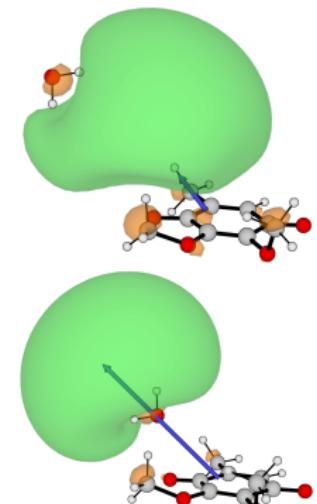
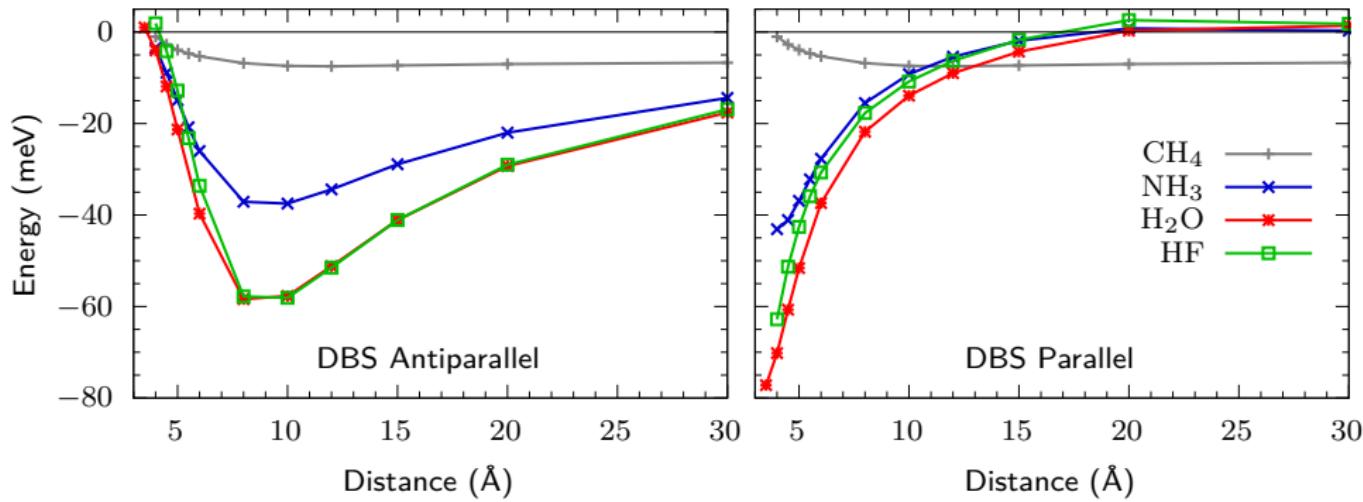
Distinct populations of dipole-bound anions (DBS) are observed

- Different regions correlate differently to the dipole strength
- **Region A:** Nearly linear relationship between binding energy and dipole strength
- **Regions B & C:** Less pronounced correlation. DBS closer to  $\pi$  system



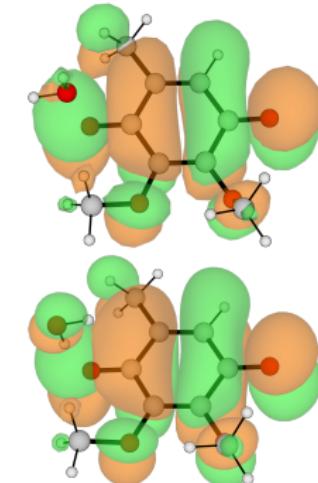
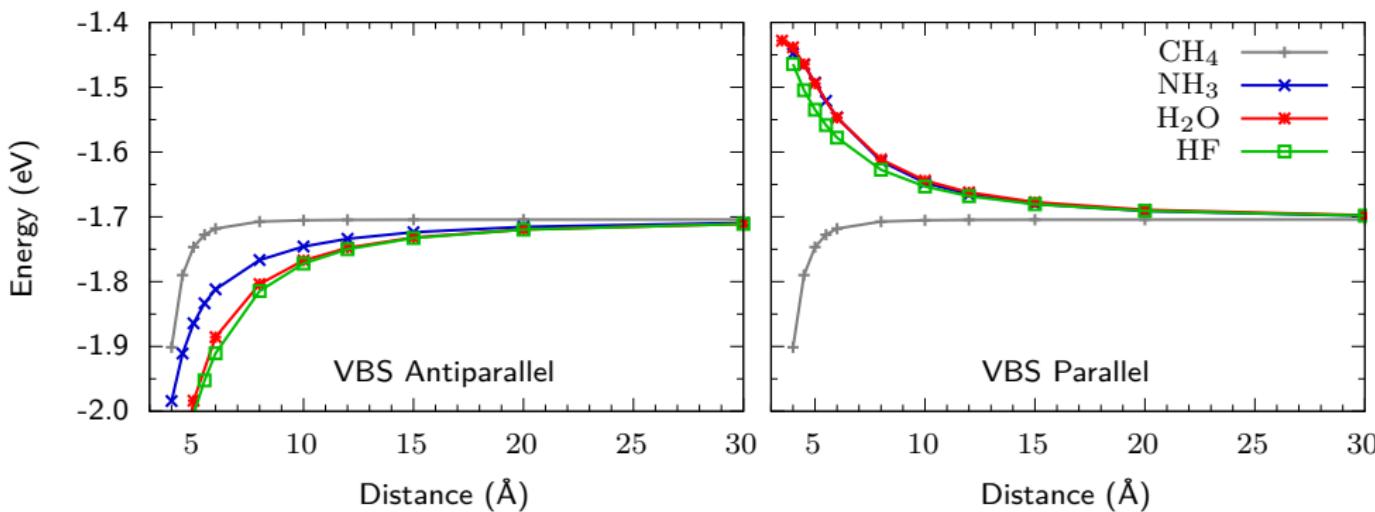
# Interaction with solvent molecules (DBS)

- **Antiparallel dipoles:** Polar molecules create a potential well with up to 10x in electron binding energy.
- **Aligned dipoles:** Repulsion at large distances. At short range, dipoles add up.



# Interaction with solvent molecules (VBS)

- **Antiparallel dipoles:** VBS strongly stabilised at short distances.
- **Aligned dipoles:** VBS destabilised.
- Intermolecular interactions larger effect on VBS than methoxy chain rotations.



# Conclusions

- Methoxy chain rotation in Q0 and Q1 significantly alters dipole moment, VBS, and DBS energies.
- In general, DBS electron binding energy is loosely correlated with dipole strength.
- For equivalent conformers, the correlation can be very strong
- Solvent interactions dramatically affect VBS and DBS stability
- Intermolecular interactions larger effect on VBS than methoxy chain rotations.

**Thanks for your attention!**

# Acknowledgements



European Research Council  
Established by the European Commission



# DBS Basis set convergence

Table: Electron affinity of dipole-bound radical anions computed using different augmented Dunning basis sets and EOM-EA RI-CC2 and EOM-EA RI-CCSD. Koopman' theorem (KT), and dipole moment,  $\mu$ , calculated at the HF/aug-cc-pVTZ+6s3p level, and mean absolute error (MAE) taking CCSD/aug-cc-pVTZ+6s3p as reference are also given. The values are in meV and Debye respectively.

Molecule		RI-CC2				RI-CCSD				KT	$\mu$		
		2s1p	aug-cc-pVTZ			pVDZ 6s3p	pVQZ 6s3p	pVDZ 6s3p	pVTZ 6s3p				
			4s2p	6s3p	8s4p								
Acetaldehyde	CH <sub>3</sub> CHO	-156.7	-27.8	-3.2	0.8	-4.6	-3.2	-4.6	-3.1	-0.4	3.29		
Acetone	(CH <sub>3</sub> ) <sub>2</sub> CO	-114.9	-16.8	1.3	3.3	-0.3	0.9	-0.5	0.9	-5.1	3.46		
Acetonitrile	CH <sub>3</sub> CN	-61.2	12.6	19.9	20.1	18.2	20.3	17.1	18.4	4.2	4.29		
Benzaldehyde	C <sub>6</sub> H <sub>5</sub> CHO	-97.1	-2.1	8.9	9.6	7.4	9.1	3.4	4.6	-4.9	3.77		
N,N-Dimethylformamide	(CH <sub>3</sub> ) <sub>2</sub> NCHO	-81.1	5.4	14.1	14.4	13.2	14.4	13.3	13.7	1.9	4.48		
DMSO	(CH <sub>3</sub> ) <sub>2</sub> SO	-84.5	4.0	15.4	16.1	14.8	15.5	14.7	14.9	2.1	4.63		
Formamide	CH <sub>3</sub> NO	-92.2	1.1	16.2	17.2	15.1	17.0	15.1	15.9	3.4	4.28		
Methylisocyanide	CH <sub>3</sub> NC	-95.1	-0.5	10.0	10.5	9.5	10.1	8.8	9.0	-1.8	3.59		
Nitrobenzene	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	-63.6	30.6	34.8	34.8	32.5	—	25.0	25.9	5.4	5.15		
Nitromethane	CH <sub>3</sub> NO <sub>2</sub>	-82.9	5.7	14.2	14.7	13.0	14.7	12.9	13.7	3.5	4.10		
Nitrosobenzene	C <sub>6</sub> H <sub>5</sub> NO	-125.0	1.0	11.4	—	9.9	—	5.1	6.0	-4.1	3.73		
Phenylisocyanide	C <sub>6</sub> H <sub>5</sub> NC	-82.7	8.6	16.3	16.5	15.2	16.7	9.0	9.2	-4.9	3.61		
Pyridazine	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	-80.7	20.5	26.3	26.4	25.0	26.7	18.6	19.1	1.7	4.41		
Vinylene carbonate	C <sub>3</sub> H <sub>2</sub> O <sub>3</sub>	-82.5	20.9	27.2	27.4	26.4	27.7	25.1	25.5	10	5.05		
		MAE	105.3	8.8	2.8	3.4	2.3	2.4	0.8	0.0	12.0		