

# Exploring biologically relevant non-valence anions with the CC2 method

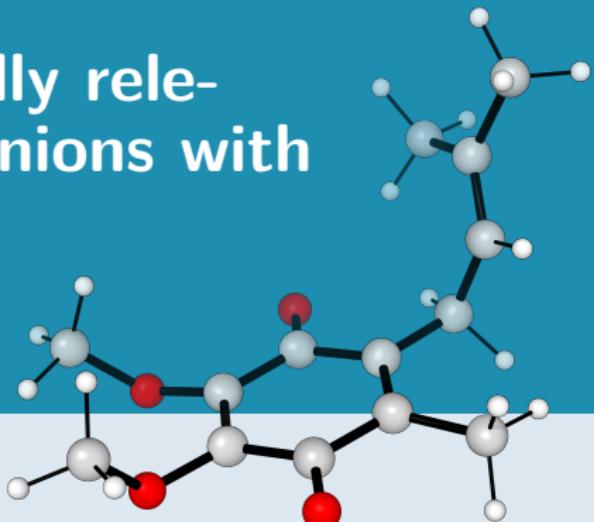
TCCM

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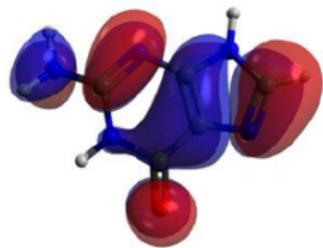
# Outline

- **Background**
- Non-Valence anions
- Equation-of-Motion CC
- Ubiquinone
- **Results**
- Dipole Surface
- A Simple Cluster Model
- **Future steps**

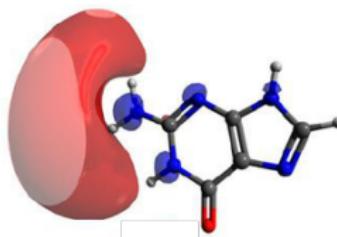
# Non-Valence anions

In non-valence anions (NVAs) the excess electron resides in a diffuse orbital stabilized by long-range interactions

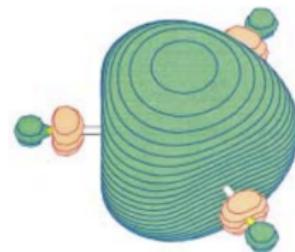
- Relevant for electron scattering and transfer processes and can act as a doorway for a valence state
- Require huge basis sets and accurate correlation treatment



G valence anion



G dipole anion



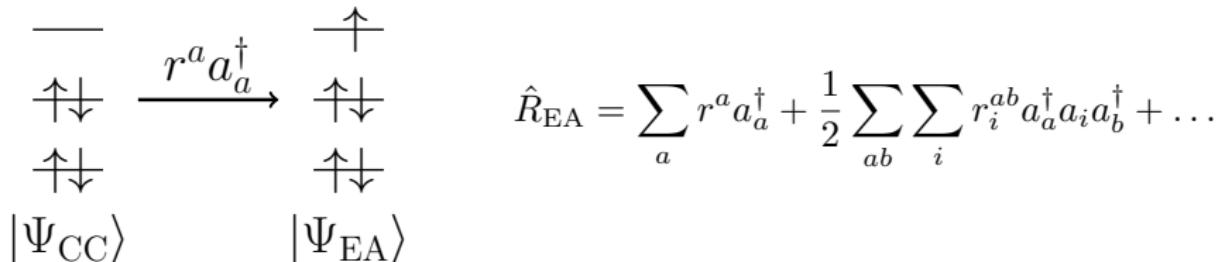
$(HF)_3$  solvated electron

Dutta, A. Int. J. of Quant. Chem., 2015  
Gutowski, M., Phy. Rev. Lett., 2002

# EOM-EA

Equation-of-motion electron-attachment coupled-cluster (EOM-EA-CC) methods are particularly well suited to study NVAs

- The description is based on the wavefunction of the parent neutral molecule
- The computational cost and memory requirements limit the EOM-EA-CCSD applications to small molecules



## CC2

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

- Lowers computational scaling from CCSD
- Allows treatment of “big” molecules: > 25 heavy atoms

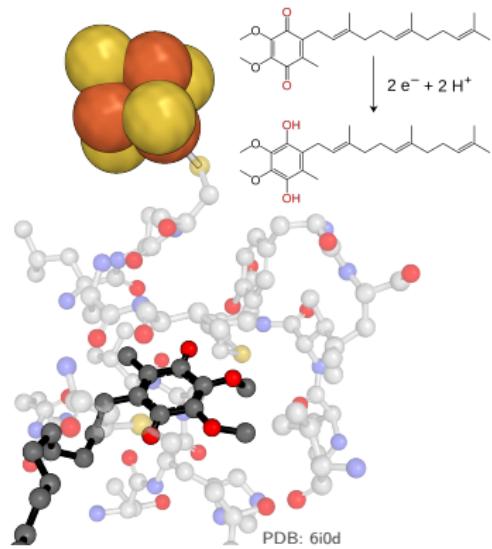
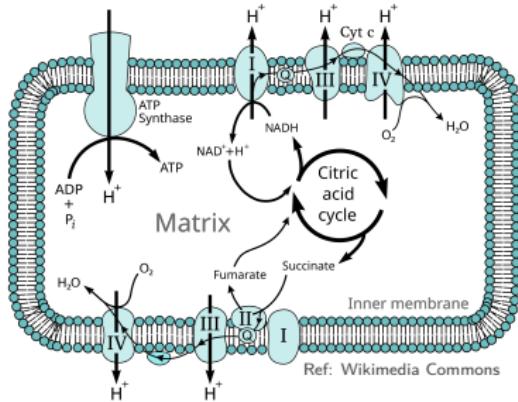
Method	Scaling	Memory
CCSD	$O(N^6)$	$O(N^4)^*$
CC2	$O(N^5)$	$O(N^4)^*$

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

# Biological Quinones: Ubiquinone (CoQ)

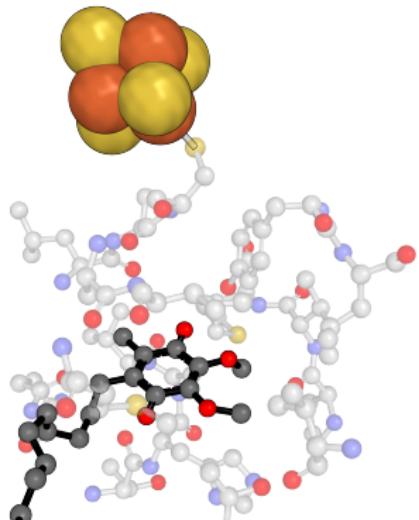
Quinones are essential electron carriers in biological mechanisms

- CoQ: component of electron transport chains in bacterial photosynthesis and aerobic respiration
- It is capable of both a valence and dipole bound anion states

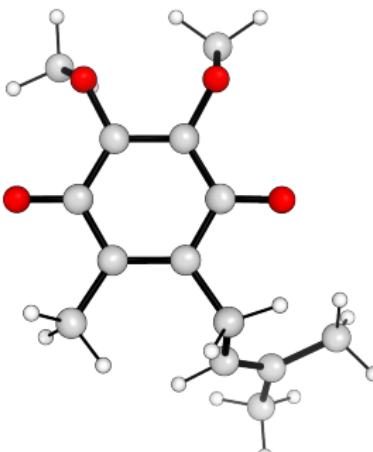


# Quinone models

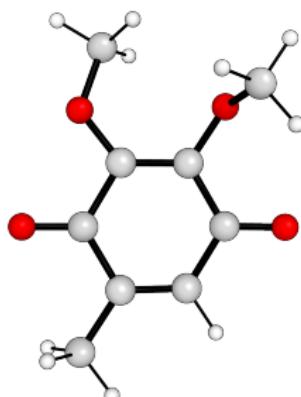
- Quinone head involved in the electron transfer
- Isoprenoid tail responsible for the solubility in the membrane
- Methoxy chains determine the dipole moment



Q10, Cluster Model



Q1



Q0

# Objectives

- Characterize dipole bound state for different CoQ models and conformations
- Explore effect of environment
- Possible involvement in charge transfer reactions

## Computational methods

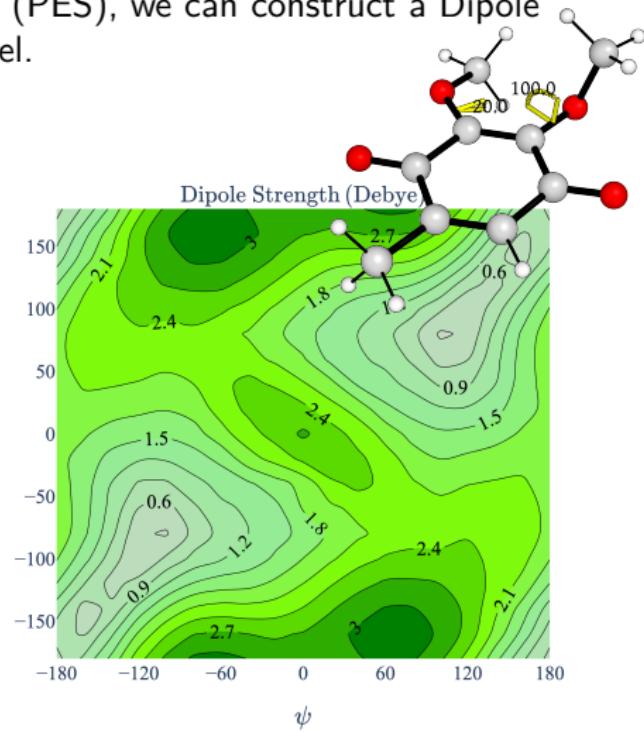
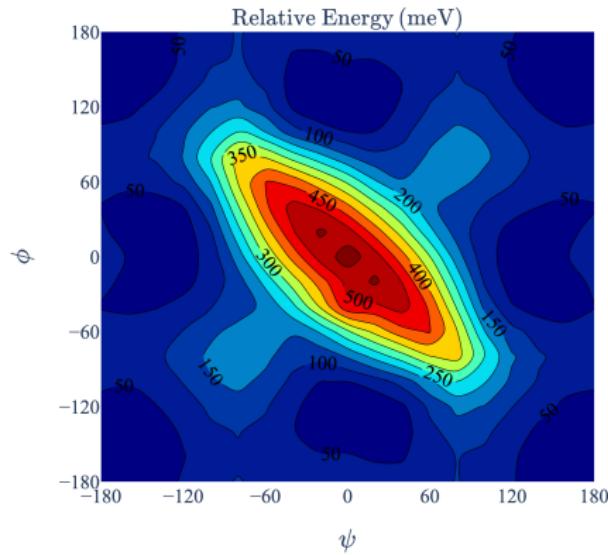
- Optimizations performed at TPSS+D3BJ/ma-def2-TZVP EA calculated at the RI-EOM-EA-CC2 using the neutral ground state as CC reference state
- aug-cc-pVTZ or DVZ basis further augmented by 3 s-shells on Hydrogen atoms and 6 s- and 3 p-shells on all non-hydrogen atoms



# Q0 Dipole PES

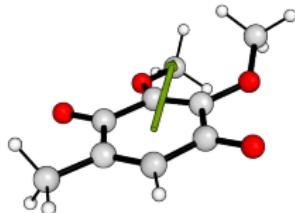
Similarly to a Potential Energy Surface (PES), we can construct a Dipole Moment Surface (DMS) for the Q0 model.

- $\Psi$  and  $\Phi$  are the methoxy dihedrals.

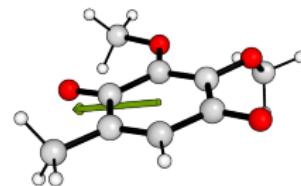


# Q0 Dipole PES

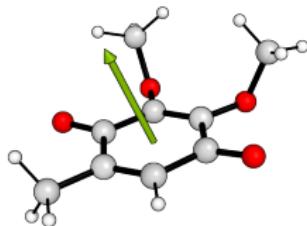
Dipole strength is not the whole picture



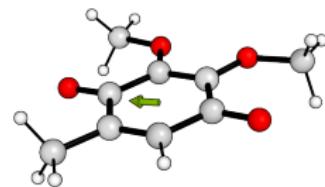
$\mu$  2.4 D EA<sub>dba</sub> +12.3 meV



$\mu$  2.8 D EA<sub>dba</sub> +3.6 meV



$\mu$  3.2 D EA<sub>dba</sub> +4.7 meV

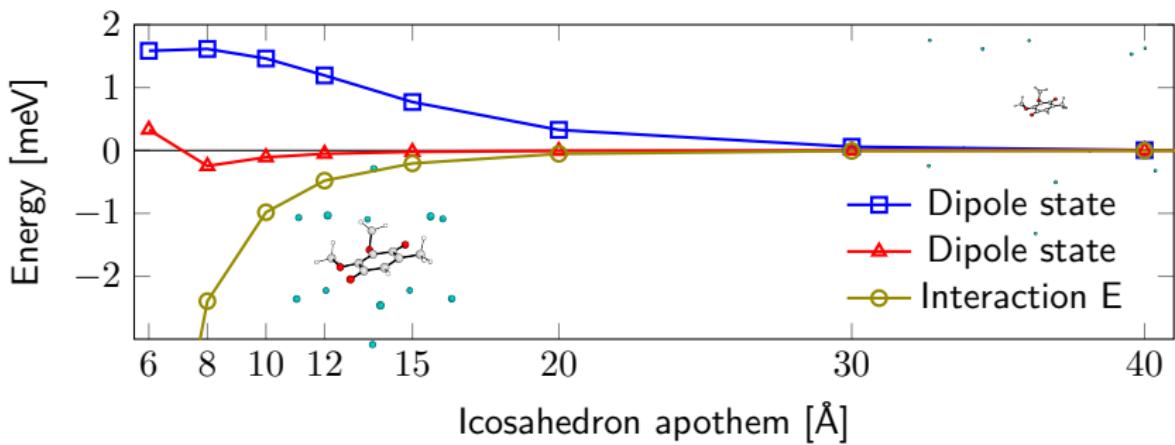


$\mu$  0.5 D EA<sub>dba</sub> -7.9 meV

# A simple cluster model

Encase Q0 in a Helium icosahedron.

- Valence state gets stabilized by the "solvent"
- Dipole state gets destabilized



## Future steps

- More realistic cluster model: polar residues might help “solvate” the electron
- Effect of isoprenoid tail
- Study other species: plastoquinone, vitamin K

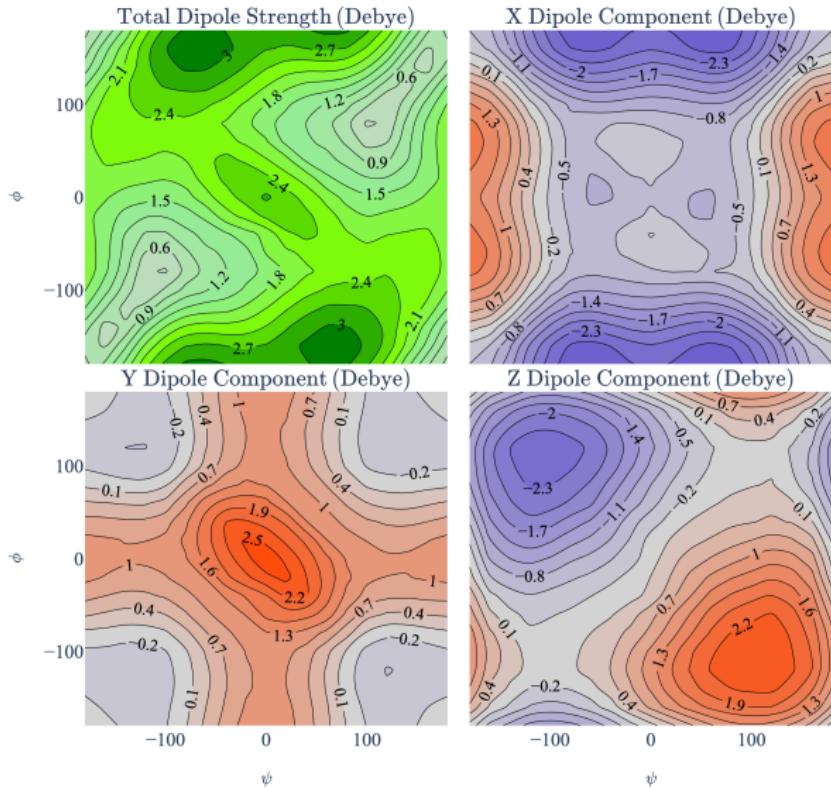
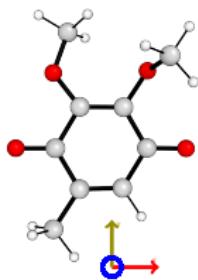
**Thanks for your attention!**

# Basis set convergence

Basis size and # of extra diffuse functions effect on dipole bound states

	RI-CC2			RI-CCSD	
	pVDZ+6s3p	pVTZ+6s3p	pQDZ+6s3p	pVDZ+6s3p	pVTZ+6s3p
acetaldehyde	4.6	3.2	3.2	4.6	3.1
acetone	0.3	-1.3	-0.9	0.5	-0.9
acetonitrile	-18.2	-19.9	-20.3	-17.1	-18.4
benzaldehyde	7.4	8.9	9.1	3.4	4.6
dimethylformamide	13.2	14.1	14.4	13.3	13.7
dmso	14.8	15.4	15.5	14.7	14.9
formamide	-16.1	-16.2	-17.0	-15.1	-15.9
methylisocyanide	-9.5	-10.0	-10.1	-8.8	-9.0
nitrobenzene	-32.5	-34.8	-	-28.0	-25.9
nitromethane	-13.0	-14.2	-14.7	-12.9	-13.7
nitrosobenzene	-9.9	-11.4	-	-5.1	-6.0
phenylisocyanide	-15.2	-16.3	-16.7	-9.0	-9.2
pyridazine	-26.0	-26.3	-26.7	-18.6	-19.1
vinylene carbonate	-26.4	-27.2	-27.7	-25.1	-25.5
<b>MAE</b>	<b>2.3</b>	<b>2.8</b>	<b>2.4</b>	<b>0.8</b>	-

# Q0 Dipole PES



# Computational methods

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