

Computational Exploration of Non-Valence Anions from Biological Quinones

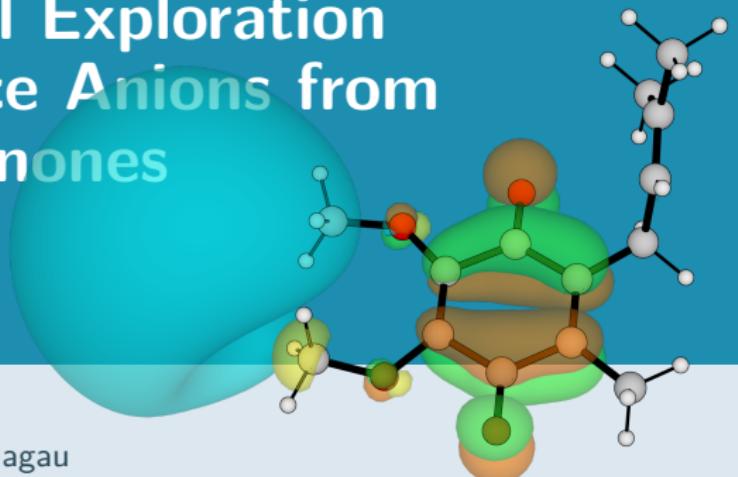
TCCM Thesis Defense

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Outline

- **Background**
 - Non-Valence Anions
 - Equation-of-Motion CC
 - Ubiquinone
- **Results**
 - Potential Energy Surfaces
 - Simple Cluster Models
- **Conclusions and Outlook**

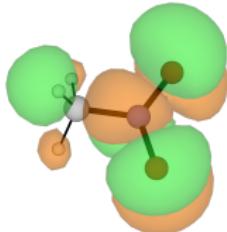
Non-valence anions

The excess electron is bound by long-range forces (e.g., dipole, quadrupole).

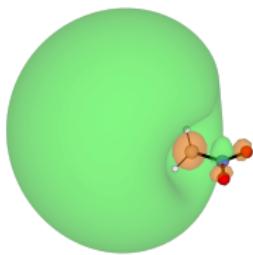
The 'extra' electron density is located far from the molecule.

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

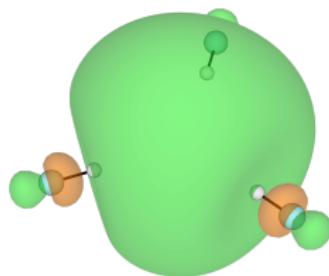
- Extremely diffuse electron clouds
- Sensitive to correlation and environmental effects
- Require huge basis sets and accurate correlation treatment



Valence-bound anion of
nitromethane



Dipole-bound anion of
nitromethane



(HF)₃ solvated electron

CC2

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

- 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	$O(N^5)$	$O(N^4)^*$

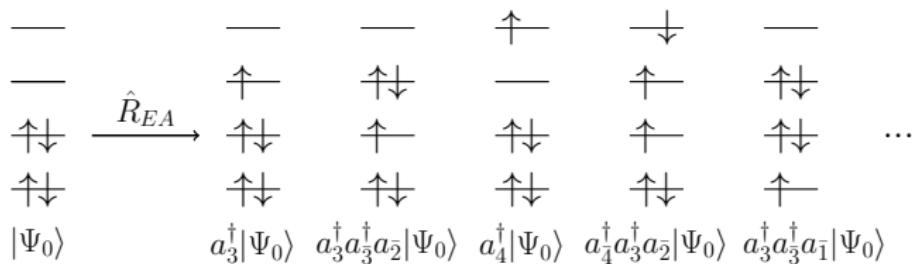
* $O(N^3)$ with RI approximation.

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

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

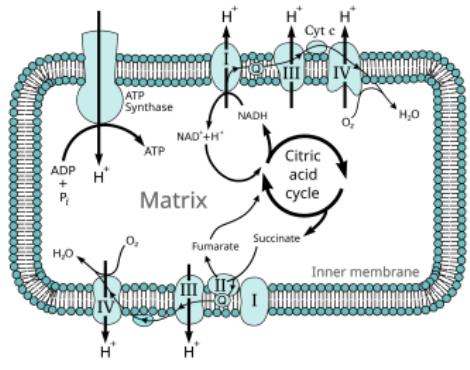
$$\hat{R}_{\text{EA}} = \sum_a r^a a_a^\dagger + \frac{1}{2} \sum_{ab} \sum_i r_i^{ab} a_a^\dagger a_i a_b^\dagger + \dots$$



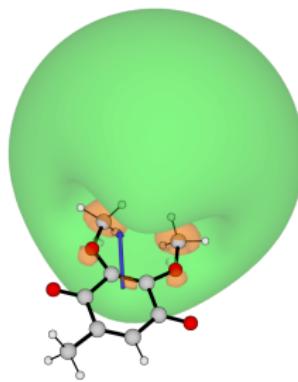
Biological Quinones: Ubiquinone (CoQ)

Quinones are essential electron carriers in biological processes

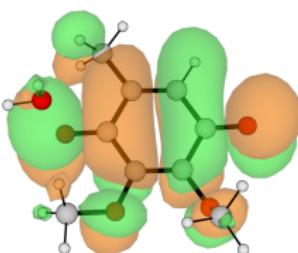
- Component of electron transport chains in bacterial photosynthesis and aerobic respiration
- Capable of both valence and dipole bound anion states



From Wikimedia Commons



Dipole-bound state

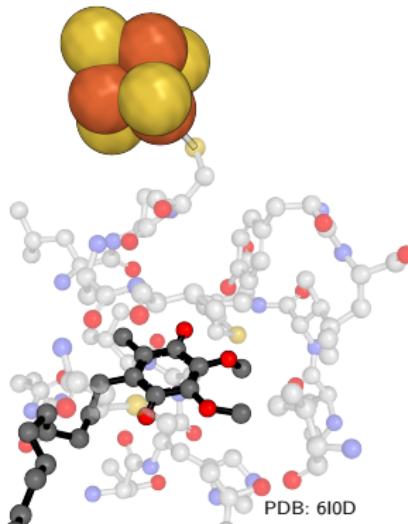


Valence-bound state

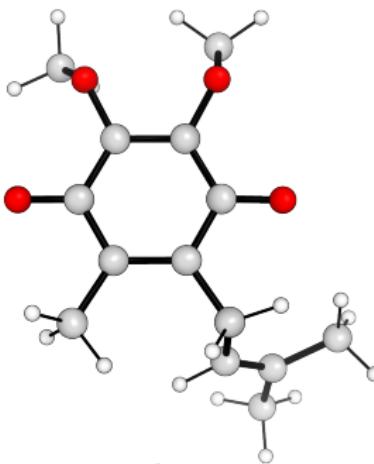
Quinone structure

Each part of the molecule plays a distinct function:

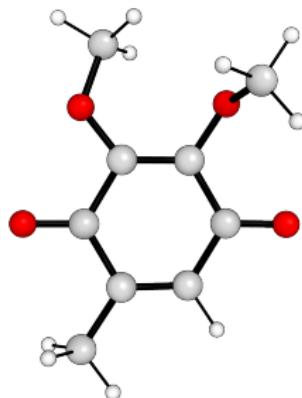
- Quinone head involved in the electron transfer
- Isoprenoid tail responsible for the solubility in the membrane
- Methoxy chains determine the dipole moment



Q10, Cluster Model



Q1



Q0

Computational methods

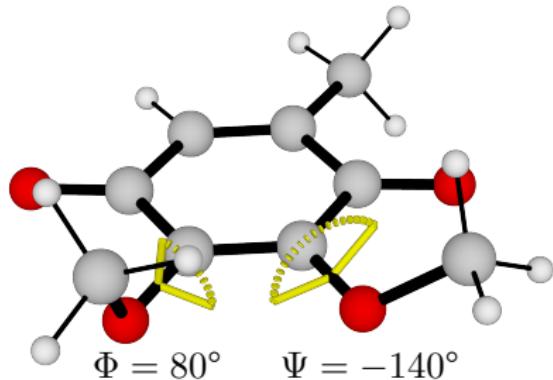
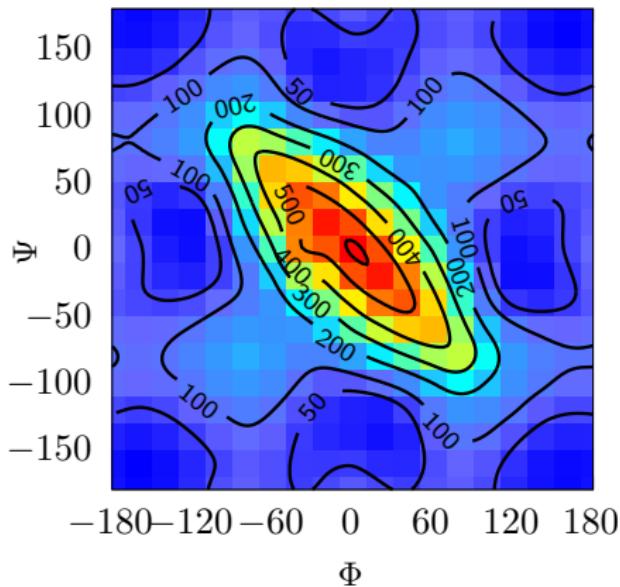
All calculations were performed using the *Q-Chem* software.

- 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)



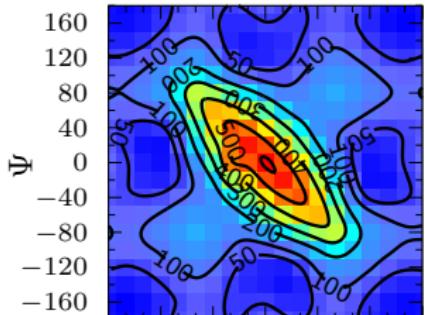
Potential Energy Surface

We can construct surfaces from the methoxy rotations (Ψ and Φ) of the Q0 model.

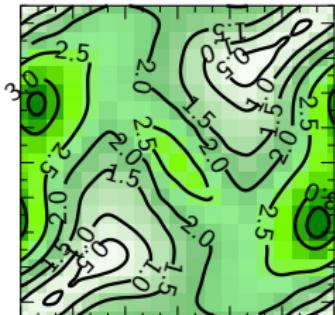


Potential Energy Surfaces of Q0

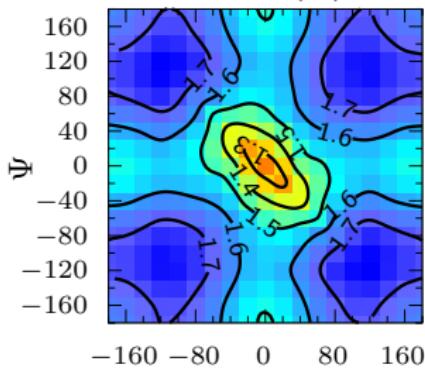
Conformational Energy (meV)



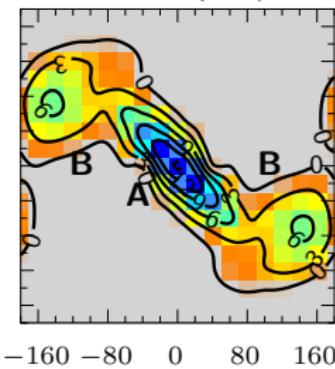
Dipole Strength (Debye)



VBA EA (eV)

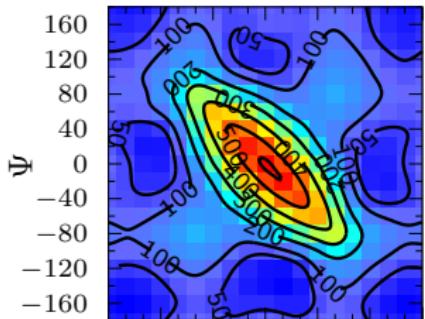


DBA EA (meV)

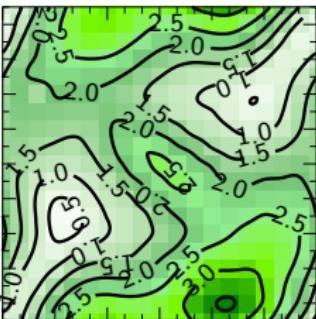


Potential Energy Surfaces of Q1

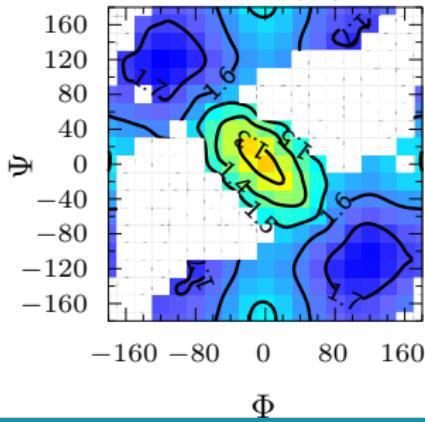
Conformational Energy (meV)



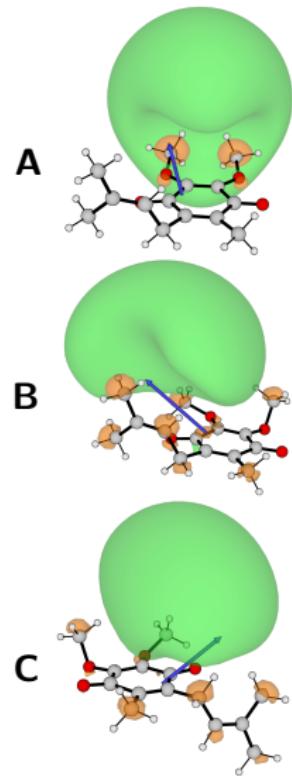
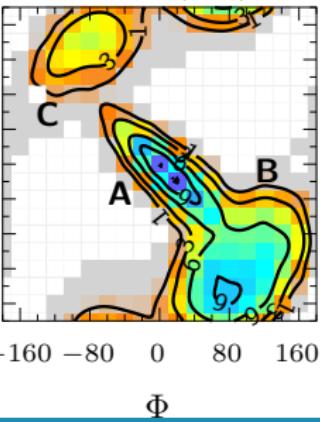
Dipole Strength (Debye)



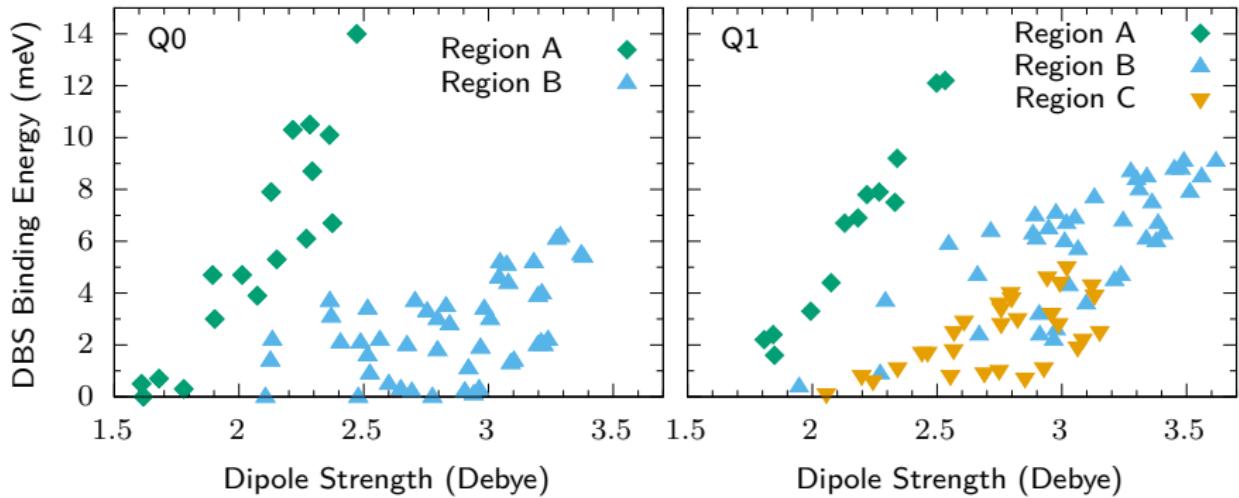
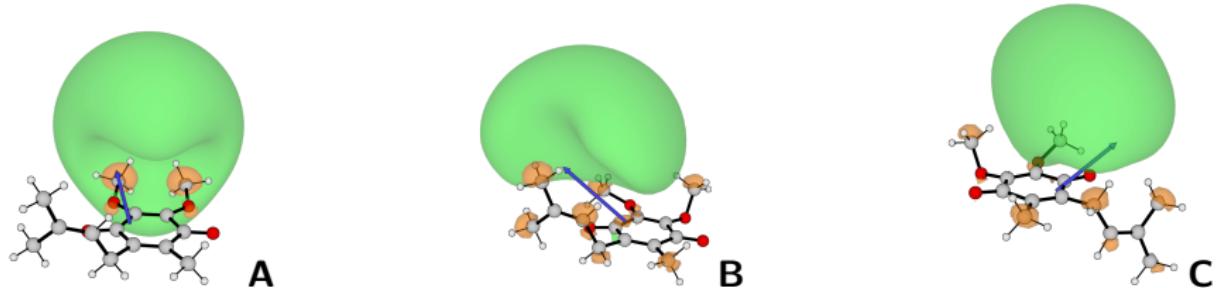
VBA EA (eV)



DBA EA (meV)

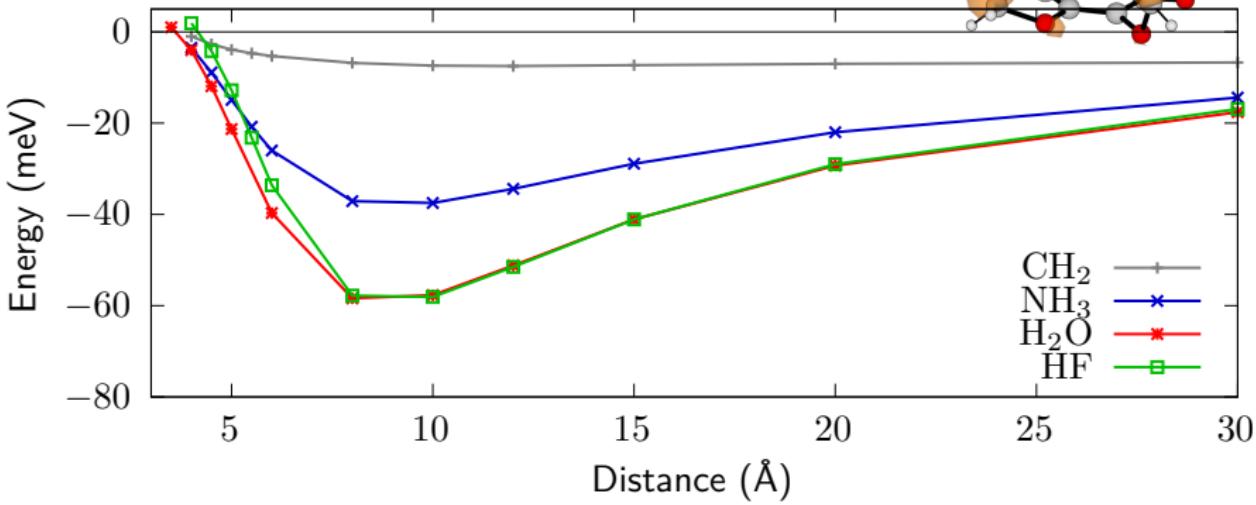
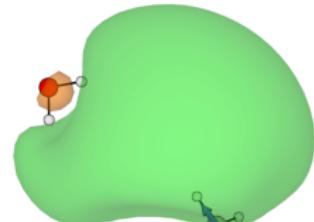


DBA Populations



A simple cluster model

A directed interaction with small molecules strongly stabilises the DBA.



Conclusions

- No conclusions

Thanks for your attention!

Acknowledgements



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CENTRUM



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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's theorem (KT), and dipole moment, μ , 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				
		2s1p	aug-cc-pVTZ 4s2p	6s3p	8s4p	pVDZ 6s3p	pVQZ 6s3p	pVDZ 6s3p	pVTZ 6s3p	KT	μ
Acetaldehyde	CH ₃ CHO	-156.7	-27.8	-3.2	0.8	-4.6	-3.2	-4.6	-3.1	-0.4	3.29
Acetone	(CH ₃) ₂ CO	-114.9	-16.8	1.3	3.3	-0.3	0.9	-0.5	0.9	-5.1	3.46
Acetonitrile	CH ₃ CN	-61.2	12.6	19.9	20.1	18.2	20.3	17.1	18.4	4.2	4.29
Benzaldehyde	C ₆ H ₅ 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 ₃) ₂ NCHO	-81.1	5.4	14.1	14.4	13.2	14.4	13.3	13.7	1.9	4.48
DMSO	(CH ₃) ₂ SO	-84.5	4.0	15.4	16.1	14.8	15.5	14.7	14.9	2.1	4.63
Formamide	CH ₃ NO	-92.2	1.1	16.2	17.2	15.1	17.0	15.1	15.9	3.4	4.28
Methylisocyanide	CH ₃ NC	-95.1	-0.5	10.0	10.5	9.5	10.1	8.8	9.0	-1.8	3.59
Nitrobenzene	C ₆ H ₅ NO ₂	-63.6	30.6	34.8	34.8	32.5	—	25.0	25.9	5.4	5.15
Nitromethane	CH ₃ NO ₂	-82.9	5.7	14.2	14.7	13.0	14.7	12.9	13.7	3.5	4.10
Nitrosobenzene	C ₆ H ₅ NO	-125.0	1.0	11.4	—	9.9	—	5.1	6.0	-4.1	3.73
Phenylisocyanide	C ₆ H ₅ NC	-82.7	8.6	16.3	16.5	15.2	16.7	9.0	9.2	-4.9	3.61
Pyridazine	C ₄ H ₄ N ₂	-80.7	20.5	26.3	26.4	25.0	26.7	18.6	19.1	1.7	4.41
Vinylene carbonate	C ₃ H ₂ O ₃	-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	