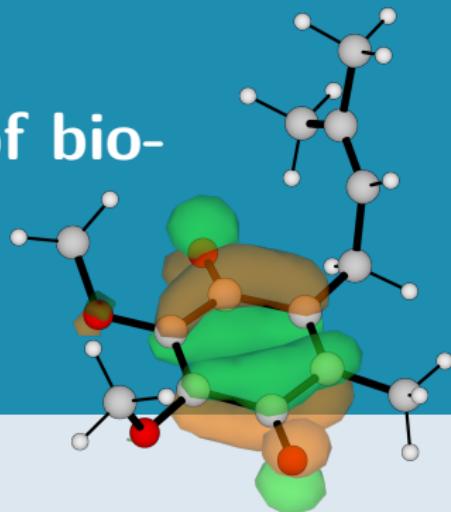


Enon-valence anions of bio-logical molecules

TCCM

Mauro Gascón
HPC User Day

June 2, 2025



What is an anion?

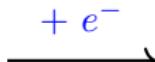
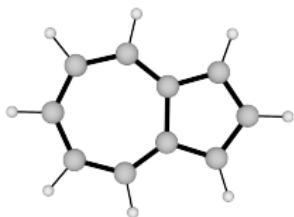
An anion is a negatively charged ion, formed when an atom or molecule gains one or more electrons.

They are fundamental in chemistry, biology, and materials science and play key roles in almost all chemical processes, including:

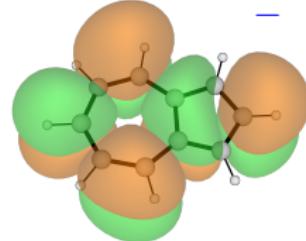
- Acid-base chemistry
- Redox reactions
- Biological processes
- Environmental and atmospheric chemistry

One can distinguish between valence and non-valence anions.

Neutral azulene

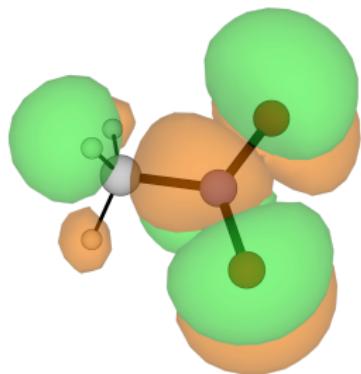


Azulene anion



Valence anions

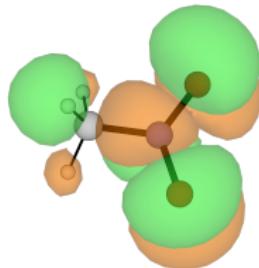
- In **valence anions**, the extra electron occupies a valence orbital (localized on the molecule).
- These are the most common type of anions (e.g., Cl^- , NO_2^-).



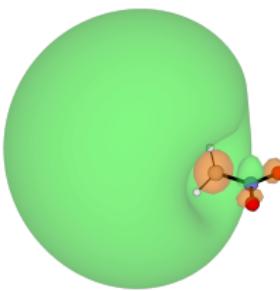
Valence-bound anion of nitromethane

Nonvalence anions: importance and challenges

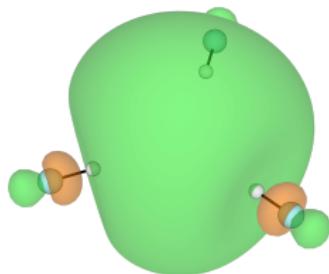
- **Nonvalence anions (NVAs):** the excess electron is bound by long-range forces (e.g., dipole, quadrupole)
- The ‘extra’ electron density is located far from the molecule.
- Found in atmospheric, interstellar, and biological environments.
- **Challenges:**
 - Extremely diffuse electron clouds
 - Sensitive to correlation and environmental effects



Valence-bound anion of
nitromethane



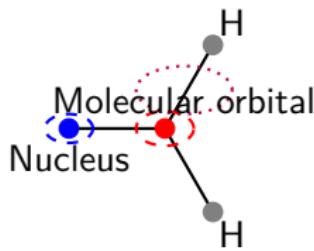
Dipole-bound anion of
nitromethane



(HF)₃ solvated
electron

Theoretical treatment of electronic structure

- Quantum chemistry describes molecules by solving the Schrödinger equation for electrons and nuclei.
- Approximations are needed for all but the smallest systems.
- Key concepts:**
 - Molecular orbitals
 - Electron correlation
 - Basis sets

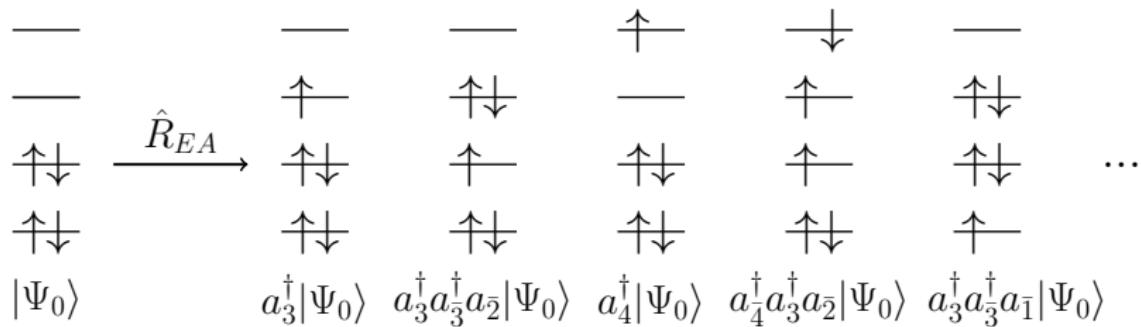


EOM-EA

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

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



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

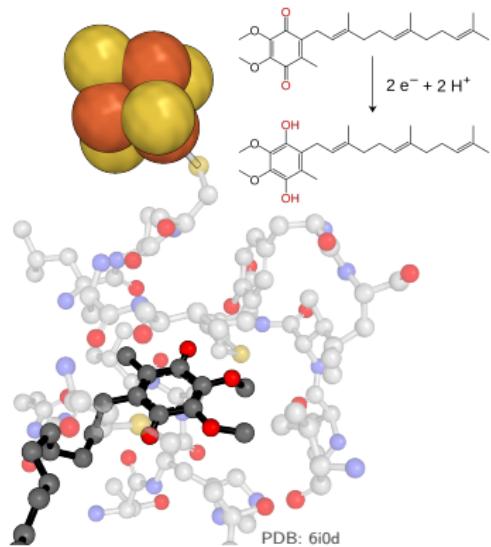
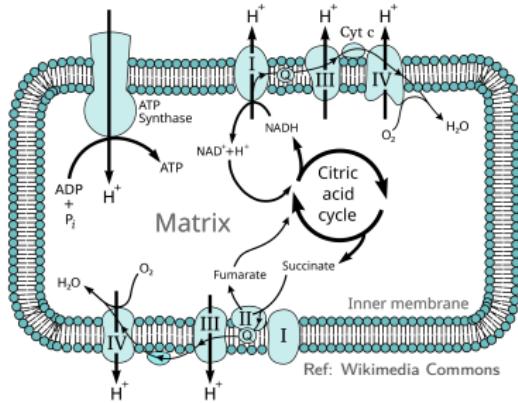
Method	Scaling	Memory
CCSD	$O(N^6)$	$O(N^4)^*$
CC2	$O(N^5)$	$O(N^4)^*$

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

Biological Quinones: Ubiquinone (CoQ)

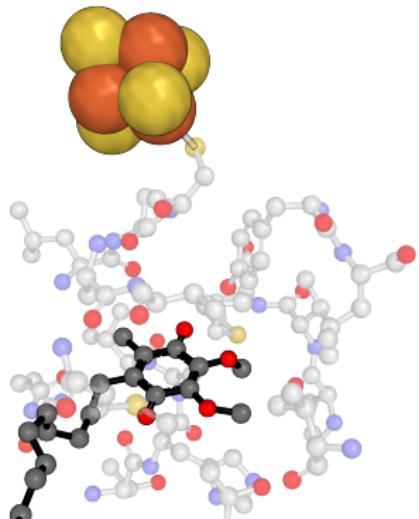
Quinones are essential electron carriers in biological mechanisms

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

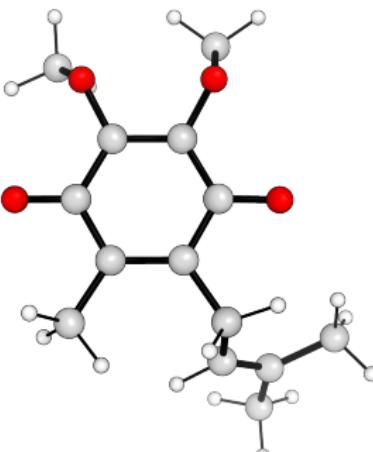


Quinone models

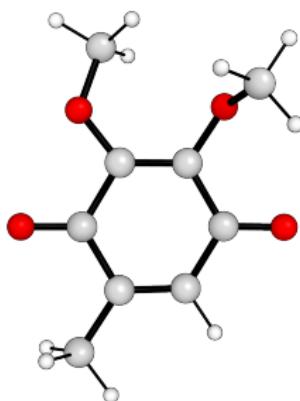
- Quinone head involved in the electron transfer
- Isoprenoid tail responsible for the solubility in the membrane
- Methoxy chains determine the dipole moment



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

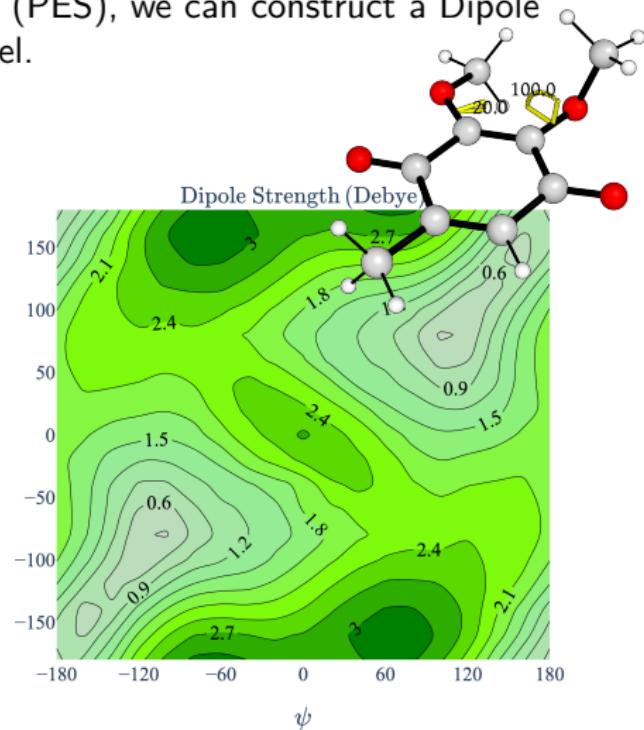
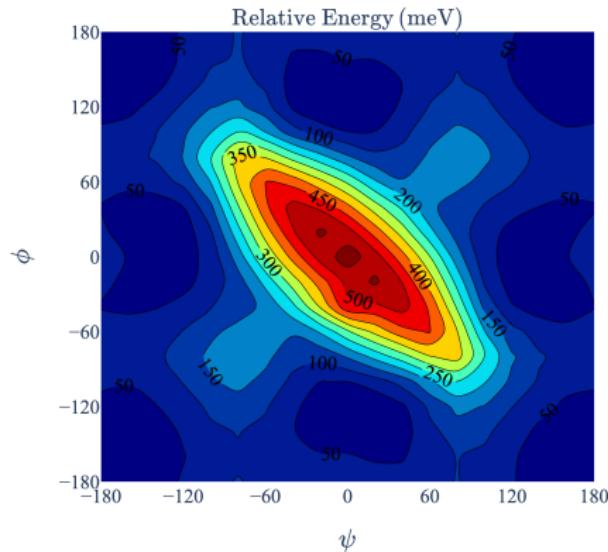
- Optimizations performed at TPSS+D3BJ/ma-def2-TZVP EA calculated at the RI-EOM-EA-CC2 using the neutral ground state as CC reference state
- aug-cc-pVTZ or DVZ basis further augmented by 3 s-shells on Hydrogen atoms and 6 s- and 3 p-shells on all non-hydrogen atoms



Q0 Dipole PES

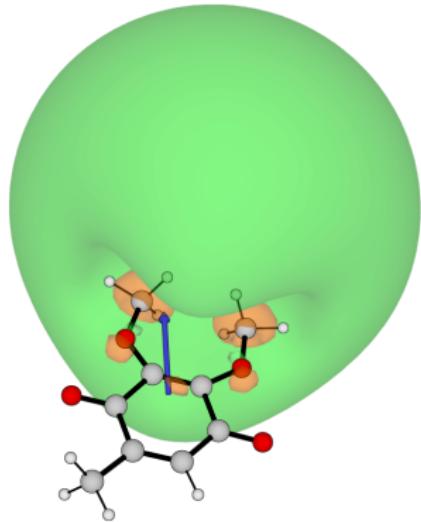
Similarly to a Potential Energy Surface (PES), we can construct a Dipole Moment Surface (DMS) for the Q0 model.

- Ψ and Φ are the methoxy dihedrals.

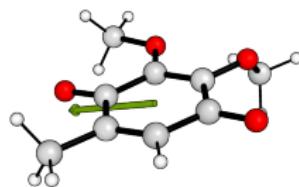


Q0 Dipole PES

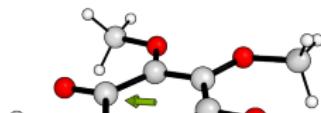
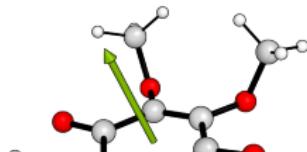
Dipole strength is not the whole picture



μ 2.4 D EA_{dba} +12.3 meV



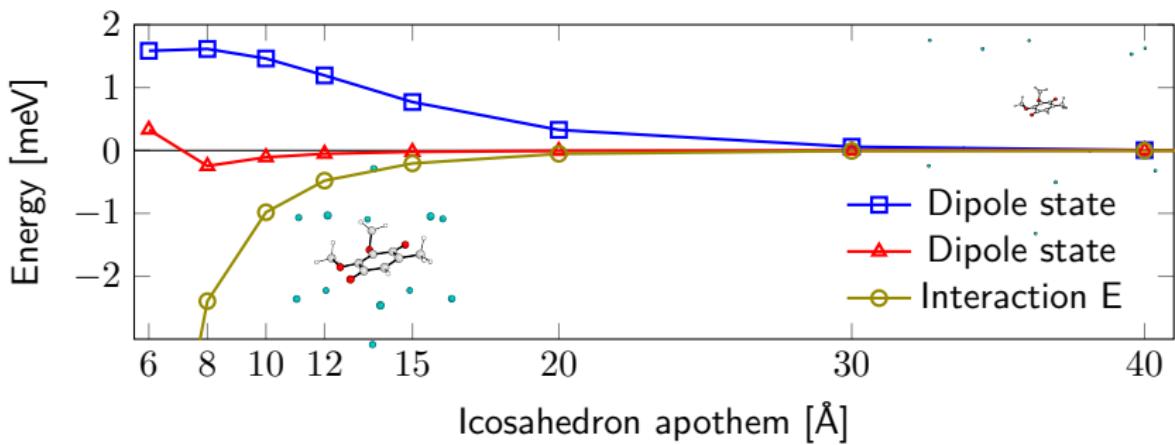
μ 2.8 D EA_{dba} +3.6 meV



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

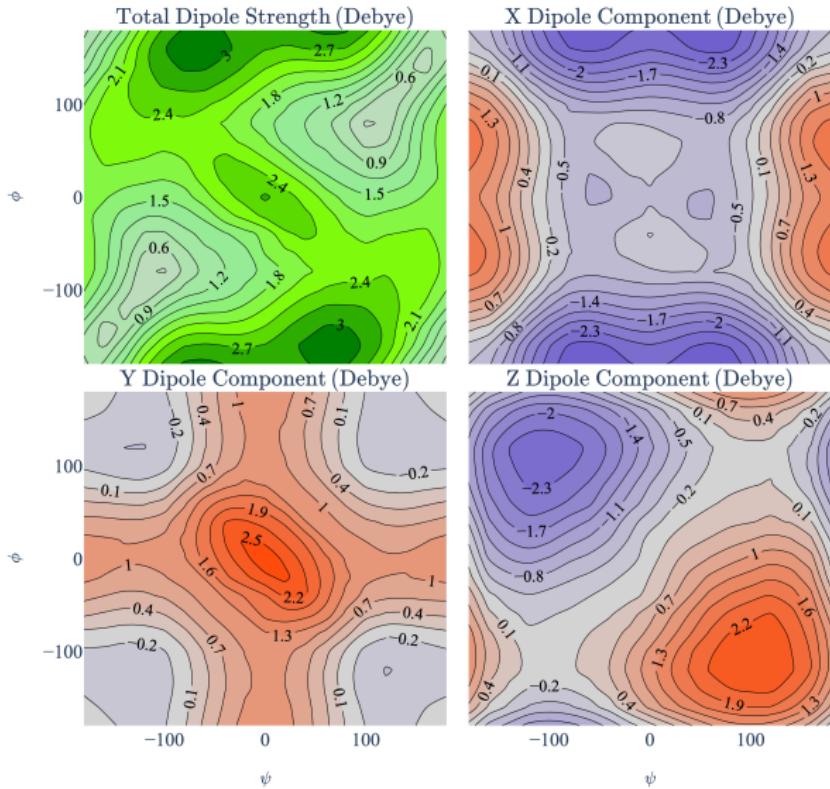
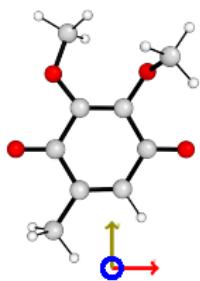
Thanks for your attention!

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
MAE	2.3	2.8	2.4	0.8	-

Q0 Dipole PES



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 basis further augmented by 3 s-shells on Hydrogen atoms and 6 s- and 3 p-shells on all non-hydrogen atoms

