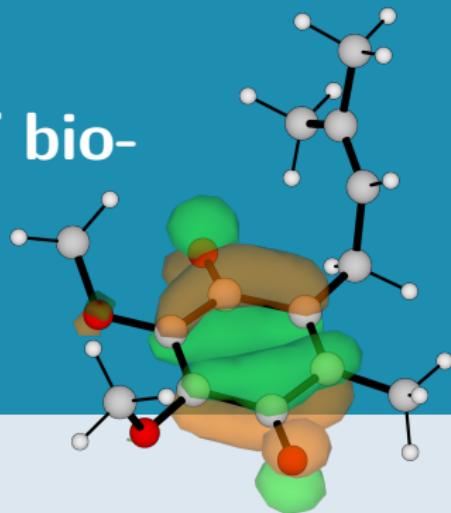


Non-valence anions of biological molecules

TCCM

Mauro Gascón
HPC User Day

June 2, 2025



What is an anion?

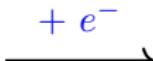
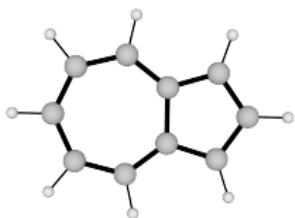
An anion is a **negatively charged ion**, formed when an atom or molecule gains one or more electrons.

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

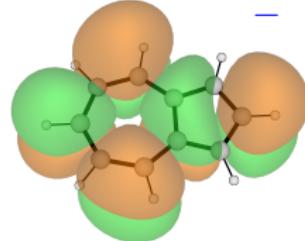
- Acid-base chemistry
- Redox reactions
- Biological processes
- Environmental and atmospheric chemistry

One can distinguish between valence and non-valence anions.

Neutral azulene

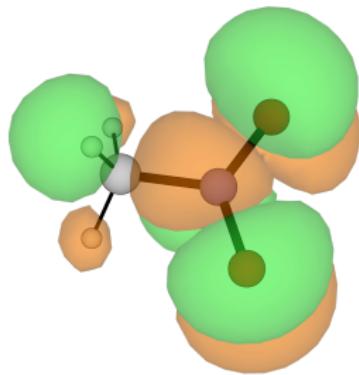


Azulene anion



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^-).



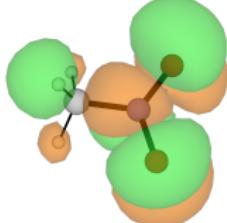
Valence-bound anion of nitromethane

Nonvalence anions

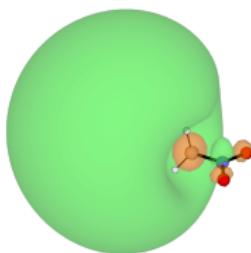
Nonvalence anions (NVAs): the excess electron is bound by long-range forces (e.g., dipole, quadrupole). The 'extra' electron density is located far from the molecule.

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

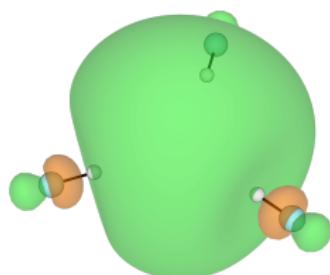
- Extremely diffuse electron clouds
- Sensitive to correlation and environmental effects
- Difficult to describe theoretically



Valence-bound anion of
nitromethane



Dipole-bound anion of
nitromethane



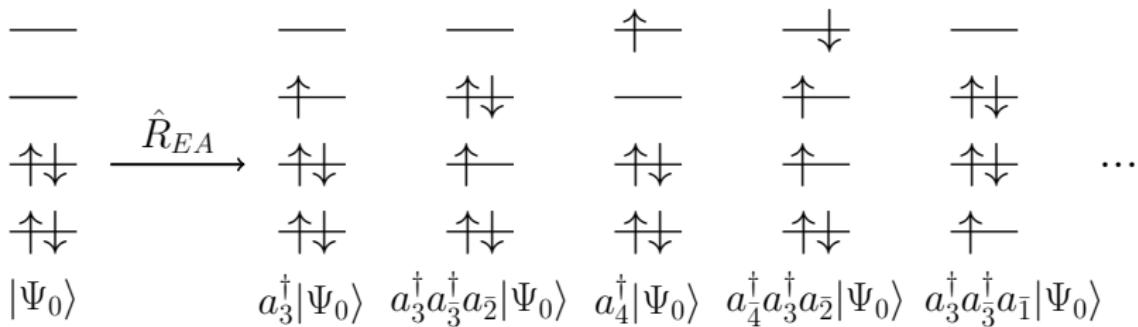
(HF)₃ solvated electron

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

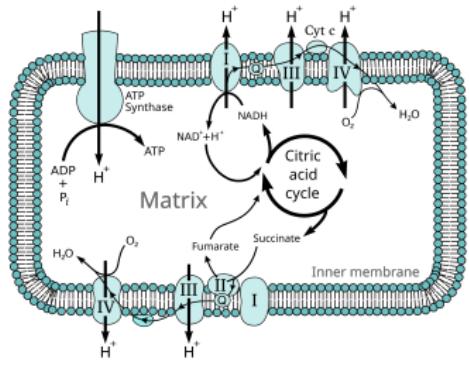
$$\hat{R}_{EA} = \sum_a r^a a_a^\dagger + \frac{1}{2} \sum_{ab} \sum_i r_i^{ab} a_a^\dagger a_i a_b^\dagger + \dots$$



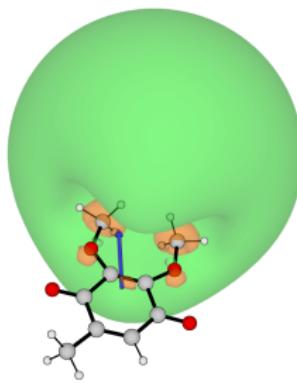
Biological Quinones: Ubiquinone (CoQ)

Quinones are essential electron carriers in biological mechanisms

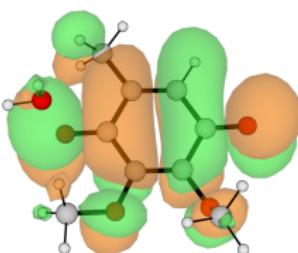
- CoQ: component of electron transport chains in bacterial photosynthesis and aerobic respiration
- It is capable of both a valence and dipole bound anion states



From Wikimedia Commons



Dipole-bound state

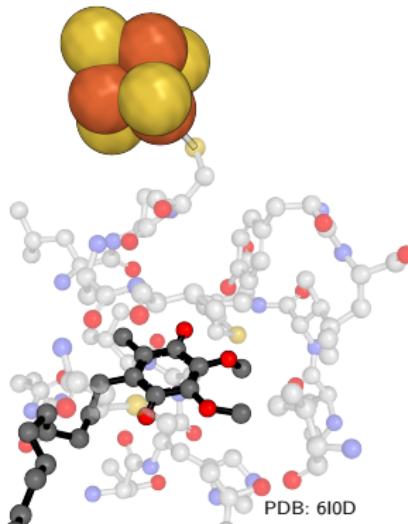


Valence-bound state

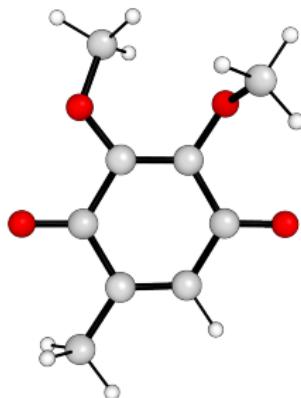
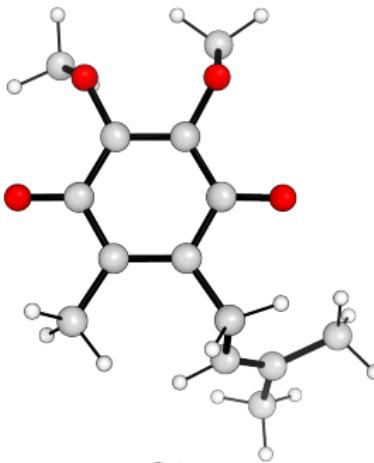
Quinone models

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

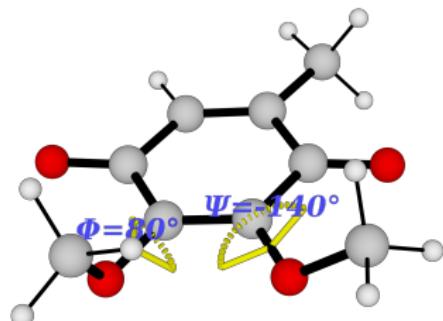
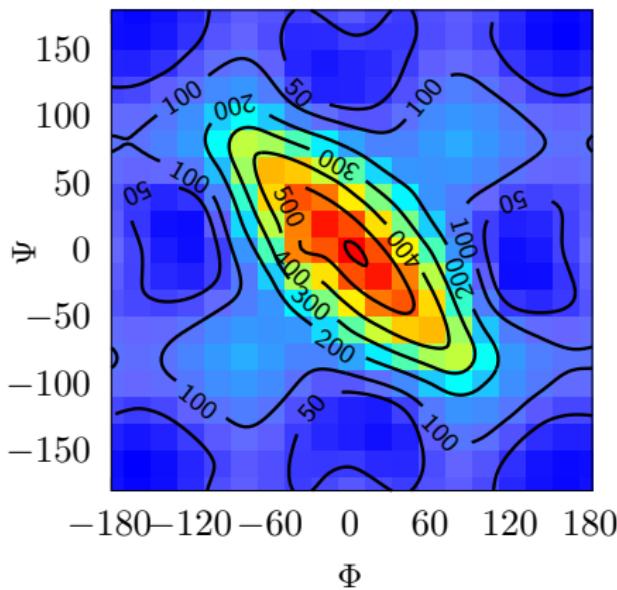


Q10, Cluster Model

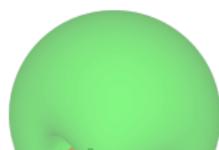
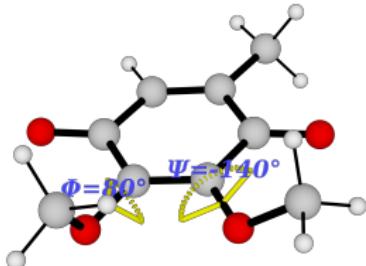
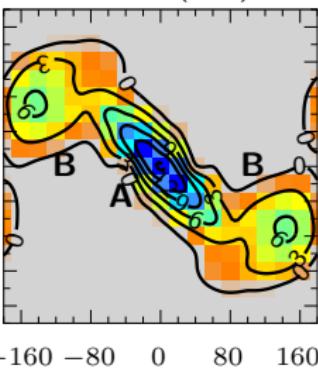
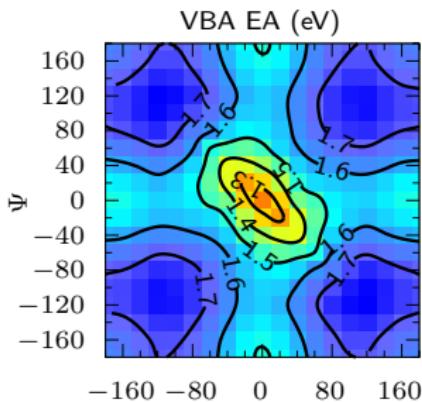
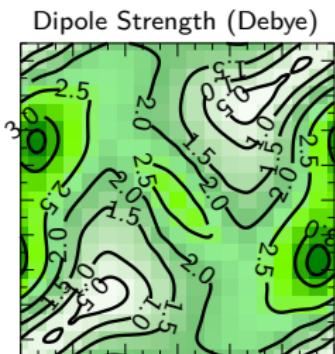
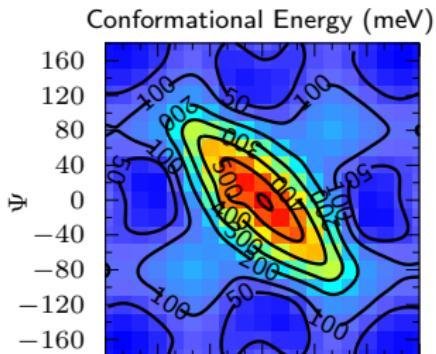


Potential Energy Surface

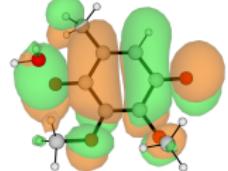
We can construct Surfaces from the methoxy rotations (Ψ and Φ) of the Q0 model.



Potential Energy Surfaces



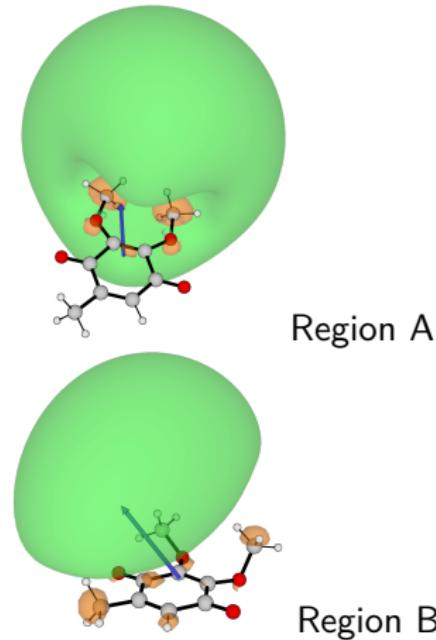
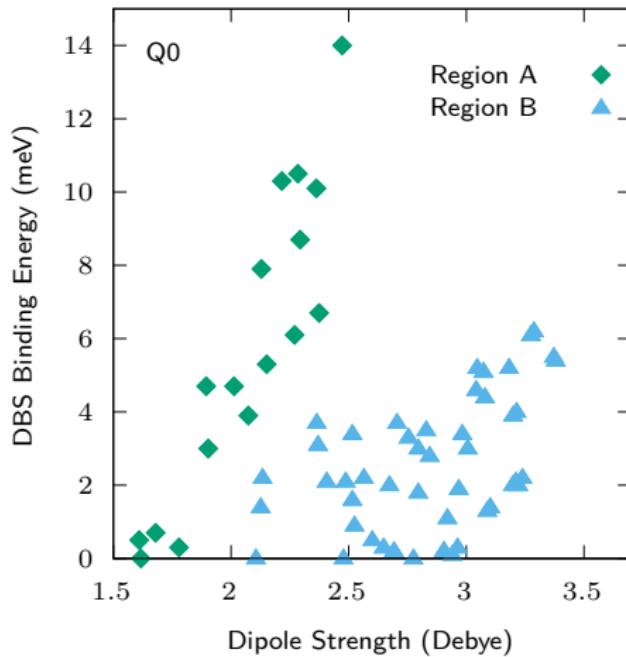
DBA



VBA

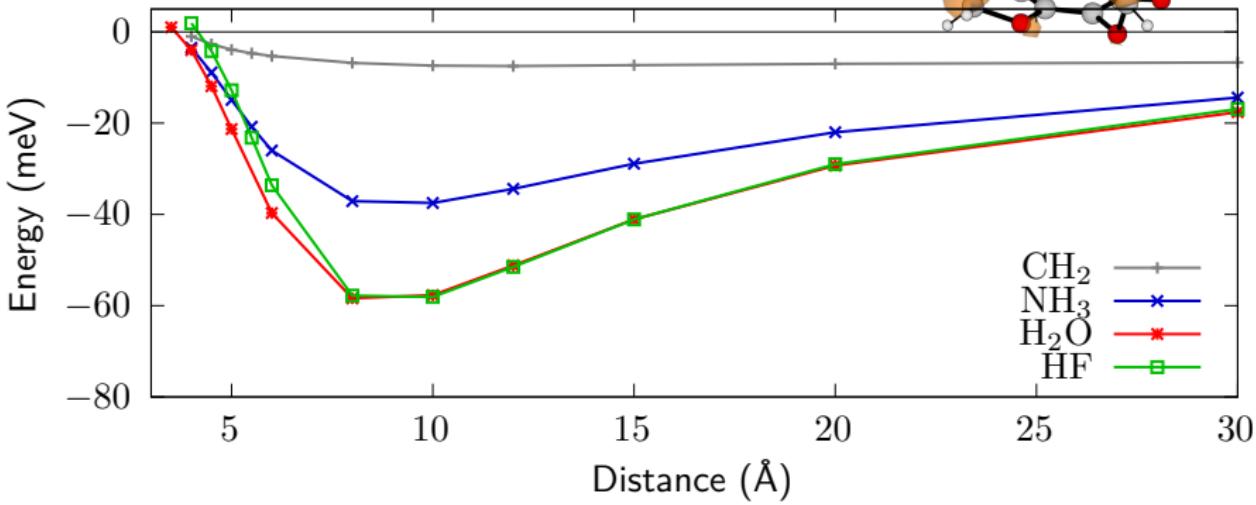
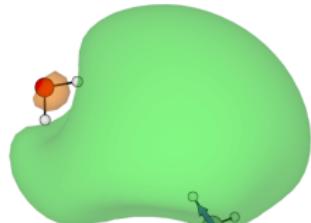
DBA populations

Two distinct types of dipole-bound anions (DBA) are observed.



A simple cluster model

A proper interaction with small molecules deeply stabilizes the DBA.



Conclusions

- Distinction between valence and Non-valence anions.
- Dipole Strength is correlated with DBA energy for similar chemical contexts.
- Surrounding molecules can have a big effect on the states.

Thanks for your attention!

Acknowledgements



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