

KU LEUVEN

FACULTY OF SCIENCE
Department of Chemistry

Computational Exploration of Non-Valence Anions from Biological Quinones

A Second Order Approximate Coupled
Cluster Study

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Mauro Gascón Navas

Dissertation presented in partial fulfillment
of the requirements for the degree of
Erasmus Mundus Master of Science in
Theoretical Chemistry and Computational
Modelling

Supervisors:
Robin Moorby
Prof. Dr. Thomas Jagau

June 2025



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(Far Away)

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Abstract

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Beknopte samenvatting

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List of Abbreviations

MD molecular dynamics. 4



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Chapter 1

Introduction

This chapter provides an overview of non-valence anions in general and particularly dipole bound anions. The current research that has viewed the presence of both dbas and biological systems is presented. It then presents the system of interest, biological quinones, and their role in biological process. Finally the research goals are specified.

1.1 Nonvalence Anions

Anions are molecules with an excess electron. Anions generally require specific care in terms of their ab initio description because of the more diffuse nature of the valence orbitals [1, 2]. The first conception of the NBS was given in 1947 by Fermi and Teller, who predicted that an excess electron could be held by a non-rotating dipole field of a neutral core if its dipole moment exceeds 1.625 D [3]. Nonvalence anions (NBS) represent a class of molecular anions where the extra electron occupies a diffuse orbital that is spatially decoupled from the usual valence orbitals of the molecule.[4]. These have been studied extensively by spectroscopic means in the gas phase in the last years, they have weakened a lot of interest [5]. Solvated electrons could be considered a nonvalence state, although still a debated topic, the main theory and observations point to the electron residing in a cavity of 2.5 Å [6].

1.1.1 Dipole Bound Anions

When it comes to the theoretical study of DB anions, two challenges are faced. First, one must use atomic orbital basis functions that are sufficiently diffuse to describe the spatial extent of the DB orbital, usually this means using custom basis sets [7]. Although the electron bound within the DB orbital resides to a large extent far away from the precursor’s valence electrons, it still has a significantly large dispersion-like interaction with the latter electrons to contribute substantially to the EBE. That is, the DB orbital is quite polarizable, so it would be expected to have a substantial van der Waals (i.e., dispersion) interaction with other nearby electron densities [8]. Apart from the esoteric nature of their studies as theoretical objects and in carefully prepared experiments, dipole bound anions are of great interest due to their presence in various fields, including astrochemistry [9], and radiation biology [10, 11]. The main interest for them is when the parent molecule also supports a valence anion state. In this case, the DBA can act as a doorway state electrons for the more stable VBA.

When solvent molecules are considered, be captured by nearby solvent molecules which have undergone reorientation to form a solvation cage around the electron, or (c) be captured by nearby solvent molecules whose instantaneous dipole orientations happen to be favorable to forming a DB state. The latter two cases arise in so-called charge-transfer-to-solvent (CTTS) electronic transitions [12, 13].

1.2 Dipole Bound Anions in Biology

The vast majority of research on dipole bound anions has been conducted in gas phase. Related to biological research, the most relevant work has been done on the interaction of dipole bound anions with DNA. The main focus of these studies has been on the radiation damage to DNA [10] and the role of dipole bound anions as radiosensitizers [11].

The existence of NBS in condensed matter is still debated. For instance, A QM study of the effects of hydration on the DB state of a model polar species showed that the excess electron migrates into an orbital localized on the outer surface of the water solvent cage [14]. However, it has been experimentally shown that a DBS is not destroyed by the presence of an alkyl chain [15]. Another study found that a DBS mediated doorway mechanism exists in both microsolvated and bulk-solvated uracil-DEG systems [16]. This leads to the questions of can the NBS survive in the bulk? In an apolar solvent, the density of molecules is too large and the excluded volume will not allow a DBS to exist. In polar solvents, the solvent itself can provide a dipolar stabilisation as is the case for

charge-transfer-to-solvent (CTTS) states,[12, 13] which may be viewed as a DBS. However, much of biology exists as softmatter, for which the molecular density can be much lower. For example, proteins contain large vacant pockets, which could accommodate a DBS that may have small molecular fragments poking into it.

Little work has been done to assess their role in natural pathways. It is possible that they could provide an elegant way to regulate long-range electron transfer. Due to their strong dependence on to the surroundings, they could provide. Uracil water [17]. This has been limited by the expensive methods needed to study these states, only allowing to study small systems.

1.2.1 Experimental Studies overview

1.2.2 overlap with biochemical systems

Interactions of electrons with bare and hydrated biomolecules: From nucleic acid bases to DNA segments [18]. It has been suggested that the dipole bound anions could be important in the cases of flavines [19]

1.3 Biological quinones

To trace this history from its source we must go back to 1785, when an apothecary of the name of Hofmann obtained the calcium salt of an acid called quinic acid from Cinchona bark. This acid is now known to be of common occurrence in plants ; it exists in the bilberry and in coffee, in holly, ivy, oak, elm, and ash leaves, and probably many other leaves. Liebig also prepared the calcium salt, and was the first to give a complete analysis... he proposed in place of it the name quinone, by which it is still known The origin of the name “quinone” itself is interesting. It comes from quinic acid, as quinone was first obtained in the oxidation reaction of this acid, which at its time is obtained from the bark of cinchona and the word ending -one comes from the ketone group (ketone)[20, 21]. The role of ubiquinones in biological processes cannot be overestimated...[22]. Quinones are a class of molecules that are ubiquitous in biological systems. Quinones act as electron carriers between different enzymes, facilitating the transfer of electrons and protons in redox reactions. It is generally accepted that the isoprenoid side chain of the coenzyme takes part in intermolecular interactions. The mitochondrial Complex I has an L-shaped structure. Electrons produced by NADH oxidation are transported along the

hydrophilic arm through a series of Fe-S clusters. The second arm, embedded in the mitochondrial inner membrane, provides an amphipathic environment composed of charged and hydrophobic ends. The ubiquinone chamber stretches through the boundary between the two arms, and recently reported free energy profiles unveiled the interplay between the interactions of the ubiquinone head and tail. Electron transfer takes place as the CoQ 0 head approaches the closest lying cluster, labelled N2, while diffusion of the isoprenoid tail along the mitochondrial inner membrane carries the electrons to the subsequent stages of aerobic cell respiration. The CoQ 0 head can form hydrogen bonds with water molecules (micro-hydration) and nearby amino acid residues in the hydrophilic arm, while the tail is responsible for hydrophobic interactions in the membrane, although with some degree of hydration.

Coenzyme Q (ubiquinone) is one of the most common quinones found in nature, and its structure allows for the stabilization of both valence and dipole-bound anionic states. This unique property makes quinones an interesting subject for studying the potential existence and role of nonvalence anions in biological systems.

The dipole bound anion in 2-3-dimethoxy-para-benzoquinone (CoQ0), has been observed experimentally [23, 24, 25, 26]. for CoQ1 it is still seen but much weaker, and for CoQ2 it is not.

1.4 Research Goals

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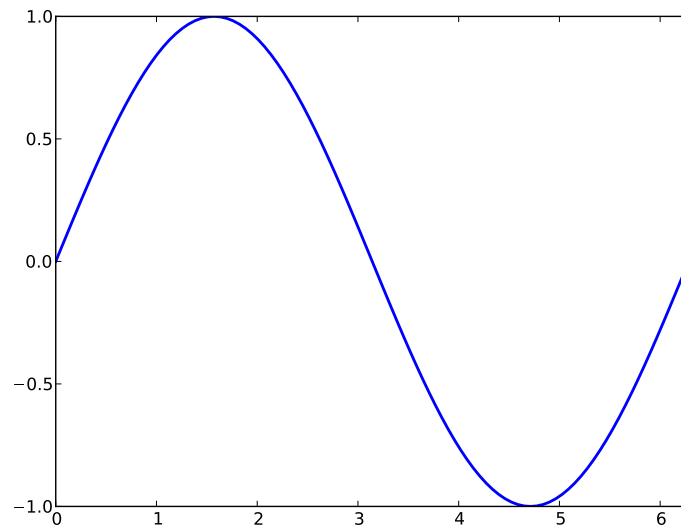


Figure 1.1: Illustration of how to include a figure (long text, should not go to Table of Figures).

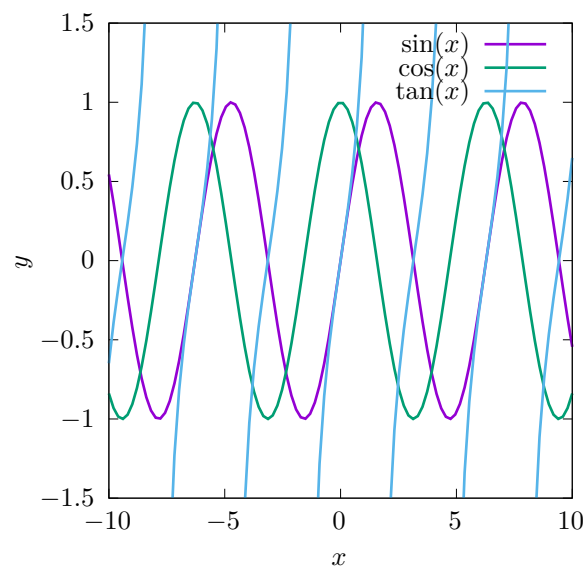


Figure 1.2: Illustration of how to include a figure (long text, should not go to Table of Figures).

Chapter 2

Theoretical Background

2.1 Self Consistent Field Methods

The objective of any quantum chemical calculation is to solve the time-independent Schrödinger equation (TISE) for a many-electron system:

$$\hat{H}\Psi = E\Psi \quad (2.1)$$

However, solving the TISE exactly for systems with more than one electron is computationally infeasible due to the complexity of electron-electron interactions. To address this, approximate methods such as the Hartree-Fock (HF) method have been developed[27].

The Hartree-Fock (HF) method stands as the cornerstone electronic structure calculations. Its primary objective is to provide an approximate solution to the many-electron time-independent Schrödinger equation within the Born-Openheimer approximation, which governs the behavior of electrons within atoms and molecules: The HF method achieves this by assuming that each electron moves independently within an average electrostatic field generated by the other electrons in the system. In the HF method the N -electron wavefunction is represented by a Slater determinant, which is formed by taking the antisymmetrized product of N individual one-electron spin-orbitals (χ):

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{r}_1) & \chi_2(\mathbf{r}_1) & \cdots & \chi_N(\mathbf{r}_1) \\ \chi_1(\mathbf{r}_2) & \chi_2(\mathbf{r}_2) & \cdots & \chi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{r}_N) & \chi_2(\mathbf{r}_N) & \cdots & \chi_N(\mathbf{r}_N) \end{vmatrix} \quad (2.2)$$

The choice of using a determinant inherently satisfies both the Pauli exclusion principle, and the antisymmetry requirement of fermions. The energy expectation for a Slater determinant according to HF is variational and can be computed as:

$$\begin{aligned}
 E_{HF} &= \langle \Psi | \sum_{i=1}^N \hat{F}_i | \Psi \rangle \\
 &= \langle \Psi | \sum_{i=1}^N \hat{h}(i) + \sum_{i,j=1}^N (2\hat{J}_j(i) - \hat{K}_j(i)) | \Psi \rangle \quad (2.3) \\
 &= \sum_{i=1}^N \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{i,j=1}^N \langle \chi_i \chi_j | | \chi_i \chi_j \rangle
 \end{aligned}$$

Where, \hat{F} is the Fock operator. \hat{F} is made up from \hat{h} , the one-electron core Hamiltonian operator (kinetic energy and electron-nucleus attraction); $\hat{J}_j(i)$, the Coulomb operator, describing the electrostatic repulsion between electron i and the average charge distribution of electron j , and $\hat{K}_j(i)$ is the exchange operator, a purely quantum mechanical term arising from the antisymmetry principle. Because of the two electron terms, the computational cost of HF scales as $O(N^4)$.

The Hartree-Fock equations are inherently non-linear: because the Fock operator depends on the wavefunctions of all the other electrons, their interactions are coupled. Consequently, these equations cannot be solved analytically and are solved using an iterative procedure known as the self-consistent field (SCF) method, where the final field experienced by the electrons must be consistent with the electron distribution that generates that field. The SCF procedure involves the following steps: An initial guess for the spin-orbitals is made. Using this initial guess, the Fock operator is constructed. The Hartree-Fock equations are then solved by diagonalizing the Fock operator to obtain a new set of molecular orbitals and their corresponding energies. This new set of orbitals is compared to the previous set. If the change is below a predefined threshold, the procedure is considered converged, and the SCF is achieved. If convergence is not reached, the new set of orbitals is used to construct a new Fock operator, and the process is repeated. Convergence signifies that a stable electronic configuration has been reached within the limitations of the Hartree-Fock approximation.

In practical Hartree-Fock calculations, the spinorbitals are expressed as linear combinations of predefined mathematical functions known as basis functions. The set of these functions is called a basis set. Because a finite basis set cannot exactly represent the spinorbitals, they greatly define the level of accuracy

and computational cost of the calculation. Larger basis sets generally lead to more accurate descriptions of the electronic structure at the cost of increased computational effort.

2.1.1 Electron Correlation

The Hartree-Fock (HF) method is inherently limited by its neglect of the instantaneous interactions of electrons. In the HF approximation, each electron is treated as moving independently within a static, average field created by the other electrons. This mean-field approach fails to account for the fact that electrons will instantaneously repel each other, leading to a correlated movements as they try to avoid each other in space.

The primary consequence of neglecting electron correlation in the HF approximation is an overestimation of the electron-electron repulsion energy. While the HF method does account for the exchange interaction exactly as a consequence of the antisymmetry of the Slater determinant (Fermi correlation), it completely neglects the Coulomb, or dynamic, correlation. This omission leads to a higher electronic energy than the exact solution, and an inability to accurately predict certain phenomena, such as London dispersion forces.

The difference between the exact non-relativistic energy of the system and the energy obtained in the HF complete basis limit is defined as the correlation energy and is always negative due to the variational principle. Correlated methods aim to include the effects of the instantaneous interactions between electrons that are neglected in the mean-field approximation of HF theory. In the following sections, several correlated methods relevant to this work are presented.

2.1.2 Møller-Plesset Perturbation Theory

Møller-Plesset (MP) perturbation theory offers a way to improve upon the HF energy by the use of Raylei-Schro perturbation theory: the electron correlation is treated as a perturbation to the HF Hamiltonian. The energy and wavefunction are then expanded as a series in terms of the perturbation strength. The first-order energy correction in MP theory is zero, so the first non-trivial correction to the HF energy appears at the second order, giving rise to the MP2 method. The MP2 energy correction for a closed-shell molecule is given by:

$$E_{\text{MP2}} = -\frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{|\langle ij || ab \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \quad (2.4)$$

Where i, j denote occupied molecular orbitals, a, b denote virtual molecular orbitals, and ϵ are the corresponding orbital energies from the HF calculation. MP theory can be extended to higher orders (MP3, MP4, etc.) to achieve greater accuracy, although the computational cost increases significantly with each order. The computational cost of MP2 scales as $O(N^5)$.

2.1.3 Density Functional Theory

Density Functional Theory (DFT) provides an alternative approach to incorporating electron correlation by parametrizing the energy on the electron density rather than the wavefunction, reducing the degrees of freedom of the system from $3N - 3$ to just 3. In the most commonly used form of DFT, the Kohn-Sham method, the problem is formulated in terms of orbitals that are not physical, but are chosen to reproduce the electron density of the system. The fundamental principle of DFT is that the ground state energy of a system is a unique functional of its electron density:

$$\left(-\frac{1}{2}\nabla^2 + \hat{V}_{\text{ext}}(\mathbf{r}) + \hat{V}_{\text{H}}(\mathbf{r}) + \hat{V}_{\text{XC}}[\rho(\mathbf{r})] \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2.5)$$

Where \hat{V}_{ext} represents the external potential, $\hat{V}_{\text{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$ is the Hartree potential, \hat{V}_{XC} is the Exchange-Correlation potential and $\rho(\mathbf{r})$ is the electron density. The exchange-correlation functional is the most challenging part of DFT, as it is not known exactly and must be approximated. The accuracy of DFT calculations depends heavily on the choice of exchange-correlation functional. The computational cost of DFT scales as $O(N^4)$.

2.1.4 Configuration Interaction

Configuration Interaction (CI) methods improve upon HF by expressing the electronic wavefunction as a linear combination of the HF ground state determinant and excited state determinants:

$$|\Psi_{\text{CI}}\rangle = c_0|\Phi_0\rangle + \sum_{ia} c_{ia}|\Phi_{ia}\rangle + \sum_{ijab} c_{ijab}|\Phi_{ijab}\rangle + \dots \quad (2.6)$$

Where $|\Phi_0\rangle$ is the HF ground state determinant, $|\Phi_{ia}\rangle$ represents a determinant with a hole in spin-orbital i and a particle in the spin-orbital a , and c are the CI coefficients. Full CI (FCI), includes all possible excitations within a given one-electron basis set and represents the exact solution to the non-relativistic Schrödinger equation in that basis. However, is computationally prohibitive

for all but the simplest systems. Full Configuration Interaction (FCI) includes all possible excitations within a given one-electron basis set and represents the exact solution to the non-relativistic Schrödinger equation in that basis. However, it is computationally prohibitive for all but the simplest systems. Truncated CI methods, such as CISD (singles and doubles), are more practical but lack size extensivity — a property ensuring that the energy of a system scales correctly with the number of non-interacting subsystems. A method is size-extensive if, for two infinitely separated molecules A and B , the total energy satisfies $E(A + B) = E(A) + E(B)$. Truncated CI methods fail to satisfy this condition because they do not include all necessary higher-order excitations, leading to an underestimation of the total energy as system size grows. CI are, however, size-consistent, meaning that the energy behaviour remains consistent when interaction between the involved molecular subsystems is nullified (by distance, for instance). While CISD is size-consistent, its lack of size extensivity makes it unsuitable for extensive systems.

2.1.5 Coupled Cluster Theory

Similarly to CI, the coupled cluster CC method expands the wavefunction as a linear combination of Slater determinants. However, the CC wavefunction is size-extensive and size-consistent by using an exponential ansatz,

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Psi_0\rangle \quad (2.7)$$

where \hat{T} is the cluster operator, which is the central component of CC theory and is defined as a sum of excitation operators,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N \quad (2.8)$$

where N is the total number of electrons in the system. Each term in this sum corresponds to a specific level of excitation and is expressed within the second quantization formalism:

- $\hat{T}_1 = \sum_i^{\text{occ}} \sum_a^{\text{virt}} t_i^a a_a^\dagger a_i$ represents single excitations.
- $\hat{T}_2 = \frac{1}{4} \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{virt}} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$ represents double, *coupled* excitations.
- Higher-order excitation operators $\hat{T}_3, \hat{T}_4, \dots$ describe coupled excitation of three, four, and more electrons, respectively.

The coefficients t_i^a , t_{ij}^{ab} , etc., are cluster amplitudes to be determined by projection of the CC Schrödinger equation onto the excited determinant. The exponential

form, expanded as a Taylor series,

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \dots \quad (2.9)$$

inherently includes terms that represent disconnected clusters, which ensures for size consistency. The energy is obtained by projecting onto the HF reference determinant:

$$E_{\text{CC}} = \langle \Psi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle \quad (2.10)$$

Using the Baker-Campbell-Hausdorff expansion, the exponential operators in Eq. 2.10 can be simplified to a series of commutators which ends at the fourth order. The cluster operator \hat{T} can be truncated at different levels of excitation:

- **CCD** (Coupled Cluster Doubles): This is the simplest approximation in the CC family, where the cluster operator is truncated to include only double excitations: $\hat{T} \approx \hat{T}_2$. There is no CC Singles since the Brillouin’s theorem implies that the amplitudes of single excitations alone are null.
- **CCSD** (Coupled Cluster Singles and Doubles): This is one of the most widely used and generally accurate *ab initio* methods, where the cluster operator includes both single and double excitations: $\hat{T} \approx \hat{T}_1 + \hat{T}_2$.
- **CCSDT** (Coupled Cluster Singles, Doubles, and Triples): $\hat{T} \approx \hat{T}_1 + \hat{T}_2 + \hat{T}_3$.
- ...

The hierarchy can be extended to include even higher levels of excitation, with the properties converging to the FCI limit. The computational cost of CC methods increases rapidly with the level of truncation, as shown in Table 2.1.

Method	Operation count	Memory
HF	$O(N^4)$	$O(N^4)$
DFT	$O(N^4)$	$O(N^4)$
MP2	$O(N^5)$	$O(N^4)$
CCD/CCSD	$O(N^6)$	$O(N^4)$
CCSDT	$O(N^8)$	$O(N^6)$
CC2	$O(N^5)$	$O(N^4)$

Table 2.1: Computational scaling of quantum chemistry methods.

2.1.6 Second Approximate Coupled Cluster

Second Approximate Coupled Cluster (CC2) belongs to the broader family of CCn approximate coupled cluster methods, where the ‘n’ in CCn indicates the truncation of the cluster operator within a perturbative hierarchy. These methods aim to reduce the computational cost associated with standard CC truncations while still retaining a reasonable level of accuracy.

In CC2, the equations for the single amplitudes, t_i^a , are the same as CC theory (Eq. 2.7) under the constraint that the doubles amplitudes, t_{ij}^{ab} , are calculated using the non-iterative expression for MP2 (Eq 2.4). The resulting expression for the CC2 correlation energy is:

$$E_{CC2} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{|\langle ij || ab \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} + \sum_i^{\text{occ}} \sum_a^{\text{virt}} \hat{F}_{ai} t_i^a \quad (2.11)$$

The perturbative treatment of the doubles amplitudes in CC2, reduces the computational cost compared to CCSD, Table 2.1. While this approximation can lead to a less accurate description of electron correlation, the inclusion of singles amplitudes allows for an approximate description of orbital relaxation, which often leads to higher quality wavefunction, and hence properties, compared to MP2.

2.2 Equation-of-Motion Methods

Equation-of-Motion Coupled Cluster (EOM-CC) methods are an extension of ground-state coupled cluster theory which provide a framework for calculating a variety of excited (EE), ionized (IP) and electron-attached (EA) states. In the EOM-CC, the target electronic state is generated by applying a linear excitation operator \hat{R} to a reference state, which typically is the coupled cluster wavefunction of the ground state. The target state wavefunction can then be expressed as $|\Psi_{\text{EOM}}\rangle = \hat{R}|\Psi_{\text{CC}}\rangle = \hat{R}e^{\hat{T}}|\Phi_{\text{HF}}\rangle$. Figure 2.1, shows some of the determinats of $|\Psi_{\text{EA}}\rangle$, where the target state has one more α electron.

The form of the operator \hat{R} is similar to the cluster operator and chosen to access the desired target state. In the case of EOM-EA, the electron attachment operator R^{EA} includes terms that describe the creation of one electron to an unoccupied orbital, terms that describe the creation of one electron accompanied by the excitation of another electron from an occupied to an unoccupied orbital,

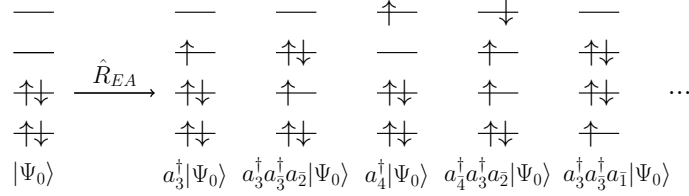


Figure 2.1: EOM-EA.

and so on:

$$\hat{R}^{\text{EA}} = \hat{R}_1^{\text{EA}} + \hat{R}_2^{\text{EA}} + \dots = \sum_a r^a a_a^\dagger + \frac{1}{2} \sum_{ab} \sum_i r_i^{ba} a_b^\dagger a_a^\dagger a_i + \dots \quad (2.12)$$

Where a and b denote virtual orbitals, i denotes an occupied orbital, and r^a and r_i^{ba} are the coefficients to be determined. By truncating at the same excitation level as the cluster operator, the method is rigorously size-extensive and size-consistent. The EA energies, or any other EOM energy, can be obtained as the eigenvalues of the similarity-transformed Hamiltonian, \bar{H}_N :

$$\bar{H}_N \hat{R} |\Psi_0\rangle = \Delta E_{\text{EOM}} \hat{R} |\Psi_0\rangle \quad (2.13)$$

$$\bar{H}_N = e^{-\hat{T}} \hat{H} e^{\hat{T}} - \langle \Psi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle \quad (2.14)$$

Since the similarity transformed hamiltonian is non-hermitian, the left and right are different but correspond to the same eigenvalues. This means that the properties have ‘right’ and ‘left’ expectation values.

The strength of the EOM-CC ansatz is the use of a closed shell reference to access open shell states, which are eigenfunctions of the \hat{S}^2 operator. The EOM-CC methods are also size-extensive and size-consistent. The computational cost of EOM-CC methods is similar to that of the corresponding ground-state CC methods.

2.3 Dyson Orbitals

Dyson orbitals are defined as the overlap between the wavefunction of an initial N -electron state ($|\Psi_0^N\rangle$) and the wavefunction of the final state with $N \pm 1$ electrons ($|\Psi_f^{N \pm 1}\rangle$).

$$\phi_d(r_1) = \sqrt{N} \int \Psi^N(r_2, \dots, r_N) \Psi^{N+1}(r_1, r_2, \dots, r_N) dr_2 \dots dr_N \quad (2.15)$$

Because the the terms differ in one electron, the result of the overlap is a vector instead of a scalar, and can be expressed as a linear combination of the molecular orbitals ($\phi_p(r)$) of the reference wavefunction:

$$\phi_d(r) = \sum_p \gamma_p \phi_p(r) \quad (2.16)$$

where γ_p are the coefficients that quantify the contribution of each molecular orbital to the Dyson orbital. Physically, Dyson orbitals can be interpreted as the correlated analog to the orbital of the electron that is either removed or attached.

The norm squared of the Dyson orbital, (P), is calculated by integrating the squared modulus of the Dyson orbital over all space:

$$P = \int |\phi_{Dyson}(r)|^2 dr = \sum_{p,q} \gamma_p^* \gamma_q \langle \phi_p | \phi_q \rangle \quad (2.17)$$

The pole strength ranges from 0 to 1 and provides a direct measure of the one-electron character of the ionization or electron attachment process. As the open shell wavefunction is usually obtained by means of a EOM-CC method, there are a ‘left’ and ‘right’ Dyson orbital.

They can be used for the interpretation and prediction of photoelectron spectra as they contain all the information required to calculate differential cross-sections, $\frac{d\sigma}{d\Omega_k}$:

$$\frac{d\sigma}{d\Omega_k} = \frac{4\pi^2 k E}{c} |\langle \phi_d | \mu | \Psi_k^{el} \rangle|^2 \quad (2.18)$$

where where k is the magnitude of the photoelectron wavevector, E is the energy of the ionizing radiation, and c is the speed of light, μ is the dipole operator, and Ψ_k^{el} is the photoelectron wavefunction, and a strong orthonormality is assumed between the reference and continuum wavefunction.

2.3.1 EOM-CC2 Dyson Orbital Equations

Justify that the expression doesnt change from CCSD (see TJ email).

EOM-EA-Dyson Equations

A derivation of the algebraic expression of Dyson orbitals in terms of the t , r , l , λ amplitudes is presented. It is importnat to realize that the operators

involved ($\hat{T}, \hat{\Lambda}, \hat{R}, \hat{L}$) affect the occupation of the spin-orbitals, and thus only the combinations of terms which leave the reference wavefunction, $|0\rangle$, unchanged survive. To find these combinations, commutators can be used to reorder the operators involved:

In the case of the right EOM-EA-Dyson orbital amplitudes:

$$\gamma_i^{\text{EA,R}} = \langle EA | \hat{a}_i^\dagger | CC \rangle = \langle 0 | \hat{L}^{EA} e^{-\hat{T}} \hat{a}_i^\dagger e^{\hat{T}} | 0 \rangle$$

The following equalities are useful:

$$e^{-\hat{T}} e^{\hat{T}} = e^{\hat{T}} e^{-\hat{T}} = 1$$

$$[e^{\pm \hat{T}}, \hat{a}_p^\dagger] = \cancel{[1, \hat{a}_p^\dagger]} \overset{0}{\pm t_j^b [\hat{b}^\dagger \hat{j}, \hat{a}_p^\dagger]} \pm t_{jk}^{bc} [\hat{b}^\dagger \hat{c}^\dagger \hat{k} \hat{j}, \hat{a}_p^\dagger] + \dots$$

Where a change of notation, $a_p^\dagger \rightarrow p^\dagger$, upon expansion is done for readability. Two cases are distinguished, p is a virtual orbital, a , or an occupied orbital, i . For virtual orbitals, $p = a$:

$$[\hat{b}^\dagger \hat{j}, \hat{a}^\dagger] = \hat{b}^\dagger \hat{j} \hat{a}^\dagger - \hat{a}^\dagger \hat{b}^\dagger \hat{j} = (-1)^2 \hat{a}^\dagger \hat{b}^\dagger \hat{j} - \hat{a}^\dagger \hat{b}^\dagger \hat{j} = 0$$

Similarly with higher order terms, it is arrived to:

$$[e^{\pm \hat{T}}, \hat{a}_a^\dagger] = 0$$

For occupied orbitals, $p = i$:

$$[\hat{b}^\dagger \hat{j}, \hat{i}^\dagger] = \hat{b}^\dagger \hat{j} \hat{i}^\dagger \overset{0}{\cancel{- \hat{i}^\dagger \hat{b}^\dagger \hat{j}}} - \hat{i}^\dagger \hat{b}^\dagger \hat{j}$$

And similarly with higher order terms:

$$[e^{\pm \hat{T}}, \hat{a}_i^\dagger] = -\hat{a}_i^\dagger (e^{\pm \hat{T}} - 1)$$

These relations can now be used to derive the expression for the occupied and virtual Right EOM-EA-Dyson orbital amplitudes:

$$\phi_D^{\text{EA,R}} = \sum_p \gamma_p^{\text{EA,R}} \phi_p = \sum_i^{\text{occ}} \gamma_i^{\text{EA,R}} \phi_i + \sum_a^{\text{vir}} \gamma_a^{\text{EA,R}} \phi_a$$

The general expression can be reordered:

$$\begin{aligned} \gamma_p^{\text{EA,R}} &= \langle EA | \hat{a}_p^\dagger | CC \rangle = \langle 0 | \hat{L}^{EA} e^{-\hat{T}} \hat{a}_p^\dagger e^{\hat{T}} | 0 \rangle \\ &= \langle 0 | \hat{L}^{EA} (\hat{a}_p^\dagger e^{-\hat{T}} + [e^{-\hat{T}}, \hat{a}_p^\dagger] e^{\hat{T}}) | 0 \rangle \end{aligned} \quad (2.19)$$

For virtual orbitals, $p = a$:

$$\begin{aligned}
 \gamma_a^{\text{EA,R}} &= \langle 0 | \hat{L}^{EA} (\hat{a}_a^\dagger e^{-\hat{T}} + [e^{-\hat{T}}, \hat{a}_a^\dagger]) e^{\hat{T}} | 0 \rangle \\
 &= \langle 0 | \hat{L}^{EA} \hat{a}_a^\dagger e^{-\hat{T}} e^{\hat{T}} | 0 \rangle = \langle 0 | \hat{L}^{EA} \hat{a}_a^\dagger | 0 \rangle \\
 &= \langle 0 | l_a \hat{a} \hat{a}^\dagger | 0 \rangle \\
 &= l_a
 \end{aligned} \tag{2.20}$$

For occupied orbitals, $p = i$:

$$\begin{aligned}
 \gamma_i^{\text{EA,R}} &= \langle 0 | \hat{L}^{EA} (\hat{a}_i^\dagger e^{-\hat{T}} + [e^{-\hat{T}}, \hat{a}_i^\dagger]) e^{\hat{T}} | 0 \rangle \\
 &= \langle 0 | \hat{L}^{EA} (\hat{a}_i^\dagger e^{-\hat{T}} - \hat{a}_i^\dagger e^{-\hat{T}} + \hat{a}^\dagger) e^{\hat{T}} | 0 \rangle = \langle 0 | \hat{L}^{EA} \hat{a}_i^\dagger e^{\hat{T}} | 0 \rangle \\
 &= \langle 0 | l_b t_i^b \hat{b} \hat{i}^\dagger \hat{b}^\dagger \hat{i} + l_{bc}^j t_{ij}^{bc} \hat{b} \hat{c} \hat{j}^\dagger \hat{i}^\dagger \hat{b}^\dagger \hat{c}^\dagger \hat{i} \hat{j} | 0 \rangle \\
 &= - \sum_c t_{ic} l_c - \frac{1}{2} \sum_{kcd} t_{ki}^{dc} t_{dc}^k
 \end{aligned} \tag{2.21}$$

A similar approach can be applied to the other Dyson equations to obtain the expressions.

Left EOM-EA-Dyson orbital, $\phi_D^{\text{EA,L}} = \sum_i^{\text{occ}} \gamma_i^{\text{EA,L}} \phi_i + \sum_a^{\text{vir}} \gamma_a^{\text{EA,L}} \phi_a$:

$$\begin{aligned}
 \gamma_i^{\text{EA,L}} &= \langle CC | \hat{a}_i | EA \rangle \\
 &= - \sum_c \lambda_{ic} r_c - \frac{1}{2} \sum_{kcd} \lambda_{ik}^{cd} t_k^{dc}
 \end{aligned} \tag{2.22}$$

$$\begin{aligned}
 \gamma_a^{\text{EA,L}} &= \langle CC | \hat{a}_a | EA \rangle \\
 &= r_a + \sum_{kc} \lambda_{kc} r_{ca}^k + \sum_k \gamma_k^{\text{EA,L}} t_{ka} - \frac{1}{2} \sum_{klcd} \lambda_{lk}^{dc} t_{lk}^{da} r_c
 \end{aligned} \tag{2.23}$$

EOM-EA-EE-Dyson Equations

Right Dyson orbital, $\phi_D^{\text{EA-EE,R}} = \sum_i^{\text{occ}} \gamma_i^{\text{EA-EE,R}} \phi_i + \sum_a^{\text{vir}} \gamma_a^{\text{EA-EE,R}} \phi_a$:

$$\begin{aligned}\gamma_i^{\text{EA-EE,R}} &= \langle EA | \hat{a}_i^\dagger | EE \rangle \\ &= r_0 \gamma_a^{\text{EA,R}} - \sum_c r_{ic} l_c - \frac{1}{2} \sum_{lcd} r_{il}^{cd} l_{dc}^l - \sum_{lcd} l_{dc}^l t_{ic} r_{ld}\end{aligned}\quad (2.24)$$

$$\begin{aligned}\gamma_a^{\text{EE-EA,R}} &= \langle EA | \hat{a}_a^\dagger | EE \rangle \\ &= r_0 l_a + \sum_{kc} l_{ca}^k r_{kc}\end{aligned}\quad (2.25)$$

Left Dyson orbital, $\phi_D^{\text{EE-EA,L}} = \sum_i^{\text{occ}} \gamma_i^{\text{EE-EA,L}} \phi_i + \sum_a^{\text{vir}} \gamma_a^{\text{EE-EA,L}} \phi_a$:

$$\begin{aligned}\gamma_i^{\text{EE-EA,L}} &= \langle EE | \hat{a}_i | EA \rangle \\ &= - \sum_c l_{ic} r_c - \frac{1}{2} \sum_{kcd} l_{ik}^{cd} r_k^{dc}\end{aligned}\quad (2.26)$$

$$\begin{aligned}\gamma_a^{\text{EE-EA,L}} &= \langle EE | \hat{a}_a | EA \rangle \\ &= \sum_{kc} l_{kc} r_{ca}^k + \sum_k \gamma_k^{\text{EE-EA,L}} t_{ka} - \frac{1}{2} \sum_{klcd} l_{lk}^{dc} t_{lk}^{da} r_c\end{aligned}\quad (2.27)$$

EOM-IP-Dyson Equations

Right Dyson orbital, $\phi_D^{\text{EE,R}} = \sum_i^{\text{occ}} \gamma_i^{\text{IP,R}} \phi_i + \sum_a^{\text{vir}} \gamma_a^{\text{IP,R}} \phi_a$:

$$\begin{aligned}\gamma_a^{\text{IP,R}} &= \langle CC | \hat{a}_a^\dagger | IP \rangle \\ &= \lambda_{ka} r_k + \frac{1}{2} \lambda_{lk}^{ca} r_{klc}\end{aligned}\quad (2.28)$$

$$\begin{aligned}\gamma_i^{\text{IP,R}} &= \langle CC | \hat{a}_i^\dagger | IP \rangle \\ &= r_i + \sum_{kc} \lambda_{kc} r_{ik}^c - \sum_c \gamma_c^{\text{IP,R}} t_{ic} - \frac{1}{2} \sum_{klcd} \lambda_{lk}^{dc} t_{li}^{dc} r_k\end{aligned}\quad (2.29)$$

Left Dyson orbital, $\phi_D^{\text{IP,L}} = \sum_i^{\text{occ}} \gamma_i^{\text{IP,L}} \phi_i + \sum_a^{\text{vir}} \gamma_a^{\text{IP,L}} \phi_a$:

$$\begin{aligned} \gamma_i^{\text{IP,L}} &= \langle IP | \hat{a}_i | CC \rangle \\ &= l_i \end{aligned} \quad (2.30)$$

$$\begin{aligned} \gamma_a^{\text{IP,L}} &= \langle IP | \hat{a}_a | CC \rangle \\ &= \sum_k t_{ka} l_k + \frac{1}{2} \sum_{klc} t_{kl}^{ac} l_{kl}^c \end{aligned} \quad (2.31)$$

EOM-EE-IP-Dyson Equations

Right Dyson orbital, $\phi_D^{\text{EE-IP,R}} = \sum_i^{\text{occ}} \gamma_i^{\text{EE-IP,R}} \phi_i + \sum_a^{\text{vir}} \gamma_a^{\text{EE-IP,R}} \phi_a$:

$$\begin{aligned} \gamma_i^{\text{EE-IP,R}} &= \langle EE | \hat{a}_i^\dagger | IP \rangle \\ &= \sum_{kc} l_{kc} r_{ik}^c - \sum_c \gamma_c^{IP-EE} t_{ic} - \frac{1}{2} \sum_{klcd} l_{lk}^{dc} t_{li}^{dc} r_k \end{aligned} \quad (2.32)$$

$$\begin{aligned} \gamma_a^{\text{EE-IP,R}} &= \langle EE | \hat{a}_a^\dagger | IP \rangle \\ &= l_{ka} r_k + \frac{1}{2} l_{lk}^{ca} r_{klc} \end{aligned} \quad (2.33)$$

Left Dyson orbital, $\phi_D^{\text{IP-EE,L}} = \sum_i^{\text{occ}} \gamma_i^{\text{IP-EE,L}} \phi_i + \sum_a^{\text{vir}} \gamma_a^{\text{IP-EE,L}} \phi_a$:

$$\begin{aligned} \gamma_i^{\text{IP-EE,L}} &= \langle IP | \hat{a}_i | EE \rangle \\ &= r_0 l_i + \sum_{kc} l_{ik}^c r_{kc} \end{aligned} \quad (2.34)$$

$$\begin{aligned} \gamma_a^{\text{IP-EE,L}} &= \langle IP | \hat{a}_a | EE \rangle \\ &= r_0 \gamma_a^{\text{IP,L}} + \sum_k r_{ka} l_k + \frac{1}{2} \sum_{klc} r_{kl}^{ac} l_{kl}^c + \sum_{klc} l_{kl}^c t_{ka} r_{cl} \end{aligned} \quad (2.35)$$



Chapter 3

Computational Methods

All electronic structure calculations were performed using the developer’s copy of the *Q-Chem* software [28]. In all computations the frozen-core approximation is used, only the valence electrons are correlated, as well as the resolution of the identity (RI) approximation, auxiliary basis functions are used to approximate the two-electron integrals, reducing its scaling to $N(O^3)$ [29].

For the EOM-EA calculations, the reference wavefunction was obtained as the restricted Hartree-Fock (RHF) solution of the ground state of the neutral molecule. Unless explicitly mentioned, calculations were performed at using the aug-cc-pVDZ basis set [30] further augmented by 3 s-shells on hydrogen atoms and 6 s- and 3 p-shells on all non-hydrogen atoms [31] to properly model the non-valence states. The coefficients of the extra functions were obtained by successively halving the most diffuse function of the original set.

CC2 Dyson orbitals for EOM variants described in section 2.3.1 and appendix ?? were implemented as described, and will be released in an upcoming version of *Q-Chem*.

All closed-shell quinone model geometries were optimized using the TPSS functional[32] with Grimme’s pair-wise dispersion corrections with Becke-Johnson damping (D3BJ)[33], and the minimally augmented[34] def2-TZVP basis sets[35] (ma-def2-TZVP), following the work in [36]. For the scan calculations, each singlepoint was optimized constraining its relevant angles by the method of Lagrange multipliers; dihedrals of the methoxy chains of Q0 and Q1, and the isoprene tail of Q1. In the case of quinone + aminoacid models, crystal structures were taken from the Protein Data Bank (PDB). Hydrogens were added using *PyMOL*’s [37] `add_H` functionality, and relaxed using the

method above (fixing the rest of the heavy atoms).

For the scans of quinone + molecule, each subsystem was independently optimized and and put together with any further refinement.

For quinone stystems, only EOM-EA right Dyson orbitals were computed to speed up the calculations by avoiding the need to compute the lamda terms.

Photoionization and Photodetachment crossections were calculated using the *ezDyson* package [38, 39].

Chapter 4

Results and Discussion

4.1 Performance of EOM-CC2 Related Methods

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4.1.1 Basis Set Dependence of EA-EOM-CC2 in Dipole Bound Anions

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Molecule		RI-CC2						RI-CCSD				KT	μ (D)
		aug-cc-pVTZ				pVDZ		pVQZ		pVDZ			
		2s1p	4s2p	6s3p	8s4p	6s3p	6s3p	6s3p	6s3p	6s3p	6s3p		
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	ref.	12.0			

Table 4.1: EOM-EA binding energies of dipole-bound radical anions computed using different augmented Dunning basis sets and RI-CC2 and RI-CCSD for the the test set of moluces [31]. A positive value corresponds to a bound electron. Koopmans’ theorem (KT), and dipole momment (μ), calculated at the HF level, and mean absolute error (MAE) are also given. The values are in meV and D respectively.

4.1.2 Performance of EA-EOM-CC2 on Valence Bound Radical Anion States of Quinones

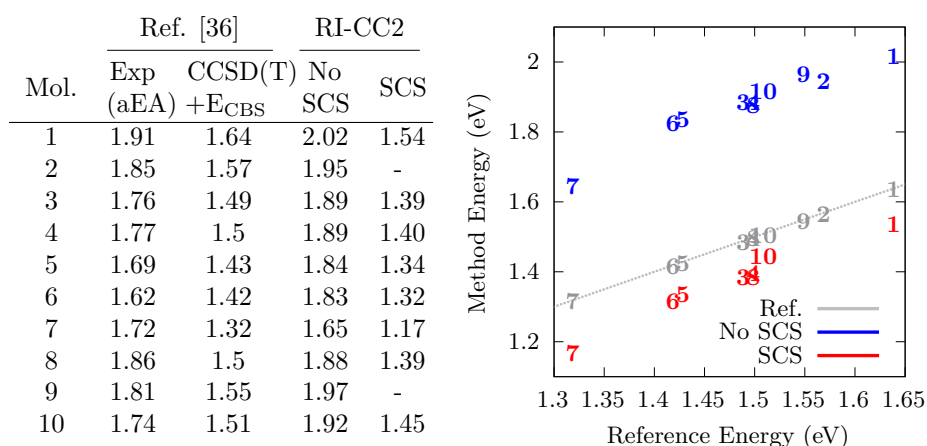


Table 4.2 and **Figure 4.1**: Comparison between reference and RI-CC2 data for quinones. The table also includes the experimental value (adiabatic EA instead of vertical EA).

SCS improves the result for valence state of CC2, which is in accordance with the conclusions from [31]. Something to note is that when comparing the results with experiments, one can think that CC2 gets close than CCSD. This however, can be explained by the fact that the experiment measures the adiabatic electron binding energy, while the calculations are performed for the vertical EA. As the former energy

As the trend is recovered without SCS, albeit the larger (0.2 eV) but consistent error the subsequent calculations do not use this method, as SCS worsens the results for dipole bound anions. A strength of this approach is that both states can be calculated from the same Hamiltonian, and the results are consistent.

Dipole bound states are worsened by SCS [31]. This is explained by the fact that the DBS resides in a diffuse state; the extra spin is far from the other electrons, meaning that the exchange interaction is much smaller than the Coulomb interaction. ...

4.1.3 Photoelectron Cross-section Calculations from EOM-CC2/CCSD

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4.2 Study on the Anion States of Ubiquinone

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4.2.1 Energy and Dipole Surfaces of CoQ

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Q0

aa

...

Q1

...

4.2.2 A Simple Cluster Model

...

4.2.3 Interaction with Water

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4.2.4 Effect of Nearby Aminoacids

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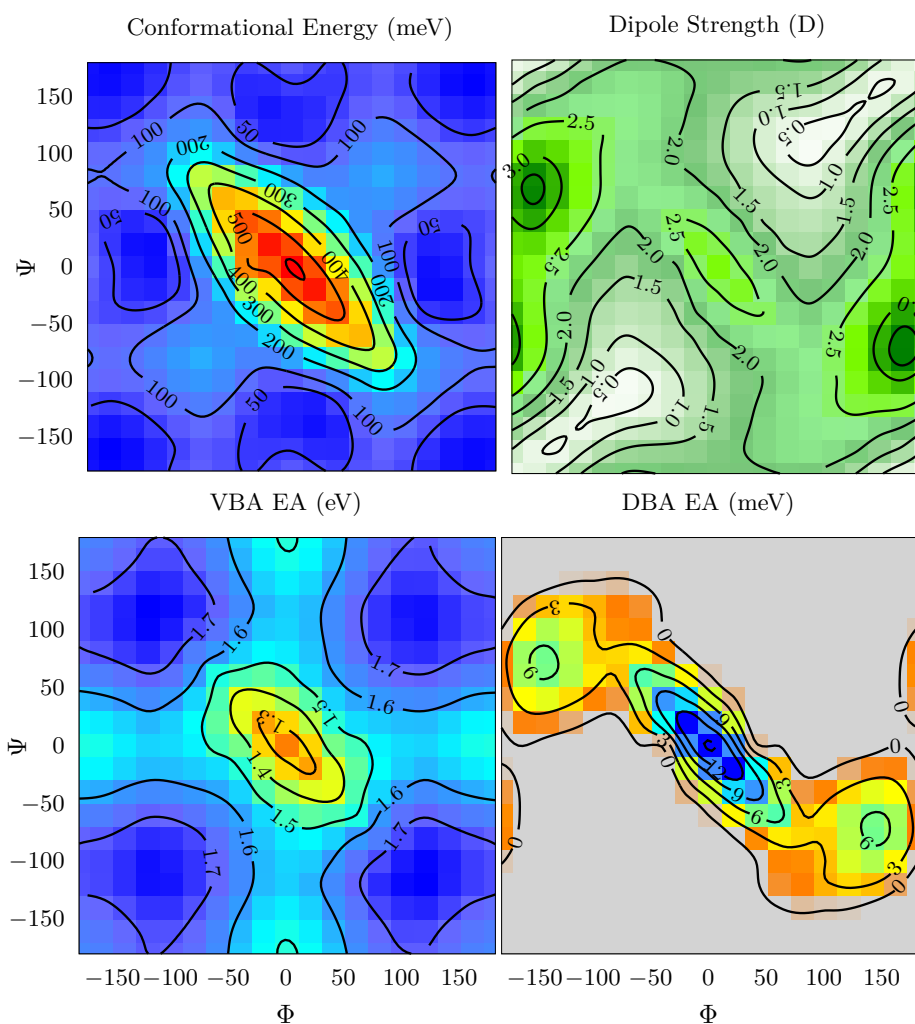


Figure 4.2: Surfaces of Q0. Left: Energy surface. Right: Dipole moment surface.

Serine

...

Threonine

...

Apsaragine

...

Isoleucine

...

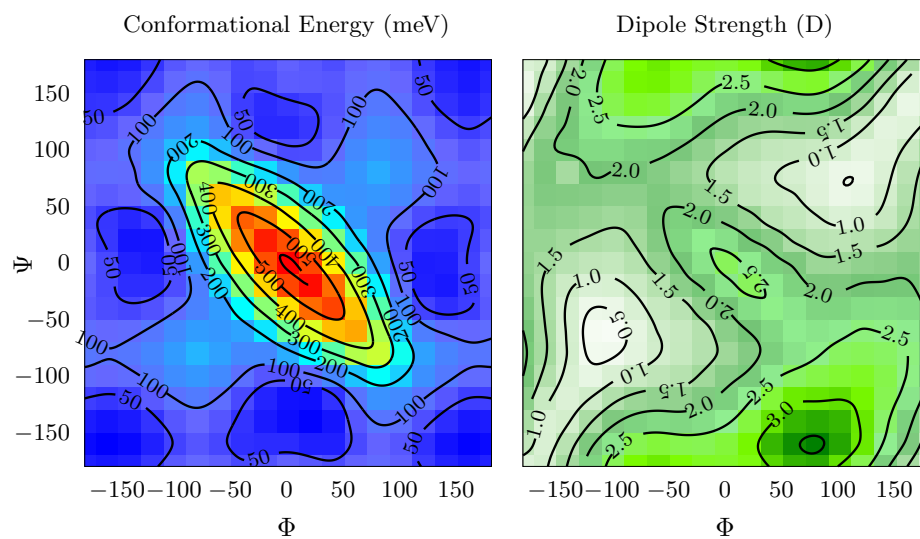


Figure 4.3: Surfaces of Q1. Left: Energy surface. Right: Dipole moment surface.

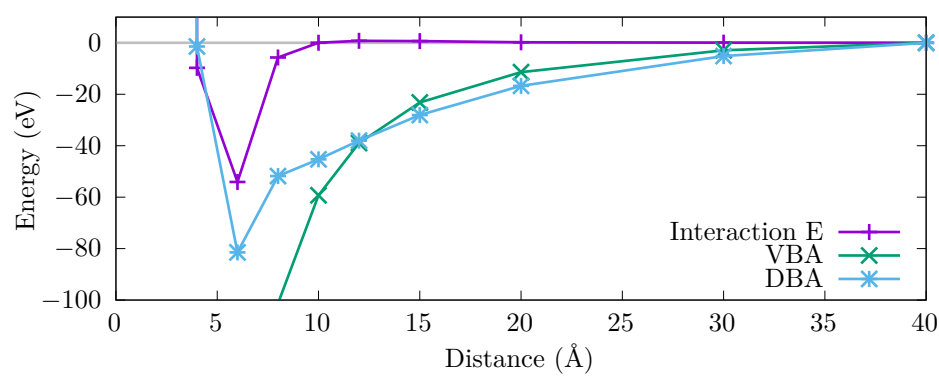


Figure 4.4: Favorable Interaction with water.



Chapter 5

This is conclusion

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Instructions by the Arenberg Doctoral School:

An extensive conclusion, including a global discussion of the research results, a discussion of the implications of the PhD research and future perspectives in regards to follow-up research.



Appendix A

This is myappendix

...

Instructions by the Arenberg Doctoral School:

Appendices: The appendices should include parts of the research which are essential for the work, but which may hamper the readability of the text, e.g. because of their length (mathematical deductions, experimental data, examples, figures, etc.).



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Generative AI was used for language and coding assistance (ChatGPT, MicrosoftCopilot, LeChat).

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