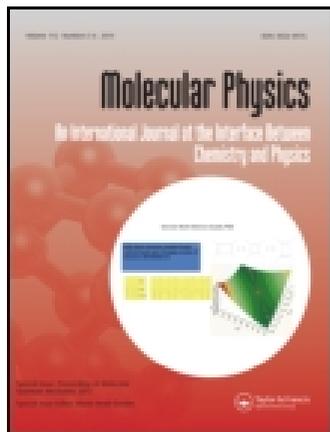


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### Structure and photochemistry of a bio-inspired model for photocatalytic H<sub>2</sub>O splitting: Improved calculations of the Sobolewski and Domcke's Chlorophyll-Imidazole-Benzoquinone model complex

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## INVITED ARTICLE

# Structure and photochemistry of a bio-inspired model for photocatalytic H<sub>2</sub>O splitting: Improved calculations of the Sobolewski and Domcke's Chlorophyll-Imidazole-Benzoquinone model complex

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The photoelectron spectrum of a bio-inspired model supramolecule that consists of a truncated chlorophyll, imidazole, and benzoquinone is explored with the equation of motion coupled cluster method (EOM-CCSD). The motivation for this study is to highlight the capabilities of the massively parallel implementations of closed- and open-shell CC methods in ACES III and to augment recently published results with the approximate resolution of identity CC singles and doubles (RI-CC2) method. Furthermore, we have also obtained the structure of the supramolecule at the second-order many body perturbation theory (MBPT(2)) level with two different basis sets and compared our structure with previous density functional theory (DFT) results.

**Keywords:** artificial photosynthesis; bio-inspired models; hydrogen fuel; equation of motion coupled cluster method

### Introduction

Industrial societies are mostly dependent on limited sources of energy, such as fossil fuels, natural gas etc., for energy requirements. As a result of the growing needs for new sources of energy and the adverse impact on the environment from extracting and utilising fossil fuels, alternative renewable and green energy sources have been sought. The 'hydrogen economy' envisions H<sub>2</sub> [1–4] as the primary fuel source. Since hydrogen is abundant in nature but not commonly found in the free form of H<sub>2</sub>, an economical carbon-neutral process to generate free H<sub>2</sub> is imperative for the long-term success of the evolving 'hydrogen economy' [4]. A seemingly effortless process that converts the most abundant material on earth, H<sub>2</sub>O, into its components, hydrogen and oxygen, utilising the unlimited source of the sun's energy during photosynthesis would hold the secret for a carbon-neutral continuous source of H<sub>2</sub> [5,6]. The question as to whether we can design a molecular machinery to mimic nature's photosynthetic reaction centre to directly convert sunlight into energy to split H<sub>2</sub>O has fascinated scientists for decades [7–12].

The oxidation of H<sub>2</sub>O into its components,  $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}$ , is a highly energetically unfavourable reaction ( $\Delta H^\circ = 275 \text{ KJ/mol}$ ). The uncatalysed dissociation reaction requires a temperature of 2500°C to break the four strong OH bonds (the bond enthalpy is 494 KJ/mol per each OH bond). However, the energy barrier can be substantially lowered if the dissociation is coupled to an energy releasing step of O–O bond formation ( $\Delta H^\circ = -494 \text{ KJ/mol}$ ) and

with the aid of a catalyst. The precision that 'the catalyst' must achieve is made abundantly clear in a recent article from which we quote: 'This can, however, only occur via the intermediacy of a catalyst that is constrained to rearrange these five bonds in a coordinated sequence with a picometer precision and without releasing reactive intermediates' [13]. Delivering the necessary energy input into these bonds while overcoming the mechanistic complexity is among the 'Holy Grails of chemistry' [14–16].

Nature's invention to accomplish this complex chemistry is the photosystem II (PSII) and the oxo-manganese catalyst (OMC) [5,6]. The light harvesting molecules in PSII absorb light in a region of the spectrum high enough to generate the potential required to initiate the electron transfer from the weakly oxidising H<sub>2</sub>O in the presence of a catalyst. The collection of molecules that directly participate in the H<sub>2</sub>O oxidation is designated as the oxygen evolving centre (OEC). Our current understanding of the OEC comes from the catalytic cycle involving the oxo-manganese complex (OMC) proposed by Joilot and Kok [17,18] and from recent high-resolution X-ray diffraction experiments [19,20]. It has been argued that if we can fully characterise the mechanism by which PSII splits H<sub>2</sub>O, we will be able to design a much simpler, robust and efficient artificial system to accomplish the same task. While a detailed microscopic understanding of the electron- and proton-transfer processes of the natural photosynthetic reaction is still missing, the structures of the PSII and the basic processes of the electron transport chains are known with a sufficient degree of

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accuracy. The key components of the PSII consist of a light harvesting molecule (substituted porphyrines),  $\text{H}_2\text{O}$ , the  $\text{Mn}_4\text{CaO}_x$  catalyst and electron acceptors (the quinone cofactor, pheophytin, and the redox active tyrosine residue) [19,20].

There have been numerous efforts to artificially split  $\text{H}_2\text{O}$  by using bio-inspired models. These models are designed so that they are the closest prototypes of the natural system, and consist of porphyrine- or phthalocyanine-type photo sensitiser, – usually, a catalyst and quinone-type electron acceptors that are held together by water or other suitable substrates through hydrogen bonds. An efficient process to screen these models for their potential to split  $\text{H}_2\text{O}$  avoiding the cost and time of fabricating them in a laboratory would be an invaluable tool. Computational modelling, specifically, high-level quantum mechanical (QM) methods or multi-scale modelling using QM and molecular mechanics (QM/MM) provides such a tool [21]. In this work, we report an application of high-level QM methods to a bio-inspired model system to obtain the basic molecular parameters that govern  $\text{H}_2\text{O}$  splitting.

Impetus for this work comes from recently published articles by Sobolewski and Domcke's (henceforth referred to as SD) [22,23], where they report the computational study of the bio-inspired Chl-Im-Q model system that consists of a chlorophyll fragment (photo-sensitiser), imidazole and  $\text{H}_2\text{O}$ , and p-benzoquinone (electron acceptor) held together by hydrogen bonds. They find a charge-transfer excited state in the supermolecule that is absent in any of the individual fragments, and speculate that it can initiate an electron-transfer chain as in the natural system. The excitation energies are computed with the resolution of identity approximate coupled cluster singles and doubles (RI-CC2) model [24,25] using geometries optimised at the density functional theory (DFT) level [26,27] using the B3LYP exchange-correlation potential [28]. They recommend further studies, in particular, molecular dynamical studies of electron- and proton-transfer processes, in order to fully characterise the model's viability as an artificial  $\text{H}_2\text{O}$  splitting system. However, we believe it is also worthwhile to scrutinise the DFT and RI-CC2 results with superior theoretical methods. There are two primary reasons for this. First, according to B3LYP-DFT, the structure of Chl-Im-Q is held together only by weak hydrogen bonds, but the accuracy of the B3LYP-DFT description of weak interactions has been questioned [29]. Second, the RI-CC2 approximation employed to obtain the excitation energies has also been shown to have weaknesses [30,31]. The charge-transfer excitation is a critical step in the initiation of the photo-driven  $\text{H}_2\text{O}$  splitting.

In this study, we use the many perturbation theory (MBPT), coupled cluster (CC) [32,33], and equation of motion CC (EOM-CC) [34,35] methods to characterise the electronic structure and the photochemistry of the Chl-Im-Q complex. Only with the recent development

and implementation of CC algorithms in massively parallel programs such as ACES III [36], it has become possible to apply CC/MBPT methods to electronic structure problems of the size of the Chl-Im-Q complex.

### Computational methods

The geometry of the Chl-Im-Q complex is optimised at the MBPT(2)/6-31G\* [37] and MBPT(2) levels using the 6-31G(3DF,3PD) [37,38] basis set for Mg and the cc-pVDZ [39] basis set for all the other atoms (this particular mixed basis set is henceforth designated as PVDZ). The vertical excitation energies of the complex is computed using EOM-CCSD at the DFT geometry obtained by Sobolewski and Domcke and at the MBPT(2)/PVDZ geometry obtained in this work. The EOM-CCSD excitation energy calculations employ Ahlrichs' split-valence double zeta basis set with added polarisation functions on Mg and Ahlrichs' PVDZ and VDZ basis set for the other heavy atoms and the hydrogens, respectively [40,41]. As in SD, we designate this basis set as def-SV(P). The core orbitals are kept frozen for the EOM-CCSD excited state calculations.

### Results and discussion

The MBPT(2)/PVDZ geometry of the Chl-Im-Q complex is shown in Figure 1. In Table 1, a few selected bond lengths that are critical to the stability of the complex obtained at the B3LYP/def-SV(P) level by SD is compared with the MBPT(2) results obtained with two different basis sets. The 6-31G\* basis set and the designated PVDZ basis sets have 646 and 747 basis functions, respectively. Purely in terms of the number of basis functions, these calculations do not constitute a very large MBPT(2) optimisation effort in terms of today's standards; however, it is important to point out that there are 308 active electrons that significantly influence the cost of these optimisations.

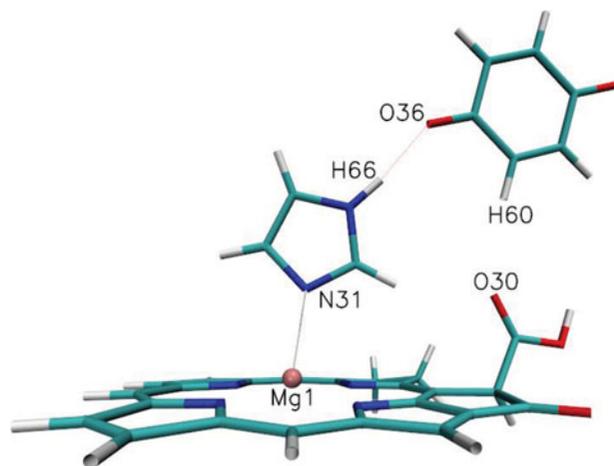


Figure 1. The MBPT(2)/PVDZ optimised structure of the Chl-Im-Q complex.

Table 1. A selection of bond lengths of the Chl–Im–Q complex obtained at different levels of theory (in Angströms).

Bond	B3LYP/ def–SV(p)	MBPT(2) / 6–31G**	MBPT(2)/ PVDZ
O30–H60	2.398	2.425	2.413
O36–H66	1.861	1.877	1.869
Mg1–N31	2.172	2.132	2.124

The basic conclusions of the SD B3LYP optimization: that the imidazole shows a strong coordination to the porphyrin structure (short Mg1–N30 bond) and that one of the oxygen atoms in the quinone forms a relatively strong hydrogen bond with the azine group of the imidazole (O36–H66), is also supported by our calculations. The weak hydrogen bond between O30 and H60 is somewhat elongated at the MBPT(2) level compared to that at the B3LYP–DFT level. It is known that weak interactions are not very well described by DFT. These hydrogen bonded interactions are critical in maintaining the rigidity of the complex and even a slight elongation (0.1 Å) may influence its viability as an artificial model for H<sub>2</sub>O splitting. The MBPT(2) geometries obtained from the two different basis sets show that there is only a very slight variation between the results as we increase the basis set quality.

The EOM–CCSD vertical excitation energies computed at the B3LYP/def–SV(P) and MBPT(2)/PVDZ geometries are shown in Table 2 along with the RI–CC2 results of SD, which are computed at the B3LYP/def–SV(P) geometry.

We also use the same designations of SD to label the excited states. The locally excited states of Chlorophyll singlets are designated as <sup>1</sup>LE<sub>C</sub>, those of the quinone as <sup>1</sup>LE<sub>Q</sub>, and the charge-transfer states as <sup>1</sup>CT<sub>CQ</sub>. The EOM–CCSD excited state calculations consist of 617 basis functions and 220 active electrons. In terms of the number of active electrons to the number of basis function ratio, these UHF–EOM–CCSD calculations (to obtain both singlet and triplet states simultaneously) are the largest that have been attempted so far. This is evident from the fact that it takes about 30 days on 760 cores to complete the entire calculation that solves 10 EOM–CCSD roots.

We can make a direct assessment of the quality of the RI–CC2 results compared to the EOM–CCSD ones from the results shown in the 2<sup>nd</sup> and 3<sup>rd</sup> columns of Table 2 since they both employ the same geometry and basis set. The results in the 4<sup>th</sup> column of Table 2 are obtained to gauge the effect of the geometry on the photoelectron spectrum of the complex. As can be seen from Table 2, we are not able to locate all the singlet states that were previously obtained at the RI–CC2 level. At first, we concluded that this is because we are trying to obtain both singlets and triplets simultaneously. However, singlet-only EOM–CCSD calculations did not yield additional singlet states that can be matched with those obtained at the RI–CC2 level. Nevertheless, it is premature at this stage to conclude that the unmatched RI–CC2 states do not exist at a more accurate EOM–CCSD level without a thorough investigation since the obtained EOM–CCSD states are conditioned by the configuration interaction singles (CIS) initial guess. It is possible that our

Table 2. Vertical excitation energies of the Chl–Im–Q complex. A comparison of RI–CC2 and EOM–CCSD results.

Transition	Excitation Energy (eV)			Oscillator Strength <sup>a</sup>
	CC2/def–SV(P)	EOM–CCSD		
	B3LYP/def–SV(P) geometry	B3LYP/def–SV(P) geometry	MBPT(2)/PVDZ geometry	
<sup>3</sup> LE <sub>C</sub> ( $\pi\pi^*$ )		1.38	1.61	0.0
<sup>3</sup> LE <sub>C</sub> ( $\pi\pi^*$ )		1.50	1.80	0.0
<sup>1</sup> LE <sub>C</sub> ( $\pi\pi^*$ )	2.27	2.21	2.09	0.1
<sup>3</sup> LE <sub>C</sub> ( $\pi\pi^*$ )		2.43	2.35	0.0
<sup>1</sup> LE <sub>C</sub> ( $\pi\pi^*$ )	2.32			
<sup>1</sup> CT <sub>CQ</sub> ( $\pi\pi^*$ )	2.66	2.53	2.38	0.1
<sup>1</sup> CT <sub>CQ</sub> ( $\pi\pi^*$ )	2.75			
<sup>3</sup> CT <sub>CQ</sub> ( $\pi\pi^*$ )			2.65	
<sup>3</sup> CT <sub>CQ</sub> ( $\pi\pi^*$ )			2.93	
<sup>1</sup> LE <sub>Q</sub> ( $n\pi^*$ )	2.85	3.10	3.03	~0.0
<sup>1</sup> LE <sub>Q</sub> ( $n\pi^*$ )	3.24	3.35	3.04	~0.0
<sup>1</sup> LE <sub>C</sub> ( $\pi\pi^*$ )	3.34	3.47	3.04	$1.0 \times 10^{-5}$
<sup>1</sup> LE <sub>C</sub> ( $\pi\pi^*$ )	3.45	3.50	3.38	$3.0 \times 10^{-5}$

<sup>a</sup>The oscillator strengths are obtained subjected to the approximation that a left-hand EOM–CCSD state is the transpose of a right-hand EOM–CCSD state. Note that the oscillator strengths reported here are not meant to be quantitatively accurate.

CIS implementation needs more refinements. Also, the less costly spin-adapted form of the EOM equations is better suited for these calculations. These considerations are being investigated and we are planning to report those findings in a more detailed follow-up paper.

We note that both EOM-CCSD calculations locate two very low lying triplet states ( $<2$  eV) along with several other triplet states. In our calculations, we are not able to locate the corresponding EOM-CCSD state for the second RI-CC2 charge-transfer singlet state ( $CT_{CQ}(\pi\pi^*)$ ) obtained by RI-CC2 at 2.75 eV. We observe that for the matching charge-transfer state, the EOM-CCSD result is about 0.1 eV smaller than the RI-CC2 result. This is in contrast to our findings in an earlier study of the excited states of DNA bases that the CC2 results are consistently lower compared to the EOM-CCSD results [30,31]. Moreover, our experience from previous studies is that the CC2 valence excitation energies are surprisingly accurate for  $\pi \rightarrow \pi^*$  transitions but fails for  $n \rightarrow \pi^*$  and Rydberg transitions [30,31]. The comparisons for charge-transfer states are scarce to make a definitive statement. The largest differences that we see are for the  $LE_Q(n\pi^*)$  and  $LE_C(n\pi^*)$  states where the EOM-CCSD results are about 0.1 eV higher than the RI-CC2 results.

Let us exclusively focus on the EOM-CCSD results obtained at the MBPT(2)/PVDZ geometry. The weak 2.09 eV (matching RI-CC2 value is 2.27 eV) and stronger 3.04 eV (matching RI-CC2 value is 3.24 eV) are in the same region of widely known  $Q_{x,y}$  and 'Soret' bands of Chlorophyll [42]. A comparison of the results obtained at different geometries shows that both bands display significant changes due to geometry differences. The most important feature of the spectrum of the complex is the appearance of charge-transfer excitations. These excitations are absent in the molecular components of the complex. The  $\pi \rightarrow \pi^*$  charge-transfer excitations transfer an electron from the  $\pi$  orbital of the porphyrin to the vacant  $\pi^*$  orbital of the quinone. The resulting electric field gradient (potential) is responsible for the initiation of proton transfer to reduce the quinone to semiquinone. The photo-assisted electron transfer, subsequent proton transfer, and maintaining and generating a sufficient potential to oxidise water are the features of the natural system that artificial systems are designed to mimic.

A discussion of the viability of the Chl-Im-Q model as an artificial photosynthesis complex within the context of generic electron-driven proton-transfer (EDPT) processes of intramolecularly hydrogen bonded-aromatic systems [43,44] and a qualitative description of photon-assisted electron-transfer reactions that Chl-Im-Q undergoes upon light absorption are explained in detail by SD and is not repeated here [22,23]. In this work, we only focused on assessing the quality of the electronic structure calculations of SD. Based on our results we conclude that the RI-CC2 results are sufficiently close to the EOM-CCSD ones

and may be used in the dynamical simulations of charge-transfer reactions of the Chl-Im-Q model complex. However, it is important to note that our MBPT(2) optimisations and the EOM-CCSD calculations are by no means conclusive benchmark calculations. They only provide minimum thresholds due to the absence of triple excitation effects that are included in the CCSD(T) or EOM-CCSD(T) models, but the highly unfavourable occupied-to-virtual ratio (for a good quality basis set) in this system means that such calculations are currently beyond reach.

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