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Excitation Energies of Zinc Porphyrin in Aqueous Solution Using Long-Range Corrected Time-Dependent Density Functional Theory

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We study the low-lying excited states of the zinc porphyrin molecule in aqueous solution using long-range corrected TDDFT. We report results using the CAM-B3LYP and CAM-PBE0 functionals and compare them with previously reported excited states based on high-level coupled cluster (CC) methods. The aqueous environment is treated via a QM/MM approach.

Introduction

Time-dependent density functional theory (TDDFT)[1] is becoming an attractive tool for reliable excited-state calculations involving single excitations in a wide variety of systems ranging from molecules to materials.[2] However, the results are dependent on the exchange−correlation functionals. Even though TDDFT in conjunction with various standard functionals is reasonably accurate for valence excited states, the inaccuracies of these functionals in the prediction of charge-transfer (CT) and Rydberg states are well documented.[3,4]

The porphyrin system is an ideal case that highlights the typical problems encountered with traditional DFT functionals.[5−7] Porphyrins and their derivatives are vital to the biochemistry of living organisms as they are an integral part of pigments like heme and chlorophyll. A fundamental understanding of the excited states of these systems is therefore of key importance to a variety of biological processes like catalysis, electron transfer, oxygen binding, and photochemical processes in photosynthesis to name a few. In this paper, we focus on the zinc porphyrin (ZnP) system because of its importance to the photochemical properties of π-conjugated systems.[8−11] The vertical excitation energies corresponding to the Q/B bands of the ZnP monomer and dimers as well as the CT states in a phenylene-linked zincbacteriochlorin−bacteriochlorin complex have been studied intensively over the past few years using a variety of ab initio methods.[3,13,14] A recent study[15] of ZnP in aqueous solution showed the importance of including higher-order correlation effects as well as the impact of the environment on the excited states of ZnP. In addition to showcasing large-scale EOMCCSD, CR-EOMCCSD(T), and QM/MM calculations, the paper also clearly demonstrated the failure of TDDFT calculations based on the B3LYP exchange−correlation functional in predicting the CT states in this system in an aqueous environment.

In this paper, we extend the previous calculations[15] to long-range corrected (LC) functionals. To the best of our knowledge, this is the first investigation of the performance of these functionals in systems in the presence of an explicit aqueous environment using a QM/MM approach. We report results using the CAM-B3LYP[16,17] and CAM-PBE0[18] functionals. We compare our results with previously reported high-level-based excited-state methods as well as the base hybrid functionals B3LYP[19] and PBE0.[20]

Theory and Implementation

In the long-range corrected (LC) or Coulomb attenuated (CAM) DFT approach, the electron repulsion is separated into long- and short-range parts as[16,21,22]

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta\,\mathrm{erf}(\gamma r_{12})]}{r_{12}} + \frac{\alpha + \beta\,\mathrm{erf}(\gamma r_{12})}{r_{12}} \quad (1)$$

where α and β are dimensionless constants satisfying the relations $0 \le \alpha \le 1$, $0 \le \beta \le 1$, and $0 \le \alpha + \beta \le 1$ and γ is the attenuation or range separation parameter with dimensions of inverse length. With this, the exchange energy E_{xc} can be partitioned into short- and long-range components

$$E_x = E_x^{sr} + E_x^{lr} \quad (2)$$

In this approach the short-range part is treated with traditional DFT while the long-range component is treated with exact exchange. A crucial issue in the construction of these functionals is the choice of the parameters α, β, and γ. The CAM-B3LYP and CAM-PBE0 functionals combine the features of the popular hybrid DFT functionals B3LYP and PBE0 with suitable LC extensions proposed by Hirao and co-workers.[22]

Since the long-range part of these functionals has to be calculated explicitly, the two-electron integrals have to be dealt with care. In particular, the exchange interactions have to be treated separately from the pure Coulomb interactions because the attenuation just affects the exchange. We have implemented[23] two approaches to deal with this. The first approach utilizes the well-known Dunlap charge fitting method[24] to deal with Coulomb interactions, and the exchange contribution (including the attenuation) is treated in the conventional manner. A second approach involves performing all of the integrals on the fly or

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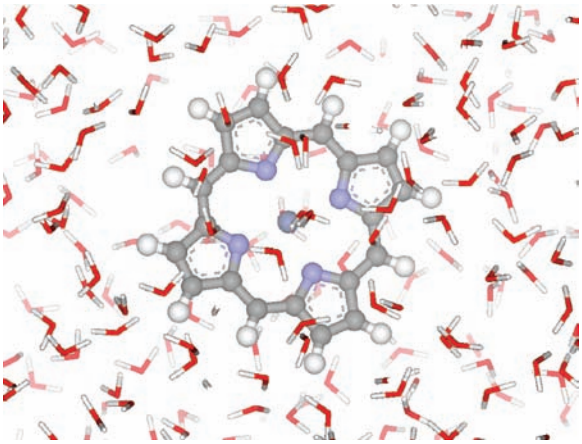

Figure 1. Zinc porphyrin molecule in an aqueous environment.

the direct approach. In this paper, we only report results using the second approach.

Computational Details

All of the calculations were performed using a development version of the NWChem computational chemistry package.[25] For our QM/MM[26] simulation, we considered one ZnP monomer embedded in a 30 Å cubic box of 869 water molecules (see Figure 1). The ZnP monomer (solute) was treated quantum mechanically (QM), while the rest of the system (solvent) was treated at the molecular mechanics (MM) level using the SPC/E water model.[27] Further details of the QM/MM simulation setup can be found in ref 15. All geometry optimizations were performed at the B3LYP level. The Ahlrichs VTZ basis set[28] was used for the Zn atom, and the 6-31G* basis set[29] was used for the remaining atoms (C,H,N).

A DFT(B3LYP)/MM optimization of the entire system was first performed followed by a solvent equilibration run for 60 ps. The equilibration was performed using constant-temperature (298.15 K) classical molecular dynamics with a 15 Å cutoff. During this procedure, the QM region was kept fixed and was represented by a set of effective charges obtained from a prior optimization procedure. At the end of the equilibration run, the entire system was optimized once more at the DFT(B3LYP)/MM level. The resulting configuration was then used for the calculation of vertical excitation energies using the QM/MM approach with all of the classical charges included.

It should be noted that the optimized ZnP geometry in solution exhibits a small out-of-plane bend. As a result, we have performed our excited-state calculations using C_1 symmetry. The excitation energies of the 2^1A and 3^1A (4^1A and 5^1A) states, however, are almost degenerate and should be attributed to 1^1E_u (2^1E_u) states or to the Q band (B band) of ZnP in D_{4h} symmetry.[5,12]

Results and Discussion

All of our gas-phase and aqueous environment results are reported in Table 1. The results from Table 2 in ref 15 are also included for completeness. Within the wave-function-based approaches (SAC-CI, EOMCCSD, CR-EOMCCSD(T)), we observe that the energy difference (ΔE_{BN}) between the B band (2^1E_u) and the nearly degenerate 6^1A and 7^1A states or N band (3^1E_u) is greater than 0.25 eV. However, this is not the case with the TDDFT-B3LYP results where the spacing is only about ~0.13−0.14 eV in the gas phase. Analysis of the leading excitations indicate that the N bands[14] are almost entirely dominated by a charge transfer from the orbital localized on the zinc and central nitrogen atoms to the orbital localized on the carbon atoms. This explains the smaller ΔE_{BN} seen in the B3LYP calculations. This shortcoming in describing CT states is well-known.[3,4] The TDDFT-B3LYP results in solution pose a more serious problem because the B and N band states are switched. It is known that increasing the Hartree−Fock (HF) content in the exchange−correlation improves the description of the CT states.[30] In order to briefly assess this, we considered the PBE0 functional, which has 25% HF content compared with 20% for B3LYP. Our results show that the ΔE_{BN} is increased in the gas phase (~0.20 eV). However, we observe that the switching persists (albeit by a smaller amount) in the solution phase. This analysis can be continued by increasing the HF content, and it is likely that these states will be better described, but our motivation for this paper is to assess how long-range corrected functionals perform for this system.

TABLE 1: TDDFT (B3LYP, PBE0, CAM-B3LYP, CAM-PBE0), SAC-CI, and EOMCC Excitation Energies (in eV) of Various States for the ZnP System in the Gas-Phase and/or in Solution[a]

method	2^1A	3^1A	4^1A	5^1A	6^1A	7^1A
B3LYP (G)	2.40 (0.001)	2.40 (0.001)	3.52 (0.861)	3.52 (0.896)	3.65 (0.004)	3.66 (0.043)
B3LYP (S)	2.40 (0.001)	2.41 (0.002)	3.51 (0.795)	3.51 (0.808)	3.36 (0.009)	3.38 (0.022)
PBE0 (G)	2.44 (0.001)	2.44 (0.001)	3.58 (0.943)	3.58 (0.957)	3.79 (0.003)	3.79 (0.022)
PBE0 (S)	2.44 (0.001)	2.44 (0.002)	3.57 (0.878)	3.58 (0.735)	3.50 (0.065)	3.52 (0.102)
CAM-B3LYP-A (G)	2.34 (0.004)	2.34 (0.004)	3.66 (1.071)	3.66 (1.075)	4.17 (0.002)	4.18 (0.006)
CAM-B3LYP-A (S)	2.35 (0.003)	2.35 (0.006)	3.65 (1.023)	3.66 (1.039)	3.89 (0.004)	3.92 (0.013)
CAM-B3LYP-B (G)	2.14 (0.006)	2.14 (0.006)	3.75 (1.152)	3.75 (1.158)	4.55 (0.003)	4.55 (0.005)
CAM-B3LYP-B (S)	2.15 (0.006)	2.17 (0.009)	3.75 (1.123)	3.76 (1.129)	4.27 (0.001)	4.30 (0.005)
CAM-PBE0 (G)	2.17 (0.007)	2.17 (0.007)	3.79 (1.179)	3.79 (1.186)	4.62 (0.003)	4.62 (0.005)
CAM-PBE0 (S)	2.18 (0.006)	2.20 (0.010)	3.78 (1.149)	3.80 (1.154)	4.35 (0.002)	4.38 (0.005)
SAC-CI	1.84	1.84	3.50	3.50	3.92	3.92
EOMCCSD	2.49	2.50	4.01	4.02	4.29	4.32
CR-EOMCCSD(T)	2.25	2.26	3.74	3.75	4.18	4.20

[a] The α, β, and γ parameters for CAM-B3LYP-A are 0.19,0.46,0.33, those for CAM-B3LYP-B are 0.19,0.81,0.33, and those for CAM-PBE0 are 0.25,0.75,0.33. Oscillator strengths are reported in parentheses. For the TDDFT results, G refers to the gas phase and S to the solution phase. The SAC-CI gas-phase results are from ref 14. The solution-phase EOMCCSD and CR-EOMCCSD(T) results are from ref 15. Pairs of degenerate states ((2^1A, 3^1A), (4^1A, 5^1A), and (6^1A, 7^1A)) correspond to the 1^1E_u (Q band), 2^1E_u (B band), and 3^1E_u (N band) states of Zn porphyrin in D_{4h} symmetry.

We have performed calculations using two long-range corrected functionals, namely, CAM-B3LYP and CAM-PBE0. This allowed us to compare their performance against the base functionals from which they were constructed. For CAM-B3LYP, we have considered two sets of parameters for α, β, and γ, (1) $\alpha = 0.19$, $\beta = 0.46$, $\alpha + \beta = 0.65$ and (2) $\alpha = 0.19$, $\beta = 0.81$, $\alpha + \beta = 1.0$. We shall refer to these as CAM-B3LYP-A and CAM-B3LYP-B, respectively. For CAM-PBE0, we have used $\alpha = 0.25$, $\beta = 0.75$, and $\alpha + \beta = 1.0$. The γ parameter was kept fixed at 0.33, so that we had the same attenuation strength in all of the functionals. There is empirical evidence[16,17,23,31,32] that this choice of γ may be reasonable for some systems but must be tuned using a well-defined procedure.[31] For CT complexes, care must be taken so that the ionization potential (IP) of the donor and electron affinity (EP) of the acceptor are properly balanced.

Analyzing the results of our CAM functional calculations (Table 1), we see that the ΔE_{BN} between the B and N band states in the solution phase, as predicted by CAM-B3LYP-A (which falls off as $0.65/r$ asymptotically), is ~0.25 eV. This is in reasonable agreement with the solution-phase results using the CR-EOMCCSD(T) method. The individual energies of the Q, B, and N bands are also in reasonable agreement. We also do not see any state switching in the solution phase.

The agreement is further improved when the asymptotic falloff is $1/r$ as with the CAM-B3LYP-B and CAM-PBE0 functionals. In these cases, the ΔE_{BN} values of ~0.50 and ~0.55 eV, respectively, in the solution phase between the B and N bands are in excellent agreement with the CR-EOMCCSD(T) results. The individual excitation energies are also greatly improved and are within ~±0.15 eV. It is clear that the stronger $1/r$ dependence helps stabilize the B band and shifts the N band states further away, which is a key ingredient in the proper description of CT states. This is consistent with the $1/r$ dependence expected for CT states.[33] Our calculations also indicate that the energy difference between the B and N bands gets smaller in the aqueous solution phase. The increased ΔE_{BN} separation that we observe in the gas phase greatly helps in the stabilization of these states in the solution phase and prevents state switching. The CAM-based functionals clearly outperform their base counterparts for CT transitions for this system and are even comparable to the highest-level excited-state methods considered in this paper. While these results are extremely encouraging, there is a lot more work needed, and we are currently assessing these functionals in different systems involving CT excitations.

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