Computational and Theoretical Chemistry 1046 (2014) 6–9

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

A quantum Monte Carlo study of zinc-porphyrin: Vertical excitation between the singlet ground state and the lowest-lying singlet excited state

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ARTICLE INFO

Article history:
Received 17 June 2014
Received in revised form 11 July 2014
Accepted 12 July 2014
Available online 23 July 2014

Keywords:
Quantum Monte Carlo
Fixed-node approximation
Zinc porphyrin
Excited states

ABSTRACT

We have calculated the vertical excitation energy between the singlet ground state (1^1A_g) and the lowest-lying singlet excited state (1^1E_u) of Zn-porphyrin employing the fixed-node diffusion Monte Carlo technique. The determinantal parts of trial wave functions were constructed using results from Configuration Interaction and time-dependent Density Functional Theory.

1. Introduction

Porphyrins and their derivatives are very important molecules as they hold key roles in many biochemical processes such as photosynthesis, oxygen transport and photo-induced electron-transfer [1–3]. In addition, they are constituent units of systems that have raised considerable interest in a variety of research areas, for instance, in photodynamic therapy (in medicine), molecular electronics, supramolecular chemistry, molecular computers [4], and light-harvesting [5].

Due to the importance of porphyrins, it is crucial to understand and accurately describe the ground and excited states in these molecules. For a reliable treatment of metal-porphyrins, one needs to employ methods that capture the electron correlation with high accuracy. This is especially true for transition-metal porphyrins due to the strong correlations and exchange effects present as well as for proper description of p—d bondings [6].

Porphyrins and their derivatives have been intensively studied by Density Functional Theory (DFT) methods. DFT methods, by the virtue of including electron correlations by construction, are computationally very appealing. Unfortunately, DFT is biased by empirical choices and by the approximate character of the available functionals. In addition to DFT methods, porphyrins have been investigated by wave function-based correlated methods such as Coupled Cluster (CC) and its variants. These high order quantum chemical techniques usually provide very accurate results, however, they do not scale very well with the system size. Hence, it is very difficult to extend the study to larger systems of porphyrins. On the other hand, quantum Monte Carlo (QMC), a sophisticated quantum many-body method, offers high accuracy along with a better scaling than CC does [7]. As such, it is a promising method of choice for studying these types of systems.

In our work, we investigate ground and excited states of a porphyrin using the QMC methods. A monomer metal-porphyrin has D_{4h} symmetry and without side chains its molecular formula is $C_{20}H_{12}N_4M$ where M is the metal atom (see Fig. 1). According to Gouterman's porphyrin model the visible absorption bands (Q band) are associated with π—π transitions with E_u symmetry that correspond to two equivalent transitions in the molecular plane [1]. For our study we have chosen the Zinc-porphyrin (ZnP), a well-known example of p-conjugated systems with an important role in photo-chemical processes [8].

In our study we aim to calculate the vertical excitation energy in the Q band corresponding to the excitation from the singlet ground state (1^1A_g) to the lowest-lying singlet excited state (1^1E_u) of ZnP by means of the diffusion Monte Carlo method (DMC), a variant of QMC. DMC is essentially a stochastic solution of the many-body Schrödinger equation in which the state with the lowest energy of a given symmetry is projected out of a trial wave function. Although formally exact, it suffers from the

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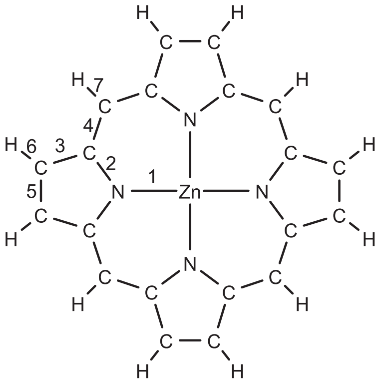
http://dx.doi.org/10.1016/j.comptc.2014.07.006



(a)

Bonds	Bond-Lengths(A^o)
Zn-N (1)	2.053
N-C (2)	1.373
C-C (3)	1.446
C-C (4)	1.397
C-C (5)	1.364
C-H (6)	1.086
C-H (7)	1.086

(b)

Fig. 1. (a) Zn-porphyrin (ZnP) $C_{20}H_{12}N_4Zn$ geometry. (b) The bond lengths of ZnP in the singlet ground state. The numbers in parenthesis next to the bonds refer the order of bonds given in (a).

well-known fermion sign problem that we circumvent by the fixed-node approximation (FN-DMC). We construct the trial wave functions using orbitals Hartree–Fock (HF), post-HF and DFT techniques. More specifically, the trial wave functions of the excited state were obtained by Configuration Interaction Singles (CIS), DFT and time-dependent DFT (TDDFT) methods (see, for example, studies Refs. [9,10]).

The rest of our paper will be as follows: First, the fixed-node DMC method is briefly introduced. Second, we explain the computational details. Third, the results and discussion are presented. Finally, the paper ends with concluding remarks.

2. Method

This part presents a brief overview of the fixed-node DMC method. A more detailed discussion of this formalism can be found in many reviews, for instance, Refs. [11,12,7].

2.1. Fixed-node diffusion Monte Carlo

DMC is a projection approach: the state with the lowest energy is projected out of a trial wave function. Let ψ_T be a trial wave function defined in a space spanned by the eigenstates of the Hamiltonian of the system as follows:

$$\psi_T = \sum_{i=0} a_i \Phi_i, \tag{1}$$

where $\{\Phi_i\}$ is the set of eigenstates with eigenvalues $\{E_i\}$, i.e. $H\Phi_i = E_i\Phi_i$. Assuming that $a_0 \neq 0$, the state with the lowest energy (Φ_0) can be singled out by applying the projection operator, $e^{-(H-E_T)t}$ to the trial wave function as follows

$$\Phi_0 = \lim_{t\to+\infty} e^{-(H-E_T)t}\psi_T. \tag{2}$$

provided that E_T becomes E_0. We note that the parameter t (imaginary time) in the projection operator is a positive real number.

For higher efficiency, the importance sampling by ψ_T can be introduced so that the resulting product, $f(\mathbf{R},t) = \Phi_0(\mathbf{R},t)\psi_T(\mathbf{R})$, obeys the following integral equation:

$$f(\mathbf{R},t+\tau) = \int d\mathbf{R}'\,\widetilde{G}(\mathbf{R}'\to\mathbf{R},\tau)f(\mathbf{R}',t), \tag{3}$$

where $\widetilde{G}(\mathbf{R}'\to\mathbf{R},\tau) = \langle\mathbf{R}\mid e^{-\tau(H-E_T)}\mid\mathbf{R}'\rangle\psi_T(\mathbf{R})\psi_T(\mathbf{R}')^{-1}$ is the Green's function with the propagation time step τ, and $\mathbf{R}$ and $\mathbf{R}'$ denote electronic system configurations. In the long time limit, $f(\mathbf{R},t)$ converges in the following form: $\lim_{t\to\infty} f(\mathbf{R},t) = \Phi_0(\mathbf{R})\psi_T(\mathbf{R})$.

The simulation formulated above begins with sampling of $|\psi_T(\mathbf{R})|^2$ by an ensemble of configurations (or walkers) which subsequently evolve in accordance with the Green's function $\widetilde{G}(\mathbf{R}'\to\mathbf{R},\tau)$ into the product of the ground state $\Phi_0(\mathbf{R})$ and the trial wave function $\psi_T(\mathbf{R})$. An analysis of the Green's function shows that the evolution of the configurations can be represented by stochastic realization of processes such as diffusion, branching and drift. Once the simulation reaches equilibrium, calculations of desired expectations are carried out.

Unfortunately, application of this procedure to an electronic system leads to the well-known fermion sign problem. It stems from the fact that the function $f(\mathbf{R},t) = \Phi_0(\mathbf{R})\psi_T(\mathbf{R})$ is not non-negative for the entire configuration space due to the antisymmetry of fermionic wave functions. One possible way how to circumvent the sign problem is to force the ground state (Φ_0) to adopt the nodes (zero locus) of the trial wave function (ψ_T). In this way, the product of the ground state (Φ_0) and the trial wave function (ψ_T) will be non-negative in the entire configuration space. This approach is known as the fixed-node approximation, ameliorates the inefficiency of inherent to the fermion signs at the cost of introducing the fixed-node bias. The fixed-node bias will vanish as the nodes of the trial wave function get closer to the exact nodes. Therefore, the quality of the nodes of a trial wave function is crucial in FN-DMC.

Since the state projected out in the fixed-node DMC is the state with the lowest energy of a given nodal symmetry; a desired excited state, ideally speaking, can be projected out by the fixed-node DMC if the nodal surface imposed by the trial wave function is the same as the nodal surface of the exact state [7]. The nodal constraint enforced by the fixed-node approximation enables DMC to calculate also excited states.

2.2. Trial wave functions

The trial wave functions used in our work are of the Slater–Jastrow type written as follows:

$$\psi_T(\mathbf{R}) = \sum_i d_i D_i^{\alpha}(\mathbf{R}) D_i^{\beta}(\mathbf{R}) e^{J(\mathbf{R})}, \tag{4}$$

where $D_i^{\alpha(\beta)}(\mathbf{R})$ is a Slater determinant of spin $\alpha(\beta)$ electrons, d_i is the coefficient and $J(\mathbf{R})$ is the Jastrow function. The nodes of a trial wave function are clearly determined by the antisymmetric Slater component. The Jastrow function containing one-body and two-body explicit correlation terms can be given by

$$J(\mathbf{R}) = \sum_{i>j} u(r_{ij}) + \sum_I \sum_i \chi_I(r_{iI}), \tag{5}$$

where $i(j)$ and I are electron and nuclei indices, respectively, and r_{iI}, r_{ij} are the corresponding distances. The u and χ terms describe electron–electron and electron–nucleus correlations, respectively.

Although the accuracy of the nodal approximation in the fixed-node DMC relies on the Slater component, the Jastrow factor is still important for the efficiency of the simulation since it helps to reduce the fluctuations and hence the cost of the computation.

2.3. Effective core potentials

QMC allows for use of effective core potentials (ECP), a well-known technique that is used to eliminate the core electrons. ECP in QMC calculations offers significant advantages. First, the computational cost, growing with $Z_{eff}^{5.5-6.5}$ where Z_{eff} is the effective nuclear charge, can be reduced [7]. This is mainly due to decreasing the energy fluctuations close to the nuclei but also due to the smoother electron density of the valence-only setting. Second,