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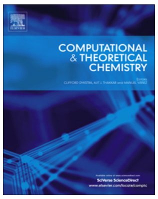

SORCI for photochemical and thermal reaction paths: A benchmark study

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ABSTRACT

Dynamic electron correlation is very important for the correct description of potential energy surfaces, especially surface with differential dynamic electron correlation. Moreover, an accurate description of both the ground and excited state potential energy surfaces is essential to understand thermal and photochemical reactions of molecular systems. In the present work we test the performance of the Spectroscopy ORiented Configuration Interaction (SORCI) method that was originally designed to account for the dynamic electron correlation in an efficient manner at fixed geometry. Here, we assess the performance of SORCI along several paths on the ground and excited state potential energy surfaces that are related to the thermal and photochemical isomerization of a reduced retinal chromophore model. The ground state mapping involves three paths. Two of them are minimum energy paths that lead through different transitions states from one *cis*/*trans* stereoisomer to the other. One transition state has a diradical (open-shell) character while the other one has a charge-transfer character. The third ground state path connects these two transition states via a conical intersection. In addition, we assess the performance of SORCI for three excited state paths that comprise a minimum energy path starting from each of the *cis* and from the *trans* chromophore. These two pathways arrive at different conical intersections that are part of one seam of conical intersections. The third excited state path presents a profile along this seam.

Despite the high complexity and varying mixture of different electronic structures involved in this benchmark, SORCI produces energy differences and energy profiles in good agreement with the multireference configuration interaction plus quadruples correction (MRCISD + Q) reference along all six paths. We find that SORCI is capable of producing smooth energy profiles, which require tighter thresholds than the present default. A further tightening of these thresholds by one order of magnitude yields converged SORCI values as compared to the limit of the method obtained by setting the three cutoffs to zero. However, we note also some deficiencies relative to MRCISD + Q in the description of relative energy differences. When comparing energies of structures that have very different geometries on the same potential energy surface we find that SORCI underestimates the reference values. Here SORCI underestimates the corresponding MRCISD + Q reference values thus indicating a non-negligible effect of the inactive double excitations. In addition we observe some artifacts at conical intersections due to the Davidson correction for higher excitations. Ways to overcome these drawbacks are discussed.

1. Introduction

The *cis*–*trans* isomerization is one of a relatively small number of chemical reactions that is exploited by nature [1]. Despite its conceptual simplicity this basic type of reaction can significantly change the physical and chemical properties of biomolecules, and hence also can control their biological activities. One good example is the isomerization of retinal protonated Schiff base (RPSB). RPSB is a polyene that contains in total six conjugated double bonds. It serves as a chromophore in a large variety of biological systems where it is covalently bound to a protein via a lysine sidechain.

Abbreviations: CI, configuration interaction; DDCI, difference-dedicated configuration interaction; SORCI, Spectroscopy ORiented Configuration Interaction; CASSCF, complete active space self-consistent field; CASPT2, complete active space second order perturbation theory; NEVPT2, second order N-electron valence perturbation theory; XMCQDPT2, extended multi-configuration quasi-degenerate perturbation theory; MRCI, multireference configuration interaction; MRPT, multireference perturbation theory; CC, coupled cluster; EOM, equation of motion; FOIS, first-order interacting space space; MEP, minimum energy path; BLA, bond length alternation; DIR, diradical; CT, charge transfer.

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In different biological systems, RPSB is at the center of many important processes such as vertebrate vision, ion-pumping and phototaxis in organisms ranging from species as primitive as archea to as complex as mammals [2–4]. In all cases the primary reaction is the photo-induced isomerization of RPSB. For instance, the prototypal bovine rhodopsin in the dark-adapted state hosts 11-*cis*-RPSB (Fig. 1), which then isomerizes around the C11 = C12 double bond upon photoexcitation. The photoisomerization is ultrafast and occurs in 100 femtoseconds (fs) [5,6]. However, the photoisomerization is only ultrafast but also highly efficient, making it a prototype for conversion from solar to chemical energy at the molecular level. Many experimental [5–7] as well as computational [8–11] studies have investigated the photochemical isomerization of RPSB in bovine rhodopsin as well as in other systems. Recent computational studies have also investigated the mechanism of thermal isomerization in RPSB, which is also important since its affects visual sensitivity [12].

The systematic and detailed studies of such systems require computational tools that are accurate but inexpensive to be applied for large, realistic systems. One promising candidate is the "Spectroscopy ORiented Configuration Interaction" [13] (SORCI) method that is implemented in the ORCA [14] program system. SORCI was developed 10 years ago as a simplified multireference method for the calculation of excitation energies as well as optical and magnetic spectra. The main goal of the method is to achieve a balance between computational efficiency, which allows application to large molecules, and accuracy for the description of energy differences for a predefined set of many-electron states. The approach combines the concepts of multireference configuration interaction (MRCI) and multireference perturbation theory (MRPT) by dividing the first-order interaction space (FOIS) into strongly and weakly interacting subspaces. Through such a classification the configurations of the former subspace can be treated variationally, while those of the latter space are treated using multireference Møller–Plesset perturbation theory to second order. Despite its multi-reference character, SORCI was designed to be as much of a "black-box" as possible. Therefore, among the available multireference methods, it stands out by simplicity and generality with respect to the choice of starting orbitals, lack of the sensitivity to multireference character of the reference wave function and absence of the intruder states problem. In order to achieve further efficiency a combination of truncation techniques is used. A detailed discussion can be found in the original work [13]. Briefly, the most important features and most important thresholds of the method are:

(i) In the first step of the procedure the reference space is reduced in order to achieve computational efficiency. It starts with the diagonalization of the Hamiltonian over an initial reference space. The initial configurations can originate from a complete active space (CAS), restricted active space (RAS) or an arbitrary list of configurations, using any type of input molecular orbitals. The most important configurations are selected if their contribution to any of the requested states according to a threshold T_{pre}. The selected space is rediagonalized to give the zeroth order wave functions for all states of interest. In the original formulation $T_{\mathrm{pre}} = 10^{-2}$ was used as default value, which selects only the truly essential CSFs for the description of a given state. Following further calibration [15] $T_{\mathrm{pre}} = 10^{-4}$ became the default cutoff as this resulted in very small errors.

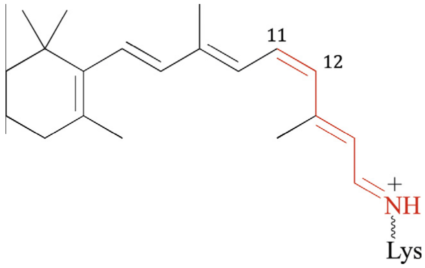

Fig. 1. Structure of the 11-cis-retinal protonated Schiff base (RPSB) connected to a lysine sidechain of a retinal protein. The penta-2,4-dieniminium cation which serves as a minimal model of RPSB is highlighted in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(ii) In the second step of the procedure the reference space is divided into a strongly- and weakly-interacting subspace (R' and R'', respectively) using a configuration selection threshold T_{sel}. The main idea is that only weakly interacting perturbers are described accurately using a perturbative approach. For this classification an uncontracted second order multireference perturbation calculation (MRPT2) is carried out. If the second order energy of a configuration is larger than T_{sel} it is assigned to the strongly interacting space.

(iii) The CI step makes use of the difference-dedicated CI (DDCI) approach [16–18] developed by Malrieu, Caballol and coworkers, where only configurations giving nonzero contributions to energy differences are included. This essentially excludes the most numerous excitations with four 'degrees of freedom' (a degree of freedom is defined as a hole in the internal orbital space or as a particle in the external orbital space). As shown by Malrieu and co-workers [17,18], the latter excitation class brings in most of the size-inconsistency error but does, to second-order in the energy, not contribute to energy differences between different electronic states. This most expensive version of DDCI is called DDCI3 and is only used in the second step of the SORCI procedure described below. The first step includes only excitations with up to two degrees of freedom (DDCI2).

(iv) The Hamiltonian in the basis of the reference CSFs and strongly-interacting CSFs from the first-order interacting space (FOIS) is diagonalized to give CI energies and wave functions. This step relaxes the reference space coefficients from their initial CASCI values and formally treats the dynamic correlation contributions from the most strongly interacting CSFs in the FOIS to infinite order. This step also removes any potentially present intruder states that plague methods relying entirely on perturbation theory.

(v) The effect of higher excitations is estimated by a multireference analog of the Davidson correction [19].

(vi) The contribution from the CSFs that were excluded from the diagonalization (part of the weakly interacting subspace) is estimated at the second-order MR-MP2 level. This effect can be optionally estimated using the relaxed and renormalized reference part of the CI wave functions.

(vii) The average density matrix of all states is computed and diagonalized in order to obtain approximate average natural orbitals (AANOs). A third threshold termed T_{nat} is reducing the number of AANOs for the subsequent iteration. The AANOs that have occupation numbers less than T_{nat} are excluded, while those that are closer than T_{nat} to 2.0 are frozen. This set of AANOs is designed to remove any bias that the initial set of MOs might have had. In addition it often drastically reduces the one-particle space, which may lead to dramatic computational savings.

(viii) In the second iteration the whole procedure is repeated with the AANOs in place of the input MOs.

(ix) The effect of the neglected inactive double excitations can be computed optionally using second order MRPT.

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