

Performance of RIJCOSX approximation in modeling of excited state intramolecular proton transfer

Y. Syetov

*Department of Experimental Physics, Oles Honchar Dnipro National University, Dnipro, Ukraine;
e-mail: setov2003@yahoo.com*

Results of calculations of structure, vibrations, vertical transitions and features of potential energy surface in the ground and first excited states of an isolated molecule of 2-(2'-hydroxyphenyl)benzoxazole by density functional theory and time-dependent density functional theory in conventional approach and RIJCOSX approximation are considered. It is found that results obtained by the RIJCOSX approximation are close to those obtained by conventional approach for the properties of the ground state and vertical transitions. RIJCOSX approximation provides good correspondence of values for geometrical parameters and relative energies of the structures in the excited state. For calculated vibrations in the excited state the difference in frequency reaches 40 cm^{-1} and there are permutation of modes and difference in forms.

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods are routinely used nowadays for calculations of properties of molecules and solids [1,2]. One of the most popular density functional used for the calculations of properties of organic molecules is a hybrid functional B3LYP [3]. Combination of 'resolution of the identity Coulomb approximation' (RI-J) and 'chain of spheres exchange' (COSX) approximation for treatment of the exchange part, proposed in [4] and implemented in the ORCA program suit [5,6] allows to speed up the calculations with the hybrid functional. However, the approximated results deviate from the values obtained with ordinary DFT calculations.

2-(2'-hydroxyphenyl)benzoxazole (HBO) (Fig. 1) is an organic compound that exhibits excited state intramolecular proton transfer. In the ground state a molecule of HBO has enol structure with an OH...N hydrogen bond (Fig. 1a). DFT calculations of infrared absorption spectra of HBO performed with the B3LYP functional

demonstrate good correspondence with the experimental spectrum except the bands attributed to the out-of-plane vibrations that involve OH bond. Calculated frequencies and forms of these vibrations are found to be dependent on the basis set used [7].

Redistribution of electron density occurs in the molecule upon absorption of a photon that makes the keto structure with the O...HN hydrogen bond (Fig. 1b) to be energetically preferable in the excited state. Transition to the ground state in the keto structure causes luminescence with an anomalously large Stokes shift. In the ground state the proton shifts back to the oxygen atom restoring the enol structure. Calculations of the excited state with the TDDFT methods demonstrate good correspondence to experiments in absorption and luminescence wavelengths as well as enol-keto structure energy relation in the excited state [8]. In this paper we consider performance of the RIJCOSX in modeling of the excited state proton transfer in the isolated molecule of HBO. The aim of the study is to evaluate of the accuracy of the approximation and determine overall speedup for this type of calculations.

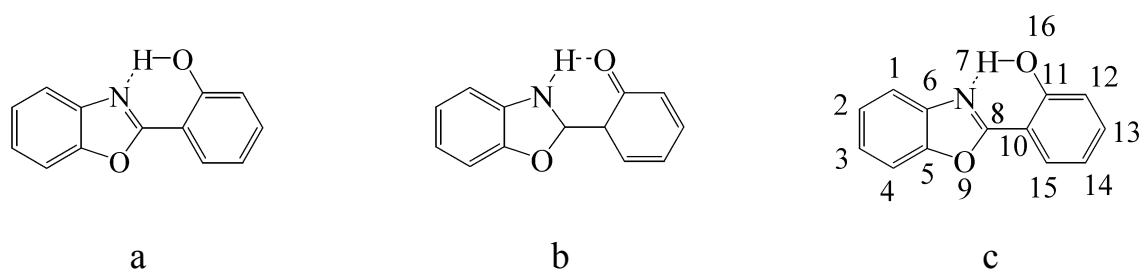


Fig. 1. Enol (a), keto (b) structures and atom numbering scheme (c) of molecule of HBO.

The calculations were performed using the ORCA software package [5,6], the B3LYP functional [3], def2-SVP and corresponding auxiliary basis sets [9–11]. For calculations with the RIJCOSX approximation, the default parameters were used, for calculations with the usual DFT (TDDFT) methods a larger grid for numerical integration (Grid6) was used. The criteria for the convergence of the self-consistent field equations were set TightSCF (10^{-7} Hartree) in both cases. The vibrations were calculated in harmonic approximation using analytical second energy derivatives for the ground state and numerical ones for the excited state. Optimization of geometrical

parameters was performed initially with RIJCOSX. Then the obtained structures were taken as start for the conventional DFT optimization.

Ground State. There is no minimum for the keto structure in the ground state of the molecule of HBO. The geometrical parameters of the enol structure, calculated with the RIJCOSX approximation, are very close to those obtained by calculation with the conventional DFT method. Difference in bond lengths is small; the largest deviation is found for the C₁₁-O₁₆ (Fig. 1c) bond and is 10⁻³ Å. Difference in the values of dihedral angles does not exceed 0.02°. The largest deviation of the values of valence angles is found for the angles that determine the relative position of benzoxazole and phenolic fragments (O₉-C₈-C₁₀, N₇-C₈-C₁₀, C₈-C₁₀-C₁₁, C₈-C₁₀-C₁₅) and the magnitude is about 0.2°.

For most normal vibrations, the frequency deviation does not exceed 2 cm⁻¹, including for out-of-plane modes that involve the OH bond. Larger deviations are found for some stretching vibrations of CH bonds (up to 4 cm⁻¹) and stretching OH vibration (deviation of 9.5 cm⁻¹). For the intensities of the absorption bands, the deviation for most vibrations does not exceed 10%. A more noticeable deviation is found for several weak bands and is insignificant, because the accuracy of the intensities calculated by DFT methods allows only a semi-quantitative comparison with the experimental values.

The energy of vertical transitions from the ground to the first five singlet excited states is underestimated by the RIJCOSX approximation in comparison with conventional DFT, however, the difference does not exceed 80 cm⁻¹. Oscillator strengths differ within 20 %.

Excited State. Two energy minima corresponding to the enol and keto structures are found in the first singlet excited state. The difference in energy of the enol and keto structures is about 1380 cm⁻¹ (RIJCOSX) and 1530 cm⁻¹ (conventional). Energy of the transition state for the excited state proton transfer (energy barrier between the enol and keto structures) is 207 cm⁻¹ (RIJCOSX) and 140 cm⁻¹ (conventional). Minimum energy curves along OH stretching coordinates obtained by RIJCOSX in the ground and excited states are shown in Fig. 2. The

values of energy for the points in the curve are underestimated by RIJCOSX within 35 cm^{-1} in the ground state and overestimated by about $1100 - 1500\text{ cm}^{-1}$ in the excited state.

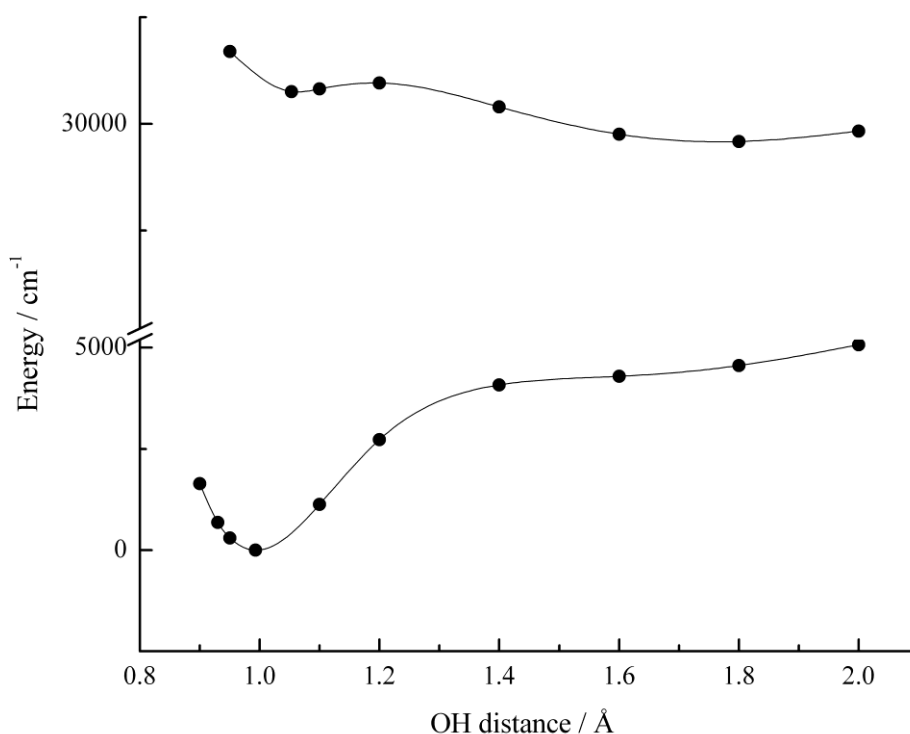


Fig. 2. Minimum potential energy curves along OH stretching coordinate in the ground and excited states of a molecule of HBO.

The difference in geometrical parameters for the enol structure in the excited state is larger than in the ground state. The largest deviation in bond length is 0.01 Å for the $\text{C}_8\text{-C}_{10}$ bond linking the benzoxazole and phenol moieties. The largest deviation in angle is found to be 0.5° for $\text{C}_8\text{-C}_{10}\text{-C}_{15}$. For the keto structure the difference reaches 0.018 Å for the $\text{N}_7\text{-C}_8$ bond and 1.2° for the $\text{C}_3\text{-C}_4\text{-C}_5$ angle. The largest deviation for dihedrals in the keto structure is 0.1° for $\text{C}_8\text{-C}_{10}\text{-C}_1\text{-O}_{16}$. The geometrical parameters of the transition state structures deviate by less than 0.023 Å in bond length and less than 0.83° in angles.

Energies of vertical transitions from the first excited state to the ground state are estimated by RIJCOSX with deviations of about 1100 cm^{-1} for the enol and keto

structures. The difference in energy of the vertical transitions is related to the deviation in the excited state. Nevertheless, calculations by RIJCOSX performed on the structures, obtained by conventional TDDFT optimization, show that the large deviation is caused by difference in geometrical parameters rather than accuracy of energy of the vertical transitions. In this case of the same geometry the deviation is only 30 cm^{-1} for the enol and 8 cm^{-1} – for the keto structures.

Calculated vibrational frequencies in the excited state are noticeably less accurate than in the ground state. The largest deviation for the enol structure is about 44 cm^{-1} and found for the in-plane mode with the calculated frequency of 2202 cm^{-1} (conventional DFT). Moreover, there is permutation for several modes with close frequencies. Conventional DFT yields vibrations at 482 and 484 cm^{-1} for the enol structure, the similar modes obtained by RIJCOSX demonstrate frequencies of 486 and 484 cm^{-1} . Frequency permutation is found also for modes 904 and 910 cm^{-1} , they become vibrations at 902 and 898 cm^{-1} . For the keto structure the deviation reaches 40 cm^{-1} , there is permutation of the modes and even noticeable difference in form for a number of vibrations.

The most time-consuming calculations are computations of vibrations in the excited state. The RIJCOSX approximation provides acceleration by about 1.5 times for this type of calculations. Analytical calculations of vibrations in the ground state are accelerated by about 3.5 times, calculations of vertical transitions – by about 2 times.

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