PERFORMANCE OF RIJCOSX APPROXIMATION AND NUMERICAL DIFFERENTIATION IN MODELING OF STRUCTURE AND SPECTRA OF 2-(2'-HYDROXYPHENYL)BENZOXAZOLE

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Structure, vibrations, vertical transitions 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 are calculated by DFT and TDDFT methods with conventional approach and RIJCOSX approximation. It is found that results obtained by the RIJCOSX approximation are close to those obtained by conventional approach for the properties in the ground state and vertical transitions. RIJCOSX approximation provides good correspondence of values for 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. Deviations in the calculated vibrational spectra related to the usage of numerical derivatives instead of analytical are considered for the molecule in the ground state.

Keywords: density functional theory, numerical differentiation, performance, electronic spectra, vibrational spectra, excited-state intramolecular proton transfer.

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1. Introduction

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). 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.

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]. 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 [4-8]. 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 [5].

The 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 [6] and implemented in the ORCA program suit [7, 8] allows to speed up the calculations with the hybrid functionals. However, the approximated results could deviate from the values obtained with the accurate DFT calculations. To model vibrational spectra in the harmonic approximation, it is necessary to calculate the second derivatives of the energy of the molecule with respect to the deviation of atoms from the equilibrium position, which corresponds to the minimum energy. For many electron density functionals, analytical calculation of the second derivative has been implemented, but for some functionals analytical calculations are possible only for the first derivative of the energy with respect to the position of atoms (energy gradient), in particular for excited states. In this case, the second derivative can be calculated using numerical differentiation of the first derivative [9].

By reducing the differentiation step, the accuracy of the derivative calculation can be increased, but the calculation of the molecule energy and its gradient is also approximate and has its own error.

Fig. 1. Enol (a) and keto (b) structures of a HBO molecule with the atomic numbering scheme.

In this work we address to accuracy of performance of the RIJCOSX and numerical differentiation in modeling the structure and optical spectra of an isolated molecule of HBO.

2. Calculations details

The calculations were performed using the ORCA software package [7, 8], the B3LYP functional [3], def2-SVP and corresponding auxiliary basis sets [10-12]. 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 10^{-7} Hartree in both cases. The optimization of geometrical parameters was performed initially with RIJCOSX. Then the obtained structures were taken as starting for the conventional DFT optimization with the same convergence thresholds. The molecular vibrations were calculated in the harmonic approximation analytically and using numerical differentiation based on central derivatives in the ground state, as implemented in this software package. In the excited state, only numerical second derivatives of energy are available. The symmetry of the molecule was not used in calculating the vibrational spectrum. The use of central numerical derivatives provides a smaller error but requires more computational time because of the need to calculate gradients for two positions of the displaced atoms.

3. Results and discussion

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 calculations with the conventional DFT method. Difference in bond lengths is small; the largest deviation is found for the C_{11}-O_{16} (Fig. 1) 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 (O_9-C_8-C_{10}, N_7-C_8-C_{10}, C_8-C_{10}-C_{11}, C_8-C_{10}-C_{15}) 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.

Numerical derivatives from the values obtained using analytical derivatives for the atomic displacement step of 0.002, 0.005, 0.015 and 0.02 Bohr (1 Bohr is an atomic unit of length equal to the Bohr radius).

The displacement step value used by default in ORCA is 0.005 Bohr. For this value, the rms frequency deviation is 3 cm^{-1}, and the maximum is 14 cm^{-1}. The maximum deviation occurs for oscillation with the lowest frequency. The deviation of the frequencies obtained numerically from those obtained analytically is within the rms deviation between the experimental and calculated values for similar methods, which is approximately 20 cm^{-1} [4-8] (using an appropriate scaling factor). The calculated values of the band intensities in the spectra calculated analytically and numerically differ noticeably only for very weak bands, and therefore numerical calculations can be used. Increasing the numerical differentiation step allows us to bring the results of the numerical calculation closer to the results of the analytical one. The smallest root mean square deviation occurs for the atomic displacement step of 0.015 Bohr (0.4 cm^{-1}) with a maximum deviation of 3 cm^{-1}.

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 %.

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). 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 C_8-C_{10} bond linking the benzoxazole and phenol moieties. The largest deviation in angle is found to be 0.5° for C_8-C_{10}-C_{15}. For the keto structure the difference reaches 0.018 Å for the N_7-C_8 bond and 1.2° for the C_3-C_4-C_5 angle. The largest deviation for dihedrals in the keto structure is 0.1° for C_8-C_{10}-C_1-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 deviations are 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 several 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. The numerical calculations of vibrations are approximately 4 times slower than the analytical calculations.

4. Conclusions

The RIJCOSX approximation reduces computational time providing results that are close to those obtained by conventional approach for the properties in the ground state and vertical transitions. For the excited state, this approximation yields good evaluation of relative energies of the structures. At the same time, geometrical parameters and vibrations are less accurate in the excited state due to lower gradients of energy in relation to the atom positions. Numerical calculations of vibrations can be used to interpret experimental spectra and to select the differentiation step allows increasing the accuracy of such calculations. The numerical calculations require significantly more computational time but can be effectively carried out in parallel on a computer cluster where a batch of the atomic displacements is calculated on a separated node independently.

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