

## EXPERIMENTAL AND THEORETICAL STUDY OF UV-VIS SPECTRA OF SCHIFF BASES

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**Abstract:** The UV-Vis properties of ten Schiff bases were systematically investigated. The time-dependent density functional theory (TDDFT) approach in combination with the B3LYP functional was used for simulation of UV-Vis spectra of examined compounds. The shapes of the Kohn-Sham molecular orbitals involved in electronic transitions were misleading. To provide better understanding of distribution of electron density natural bond orbital (NBO) analysis was used. NLMO clusters were constructed and they represent a part of a molecule characterized with eminent electron density. The TDDFT and NBO theories are complementary, and the results from these two approaches are combined to interpret the UV-Vis spectra.

**Key words:** UV-Vis spectra, TDDFT, Schiff bases, Kohn-Sham orbitals, NLMO clusters

### Introduction

It is known that phenolic compounds, both natural and synthetic, represent potent antioxidants (Rice-Evans et al., 1996). One important class of synthetic phenolic compounds are Schiff bases. This class of compounds was first produced in condensation reactions of aldehydes and aromatic amines by Hugo Schiff in 1864 (Schiff, 1864). These compounds found application in medicine and pharmacy through their antitumor, antiviral, antifungal and antibacterial activity (Radecka-Paryzek et al., 2007). Those biological properties make Schiff bases favorable for the synthesis of many drugs (Lozier et al., 1975). Some phenolic Schiff bases show effective antioxidant activity and act as possible drugs which can prevent disease caused by free radical damage. In two recent studies, we reported the antioxidative properties of some salicylaldehyde and vanillic Schiff bases (Petrović et al., 2015; Marković et al., 2015). However, this group of multifunctional compounds deserves further examination. Bearing that on mind, we put under consideration the UV-Vis properties of the series of synthetic Schiff bases (Fig.1). The quantum-chemical interpretation of UV-Vis spectra of conjugated phenolic compounds has become a crucial support for experimental data. The UV-Vis spectra of polyphenols are based on electronic transition between  $\pi$ -type molecular orbitals. There is a large panel of (time-dependent) quantum chemical methods which rationalize UV-Vis spectra of atomic and molecular systems. The time-

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depend density functional theory (TDDFT) appear to be an effective tool to estimate UV-Vis absorption of medium sized  $\pi$  conjugated compounds.

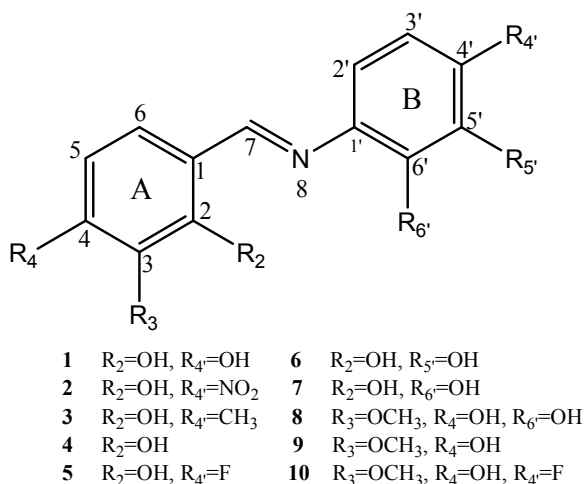


Figura 1: Opšta struktura ispitivanih Šifovih baza  
 Figure 1: General structure of the investigated Schiff bases.

### Material and methods

The UV/Vis measurements were performed at room temperature in the area of 200–500 nm range on the Agilent Technologies, Cary 300 series UV-Vis spectrophotometer. The solutions ( $2.5 \times 10^{-5}$  M concentration) of all compounds (1–10) were prepared in methanol, and measurements were recorded in a 10 mm quartz cell.

All calculation were carried out using the Gaussian program package (Frisch et al., 2009) at the B3LYP/6-311+G(d,p) level of theory. This method was selected because it proved to be the most suitable for constructing the NLMO clusters (Marković and Tošović, 2015). The influence of methanol as solvent (dielectric constant = 32.6) was simulated by the Polarizable Continuum Model (PCM). The geometries of the ground states were confirmed by the absence of any imaginary frequency. Absorption spectra were computed using the TDDFT method in combination with the same functional, basis set and solvation model. Namely, all allowed vertical transitions ( $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$ ) were inspected, and the resultant wavelengths ( $\lambda_{max}$ ) and oscillator strengths ( $f$ ) were determined. The NBO analysis was performed for all examined compounds. The GenNBO 5.0 computer program was used to describe all  $\pi$ -bonding, lone pair, and  $\pi^*$  antibonding NLMOs of the investigated molecules. The Chemcraft 1.7 program package was used to construct the NLMO clusters. For presentation of the simulated UV–vis spectra and Kohn–Sham orbital shapes the GaussView 5.0 software was used.

### Results and discussion

To gain deeper insight structure of above mentioned ten Schiff bases the UV-Vis spectra have been studied with both experimental and theoretical approaches. Experimental UV-Vis spectra for the compounds included in this study, were performed for series of Schiff bases (Fig. 1). The obtained experimental and theoretical data: vertical transition wavelength ( $\lambda_{\max}$ ), oscillator strength ( $f$ ), and orbital contribution coefficient values for all absorption bands are listed in Table 1.

Tabela 1. Rezultati eksperimentalnih i TDDFT simulacija ispitivanih jedinjenja.  
 Table 1. Results of the experimental and TDDFT calculations for examined compounds.

compound	$\lambda_{\max}$	$f$	orbital description	expt $\lambda_{\max}$ (nm)
1	357	0.68	H→L (70%)	349
	272	0.15	H-3→L (46%)	269
	207	0.19	H-1→L+3 (46%)	207
2	356	0.51	H-1→L (70%)	353
3	347	0.63	H→L (69%)	339
	271	0.22	H-3→L (56%)	269
	225	0.07	H-1→L+1 (46%)	225
4	200	0.02	H-1→L+4 (46%)	200
	340	0.50	H→L (69%)	337
	270	0.25	H-3→L (59%)	268
5	223	0.12	H→L+3 (58%)	221
	334	0.51	H→L (69%)	337
	310	0.14	H-1→L (67%)	314
6	269	0.11	H-3→L (44%)	269
	216	0.04	H→L (59%)	218
	204	0.03	H→L+6 (63%)	204
7	348	0.49	H→L (70%)	340
	271	0.25	H-3→L (57%)	266
8	366	0.46	H→L (70%)	349
	266	0.28	H-3→L (58%)	268
9	318	0.11	H-1→L (68%)	315
	285	0.07	H-3→L (56%)	283
	247	0.11	H→L+2 (63%)	231
10	340	0.67	H→L (67%)	325
	228	0.03	H-1→L+1 (63%)	227
	201	0.24	H-2→L+2 (42%)	200
10	342	0.69	H→L (67%)	327
	279	0.12	H-2→L (58%)	284
	201	0.22	H-4→L (37%)	202

In Fig 2 are illustrated experimental and simulated spectra for representative investigated Schiff bases, compounds 7 and 8, one salicylaldehyde and one vanillic,

respectively. From our previous work results for this compounds showed very good antioxidant activity, and we focus our further examination on this compounds.

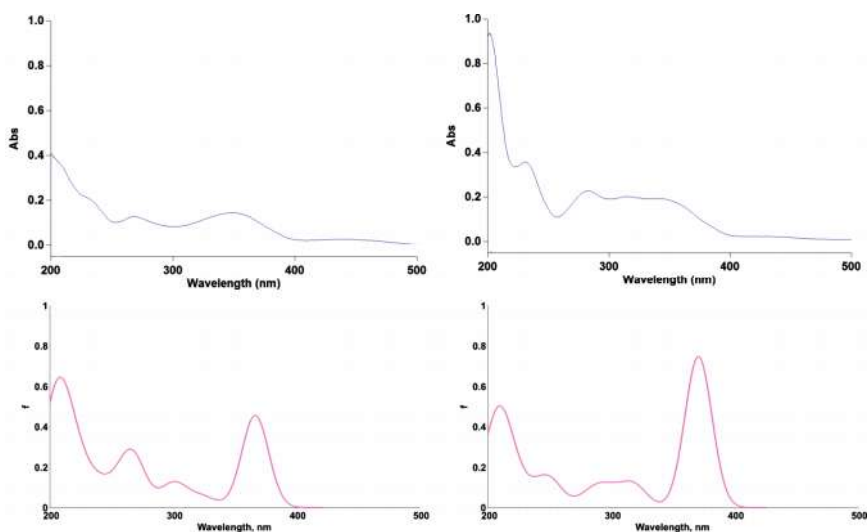


Figura 2: Eksperimentalni (gore) i simulirani (dole) UV/Vis spektri za jedinjenja 7 i 8  
 Figure 2: Experimental (up) and simulated (down) UV/Vis spectra for compounds 7 and 8

The simulated TDDFT spectra very often calculated electronic transition that do not really appear in experimental data, but also sometimes some experimental bands are not reproduced in calculated spectra. To confirm the exactness of the calculated results and to gain deeper insight into UV-Vis spectra of all examined compounds Kohn–Sham orbitals and corresponding NLMO clusters were constructed. Due to Kohn-Sham orbitals all HOMO and LUMO orbitals, including HOMO-1, HOMO-2, HOMO-3, and LUMO+1, LUMO+2 are delocalized over the whole entire molecular skeletons. Due to that fact all electronic transitions are possible. On the one hand, taking into account the shapes of the orbital only limited information are revealed about UV-Vis light absorption of the examined molecules. On the other hand, there is some crucial question such as which parts of molecules are involved in the electronic transitions, possible intramolecular charge transfer, small oscillator strengths at long wavelengths in the spectra, etc. For construction of NLMO clusters the NBO analysis results were used. According to the results of the parent NBOs of these two selected investigated compounds it is notable low occupancies in the bonding regions, and high occupancies in the antibonding regions. This observation prompts us to conclude that this is in agreement with expected results for aromatic systems. For this acknowledge is responsible the donation of electron density from bonding to antibonding orbitals. In bonding region the  $\pi$  NLMO from the C=N group possess the lowest energy value. This NLMO forms the lowest-lying HOMO-3 cluster. The HOMO-2 clusters are constructed from the lone electrons pair from p orbitals of the oxygen of hydroxyl group. The

HOMO-1 and HOMO cluster are consists of three  $\pi$  NLMOs from A and B ring, respectively. LUMO cluster is located in antibonding region and it is formed from  $\pi^*$  orbitals of the C=N group. The LUMO+1 cluster is built from three  $\pi^*$  NLMOs of the A ring, while three  $\pi^*$  NLMOs of the B ring create the LUMO+2 cluster (Fig. 3).

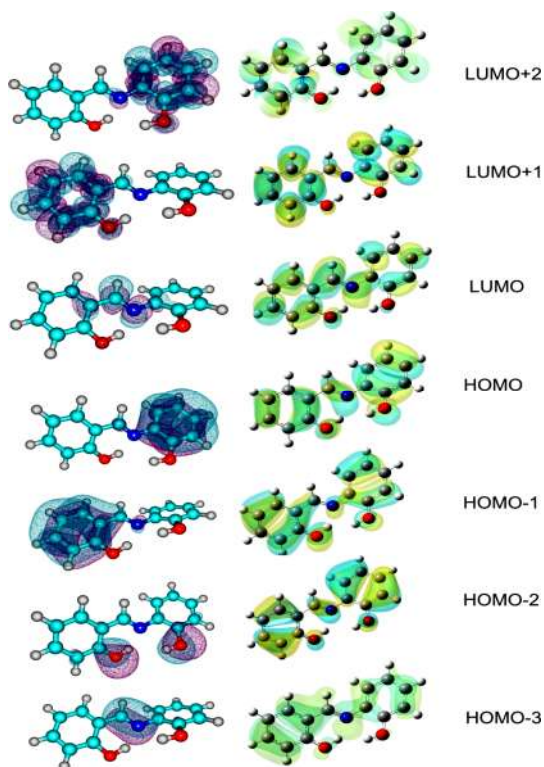


Figura 3: NLMO klasteri (levo) i odgovarajuće Kohn-Shamove orbitale (desno) za jedinjenje 7

Figure 3: NLMO clusters (left) and corresponding Kohn–Sham orbitals (right) for compound 7

### Conclusion

Synergism between the TDDFT and NBO theory help for better understanding of electronic transitions engaged in the UV-Vis light absorption of the examined compounds. The excitation energies which are available from TDDFT calculations are dependent from MO energies which can be calculated with NBO theory which ensures good approximation of the energies of the localized molecular orbitals (NLMOs). The Kohn–Sham orbitals can be replaced with NLMO clusters since they are described with specified energies and shapes. NLMO clusters provide delocalization over the definite

part of molecule while the Kohn-Sham orbitals are delocalized through the whole structure.

### Acknowledgment

The authors gratefully acknowledge financial support from the Ministry of Science of Republic of Serbia (Projects No. 172016, 172015 and 174028).

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