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Evaluation of Electronic Spectra of Unsaturated Organic Compounds Using the Pariser-Parr-Pople Method with Adaptation of Parameters

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The possibility of quantitative predictions of absorption maxima in electronic spectra of unsaturated organic compounds by means of the Pariser-Parr-Pople method with adaptation of parameters is examined. A schematic classification of quantum chemical methods is proposed which is based on the idea of extrapolation from elementary particles (physical constants) to the molecule, from atoms to the molecule and, finally, from fragments to the molecule.

INTRODUCTION

For indirect confirmation of the structure of reaction products, especially for those which cannot be preparatively isolated, calculations of electronic spectra and a comparison with experiments are expedient.

For calculations of electronic spectra, different all-valent semiempirical quantum chemical methods are often applied: SCF-CI MO,[1] CNDO/S,[2–6] CNDO/S1,[7] CNDO/S2,[7] CNDO/S3,[7–8] CNDO-MO-SCF-CI,[9] INDO/1,[10] INDO+CI,[11] INDO/2 SCF-CI,[12] INDO/S,[13–17] INDO/S-CI,[18,19] a modified version of the INDO method with a charge-iterative Hamiltonian,[20] LNDO/S,[21] RINDO/S,[22] MRINDO/S,[23] LCVO-MO,[24] CI of virtual orbitals and the method of »differences of energies«,[25] MNDOC,[26] AM1,[27] the scheme of Yonezawa based on the Mulliken approach with approximation of differential overlap,[28,29] as well as methods of the *ab initio* type.[30–32]

The methods above are often unsuitable for identification because of their inability to accurately reproduce absorption maxima, the great complexity of the systems investigated, and the difficulty of effectively including medium considerations.

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At the same time, for conjugated organic compounds, in the molecules in which the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions occur, the SCF MO LCAO Pariser-Parr-Pople (PPP) method[33,34] is used.[35–42] In contrast to the aforementioned models, it does not consider the Rydberg states, states involving excitations to or from σ-type orbitals, spin-orbital interactions, *etc.* However, the PPP method has not lost its significance and is now considered to be a fundamental physical model.[41] Furthermore, method describes the $\pi \rightarrow \pi^*$ excitations better than, for example, the CNDO/S approximation.[43]

Within the framework of the PPP method, two-centre Coulomb integrals are evaluated using the formulae of Mataga and Nishimoto,[44,45] Ohno and Klopman[46,47] and some other: resonance integrals – by means of the formulae of Pariser and Paar[48,49] and Linderberg,[50] as well as with the aid of the spectral,[5] CNDO/S[2–6] parameterizations; in all, about 20 different formulae for resonance integrals are used..

The aim of the present work is to elucidate the possibility of reproducing absorption maxima of rather complicated unsaturated organic compounds using the PPP method with adaptation of parameters and an attempt of schematic classification of quantum chemical methods in connection with the latter.

For calculations by means of the PPP method, the spatial parameters of molecules selected on the basis of the structural data[51] were used.

RESULTS AND DISCUSSION

We have developed a program involving the PPP method with minimal configuration interaction (CI) for the IBM PC XT/AT computers, having provided that the CI algorithm involves up to five lower vacant MO and an equal number of higher occupied ones. For diagonalization of matrices, the method of Householder and QL-algorithm with implicit shift[52] were used.

Even at the stage of testing on sufficiently simple molecules (*e. g.* aniline, phenol, pyridine *etc.*, some certain deviations from experimental results were observed, being in agreement with the data mentioned in the monograph,[43] and in going to more complicated chemical systems these deviations increased enormously.

Analysis of the negative phenomena brought us back to the theoretical bases of quantum chemical methods.

As it is known, scientific research includes analysis and synthesis as its most important components. In applied quantum chemistry they are featured by the following: (i) imaginary disassembling of a complicated molecule into separate atoms and application of atomic spectroscopy for determination of the parameters of each type of atoms (the analytical component of the methods); (ii) imaginary assembling of the atoms into the initial molecule and calculation of its properties using the atomic parameters obtained (the synthetic component). It is easily noticeable that the extent of the depth of the analysis is not unique: *ab initio* methods do reproduce the properties of complicated chemical systems on the basis of the properties of elementary particles (*i. e.* nucleons and electrons) using only fundamental physical constants. In order to overcome such a high leap (elementary particles – molecule, or physical constants – molecule), a developed mathematical apparatus and considerable computing power must be provided, which are often inaccessible to the majority of chemists. Besides, the results of *ab initio* calculations depend significantly, and not always monotonously, on the selected basis and consideration of correlation ef-

fects.[53–56] Hence, there is a tendency towards an increase of the role of narrowly specialized semiempirical methods. However, the extrapolation from atoms to molecule which lies in their basis does not appear to be absolutely satisfactory in all cases.

As a matter of fact, when dealing with atomic spectroscopy, information is obtained from isolated atoms, while in the case of electronic spectrophotometry, radiation is absorbed by molecules in solution. Not universal but specific interactions are especially hindering, *e. g.* protonation in acidic solutions. The spectra of atoms existing under the same conditions as the molecule »constructed« of them do not appear feasible.

A possible solution is a decrease of the »height« of the leap involved in the method, which may now be designated as »fragments – molecule«. Its advantages are the following:

1. Fragments, being separate molecules, may be placed into the same medium as the initial molecule. It is of importance since an explicit consideration of the solvation effects in electronic spectroscopy represents a complicated problem (*e. g.* Ref. 57 and references quoted therein). Numerous calculations of the spectra for chromophores with specific solvents bound as supermolecules have been performed (Refs. 12, 57 and references therein). General trends of the spectral behaviour in a series of solvents have been formulated. However, it is rarely possible to attain quantitative agreement of the calculated transition energies with experimental data.

2. The choice of the parameters is made using electronic molecular spectroscopy, which is more accessible than atomic spectroscopy.

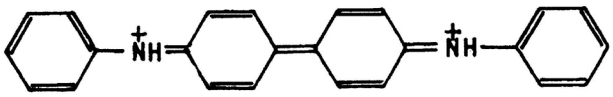
3. Fragments, in contrast to atoms and elementary particles, allow for a gradual complexation, which provides for possible correction of errors at each step; the total error is the error of the last step, thus being minimal.

For implementation of the above-described idea it is advisable that, at a minimal complexation of the molecule, only one unknown parameter should appear. In the case of the PPP method, the parameter to be corrected is the two-electron one-centre Coulomb integral (its evaluation is the main object of criticism in the whole method[5]). The correction implies that deviations exceeding their conventional values by more than 30% are highly indesirable.

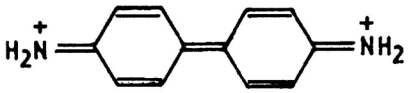
Practical use of the method consists of the following. A series of compounds is built, at the beginning of which there is an appropriate conjugated hydrocarbon (corresponding to the first parameter in the scheme to be corrected, *i. e.* the Coulomb integral of the carbon atom), and the terminal is the molecule under study. In going from one compound in the seriers to the neighbouring one, a new type of π centre corresponding to the latter must appear (note that there might be several identical π centres). The spectra of the compounds in this series should, as far as possible, be recorded under similar conditions. After that, the parameters of each π centre, one in each step, are selected with fixation of all the parameters determined in preceding steps.

Thus, the calibrated parameter »remembers« all the factors accounting for deviations of the experimental spectrum from the theoretical one and reproduces them in each following step.

The approach to the simulation of electronic spectra was checked on the example of the product of diphenylamine oxidation in the sulphuric acid medium – *N,N'*-diphenyl-*p*-diphenoquinonediimine dication (I)[58]:



This dication contains two types of π centres: C and $=\overset{+}{N}H$. The following two species were chosen as model ones: benzene and *p*-diphenoquinonediimine dication (II):



in a sulphuric acid solution.

The value of γ_C = 11.13 eV (according to Hinze and Jaffé[59] appears to describe well the absorption band of benzene with λ_{max} = 255 nm[5,53,54] and needs no correction.

In order to obtain compound II, we performed oxidation of benzidine using ammonium vanadate in 10 M sulphuric acid medium. Five millilitres of sulphuric acid and 2 ml of 10^{-3} M ammonium vanadate solution were added to 1 ml of 10^{-3} M benzidine solution in ethanol, and the reaction mixture was diluted with the sulphuric acid solution up to 25 ml. The analytical concentration of the oxidation product, *i. e.* substance II, was 4 x 10^{-5} mol/l, assuming a 100% yield. Electronic absorption spectrum of the oxidized form of benzidine (II) was recorded using a Specord M40 spectrophotometer. The absorption maximum of the oxidized form of benzidine (II) was detected at 436 nm, which is in good agreement with the value of 434 nm given in the monograph[60] (acidity not specified). The calibrated parameter γ_N took the value of 13.63 eV (in contrast to its initial value of 12.78 eV). Note that the uncertainty of spectrophotometric measurements (± 1 nm) corresponds to the calibration accuracy of the parameters up to some deV.

The spectrum of compound I calculated using these γ_C and γ_N parameters (the formula of Mataga and Nishimoto for $\gamma_{\mu\nu}$, the spectral approximation for $\beta_{\mu\nu}$) coincides with an experimental spectrum: λ_{max} = 580.9 nm (theor.), 580 nm (exper.).[58] This result may be regarded as a confirmation of the approach applied.

For a correct reproduction of spectral wavelengths, the construction of complete series of compounds, beginning with a hydrocarbon, with the appearance of a new type of π centre at each step is not always necessary; spectra may be calculated according to a »cut-down« scheme using one or more model systems for the calibration of parameters.

A confirmation of the validity of the approach presented here for the calculation of electronic spectra is the reproduction of the spectral characteristics of different organic substances using the calibration of Coulomb integrals by model compounds (Tables I and II). The experimental values of λ_{max} for the studied and model compounds, were obtained, as far as possible, under identical or similar conditions.[61–71]

TABLE I

Calibration of one-centre Coulomb integral against model compounds

Model compound	λ exper. nm	The atom for which $\gamma_{\mu\mu}$ is calibrated	Standard value of $\gamma_{\mu\mu}$/eV	Formulae for calculating $\gamma_{\mu\nu}$ and $\beta_{\mu\nu}$*	λ theor. before calibration/nm	$\gamma_{\mu\mu}$ after calibration/eV	λ theor. after calibration/nm
1	2	3	4	5	6	7	8
Glyoxal	464	$\dot{O}$	15.23	MP	460.2	16.20	464.9
Acrolein	345	$\dot{O}$	15.23	MP	344.2	15.26	345.2
Divinyl sulphide	275	$\ddot{S}$	11.92	MP	288.1	13.50	275.1
	255				272.3		260.2
				OP	247.9	12.32	274.9
Benzaldehde	280	$\dot{O}$	15.23	MP	288.5	15.90	280.0
	244			OP	286.8	16.10	280.1
					242.9		241.3
Benzoic acid	272	$\dot{O}$	15.23	OP	279.5	18.10	272.1
Aniline	281	$\ddot{N}$	16.76	MP	267.1	21.00	280.3
				OP	268.1	22.05	280.0
Phenol	271	$\ddot{O}$	18.82	MP	264.7	24.00	271.0
				OP	265.5	24.40	270.7
1,4-Benzoquinone	434	$\dot{O}$	15.23	OP	436.3	15.30	434.0
	285				206.1		285.0
1,2-Naphthoquinone	520	$\dot{O}$	15.23	MP	536.1	16.20	525.6
	400				415.2		400.1
Pyridine	257	$\dot{N}$	12.34	MP	260.8	12.60	257.1
Pyrimidine	267	$\dot{N}$	12.34	MP	240.3	16.20	267.3
Furan	200	$\ddot{O}$	18.82	MS	207.3	22.50	200.3

* Designations of formulae for calculating two-centre Coulomb integrals: M – the formula of Mataga and Nishimoto; O – the formula of Ohno and Klopman.

Desigations of formulae for calculating resonance integrals: S – spectral approximation, P – the interpolation formula of Pariser and Parr.

$\gamma_{\mu\mu}$Let us now elucidate theoretical premises. The historically accepted classification of quantum chemical methods, including the *ab initio*, semiquantitative and semiempirical ones, is mainly oriented to the elucidation of their mathematical aspects. Not refuting the positive sides of such a division of methods into groups, we would like to propose a new schematic classification, as a supplement to the aforementioned. It is based on the statement generally accepted in science that the aim of application of any theory is to predict the properties and behaviour of a system on the basis of studying its subsystems, *i. e.* going »from the inferior to the superior«. Thus, it seems reasonable to classify all the known methods by the qualitative originality of such a leap, three types of which can be distinguished.

The methods of the first group (*i. e. ab initio* and semiquantitative ones) extrapolate from elementary particles (or physical constants) to the molecule. Within this group, a simple correlation is observed: the more simplifications are introduced, the less precise the calculations are; and there are no other possible ways for further development than purely mathematical, and there is no »intermediate point« of the leap.

The extrapolation from atoms to the molecule is the basis of the methods belonging to the second group, which are called semiempirical (although all calculation schemes require a knowledge of fundamental physical constants, and »empiricism«

TABLE II

Calculation of electronic spectra of substances in accordance with model compounds

Model compounds	Compound under study	λ exper. nm	Formulae for calculating $\gamma_{\mu\nu}$ and $\beta_{\mu\nu}$	λ theor. before calibration/nm	λ theor. after calibration/nm
1	2	3	4	5	6
Glyoxal	Fumaric dialdehyde	354	MP	364.2	358.8
Acrolein	Acrylic acid	200	MP	198.1	199.2
Divinyl sulphide	Vinyl phenyl sulphide	266	MP	275.2	268.3
Benzaldehyde and phenol	2-Hydroxybenzaldehyde	256	MP	256.2	257.3
Banzaldehyde and phenol	3-Hydroxybenzaldehyde	254.5	MP	262.6	256.4
Benzaldehyde and phenol	4-Hydroxybenzaldehyde	283.5	MP	266.5	278.3
Benzoic acid and aniline	2-Aminobenzoic acid	327	OP	298.5	325.7
Benzoic acid and aniline	3-Aminobenzoic acid	310	OP	312.4	311.1
Benzoic acid and aniline	4-Aminobenzoic acid	284	OP	321.2	285.5
Benzoic acid and phenol	2-Hydroxybenzoic acid	302.5	OP	295.0	300.2
Benzoic acid and phenol	3-Hydroxybenzoic acid	296	OP	309.2	295.2
Benzoic acid	1-Naphthoic acid	290	OP	285.3	288.4
Benzoic acid	2-Naphthoic acid	333	OP	323.6	335.8
Aniline	1-Naphthylamine	324	OP	348.1	329.4
Aniline	2-Naphthylamine	338	OP	352.7	340.5
Phenol	Pyrocatechol	275	OP	270.6	277.3
		272		268.3	272.3
Phenol	Resorcinol	270	OP	266.5	269.4
1,2-Naphthoquinone and Phenol	5-Hydroxy-1,2-naphthoquinone	370	MP	382.5	376.4
Pyridine	2-Vinylpyridine	278.5	MP	284.8	281.9
Pyridine	3-Vinylpyridine	290	MP	289.6	291.3
Pyridine	2-Phenylpyridine	275	MP	263.4	268.1
Pyridine	4-Phenylpyridine	260	MP	265.0	264.6
Pyridine	2,2'-Bipyridine	280	MP	272.0	273.0
		237		237.7	238.7
Pyridine	4,4'-Bipyridine	280	MP	286.4	285.3
		236		234.6	234.5
Pyridine and aniline	2-Aminopyridine	287	MP	259.4	287.9
Pyridine and aniline	3-Aminopyridine	288	MP	274.6	290.0
Pyridine and phenol	2-Hydroxypyridine	277	MP	251.6	278.7
Pyridine and phenol	3-Hydroxypyridine	283	MP	270.6	278.9
Pyridine	Pyrimidine	267	MP	272.3	265.8
Pyridine	2-Azaanthracene	672	MP	684.4	682.0
		372		388.0	388.6
		250		250.9	250.9
Pyridine	1,8-Naphtyridine	330	MP	347.9	347.0
		308		300.0	298.7
Pyridine	1,4,5-Triazanaphthalene	359	MP	355.8	358.7
		308		295.4	291.7
		256		251.9	255.0
Pyridine	1,4,6-Triazanaphthalene	350	MP	404.3	358.9
		308		304.0	306.5
Pyridine	1,3,5,8-Tetraazanaphthalene	387	MP	359.8	370.6
		301		311.7	311.2
		235		233.8	229.6
		210		209.3	212.1
Pyrimidine and aniline	2-Aminopyrimidine	224	MP	237.3	234.0
Pyrimidine and phenol	6-Hydroxypyrimidine	223	MP	291.2	236.5
Divinyl sulphide and 1,4-benzoquinone	1-Thiopyranone-4	290	OP	319.2	302.1
Divinyl sulphide and acrolein	1-Thiopyranone-4	290	OP	319.2	305.4
Divinyl sulphide and benzaldehyde	1-Thiopyranone-4	290	OP	319.2	291.4
Furan	Furfurol	278	MS	294.8	281.7

appears necessary). During their development, various mathematical methods and physical assumptions are used to include into equations, the information obtained from isolated atoms by means of spectroscopy (by the way, it seems paradoxical that the equations are transformed in order to include the data from atomic spectroscopy, while these data are used to compensate for the errors involved in the transformation step). At this level, the universality is lost (as a price for decreased laboriousness and a number of models appear, each with its respective method. In spite of the fact that only some correction of the atomic spectroscopy data can be considered, there are a number of parameterizations and similar formulae even within the same methods (see, for example, the difference between the parameterizations of Peacock[72] and Hinze and Jaffé[59] within the PPP method). Such a negative tendency towards an increase of the volume of not wholly reliable information provides evidence that there are some reserves not yet used for further development of semiempirical methods.

Thus, there are now well-grounded bases for distinguishing the third group of methods which extrapolate from fragments to the molecule. There is a similarity consisting of the following: in going from *ab initio* methods to semiempirical ones, the most unreliable component of the equations is revealed and spectral information is used for its correction, while the methods of the third group a certain quantity is also found, the evaluations of which appear most doubtful (*e. g.* one-centre Coulomb integral in the PPP method, resonance integral in the Hückel molecular orbital, HMO, method and the extended Hückel theory, EHT), and its calibration is performed using the experimental data (in particular, electronic spectra) of specially selected compounds.

The approach extrapolating from fragments to the molecule is rather old. It was successfully used in the crystal field theory (Ref. 73 and references therein). The fragment molecular orbital and the »divide and conquer« methods[5,54] are built on this idea. There are many examples of parameterizing by known compounds, then using these specialized parameters for higher accuracy when performing calculations for similar molecules, *e. g.* within the framework of the HMO, the EHT, and the PPP method.[5,54]

In the previous works involving the »fragments-molecule« approach, the possibility of indirect medium consideration by means of experimental conditions unification for model substances and compounds under study was not emphasized. The schemes of minimization of inaccuracy of the quantum chemical calculation by means of the series of structurally related molecules (diminishing of the leap of the method) was not grounded.

The third group can hardly be expected to expand on account of all-valent methods, since the latter do not provide for the appearance of a single parameter to be calibrated, and not several ones simultaneously, after a minimal complexation of the molecular structure.

Let us discuss the relation between the methods of the first and the second groups on the one hand, and the third group, on the other. There is an important advantage that the *ab initio* approach and the all-valent semiempirical models, such as CNDO, INDO, PNDO, NDDO *et al.*, have over the PPP, the latter even with adaptation of parameters. Through automatic core (sigma) relaxation they need not distinguish between different kinds of the same atom, *e. g.* aniline (pyrrole) and pyridine type nitrogen, phenol (furan) and carbonyl type oxygen, etc.

The above-mentioned all-valent semiempirical methods, unlike the PPP method with adaptation of parameters, use unique sets of parameters for all molecular systems. Therefore, they are, in general, less accurate in predicting electronic transition energies, especially for large molecules. Some of them[22,23] give only qualitative agreement with experiment. The fact that the PPP approach uses different sets of parameters for different kinds of molecules reduces the predictive power of the method. However, it gives an opportunity to reproduce, in many cases, real absorption wavelengths of rather complicated organic compounds within nimimal CI and without explicit consideration of medium effects.

The methods of the third group seem to have some advantages at present, in the cases when the quantitative reproducing of any characteristic is desired, in particular a maximum wavelength in electronic spectrum, which is necessary, for example, in identification of chemical substances. Detailed analyses of the energetics and nature of molecular systems stationary states, and determination of the corresponding regularities in the series of compounds require the methods belonging to the first or the second group.

CONCLUSION

In order to prove the legitimacy of adaptation of the parameters of semiempirical quantum chemical methods, a schematic classification is suggested based on the ideas of extrapolating from elementary particles (physical constants) to the molecule, from atoms to the molecule, and from fragments to the molecule.

The PPP method with adaptation of parameters has been used to calculate the electronic spectra of some unsaturated, aromatic and heterocyclic compounds, such as: *N,N'*-diphenyl-*p*-diphenoquinonediimine dication and derivatives of ethylene, benzene, naphthalene, quinone, pyridine (substituted and condensed), pyridine, some other azaheterocycles, thiopyranone and furan.

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SAŽETAK

Proračun elektronskih spektara nezasićenih organskih spojeva PPP-postupkom uz prilagodbu parametara

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Ispitana je mogućnost kvantitativnog predviđanja apsorpcijskih maksimuma u elektronskim spektrima nezasićenih organskih spojeva s pomoću Pariser-Parr-Pople-ova postupka uz prilagodbu parametara. Predložena je klasifikacija kvantno-kemijskih metoda zasnovana na načelu ekstrapolacije: od elementarnih čestica (fizikalnih konstanti) do molekula, od atoma do molekula i, konačno, od fragmenata do molekula.