Pars Orbital Method for Excited States

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Based on a projection operator formalism the pars orbital method is reformulated for the general case that both the molecule M as well as the reference molecule L_i are described by a CI-expansion of the wave function. Some numerical examples in which the method is used for the interpretation of the ultraviolet spectra of simple organic molecules (butadiene, aniline, benzonitrile, o-, m-, and p-aminobenzonitrile, 2,5-diamino-p-benzoquinone) in terms of the various states (ground as well as excited) of the respective reference molecules are discussed in some detail to illustrate the scope and limitations of the proposed formalism. The results of these calculations are in addition compared to results obtained by two other methods (configuration analysis and specific measures of partial distances) designed to allow an analysis of molecules in terms of the constituent fragments.

Introduction

It is common usage in chemistry to discuss chemical and physical properties of a complex molecule in terms of its constitutent fragments, e.g. in terms of a hydrocarbon skeleton and functional groups. This "principle of analogy" as it has been designated [1] is based on the chemical evidence that properties of individual bonds or groups are to a good approximation independent of the rest of the molecule and, therefore, may be transferred from one molecule to another one. For example, the similarity between the benzenoid fragments of polycyclic aromatic hydrocarbons led Clar to his well-known classification of this class of compounds [2]. Since this concept of a similarity between the essential characteristics of different molecules proved to be very useful for the classification and systematization of a large body of chemical as well as physical properties, several attempts have been made to put this concept on a more quantitative footing, e.g. the pars orbital method [3], the pseudo pars orbital method [4] and the fragments-in-molecule method [5, 6]. Since the first description of the original pars orbital method [3] a number of applications of this method to problems in chemical reactivity [7–14], NMR-spectroscopy [15–17], UV-spectroscopy [18, 19] and triplet state properties [20] have been described. Originally formulated within the framework of the HMO model and for ground states [3], an extension of the pars orbital method to all valence electron methods [21, 22] and excited states [23, 24] has been formulated. Within the framework of a π-electron approximation the unnormalized character order $\bar{r}^{\alpha}_{L_i}$ of a molecule M in its electronic state α referred to the ground state of the fragment L_i is simply given by [24]

$$\bar{r}^{\alpha}_{L_i} = \mathrm{tr}(P^{\alpha}_{M_i} R_{L_i}) = 1/2\,\mathrm{tr}(P^{\alpha}_{M_i} P_{L_i}), \tag{1}$$

where R_{L_i} is the projector onto the subspace of the pars orbitals occupied in the reference molecule L_i. Since the density matrix P_{L_i} is idempotent only for one-determinantial wave functions it immediately follows that only comparisons of excited states of the molecule M with the ground state of the fragment L_i are possible. For the treatment of photochemical reactivity as well as for interpretative purposes in electronic spectroscopy a comparison with excited states of the reference molecule would be highly desireable. Based on the concept of distance and similarity measures [1, 25] Mehlhorn et al. [26–28] have used a somewhat different approach to circumvent the difficulties involved with the non-idempotency of the excited state density matrix.

The present paper gives a general formulation of the pars orbital method, which may be used with any quantum chemical computational scheme (semiempirical as well as ab initio) and which allows the calculation of the character orders for any states of both the molecule M as well as the fragment L_i.

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Method

Let Ψ_I be the wave function for the I-th electronic state of the molecule M and similarly Ψ_J^0 the wave function for the J-th electronic state of the fragment $\mathrm{L_i}$:

$$\Psi_I = \sum_i c_{iI} \Phi_i \quad \text{and} \quad \Psi_J^0 = \sum_j c_{jJ}^0 \Phi_j^0 , \tag{2}$$

where Φ_i and Φ_j^0 denote Slater determinants of M and $\mathrm{L_i}$ respectively. Use of the projection operator $\hat{P}_J = |\Psi_J^0\rangle\langle\Psi_J^0|$ yields for the projection P_{IJ} of the I-th molecular electronic state onto the J-th reference state the expression

$$\begin{aligned} P_{IJ} &= \langle \Psi_I | \hat{P}_J | \Psi_I \rangle \\ &= \sum_i \sum_j \sum_k \sum_l c_{iI}^* c_{jJ}^0 c_{kJ}^{0*} c_{lI} \langle \Phi_i | \Phi_j^0 \rangle \langle \Phi_k^0 | \Phi_l \rangle . \end{aligned} \tag{3}$$

In (3) the summation is over single Slater determinants, thus a factor of $(1/2)^{-1/2}$ may be contained in the CI-coefficients c_{iI} or c_{jJ}^0.

Since the Slater determinants Φ_i and Φ_j^0 are built up by a different number of electrons (n_M and $n_{\mathrm{L_i}}$, respectively) it is necessary first to integrate over $n_\mathrm{M} - n_{\mathrm{L_i}}$ electrons. According to [29] Φ_i may be written as

$$\begin{aligned} \Phi_i = \binom{n_\mathrm{M}}{n_{\mathrm{L_i}}}^{-1/2} & \sum_{j_1 < j_2 < \ldots < j_{n_{\mathrm{L_i}}}} (-1)^J (n_{\mathrm{L_i}}!)^{-1/2} \\ & \times |\psi_{j_1}(1) \psi_{j_2}(2) \ldots\ldots \psi_{j_{n_{\mathrm{L_i}}}}(n_{\mathrm{L_i}})| \, [(n_\mathrm{M} - n_{\mathrm{L_i}})!]^{-1/2} \\ & \times |\psi_{j_{n_{\mathrm{L_i}}+1}}(n_{\mathrm{L_i}}+1) \ldots\ldots \psi_{j_{n_\mathrm{M}}}(n_\mathrm{M})| , \end{aligned} \tag{4}$$

where $J = \sum_{i=1}^{n_{\mathrm{L_i}}} (j_i - i)$.

Inserting (4) one obtains for typical term of (3):

$$\begin{aligned} \langle \Phi_j | \Phi_i^0 \rangle \langle \Phi_i^0 | \Phi_j \rangle = & \binom{n_\mathrm{M}}{n_{\mathrm{L_i}}}^{-1} (n_{\mathrm{L_i}}!)^{-2} [(n_\mathrm{M} - n_{\mathrm{L_i}})!]^{-1} \\ & \times \sum_{j_1 < j_2 < \ldots < j_{n_{\mathrm{L_i}}}} (-1)^J \langle |\psi_{j_1}(1) \psi_{j_2}(2) \ldots\ldots \psi_{j_{n_{\mathrm{L_i}}}}(n_{\mathrm{L_i}})| \, \big| \, |\psi_1^0(1) \ldots \psi_{n_{\mathrm{L_i}}}^0(n_{\mathrm{L_i}})| \rangle \\ & \times \sum_{i_1 < i_2 < \ldots < i_{n_{\mathrm{L_i}}}} (-1)^I \langle |\psi_1^0(1) \ldots \psi_{n_{\mathrm{L_i}}}^0(n_{\mathrm{L_i}})| \, \big| \, |\psi_{i_1}(1) \ldots \psi_{i_{n_{\mathrm{L_i}}}}(n_{\mathrm{L_i}})| \rangle \\ & \times \langle \psi_{j_{n_{\mathrm{L_i}}+1}}(n_{\mathrm{L_i}}+1) \ldots \psi_{j_{n_\mathrm{M}}}(n_\mathrm{M})| \, \big| \, |\psi_{i_{n_{\mathrm{L_i}}+1}}(n_{\mathrm{L_i}}+1) \ldots \psi_{i_{n_\mathrm{M}}}(n_\mathrm{M})| \rangle . \end{aligned} \tag{5}$$

In order to evaluate (5), the non-orthogonality between $\{\psi_i\}$ and $\{\psi_i^0\}$ has to be taken into account ($\{\psi_i\}$ as well as $\{\psi_i^0\}$ for themselves alone are of course orthonormal). Using the well-known relationship for the overlap integral between Slater determinants involving non-orthonormal spin orbitals [30], (5) yields

$$\begin{aligned} \langle \Phi_j | \Phi_i^0 \rangle \langle \Phi_i^0 | \Phi_j \rangle = & \frac{n_{\mathrm{L_i}}!(n_\mathrm{M} - n_{\mathrm{L_i}})!}{n_\mathrm{M}!} \\ & \times \sum_{j_1 < j_2 < \ldots < j_{n_{\mathrm{L_i}}}} |S_{j_1 j_2 \ldots j_{n_{\mathrm{L_i}}}}|^2 . \end{aligned} \tag{6}$$

Using furthermore the Löwdin normalization of reduced density matrices [31], (3) thus finally leads to

$$\begin{aligned} P_{IJ} = & \sum_i \sum_j \sum_k \sum_l c_{iI}^* c_{jJ}^0 c_{kJ}^{0*} c_{lI} \\ & \times \sum_{i_1 < i_2 < \ldots < i_{n_{\mathrm{L_i}}}} \; \sum_{j_1 < j_2 < \ldots < j_{n_{\mathrm{L_i}}}} (-1)^{J_1 + J_2} \\ & \times |S_{i_1 i_2 \ldots i_{n_{\mathrm{L_i}}}}^{ij}|^* |S_{j_1 j_2 \ldots j_{n_{\mathrm{L_i}}}}^{kl}| \\ & \times \delta_{i_{n_{\mathrm{L_i}}}+1, \, j_{n_{\mathrm{L_i}}}+1} \ldots \delta_{i_{n_\mathrm{M}}, \, j_{n_\mathrm{M}}} , \end{aligned} \tag{7}$$

where $J_1 = \sum_{k=1}^{n_{\mathrm{L_i}}} (i_k - k)$ and $J_2 = \sum_{k=1}^{n_{\mathrm{L_i}}} (j_k - k)$, and $|S_{i_1 i_2 \ldots i_{n_{\mathrm{L_i}}}}^{ij}|$ is the determinant of overlap integrals between the spin orbitals in Φ_j^0 and those of the cofactor of Φ_i obtained by dropping the rows $n_{\mathrm{L_i}} + 1, \ldots, n_\mathrm{M}$ and the columns $i_{n_{\mathrm{L_i}}+1}, \ldots, i_{n_\mathrm{M}}$. If the MO's of the molecule M and the fragment $\mathrm{L_i}$ (the pars orbitals) are denoted by $\{\varphi_k^\mathrm{M}\}$ and $\{\chi_\mu^{\mathrm{L_i}}\}$, respectively, the determinant $|S_{i_1 i_2 \ldots i_{n_{\mathrm{L_i}}}}^{ij}|$ consists of overlap integrals of the form $\langle \chi_\mu^{\mathrm{L_i}} | \varphi_k^\mathrm{M} \rangle$. These may be conveniently arranged in ma-

Table 1. Results of pars orbital calculations (P_{IJ}), measures of specific partial distances ($\bar{d}_{IJ}$) and configuration analysis (m_{IJ}^2) for the fragmentation of butadiene (**I**) into ethylene (**IA**: terminal bond; **IB**: central bond).

	S_0 (**I**)			1 B_u (**I**)			2 A_g (**I**)			3 A_g (**I**)			2 B_u (**I**)		
	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2
S_0 (**IA**)	0.935	0.022	0.874	0.491	0.178	0.000	0.499	0.178	0.120	0.483	0.178	0.000	0.492	0.178	0.000
S_1 (**IA**)	0.032	0.311	0.000	0.383	0.156	0.502	0.234	0.156	0.000	0.484	0.156	0.935	0.367	0.156	0.432
S_0 (**IB**)	0.461	0.214	0.138	0.678	0.107	0.482	0.448	0.274	0.301	0.448	0.274	0.000	0.001	0.440	0.003
S_1 (**IB**)	0.218	0.119	0.062	0.212	0.226	0.063	0.141	0.060	0.042	0.359	0.060	0.000	0.569	0.106	0.994

trix form (b_{M} and $b_{\mathrm{L_i}}$ are the number of basis functions of the molecule M and the fragment $\mathrm{L_i}$, respectively):

$$\boldsymbol{S} = \langle \chi_1^{\mathrm{L_i}}, \bar{\chi}_1^{\mathrm{L_i}}, \ldots, \bar{\chi}_{b_{\mathrm{L_i}}}^{\mathrm{L_i}} | \varphi_1^{\mathrm{M}}, \bar{\varphi}_1^{\mathrm{M}}, \ldots, \bar{\varphi}_{b_{\mathrm{M}}}^{\mathrm{M}} \rangle \tag{8}$$

$$= \begin{pmatrix} \langle \chi_1^{\mathrm{L_i}} | \varphi_1^{\mathrm{M}} \rangle & 0 & \langle \chi_1^{\mathrm{L_i}} | \varphi_2^{\mathrm{M}} \rangle & \ldots\ldots & \langle \chi_1^{\mathrm{L_i}} | \varphi_{b_{\mathrm{M}}}^{\mathrm{M}} \rangle & 0 \\ 0 & \langle \chi_1^{\mathrm{L_i}} | \varphi_1^{\mathrm{M}} \rangle & 0 & \ldots\ldots & 0 & \langle \chi_1^{\mathrm{L_i}} | \varphi_{b_{\mathrm{M}}}^{\mathrm{M}} \rangle \\ \vdots & & & & & \\ 0 & \langle \chi_{b_{\mathrm{L_i}}}^{\mathrm{L_i}} | \varphi_1^{\mathrm{M}} \rangle & 0 & \ldots\ldots & 0 & \langle \chi_{b_{\mathrm{L_i}}}^{\mathrm{L_i}} | \varphi_{b_M}^{\mathrm{M}} \rangle \end{pmatrix}.$$

Here, the rows and columns correspond to the indices of the spin orbitals contained in the Slater determinants of $\mathrm{L_i}$ and M, respectively. Expansion of these matrix elements into basis functions (atomic orbitals) leads to

$$\langle \chi_\mu^{\mathrm{L_i}} | \varphi_k^{\mathrm{M}} \rangle = \sum_i^{b_{\mathrm{L_i}}} \sum_j^{b_{\mathrm{M}}} f_{\mu i}^{\mathrm{L_i}\top} S_{ij} c_{jk}^{\mathrm{M}}. \tag{9}$$

Since the number of terms appearing in (7) is given by (NCI and NCJ are the numbers of configurations used to describe the I-th and J-th electronic state of M and $\mathrm{L_i}$, respectively)

$$(2 * \mathrm{NCI})^2 * (2 * \mathrm{NCJ})^2 \binom{n_{\mathrm{M}}}{n_{\mathrm{L_i}}}^2, \tag{10}$$

the evaluation of (7) becomes rather cumbersome and time consuming with an increasing number of electrons or basis functions. Since the numerical examples given in the next section are only intended to illustrate the formalism described above the semiempirical *PPP*-method [32, 33] has been used for the calculations. In this case (9) simplifies to

$$\langle \chi_\mu^{\mathrm{L_i}} | \varphi_k^{\mathrm{M}} \rangle = \sum_i f_{\mu i}^{\mathrm{L_i}\top} c_{jk}^{\mathrm{M}}, \tag{11}$$

where the summation now is over those basis functions (in the *PPP*-approximation equivalent to atomic centres) common to both the molecule M and the fragment $\mathrm{L_i}$. The main computational effort thus consists in calculating the overlap matrix elements $\langle \chi^{\mathrm{L_i}} | \varphi^{\mathrm{M}} \rangle$ according to (11), selecting the appropriate elements of the matrix $\boldsymbol{S}$ as determined by the MO's contained in the Slater determinants Φ_i and Φ_j^0, respectively, evaluation of the respective determinant of overlap integrals $|S_{i_1 i_2 \ldots i_{n_{\mathrm{L_i}}}}^{ij}|$ and summation according to (7).

Numerical Examples

In this section the method outlined above will be illustrated on some simple organic molecules, and the results will be compared to those obtained by a configuration analysis [34] as well as with measures of specific partial distances [26, 27]. As mentioned previously, all calculations were performed with the *PPP*-method [32, 33].

The first example to be discussed is provided by the fragmentation of butadiene (**I**) into ethylene. The results for both possible fragmentations (**IA**: terminal bond; **IB**: central bond) are given in Table 1.

In this table the values P_{IJ} of the extended pars orbital method and the measures of specific partial distances $\bar{d}_{IJ}$ should be directly compareable. Some difficulties arise in the comparison of these two methods with the results obtained by the configuration analysis: For the ground state of the reference molecule the given value of m_{IJ}^2 is the contribution of the no-bond configuration, i.e. a single Slater determinant describing two or more non-interacting molecular subunits in their respective ground states, to the respective electronic state of the molecule M. For example, the value of m_{00}^2 of the no-bond configuration of fragmentation **IA** for the ground state of butadiene simply equals P_{00}^2. In other circumstances the connection between these two methods is not as simple as in this case. For S_i $(i \neq 0)$ in the following tables m_{IJ}^2 corresponds to the contribution of the respective locally excited state of the fragment under consideration except for fragmentation **IA** of butadiene, where the contributions of the symmetric (1 $\mathrm{B_u}$ and 2 $\mathrm{B_u}$) and antisymmetric (3 $\mathrm{A_g}$) excitonic state $\Psi_1^{-1} \pm \Psi_{1'}^{-1'}$ of the combined system of two ethylene molecules are listed. Consider first fragmentation **IA** of butadiene: of course the value P_{00} – corresponding to the double bond nature of the terminal bond – is very large. In the first excited state this value (i.e. P_{01}, cf. Table 1) is drastically reduced whereas the "character order" P_{11} of S_1-ethylene in the 1 $\mathrm{B_u}$ state of butadiene significantly is enhanced (0.383 as compared to 0.032 in the ground state of **I**). In contrast, the value P_{00} for fragmentation **IB** of butadiene is rather low – correspond-

Table 2. Values of P_{IJ}, $\bar{d}_{IJ}$ and m_{IJ}^2 for the fragmentation of aniline (**II**) into benzene.

	S_0 (**II**)			S_1 (**II**)			S_2 (**II**)		
	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2
S_0 (benzene)	0.997	0.012	0.831	0.303	0.039	0.000	0.518	0.050	0.135
S_1 (benzene)	0.036	0.032	0.000	0.764	0.022	0.701	0.136	0.044	0.000
S_2 (benzene)	0.037	0.032	0.001	0.074	0.022	0.000	0.476	0.044	0.353

Table 3. Values of P_{IJ}, $\bar{d}_{IJ}$ and m_{IJ}^2 for the fragmentation of benzonitrile (**III**) into benzene.

	S_0 (**III**)			S_1 (**III**)			S_2 (**III**)		
	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2
S_0 (benzene)	0.942	0.006	0.928	0.014	0.036	0.000	0.045	0.038	0.008
S_1 (benzene)	0.003	0.033	0.000	0.881	0.010	0.924	0.005	0.020	0.000
S_2 (benzene)	0.004	0.033	0.001	0.003	0.010	0.000	0.797	0.020	0.831

ing to the essential single bond nature of the central bond. In the first excited state 1 B_u the "character order" P_{01} of ground state ethylene is significantly enhanced (0.678 as compared to 0.461, cf. Table 1) – thus clearly reflecting the change of bond orders and geometry upon excitation.

Further examples which may be discussed on the basis of such a composite molecule approach are provided by the interesting features of the electronic absorption spectra of simple substituted aromatic compounds. For instance, it is well known experimentally that ortho as well as meta donator-acceptor disubstituted benzene derivatives show quite similar ultraviolet spectra and both absorb at longer wavelengths than the corresponding para derivative. Before discussing these experimental results on the basis of the method described in the previous section it seems appropriate first to consider the prototypes of a donator as well as an acceptor mono-substituted benzene, namely aniline (**II**) and benzonitrile (**III**). The results for these two compounds in terms of a fragmentation into benzene + substituent are collected in Tables 2 and 3, respectively.

The differences in the values of P_{11} and P_{22} for aniline (Table 2) and benzonitrile (Table 3) may be connected with the UV-spectroscopic properties of these two compounds: the first electronic transition is much less affected by the substituent than the second one. In fact, the latter one has been shown to contain an appreciable amount of an intramolecular charge transfer transition [35] – hence the relatively low value of P_{22}, especially in the case of aniline. The much higher values of P_{11} (0.764 and 0.881 as compared to 0.476 and 0.797 for **II** and **III**, respectively, cf. Tables 2 and 3) are in complete agreement with the experimental observations indicative for a considerably less disturbed "benzenoid" character of the first electronic transition in these two compounds. As examples for the above mentioned donator-acceptor disubstituted benzene derivatives, Tables 4–6 show the results for ortho- (**IV**) meta- (**V**), and para-aminobenzonitrile (**VI**), where fragmentations into benzene + substituents (**A**), aniline + nitrile group (**B**) as well as benzonitrile + amino group (**C**) are considered.

On the basis of various methods designed for the analysis of electronic states and transitions in terms of molecular subunits the previously mentioned unexpected UV-spectroscopic behaviour of this type of compounds has been explained by the fact that intramolecular charge transfer configurations contribute predominantly to the first absorption band in the case of both ortho- as well as meta-derivatives, whereas in the para-compounds this interaction is restricted to the S_2-state [35]. The data presented in Tables 4–6 clearly conform to this interpretation.

Finally, a rather crucial and interesting example is provided by the extensively studied compound 2,5-diamino-p-benzoquinone (**VII**) which either may be regarded as a substituted quinone [36] (fragmentation **A** in Table 7) or as two coupled trimethinemerocyanine chains [37] (fragmentation **B** in Table 7).

For fragmentation **B** of this compound similar problems are encountered as with fragmentation **A** of butadiene when the method of configuration analysis

Table 4. Values of P_{IJ}, $\bar{d}_{IJ}$ and m^2_{IJ} for the fragmentation of o-aminobenzonitrile (**IV**) into benzene (**A**), aniline (**B**), and benzonitrile (**C**).

	S_0 (**IV**)			S_1 (**IV**)			S_2 (**IV**)		
	P_{IJ}	$\bar{d}_{IJ}$	m^2_{IJ}	P_{IJ}	$\bar{d}_{IJ}$	m^2_{IJ}	P_{IJ}	$\bar{d}_{IJ}$	m^2_{IJ}
S_0 (**A**)	0.927	0.016	0.752	0.370	0.039	0.040	0.414	0.045	0.167
S_1 (**A**)	0.040	0.031	<0.001	0.295	0.025	0.501	0.044	0.035	0.111
S_2 (**A**)	0.043	0.032	0.004	0.032	0.025	0.010	−0.011	0.036	0.321
S_0 (**B**)	0.922	0.006	0.910	0.021	0.039	0.009	0.021	0.042	0.007
S_1 (**B**)	0.004	0.033	0.001	0.443	0.014	0.771	−0.082	0.037	0.112
S_2 (**B**)	0.003	0.049	0.001	0.049	0.042	0.064	0.048	0.016	0.791
S_0 (**C**)	0.996	0.010	0.808	0.367	0.030	0.027	0.422	0.034	0.122
S_1 (**C**)	0.040	0.024	<0.001	0.571	0.018	0.570	−0.024	0.030	0.104
S_2 (**C**)	0.041	0.028	0.002	0.090	0.021	0.029	0.033	0.033	0.368

Table 5. Values of P_{IJ}, $\bar{d}_{IJ}$ and m^2_{IJ} for the fragmentation of m-aminobenzonitrile (**V**) into benzene (**A**), aniline (**B**), and benzonitrile (**C**).

	S_0 (**V**)			S_1 (**V**)			S_2 (**V**)		
	P_{IJ}	$\bar{d}_{IJ}$	m^2_{IJ}	P_{IJ}	$\bar{d}_{IJ}$	m^2_{IJ}	P_{IJ}	$\bar{d}_{IJ}$	m^2_{IJ}
S_0 (**A**)	0.940	0.010	0.777	0.347	0.039	<0.001	0.438	0.045	0.091
S_1 (**A**)	0.038	0.030	<0.001	0.231	0.024	0.561	0.050	0.036	0.024
S_2 (**A**)	0.038	0.030	<0.001	0.008	0.024	0.084	0.018	0.036	0.690
S_0 (**B**)	0.941	0.005	0.927	0.005	0.038	<0.001	0.008	0.045	0.001
S_1 (**B**)	0.004	0.033	<0.001	0.680	0.010	0.871	−0.032	0.039	0.025
S_2 (**B**)	0.001	0.049	<0.001	0.013	0.046	0.015	0.084	0.009	0.935
S_0 (**C**)	0.997	0.009	0.827	0.351	0.029	0.001	0.472	0.034	0.121
S_1 (**C**)	0.030	0.024	<0.001	0.326	0.016	0.632	−0.012	0.031	0.020
S_2 (**C**)	0.025	0.028	0.001	0.102	0.023	0.012	0.054	0.036	0.382

Table 6. Values of P_{IJ}, $\bar{d}_{IJ}$ and m^2_{IJ} for the fragmentation of p-aminobenzonitrile (**VI**) into benzene (**A**), aniline (**B**), and benzonitrile (**C**).

	S_0 (**VI**)			S_1 (**VI**)			S_2 (**VI**)		
	P_{IJ}	$\bar{d}_{IJ}$	m^2_{IJ}	P_{IJ}	$\bar{d}_{IJ}$	m^2_{IJ}	P_{IJ}	$\bar{d}_{IJ}$	m^2_{IJ}
S_0 (**A**)	0.930	0.015	0.762	0.273	0.037	0.000	0.470	0.046	0.186
S_1 (**A**)	0.039	0.032	0.000	0.458	0.014	0.716	0.046	0.039	0.000
S_2 (**A**)	0.044	0.032	0.004	0.032	0.014	0.000	<0.001	0.039	0.311
S_0 (**B**)	0.932	0.006	0.919	0.012	0.032	0.000	0.029	0.045	0.010
S_1 (**B**)	0.001	0.036	0.000	0.909	0.008	0.959	0.001	0.041	0.000
S_2 (**B**)	0.005	0.048	0.001	0.002	0.042	0.000	0.495	0.012	0.851
S_0 (**C**)	0.997	0.009	0.817	0.263	0.028	0.000	0.477	0.035	0.129
S_1 (**C**)	0.044	0.025	0.000	0.545	0.017	0.735	0.075	0.029	0.000
S_2 (**C**)	0.048	0.027	0.002	0.027	0.021	0.000	0.349	0.025	0.430

is used: here the contribution of the first and second symmetric excitonic state of the two merocyanine fragments to S_0 and S_1 of **VII** are listed. For S_2 of **VII** the corresponding antisymmetric combinations are given in Table 7.

As can be seen from the data collected in Table 7, this compound provides an example for which the results of the pars orbital method as described in the previous section are at variance with the two other methods. According to the method of specific mea-

Table 7. Values of P_{IJ}, $\bar{d}_{IJ}$ and m_{IJ}^2 for the fragmentation of 2,5-diamino-p-benzoquinone (**VII**) into quinone (**A**) and trimethinemerocyanine (**B**).

	S_0 (**VII**)			S_1 (**VII**)			S_2 (**VII**)		
	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2	P_{IJ}	$\bar{d}_{IJ}$	m_{IJ}^2
S_0 (**A**)	0.973	0.025	0.554	0.491	0.044	0.242	0.468	0.039	0.000
S_1 (**A**)	0.175	0.045	0.015	0.001	0.026	0.539	<0.001	0.035	0.000
S_2 (**A**)	0.144	0.036	0.000	0.055	0.032	0.000	<0.001	0.029	0.419
S_0 (**B**)	0.932	0.010	0.875	0.472	0.050	0.003	0.472	0.042	0.000
S_1 (**B**)	0.016	0.074	0.001	0.194	0.057	0.212	0.003	0.046	0.165
S_2 (**B**)	0.018	0.079	0.001	0.002	0.076	0.006	-0.001	0.066	0.001

sures of partial distances as well as to the configuration analysis, the ground state of **VII** can best be represented by fragmentation **B** whereas the pars orbital method yields a higher value of P_{00} for fragmentation **A**, i.e. according to this latter method 2,5-diamino-p-benzoquinone should be regarded as a substituted quinone. This result, which already was obtained previously by the original formulation of the pars orbital method [38] is modified if in addition the two amino groups are taken into account [25]. Similar discrepancies pertain in the excited states of **VII**: for fragmentation **A** as well as fragmentation **B** the pars orbital method yields significant contributions only for the respective ground states of the fragments under consideration (**A** or **B**) to both S_1 and S_2 of **VII**. In contrast, both the values of $\bar{d}_{IJ}$ and m_{IJ}^2 point to the predominance of the respective excited state of the quinonoid fragment. Although the differences between the pars orbital method and the configuration analysis are most probably due to the different approach – P_{IJ} refers to a single fragment while m_{IJ}^2 refers to the fragmented analogue as a whole – the different conclusions obtained by P_{IJ} and $\bar{d}_{IJ}$ are less clear cut.

Summary

A general formulation of the pars orbital method has been presented with special emphasis for the description of excited state character orders. The applicability as well as limitations of this formalism were tested on some simple organic molecules especially with respect to the interpretation of their UV-spectroscopic properties. In addition, the results obtained by the proposed method were compared to those of similar methods.

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