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# Bond Orbital Approach for Optical Rotatory Strength Calculations

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Directly determined localized approximate molecular orbitals are used in excitation energy and optical rotatory strength calculations within the CNDO/2 scheme. Using strictly localized bond orbitals one obtains qualitatively good excitation energies, but quantitative agreement can be found only by considering delocalization effects, which have been proved to be crucial in determining the optical rotatory strength. The delocalization interactions are classified as through space and through bond ones and even the latter is found to have significant contributions. The chiroptical properties of the lowest lying transitions in the twisted glyoxal molecule are analysed in terms of localized molecular orbital contributions.

**Key words:** Optical rotatory strength – Localized orbitals – Delocalization corrections – Through space interactions – Through bond interactions – Twisted glyoxal.

## 1. Introduction

The concept of localized orbitals has been widely used in the description of molecular ground states [1]. Recently there is an increasing interest in the use of localized molecular orbitals (LMO-*s*) to study the excited states as well [2–5]. Localized orbitals offer a valuable tool to analyse the characteristics of the electronic transitions according to the well-known chromophore concept which has a basic importance in the models of the optical activity [6–9]. On the basis of the success of these theories in understanding the circular dichroism of organic and inorganic molecules, one can hope that the localized MO approach has not only an interpretative value, but it may serve also as a good starting point at different levels of sophistication to calculate the chiroptical properties of molecules.

The $R_{0i}$ optical rotatory strength, associated to the $0 \rightarrow i$ electron transition, is defined in the dipole velocity form [10] as:

$$R_{0i} = -\frac{e^2\hbar^3}{2m^2c\Delta E_{0i}} \langle 0|\hat{\nabla}|i\rangle\langle i|\hat{r} \times \hat{\nabla}|0\rangle \tag{1}$$

where $\Delta E_{0i} = E_i - E_0$ is the transition energy; the constants $e$, $m$, $\hbar$ and $c$ have the usual meaning. In most quantum chemical calculations of $R_{0i}$ the $\langle 0|$ ground state wave function is represented as a single determinant of *canonical* molecular orbitals [11], while the excited state wave function is approximated by linear combination of singly excited determinants. This computational scheme gives more or less reliable rotational strengths, but the delocalized nature of the canonical orbitals makes very difficult the interpretation of the results in terms of interacting molecular fragments and chromophores.

The need for a deeper understanding of the optical rotatory phenomena led to the development of calculational tools which permit such type of analyses. One possibility is to use *a posteriori* localized molecular orbitals, i.e. orbitals obtained from the SCF canonical ones according to some localization criteria [12–14]. These orbitals afford a systematic investigation of the most important intramolecular interactions determining the sign of the rotational strength [15–18]. However, due to the large amount of computational work necessary in the treatment of larger molecular systems with the usual SCF MO methods, the development of new calculational schemes would be advantageous.

Recently an efficient method, based on *a priori* localized molecular orbitals, was proposed to investigate ground-state properties (conformational energies) of large molecules [19, 20]. The aim of the present paper is to examine the usefulness and the reliability of this scheme for the determination of excitation properties, namely the excitation energy and the optical rotatory strength. After summarizing the methodological details we present some applications at the CNDO/2 level on simple molecules, such as $H_2O$, $H_2CO$ and the twisted glyoxal molecule, which is a typical example for an optically active chromophoric system.

## 2. Method

In the construction of a single determinantal ground state wave function from *a priori* localized bonding orbitals, the simplest approximation is to use strictly localized molecular orbitals (SLMO-*s*). These orbitals are built up from one or two atomic hybrids (lone pairs or bonds, respectively). This simple wave function describes rather poorly the electronic structure because of the neglection of all delocalization effects [21].

The delocalization corrections (tails) to the SLMO-*s* can be accounted for by choosing the localized molecular orbitals (LMO-*s*) in the following way:

$$\psi_i = \psi_1^0 + \sum_k^{\text{virt}} \eta_{ik}\psi_k^{0*} \tag{2a}$$

$$\psi_i^* = \psi_i^{0*} - \sum_k^{\text{occ}} \eta_{ki}\psi_k^0 \tag{2b}$$

where $\psi_i^0$ ($\psi_i^{0*}$) is the occupied (virtual) SLMO, and the sums represent the tails. The bonding LMO-*s* (2a) have tails only on the antibonding orbitals, while the antibonding ones (2b) have tails only on bonding orbitals. This assumption does not imply any approximation, since the exact nonorthogonal (SCF) LMO-*s* can always be written in such a form [22, 23].

One way to determine the $\eta_{ik}$ coefficients is the recently proposed linearized SCF (LSCF) method [19], which gives the most important part of the delocalization corrections corresponding to the through space interactions (TSI) [23]. In this procedure the SCF Hartree–Fock–Roothan equations are written in the bonding-antibonding basis of SLMO-*s* and are solved analytically for the unknown small delocalization corrections within a linearized approximation. The linearization means here, that all the terms containing squares or products of tails are dropped from the SCF equations. In this approximation the following formula is obtained for the tails [20]:

$$\eta_{ik} \approx \eta_{ik}^{\text{TSI}} = \frac{\Delta E_{k\to i^*} F^0_{ik^*} + (ii^*|kk^*)F^0_{ki^*}}{(ii^*|kk^*) - \Delta E_{i\to k^*}\Delta E_{k\to i^*}} \tag{3}$$

where $F^0$ is the Fockian constructed on the basis of the SLMO-*s*, $\Delta E_{i\to k}$ is the energy of the $i\to k$ excitation, the two-electron integrals are written in the (11|22) convention.

Another type of the delocalization corrections originates from the through bond interactions (TBI) [23]. This can also be partly taken into account introducing a further term in the tail formula [23]:

$$\eta_{ik} \approx \eta_{ik}^{\text{TSI}} + \eta_{ik}^{\text{TBI}} \tag{4}$$

where

$$\eta_{ik}^{\text{TBI}} = \frac{\sum_j F^0_{ij}\eta^{\text{TSI}}_{jk} - \sum_j F^0_{j^*k^*}\eta^{\text{TSI}}_{ij}}{\Delta E_{i\to k^*}} \tag{5}$$

The formulas (3–5) may turn out to be useful for the systematic investigation of the different types of the delocalization corrections. It should be emphasized that the terminology of the "through space" and "through bond" interactions was used in a somewhat different manner in a recent paper of Imamura and Hirao [17]. In the present article we prefer the formulation developed very recently by Surján et al. [23], where the concept of TSI and TBI is directly connected to the nature of the electron delocalization. The general characteristics of tails (3) is that they give almost exactly the *first-neighbour* delocalization corrections, while the tails (5) account for the *second-neighbour* delocalization interactions. The long range tails arise due to through-many-bond effects [23] and they are neglected throughout this work.

To avoid difficulties arising from the nonorthogonality of the approximate LMO-*s* obtained in the above schemes, we subject the LMO-*s* to an orthonormalization procedure. The Löwdin orthogonalization is chosen, because its maximum resemblance property preserves the localized character of the molecular orbitals to an optimal extent. Having orthonormal LMO-*s* the expectation values and the matrix elements of the operators can be computed in the usual way. This feature of the present method has considerable advantages with respect to the perturbative approaches such as PCILO [24] where the calculation of these quantities is not always straightforward.

After discussing the actual form of the approximate *a priori* localized molecular orbitals, let us turn to the problem of representing the excited state wave function. It is well-known that the SCF canonical MO-*s* have a privileged role in the description of excited states. Using canonical orbitals a simple single transition approximation:

$$|k\rangle \approx \frac{1}{\sqrt{2}}(\overset{+}{a}_{j^*\alpha}\overset{-}{a}_{i\alpha} + \overset{+}{a}_{j^*\beta}\overset{-}{a}_{i\beta})|\Phi_0\rangle = \Phi_{i\to j^*} \tag{6}$$

(here $\overset{+}{a}_{j^*\alpha}$ and $\overset{-}{a}_{i\alpha}$ are the creation and annihilation operators respectively, $\Phi_0$ is the ground state determinant of doubly occupied spin orbitals) usually preserves the symmetry properties of the excited state, which remains eigenfunction of the molecular symmetry operators. On the other hand, using localized orbitals an excited state wave function of the form (6) is no more eigenfunction of the symmetry operators, consequently the single transition approximation may lead to serious errors.

A more sophisticated method, which overcomes the above difficulty, involves a CI treatment of the singly excited determinants. The exact SCF orbitals have the important property, that as a consequence of the Brillouin theorem, the singly excited configurations constructed from them do not interact with the ground state. Thus the ground state remains the single determinant $\Phi_0$ after an "all single" CI and the matrix elements of any one electron operator $\hat{A} = \sum \hat{a}_i$ can be calculated as:

$$\langle 0|\hat{A}|k\rangle \approx \sum_{i\to j^*} C^k_{i\to j^*}\langle\Phi_0|\hat{A}|\Phi_{i\to j^*}\rangle = \sum_{i\to j^*}\frac{1}{\sqrt{2}}C^k_{i\to j^*}\langle\varphi_i|\hat{a}|\varphi_{j^*}\rangle \tag{7}$$

where $C^k_{i\to j^*}$ are the CI expansion coefficients, $\varphi_i$ and $\varphi_j$ are the occupied and virtual molecular orbitals, respectively. As it is known, orbitals spanning exactly the occupied and virtual subspaces lead to identical results at the all single CI level (Tamm–Dankoff approximation, TDA), irrespectively from the actual – canonical or localized – nature of the orbitals.

The localized orbitals proposed in the present work, even with delocalization corrections (tails), are of approximate nature, so the Brillouin theorem is violated. A ground state determinant, constructed from SLMO-s, interacts rather strongly with the corresponding singly excited determinants, so a "first order description" [3] of the excited states have to be handled with some care. However, the consideration of the tail corrections may amend this situation. The TSI tail corrections are obtained in the LSCF framework in such a way, that the local Brillouin theorem

$$\langle \psi_i | \hat{F} | \psi_{j^*} \rangle = 0$$

be satisfied up to the first order. As this theorem is the condition of the selfconsistency, and is equivalent to the usual Brillouin theorem [25–27]

$$\langle \Phi_{i \to j^*} | \hat{H} | \Phi_0 \rangle = 0,$$

the present wave function satisfies the Brillouin theorem to the first order. The introduction of higher order tail corrections (e.g. TBI) leads to further improvement in this respect. In the light of the above argument it seems reasonable to neglect the matrix elements of the Hamiltonian between the ground state and the singly excited determinants, since their contribution is only a higher order effect.

Finally, let us emphasise that our approach to construct the excited states differs significantly also from the more refined methods of Langlet and her coworkers [3–5]. These authors performed a (perturbative) CI in the basis of the SLMO-*s* according to the philosophy of the PCILO method, so both electron and exciton delocalization effects are considered within the same CI procedure. Our method accounts for these effects in two separate steps. The electron delocalization is accounted for by the appropriate tail corrections added to the occupied and virtual SLMO-*s*, while the role of the CI performed in the basis of these corrected LMO-*s* is to consider the exciton delocalization in the excited states.

## 3. Results

The calculations presented in this section were done at the CNDO/2 level of approximation. The results obtained by using four types of molecular orbitals will be discussed, namely:

(1) strictly localized molecular orbitals (SLMO-*s*);
(2) tail corrections to the SLMO-*s* are calculated within the LSCF scheme (Eq. (3)), when only TSI is accounted for;
(3) tails originating from TBI (Eq. (5)) are also considered in addition to the TSI ones;
(4) canonical molecular orbitals obtained from a full SCF calculation.

As it was mentioned in the previous section, the ground state wave function was represented as a single determinant and the excited states were approximated at the all single CI level.

### *3.1. Excitation Energies in Small Molecules*

Table 1 summarizes the excitation energies obtained with the approximations (1) to (4) for water and formaldehyde. The wave function built up from SLMO-*s* already gives excitation energies in a rather fair agreement with the full SCF

**Table 1.** Excitation energies (eV) of water and formaldehyde calculated with different approximations

| | SLMO | TSI | TSI+TBI | SCF |
|---|---|---|---|---|
| $H_2O$ | 9.51 | 9.53 | 9.61 | 9.57 |
| | 10.01 | 10.01 | 10.07 | 10.07 |
| | 12.70 | 12.72 | 12.77 | 12.79 |
| | 12.94 | 12.94 | 13.03 | 13.00 |
| | 17.30 | 17.33 | 17.33 | 17.33 |
| $H_2CO$ | 3.58 | 4.10 | 4.40 | 4.46 |
| | 9.01 | 9.01 | 9.28 | 9.16 |
| | 10.44 | 11.33 | 11.65 | 11.10 |
| | 11.92 | 11.61 | 11.75 | 11.37 |
| | 12.16 | 12.45 | 12.93 | 13.10 |
| | 13.06 | 14.02 | 14.47 | 14.12 |
| | 14.32 | 14.15 | 14.67 | 14.27 |

results, however the tail corrections arising from TSI and TBI provide for a considerable improvement in the results. In the case of these small molecules the considered tail corrections account for almost the whole delocalization effect, since there are no long range interactions.

### *3.2. Excitation Energies in Glyoxal*

The excitation energies obtained with different approximations for the six lowest-lying transitions of the trans planar glyoxal are summarized in Table 2. The first two transitions are of $n \rightarrow \pi^*$ type in accordance with the experiments. The CNDO/2 parametrization fails to describe properly the ordering of the further transitions: we found two $\sigma \rightarrow \pi^*$ type transitions before the $\pi \rightarrow \pi^*$ ones. A general observation is that the stepwise improvement of the wave function by considering the delocalization corrections (see approximations (1) to (3)), brings the transition energies closer to the full SCF results.

Fig. 1 depicts the excitation energies of the lowest lying and of the next to the lowest lying transitions as the function of the twist angle $\vartheta$ (for definition of $\vartheta$ see Fig. 2), calculated by the two type of tail corrected and by the full SCF wave functions. The planar *trans* and *cis* conformations belong to the $C_{2h}$ and $C_{2v}$

**Table 2.** Excitation energies (eV) in planar *trans* glyoxal ($\vartheta = 0°$)

| Transition | SLMO | TSI | TSI+TBI | SCF |
|---|---|---|---|---|
| $A_u$ | 2.44 | 2.65 | 2.77 | 2.77 |
| $B_g$ | 2.97 | 3.44 | 3.64 | 3.84 |
| $A_u$ | 7.22 | 6.96 | 7.03 | 6.65 |
| $B_g$ | 7.06 | 7.78 | 7.75 | 7.42 |
| $B_u$ | 7.81 | 8.11 | 8.33 | 8.22 |
| $A_g$ | 9.88 | 10.17 | 10.20 | 9.86 |

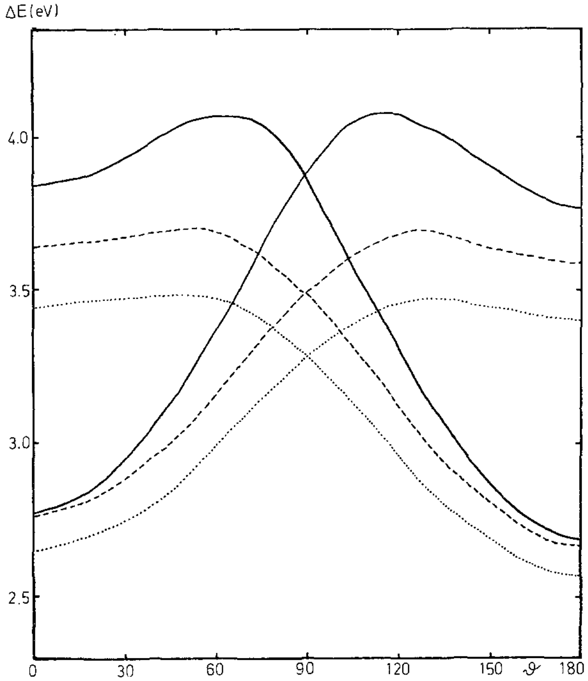

**Fig. 1.** Transition energies of the first two $n \to \pi^*$ excitations in glyoxal as a function of the twist angle $\vartheta$, calculated by different approximations: full SCF (———), TSI+TBI (- - - - -), TSI (· · · ·)

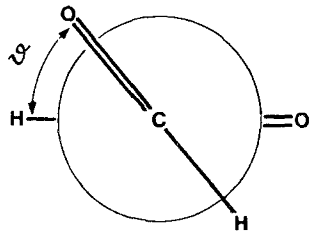

**Fig. 2.** Definition of the twist angle $\vartheta$. The chirality (helicity) of the glyoxal is positive in the figure

point groups respectively, while the nonplanar conformations are of $C_2$ symmetry. The excited states can be classified according to the irreducible representations of these point groups. In agreement with previous studies on this system [28, 29], we found that at transoid conformations the transition of symmetry $A$ (symmetric with respect to the $C_2$ axis) lies at the lowest energy, while at cisoid conformations the transition of symmetry $B$ (anti-symmetric with respect to the $C_2$ axis) is the lowest lying. A crossing is found at about $\vartheta = 90$ degrees. These overall qualitative features of the curves are correctly reproduced by all the approximations, including the SLMO method which is not presented in the Fig. 1.

As to the quantitative agreement, the SLMO method strongly underestimates the splitting between the two $n \to \pi^*$ transitions in the whole twist angle region.

The results obtained with the tail corrected wave functions run nearly parallel to the full SCF results, although the splitting is underestimated here also. The introduction of the tail corrections due to TBI leads to a further significant improvement of the excitation energies: half of the error relative to the simple tails (3) from TSI is accounted for. Practically quantitative agreement was found between the TBI and the full SCF results in the two nearly planar conformation regions.

### *3.3. Rotational Strengths of the Twisted Glyoxal*

The chiroptical properties of the optically active vicinal diketo compounds can be interpreted in terms of the inherently chiral $\alpha$-dicarbonyl chromophore. The twisted glyoxal molecule, the simplest model for this chromophoric system, was studied previously by Hug and Wagnière [28, 29] using semiempirical quantum chemical methods. In the localized picture adopted here the $\alpha$-diketo system can be considered as a dimer of two carbonyl moieties interacting *via* the carbon-carbon bond. This interaction is rather strong because of the proximity of the carbonyl groups, so this molecule may be a stringent test to the reliability of the approximate scheme proposed here.

The geometrical parameters of the glyoxal molecule were taken from [28], in all the calculations reported the helicity of the glyoxal was held positive, according to the definition of Hug and Wagnière [30] (see Fig. 2).

The rotational strengths of the first two $n \to \pi^*$ transitions of $A$ and $B$ symmetry are depicted in Figures 3a and 3b respectively, as a function of the twist angle $\vartheta$. Only results obtained with the full SCF and the tail corrected methods are presented; the SLMO rotational strengths are completely erroneous compared to the full SCF ones. Our full SCF rotational strengths do not obey to the well-known $C_2$ rule [30] (for positive chirality positive rotational strength for a $B$ transition, negative one for an $A$ transition): we get the predicted sign only in a small range of the twist angle ($155° < \vartheta < 180°$). However it is interesting to note that our results are probably not in disagreement with experimental findings, since in most of the $\alpha$-diketo compounds reported by Hug and Wagnière [29] as examples for the rule, the twist angle is in the $160° < \vartheta < 170°$ range.

Rather good agreement is found between the TSI and the full SCF results for the $A$ transition; the consideration of the TBI tail corrections leads to a nearly quantitative agreement. The situation for the $B$ transition is somewhat different: the TSI tail corrected LMO-*s* fail to reproduce the full SCF results, even the sign of the rotational strength is incorrect practically in the whole twist angle region. The introduction of the TBI tails leads to a significant improvement, as the correct sign of the rotational strength is retrieved in the nearly planar conformations and the overall shape of the curve is better approximated.

An analysis of the transition moment components based on the localized molecular orbitals may give some insight into the fine details of the optical rotatory strength of the transitions. In the localized basis we may divide the

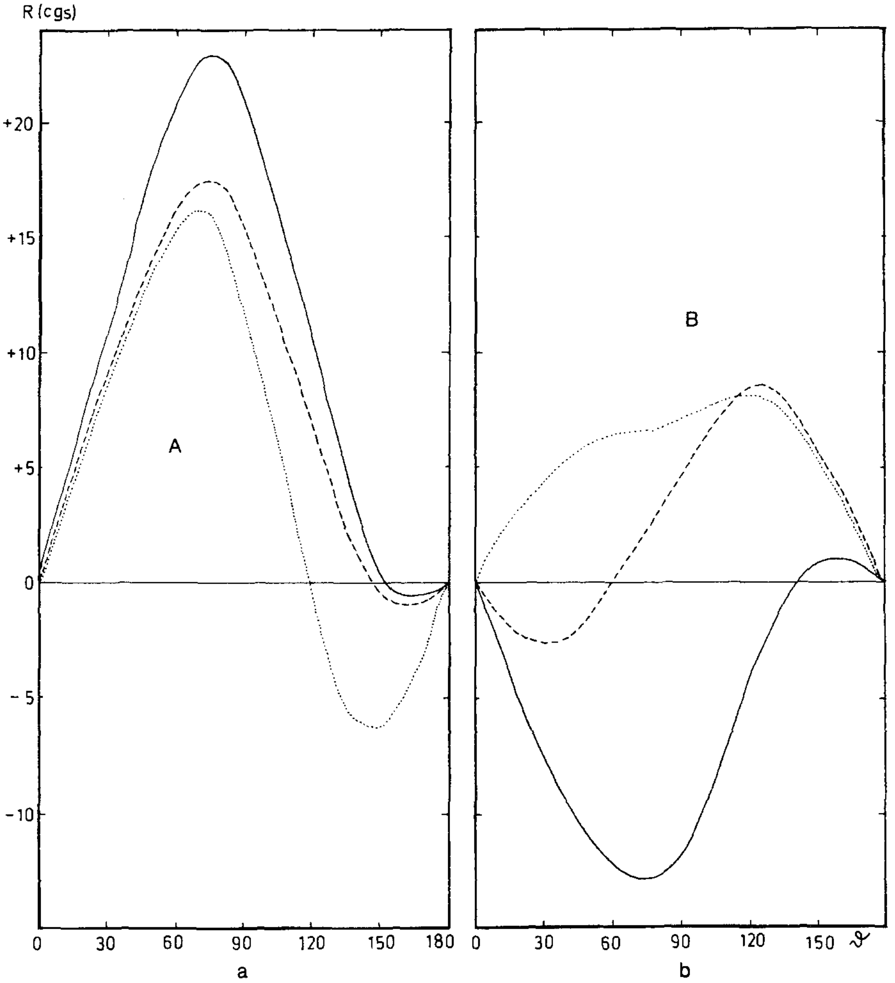

**Fig. 3.** Rotational strengths of the first two $n-\pi^*$ transitions in glyoxal as a function of the twist angle $\vartheta$. For designations see Fig. 1. (*a*) transition of symmetry *A*. (*b*) transition of symmetry *B*

singly excited configurations into two groups. One group contains configurations arising from excitation from a bonding or nonbonding orbital to an antibonding one, both localized on the same chromophore: this can be called a localized excitation. The other type of configurations comes from excitations from a bonding or nonbonding orbital to an antibonding one on another chromophore: this is an interchromophoric charge transfer configuration. We can expect that the latter type of configurations are not as well described as the locally excited ones, so the errors inherent in the method accumulate when the charge transfer configurations dominate.

The above idea is fairly supported by our findings, namely that the rotational strength of the *A* transition is well reproduced by the approximate localized orbital scheme, while the agreement is rather poor for the $B$ transition. It follows from symmetry considerations that the transition moment components in the plane perpendicular to the $C_2$ axis – and so in the plane containing the interchromophoric bond – are forbidden. This selection rule is realized in the localized picture in such a way that the transition moment components arising from the $1 \rightarrow 2$ charge transfer are completely annihilated by the contributions coming from the corresponding $2 \rightarrow 1$ charge transfer configurations. (1 and 2 are the labels of the chromophores here.) Consequently the "delicate" charge transfer configurations do not play any role in the final transition moments of the $A$ excitation.

On the other hand, in the case of the $B$ excitations the transition moment components lying in the interchromophoric axis are permitted. The origin of the

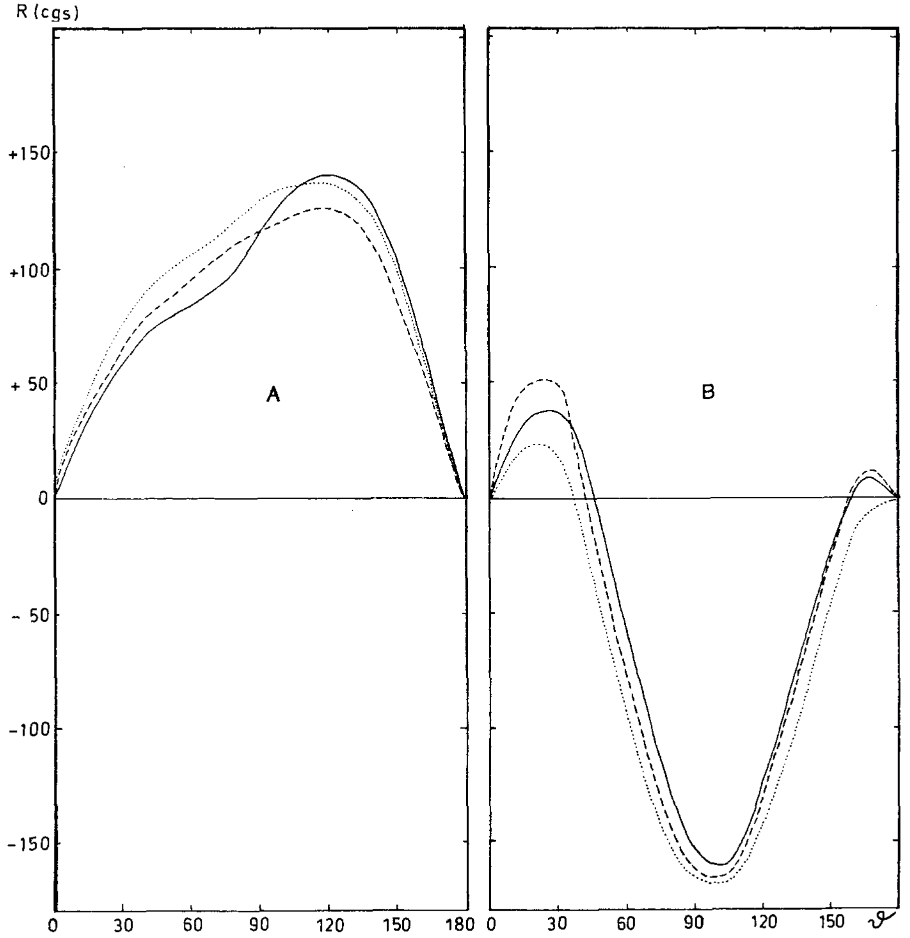

**Fig. 4.** Rotational strengths of the third and fourth transitions in glyoxal. For designations see Fig. 1. (*a*) transition of symmetry $A$. (*b*) transition of symmetry $B$

most important transition moment contributions in this direction are the interchromophoric charge transfer configurations. Since these configurations are poorly described due to the approximate nature of the long range delocalization corrections, errors can be expected. Really, the calculations using only the TSI tail corrections are erroneous, but significant improvement is found, when the description of the long range corrections is improved *via* the consideration of the through-one-bond interactions (TBI).

The rotational strengths of the third and fourth transitions lying at about 7.0–7.7 eV, are depicted in Figure 4. Good agreement is found for both *A* and *B* transitions with the TSI and with the TSI+TBI corrected wave functions. We can suppose that the role of the charge transfer configurations in this second *B* transition is not so important as in the first one, since the TSI method alone gives satisfactory agreement with the full SCF results.

## 4. Conclusions

Using the SLMO-*s* we have a qualitatively correct description of the excitation energies, but this method is completely inapplicable to the investigation of the fine details of the conformation dependence of the excitation energies and for the description of the very sensitive quantity, the rotational strength. The consideration of the delocalization corrections has proved to be of crucial importance to calculate the latter quantities. The method proposed here, involving the simultaneous evaluation of the through space and through bond delocalization corrections, can be useful for the calculation of the rotational strength in large systems, if the role of the long range electron delocalization is only of minor importance.

Another possible advantage of the present scheme is that it can serve as a natural way to truncate the CI expansion of the excited state wave function. Pairs of LMO-*s*, localized in far regions of the space, are expected to have small contributions to the corresponding CI matrix elements. Thus one can perform a much more effective CI calculation for the excited states of large molecules. Work on this line is in progress.

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