

Role of the Configuration Interaction in the CNDO/S Calculation of Optical Rotatory Strengths

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The rotatory strengths calculated directly by the CNDO/S method exhibit a pronounced dependence on the size of configuration interaction (CI). In order to elucidate the role of highly excited configurations in such calculations the perturbation theory is employed. It is shown that the restriction of the CI size to 20–40 may be quite inadequate in some cases. The calculations of rotatory strengths of several optically active molecules containing carbonyl and amide chromophores has shown that the best results can be obtained for half of full CI but sometimes it is possible to restrict the CI size to 100 configurations. The agreement with experiment for all molecules considered is satisfactory.

Key words: Optical rotatory strengths – Amide chromophores – Carbonyl chromophores

1. Introduction

Semi-empirical quantum chemical methods (CNDO, INDO, EHT etc.) make it possible to calculate the rotational strengths (R_i) of molecules directly from molecular orbital wave functions. Such calculations (see, e.g., Refs. [1–10]), in some cases, give quite satisfactory results. INDO and CNDO/S methods seem very promising in this respect. In particular Richardson and his colleagues have successfully applied the INDO method to the problem of optical activity of different cyclic compounds [6–8].

For obtaining, in CNDO/S and INDO, approximations of satisfactory quantitative description of different features of electronic spectra it is necessary to take into account the configuration interaction (CI) of some singly excited configurations. When calculating energy, oscillator strength and polarization of electronic transitions the CI may be restricted to a limited number of low-energy states (usually from 15 to 50 configurations). In these cases the enlargement of the CI size does not appreciably affect the calculated values. However, the calculated rotatory strengths critically depend on the CI size. According to Richardson and Pitts [8], in the case of methyl-substituted diketopiperazines the enlargement of the CI basis may even lead to a change of sign

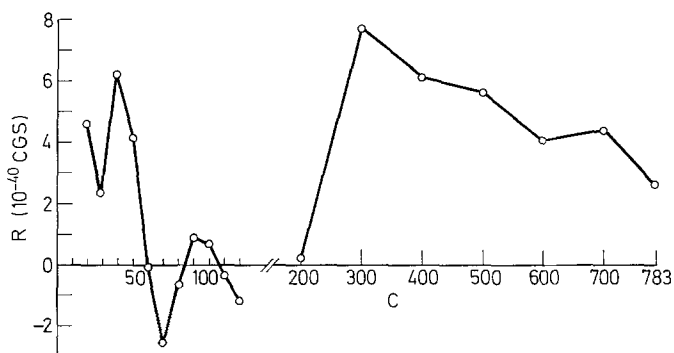


Fig. 1. The dependence of the calculated rotatory strength of $n \rightarrow \pi^*$ transition of $H_7-H_8-H_{13}$ -trimethyl-substituted cyclohexanone on the number of configurations included in CI

of the calculated rotatory strengths of some low-energy transitions. Rudolph and Wagnière have also stressed [9] the influence of the CI size on the magnitude of calculated rotatory strengths.

Our calculations of the rotatory strength of $n \rightarrow \pi^*$ transition in trimethylcyclohexanone carried out by the method reported previously [10] give a striking example of the role of CI. As follows from Fig. 1, not only the magnitude but also the sign of the rotatory strength depends on the number of configurations included. The rotatory strength does not exhibit an asymptotic behaviour when the CI size approaches 120 and its sign is opposite to the experimental one. Recently Bouman and Lightner [10a] also discovered the oscillatory behaviour of $R_{n\pi^*}$ in carbonyl-containing compounds when the CI size increased.

It is evident that for a successful application of semi-empirical methods for the calculation of R_i it is necessary to determine what number of singly excited configurations must be included into CI for obtaining the most reliable results. In this paper we investigate how the magnitude of R_i changes when the CI size increases from a few tens up to the full CI of all singly excited configurations. The results obtained allow us to suggest a simple procedure for the semi-empirical calculation of rotatory strengths.

It is well known that serious difficulties arise when a large number of configurations is included into CI. The direct diagonalization of the CI matrix becomes very complicated and the computer time necessary for the calculation of all elements of such matrices may significantly surpass the time spent on iterative self-consistent procedures. For these reasons we employed the following approach. As only the rotatory strengths of several low-energy transitions are of practical interest we at first diagonalized the CI matrix of a restricted number of low-energy configurations and then estimated the contribution of high-energy configurations to the rotatory strengths of interest by perturbation theory (PT) technique. The validity of such an approach is demonstrated for a model molecule where the direct diagonalization of the full singly excited CI matrix may easily be carried out.

The procedure described is then applied for the calculation of rotatory strengths of some optically active molecules containing carbonyl and amide chromophores.

2. Method of Calculation

When the CI size becomes large the Rayleigh–Schrödinger perturbation theory is often applied. In the case of the correlation correction to the ground state the CI problem may be completely reduced to PT calculations [11]. But this is not so in our case as denominators in the Rayleigh–Schrödinger series for excited state functions may be of the same order as the CI matrix element. Therefore we build the excited state function as follows.

The ground-state wave function φ_0 is a Slater determinant. Singlet excited state wave functions φ_i are constructed from the ground-state configuration φ_0 by replacing one of the occupied spin orbitals by a virtual spin orbital. As usual φ_i is an appropriate combination of two determinants.

The functions φ_i form the basis of the CI calculation which is carried out in two steps. Firstly, the lowest energy basis functions φ_s ($1 \leq s \leq d$) are used to build the CI matrix of order d . The diagonalization of this CI matrix allows us to obtain functions ψ_i^d ($i \leq d$):

$$\psi_i^d = \sum_{s=1}^d \mathcal{A}_{is} \varphi_s. \quad (1)$$

Those functions ψ_i^d which correspond to the transitions of interest are then expanded into the Rayleigh–Schrödinger series with functions φ_t not included in the CI matrix ($t > d$):

$$\psi_i^{c,d} = \psi_i^d + \sum_{t=d+1}^c \frac{\langle \psi_i^d | H' | \varphi_t \rangle}{E_i^d - E_t} \varphi_t, \quad (2)$$

where c is the overall number of excited functions included in $\psi_i^{c,d}$ ($c > d$).

Taking (1) into account we obtain

$$\psi_i^{c,d} = \sum_{s=1}^d \mathcal{A}_{is} \left(\varphi_s + \sum_{t=d+1}^c \frac{\langle \varphi_s | H' | \varphi_t \rangle}{E_i^d - E_t} \varphi_t \right). \quad (3)$$

As usually practised in similar cases (see, for example, [12]), to make the connection with CI we equate matrix elements $\langle \varphi_s | H' | \varphi_t \rangle$ in (3) with matrix elements $\langle \varphi_s | H | \varphi_t \rangle$ of the CI matrix. The accuracy of the function $\psi_i^{c,d}$, i.e., its closeness to the corresponding wave function calculated by diagonalization of the CI matrix of order c , depends mainly on the relation between $\langle \varphi_s | H | \varphi_t \rangle$ and $E_i^d - E_t$, and sufficiently accurate wave functions $\psi_i^{c,d}$ may be obtained only if $i \leq d$. For systems considered in this paper we calculated the rotatory strengths for a few of the lowest energy transitions ($i < 10$) and satisfactory results are secured for d of the order of a few tens.

Trial calculations have shown that the calculated rotatory strengths are substantially affected by those functions φ_s which have comparatively small coefficient \mathcal{A}_{is} in the expansion (1) for ψ_i^d and it is necessary when calculating $\psi_i^{c,d}$ according to (3), to keep all φ_s with $|\mathcal{A}_{is}| > 0.001$.

For the calculation of the rotatory strength of $0 \rightarrow i$ transition we used the expression

$$R_i = \frac{e\hbar}{m\Delta E_i} \langle \psi_0 | \hat{p} | \psi_i \rangle \langle \psi_i | \hat{m} | \psi_0 \rangle \quad (4)$$

where ΔE is the transition energy, \hat{p} and \hat{m} are linear momentum and magnetic dipole operators respectively. The use of expression (4) in a dipole velocity form insures origin independence of the results. In further discussions R_i^d and $R_i^{c,d}$ would designate the rotatory strengths calculated respectively with functions ψ_i^d and $\psi_i^{c,d}$.

To obtain ψ_0 and ψ_i we used the CNDO/S variant of the CNDO/2 method [13]. A substantial part of the calculations is the evaluation of the matrix elements of \hat{p} and \hat{m} over atomic orbitals. In particular we applied Linderberg's equation [14]

$$i\hbar \langle \chi_{\mu A} | \hat{p} | \chi_{\nu B} \rangle = (\vec{R}_A - \vec{R}_B) \beta_{\mu A \nu B} \quad (5)$$

where $\chi_{\mu A}$ is μ th orbital of an atom A, $\beta_{\mu A \nu B}$ is the resonance integral, \vec{R}_A is a position vector of atom A. Explicit expressions for matrix elements over atomic orbitals are given in our earlier paper [10].

3. Model Molecule

The optically active molecules are complex compounds and the order of the full CI matrix, even in the simplest cases, is of several hundreds. For this reason, for illustrative purposes we investigated the model molecule with carbonyl chromophore (HCOC_2H_5) in conformation in Fig. 2. For this molecule the maximum number of singly excited wave functions is 120 and the comparison between CI matrix calculations and the PT approach is easily carried out.

Let us compare the rotatory strengths $R_i^{c,d}$ calculated through PT with R_i^c obtained by the usual CI matrix procedure. Series of calculations performed for $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $n \rightarrow \sigma'^*$ and $\pi \rightarrow \pi^*$ transitions of the model molecule gave encouraging results. Typical values are given in Table 1. The interaction of the 50 lowest basis functions ϕ_s was considered by the matrix method (i.e., $d = 50$ in Eq. (1)) and then the excited wave functions of interest were obtained by Equation (3) for $c = 60, 80, 100$ and 120. The transitions $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ were considered as one transition since their energies are close to each other. The values of $R_i^{c,50}$ are close enough to R_i^c . As follows from the data of Table 2, which contains values of $R_i^{120,d}$ for different d , the calculation of excited

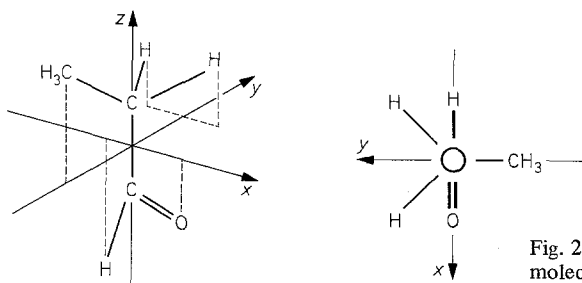


Fig. 2. The absolute configuration of model molecule

Table 1. Rotational strength (in 10^{-40} cgs) of the model molecule obtained by the CI matrix and by PT procedures^a

Number of Configurations (c)	$R_{n\pi}^c$	$R_{n\pi}^{c,50}$	$R_{\pi\pi}^c + R_{n\sigma}^c$	$R_{\pi\pi}^{c,50} + R_{n\sigma}^{c,50}$	$R_{n\sigma'}^c$	$R_{n\sigma'}^{c,50}$
0	-34.7		+3.6		-22.5	
20	+2.8		-6.4		+53.0	
40	-2.3		-35.1		+36.3	
60	-6.9	-6.3	-29.4	-31.5	+34.2	+34.3
80	-3.4	-3.2	-26.9	-27.6	+33.5	+31.6
100	-2.7	-2.4	-18.6	-23.3	+28.6	+28.9
120	-1.3	-1.2	-7.6	-10.9	+22.9	+23.2
Energy of transition (eV) calculated for $c = 40$	3.49		8.67 ($\pi \rightarrow \pi^*$) 8.76 ($n \rightarrow \sigma^*$)		9.34	

^a For notation and definition of R^c and $R^{c,50}$ see text.

state functions through the PT is sufficiently reliable for $d \geq 40$. For $d = 40$ the minimal value of $E_i^d - E_t$ [see Eq. (4)] for the transitions considered is 5.9 eV.

An analysis of rotatory strengths R_i^c and $R_i^{c,50}$ (Table 1), calculated for different values of c , shows that the inclusion of highly excited configurations ($c > 60$) substantially diminishes the absolute values of R_i^c and $R_i^{c,50}$. This fact probably reflects the inadequacy of semi-empirical wave functions for the description of high-energy transitions. This was also noted by Rauk *et al.* [15]. Therefore we consider it reasonable to include into CI only two groups of transitions:

- 1) Transitions between two such orbitals, i and j , where either i or j belongs to the orbitals taking part in the transitions for which the rotatory strengths are to be calculated.
- 2) All those transitions which have energies that are less than the highest transition energy of the first group.

Table 2. Rotational strengths (in 10^{-40} cgs) of the model molecule calculated by PT for full CI and different d

Number of Configurations (d)	$R_{n\pi}^{120,d}$	$R_{\pi\pi}^{120,d} + R_{n\sigma}^{120,d}$	$R_{n\sigma'}^{120,d}$
20	-1.9	-50.4	+56.9
40	-1.1	-10.3	+25.2
60	-1.5	-9.7	+23.3
80	-1.3	-11.0	+25.5
100	-1.3	-8.1	+24.0
R^{120}	-1.3	-7.6	+22.9

These two groups of transitions form approximately half of all singly excited transitions. As will be shown in the following sections, the agreement between experimental R_f and $R_f^c,^d$, calculated with a CI of half of all the singly excited configurations, is usually satisfactory.

In conclusion, it may be noted that the dependence of R_f^c on the size of CI is not the same for different transitions. For values of c from 40 to 80 the rotatory strengths $R_{\pi\pi}^c + R_{n\sigma}^c$ and $R_{n\sigma'}^c$ vary less than $R_{n\pi}^c$.

4. Methyl-Substituted Cyclohexanones

As noted the rotatory strengths of methyl-substituted cyclohexanones depend appreciably on the number of configurations in CI. We calculated the rotatory strengths of two such molecules: H₇-H₈-H₁₃-trimethyl-substituted and H₇-H₁₃-dimethyl-substituted cyclohexanones for different CI sizes. The structures of these molecules are represented in Fig. 3. If the CI size was less than 100 then direct diagonalization was carried out; otherwise only the first hundred configurations were considered by the matrix method and then PT was applied. The coordinates of the cyclohexanones considered were taken from [1].

The experimental value of the rotatory strength of $n \rightarrow \pi^*$ transition of trimethylcyclohexanone is $+6.7 \times 10^{-40}$ cgs [16]. The dependence of the calculated rotatory strength of this transition on the number of excited state functions (c) is given in Fig. 1. For values of c less than 200 the calculated rotatory strength $R_{n\pi^*}$ exhibits an obvious oscillatory behaviour; with further increase of c the calculated $R_{n\pi^*}$ reaches a stable positive value close to an experimental one. When the number of excited state functions taken into account becomes more than 500 the calculated $R_{n\pi^*}$ gradually diminishes but its sign remains positive. Here, as in the case of the model molecule, the poor quality of the functions for highly excited configurations is probably responsible for the noticeable decrease of the calculated $R_{n\pi^*}$. It may be noted that the calculation with half of the excited state functions ($c \sim 400$), as was recommended in the previous section, gives for $R_{n\pi^*}$ of trimethylcyclohexanone a value close to the experimental one.

A comparison of the rotatory strength of $n \rightarrow \pi^*$ transition of H₇-H₁₃-dimethyl-substituted cyclohexanone, calculated for different c with the sum of $R_{n\pi^*}$ of H₇- and H₁₃-monomethyl-substituted cyclohexanones obtained for an appropriate CI, shows an additivity of the contributions of separate asymmetrical centres to rotatory strength

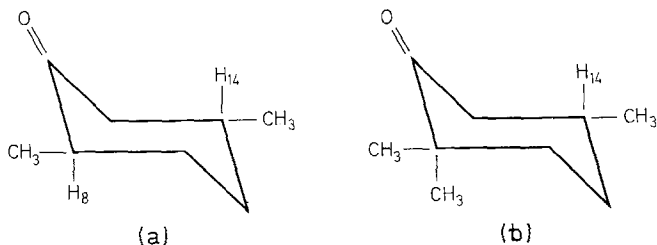


Fig. 3. The absolute configurations of H₇-H₁₃-dimethyl-substituted cyclohexanone (a) and H₇-H₈-H₁₃-trimethyl-substituted cyclohexanone (b)

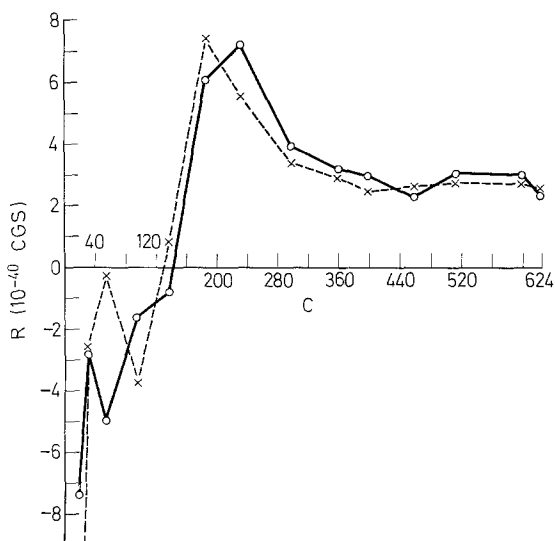


Fig. 4. The dependence of the calculated rotatory strength of $n \rightarrow \pi^*$ transition of H_7 - H_{13} -dimethyl-substituted cyclohexanone (—○—○—○) on the number of configurations included in CI. The sum of calculated rotatory strengths of $n \rightarrow \pi^*$ transition of H_7 - and H_{13} -monomethyl-substituted cyclohexanones is designated as (x--x--x)

(Fig. 4). The number of configurations in CI for monomethylcyclohexanones, in order to conform with the CI for dimethylcyclohexanones, were chosen in such a way that the energies of the highest excited states included for all the three molecules were the same. The calculation has shown that $R_{n\pi^*}$ of dimethylcyclohexanone becomes positive only for $c > 150$ and only when slightly more than half of all singly excited functions had been taken into account (~ 300 - 350) does the value of $R_{n\pi^*}$ become more or less close to the experimental value, $+1.8 \times 10^{-40}$ cgs (as reported in [16]).

We now discuss the rotatory strengths of transitions other than $n \rightarrow \pi^*$ transition. The calculated rotatory strengths of $\sigma \rightarrow \pi^*$, $\sigma' \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of dimethyl- and trimethylcyclohexanones are given in Table 3. For transitions $\sigma' \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ only the sum of their rotatory strengths is given because of the closeness of energies of these transitions. The values of $R_{\sigma\pi^*}$ of both molecules do not change significantly after c reaches 100. But the sums $R_{\sigma'\pi^*} + R_{\pi\pi^*}$ exhibit a more pronounced dependence on c . Unfortunately for these transitions the experimental data are not available.

5. L-Pyrrolid-2-One-5-Carboxamide

Until now we have considered molecules containing a carbonyl chromophore. In this section we give the results of the calculation of rotatory strengths of L-pyrrolid-2-one-5-carboxamide (Fig. 5), which is a cyclic dipeptide containing two amide chromophores. As for the di- and trimethylcyclohexanones the first one hundred excited state functions were considered by the matrix method and then PT was applied. The geometry and the conformation of the molecule were taken from [17]. The rotatory strengths of the two

Table 3. The calculated rotatory strengths of $\sigma \rightarrow \pi^*$, $\sigma' \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of dimethyl- and trimethylcyclohexanones^a

Number of Configurations (<i>c</i>)	H ₇ -H ₁₃ -Methyl-Substituted Cyclohexanone		H ₇ -H ₈ -H ₁₃ -Methyl-Substituted Cyclohexanone	
	$R_{\sigma\pi^*}$	$R_{\sigma'\pi^*} + R_{\pi\pi^*}$	$R_{\sigma\pi^*}$	$R_{\sigma'\pi^*} + R_{\pi\pi^*}$
0	-14.9	+4.8	-12.1	+5.5
20	-5.5	-12.1	-19.3	-2.7
40	-3.2	-16.3	-16.0	-17.1
60	-9.1	-7.5	-9.2	-9.2
100	-1.1	-1.0	-5.6	-22.8
200	-3.9	-4.5	-2.4	-20.1
300	-1.4	+2.4	-4.1	-23.2
400	-3.9	+0.9	-5.5	-27.1
500	-2.4	+5.9	-6.3	-35.4
600	-3.6	+6.6	-6.0	-37.9
624	-2.5	+8.2	-	-
700	-	-	-5.6	-39.1
783	-	-	-5.1	-43.6
Energy of transition (eV) calculated for <i>c</i> = 40	8.58	8.88 ($\sigma' \rightarrow \pi^*$) 9.04 ($\pi \rightarrow \pi^*$)	8.51	8.79 ($\sigma' \rightarrow \pi^*$) 8.93 ($\pi \rightarrow \pi^*$)

^a For $c \leq 100$ the rotational strengths were calculated by the CI matrix method, for $c > 100$, R^c ,¹⁰⁰ are cited.

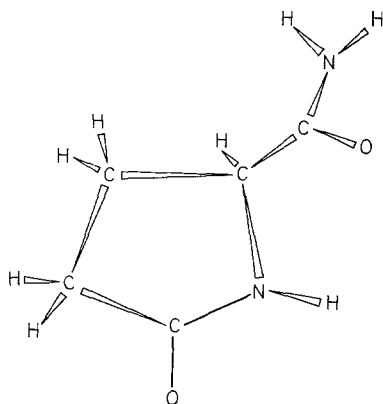


Fig. 5. The absolute configuration of L-pyrrolid-2-one-5-carboxamide

Table 4. Rotatory strengths (in 10^{-40} cgs) of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of L-pyrrolid-2-one-5-carboxamide calculated for different number of configurations in CI^a

Number of Configurations (c)	$R_{n\pi^*}$	$R_{\pi\pi^*}$	$R_{\pi\pi'^*}$	
0	+71.3	+35.8	-49.1	
40	+9.2	+5.2	-7.7	
100	+4.6	+7.7	-11.5	
200	+4.4	+15.2	-18.2	
300	+3.7	+11.2	-15.0	
400	+3.2	+10.9	-13.7	
475	+1.7	+10.1	-4.7	
Energy of transition (eV) calculated for $c = 40$	4.16	7.12	7.63	^a For $c \leq 100$ the rotational strengths were calculated by the CI matrix method, for $c > 100$ $R^{c,100}$ are cited.

$n \rightarrow \pi^*$ transitions and the two higher $\pi \rightarrow \pi^*$ transitions were calculated for different c (Table 4). As the energies of two $n \rightarrow \pi^*$ transitions are almost the same only the sum of their rotatory strengths is given in Table 4. The main feature of these results is the absence of oscillatory behaviour of the rotatory strengths of all the transitions considered. This fact gives rise to the hope that in some cases for establishment of the sign and order of magnitude of rotatory strengths it would be possible to restrict calculations to a comparatively small CI size. The rotatory strengths change less than two times when c increases from 100 to 200, the latter figure being a little less than half of full CI. The comparison with experiment is possible only for $R_{n\pi^*}$, which according to [17] is equal to $+9.4 \times 10^{-40}$ cgs.

6. Conclusions

The results for the model molecule have shown that dependence of the rotatory strengths of low-energy transitions on the CI size may be studied by the PT technique. The calculated rotatory strengths of optically active molecules considered have exhibited a sig-

nificant dependence on the CI size. In some cases the restriction of the CI size to 20–40 interacting excited state functions is found quite inadequate as the increase of the CI size leads to changes in magnitude and even in sign of the calculated rotatory strengths. It appears that for semi-empirical wave functions the best results are obtained when approximately half of the full CI is taken into account.

The rotatory strength of $n \rightarrow \pi^*$ transition of carbonyl chromophore displays a pronounced oscillatory behaviour when the CI size increases from 20 to 100 and $R_{n\pi^*}^{100}$ for methyl-substituted cyclohexanones is opposite in sign to the $R_{n\pi^*}$ calculated for half of full CI. In other cases R_i^{100} has the same sign as R_i calculated for half of full CI, differing from it in magnitude not more than by a factor of two.

Thus from our results it follows that in semi-empirical calculations of rotatory strengths it is advisable to distinguish two possibilities. If the calculated rotatory strengths oscillate when the CI size varies within a few tens then it is necessary to include into the CI half of all singly excited configurations. Otherwise the CI may be restricted to approximately 100 configurations. However, in the latter case, it is necessary to bear in mind that the calculated R_i may be somewhat different in magnitude (but not in sign!) from R_i for half of full CI. Unfortunately, at this stage, we are not certain of the reason why there are two modes of dependence of the calculated rotatory strengths on the CI size.

In all cases where it was possible to compare R_i calculated by this procedure with experimental ones the agreement in order of magnitude and in sign was satisfactory.

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