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Optical Rotatory Strength Calculation by Evaluating the Gradient Matrix through the Equation of Motion

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A straightforward generalization of Linderberg's equation–of–motion–based formula for the matrix elements of the linear momentum operator is proposed. The essential feature of the modification is the abandonment of the zero differential overlap (ZDO) approximation for the electric transition integrals. It is expected that this new formula gives better transition moments and, consequently, better optical rotatory strength values. The results of this modification are analysed numerically for the rotatory strengths of the twisted hydrogen peroxide and for the 1,6-diazaspiro[4,4]-nonane-2,7-dione, $C_7H_{10}N_2O_2$, molecule, using a CNDO Hamiltonian. For both systems a definitive improvement of calculated rotatory strengths resulted.

Key words: Optical rotatory strength – Linderberg's equation of motion

1. Introduction

The basic characteristics of the optical rotatory dispersion (ORD) and circular dichroism (CD) spectra of molecules are the R_i rotatory strengths belonging to the $0 \to i$ transition of the molecule [1]:

$$R_i^r = -\frac{e^2\hbar}{2mc}\langle 0|\sum_k \hat{r}_k|i\rangle\langle i|\sum_k \hat{r}_k \times \hat{\nabla}_k|0\rangle \tag{1}$$

(dipole length form)

$$R_i^\nabla = -\frac{e^2\hbar^3}{2m^2c\omega_i}\langle 0|\sum_k \hat{\nabla}_k|i\rangle\langle i|\sum_k \hat{r}_k \times \hat{\nabla}_k|0\rangle \tag{2}$$

(dipole velocity form)

where $\omega_i = (E_i - E_0)$[1] the excitation energy, $|i\rangle$ is the ith excited state, $\hat{r}$, $\hat{\nabla}$ are the one-electron position and gradient operators, respectively. The accurate quantum chemical evaluation of R_i is not trivial due to the observed strong dependence on molecular geometry [2], size of the configuration interaction (CI) [3, 4], and on the position and gradient matrix elements over atomic orbitals.

According to the off-diagonal hypervirial theorem [5, 6] the (1) and (2) rotatory strengths are identical if the $|i\rangle$ states are exact eigenstates of the model Hamiltonian and if the $\hat{\nabla}$ and $\hat{r}$ operators fulfil the $\hat{\nabla} = [\hat{r}, \hat{H}]$ Heisenberg equation of motion [7].

An approximate wave function may violate the off-diagonal hypervirial theorem, therefore in this case the R^∇ and R^r values for a transition are not automatically identical. However, both of these formulae have their own significance: the R^∇ rotatory strengths are origin independent [8], and the R^r values fulfil the $\sum_i R_i^r = 0$ sum rule [6, 9, 10]. Hence the equivalence of the dipole velocity and dipole length forms is very important in quantum chemical calculation of R.

The calculation of the rotatory strength consists in the evaluation of the 1) Hartree–Fock linear combination of atomic orbitals (LCAO) and CI coefficients as well as 2) the matrix elements of position, linear and angular momentum operators over atomic orbitals. In this paper we restrict the discussion to the latter question. For this two different procedures have been proposed. The first consists of integration over (e.g. Slater-type) atomic orbitals [11, 12]. The second one is the Linderberg approximation, which was used in connection with the Pariser–Parr–Pople (PPP) [13, 14] and complete neglect of differential overlap (CNDO) [15] models [16, 17]. Within the second scheme the ZDO approximation was applied for $\boldsymbol{r}_{\mu\nu}$:

$$\boldsymbol{r}_{\mu\nu} \equiv \langle\mu|\hat{\boldsymbol{r}}|\nu\rangle \approx \boldsymbol{r}_a \tag{3}$$

μ on atom a; $\boldsymbol{r}_a$ is the position vector of atom a in the molecular frame of reference. The matrix elements of the gradient operator are calculated by the ($4b$) Linderberg equation [17], which can be obtained by substituting Eq. (3) into the equation of motion ($4a$):

$$\hat{\nabla}_{\mu\nu} = [\hat{r}, \hat{H}]_{\mu\nu} \tag{4a}$$

$$\hat{\nabla}_{\mu\nu} = (\boldsymbol{r}_a - \boldsymbol{r}_b)\beta_{\mu\nu} \tag{4b}$$

ν on atom b, the $\beta_{\mu\nu}$'s are the resonance integrals. This formula gives automatically zero gradient matrix elements between orbitals on the same atom. This

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[1] From here in all formulae atomic units are used.

method differs from the first one (analytic integration) also in its results: 1) because it enforces directly the Heisenberg equation of motion for $\hat{\boldsymbol{r}}$; 2) because of the ZDO assumption in Eq. (3). It may be noted that the equation of motion is violated by the Hartree–Fock and by the finite basis set approximations if the analytic procedure is applied [9, 18].

The use of Eq. (4) is justified because, according to quantum mechanical formalism, the matrix elements of the $\hat{\boldsymbol{r}}$ and the $\hat{\boldsymbol{\nabla}}$ operators are not independent. Therefore one is free to choose the matrix elements of $\hat{\boldsymbol{r}}$ e.g. by using formula (3), but then the matrix elements of $\hat{\boldsymbol{p}}$ are already fixed by Eq. (4*a*) as a consequence of quantum mechanics.

The Linderberg method was successfully used for the ordinary and magneto-optical calculations, in connection with CNDO wave functions in several cases [3, 19–26].[2]

Eq. (3) is a rough approximation involving neglect of all one- and two-center electronic transition moment integrals (off-diagonal elements of $\boldsymbol{r}_{\mu\nu}$). However, it is well known that "omission of the atomic transition moment integrals makes it practically impossible to obtain realistic molecular (...) transition moments" [28]. Therefore Linderberg and Seamans [28] calculated the $\boldsymbol{r}_{\mu\nu}$ integrals according to the neglect of diatomic differential overlap (NDDO) [15] scheme, and consequently correction terms occurred in Eq. (4*b*). As far as we know, this generalized equation has not yet been applied in any actual optical activity calculation.

In this paper according to the original concept of Linderberg, we are giving a modification of the (4*b*) formula when the ZDO hypothesis is dropped from Eq. (3). From this modification we expect better numerical results for those transitions which involve large contributions of one-center matrix elements.

2. Method

The matrix elements of the position operator are defined by the general second quantized form:

$$\hat{\boldsymbol{r}} = \sum_{\mu,\nu,s} \boldsymbol{r}_{\mu\nu} a^{+}_{\mu s} a_{\nu s} \tag{5}$$

s is the spin label, and the CNDO model Hamiltonian [29] is applied:

$$\hat{H} = \sum_{\mu,\nu,s} \beta_{\mu\nu} a^{+}_{\mu s} a_{\nu s} + \tfrac{1}{2} \sum_{\substack{\mu,\nu,s \\ \mu\neq\nu}} \gamma_{\mu\nu} \hat{n}_{\mu s} \hat{n}_{\nu s} + \\ + \tfrac{1}{2} \sum_{\mu,s} \gamma_{\mu\mu} \hat{n}_{\mu s} \hat{n}_{\mu -s} \tag{6}$$

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[2] Note that the CNDO model is not the only possibility to combine with the Linderberg method. It is easy to show that the INDO [27] or the NDDO [15] Hamiltonians are also compatible with Eq. (4*b*).

According to ($4a$) the explicit calculation shows that the commutator of (5) and (6) gives:

$$\boldsymbol{\nabla}_{\mu\nu} = \sum_{\lambda} (\boldsymbol{r}_{\mu\lambda}\beta_{\lambda\nu} - \boldsymbol{r}_{\nu\lambda}\beta_{\lambda\mu}) \tag{7}$$

It may be noted that the electron repulsion part of (6) drops out from the $[\hat{r}, \hat{H}]$ commutator even in the NDDO case [30].

We propose this formula to calculate the gradient matrix elements in the magnetic and in the dipole velocity electric transition moments. In Eq. (7) not only the $\beta_{\mu\nu}$, $\mu \neq \nu$ off-diagonal resonance matrix elements occur, but also the β_{ss} and β_{pp} s- and p-type ionization potentials, respectively. Naturally, in the ZDO limit this equation reduces to Linderberg's one ($4b$). Note that we restrict ourselves to the case of the CNDO method, because of the special form of our model Hamiltonian (6).

It may be argued that the use of the ZDO assumption is more consequent in a CNDO scheme, thus Eq. ($4b$) is to be preferred over Eq. (7). However, the undermentioned numerical examples will demonstrate that approximation (3), also in connection with the CNDO model is sometimes unreasonably rough, in particular in the case of the one-center matrix elements, which may have relatively large values. This fact justifies a procedure which uses ZDO for the calculation of the wave function but is a non-ZDO method for the evaluation of other physical parameters.

It must be noted that in general Eq. (7) has an origin dependence. A change of origin ($\boldsymbol{\delta}$) leads to a $\boldsymbol{\delta}$-dependence in $\boldsymbol{\nabla}_{\mu\nu}$:

$$\boldsymbol{\nabla}_{\mu\nu}(\boldsymbol{\delta}) = [\boldsymbol{r}, \boldsymbol{\beta}]_{\mu\nu} + \boldsymbol{\delta}[\boldsymbol{S}, \boldsymbol{\beta}]_{\mu\nu}$$

where $\boldsymbol{S}$ is the overlap matrix, which does not commute with the $\boldsymbol{\beta}$ resonance integral matrix in finite basis. If we restrict us to the CNDO model, $\beta_{\mu\nu} = [(\beta^0_a + \beta^0_b)/2]S_{\mu\nu}$ than the last term reduces to

$$[\boldsymbol{S}, \boldsymbol{\beta}]_{\mu\nu} = \frac{\beta^0_b - \beta^0_a}{2}(\boldsymbol{S}^2)_{\mu\nu} = \frac{\beta^0_b - \beta^0_a}{2}[\delta_{\mu\nu} + 2S_{\mu\nu} + (S^2_{\mu\nu})]$$

Eq. (7) has been derived by supposing that a^+_μ refers to a ZDO basis. Since we have kept $\boldsymbol{r}_{\mu\nu}(\mu \neq \nu)$ integrals, it may be also argued, that the basis set in question is not ZDO in fact. This may be visualized by applying a translation $\boldsymbol{\delta}$ of the coordinate system:

$$\boldsymbol{r}_{\mu\nu}(\boldsymbol{\delta}) = \boldsymbol{r}_{\mu\nu}(0) + \boldsymbol{\delta}S_{\mu\nu}$$

Since we use for $\boldsymbol{r}_{\mu\nu}$ an analytic procedure, this effect actually occurs. In order to compensate the origin dependence of $\boldsymbol{\nabla}_{\mu\nu}$ in Eq. (7) one can use instead of Eq. (7) the following expression (Biczó, private communication and [18]):

$$\boldsymbol{\nabla}_{\mu\nu} = \sum_{\lambda\sigma} [\boldsymbol{r}_{\mu\lambda}(S^{-1})_{\lambda\sigma}\beta_{\sigma\nu} - \beta_{\mu\lambda}(S^{-1})_{\lambda\sigma}\boldsymbol{r}_{\sigma\nu}] \tag{7'}$$

Unfortunately, this formula is not consistent from another point of view: in case of CNDO wave functions we have a ZDO Hamiltonian for which $S_{\mu\nu} = 0$ $(\mu \neq \nu)$. The ZDO assumption and consequently Eq. (4*b*) leads automatically to translationally invariant results. This violation is the cost we have to pay in order to get better numerical results by the abandoned ZDO assumption.

For the matrix elements of the $\hat{\boldsymbol{r}} \times \hat{\boldsymbol{\nabla}}$ operator, which is needed in Eqs. (1) and (2), we used the following formula:

$$\langle \nu | (\hat{\boldsymbol{r}} \times \hat{\boldsymbol{\nabla}})^{\lambda} | \mu \rangle = -\sum_{\rho \in a} \varepsilon_{\lambda \bar{\mu} \bar{\rho}} S_{\nu\rho} + (\boldsymbol{r}_a \times \boldsymbol{\nabla}_{\nu\mu})^{\lambda} \tag{8}$$

where ε is the total antisymmetric unit tensor (the Levi–Civitta symbol), $\lambda \doteq 1, 2, 3$ corresponds to the x, y, z components of the $\hat{\boldsymbol{r}} \times \hat{\boldsymbol{\nabla}}$ vector operator, respectively. The μ, ρ and ν labels denote AOs on atoms a and b, respectively. The $\bar{\mu}$, $\bar{\rho}$ orbital indices are 1, 2, 3 corresponding to the type of the AOs in the p_x, p_y and p_z order, respectively. If any of the μ or ρ AOs is s-type, the first term in Eq. (8) is absent. During the derivation of Eq. (8) we followed the same way as Linderberg and Michl [17] did, the only difference was that we did not approximate the $S_{\nu\rho}$ overlap matrix with the $\delta_{\nu\rho}$ unit matrix, this approximation being consistent with the retention of the differential overlap in Eqs. (5) and (7).

The use of Eq. (8) together with Eq. (7) leads to some consistency problem for the angular momentum operator [28], such as e.g. 1) the violation of the gauge- and translational invariance [28, 31] and 2) the fact that the $(\hat{\boldsymbol{r}} \times \hat{\boldsymbol{\nabla}})_{\mu\nu}$ matrix is not antisymmetric through the $\hat{\boldsymbol{r}} \times \hat{\boldsymbol{\nabla}}$ operator is anti-Hermitian. The first problem appears in magnetic field only, and it can be solved by use of London-type AOs [32–34]. The second problem is more essential, but we refer to a lot of direct rotatory strength calculations where Eq. (8) was applied [2, 11, 35, 36]. For instance, the analytic procedure [11], which was used to check our results, calculates the angular momentum integrals also by Eq. (8). Despite of this inconsistency we adopted Eq. (8) in order to have a basis of comparison with the analytic procedure. We note that numerical checks showed ~10% change in R while replacing $(\boldsymbol{r} \times \boldsymbol{\nabla})_{\mu\nu}$ with $-(\boldsymbol{r} \times \boldsymbol{\nabla})_{\nu\mu}$.

We have now an objection to the usual rotatory strength calculation using Eq. (4*b*). This formula is valid only together with the $r_{\mu\nu} \sim \delta_{\mu\nu}$ approximation. However, in the calculations of the dipole length electric transition moments it is not customary to neglect for instance the $(3s|\hat{z}|3p_z)$ type integrals, e.g. of a sulphur atom [17]. But then it is slightly inconsistent to use Eq. (4*b*) to calculate the magnetic or dipole velocity electric transition moments. This inconsistency probably leads to an unreasonably large difference between the dipole velocity and dipole length rotatory strength values.

3. Results

The effect of the above described modification is demonstrated first on the numerical values of $\boldsymbol{\nabla}_{\mu\nu}$ and $(\boldsymbol{r} \times \boldsymbol{\nabla})_{\mu\nu}$ matrix elements over AOs for the twisted hydrogen peroxide (H_2O_2) model molecule (its geometry is given in Table 1). In

	x	y	z	(Å)
H_1	−0.0795	−0.4734	0.8199	
H_2	1.5545	0.9467	0	
O_1	0	0	0	
O_2	1.4750	0	0	

Table 1. Cartesian coordinates of atoms in H_2O_2 according to experimental data [38]: $r(OH) = 0.96$ Å, $r(OO) = 1.475$ Å and the HOO bond angle is 94.8°. Here and in Table 2 the dihedral angle is 120°

Table 2 there are one-center oxygen matrix elements, two-center oxygen–hydrogen and two-center oxygen–oxygen matrix elements, in three approximations. The first one is the original Linderberg's, i.e. "full ZDO" in $r_{\mu\nu}$ (see Eq. (4*b*) for $\nabla_{\mu\nu}$); the second one is the present modification according to Eqs. (7) and (8) by means of the CNDO Hamiltonian of the molecule; and the last is the direct integration with Slater-type AOs (analytic), where the equation of motion plays no role. The modified values are obtained by the direct integration of the $r_{\mu\nu}$s with Slater-orbitals [37].

Let us see first the gradient integrals. We have written down only the values significantly larger than zero. It seems that the "full ZDO" approximation neglects the integrals in a few important cases (rows 1, 4, 10 and 12 in Table 2). In row 5 the "full ZDO" result has the wrong sign. In some cases the values have the same sign and order of magnitude in all three approximations (rows 2, 3, 6, 7, 8, 9, 11). However, sometimes the present modification changes the "full ZDO" values in the wrong direction (rows 2, 3, 6, 7).

It is interesting that in the present method certain integrals e.g. $(2s|\hat{\nabla}|2p_\sigma)$, etc. have no exactly fixed values (see rows 1, 10 and 12 in Table 2). This is a natural consequence of the fact that the computation of $\nabla_{\mu\nu}$ according to Eq. (7) is a "nonlocal" procedure: the $\nabla_{\mu\nu}$ value is determined by the molecule as a whole through certain $\beta_{\lambda\sigma}$ and certain $r_{\lambda\sigma}$ integrals. In the case of the usual integration technique (i.e. the analytic way) the $\nabla_{\mu\nu}$ value depends only on the μ and ν AOs. In the original Linderberg method this problem is avoided by use of the very simple form of Eq. (4*b*).

The differences are more remarkable in the case of the $r \times \nabla$ integrals (see rows 13–17 in Table 2). We wrote down here also the matrix elements significantly larger than zero. It seems that the "full ZDO" approximation keeps the trivial integrals (row 14) only, and the present modification gives results very similar to the analytic values.

The change of the rotatory strength caused by the present modification is demonstrated first on the rotatory strength values of the first four lowest transitions of hydrogen peroxide. For the rotatory strength of H_2O_2 no experimental data are available, and therefore the analytic method was chosen as a reference. The analytic rotatory strengths are calculated in dipole velocity form which is origin independent [8]. The present and the "full ZDO" values are calculated in both (dipole velocity and dipole length) formalisms. The geometry of H_2O_2 was chosen according to experiment [38], except the dihedral angle α_D which was

Table 2. One- and two-center ∇ and $\boldsymbol{r}\times\nabla$ integrals for hydrogen and oxygen atoms in H_2O_2 molecule (the molecular geometry is shown in Table 1)

	approximation		
Integral type	"full ZDO"	present	analytical
one-center ∇			
1. $\left(2s\middle\vert\frac{\partial}{\partial x}\middle\vert 2P_x\right)$	0	0.38 0.40 0.43 0.45	0.66
two-center H_1–O_1 ∇			
2. $\left(1s\middle\vert\frac{\partial}{\partial x}\middle\vert 2s\right)$	−0.55	−0.73	−0.30
3. $\left(1s\middle\vert\frac{\partial}{\partial y}\middle\vert 2s\right)$	0.32	0.42	0.17
4. $\left(1s\middle\vert\frac{\partial}{\partial x}\middle\vert 2p_x\right)$	−0.0	0.21	0.21
5. $\left(1s\middle\vert\frac{\partial}{\partial y}\middle\vert 2p_y\right)$	−0.13	0.09	0.12
6. $\left(1s\middle\vert\frac{\partial}{\partial y}\middle\vert 2p_z\right)$	0.22	0.24	0.17
7. $\left(1s\middle\vert\frac{\partial}{\partial z}\middle\vert 2p_y\right)$	0.22	0.24	0.17
two-center O_1–O_2 ∇			
8. $\left(2s\middle\vert\frac{\partial}{\partial x}\middle\vert 2s\right)$	0.50	0.30	0.19
9. $\left(2s\middle\vert\frac{\partial}{\partial x}\middle\vert 2p_\sigma\right)$	−0.61	−0.54	−0.20
10. $\left(2s\middle\vert\frac{\partial}{\partial y}\middle\vert 2p_\pi\right)$	0	0.08 0.06	0.07
11. $\left(2p_x\middle\vert\frac{\partial}{\partial x}\middle\vert 2p_x\right)$	−0.70	−0.42	−0.18
12. $\left(2p_\pi\middle\vert\frac{\partial}{\partial_x}\middle\vert 2p_\pi\right)$	0	0.14 0.16	0.11
one-center $\boldsymbol{r}\times\nabla$ O_2			
13. $(2p_z\vert(\boldsymbol{r}\times\nabla)^y\vert 2s)$	0	1.06	1.83
14. $(2p_z\vert(\boldsymbol{r}\times\nabla)^y\Vert 2p_x)$	1.0	1.0	1.0
two-center O_1–H_1 $\boldsymbol{r}\times\nabla$			
15. $(2p_y\vert(\boldsymbol{r}\times\nabla)^x\vert 1s)$	0	0.35	0.33
16. $(2p_z\vert(\boldsymbol{r}\times\nabla)^x\vert 1s)$	0	0.20	0.19
two-center O_2–O_1 $\boldsymbol{r}\times\nabla$			
17. $(2p_x\vert(\boldsymbol{r}\times\nabla)^y\vert 2p_z)$	0	0.22	0.22

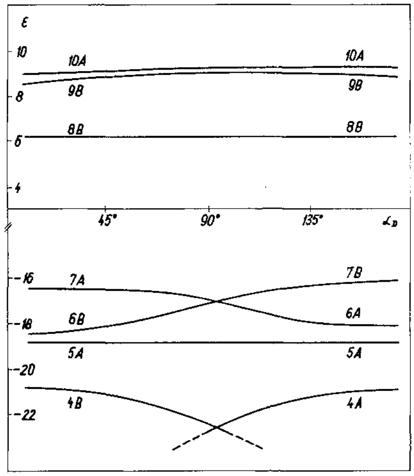

Fig. 1. Correlation diagram for molecular orbitals of H_2O_2. The MO energies are in eV units. The orbitals are numbered in order of ascending energy and denoted by C_2 point group symmetry

varied in our calculations in the 0° to 180° range. Our wave function is a result of a CNDO/2-CI calculation (the latter includes all the single excitations).

In the case of the first and second lowest transitions neither the "full ZDO",[3] nor the "modified" values are similar to the analytic rotatory strengths. The present and the analytic results are opposite in sign, and the "full ZDO" values are too small. The numerical analysis of matrix elements showed that the sign difference between the present and analytical values is caused by the $\approx 40\%$ difference between the present and analytic one-center gradient integrals (Table 2, first row). These matrix elements have relatively large weight in the first and second lowest transitions.

On Fig. 2 the rotatory strength of the first lowest (from 0° to 90°) and second lowest (from 90° to 180°) transitions of H_2O_2, in the above mentioned three approximations, are given as a function of dihedral angle α_D. These two transitions give a continuous curve because of the degeneracy and level crossing at about 90° (see Fig. 1). Fig. 2 illustrates well the sign difference between the present and analytical values and that the "full ZDO" rotatory strengths are too small. It seems that the present dipole length and dipole velocity results are in very good agreement with each other.

The situation is more fortunate in the case of the third and fourth lowest transitions of H_2O_2 (Figs. 3 and 4). The sign of rotatory strengths is generally the same in all three approximations, and the curves are more or less similar, however the numerical differences are not small.

In the case of the transition shown in Fig. 3 (this corresponds to the $7A \rightarrow 9B$ one-electron transition for $\alpha_D < 90°$ and to the $7B \rightarrow 9B$ for $\alpha_D > 90°$; see Fig. 1)

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[3] In the calculation of rotatory strength by the original Linderberg (ZDO) method we have neglected the differential overlap in the $(\mu|\vec{r}|\nu)$ electric transition moment integrals, as it is consistent with the use of Eq. (4*b*).

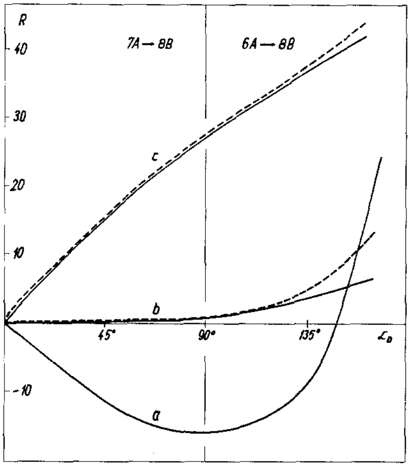

Fig. 2. Optical rotatory strengths in 10^{-40} CGS units of first and second lowest transition of H_2O_2, by analytical (*a*), "full ZDO" (*b*) and present (*c*) methods in dipole velocity (———) and dipole length (– – – –) forms. The designation of transitions are shown in Fig. 1

the "full ZDO" rotatory strengths are everywhere too small. The present curves between the dihedral angles 90° and 180° are similar to the analytic one, but they are opposite in sign for angles less than 60°. The local minimum at about 80° and the maximum at about 40° are the characteristics of all curves, but the large minimum at 15° occurs only for the present method.

In the case of the $7A \rightarrow 10A$ for $\alpha_D < 90°$ and $7B \rightarrow 10A$ for $\alpha_D > 90°$ transitions (see Fig. 4) the present modification shifts the "full ZDO" curves towards the theoretical one.

For the third and fourth lowest transitions the present rotatory strengths in dipole length and dipole velocity forms do not agree as well as on Fig. 2, however they are near to one another. This may be a consequence of the fact that the transition energies of higher excitations are less accurate, and they appear in the dipole

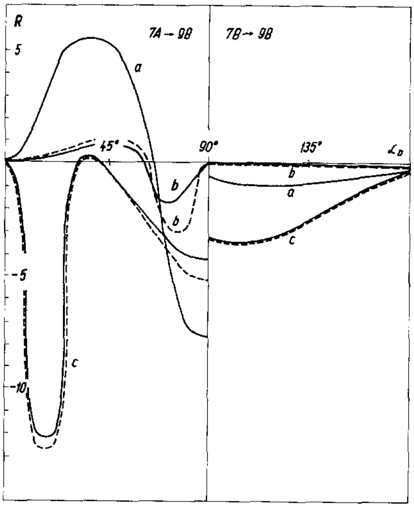

Fig. 3. Rotatory strength curves of $7 \rightarrow 9$ transition of H_2O_2 in 10^{-40} CGS units. Designations see in Fig. 2

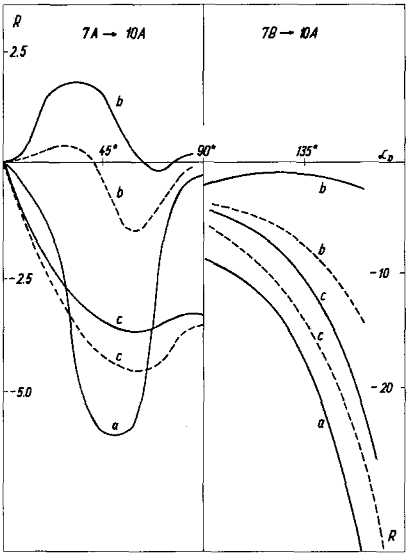

Fig. 4. Rotatory strengths of 7→10 transition of H_2O_2 in 10^{-40} CGS units. Designations see in Fig. 2

velocity rotatory strength explicitly (see formula (2)). Certainly, the "full ZDO" dipole velocity and dipole length values differ more pronouncedly from each other than those of the present method.

We have mentioned in the Introduction that the equivalence of rotatory strengths (1) and (2) require exact wave functions and the validity of the Heisenberg

Table 3. Rotatory strengths, R, [10^{-40} CGS] of first five lowest transition of H_2O_2 calculated in dipole length (r) and in dipole velocity (∇) formalisms. The molecular geometry is the same as in Table 1

		approximation			
Transition	Form	analytic	"full ZDO"	*a*	*b*
1	r	−12.2	0.2	−18.7	−16.2
	∇	17.7	0.3	−18.5	−15.5
2	r	24.7	2.6	33.5	31.9
	∇	−13.7	2.2	33.0	33.9
3	r	−13.8	−5.2	−9.7	−5.7
	∇	−12.7	−1.0	−7.1	−2.4
4	r	3.6	−0.0	−3.1	−6.3
	∇	−0.8	+0.0	−3.1	−10.3
5	r	−18.3	−13.1	−22.7	−23.2
	∇	3.7	−27.9	−34.7	−26.9

[a] R values by use of Eq. (7) for $\nabla_{\mu\nu}$.
[b] R values by use of Eq. (7') for $\nabla_{\mu\nu}$.

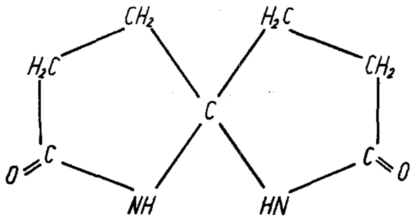

Fig. 5. 1,6 diazaspiro[4,4]nonane-2,7-dione molecule.

equation of motion. This second condition is satisfied in all procedures using Linderberg's concept, thus also in the present method. This is not true for methods using the direct integration technique, hence the difference between the (1) and (2) rotatory strengths is much larger in the case of these methods (see Refs. [9, 39–42], Table 3). Translational invariance is hurt by about 1% by using 1 Å translation in case of $\nabla_{\mu\nu}$ calculated by Eq. (7). Application of the translationally invariant Eq. (7′) leads to qualitatively similar results (see last column of Table 3). We note that even use of Eq. (7′) in the dipole length formalism is *not* translationally invariant.

Further on we demonstrate the effect of the present modification on a chemically more interesting larger molecule, 1,6-diazaspiro[4,4]nonane-2,7-dione (see Fig. 5). The geometry was taken from experimental X-ray diffraction data [43].

The calculated excitation energies and rotatory strengths of the first five lowest transitions of this molecule are shown in Table 4. The wave function is a result of a CNDO/2-CI calculation. The CI basis set is built from the single excitations between molecular orbitals localized on the carbonyl chromophores.

The present rotatory strengths (third row) are in qualitative agreement with the analytic (first row) values, and the "full ZDO" results differs from these in particular at the second and fifth lowest transitions. The present dipole velocity

Table 4. Excitation energies and rotatory strengths (10^{-39} CGS) of the first five lowest transitions of 1,6 diazaspiro[4,4]nonane-2,7-dione molecule, using dipole length (r) and dipole velocity (∇) formalisms

Transition			1	2	3	4	5
	energy (eV)		6.63	6.64	11.24	11.74	12.08
	analytical	∇	−8.0	5.9	0.5	−1.1	−2.1
Calculated R							
	"full ZDO"	r	−1.9	0.2	1.2	−2.6	0.9
		∇	−2.7	−1.0	1.0	−1.7	1.2
	present	r	−4.7	3.3	2.2	−2.8	−2.0
		∇	−7.7	3.3	1.5	−1.6	−4.0
Observed	R		±3.9				
	energy (eV)		6.4				

and dipole length rotatory strengths have the same sign, the Linderberg's values at the second lowest transition are opposite in sign.

According to the circular dichroism measurements the molecule has a transition of 6.4 eV with rotatory strength $\pm 3.9 \times 10^{-39}$ CGS, the sign is unknown [44]. The theoretical calculations make the negative sign probable (see Table 4).

4. Conclusion

The present generalization of Linderberg's method gives more real numerical results because the applied approximations are less rough. It has not the inconsistency caused by the combination of the (4*b*) Linderberg equation and the retention the differential overlap in electric transition moment. Its numerical quality is illustrated well by Table 4. The rotatory strengths of the H_2O_2 molecule are more uncertain because this molecule is too small and simple and therefore some defective matrix elements have relatively large weights, leading to enlarged or incompensated errors.

It appears as an important feature of the present method that it yields dipole length and dipole velocity rotatory strength values which are relatively close to one another.

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