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OPTICAL ROTATORY POWER BY THE ONE-DIMENSIONAL ELECTRON GAS MODEL—I

THEORY AND APPLICATION TO SKEW CONFORMATIONS OF BUTADIENE†

H. J. NOLTE and V. BUSS
Max-Planck Institut für Biophysikalische Chemie D-34 Göttingen, Am Fassberg

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Abstract—A quantum-mechanical model for the theoretical calculation of optical activity in "pseudo" π-systems is presented. Based on refined one-dimensional electron gas theory, the model allows for a rapid evaluation of electric and magnetic transition moments and of origin-independent rotational strengths. The influence of varying wave functions and geometry on the rotational strengths of skew butadiene conformations is discussed.

Zusammenfassung—Ein quantenmechanisches Modell zur Berechnung der optischen Aktivität von "Pseudo" π-Systemen wird entwickelt. Auf der Grundlage der verfeinerten eindimensionalen Elektronengastheorie erlaubt das Modell die schnelle Berechnung von elektrischen und magnetischen Übergangsmomenten und von koordinatenursprungsunabhängigen Rotationsstärken. Der Einfluss der Wellenfunktionen und der Geometrie auf die Rotationsstärken von chiralen Butadienkonformeren wird diskutiert.

INTRODUCTION

In the past there have been numerous applications of the quantum-mechanical theory of optical activity to large molecular systems of biological importance in order to obtain information about the molecular configuration which is difficult to get otherwise. A few examples are: the studies of vitamin B12 and its derivatives on the basis of LCAO–MO-theory,[1] the use of Kirkwood's polarizability approximation in the analysis of the CD spectra of chlorophyll and its aggregates,[2] and the many applications of exciton and classical oscillator theory to the study of biopolymer configurations.[3]

One-dimensional electron gas theory has been applied with success to the analysis of ordinary absorption spectra of many similar systems, ranging from the theoretical treatment of the corrinoid absorption[4] and the investigation of the typical absorption pattern of porphin ring systems[5] to the presentation of new proposals for the molecular structure of dye aggregates.[6] No general effort has been made, however, to use electron gas theory in the calculation of optical activity of dissymmetric molecules, but only very special helical arrangements without explicit consideration of the actual atomic loci in space have been treated.[7,8] We have developed a scheme which allows the use of one-dimensional electron gas wave functions to calculate the rotational strengths of electronic transitions in non-planar "pseudo" π-systems of any given configuration. The basis for σ–π separability in such molecules is more questionable than in planar π-systems. However, from the results obtained so far we conclude that π-electron wave functions form a basis for the calculation of transition densities which compares well with more elaborate methods. The ease with which these functions are obtained allows the calculation of many different nuclear configurations and through potential corrections[9] these functions may represent largely delocalized as well as localized systems with a high degree of double bond fixation. This corresponds to an almost continuous transition from the quantum-chemical view of delocalized molecular orbitals to the classical coupled-oscillator concept.[10]

THEORY

The quantum-mechanical expression for the rotational strength R_k associated with the transition of a system from the ground state Ψ_0 to the electronically excited state Ψ_k was derived almost half a century ago:[11]

$$R_k = \mathrm{Im}\,\{\langle\Psi_0|\boldsymbol{\mu}_e|\Psi_k\rangle \,.\, \langle\Psi_k|\boldsymbol{\mu}_m|\Psi_0\rangle\}. \tag{1}$$

The electric and magnetic moment vectors are defined as sums of one-electron operators,

$$\boldsymbol{\mu}_e = e\sum_n \mathbf{r}_n \tag{2}$$

$$\boldsymbol{\mu}_m = \frac{e\hbar}{2mci}\sum_n \mathbf{r}_n \times \bar{\nabla}_n \tag{3}$$

the summation being over all electrons n. Im in (1) means that only the imaginary part of the dot product of the electric and magnetic dipole moment is to be taken. In (2) and (3), m and e are, respectively, mass and charge of an

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†Taken in part from the dissertation of H. J. Nolte, Marburg (1973).

electron, $\mathbf{r}_n$ the position vector to the n-th electron, and for the tilde ($\tilde{}$) on the nabla operator see below.

(a) *The orbitals.* In electron gas theory the wave functions Ψ are formed as simple products of one-electron orbitals ψ_i of energies E_i which are solutions of the one-dimensional Schroedinger equation:

$$\frac{d^2\psi_i}{ds^2}+\frac{2m}{\hbar^2}(E_i-V(s))\psi_i=0. \tag{4}$$

In (4), s represents the internal one-dimensional coordinate, and V(s) the potential in which the electrons are assumed to move. This potential is adjusted to the molecular geometry in two respects. First, it reflects, in a manner already described[9] the different bond lengths in the molecule which arise from the charge density of all occupied orbitals. Second, the decreased overlap of the π-system in the distorted, non-planar σ-skeleton of the actual nuclear configuration is taken into account (see the calculated example). Self-consistence of the orbitals ψ_i with the potential V(s) is then achieved in the usual way.[9] Eqn (4) is solved in the finite-differences approximation of Stratmann and Seelig.[12] Note that up to this point the actual nuclear configuration of the molecule is of no influence on the orbitals, except for the second potential correction. The calculation is purely topological taking into account only the connectedness of the different atoms in the molecule. Finally the orbitals are attached to the nuclear skeleton in the given configuration in space, and electric and magnetic transition moments are calculated in the external coordinate system.

(b) *The moments.* The electric transition moment (2) presents no difficulties, its calculation in a non-planar system being analogous to a planar system.[13] With respect to the magnetic moment one has to be careful to use a hermitian momentum operator for which we define the gradient operator $\tilde{\nabla}$ by

$$\int_{s_i}^{s_{i+1}}\psi_0\tilde{\nabla}\psi_k\,ds=\mathbf{A}_i\int_{s_i}^{s_{i+1}}\psi_0\frac{d}{ds}\psi_k\,ds-\frac{\mathbf{A}_i}{2}[\psi_0\psi_k]_{s_i}^{s_{i+1}}, \tag{5}$$

where (Fig. 1)

$$\mathbf{A}_i=\mathbf{i}\alpha_i+\mathbf{j}\beta_i+\mathbf{k}\gamma_i \tag{5a}$$

is the vectorial coefficient of the direction cosines of the ith straight chain segment with end points s_i and s_{i+1}, usually two atoms linked by a bond. The term in brackets is defined as

$$[\psi_0\psi_k]_{s_i}^{s_{i+1}}=\psi_0(s_{i+1})\psi_k(s_{i+1})-\psi_0(s_i)\psi_k(s_i). \tag{5b}$$

With the gradient operator in this form, the following relation holds exact (Appendix):

$$\sum_i\int_{s_i}^{s_{i+1}}\psi_0\tilde{\nabla}\psi_k\,ds=\frac{m(E_k-E_0)}{\hbar^2}\sum_i\int_{s_i}^{s_{i+1}}\psi_0\mathbf{r}\psi_k\,ds, \tag{6}$$

where the summation is over all straight chain segments in the molecule. From Eqn (6) it follows directly that rotational strengths calculated in this manner will be independent of the choice of origin.[14]

In the finite difference approximation[12] the wave functions are obtained in terms of their numerical values at points q of equal distance Δ along the coordinate s, and the moments are obtained, instead of integration, by summation over all points q. For the electric moment*

$$\boldsymbol{\mu}_e=e\Delta\sum_q\psi_0(q)\mathbf{r}\psi_k(q) \tag{7a}$$

and for the magnetic moment

$$\boldsymbol{\mu}_m=\frac{e\hbar}{2mci}\left\{\Delta\sum_q(\mathbf{r}\times\mathbf{A}_q)\psi_k(q)\frac{d}{ds}\psi_0(q)-\frac{1}{2}\sum_i(\mathbf{r}\times\mathbf{A}_i)\times[\psi_0\psi_k]_{s_i}^{s_{i+1}}\right\} \tag{7b}$$

where the index i extends over all chain segments and $\mathbf{A}_q=\mathbf{A}_i$ for all points on the i-th segment. For the differential d/ds in this approximation see Ref 12.

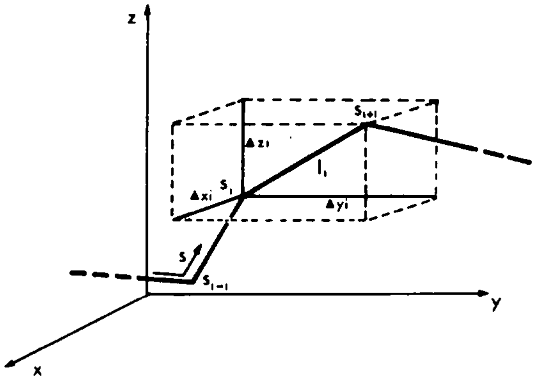

Fig. 1. Part of the σ-skeleton of a molecule in arbitrary conformation in a cartesian coordinate system. The direction cosines α_i, β_i and γ_i of the *i*th chain segment used in the vectorial coefficient A_i of Eqn (5) are defined as, respectively, $\Delta x_i/l_i$, $\Delta y_i/l_i$ and $\Delta z_i/l_i$.

RESULTS

Though our aim is the calculation of rotational strengths of large unsaturated systems, we have applied our method as the first test case to a small chiral system, the skew conformations of butadiene, which has been the subject of several investigations before.[8,15–17] In the calculations, three different sets of wave functions were employed: (a) in the simplest form of electron gas theory V(s) is set equal to zero in Eqn (4). The wave functions are then given by $\psi_i=\sqrt{2/L}\sin(i\pi s/L)$. L, the length of the chain, is taken to be 5·1. 39 Å = 6·95 Å, since the functions are assumed to extend one bond length beyond the last atom in a chain; (b) to account for the localization of the π-electrons in the double bonds, a correction potential V(s) was employed which depends linearly on the charge

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*In the actual program, electric moments are still computed in the dipole velocity formalism which we originally had believed necessary for obtaining origin independent rotational strengths.

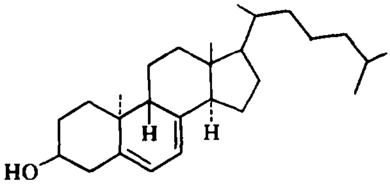
density in each bond. In this way self-consistent wave functions[9] are obtained; (c), since the localization of the π-electrons presumably increases when the dihedral angle between the two double bonds is increased from zero in the planar to 90° in the perpendicular form, we have added a correction to the potential by assuming that the electrons move on the average at a distance d above and below the σ-skeleton.[6] Then in a non-planar molecule the path length l between two atoms a distance l_0 apart is increased to

$$l = (l_0^2 + d^2\theta^2)^{1/2}, \qquad (8)$$

θ being the dihedral angle between the neighboring bonds. With d set equal to 0·75 Å[6] l is converted via the bond length bond potential relationship into a potential correction which slightly modifies the wave functions.

In Fig. 2 the rotational strengths of the four longest wave length electronic transitions between the calculated π-orbitals in butadiene are plotted against the dihedral angle of the two double bonds. The shaded area in each curve shows the range of R-values obtained with the different sets of wave functions, the lower limit of |R| corresponding to set a and the upper to set c. There is a difference of less than 5% between sets c and b. From this we conclude that it is important to account for double bond fixation in the calculation of the chiroptical properties of polyenic systems, but that the additional localization of the π-electrons due to non-planarity appears to be of little influence on the calculated rotational strengths.

Comparison with experiment. A rigid non-planar butadiene subunit is found in a number of steroid molecules.[18] For lumisterol



a crystal structure was reported by Hodgkin and Sayre,[19] and the ORD-spectrum of the compound was measured by Charney.[15] From the crystal atomic coordinates, we obtain a dihedral angle of ~4° between the two double bonds in the molecule† and have constructed an ORD-spectrum of lumisterol from the relation

$$[M] = \frac{48}{\hbar c} N_A \sum_j R_j \frac{\lambda_j^2(\lambda^2 - \lambda_j^2)}{(\lambda^2 - \lambda_j^2)^2 + \lambda^2\Lambda_j^2}. \qquad (9)$$

In (9), [M] is the molar rotation, N_A Avogadro's number and Λ_j the half band width of the j-th transition. We have considered two electronic transitions, at $\lambda_1 = 271$ nm and $\lambda_2 = 207$ nm as contributing to the experimental spectrum,[8] and with the rotational strengths R_{23} and R_{13} calculated for these transitions and Λ-values taken from literature data,[8] we obtain the spectrum shown in Fig. 3. The agreement between the theoretical and experimental curves is remarkable.

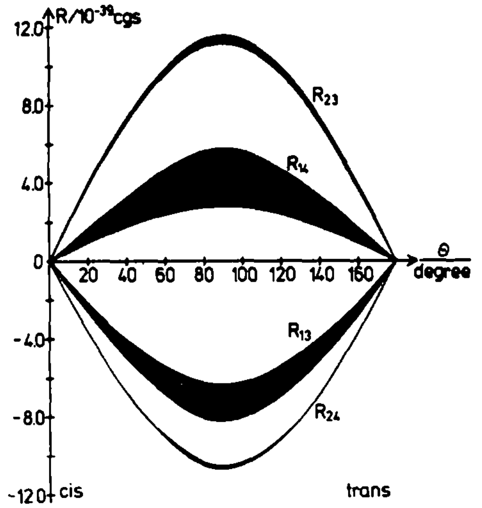


Fig. 2. Calculated rotational strengths R_{ij} of the electronic transitions from state i to state j in skew butadiene of right handed chirality. θ = dihedral angle between double bonds. Maximum value $|R|$ in shaded areas: calculation according to set c; minimum value: according to set a (see text).

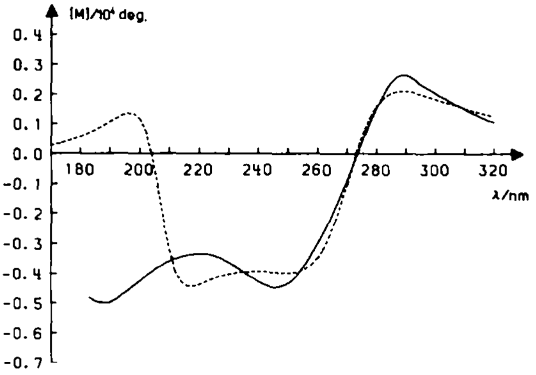


Fig. 3. Experimental (———)[15] and calculated (····) ORD-spectrum of lumisterol. A dihedral angle of 4° between the double bonds was used in the calculation.

DISCUSSION

We want to point out that other models with wave functions of accuracy comparable to ours would have yielded equally good results provided a dihedral angle of 4° in the chromophore had been used. It was the discrepancy between calculated and experimental [M]-values that initiated our recalculation of the experimental twist angle. However, the chiral diene chromophore in lumisterol appears to be of considerably less complexity than in many other steroids the CD-spectra of which do not even seem to reflect the handedness of the conjugated diene.[20] Therefore we do not think it is admissable at this time to

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†An angle of 8·3° has been used by others[8,15] in theoretical calculations with the result that rotational strengths are too large by a factor of ~2.

judge the reliability of our model from the successful calculation of one simple system and further work to test the range of applicability of the method is under way.

We would like to stress the transparency of the model which should prove useful in the interpretation of CD- and ORD-spectra. As an example, consider the two long wave length transitions in butadiene, $\psi_2 \to \psi_3$ and $\psi_1 \to \psi_3$. The dependence of the rotational strengths associated with these transitions on the dihedral angle between the double bonds has already been presented in Fig. 2. The orbitals involved in the excitations are drawn schematically in Figs. 4 and 5, together with the transition densities $\psi_2\psi_3$ and $\psi_1\psi_3$ which correspond, respectively, to a low energy in-phase coupling (B symmetry in C_2 point group) and a high energy out-of-phase coupling (A symmetry) of two transition dipoles located at the double bonds. The analysis of the different electric and magnetic moments in the molecule as it is twisted along its single bond from cis-configuration ($\theta = 0$) to trans ($\theta = 180°$) shows that their relative orientation causes rotational strength of positive sign for the $\psi_2 \to \psi_3$ transition and of negative sign for the $\psi_1 \to \psi_3$ transition (provided right-handed helicity of the diene) with maximum values around the perpendicular form ($\theta = 90°$).

It is seen from Fig. 4 that in the low energy excitation rotational strength near $\theta = 0$ is connected with a small electric and a considerable magnetic moment whilst the reverse holds for dihedral angles near $\theta = 180°$. This demonstrates the well known fact that optical activity of considerable amount may be associated with weak and with strong absorption bands.[21,22] One should note that for the high energy transition $\psi_1 \to \psi_3$ (Fig. 5) the rotational strength associated with strong absorption is found at the *cis* side, opposite to the low energy transition. This indicates that not only the molecular frame work, but also the mode of coupling determines the appearance of absorption and CD bands.

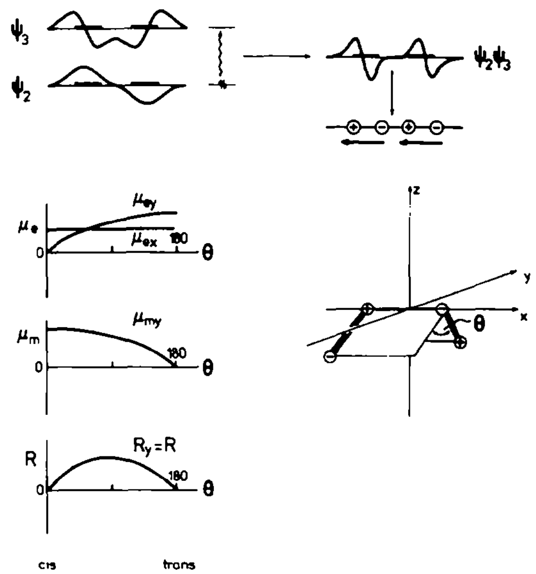

Fig. 4. The low energy in-phase B-type coupling of two transition dipoles arising from excitation of an electron from ψ_2 to ψ_3 in chiral butadiene. This coupling is seen to give rise to positive R-values for $0 < \theta < 180°$. Strong absorption occuring at trans-side.

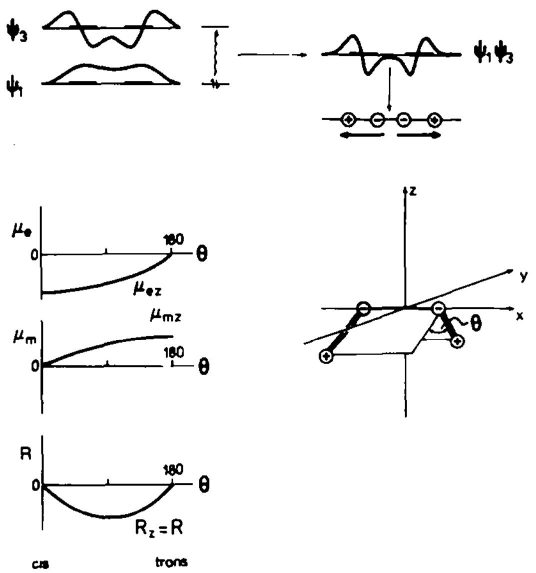

Fig. 5. The high energy out-of-phase A-type coupling of two transition dipoles arising from excitation of an electron from ψ_1 to ψ_3 in chiral butadiene. Coupling gives rise to negative R-values for $0 < \theta < 180°$. Strong absorption at the cis-side.

We are presently engaged in the theoretical study of other chiral systems, the results of which will be presented in forthcoming papers.[23]

Calculations were performed at the GWD computing center, Göttingen.

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APPENDIX

For the proof of Eqn (6) we confine ourselves, for simplicity, to the y-component. Consider the expression

$$a_i = \frac{m(E_k - E_0)}{\hbar^2} \int_{s_i}^{s_{i+1}} \psi_0 y \psi_k ds. \tag{A1}$$

The cartesian value y of a point on the i-th chain segment must be expressed in terms of the internal onedimensional coordinate s:

$$y = y_i + (s - s_i)\beta_i; \tag{A2}$$

y_i and s_i denote the fixed values y and s of the starting point of the i-th segment and β_i is the direction cosine of this segment with the y-axis. Since the wave functions are assumed to be exact solutions of the time-independent Schrödinger equation we obtain from (A1) by introducing (4) after some manipulation

$$a_i = -\frac{1}{2}\left\{\int_{s_i}^{s_{i+1}} \psi_0 y \psi_k'' ds - \int_{s_i}^{s_{i+1}} \psi_0'' y \psi_k ds\right\} \tag{A3}$$

where we have used the abbreviations $\psi_0'' = (d^2/ds^2)\psi_0$ and similarly for ψ_k''.

With the explicit expression for y in (A2) the second integral in (A3) is twice integrated by parts and we obtain after some straightforward calculation

$$a_i = \left[\frac{y}{2}\left(\psi_0'\psi_k - \psi_0\psi_k'\right)\right]_{s_i}^{s_{i+1}} + \beta_i\left\{\int_{s_i}^{s_{i+1}} \psi_0\psi_k' ds - \frac{1}{2}[\psi_0\psi_k]_{s_i}^{s_{i+1}}\right\}. \tag{A4}$$

Here we have used the abbreviations $\psi_0' = (d/ds)\psi_0$ and similarly ψ_k' and the terms in brackets are defined as in (5b). In the following summation over all segments i of the molecular frame, the sum of the first brackets in (A4) vanishes identically, if the wave functions obey the branching conditions[13] and vanish at any free end point of the internal coordinate.

Thus we get from (A4)

$$a = \sum_i a_i = \sum_i \beta_i\left\{\int_{s_i}^{s_{i+1}} \psi_0\psi_k' ds - \frac{1}{2}[\psi_0\psi_k]_{s_i}^{s_{i+1}}\right\} \tag{A5}$$

and similarly from (A1)

$$a = \frac{m(E_k - E_0)}{\hbar^2} \sum_i \int_{s_i}^{s_{i+1}} \psi_0 y \psi_k ds. \tag{A6}$$

Since the right-hand sides of (A5) and (A6) are identical, the same is true if we take the vector sums of all cartesian components being obtained in a way analogous as described above. With the definition (5) of the nabla operator the relation (6) results.