278. The MO-theoretical Description of Optical Properties in Polymers
Selection Rules due to Cyclic Symmetry

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Summary. The possibility is considered of applying routine semiempirical SCF-MO-CI procedures to the optical properties of polymers, such as polyamino acids, for instance. The polymer is assumed to be of intermediate length, namely, long enough that cyclic boundary conditions may be applied, but definitely shorter than the wavelength of incident light. Selection rules such as those which were derived by *Moffitt* in the frame of the exciton model are here translated into the MO picture. In the case of a helix the transitions polarized perpendicular to the axis of the helix are governed by clear-cut selection rules only if the number of repeating units N strictly corresponds to an integral multiple of a translational identity period. Questions concerning the tractability of the configuration interaction calculation are discussed.

1. Introduction. – Theoretical investigations of the optical properties of polymers have until now practically exclusively been based on the exciton model. Interest in a molecular orbital description of polymers has been increasing, however. The eventual advantage of the latter approach rests in the possibility to explicitly take into account structural changes within the individual monomers or elementary cells in the polymer. For smaller polyatomic molecules the calculation of electronic spectral properties starting from one-electron molecular orbitals extending over all atomic centers has become a routine procedure, at least within a semiempirical frame. In the basis of appropriate SCF-LCAO-MO's singly excited configurations are constructed, using the virtual canonical orbitals. A configuration interaction (CI) calculation in the basis of these configurational functions gives a first approximation to the lower excited states. There are of course cases where higher excited configurations possibly also should be included.

In the present note we want to discuss the practical applicability of such a molecular orbital procedure to polymers built from repeating units such that, neglecting end effects, cyclic boundary conditions may be applied. We assume the polymer to be small enough though – containing perhaps between 10 and 100 elementary units – that higher retardation effects may be neglected in computing optical properties. Our particular interest concerns the tractability of the singly excited configuration interaction part. The way retardation effects come into play when the length of the polymer becomes comparable to the wavelength of incident light has been studied in the molecular orbital frame by *Avery* [1]. In this latter case the approach outlined here is no longer applicable.

2. The molecular orbital scheme. – We consider a polymer built from N monomers or repeating units, in which each unit contains n_e valence electrons. We assume that per monomer n valence orbitals have to be taken into account, leading

to a correspondingly large LCAO basis of the order of n · N. Cyclic symmetry will, however, factorize the *Hartree-Fock* matrix according to the irreducible representations of the group C_N, namely, for N even into

$$a, e_{+1}, e_{-1}, \ldots e_{+j}, e_{-j}, \ldots e_{+(N/2-1)}, e_{-(N/2-1)}, b.$$

There are consequently N matrices of dimension n to be diagonalized. As will become obvious in Sections 3 and 4, matrix elements of the *Fock* operator between MO's of symmetry e_{+j} and e_{-j} vanish also. Other details concerning the SCF equations are to be found in [2]. The general form of a molecular orbital is

$$|jm\rangle = \sum_p \sum_s \omega^{jp} c_{jm,s} |ps\rangle \tag{1}$$

with m running from 1 to n, j taking on the values 0, ± 1, ... $\pm (N/2-1)$, N/2. ω stands for exp $(2\pi i/N)$, and s numbers an AO within the elementary cell p. Each one-electron monomer state m is formally split into an N-fold band of mostly doubly degenerate one-electron polymer states j. It is easily seen that there are $N \cdot n_e/2$ filled MO's and consequently $N \cdot \mathcal{n}$ possible single excitations, where

$$\mathcal{n} = N \cdot \frac{n_e}{2} \left(n - \frac{n_e}{2} \right). \tag{2}$$

With respect to their symmetry these singly excited configurations are also evenly distributed over all irreducible representations of the group C_N[1]). Consequently there will be $\mathcal{n}$ singly excited configurations belonging to each of the N representations[2]) A, B and sub-representations E_{+j} and E_{-j} (see also Section 4). As N, n_e and n grow, the computational labor of eventually diagonalizing these N CI-matrices rapidly becomes immense. It is therefore essential i) to reduce the number of matrices to be diagonalized, ii) to decrease their dimension.

3. Selection rules for transition moments. – Being interested in optical properties, the first problem i) may be approached by considering selection rules for electric dipole transition moments. Such selection rules were derived by *Moffitt* [3] in the frame of the exciton model. In the MO picture the transition moment between the ground state and an excited state will be a linear combination of matrix elements between polymer MO's of the form

$$\langle jm | \nabla | j'm' \rangle = \sum_{s=1}^{n} \sum_{s'=1}^{n} c^*_{jm,s} c_{j'm',s'} \sum_{p=1}^{N} \sum_{p'=1}^{N} \omega^{(j'p'-jp)} \langle ps | \nabla | p's' \rangle \tag{3}$$

We now focus our attention on the second double summation in (3), running over elementary cells, and we notice that it is independent of m and m'.

Assuming that s and s' have a definite constant value and that, on going from one elementary cell to the next, they always designate a pair of equivalent AO's,

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[1]) Unless an overlap occurs between the energies of bands for which $m \leq n_e/2$ and bands for which $m > n_e/2$. This limitation does, however, not affect our basic argument.

[2]) To characterize many-electron states, capital letters are used.

we may for our purposes drop these indices and abbreviate $\langle ps | \nabla | p's' \rangle$ by $\mathbf{b}_{pp'}$. We now perform the summation over p and p' in (3) in the following manner:

$$\sum_{p=1}^{N} \sum_{p'=1}^{N} \omega^{(j'p'-jp)} \mathbf{b}_{pp'} =$$

$$= \sum_{p=1}^{N} \omega^{p(j'-j)} \{\mathbf{b}_{pp} + \omega^{j'} \mathbf{b}_{p(p+1)} + \omega^{2j'} \mathbf{b}_{p(p+2)} + \ldots + \omega^{(N-1)j'} \mathbf{b}_{p(p+N-1)}\} \quad (4)$$

where we remember that $p' = N + \alpha$ is equivalent to $p' = \alpha$, α being an integer.

It now becomes essential to distinguish between the formal symmetry C_N of the polymer and its actual geometry. We consider different simple cases:

a) *Linear geometry*: We find $\mathbf{b}_{11} = \mathbf{b}_{22} = \ldots$ etc., $\mathbf{b}_{12} = \mathbf{b}_{23} = \ldots$ etc.: The expression in curly brackets in (4) is independent of p. Therefore expression (4) vanishes identically due to the cyclic phase factor, unless $j' = j$.

b) *Cyclic geometry*: Formal and geometric symmetric are identical. It is immediately apparent that the z-components of the vectors $\mathbf{b}_{p(p+\alpha)}$, parallel to the N-fold symmetry axis, lead to the same selection rule as in case a), namely $j' - j = 0$. The in-plane components x,y may, as *Moffitt* showed (see expressions (17)–(19), (44) and (45) in [3], be written in the form

$$\mathbf{b}_{p(p+\alpha)}^{(x,y)} = \omega^p \mathbf{v}_\alpha + \omega^{-p} \mathbf{v}_\alpha^*, \quad (5)$$

where $\alpha = 0, 1 \ldots N - 1$, and $\mathbf{v}_\alpha$ is a complex vector quantity independent of p. Introducing (5) into (4) and factoring into p-dependent and p-independent terms, we obtain the phase factors $\omega^{p(j'-j+1)}$ and $\omega^{p(j'-j-1)}$, leading to the selection rule $j' = j \pm 1$.

c) *Helical geometry*: This case is the one actually discussed in detail in [3]. For the z-components of the vectors $\mathbf{b}_{p(p+\alpha)}$, chosen parallel to the helical axis, the selection rule is $j' = j$. For the components perpendicular to the helical axis we find an analogy to (5):

$$\mathbf{b}_{p(p+\alpha)}^{(x,y)} = \omega^{Mp} \mathbf{v}_\alpha + \omega^{-Mp} \mathbf{v}_\alpha^*. \quad (6)$$

$M = N/Q$, where Q is the number of monomers per helical turn and in general not an integer. Introducing (6) into (4), the p-dependent phase factors become $\omega^{p(j'-j+M)}$ and $\omega^{p(j'-j-M)}$. Expression (3) consequently vanishes, unless $j' = j \pm M$. Now by definition $j' - j$ can only be an integral number, so M must be an integer. A clear-cut selection rule will consequently only hold for values of N that correspond to one or several translational identity periods along the axis of the helix.

For the sake of completeness we mention the obvious fact that an expression like (3) vanishes for any scalar one-electron operator – such as the kinetic or nuclear attraction hamiltonian – unless $j' = j$.

4. Many-electron integrals. – We consider an electron repulsion integral between polymer MO's of the general form $\langle jm\ l'n' | j'm'\ ln \rangle =$

$$\sum_s \sum_{t'} \sum_{s'} \sum_t c_{jm,s}^* c_{l'n',t'}^* c_{j'm',s'} c_{ln,t} \cdot$$

$$\cdot \sum_p \sum_{q'} \sum_{p'} \sum_b \omega^{(-jp-l'q'+j'p'+lq)} \langle ps\ q't' | p's'\ q\ t \rangle \quad (7)$$

and consider in particular the summation over elementary-cell indices p, q' p', q. In analogy to our procedure in the previous section, we assume definite and constant values for s, t', s' and t, that is, we consider in every monomer a particular equivalent quadruplet of AO's. With this in mind we can drop these latter indices and write:

$$\sum_p \sum_{q'} \sum_{p'} \sum_q \omega^{(-j\,p-l'\,q'+j'p'+l\,q)} \langle p\,q' \mid p'\,q \rangle =$$

(8)

$$\sum_p \omega^{(-j-l'+j'+l)}\,p \left\{ \sum_{\alpha=0}^{N-1} \sum_{\beta=0}^{N-1} \sum_{\gamma=0}^{N-1} \omega^{(-l'\alpha+j'\beta+l\gamma)} \langle p(p+\alpha) \mid (p+\beta)(p+\gamma) \rangle \right\}$$

Because of the cyclic symmetry the value of the triple sum in brackets is independent of p. This may be visualized for a particular value of α, β and γ. For instance, if $\alpha = 2$, $\beta = 1$, $\gamma = 3$ we indeed find $\langle 13 \mid 24 \rangle = \langle 24 \mid 35 \rangle = \langle 35 \mid 46 \rangle = \ldots$ etc. Therefore the sum over p consists of constant terms times a complex phase factor and vanishes cyclically, unless

$$(-j - l' + j' + l) = 0. \tag{9}$$

Relation (9) is of course also deducible on purely group theoretical grounds. The right-hand side of (8) may prove convenient for computer programming. The fall-off of the value of the electron repulsion integrals with distance will enable one to break-off the summation at relatively small values of α, β and γ. We now also immediately see that the matrix elements of the Fock operator

$$\langle j\,m \mid F \mid j'\,m' \rangle =$$

$$= \langle j\,m \mid h \mid j'\,m' \rangle + \sum_{ln} \{2 \langle j\,m\;ln \mid j'm'\;ln \rangle - \langle j\,m\;ln \mid ln\;j'm' \rangle \} \tag{10}$$

vanish, unless $j' = j$.

Integrals such as (7) appear in the energy matrix elements between excited configurations. j'm' and l'n' may then be virtual polymer MO's. Suppose $j' = j + M$, to take an example of the previous section, then we must have $l' = l + M$ to fulfill (9). This also illustrates that matrix elements between singly excited configurations transforming like E_{+M} and ones transforming like E_{-M} vanish.

5. Configuration interaction. – The selection rule $j' = j$ (see Section 3) implies that there is only one CI submatrix of dimension $\mathcal{n}$ between singly excited configurations of symmetry A to be considered. Similarly $j' = j \pm 1$ is related to two CI matrices of symmetry E_{+1} and E_{-1} respectively, and $j' = j \pm M$ to two matrices of respective symmetry E_{+M} and E_{-M}. If in the helical case N/Q is not an integer, preventing a clear-cut selection rule for transitions polarized perpendicular to the axis of the helix, then the number of relevant CI submatrices is correspondingly increased, 'spreading' the electric dipole intensity over transitions of different symmetries.

The problem ii) now remains of reducing the dimension of the matrices of given symmetry which actually have to be diagonalized. There is no clear-cut criterion for this. The suggested procedure consists in primarily taking into account configura-

tions which make dominant numerical contributions to the transition moments (both electric dipole and magnetic dipole, if one is interested in optical activity), possibly even at the expense of accuracy in assessing transition energies. The selection of these dominant configurations may be carried out on oligomers without cyclic boundary conditions, where N is very small. The number of monomers in the polymer is then increased stepwise, cyclic boundary conditions are introduced, with the hope of finding a convergence of the results.

The question of how important are doubly and higher excited configurations is not only relevant to polymers. But here it may become particularly important, due to the reduced energy gap between filled and empty MO's and the great number of possible configurations. Double excitations will unquestionably affect the energy of even the lowest excited states with respect to the ground state. It appears unlikely, though, that they will in general invert the sequence of predicted longest-wavelength transitions. In general their contribution to the transition moments may be of limited importance for the following reason: There are no matrix elements of the transition moment operator between the ground configuration and the doubly excited ones. There are nonvanishing contributions to the transition moment between selected singly and doubly excited configurations making up a given excited state wavefunction and some doubly excited configurations belonging to the ground state wavefunctions. The coefficients of the doubly excited configurations in the ground state wavefunction will always be relatively small, however. Still, one cannot exclude that many such small contributions might finally add up to a big one.

The acid test for the numerical procedure outlined here, based on the interaction of only a limited number of singly excited configurations, will not so much be the prediction of absorption spectra, but possibly rather of CD. spectra, wherever optical activity occurs, and where every transition will also be associated with a definite sign. Numerical work is in progress.

REFERENCES

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