

SYMMETRY AND ELECTRON SPECTRA OF POLYMERS

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The one-electron calculations of electronic energy spectra (band structures) have been reported for a number of polymer molecules. Different methods are used ranging from the simple HMO's to the extensive ab initio SCF HF LCAO CO's [1]. Such computations—in the case of some important biopolymers [2], as well as in that of the one-dimensional metals [3]—have received much attention recently.

In principle, the basic problem to be solved here is a secular equation of the form

$$\det(H_{\alpha\alpha} - E O_{\alpha\alpha}) = 0, \text{ where } H_{\alpha\alpha} = \langle \alpha | \hat{H} | \alpha \rangle, O_{\alpha\alpha} = \langle \alpha | \alpha \rangle, \quad (1)$$

where \hat{H} is the one-electron Hamiltonian and $|\alpha\rangle$ the orbitals forming the variational basis set. Even for the medium-size basis sets computations turn out to be very extensive, and it would be highly desirable to reduce them, without any loss in the accuracy of the results obtained. However, this is exactly what happens if the symmetry of the macromolecule considered, is properly exploited.

Symmetry of each stereoregular polymer molecule can be described by one of the line groups. All of the irreducible representations (IR's) of these groups were derived recently [4,5]. These IR's can be denoted by $D_{k,j}^{\rho}$, $k \in (-\pi/a, \pi/a]$, $j \in \{0, 2\pi/n, 2 \cdot 2\pi/n, \dots, (n-1)2\pi/n\}$ where a is the translational period of the molecule and n the order of the main axis. ρ can take 1, 2 or 4 values according to the dimension of the representation. j and k are the quantum numbers of \underline{L}_n [4,5]; an additional symmetry element can connect some of their values given above.

Once the mentioned IR's are known it is possible (e.g. making use of the symmetry projection operators, [5])

to introduce a symmetry-adapted basis $|k, j, \rho, r, \tau\rangle$ - where r is the row label of $D_{k,j}^\rho$ and where τ completes the set of quantum numbers-transforming according to these IR's. But then one has:

$$H_{k_j \rho r \tau, k' j' \rho' r' \tau'} = \delta_{kk'} \delta_{jj'} \delta_{\rho\rho'} H(k, j, \rho)_{\tau, \tau'} \quad (2)$$

and similarly for the overlap matrix. This block-diagonalization immediately splits (1) into:

$$\det |H(k, j, \rho)_{\tau, \tau'} - E(k, j, \rho) O(k, j, \rho)_{\tau, \tau'}|_{\dim D_{k,j}^\rho} = 0 \quad (3)$$

for each k, j and ρ . For sufficiently large macromolecules, k varies quasi-continuously; j, r and τ label the energy bands.

Apart from the reduction of the computational effort and time, use of the full, line group symmetry enables one (in view of (3)) to predict the degeneracies of the energy bands. Furthermore, the quantum numbers k and j bear direct physical interpretation (quasi-momentum and quasi-angular momentum; note that the latter one can take only a finite number of values). Hence, it becomes possible to analyze different physical processes - such as the direct optical absorption, the influence of the external or the crystal fields, etc. - in terms of (the selection rules involving) simple and intuitively clear physical notions.

The application of the above consideration to some particular polymers, such as polyoxyethylene (with line group $\underline{L7}_4 2$) or polyoxymethylene ($\underline{L9}_2 2$) is omitted here for brevity, but can be found in [5] and will be published elsewhere.

References:

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