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SYMMETRY ADAPTED BASES AND SELECTION RULES FOR POLYMER MOLECULES

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1. INTRODUCTION

Symmetries of the stereoregular polymer molecules are described adequately in terms of line groups, which were derived and classified in Ref. 1. In quantum theoretical studies of these physical systems, such as calculations of their electronic spectra (band structure) one should use the irreducible representations(ireps) of the line groups [2], as these ireps describe the action of the symmetry operations in the corresponding state space. The ireps of all the line groups were derived and tabulated in Refs 3 and 4.

In the sequel we are concerned with a quantum theoretical description (by means of an effective one-electron Hamiltonian $\hat{H}_{eff}$) of the motion of an electron in a potential created by a stereoregular polymer molecule having the symmetry Ln_p. These are the simplest among the line groups, they appear as subgroups of all the others, so that the following results have general validity. Every element of Ln_p is of the form $(C_n^s|\tau+t)$, moving (ρ,ϕ,z) into $(\rho,\phi-s\alpha,z-(t+\tau)a)$, where $\alpha=2\pi/n$, n is the order of the main axis, $p,s=0,1,\dots,n-1$, $t=0,\pm1,\pm2,\dots,\pm N/2$ $=Fr(sp/n)$, a is the fiber period. Hence, the screw axis n_p

characterizes this family of line groups.

The ireps of Ln_p are given by

$$ {}_kA_m(C_n^s|t+\tau) = \exp[ik(t+\tau)a]\exp(ims\alpha) \quad , \qquad (1)$$

where $k\in(-\pi/a,\pi/a]$ and $m=0,\pm1,\dots,\pm(n-1)/2$ for n odd, $m=0,\pm1,\dots,\pm(n-2)/2,n/2$ for n even. These are good quantum numbers originating in the symmetry of the system. They furthermore possess physical meaning and are related to the observables of the linear and/or the angular momentum type.

2. SYMMETRY-ADAPTED BASES

Once the ireps ${}_kA_m$ of Ln_p are known, one can adapt a given function $f(\vec{r})$ to this symmetry applying the corresponding projection operator:

$$f_{km}(\vec{r})= {}_k\mathcal{P}_m f(\vec{r}) = (1/nN)\sum_{s,t}\exp(-ims\alpha)\exp[-ik(t+\tau)a]f(\vec{r}\,'), \qquad (2)$$

where $\vec{r}\,' = (C_n^s|t+\tau)^{-1}\vec{r}$. The functions f_{km} are analogous to the so-called Bloch sums, well known in solid state physics, where one sums over the translations only.

Next, one can easily show that for each $f(\vec{r})$ one can write

$$f_{km}(\vec{r}) = \exp(-ikz)\exp(-im\phi)u_{km}(\vec{r}) \quad , \qquad (3)$$

where $u_{km}(\vec{r})$ is invariant under all the operations from Ln_p . This statement is analogous to Bloch's theorem.

One can also show that in the orbital state space there exists a complete orthonormal basis $\{e_{km\lambda}(\vec{r})\}$ such that it is (quasi)continuous in k , and periodic in k,m (as required by the equivalence of the ireps), in addition to the property that each function $e_{km\lambda}(\vec{r})$ is of the form (3).

3. ADVANTAGES OF THE USE OF THE SYMMETRY-ADAPTED BASES

The first and obvious benefit is the block diagonalization of the Hamiltonian $\hat{H}_\psi$ in $\{e_{km\lambda}\}$, which means

$$(e_{k'm'\lambda'},\hat{H}_\psi e_{km\lambda}) = 0 \text{ unless } k'=k \text{ , } m'=m \text{ .}$$

This greatly facilitates the task of finding energy spectra and eigenfunctions. Furthermore, the latter are completely determined once their values in $0 \leq \rho < \infty$, $0 \leq \phi < \alpha$, $0 \leq z < a$ are known. The energy eigenvalues can be denoted by $E_m(k)$. These functions are continuous and analytic in k , and periodic in k and m ; thus one has the energy bands. Next, one can show that m is conserved along one fixed band, i.e. that the energy bands are labelled by the symmetry quantum number m . This finds application in understanding the different physical processes in such systems through the selection rules.

4. SELECTION RULES

Let $\hat{B}_{q\mu}$ be an observable satisfying

$$(C_n^s|t+\tau)\hat{B}_{q\mu}(C_n^s|t+\tau)^{-1}=\exp[iq(t+\tau)a]\exp(i\mu s\alpha)\hat{B}_{q\mu} \text{ ,}$$

i.e. transforming according to the irep ${}_qA_\mu$ of Ln_p . In other words, $\hat{B}_{q\mu}$ is an irreducible tensor operator of Ln_p . Then one has the following selection rule:

$$(\varphi_{k'm'},\hat{B}_{q\mu}\psi_{km}) = 0 \quad \text{unless} \quad \Delta k \doteq q \quad \text{and} \quad \Delta m \doteq \mu \text{ .} \tag{4}$$

Here $\Delta k=k'-k$, $\Delta m=m'-m$, and "$\doteq$" means "equal up to equivalence of the ireps. Note that this selection rule in principle allows the "Umklapp" processes such as $k'=k+q-2\pi/a$, $m'=m+\mu-p$ etc. But these interesting possibilities cannot be discussed here for reasons of brevity.

Let us assume that an electron is in a stationary initial state ψ^{i}_{km} of the unperturbed effective Hamiltonian $\hat{H}_{eff}$, and that it is excited into $\varphi^{f}_{k'm'}$ by the action of a (time-dependent) perturbation $\hat{H}_{pert}$. The transitional probability $v(\psi_i \to \varphi_f)$ is proportional to $(\varphi^{f}_{k'm'}, \hat{H}_{pert}\psi^{i}_{km})^2$ in first order of time-dependent perturbation theory. To apply the selection rules (4) one has to decompose $\hat{H}_{pert}$ into its irreducible components.

In Ref 5 this technique is applied to the analysis of the interaction of light with the electrons of a polymer molecule. It turns out that the mere knowledge of the line group describing the symmetry of the system suffices to obtain some important qualitative features of the absorption spectra discussed.

REFERENCES

1 M. Vujičić,I.B. Božović,F. Herbut, J. Phys. A, 10 (1977)1271

2 I.B. Božović, Fizika 8 Suppl. (1976) 100

3 I.B. Božović,M. Vujičić,F. Herbut, to appear in the October 1978 issue of J. Phys. A

4 I.B. Božović, Doctoral Thesis, University of Belgrade, 1975 (in Serbo-Croate)

5 M. Džambazovski,I.B. Božović,M. Vujičić,F. Herbut, this Supplement