SYMMETRY AND DYNAMICS OF POLYMERS

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I. INTRODUCTION

Systems we are dealing with here are physical objects translationally periodic along the line. Stereoregular polymers belong to this class, but in quasi-one dimensional conductors and semiconductors we find other important examples.

Properties we are interested in are molecular ones, viz. those that reflect and are essentially dependent on the primary "stereochemical" structure of the polymer and much less (and in a distinguishable way) on its secondary and tertiary structure. The single infinite chain model provides a basis for calculation of electron band structure and phonon dispersion curves for polymers, and for interpretation of related X- and UV- photoelectron, IR and Raman spectra, etc.

Research interest for the above problems is both fundamental (e.g. Peierls transitions, CDW's and SDW's, comensurability, solitons) /1,2/ and applicational (e.g. role of polymers as electronic materials has been reviewed in /3/). The number of attractive systems is increasing and in addition to "old" ones like $(SN)_x$, $(CH)_x$, TTF-TCNQ, ..., we now have poly(pyrrole) and poly(p-phenylene); a most recent (and very promising) one is the $(Se)_x$ chain structure in a zeolite matrix.

Symmetries of these objects are not trivial (note that there are lateral degrees of freedom!): they are properly described in terms of *line groups* /4/. Irreducible representations of these groups are derived in /5/.

Applications of symmetry considerations include assignation of the spectra, derivation of symmetry-adapted bases, block-diagonalization of Hamiltonians and other (in general, tensor) observables, compatibility relations,

selection rules, etc. Electron band structure was extensively analysed from this point of veiw in /6/, and in the sequel we will discuss - in terms of a simple example - the case of phonons, and electron-phonon interaction.

II. SMALL VIBRATIONS OF THE $(BeH_2)_x$ CHAIN

Beryllium hydride polymeric solid consists of molecular chains, the "most likely" /7/ geometry of which is represented in Fig. 1. The symmetry of such a chain is described by the $\underline{L}4_2/mcm$ line group. The characteristic symmetry elements of this group include a screw axis (4_2), and the vertical and horizontal mirror planes, as indicated in the picture.

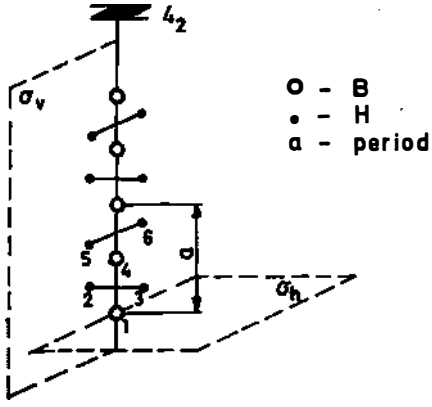

Fig. 1.

However, we will - for simplicity - consider $\underline{L}4_2mc$, which is a subgroup of $\underline{L}4_2/mcm$, in what follows. The irreducible representations of $\underline{L}4_2mc$ are either one-dimensional ($_kA_0$, $_kA_2$, $_kB_0$, $_kB_2$) or two-dimensional ($_kE_{1,-1}$); the matrices are given in /5/. The guantum numbers are the guasi-momentum k ($-\pi/a<k\leq\pi/a$), the quasi-angular momentum m (m=0 ±1, 2) and the parity with respect to the vertical mirror plane (A = even, B = odd).

Let $\binom{t}{i}$ label the i-th atom (i=1,2,....,6) in the t-th elementary cell (t=0,±1, ..., ±N), and let $e_\alpha\binom{t}{i}$ describe the displacement of this atom in the direction α(α=x,y,z) for a length unit. The set of all $e_\alpha\binom{t}{i}$ spans a 18(2N+1)-dimensional vector space V^{dis}, and transforms according to a certain reducible representation $D^{dis}(\underline{L}4_2mc)$. One can show that

$$D^{dis}(\underline{L}4_2mc) \sim \bigoplus_k (3_kA_0 \oplus 3_kA_2 \oplus {}_kB_0 \oplus {}_kB_2 \oplus 5_kE_{1,-1} \qquad (1)$$

Thus we have determined the number and degeneracy of vibration branches for each symmetry species.

More detailed information is obtained by constructing a symmetry-adapted basis (SAB) in V^{dis}. For each value of k, this SAB contains 18 vectors, derived e.g. by symmetry-projecting the $\vec{e}_\alpha(^t_i)$'s. One thus finds

$$ {}_k\vec{f}_1 = P({}_kA_o)\vec{e}_z(^0_1) = \frac{1}{2}\left[{}_k\vec{e}_{1z}+\exp(-ika/2)\,{}_k\vec{e}_{4z}\right] $$

where

$$ {}_k\vec{e}_i = \frac{1}{2N+1}\sum_t \exp(-ikta)\vec{e}_\alpha(^t_i) $$

$$ {}_k\vec{f}_2 = P({}_kA_o)\vec{e}_z(^0_2) = \frac{1}{4}\left[{}_k\vec{e}_{2z}+{}_k\vec{e}_{3z}+\exp(-ika/2)({}_k\vec{e}_{5z}+{}_k\vec{e}_{6z})\right] $$

etc, through $\vec{f}_{18}$.

Appropriately combining ${}_k\vec{f}_{i\alpha}$'s within each symmetry species one can further separate longitudinal (L) from transversal (T) vibrations and also acoustical (A) from optical (O) ones. The resulting classification is given in Table 1.

${}_kA_o$ { TO, LO, LA	${}_kA_2$ { TO, 2xLO	${}_kB_o$ { TA	${}_kB_2$ { TO	${}_kE_{1,-1}$ { 2xLO, 6xTO, 2xTA

Table 1.

In this basis the dynamical problem is evidently greatly simplified; in addition, one obtains some geometrical and (via the quantum numbers) physical insight into the nature of the vibrational modes. We illustrate some of them in Fig. 2.

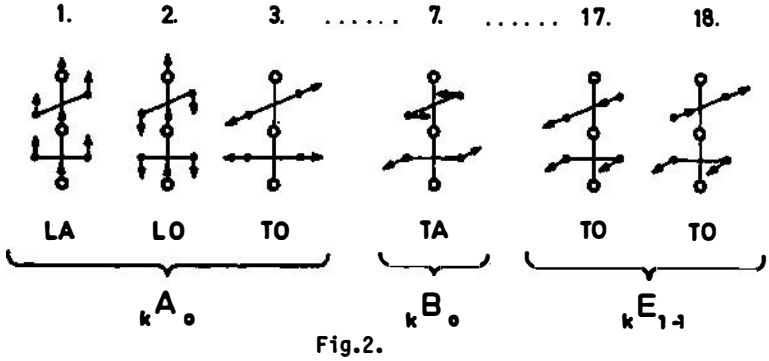

Fig.2.

III. VIBRONIC COUPLING IN THE $(BeH_2)_x$ CHAIN

Band structure. The dynamics of electrons in a polymer chain can be described in terms of the following Hamiltonian:

$$H_e(R,r) = T_e+V_{ee}+V(R,r); \quad V(R,r) \equiv V_{Ne}(R,r)+V_{NN}(R)$$

where R and r denote the totality of nuclear and electronic coordinates, respectively. If R_0 is the equilibrium chain configuration, the electron band structure is obtained by solving

$$H_e(R_0,r)\psi^0_{k\lambda} = \varepsilon^0_\lambda(k)\psi^0_{k\lambda} \qquad (2)$$

for each k-point; λ is the band index.

Symmetry analysis of the band structure of the $(BeH_2)_x$ chain shows that some of the bands (viz. those of ${}_kE_{1,-1}$ symmetry species) are twofold degenerate throughout the Brillouin zone. From the *ab initio* SCF HF LCAO computations of /7,8/ we know this to be the case for the highest occupied valence band (which is of $1s(H),2p_x(Be)_1$, $2p_y(Be)_4$ character). Notice that dimers, trimers etc. do not exhibit degeneracy so that the effect is an essentially polymeric one. More precisely, it appears when the number of monomers is great enough for 4_2- screw axis symmetry to be felt.

Vibronic coupling. Now let the chain change slightly its configuration from R_0 into $R = R_0+Q_i$, where Q_i is a vibrational mode. The electrons are perturbed by

$$V = \sum_i \left(\frac{\partial V}{\partial Q_i}\right)_0 Q_i + \frac{1}{2}\sum_i\sum_j \left(\frac{\partial^2 V}{\partial Q_i \partial Q_j}\right)_0 Q_i Q_j + \cdots\cdots$$

For a nondegenerate energy level, the linear terms should vanish; however, this need not be true for the degenerate ${}_kE_{1,-1}$ -type band that we are considering. If we denote this band calculated at R_0 by $\varepsilon^0(k)$ and the corresponding eigenstates by ψ^0_{1k}, ψ^0_{2k}, one finds that

$$\frac{\partial \varepsilon^0_\alpha}{\partial Q_i} = \int \psi^{0*}_{\alpha k}(r)\,\frac{\partial V}{\partial Q_i}\,\psi^0_{\alpha k}(r)\,d^3r \neq 0,$$

where α=1,2, for certain modes Q_i of specified symmetry properties. We have

identified these active modes for each of the line groups, thus establishing a complete polymeric analogue of the Jahn-Teller theorem.

In our $\underline{L}4_2mc$ case the Jahn-Teller active modes are determined by comparing (1) with

$$\left[{}^{k}E_{1,-1}{}^{2}\right] \sim \begin{cases} q^{A}{}_{0} \oplus q^{A}{}_{2} \oplus q^{B}{}_{2} \text{ with } q=2k \\ q^{A}{}_{0} \oplus q^{A}{}_{2} \oplus q^{B}{}_{0} \text{ with } q=2k\pm 2\pi/a \end{cases} \qquad (3)$$

where $-\pi/a<q\leq\pi/a$. Notice that these modes include some TO modes, like Q_3 in Fig. 2. Lateral instabilities in quasi-1D systems have not been studied in much detail yet and a symmetry argument provides a good starting point.

Next, let us stress that a "paradox" actually exists concerning the band structure of $(BeH_2)_x$ /8/: the stabilization energy for the dimer $(BeH_2)_2$ was calculated to be greater than for the polymer $(BeH_2)_x$. Notice that geometry optimization performed in that computations did not go beyond the full $\underline{L}4_2/mcm$ symmetry. The answer may be sought for in either static (distorsion) or dynamic (vibronic states) effects.

Finally, let us remark that the degeneracy along some special lines or planes in the k-space of 2D- and 3D-systems is in general relatively unimportant, since symmetric k-vectors are outnumbered by the rest. Here, on the contrary, we have bands degenerate for every k; the consequences of this fact might be rather pronounced in some cases.

References

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