Irreducible representations of the symmetry groups of polymers. IV. The relevant subset of a

line group

Irreducible representations of the symmetry groups of polymers: IV. The relevant subset of a line group

Ivan Božović

Department of Physics, Faculty of Science, The University, PO Box 550, 11001 Belgrade, Yugoslavia

Abstract. The irreducible representations of the line groups (constructed in the preceding papers of this series) provide a useful labelling scheme for electron energy bands of stereo-regular polymers and quasi one-dimensional solids. To implant automatic symmetry assignation into a band-structure computing routine one needs a method of dealing with representations of line groups, which are of infinite order. We demonstrate here that the set K of coset representatives of the translational subgroup T of the line group L—which has a finite (and usually quite small) number of elements—contains all the relevant information. Dealing only with K, one can complete the symmetry assignation, decompose a reducible representation and derive selection rules.

1. Introduction

Fundamental and applicative interest in electronic properties of polymers and quasi one-dimensional solids motivated extensive band-structure computations on chain-like atomic models (André *et al* 1980). The spatial symmetry groups of physical objects periodic along a line are *line groups* (Vainshtein 1966, Vujičić *et al* 1977, to be referred to as LG); hence, energy bands of a polymer can be labelled by unitary irreducible representations (reps) of the corresponding line group. Utilising these reps one can derive selection rules, compatibility relations (Božović *et al* 1981) etc.

For a periodic array of atoms, the state space V is a direct sum of subspaces V_k ($-\pi/a < k \leq \pi/a$, a being the repeat length) belonging to the reps d_k of the one-dimensional translational subgroup T. In general, V_k need not be invariant with respect to the whole line group L; hence in *the subgroup method*—which we utilise in the present paper—one replaces L by L_k, the maximal subgroup of L leaving V_k invariant. (If L is of L^+ type, $L_k = L$; if $L = L^- = L^+ + (R^-|0)L^+$, then $L_k = L$ for $k = 0$ and $k = \pi/a$, and $L_k = L^+$ otherwise.) The reps of L_k determine systematic band degeneracies, band touchings at the Brillouin-zone edges etc; the remaining symmetry elements (including the time reversal) impose star degeneracies (Božović and Božović 1981, to be referred to as III). Since L_k is also a line group, its reps can be easily selected out of tables of Božović *et al* (1978), Božović and Vujičić (1981) (to be referred to as I and II, respectively), but one still has to deal with infinite arrays of matrices or character components.

In this paper we prove that in all mentioned applications it is sufficient to consider the set K of coset representatives of T in L_k; the number of elements of K is finite

(in fact, quite small for real polymers), hence the symmetry assignation can readily be automatised.

2. Relevant subset of L_k

The elements of a line group L_k are of the form $(R|v+t)$ where R is a proper or improper rotation, $0 \leq v < 1$ and $t = 0, \pm1, \pm2, \ldots$ (cf LG). Our results are based on the following lemma.

Lemma. Let $_kD$ be a representation (in general, reducible) of L_k in V_k; then

$$_kD(R|v+t) = \exp(ikta)_kD(R|v) \tag{1}$$

for every $(R|v+t) \in L_k$.

The proof of this statement is straightforward but somewhat lengthy; we sketch it in the appendix. Let K denote the set $\{(R|v)|(R|v) \in L_k\}$ of coset representatives of T in L_k; then (1) implies the following theorem.

Theorem 1. Two reps $_kD$ and $_kD^m$ of L_k in V_k are equivalent iff $_k\chi(R|v) = {_k\chi}^m(R|v)$ for every $(R|v) \in K$.

Let $[R|v+t]$ denote the symmetry operator defined in V by $[R|v+t]f(r) \equiv f[(R|v+t)^{-1}r]$ where $f(r) \in V$. To determine the symmetry labels of a given energy level $E_\lambda(k)$ it is sufficient, in view of theorem 1, to represent the operators $[R|v]$, for $(R|v) \in K$, in an eigenbasis belonging to $E_\lambda(k)$ and to compare the traces to the tabulated ones, $_k\chi^m(R|v)$. Hence K conveys all the relevant information. The same fact is observed when one decomposes a reducible representation $_kD$ of L_k in V_k. Let Σ' denote a direct sum and $\sim$ the equivalence of representations; then we have the following theorem.

Theorem 2. Let $_kD \sim \Sigma' n^m {_kD}^m$; then

$$n^m = \frac{1}{|K|} \sum_{(R|v) \in K} {_k\chi}(R|v)^* {_k\chi}^m(R|v) \tag{2}$$

where $_k\chi$ and $_k\chi^m$ denote the traces of $_kD$ and $_kD^m$, respectively. Notice that summation in (2) runs over only $|K|$ elements.

To prove this statement, let us multiply both sides of $_k\chi(R|v+t) = \Sigma_m n^m {_k\chi}^m(R|v+t)$ by $_k\chi^m(R|v+t)^*$ and average over L_k; in view of the above lemma it reduces onto the average over K, and (2) follows.

To derive selection rules for different processes, one has to reduce Kronecker products of reps of L_k. It is not difficult to check that, in view of (1), $_{k_1}D^{m_1}(L_k) \otimes {_{k_2}D}^{m_2}(L_k)$ is a representation of L_k (equal to the smaller of L_{k_1}, L_{k_2}) in V_k, where $k = k_1 + k_2 + 2\pi/a$ if $-2\pi/a < k_1 + k_2 \leq -\pi/a$, $k = k_1 + k_2$ if $-\pi/a < k_1 + k_2 \leq \pi/a$ and $k = k_1 + k_2 - 2\pi/a$ if $\pi/a < k_1 + k_2 \leq 2\pi/a$. Hence one can apply (2), and this considerably facilitates derivation of selection rules. In particular, the wavevector selection rules are immediately obtained:

$$\langle \psi_{k_1}, \hat{A}_q \psi_{k_2} \rangle = 0 \text{ unless } k_1 \doteq q + k_2 \text{ where } \doteq \text{ means 'equal mod}(2\pi/a)'.$$

Finally, dealing only with K, one can construct symmetry adapted bases (SAB's) in V_k, in view of

$$_k\hat{P}^m_{\mu\nu} = \frac{d}{|L_k|} \sum_{(R|v+t)\in L_k} {}_kD^m_{\mu\nu}(R|v+t)^*[R|v+t]$$

$$= \frac{d}{|K|} \sum_{(R|v)\in K} {}_kD^m_{\mu\nu}(R|v)^*[R|v] \tag{3}$$

where d is the dimension of $_kD^m$. Namely, $[R|v+t]f_k(r) = [R|v][E|t]f_k(r) = [R|v]\exp(ikta)f_k(r)$ for every $f_k(r) \in V_k$, so that $[R|v+t] \equiv \exp(ikta)[R|v]$ (in V_k) for every $(R|v+t) \in L_k$ and (3) follows in view of (1) and $|L_k| = |T| \cdot |K|$.

3. Conclusions

Line-group theoretical considerations can be efficiently implanted into computer programs for electron band-structure calculations on polymers and quasi-1D solids, since it is sufficient to deal explicitly with only few symmetry elements. Considering the set K of coset representatives of T in L_k, one can label the energy bands and derive SAB's, selection rules and compatibility relations.

A few remarks might be in order. First, further reductions are visible in some cases: (i) for one-dimensional reps, generators of L_k are sufficient; (ii) for L^+ type line groups, $_kD^m(R|v) = \exp(ikva)D^m(R)$, cf I, etc. However, dealing with K in computer applications one retains—on the account of negligible increase of numerical work—uniform treatment of every rep of every line group, as well as maximal conceptual simplicity.

Finally, notice that all the results given here apply also to vibration branches, exciton bands etc, since the corresponding Hamiltonians also commute with L.

Acknowledgment

Appendix 1

To prove the Lemma, let us first note that if (1) is true for a certain representation $_kD$ of L_k it is also valid for any other representation $_kG$ equivalent to $_kD$. Namely, if $_kG(R|v+t) = P^{-1}{}_kD(R|v+t)P$ for some non-singular matrix P, then $_kG(R|v+t) = \exp(ikta)P^{-1}{}_kD(R|v)P = \exp(ikta)_kG(R|v)$. Thus without any loss of generality we can consider only the representations actually decomposed into irreducible blocks, the latter being in the 'standard' form given in I and II. If (1) is true for the reps $_kD^m$ it is also valid for any $\Sigma'_m n^m{}_kD^m$; hence it remains to analyse each type of the reps of L_k. We proceed to that now, assuming familiarity with I and II, omitting the unnecessary indices and choosing a for length unit, so that $-\pi < k \le \pi$.
  (i) If L_k is of L^+ type, one has $_kD(R|v+t) = \exp[ik(v+t)]D(R)$ and (1) follows.
  (ii) If L_k is of L^- type and $k = 0$ one has $_0D(R|v+t) = {}_0D(R)$; (1) is true.

(iii) If L_k is of L^- type and symmorphic, then $v = 0$ and for $k = \pi$ one has $_\pi D(R|t) = (-1)^t D(R)$; (1) is fulfilled.

(iv) If L_k is of L^- type and non-symmorphic, if $k = \pi$ and $_\pi D(L^- \downarrow L^+) = {}_\pi d(L^+)$, i.e. if $_\pi D$ subduces onto a rep $_\pi d$ of L^+ (which is an order two subgroup of L_k), one has $_\pi D(R^+|v + t) = {}_\pi d(R^+|v + t) = (-1)^t {}_\pi D(R^+|v)$ and either

$$_\pi D(R^- R^+|-v - t) = {}_\pi d(R^+|v + t) = (-1)^t {}_\pi D(R^- R^+|-v)$$

or

$$_\pi D(R^- R^+|-v - t) = -{}_\pi d(R^+|v + t) = (-1)^t {}_\pi D(R^- R^+|-v)$$

so that (1) is true in either case.

(v) The last possibility is that L_k is of L^- type, non-symmorphic, $k = \pi$ and

$$_\pi D(R^+|v + t) = \begin{pmatrix} {}_\pi d(R^+|v + t) & 0 \\ 0 & {}_\pi d(R^- R^+(R^-)^{-1}|-v - t) \end{pmatrix} = (-1)^t {}_\pi D(R^+|v)$$

$$_\pi D(R^- R^+|-v - t)$$

$$= \begin{pmatrix} 0 & {}_\pi d(R^- R^+(R^-)^{-1}|-v - t) \\ {}_\pi d((R^-)^2 R^+|v + t) & 0 \end{pmatrix} = (-1)^t {}_\pi D(R^- R^+|-v)$$

where $_\pi d$ (as well as $_\pi \bar{d}$) is a rep of L^+; (1) is evidently valid in this case also, and the lemma is proved.

References

André J-M, Brédas J-L, Delhalle J, Ladik J, Leroy G and Moser C (ed) 1980 *Recent Advances in the Quantum Theory of Polymers: Lecture Notes in Physics* vol 113 (Berlin: Springer)
Božović I and Božović N 1981 *J. Phys. A: Math. Gen.* **14** 1825-34
Božović I, Delhalle I and Damnjanović M 1981 *Int. J. Quantum Chem.* **20** 1143-63
Božović I and Vujičić M 1981 *J. Phys. A: Math. Gen.* **14** 777-95
Božović I, Vujičić M and Herbut F 1978 *J. Phys. A: Math. Gen.* **11** 2133-47
Vujičić M, Božović I and Herbut F 1977 *J. Phys. A: Math. Gen.* **10** 1271-9
Vainshtein B K 1966 *Diffraction of X-Rays by Chain Molecules* (Amsterdam: Elsevier) p 53