Selection rules for vibronic coupling in quasi-one-dimensional solids: I. Eclipsed molecular stacks

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Abstract. Symmetrised Kronecker squares of irreducible representations of line groups are decomposed into irreducible constituents. Selection rules for linear vibronic-coupling matrix elements are derived. They provide a systematic method of identification of the Peierls modes in conducting polymers and quasi-one-dimensional metals.

1. Introduction

Quasi-one-dimensional (QID) metals have attracted a lot of interest in the last decade (Miller 1982, Kuzmany *et al* 1985, Monceau 1985, Kamimura 1985, Skotheim 1986). They frequently show some remarkable topological effects of reduced dimensionality, the best known of which is the Peierls instability (Peierls 1955). The total adiabatic energy of a monatomic periodic chain with a partially filled conduction band contains a term proportional to $Q^2 \ln Q$, where Q is a small longitudinal distortion of wavelength $\lambda = \pi/k_F$; here k_F is the wavevector corresponding to the Fermi level E_F. Consequently, the chain distorts along Q.

The actual QID crystals and polymers may contain many atoms in the unit cell; nevertheless, the above Peierls theorem can be generalised (Božović 1985a) to such complex chains. In most real cases only one or two out of many possible normal modes of such a system turn out to be 'Peierls active', i.e. of such a symmetry that the matrix element of linear electron-phonon coupling, $\langle e | Q \cdot (\partial V/\partial Q)_0 | e' \rangle$, does not vanish identically. (Here V denotes the effective one-electron potential, and $|e\rangle, |e'\rangle$ are the degenerate one-electron eigenstates at E_F.)

A systematic method of determining all such linearly vibronically allowed modes is as follows: (i) identify the (grey) line group L of the polymer under study, (ii) find the irreducible (co)representation D of the states $|e\rangle, |e'\rangle, \ldots,$ at E_F, (iii) construct the symmetrised Kronecker square $[D^2]$, (iv) decompose $[D^2]$ into its irreducible components D_i, $i = 1, 2, \ldots, r$, and (v) identify the corresponding normal modes (e.g. by constructing the symmetry-adapted bases of D_i, cf Božović and Delhalle (1984) or Koch and Seelig (1987)).

Vibronic instabilities in molecules with electronic degeneracies had been predicted long ago (Jahn and Teller 1937) by applying the above algorithm to all the point groups; the result was the well known Jahn-Teller theorem. Several space groups had also been explored along these lines (Birman 1959). Despite the extensive experimental

and theoretical research on vibronic instabilities in Q1D and Q2D metals, no comprehensive group-theoretical treatment has appeared yet. (A few representative cases were analysed in some detail in Božović (1984).) In this paper, we report the selection rules for linear vibronic coupling for all the symmorphic line groups (Ln, Lnm, $Lnmm$, Ln/m, $Ln2$, $Ln22$, $L\bar{n}$, $L(\overline{2n})$, $L\bar{n}m$, $L(\overline{2n})2m$, Ln/mmm). They enable direct identification of the Peierls modes in every Q1D eclipsed-stack molecular conductor, such as TTF—TCNQ, Ni—phtalocyanine or the platinum salts such as $PtCl_4PtN_4$. The same selection rules also govern the two-photon infrared absorption processes involving the overtones of a degenerate normal mode (Cracknell 1975).

The results are presented in tables 1–7 below. Three independent methods (the group character formula, the symmetry-adapted basis construction and the direct summation) were utilised to derive and check the entries. The details of the method and the proofs are omitted for brevity; instead, a brief reminder of the line group notation is added for self-containedness.

2. Notation

A one-dimensional irreducible representation of a line group L is denoted by A if it is even with respect to the vertical mirror reflection (or if that symmetry element is absent from L) and by B if it is odd. Two- and four-dimensional representations are denoted by E and G, respectively. Other relevant quantum numbers include the quasimomentum $\hbar k$ and the quasi-angular momentum $\hbar m$ (Božović *et al* 1978, Božović and Vujičić 1981). Since the time-reversal symmetry has to be included we have to use the irreducible corepresentations or, equivalently, the unitary-antiunitary representations (Herbut *et al* 1980) or the physical representations (Landau and Lifshitz 1977). These are denoted below by the same (short) symbol as its subduced ordinary irreducible representation, if the latter is real; in the opposite case (Frobenius–Schur type (b) and (c) representations, Božović and Božović (1981)) a pair of such symbols, denoting the two complex-conjugate ordinary representations, is enclosed in a single bracket. To simplify the notation, we take $\hbar = 1$ and the translation period $a = 1$, so that

$$0 \leqslant k < \pi \qquad m = \begin{cases} 1, 2, \ldots, (n-2)/2 & \text{for } n \text{ even} \\ 1, 2, \ldots, (n-1)/2 & \text{for } n \text{ odd} \end{cases} \qquad (1)$$

where n is the order of the principal rotation axis.

In table 1 we reproduce the characters of all the representations of the symmorphic line groups isogonal to D_{nh}, $n = 1, 2, \ldots$. Since all the other line groups considered here are their subgroups, this is sufficient to define their representations, too. Matrices of all the representations of line groups were given explicitly by Božović *et al* (1978) and Božović and Vujičić (1981).

3. Irreducible components of the symmetrised Kronecker squares of corepresentations of all symmorphic line groups

Symmetrised Kronecker squares (SKS) of real irreps of all the symmorphic line groups are presented in tables 2–8. Further abbreviations, utilised in these tables, are

$$p = 2k \qquad t = 2\pi - 2k \qquad (2)$$

$$w = 2m \qquad v = 2m - n. \qquad (3)$$

Table 1. The characters of the irreducible representations of the line groups $L(\overline{2n})2m$ $(n = 1, 3, \ldots)$ and Ln/mmm $(n = 2, 4, \ldots)$. Here $s = 0, 1, \ldots, n-1$ and $t = 0, \pm 1, \ldots$; C_n denotes the rotation around the z axis by $\alpha = 2\pi/n$; σ_v and σ_h denote the reflections in the xz and xy planes, respectively. $(C_n^s|t)$ denotes the rotation C_n^s followed by the translation for tae_z, where a is the translation period.

Representation	$(C_n^s\|t)$	$(\sigma_v C_n^s\|t)$	$(\sigma_h C_n^s\|-t)$	$(\sigma_h\sigma_v C_n^s\|-t)$
$(_0A_{0+})$	1	1	1	1
$(_0B_{0+})$	1	-1	1	1
$(_0E_{m+})$	$2\cos ms\alpha$	0	$2\cos ms\alpha$	0
$(_kEA_0)$	$2\cos kt$	$2\cos kt$	0	0
$(_kEB_0)$	$2\cos kt$	$-2\cos kt$	0	0
$(_kG_m)$	$4\cos kt\cos ms\alpha$	0	0	0
$(_\pi A_{0+})$	$(-1)^t$	$(-1)^t$	$(-1)^t$	$(-1)^t$
$(_\pi B_{0+})$	$(-1)^t$	$-(-1)^t$	$(-1)^t$	$(-1)^t$
$(_\pi E_{m+})$	$(-1)^t 2\cos ms\alpha$	0	$(-1)^t 2\cos ms\alpha$	0
$(_0A_{q+})$	$(-1)^s$	$(-1)^s$	$(-1)^s$	$(-1)^s$
$(_0B_{q+})$	$(-1)^s$	$-(-1)^s$	$(-1)^s$	$(-1)^s$
$(_kEA_q)$	$(-1)^s 2\cos kt$	$(-1)^s 2\cos kt$	0	0
$(_kEB_q)$	$(-1)^s 2\cos kt$	$-(-1)^s 2\cos kt$	0	0
$(_\pi A_{q+})$	$(-1)^{s+t}$	$(-1)^{s+t}$	$(-1)^{s+t}$	$(-1)^{s+t}$
$(_\pi B_{q+})$	$(-1)^{s+t}$	$-(-1)^{s+t}$	$(-1)^{s+t}$	$(-1)^{s+t}$

A dagger (†) indicates that the result is valid for $n = 2q = 2, 4, \ldots$, only; two daggers (††) mean 'for $n = 2q = 4, 8, \ldots$, only'.

Since the totally symmetric (identical) representation appears in every symmetrised Kronecker square $[D^2]$, it is subtracted from the result of the decomposition of $[D^2]$ to reduce the tables.
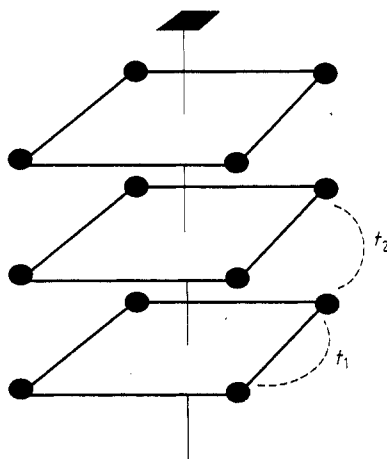
Figure 1. The model polymer of $L4/mmm$ line-group symmetry: a periodic array of equidistant square planar molecules in the eclipsed position.

Table 2. Symmetrised Kronecker squares (SKS) of real ireps of the line groups Ln ($n = 1, 2, \ldots$).

D			$[D^2] - (_0A_0)$
$(_0A_m, _0A_{-m})$		$m < n/4$	$(_0A_w, _0A_{-w})$
		$m = n/4\dagger\dagger$	$2(_0A_q)$
		$m > n/4$	$(_0A_v, _0A_{-v})$
$(_kA_0, _{-k}A_0)$	$k < \pi/2$		$(_pA_0, _{-p}A_0)$
	$k = \pi/2$		$2(_\pi A_0)$
	$k > \pi/2$		$(_tA_0, _{-t}A_0)$
$(_kA_m, _{-k}A_{-m})$	$k < \pi/2$	$m < n/4$	$(_pA_w, _{-p}A_{-w})$
		$m = n/4\dagger\dagger$	$(_pA_q, _{-p}A_q)$
		$m > n/4$	$(_pA_{-v}, _{-p}A_v)$
	$k = \pi/2$	$m < n/4$	$(_\pi A_w, _\pi A_{-w})$
		$m = n/4\dagger\dagger$	$2(_\pi A_q)$
		$m > n/4$	$(_\pi A_v, _\pi A_{-v})$
	$k > \pi/2$	$m < n/4$	$(_tA_{-w}, _{-t}A_w)$
		$m = n/4\dagger\dagger$	$(_tA_q, _{-t}A_q)$
		$m > n/4$	$(_tA_v, _{-t}A_{-v})$
$(_kA_{-m}, _{-k}A_m)$	$k < \pi/2$	$m < n/4$	$(_pA_{-w}, _{-p}A_w)$
		$m = n/4\dagger\dagger$	$(_pA_q, _{-p}A_q)$
		$m > n/4$	$(_pA_v, _{-p}A_{-v})$
	$k = \pi/2$	$m < n/4$	$(_\pi A_w, _\pi A_{-w})$
		$m = n/4\dagger\dagger$	$2(_\pi A_q)$
		$m > n/4$	$(_\pi A_v, _\pi A_{-v})$
	$k > \pi/2$	$m < n/4$	$(_tA_w, _{-t}A_{-w})$
		$m = n/4\dagger\dagger$	$(_tA_q, _{-t}A_q)$
		$m > n/4$	$(_tA_{-v}, _{-t}A_v)$
$(_kA_q, _{-k}A_q)\dagger$	$k < \pi/2$		$(_pA_0, _{-p}A_0)$
	$k = \pi/2$		$2(_\pi A_0)$
	$k > \pi/2$		$(_tA_0, _{-t}A_0)$
$(_\pi A_m, _\pi A_{-m})$		$m > n/4$	$(_0A_w, _0A_{-w})$
		$m = n/4\dagger$	$2(_0A_q)$
		$m > n/4$	$(_0A_v, _0A_{-v})$

4. Examples

Let us now illustrate how these tables can be used to analyse vibronic instabilities in Q1D metals. We shall consider an eclipsed stack of square planar molecules shown in figure 1. This model is rich enough to include some of the most complex cases possible—such as ten-dimensional $[D^2]$ representations—and yet simple enough to make the analysis transparent. Furthermore, a detailed account of the underlying physics—complementary to the present one since it omitted the group-theoretical aspects which are our principal interest here—is already available (Božović 1984).

The line group of the model polymer shown in figure 1 is L4/mmm. The corresponding vibronic-coupling selection rules are given in table 8. To be specific, let us further

Table 3. SKS of real ireps of the line groups Lnm ($n = 1, 3, \ldots$) and Lnmm ($n = 2q = 2, 4, \ldots$).

D			$[D^2] - (_0A_0)$
$(_0E_m)$		$m < n/4$	$(_0E_w)$
		$m = n/4$††	$(_0A_q) + (_0B_q)$
		$m > n/4$	$(_0E_v)$
$(_kA_0, _{-k}A_0)$	$k < \pi/2$		$(_pA_0, _{-p}A_0)$
	$k = \pi/2$		$2(_\pi A_0)$
	$k > \pi/2$		$(_tA_0, _{-t}A_0)$
$(_kE_m, _{-k}E_m)$	$k < \pi/2$	$m < n/4$	$(_pE_w, _{-p}E_w) + (_pA_0, _{-p}A_0) + (_0E_w) + (_0B_0)$
		$m = n/4$††	$(_pA_q, _{-p}A_q) + (_pB_q, _{-p}B_q) + (_pA_0, _{-p}A_0) + (_0A_q) + (_0B_q)$
			$+ (_0B_0)$
		$m > n/4$	$(_pE_v, _{-p}E_w) + (_pA_0, _{-p}A_0) + (_0E_v) + (_0B_0)$
	$k = \pi/2$	$m < n/4$	$2(_\pi E_w) + 2(_\pi A_0) + (_0E_w) + (_0B_0)$
		$m = n/4$††	$2(_\pi A_q) + 2(_\pi B_q) + 2(_\pi A_0) + (_0A_q) + (_0B_q) + (_0B_0)$
		$m > n/4$	$2(_\pi E_v) + 2(_\pi A_0) + (_0E_v) + (_0B_0)$
	$k > \pi/2$	$m < n/4$	$(_tE_w, _{-t}E_w) + (_tA_0, _{-t}A_0) + (_0E_w) + (_0B_0)$
		$m = n/4$††	$(_tA_q, _{-t}A_q) + (_tB_q, _{-t}B_q) + (_tA_0, _{-t}A_0) + (_0A_q) + (_0B_q)$
			$+ (_0B_0)$
		$m > n/4$	$(_tE_v, _{-t}E_v) + (_tA_0, _{-t}A_0) + (_0E_v) + (_0B_0)$
$(_kA_q, _{-k}A_q)$†	$k < \pi/2$		$(_pA_0, _{-p}A_0)$
	$k = \pi/2$		$2(_\pi A_0)$
	$k > \pi/2$		$(_tA_0, _{-t}A_0)$
$(_kB_q, _{-k}B_q)$†	$k < \pi/2$		$(_pA_0, _{-p}A_0)$
	$k = \pi/2$		$2(_\pi A_0)$
	$k > \pi/2$		$(_tA_0, _{-t}A_0)$
$(_\pi E_m)$		$m < n/4$	$(_0E_w)$
		$m = n/4$††	$(_0A_q) + (_0B_q)$
		$m > n/4$	$(_0E_v)$

assume that each atom contributes one atomic orbital of the $l = 0$ type (i.e. s, p, d_z, etc), and let t_1 and t_2 denote the intra- and inter-molecular transfer integrals (see figure 1). Then the tight-binding electron energy bands are given by

$$E(_kA_0) = 2t_1 + 2t_2 \cos ka$$
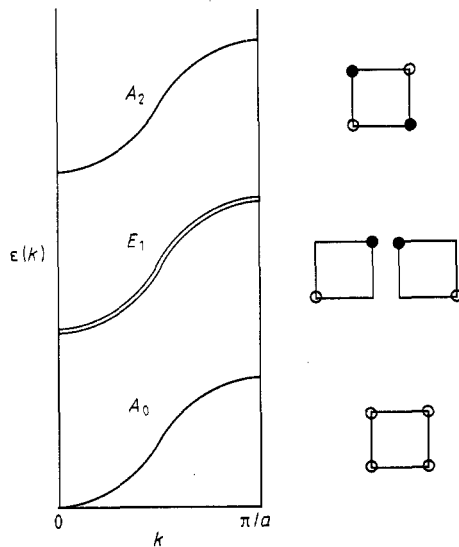
$$E(_kE_1) = 2t_2 \cos ka$$

$$E(_kE_2) = -2t_1 + 2t_2 \cos ka.$$

These bands are shown in figure 2 for $t_1 < 0$, $t_2 < 0$ and $|t_2| > 2|t_1|$, together with the corresponding one-electron states. Note that the middle E_1 band is twofold degenerate throughout the Brillouin zone.

Case 1. If each molecule contributes one electron, the lowest (A_0) band is half filled. The Fermi-level states transform according to $D = (_{\pi/2}A_0) + (_{\pi/2}A_0) = (_{\pi/2}EA_0)$. The matrix element $\langle e' | \boldsymbol{Q} \cdot (\partial v / \partial \boldsymbol{Q})_0 | e \rangle$ is non-zero only if $[D^2] = [_{\pi/2}EA_0^2]$ contains the representation D_Q of that particular phonon $\boldsymbol{Q}$. From table 8, entry $(_kEA_0)$, case

Table 4. SKS of real ireps of the line groups Ln/m ($n = 1, 2, \ldots$). Here $w = 2m$, $v = 2m - n$, $p = 2k$ and $t = 2\pi - 2k$.

D			$[D^2] - ({}_0A_{0+})$
$({}_0A_{m\pm}, {}_0A_{-m\pm})$		$m < n/4$	$({}_0A_{w+}, {}_0A_{-w+})$
		$m = n/4$††	$2({}_0A_{q+})$
		$m > n/4$	$({}_0A_{v+}, {}_0A_{v-})$
$({}_kE_0)$	$k < \pi/2$		$({}_pE_0)$
	$k = \pi/2$		$({}_\pi A_{0+}) + ({}_\pi A_{0-})$
	$k > \pi/2$		$({}_tE_0)$
$({}_kE_m, {}_kE_{-m})$	$k < \pi/2$	$m < n/4$	$({}_pE_w, {}_pE_{-w}) + ({}_pE_0) + ({}_0A_{w+}, {}_0A_{-w+}) + ({}_0A_{0-})$
		$m = n/4$††	$2({}_pE_q) + ({}_pE_0) + 2({}_0A_{q+}) + ({}_0A_{0-})$
		$m > n/4$	$({}_pE_v, {}_pE_{-v}) + ({}_pE_0) + ({}_0A_{v+}, {}_0A_{-v+}) + ({}_0A_{0-})$
	$k = \pi/2$	$m < n/4$	$({}_\pi A_{w+}, {}_\pi A_{-w+}) + ({}_\pi A_{w-}, {}_\pi A_{-w-}) + ({}_\pi A_{0+}) + ({}_\pi A_{0-})$ $+ ({}_0A_{w+}, {}_0A_{-w+}) + ({}_0A_{0-})$
		$m = n/4$††	$2({}_\pi A_{q+}) + 2({}_\pi A_{q-}) + ({}_\pi A_{0+}) + ({}_\pi A_{0-}) + 2({}_0A_{q+}) + ({}_0A_{0-})$
		$m > n/4$	$({}_\pi A_{v+}, {}_\pi A_{-v+}) + ({}_\pi A_{v-}, {}_\pi A_{-v-}) + ({}_\pi A_{0+}) + ({}_\pi A_{0-})$ $+ ({}_0A_{v+}, {}_0A_{-v+}) + ({}_0A_{0-})$
	$k > \pi/2$	$m < n/4$	$({}_tE_w, {}_tE_{-w}) + ({}_tE_0) + ({}_0A_{w+}, {}_0A_{-w+}) + ({}_0A_{0-})$
		$m = n/4$††	$2({}_tE_q) + ({}_tE_0) + 2({}_0A_{q+}) + ({}_0A_{0-})$
		$m > n/4$	$({}_tE_v, {}_tE_{-v}) + ({}_tE_0) + ({}_0A_{v+}, {}_0A_{-v+}) + ({}_0A_{0-})$
$({}_kE_q)$†	$k < \pi/2$		$({}_pE_0)$
	$k = \pi/2$		$({}_\pi A_{0+}) + ({}_\pi A_{0-})$
	$k > \pi/2$		$({}_tE_0)$
$({}_\pi A_{m\pm}, {}_\pi A_{-m\pm})$		$m < n/4$	$({}_0A_{w+}, {}_0A_{-w+})$
		$m = n/4$††	$2({}_0A_{q+})$
		$m > n/4$	$({}_0A_{v+}, {}_0A_{-v+})$

Figure 2. The tight-binding one-electron band structure of the polymer in figure 1.

Table 5. SKS for real ireps of the line groups Ln2 ($n = 1, 3, \ldots$) and Ln22 ($n = 2, 4, \ldots$). Here $w = 2m$, $v = 2m - n$, $p = 2k$ and $t = 2\pi - 2k$.

D			$[D^2] - (_0A_{0+})$
$(_0E_m)$		$m < n/4$	$(_0E_w)$
		$m = n/4$††	$(_0A_{q+}) + (_0A_{q-})$
		$m > n/4$	$(_0E_v)$
$(_kE_{\pm m})$	$k < \pi/2$	$m \leqslant n/4$	$(_pE_w)$
		$m > n/4$	$(_pE_v)$
	$k = \pi/2$	$m < n/4$	$(_\pi E_w)$
		$m = n/4$††	$(_\pi A_{q+}) + (_\pi A_{q-})$
		$m > n/4$	$(_\pi E_v)$
	$k > \pi/2$	$m \leqslant n/4$	$(_t E_w)$
		$m > n/4$	$(_t E_v)$
$(_kE_q)$†	$k < \pi/2$		$(_pE_0)$
	$k = \pi/2$		$(_\pi A_{0+}) + (_\pi A_{0-})$
	$k > \pi/2$		$(_t E_0)$
$(_\pi E_m)$		$m < n/4$	$(_0E_w)$
		$m = n/4$	$(_0A_{q+}) + (_0A_{q-})$
		$m > n/4$	$(_0E_v)$

$k = \pi/2$, we find that

$$[_{\pi/2}EA_0^2] = (_\pi A_{0+}) + (_\pi A_{0-}) + (_0A_{0+}).$$

(Here we have added the identity representation $(_0A_{0+})$, which appears in every $[D^2]$.) The next step is to construct the vibration modes which transform according to $(_\pi A_{0+})$ and $(_\pi A_{0-})$ respectively. This can be done by utilising the standard methods for construction of symmetry-adapted bases (see Božović (1984) and references therein); the results are shown in figure 3. Hence, in this case, there are two competing instabilities, one of which, $(_\pi A_{0-})$, is longitudinal and displacive, while the other, $(_\pi A_{0+})$, is transverse and distortive. The first of these two types of vibronically induced transitions is most frequent in organic molecular stacks, while the second is found in many transition-metal chalcogenides.

Case 2. If each atom contributes one electron, the middle (E_1) band will be half filled. The Fermi-level states belong to

$$(_{\pi/2}E_1) + (_{-\pi/2}E_1) = (_{\pi/2}G_1).$$

From table 8, entry $(_kG_m)$, case $k = \pi/2$, $m = n/4 = 1$, and noting that $q = n/2 = 2$, we find that

$$[_{\pi/2}G_1^2] = (_\pi A_{2+}) + (_\pi B_{2+}) + (_\pi A_{2-}) + (_\pi B_{2-}) + (_\pi A_{0+})$$
$$+ (_\pi A_{0-}) + (_0A_{2+}) + (_0B_{2+}) + (_0B_{0-}) + (_0A_{0+}).$$

Out of these ten representations one, $(_0A_{0+})$, is trivial and for two others, $(_0B_{0-})$ and $(_\pi B_{2-})$, there are no corresponding phonons. The modes of $(_\pi A_{0+})$ and $(_\pi A_{0-})$ symmetry were already given in figure 3; the remaining five modes are shown in figure 4.

In an analogous way, all vibronically active modes can be determined for any given polymer provided its spatial and electronic structures are known.

Table 6. SKS of real ireps of the line groups $L\bar{n}$ $(n = 1, 3, \ldots)$ and $L(\overline{2n})$, $(n = 2, 4, \ldots)$. For $D = ({}_0A_{0\pm})$ and $D = ({}_\pi A_{0\pm})$, $[D^2] = ({}_0A_{0+})$.

D			$[D^2] - ({}_0A_{0+})$
$({}_0A_{m\pm}, {}_0A_{-m\pm})$		$m < n/4$	$({}_0A_{w+}, {}_0A_{w-})$
		$m = n/4$††	$({}_0A_{q+}, {}_0A_{q-})$
		$m > n/4$	$({}_0A_{v+}, {}_0A_{-v+})$
$({}_0A_{q+}, {}_0A_{q-})$†			$({}_0A_{0+}) + ({}_0A_{0-})$
$({}_kE_0)$	$k < \pi/2$		$({}_pE_0)$
	$k = \pi/2$		$({}_\pi A_{0+}) + ({}_\pi A_{0-})$
	$k > \pi/2$		$({}_tE_0)$
$({}_kE_m, {}_kE_{-m})$	$k < \pi/2$	$m < n/4$	$({}_pE_w, {}_pE_{-w}) + ({}_pE_0) + ({}_0A_{w+}, {}_0A_{-w+}) + ({}_0A_{0-})$
		$m = n/4$††	$({}_pE_q, {}_pE_q) + ({}_pE_0) + ({}_0A_{q+}, {}_0A_{q-}) + ({}_0A_{0-})$
		$m > n/4$	$({}_pE_v, {}_pE_{-v}) + ({}_pE_0) + ({}_0A_{v-}, {}_0A_{-v-}) + ({}_0A_{0-})$
	$k = \pi/2$	$m < n/4$	$({}_\pi A_{w+}, {}_\pi A_{-w+}) + ({}_\pi A_{w-}, {}_\pi A_\pi A_{-w-}) + ({}_\pi A_{0+})$
			$({}_\pi A_{0-}) + ({}_0A_{w+}, {}_0A_{-w+}) + ({}_0A_{0-})$
		$m = n/4$††	$2({}_\pi A_{q+}, {}_\pi A_{q-}) + ({}_\pi A_{0+}) + ({}_\pi A_{0-}) + ({}_0A_{q+}, {}_0A_{q-})$
			$+ ({}_0A_{0-})$
		$m > n/4$	$({}_\pi A_{v+}, {}_\pi A_{-v+}) + ({}_\pi A_{v-}, {}_\pi A_{-v-}) + ({}_\pi A_{0+})$
			$({}_\pi A_{0-}) + ({}_0A_{v-}, {}_0A_{-v-}) + ({}_0A_{0-})$
	$k > \pi/2$	$m < n/4$	$({}_tE_w, {}_tE_{-w}) + ({}_tE_0) + ({}_0A_{w+}, {}_0A_{-w+}) + ({}_0A_{0-})$
		$m = n/4$††	$({}_tE_q, {}_tE_q) + ({}_tE_0) + ({}_0A_{q+}, {}_0A_{q-}) + ({}_0A_{0-})$
		$m > n/4$	$({}_tE_v, {}_tE_{-v}) + ({}_tE_0) + ({}_0A_{v-}, {}_0A_{-v-}) + ({}_0A_{0-})$
$({}_kE_q, {}_kE_q)$†	$k < \pi/2$		$3({}_pE_0) + 2({}_0A_{0-}) + ({}_0A_{0+})$
	$k = \pi/2$		$3({}_\pi A_{0+}) + 3({}_\pi A_{0-}) + 2({}_0A_{0-}) + ({}_0A_{0+})$
	$k > \pi/2$		$3({}_tE_0) + 2({}_0A_{0-}) + ({}_0A_{0+})$
$({}_\pi A_{m\pm}, {}_\pi A_{-m\pm})$		$m < n/4$	$({}_0A_{w+}, {}_0A_{-w+})$
		$m = n/4$††	$({}_0A_{q+}, {}_0A_{q-})$
		$m > n/4$	$({}_0A_{v-}, {}_0A_{-v-})$
$({}_\pi A_{g+}, {}_\pi A_{g-})$			$({}_0A_{0+}) + ({}_0A_{0-})$

5. Conclusions and discussions

A detailed inspection of tables 2–8 reveals several interesting facts. First, the quasi-momentum, the quasi-angular momentum and the well defined parities with respect to vertical or horizontal mirror planes, or the dihedral axes, are all conserved in the scattering processes studied here. Indeed, these are good quantum numbers, which can be conveniently used to identify and label the corresponding linearly vibronically active modes. (Some concrete physical examples have been worked out in Božović (1984, 1985a, 1986).)

Second, not all the Clebsh-Gordan (or frequency) coefficients are one (or zero); for several four-dimensional representations $[D^2]$ contains some irreducible components twice. One can use the Wigner-Eckart theorem in these cases to obtain some further selection rules.

Table 7. SKS of real ireps of the line groups $L\tilde{n}m$ ($n = 1, 3, \ldots$) and $L(\overline{2n})2m$ ($n = 2, 4, \ldots$).

D			$[D^2] - (_0A_{0+})$
$(_0E_{m\pm})$	$m < n/4$		$(_0E_{w+})$
	$m = n/4$††		$(_0E_q)$
	$m > n/4$		$(_0E_{v-})$
$(_0E_q)$†			$(_0A_{0-}) + (_0B_{0+})$
$(_kEA_0)$	$k < \pi/2$		$(_pEA_0)$
	$k = \pi/2$		$(_\pi A_{0+}) + (_\pi A_{0-})$
	$k > \pi/2$		$(_tEA_0)$
$(_kEB_0)$	$k < \pi/2$		$(_pEA_0)$
	$k = \pi/2$		$(_\pi A_{0+}) + (_\pi A_{0-})$
	$k > \pi/2$		$(_tEA_0)$
$(_kG_m)$	$k < \pi/2$	$m < n/4$	$(_pG_w) + (_pEA_0) + (_0E_{w+}) + (_0B_{0+})$
		$m = n/4$††	$(_pEA_q, {_p}EB_q) + (_pEA_0) + (_0E_q) + (_0B_{0+})$
		$m > n/4$	$(_pG_v) + (_pEA_0) + (_0E_{v-}) + (_0B_{0+})$
	$k = \pi/2$	$m < n/4$	$(_\pi E_{w+}) + (_\pi E_{w-}) + (_\pi A_{0+}) + (_\pi A_{0-}) + (_0E_{w+}) + (_0B_{0+})$
		$m = n/4$††	$2(_\pi E_q) + (_\pi A_{0+}) + (_\pi A_{0-}) + (_0E_q) + (_0B_{0+})$
		$m > n/4$	$(_\pi E_{v+}) + (_\pi E_{v-}) + (_\pi A_{0+}) + (_\pi A_{0-}) + (_0E_{v-}) + (_0B_{0+})$
	$k > \pi/2$	$m < n/4$	$(_tG_w) + (_tEA_0) + (_0E_{w+}) + (_0B_{0+})$
		$m = n/4$††	$(_tEA_q, {_t}EB_q) + (_tEA_0) + (_0E_q) + (_0B_{0+})$
		$m > n/4$	$(_tG_v) + (_tEA_0) + (_0E_{v-}) + (_0B_{0+})$
$(_kEA_q, {_k}EB_q)$†	$k < \pi/2$		$2(_pEA_0) + (_pEB_0) + (_0A_{0-}) + (_0B_{0+}) + (_0B_{0-})$
	$k = \pi/2$		$2(_\pi A_{0+}) + 2(_\pi A_{0-}) + (_\pi B_{0+}) + (_\pi B_{0-}) + (_0A_{0-}) + (_0B_{0+})$ $+ (_0B_{0-})$
	$k > \pi/2$		$2(_tEA_0) + (_tEB_0) + (_0A_{0-}) + (_0B_{0+}) + (_0B_{0-})$
$(_\pi E_{m\pm})$	$m < n/4$		$(_0E_{w+})$
	$m = n/4$††		$(_0E_q)$
	$m > n/4$		$(_0E_{v-})$
$(_\pi E_q)$†			$(_0A_{0-}) + (_0B_{0+})$

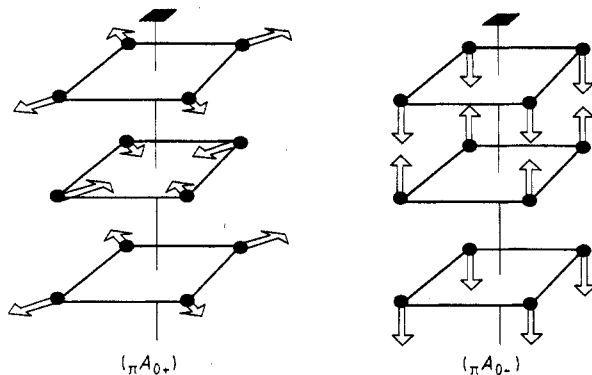$(_\pi A_{0+})$ $(_\pi A_{0-})$

Figure 3. The vibronically active modes of the polymer in figure 1, in the case when the (A_0) band is half filled.

Table 8. SKS for real ireps of the line groups $L(\overline{2n})2m$ ($n = 1, 3, ..$) and Ln/mmm ($n = 2, 4, \ldots$).

D			$[D^2] - ({}_0A_{0+})$
$({}_0E_{m\pm})$		$m < n/4$	$({}_0E_{w+})$
		$m = n/4\dagger\dagger$	$({}_0A_{q+}) + ({}_0B_{q+})$
		$m > n/4$	$({}_0E_{v+})$
$({}_kEA_0)$	$k < \pi/2$		$({}_pEA_0)$
	$k = \pi/2$		$({}_\pi A_{0+}) + ({}_\pi A_{0-})$
	$k > \pi/2$		$({}_lEA_0)$
$({}_kEB_0)$	$k < \pi/2$		$({}_pEA_0)$
	$k = \pi/2$		$({}_\pi A_{0+}) + ({}_\pi A_{0-})$
	$k > \pi/2$		$({}_lEA_0)$
$({}_kG_m)$	$k < \pi/2$	$m < n/4$	$({}_pG_w) + ({}_pEA_0) + ({}_0E_{w+}) + ({}_0B_{0-})$
		$m = n/4\dagger\dagger$	$({}_pEA_q) + ({}_pEB_q) + ({}_pEA_0) + ({}_0A_{q+}) + ({}_0B_{q+}) + ({}_0B_{0-})$
		$m > n/4$	$({}_pG_v) + ({}_pEA_0) + ({}_0E_{v+}) + ({}_0B_{0-})$
	$k = \pi/2$	$m < n/4$	$({}_\pi E_{w+}) + ({}_\pi E_{w-}) + ({}_\pi A_{0+}) + ({}_\pi A_{0-}) + ({}_0E_{w+}) + ({}_0B_{0-})$
		$m = n/4\dagger\dagger$	$({}_\pi A_{q+}) + ({}_\pi B_{q+}) + ({}_\pi A_{q-}) + ({}_\pi B_{q-}) + ({}_\pi A_{0+})$
			$({}_\pi A_{0-}) + ({}_0A_{q+}) + ({}_0B_{q+}) + ({}_0B_{0-})$
		$m > n/4$	$({}_\pi E_{v+}) + ({}_\pi E_{v-}) + ({}_\pi A_{0+}) + ({}_\pi A_{0-}) + ({}_0E_{v+}) + ({}_0B_{0-})$
	$k > \pi/2$	$m < n/4$	$({}_lG_w) + ({}_lEA_0) + ({}_0E_{w+}) + ({}_0B_{0-})$
		$m = n/4\dagger\dagger$	$({}_lEA_q) + ({}_lEB_q) + ({}_lEA_0) + ({}_0A_{q+}) + ({}_0B_{q+}) + ({}_0B_{0-})$
		$m > n/4$	$({}_lG_v) + ({}_lEA_0) + ({}_0E_{v+}) + ({}_0B_{0-})$
$({}_kEA_q)\dagger$	$k < \pi/2$		$({}_pEA_0)$
	$k = \pi/2$		$({}_\pi A_{0+}) + ({}_\pi A_{0-})$
	$k > \pi/2$		$({}_lEA_0)$
$({}_kEB_q)\dagger$	$k < \pi/2$		$({}_pEA_0)$
	$k = \pi/2$		$({}_\pi A_{0+}) + ({}_\pi A_{0-})$
	$k > \pi/2$		$({}_lEA_0)$
$({}_\pi E_{m\pm})$		$m < n/4$	$({}_0E_{w+})$
		$m = n/4\dagger\dagger$	$({}_0A_{q+}) + ({}_0B_{q+})$
		$m > n/4$	$({}_0E_{v+})$

Third, again in the case of a four-dimensional starting representation D, some of the irreducible components of $[D^2]$ frequently happen to be four dimensional themselves. In more physical terms, this means that for a Q1D molecular metal with the conduction band twofold degenerate throughout the Brillouin zone—which indeed is the case with some molybdenum oxides and some transition-metal tetrachalcogenides (Miller 1982, Kamimura 1985, Monceau 1985)—the Peierls mode can be fourfold degenerate itself. A four-dimensional order parameter can generate physics quite different from that of the usual simple 'Peierls' model, e.g. two Goldstone modes may emerge (Božović 1985b).

Finally, to complete the task of proving the polymer (or line-group) analogue of the Jahn–Teller theorem, only one further step is needed—to construct the vibrational symmetry-adapted bases for all the graphs of the line groups (in analogy with Božović and Delhalle (1984); see also Koch and Seelig (1987)) and to verify that indeed in each case at least one of the vibronically allowed modes is involved. This, however, is a lengthy task and goes beyond the scope of the present paper.
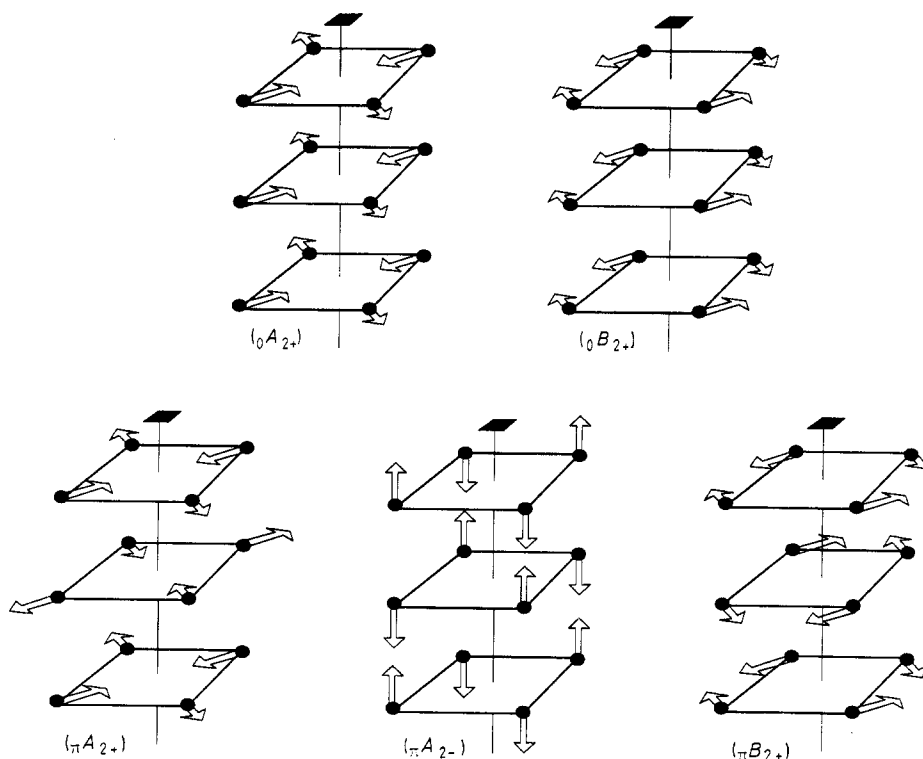
Figure 4. Additional vibronically active modes of the polymer in figure 1, in the case when the (E_1) band is half filled.

References

Birman J L 1959 *Phys. Rev.* **125** 1959
Božović I 1984 *Phys. Rev.* B **29** 6586
——— 1985a *Phys. Rev.* B **32** 8136
——— 1985b *Mol. Cryst. Liquid Cryst.* **119** 47
——— 1986 *Phys. Rev.* B **33** 5956
Božović I and Božović N 1981 *J. Phys. A: Math. Gen.* **14** 1825
Božović I and Delhalle J 1984 *Phys. Rev.* B **29** 4733
Božović I and Vujičić M 1981 *J. Phys. A: Math. Gen.* **14** 777
Božović I, Vujičić M and Herbut F 1978 *J. Phys. A: Math. Gen.* **11** 2133
Cracknell A P 1975 *Group Theory in Solid State Physics* (London: Taylor and Francis)
Herbut F, Vujičić M and Papadopolos Z 1980 *J. Phys. A: Math. Gen.* **13** 2577
Jahn H A and Teller E 1937 *Proc. R. Soc.* A **161** 220
Landau L D and Lifshitz E M 1977 *Quantum Mechanics* (Oxford: Pergamon) 3rd edn
Kamimura H (ed) 1985 *Theoretical Aspects of Band Structures and Electronic Properties of Pseudo-One-Dimensional Solids* (Dordrecht: Reidel)
Koch W and Seelig F F 1987 *Int. J. Quant. Chem.* **32** 249
Kuzmany H, Mehring M and Roth S (ed) 1985 *Electronic Properties of Polymers and Related Compounds* (Berlin: Springer)
Miller J (ed) 1982 *Extended Linear Chain Compounds* (New York: Plenum)
Monceau P (ed) 1985 *Electronic Properties of Inorganic Quasi-One-Dimensional Compounds*, vols I, II (Dordrecht: Reidel)
Peierls R E 1955 *Quantum Theory of Solids* (Oxford: Oxford University Press)
Skotheim T 1986 *Handbook of Conducting Polymers*, vols I, II (New York: Dekker)