

Group theoretical analysis of lattice vibrations in molecular crystals

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Abstract. Computer programs have been developed by Warren and Worlton, for the external modes in ionic crystals where the principal axes of the radicals of groups coincide with the crystallographic axes. In this paper, we discuss the generalisation of these computer programs for molecular crystals where the principal axes do not coincide with the crystallographic axes and for molecular crystals with linear molecules having a redundant rotational degree of freedom. Our results are discussed for the $q \rightarrow 0$ modes of solid NH_3 , N_2 and CS_2 .

Keywords. Group theory; lattice vibrations; complex crystals.

1. Introduction

Group theory has been extensively used in the study of lattice vibrations in crystals. The distribution of normal modes into the various irreducible representations of the little group of the wave vector, their activities in one and two phonon optical spectra and an analysis of inelastic neutron scattering in crystals can all be carried out effectively by employing standard group theoretical methods. Further, one can evaluate the interatomic forces in crystals, from the experimental Raman and infrared data with the help of the group theoretical expressions for frequencies of these modes, in terms of a general interaction potential. For this, one can use the symmetry of the crystal to set up a dynamical matrix and find out the number of independent elements of this matrix. The projection operators can then be set up for the various irreducible representations and can be used to block diagonalise the dynamical matrix into matrices of smaller dimensions corresponding to each of the irreducible representations. From the corresponding frequencies, as obtained from laser Raman and far infrared spectra, one can evaluate the parameters of the interatomic potentials. These parameters will then enable us to study interesting problems like the equilibrium conditions of the lattice, soft modes, etc.

Even for a crystal with a small number of atoms, this is a tedious task to accomplish. However, Worlton and Warren (1972) have developed a computer program, for crystals containing up to 20 atoms in the unit cell, to enumerate their vibration spectra, selection rules, the dynamical matrix and its block-diagonalised forms with using cell dimensions, atomic positions, wave vector and the character table as the input data. Following this work, Worlton (1973) has developed a subroutine to generate the character tables for the wave vector, in order to reduce the input data to a mini-

mum. The limitation of this program is that it cannot be extended to crystals containing more than 20 atoms, on account of storage problems in the computer. Boyer (1974) has developed programs of considerably shorter lengths for crystals containing more than 20 atoms.

In complex crystals, where one can separate out the 'internal' vibrations of the groups of atoms from the 'external' vibrations of the groups against each other, the size of the dynamical matrix can further be reduced. For example, in a crystal of CaWO_4 , where the interactions between W—O of WO_4 are stronger than those between Ca and WO_4 units, one can separate the internal vibrations of WO_4 groups as non-interacting with those of the external vibrations of Ca and WO_4 treated as rigid units. With this assumption, one has to set up only a 18×18 matrix for the external vibrations of the 2CaWO_4 molecules in the unit cell, as against a 36×36 matrix for all the vibrational modes of the unit cell. In order to facilitate this, Worlton (1972) has modified the original computer program of Worlton and Warren (1972). The two limitations of this program are that it cannot be employed for crystals containing groups or molecules whose principal axes of inertia do not coincide with the crystal axes and for linear molecules which do not have a rotational degree of freedom about their own axis. In the course of our investigations on the lattice vibrations in molecular crystals, we found it necessary to further generalise the computer program of Worlton (1972), to derive the atom-atom potentials in boron trihalides (Binbrek and Anderson, 1974), ammonia, nitrogen, carbondisulfide, etc. in their condensed phases. For boron trihalides, the flat BX_3 molecules—the symmetric tops, have their principal axes parallel to the crystal axes while for other crystals, principal axes transformations and the removal of redundancies become important.

Dynamics in the principal axes frame

In the case of groups of atoms like WO_4 , NH_4^+ , etc, called the spherical tops, all the three moments of inertia are equal and the inertia ellipsoid is a sphere. Any set of three axes can be chosen as principal axes. For convenience, the crystal axes themselves can be chosen as principal axes and the original program of Worlton (1972) can be used. For molecular groups like BCl_3 , CO_3^- , etc., called symmetric tops, one of the principal axes coincides with the crystallographic unique axis while the other two can be chosen at will. For asymmetric tops H_2O , NO_2 , etc., the principal axes are uniquely fixed relative to the molecular group. Only in some fortunate instances, these principal axes coincide with the crystal axes as in NO_2 groups of NaNO_2 . In general, for many molecular crystals like NH_3 , CS_2 , N_2 , IBr , naphthalene, etc., the principal axes do not coincide with the crystal axes and the inertia tensor is not diagonal. One has to perform computations with respect to the principal axes frame where the moment of inertia tensor is purely diagonal and the dynamical matrix has its simpler form. In the notation of Venkataraman and Sahni (1970), the elements of the dynamical matrix involve the computation of the following terms:

$$\phi_{\alpha\beta}^{tt} (IK; I'K') = \sum_{kk'} \phi_{\alpha\beta} (IKk; I'K'k')$$

$$\phi_{\alpha\beta}^{tr} (IK; I'K') = \sum_{kk'} \sum_{\gamma\delta} \phi_{\alpha\gamma} (IKk; I'K'k') \epsilon_{\gamma\beta\delta} X_{\delta}(k')$$

$$\phi_{\alpha\beta}^{rt} (IK; l'K') = \sum_{kk'} \sum_{\mu\nu} \phi_{\mu\nu} (IKk; l'K'k') \epsilon_{\mu\alpha\nu} X_{\nu} (k)$$

$$\phi_{\alpha\beta}^{rr} (IK; l'K') = \sum_{kk'} \sum_{\mu\nu} \sum_{\gamma\delta} \phi_{\mu\nu} (IKk; l'K'k') \epsilon_{\gamma\beta\delta} \epsilon_{\mu\alpha\nu} X_{\nu} (k) X_{\delta} (k')$$

where $\phi_{ij} (IKk; l'K'k')$ represents the intermolecular interactions between molecules $(IK; l'K')$ which is taken as the sum of the various interactions between different pairs of atoms $(IKk; l'K'k')$ on different molecules.

If $\mathbf{A}(K)$ is the orthogonal transformation which transforms a set of axes on a vibrating unit of the K -th sublattice located parallel to the fixed frame, to the principal axes, then

$$\phi_{\alpha\beta}^{ii'} (IK; l'K') = \sum_{\gamma\delta} \mathbf{A}_{\alpha\gamma} (K) \phi_{\gamma\delta}^{ii'} (IK; l'K') \mathbf{A}_{\beta\delta} (K')$$

For monatomic groups, as their local axes can be chosen as we wish and as it is convenient to have them all parallel to the crystal axes, we can define

$$\mathbf{A}(K) = \mathbf{I}_3$$

where \mathbf{I}_3 is a three dimensional unit matrix. For molecular groups $\mathbf{A}(K)$ is defined by the three Eulerian angles (ξ, η, ζ) transforming the axes on a fixed frame to the principal axes. In terms of the principal axes, the displacements of the molecules have to be written as

$$u_p^i (IK) = \mathbf{A}(K) u^i (IK).$$

These two changes have been incorporated in the program for the lattice vibrations in molecular crystals. The $\mathbf{A}(K)$ matrices, as defined by Venkataraman and Sahni (1970) can be easily worked out from (ξ, η, ζ) which can be determined from the crystal structure data. Alternatively, one can compute the moments of inertia tensor in the crystal axes frame and diagonalise it, to obtain the eigen values and eigen vectors. The eigen values give the principal moments of inertia and the eigen vector matrix gives $\mathbf{A}(K)$. This can be carried out in the computer programs. Symmetry reduced and block diagonalised dynamical matrix for solid NH_3 are given in appendix 1. The other details can be provided by the author on request.

Linear molecules

For linear molecules, even if their principal axes coincide with the crystallographic axes, as in the case of (OH) ions in $\text{Mg}(\text{OH})_2$ crystals (Mitra 1962), there is still a redundant rotational degree of freedom about the axis of the molecule. The program has to be modified to eliminate this extra rotational degree of freedom.

If U_x^r , U_y^r and U_z^r represent the components of the angular displacement of a linear molecule with respect to the crystal axes (xyz) and if we choose another set of

axes ($x'y'z'$) such that z' is along the length of the molecule, then with respect to the new axes only the x' and y' component of \mathbf{U}^r will be non-vanishing. The component along z' will be zero, since a linear molecule does not have a rotational degree of freedom about its axis. If $U_{x,P}^r$, $U_{y,P}^r$ and $U_{z,P}^r$ are the new components of \mathbf{U}^r , then $U_{z,P}^r = 0$. This transformation is written as

$$\begin{bmatrix} U_{x,P}^r \\ U_{y,P}^r \\ U_{z,P}^r = 0 \end{bmatrix} = A \begin{bmatrix} U_x^r \\ U_y^r \\ U_z^r \end{bmatrix}.$$

Using this, we can eliminate U_z^r in the expressions for the second order term Φ_2 .

We obtain, the following expressions for the various interaction terms $\phi_{\alpha\beta}^{ii'}$:

(i) $\phi_{xy,P}^{ii}$ ($IK; I'K'$) remain unchanged.

$$(ii) \quad \phi_{xx,P}^{tr} = A_{xx}(K') \phi_{xx}^{tr} + A_{xy}(K') \phi_{xy}^{tr} + A_{xz}(K') \phi_{zx}^{tr}$$

$$\phi_{yy,P}^{tr} = A_{yx}(K') \phi_{yx}^{tr} + A_{yy}(K') \phi_{yy}^{tr} + A_{yz}(K') \phi_{yz}^{tr}$$

$$\phi_{xy,P}^{tr} = A_{yx}(K') \phi_{xx}^{tr} + A_{yy}(K') \phi_{xy}^{tr} + A_{yz}(K') \phi_{xz}^{tr}$$

$$\phi_{zx,P}^{tr} = A_{xx}(K') \phi_{zx}^{tr} + A_{xy}(K') \phi_{zy}^{tr} + A_{xz}(K') \phi_{zz}^{tr}$$

$$\phi_{yx,P}^{tr} = A_{xx}(K') \phi_{yx}^{tr} + A_{xy}(K') \phi_{yy}^{tr} + A_{xz}(K') \phi_{yz}^{tr}$$

$$\phi_{zy,P}^{tr} = A_{yx}(K') \phi_{zx}^{tr} + A_{yy}(K') \phi_{zy}^{tr} + A_{yz}(K') \phi_{zz}^{tr}$$

the rest are $\equiv 0$

$$(iii) \quad \phi_{xx,P}^{rt} = A_{xx}(K) \phi_{xx}^{rt} + A_{xy}(K) \phi_{yx}^{rt} + A_{xz}(K) \phi_{zx}^{rt}$$

$$\phi_{yy,P}^{rt} = A_{yx}(K) \phi_{xy}^{rt} + A_{yy}(K) \phi_{yy}^{rt} + A_{yz}(K) \phi_{zy}^{rt}$$

$$\phi_{xy,P}^{rt} = A_{xx}(K) \phi_{xy}^{rt} + A_{xy}(K) \phi_{yy}^{rt} + A_{xz}(K) \phi_{yz}^{rt}$$

$$\phi_{yz,P}^{rt} = A_{yx}(K) \phi_{xz}^{rt} + A_{yy}(K) \phi_{yz}^{rt} + A_{yz}(K) \phi_{zz}^{rt}$$

$$\phi_{yx,P}^{rt} = A_{yx}(K) \phi_{xx}^{rt} + A_{yy}(K) \phi_{yx}^{rt} + A_{yz}(K) \phi_{zx}^{rt}$$

$$\phi_{xz,P}^{rt} = A_{xx}(K) \phi_{xz}^{rt} + A_{xy}(K) \phi_{yz}^{rt} + A_{xz}(K) \phi_{zz}^{rt}$$

the rest are $\equiv 0$

$$\begin{aligned}
\text{(iv)} \quad \phi_{xx, P}^{rr} &= A_{xx}(K) A_{xx}(K') \phi_{xx}^{rr} + A_{xy}(K) A_{xy}(K') \phi_{yy}^{rr} \\
&+ A_{xz}(K) A_{xz}(K') \phi_{zz}^{rr} + A_{xx}(K) A_{xy}(K') \phi_{xy}^{rr} \\
&+ A_{xy}(K) A_{xz}(K') \phi_{yz}^{rr} + A_{xz}(K) A_{xx}(K') \phi_{zx}^{rr} \\
&+ A_{xy}(K) A_{yy}(K') \phi_{yx}^{rr} + A_{xz}(K) A_{xy}(K') \phi_{zy}^{rr} \\
&+ A_{xx}(K) A_{xz}(K') \phi_{xz}^{rr} \\
\phi_{yy, P}^{rr} &= A_{yx}(K) A_{yx}(K') \phi_{xx}^{rr} + A_{yy}(K) A_{yy}(K') \phi_{yy}^{rr} \\
&+ A_{yz}(K) A_{yz}(K') \phi_{zz}^{rr} + A_{yx}(K) A_{yy}(K') \phi_{xy}^{rr} \\
&+ A_{yy}(K) A_{yz}(K') \phi_{yz}^{rr} + A_{yz}(K) A_{yx}(K') \phi_{zx}^{rr} \\
&+ A_{yy}(K) A_{yx}(K') \phi_{yx}^{rr} + A_{yz}(K) A_{yy}(K') \phi_{zy}^{rr} \\
&+ A_{yx}(K) A_{yz}(K') \phi_{xz}^{rr} \\
\phi_{xy, P}^{rr} &= A_{xx}(K) A_{yx}(K') \phi_{xx}^{rr} + A_{xy}(K) A_{yy}(K') \phi_{yy}^{rr} \\
&+ A_{xz}(K) A_{yz}(K') \phi_{zz}^{rr} + A_{xx}(K) A_{yy}(K') \phi_{xy}^{rr} \\
&+ A_{xy}(K) A_{yz}(K') \phi_{yz}^{rr} + A_{xz}(K) A_{yx}(K') \phi_{zx}^{rr} \\
&+ A_{xy}(K) A_{yx}(K') \phi_{yx}^{rr} + A_{xz}(K) A_{yy}(K') \phi_{zy}^{rr} \\
&+ A_{xx}(K) A_{yz}(K') \phi_{xz}^{rr} \\
\phi_{yx, P}^{rr} &= A_{yx}(K) A_{xx}(K') \phi_{xx}^{rr} + A_{yy}(K) A_{xy}(K') \phi_{yy}^{rr} \\
&+ A_{yz}(K) A_{xz}(K') \phi_{zz}^{rr} + A_{xy}(K) A_{xy}(K') \phi_{xy}^{rr} \\
&+ A_{yy}(K) A_{xz}(K') \phi_{yz}^{rr} + A_{yz}(K) A_{xx}(K') \phi_{zx}^{rr} \\
&+ A_{yy}(K) A_{xx}(K') \phi_{yx}^{rr} + A_{yz}(K) A_{xy}(K') \phi_{zy}^{rr} \\
&+ A_{yx}(K) A_{xz}(K') \phi_{xz}^{rr}
\end{aligned}$$

the rest are $\equiv 0$

The computer programs developed by Warren and Worlton (1974) read the basis vectors $A(I, J)$ and crystal structure data $X(I, K)$ of the material. The reciprocal lattice vectors $A^{-1}(I, J)$ are determined. From the rotation matrices $R(N, I, J)$ defined in the subroutine ROT and by removing the lattice vectors defined in a helper subroutine RLV, the point group of the lattice is determined in the subroutine PGL. For the given wavevector components and the character tables, the subroutine PGWV

determines the group of the wavevector. The various functions needed in the calculations, such as $F\phi$, V and MT and the Brillouin zone boundary are determined in the subroutines ATFTMT and BZB respectively. The irreducible multiplier representations can be generated and their orthonormality tested, if the later version of the programs of Worlton (1973) containing the subroutine GIR is used. A random dynamical matrix is created in TMAT, from the subroutine RANVEC generating a random number matrix. The symmetry operations of the little group of the wavevector are applied on this random matrix and its number of independent elements are found out. The time reversal and extra degeneracies are checked in TRINV and TRDEG. Subroutine POASC construct the projection operators and the symmetry coordinates and with the help of these, the block diagonalisation of the dynamical matrix and the calculation of the selection rules are carried out in BDODM.

The changes indicated in sections (a) and (b), for molecular crystals with non-linear and linear molecules respectively, are incorporated in the subroutines TMAT and POASC, so that the appropriate dynamical matrix is stored for the block diagonalisation in BDODM. The modified version has been tested on the IBM 370 computer at IIT, Madras and gives satisfactory results.

2. Results

2.1. Non-linear molecules

Solid ammonia belongs to the first class of a molecular crystal having non-linear molecules. The principal axes of these molecules do not coincide with the crystallographic axes. The long wavelength phonons of solid NH_3 are distributed as $A+E+2F$ translational modes and $A+E+3F$ librational modes. The zero frequency acoustic modes come under the F representations of the T^4 space group. The dynamical matrix is of order 24×24 and the block diagonalised matrices are of dimensions 2×2 , 2×2 and 6×6 corresponding to the A , E and F representations respectively (appendix 1). Using the experimental data of Binbrek and Anderson (1972), we have tried to find a set of parameters for N-N, N-H and H-H interactions in NH_3 . Our experience shows that no realistic values of these parameters for a Lennard-Jones or Exp-6 or Buckingham potentials and with long range interactions can explain the observed Raman and infrared spectra. This shows the need to develop quantum mechanical calculations in crystals having hydrogen atoms.

2.2. Linear molecules

Solid nitrogen comes under this category with the crystal structure having linear N_2 molecules with their principal axes having a definite orientation with respect to the crystal axes. Lattice dynamics of the cubic phase of solid nitrogen has been studied by Anderson, Sun and Donkersloot (1970). Since it is a linear molecule, we have to employ the modifications in the program as explained before. The unit cell has four molecules and though we have set up a 24×24 matrix with the normal modes coming under $2A+2E+6F$ representations, we find from the block diagonalised matrices, there are only a 5×5 and 1×1 submatrices coming under F and A representations, thus automatically removing the 4 redundant rotational degrees of freedom

(appendix 2). This program has been tested numerically from our calculations on the $q=0$ phonons in NH_3 , N_2 and CS_2 (Anderson *et al* 1973) crystals. Frequencies obtained by solving the full dynamical matrix and the block diagonalised matrices agree well in all these crystals. This has considerably reduced the computer times and has helped us to study several potential functions in molecular crystals.

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Appendix 1.

Group theoretical analysis of lattice vibrations in non-linear molecules—ammonia

(a) Symmetry reduced dynamical matrix warning the number of independent elements is too large

	Amplitudes																							
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	AA	AB	AC	..	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP	AQ	AR	AS	AT	AU
2	..	AA	..	AC	AB	..	AE	AV	AW	AX	AY	AZ	AK	BA	BB	BC	BD	BE	AQ	BF	BG	BH	BI	BJ
3	BK	BL	AF	AW	BM	BN	BU	BP	AL	BB	BM	BQ	BR	BP	AR	BG	BM	BS	BT	BP
4	AB	AC	..	BU	AG	AX	BN	BV	BW	BX	AM	BC	BQ	BY	BZ	CA	AS	BH	BS	CB	CC	CD
5	AC	AB	BU	..	AH	AY	BO	BW	CE	CF	AN	BD	BR	BZ	CG	CH	AT	BI	BT	CC	CI	CJ
6	BL	CK	AI	AZ	BP	BX	CF	CL	AO	BE	BP	CA	CH	CL	AU	BJ	BP	CD	CJ	CL
7	AD	AE	AF	AG	AH	AI	AA	AB	AC	..	AP	AQ	AR	AS	AT	AU	AJ	AK	AL	AM	AN	AO
8	AE	AV	AW	AX	AY	AZ	..	AA	..	AC	AB	..	AQ	BF	BG	BH	BI	BJ	AK	BA	BB	BC	BD	BE
9	AF	AW	BM	BN	BO	BP	BK	BL	AR	BG	BM	BS	BT	BP	AL	BB	BM	BQ	BR	BP
10	AG	AX	BN	BV	BW	BX	AB	AC	..	BU	AS	BH	BS	CB	CC	CD	AM	BC	BQ	BY	BZ	CA
11	AH	AY	BO	BW	CE	CF	AC	AB	BU	..	AT	BI	BT	CC	CI	CJ	AN	BD	BR	BZ	CG	CH
12	AI	AZ	BP	BX	CF	CL	BL	CK	AU	BJ	BP	OD	CJ	CL	AO	BE	BP	CA	CH	CL
13	AJ	AK	AL	AM	AN	AO	AP	AQ	AR	AS	AT	AU	AA	AB	AC	..	AD	AE	AF	AG	AH	AI
14	AK	BA	BB	BC	BD	BE	AQ	BF	BG	BH	BI	BJ	..	AA	..	AC	AB	..	AE	AV	AW	AX	AY	AZ
15	AL	BB	BM	BQ	BR	BP	AR	BG	BM	BS	BT	BP	BK	BL	AF	AW	BM	BN	BO	BP
16	AM	BC	BQ	BY	BZ	CA	AS	BH	BS	CB	CC	CD	AB	AC	..	BU	AG	AX	BN	BV	BW	BX
17	AN	BD	BR	BZ	CG	CH	AT	BI	BT	CC	CI	CJ	AC	AB	BU	..	AH	AY	BO	BW	CE	CF
18	AO	BE	BP	CA	CH	CL	AU	BJ	BP	CD	CJ	CL	BL	CK	AI	AZ	BP	BX	CF	CL

Appendix 1(Contd)

19	AP	AQ	AR	AS	AT	AU	AJ	AK	AL	AM	AN	AO	AD	AE	AF	AG	AH	AI	AA	AB	AC	..
20	AQ	BF	BG	BH	BI	BJ	AK	BA	BB	BC	BD	BE	AE	AV	AW	AX	AY	AZ	..	AA	..	AC	AB	..
21	AR	BG	BM	BS	BT	BP	AL	BB	BM	BQ	BR	BP	AF	AW	BM	BN	BO	BP	BK	BL
22	AS	BH	BS	CB	CC	CD	AM	BC	BQ	BY	BZ	CA	AG	AX	BN	BV	BW	BX	AB	AC	..	BU
23	AT	BI	BT	CC	CI	CJ	AN	BD	BR	BZ	CG	CH	AH	AY	BO	BW	CE	CF	AC	AB	BU	..
24	AU	BJ	BP	CD	CJ	CL	AO	BE	BP	CA	CH	CL	AI	AZ	BP	BX	CF	CL	BL	CK

(b) Elements of the block-diagonalized dynamical matrix

$$\begin{aligned}
 D(1, 1) &= (1.0000, 0.0))BK + (-3.0000, -0.0000)BM \\
 D(1, 2) &= (1.0000, 0.0))BL + (-3.0000, -0.0000)BP \\
 D(2, 2) &= (1.0000, 0.0))CK + (-3.0000, -0.0000)CL
 \end{aligned}$$

This block belongs to IR (1) and occurs 1 times on the diagonal

$$\begin{aligned}
 D(3, 3) &= (1.0000, 0.0))AA + (-0.5000, -0.0000)AD + (0.5000, 0.0000)AJ + (-0.5000, 0.0))AP + (-0.5000, -0.0000)AV \\
 &+ (-0.5000, 0.0))BA + (0.5000, 0.0000)BF \\
 D(3, 4) &= (1.0000, 0.0))AB + (-0.0000, 1.0000)AC + (0.5000, 0.0))AG + (-0.0000, 0.5000)AH + (-0.5000, 0.0))AM \\
 &+ (0.0000, -0.5000)AN + (-0.5000, 0.0))AS + (0.0000, 0.5000)AT + (0.0000, -0.5000)AX + (-5.000, -0.00000)AY \\
 &+ (-0.0000, 0.5000)BC + (-0.5000, 0.0))BD + (0.0000, -0.5000)BH + (0.5000, 0.0000)BI \\
 D(4, 4) &= (1.0000, 0.0))BU + (0.5000, 0.0))BV + (0.5000, 0.0000)BY + (-0.5000, 0.0))CB + (-0.5000, -0.0000)CE \\
 &+ (-0.5000, 0.0))CG + (0.5000, 0.0000)CI
 \end{aligned}$$

This block belongs to IR (2) and occurs 1 times on the diagonal

$$\begin{aligned}
 D(5, 5) &= (1.0000, 0.0))AA + (-0.5000, -0.0000)AD + (0.5000, 0.0000)AJ + (-0.5000, 0.0))AP + (-0.5000, -0.0000)AV \\
 &+ (-0.5000, 0.0))BA + (0.5000, 0.0000)BF \\
 D(5, 6) &= (1.0000, 0.0))AB + (-0.0000, -1.0000)AC + (0.5000, 0.0))AG + (0.0000, -0.5000)AH + (-0.5000, 0.0))AM \\
 &+ (-0.0000, 0.5000)AN + (-0.5000, 0.0))AS + (0.0000, -0.5000)AT + (-0.0000, 0.5000)AX + (-0.5000, -0.0000)AY \\
 &+ (0.0000, -0.5000)BC + (-0.5000, 0.0))BD + (0.0000, 0.5000)BH + (0.5000, 0.0000)BI
 \end{aligned}$$

Appendix I(Contd)

$$D(6,6) = \begin{pmatrix} 1.0000, 0.0 \\ -0.5000, 0.0 \end{pmatrix} BU + \begin{pmatrix} 0.5000, 0.0 \\ -0.5000, 0.0000 \end{pmatrix} BV + \begin{pmatrix} 0.5000, 0.0000 \\ -0.5000, 0.0000 \end{pmatrix} BY + \begin{pmatrix} -0.5000, 0.0 \\ -0.5000, -0.0000 \end{pmatrix} CB + \begin{pmatrix} -0.5000, -0.0000 \\ -0.0000, 0.0 \end{pmatrix} CE$$

This block belongs to IR (3) and occurs 1 times on the diagonal

$$D(7,7) = \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} AD + \begin{pmatrix} -1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} AM + \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, 0.0 \end{pmatrix} AP$$

$$D(7,8) = \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} AE + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} AK + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} AQ$$

$$D(8,8) = \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} AV + \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} BA + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} BF$$

$$D(7,9) = \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} AF + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} AL + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} AR$$

$$D(8,9) = \begin{pmatrix} 1.0000, 0.0000 \\ -1.0000, -0.0000 \end{pmatrix} AW + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} BB + \begin{pmatrix} 1.0000, 0.0000 \\ -1.0000, 0.0000 \end{pmatrix} BG$$

$$D(9,9) = \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, 0.0000 \end{pmatrix} BM + \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} BC + \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, 0.0 \end{pmatrix} AS$$

$$D(7,10) = \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, 0.0000 \end{pmatrix} AB + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} AX + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} BH$$

$$D(8,10) = \begin{pmatrix} 1.0000, 0.0000 \\ -1.0000, -0.0000 \end{pmatrix} AC + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} BX + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} BS$$

$$D(9,10) = \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} BN + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} BQ + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} BY$$

$$D(10,10) = \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} BU + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} AH + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} AN + \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} AT$$

$$D(7,11) = \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} AB + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} AY + \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} BI$$

$$D(8,11) = \begin{pmatrix} 1.0000, 0.0000 \\ -1.0000, -0.0000 \end{pmatrix} BO + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} BR + \begin{pmatrix} 1.0000, 0.0000 \\ -1.0000, -0.0000 \end{pmatrix} BT$$

$$D(10,11) = \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} BW + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} BZ + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} CC$$

$$D(11,11) = \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} BU + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0 \end{pmatrix} CE + \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} CG + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} AU$$

$$D(7,12) = \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} AI + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} AO + \begin{pmatrix} 1.0000, 0.0000 \\ -1.0000, 0.0000 \end{pmatrix} BJ$$

$$D(8,12) = \begin{pmatrix} 1.0000, 0.0000 \\ -1.0000, -0.0000 \end{pmatrix} AZ + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} BE + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} CD$$

$$D(9,12) = \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, -0.0000 \end{pmatrix} BL + \begin{pmatrix} 1.0000, 0.0000 \\ -1.0000, -0.0000 \end{pmatrix} BP + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} CH$$

$$D(10,12) = \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} BX + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} CA + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} CJ$$

$$D(11,12) = \begin{pmatrix} 1.0000, 0.0000 \\ -1.0000, -0.0000 \end{pmatrix} CF + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} CH + \begin{pmatrix} -1.0000, -0.0000 \\ 1.0000, 0.0000 \end{pmatrix} CL$$

$$D(12,12) = \begin{pmatrix} 1.0000, 0.0 \\ -1.0000, 0.0000 \end{pmatrix} CK + \begin{pmatrix} 1.0000, 0.0000 \\ -1.0000, 0.0000 \end{pmatrix} CL$$

This block belongs to IR (4) and occurs 3 times on the diagonal

Appendix 2 (Contd)

19	AN	AK	AF	AO	AP	..	AJ	AG	AK	AL	AM	..	AE	AF	AG	AH	AI	..	AA	AB	AB	AC	AD	..
20	AK	AJ	AG	AW	AX	..	AG	AE	AF	AU	AV	..	AF	AN	AK	AS	AT	..	AB	AA	AB	AQ	AR	..
21	AF	AG	AE	BE	BF	..	AK	AF	AN	BC	BD	..	AG	AK	AJ	BA	BB	..	AB	AB	AA	AY	AZ	..
22	AO	AW	BE	BL	BM	..	AL	AU	BC	BJ	BK	..	AH	AS	BA	BH	BI	..	AC	AQ	AY	BG
23	AP	AX	BF	BM	BP	..	AM	AV	BD	BK	BO	..	AI	AT	BB	BI	BN	..	AD	AR	AZ	..	BG	..
24

(b) Elements of the block-diagonalized dynamical matrix

$$D(1, 1) = (1.0000, 0.0)AA + (+ 1.0000, 0.0)AE + (1.0000, 0.0)AJ + (1.0000, 0.0)AN$$

This block belongs to IR (1) and occurs 1 times on the Diagonal.

$$\begin{aligned} D(3, 3) &= (1.0000, 0.0)AA + (-1.0000, 0.0000)AJ \\ D(3, 4) &= (0.5000, 0.0)AC + (-0.0000, 0.5000)AD + (0.5000, 0.0)AH + (-0.0000, 0.5000)AI + (-0.5000, 0.0)AL \\ &= (0.0000, -0.5000)AM + (-0.5000, 0.0)AO + (0.0000, -0.5000)AP \\ D(4, 4) &= (1.0000, 0.0)BG + (0.5000, 0.0)BH + (0.5000, 0.0000)BJ + (-0.5000, 0.0)BL + (-0.5000, -0.0000)BN \\ &= (-0.5000, 0.0)BO + (0.5000, 0.0000)BP \end{aligned}$$

This block belongs to IR (2) and occurs 1 times on the diagonal.

$$\begin{aligned} D(5, 5) &= (1.0000, 0.0)AA + (-1.0000, -0.0000)AJ \\ D(5, 6) &= (0.5000, 0.0)AC + (0.0000, -0.5000)AD + (0.5000, 0.0)AH + (0.0000, -0.5000)AI + (-0.5000, 0.0)AL \\ &= (-0.0000, 0.5000)AM + (-0.5000, 0.0)AO + (-0.0000, 0.5000)AP \\ D(6, 6) &= (1.0000, 0.0)BG + (0.5000, 0.0)BH + (0.5000, 0.0000)BJ + (-0.5000, 0.0)BL + (-0.5000, -0.0000)BN \\ &= (-0.5000, 0.0)BO + (0.5000, 0.0000)BP \end{aligned}$$

This block belongs to IR (3) and occurs 1 times on the diagonal

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