

# A NEW LOOK AT THE EVALUATION OF CARTESIAN SYMMETRY COORDINATES IN MOLECULAR VIBRATIONS. APPLICATION TO NORMAL COORDINATE ANALYSIS

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A new method for evaluating symmetry coordinates for molecular potential function  $V$  expressed in Cartesian coordinates is described. The transformation which factorizes  $V$  is represented as a Kronecker product of  $N$ - and 3-dimensional matrices: a simple method of finding these matrices is also described.

The problem of redundant coordinates does not exist in this proposed method.

## 1. Introduction

In 1939 and 1941 Wilson [1, 2] showed how to express the kinetic energy of any molecule in terms of the time derivatives of bond-length changes and interbond angle changes. Essentially all normal coordinate treatments published since that time have expressed potential functions in terms of interbond angle changes and bond-length changes and have used the Wilson  $F$ - $G$  matrix method to set up the secular equations. However, in 1965 Pariseau, Zuzuki and Overend [3] used mass-weighted Cartesian coordinates in their study of the anharmonic potential field of small molecules. Next, in 1971, Tyson, Classen and Kim [4] developed a straightforward way to derive the necessary potential matrices for any  $XY_n$  type of molecule with  $n$  bonds to a central atom  $X$ . In their work it proved to be convenient to use Cartesian coordinates rather than internal coordinates. The procedure outlined in their paper may seem to ignore molecular symmetry and the possibility this provides for the factorization of the secular equation, because the emphasis is on a physically meaningful force field model. For this, they do not need symmetry coordinates. In [5] Gwinn has described a method of performing normal coordinate analysis using Cartesian coordinates, which is more suitable for use with electronic computers than the current methods, but he has not considered group theoretical aspects in detail, as well. In the present paper we propose a simple method of finding symmetry coordinates for molecular problems expressed in Cartesian coordinates (corresponding to the computational method used in [4, 5, 6]).

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## 2. Basic theory

Let  $G = \{g\}$  be the point symmetry group of an  $N$ -atomic molecule. The vibration of this molecule (including translations and rotations) are specified by the vector  $x$  in the  $3N$  dimensional vector space  $L^{3N}$ . The Cartesian displacement coordinates in the column matrix,  $x$ , where  $x^T = (x_1, x_2, \dots, x_N) = (x_1, x_2, x_3, x_4, \dots, x_{3N})$  are defined in the usual way so that  $x_1, x_2$  and  $x_3$  are the  $x$ -,  $y$ - and  $z$ -displacement coordinates, respectively, from the equilibrium point of the first atom,  $x_4, x_5$  and  $x_6$  similarly refer to the second atom, *etc.*, up to  $x_{3N}$  the  $z$ -coordinate of the  $N$ -th atom. On the vector space  $L^{3N}$  is defined also the representation  $T_{(g)}^{3N}$  of the group  $G$ .

If we want to find the symmetry adapted basis in  $L^{3N}$ , following the standard method [7, 8] we ought to construct the well known projection operators,

$$P_\gamma = \int_G dg \overline{\tau_{mm(g)}^\gamma} T_{(g)}^{3N} \quad (1)$$

where  $\overline{\tau_{mm(g)}^\gamma} = \tau_{mm(g^{-1})}^\gamma$  is the diagonal  $(m, m)$  th element of the irreducible representation  $\Gamma^\gamma$  of  $G$ , and operate them on a given basis in  $L^{3N}$ . For a finite group  $\int_G dg \rightarrow \frac{1}{\text{order } G} \sum_{g \in G}$ .

However, in more complicated applications, from the practical point of view using equation (1) can present formidable problems because the size of  $T_{(g)}^{3N}$  matrices is considerable. Operating with these large matrices is very difficult, very time-consuming and subject to error. Below we outline a simpler way of constructing the set of symmetry adapted coordinates for a given molecule.

It is well known that every operation  $g \in G$  induces rotation (reflection, inversion) and permutation of the displacement vectors  $x_i$  in  $x$ .

Formally, we can write  $T_{(g)}^{3N}$  as a direct product,

$$T_{(g)}^{3N} = T_{(g)}^N \otimes T_{(g)}^3 \quad (2)$$

where

$T_{(g)}^N$  — is the  $N$ -dimensional permutation matrix which takes  $x_i$  into  $x_j$  (*i. e.* which permutes the displacement vectors in  $x$  in the same way  $g \in G$  permutes the atoms of the equilibrium molecule),  $T_{(g)}^3$  — is the 3-dimensional transformation matrix which describes the effect of the symmetry operation  $g \in G$  on the displacement vectors  $x_i$  (*i. e.* which describes the change of the directions of these displacements  $x_i$  under  $g \in G$  leaving the atoms in their equilibrium positions in the molecule). From (2) we obtain automatically a useful relation for the characters  $\chi_{(g)}^{3N}, \chi_{(g)}^N, \chi_{(g)}^3$  of the reducible representation  $T_{(g)}^{3N}, T_{(g)}^N, T_{(g)}^3$  respectively:

$$\chi_{(g)}^{3N} = \chi_{(g)}^N \chi_{(g)}^3 \quad (3)$$

This in itself represents no innovation [7,8] and [16]. It is worth to note here that formally we can write:

$$L^{3N} = L^N \otimes L^3 \quad (4)$$

if  $L^N$  and  $L^3$  are the carrier spaces of the representation  $T_{(g)}^N$  and  $T_{(g)}^3$  of  $G$ , respectively.

The innovation of the present paper relies on the fact that we do not construct the symmetry subspaces in  $L^{3N}$  in a straightforward manner, operating the large matrices  $T_{(g)}^{3N}$ , but we reduce the spaces  $L^N$  and  $L^3$  separately. Then, in our method, the construction of the symmetry adapted to the  $G$  basis in  $L^{3N}$  is a two-step process: first, from a given basis  $\{e_i^N\}$  in  $L^N$  ( $i = 1, 2, \dots, N$ ) and  $\{e_\alpha^3\}$  in  $L^3$  ( $\alpha = 1, 2, 3$ ) we construct the irreducible subspaces in  $L^N$  and  $L^3$  separately, and, second, we find the symmetry adapted basis in  $L^{3N}$  as the Kronecker product of the symmetry adapted basis vectors  $\{e_{\gamma j}^N\}$  in  $L^N$  ( $j = 1, \dots, n_\gamma$ ;  $n_\gamma = \int_G dg \overline{\chi_{(g)}^\gamma} \chi_{(g)}^N$ ) and  $\{e_{\gamma' j'}^3\}$  in  $L^3$  ( $j' = 1, \dots, n_{\gamma'}$ ;  $n_{\gamma'} = \int_G dg \overline{\chi_{(g)}^{\gamma'}} \chi_{(g)}^3$ ).

In other words, knowing the symmetry adapted basis  $\{e_{\gamma j}^N\}$  in  $L^N$  and  $\{e_{\gamma' j'}^3\}$  in  $L^3$  it is possible to obtain simply the symmetry adapted basis  $\{e_{\gamma'' j''}^{3N}\}$  in  $L^{3N}$  ( $j'' = 1, \dots, n_{\gamma''}$ ;  $n_{\gamma''} = \int_G dg \overline{\chi_{(g)}^{\gamma''}} \chi_{(g)}^{3N}$ ) performing the Kronecker product (see Appendix A):

$$\{e_{\gamma j}^N\} \otimes \{e_{\gamma' j'}^3\} = \{e_{\gamma'' j''}^{3N}\}. \quad (5)$$

The procedure for the reduction of the  $L^3$  space is trivial (one operates only 3-dimensional matrices): a systematic method for accomplishing the reduction of the  $L^N$  space (or the  $T_{(g)}^N$  reducible representation) will now be described.

### Reduction of the $L^N$ space

It is possible to achieve a high degree of simplicity of the reduction of the  $L^N$  space if we note the obvious fact that, when the atoms are permuted among each other after the operation  $g \in G$ , only identical atoms (nuclei) are interchanged. Suppose that among  $N$ -atoms of the molecule there are  $n_k$  atoms of the same kind  $k$  ( $k = 1, 2, \dots, p$ ;  $\sum_{k=1}^p n_k = N$ ). For example, for nitromethane  $\text{CH}_3\text{NO}_2$  we have:

$$n_C = 1, n_H = 3, n_N = 1, n_O = 2; \quad n_C + n_H + n_N + n_O = 7; \quad p = 4.$$

Therefore, we can write

$$T_{(g)}^N = \bigoplus_{k=1}^p T_{(g)}^{n_k} \quad (6)$$

and, using (1)

$$P_\gamma^N = \int_G dg \tau_{mm(g)}^\gamma T_{(g)}^N = \bigoplus_{k=1}^p P_\gamma^{n_k} \quad (7)$$

where

$$P_\gamma^{n_k} = \int_G dg \tau_{mm(g)}^\gamma T_{(g)}^{n_k}. \quad (8)$$

It is therefore shown, that a symmetry adapted basis in  $L^N$  can be constructed using  $n_k$ -dimensional matrices.

## 3. Simple example

This section is intended to illustrate, on an extremely simple example, the ideas set out in the previous pages.

Consider the  $C_{2v}$  bent symmetrical  $XY_2$  molecule (Fig. 1).

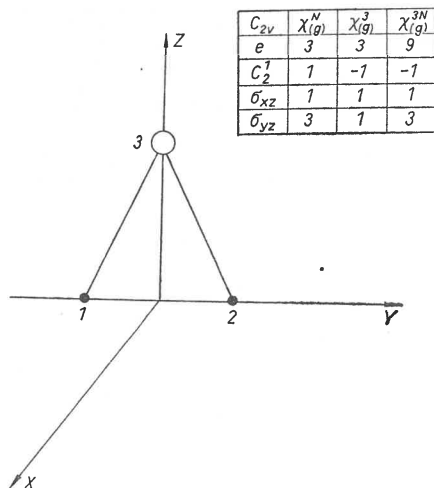


Fig. 1. Bent symmetrical  $XY_2$  molecular model (symmetry  $C_{2v}$ ) and characters of the reducible representations  $T_{(g)}^{3N}$ ,  $T_{(g)}^N$ ,  $T_{(g)}^3$

Using the common group theoretical formula  $n_\gamma = \int_G \overline{\chi_\gamma^i} \chi_{(g)}$  for finding the irreducible representations of  $T_{(g)}^{3N}$ ,  $T_{(g)}^N$ ,  $T_{(g)}^3$  we have,

$$T_{(g)}^{3N} = 3A_1 + A_2 + 2B_1 + 3B_2 \quad (9)$$

$$T_{(g)}^N = 2A_1 + B_2 \quad (10)$$

$$T_{(g)}^3 = A_1 + B_1 + B_2. \quad (11)$$

Of course, in agreement with (2) and (4),

$$(2A_1 + B_2) \otimes (A_1 + B_1 + B_2) = 3A_1 + A_2 + 2B_1 + 3B_2.$$

Reduction of the  $L^3$  space

With the geometrical interpretation of the  $C_{2v}$  point group we instantly find the symmetry adapted basis in  $L^3$ :

$$e_{A_1}^3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad e_{B_1}^3 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad e_{B_2}^3 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}. \quad (12)$$

Of course, the same results can be obtained formally by using equation (1).

Reduction of the  $L^N$  space

Operating with the projection operators (7) or (8) on the reducible basis  $\{e_i^N\}$  in  $L^N$  ( $N = 3, i = 1, 2, 3$ ) we construct the symmetry adapted basis in  $L^N$ :

$$e_{A_{1,1}}^N = \frac{1}{\sqrt{2}}(e_1^N + e_2^N) = \frac{1}{\sqrt{2}} \left\{ \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \right\} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$$

$$e_{A_{1,2}}^N = e_3^N = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$e_{B_2}^N = \frac{1}{\sqrt{2}}(e_1^N - e_2^N) = \frac{1}{\sqrt{2}} \left\{ \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} - \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \right\} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}. \quad (13)$$

In other words, the atom number 3 (Fig. 1) is not permuted for every  $g \in C_{2v}$ , therefore, the vector  $e_3^N$  which represents this atom in  $L^N$  space, belongs to the  $A_1$  symmetry space. Atom number 1 and 2 are permuted under the operations  $\{\sigma_{xz}, C_2^1\} \in C_{2v}$  then operating with the projection operators (7) on the vectors  $e_1^N$  and  $e_2^N$  which represent these atoms in  $L^N$  space, we obtain  $e_{A_{1,1}}^N$  and  $e_{B_2}^N$  (for the characters of irreducible representations see, e. g., reference [2]).

Reduction of the  $L^{3N}$  space

The symmetry adapted basis in  $L^{3N}$  is found automatically in agreement with equation (5):

$L^N \otimes L^3$	$e_{A_1}^3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$	$e_{B_1}^3 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$	$e_{B_2}^3 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$
$e_{A_{1,1}}^N = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$	$e_{A_{1,1}}^{3N}$	$e_{B_{1,1}}^{3N}$	$e_{B_{2,1}}^{3N}$
$e_{A_{1,2}}^N = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$	$e_{A_{1,2}}^{3N}$	$e_{B_{1,2}}^{3N}$	$e_{B_{2,2}}^{3N}$
$e_{B_2}^N = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}$	$e_{B_{1,3}}^{3N}$	$e_{A_2}^{3N}$	$e_{A_{1,3}}^{3N}$

#### 4. Application to normal coordinate analysis

Consider the  $D_{\infty h}$  linear molecule of the type  $XY_2$  (Fig. 2).

The model for the molecule that we consider is the one that Heath and Linnett [9] suggested and designated the orbital valency force field (OVFF).

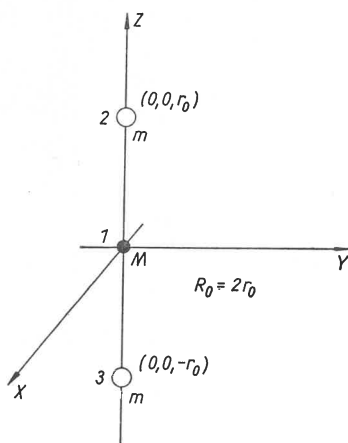


Fig. 2. Coordinate system for the linear  $XY_2$  molecule

This model, as was shown [9, 10, 11, 4] to be a very satisfactory for symmetrical  $XY_n$  molecules. In our case, the assumed potential function for  $XY_2$  linear molecule is

$$2V = K \sum_{i=1}^2 \Delta r_i^2 + 2r_0 K' \sum_{i=1}^2 \Delta r_i + F \Delta R_{12}^2 + 2R_0 F' \Delta R_{12} + r_0^2 D \sum_{i=1}^2 \beta_i^2 \quad (15)$$

with the common assumption  $K' = 2F'$  [4].

The notation is fairly standard as it is used in most Urey-Bradley treatments:  $\beta_i$  is the angle between the actual position of the  $i$ -th ligand atom and the direction where the  $i$ -th orbital is centered when the orbital energy is minimized (the notation is the same as that used in [4]). The potential function (15) expressed in terms of Cartesian displacement coordinates is elsewhere [4, page 3148] as the potential-energy matrix  $A$ :  $2V = x^T A x$ .

The secular equation in the Cartesian coordinates is the following

$$|M^{-1}A - \lambda I| = 0 \quad (16)$$

where

$M$  is the diagonal  $3N \times 3N$  matrix of atomic masses [12]

$I$  — unit matrix.

The next step is the construction of the symmetry adapted basis in  $L^{3N}$  space, in agreement with the procedure outlined above.

Using the common group theoretical method [13] we have,

$$\begin{aligned} T_{(g)}^{3N} &= 2\Pi_u + 2\Sigma_u^+ + \Pi_g + \Sigma_g^+ \\ T_{(g)}^N &= 2\Sigma_g^+ + \Sigma_u^+ \\ T_{(g)}^3 &= \Pi_u + \Sigma_u^+. \end{aligned} \quad (17)$$

Of course, in agreement with (2) and (4),

$$(2\Sigma_g^+ + \Sigma_u^+) \otimes (\Pi_u + \Sigma_u^+) = 2\Pi_u + 2\Sigma_u^+ + \Pi_g + \Sigma_g^+. \quad (18)$$

With the geometrical interpretation of the  $D_{\infty h}$  point group we instantly find the symmetry adapted basis in  $L^3$

$$e_{\Pi_u,1}^3 = e_1^3 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad e_{\Pi_u,2}^3 = e_2^3 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad e_{\Sigma^+_u}^3 = e_3^3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (19)$$

In the  $L^N$  space, the atom number  $i$  is represented by the vector  $e_i^N$ . Operating with the projection operators (7) on the reducible basis  $\{e_i^N\}$  in  $L^N$  ( $N = 3, i = 1, 2, 3$ ) we construct the symmetry adapted basis in  $L^N$ :

$$\begin{aligned} e_{\Sigma^+_g,1}^N = e_1^N &= \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad e_{\Sigma^+_g,2}^N = \frac{1}{\sqrt{2}}(e_2^N + e_3^N) = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} \\ e_{\Sigma^+_u}^N &= \frac{1}{\sqrt{2}}(e_2^N - e_3^N) = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}. \end{aligned}$$

The symmetry adapted basis in  $L^{3N}$  is found in agreement with equation (5).

Factorizing the matrices  $A$  and  $M^{-1}$  in these symmetry coordinates one can obtain three non-zero, separate secular equations:

$$\begin{aligned} \Pi_u: \begin{vmatrix} \frac{-4F' + 2D}{M} - \lambda, & \frac{\sqrt{2}(2F' - D)}{M} \\ \frac{\sqrt{2}(2F' - D)}{m}, & \frac{-2F' + D}{m} - \lambda \end{vmatrix} = 0 & \quad \Sigma_u^+: \begin{vmatrix} \frac{2K}{M} - \lambda, & -\frac{\sqrt{2}K}{M} \\ -\frac{\sqrt{2}K}{m}, & \frac{K}{m} - \lambda \end{vmatrix} = 0 \\ \Sigma_g^+: \begin{vmatrix} \frac{K + 2F}{m} - \lambda \end{vmatrix} = 0. & \end{aligned} \quad (21)$$

At last, we obtain the force constants by solving equations (21),

$$\begin{aligned} K &= \frac{Mm}{M + 2m} \lambda_{\Sigma^+_u} \\ F &= \frac{1}{2}(m\lambda_{\Sigma^+_g} - K) \\ D - 2F' &= \frac{Mm}{M + 2m} \lambda_{\Pi_u} \end{aligned}$$

where  $\lambda_\gamma = 4\pi^2\nu^2$  the frequencies corresponding to the normal coordinates ( $\gamma = \Sigma_u^+, \Sigma_g^+, \Pi_u$ ).

The values  $K$ ,  $F$  and  $D-2F'$  calculated in agreement with (22) for typical linear molecules  $XY_2$  are given in Table I.

TABLE I

Calculated orbital valency force constants for  $XY_2$  linear molecules (milidynes per angstrom)

Molecule	$\nu_{\Sigma_u^+}$ ( $\text{cm}^{-1}$ )	$\nu_{\Sigma_g^+}$ ( $\text{cm}^{-1}$ )	$\nu_{\Pi_u}$ ( $\text{cm}^{-1}$ )	$K$	$F$	$D-2F'$
CO <sub>2</sub>	2349	1388	667.4	14.2	2.0	1.14
CS <sub>2</sub>	1532.5	658	397	6.95	0.6	0.47

The value of the usual bond-stretching force constants  $K$  are in excellent agreement with the early results [15]. For the separation of translations and rotations see Appendix B.

### APPENDIX A

It is well known [14] that, generally, the Kronecker product of irreducible representations  $\Gamma_\gamma$  and  $\Gamma_{\gamma'}$  of a given group  $G$  is reducible (if  $n_\gamma$  and  $n_{\gamma'} \geq 2$ ). Therefore, in the case when as the  $L^N$  as the  $L^3$  spaces simultaneously contain the irreducible subspaces of dimension higher than one ( $n_\gamma$  and  $n_{\gamma'} \geq 2$ ) it is not possible to obtain the complete reduction of the  $L^{3N}$  space on performing the Kronecker product (5), although the  $L^N$  and  $L^3$  spaces are reduced completely.

In this case we ought to use the Clebsch-Gordan coefficients for a full adaptation of the  $L^{3N}$  space. The usual procedure for this is described in detail, *e. g.* [14].

The orthonormal basis  $\{e_\alpha^3\}$  ( $\alpha = 1, 2, 3$ ) in  $L^3$  and  $\{e_i^N\}$  ( $i = 1, 2, \dots, N$ ) in  $L^N$  is defined in the usual way:  $e_1^3 = (1, 0, 0) \dots e_3^3 = (0, 0, 1)$ ;  $e_1^N = (1, 0 \dots 0)$ ,  $\dots e_N^N = (0, 0, \dots, 1)$ .

### APPENDIX B

If we want to separate the translations and rotations of our molecule as a whole, we construct in  $L^N$  another set of the symmetry adapted vectors as following,

$$\begin{aligned}\tilde{e}_{\Sigma^+g,1}^N &= \frac{1}{\sqrt{3}} (e_{\Sigma^+g,1}^N + \sqrt{2} e_{\Sigma^+g,2}^N) = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \\ \tilde{e}_{\Sigma^+g,2}^N &= \frac{1}{\sqrt{6}} (-2e_{\Sigma^+g,1}^N + \sqrt{2} e_{\Sigma^+g,2}^N) = \frac{1}{\sqrt{6}} \begin{pmatrix} -2 \\ 1 \\ 1 \end{pmatrix} \\ \tilde{e}_{\Sigma^+u}^N &= e_{\Sigma^+u}^N = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}\end{aligned}$$



Then, for the symmetry adapted basis in  $L^{3N}$  we have

$L^N \otimes L^3$	$e_{\Pi_u,1}^3 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$	$e_{\Pi_u,2}^3 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$	$e_{\Sigma_u^+}^3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$
$\tilde{e}_{\Sigma_g^+,1}^N = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$	$T_x$	$T_y$	$T_z$
$\tilde{e}_{\Sigma_g^+,2}^N = \frac{1}{\sqrt{6}} \begin{pmatrix} -2 \\ 1 \\ 1 \end{pmatrix}$	$e_{\Pi_u,1}^{3N}$	$e_{\Pi_u,2}^{3N}$	$e_{\Sigma_u^+}^{3N}$
$\tilde{e}_{\Sigma_u^+}^N = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}$	$R_x$	$R_y$	$e_{\Sigma_g^+}^{3N}$

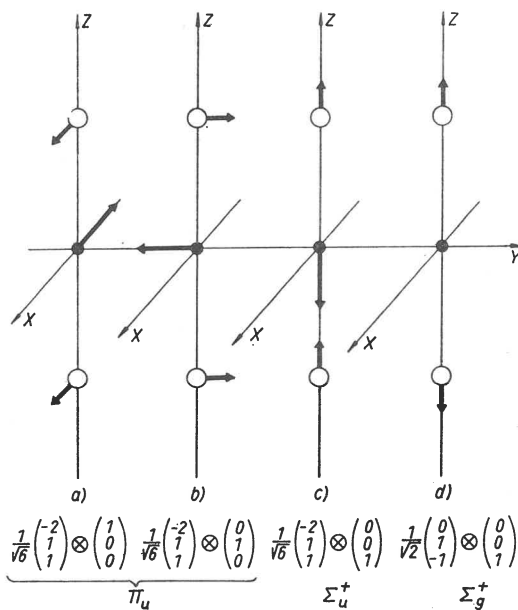


Fig. 3. The set of the pure vibrational symmetry adapted basis vectors for the linear  $XY_2$  molecule

The set of the pure vibrational symmetry adapted basis vectors is shown in the Fig. 3 a, b, c, d. This result is, of course, well known [15].

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