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Symmetry Adaption

IV. The Force Constant Matrix of Symmetric Molecules

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The matrix of force constants of a symmetric molecule is reduced to its invariants (nearly diagonal form). For the case of distance dependent potentials these invariants are expressed by the derivations of the potentials and geometric factors. For the purpose of parametrization the inversions of these formulae are derived. The general equilibrium condition and the elimination of the translational and rotational coordinates are discussed. The example of the tetrahedral AB_4 structure is worked out.

Key words: Force constants – Symmetry coordinates – Normal vibrations – Tetrahedral molecule

1. Introduction

As a further application of the SALC coefficients proposed in I [1] we want to attack a problem connected with symmetry coordinates. In doing so we shall use the mathematics worked out in II [2]. Our notations refer to this paper and the closely related example III [3] of the molecular overlap matrix. The problem is as follows: In a molecule $A_mB_nC_p\ldots$ with symmetry group G there are given distance dependent potentials $\Phi(|\boldsymbol{A}_i-\boldsymbol{B}_k|)$. For sake of generality we allow different potentials for symmetrically inequivalent edge vectors $\boldsymbol{S}_l=\boldsymbol{A}_i-\boldsymbol{B}_k$: $\Phi(S, |\boldsymbol{A}_i-\boldsymbol{B}_k|)$. It is clear from the first that the normal vibration frequencies in harmonic approximation will depend on the first and second derivatives of the potential only. We want to derive an explicit formula for the force constants with respect to symmetry coordinates as functions of these derivatives. The force constants will still form matrices with non-diagonal elements if there is more than one coordinate of one symmetry species. But the remaining diagonalization depends on the masses of the atoms A, B, etc. and cannot be achieved by group algebraic methods.

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2. General Potentials

For the first step to our aim it is not necessary to restrict the molecular potential in any way. We therefore start with an arbitrary potential $V(\boldsymbol{A}_1', \boldsymbol{A}_2', \ldots, \boldsymbol{B}_1', \boldsymbol{B}_2', \ldots)$, where the vectors $\boldsymbol{A}_i'$ etc. mean the actual nonequilibrium position and $\boldsymbol{A}_i$ the equilibrium. Thus the deviations are

$$\Delta \boldsymbol{A}_i = \boldsymbol{A}_i' - \boldsymbol{A}_i \tag{1}$$

For the partial differential operator with reference to component ΔA_{im} of vector $\Delta \boldsymbol{A}_i$ we write:

$$\nabla(Aim) = \partial / \partial \Delta A_{im}^* \tag{2}$$

The component indices refer to the complex basis of the spherical harmonics $|1m\rangle$. The formal complication of using complex coordinates has, of course, no consequences for our final results, but conforms to the definition of the gradient operator in the algebra of spherical harmonics [4]. The Cartesian force constants then are:

$$F(Aim, Bkn) = \nabla(Aim)\nabla(Bkn)V|_{\Delta \boldsymbol{A}_i = 0} \text{ etc.} \tag{3}$$

Since the elongations $\Delta \boldsymbol{A}_i$ belong to the angular momentum quantum number $l=1$, according to Eq. (20) of II the symmetry coordinates Q of symmetry species c (component p) are given by

$$Q(\gamma cp, A\alpha a\ell) = \sum_{im} M(\gamma cp, Ai\alpha a, (\ell)1m) \cdot \Delta A_{im} \tag{4}$$

Here we have omitted the multiplicity index β, because with the exception of the very low symmetries C_2, C_s, and C_{2h} the representations resulting from $l=1$ by subduction are different from each other. So we can save space and β may be supplemented afterwards, if necessary. The symmetry coordinates of the same species are distinguished according to the equivalent atomic set A, the irreducible representations a and ℓ, which occur in the reduction of σ^A and $l=1$, and by the multiplicity indices α of a in σ^A and γ of c in $a \times \ell$. The techniques of I and II allow the numerical calculation of the coefficients M for arbitrary structures via tabulated quantities without projection operators. But the algebraic formulae Eqs. (21), (15) of II or Eq. (7) of III moreover permit the tensor algebraic evaluation of the symmetry force constants leading to expressions which do neither depend on the chosen coordinates nor on the numeration of the equivalent atoms. Thus there is no need to know the numerical values of (4).

The differential operators of the symmetry coordinates are

$$\nabla(Q, \gamma cp, A\alpha a\ell) = \partial / \partial Q(\gamma cp, A\alpha a\ell)^* = \sum_{im} [\partial \Delta A_{im} / \partial Q(\gamma cp, A\alpha a\ell)] \cdot \nabla(Aim)$$

and with the inversion of (4):

$$\nabla(Q, \gamma cp, A\alpha a\ell) = \sum_{im} M(\gamma cp, Ai\alpha a, (\ell)1m) \cdot \nabla(Aim) \tag{5}$$

The matrix of the symmetry invariant force constants then is

$$F(c, \gamma A\alpha a\mathscr{b}, \gamma' B\alpha' a'\mathscr{b}') = V(Q, \gamma cp, A\alpha a\mathscr{b})^* V(Q, \gamma' cp, B\alpha' a'\mathscr{b}')V/_{\text{all } Q=0} \tag{6}$$

The connection between the two force constant matrices is because of (5):

$$F(c, \gamma A\alpha a\mathscr{b}, \gamma' B\alpha' a'\mathscr{b}') = \sum_{iknm} M(\gamma cp, Ai\alpha a, (\mathscr{b})1m)^* M(\gamma' cp, Bk\alpha' a', (\mathscr{b}')1n)F(Aim, Bkn) \tag{7}$$

and by inversion:

$$F(Aim, Bkn) = \sum_{\alpha a\mathscr{b}\gamma} \sum_{\alpha' a'\mathscr{b}'\gamma'} \sum_{cp} M(\gamma cp, Ai\alpha a, (\mathscr{b})1m)M(\gamma' cp, Bk\alpha' a', (\mathscr{b}')1n)^* F(c, \gamma A\alpha a\mathscr{b}, \gamma' B\alpha' a'\mathscr{b}') \tag{8}$$

This is in accordance with Eqs. (5) and (6) of III. For the numerical calculation of the invariants one again must calculate an equal number of elements $F(Aim, Bkn)$ and then use (8). For the derivation of an explicit formula from (7) one needs more information on the potential.

3. The Distance Dependent Potential

As already mentioned in the introduction the potential between $\boldsymbol{A}_i'$ and $\boldsymbol{B}_k'$ is supposed to be $\Phi(S, |\boldsymbol{A}_i' - \boldsymbol{B}_k'|)$, if $\boldsymbol{A}_i' - \boldsymbol{B}_k' = \boldsymbol{S}_n'$ or $|\boldsymbol{A}_i - \boldsymbol{B}_k| = S$. This condition can be formalized by the triangular matrices defined in Eq. (37) of II. Since $-\boldsymbol{A}_i + \boldsymbol{B}_k + \boldsymbol{S}_n = \boldsymbol{O}$, the potential of $\boldsymbol{A}_i - \boldsymbol{B}_k$ is

$$\Phi(S, |\boldsymbol{A}_i' - \boldsymbol{B}_k'|) = \sum_{Tr} Z(-ABT)^{1/2}\tau \begin{pmatrix} -A & B & T \\ i & k & r \end{pmatrix} \Phi(T, |\boldsymbol{T}_r'|)$$

and the total potential of the molecule:

$$V(\boldsymbol{A}_1', \boldsymbol{A}_2', \ldots, \boldsymbol{B}_1', \boldsymbol{B}_2', \ldots) = (1/2) \sum_{S \neq 0} \sum_{rCp} \sum_{Dq} Z(-CDS)^{1/2}\tau \begin{pmatrix} -C & D & S \\ p & q & r \end{pmatrix} \Phi(S, |\boldsymbol{S}_r'|) \tag{9}$$

The essential of Eq. (9) is the enumeration of the potentials not by the position vectors, but by the sets S of equivalent edge vectors. Only this sum of physical interest will survive till the final formulae.

The first derivatives are:

$$\nabla(Bkn)V = -(1/2) \sum_{S \neq 0} \sum_{rCp} Z(-CBS)^{1/2}\tau \begin{pmatrix} -C & B & S \\ p & k & r \end{pmatrix} \nabla(Srn)\Phi(S, |\boldsymbol{S}_r'|) \tag{10}$$

As for the second derivatives we have to distinguish two cases:

$$\nabla(Aim)^*\nabla(Bkn)V = -\sum_{S \neq 0} \sum_{r} Z(-ABS)^{1/2}\tau \begin{pmatrix} -A & B & S \\ i & k & r \end{pmatrix} \nabla(Srm)^*\nabla(Srn)\Phi(S, |\boldsymbol{S}_r'|) \tag{11}$$

with $A_i \neq B_k$, and

$$\nabla(Aim)^*\nabla(Ain)V = \sum_{S\neq 0}\sum_{Dqr} Z(-ADS)^{1/2}\tau\begin{pmatrix} -A & D & S \\ i & q & r \end{pmatrix} V(Srm)^*V(Srn)\Phi(S, |\boldsymbol{S}'_r|) \tag{12}$$

In order to get compact formulae for the derivatives at the right-hand side we express them in spherical harmonics using the gradient formula (1.35) of [4]. We write

$$\Phi(S, |\boldsymbol{S}'_r|) = (4\pi)^{1/2}\Phi(S, |\boldsymbol{S}'_r|)\langle \boldsymbol{S}'_r \mid 00\rangle$$

and get for the first derivatives

$$\nabla(Srn)\Phi(S, |\boldsymbol{S}'_r|) = (4\pi/3)^{1/2}\,\Phi'(S, |\boldsymbol{S}'_r|)\langle \boldsymbol{S}'_r \mid 1n\rangle, \tag{13}$$

where $\Phi'(S, x) = d\Phi(S, x)/dx$. The second derivatives are

$$\nabla(Srm)^*\nabla(Srn)\Phi(S, |\boldsymbol{S}'_r|)/\boldsymbol{S}'_r = \boldsymbol{S}_r = \sum_{LM} \sigma(L, S)\begin{pmatrix} L^+ & 1^+ & 1 \\ M & m & n \end{pmatrix}\langle \boldsymbol{S}_r \mid LM\rangle \tag{14}$$

with $\sigma(L, S) = (4\pi/3)^{1/2}\langle L\|\nabla(Sr)\|1\rangle\Phi'(S, S)$. For L^+ cf. Eq. (58) of II. Because we use the spherical harmonics in the phase convention $\langle \mathbf{r} \mid lm\rangle = il\,Y_{lm}(\vartheta, \varphi)$ we repeat the reduced matrix element:

$$\langle L\|\nabla^r\|l\rangle = [\delta(L, l+1)L^{1/2} + \delta(L, l-1)l^{1/2}]\cdot\left[\frac{1}{r}\frac{d}{dr}r + \frac{l(l+1) - L(L+1)}{2r}\right]$$

According to the selection rules there are two functions:

$$\begin{aligned} \sigma(0, S) &= (4\pi/3)^{1/2}[\Phi''(S, S) + 2\Phi'(S, S)/S] \\ \sigma(2, S) &= (8\pi/3)^{1/2}[\Phi''(S, S) - \Phi'(S, S)/S] \end{aligned} \tag{15}$$

We mention that $\sigma(0, S)$ vanishes for Coulomb potentials ($S \neq 0$). We now can substitute (11), (12) and (14) into (7). For the force constants between inequivalent set $A \neq B$ we only need (11) and (14):

$$\begin{aligned} F(c, \gamma A\alpha a\ell, \gamma' B\alpha' a'\ell') = -\sum_{LS\neq 0}\sigma(L, S)\sum_{imk}\sum_{nrM} M(\gamma cp, Ai\alpha a, (\ell)1m)^* \\ \cdot M(\gamma' cp, Bk\alpha' a', (\ell')1n)Z(-ABS)^{1/2}\tau\begin{pmatrix} -A & B & S \\ i & k & r \end{pmatrix}\begin{pmatrix} L^+ & 1^+ & 1 \\ M & m & n \end{pmatrix}\langle \boldsymbol{S}_r \mid LM\rangle \end{aligned}$$

The second sum is in exact accordance with Eq. (12) of III and we can express the force constants in close analogy with Eq. (11) of III by a "physical factor" $\sigma(L, S)$, i.e. the derivatives of the potentials, and a geometrical one:

$$F(c, \gamma A\alpha a\ell, \gamma' B\alpha' a'\ell') = -\sum_{LS\neq 0}\sigma(L, S)\cdot G(A\alpha a1\ell, B\alpha' a'1\ell', \gamma\gamma' c, L, S) \tag{16}$$

Because the geometrical factor can be evaluated via Eq. (15) of III, we have solved our problem in this case. Of course the factors can be taken over if LCAO calculations involving p-orbitals already have been worked out. We shall profit by this in our example.

In the case of force constants within an equivalent set A we get two sums, one for $i \neq k$ and one for $i=k$. Using (11) and (12) we derive from (7):

$$F(c, \gamma A\alpha a\ell, \gamma' A\alpha' a'\ell') = \sum_{S\neq 0} \sum_{irmn} M(\gamma cp, Ai\alpha a, (\ell)1m)^* \nabla(Srm)^* \nabla(Srn) \Phi(S, |\boldsymbol{S}_r'|)$$
$$\cdot \Bigg[-M(\gamma' cp, Ak\alpha' a', (\ell')1n) Z(-AAS)^{1/2} \tau \begin{pmatrix} -A & A & S \\ i & k & r \end{pmatrix}$$
$$+ \sum_{Dq} M(\gamma' cp, Ai\alpha' a', (\ell')1n) Z(-ADS)^{1/2} \tau \begin{pmatrix} -A & D & S \\ i & q & r \end{pmatrix} \Bigg]_{\boldsymbol{S}_r' = \boldsymbol{S}_r}$$

Inserting (14) again we get two terms, the first of which has the same structure as (16) and the second one leading to a second geometrical factor:

$$F(c, \gamma A\alpha a\ell, \gamma' A\alpha' a'\ell') = \sum_{LS\neq 0} \sigma(L, S)[-G(A\alpha a1\ell, A\alpha' a'1\ell', \gamma'\gamma' c, L, S)$$
$$+ H(A\alpha a1b, A\alpha' a'1\ell', \gamma\gamma' c, L, S)] \tag{17}$$

The second factor is defined by

$$H(A\alpha a1\ell, A\alpha' a'1\ell', \gamma\gamma' c, L, S)$$
$$= \sum_{irmn} \sum_{DqM} M(\gamma cp, Ai\alpha a, (\ell)1m)^* M(\gamma' cp, Ai\alpha' a', (\ell')1n)$$
$$\cdot Z(-ADS)^{1/2} \tau \begin{pmatrix} -A & D & S \\ i & q & r \end{pmatrix} \begin{pmatrix} L^+ & 1^+ & 1 \\ M & m & n \end{pmatrix} \langle \boldsymbol{S}_r \mid LM \rangle \tag{18}$$

and is evaluated in analogy to the G factor. As in this case we start with Eq. (7) of III, express the $3jm$-symbol in the s.a. basis as in Eq. (13) of III and insert this into (18). Now there are three V-coefficients, which again are collected in a Racah- and one V-coefficient. We then have:

$$H(A\alpha a i\ell, A\alpha' a'1\ell', \gamma\gamma' c, L, S)$$
$$= \Theta_\gamma(a\ell c^+) \sum_{\eta nn'} \sum_{irDq} \sum_{\mu ds} Is_\varepsilon \begin{pmatrix} L^+ & 1^+ & 1 \\ \mu d^+ & \ell^+ & \ell' \end{pmatrix} W \begin{pmatrix} d^+ & a'^+ & a \\ c & \ell & \ell' \end{pmatrix}_{\varepsilon\gamma\gamma'\eta}$$
$$\cdot V_\eta \begin{pmatrix} d^+ & a'^+ & a \\ s & n' & n \end{pmatrix} (A\alpha an \mid \boldsymbol{A}_i)(\boldsymbol{A}_i \mid A\alpha' a'n') \langle \boldsymbol{S}_r \mid L\mu ds \rangle Z(-ADS)^{1/2} \tau \begin{pmatrix} -A & D & S \\ i & q & r \end{pmatrix}$$

In difference to the G factor in III we now have the product of two standard functions of $\boldsymbol{A}_i$. According to Eq. (43) of II this can be expressed by a sum of standard functions. With the convention, Eq. (9) of II we get:

$$(A\alpha an \mid \boldsymbol{A}_i)(\boldsymbol{A}_i \mid A\alpha' a'n') = (\boldsymbol{A}_i \mid A\alpha' a'n')(\boldsymbol{A}_i \mid A\alpha a^+ n)$$
$$= \sum_{\beta\varphi\ell p} P_\beta(A, \varphi\ell \| \alpha' a' \| \alpha a^+) V_\beta \begin{pmatrix} \ell^+ & a' & a^+ \\ p & n' & n \end{pmatrix} (\boldsymbol{A}_i \mid A\varphi\ell p)$$

The sum over V_η and V_β can be evaluated immediately. In addition we expand $\langle \boldsymbol{S}_r | L\mu d s\rangle$ in standard functions as in Eq. (12) of II:

$$H(A\alpha a 1\ell, A\alpha' a' 1\ell', \gamma\gamma' c, L, S)$$
$$= \Theta_\gamma(a\ell c^+) \sum_{irDq} \sum_{\mu} \sum_{\delta\varphi\eta\varepsilon} Is_\varepsilon \begin{pmatrix} L^+ & 1^+ & 1 \\ \mu d^+ & \ell^+ & \ell \end{pmatrix} W \begin{pmatrix} d^+ & a'^+ & a \\ c & \ell & \ell' \end{pmatrix}_{\varepsilon\gamma\gamma'\eta}$$
$$\cdot P_\eta(A, \varphi d^+ \| \alpha' a' \| \alpha a^+)(\boldsymbol{A}_i | A\varphi d^+ s) c(S\delta d, L\mu)$$
$$\times (\boldsymbol{S}_r | S\delta d s) Z(-ADS)^{1/2} \tau \begin{pmatrix} -A & D & S \\ i & q & r \end{pmatrix} / \dim d$$

Finally the two standard functions and the τ matrix form a special polyhedral isoscalar, cf. Eq. (42) of II:

$$H(A\alpha a 1\ell, A\alpha' a' 1\ell', \gamma\gamma' c, L, S)$$
$$= \Theta_\gamma(a\ell c^+) \sum_{\varepsilon\delta\mu} \sum_{\varphi d D\eta} Is_\varepsilon \begin{pmatrix} L^+ & 1^+ & 1 \\ \mu d^+ & \ell^+ & \ell' \end{pmatrix} W \begin{pmatrix} d^+ & a'^+ & a \\ c & \ell & \ell' \end{pmatrix}_{\varepsilon\gamma\gamma'\eta} \tag{19}$$
$$\cdot P_\eta(A, \varphi d^+ \| \alpha' a' \| \alpha a^+) PIs \begin{pmatrix} -A & D & S' \\ \varphi d^+ & o & \delta d \end{pmatrix} c(S\delta d, L\mu) [Z(D) Z(-ADS)/\dim d]^{1/2}$$

The essential sums are d and D, the rest being due to multiplicities. Thus the structural coefficients defined in II, PIs, P and c, suffice to calculate all the geometrical factors in (17). In the following sections we work out some further consequences. But first we must come back to the tacitly presupposed equilibrium.

4. The Equilibrium Condition

The general equilibrium condition is:

$$\nabla(Akn) V/_{A\boldsymbol{A}_i = 0} = 0 \tag{20}$$

The insertion of (10) and (13) yields:

$$\sum_{S\neq 0} \sum_{rCp} Z(-CAS)^{1/2} \tau \begin{pmatrix} -CAS \\ pkr \end{pmatrix} \Phi'(S, S) \langle \boldsymbol{S}_r \mid 1n\rangle = 0$$

Now follow the manipulations: Transformation of $\langle \boldsymbol{S}_r \mid 1n\rangle$ into the s.a. form $\langle \boldsymbol{S}_r \mid 1\ell t\rangle$ and expansion of the latter in standard functions according to Eq. (12) of II, multiplication by $(\boldsymbol{A}_k \mid A\alpha a s)$ and summation over k. This yields:

$$\sum_{S\neq 0} \sum_{rCp} \sum_{\beta k} Z(-CAS)^{1/2} \tau \begin{pmatrix} -CAS \\ pkr \end{pmatrix} (\boldsymbol{A}_k \mid A\alpha a s)(\boldsymbol{S}_r \mid S\beta\ell t) c(S\beta\ell, 1) \Phi'(S, S) = 0$$

Because the sum over p is invariant under the symmetry transformations the equation is trivially zero for $a \neq \ell^+$. So we consider $a = \ell^+$. From Eq. (42) of II follows the special case:

$$PIs \begin{pmatrix} -C & A & S \\ o & \alpha a & \beta\ell \end{pmatrix} = \delta(a, \ell^+) [Z(S) \dim \ell]^{-1/2} \sum_{pikl} \tau \begin{pmatrix} -C & A & S \\ i & k & l \end{pmatrix}$$
$$(\boldsymbol{A}_k \mid A\alpha\ell^+ p)(\boldsymbol{S}_l \mid S\beta\ell p)$$

where o again means the totally symmetric representation. Inserting this we finally get the equilibrium conditions in the invariant form:

$$\sum_{S\neq 0}\sum_{C\beta}[Z(C)Z(-CAS)]^{1/2}PIs\begin{pmatrix}-C & A & S\\ o & \alpha\ell^{+} & \beta\ell\end{pmatrix}c(S\beta\ell,\,1)\Phi'(S,\,S)=0 \tag{21}$$

(21) implies a condition for every set A and for each representation ℓ, which is simultaneously contained in σ^A, σ^S and $\mathscr{D}^1(0(3))$. We shortly discuss the example $C(CH_3)_4$. There are two independent shape parameters, the radii of the C and the H spheres. The only possible representation is $\ell=T_2$, which is contained in σ^C and σ^H. Thus there are two Eqs. (21), the set A representing either the C atoms or the H atoms.

In general the different potentials $\Phi(S,\,S)$ will compensate each other at the equilibrium, which implies inner stresses in the molecular framework. If this is not the case, all potentials take on their minima simultaneously:

$$\Phi'(S,\,S)=0$$

This assumption halves the number of independent parameters in (15) and produces additional connections between the force constants.

5. Special Cases and Sum Rules

We discuss the special case of one of the equivalent sets containing the central atom only, $\boldsymbol{B}=\boldsymbol{O}$. (16) then becomes

$$F(b',\,\gamma A\alpha a\ell,\,Oo\ell')=-\sum_{L}\sigma(L,\,A)G(A\alpha a1\ell,\,Oo1\ell',\,\gamma1\ell',\,L,\,A) \tag{22}$$

where the special G factor is given by Eq. (16) of III.

For the diagonal elements with $\boldsymbol{A}=\boldsymbol{B}=\boldsymbol{O}$ we must specialize (17). As (15) shows the factor G vanishes in this case for $S\neq 0$ and we only get terms with H factors:

$$F(\ell,\,Oo\ell,\,Oo\ell')=\delta(\ell,\,\ell')\sum_{LS}\sigma(L,\,S)H(Oo1\ell,\,Oo1\ell,\,11\ell,\,L,\,S) \tag{23}$$

where the special factor is:

$$H(Oo1\ell,\,Oo1\ell,\,11\ell,\,L,\,S)=[Z(S)/\dim\ell]^{1/2}\sum_{\mu}Is\begin{pmatrix}L^{+} & 1^{+} & 1\\ \mu o & \ell^{+} & \ell\end{pmatrix}c(So,\,L\mu) \tag{24}$$

To get (24) one needs Eqs. (45) and (46) of II. Because L has only the values 0 and 2 in the expressions (16) and (17), it will be helpful to explicate the simple geometric factors for $L=0$:

$$G(A\alpha a1\ell,\,B\alpha' a'1\ell',\,\gamma\gamma' c,\,0,\,S)=\delta(\ell,\,\ell')\delta(a,\,a')\delta(\gamma,\,\gamma')[Z(-ASB)/\dim a]^{1/2}\cdot PIs\begin{pmatrix}-A & S & B\\ \alpha a^{+} & o & \alpha' a'\end{pmatrix}(Z(S)/4\pi)^{1/2}$$

$$H(A\alpha a1\ell,\,A\alpha' a'1\ell',\,\gamma\gamma' c,\,0,\,S)=\delta(\alpha,\,\alpha')\delta(a,\,a')\delta(\ell,\,\ell')\delta(\gamma,\,\gamma')Z(-ADS)(4\pi)^{-1/2}$$

where we used Eq. (46) of II and the special case:

$$PIs\begin{pmatrix} -ADS \\ ooo \end{pmatrix} = [Z(-ADS)/Z(A)Z(D)Z(S)]^{1/2} \tag{25}$$

As in III we can set up several sum rules for the diagonal elements of (17). In simple cases as for instance P_4 or if the non-diagonal elements can be neglected, these sum rules apply immediately to the quadrates of the normal vibration frequencies. One has to calculate the analogues of Eqs. (20–22) of III for the factor H. The analogue of Eq. (21) of III is

$$\sum_{\ell\gamma c} \dim c \cdot H(A\alpha a 1\ell, A\alpha a 1\ell, L, S) = \delta(L, 0)(3/4\pi)^{1/2} Z(-ADS)\dim a/Z(A) \tag{26}$$

where we suppose $Z(-ADS)=0$, if $-ADS$ is no triangle. This yields the sum rule:

$$\begin{aligned} \sum_{\ell\gamma c} \dim c \cdot F(c, \gamma A\alpha a\ell, \gamma A\alpha a\ell) = &- \sum_{S\neq 0} [\Phi''(S, S) + 2\Phi'(S, S)/S] \\ &\cdot [(Z(-ASA)Z(S)\dim a)^{1/2} PIs\begin{pmatrix} -A & S & A \\ \alpha a^{+} & o & \alpha a \end{pmatrix} - Z(-ADS)\dim a/Z(A)] \end{aligned} \tag{27}$$

and with further summation simply:

$$\sum_{\alpha a\ell} \sum_{\gamma c} \dim c \cdot F(c, \gamma A\alpha a\ell, \gamma A\alpha a\ell) = \sum_{S\neq 0} [\Phi''(S, S) + 2\Phi'(S, S)/S] Z(-ADS) \tag{28}$$

We again remark that the right side vanishes for purely Coulombic interaction. In this case the matrix of the force constants would not be positively definite.

6. Parametrization

If it is possible to determine all the invariant force constants by experiment one can regard $\Phi''(S, S)$ and $\Phi'(S, S)$ as fitting parameters. For this purpose one needs the inversion of (16) and (17). One again uses the orthogonality relation (24) of III. We derive from (16)

$$\begin{aligned} \sigma(L, S) = -(4\pi/Z(-ASB)) &\sum_{\alpha a\alpha' a'\ell\ell'} \sum_{\gamma\gamma' c} \dim c \\ &\cdot G(A\alpha a 1\ell, B\alpha' a' 1\ell' \gamma\gamma' c, L, S)^* \cdot F(c, \gamma A\alpha a\ell, \gamma' B\alpha' a'\ell'), \end{aligned} \tag{29}$$

which gives the parameters $\sigma(L, S)$ for the edge vectors S connecting different sets A and B. For the parameters within one equivalent set we have to invert (17). The second term in (17) makes no trouble, because we fortunately have the following orthogonality of the factors G and H:

$$\begin{aligned} \sum_{\alpha a\alpha' a'\ell\ell'} \sum_{\gamma\gamma' c} &\dim c \\ &\cdot G(A\alpha a 1\ell, A\alpha' a' 1\ell', \gamma\gamma' c, L, S) H(A\alpha a 1\ell, A\alpha' a' 1\ell', \gamma\gamma' c, L, S) \\ &= \delta(L, L')\delta(L, 0)\delta(S, 0)[4\pi Z(-ADS)]^{-1} \end{aligned} \tag{30}$$

Therefore (29) is the inversion of (17) too (with $A=B$, $S\neq 0$), and we can calculate all free parameters from the force constants. In order to prove (30) one uses the orthogonality relations of the W coefficients and isoscalars as in the case of Eq. (24) of III. The essential point then is the relation

$$\sum_{\alpha a}\sum_{\alpha' a'\eta} PIs^{*}_{\eta}\begin{pmatrix} -A & S & A \\ \alpha a^{+} & \delta d & \alpha a \end{pmatrix} P_{\eta}(A, \varphi d^{+}\|\alpha' a'\|\alpha a^{+}) = \delta(S, O)\delta(\delta, 1)\delta(\varphi, 1)\delta(d, o), \tag{31}$$

from which (30) follows immediately.

7. The Elimination of Translation and Rotation

Since we have started with the Cartesian coordinates of all atoms, the symmetry-invariant force-constant-matrix contains still the two zero-frequency eigenvalues of the translation and rotation of the whole molecule. In order to reduce the rank of the matrix it may be desirable to eliminate them. This is done by the conditions introduced by Eckart [5]:

$$\sum_{Ai} m(A)\cdot \Delta A_i = 0 \tag{32}$$

$$\sum_{Ai} m(A)\cdot A_i \times \Delta A_i = 0 \tag{33}$$

where $m(A)$ is the mass of one atom of set A. By inversion of (4) and insertion into (32) we get:

$$\sum_{Ai} m(A) \sum_{\alpha a \ell}\sum_{\gamma c p} M(\gamma c p, Ai\alpha a, (\ell)1m)\cdot Q(\gamma c p, A\alpha a\ell) = 0$$

We first evaluate the sum over i. Because of

$$\sum_{i} (A_i|A\alpha a q) = \delta(\alpha, 1)\delta(a, o)\delta(q, 0)Z(A)^{1/2}$$

we get:

$$\sum_{i} M(\gamma c p, Ai\alpha a, (\ell)1m) = \delta(\alpha, 1)\delta(a, o)\delta(\ell, c)\delta(\gamma, 1)Z(A)^{1/2}\langle 1m \mid 1cp\rangle$$

and therefore:

$$\sum_{Acp} m(A)\cdot Q(1cp, A1oc)Z(A)^{1/2}\langle 1cp \mid 1m\rangle = 0$$

By summation with $\langle 1m \mid 1\ell r\rangle$ the first condition yields:

$$\sum_{A} m(A)Z(A)^{1/2}Q(1\ell r, A1o\ell) = 0 \tag{34}$$

In order to evaluate (33) we have to express the vector product by Clebsch–Gordan coefficients or $3jm$-symbols, cf. formulae (5.1.5), (5.1.8) and (3.7.3) of [6]:

$$(A_i \times \Delta A_i)_p = i\cdot 2^{1/2}\sum_{nm} A_{in}\Delta A_{im}\langle 1n1m \mid 1p\rangle$$

We insert this into (33), write $A_{in}=(4\pi/3)^{1/2}A\langle A_i \mid 1n\rangle$, and express ΔA_{im} again by (4). This yields except for an irrelevant factor:

$$\sum_{Ainm} m(A)\cdot A\langle A_i \mid 1n\rangle \begin{pmatrix} 1^+ & 1^+ & 1 \\ n & m & p \end{pmatrix} \sum_{\alpha a b} \sum_{\gamma c q} M(\gamma c q,\, Ai\alpha a,\, (b)1m) \cdot Q(\gamma c q,\, A\alpha a b)=0$$

We convert the $|1n\rangle$ basis into the s.a. one, $|1dr\rangle$ etc., express the 3*jm*-symbol by an isoscalar and use Eq. (7) of III. Thus the condition becomes:

$$\sum_{Ai\alpha a b} \sum_{\gamma c q} \sum_{drsft\varepsilon} m(A)A\langle A_i \mid 1dr\rangle Is_\varepsilon \begin{pmatrix} 1^+ & 1^+ & 1 \\ d^+ & b^+ & f \end{pmatrix} V_\varepsilon \begin{pmatrix} d^+ & b^+ & f \\ r & s & t \end{pmatrix} \langle 1ft \mid 1p\rangle \dim c^{1/2}\cdot V_\gamma \begin{pmatrix} abc^+ \\ ksq \end{pmatrix} (A\alpha a k \mid A_i) Q(\gamma c q,\, A\alpha a b)=0$$

With (II.13) and the orthogonality of the coefficients V we get

$$\sum_{A\alpha a b} \sum_{\gamma c q} m(A)A\cdot c(A\alpha a,\, 1) Is_\gamma \begin{pmatrix} 1^+ & 1^+ & 1 \\ a^+ & b^+ & c \end{pmatrix} \langle 1cq \mid 1p\rangle Q(\gamma c q,\, A\alpha a b)\cdot \dim c^{-1/2}=0$$

and finally by summation with $\langle 1p \mid 1dr\rangle$:

$$\sum_{A\alpha a b} \sum_{\gamma} m(A)\cdot A\cdot c(A\alpha a,\, 1)\cdot Is_\gamma \begin{pmatrix} 1^+ & 1^+ & 1 \\ a^+ & b^+ & d \end{pmatrix} \cdot Q(\gamma dr,\, A\alpha a b)=0 \tag{35}$$

This is a condition for those symmetry coordinates for which a and b are contained in the representation $\mathscr{D}^{1-}(0(3))$, d in $\mathscr{D}^{1+}(0(3))$ and of course d in $a\times b$.

One can take account of the conditions (34) and (35) by forming linear combinations of the coordinates involved, which are orthogonal to (34) or (35) as is done in [7]. As an example we point to the Eqs. (39) and (40) below. An alternative procedure is to use (34) and (35) for the elimination of one of the involved symmetry coordinates and the related velocity from the energy function.

8. Example

As an example we study the vibrations of AB_4 type molecules or complexes. In accordance with the notations of the example in III we designate the positions of the four ligands by $\boldsymbol{R}_i$, the central atom by $\boldsymbol{O}$, and the distance vectors between the ligand atom by $\boldsymbol{S}_{ik}=\boldsymbol{R}_i-\boldsymbol{R}_k$. Since the elongation vectors $\Delta\boldsymbol{A}_i$ (i.e. $\Delta\boldsymbol{R}_i$ and $\Delta\boldsymbol{O}$ in our example) belong to the symmetry species T_2 like the *p*-orbitals, they induce the representations

$$T_2\times\sigma^R=T_2\times(A_1+T_2)=A_1+E+T_1+T_2$$

and

$$T_2\times\sigma^0=T_2\times A_1=T_2.$$

The geometric factors G for the R-sphere have been listed up in Table 5 of III, those for the O-R interaction in the subsequent discussion.

For the calculation of the factors H according to (19) we have to add to the polyhedral isoscalars already included in III the factors P defined by Eq. (44) of II. These are:

$$P(R, A_1\|A_1\|A_1)=1/2,\ P(R, A_1\|T_2\|T_2)=\sqrt{3}/2,\ P(R, T_2\|T_2\|T_2)=-\sqrt{3}/2$$

Since the polyhedral isoscalars could be tested by Eq. (49) of II we mention an analogous formula for the factors P:

$$\sum_{\alpha a}\sum_{\beta\delta\varepsilon} P^*_\varepsilon(S, \alpha a\|\beta\delta\|\gamma c)P_\varepsilon(S, \alpha a\|\beta\delta\|\gamma' c)=\delta(\gamma, \gamma')\dim c \tag{36}$$

Likewise condition (31) must be met. We then can list up the factors H calculated by (19).

Table 1. Geometric factors $H(Aa1\delta, A\alpha1\delta, c, L, P)\cdot\sqrt{4\pi}$ for the tetrahedral positions $\boldsymbol{R}_i$ and center $\boldsymbol{O}$

	$(L, P)=$			
$Aa1\delta, A\alpha1\delta, c$	$(0, S)$	$(2, S)$	$(0, R)$	$(2, R)$
RA_11T_2, RA_11T_2, T_2	$\sqrt{3}$	0	$1/\sqrt{3}$	0
RT_21T_2, RA_11T_2, T_2	0	$-\sqrt{3}/2$	0	$1/\sqrt{3}$
RT_21T_2, RT_21T_2, A_1	$\sqrt{3}$	$\sqrt{6}/2$	$1/\sqrt{3}$	$2/\sqrt{6}$
RT_21T_2, RT_21T_2, E	$\sqrt{3}$	$-\sqrt{6}/4$	$1/\sqrt{3}$	$-1/\sqrt{6}$
RT_21T_2, RT_21T_2, T_1	$\sqrt{3}$	$-\sqrt{6}/4$	$1/\sqrt{3}$	$-1/\sqrt{6}$
RT_21T_2, RT_21T_2, T_2	$\sqrt{3}$	$\sqrt{6}/4$	$1/\sqrt{3}$	$1/\sqrt{6}$
OA_11T_2, OA_11T_2, T_2	·	·	$4/\sqrt{3}$	0

We again mention a control formula:

$$\sum_{\alpha a\alpha' a'\delta}\sum_{\delta'\gamma\gamma' c}\dim c\cdot|H(Aa\alpha1\delta, A\alpha' a'1\delta', \gamma\gamma' c, L, S)|^2$$
$$=[Z(D)Z(-ADS)/(2L+1)]\cdot\sum_{d\mu\varphi}\left|\sum_\delta PIs\begin{pmatrix}-A & D & S\\ \varphi d^+ & c & \delta d\end{pmatrix}c(S\delta d, L\mu)\right|^2 \tag{37}$$

Since the symmetry species A_1, E, T_1 occur only once, we can write down their force constants immediately:

$$F(A_1, RT_2T_2, RT_2T_2)=\sqrt{4\pi}\cdot[(1/\sqrt{3}+\sqrt{3})\sigma(0, S)+(5/\sqrt{6}+\sqrt{6}/2)\sigma(2, S)$$
$$+(1/\sqrt{3})\sigma(0, R)+(2/\sqrt{6})\sigma(2, R)]$$
$$=4\Phi''(S, S)+\Phi''(R, R)$$

In the same way we get:

$$F(E, RT_2T_2, RT_2T_2)=\Phi''(S, S)+3\Phi'(S, S)/S+\Phi'(R, R)/R$$
$$F(T_1, RT_2T_2, RT_2T_2)=4\Phi'(S, S)/S+\Phi'(R, R)/R$$

Since T_1 is the symmetry species of the rotation according to (35) and $\mathscr{D}^{1+}(0(3))\to T_1(T_d)$, this force constant should be zero. In order to verify this we

have to take into account the equilibrium condition (21), which reads in our case:

$$[Z(0)Z(0R-R)]^{1/2}PIs\begin{pmatrix}0 & R & -R\\ A_1 & T_2 & T_2\end{pmatrix}c(RT_2,\,1)\Phi'(R,\,R)+[Z(R)Z(-RRS)]^{1/2}$$
$$\cdot[PIs\begin{pmatrix}-R & R & S\\ A_1 & T_2 & \alpha T_2\end{pmatrix}c(S\alpha T_2,\,1)+PIs\begin{pmatrix}-R & R & S\\ A_1 & T_2 & \beta T_2\end{pmatrix}c(S\beta T_2,\,1)]\Phi'(S,\,S)=0$$

Inserting the coefficients from III we get:

$$\Phi'(R,\,R)+\sqrt{6}\Phi'(S,\,S)=0$$

With regard to the geometric relation $S=\sqrt{8/3}\cdot R$ this yields:

$$F(T_1,\,RT_2T_2,\,RT_2T_2)=[4\Phi'(S,\,S)/\sqrt{8/3}+\Phi'(R,\,R)]/R=0$$

With respect to the symmetry species T_2 we have three coordinates $Q(T_2p,\,OA_1T_2)$, $Q(T_2p,\,RA_1T_2)$ and $Q(T_2p,\,RT_2T_2)$. The matrix elements of the force constants of this species are:

$$\begin{aligned}
F(T_2,\,RT_2T_2,\,RT_2T_2)&=2\Phi''(S,\,S)+2\Phi'(S,\,S)/S+(2/3)\Phi''(R,\,R)\\
&\quad+(1/3)\Phi'(R,\,R)/R\\
F(T_2,\,RA_1T_2,\,RA_1T_2)&=(1/3)[\Phi''(R,\,R)+2\Phi'(R,\,R)/R]\\
F(T_2,\,OA_1T_2,\,OA_1T_2)&=(4/3)[\Phi''(R,\,R)+2\Phi'(R,\,R)/R]\\
F(T_2,\,RT_2T_2,\,RA_1T_2)&=(\sqrt{2}/3)[\Phi''(R,\,R)-\Phi'(R,\,R)/R]\\
F(T_2,\,OA_1T_2,\,RA_1T_2)&=-(2/3)[\Phi''(R,\,R)+2\Phi'(R,\,R)/R]\\
F(T_2,\,OA_1T_2,\,RT_2T_2)&=-(\sqrt{8}/3)[\Phi''(R,\,R)-\Phi'(R,\,R)/R]
\end{aligned}\tag{38}$$

Because of T_2 being the species of the translation coordinate the matrix consisting of the elements (38) must have a zero eigenvalue. Indeed the transformation

$$Q(T_2p,\,\alpha)=5^{-1/2}[2Q(T_2p,\,RA_1T_2)+Q(T_2p,\,OA_1T_2)] \tag{39}$$

$$Q(T_2p,\,\beta)=(4m(R)^2+m(O)^2)^{-1/2}[m(O)Q(T_2p,\,RA_1T_2)$$
$$-2m(R)Q(T_2p,\,OA_1T_2)] \tag{40}$$

leads to the intended result. (39) is the translation coordinate, which is no more coupled to the other two, and (40) fulfils the condition (34). Thus the real vibrations of species T_2 are linear combinations of $Q(T_2p,\,\beta)$ and $Q(T_2p,\,RT_2T_2)$.

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