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# Effective Hamiltonian for multimode static Jahn–Teller effect in polycentre vibronic systems

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**Abstract.** The adiabatic potential of an arbitrary polycentre system with multimode vibronic interaction at each centre is investigated. It is shown that in the case when the extrema of this adiabatic potential are considered, an effective Hamiltonian for the static Jahn–Teller effect depending only on active one-centre nuclear displacements can be proposed. The expressions for the parameters of this Hamiltonian are obtained and its symmetry properties are elucidated.

## 1. Introduction

Multicentre vibronic interactions are manifested in a wide number of systems such as impurity Jahn–Teller centres [1], multicentre molecular clusters [2] and Jahn–Teller crystals [3]. However, the theory of vibronic interactions in these systems is not well-developed when compared with one-centre systems, due to some peculiarities which arise in the multicentre case. The latter consist of a great number of electronic states and vibrational modes of the multicentre system involved in vibronic mixing and offer difficulties even at the stage of investigating the adiabatic potential. The only exceptions are the cases of vibronic interactions of  $E \otimes b_1$  and  $T \otimes e$ -type at the centres, i.e. when one-centre electronic states are not mixed by vibrational modes [4]. In these cases each electronic state of the multicentre system becomes a sheet of the adiabatic potential, but the vibronic interaction is manifested only in the shift of the equilibrium points of normal vibrations of the zeroth-order harmonic Hamiltonian [5].

In the general case, when the operators of vibronic interaction at the centres are of non-diagonal form, the expressions for the sheets of the adiabatic potential contain nonlinear combinations of normal coordinates of the zeroth-order harmonic Hamiltonian. An example of such situations are biocahedral systems with  $E \otimes e$ -interaction at each centre. An approach based on the use of the one-centre nuclear coordinates was proposed for the investigation of the adiabatic potential of molecular systems of this type [6]. However, such an approach seems to be less adequate in the case of two interacting Jahn–Teller impurities in the crystal. That is why in the work [7] a model Hamiltonian for the static Jahn–Teller effect in this system was used without due substantiation. Another approach [8, 9] is based on the assumption that the displacement fields due to the impurities are independent. Obviously, such an approximation is justified only for sufficiently distant impurities, when the effects of their interaction on the one-centre vibronic instability generating these displacement fields, can be neglected.

In the present paper it is shown that the problem of the investigation of the static Jahn–Teller effect in an arbitrary polycentre system with multimode vibronic interaction is reduced exactly to the consideration of an effective Hamiltonian depending on active one-centre nuclear displacements only.

## 2. Effective Hamiltonian for static Jahn–Teller effect

Consider an arbitrary multiatomic system with Jahn–Teller centres, which are not supposed to be equivalent. The distortions of this system are described by normal coordinates  $Q_{\mu\Gamma\gamma}$ , which transform as irreducible representations  $\Gamma$  of the corresponding symmetry group  $G$ . The vibronic mixing of the set of local electronic states by a number of one-centre symmetrized nuclear displacements  $\{q_{\mu\Gamma\gamma}^{(n)}\}$  which transform as irreducible representations of the corresponding site-symmetry group  $G^{(n)}$  takes place at each centre. In the following the coordinates  $q_{\mu\Gamma\gamma}^{(n)}$  (they are also called active coordinates) and  $Q_{\mu\Gamma\gamma}$  are considered to be real. In the absence of direct intercentre interaction of electronic states the Hamiltonian of the static Jahn–Teller effect can be written as follows:

$$\hat{H} = \sum_{\mu\Gamma\gamma} \frac{1}{2} \omega_{\mu\Gamma\gamma}^2 Q_{\mu\Gamma\gamma}^2 + \sum_n \hat{U}_{\text{vib}}^{(n)}(\{q_{\mu\Gamma\gamma}^{(n)}\}) \quad (1)$$

where  $\omega_{\mu\Gamma\gamma}$  are the frequencies of the zeroth-order harmonic Hamiltonian of the multiatomic system and  $\hat{U}_{\text{vib}}^{(n)}$  is the operator of vibronic interaction at the  $n$ th centre. The matrix of this operator is written in the basis of the electronic states of the corresponding centre. The eigenvalues of the operator (1) (the sheets of the adiabatic potential) can be obtained after the unitary transformation:

$$\hat{H} = S^+ \hat{H} S. \quad (2)$$

Obeying the condition under which the Hamiltonian (1) was written, i.e. when the commutation of the electronic operators of different centres takes place, the operator of the unitary transformation takes the form [10]:

$$S = S^{(1)}(\{q_{\mu\Gamma\gamma}^{(1)}\}) \otimes S^{(2)}(\{q_{\mu\Gamma\gamma}^{(2)}\}) \otimes \dots \quad (3)$$

where  $S^{(n)}(\{q_{\mu\Gamma\gamma}^{(n)}\})$  is the matrix of the unitary transformation which diagonalizes the operator of vibronic interaction of the  $n$ th centre. These matrices are known for most vibronic problems [4]. Fulfilling the transformations (2), (3) we obtain the following expression for the sheets of the adiabatic potential:

$$U_{\alpha_1\alpha_2\dots} = \sum_{\mu\Gamma\gamma} \frac{1}{2} \omega_{\mu\Gamma\gamma}^2 Q_{\mu\Gamma\gamma}^2 + \sum_n \varepsilon_{\alpha_n}^{(n)}(\{q_{\mu\Gamma\gamma}^{(n)}\}) \quad (4)$$

where the index  $\alpha_n$  numbers the eigenvalues of the operator of vibronic interaction at the  $n$ th centre. To find the extrema of the sheets of the adiabatic potential it is necessary to express  $\varepsilon_{\alpha_n}^{(n)}$  in terms of  $Q_{\mu\Gamma\gamma}$  using the expansion

$$q_{\mu\Gamma\gamma}^{(n)} = \sum_{\mu\Gamma\gamma} a_{\mu\Gamma\gamma}^{(n)}(\mu\Gamma\gamma) Q_{\mu\Gamma\gamma} \quad (5)$$

and to solve the corresponding extrema equations. However, as was mentioned above, the eigenvalues  $\varepsilon_{\alpha_n}^{(n)}$  are complicated functions of  $Q_{\mu\Gamma\gamma}$  when the operators of vibronic interaction at the centres have a non-diagonal form. In this case the corresponding

extrema equations become practically unsolvable for systems with a large number of vibrational modes.

The above complication can be avoided if we search the extrema in the space of both the coordinates  $Q_{\mu\Gamma\gamma}$  and  $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}$ . Due to the coupling conditions imposed on these coordinates by the equations (5) the following functional must be considered:

$$F_{\alpha_1\alpha_2\dots} = U_{\alpha_1\alpha_2\dots} + \sum_n \sum_{\bar{\mu}\bar{\Gamma}\bar{\gamma}} \lambda_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)} \left( q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)} - \sum_{\mu\Gamma\gamma} a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma) Q_{\mu\Gamma\gamma} \right) \tag{6}$$

where  $\lambda_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}$  are the Lagrange multipliers [11]. The extrema equations in this case take the following form:

$$\left. \begin{aligned} \frac{\partial F_{\alpha_1\alpha_2\dots}}{\partial Q_{\mu\Gamma\gamma}} &= \omega_{\mu\Gamma}^2 Q_{\mu\Gamma\gamma} - \sum_n \sum_{\bar{\mu}\bar{\Gamma}\bar{\gamma}} \lambda_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)} a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma) = 0 \\ \frac{\partial F_{\alpha_1\alpha_2\dots}}{\partial q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}} &= \frac{\partial \varepsilon_{\alpha_n}^{(n)}(\{q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}\})}{\partial q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}} + \lambda_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)} = 0 \\ q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)} - \sum_{\mu\Gamma\gamma} a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma) Q_{\mu\Gamma\gamma} &= 0 \end{aligned} \right\} \tag{7}$$

Multiplying the first equation from (7) by  $a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma)/\omega_{\mu\Gamma}^2$  and fulfilling the summation over  $\mu\Gamma\gamma$  we have, after using the third equation from (7), the expression:

$$q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)} = \sum_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'} \lambda_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n')} \zeta_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{n\bar{\mu}\bar{\Gamma}\bar{\gamma}} \tag{8}$$

where the following notation is introduced

$$\zeta_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{n\bar{\mu}\bar{\Gamma}\bar{\gamma}} = \sum_{\mu\Gamma\gamma} \frac{a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma) a_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n')}(\mu\Gamma\gamma)}{\omega_{\mu\Gamma}^2} \tag{9}$$

The matrix  $\zeta$  is Hermitian and depends on the elastic parameters of the multiatomic system only. Using the inverse matrix  $\zeta^{-1}$  (in the following denoted by  $\mathcal{K}$ ) which is Hermitian too, the Lagrange multipliers can be expressed from (8):

$$\lambda_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)} = \sum_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'} \mathcal{K}_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{n\bar{\mu}\bar{\Gamma}\bar{\gamma}} q_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n')} \tag{10}$$

Substituting the expression (10) into the second equation from (7) we obtain

$$\frac{\partial \varepsilon_{\alpha_n}^{(n)}(\{q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}\})}{\partial q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}} + \sum_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'} \mathcal{K}_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{n\bar{\mu}\bar{\Gamma}\bar{\gamma}} q_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n')} = 0 \tag{11}$$

So we have reduced the system of extrema equations for the sheet  $U_{\alpha_1\alpha_2\dots}$  to a limited number of equations depending on active invibronic interaction one-centre symmetrized displacements only. Solving the system of equations (11), the equilibrium values of these coordinates in the extrema points  $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n(0))}$  are obtained. Substituting these values into (10) and then into the first equation from (7) we obtain the expression for the equilibrium values of all nuclear coordinates in the extrema points:

$$Q_{\mu\Gamma\gamma}^{(0)} = \frac{1}{\omega_{\mu\Gamma}^2} \sum_{n\bar{\mu}\bar{\Gamma}\bar{\gamma}} a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma) \sum_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'} \mathcal{K}_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{n\bar{\mu}\bar{\Gamma}\bar{\gamma}} q_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n'(0))} \tag{12}$$

Finally the energies of stabilization in the extrema points can be obtained after substituting (12) into (4):

$$U_{a_1 a_2 \dots} = \frac{1}{2} \sum_{\substack{n\bar{\mu}\bar{\Gamma}\bar{\gamma} \\ n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}} \mathcal{K}_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{n\bar{\mu}\bar{\Gamma}\bar{\gamma}} q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)(0)} q_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n')(0)} + \sum_n \varepsilon_{a_n}^{(n)} (\{q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)(0)}\}). \quad (13)$$

As follows from expressions (12) and (13), the extrema of the adiabatic potential are completely determined by equilibrium values of active one-centre displacements. The expression (13) can be treated as the sheets of an effective adiabatic potential. Indeed when replacing the equilibrium values in (13) by the corresponding variables, the expressions (11) can be considered as extrema equations for this effective adiabatic potential. Making a unitary transformation inverse to (2), the effective Hamiltonian for the static Jahn-Teller effect in polycentre vibronic systems is obtained:

$$\hat{H} = \frac{1}{2} \sum_{\substack{n\bar{\mu}\bar{\Gamma}\bar{\gamma} \\ n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}} \mathcal{K}_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{n\bar{\mu}\bar{\Gamma}\bar{\gamma}} q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)} q_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n')} + \sum_n \hat{U}_{\text{vib}}^{(n)} (\{q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}\}). \quad (14)$$

This Hamiltonian is equivalent to that given by expression (1) when the extrema of adiabatic potential are considered, but depends on active one-centre nuclear displacements only. It does not mean, however, that only these one-centre displacements are different from zero in the extrema points. Some non-active one-centre nuclear displacements  $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}$  are also different from zero. Indeed, expressing them through normal coordinates

$$q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)} = \sum_{\mu\Gamma\gamma} a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma) Q_{\mu\Gamma\gamma} \quad (15)$$

and using (12) we obtain

$$q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)(0)} = \sum_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'} \zeta_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{n\bar{\mu}\bar{\Gamma}\bar{\gamma}} \sum_{n''\bar{\mu}''\bar{\Gamma}''\bar{\gamma}''} \mathcal{K}_{n''\bar{\mu}''\bar{\Gamma}''\bar{\gamma}''}^{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'} q_{\bar{\mu}''\bar{\Gamma}''\bar{\gamma}''}^{(n'')(0)} \quad (16)$$

where the matrix  $\zeta$  has the form:

$$\zeta_{n'\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{n\bar{\mu}\bar{\Gamma}\bar{\gamma}} = \sum_{\mu\Gamma\gamma} \frac{a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma) a_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n')}(\mu\Gamma\gamma)}{\omega_{\mu\Gamma}^2}. \quad (17)$$

So  $\zeta$  has the same form as  $\zeta$  but is determined on the basis of both active and non-active one-centre nuclear displacements.

### 3. Properties of the force constants matrix $\mathcal{K}$

The Hamiltonian (14), as well as (1), is an invariant of the symmetry group  $G$ . The matrix  $\zeta$  is an inverse one for the force constants matrix  $\mathcal{K}$  and, therefore, have the same symmetry properties. So, if any elements of the matrix  $\zeta$  are equal to zero from symmetry reasons, the same matrix elements in  $\mathcal{K}$  will be also equal to zero. The symmetry properties of the matrices  $\mathcal{K}$  and  $\zeta$  are established below.

Consider an arbitrary matrix element of  $\zeta$ . The expansion coefficients  $a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma)$  contained in the matrix element (9) obviously will be different from zero only if  $\bar{\Gamma} \in \Gamma$  when the reduction of group  $G \rightarrow G^{(n)}$  takes place. The normal coordinates of the multi-atomic system  $Q_{\mu\Gamma\gamma}$  can be classified using irreducible representations  $\bar{\Gamma}$  of the symmetry

group of the  $n$ th centre. Because  $G^{(n)}$  is a subgroup of  $G$  we can generally expect the following reduction of the representations:

$$\Gamma = \sum_i^{\oplus} \bar{n}_i \bar{\Gamma}_i \quad (18)$$

where  $\bar{n}_i$  is the number of repeating representation  $\bar{\Gamma}_i$ . Each set of normal coordinates  $\{Q_{\mu\Gamma\gamma}\}$  with fixed  $\mu$  and  $\Gamma$  can be transformed into another set of normal coordinates  $\{\tilde{Q}_{\bar{\mu}_1\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma)\}$  which forms a basis of the irreducible representation of the group  $G^{(n)}$ :

$$\tilde{Q}_{\bar{\mu}_1\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma) = \sum_{\gamma} (C^{(n)}(\mu\Gamma))_{\gamma}^{\bar{\mu}_1\bar{\Gamma}\bar{\gamma}} Q_{\mu\Gamma\gamma} \quad (19)$$

where  $C^{(n)}(\mu\Gamma)$  is a unitary matrix and the superscript  $(n)$  on both sides of equation (19) indicates the centre under consideration. Obviously, the irreducible representations  $\bar{\Gamma}$  from (19) can be only those contained in (18) and the corresponding index  $\bar{\mu}_1$  takes the values  $1 \leq \bar{\mu}_1 \leq \bar{n}_i$  for a given  $\Gamma$ .

The one-centre nuclear coordinates  $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}$  can now be decomposed using a new set of normal coordinates (19):

$$q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)} = \sum_{\mu\Gamma} \sum_{\bar{\mu}_1} \tilde{a}_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\bar{\mu}_1\mu\Gamma) \tilde{Q}_{\bar{\mu}_1\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma) \quad (20)$$

where  $\tilde{a}_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\bar{\mu}_1\mu\Gamma)$  are new expansion coefficients. Substituting (19) into (20) we obtain for the expansion coefficients  $a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma)$  the following expression:

$$a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma) = \sum_{\bar{\mu}_1} \tilde{a}_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\bar{\mu}_1\mu\Gamma) (C^{(n)}(\mu\Gamma))_{\gamma}^{\bar{\mu}_1\bar{\Gamma}\bar{\gamma}}. \quad (21)$$

Using (21) the following relations are found:

$$\begin{aligned} & \sum_{\mu\Gamma\gamma} a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma) a_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n)}(\mu\Gamma\gamma) f(\omega_{\mu\Gamma}) \\ &= \sum_{\mu\Gamma} \sum_{\bar{\mu}_1\bar{\mu}_2} \tilde{a}_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\bar{\mu}_1\mu\Gamma) \tilde{a}_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n)}(\bar{\mu}_2\mu\Gamma) f(\omega_{\mu\Gamma}) \sum_{\gamma} (C^{(n)}(\mu\Gamma))_{\gamma}^{\bar{\mu}_1\bar{\Gamma}\bar{\gamma}} (C^{(n)}(\mu\Gamma))_{\gamma}^{\bar{\mu}_2\bar{\Gamma}'\bar{\gamma}'} \\ &= \delta_{\bar{\Gamma}\bar{\Gamma}'} \delta_{\bar{\gamma}\bar{\gamma}'} \sum_{\mu\Gamma\gamma} a_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}(\mu\Gamma\gamma) a_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n)}(\mu\Gamma\gamma) f(\omega_{\mu\Gamma}) \end{aligned} \quad (22)$$

where the orthogonality of the coefficients of the unitary transformation (19) has been used and  $f(\omega_{\mu\Gamma})$  is an arbitrary function of  $\omega_{\mu\Gamma}$ . Thus the one-centre matrix elements of  $\zeta$  and  $\mathcal{K}$  are diagonal after both the irreducible representation and row indices.

The same symmetry properties can be established for an expression of type (19) written for two different centres  $n$  and  $n'$ . The selection rules for the matrix elements of  $\zeta$  and  $\mathcal{K}$  are determined in this case by the pair symmetry of these centres. Consider first a system consisting of two centres only. In this case the pair symmetry group coincides with the group  $G$  and the equality  $G^{(n)} = G^{(n')}$  obviously takes place. Therefore the local symmetrized nuclear displacements at the centre  $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}^{(n)}$  and  $q_{\bar{\mu}'\bar{\Gamma}'\bar{\gamma}'}^{(n')}$  can always be chosen in such a way as to transform identically under the symmetry operations of the group  $G$ . In this case the effective elastic Hamiltonian in (14) will contain as invariants of the group  $G$  only such bilinear terms of symmetrized nuclear displacements of different centres which are diagonal after the indices  $\bar{\Gamma}$  and  $\bar{\gamma}$ . In accordance with the symmetry equivalence of matrices  $\mathcal{K}$  and  $\zeta$  mentioned above, the corresponding matrix elements will be different from zero also in the matrix  $\zeta$ . When a multicentre system is considered, the pair symmetry of two arbitrary centres is generally a subgroup of  $G$ .

The selection rules are the same as in the two-centre case if the symmetrized displacements are classified after the irreducible representations of the subgroup  $\tilde{G}^{(n)}$  of the site symmetry group  $G^{(n)}$  of the corresponding centre. This subgroup includes those symmetry operations of the group  $G^{(n)}$  which do not affect the position of the pair axis.

The established symmetry properties of the matrices  $\zeta$  and  $\mathcal{K}$  allow one to reduce substantially the number of independent matrix element. Consider, as an example, a system of two impurities in the rock salt lattice. A single impurity has the site symmetry group  $O_h$ . Let us suppose that this impurity forms a vibronic centre with the active one-centre displacements of type  $E_g$ . In the case of two such impurities, the site symmetry groups  $G^{(n)}$  and the symmetry group  $G$  are determined by their mutual position. We consider below three situations when the impurity centres are on the three-, four- and two-fold symmetry axis of the crystal. The local active displacements of the different centres pass into each other under reflection relative to the plane perpendicular to the axis connecting these centres. As can be seen from table 1 the matrices  $\zeta$  and  $\mathcal{K}$  contain two independent parameters in the case of three-fold symmetry axis and four in the other two cases.

Table 1. Force constants for two-centre impurity systems in the rock salt lattice.

Pair axis	(111)	(100)	(110)
Pair symmetry group $G$	$D_{3d}$	$D_{4h}$	$D_{2h}$
Site symmetry group $G^{(n)}$	$C_{3v}$	$C_{4v}$	$C_{2v}$
Reduction of the representation $E_g$ in the $G^{(n)}$ group	$E$	$A_1 + B_1$	
Non-zero elements of the matrix $\zeta$	$\zeta_{1E_g^2}^1 = \zeta_{1E_g^2}^1 = \zeta_{2E_g^2}^2 = \zeta_{2E_g^2}^2$ $= \zeta_{2E_g^2}^2 = \zeta_0$ $\zeta_{2E_g^2}^1 = \zeta_{1E_g^2}^2 = \zeta_{2E_g^2}^1$ $= \zeta_{1E_g^2}^1 = \zeta_1$	$\zeta_{1A_1}^1 = \zeta_{2A_1}^2 = \zeta_{A_1}$ $\zeta_{1B_1}^1 = \zeta_{2B_1}^2 = \zeta_{B_1}$ $\zeta_{2A_1}^1 = \zeta_{1A_1}^2 = \zeta_{A_1 A_1}$ $\zeta_{2B_1}^1 = \zeta_{1B_1}^2 = \zeta_{B_1 B_1}$	
Non-zero elements of the matrix $\mathcal{K}$	$\mathcal{K}_{1E_g^2}^1 = \mathcal{K}_{1E_g^2}^1 = \mathcal{K}_{2E_g^2}^2$ $= \mathcal{K}_{2E_g^2}^2 = \frac{\zeta_0}{\zeta_0^2 - \zeta_1^2}$ $\mathcal{K}_{2E_g^2}^1 = \mathcal{K}_{1E_g^2}^2 = \mathcal{K}_{2E_g^2}^1$ $= \mathcal{K}_{1E_g^2}^1 = -\frac{\zeta_1}{\zeta_0^2 - \zeta_1^2}$	$\mathcal{K}_{1A_1}^1 = \mathcal{K}_{2A_1}^2 = \frac{\zeta_{A_1}}{\zeta_{A_1}^2 - \zeta_{A_1 A_1}^2}$ $\mathcal{K}_{1B_1}^1 = \mathcal{K}_{2B_1}^2 = -\frac{\zeta_{B_1}}{\zeta_{B_1}^2 - \zeta_{B_1 B_1}^2}$ $\mathcal{K}_{2A_1}^1 = \mathcal{K}_{1A_1}^2 = -\frac{\zeta_{A_1 A_1}}{\zeta_{A_1}^2 - \zeta_{A_1 A_1}^2}$ $\mathcal{K}_{2B_1}^1 = \mathcal{K}_{1B_1}^2 = -\frac{\zeta_{B_1 B_1}}{\zeta_{B_1}^2 - \zeta_{B_1 B_1}^2}$	

As follows from (9), the elements of the matrix  $\zeta$  (and of the matrix  $\mathcal{K}$  as well) become available if the expansion coefficients (5) and the frequencies of the zeroth-order vibrations are known. The latter imply a knowledge of the normal coordinates, i.e. the solution of the corresponding vibrational problem. In the case of a crystal-type system the matrix  $\zeta$  can be found in another way. To obtain the expansion coefficients, first we must express the one-centre active coordinates  $q_{\mu\bar{\mu}\bar{\nu}}^{(n)}$  through the displacements of the atoms from the vicinity of the corresponding centre:

$$q_{\mu\bar{\mu}\bar{\nu}}^{(n)} = \sum_{n'\kappa\alpha} C_{\mu\bar{\mu}\bar{\nu}}(n-n', \kappa, \alpha) x_{\kappa\alpha}(n') \quad (23)$$

where  $x_{\kappa\alpha}(\mathbf{n}')$  is the Cartesian displacement of the atom of type  $\kappa$  at the unit cell  $\mathbf{n}'$  of the crystal,  $\alpha$  denotes the Cartesian axis. If the one-centre vibronic mixing involves localized electronic states of a given centre, the active nuclear coordinates contain the displacements of the corresponding nearest neighbour atoms. Thus only a few terms are contained in the sum (23). The atomic displacements are further expressed through normal coordinates, i.e. the phonon coordinates  $Q_{kj}$  as follows [12]:

$$x_{\kappa\alpha}(\mathbf{n}) = \frac{1}{\sqrt{NM_\kappa}} \sum_{kj} e_{\kappa\alpha}(j)^k Q_{kj} \exp(ik\mathbf{n}) \quad (24)$$

where  $k$  and  $j$  denote the momentum and the branch of the phonon,  $M_\kappa$  is the mass of the  $\kappa$  atom,  $N$  is the number of the unit cells in the crystal, and  $e_{\kappa\alpha}(j)^k$  denotes the polarization vector. The phonon coordinates from (24) are complex and obey the relation  $Q_{kj} = Q_{kj}^*$ . Substituting (24) into (23) and using equation (5), the expansion coefficients  $a_{\mu\bar{\Gamma}\bar{\gamma}}^{(n)}(kj)$ , i.e. the Van Vleck coefficients [13], are obtained. The expression (9) takes the form:

$$\begin{aligned} \zeta_{\mathbf{n}'\mu\bar{\Gamma}\bar{\gamma}\mathbf{n}''\mu'\bar{\Gamma}'\bar{\gamma}'} &= \sum_{kj} \frac{a_{\mu\bar{\Gamma}\bar{\gamma}}^{(n)}(kj)^* a_{\mu'\bar{\Gamma}'\bar{\gamma}'}^{(n)}(kj)}{\omega_{kj}^2} \\ &= \sum_{lm} \sum_{\kappa'\kappa} \sum_{\alpha\beta} C_{\mu\bar{\Gamma}\bar{\gamma}}(\mathbf{n}'-l, \kappa', \alpha) C_{\mu'\bar{\Gamma}'\bar{\gamma}'}(\mathbf{n}''-m, \kappa, \alpha) G_{\kappa'\alpha, \kappa\beta}(m-l) \end{aligned} \quad (25)$$

where  $G_{\kappa'\alpha, \kappa\beta}(\mathbf{n})$  are static lattice Green functions [14, 12]:

$$G_{\kappa'\alpha, \kappa\beta}(m-l) = \frac{1}{N} \sum_{kj} \frac{e_{\kappa'\alpha}(j)^k e_{\kappa\beta}(j)^k}{\sqrt{M_{\kappa'}M_\kappa} \omega_{kj}^2} \exp ik(m-l). \quad (26)$$

These Green functions were found for a number of crystals both from calculations [14, 15] and from neutron scattering measurements [16-19]. Thus the matrix  $\zeta$  can be obtained for these crystals avoiding the solution of a complicated phonon problem.

The equation (25) is correct, strictly speaking, only for a system with translational symmetry. So the multicentre vibronic system must form a Jahn-Teller crystal. Concerning an impurity system, the zeroth-order phonon Hamiltonian can be used only if the defects of mass and force constants induced by the impurities in the regular lattice can be neglected. When this approximation is not justified the impurity effects on the force constants matrix  $\mathcal{K}$  are to be taken into account, which is simpler to do within the Green functions formalism [12].

It is generally known that the one-centre elastic force constants are usually much greater than the intercentre elastic interactions. The latter change markedly with the variations of the intercentre distance [20]. For two distant centres this interaction changes as  $R^{-3}$ , where  $R$  is the intercentre distance [20, 21]. The same behaviour is expected for intercentre matrix elements of  $\zeta$  and  $\mathcal{K}$ . The relationship between one-centre and intercentre matrix elements determines the type of equilibrium nuclear configuration of the multicentre system [6], which can thus change with the variation of the intercentre distances.

After the determination of the matrix  $\mathcal{K}$  the investigation of the extrema of the adiabatic potential using equation (11) becomes equivalent to the corresponding molecular problem. So the three situations considered in table 1 (with the arbitrary intercentre distances) are equivalent to face-, corner- and edge-shared biotahedra, respectively. The adiabatic potential of these systems with the vibronic interaction of  $E \otimes e$  type at the centres was investigated earlier [6]. The only difference between the



impurity system and the corresponding molecular one is contained in the matrix elements of  $\zeta$ .

#### 4. Concluding remarks

To conclude, the investigation of the extrema of the adiabatic potential of an arbitrary multicentre and multimode vibronic system can be reduced exactly to the investigation of an effective adiabatic potential in the space of active one-centre displacements only. In the case of a few centres this problem becomes a molecular one.

The non-Jahn-Teller distortions are different from zero together with the Jahn-Teller ones in the extrema points of the adiabatic potential of multicentre system as shown by expression (16). This expression also indicates that the non-active nuclear displacements of a given vibronic centre are induced in the main by the active one-centre displacements of the neighbour centres. Indeed, the corresponding contributions in (16) are linear in the non-diagonal matrix element of  $\zeta$ . The direct effect of the active one-centre displacements on non-active displacements of the same centre cannot take place due to symmetry reasons (19). It can be manifested indirectly at higher order in non-diagonal elements of  $\zeta$  and  $\mathcal{H}$ .

In the absence of intercentre elastic interaction the effective elastic Hamiltonian in (14) contains only one parameter  $\zeta^{-1}$ . The latter corresponds exactly to the parameter  $\omega_{E_g}^{-2}$  (formulae 3.5.33 from [22]), which appears in the expressions for the adiabatic potential of the one-centre multimode Jahn-Teller effect.

The effective vibronic Hamiltonian was derived above without detailing the zeroth-order vibrations of the multiatomic system. However, special attention must be paid to the case of crystal vibrations including the interaction with the free surface, which is important, for example in crystals with finite dimensions. The same is true for the interactions with the bulk deformation of the crystal. Formally these effects can be included in the frame of the above approach, analogously to other vibrations, if they can be presented as interactions with independent vibrational degrees of freedom. However, complications can arise because, for example, uniform deformations of the crystal cannot be simply treated as vibrational degrees of freedom [23, 24]. We shall discuss this point more thoroughly in another paper.

The theory developed will be useful to rationalize experimental data concerning multicentre systems where intercentre correlation of one-centre Jahn-Teller distortions are important. Besides cooperative Jahn-Teller systems [3, 24] and polynuclear molecular clusters [2], multicentre vibronic interactions are manifested in systems of substitution impurities in crystals with high symmetry lattice. Examples of such kind are EPR evidence of  $\text{Cu}^{2+}$  ion pairs in single crystals  $\text{CaO}$  [25],  $\text{CsMgCl}_3$  [26],  $\text{Zn}(\text{pyO})_6(\text{ClO}_4)_2$  [27]. Apart from substitution impurities there are also complex colour centres (M, R and others) in alkali halides and multiple defects of N in diamond (see, for examples [28] and references therein) which would be objects for application of the above theory.

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