

# Jahn-Teller effect

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March 14, 2011

## Abstract

We investigate the condition under which a polyatomic molecule is stable, when its electronic state has orbital degeneracy (degeneracy not arising from spin). Jahn-Teller theorem says that stability and degeneracy are not possible simultaneously unless the molecule is colinear. After an introduction into adiabatic approximation and quantum-mechanical description of the molecular vibration we formulate Jahn-Teller problem and sketch the original theorem's proof. In the end we discuss an application of the theorem.

## 1 Introduction

Jahn-Teller effect describes the distortion of a non-linear molecule if its electronic states are degenerated. The effect is named after Hermann Arthur Jahn and Edward Teller, who proved the theorem using group theory. The problem was first discussed in 1934 when E. Teller and Lev Landau had many discussions on the stability of the  $\text{CO}_2$  molecule. Teller's student R. Renner showed that a linear molecule, which has degenerated electronic states, should be stable; but Landau objected. His arguments were that in the degenerate electronic state the symmetry on which the degeneracy is based will be destroyed. Teller first showed that this is not true for colinear configuration of nuclei. But the question was if there are some other exceptions. Teller and Jahn found out by a quite inelegant method that this is the only case.

## 2 Adiabatic approximation

Molecule is composed of electrons and nuclei interacting by electrical forces. The idea for adiabatic or Born-Oppenheimer approximation starts with the notion that nuclei are more than thousand times heavier than electrons and therefore move much more slowly than the electrons. We can therefore separate nuclear and electronic motion. The first step is to calculate the electronic motions at assumption that nuclei are fixed and then calculate the equilibrium positions of nuclei.

The total Hamiltonian of a molecule or a crystal may be written as ([1],[2])

$$H = H_{el} + H_{ions} + H_{ions-el} = \sum_i \frac{P_i^2}{2M_i} + \sum_j \frac{p_j^2}{2m_j} + V(R, r),$$

where the first sum is over all nuclei and  $P_i, M_i$  are the momentum operator and mass of the nuclei, the second sum is over all electrons and the last term is the potential energy between electron-nuclei, electron-electron and nuclei-nuclei, where  $R$  and  $r$  marks the set of nuclei and electron coordinates. In the adiabatic approximation one first solves the Schrödinger equation for electrons where nuclei are fixed:

$$H_0\phi_n(r, R) = \left[ \sum_j \frac{p_j^2}{2m_j} + V(R, r) \right] \phi_n(r, R) = E_n(R)\phi_n(r, R), \quad (1)$$

where  $\phi_n$  are eigenfunctions of this Hamiltonian. The set of nuclear coordinates are regarded as parameters with respect to the electronic motion; physically this means that nuclei move much more slowly than electrons. Even this simplified problem is a formidable task. Now we assume that the total solution can be written as

$$\Phi(r, R) = \phi_n(r, R)\chi(R) \quad (2)$$

and substitute the ansatz into the full Schrödinger equation:

$$H(R, r)\Phi_{r,R} = \left[ \sum_i \frac{P_i^2}{2M_i} + \sum_j \frac{p_j^2}{2m_j} + V(R, r) \right] \phi_n(r, R)\chi(R) = E\Phi_{r,R} \quad (3)$$

$$\approx \left[ \sum_i \frac{P_i^2}{2M_i} + E_n(R) \right] \chi_n(R) = E\chi_n(R), \quad (4)$$

on going from the second to the third line we used Eq.(1) and neglected the second derivative of  $\phi_n(r, R)$  with respect to  $R$ . The last assumption is the main assumption in the adiabatic approximation. Knowing the electrons energies for fixed  $R$  the Eq.(3) allows us to get the solution of the whole problem. Electron energy can be seen as an effective potential.

It is a common practice to solve vibrational problems by making expansion of the electrons energy, around the assumed equilibrium configuration  $R_0$  in powers of the deviations from the equilibrium position  $u_i = R - R_0$ :

$$E_n(R) = E_n(R_0) + \sum_i \left( \frac{\partial E}{\partial u_i} \right) u_i + \frac{1}{2} \sum_{i,i'} \left( \frac{\partial^2 E_{n,i}}{\partial u_i \partial u_{i'}} \right) u_i u_{i'} + \dots, \quad (5)$$

where we have ignored the anharmonic terms. We can now make the transformation to normal modes  $q = \sum_i D_{i,j} u_i$ , where nuclear kinetic energy and the quadratic terms in the potential will be diagonal. The term  $E_n(R_0)$  in Eq.(5) is only an constant term and in the vibrational theory the vanishing of the linear term is taken as a condition for the establishment of an equilibrium configuration. Jahn and Teller showed that this equilibrium configuration usually does not exist if electron states are degenerated.

### 3 Quantum-mechanical description of molecular vibrations

The classical description of the molecular vibrations should be a known subject to reader [1]. We can do completely analogous quantum-mechanical treatment of the problem. The

harmonic Hamiltonian operator in normal coordinates is written as

$$H = \sum_{k=1}^{3N} \left( -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \omega_k^2 Q_k^2 \right), \quad (6)$$

where  $Q_k$  denote the normal coordinates. The Hamiltonian is decomposed into the sum of harmonic oscillators, therefore we can compose the solution as

$$\Phi(n_1, n_2, n_3, \dots) = \prod_k \phi_{n_k}(Q_k),$$

where

$$\phi_{n_k}(Q_k) = A H_{n_k}(\mu_k Q_k) \exp\left(-\frac{1}{2} \mu_k^2 Q_k^2\right) \quad (7)$$

are solutions of quantum harmonic oscillator and  $H_{n_k}$  are Hermitian polynomial, A normalizing constant and  $\mu_{n_k} = (\omega_k/\hbar)^{\frac{1}{2}}$ . The total energy is  $E = \sum_k (n_k + \frac{1}{2}) \hbar \omega_k$ .

The general vibration state is labeled by the set of quantum numbers  $n_k$ , which tells us the number of quantum excitations. Since we are only interested in the internal degrees of freedom of a molecule, we must exclude six zero frequency modes, which corresponds to the translation and rotation, from the wave function  $\Phi = \Phi(n_1, n_2, \dots, n_{3N-6})$ .

The exponent in Eq.(7)

$$\sum_k \mu_k^2 Q_k^2 = \frac{1}{\hbar} \sum_{\alpha} \sum_{p=1}^{m_{\alpha}} \omega_{\alpha,p} \sum_i^{s_{\alpha}} Q_{\alpha pi}, \quad (8)$$

where  $\alpha$  labels the irreducible representation of symmetry group,  $i$  labels the row of certain irreducible representation and  $p$  is label if there are two or more irreducible representation with the same  $\alpha$ . The dimension of the certain irreducible representation is  $s_{\alpha}$ . We transform the coordinates  $Q_{\alpha pi}$  by a symmetry operation T:

$$Q'_{\alpha pi} = \sum_j T_{ij}^{\alpha} Q_{\alpha pj}$$

and the exponent can be written as

$$\sum_i (Q'_{\alpha pi})^2 = \sum_{i,j,k} T_{ij}^{\alpha} T_{ik}^{\alpha} Q_{\alpha pj} Q_{\alpha pk} = \sum_j Q_{\alpha pj}^2, \quad (9)$$

where we used the fact that matrix  $T$  is unitary and real, therefore orthogonal. The exponent in the wave function is invariant and the symmetry properties of the total wave function is given by the product of the Hermitian polynomials. The ground state will transform according to the  $H_0$ , which is a constant—invariant under symmetry operation. The first excited state is of form  $n_{\alpha_i p_i} = 1$  for certain  $i$  and all the rest of the  $n$ 's are zero. The symmetry properties of such a state are symmetry properties of the hermitian polynomial  $H_1(x) \propto x$ , which is just the symmetry of the normal coordinates  $Q_{\alpha_i p_i}$ . The first excited states are transformed just as the normal modes under irreducible representation  $T_{\alpha_i}$ , their energies are  $\hbar \omega_{\alpha_i}$  and degeneracies  $s_{\alpha}$ . The states are called *fundamental*.

### 3.1 Higher excited states

There are two types of higher excited states. First are called *combination levels*, where two or more modes of different frequency are excited, and second are called *overtone levels*, where single mode is excited with more than one quantum.

For example consider the most simple combination level, where  $n_{\alpha_1} = n_{\alpha_2} = 1$  and the remaining  $n_i = 0$ , is described by a wave function proportional to  $H_1(x_{\alpha_1})H_1(x_{\alpha_2})$  which transform as the direct product of the representation  $T^{\alpha_1} \otimes T^{\alpha_2}$ . This simple combination levels can now be labeled by a product representation. In general this product representation is reducible and if we add anharmonic terms in the potential without disturbing the symmetry the product representation breaks down into the irreducible representation.

Overtone levels are a bit more complicated, since the product states do not transform according to a product representation. If  $x_{\alpha p_1}$  and  $x_{\alpha p_2}$  are coordinates of the degenerated doublet of the wave functions which transform according to  $T^\alpha$ , ( $p_i$  is label for function), then we can form only three wave functions  $H_2(x_{\alpha p_1})$ ,  $H_1(x_{\alpha p_1})H_1(x_{\alpha p_2})$  and  $H_2(x_{\alpha p_2})$ , since  $H_1(x_{\alpha p_1})H_1(x_{\alpha p_2})$  and  $H_1(x_{\alpha p_2})H_1(x_{\alpha p_1})$  are equal. Only those functions which are symmetric in the factors will exist and they form so-called *symmetrised product representation*. We would like to make a decomposition of this symmetrised product representation into the irreducible representations and therefore we need to know the character of this representation for a certain group element. It can be shown, although we will not do it here (The reader can check Ref.[1]), that character of this symmetrised product representation is given by

$$\chi_{sym}^{\alpha \times \alpha}(a) = \frac{1}{2}[\chi^\alpha(a)]^2 + \frac{1}{2}\chi^\alpha(a^2), \quad (10)$$

where  $\chi_{sym}^{\alpha \times \alpha}$  denotes the character of the symmetrised product representation and  $a$  is a group element. Using Eq.10 we can decompose the symmetrised product representation into irreducible components.

## 4 Two examples

Before the more formal formulation of the problem, we will consider two examples. In the first example consider the motion of a single electron in the field of three nuclei lying on a straight line. The symmetry group of the problem is  $C_{\infty v}$ , meaning 2D rotational symmetry plus reflection over the vertical plane, if  $y$ -plane is the line of nuclei. The states of the electrons transform under 1D irreducible representations with basis states  $e^{\pm im\phi}$ , where  $m = 0, \pm 1, \pm 2, \dots$ . All states are two fold degenerated, except the state with  $m = 0$ . Now if one of the nuclei is misplaced from the equilibrium position perpendicular to the axis for a distance  $d$ , the axial symmetry is broken and the degeneracy is removed. Each twofold degenerated state will split into two states. One state will be symmetrical with respect to the reflection about the symmetry plane and the second one will be antisymmetrical. These states will have different energies and these energies will change continuously with the displacement. It is clear that when the displacement is  $-d$  the states and energies will be the same. Therefore the energy is even function of  $d$ . The requirement for stability is fulfilled, since the linear term in Eq.5 is zero.

The second example is motion of an single electron in the field of a plane square configuration of four identical nuclei. The symmetry group of this problem is  $D_4^h$  and when wave function is determined in one half-plane perpendicular to the axis through the center of the square, it is determined on all four half-planes perpendicular to each other. The wave function is multiplied by  $e^{i\lambda\phi}$ , where  $\phi$  is restricted to  $\pm\frac{\pi}{2}, \pi$ ,  $\lambda$  has values  $0, \pm 1$  and state with  $|\lambda| = 1$  is again two fold degenerated.

What can we say about the stability of the square configuration for this degenerated electronic states? The displacement of the nuclei shown in Fig.1 may be regarded as positive and negative value of the same displacement. This displacement clearly destroys the four-fold axis, replacing it by a twofold one. The degenerated states will split into two states, let us mark them with  $\phi_1, \phi_2$ , the first one having node in horizontal plane of symmetry and the second one in the vertical plane of symmetry. The left configuration (*conf1*) is geometrically similar to right configuration (*conf2*), since the horizontal plane in *conf1* corresponds to vertical plane in *conf2* and vice versa. If we denote energies of the wave functions by  $E_{1,2}$ , we have the relation:

$$\begin{aligned} E_1(\text{conf1}) &= E_2(\text{conf2}) \\ E_1(\text{conf2}) &= E_2(\text{conf1}). \end{aligned}$$

The two levels crosses at zero displacement, but there is no reason (at least symmetrical reason), which would forbid a linear dependence of the energy levels. The conclusion is that the square configuration in general will not be stable configuration.

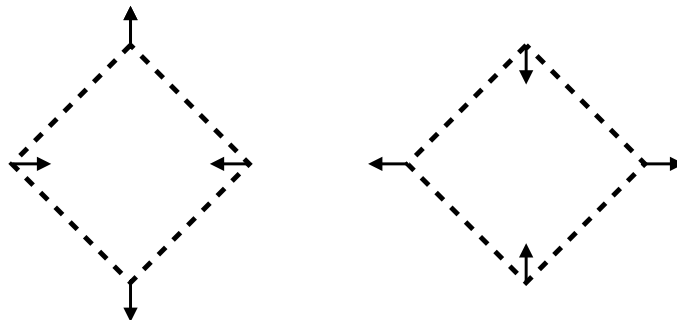


Figure 1: The displacement of nuclei in the square configuration.

## 5 Formulation of the problem

In the first subsection we will just state the theorem without any further explanation. The next subsection will form a basis for physical formulation of the problem. In the end we will repeat the two examples already mentioned, using the formulation.

### 5.1 Jahn-Teller theorem

A geometrical configuration of a molecule in which the electronic state is degenerate cannot be stable (on symmetry grounds alone) unless when the configuration of nuclei is collinear or the electronic degeneracy is the Kramer twofold degeneracy [1].

## 5.2 Physical formulation

The starting point is Eq.5, where we expand the energy in terms of the nuclei positions  $V_i = \partial E / \partial u_i$  and  $V_{i,j} = \partial^2 E / \partial u_i \partial u_j$ , which are functions of nuclei positions only. Let  $E_0$  be the energy of the degenerated electronic state and  $\phi_i$  a complete set of orthogonal wave functions

$$H_0 \phi_i = E_0 \phi_i,$$

where  $H_0$  stands for the Hamiltonian in equilibrium (Eq.1). After the displacement this energy levels can split or not (meaning, that they merely change the value). The equilibrium configuration will be stable if linear term will vanish. We can use perturbation theory, to check the linear term. The perturbed energies in first order are

$$E_1 = \sum_i u_i \langle \phi_1 | V_i | \phi_2 \rangle$$

and since perturbation is linearly dependent of  $u_i$ ,  $E_1 \rightarrow -E_1$  if all displacements changes sign. The configuration can not be stable unless all (!) the perturbation elements vanish in the first order.

Here comes the role of the symmetry.  $V_i = \partial E / \partial u_i$  and  $u_i$  transforms according to irreducible representation  $T^\beta$  of the symmetry group, and  $E$  transforms according to identical representation.  $V_i$  has to transform according to the complex conjugate representation  $T^{(\beta)*}$ , but since the representation is real  $T^{(\alpha)*} = T^\alpha$ . In the chapter about quantum vibrations we showed that wave functions transforms according to certain representation of symmetry group as the normal coordinates does; let us mark this representation by  $T^\alpha$ . If  $T^\alpha$  does not encounter in the reduction of the product representation  $T_\beta \otimes T_\alpha$  the perturbation is zero. If this condition is not fulfilled, then the integrals in general will not vanish. Now we have a defined quantity, which is responsible for stability of the equilibrium state. Since  $E_1$  is a number it is invariant under all group transformation and if reduction of the representation of the product  $\phi_1 V_i \phi_2$  does not contain the identity representation, the perturbation will be zero. This is just another point of view of the same argument as before, although it is sometimes easier to use. We will restrict ourself only to the orbital degeneracy <sup>1</sup> where representation  $T^\alpha$  can always be chosen real and the product of the functions transform according to the product representation

$$T^\beta \otimes [T^{(\alpha)2}], \quad (11)$$

where  $[T^{(\alpha)2}]$  denotes the symmetrised product of the representation  $T^\alpha$ .

There are four interesting cases:

1. Electronic state is non-degenerated  $[T_\alpha^2] = T_1$  and vibrational state is symmetric  $T_1$ . In this case perturbation is not necessarily zero. But system will readjust until it is "accidentally zero", since it evolves a symmetric mode and does not destroy the symmetry of the system.
2. Electronic state is non-degenerated  $[T_\alpha^2] = T_1$  and vibrational state is asymmetric  $T_\gamma \neq T_1$ . The perturbation is always zero.

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<sup>1</sup>We will not consider the degeneracy arising from the invariance of the wave function with respect to time reversal. The spin wave function and its role in Jahn-Teller effect will be briefly considered at the end of the section.

3. Electronic state is degenerated  $[T_\alpha^2] = T_1 + \dots$  and vibrational state is symmetric  $T_1$ . The perturbation is not necessarily zero, but situation is analog to the first situation.
4. Electronic state is degenerated  $[T_\alpha^2] = T_1 + \dots$  and vibrational state is asymmetric. In this case we have Jahn-Teller effect, since the product of the states nearly always contains  $T_1$  and the equilibrium is obtained by changing the original symmetry.

### 5.3 Two examples

Let us illustrate the general considerations on the two examples given in the previous section. In the first example the symmetry group is  $C_\infty^v = \mathcal{R}^2 \times S_2$ . The degenerate irreducible representations (there is also one non-degenerate representation) of the group are all two-dimensional and there is an infinite series of them:  $E_1, E_2, \dots$ . Using Eq.10 we can decompose the symmetrised product:

$$[E_k^2] = A_1 \oplus E_{2k}, \quad (12)$$

where  $A_1$  is identical representation. For linear nuclear configuration non-totally symmetric solutions are of type  $E_1$  and the decomposition of the whole product is

$$E_1[E_k^2] = E_1(A_1 \oplus E_{2k}) = E_1 \oplus E_{2k+1} \oplus E_{2k-1}, \quad (13)$$

where the last equality comes from simple decomposition of the product representation  $E_1 \otimes E_{2k}$ . The decomposition does not contain the identity representation so all the linear terms in perturbation are zero. The molecule is stable.

The analysis of the second example is equivalent. The symmetry group is  $D_4^h$  and this group has two degenerated irreducible representations  $E_{g,u}$ , which are 2 dimensional. The square configuration possesses non-totally symmetrical displacements of types  $B_{1g,1u,2g}, E_u$ . Using Eq.10 we can show

$$[E_{g,u}^2] = A_{1g} + B_{1g} + B_{2g} \quad (14)$$

and from character table we can see that  $B_{1g,2g}^2 = A_{1g}$ , therefore  $B_{1g,2g}[E_{g,u}^2]$  all contain the identical representation. We can conclude (but only from symmetry point of view) that this molecule is not stable for a degenerate electronic state of either type.

## 6 Sketch of proof

The original proof of Jahn-Teller theorem [2] is a tedious job. After initial plan the calculations are straightforward, but very time-consuming, or as the Teller said[3]: "It was not a proof that a mathematician would enjoy." We will just make a sketch of the proof with an example. All further calculations should be straightforward.

We have to show, for all configurations and any degenerate representation of electronic symmetry group  $T_\alpha$ , that a nuclear configuration possesses non-totally symmetrical normal displacements, which transform according to the irreducible representation  $T_\beta$ . The perturbation is zero if  $T^\beta$  occur in the reduction of  $[T^{(\alpha)^2}]$ .

We know how to calculate for any given nuclear displacement how many normal displacements of certain irreducible type occur in the reduction. To apply this calculations to all possible symmetrical molecules we note that any symmetrical configuration must contain a set on nuclei, which transform into each other under symmetry operation. This nuclei form a set of the *equivalent points* and for given group there are various possible kinds of such equivalent sets. Imagine a random point in the space<sup>2</sup> and if we act with all the symmetry operations of certain group on this point we get a set of equivalent points. Now if this point lie on certain symmetry line, then the set of equivalent points will be smaller, since some operations will produce the same point. Example for group  $D_3$  is shown in Fig.2.

Jahn and Teller actually checked all the possible sets of equivalent points for all points groups and for each set they found what types of normal displacements occur<sup>3</sup>. They investigated what is the minimum number of equivalents points from which a molecule of a certain symmetry can be composed. In the end they checked all the symmetrised products of all possible degenerated representations. Now the theorem was easily checked, just by comparing the decomposition of a group representations according to the vibrational normal modes and the decomposition of the symmetrised products for every points group.

Let us consider just one example  $D_3$ . First we must find sets of equivalent points and check the reduction of group representation according to vibration. The vibrational characters is calculated using

$$\chi(R(\theta)) = (N_R - 2)(2 \cos(\theta) + 1), \quad (15)$$

where  $\theta$  is angle of rotation and  $N_R$  is number of point, which stays fixed for a certain group operation. Here we have to emphasize that different kind of equivalent points has different number of fixed points for certain operation.

There are four kinds of equivalent points and graphical representation is seen in Fig.2:

1. Initial point is random: we have 6 equivalent points in a set, which is the same as the number of group elements. Using formula 15 the reduction into irreducible representation for the whole set of nuclear displacements, without rigid rotations and translations, is  $3A_1 \oplus 4E \oplus A_2$ . With 6 molecule we have  $3 \times 6 = 18$  degrees of freedom and if rigid translation and rotation have  $3 + 3$  degrees of freedom we are left with  $12 = 3 \times 1 + 4 \times 2 + 1$  which agrees with the reduction.
2. Initial point lie on  $C_2$  axis of rotation: we have 3 equivalent points in a set. The irreducible components are  $A_1 \oplus E$ . With 3 molecules we have  $3 \times 3 = 9$  degrees of freedom and without rigid translations and rotations we are left with  $3 = 1 + 2$ .
3. Initial point lie on  $C_3$  axis of rotation: we have 2 equivalent points in a set. The irreducible components are  $A_1 \oplus E_2$ , but be aware that in this case we do not have rigid rotations.
4. Initial point lie in the center: we have just one trivial point in a set. The irreducible components are  $A_2 + E_1$ , where we do not have rigid translations and rotations.

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<sup>2</sup>Random in sense that it does not lie on any symmetry line or plane.

<sup>3</sup>The reader is invited to check the 4 page long table in the original article [2].



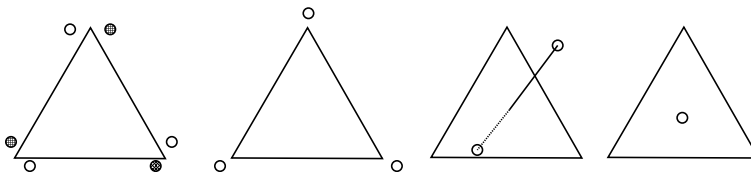


Figure 2: Four kinds of equivalent points for group  $D_3$ , where filled circles marks the point under the horizontal plane and open circles mark the points above the horizontal plane. The order of different plane points set's is the same as in the text.

When we construct the table of irreducible components for all the sets of equivalent points for each point group, we still need a table for minimum number of equivalent points from which a molecule can be composed. In case of  $D_3$  we need one set of equivalent points, where initial point is random (type 1). This is also the only possible choose, since all other combinations of the equivalent points have higher symmetry. Another nontrivial example is a molecule of the tetragonal symmetry. We can take random initial point and set of equivalent points will form a tetrahedron, but if we take six points and put them on two fold axes, then this configuration will have higher octahedron symmetry. The last step in this proof is to construct the table of symmetrical products for all of the degenerated representations. By trivial but tedious comparison of all the tables, the proof is finished.

Of course later more mathematical rigorous proof were established, but here we do not have enough space to introduce the whole new pallet of group-theoretical tool. The main idea is to get well defined tool from theory of groups that is able to describe equivalent points and then study the reduction of the representations. In Ref.[4] and references therein the reader can find group theoretical proof of Jahn-Teller theorem.

We have to point out that effect will be important only if the degenerated electrons participate strongly in the binding of the molecule and if the perturbation arising from nuclei displacement is appreciable. The effect is small if the degenerated electrons are in inner atomic shells or if they are in highly excited states. The case with inner degenerated electronic shells that do not contribute much to binding, are paramagnetic rare earth ionic salts.

An extension of the theorem to cover the additional degeneracy arising from the spin [5], shows that if total orbital and spin electronic state is degenerated, then a non-linear molecule will be unstable, unless the degeneracy is Kramer degeneracy (only an odd number of electrons). The additional instability because of the spin degeneracy alone is shown to be very small. The additional idea was that spin could stabilize a non-linear molecule, but it was shown that this is not possible, because the effect of spin is not large enough.

## 7 Description of vibronic systems

In the next section we will explain basic tools for description of the systems where Jahn-Teller effect take place. Although the tools are rather general, we will make example from transition metal oxides. The first subsection will provide short description of Cu

or Mn based compounds. In the second subsection we will derive effective Hamiltonian for Jahn-Teller distortion. In the third subsection we will consider the simplest case of coupling doubly degenerated electronic state to the single vibrational mode. In the last subsection we will describe first non-trivial coupling of electronic doublet with two vibrational modes. At the end the short discussion of the higher terms is included. The notation used in this section:  $E$  will denote doubly degenerated electronic state and with Greek letters we will mark vibronic state (example  $\epsilon$  is two dimensional irreducible representation).

## 7.1 $\text{Cu}^{2+}$ and $\text{Mn}^{3+}$ oxides

The valence orbitals in  $\text{Cu}^{2+}$  are  $3d$  orbitals and in many cases (like  $\text{La}_2\text{CuO}_4$ ,  $\text{CuFe}_2\text{O}_4$ ) the transition metal ions are surrounded by 6 oxygen ions forming octahedron. The structure is often called perovskite structure.  $3d$  orbitals are five fold degenerated, but in the crystal field of  $\text{O}^{2-}$  the spherical symmetry is broken into octahedral. A simple reduction of  $3d$  orbitals in the cubic crystal field show that five-fold degeneracy reduce into two-fold degenerated orbitals:  $d_{x^2-y^2}, d_{3z^2-r^2}$  often marks as  $e_g$  orbitals and  $d_{xy}, d_{yz}, d_{zx}$  or  $t_{2g}$  orbitals. These functions are plotted in Fig.3a. The  $e_g$  orbitals extends towards the oxygen ions which have negative charge so in these orbitals the energy is raised by the Coulomb interaction. On the other hand  $t_{2g}$  orbitals point away from the oxygen ions and therefore have lower energy<sup>4</sup>.

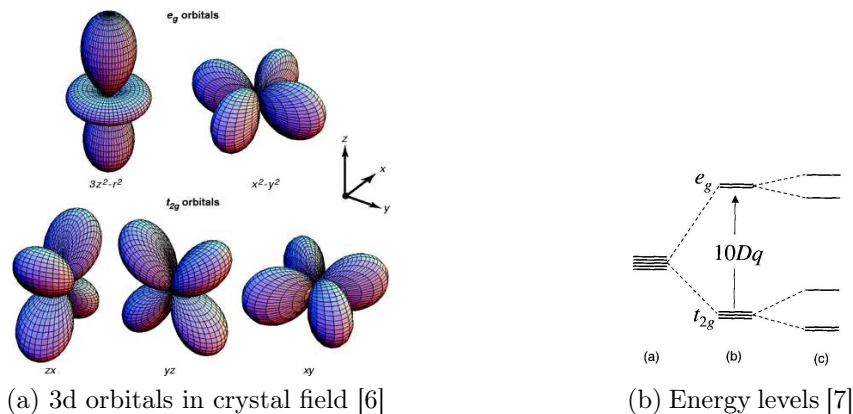


Figure 3: Energy levels in the crystal field are drawn for (a) spherical, (b) cubic and (c) tetragonal symmetry. In the tetragonal symmetry the octahedron is elongated in  $z$  direction.

Since  $e_g$  levels lie higher, we can describe the configuration of  $\text{Cu}^{2+}$  as having one hole in the highest orbital. Hole is in the electronic doublet, which belongs to the E irreducible representation of  $O_h$  symmetry group and because of Jahn-Teller effect it has to be unstable.

<sup>4</sup>Reader is invited to calculate the splitting using perturbation theory. The result is that energy of splitting for  $e_g$  versus  $t_{2g}$  is 3:2.

## 7.2 Linear coupling term

The starting point for linear coupling is once again Eq.5, actually just linear term. The system is in one of the degenerated electronic states

$$\phi^{T_a}(\vec{r}, \vec{u}) = \sum_i a_i^{T_a}(\vec{u}) \phi_i^{T_a}(\vec{r}), \quad (16)$$

where  $\phi^{T_a}$  is a linear combination of the electronic eigenstates which transform according to the degenerated irreducible representation  $T_a$  and  $a_i^{T_a}$  are coefficients in the expansion. The linear part can be rewritten

$$\sum_{T_b, i, j, k} q_i^{T_b} a_j^{T_a*} a_k^{T_a} \left\langle \phi_j^{T_a} \left| \frac{\partial H}{\partial u_i^{T_b}} \right| \phi_j^{T_a} \right\rangle = \quad (17)$$

$$\sum_{T_b, i, j, k} q_i^{T_b} a_j^{T_a*} a_k^{T_a} \langle T_a | H^{T_b} | T_a \rangle \langle T_a T_b T_a j | T_a T_b k i \rangle \quad (18)$$

where  $T_b$  marks irreducible representations of normal modes,  $i$  is component of the representation  $T_b$  and  $j$  and  $k$  marks linear combination of electronic states. From first to the second line we used Wigner-Eckart theorem, where  $\langle T_a | H^{T_b} | T_a \rangle$  is the reduced matrix element and  $\langle T_a T_b T_a j | T_a T_b k i \rangle$  are the Clebsch-Gordan coefficients. The coupling is described by direct product of the irreducible representation and standard notation is that we mark certain coupling as  $T_a \otimes T_b$ .

Variation of Eq.18 with the respect to the undetermined coefficients  $a_j^{T_a}$  leads to the effective potential part of the Hamiltonian, which acts on certain degenerate representation  $T_a$ . Matrix form of this potential is

$$(H_{JT})_{i,j} = \sum_{T_b k} q_i^{T_b} \langle T_a | H^{T_b} | T_a \rangle \langle T_a T_b T_a i | T_a T_b j k \rangle. \quad (19)$$

The complete Hamiltonian includes diagonal kinetic and elastic part as well higher that linear vibrational terms, whenever they are important.

## 7.3 $E \otimes \beta$

$E$  is two dimensional irreducible representation of electronic states  $|E_1\rangle, |E_2\rangle$ , which is coupled to the single normal mode vibration  $\beta$ . The Clebsch-Gordan coefficients for this case are  $\pm 1$  and simple Hamiltonian can be written:

$$H = \left( -\frac{1}{2} \frac{\partial^2}{\partial u^2} + \frac{1}{2} u^2 \right) + Lu\sigma_z, \quad (20)$$

where  $I$  stands for the identity matrix,  $\sigma_z$  is the third Pauli matrix and  $L = \langle T_a | H^{T_b} | T_a \rangle$ . The solutions of this problem are trivial, since the origin of the harmonic oscillator is only displaced for a distance  $\pm L$  and now the potential minima are  $-L^2/2$ . The eigenfunctions are harmonic oscillator wave function with origins in  $\pm k$  and are two fold degenerated.

## 7.4 $E \otimes \epsilon$

$\epsilon$  is two dimensional irreducible representation of the normal mode and  $E \otimes \epsilon$  marks the coupling of electronic doublet with vibrational doublet. After calculating Clebsch-Gordan coefficients we get the Hamiltonian:

$$H = \frac{1}{2} \left( \frac{\partial^2}{\partial u_1} + \frac{\partial^2}{\partial u_2} + u_1^2 + u_2^2 \right) I - L \begin{bmatrix} -u_1 & u_2 \\ u_2 & u_1 \end{bmatrix} \quad (21)$$

where  $u_{1,2}$  marks normal coordinates,  $L$  reduced matrix element and  $I$  is the identity matrix. The potential part of the Hamiltonian in the  $u_1, u_2$  plane is seen on Fig.4 and the shape is so-called Mexican hat. The potential part is often referred as adiabatic potential energy sheet or APES; since it is the solution of the problem in adiabatic limit.

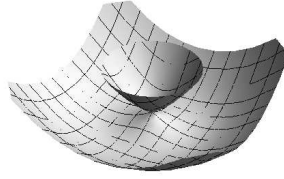


Figure 4: Potential surface in the  $u_1, u_2$  plane for coupling of electronic doublet with vibrational doublet.

From the shape of the potential part we can notice that ground state should be continuously degenerated. Useful parameterization is  $u_1 = u \sin(\phi)$  and  $u_2 = u \cos(\phi)$  and since we are interested only in the ground state, the potential part should be diagonalized. The transformation matrix is

$$T = \begin{bmatrix} \cos \frac{\phi}{2} & \sin \frac{\phi}{2} \\ -\sin \frac{\phi}{2} & \cos \frac{\phi}{2} \end{bmatrix} \quad (22)$$

and Hamiltonian in the new basis is

$$H' = THT^{-1} = \left( -\frac{\partial^2}{\partial u^2} - \frac{1}{u} \frac{\partial}{\partial u} - \frac{1}{u^2} \begin{bmatrix} -\frac{1}{4} + \frac{\partial^2}{\partial \phi^2} & \frac{\partial}{\partial \phi} \\ -\frac{\partial}{\partial \phi} & -\frac{1}{4} + \frac{\partial^2}{\partial \phi^2} \end{bmatrix} + u^2 \right) + \frac{1}{2} Lu \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \quad (23)$$

and the basis states are  $|1, 2\rangle = \cos(\phi)|E_1\rangle \mp \sin(\phi)|E_2\rangle$ . If the kinetic energy is neglected, the ground state is  $|1\rangle$  with energy  $-\frac{1}{2}L^2$ . Solution of the whole Hamiltonian goes beyond the scope of this seminar. The ground state solutions are still degenerate, so others terms are needed for some more symmetry breaking. Derivation of higher orders term is based on the theory of tensorial sets and also goes beyond this seminar, but idea is still the same: Find which terms in the electronic-vibrational coupling are allowed by symmetry group and in the same manner as in the linear term derive the effective Hamiltonian. It turns out that the quadratic term is

$$\frac{1}{4}k \begin{bmatrix} -u_1^2 - u_2^2 & 2u_1u_2 \\ 2u_1u_2 & u_2^2 - u_1^2 \end{bmatrix} + u^2 = \frac{1}{4}ku^2 \begin{bmatrix} -\cos(3\phi) & \sin(3\phi) \\ \sin(3\phi) & \cos(3\phi) \end{bmatrix}. \quad (24)$$

where first is written in base  $|1\rangle, |2\rangle$  and second in the potential diagonal base  $|1\rangle, |2\rangle$ . This term becomes important only when  $R$  is large, since  $R^2$  dependence, and it is important when linear coupling is strong. The potential surface becomes so-called warped Mexican hat with 3 minima. The lowest energy is now at the angles  $\phi = 0, \pm 2\pi/3$ .

## 7.5 Case of $\text{Cu}^{2+}$

$\text{Cu}^{2+}$  ion together with the 6 oxygen ions forms the octahedron. We would like to find what is the Jahn-Teller deformation of such system. First we need to find 2 dimensional normal modes of the octahedron. This means reducing the  $3 \times 8 = 24$  dimensional representation and find basis states for certain 2 dimensional representation. This task is straightforward but time consuming, so we will just write down the basis vector for the normal mode in cartesic representation:  $u_1 = (x_1 - x_4 - y_2 + y_5)/\sqrt{2}$  and  $u_2 = (2z_3 - 2z_6 - x_1 + x_4 - y_2 + y_5)/\sqrt{6}$ , where  $x, y, z$  are coordinates of ions and suffixes denote the ion number as marked on figure 5.

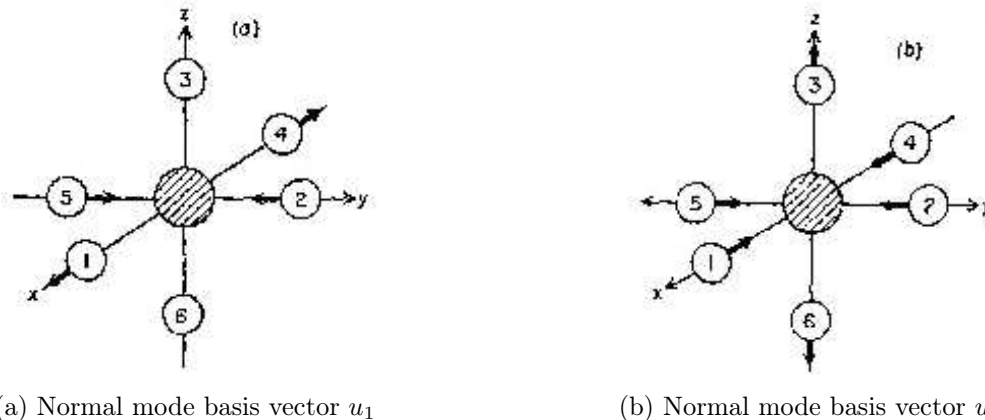


Figure 5: Normal modes of the 2 dimensional irreducible representation for octahedron [8].

In the previous subsection we saw that using linear and quadratic terms the minimum of the potential energy is at three angles  $\phi = 0, \pm 2\pi/3$  in the  $u_1 - u_2$  plane. The angle  $\phi = 0$  correspond to the  $u_2$  vector and is tetragonal distortion along the  $z$  axis as seen on figure 5b. The solutions at the angle  $\phi = \pm 2\pi/3$  are just the other two tetragonal distortion in  $x$  and  $y$  directions. The later is easily seen by forming appropriate linear combination of  $u_{1,2}$ :  $-1/2u_1 \pm \sqrt{3}/2u_2$  in the Cartesian coordinates.  $\text{Cu}^{2+}$  ions in the perovskite structure has usually strong tendency to form a complexes in which two nearest neighbors form a square and other neighbors out of the plane form an extended octahedron. Probably the most famous case is the  $\text{La}_2\text{CuO}_4$ , where the in-plane  $\text{Cu} - \text{O}$  distances are  $1.90 \text{ \AA}$  and perpendicular to the plane the distances are  $2.5 \text{ \AA}$ . The tetragonal distortion has strong influences on the electronic properties of the crystal, but this is now another story ...

## 8 Conclusion

The intension of this seminar was to give a gentle introduction to the Jahn-Teller effect. This is why on basic notions are given, although there are many related phenomena, which could also be described. Reader should be aware that Jahn-Teller (and related types of) effects are a large field of research, with strong interplay of theory and experiment. It is important effect in various different systems like transition metal oxides, fullerenes . . . The example of  $\text{Cu}^{2+}$  from the last section was actually research motif of the Karl Müller and Johannes Bednorz, who unexpectedly discovered high-temperature superconductivity in cuprate-perovskite ceramics of  $\text{LaBaCuO}$ . Fascinating thing is that it all started with a simple problem of  $\text{CO}_2$  stability and rather “long exercise” from the group theory.

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