Analogy Between Particle in a Box and Jahn–Teller Effect

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The energy levels of a particle in a box are degenerate. The degeneracy of an energy level is reduced or removed on slight distortion in the dimensions of the box without changing its volume. This phenomenon is analogous to the Jahn–Teller Effect, which states that in an electronically degenerate state (i.e., more than one degenerate orbital is available for an electron), a nonlinear molecule undergoes distortion to remove the degeneracy by lowering the symmetry and thus lowering the energy.

Particle in a Cubical Box

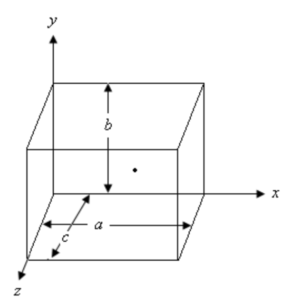

Figure 1. Particle moving freely in a rectangular box.

A particle is enclosed inside a rectangular box having edges a, b and c in length (*Figure* 1). The potential $U(x, y, z)$ of the particle is defined by

$$\left.\begin{aligned} U(x,y,z) &= 0 \text{ for } 0 \leq x \leq a, 0 \leq y \leq b, \\ &\qquad\qquad 0 \leq z \leq c \\ &= \infty, \text{otherwise.} \end{aligned}\right\} \quad (1)$$

Solving the Schrödinger equation, the allowed energy levels of the particle are given by

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right), \quad (2)$$

where h = Planck's constant $= 6.63 \times 10^{-34}$Js, m = mass of the particle, and quantum numbers $n_x, n_y, n_z = 1, 2, 3, 4, \ldots$.

For a cubical box, $a = b = c$ and energy can be expressed as

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right). \quad (3)$$

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Degeneracy, distrortion, Jahn–Teller effect.

Equation (3) shows that only certain values of energy E may occur, i.e., the energy is quantized. It can be seen that different sets of quantum numbers n_x, n_y and n_z have exactly the same energy. This situation is known as *degeneracy*, and the energy levels are said to be *degenerate*.

Degeneracy occurs in general whenever a system is labelled by two or more quantum numbers and different combinations of quantum numbers give the same value of the energy. In case of atomic physics, the degeneracy is a major contributor to the structure and properties of atoms.

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Figure 2 shows the energy levels for a particle in a cubical box. These energy levels are degenerate to some degree. For convenience, let $E_0 = \frac{h^2}{8ma^2}$. Then the only allowed energies for the particle are $3E_0, 6E_0, 9E_0, \ldots$, etc., and all intermediate values are forbidden. The lowest energy state is known as the *ground state* and the states with higher energies are known as *excited states*.

The ground state energy E_{111} is obtained from (3) by putting $n_x = n_y = n_z = 1$:

$$E_{111} = \frac{3h^2}{8ma^2} = 3E_0 \ . \qquad (4)$$

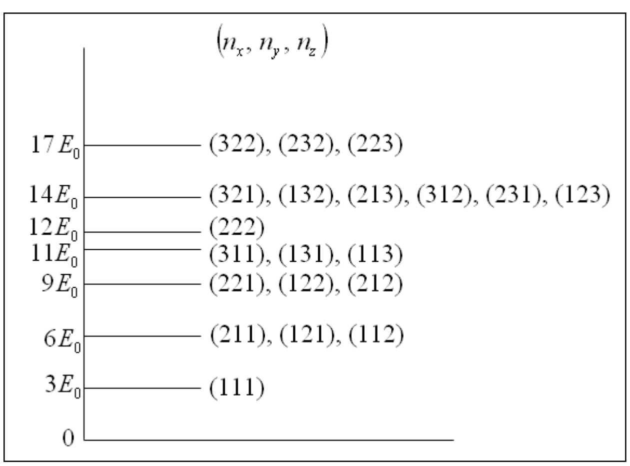


Figure 2. Energy levels and quantum numbers of a particle in a cubical box.

The wave functions corresponding to three sets of quantum numbers of the triply degenerate second energy level are different.

There is only one set of quantum numbers that gives this energy state and hence the ground state is said to be non-degenerate.

If we now consider the second energy state, it is seen that there are three sets (211), (121) and (112) of the quantum numbers n_x, n_y and n_z that will give the same energy level. From (3), the energy of this level is given by

$$E = \frac{6h^2}{8ma^2} = 6E_0\,. \tag{5}$$

Such a level is said to be triply degenerate or *three-fold* degenerate and we can also say that the degeneracy of this level is 3. The wave functions corresponding to the three sets of quantum numbers of this energy level are different.

Distortion of the Box

Consider a rectangular box of sides x, y and z. For small distortions $+dx$ and $-dy$ along x and y axes respectively, keeping volume constant, we have

$$(x + dx)\,(y - dy)\,z = xyz$$

or $y\,dx - x\,dy = 0$ (neglecting $dx\,dy$) ,

or

$$\frac{x}{y} = \frac{dx}{dy}.$$

For a cubical box, $x = y = z$ and hence $dx = dy$.

Now we consider a slight distortion of the cubical box by $+da$ along x-axis and $-da$ along y-axis, keeping its volume constant.

Using (3), the ground state energy is now

$$E_{111} = \frac{h^2}{8m}\left[\frac{1}{(a+da)^2} + \frac{1}{(a-da)^2} + \frac{1}{a^2}\right]$$

$$= \frac{h^2}{8ma^2}\left[\left(1+\frac{da}{a}\right)^{-2}+\left(1-\frac{da}{a}\right)^{-2}+1\right]$$

$$= \frac{h^2}{8ma^2}\left[1-\frac{2da}{a}+1+\frac{2da}{a}+1\right]$$

$$= \frac{3h^2}{8ma^2}$$

which is the same as (4).

Therefore the ground state energy remains the same due to slight distortion of the cube.

Using (3), the new energy of the 2nd energy state having wave function $\psi\,(2,1,1)$ is given by

$$E'_{211} = \frac{h^2}{8m}\left[\frac{4}{(a+da)^2}+\frac{1}{(a-da)^2}+\frac{1}{a^2}\right]$$

$$= \frac{h^2}{8ma^2}\left[4\left(1+\frac{da}{a}\right)^{-2}+\left(1-\frac{da}{a}\right)^{-2}+1\right]$$

$$= \frac{h^2}{8ma^2}\left[4\left(1-\frac{2da}{a}\right)+\left(1+\frac{2da}{a}\right)+1\right]$$

$$= \frac{6h^2}{8ma^2}-\frac{3h^2}{4ma^3}da\,. \qquad (6)$$

Similarly the new energies of the 2nd energy state for the other two states $\psi\,(1,\,2,\,1)$ and $\psi\,(1,\,1,\,2)$ are given by

$$E'_{121} = \frac{h^2}{8m}\left[\frac{1}{(a+da)^2}+\frac{4}{(a-da)^2}+\frac{1}{a^2}\right]$$

$$= \frac{h^2}{8ma^2}\left[\left(1+\frac{da}{a}\right)^{-2}+4\left(1-\frac{da}{a}\right)^{-2}+1\right]$$

$$= \frac{6h^2}{8ma^2}+\frac{3h^2}{4ma^3}da\ , \qquad (7)$$

$$E'_{112} = \frac{h^2}{8m}\left[\frac{1}{(a+da)^2}+\frac{1}{(a-da)^2}+\frac{4}{a^2}\right]$$

The degeneracy of an energy level is reduced or removed on slight distortion of a system. This phenomenon is analogous to the Jahn–Teller Effect (Distortion).

The Jahn–Teller theorem states that in a nonlinear molecule, if degenerate orbitals are asymmetrically occupied a distortion will occur to remove the degeneracy.

$$= \frac{h^2}{8ma^2}\left[\left(1+\frac{da}{a}\right)^{-2}+\left(1-\frac{da}{a}\right)^{-2}+4\right]$$

$$= \frac{6h^2}{8ma^2}\,. \tag{8}$$

Thus, the initial three-fold degenerate 2nd energy level given by (5), is split on slight distortion of the cube into three different energy levels given by (6), (7) and (8). Hence the degeneracy is removed. In general the degenergy of an energy level is reduced or removed on slight distortion of a system. This phenomenon is analogous to the Jahn–Teller effect (distortion).

Jahn–Teller Effect

The Jahn–Teller effect, sometimes also known as Jahn–Teller distortion, describes the geometrical distortion of non-linear molecules under certain situations.

This effect was first predicted in 1937 by Hermann Arthur Jahn and Edward Teller, using group theory. The Jahn–Teller theorem states that in a nonlinear molecule, if degenerate orbitals are asymmetrically occupied, a distortion will occur to remove the degeneracy. This theorem essentially states that any non-linear molecule with a degenerate electronic ground state will undergo a geometrical distortion that removes the degeneracy.

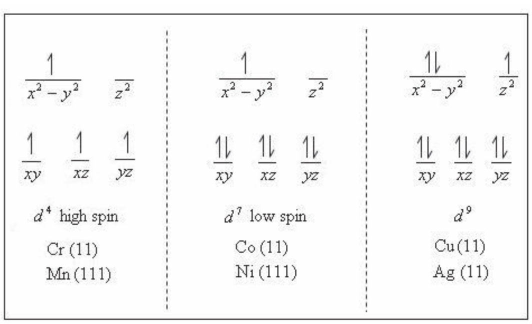
An electronically degenerate state represents the availability of more than one degenerate orbital for an electron. In this condition the degenerate orbitals are asymmetrically occupied and get more energy. Therefore the system tries to get rid of this extra energy by lowering the overall symmetry of the molecule, i.e., undergoing distortion, which is otherwise known as Jahn–Teller distortion.

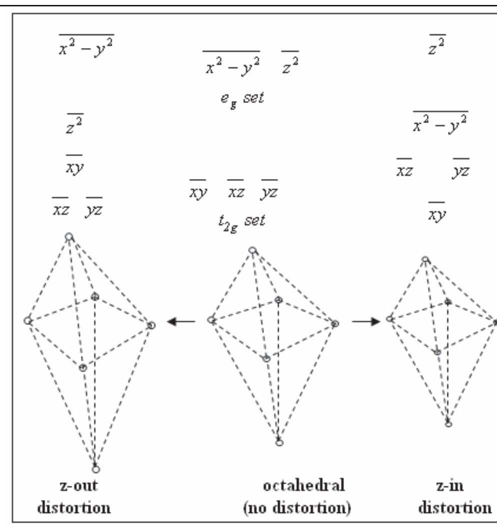
The Jahn–Teller effect is most often encountered in octahedral complexes of the transition metals, whose ions have incompletely filled *d* orbitals.

The Jahn–Teller effect is most often encountered in octahedral complexes of the transition metals, whose ions have incompletely filled d orbitals. In an octahedral crystal, the t_{2g} orbitals occur at lower energy than the e_g orbitals. Considerable distortions are observed when an odd number of electrons occupy the e_g orbitals in d^9 [Cu(11), Ag(11)], low spin d^7 [Co(11), Ni(111)] and high spin d^4[Cr(11), Mn(111)] configurations in the octahedral environment (*Figure* 3). Jahn–Teller distortion is significant in these configurations due to asymmetrically occupied e_g orbitals. The ground states of all these complexes are doubly degenerate. The degeneracy of the orbitals is removed by lowering the symmetry of the molecule either by elongation of bonds along the z-axis (z-out distortion) or by shortening of the bonds along the z-axis (z-in distortion). Thus an octahedrally symmetrical molecule is distorted to tetragonal geometry.

In case of z-out distortion, the energies of d-orbitals with z factor are lowered. The energies of orbitals with z factor are increased in case of z-in distortion (*Figure* 4). Usually the octahedral d^2, d^4 high spin, d^7 low spin, d^8 low spin and d^9 configurations show the z-out distortion. The octahedral d^1 configuration like Ti (111) in $[Ti(H_2O)_6]^{3+}$ shows z-in distortion.

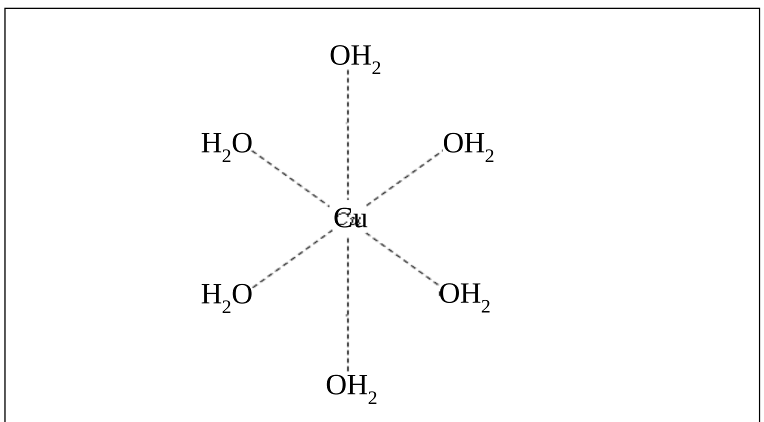
Figure 3 (left). Configuration with considerable Jahn–Teller distortion.
Figure 4 (right). *z*-out and *z*-in distortions in octahedral complexes.





Jahn–Teller Distortion in $[Cu(OH_2)_6]^{2+}$ Ion

The Jahn–Teller effect is responsible for the tetragonal distortion of the hexaacquacopper(11) complex ion, $[Cu(OH_2)_6]^{2+}$. The Cu(11) ion in the acqueous medium is surrounded by six water molecules in tetragonal geometry – four of these are at the corners of a square plane and at shorter distances with stronger interactions, whereas the remaining two are weakly interacting with the metal ion at distant axial positions as shown in *Figure* 5. The two axial Cu-O distances are 238pm, whereas the four equatorial Cu-O distances are $\sim$ 195pm. The d^9 electronic configuration of this ion gives three electrons in e_g orbitals and the two ways of filling the e_g level gives doubly-degenerate electronic ground state (*Figure* 6). The distortion occurs along one of the molecular four-fold axes (always labelled as z-axis). This distortion normally takes the form of elongating the bonds to the ligands lying along the z-axis, but occasionally



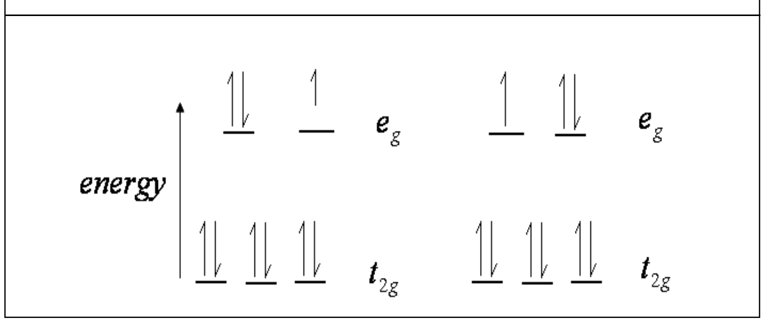


Figure 5 (top). Structure of $[Cu(OH_2)_6]^{2+}$ ion.
Figure 6 (bottom). Two ways of filling e_g level of $[Cu(OH_2)_6]^{2+}$ ion.

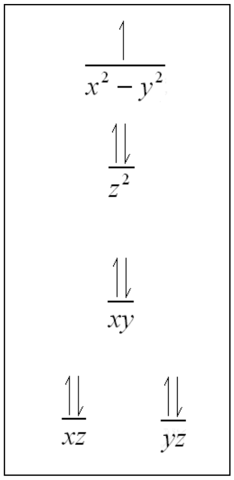


Figure 7. Removal of degeneracy in Cu(11) ion.

occurs as a shortening of these bonds instead. The removal of degeneracy or J–T distortion is shown in *Figure* 7.

Dynamic Jahn–Teller Distortion

In some molecules, the distortion is negligible. However the distortion can be seen by freezing the molecule at lower temperatures. This condition is known as dynamic Jahn–Teller distortion. The complexes of the type $M_2PbCu(NO_2)_6$ show dynamic J–T distortion. Here, M = K, Rb, Cs, Tl.

Suggested Reading

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