Two Equivalent e_g Orbitals for the Discussion of Bonding in Octahedral Complexes

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Transition-metal complexes form a crucial part of lecture courses on coordination, organometallic, and bioinorganic chemistry. The bonding situation in these compounds is often described by either crystal or ligand field theory *(1)*. Since transition metals generally have partly filled or empty d orbitals, these orbitals are usually assumed to be involved in the formation of bonds between the metal atom and the ligands; in almost every textbook, the omnipresent set of the real-valued d orbitals, d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, and d_{z^2}, is used, which is obtained by one particular linear combination of the complex canonical solutions of the Schrödinger equation for the H atom *(2)*. From this exclusive use, students might think that this is the only existing set. Nevertheless, this is clearly not the case, since every appropriate linear combination of the canonical orbitals (or of the standard d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, and d_{z^2} orbitals) also represents a valid set and could be used instead *(3)*. For instance, it has been shown by Powell *(4)* and others *(5–9)* that a set of five equivalent real-valued d orbitals can be constructed that have the same shape and only differ in their orientation along the slant edges of a pentagonal pyramid. For didactic reasons, the presentation of these equivalent orbitals during a lecture could help students to accept the degeneracy of the standard textbook d orbitals despite their different appearance. In a similar fashion, bonding considerations for octahedral complexes afford two sets of degenerate t_{2g} (d_{xy}, d_{yz}, d_{xz}) and e_g orbitals ($d_{x^2-y^2}$, and d_{z^2}), whereby the latter often confuse students because of their totally different shape. The reader should be reminded that the interpretation of one-electron wavefunctions (orbitals) in the context of chemical bonding is a frequently discussed topic in this *Journal (10–14)*.

It is the aim of this article to present a new set of d orbitals featuring equivalent e_g orbitals, which might be intuitively more appropriate for the discussion of the bonding situation in transition-metal complexes, for example, by means of ligand field theory.

The Canonical Set

The canonical set of d orbitals is obtained as solutions of the Schrödinger equation for the H atom, which are the so-called spherical harmonics *(3)*, Y_{l,m_l} with the quantum number $l = 2$ and $m_l = -l, ..., l$ (the associated Laguerre function is set to 1 for the discussion):

$$Y_{2,-2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \; e^{-2i\varphi} \tag{1}$$

$$Y_{2,-1} = \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta \; e^{-i\varphi} \tag{2}$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}} \left(3\cos^2\theta - 1\right) \tag{3}$$

$$Y_{2,1} = -\sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta \; e^{i\varphi} \tag{4}$$

$$Y_{2,2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \; e^{2i\varphi} \tag{5}$$

The Standard Textbook Set

The standard textbook set can be obtained by linear combinations of the spherical harmonics Y_{l,m_l}:

$$d_{z^2} = Y_{2,0} \tag{6}$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}\left(Y_{2,2} + Y_{2,-2}\right) \tag{7}$$

$$d_{xy} = -\frac{i}{\sqrt{2}}\left(Y_{2,2} - Y_{2,-2}\right) \tag{8}$$

$$d_{yz} = -\frac{i}{\sqrt{2}}\left(Y_{2,1} + Y_{2,-1}\right) \tag{9}$$

$$d_{xz} = \frac{1}{\sqrt{2}}\left(Y_{2,1} - Y_{2,-1}\right) \tag{10}$$

Every chemist is familiar with this set of d orbitals, and it is extensively used for the description of the bonding in transition-metal complexes. The standard set is chosen such that the orbitals d_{z^2} and $d_{x^2-y^2}$ are directed along the axes of a Cartesian coordinate system, while the remaining three orbitals, d_{xy}, d_{yz}, and d_{xz}, span the space between them (Figure 1).

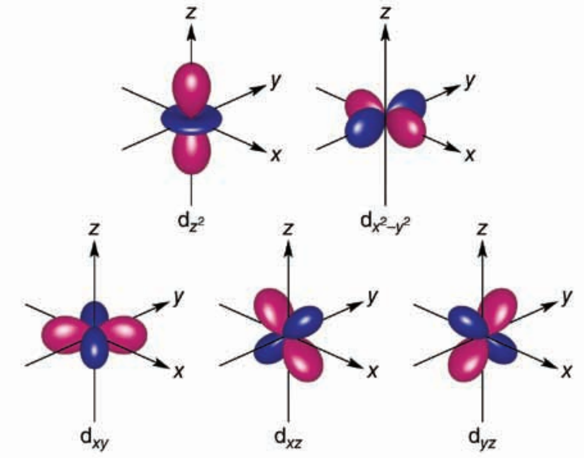

Figure 1. Standard set of d orbitals. Depicted are the corresponding spherical harmonics.

This set allows for any description of bonding by means of ligand field theory; however, if octahedral complexes are discussed, the ligand field splits the degenerate set of d orbitals into two sets of t_{2g} and e_g symmetry, respectively. The t_{2g} set consists of the d_{xy}, d_{yz}, and d_{xz} orbitals and these are all of the same shape. In contrast, this is not the case for the e_g orbitals, d_{z^2} and $d_{x^2-y^2}$, which exhibit a totally different shape but are still energetically degenerate. This is somewhat counterintuitive, and the question arises whether a set of equivalent and equally shaped e_g orbitals exists, while the t_{2g} orbitals remain unchanged.

The New Set

The new set can be obtained by the transformation

$$\begin{bmatrix} e_{g1} \\ e_{g2} \\ d_{xy} \\ d_{xz} \\ d_{yz} \end{bmatrix} = \begin{bmatrix} a & b & 0 & 0 & 0 \\ c & d & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} d_{z^2} \\ d_{x^2-y^2} \\ d_{xy} \\ d_{xz} \\ d_{yz} \end{bmatrix} \qquad (11)$$

where *a*–*d* are constants to be determined. In addition, the new e_g orbitals must be orthogonal and normalized, which means that the following conditions have to be fulfilled:

$$\int_0^{2\pi}\int_0^{\pi} e_{g1} e_{g1}^{*} \sin\theta \, d\theta \, d\varphi = 1 \qquad (12)$$

$$\int_0^{2\pi}\int_0^{\pi} e_{g1} e_{g2}^{*} \sin\theta \, d\theta \, d\varphi = 0 \qquad (13)$$

$$\int_0^{2\pi}\int_0^{\pi} e_{g2} e_{g2}^{*} \sin\theta \, d\theta \, d\varphi = 1 \qquad (14)$$

Table 1. General Set of Coefficients that Satisfy Equations 17–19

a	*b*	*c*	*d*
$-d$	$(1-d^2)^{1/2}$	$(1-d^2)^{1/2}$	$d > 0$
d	$-(1-d^2)^{1/2}$	$(1-d^2)^{1/2}$	$d > 0$
d	$(1-d^2)^{1/2}$	$-(1-d^2)^{1/2}$	$d > 0$
$-d$	$(1-d^2)^{1/2}$	$(1-d^2)^{1/2}$	$d < 0$
$-d$	$-(1-d^2)^{1/2}$	$-(1-d^2)^{1/2}$	$d < 0$
d	$(1-d^2)^{1/2}$	$-(1-d^2)^{1/2}$	$d < 0$
d	$-(1-d^2)^{1/2}$	$(1-d^2)^{1/2}$	$d < 0$
$-d$	$-(1-d^2)^{1/2}$	$-(1-d^2)^{1/2}$	$d > 0$

By noticing that the standard set of d orbitals is already orthonormal, this set of equations can be simplified, as is shown in detail for eq 12:

$$\int_0^{2\pi}\int_0^{\pi} \left(a d_{z^2} + b d_{x^2-y^2}\right)^2 \sin\theta \, d\theta \, d\varphi = 1 \qquad (15)$$

$$a^2 \underbrace{\left\langle d_{z^2} \middle| d_{z^2} \right\rangle}_{1} + 2ab \underbrace{\left\langle d_{z^2} \middle| d_{x^2-y^2} \right\rangle}_{0} + b^2 \underbrace{\left\langle d_{x^2-y^2} \middle| d_{x^2-y^2} \right\rangle}_{1} = 1 \qquad (16)$$

$$a^2 + b^2 = 1 \qquad (17)$$

Simplifying eqs 13 and 14 results in

$$ac + bd = 0 \qquad (18)$$

$$c^2 + d^2 = 1 \qquad (19)$$

Equations 17–19 contains four unknowns, which requires a fourth condition for its unique solution. Eight solutions that depend on the coefficient *d* can be obtained, which are listed in Table 1. The requirement for a specific sign of the coefficient *d* stems from the orthogonality condition (cf. eq 18). From eq 18 it is obvious that exactly one of the coefficients *a, b, c,* or *d* must differ in sign from the others. That means that the e_{g1} orbital is constructed formally by adding the d_{z^2} orbital to the $d_{x^2-y^2}$ orbital, while the e_{g2} orbital is obtained by subtracting d_{z^2} from $d_{x^2-y^2}$. A more concise formulation of this requirement is

$$e_{g1} = d_{z^2} \cos\lambda + d_{x^2-y^2} \sin\lambda \qquad (20)$$

$$e_{g2} = -d_{z^2} \sin\lambda + d_{x^2-y^2} \cos\lambda \qquad (21)$$

Table 2. All Possible Coefficients for the Generation of Two e_g Orbitals of the Same Shape

a	*b*	*c*	*d*
$-(1/2)^{1/2}$	$(1/2)^{1/2}$	$(1/2)^{1/2}$	$(1/2)^{1/2}$
$(1/2)^{1/2}$	$-(1/2)^{1/2}$	$(1/2)^{1/2}$	$(1/2)^{1/2}$
$(1/2)^{1/2}$	$(1/2)^{1/2}$	$-(1/2)^{1/2}$	$(1/2)^{1/2}$
$(1/2)^{1/2}$	$(1/2)^{1/2}$	$(1/2)^{1/2}$	$-(1/2)^{1/2}$
$(1/2)^{1/2}$	$-(1/2)^{1/2}$	$-(1/2)^{1/2}$	$-(1/2)^{1/2}$
$-(1/2)^{1/2}$	$(1/2)^{1/2}$	$-(1/2)^{1/2}$	$-(1/2)^{1/2}$
$-(1/2)^{1/2}$	$-(1/2)^{1/2}$	$(1/2)^{1/2}$	$-(1/2)^{1/2}$
$-(1/2)^{1/2}$	$-(1/2)^{1/2}$	$-(1/2)^{1/2}$	$(1/2)^{1/2}$

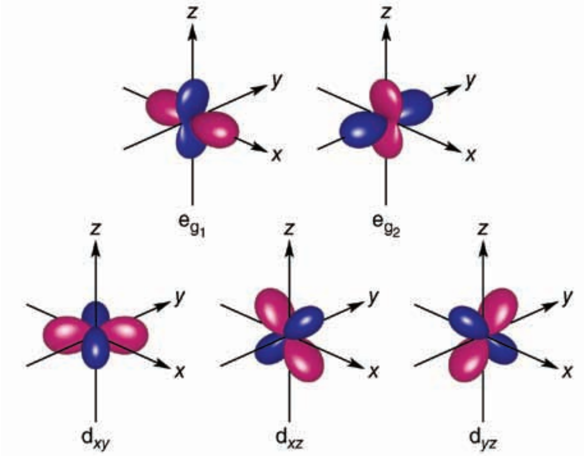

Figure 2. New set of d orbitals with modified e_g orbitals. Depicted are the corresponding spherical harmonies.

Since we wish to find a set of e_g orbitals where both orbitals should have the same shape, the coefficient *d* (or λ, respectively) has to be chosen such, that this condition is fulfilled. Because of the $D_{\infty h}$ symmetry of the d_{z^2} orbital and the shape of the $d_{x^2-y^2}$ orbital, the addition and subtraction of the d_{z^2} orbital to and from the $d_{x^2-y^2}$ orbital will result in two e_g orbitals with either a bigger positive or negative lobe along the *x* and *y* axis, respectively. However, for both e_g orbitals to be equally shaped it is necessary that these lobes are equivalent. This is only satisfied if the d_{z^2} contribution to either of the e_g orbitals is the same. From this requirement one can infer that $|a| = |c|$ (or $\cos\lambda = \sin\lambda$). That means $|d| = |(1 - d^2)^{1/2}|$ (cf. Table 1). This equation has the two solutions $d = \pm(1/2)^{1/2}$, of which only one fulfils the orthogonality condition. Therefore there are eight possible sets of coefficients *a, b, c,* and *d* satisfying eqs 17–19 that result in a pair of equally shaped e_g orbitals. These are listed in Table 2.

Apart from sign, all eight sets of coefficients lead to only one set of e_g orbitals, which is given by (here the coefficients of the first row in Table 2 have been used)

$$e_{g_1} = -A\left[\left(\cos^2\theta - 1\right)\left(1 + \frac{B}{A}\right) + 2\cos^2\theta\right] \quad (22)$$

$$e_{g_2} = A\left[\left(\cos^2\theta - 1\right)\left(1 - \frac{B}{A}\right) + 2\cos^2\theta\right] \quad (23)$$

$$A = \sqrt{\frac{5}{32\pi}} \quad (24)$$

$$B = \sqrt{\frac{15}{32\pi}}\cos 2\varphi \quad (25)$$

The new set of orbitals is depicted in Figure 2. The new e_g orbitals exhibit D_{2h} symmetry and have their greatest extension along the *x* and *y* axis, respectively, whereas the extension along the *z* axis is the same for both orbitals. In accordance with the usual interpretation in terms of crystal field theory for octahedral complexes, six ligands oriented along the Cartesian axes split the degenerate set into two sets, whereby the energy of the e_g orbitals is higher than that of the t_{2g} set. But whereas the degeneracy within the e_g set is not very intuitive if the textbook orbitals d_{z^2} and $d_{x^2-y^2}$ are considered, the degeneracy of the newly derived e_g orbitals is obvious owing to their identical spatial appearance.

To suggest an appropriate nomenclature for the new e_g orbitals, we express the two orbitals in terms of Cartesian coordinates. The relation between spherical and Cartesian coordinates is given by

$$x = r\sin\theta\cos\varphi \quad (26)$$

$$y = r\sin\theta\sin\varphi \quad (27)$$

$$z = r\cos\theta \quad (28)$$

Substitution into the e_g orbital expressions (eqs 22 and 23) leads to

$$e_{g_1} = \frac{\sqrt{10}}{8\sqrt{\pi}\,r^2}\left[\left(\sqrt{3} + 1\right)x^2 - \left(\sqrt{3} - 1\right)y^2 - 2z^2\right] \quad (29)$$

$$e_{g_2} = \frac{\sqrt{10}}{8\sqrt{\pi}\,r^2}\left[\left(\sqrt{3} - 1\right)x^2 - \left(\sqrt{3} + 1\right)y^2 + 2z^2\right] \quad (30)$$

Therefore, the two e_g orbitals may be denoted $d_{x^2-y^2-z^2}$ and $d_{x^2-y^2+z^2}$, respectively. This notation can also be derived from the transformation (eq 11) after substitution of the coefficients *a, b, c,* and *d* (Table 2), resulting in

$$e_{g_1} = \sqrt{\tfrac{1}{2}}\left(d_{x^2-y^2} - d_{z^2}\right) \quad (31)$$

$$e_{g_2} = \sqrt{\tfrac{1}{2}}\left(d_{x^2-y^2} + d_{z^2}\right) \quad (32)$$

which clearly show that the orbitals $d_{x^2-y^2-z^2}$ and $d_{x^2-y^2+z^2}$ represent the simplest normalized linear combination of the standard e_g orbitals d_{z^2} and $d_{x^2-y^2}$.

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