

# On the choice of $d$ -orbital coordinate system in charge-density studies of low-symmetry transition-metal complexes

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The distribution of the  $d$  electrons over the corresponding orbitals in transition-metal complexes is a central concept in the theory of metal–ligand bonding. The description requires the assignment of an axis of quantization, which is unambiguous in symmetric environments but not clear-cut in the now commonly encountered case of a low-symmetry coordination environment. As the  $d$ -electron population can be derived from accurate diffraction data using the methods of charge-density analysis [Holladay *et al.* (1983). *Acta Cryst.* **A39**, 377–387], the need for an appropriate procedure is relevant in this area of crystallography. Several criteria for the choice of coordinate system based on the resulting orbital populations are discussed. They are tested on a cobalt atom in a trigonal bipyramidal site and applied to transition-metal sites in Cu<sup>II</sup>-alanyl-valine, and an open zirconocene. The population of the  $d$ -orbital cross terms for the different coordinate-system orientations is used to judge the results. In the cases examined, the intuitively most reasonable coordinate system corresponds to the one with smaller value of the sum of the populations of the  $d$ -orbital cross terms.

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## 1. Introduction

When the field exerted by the local environment on the site of a transition-metal atom deviates from spherical symmetry, as is the case in any crystal, the degeneracy of the  $d$  orbitals is lifted, and for all but fully occupied shells preferential occupancy will occur. The analysis of  $d$ -orbital occupancies and their interpretation in terms of metal–ligand bonding continues to play a central role in inorganic and metallo-organic chemistry (Ballhausen, 1962; Sugano *et al.*, 1970; Allbright *et al.*, 1985).

In X-ray charge-density analysis, the  $d$ -orbital populations can be derived from the multipole population parameters (Holladay *et al.*, 1983), as obtained with refinements based on the atom-centered spherical harmonic expansion of the electron density (Stewart, 1976; Hansen & Coppens, 1978; Coppens, 1997). By necessity, the numerical values of the refined multipole population parameters are a function of the choice of the local coordination system (LCS), and so are the  $d$ -orbital populations derived from the multipole population parameters. For highly symmetric environments, such as octahedral, trigonal, square-planar, pyramidal, the appropriate orientation is unambiguous and prescribed by ligand-field theory. In octahedral complexes, for example, the  $x$ ,  $y$  and  $z$  axes are oriented in the direction of the ligands, while in a tetrahedral environment they are oriented along the fourfold inversion axes which bisect the ligands. But with the dramatic

growth of crystal structure analysis structures in which the metal site is distorted from idealized symmetry, or has a very low symmetry, have become much more common. In such cases, the choice of the LCS is not obvious. It thus becomes desirable to explore the optimal choice of coordinate system to allow interpretation of the results.

## 2. Choice of criteria

In the electrostatic crystal field theory, electrons in orbitals pointing towards the negatively charged ligands are repelled, leading to higher energy and thus lower population of these orbitals in all but weak fields. This is generally confirmed by more advanced treatments as well as experimental charge-density studies, which generally show, for instance, lower populations of the  $d(z^2)$  and  $d(x^2 - y^2)$  orbitals in the case of octahedral coordination. The criteria adopted are derived from the idealized symmetries. For a sixfold coordination distorted from octahedral, the coordinate system that minimizes the sum of the  $d(z^2)$  and  $d(x^2 - y^2)$  populations is searched for. For a fourfold environment distorted from tetrahedral, this sum is maximized, while in an approximately square-planar or square-pyramidal environment with distant fifth axial ligand, the  $d(x^2 - y^2)$  population is minimized. Other criteria can be explored depending on the details of the coordination environment. It is important to point out that the

**Table 1**  
Percentage  $d$ -orbital population of Co1 in  $\text{Co}_2(\text{CO})_6(\text{AsPh}_3)_2$ .

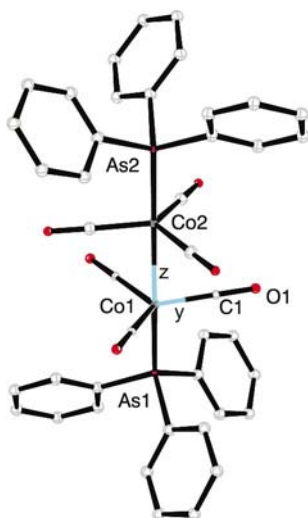
	$d(z^2)$	$d(xz)$	$d(yz)$	$d(x^2 - y^2)$	$d(xy)$
%	9.4	26.2	26.2	19.1	19.1

total density is invariant to a change in coordinate system, but that the interpretation of the asphericity of the  $d$ -orbital density in terms of the bonding interactions with the ligands will be affected.

In addition to orbital populations, the electron density in all but the highest symmetry environments includes non-zero populations of the cross terms of the orbital product functions (Coppens, 1997). If  $\phi(d_i)$  is the atomic  $d$ -orbital basis set, the corresponding  $d$ -orbital density is given by

$$\rho_d = \sum_i \sum_j P_{ij} \phi(d_i) \phi(d_j),$$

where  $P_{ij}$  is the population of the  $ij$  orbital product. The cross terms  $\phi(d_i)\phi(d_j)$  with  $i \neq j$  do not occur for the isolated atom and will only be nonzero in the molecular case for orbitals belonging to the same representation of the point group of the molecule. They are progressively removed as the site symmetry increases, no cross terms are allowed in the highest-symmetry environments. Thus, a low set of values of the cross terms after coordinate rotation indicates that a higher-symmetry environment has been more closely approximated. The progress of the search for an optimal coordinate system may therefore be monitored by examination of the population of the orbital cross terms. The size of the populations of the orbital products may be used as a test of the suitability of the criteria applied in the procedure, as illustrated below.

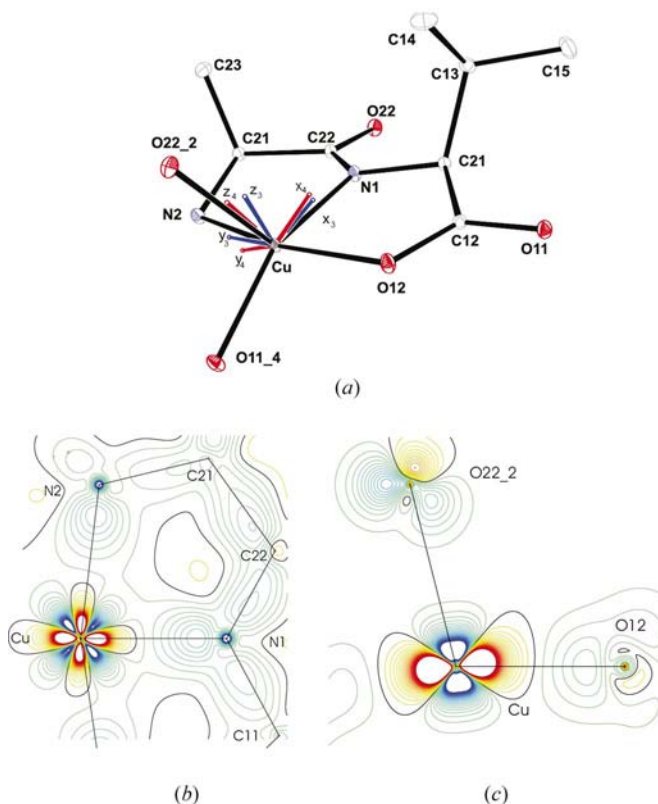


**Figure 1**  
Structure of the  $\text{Co}_2(\text{CO})_6(\text{AsPh}_3)_2$  complex. The blue lines are the  $z$  and  $y$  axes of the original LCS. The search for an orientation with a minimum in the  $d(z^2)$  population reproduces the symmetry-imposed LCS, which also corresponds to a minimum in the sum of the squares of the  $d$ -orbital cross terms.

### 3. Application

#### 3.1. Test calculation: cobalt on a trigonal bipyramidal site

The charge density of  $\text{Co}_2(\text{CO})_6(\text{AsPh}_3)_2$  has been studied with the multipole model by Macchi *et al.* (1998). The cobalt atoms reside at the  $\bar{3}$  special position of the  $R\bar{3}$  space group. The valence-shell configuration of the pentacoordinate Co atoms is  $3d^7$  and the refined monopole value is 6.95 e. Because of the local site symmetry of the Co atoms, the multipole refinement was performed with the  $z$  axis along the Co–Co bond direction, and with the  $zy$  plane defined by the atoms Co2, Co1 and C1 (Fig. 1). Since only a small charge concentration is found in the Co–Co bond, a small population is expected in the  $d(z^2)$  orbital. The LCS search program was tested by changing the starting coordinate system to several general orientations. In all cases, the original orientation was successfully recovered. The  $d$ -orbital population is given in Table 1.



**Figure 2**  
(a)  $\text{Cu}^{\text{II}}$ -alanyl-valine showing the distorted five coordination of the Cu atom. The blue coordinate system labeled  $(x_3, y_3, z_3)$  corresponds to the best orientation for minimum  $d(x^2 - y^2)$  population; the red coordinate system labeled  $(x_4, y_4, z_4)$  corresponds to the best orientation for minimum  $d(z^2) + d(x^2 - y^2)$ . The  $z_3$  direction is almost parallel to the normal vector of the least-squares plane through  $\text{N1} \cdots \text{N2} \cdots \text{O11}_4 \cdots \text{O12}$ . (b) Model deformation density in the plane  $\text{N2}-\text{Cu}-\text{N1}$ ; (c) in the plane  $\text{O22}_2-\text{Cu}-\text{O12}$ . Blue and green contours positive, red and yellow contours negative, zero contour black. Contour interval  $0.1 \text{ e } \text{\AA}^{-3}$ .

### 3.2. The Cu<sup>II</sup>-alanyl-valine complex

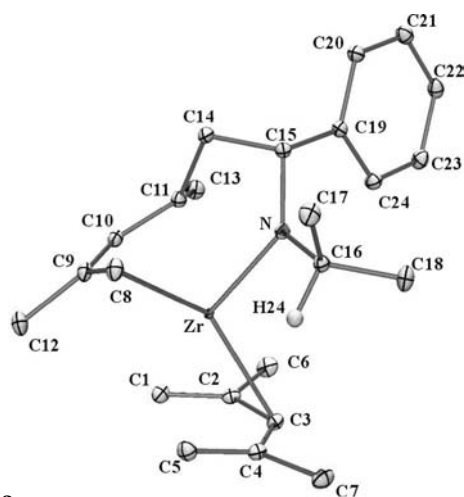
In Cu<sup>II</sup>-alanyl-valine, the copper atom is in a distorted pentacoordinated site as illustrated in Fig. 2(a), with the  $3d^94s^0$  valence configuration. Starting with this configuration, only  $d$ -electron occupancies were refined on the Cu atom to give a total of 9.84 valence electrons. The complete charge-density study of Cu<sup>II</sup>-alanyl-valine will be reported elsewhere (Sabino *et al.*, 2003). The model deformation densities in two planes through the Cu atom are shown in Fig. 2(b).

Although the atoms N1, O12, O11\_4 and N2 are not coplanar, spectroscopic results have been interpreted in terms of an approximately square-pyramidal environment with these four atoms in the square base, and an underpopulated  $d(x^2 - y^2)$  orbital (Facchin *et al.*, 2000). Because of this, searches for minimal  $d(x^2 - y^2)$  populations were included in the analysis.

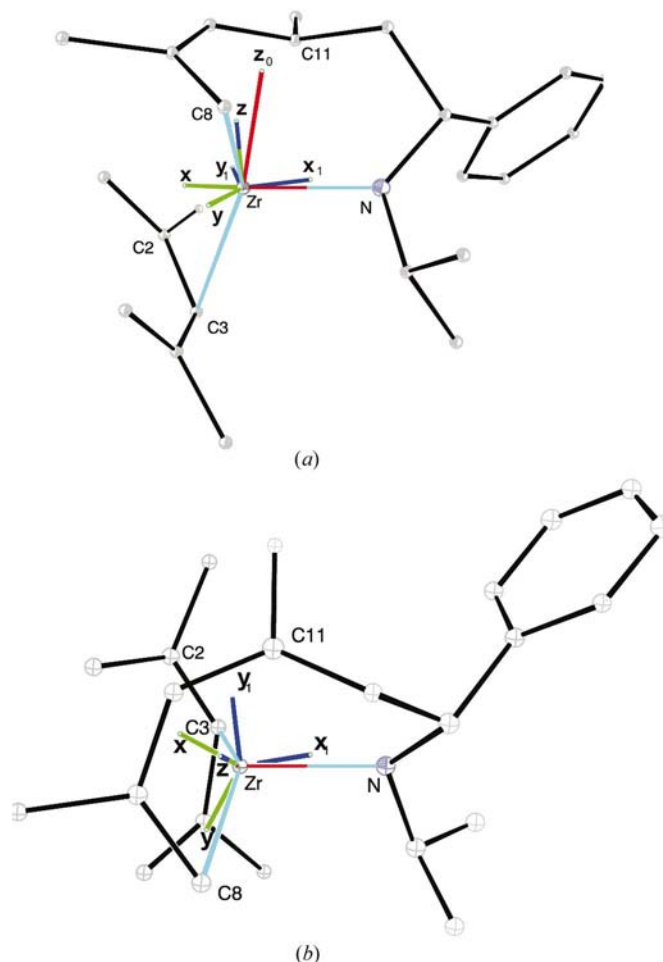
In the LCS used in the original multipole refinement (I), the  $x$  axis is oriented along Cu–N1 [Cu–N1 and Cu–N2 have lengths of 1.9115 (4) and 2.0299 (4) Å, respectively] and the  $xy$  plane is defined by Cu–N1 and Cu–O12 [bond lengths of Cu–O12 and Cu–O11\_4 are 1.9986 (4) and 1.9939 (4) Å, respectively]. First the LCS choice with  $z$  along Cu–O22\_2 (II) [2.2232 (4) Å] was tested, as it conforms to the approximation of a square-pyramidal geometry around the Cu atom.

Subsequent searches with either minimal  $d(x^2 - y^2)$  or minimal  $d(z^2) + d(x^2 - y^2)$  populations give (III) and (IV), respectively. Relative  $d$ -orbital populations (in %) are listed in Table 2(a), while the LCS corresponding to (III) and (IV) are illustrated in Fig. 2(a).

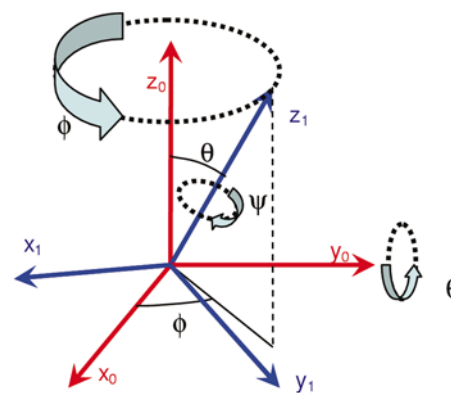
The cross terms obtained for the various coordinate systems are listed in Table 2(b). The choice of (III), arrived at by minimization of  $d(x^2 - y^2)$  as suggested by the spectroscopic study, minimizes the populations of the  $d$ -orbital cross terms (Table 2b), and is therefore preferred over IV.



**Figure 3**  
ORTEP view and atom numbering scheme of Zr(2,4-C<sub>7</sub>H<sub>11</sub>)-(NMe<sub>2</sub>)<sub>2</sub>CHPhCH<sub>2</sub>CMe=CHCMe=CH<sub>2</sub>. Ellipsoids drawn at the 50% level probability and arbitrary radius for H24. H atoms (except H24) omitted for clarity.



**Figure 4**  
(a) View normal to the plane N–Zr– $z_0$ . (b) View along the  $z_0$  vector towards the Zr atom, in the distorted site of the zirconium atom. Light blue lines indicate the bond paths from the topological analysis. The red lines represent the initial LCS, with  $z_0$  defining the starting  $z$  direction and  $z_0$ , Zr and N defining the plane  $zx$ . The green LCS, labeled  $(x, y, z)$ , corresponds to the maximum  $d(z^2)$  population (I in Table 3); the dark blue LCS, labeled  $(x_1, y_1, z)$ , corresponds to the orientation of maximum population in the  $d(z^2)$  and  $d(x^2 - y^2)$  orbitals (II in Table 3). The green and dark blue coordinate systems share the  $z$  axis.



**Figure 5**  
The search is performed for all orientations starting with the original LCS  $(x_0, y_0, z_0)$  in red. The search grid is spanned in the following way: the vector  $z_1$  circles around  $z_0$  forming a cone with opening angle  $\theta$ ; for each orientation of  $z_1$ , a stepped rotation around  $z_1$  is performed (the angle  $\psi$ ).

**Table 2**

Percentage populations of the Cu<sup>II</sup> *d* orbitals in Cu<sup>II</sup>-alanyl-valine and *d* cross terms for the cases (I)–(IV).

(a) Percentage populations of the Cu<sup>II</sup> *d* orbitals in Cu<sup>II</sup>-alanyl-valine with refined monopole 983 e.

	$d(z^2)$	$d(xz)$	$d(yz)$	$d(x^2 - y^2)$	$d(xy)$
I (%)	23.2	21.4	21.4	13.6	20.6
II (%)	21.8	21.1	21.0	14.2	21.9
III (%)	22.8	21.5	21.4	13.3	21.1
IV (%)	21.4	21.6	21.0	14.2	21.8

(b) *d* cross terms for the cases (I)–(IV).  $\sum(d_i/d_j)^2$  is the sum of the squares of cross terms.

	$dz^2/xz$	$dz^2/yz$	$dz^2/x^2 - y^2$	$dz^2/xy$	$dxz/yz$	$dxz/x^2 - y^2$	$dxz/xy$	$dyz/x^2 - y^2$	$dyz/xy$	$dx^2 - y^2/xy$	$\sum(d_i/d_j)^2$
I	0.161	-0.215	0.017	-0.052	0.061	0.502	-0.145	0.166	0.229	-0.764	1.016
II	-0.016	-0.087	0.120	-0.032	0.034	0.205	-0.154	-0.153	-0.204	-0.694	0.637
III	0.080	-0.148	0.118	0.001	-0.045	0.006	-0.153	0.024	0.232	-0.097	0.132
IV	-0.267	-0.125	-0.172	0.096	-0.040	-0.454	-0.202	0.225	-0.154	0.017	0.449

**Table 3**

Percentage *d*-orbital population of the Zr atom in the open zirconocene complex and *d* cross terms for the models listed.

(a) Percentage *d*-orbital population of the Zr atom in the open zirconocene complex. The total (*4d* + *5s*) monopole population is 2.47 e.

	$d(z^2)$	$d(xz)$	$d(yz)$	$d(x^2 - y^2)$	$d(xy)$
I (%)	36.5	22.5	11.5	6.5	23.0
II (%)	36.5	32.0	2.0	24.9	4.7

(b) *d* cross terms for the models listed in (a).  $\sum(d_i/d_j)^2$  is the sum of the squares of cross terms.

	$dz^2/xz$	$dz^2/yz$	$dz^2/x^2 - y^2$	$dz^2/xy$	$dxz/yz$	$dxz/x^2 - y^2$	$dxz/xy$	$dyz/x^2 - y^2$	$dyz/xy$	$dx^2 - y^2/xy$	$\sum(d_i/d_j)^2$
I	-0.009	0.014	-0.044	-0.057	-0.688	-0.056	0.105	-0.206	0.042	-0.408	0.704
II	-0.001	-0.016	0.041	-0.060	0.044	-0.053	-0.192	0.068	0.119	0.500	0.316

### 3.3. Organozirconium complex

The zirconium atom in the open zirconocene, Zr(2,4-C<sub>7</sub>H<sub>11</sub>)[(<sup>1</sup>Pr)NCHPhCH<sub>2</sub>CMe=CHCMe=CH<sub>2</sub>] (C<sub>7</sub>H<sub>11</sub> = dimethylpentadienyl) (Pillet *et al.*, 2003) is at a complex distorted site, as shown in Fig. 3.

In the original analysis, refinements were performed both with and without an occupied 5*s* shell. As the agreement factors were almost identical, and a fully occupied 5*s* shell gave negative populations in one of the *d* orbitals (*4d*<sub>*yz*</sub>), some of the 5*s* electrons were distributed equally over all *d* orbitals, such as to eliminate the negative population, as described fully in the original publication (Pillet *et al.*, 2003).

A search for the highest population in *d*(*z*<sup>2</sup>) produces coordinate system (I), while a search for highest *d*(*z*<sup>2</sup>) followed by a search for the highest *d*(*x*<sup>2</sup> - *y*<sup>2</sup>) population gives system (II). The latter search is based on the approximation to the tetrahedral symmetry as suggested by bond paths connecting Zr with the N, C8 [Zr–C8 = 2.3535 (6) Å] and C3 [Zr–C3 = 2.4714 (6) Å] atoms in the charge-density study of Pillet *et al.* (2003), and the proximity of C11 at 2.4963 (6) Å from the Zr atom (though no bond path was found between Zr and C11). The orientation corresponding to (II) produces the lowest value of the sum of the squares of the *d* cross-term populations (Table 3*b*), supporting its selection. It is noticeable that this orientation also minimizes the *d*(*yz*)

orbital population. The coordinate systems are illustrated in Fig. 4.

### 4. Conclusions

The search for an appropriate coordinate system for the definition of the *d*-orbital orientations at a transition-metal site, based on the approximate site symmetry and ligand field considerations, is of importance in the interpretation of metal *d*-orbital populations and the analysis of chemical bonding. The LCS choice for high-symmetry metal sites (*e.g.* octahedral, trigonal *etc.*) is unambiguous and no deviation from the standard orientation is obtained. For low-symmetry metal sites, the coordinate system can be chosen to optimize the fit to the approximate site symmetry. For Cu<sup>II</sup>-alanyl-valine, minimization of the population in the *d*(*x*<sup>2</sup> - *y*<sup>2</sup>) orbital leads to the optimal choice as judged by the population of the *d*-orbital cross terms, a result also in satisfactory agreement with the interpretation of the spectroscopic data by Facchin *et al.* (2000). The criterion based on fourfold, approximately tetrahedral, coordination of the Zr atom in the open zirconocene again leads to a significant decrease in the *d*-orbital cross-term populations, which are obviously important in judging the success of the procedure.

Finally, the need for a proper choice of coordinate system for transition metals in low-symmetry environments is not limited to experimental charge-density analysis but is similarly relevant in the interpretation of theoretical studies of transition-metal complexes.

## APPENDIX A

### A1. Method

The *d*-orbital populations are calculated from the multipole model (MM) population parameters with the appropriate transformation matrix, described by Holladay *et al.* (1983) and by Coppens (1997). The projection matrix **P** of the old LCS (**x**<sub>0</sub>, **y**<sub>0</sub>, **z**<sub>0</sub>) into the new LCS (**x**<sub>1</sub>, **y**<sub>1</sub>, **z**<sub>1</sub>) is given by

$$P = \begin{vmatrix} x_1 \cdot x_0 & x_1 \cdot y_0 & x_1 \cdot z_0 \\ y_1 \cdot x_0 & y_1 \cdot y_0 & y_1 \cdot z_0 \\ z_1 \cdot x_0 & z_1 \cdot y_0 & z_1 \cdot z_0 \end{vmatrix}.$$

Starting from the projection matrix, the angles  $\alpha$ ,  $\beta$  and  $\gamma$  of an Eulerian rotation matrix (corresponding to rotations by  $\gamma$  around **z**<sub>0</sub>,  $\beta$  around the intermediate **y**'<sub>1</sub> and of  $\alpha$  around **z**<sub>1</sub>) and the spherical harmonic (SH) rotation matrix are obtained as described by Su & Coppens (1994). The SH population parameters are transformed by the inverse of the transpose of the rotation matrix.

In the search for the best LCS orientation, which is dependent on the criterion selected, the new LCS is determined by explicit rotation of the LCS in which the multipole refinement was performed. A rotation of the vector **r** by an angle  $\Phi$  around the unit direction **n** is based on the rotation formula described by Goldstein *et al.* (2002), and given by

$$\mathbf{r}' = \mathbf{r} \cos \Phi + \mathbf{n}(\mathbf{n} \cdot \mathbf{r})(1 - \cos \Phi) + (\mathbf{r} \times \mathbf{n}) \sin \Phi.$$

The search is performed in a grid over a hemisphere, where the tip of the **z**<sub>1</sub> axis spans the sphere surface in successive circular paths (Fig. 5). The blue coordinate system (Fig. 5) starts at the original LCS (the red vectors in Fig. 5). A stepped rotation in the angle  $\theta$  is performed around **y**<sub>0</sub>, for each step in  $\theta$  the vector **z**<sub>1</sub> spans a circle on the spherical surface by steps in  $\phi$ , and for each step in  $\phi$  the system is rotated around the vector **z**<sub>1</sub> by steps in  $\psi$ . In each orientation, the Euler angles and the new SH populations are calculated and the criterion is tested. The angles  $\theta$ ,  $\phi$  and  $\psi$  range from 0 to 90°, 0 to 360° and 0 to 180°, respectively.

### A2. Software (available from jrsabino@if.sc.usp.br)

The coordinate system rotation and search according to specific population criteria have been implemented in the

program *ERD*. The program obtains the angles  $\alpha$ ,  $\beta$  and  $\gamma$  for an Eulerian rotation, calculates the SH rotation matrix, the multipole populations in the new LCS and the corresponding *d*-orbital populations. The geometry is read from an input file in which the user specifies the atom for which the calculation is to be performed and, if required, two local coordinate systems. Alternatively, it is possible to analyze a stepped rotation around a single axis starting from the initial coordination system axis and to search for the best orientation in all orientation space with the specified criterion for the *d*-orbital populations or with minimization of sum of the squares of the cross terms. The program is available for PC and workstations. It has been compiled successfully in Linux RH 7.1, SGI IRIX 6.5, SunOS 5.8 and Windows XP; and can be compiled for all platforms with a standard C/C++ compiler without any major changes. Complete documentation on how to run the program is included in the distribution, which can be obtained from <http://zappa.if.sc.usp.br> or by an e-mail request to JRS. The mathematical background is described in the references.

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