# The Meaning of d-Orbital Labels

**Guy Ashkenazi**
Department of Science Teaching, The Hebrew University, Jerusalem 91904, Israel; *guy@fh.huji.ac.il*

Crystal field theory is a standard topic in current U.S. textbooks for undergraduate general chemistry. The key concept that guides this theory is the spatial orientation of the different d orbitals: while $d_{xy}$, $d_{yz}$, and $d_{xz}$ lie between the axes, $d_{x^2-y^2}$ and $d_{z^2}$ are aligned along in the *x, y,* and *z* direction. The interaction of ligands with the two different sets of orbitals induces a splitting in the d-orbital energy levels, and this splitting gives rise to the color of transition-metal complexes. d Orbitals are introduced early in many textbooks, usually in the chapter about atomic structure. Many textbooks (for example, *1–3*) present a diagram of the orbital shapes and their labels, without any reference to the meaning of the labels. Students who study crystal field theory need to know the shapes of the five d orbitals, the labels of the five d orbitals, and how to match the labels to the shapes. This is a lot of data to memorize! When faced with this quantity of unrelated data, most students learn it by rote memorization.

**Table 1. Polar and Cartesian Representations of the Angular Part of d-Type Real Hydrogen-like Wave Functions**

| Orbital | Polar Representation | Cartesian Representation on a Unit Sphere ($r$ = 1) |
|---|---|---|
| $d_{xy}$ | $\sin^2\theta \sin 2\varphi$ | $2xy$ |
| $d_{x^2-y^2}$ | $\sin^2\theta \cos 2\varphi$ | $x^2 - y^2$ |
| $d_{xz}$ | $\cos\theta \sin\theta \cos\varphi$ | $xz$ |
| $d_{yz}$ | $\cos\theta \sin\theta \sin\varphi$ | $yz$ |
| $d_{z^2}$ | $3\cos^2\theta - 1$ | $2z^2 - (x^2 + y^2)$ |

## An Inclusive Principle

To achieve meaningful learning, as defined by Ausubel *(4),* an inclusive principle must be presented to the students. The students can then connect specific details to the inclusive principle, thereby creating a cognitive structure, rather than an incoherent collection of facts. The inclusive principle can be viewed as the scaffolding, on which individual bricks are carefully structured, rather than tossed into a pile. The product of meaningful learning is not just better memorization, but the ability to use specific facts in other contexts, by identifying commonalities and differences with other inclusive concepts.

Some textbooks (for example, *5–7*) give only a partially inclusive principle in their introduction to d orbitals. They argue that in the same way the labels of the p orbitals identify the *axis* on which the orbitals lies (*x, y,* or *z*), the labels of the d orbitals identify the *plane* in which the orbital lies (*xy, yz,* or *xz*). This principle is inclusive for three of the five orbitals, but still does not include $d_{x^2-y^2}$ and $d_{z^2}$, which have to be memorized separately, and does not offer insight as to which orbitals lie *on* the axes and which *in between*.

The most inclusive concept for labeling d orbitals can be found in advanced level textbooks (physical or quantum chemistry). It turns out that the labels are not arbitrary names given to the orbitals to distinguish them, but have an actual mathematical meaning. They are the angular part of the hydrogen-like wave function, expressed in Cartesian coordinates (Table 1).

In the quantum mechanical solution of the hydrogen atom, the spherical symmetry of the system lends itself to a simple solution in polar coordinates ($r$, $\theta$, and $\varphi$). The energy eigen functions can be written as the product of a radial part ($r$ dependent) and an angular part ($\theta$ and $\varphi$ dependent). The angular part can be transformed into Cartesian coordinates on a unit sphere ($r$ = 1) by the substitutions:

$$\sin\theta \cos\varphi \rightarrow x, \qquad \sin\theta \sin\varphi \rightarrow y, \qquad \cos\theta \rightarrow z$$

This means that if you draw a unit sphere centered on the origin and calculate the value of the Cartesian function at each point on the sphere, you would get the angular distribution of the wave function. By looking at the data presented in Table 1, it is clear that the labels of the d orbitals are derived from the Cartesian representation of the angular wave function.

There are two reasons why Cartesian coordinates are used to represent an angular function instead of the natural polar coordinates. The first is for the sake of brevity: "*xy*" is shorter than "$\sin^2\theta \sin 2\varphi$". The second, and more important to our case, is that it is easier to interpret the spatial orientation of the orbital from the Cartesian representation. For example, the angular function of $d_{xy}$ is:

$$\sin^2\theta \sin 2\varphi = 2(\sin\theta \cos\varphi)(\sin\theta \sin\varphi) = 2xy$$

When either *x* or *y* equal 0, the function equals 0, that is, there are two nodal planes at *yz* ($x = 0$) and *xz* ($y = 0$). The function has a maximum absolute value when $|x| = |y|$, that is, the maxima are pointing between the *x* and *y* axes. The sign of the lobes can also be deduced from the function—it is positive when *x* and *y* have the same sign and negative when their signs oppose, that is, the function is positive in the first and third quadrants on the *xy* plane, and negative in the second and fourth. We can compare this to $d_{x^2-y^2}$, which has the angular function:

$$\sin^2\theta \cos 2\varphi = (\sin\theta \cos\varphi)^2 - (\sin\theta \sin\varphi)^2 = x^2 - y^2$$

This orbital has a maximum absolute value on the $x$ and $y$ axes; its sign is positive on the $x$ axis and a negative on the $y$ axis; the nodal planes intersect the origin in between the axes, where $|x| = |y|$. Similar reasoning can be used to deduce the spatial orientation of $d_{yz}$ and $d_{xz}$ (this is left to the reader as an exercise). The only orbital that does not seem to fit in this scheme is $d_{z2}$. The $z^2$ term only produces the dumbbell lobe along the $z$ axis—but where is the doughnut? The answer is that this label is shorthand for the full angular function: $2z^2 - (x^2 + y^2)$. The term $x^2 + y^2$ is the formula of a circle centered at the origin, and is responsible for the round shape of the doughnut. The minus sign is responsible for the two conical nodal planes separating the dumbbell and the doughnut.

## Conclusion

It was shown that considering orbital labels as the angular part of the wavefunction can serve as an inclusive principle, which the students can use to construct the spatial shapes of the d orbitals from their labels. This scheme is not unique to d orbitals. It is inclusive of p and f orbitals labels as well. It gives the orientation and sign of $p_x$, $p_y$, and $p_z$, and can be used to interpret the complicated labels of the seven f orbitals.

## Literature Cited


1. Jones, L.; Atkins, P. *Chemistry: Molecules, Matter, and Change,* 4th ed.; W. H. Freeman: New York, 2000; pp 278–280.
2. McMurry, J.; Fay, R. C. *Chemistry,* 4th ed.; Prentice Hall: Upper Saddle River, NJ, 2004; pp 177–178.
3. Hill, J. W.; Petrucci, R. H. *General Chemistry: An Integrated Approach,* 3rd ed.; Prentice Hall: Upper Saddle River, NJ, 2002; pp 306–308.
4. Ausubel, D. P.; Novak, J. D.; Hanesian, H. *Educational Psychology—A Cognitive View,* 2nd ed.; Holt, Rinehart & Winston: New York, 1978; pp 163–203.
5. Zumdahl, S. S.; Zumdahl S. *Chemistry,* 6th ed.; Houghton Mifflin: Boston, MA, 2003; pp 309–311.
6. Kotz, J. C.; Treichel, P. *Chemistry and Chemical Reactivity,* 4th ed.; Saunders College Publishing: Fort Worth, TX, 1999; pp 320–322.
7. Brown, T. L.; LeMay, H. E.; Bursten, B. E. *Chemistry: The Central Science,* 8th ed.; Prentice Hall: Upper Saddle River, NJ, 2000; pp 205–206.