

**Figure 2.**

By the fact stated in the previous paragraph, each of these integrals is zero and hence the integral over the big rectangular region is also zero. Once again applying the same fact gives us that one of the sides of the big rectangle must have integer length.

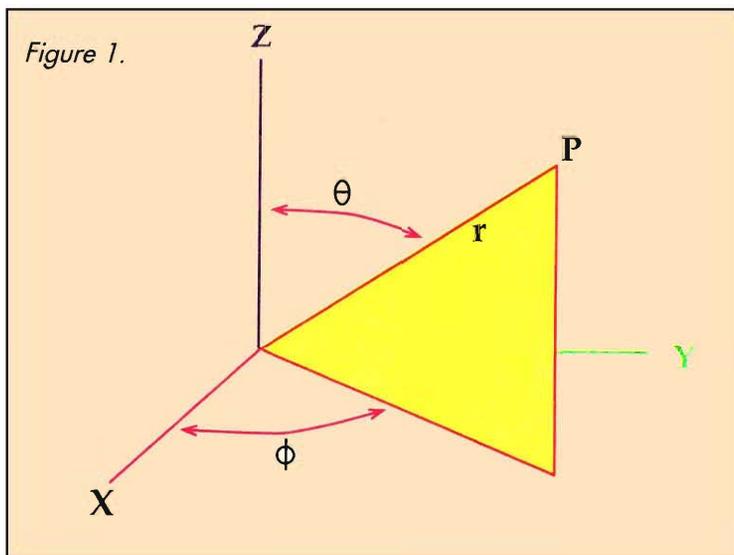
There will be more discussion on this problem in the Classroom section in one of the forthcoming issues of *Resonance*.

Question posed by:  
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### What are the Shapes of *f* - Orbitals?

The electron has a particle and a wave nature. Due to its wave nature, the electron in a stationary state of the Hydrogen atom is characterized by its wave function  $\psi_{nlm}(r, \theta, \phi)$ . Here  $(r, \theta, \phi)$  are the spherical polar coordinates, used to specify the position of the electron in space (see the figure) and  $n, l, m$  are the principal, azimuthal and magnetic quantum numbers.

The wave functions for a single electron are usually referred to as atomic orbitals and have the form  $\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$ . (These are discussed in detail in the book by Atkins). Here  $R_{nl}(r)$ , the radial part of the wave-function determines the variation of the wave function with the distance  $r$ .  $Y_{lm}(\theta, \phi)$  are the spherical harmonics and determine the shapes (direction dependence) of the wave



functions. These are of considerable interest, as they arise in any problem involving the motion of an electron in an arbitrary spherically symmetric potential. Therefore they occur as angular parts of the one-electron wave functions (atomic orbitals) in many electrons atoms too.

A knowledge of the shapes of the atomic orbitals is of importance in understanding their role in the formation of chemical bonds. The shapes of the different atomic orbitals are usually shown using polar plots. For example, the angular part of the  $d_{z^2}$  orbital is the function  $Y_{20}(\theta, \phi) = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$ . The polar plot for this is constructed as follows: Consider any line starting from the origin. Its direction in space is specified by its values for  $(\theta, \phi)$ . In each such direction, one puts a point whose distance from the origin is equal to  $|Y_{20}(\theta, \phi)|$ . The surface formed by all these points is the polar plot of the function  $Y_{20}(\theta, \phi)$ . Usually, the information on the sign (whether  $Y_{20}(\theta, \phi)$  is positive or negative) is then added on by putting positive or negative signs on appropriate lobes. Equivalently, the sign information is given using different colours, eg: blue colour to indicate directions in which the function is positive and red for negative.

### Note to the Readers

We have frequently been asked why *Resonance* does not carry a 'Correspondence' section. We have occasionally even been accused of being insensitive to reader's views. We would like to assure you that the *Resonance* team takes the feedback we receive, formally and informally, quite seriously. We try to act upon all constructive suggestions. A case in point is a letter from one of our readers containing a simple, one-line request: Name the seven *f*-orbitals. In this issue, K L Sebastian provides a detailed answer. As a bonus, a poster containing the figures of all atomic orbitals of chemical interest is included. Although there may be some inevitable delay, we hope to respond to readers' suggestions in a similar positive manner.

Many of the spherical harmonics are complex functions (they contain  $i = \sqrt{-1}$ !),  $Y_{11}(\theta, \phi) = -\sqrt{3/8\pi} \sin\theta e^{i\phi}$  and  $Y_{1-1}(\theta, \phi) = \sqrt{3/8\pi} \sin\theta e^{-i\phi}$ . It is rather difficult to visualize them. In such cases, one combines the functions linearly to obtain new functions which are real. Typical linear combinations are  $1/\sqrt{2}(-Y_{11}(\theta, \phi) + Y_{1-1}(\theta, \phi))$ , which leads to the  $p_x$  atomic orbital and  $i/\sqrt{2}(Y_{11}(\theta, \phi) - Y_{1-1}(\theta, \phi))$  which corresponds to  $p_y$ . Such combinations are quite acceptable as the orbitals which are combined have the same energy. However, the new orbitals,  $p_x$  and  $p_y$  do not have a unique value for the magnetic quantum number  $m$ ! Similar combinations are done with  $d$  and  $f$  orbitals too. Thus one obtains the familiar set of five  $d$ -orbitals  $d_{z^2}$ ,  $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ .

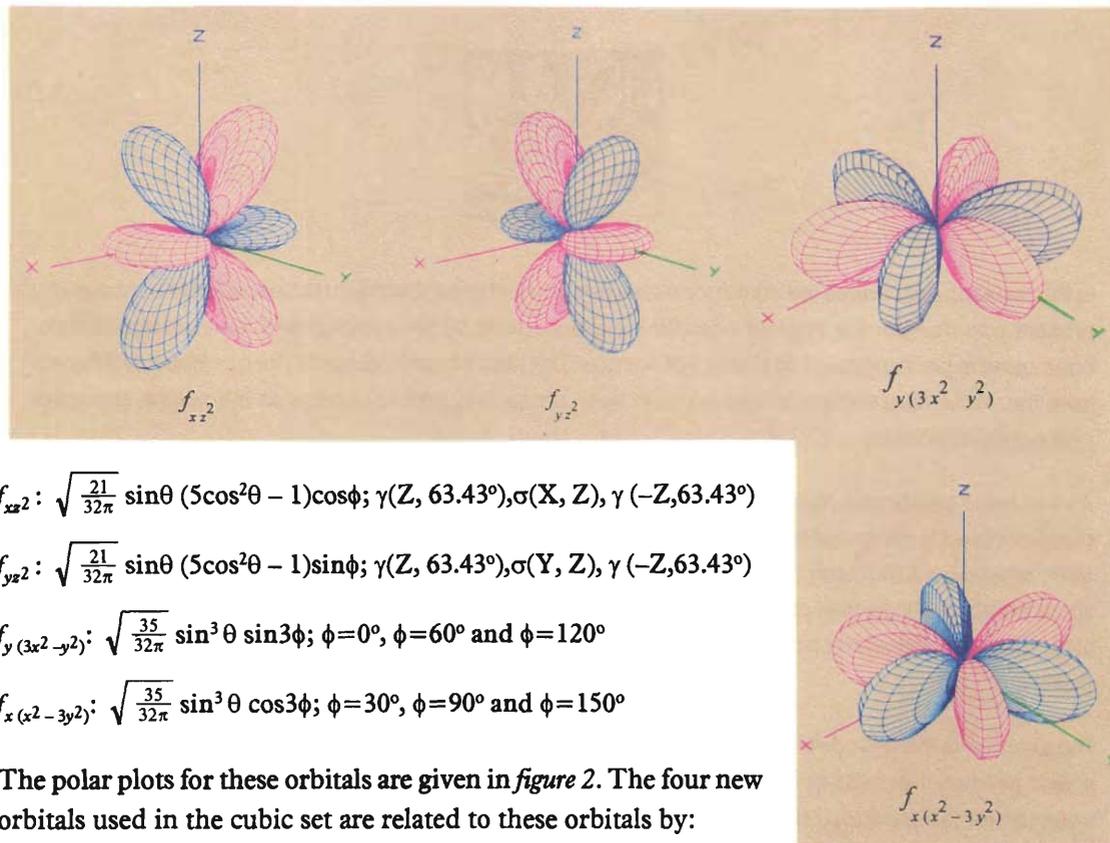
There are two alternative ways in which  $f$ -orbitals are represented: the general set and the cubic set.

Coming to Deepali's question, the seven  $f$ -orbitals that are obtained as combinations of the spherical harmonics are (see the paper by H G Friedmann et al in Suggested Reading):

$$f_{z^3}, f_{z(x^2-y^2)}, f_{xyz}, f_{xz^2}, f_{yz^2}, f_{x(x^2-3y^2)} \text{ and } f_{y(3x^2-y^2)}$$

These are referred to as the general set. The shapes of the last four orbitals are somewhat more difficult to visualize. Therefore, one combines them linearly to obtain four new orbitals. The set consisting of the first three of the general set and the four new orbitals are referred to as the cubic set. These are not only easier to visualize, but one can also easily predict how their energy levels will be split in a ligand field having cubic symmetry. In the poster included in this issue, plots for all the atomic orbitals that are of common interest are given. For the  $f$ -orbitals, the cubic set is shown. For the sake of completeness, the angular parts for the last four orbitals of the general set are given below. The functions are followed by the description of the nodal surfaces (see the poster for the meanings of  $\gamma$  and  $\sigma$ ;  $\phi = 30^\circ$  denotes a plane parallel to the XZ plane, having this value for  $\phi$ ).





$$f_{xz^2}: \sqrt{\frac{21}{32\pi}} \sin\theta (5\cos^2\theta - 1)\cos\phi; \gamma(Z, 63.43^\circ), \sigma(X, Z), \gamma(-Z, 63.43^\circ)$$

$$f_{yz^2}: \sqrt{\frac{21}{32\pi}} \sin\theta (5\cos^2\theta - 1)\sin\phi; \gamma(Z, 63.43^\circ), \sigma(Y, Z), \gamma(-Z, 63.43^\circ)$$

$$f_{y(3x^2 - y^2)}: \sqrt{\frac{35}{32\pi}} \sin^3\theta \sin 3\phi; \phi = 0^\circ, \phi = 60^\circ \text{ and } \phi = 120^\circ$$

$$f_{x(x^2 - 3y^2)}: \sqrt{\frac{35}{32\pi}} \sin^3\theta \cos 3\phi; \phi = 30^\circ, \phi = 90^\circ \text{ and } \phi = 150^\circ$$

The polar plots for these orbitals are given in figure 2. The four new orbitals used in the cubic set are related to these orbitals by:

$$f_{x^3} = 1/4 (-\sqrt{6} f_{xz^2} + \sqrt{10} f_{x(x^2 - 3y^2)})$$

$$f_{y^3} = -1/4 (\sqrt{6} f_{yz^2} + \sqrt{10} f_{y(3x^2 - y^2)})$$

$$f_{x(y^2 - z^2)} = -1/4 (\sqrt{10} f_{xz^2} + \sqrt{6} f_{x(x^2 - 3y^2)})$$

$$f_{y(z^2 - x^2)} = 1/4 (\sqrt{10} f_{yz^2} - \sqrt{6} f_{y(3x^2 - y^2)})$$

Figure 2.

The paper by Friedmann *et al* of Suggested Reading use  $f_{y(x^2 - z^2)}$  instead of the function  $f_{y(z^2 - x^2)}$  that we have used. The two differ only in their signs.

### Suggested Reading

- ◆ P W Atkins, *Physical Chemistry* (3rd Edn). ELBS/Oxford University Press. Oxford. p.345, 1986.
- ◆ H G Friedmann Jr. G R Choppin and D G Feurebacher. *Journal of Chemical Education*. 41.354, 1964.

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