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Textbook Errors, 91

The Graphical Representation
of Hydrogen-Like Wave Functions

The hydrogen-like wave functions depend on three coordinates. Therefore, the information which can be conveyed about them by three-dimensional figures (and, even more so, by two-dimensional diagrams) is of necessity incomplete. There exist, however, simple representations which have a well-defined physical meaning. One possibility (1) is to draw polar graphs of the values of the angular part of the wave function or its square. Three-dimensional angular distribution functions have also been constructed (2). By this method, the radial distribution obviously cannot be shown; the distance from the center of the figure measures the *value* of the wave function in a particular direction relative to its value in other directions, and is in no way connected with the distance from the center of the atom.

Another possibility is the construction of contour surfaces of constant value of the wave function. A variation of this method is the construction of a boundary surface, which is that contour which includes within its surface some definite percentage of the total electronic charge (e.g., 90%) (3). In two dimensions, contour *lines* can be drawn which are the cross-sections of the *surfaces* by an appropriate plane passing through the center of the atom.

Although the above definitions seem clear, and although the difference between the two methods of representation has been stressed in this Column some 7 years ago (4), modern textbooks[1] continue to present ill-defined pictures and to make misleading and even incorrect statements.

Firstly, the concept of boundary surfaces is often insufficiently explained, so that the student is apt to conclude that this surface indeed represents a sharp "boundary" where the probability of finding the electron suddenly drops to a very low value.
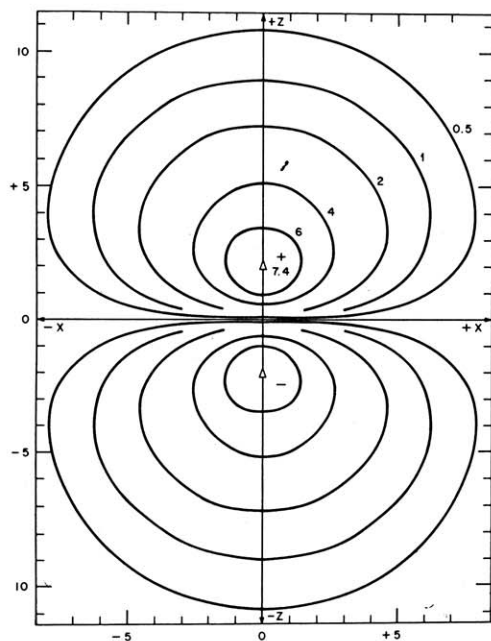
Figure 1. Contour lines of the normalized wave function

$$\psi_{2pz} = (1/4\sqrt{2\pi})\rho e^{-\rho/2}\cos\theta = (1/4\sqrt{2\pi})ze^{-\rho/2}$$

The numbers in the figure refer to $\psi \times 10^2$. The points where ψ is at its maximum are indicated by a triangle. The numbers on the coordinate axes are in units of ρ, where ρ is defined (7) as the distance from the center of the atom measured in Bohr units and multiplied by $2/n$, n being the principal quantum number. In the xz plane presented, $y = 0$ and $x^2 + z^2 = \rho^2$. Three-dimensional contour surfaces are obtained by rotation round the z-axis.

Figure 2. Contour lines of the normalized wave function

$$\psi_{3pz} = (\sqrt{2}/36\sqrt{\pi})(4-\rho)\rho e^{-\rho/2}\cos\theta = (\sqrt{2}/36\sqrt{\pi})(4-\rho)ze^{-\rho/2}$$

The meaning of the numbers is explained in Figure 1. Three-dimensional contour surfaces are again obtained by rotation round the z-axis.
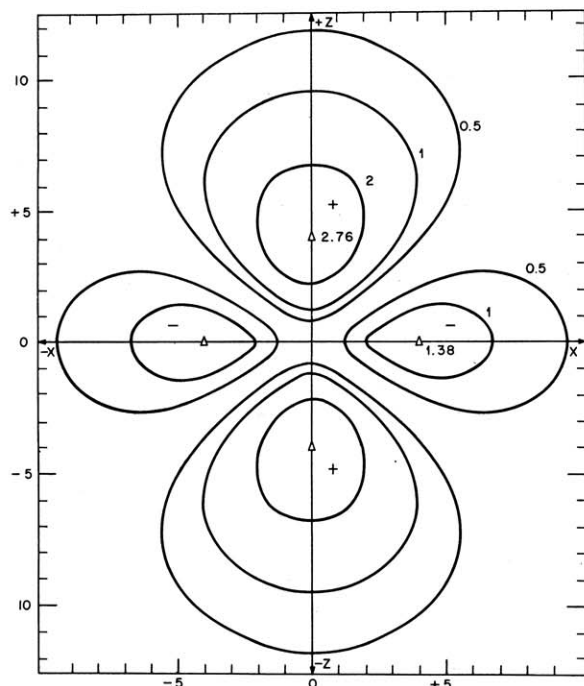

Figure 3. Contour lines of the normalized wave function

$$\psi_{3dz2} = (1/36\sqrt{6\pi})(3\cos^2\theta - 1)\rho^2 e^{-\rho/2} = (1/36\sqrt{6\pi})(3z^2 - \rho^2)e^{-\rho/2}$$

The meaning of the numbers is explained in Figure 1. Three-dimensional contour surfaces are again obtained by rotation round the z-axis.

Figure 4. Contour lines of the normalized wave function

$$\psi_{3dzz} = (\sqrt{2}/36\sqrt{\pi})\rho^2 e^{-\rho/2}\sin\theta\cos\theta\cos\phi = (\sqrt{2}/36\sqrt{\pi})zx e^{-\rho/2}$$

The meaning of the numbers is explained in Figure 1. The three-dimensional contour surfaces each consist of 4 lobes which do not have a circular cross-section (11).

Secondly, some textbooks reproduce polar graphs without explaining their meaning at all, whereas in a number of others, polar graphs or photogra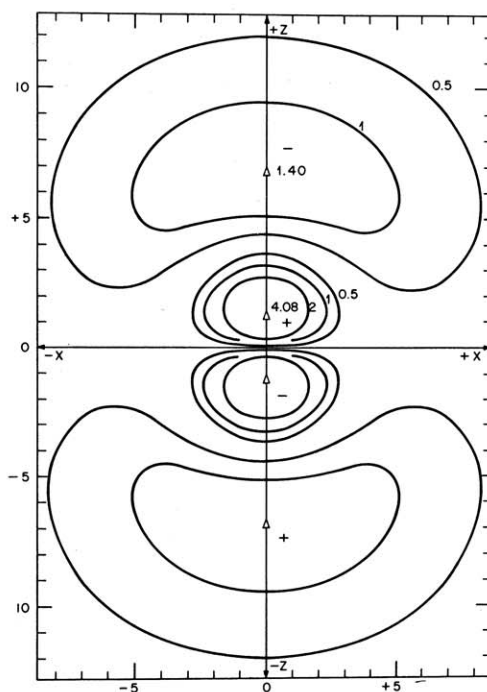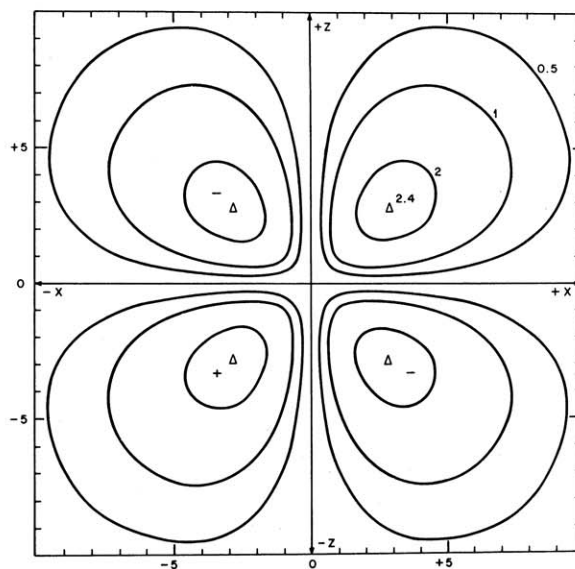phs or drawings of three-dimensional models of *angular wave functions* or their squares are misrepresented as *boundary surfaces*. Furthermore, it is often implied that hydrogen-like wave functions cannot be represented in an exact way and "orbital shapes" or "approximate representations" of boundary surfaces or of "electron clouds" are presented which usually resemble polar graphs with blurred outlines rather than (5) actual electron probability densities.

Now, polar graphs appear in many texts (1), and contour lines, though presented in only very few text-
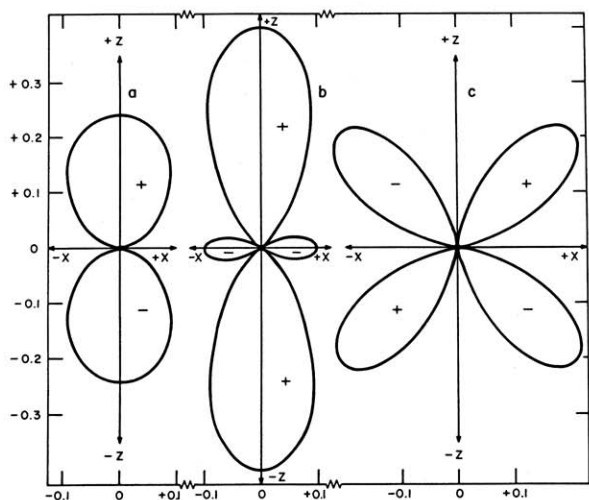
Figure 5. Squares of normalized angular distribution functions: (a) p_z; (b) d_{z^2}; (c) d_{xz}.

books, and only for p-orbitals (*6–8*) can be found in the literature (*9–10*). Nevertheless, in view of the existing confusion, a juxtaposition of detailed quantitative diagrams representing the two methods seems appropriate. In Figures 1–4 we show some contour lines in the xz plane for the $2p_z$, $3p_z$, $3d_{z^2}$, and $3d_{xz}$ orbitals, whereas Figures 5a to 5c show the squares of the p_z, d_{z^2}, and d_{xz} angular distribution functions. Definite *boundary surfaces* can be easily calculated only for the s-orbitals which are spherically symmetric in any representation. For the others, the calculation is much more complicated, and only for the $2p$-orbital has a graphical integration been carried out (*9*). They have, however, been qualitatively represented in pictorial form (*11*).

Comparison of the two sets of diagrams shows that the two methods of representation result in figures which exhibit some similarity. However, there are also significant differences. For instance, in the d_{z^2} orbital, the square of the function has a maximum in the xy plane which is one quarter of that along the z axis. For the angular distribution function this results in a small ring in the xy plane (appearing as a small lobe in our diagram), close to the origin of the coordinates. On the other hand, the contour lines of the $3d_{z^2}$ orbital show that although that part of the function which has its maximum in the xy plane is much less dense than the main part, it nevertheless for small values of ψ reaches almost as far out into space. For both parts the maxi-

mum of the electron density lies at the *same* distance from the center of the atom (*9*).

For an elementary study of quantum chemical phenomena the angular distribution functions have some advantages over the contour lines; in particular, they help the student to visualize the s, p, and d character of an orbital in a way which is independent of the principal quantum number. On the other hand, it must be kept in mind that it is, after all, electron densities and not polar graphs which, for instance, overlap in molecule formation, or which repel each other and cause ligand field splitting.

The serious student who tries to understand what he is being taught will wonder whether contour lines and electron densities should indeed, by some strange coincidence, look exactly like the angular distribution functions which he may have encountered elsewhere. As he progresses to more advanced studies he will realize that both kinds of diagrams are only a temporary aid in visualizing problems of quantum chemistry. Nevertheless, he may retain a confused picture, caused by the incorrect interpretation of diagrams presented to him at an early stage.

Literature Cited

(1) See, e.g., Pauling, L., and Wilson, E. B., "Introduction to Quantum Mechanics," McGraw Hill Book Company, New York, **1935**, pp. 148, 149.
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(5) See, e.g., Moore, W. J., "Physical Chemistry," (3rd ed.), Prentice Hall, Englewood Cliffs, N. J., **1962**, p. 496.
(6) Murrell, J. N., Kettle, S. F. A., and Tedder, J. M., "Valence Theory," John Wiley & Sons, Inc., New York, **1965**, p. 25.
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(11) Reference (8), p. 68.