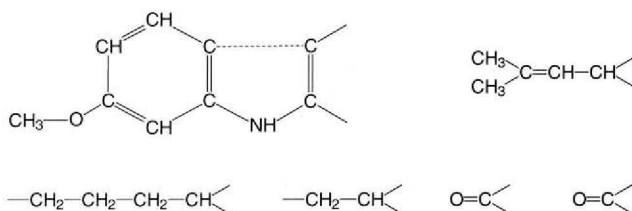nonoverlapping substructures (macro atoms, in terms of MOLGEN) $F_1, ..., F_6$.

Using these substructures, the molecular formula reduces to $F_1F_2F_3F_4F_5F_6N_2$. MOLGEN obtains (after several steps not described in detail here) 2,337 structural formulas for that reduced molecular formula, and after expansion it constructs 8,916 isomers. We used the following restrictions: no triple bond and ring sizes between 5 and 6. Only 201 candidates remained from which an expert easily obtained the correct solution.
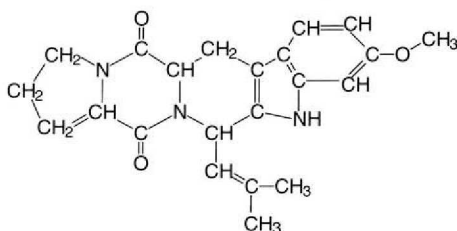
MOLGEN runs under DOS on a PC. Versions for Windows, OS/2, Macintosh and various workstations are in preparation. There exists a limited version for education and a full version for science and research. For more information contact the authors. Telephone (0921) 55-3388, Fax (0921) 55-3385, E-mail: kerber@btm2x2.mat.uni-bayreuth.de

# Three-Dimensional Graphical Visualization of One-Electron Atomic Orbitals

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Discussions of the one-electron atomic orbitals $\psi_{nlm}(r, \theta, \phi)$ in physical chemistry courses typically cover the coordinate dependence of the radial functions and the spherical harmonics separately. These ideas are then combined to obtain the shapes and the nodal patterns of atomic orbitals, which are illustrated by schematic sketches of the "shapes" of the orbitals. Contour diagrams are sometimes used (33) in order to clearly show the positions of the radial and angular nodes. On the contour plots, radial nodes appear as circles, and the angular nodes appear as straight lines. Some familiarity with the concept of contour mapping and imagination are then necessary to visualize the radial nodes as spheres and the angular nodes as planes in three-dimensional space. All this is necessary before students can visualize the spatial distribution of electron densities around the nucleus.

The shapes and the nodal structures of atomic orbitals can be studied and taught very effectively if the students (and the teacher) generated and viewed three-dimensional graphical representations of atomic orbitals. It is now entirely practical to carry out the computations and the rather sophisticated plotting required for this exercise on relatively inexpensive personal computers based on the 80486 (or 80386 with a math coprocessor) microprocessor or RISC workstations. In this article, we discuss how three-dimensional graphical representations of hydrogenic atomic orbitals may be generated (and viewed from any perspective) using the software package Mathematica.

## Generating Isosurfaces

The basis of this exercise is a program we have developed, which serves as input to Mathematica. Our program finds and plots the points in three-dimensional Cartesian space where $|\psi_{nlm}|$ has a constant value, that is, isosurfaces. Both the positive and negative regions of the functions are plotted by using the absolute value of the wave function for selecting the points. The sign of the wave function in the different regions is represented by different colors (or different gray scaling).

We illustrate our method using the case of the $2p_z$ orbital, which for the hydrogen atom (atomic number $Z = 1$), is

$$\psi_{2p_z}(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi}} r e^{(-r/2)} \cos \theta \qquad (1)$$

where the atomic units of length ($a_0 = 1$) are used. The isosurface to be plotted is the set of points $\{r, \theta, \phi\}$ or $\{x, y, z\}$ for which the absolute value of the function in eq 1 is a certain positive constant, $\kappa$. In other words, we seek all points that satisfy the equation

$$\kappa - |r e^{(-r/2)} \cos \theta| = 0 \qquad (2)$$

where the normalization constant has been absorbed into $\kappa$.

A graphical representation of the resulting surface is generated as a parametric plot of one of the variables expressed as a function of the other two. Due to the nonlinear dependence of the wave function on $r$, it is easier to express $\cos \theta$ in terms of the radial distance $r$ as

$$\cos \theta = \frac{\kappa}{r} e^{(r/2)} \qquad (3)$$
$$\kappa < 2e^{-1}; r \in (r_1, r_2)$$

where $r_1$ and $r_2$ are the roots of eq 2 when $\theta = 0$. This is schematically shown in Figure 11.

The following relationships for the set $\{x, y, z\}$ are then obtained in terms of $\{r, \phi\}$:

$$x = r \sin \theta \cos \phi = r \sqrt{1 - \left(\frac{\kappa}{r} e^{(r/2)}\right)^2} \cos\phi$$
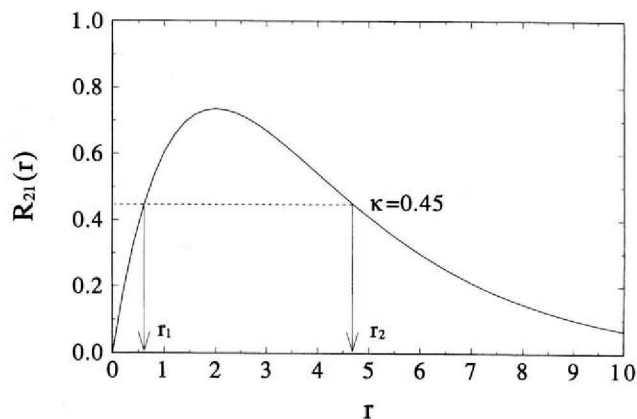


Figure 11. Schematic representation of the roots $r_1$, $r_2$ for the $2p_z$ orbital ($\theta = 0$) for an arbitrary value of $\kappa$. The normalization constants were dropped from the radial function.

**Table 2. Summary of the Equations, Parameters, and Limits Used To Generate Various Atomic Orbital Isosurfaces**

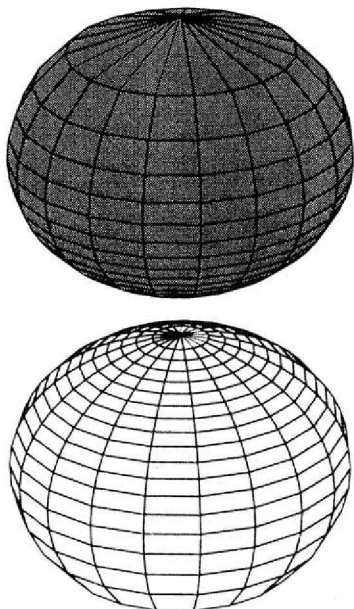| Orbital | $\Psi_{nlm}(r, \theta, \phi)$ | Positive part of $\Psi_{nlm}$ | Negative part of $\Psi_{nlm}$ | Remarks |
|---|---|---|---|---|
| 2s | $(2-r)e^{(-r/2)}$ | $r_1 = $ constant | $r_2, r_3 = $ constants | $r_1$ is the root of $\Psi_{nlm} = \kappa$ <br> $r_2, r_3$ are roots of $\Psi_{nlm} = -\kappa$ <br> $\kappa < 2e^{-2}$ |
| $2p_z$ | $re^{(-r/2)}\cos\theta$ | $\cos\theta = (\kappa/r)e^{r/2}$ <br> $r \in (r_1, r_2)$ | $\cos\theta = (-\kappa/r)e^{r/2}$ <br> $r \in (r_1, r_2)$ | $r_1, r_2$ are roots of $re^{-r/2} = \kappa$ <br> $\kappa < 2e^{-1}$ |
| 3s | $(27-18r+2r^2)e^{(-r/3)}$ | $r_1, r_4, r_5 = $ constants | $r_2, r_3 = $ constants | $r_1, r_4, r_5$ are roots of $\Psi_{nlm} = \kappa$ <br> $r_2, r_3$ are roots of $\Psi_{nlm} = -\kappa$ <br> $\kappa < 18(2+\sqrt{7})e^{-(5+\sqrt{7})/2}$ |
| $3p_z$ | $r(6-r)e^{(-r/3)}\cos\theta$ | $\cos\theta = \kappa e^{r/3}/[r(6-r)]$ <br> $r \in (r_1, r_2)$ <br> $\cos\theta = -\kappa e^{r/3}/[r(6-r)]$ <br> $r \in (r_3, r_4)$ | $\cos\theta = -\kappa e^{r/3}/[r(6-r)]$ <br> $r \in (r_1, r_2)$ <br> $\cos\theta = \kappa e^{r/3}/[r(6-r)]$ <br> $r \in (r_3, r_4)$ | $r_1, r_2$ are roots of $r(6-r)e^{-r/3} = \kappa$ <br> $r_3, r_4$ are roots of $r(6-r)e^{-r/3} = -\kappa$ <br> $\kappa < 9\sqrt{2}(2+\sqrt{2})e^{-(2+\sqrt{2})}$ |
| $3d_z^2$ | $r^2e^{(-r/3)}(3\cos^2\theta - 1)$ | $\cos^2\theta = 1/3(1 + \kappa e^{r/3}/r^2)$ <br> $r \in (r_1, r_2)$ | $\cos^2\theta = 1/3(1 + \kappa e^{r/3}/r^2)$ <br> $r \in (r_3, r_4)$ | $r_1, r_2$ are roots of $2r^2e^{-r/3} = \kappa$ <br> $r_3, r_4$ are roots of $r^2e^{-r/3} = \kappa$ <br> $\kappa < 36e^{-2}$ |
| $3d_{x^2-y^2}$ | $r^2e^{(-r/3)}(\sin^2\theta\cos 2\phi)$ | $\phi = (y/2)\cos^{-1}(\kappa e^{r/3}/r^2)$ <br> $\sin^2\theta = \kappa e^{r/3}/(r^2\cos 2\phi)$ <br> $r \in (r_1, r_2)$ | $\phi = (y/2)\cos^{-1}(-\kappa e^{r/3}/r^2)$ <br> $\sin^2\theta = -\kappa e^{r/3}/(r^2\cos 2\phi)$ <br> $r \in (r_1, r_2)$ | $y \in (-1, 1)$ <br> $r_1, r_2$ are roots of $r^2e^{-r/3} = \kappa$ <br> $\kappa < 36e^{-2}$ |



Figure 12. An isosurface for the $2p_z$ orbital, generated according to the constraints described in text and summarized in Table 2. The darker shade represents the positive part of the wavefunction and the lighter shade, the negative part.

$$y = r\sin\theta\sin\phi = r\sqrt{1 - \left(\frac{\kappa}{r}e^{(r/2)}\right)^2}\sin\phi$$

$$z = r\cos\theta = \kappa e^{(r/2)} \tag{4}$$

Limiting the value of $\kappa$ and the range of $r$ as in eq 3 ensures that the quantities in the square roots in eqs 4 are nonnegative. The set of points $\{x, y, z\}$ is used to construct the positive part of the $2p_z$ orbital, whereas the set $\{x, y, -z\}$ is used for the negative part. A typical isosurface generated using this approach is shown in Figure 12. Similar strategies are used in the generation of the other orbitals. Table 2 summarizes the relationships between the angles and $r$ for a few of the atomic orbitals, and the limits imposed on $\kappa$.

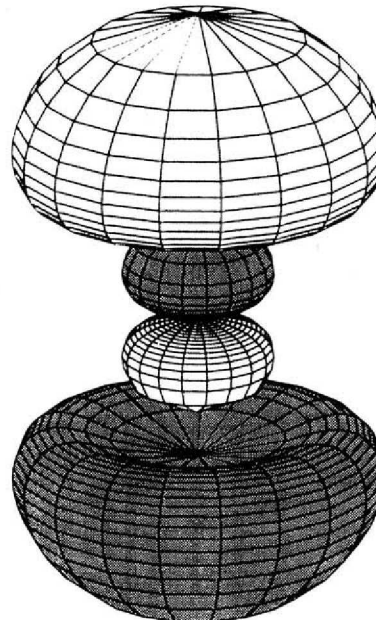Some considerations regarding the extrema of the radial functions form the basis for the limits imposed on the



Figure 13. An isosurface for the $3p_z$ orbital. The shading conventions are the same as in Figure 12.

value of $\kappa$. Figure 11 shows that no points will be selected if $\kappa$ is too large. In the case of orbitals with radial nodes (2s, 3p, etc.), the value of $\kappa$ must be selected so that points on either side of the radial node are selected. In other words, $\kappa$ must not exceed the smallest maximum in $|R_{nl}(r)|$. The default value of $\kappa$ is set at a certain percentage of the smallest maximum in $|R_{nl}(r)|$. Such a "default" isosurface of the $3p_z$ orbital is shown in Figure 13.

## Discussion

The program written for this work has been successfully used on Sun SPARCStations and on IBM RISC/6000 workstations. We will be happy to make it available to interested colleagues by e-mail. The principal author can be reached at ramu@chem.LaTech.edu.

## Acknowledgment

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