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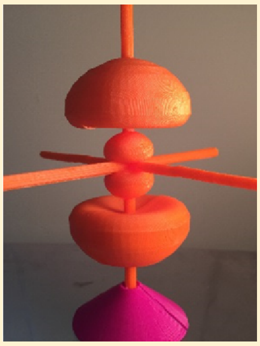
Do-It-Yourself: 3D Models of Hydrogenic Orbitals through 3D Printing

Kaitlyn M. Griffith, Riccardo de Cataldo, and Keir H. Fogarty*

Department of Chemistry, High Point University, One University Parkway, High Point, North Carolina 27268, United States

Supporting Information

ABSTRACT: Introductory chemistry students often have difficulty visualizing the 3-dimensional shapes of the hydrogenic electron orbitals without the aid of physical 3D models. Unfortunately, commercially available models can be quite expensive. 3D printing offers a solution for producing models of hydrogenic orbitals. 3D printing technology is widely available, and the cost of 3D printing "inks" is relatively low. Creation of models requires graphing electron orbital probability distributions in spherical coordinates and exporting as stereolithography (.stl) files (a common format for 3D printing). There is both freeware (CalcPlot3D), and license-requiring (Matlab, Mathematica, Maple) software capable of plotting orbital equations and exporting in the required format. The process of creating the orbitals is relatively simple, and the 3D printing methodology is cost-effective.



KEYWORDS: *First-Year Undergraduate/General, Upper-Division Undergraduate, Physical Chemistry, Inorganic Chemistry, Hands-On Learning/Manipulatives, Multimedia-Based Learning, Atomic Properties/Structure, Quantum Chemistry*

The hydrogenic orbitals are a foundational topic introduced in general chemistry and repeated throughout the chemistry curriculum.[1−9] Students are required to familiarize themselves with orbital size, shape, and orientation in relation to quantum theory. To aid with this, different orbital visualization methods have been developed throughout the years.[10−24] As computers have become more generally accessible, virtual simulations of either 3-dimensional orbital models,[10,11,13,14] or 4-dimensional models (electron density dot plots as a function of three positional variables)[16−18] have become a standard pedagogical tool in the undergraduate classroom. These simulations are advantageous because students are able to manipulate orbital representations in a 3-dimensional plot, which aids both visualization of orbital orientation and shape, and how the viewer's perspective changes as the orbital is rotated in space.

In addition to computer-simulated models of hydrogenic orbitals, a number of physical models of orbitals have been developed, both commercial and "homemade".[19−24] Physical models of hydrogenic orbitals are most commonly produced using an isosurface orbital model. In the isosurface model, a surface represents a boundary condition whose volume contains a certain fixed percentage of the total electron density of the orbital.[25] The isosurface model has been criticized, as it gives a false impression of an abrupt end to the electron cloud, and therefore does not accurately portray the probability distribution of electron density.[16,17,26] Despite this limitation, the defined surfaces of isosurface representations are the most practical for developing physical, hands-on models of hydrogenic orbitals that depict orbital size, shape, and orientation. Commercially available models are generally artistically rendered based on a qualitative interpretation of the isosurface model.[19,21] Homemade physical models have used such things as balloons and Styrofoam to model the space-filling aspect of hydrogenic orbital isosurfaces.[20,23]

Both the homemade and commercial models provide students with physically manipulable objects that qualitatively represent the features of orbitals. These physical models of hydrogenic orbitals are indirect representations, as they have been constructed as aesthetic mimics of orbital shapes, rather than directly from the mathematics of quantum mechanics. This aspect of physical models puts them at a relative disadvantage to computer simulations, as their shapes lack subtle details of hydrogenic orbitals which simulations accurately portray.

In recent years, 3D printing technology has been used to develop a variety of physically accurate models, such as molecular orbitals,[27] crystallographic models,[28−30] molecular models,[31−33] and potential energy surfaces.[34−36] These applications demonstrate the power of 3D printing to utilize mathematically accurate virtual models as "molds" for physical models. Thus, 3D printing is an ideal technique for creating physical models of hydrogenic orbitals which accurately reflect the mathematics of quantum mechanics. We have developed a method of producing physical, 3D hydrogenic orbital models, with an emphasis on method accessibility and the use of freely available software. The mathematics are first visualized using a free online applet, CalcPlot3D.[37,38] This freeware is capable of

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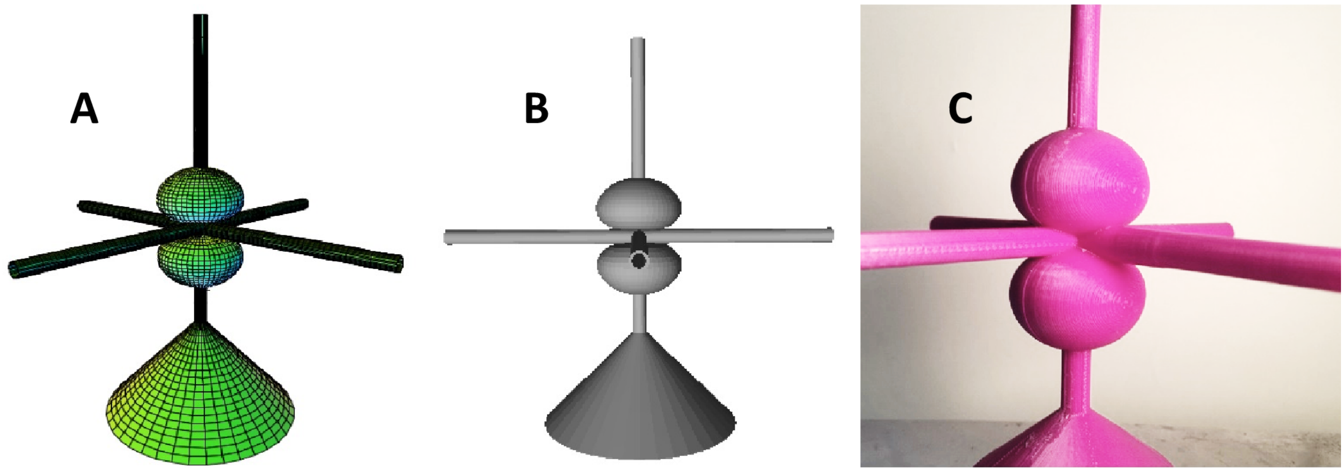

Figure 1. Process of creating a 3D printed model for a $2p_y$ orbital. Panel A represents the orbital model as prepared in CalcPlot3D using the appropriate quantum mechanical equations, and adding three cylinders and a cone for axes and structural support. Panel B represents the .stl file, as seen in the free online STL viewer, which is used to check .stl file output from CalcPlot3D. Panel C is the physical 3D printed model of the $2p_y$ orbital.

saving the simulated orbital as a stereolithography (.stl) file, which is compatible with 3D printing technology. Once the .stl file is obtained, it is relatively simple to print the model using a 3D printer. While this paper focuses on the use of CalcPlot3D freeware for the initial mathematical modeling of the hydrogenic orbitals, a variety of license-requiring mathematics visualization software (e.g., Mathematica, MatLab, and Maple) are all capable of exporting files in 3D printing format. In addition, minimal structural modifications are needed to produce free-standing, mathematically accurate, 3D printed models of the hydrogenic orbitals. The equations used to generate the orbitals were taken directly from chemistry textbooks[1,3,5] and online pedagogical resources.[39,40] It is proposed that the relative simplicity of generating the 3D printed models renders the process accessible to potential hands-on undergraduate student projects in upper-level chemistry courses, with the added benefit of generating models for use in introductory courses.

■ AN OVERVIEW OF 3D PRINTING OF HYDROGENIC ORBITALS

The process of creating a 3D printed orbital model requires three primary steps (Figure 1): (1) creation of the orbital and support structures in CalcPlot3D, and exporting the visualization as a .stl file (Panel A), (2) performing quality control procedures on the .stl file and converting it to the proper format utilized by the 3D printer (Panel B), and (3) 3D printing of the model, followed by gluing pieces of the model that are printed separately (if any) (Panel C) . A $2p_y$ orbital is used in this manuscript to illustrate the process of preparing 3D printed orbital models. To prepare other 3D-printed orbital models, one simply needs to substitute the relevant functions into the procedure outlined below, and in more detail in the Supporting Information.

■ GENERATION OF VIRTUAL ORBITAL MODELS IN CALCPLOT3D

Creating the Virtual Orbital Using the Implicit Surface Tool

Figure 1, panel A depicts a $2p_y$ orbital prepared in CalcPlot3D for export as the .stl file used for 3D printing. The graphic consists of a $2p_y$ three-dimensional isosurface plot, along with structural elements (three cylinders and a cone) that double as axes and structural support for the model. The $2p_y$ isosurface plot is based on the function for electron density (also known as the probability function), which is simply the square of the wave function[1]

$$\psi(r, \theta, \varphi)^2_{2p_y} = R(r)^2 Y(\theta, \varphi)^2 \qquad (1)$$

where $R(r)$ is the radial function, and $Y(\theta,\varphi)$ is the angular function. The radial function describes electron density in relation to distance from the atomic nucleus, and for a $2p_y$ orbital

$$R(r) = \frac{1}{\sqrt{3}}\left[\frac{Z}{2a_0}\right]^{3/2} \rho e^{-\rho/2} \qquad (2)$$

where Z is the effective nuclear charge, a_o is the Bohr radius (a_o = 52.9 pm), ρ varies with distance, r, from the nucleus ($\rho = Zr/a_o$). The angular function describes the shape and orientation of orbitals. For a $2p_y$ orbital

$$Y(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\varphi \qquad (3)$$

where θ is the angle from the z-axis, varying from 0 to π, and φ is the angle from the x axis, varying from 0 to 2π. An isosurface orbital model is generated by setting eq 1 to a constant. In CalcPlot3D, this function can be plotted using the *implicit surface* functionality. To simplify the generation of the model, all constants appearing in the radial and angular functions can be absorbed into the constant of the probability function, such that, for a $2p_y$ orbital

$$\text{constant} = (\rho e^{-\rho/2})^2(\sin\theta\sin\varphi)^2 \qquad (4)$$

In CalcPlot3D, the constant can be manipulated using the *parameters* tool, which allows one to adjust the value of the constant through the use of a sliding bar. Other parameters can be added to eq 4, such that the resulting isosurface model can be adjusted to the appropriate scale.

Generating Support Structures for Physical Model Stability

It is effectively impossible to produce a free-standing 3D printed $2p_y$ orbital, as the orbital's rounded shape and angular node would prevent the preparation of a cohesive, stable physical object. For this reason, structural supports (three cylinders and a cone) were generated in CalcPlot3D which serve three purposes: (1) they hold the orbital together in the proper orientation, (2) the cylinders also serve as axes for ascertaining orbital orientation, and (3) the cone serves as a model base for a free-standing model. These structures can be generated CalcPlot3D using the *parametric surfaces* tool. Table 1 gives the functions used to generate the three axes and the cone. Once the orbital function and parametric surfaces are tuned appropriately, the structure can be exported as a .stl file using the CalcPlot3D file menu. Please refer to the supporting document for a more in-depth procedural overview for creating models in CalcPlot3D. Topics covered in the supplemental include; a discussion of the current state and future of CalcPlot3D, a software guide for generating the orbitals, a discussion of limitations of this method, and suggestions for representing orbitals with challenging structural features, such as off-axis lobes.

Table 1. Generation of Model Axes and Base Using Parametric Surfaces[a]

variable	*x* axis (cylinder)	*y* axis (cylinder)	*z* axis (cylinder)	base (cone)[b]
x	v	$\cos(u)$	$\sin(u)$	$\cos(u)*v$
y	$\cos(u)$	v	$\cos(u)$	v-3
z	$\sin(u)$	$\sin(u)$	v	$\sin(u)*v$

[a] Parametric functions are created by varying x, y, and z parameters with respect to two parameters, u and v. The parameter u's range is $0 \leq u \leq 2\pi$, and v's is set to a range that is appropriate to the model. [b] The "v-3" function used for the y-variable is used to offset the cone from the origin.

QUALITY CONTROL IN PREPARATION FOR 3D PRINTING

Check .stl File Output for Errors Using a .stl Viewer

To check that the .stl file is in the proper format for 3D printing, it is wise to first confirm the output using a .stl file viewing tool. The .stl file output from CalcPlot3D was checked using the free online .stl viewer web page.[41] Figure 1, panel B depicts the .stl file output from CalcPlot3D for the $2p_y$ orbital. As can be seen in the figure, the .stl file has been output with no obvious errors in the shape functions.

Ensuring a Cohesive Object for 3D Printing Using .stl File Repair

As discussed above, the model output by CalcPlot3D consists of five separate surfaces (orbital, cone, and three axes). An attempt to 3D print the .stl file output from CalcPlot3D may encounter an error with intersecting surfaces. This error is due to the 3D printer treating the model to be printed as five different objects; where those objects overlap (e.g., at the origin), the 3D printer encounters an error. To combine the disparate surfaces into one cohesive object, it is necessary to "repair" the file. This was accomplished using a free online repair tool, 3D Model Repair.[42] Once the model file has been repaired, it is checked once more on the free online viewer, and then it is ready for 3D printing. A zipped folder containing repaired .stl files for s, p, d, and f orbitals is included in the supporting files. These .stl files are ready to 3D print, depending on constraints of individual 3D printers. The full set of 1s, 2p, 3d, and 4f orbitals is included, with some additional orbitals as discussed in the supporting document.

3D PRINTING OF HYDROGENIC ORBITAL MODELS

The 3D printer used to produce the orbital models is a Fusion3 Designs F306 (Fusion3 Design LLC, Greensboro, NC). The aforementioned 3D printer utilizes the Simplify3D printing slicing software package (Simplify3D Software, Cincinnati, OH) for printing of the .stl file. When an object is 3D printed, plastic filament is melted and deposited, layer by layer, in the appropriate pattern such that the orbital model is gradually generated over the period of ~2 h. The Fusion3 3D printer used to produce the models uses 1.75 mm polylactic acid polymer filament (AtomicFilament.com, Burbank, CA).

Accounting for Overhanging Structures in 3D Printing

Due to the layer-by-layer 3D printing methodology, overhang structures in the orbital models (e.g., the horizontal axes) must have a support structure, automatically generated by the Simplify3D software, so that the first overhanging layer of the model has a structure to be deposited onto. The support structures are designed by the software such that they can be removed once the model has been completed. A screenshot from Simplify3D for a $3d_{xz}$ orbital with a software generated support structure can be seen in Figure 2, panel A. Unfortunately, support structures represent a net waste of plastic, as they cannot be reused.

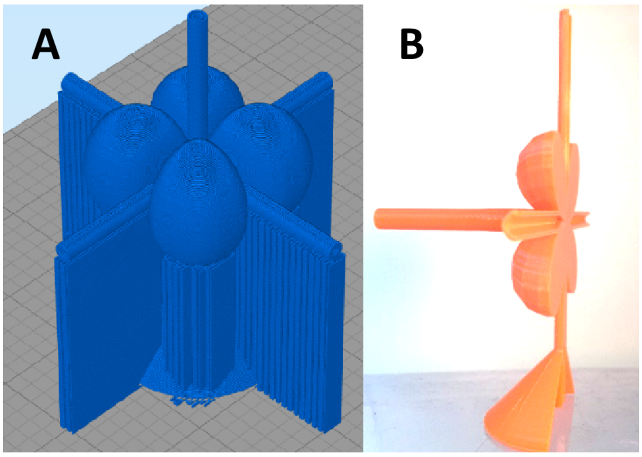

Figure 2. Alternate 3D printing methodologies for orbital models. Panel A is a screenshot of a $3d_{xz}$ virtual orbital model with a software-generated support structure that would be printed to lend support to overhanging portions of the orbital model. Support structures represent an inefficient use of printing filament as they are discarded after printing. Panel B depicts an alternative method that can be done without the need for support structures. In this method the orbital is printed in halves, with the flat, planar surface side down. Arranged this way, the orbital models exhibit no overhanging surfaces requiring support structures. The two halves can then be glued together after printing.

Alternatively, the virtual model of the orbital can be positioned in the 3D printing window of the Simplify3D software such that only one-half of the model is printed at a time. Figure 2, panel B is a photograph of one-half of a $3d_{xy}$ orbital. The model is printed with the flat side down, and, as can be seen in the figure, has no overhanging components. Thus, the model can be printed without the need for a support structure. The two halves of each orbital model can then be glued together with model glue. The $2p_y$ orbital in Figure 1, panel C was prepared in this manner.

CONCLUDING REMARKS

3D printing is an ideal technique for generating mathematically precise, physical models of chemical phenomena for use as hands-on pedagogical aids.[27−36,43] We have demonstrated a relatively simple 3D printing procedure for producing physical hydrogenic orbital models utilizing freeware. The models are produced using the mathematics of quantum mechanics, and thus exhibit quantitatively accurate shapes not present in other common physical orbital models, which are qualitative representations of hydrogenic orbitals. In addition, the models can be produced relatively cheaply; the software chosen to create the orbitals is freeware, and the amount of printing filament used per model produced averaged ∼\$2.50, as calculated by the Simplify3D software. This amount of printing filament produced models that were, on average, ∼1000 cm^3 (about the size of a grapefruit). As a comparison, three 2p orbital models from Klinger educational are listed at \$140.00 for the set on their Web site.[19] In addition, 3D printers are becoming more generally available; they can be found at many different levels of academic institutions and are appearing at locations such as public libraries. The process of constructing the models is accessible, using equations out of advanced chemistry textbooks. Thus, it is possible that the model creation process can be adapted for advanced physical or inorganic chemistry classes as a hands-on pedagogical project. Once built, the models are relatively sturdy, and can be handled without much concern for fragility.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00293.

> More detailed instructions for using CalcPlot3D to generate orbital models is included. In addition, the document discusses limitations of this method, and techniques to overcome structural challenges such as off-axis lobes. Example images of orbital .stl files generated using CalcPlot3D are included. (PDF)
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> More detailed instructions for using CalcPlot3D to generate orbital models is included. In addition, the document discusses limitations of this method, and techniques to overcome structural challenges such as off-axis lobes. Example images of orbital .stl files generated using CalcPlot3D are included. (DOCX)
>
> Folder containing a variety of ready-to-print orbital .stl files. These files include all the basic (i.e., no radial nodes) s, p, d, and f orbitals. Any orbitals used in images in either the supporting document or the main document are also included. (ZIP)

AUTHOR INFORMATION

Corresponding Author

*E-mail: kfogarty@highpoint.edu.

Notes

The authors declare no competing financial interest.

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