THE spdf ELECTRON ORBITAL MODEL PARSED

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Abstract

The currently accepted, QM, spdf electron model is a collection of individual orbital sets designed to handle 1, 3, 5 and 7 groupings. For anyone who takes enough chemistry, these mathematically generated images are some of the most memorable – as separate presentations, that is. When combined in 3D space to contain 32 electrons, they are a mess as the sets are not orthogonal to one another; nor are they dynamic. The spdf orbital sets, their shapes, orientations, and spatial overlapping are addressed.

INTRODUCTION

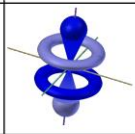
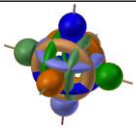
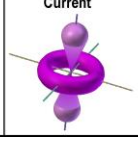
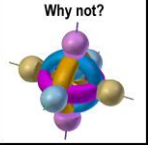
The spdf orbital model of the electrons of the elements of the periodic table is now over a century old. As such, it is deeply entrenched in scientific studies. The individual components (s, p, d and f) are presented in graphic form for all to grasp. They form some of the most recognizable images of the scientific arena. Individually, that is. Images of them combined in 3D beyond the s+p level are seldom set forth. This paper has been prepared to address that issue and to illustrate how these individual components collectively handle 32 electrons.

THE spdf MODEL

The s, p, and d orbitals are quite familiar to anyone who has studied the electronic structure of atoms. The f-orbitals, on the other hand, are not so familiar. Interestingly, while the s, p, and d orbitals are presented as singular sets, there are two (2) sets in common usage for the f-orbitals: cubic and general[1]. Images of both sets are found on the web with the cubic[2] showing up more often than the general[3].

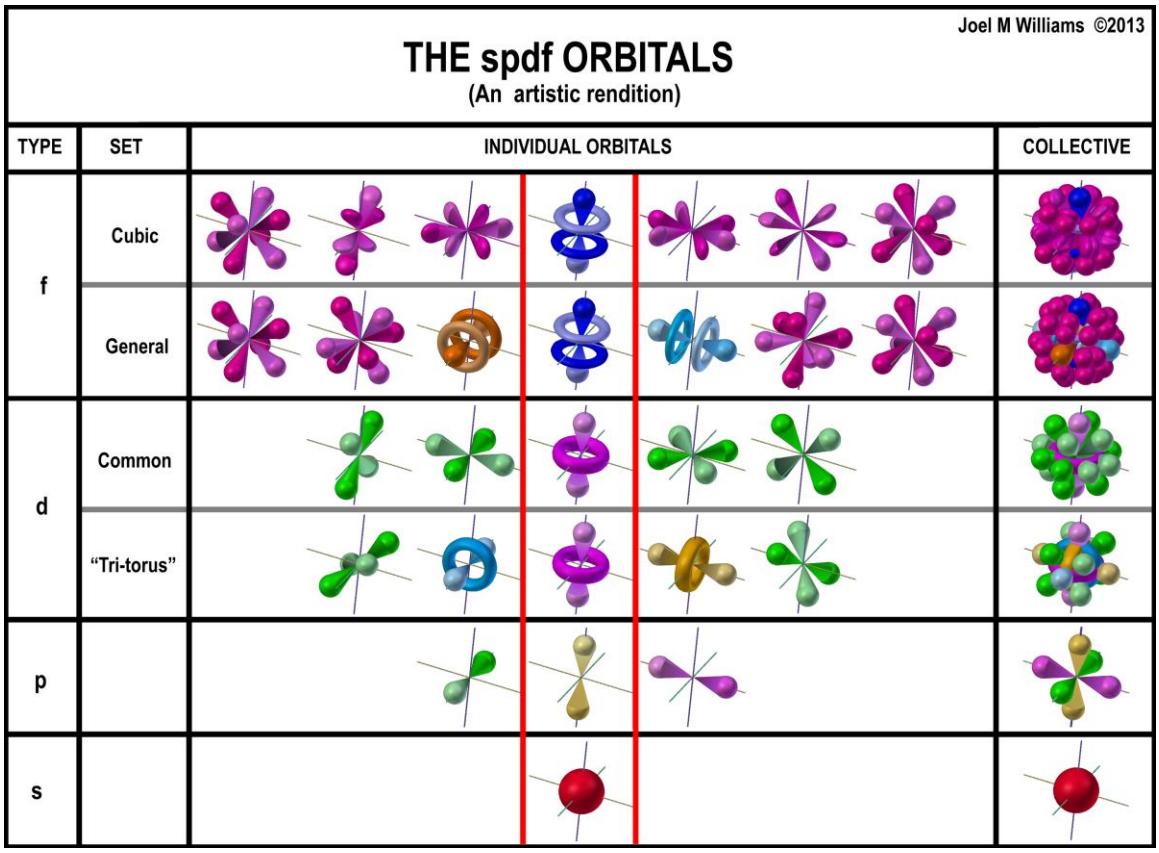
The two f-orbital sets use the three (3) orbital shapes shown in the figure at the right. Three are common to both sets[4]. The "cores" differ primarily in the number of "tori-orbitals" as shown in the figure on the left. The core of the general set gives the illusion of a "gyroscope"[5]. Why isn't a similar set presented for the d-orbitals? The four common spdf orbital sets are presented as artistic representations in the following chart in typical, but inverted, "pyramidal" fashion along with d and f tri-torus sets.

d and f Orbital Set Cores

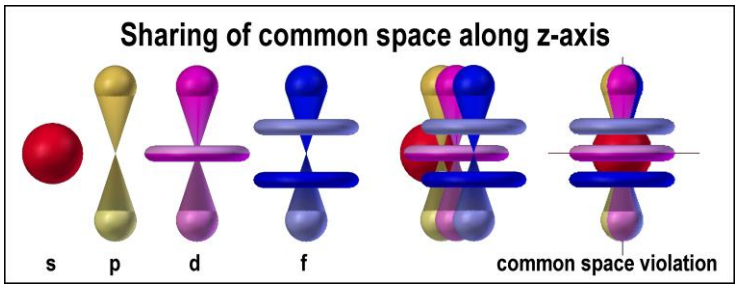
Orbitals	Orbital set tori unit: Cubic	Orbital set tori unit: General
f		
d	Current 	Why not? 

f-Orbital Shapes
(2 sets in current usage)

f-Orbital Shape	Number in Set: Cubic	Number in Set: General
	1	3
	2	4
	4	0

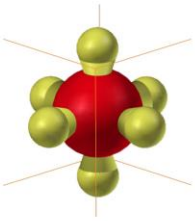
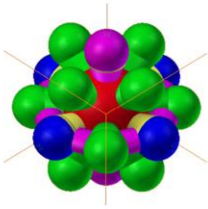
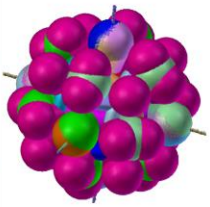


This layout of the spdf orbitals emphasizes what the orbitals are intended to do: model space for 1, 3, 5, and 7 pairs of electrons. What should be clear is that each set ignores the fact that it starts by occupying the space dedicated to the preceding one. This is seen in the center column of the above figure and emphasized in the figure at the right. Roughly, the electron density of ~6 electrons, out of 32, is concentrated along this axis. With similar overlaps along the x and y axes, ~60% of the total electron density of a period is concentrated in ~20% of the spherical volume! This may be nice for mathematics, but it is unlikely to occur in a real world situation.



While they can handle the 1, 3, 5, and 7 pairs separately, they do not present proper orbitals when the sums of the electrons are 2, 8, 18, and 32 as needed to address the periods of the periodic table of elements. The following figure illustrates how the spdf electron orbitals mesh to provide the number of electrons for a period in the periodic table. The spdf orbital model starts with a "mild" overlap as the s and p-orbitals combine to accommodate 8 electrons. The overlap is not so mild when the d-orbitals are added to the s/p group to handle 18 electrons. [The portions where the d-orbitals coexist with the p_x and p_y orbitals are tipped with blue; a bit of yellow can be seen where the p-orbitals are present. The p_z orbital coexists with the purple d_{x^2} orbital.] The overlap situation becomes extreme when the f-orbitals are added to the s/p/d sum. [The general f-orbital set is used in the figure.] Of note is the change in the number of lobes required to accommodate a

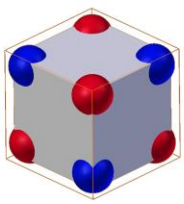
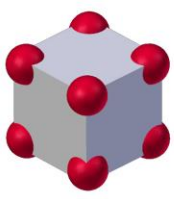
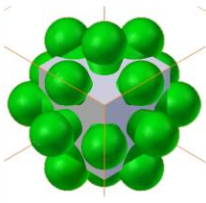
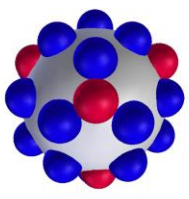
pair of electrons: 1 for 2, 7 for 8, 25 for 18, and ~64 for 32 along with a few tori. Strange! Of course, it is, but they have been mathematically generated according to the precepts of the QM nlms numbers and fitting 5 or 7-component sets into 3D space.

Accommodating Atomic Electrons at the Same Period Level				
# e in level	2	8	18	32
spdf Model				
Orbitals/Lobes/Tori	1/1/0	4/7/0	9/25/1	16/67/3 Cubic 16/63/7 General

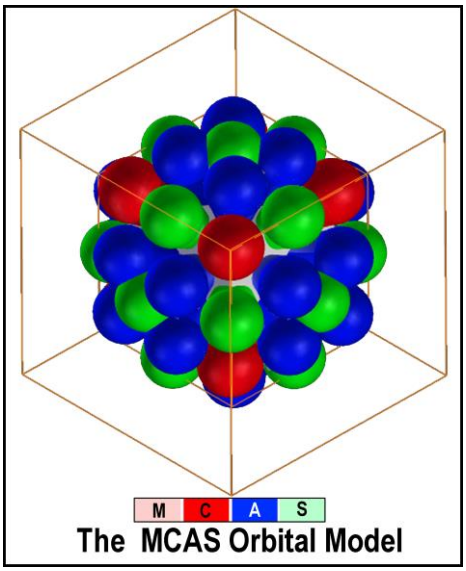
Conclusion: the spdf orbital models look neat and crisp when viewed as independent sets of orbitals, but become a garbled mess when combined beyond the simplest grouping of 8. This garbled mess becomes even worse as more periods are considered. The spdf model is simply a rigid orbital, "file cabinet" model, starting with a single drawer and stacking more on top. The spdf model is rather myopic when broad application is considered. Dogged adherence to its rigidity indicates either that little has been learned in the past century about the actual structure or that no one dares to disturb the sacred icon.

THE MCAS MODEL

Consider now the logic of starting from the standpoint of accommodating all of the electrons of each period in a symmetrical manner AND then seeing what subsets they contain. The MCAS model was developed with just this approach. The figure below shows how the MCAS model accommodates the differing numbers of electrons needed for each layer.

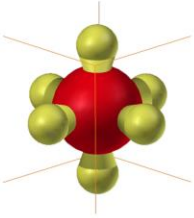
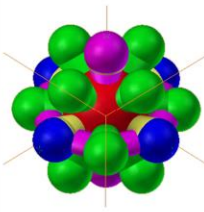
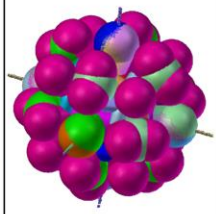
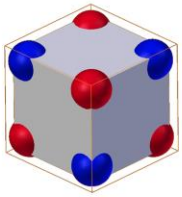
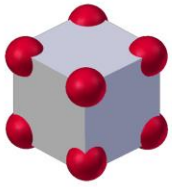
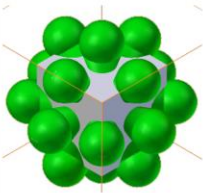
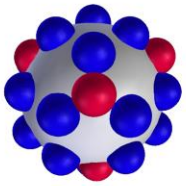
Accommodating Atomic Electrons at the Same Period Level				
# e in level	2	8	18	32
MCAS Model				
Lobes	M2x4	C8	A18	SC32

Nesting of the orbital types is clearly evident with each electron having a "dedicated" home abode. Sub-orbital units can be established to associate electrons into groups as required (that is demonstrated for the 2 electron case), but an overall symmetrical distribution of electron density (as defined by the lobes) must be maintained. The complete nesting symmetry of all of the MCAS orbital types is shown in the figure at the right.

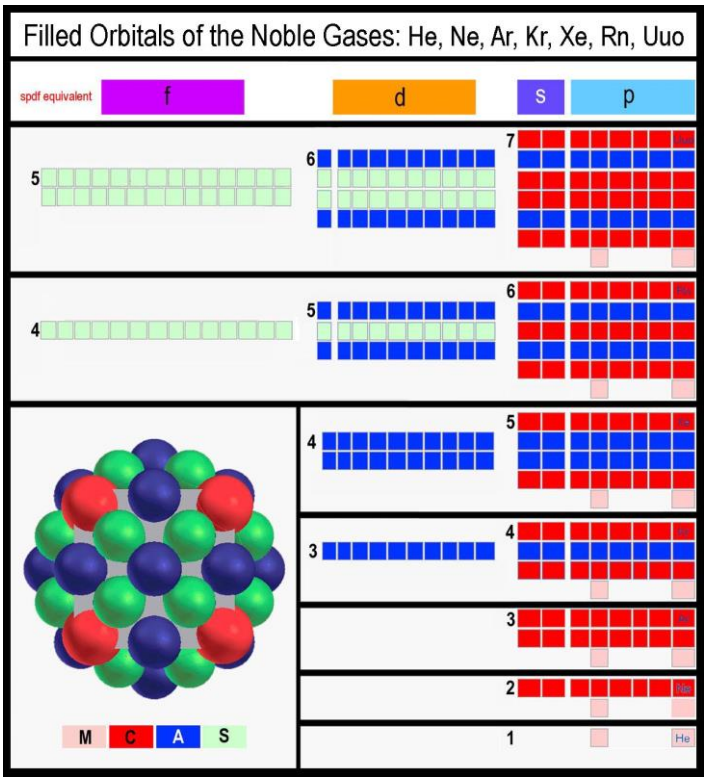


Layer nesting of orbitals is not a feature of the spdf model! Nor does the spdf model provide dedicated (orthogonal) space of the orbital sets as touted. The following figure provides a side-by-side comparison of how the spdf and MCAS models the 2, 8, 18, 32 electrons around an atom to provide an easier recognition of their differences.

Accommodating Atomic Electrons at the Same Period Level

# e in level	2	8	18	32
spdf Model				
Orbitals/Lobes/Tori	1/1/0	4/7/0	9/25/1	16/67/3 Cubic 16/63/7 General
MCAS Model				
Lobes	M2x4	C8	A18	SC32

So, what is so important about "nesting"? Consider that the currently known elements require seven (7) periods (levels) of electrons. The last element in the 7th period will contain 118 electrons in periods of 2, 8, 18, 32, 32, 18, and 8 electrons. These periods are not onion-skin layers independent of the layer above and below. "Nesting" provides the mechanism that allows electron orbitals to be placed in each period in a manner that provides the lowest energy for the total arrangement. "Nesting" of the orbitals is clearly seen in the orbital structure of the noble gases when modeling has been performed with MCAS orbitals (see figure below; its generation is presented elsewhere[6] - click here to connect). Note that only two levels of A or S sets ever need coordinating!



Electrons in similar orbital types of different "periodic levels" are coordinated as orbital dimensions range from the nucleus outward to the farthemost extent of the orbital type. Dynamic coordination is an inherent feature of the MCAS model.

SUMMARY

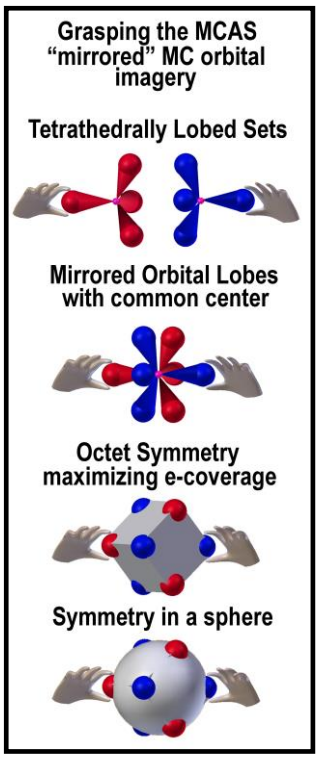
The spdf model is a stoic mathematical model that is based on creating independent sets of orbitals containing 1, 3, 5 and 7 pairs of electrons. The resulting sets have memorable 3D images of their individual components. Individually, each set is aligned along the x, y, and z axes. When combined to handle 2, 8, 18, and 32 electrons in 1, 4, 9, 16 pairs, these sets are not orthogonal to one another and overlap from the very start. The noble elements require well-coordinated groups of 2, 8, 18, and 32 electrons. When the spdf orbitals are subjected to a 3D, visual summing, they present anything but a neat assemblage of the electron spaces needed to handle the required number of "periodic" electrons. It is not a matter of how the spdf orbital sets have been generated (the mathematical logic of the individual sets can clearly be followed and taught), but whether the summation logic follows the same constraints that are applied to the individual sets. When the orbital sets are combined, it is clear that the same constraints are not followed.

In contrast to the spdf electron orbital model, the MCAS electron orbital model provides simple, nesting, configurations to handle the electrons needed for the periods of the periodic table of elements.

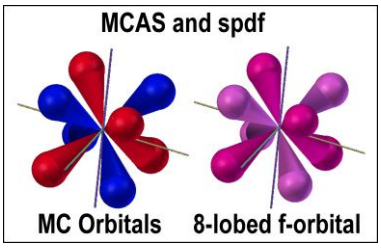
"*Comparing the Logic behind the spdf and MCAS Models*" also addresses the spd portion of the spdf model[7] - click here to connect.

ADDENDUM

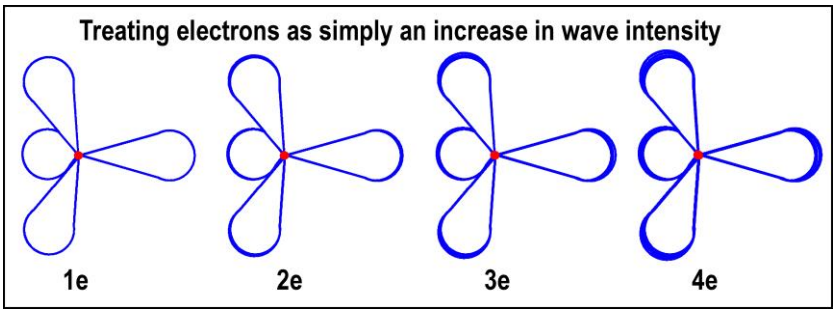
The figure at the right is given to aid in understanding the MC "mirrored" orbital concept.



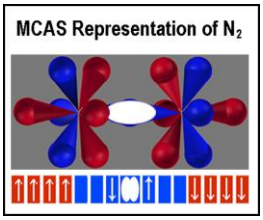
Stanch adherents to the spdf model who thus oppose tetrahedral orbitals in place of the spherical one should consider the similarity of one of their f-orbitals to the MC pair (see figure at right). Two electrons can occupy the f-orbital, but just how one or two of them can occupy those 8 lobes is not clear. How they do so in the MC orbitals is.



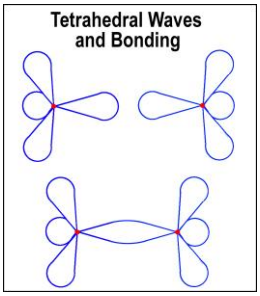
For adherents of the wave approach to electrons, think of the edges of the lobes of the tetrahedral orbital as defining the wave length. The number of electrons in the tetrahedral orbital can be thought of as the wave's intensity. This imagery is presented in the figure below. The size of the tetrahedral lobes determines how many electrons can be accommodated. The first tetrahedral unit is only large enough to handle a single electron. The wave intensity of a single tetrahedral orbital unit beyond that first level can scale to 4 (1 per lobe); the sum of the two mirrored tetrahedral orbitals can reach 8.



Bonding using the orbitals of the MCAS model has been presented elsewhere where electrostatic attracting and repelling of the electrons and nuclei are included[8]. The nitrogen molecule is shown at the right.



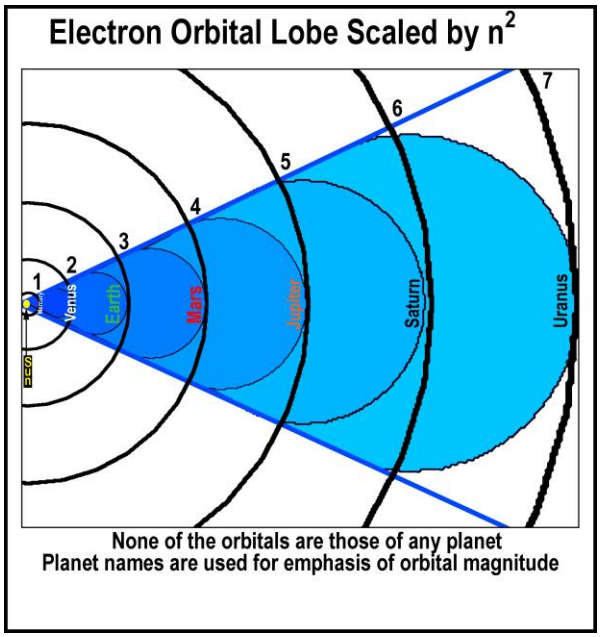
In keeping with the wave imagery above, the figure at the right shows the combination of tetrahedral waves from two separate atoms. Lower energy results from the longer (~doubled!) combined wave length. At the lowest orbital level, this would be one of the possibilities for H_2 (2 electrons). For the next level and a larger tetrahedral unit, the combined wave can accommodate up to 6 electrons (F_2). A 7^{th} electron will not be accommodated as the combined wave would be more energetic than the two individual ones. Also, a "permanent" electron presence would occur between the nuclei. Think about Ne and F not forming a bond.



For those preferring a particulate model, the combined "wave lines" indicate coordinated passage of electrons around each nucleus and then onto the other giving greater mean coverage to the nuclei. There are electrostatic interactions of these orbitals with the other tetrahedral orbitals that are not shown here.

For those preferring a probability model, the overlapped orbitals are simply a way of reducing the total orbital volume to be filled with the totality of electron density; 8 orbitals reduced to 7. A high concentration of electron negativity should NOT be expected in the overlap, however, as the other lobes have requirements, too. For N_2, 2 electrons would be distributed among the 7 and, as a first approximation, the overlapped region would have 0.29 electron; not 2. For F_2, it would have 0.86 electron.

Orbitals scale by n^2 (see the figure at the right). It is easy to see how a wave or moving particle could create such orbital spaces as they relate to defined energy levels. It takes a lot of energy to reach the outer limits. With sufficient energy an electron will escape the nuclear grip and leave a positively charge atom (ion). Otherwise, the electron remains associated with the nucleus in a *controlled* manner.



The definition of orbital space by electron probability (defined as the likelihood of finding an electron in a given spot) is less facile. Since the spdf model has electron densities concentrated in overlapped orbital spaces along the x, y, and z axes, what keeps the electrons in those overlapped probability clouds confined to a particular orbital?

Probability information reads like a census of the number of residents in tenement buildings of a complex without explaining why or how those residents got there. When thinking about forming bonds by overlapping e-rich orbitals - as is done in the current approach, consider the effect of stuffing more residents, especially hotheads, into the same tenement space while leaving other space vacant.

REFERENCES

[1] Atomic orbitals: 5f (cubic set), University of Sheffield - http://winter.group.shef.ac.uk/orbitron/AOs/5f/

[2] a) Electronic Orbitals, UCDavis - http://chemwiki.ucdavis.edu/Physical_Chemistry/Quantum_Mechanics/Atomic_Theory/Electrons_in_Atoms/Electronic_Orbitals;
b) Electron Orbitals, http://www.angelfire.com/falcon2/dirgni/orbitals.html;
c) 4f Orbitals (General Setting) Department of Chemistry - University of Oxford - http://www.chem.ox.ac.uk/icl/heyes/LanthAct/I3.html;
d) f orbitals, WikiMedia Commons - https://commons.wikimedia.org/wiki/File:F_orbitals.png;
e) seven f orbital are less well understood, Los Alamos National Labotratory - http://www.lanl.gov/orgs/nmt/nmtdo/AQarchive/04spring/VO.html

[3] a) Atomic Orbitals f orbitals, Delta School District British Columbia, Canada - https://fc.deltasd.bc.ca/~mannandale/oldchemsite/Chemistry11/Atomictheory/forbitals.htm;
b) f-orbital models on stands, University of Michigan SharePoint Portal - https://sharepoint.umich.edu/lsa/physics/demolab/DemoLab%20Asset%20Library/F%20Orbital%20Models_7B50.10.bmp

[4] fxyz, fz3, and fz(x2-y2), Atomic orbitals: 5f (cubic set), University of Sheffield - http://winter.group.shef.ac.uk/orbitron/AOs/5f/

[5] Gyroscope, from collection at the National Museum of American History at the Smithsonian Institution, Department of Physics, Kenyon College - http://physics.kenyon.edu/EarlyApparatus/Mechanics/Bohnenbergers_Apparatus/Bohnenbergers_Apparatus.html

[6] Creating the Familiar Periodic Table via MCAS Electron Orbital Filling,, Joel M Williams - http://pages.swcp.com/~jmw-mcw/The%20Familiar%20Periodic%20Table%20of%20Elements%20and%20Electron%20Orbital%20Filling.htm

[7] Comparing the Logic behind the spdf and MCAS Models, Joel Mann Williams - http://gsjournal.net/Science-Journals/Essays/View/5000

[8] a) Understanding the Bonding of Second Period Diatomic Molecules (spdf vs MCAS), Joel Mann Williams - http://gsjournal.net/Science-Journals/Essays/View/4850;
b) Comparing Several Orbital Approaches to the Hydrogen, Joel Mann Williams - http://gsjournal.net/Science-Journals/Essays/View/4885;
c) Electronic Bonding of Atoms, Joel Mann Williams - http://gsjournal.net/Science-Journals/Essays/View/4043;
d) Modeling the MCAS Way, Joel M Williams - http://arxiv.org/html/physics/9902046v2 (sharper imagery at http://pages.swcp.com/~jmw-mcw/science)