

Is It Time To Retire the Hybrid Atomic Orbital?

Alexander Grushow*

Department of Chemistry, Biochemistry & Physics, Rider University, Lawrenceville, New Jersey 08648, United States

ABSTRACT: A rationale for the removal of the hybrid atomic orbital from the chemistry curriculum is examined. Although the hybrid atomic orbital model does not accurately predict spectroscopic energies, many chemical educators continue to use and teach the model despite the confusion it can cause for students. Three arguments for retaining the model in the chemical curriculum are presented. These arguments are then refuted and methods for teaching chemistry without invoking the hybrid atomic orbital model are presented to show how the model can be removed from the chemistry curriculum with little negative effect.

KEYWORDS: First-Year Undergraduate, Organic Chemistry, Physical Chemistry, Misconceptions/Discrepant Events, Theoretical Chemistry, VSEPR Theory, Valence Bond Theory, MO Theory, Covalent Bonding

In the mid 18th century, the phlogiston model¹ held firm sway among chemists as a way to explain the change in chemical behavior of metals subjected to flame or heat. The simplified statement of the model is that, upon heating of certain elements, phlogiston “escapes” from the substance and the remaining substance (referred to as a calx) can be restored to elemental form by heating the substance with charcoal (which was thought to be pure phlogiston). This model did not account for the fact that the calx of an element was heavier than the element itself because poor precision in mass measurement of the time. Eventually this experimental detail could not be ignored and further discoveries concerning the nature of gases, oxygen in particular, showed that the phlogiston model could not be used to accurately predict the product mass after heating a metal. The phlogiston model was eventually discarded by practicing chemists because it could not provide full quantitative results and was shown to be conceptually invalid.

The story of the phlogiston model is related here because it serves to remind us that we use models to help us understand chemical phenomena, and furthermore, that chemists and chemical educators must reconsider the value of using models that have been shown to be conceptually invalid. I believe it is time to reexamine the validity of the hybrid atomic orbital model and particularly its utility in chemical education because it does not provide an accurate understanding of bonding theory and has led both students and professional chemists to make inaccurate predictions of experimental results.

■ BACKGROUND

The origin of the hybrid atomic orbital model is traced to Pauling² who developed the theoretical construct as a means to rationalize molecular shape. At the time of its initial development, quantum mechanics, as applied to chemical systems, was still in its infancy and chemical bonding was typically described using localized electron models; molecular orbital theory was still a number of years off. To chemists attempting to rationalize molecular structure and Lewis structures with emerging quantum mechanical orbital models, the notion of a hybridized atomic orbital seemed like a reasonable solution. However, the solution has proved to be too simple because photoelectron spectroscopic evidence indicates that hybrid atomic orbitals are inappropriate

models for the description of electronic energies and electron density within a molecule. Furthermore, advances in theoretical methods indicate that an appropriate description of electron density is often best made using a delocalized approach rather than the localized electron theory that basic hybrid atomic orbitals provide.

■ ARGUMENTS

Despite significant experimental evidence and theoretical advances to indicate that hybrid atomic orbitals do not exist and do not appropriately describe molecular bonding, their description still permeates chemical education at many levels, and the model still finds its way into modern chemical literature. In conversations with colleagues, there remain three common rebuttals to my request to retire the hybrid atomic orbital model and these shall be addressed in turn.

Hybrid Atomic Orbitals Help Students Understand the Three-Dimensional Structure in Molecules (Particularly Organic Compounds)

To this statement, it could be argued that introductory students do not *understand* hybrid atomic orbitals any more than they *understand* atomic orbitals in general. To students who have not fully examined the solutions to the Schrödinger equation for the hydrogen atom, atomic orbitals are no more than cartoons that indicate where they will find an electron in an atom (which in itself is also a fallacy to be discussed at another time). For most introductory students, the concept of a wave function used to describe probability is not developed, nor is the notion that functions made up of a linear combination of other solutions to the Schrödinger equation also provide possible solutions to the wave equation. So, if students do not understand how a hybrid atomic orbital is developed, all they see is another cartoon shape that their instructor has asked them to memorize.³ Thus, I would aver that this model does not help the student to *understand* three-dimensional structure, but it does provide a convenient, although false, justification for molecular shape.

Published: March 11, 2011

Hybrid Atomic Orbitals Provide a Nomenclature That Allows Chemists To Describe and Predict the Orientation of Bonded Atoms around a Particular Molecular Center (Usually Carbon)

This is a particularly common statement from the organic chemists. However, an “sp³” carbon is nothing more than a carbon that has a tetrahedral geometry. So why not just call it a tetrahedral carbon? Furthermore, the predictive power of the hybrid atomic orbital model is really based on VSEPR and the arrangement of electron domains around a central atom.⁴ That is to say the shape of a simple molecule is predicted by drawing a Lewis structure and then using VSEPR and the number of electron domains determined from the Lewis structure to predict the geometry of the bonded atoms around the central atom. Hybrid atomic orbitals are not even used to predict the shape. They are only used after-the-fact to justify the resulting shape.

The Use of Hybrid Atomic Orbitals Provides an Energetic Justification for Having Four Equivalent Bonds in Methane

The corollary to this statement is that it is not feasible to bond the 1s orbitals of hydrogen with the 2s and 2p orbitals of carbon to get four equivalent bonds, at least using a localized electron model, and this is where this particular rebuttal causes so much trouble. Although indeed the carbon–hydrogen bond lengths of methane are equivalent, photoelectron spectroscopy⁵ shows that the electron energies in methane mimic those of the 2s and 2p orbitals of a carbon atom and that the picture of four equivalent bonding orbitals each describing two electrons does not exist in methane. It is the notion that four equivalent bonds in methane (a thermodynamic measurement) results in (or from) four equivalent orbital electron energies (a quantum mechanical measurement) that causes numerous problems for students later on in their chemical education. Indeed, the localized electron model of the Lewis structure is very useful for understanding how atoms are connected within a molecule, but that is the extent of its utility. A Lewis structure is not explicitly used to predict the bond energy; it is an understanding of the relationship between bond length and bond strength that predicts bond energy. However, despite experimental evidence to the contrary, some general chemistry texts⁶ and organic chemistry texts⁷ still insist that all the bonding electrons in methane have equivalent electronic energies. It is reasonable to say that the bond lengths are equivalent, but it is not acceptable to infer a molecular orbital energy or any kind from a bond length. Indeed it is a subtle, but important, distinction to say that the bond energies in methane are the same, but that the energies of all eight bonding electrons are not the same. The bonding electrons in methane (or most any other molecule for that matter) simply cannot be properly characterized using a localized electron model. Furthermore, a molecular orbital model and the description of the probability density of the electrons and their orbital energies do not follow directly from the equivalence of the C–H bonds in methane. To paraphrase Simons,⁸ although bonds may be equivalent, they are by no means independent of one another.

■ SOLUTIONS

Now that the failings of teaching or using the hybrid atomic orbital model have been explained, what should be put in its place? This can be answered by revisiting the three “utilities” of the hybrid atomic orbital model given above and providing solutions to these issues. First, when it comes to visualizing the three-dimensional shape of molecules, most students learn the molecular shapes by applying VSEPR to an appropriate Lewis

structure. The beauty of VSEPR is that it does not require any orbitals at all. It simply answers the question, how can these electron domains be moved as far away from each other as possible? Although it does seem that this commentary is designed to refute the localized electron model, Lewis structures do more good than harm in helping students understand chemical bonding, whereas I would argue that the hybrid atomic orbital model does more harm than good. In the study of bonding of inorganic compounds, for example, the hybrid atomic orbital model has been almost completely abandoned because the model simply does not hold up to the complexities of chemistry studied in that discipline. Recent papers in this *Journal* have shown the inability of hybrid atomic orbitals to properly describe or predict molecular shape.⁹ However, in the teaching of organic chemistry, and, as a corollary, general chemistry, the hybrid atomic orbital model has unfortunately become very entrenched. Student understanding of molecular bonding is often fixated on the localized bonding model and the hybrid atomic orbital model only serves to reinforce this notion. As a result, students have a difficult time accepting other important bonding concepts in chemistry. The concept of probability of finding a particular electron anywhere on a large molecule, and not just between two particular atoms, causes no end of anguish for advanced students of chemistry because the localized electron model is so ingrained into the fabric of their understanding. Localized models do indeed serve many purposes, but to reinforce them through the construction of an incorrect model only serves to make deeper understanding of chemistry more difficult.

As to the problem of nomenclature and power of prediction, the solution has already been provided in the form of nomenclature that appropriately describes the geometry of a molecular center (tetrahedral, trigonal, and linear). Furthermore, it has been indicated that the hybrid atomic orbital is not even used to predict geometry. Where there might be some concern in the literature is in the discussion of the *character* of a molecular center as being sp³ or sp² character or having more s or p character. Such articles are doing one of two things: either they are attempting to quantify the nature of the three-dimensional arrangement around a particular atom as either being tetrahedral or trigonal or somewhere in between or they are attempting to quantify the contribution to the bonding of an s or p atomic orbital. In the first case, it should be acceptable use the nomenclature given above without referring to a hybrid atomic orbital and in the second case the use of the term hybrid or hybridization is actually anachronistic since the s or p character is referring to the level of contribution that an s or p orbital makes to a molecular orbital, whether that molecular orbital is localized or not. In cases where the author uses %s or %p character to estimate a bond angle, it is often the case that such percentages are determined empirically through correlation with some experimental measurement¹⁰ or theoretical determination.¹¹ The bond angle is then inferred from the %s or %p. Why not skip the middle step and simply correlate the experimental measurement with bond angle? The same could be done for correlations between the bond angles found on a carbon center and pK_a of a proton bound to that carbon.

For the issue of inferring equal bond orbital energies from equivalent bonds, ignoring this issue in the teaching of chemical bonding would be a blessing for general chemistry students. The justification that the textbooks use to explain how a hybrid atomic orbital is formed is not corroborated by experiment and only serves to ingrain the incorrect notion that all covalent bonding is

a localized phenomenon. Indeed a discussion of electron orbital energies is unnecessary except in the examination of the electronic spectroscopy of molecules; a subject rarely discussed in general chemistry. The more important aspect of chemical bonding for students of general chemistry is the thermodynamic quantity of bond energy, which is different from orbital energy. In introductory organic chemistry texts, orbital energies are rarely well described in the passing nod to molecular orbital theory. This leaves the issue to be brought up in physical chemistry where discussion of molecular orbital energies using quantum mechanics is appropriately developed. Furthermore, this development is much simpler if students do not have incorrect notions of localized bonding orbitals already stuck in their heads. So, the solution is to leave the discussion of orbital energies to a course that appropriately discusses the nature of orbitals and develops the proper language and mechanics to explain them.

■ FINAL REMARK

Even after development of much experimental evidence that ran counter to the phlogiston model, it took many years for the model to completely disappear.¹ Indeed some (namely Joseph Priestly) were never fully convinced that phlogiston did not exist. Surely the same will be true of the hybrid atomic orbital model. I only ask those in a position to change the chemistry curriculum (namely the textbook authors and standardized exam writers) to think carefully about the utility and validity of including a model in the curriculum that has no experimental basis and too often leads to student confusion.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: grushow@rider.edu.

■ REFERENCES

- (1) (a) Partington, J. R. *A Short History of Chemistry*, 3rd ed.; Dover: New York, 1989; pp 85–152. (b) Brock, W. H. *The Norton History of Chemistry*; W. W. Norton & Co.: New York, 1993; pp 78–127.
- (2) (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (b) Pauling, L. *J. Am. Chem. Soc.* **1931**, *59*, 1367–1400.
- (3) A typical example is described in Schreiner, P. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 3579–3581.
- (4) Gillespie, R. J. *J. Chem. Educ.* **2004**, *81*, 298–304 and references therein.
- (5) Potts, A. W.; Williams, T. A.; Price, W. C. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 104–115.
- (6) (a) Brown, T. L.; LeMay, H. E., Jr.; Bursten, B. E.; Murphy, C. J. *Chemistry: The Central Science*, 11th ed.; Prentice Hall: Upper Saddle River, NJ, 2009; pp 357–362. (b) Atkins, P. W.; Jones, L. L. *Chemical Principles: The Quest for Insight*, 4th ed.; Freeman: New York, 2008; pp 108–112. (c) Spencer, J. N.; Bodner, G. M.; Rickard, L. H. *Chemistry: Structure and Dynamics*, 4th ed., Wiley: Hoboken, NJ, 2008; pp 161–162. (d) Zumdahl, S. S.; Zumdahl, S. A. *Chemistry*, 8th ed.; Cengage: Belmont, CA, 2010; pp 404–410. (e) Ebbing, D. D.; Gammon, S. D. *General Chemistry*, 9th ed.; Houghton Mifflin: Boston, MA, 2009; pp 389–398. (f) Kelter, P.; Mosher, M.; Scott, A. *Chemistry: The Practical Science*; Houghton Mifflin: Boston, MA, 2008; pp 363–374.
- (7) (a) Solomons, T. W. G.; Fryhle, C. B. *Organic Chemistry*, 10th ed.; Wiley: Hoboken, NJ, 2009; pp 25–37. (b) Brown, W. H.; Foote, C. S.; Iverson, B. L.; Anslyn, E. V. *Organic Chemistry*, 5th ed.; Cengage: Belmont, CA, 2009; pp 32–36. (c) Carey, F. A.; Giuliano, R. M. *Organic Chemistry*, 8th ed.; McGraw-Hill: New York, 2009; p 64. (d) Smith, J. G. *Organic Chemistry*, 3rd ed.; McGraw-Hill: New York, 2009; pp 32–40.

- (8) Simons, J. *J. Chem. Educ.* **1992**, *69*, 522–528.
- (9) (a) Purser, G. H. *J. Chem. Educ.* **1999**, *76*, 1013–1018. (b) Galbraith, J. M. *J. Chem. Educ.* **2007**, *84*, 783–787.
- (10) (a) Mosher, M. D.; Ojha, S. *J. Chem. Educ.* **1998**, *75*, 888–890. (b) Gil, V. M. S. *J. Chem. Educ.* **2001**, *78*, 31. (c) Autschbach, J.; Guenic, B. L. *J. Chem. Educ.* **2007**, *84*, 156–171.
- (11) Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. J. *Am. Chem. Soc.* **2003**, *125*, 5973–5987.