Comparing Atomic versus Molecular Orbitals in Comprehensive Introductory Organic Chemistry Textbooks

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Abstract: Variations, factual inaccuracies, inconsistencies in presentation, and ordering of various topics related to atomic and molecular orbitals in comprehensive introductory organic chemistry textbooks prompted their comparison. This work analyzes atomic orbitals, molecular orbitals, and related concepts in introductory organic chemistry and provides student-identified remedies. The recommendations are fact-based, pedagogically useful, and designed to clarify discrepancies in comprehensive introductory organic chemistry textbooks and avoid the inadequacies from being carried to future editions.

Introduction

Understanding atomic and molecular orbital characteristics is important to learning molecular structure, bonding, and reactivity. Because these are basic concepts in introductory organic chemistry, their accurate presentation is critical in order for students to learn the subject. Inconsistencies in these concepts found in some current comprehensive introductory organic chemistry textbooks can impede student learning. Accordingly, we methodically compared currently used comprehensive organic chemistry textbooks in order to assess their accuracy and consistency in presenting atomic and molecular orbital characteristics.

The importance of topic sequencing in comprehensive introductory organic chemistry has been highlighted recently.[1] Therefore, we also evaluated selected additional aspects of atomic and molecular orbitals in these texts, including topic sequence.

I. Atomic Orbital and Molecular Orbital Characteristics

Discussing the variety of atomic and molecular orbitals found in chemistry is beyond the scope of this article. Therefore, the atomic and molecular orbitals considered herein are the orbitals and hybridized orbitals which are most often used in organic chemistry.

A. Atomic Orbitals

An atomic orbital (AO) is a theoretical region of space around an atomic nucleus where the probability of finding an electron is high. The AOs which are most used in organic chemistry reactions are s, p, d, and f orbitals.[2] The following descriptions and explanations seem to be the minimum needed for undergraduates to understand the role of orbitals in bonding and molecular structure in organic chemistry and should therefore be included in undergraduate organic chemistry texts.

B. Molecular Orbitals

Molecular orbitals, as the name implies, are orbitals representing the region of space occupied by electrons in molecules.[3a] A molecular orbital (MO) encompasses more than one nucleus and is obtained by combining AOs in the molecule.[3a] According to MO theory, the two ways for orbitals to interact and form a molecular bond are via an additive interaction or a subtractive interaction. The additive

interaction (constructive interference) leads to formation of a MO that is roughly egg-shaped, whereas the subtractive interaction (destructive interference) leads to formation of a MO than contains a node between the atoms.[3a] The overlap of two AOs with matching symmetry, similar energy, and close contact forms two MOs; these are one lower-energy bonding MO and one higher-energy antibonding MO, as shown in Figure 1.[3a] The symmetry properties and relative energies of AOs determine how the orbitals interact or mix to form MOs.[3a,b] AOs are less stable than the bonding MOs which they form, and more stable than the corresponding anti-bonding MOs.[3a]

Electrons populate MOs preferring lower-energy MOs.[3b] The result is that the overall energy of the electrons in the occupied MOs are lower in energy than the overall energy of the electrons in the original AOs, and the resulting molecule has a lower total energy than the separate atoms.[3b] When two AOs have quite different energies, their interaction is weak, and the resulting MOs have characteristics such as energy and shape, which are similar to those of the AOs (1s versus 2s, or 2s versus 2p).[3b] Hybridized orbitals can also combine to form MOs, provided they have matching symmetries, have similar energies, and can make close contact. AO hybridization involves mixing AOs on an atom to create hybrid AOs.[3b] These new hybrid AOs permit greater overlap when forming MOs, and the hybridization determines the shape of the molecule.[3]

1. Sigma Molecular Orbitals (σ and σ*)

The orbital resulting from end-on overlap and constructive interference of AOs is called a bonding MO, because electron(s) in this orbital spend most of the time in the region directly between the two nuclei.[3a,b] This orbital is called a sigma (σ) MO because it looks like an s orbital when viewed along the axis of the bond.[3a,b] Placing an electron in this lower-energy orbital (Figure 1) therefore stabilizes the molecule relative to the original AOs.[3a,b]

The orbital resulting from end-on overlap and destructive interference of AOs is called an antibonding MO or sigma star (σ*) MO,[3a,b] because electrons placed in one of these orbitals spend most of their time in regions away from the area between the two nuclei.[3a,b] Because the σ* antibonding MO forces the occupying electron(s) to spend most of the time away from the area between the nuclei, placing an electron in this higher-energy orbital makes the molecule less stable, relative to the original AOs (Figure 1).[3a,b]
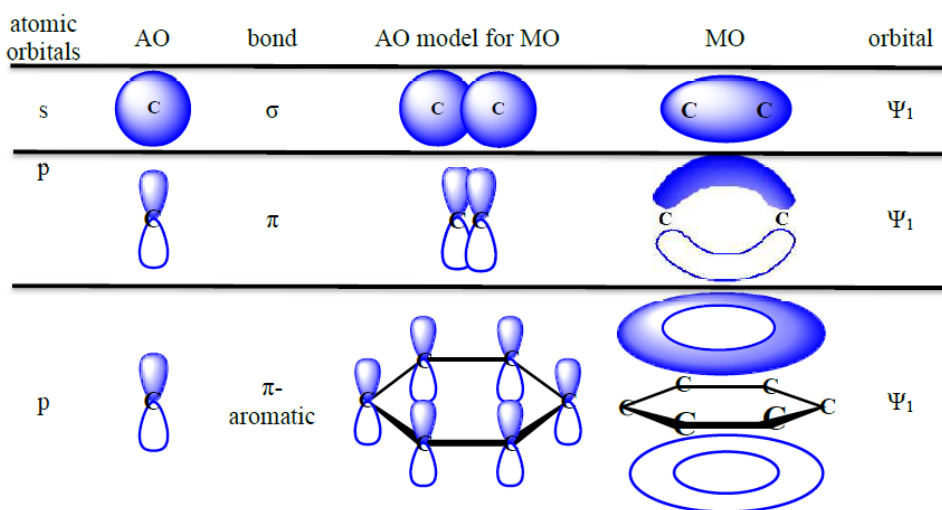
Figure 1. Schematic diagram of MOs formed from interactions between pairs of AOs.

2. Pi Molecular Orbitals (π and π^*)

The sidewise overlap of two AOs of appropriate shape and orientation results in formation of a bonding π orbital and an antibonding π^* orbital (Figure 1).[3c,d] Two atomic p orbitals constructively overlapping will result in a bonding π MO with one nodal plane in which are found the sp^2-hybridized carbons and all atoms directly bonded to them.[3c-e]

Destructive interference resulting from sideways overlap of two AOs of appropriate shape and orientation forms an antibonding π^* MO.[3c-e] The shapes of these orbitals are decided by the orbitals participating in their formation. The antibonding π^* MO should have two nodal planes; these are the nodal plane mentioned above plus an additional nodal plane resulting from destructive interference of the participating orbitals.[3c-e]

3. Nonbonding Molecular Orbitals (n)

The number of AOs which mix equals the number of resulting bonding and antibonding MOs.[3] If two AOs mix, then two MOs will result --- a bonding MO and an antibonding MO (Figure 1). However, if there are three AOs of the same symmetry and similar energy, then three MOs are formed (a low-energy bonding orbital, a high-energy antibonding orbital, and an intermediate energy nonbonding orbital).[3] AOs whose symmetries do not match, and therefore remain unchanged in the molecule, are also called nonbonding.[3] If more than three AOs are involved, even then the number of AOs will be equal to the number of MOs formed (i.e. bonding, antibonding, and nonbonding orbitals).[3]

Methodology

We compared the ordering and content of material pertaining to AOs and MOs across fourteen[4-11,13-16,18,19] currently used comprehensive introductory organic chemistry textbooks, and two additional recently used ones[12,17] (marked with asterisks (*)). In order to do this, we (A) evaluated the current edition of each textbook[4-18] and (B) compared their presentations and drawings of AOs and MOs, as well as the presentation and drawing orderings.

The same student participation as detailed in our previous publications[20] was used for textbook comparison. A group of undergraduate students, who recently had completed Organic Chemistry I and Organic Chemistry II, each enrolled in an independent study course in order to assist with the project and help formulate the recommendations discussed herein. Over two semesters, about 20 students participated, joining and leaving at different times, with flexibility in their participation. Each student brought "fresh eyes" to the project -- the valuable perspective of a student who was learning the material, rather than the perspective of a professor who had taught the course for years. Each came in at regular intervals, reviewed pertinent sections of each textbook, and offered his/her individual evaluation of each text. The results from the students for each book are compiled and compared in Tables 1-3.

Results and Discussion

Variations in the order, descriptions, and drawings of AOs and MOs are found across these textbooks.[4-19] Some texts had errors, which may be well-meant attempts to simplify the material, but which could nevertheless (1) confuse students who try to supplement their adopted text with a second text or (2) leave students ill-prepared for questions on AOs and MOs in standardized exams, such as the ACS Standardized Exam in Organic Chemistry.[21] Furthermore, recent terminology changes have not been adopted uniformly across these textbooks.

Describing AO versus MO

All textbooks explored herein[4-19] discuss and compare AOs and MOs, but some differ in the number of chapters devoted to the topics (Table 1). Textbooks also differ in how early the concepts are presented, as demonstrated by the chapter number in which AO and MO appear (Table 1, Column 5). Eight texts[4,6, 7,9,10,12,13,14] present these concepts in the first chapter, while three texts[5,16,19] discuss AO and MO in chapter three. Four texts[8,15,17,18] spread the topics across

two chapters, with the first being chapter one for AOs. One text[11] presents these concepts in chapter four.

These textbooks have appropriate figure captions except one text,[11] in which the AO and MO figure captions are missing. This textbook[11] does explain the figures (page 80-101) with in-text descriptions, but figure captions would unambiguously further explain the points (Table 1, Column 7).

Figures in the texts generally correlate well with their corresponding descriptions. Figures should help students visualize the concept, and therefore facilitate understanding it. However, figures in some texts[15,18] are less easily understood than in others (Table 1).

In another text,[10] the description of Figure 1-7 (page 26) mentions p-orbital diagrams, but the figure shows an s orbital. The text describes "the three rules for assigning electrons to atomic orbitals", on page 27 and notes Figure 1-8 as an example, but Figure 1-8 only shows an empty energy level AO diagram. Figure 1-9 in this text provides an example of filled energy diagrams, but the textbook does not provide enough examples of AO diagrams (Table 1, Column 8). This text also describes interaction of atomic p orbitals as MOs in Figures 14-2, 14-7, and

15-4 at pages 581, 590, and 648, respectively. Similarly, five other texts[11-14,16] also label atomic p orbitals as MOs (Figures at pages 147 and 159)[11]; Figures 13.16 and 14.10, pages 597 and 648[12]; Figure 20.2, page 834[13]; Figure 15.4, page 540[14]; Figures 23.5 and 24.1, pages 1206 and 1245[16].

One text[18] (Section 17.9b, page 652) has correct descriptions, but Figure 17.9 describes the interactions of atomic p orbitals of benzene as molecular orbitals, but it does not show MOs. This hinders understanding the types of orbitals represented there. Inconsistent depiction of AOs and MOs in this the section causes the "N" in the column "AO vs. MO differentiation clear" (Table 1, Column 11).

The descriptions of AOs and MOs in two texts[15,18] are not easy to understand. In one[18] (Section 17.9a, page 651), AOs are combined to form a single-colored drawing for the lower energy bonding MO and two separate antibonding MOs. The description in Section 17.9b states "Because each of the six carbon atoms of benzene has a p orbital, six atomic p orbitals combine to form six π molecular orbitals" in referring to Figure 17.9. This instance does not follow previous representations of AOs combining to form MOs. When the six p orbitals combine into the benzene model, the orbitals

Table 1. Atomic Orbital (AO) and Molecular Orbital (MO) Characteristics in Organic Chemistry Textbooks.

textbooks					figures			text			ref
first author	publisher	current edition	pub year	chapter	captions	placement in-text maximizes relevance	in-text description easy to understand	clear definitions of AO & of MO	AO vs MO differentiation included	AO vs MO differentiation clear	
Bruice	Pearson	8	2016	1							4
Hornback	Cengage	2	2006	3							5*
Loudon	Roberts	6	2016	1							6
Solomons	Wiley	12	2016	1							7
Wade	Pearson	9	2016	1,2							8
Klein	Wiley	3	2016	1							9
Vollhardt	Macmillan	8	2018	1			N				10
Clayden	Oxford Univ.	2	2012	4	N						11
Jones	Norton	5	2014	1				N			12
Brown	Cengage	8	2017	1						N	13
McMurry	Cengage	9	2015	1							14
Carey	McGraw Hill	10	2016	2			N	N			15
M Smith	CRC Press	2	2018	3							16
Sorrell	Univ. Science	2	2006	2				N			17*
J Smith	McGraw Hill	5	2015	1			N	N	N	N	18
Karty	W W Norton	2	2018	3			N	N	N	N	19

are still depicted as the author had previously referred to as AOs. The bonding MOs appear as individual AOs instead of MOs. They show no orbital overlap (Table 1, Column 9). One text[15] has difficulty in chapter 2 in describing AO and MO theories, and their respective definitions are not explicitly stated. Although in Section 2.4 an accurate description is referenced, atomic and molecular orbital theories are not restated in Chapter 10.1, which should be the appropriate location.[15] The sections should be revised, and information should be reformatted, in a way that clearly presents the main ideas in simpler labeling directly under the figures instead of only in the text (Table 1, Columns 9 & 10).[15]

The definitions of AO and MO are very clear in some texts[4-11,13,14,16] (Table 1, Column 9), while others[12,15,17,18,19] do not define them so clearly. Color can be more effectively used if AOs and MOs are represented in different colors or different shades of one color (Table 1, Column 10). Students opined that the texts[4-9,11-18] have relevant figures. Most of the textbooks discuss the differences between AO and MO,[4-17] except one[18] which omits the differentiation completely. Figure references in all texts are correct. However, in one,[13] the bottom "cartoon" representation of the "in-phase addition" in Figure 1.21 seems incorrect; the MOs should overlap if the atoms are in-phase as shown in the "computed" representation (Table 1, Column 12). In another text[17] (Section 2.4b, pages 49-50), a clear definition of AO is not given before the term is used to define valence bond theory. Furthermore, the definition of valence bond theory is related to the definition of MO theory, which is not mentioned until almost three hundred pages later (page 307).[17]

In one text[15] (pages 372-373), definitions of AO and MO are introduced in a complicated, alternative approach, which makes the descriptions unclear. While describing one situation, another is introduced in the middle of the sentence. Also, the figure description should be more theory based. Sentences with too many clauses are distracting and difficult for students to follow (Table 1, Column 10), such as, "Recalling from Section 2.4 that the number

of orbitals is equal to the number of AOs that combine to form them, we combine the three 2p AOs, one from each of the three sp^2-hybridized carbons of allyl, into the system of three π MO's shown in Figure 10.2" (page 373).

Describing and Presenting the Concept of Node in AOs and MOs

Characteristics of the description and presentation of AO node and MO node are collated in Table 2. Texts differ in the chapter number in which AO node and MO node are presented. Ten texts[4,7-10,12-15,18] discuss them in the first chapter. Two texts[5,19] present them in chapter three and another text[11] presents them in chapter 4, while the description of node is spread across two chapters in three texts[6,16,17] (Table 2, Column 2). We recommend presenting the definition and discussion of node in one chapter along with the introduction of AO structure, because spreading the discussion across multiple chapters unnecessarily splits this closely related information. Overall, the concept of node is explained clearly in all the books,[4-6,8-18] except one.[15]

The texts also differ in the number of figures used to explain the concepts of AO and MO nodes. Six[4,7,8,10,11,19] use two figures to explain them, while two[12,13] use three figures, and another two[6,9] use four. Four texts[5,15,16,18] use one figure to discuss node, while two texts[14,17] use no figures at all to explain the concept of node (Table 2, Column 4).

In addition to figures, an appropriate description is also required in order to clearly present the concept of node. However, different textbooks use different amounts of text to explain node. It is difficult to judge how many paragraphs are needed to explain the concept of node, but the descriptive text should be enough to explain node characteristics, so that it is clear and does not overwhelm students. Four texts[9,10,11,12] have four paragraphs, while one text[4] uses one and one-half paragraphs. Three texts[5,7,17] explain all properties of a node in one paragraph, while four texts[8,14,15,18] devote less than one complete paragraph to this (Table 2,

Table 2. Descriptions and Presentation of Node in AOs and MOs in Texts.

first author	chapter	# of figures showing node	# of paragraphs discussing node	figure accuracy	node	nodal plane (planar node)	others	ref
Bruice	1	2	1.5				radial node	4
Hornback	3	1	1				spherical node / nodal sphere	5
Loudon	1	4	5				spherical node / nodal sphere	6
Solomons	1	2	1				nodal surface	7
Wade	1,2	4	2					8
Klein	1	4	4			N		9
Vollhardt	1	2	3.5					10
Clayden	4	2	4				spherical node / nodal sphere	11
Jones	1	3	4				spherical node / nodal sphere	12
Brown	1	3	1	N				13
McMurry	1	0	<1			N		14
Carey	1	3	<1		N	N	nodal surface	15
M Smith	3	1	2	N		N		16
Sorrell	2	0	1			N		17
J Smith	1	1	<1			N	node of electron density	18
Karty	3	2	2					19

Column 5).

In one text,[13] Figures 1.12a, 1.14a, and 1.16a (pages 34, 35, and 36) all depict the "cartoon" versions of AOs for sp, sp^2, and sp^3 to be identical, while the computerized versions of these images show differences and only slight similarities that exist among these AOs. The size of the smaller lobe on each "computed" representation decreases as the s character increases in these hybridized orbitals. One text[16] was found to be incomplete with respect to orbital images showing the contributions from different orbitals. Although Figure 3.1 correctly depicts the orbital images and their nodes from wave functions, the shapes of the AO nodes are not shown in a manner that is easy to understand. There are some 2-D versions showing possible shapes for these orbitals but a 3-D depiction would convey a much clearer message (Table 2, Column 6). In one text,[15] (Figure 2.5b) the node is mentioned in the figure, but not in the text (Table 2, Column 7).

The use of different names for node, such as "node of electron density," "nodal surface," "radial node," and "planar node" was found during the study. One text[18] used both terms "node" and "node of electron density" interchangeably, which could lead to confusion (Table 2, Column 9). We recommend using "node" consistently throughout, because "node of electron density" might lead a student to think that a node contains electron density, which is the exact opposite of the fact that the node actually has no electron density. Two texts[7,15] use "nodal surface" in addition to "node" when explaining the area of no electron density, but one text[4] separately defines "radial node." Most texts[4-8,10-13] explain "planar node" or "nodal plane," while six texts[9,14-18] completely overlook this (Table 2, Column 8). In addition to the above-mentioned terms, four texts[5,6,11,12] use the terms "spherical node" or "nodal sphere" (Table 2, Column 9). Explaining nodal plane is important to understanding the shapes of orbitals, so it is recommended that this be included in all textbooks.

Although nine texts[4-6,8-10,12,13,16] present accurate information about node by using merely figures alone, four texts[7,10,15,18] do not have such clarity in node explanation. Similarly, nine textbooks[4,5,7-10,12,13,16] present appropriate

terms for the explanations, while five[6,11,14,15,18] do not. Some books[6,8,11-13] use multiple terms as mentioned above and clearly define and differentiate each term, while others[4,7,10,16,18] use multiple terms, but do not define and differentiate them.

Hybridization

The concept of hybridization is key in understanding the shape and geometry of a molecule. Eight texts[4,6,7,9,10,13,14,18] discuss this concept in the same chapter with AOs, while four texts[8,12,15,17] present it in the chapter immediately following AOs (Table 3, Column 2). Three texts[5,11,16] place hybridization in chapter 3, and one of them[16] splits the discussion into chapters 3 and 5. We recommend that hybridization be discussed in the same chapter with AOs, in order to understand the concept better, at a time when AOs are still fresh in students' minds. All of the textbooks[4-10,12-16,18] used appropriate terms in illustrating hybridization, with the exception of two texts.[11,17] One text[16] states, "The hybridization process is illustrated by the 'blue lobes' for electrons in the 2p-orbitals 'donated' by carbon and the 'red lobe' the electrons in the 2s-orbital".

All textbooks used appropriate figures for explaining hybridization, with accurate captions and text descriptions. Except for one text,[16] all books present the concept in a way such that it is easy for students to understand (Table 3, Column 3). Surprisingly, three texts[11,12,14] do not refer to VSEPR (Valence Shell Electron Pair Repulsion) theory in discussing hybridization, while the others do (Table 3, Column 4). VSEPR theory is a model used to predict the geometry of individual molecules from the number of electron pairs surrounding their central atoms.

Aromaticity vs Pericyclic reactions

Both AOs and MOs play a central role in explaining aromaticity as well as stereochemistry in pericyclic reactions. MO theory also enables understanding aromaticity and predicting the stability of aromatic systems. Therefore, it is important to compare across textbooks for presentation of aromaticity and pericyclic reactions with AOs and MOs. Aromaticity is explained before pericyclic reactions in nine texts,[4-6,11-14,16,18] while the reverse is true in six texts.[7-10,15,17] Aromaticity should be discussed before pericyclic reactions, because it will help understand the transition states of pericyclic reactions. If the transition state has a continuous flow of electron density, a planar geometry, and a (4n+2) number of electrons, this will satisfy the requirements for the transition state to be aromatic and more stable than expected otherwise. It is important that students know what imparts stability to a cyclic conjugated system of continuous flowing electrons. Therefore, we recommend presenting aromaticity before pericyclic reactions and conjugated systems. One text[10] only discusses electrocyclic reactions in the pericyclic reactions chapter.

The texts range widely in the number of chapters separating aromaticity and pericyclic reaction discussions. One text[8] presents aromaticity immediately followed by pericyclic reactions (0 chapters apart), two texts[13,16] separate them by two chapters, one text[5] by five, one text[12] by six, one text[18] by nine, one text[6] by eleven, one text[14] by fourteen, one text[4] by nineteen, and one text[11] has a twenty-five-chapter separation. Furthermore, one text[16] chapter on pericyclic reactions focuses on sigmatropic rearrangements only.

Eleven texts[5,7-10,13-18] explain aromaticity in the benzene and aromatic compounds chapter. Eight texts[4-6,11,12,14,16,18] discuss pericyclic reactions separately from benzene and conjugated π systems, while six texts[7-10,15,17] discuss it with the conjugated pi-electron systems. Only one text[11] discusses pericyclic reactions in two chapters while the other books discuss the topic in one chapter either alone or with π-conjugated systems. One text[13] presents pericyclic reactions with other C-C bond formation reactions, which include charge-controlled reactions (electrophilic additions to conjugated dienes) in addition to orbital-controlled pericyclic reactions (electrocyclic, cycloaddition, and sigmatropic reactions).

Table 3. Hybridization Characteristics in Textbook.

first author	hybridization			
	chapter	easy to understand	reference to VSEPR theory	ref
Bruice	1			4
Hornback	3			5
Loudon	1			6
Solomons	1			7
Wade	2			8
Klein	1			9
Vollhardt	1			10
Clayden	4		N	11
Jones	2		N	12
Brown	1			13
McMurry	1		N	14
Carey	1,2			15
M Smith	3,5	N		16
Sorrell	2			17
J Smith	1			18
Karty	3			19

Conclusion

Comparing fifteen currently used comprehensive introductory organic chemistry textbooks reveals discrepancies, variations, and inconsistencies in their presentations, figures, and discussions of AO and MO concepts. Recommendations with appropriate and reasonable justifications have been provided in order to remedy these shortcomings. In order to facilitate students learning these concepts, the recommendations are pedagogically useful, consistent, descriptive, and in agreement with research literature.

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