

Orbitals: Some Fiction and Some Facts

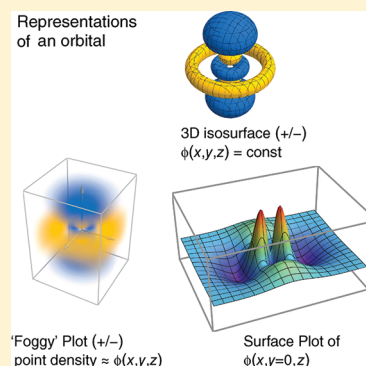
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S Supporting Information

ABSTRACT: The use of electron orbitals in quantum theory and chemistry is discussed. Common misconceptions are highlighted. Suggestions are made how chemistry educators may describe orbitals in the first and second year college curriculum more accurately without introducing unwanted technicalities. A comparison is made of different ways of graphically representing orbitals. The connection of orbital delocalization and electron delocalization is explained by using graphical representations of canonical and localized molecular orbitals for water, benzene, and linear hexatriene.

KEYWORDS: First-Year Undergraduate/General, Second-Year Undergraduate, Upper-Division Undergraduate, Interdisciplinary/Multidisciplinary, Physical Chemistry, Misconceptions/Discrepant Events, MO Theory, Quantum Chemistry



1. SOME OF THE ISSUES WITH ORBITALS

This article has been written to draw attention to some common misconceptions about electron orbitals in many-electron atoms and molecules. By the time when chemistry students get to learn details of what orbital theory is all about, they have been exposed to orbitals, qualitative aspects of molecular orbital theory, and orbital energy diagrams, for several years already. The author of the present article perceives this as problematic. The consequence of widespread misconceptions about orbitals and orbital energies is, in more innocent cases, the incorrect use of language in scientific discussions keeping these misconceptions alive. In more problematic cases, there are theoretically unfounded expectations as to how a system might behave upon ionization, electron attachment, or as a result of an electronic excitation, or whether orbitals and orbital energies can be measured. The remainder of this section furnishes some examples. Subsequently, suggestions are made as to how educators may introduce orbitals to chemistry students more accurately. Further, small changes in the descriptive language used in association with orbitals are suggested that might be helpful in avoiding misconceptions.

The author regularly teaches a course about molecular orbital (MO) theory at the advanced undergraduate level. One of the homeworks is writing an essay about orbital models, with a focus on the hierarchy of approximations. Many students have opened their essays with a statement such as 'Molecular orbitals are introduced in quantum theory to describe chemical bonds. For example, the molecular orbitals of H_2 are formed when the two s orbitals overlap and form bonding and antibonding combinations.' Such a 'linear combination of atomic orbitals' (LCAO) is not the essence of MO theory. LCAO is a narrowly defined and suboptimally named approximation of orbital theory that is unrelated to the necessity of having to introduce orbitals in

theoretical chemistry in the first place. Students who focus too narrowly on such a minimal basis approximation of orbital theory often tend to overlook entirely the approximate nature of orbital theory. It is fortunate for chemists that orbitals carry so much information about bonding, but if we were able to solve the Schrödinger equation exactly, we would perhaps be introducing first-year college students in a different way to the quantum theoretical foundation of chemical bonding.

In the same course, an exam problem has frequently been the following:

In a chemistry textbook you find an orbital diagram like the one in Figure 1. The author writes about a (hypothetical) system with 4

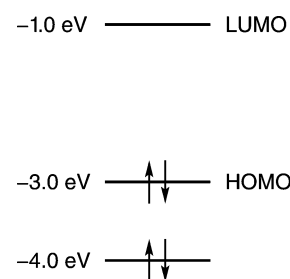


Figure 1. Example of an orbital energy level diagram.

electrons: "From the energy diagram we can see, by adding the energies of each electron, that the total valence energy of the molecule is -14 eV."

(a) Within the context of how molecular orbitals have been introduced and defined in our course, explain what an orbital

energy is. Can one measure an orbital energy? How does one calculate, from theory, the total energy of a molecule? (b) The author makes three mistakes here. One has to do with a contribution to the energy that was completely overlooked. Another has to do with a common misconception about orbital energies. The third mistake has to do with the Pauli principle. Explain what is wrong with the statement. (c) Draw a sketch of what happens to the MO diagram shown above when the system undergoes an excitation (HOMO to LUMO). The context mentioned in the problem is Hartree–Fock (HF) theory,¹ and specifically the so-called canonical orbitals that are usually the results of HF calculations. Basics of Kohn–Sham Density functional theory (DFT)^{2,3} are also introduced in the course. By attending the class the students should be well prepared to answer these questions since similar examples are discussed during the lectures. See ref 4 for possible answers.

Typically, students who do not struggle with the mathematical aspects of quantum theory also gain enough insight into more qualitative aspects of orbital theory and answer such questions correctly. Likewise, these students' homework essays on molecular orbital theory tend to be concise, to the point, and for the most part correct. Unfortunately, students who struggle with the mathematical or physical aspects of quantum theory often do not realize that there are important qualitative aspects of orbital theory that one can know without being able to calculate certain integrals. By attempting to answer the questions above, for which no calculations are needed, less mathematically adept students tend to fall back to the qualitative orbital theory from their first and second year in college. The resulting answers to the exam questions are often as confusing as the hypothetical statement from the hypothetical textbook which, short as it is, involves rather common misconceptions about orbital energies ("the sum of orbital energies is the total energy", "orbitals and electrons are interchangeable terms") and ignores the nuclear repulsion and possibly the presence of core orbitals. The same students who have trouble answering part (b) of the above sets of questions typically also have difficulties distinguishing between orbitals and the many-electron wave function, and between orbital energies and the total energy, in the homework essay and in related exam problems.

Orbitals are standard fare in introductory college chemistry classes. Since the mathematical and physical background is not provided, the discussion of orbitals rests on a pictorial representation. An issue is then the graphical representation of orbitals. To many chemistry students, an orbital seems to be an arrangement of colored 'balloons' in which one or two electrons 'bounce around'. The image is, perhaps unintentionally, reinforced by introductory chemistry textbooks such as one recently inspected by the author,⁵ where colored isosurfaces of the π MOs for benzene are shown along with a figure caption stating 'Each of these bonding pi MOs contains a pair of electrons' (emphasis by the author). Moreover, many textbooks oppose 'MO descriptions of bonding' with—presumably more intuitive—'valence bond descriptions of bonding' with the latter usually simply being a computer graphics equivalent of drawing Lewis structures.⁶ What is often not told is the following: Provided that MO theory describes the electronic structure about right, the result of a quantum chemical calculation contains information that can be used to draw a Lewis formula.⁷ There is no need to provide Lewis structures or atom valence shell hybridizations as input for *ab initio* calculations. Quite the contrary: such information can be extracted from the results of a quantum theoretical calculation, at least to some extent given by how well qualitative chemical

bonding concepts and the quantum theory of molecules can be mapped onto each other. Often, the bonding patterns are visible in the orbitals, in particular when localized orbitals are generated. In cases where a Lewis formula is not self-evident, a molecular orbital calculation or some other type of quantum chemical computation can be used for guidance.

Orbitals that are calculated from MO theory are normally delocalized by construction (canonical orbitals). This does not mean that the electronic system in every molecule is delocalized. Many chemistry textbooks use the delocalized representation of the benzene π MOs in a discussion of delocalization. The implication is that the delocalization of the π MOs of benzene indicates delocalization of the electronic system.⁸ By the same argument, however, the O–H bonds and one of the oxygen lone pairs of H₂O would be considered as delocalized because the relevant orbitals computed from all flavors of MO theory are delocalized over the whole molecule. This conclusion is not correct. There are ways to obtain information about delocalization from quantum chemical calculations. However, this is not done by generating graphical representations of MOs that, by construction, extended over many atomic centers.

Section 2 addresses some common misconceptions about orbitals. The Supporting Information (SI) provides additional theoretical details that may be of interest to readers who would like a synopsis of the technical background of Section 2. It is the hope that students can be better prepared to avoid common misconceptions related to orbitals. To this end, Section 2 lists a number of issues that should be clarified already in beginner's courses whenever molecular orbitals are mentioned. Ideally, these concepts are then reiterated in higher level courses, perhaps once on a qualitative basis and once in the context of the theory at a more technical level such that one can discuss the relevant equations. Section 3 briefly touches upon aspects of graphical representations of orbitals. The question of localization and delocalization is addressed in Section 4. Concluding remarks can be found in Section 5.

2. FACTS ABOUT ORBITALS THAT CHEMISTRY STUDENTS SHOULD KNOW

Some or all of the following concepts should be communicated to chemistry students at the earliest point when orbitals are invoked. There is no Math required. The list is likely incomplete and the author hopes that others will provide additional examples. Herein, the term 'orbital' refers exclusively to electron orbitals, that is, functions of a single electronic coordinate that are used to describe the electronic structure of many-electron atoms and molecules. It is assumed that the electronic and nuclear motions can be separated, and nuclear motion is not further considered in this article. For further details please consult the Supporting Information.

(i) *Orbitals represent an approximation to reality:* Orbitals are used to construct approximate many-electron quantum mechanical wave functions which, in turn, describe the electron distributions and other properties of molecules. This is done as a first approximation because an exact analytic solution is not possible and a sufficiently accurate numerical solution is not easy. A simple electron-label permutation antisymmetric wave function constructed from a minimal set of orbitals implies that the electrons described by this wave function do not move in a concerted (correlated) fashion, which is not true in reality.¹⁰

(ii) *Orbitals are primarily a convenience, but many chemists also like the orbital approximation for its interpretative power:* In numerous applications, it has been found that approximate

molecular orbital wave functions and orbital-based Kohn–Sham DFT provide suitable, sometimes quite accurate, quantum mechanical results. One may therefore use orbitals to develop an understanding of chemical bonding and molecular structure in terms of uncorrelated ‘quasi electrons’. Generally, chemists have grown very fond of this concept. Orbitals also make for nice intuitive looking computer graphics (see Section 3) that have relevance in the context of structure, reactivity, and spectroscopy, even if the precise meaning is not rigorously discussed.

(iii) *LCAO is not the essence of orbital theory*: Calculations with finite basis sets approximate molecular orbitals as linear combinations of a finite number of preselected functions. This approximation is often called ‘linear combination of atomic orbitals’ (LCAO). The ‘atomic orbitals’ used in calculations with atom-centered basis functions usually are not actual atomic orbitals in the sense that they are not orbitals obtained from wave function calculations for many-electron atoms. They are atom centered functions with an exponential or Gaussian radial dependence suitable for ‘atoms in molecules’, multiplied with s , p , d , f , and so on, angular momentum functions. By using a relatively small number of such functions, one may gain much chemical insight without processing a huge set of data. Therefore, chemists have grown very fond of such approximations as well. However, it is not correct to state that the essence of MO theory is the formation of MOs by taking linear combination of AOs (LCAOs). This is another approximation on top of the orbital model itself, and the ‘AOs’ are not really the orbitals of atoms.

(iv) *Orbitals and orbital energies are not observable*: Strictly speaking^{11–13} the orbitals produced by molecular orbital calculations cannot be observed,^{14,15} despite frequent statements in the literature (for example, see refs 16–19). Likewise, orbital energies are not observable in a strict sense.²⁰ This does not preclude measurements of one-electron differences defined via an experimental procedure^{18,19,21} which may also correctly be called orbitals, but this distinction should be drawn clearly. Further, instead of making statements such as ‘This molecule has three occupied π orbitals that look as follows: ...’, it would be more appropriate to explain (at least once) ‘Calculations have shown that the electronic structure of this molecule, and many of its observed properties, are reasonably well described within the orbital approximation. The orbitals were chosen such that three of them have π symmetry.’²² Graphical representations of these orbitals look as follows ...’ (more on the graphical aspect in Section 3). Claims of ‘measurements of orbitals’ (which may be phrased in a variety of ways) should state clearly what exactly was measured. It also should be stated explicitly how and at what level of theory the measured quantities relate to, for instance, orbital densities or orbital energies. Such research papers often feature very interesting science. When they are discussed in courses, it is important to mention that the chemist’s orbitals or orbital energies relate in an approximate sense to what was measured.

(v) *‘Orbital occupation’ can be a misleading term*: There is danger that ‘occupation’ conjures an image of orbital shapes ‘containing electrons’. The term ‘orbital occupation’ is potentially misleading; what it means is how often a certain spatial one-electron function is used in the construction of a simple many-electron wave function. The limitation of using one spatial orbital not more than twice has its origin in not being able to distinguish the electrons, and the strange requirement of electronic and other *fermionic* wave functions having to change sign when two electron labels are switched. One should therefore mention that ‘orbital occupation’ is a phrase that has a

well-defined meaning in quantum theory which is subtly different from referring to an electron filling a certain space. Students should be told that ‘orbital occupation’ may create in their mind a somewhat misleading picture of a shaped region of space filled with (occupied by) an electron cloud. At a more technical level, the quantum chemical concept of *population* may be invoked which quantifies a share of the total number of electrons associated with a given one-electron function.

(vi) *Orbitals are not electrons*: As a consequence of the *Pauli principle*, all (‘occupied’) orbitals describe all electrons simultaneously. Electrons are indistinguishable, so it makes no sense to say ‘ π electron’. Researchers and educators (including the author) use phrases like this, or ‘core/valence electrons’, frequently because it is tedious to always use precise language. But they should use them while knowing better. One may mentally replace ‘orbitals’ with noninteracting ‘quasi-electrons’ described by some one-particle wave functions. It is then sometimes necessary to be clear about whether a statement refers to one of the quasi-electrons used to theoretically describe chemical bonding and other phenomena of the system of interest, or to the physical electrons where it is not allowed to refer to a particular one.

(vii) *The orbitals for a molecule are not unique*: Any linear combination within the set of orbitals for a system, orthonormal or not, gives the same wave function. Thus, any such linear combination gives the same energy and the same observable properties other than the energy (not necessarily the same equations for the energy and other properties, which tend to be more compact with orthonormal orbitals sets). That does not mean, however, that the set of orbitals is arbitrary. In Hartree–Fock theory, in Kohn–Sham DFT, and in semiempirical orbital theory, a set of orbitals is determined that gives a wave function or electron density with the lowest possible energy expectation value.²³ The canonical orbitals usually shown in research articles and textbooks are a particular choice. The canonical orbitals are eigenfunctions of the so-called Fock operator (see Supporting Information). Spatially localized sets of orbitals can be constructed that are often better suited to describe individual bonds or local properties.

Further, the σ/π partitioning of orbitals associated with multiple bonds is not unique. An example is shown in Figure 2. The two equivalent ‘banana bonds’ represent an equally valid description of the C=C double bond by two orthonormal orbitals as does the usual set of σ and π orbitals. In a π -complex of a metal with ethene, it is then essentially one of the ‘banana orbitals’ that is donated to the metal. The orbitals shown in research articles and textbooks are a particular choice often selected to emphasize symmetry differences, thereby allowing other simplifications in the treatment of bonding. When comparing different systems, such as a molecule and its cation, or a molecule in its ground state and an excited state, the canonical orbitals have some distinct advantages related to the approximately observable eigenvalues (see below). Another feature of canonical orbitals is that they can be constructed to transform as symmetry species of the molecule’s point group. When linear combinations of canonical orbitals are formed to obtain localized sets, these global symmetry properties are then typically replaced by local symmetry properties. For instance, under a symmetry operation, one localized orbital may transform into another, equivalent, localized orbital.

(viii) *The sum of the orbital energies is very likely not the total electronic energy*: In *ab initio* theory, the equations that are used to determine the orbitals afford electrostatic repulsion terms of each orbital with every other ‘occupied’ orbital. This repulsion is therefore included in the orbital energy, along with the kinetic energy and nuclear attraction for the orbital.²⁴

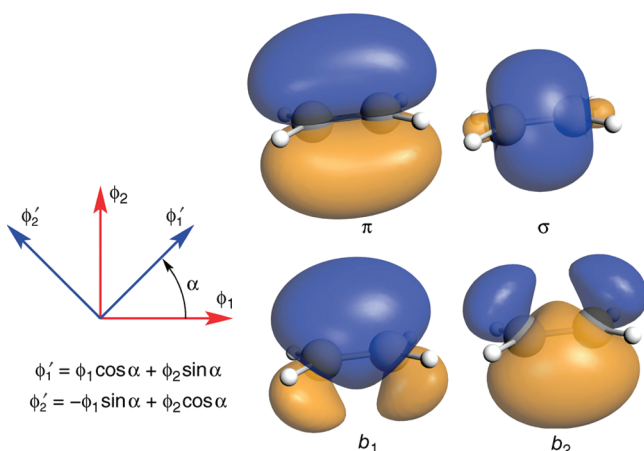


Figure 2. Representation of two orthonormal orbitals as two orthogonal vectors of unit length. Rotation by an angle α gives an alternative set of orthonormal orbitals without changing the wave function. Any other pair of distinct vectors in the same plane can also be used. The example shows isosurfaces (± 0.03 au, B3LYP/DZP//BP/DZP, see Section 3) for a set of C–C bonding σ and π orbitals of ethene. Also shown are linear combinations with $\alpha = 45^\circ$ representing two equivalent 'banana bonds' $\phi_1' = b_1$ and $\phi_2' = b_2$. Note that the orbital phases are arbitrary.

Orbital energies reported in contemporary research papers are most likely of this type, that is, including orbital repulsion energies. The energy expectation value calculated from an approximate determinant wave function (HF theory) or from the orbital partitioning of the density (in DFT) includes, rather intuitively, electrostatic repulsion terms between each unique pair of orbitals.²⁷ When adding the orbital energies, the orbital repulsion energies are counted twice. In the exam problem mentioned in Section 1, students need to realize that the hypothetical textbook author assumes that the sum of orbital energies is the total energy, although the former is missing the nuclear repulsion and double counts the orbital repulsion.

As an example, Walsh diagrams^{28–30} are used to deduce the overall stability of small molecules from a sum of orbital energies as a function of some bond angle. As in the hypothetical textbook example of Section 1, the nuclear repulsion is ignored and the electron repulsion is double-counted. For bond angle changes, the trends in the electron repulsion can be similar to the trends in the nuclear repulsion. The predictive value of the Walsh model then rests on the cancellation of two terms, if one considers the orbital energies to have properties like those calculated from Hartree–Fock theory or Kohn–Sham DFT. The articles by Walsh do not specify directly if the orbitals are supposed to come from such theories. Semiempirical one-electron theories such as (extended) Hückel theory are different in nature because there is no effective electron–electron repulsion and the approximated electronic energy is the sum of the orbital energies. This might be among the reasons for the remarkably successful application of Hückel theories to many problems in chemistry.³¹ The orbital energies of the Walsh diagram are perhaps also best understood in this semiempirical one-electron sense. See also ref 49.

(ix) *Orbital energies change when 'occupations' change:* Because of the fact that in *ab initio* theory the orbital energies include repulsion terms with all other orbitals, it means that whenever the electronic structure is modified, such as by 'changing occupations' (which, accordingly, means: removing, adding, or substituting orbitals when constructing the many-electron

wave function), these repulsion terms change. In the exam problem mentioned in Section 1, the students are supposed to indicate that the orbital energies change when they change the occupations to create an excited configuration.

The result of changing orbital occupations on the total energy can sometimes be difficult to predict. For instance, for many *free, neutral*^{32,33} transition metal atoms, the orbital configuration leading to the lowest total energy corresponds to a $(n-1)d^{g-2}ns^2$ instead of $(n-1)d^{g-1}ns^1$ configuration (with n being 4, 5, and 6, for the first, second, and third transition metal row, respectively, and g the group number). This is despite the fact that the orbital energy of ns in the more stable configuration is above those for the occupied members of the $(n-1)d$ shell. This apparent paradox has been explained by Melrose and Scerri,³⁴ see also ref 33. In a mid term exam of a course taught by the author, a class of about 20 students was given simplified equations for the orbital energies and the total electronic energy for first row transition metal $3d^{g-2}4s^2$, $3d^{g-1}4s^1$, and $3d^g4s^0$, configurations. The problem was set up to reproduce numerically the situation discussed in refs 33 and 34, where for a more stable $3d^{g-2}4s^2$ configuration, the $4s$ orbital energy is *above* the orbital energy for the $3d$ set. Most students calculated the orbital and total energies correctly, but half of the class then drew the orbital diagram with the $4s$ level below $3d$ despite their own numerical data indicating otherwise. Some students did not trust their calculations, but others stated that it simply *had* to be this way.

(x) *The orbital energy 'ladder' is not rigid:* Continuing from the previous point, in educational material the orbital energy 'ladder' of an atom or molecule is often implicitly treated as a fixed internal set of quantized energies (sometimes with the understanding that what determines the stability of the system is the sum of these energies for 'occupied' orbitals). As we have seen, the positions of the rungs of the ladder depend on many things. The mental image, rather than a stable metal or wooden ladder, should be that of a soft rope ladder where the shape stretches and the rungs move as someone climbs up.

(xi) *Almost any function of x, y, z can be an unoccupied orbital:* When calculating orbitals by using basis sets, there are typically more orbitals generated as needed to construct a wave function determinant. Most of the algorithms to solve MO equations generate as many orbitals as there are basis functions. One says: 'the calculation also yields 'unoccupied' orbitals'. There is nothing special about these in the sense that any other function orthogonal to the 'occupied' set is by definition an unoccupied orbital. Experience has shown that specific excess linear combinations resulting from atom-centered basis set expansions in molecular ground state calculations can be useful to construct approximate wave functions for excited states. Other functions that would be suitable, for example, to describe electronic polarization by an external field or by another molecule might not be obtained in the same way. In this sense, some unoccupied orbitals are suited to describe selected properties of a molecule better than random functions that are different from the set of occupied orbitals. Antibonding character of such excess orbitals typically results in large kinetic energies compared to orbitals that have smoother shapes (i.e., fewer sign changes).

(xii) *Orbitals and orbital energies can have physical meaning within a well-defined context:* Orbital energies and orbitals themselves²¹ can have well-defined physical interpretations, but one needs to be careful not to mix them indiscriminately.³⁵ For example, in Hartree–Fock theory, the energies of occupied orbitals are approximations for ionization potentials (IPs, upon

changing the sign of the orbital energy). This is often referred to as Koopmans' theorem; for an in-depth discussion see, for example, ref 37. Likewise, upon sign change, the energies of low lying unoccupied orbitals can be shown to serve as (somewhat poor) approximations for electron attachment (EA) energies. The occupied–unoccupied Hartree–Fock orbital gaps are not approximations of excitation energies. The lowest excitation energy is the fundamental gap, IP–EA, plus the negative binding energy of the quasi electron–hole pair. Hartree–Fock orbital gaps are therefore typically larger than excitation energies. Kohn–Sham DFT also makes use of orbitals, but in a very different spirit than Hartree–Fock theory. In DFT, the HOMO energy is formally identical to $-IP$ (with the exact functional). DFT calculations with approximate functionals may give HOMO energies that are very different from the negative IP unless the functional has been designed to produce a match. For a discussion and relevant references, see ref 38. Even with the elusive exact functional, in DFT the LUMO energy is not related to an electron attachment. Rather, in DFT the orbital gaps are zeroth order approximations for excitation energies. In particular, when it comes to the meaning of the LUMO, in orbital theories such as Hartree–Fock or Kohn–Sham DFT with approximate functionals one cannot have it both ways: either the orbital energy is suitable for describing how the energy changes when an extra electron is attached, or it is suitable to estimate how the total energy changes upon an electronic excitation. An illustrative, if somewhat pathological, example is the metal complex ion $(Co(en)_3)^{3+}$ which we investigated recently.³⁹ The DFT HOMO–LUMO gap was about 2.5 eV, close to the experimentally observed energies for the ligand-field transitions in the UV–vis spectrum, whereas the Hartree–Fock orbital gap was about 17 eV.

(xiii) *Orbital energy diagrams are usually computed:* The author has often perceived a sense of student frustration with orbital energy diagrams. How can they know the ordering of energies in all but the simplest cases? The short answer is: without

experience they cannot. It needs to be firmly established that orbital energy level diagrams are in principle the outcomes of quantum chemical computations. A researcher or educator can often draw a qualitatively correct orbital diagram for a molecule or a metal complex without performing a numerical computation, based on experience with the results of such computations that has been accumulated over decades. Students should be told this explicitly.

(xiv) *Lewis structures, or atomic hybridizations, are not needed as inputs for *ab initio* calculations:* If a molecule is adequately described by a simple Lewis formula, this often means that relatively low-level molecular orbital calculations describe the properties of the molecule qualitatively, and often semiquantitatively, correctly. It is then possible to extract information about bonding, hybridization, and so on, from the results of such calculations. For example, localized MOs (see Section 4) may be considered as a quantum mechanical analog of Lewis' covalent bonds and lone pairs.⁴⁰ There are other methods to extract bonding information from quantum theory, such as Bader's analysis,⁴¹ that do not rely on orbitals.

3. GRAPHICAL REPRESENTATIONS OF ORBITALS AND THE QUESTION OF DELOCALIZATION

This section briefly summarizes different approaches to generating graphical representations of orbitals. The problem, shared with every field of science or engineering where volume data has to be rendered, is that atomic and molecular orbitals are functions of three variables.⁴² Therefore, 'plotting the orbital' in the conventional sense would mean that one needs a four-dimensional coordinate system to generate the plot, one dimension each for x , y , z , and one more axis, orthogonal to the other three, for $\phi(x, y, z)$. What we *can* plot is at best a projection of a three-dimensional object onto a two-dimensional surface of paper or onto a computer screen. A reduction of variables is therefore necessary.

Figure 3 displays several different alternative graphical representations of the same $4d_{z^2}$ hydrogen atom excited state

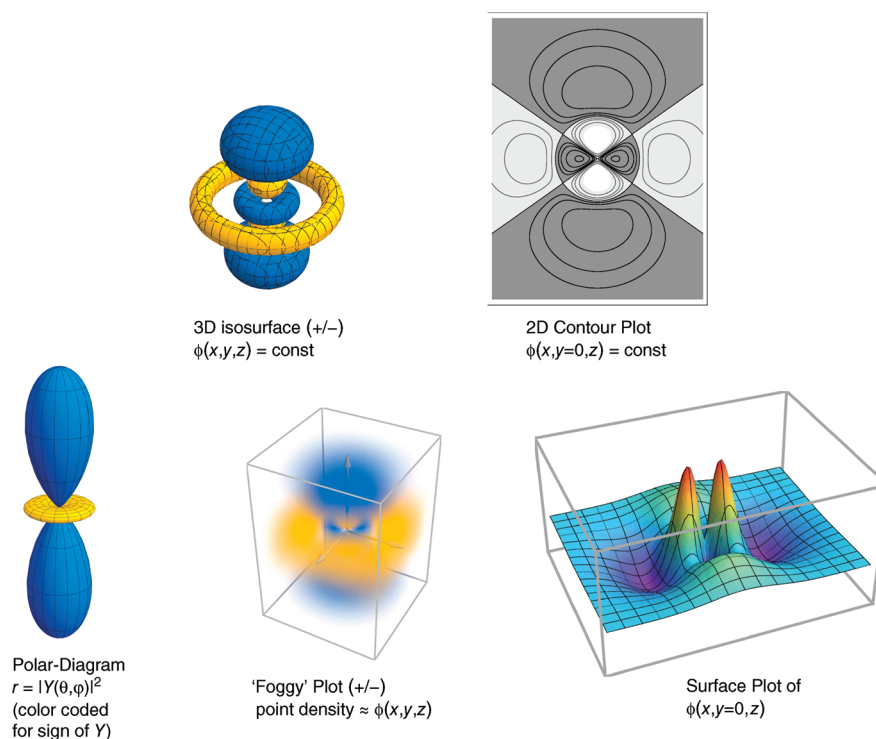


Figure 3. Different graphical representations of a $4d_{z^2}$ hydrogen atomic orbital denoted as $\phi(x, y, z)$ or $\phi(r, \theta, \varphi) = R(r)Y(\theta, \varphi)$.

wave function. Similar looking functions may be generated in quantum chemical calculations of atoms with occupied 4f shells, or be used as polarization functions (for instance, for transition metal d shells in metal complexes). The most common way to display an orbital is by showing differently colored or shaded three-dimensional (3D) isosurfaces for positive and negative orbital values. For atomic orbitals without radial nodes, lobes with different colors or shading indicate different signs of the orbitals due to nodes in the angular functions. For orbitals with additional radial nodes, in isosurface plots, one may obtain separate sets of surfaces for the function inside and outside of the radial node (depending on the chosen isosurface values). For the $4d_{z^2}$ orbital in Figure 3, the radial node creates an inward-outward 'nested' set of the familiar d_{z^2} shapes in the isosurface and contour plots. The isosurface values for such 3D plots may be chosen such that if $\phi^*\phi$ is integrated over the volume enclosed by the surfaces, a set value is obtained⁴³ (e.g., 0.9 corresponding to 90% of the orbital's density). However, this is rarely done; in practice, a fixed isosurface typically on the order of 10^{-2} au is conveniently chosen. It is important to mention in class that enclosing 90% or any other fraction of the density does not determine the general appearance of the plot. For instance, one can choose a box or a sphere and adjust the size such that 90% of an orbital's density is enclosed in the volume. Obviously, this does not mean that all orbitals look like spheres or rectangular boxes. Usually, the 'orbital shape' is the shape of the isosurface. Orbital shapes shown in the literature are sometimes rather poor sketches of actual AO isosurfaces and more closely resemble polar diagrams (see discussion below).

For planar molecules, it can be more advantageous to use a two-dimensional (2D) contour plot of a slice of the orbital because it reveals more detail. Similar information is conveyed in the plot of the slice in a 3D coordinate system ('surface plot'). The relation between these graphical representations is comparable to that between a map and a postcard image of a mountain range. As with regular maps, the 2D contour plot is preferred over the surface plot if detailed information is needed. Compared to a single 3D isosurface, the 2D contour plot shows more clearly the radial dependence of the orbital.

Polar diagrams are useful only to visualize the angular dependence of one-center functions such as AOs which may be written as a product of radial and angular functions $\phi = R(r)Y(\theta, \phi)$. A surface is drawn such that the distance r of the origin to a point (r, θ, ϕ) on the surface is proportional to the absolute value, or the square, of the angular function. There is no radial information contained in polar plots, although the image may misleadingly suggest otherwise.

The center of Figure 3 shows what may be called a 'foggy plot'. The density of points, or their opacity, is highest where the orbital function has large values, resembling regions with more or less dense fog. The image conveys the spatial fuzziness of orbitals better than the isosurface plot, and is not as easily mistaken for the aforementioned 'balloon in which electrons bounce around'. However, the fuzziness of the plot also makes it less convenient for orbital visualizations in research papers. The author recommends the juxtaposition of isosurface and 'foggy' plots when orbital graphics are first shown to students.

4. LOCALIZED OR DELOCALIZED?

The final topic of this article is the question of electron delocalization and its relation to orbital localization. As pointed out above, once the orbitals for a system are calculated, the same

wave function is obtained with linear combinations of these orbitals. That means one can choose orbital linear combinations that are spatially localized. There are many different criteria available for constructing such linear combinations.⁴⁴ We show here localized MOs (LMOs) obtained from a method introduced by Weinhold and co-workers.⁴⁵ LMOs of similar appearance can be obtained with other localization methods. Density functional calculations were performed for water, benzene, and linear hexatriene, using the Amsterdam Density Functional package (ADF)⁴⁶ with the B3LYP/DZP//BP/DZP level of theory. DZP is a split valence polarized Slater-type basis.

Figure 4 displays 2D contour plots of selected canonical orbitals and LMOs of the water molecule. The canonical

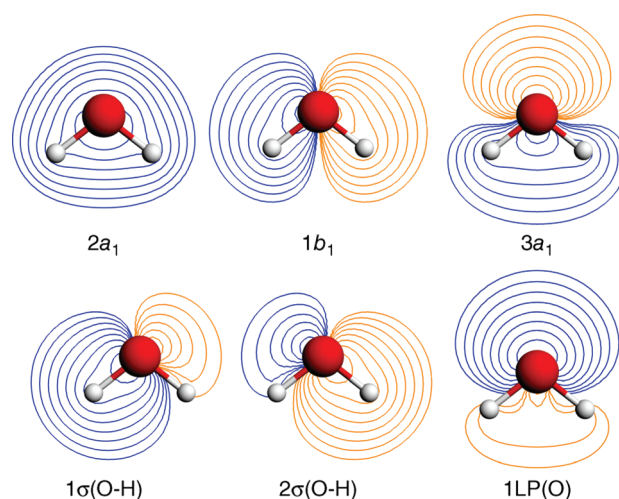


Figure 4. 2D contour plots of selected canonical (top) and localized (bottom) orthonormal molecular orbitals for water (B3LYP/DZP//BP/DZP). Contour values have logarithmic spacing, 10 contours from 0.03 to 1.0 atomic units. Orbitals plotted in the horizontal symmetry plane.

orbitals are delocalized. The LMOs are linear combinations of the three canonical orbitals shown in the figure and can be viewed as representations of the two O–H bonds in the Lewis structure and a lone pair (LP) on oxygen of local σ symmetry. The other lone pair is of local π symmetry (b_2 in the C_{2v} point group of water) and already localized in the canonical set because there are no π type bonding contributions for O–H.⁴⁷ The small size of the water molecule causes the O–H bonding LMOs to have rather pronounced contributions (orthogonalization 'tails') outside of the O–H bonding regions in order to ensure mutual orthogonality on each other and other water orbitals.

Figure 5 displays 2D contour plots for some of the canonical and localized molecular orbitals obtained for hexatriene and benzene. Both sets of canonical π orbitals are delocalized over the whole molecule, and so are the sets of canonical σ orbitals (not shown). The localized C–C bonding σ orbitals of both molecules are well localized on two centers, and they show very similar characteristics in both molecules. The set of localized MOs generated by the calculations is orthonormal. Therefore, orthogonalization 'tails' on neighboring atoms are visible in the two-center σ orbitals, but these orbitals would not be considered as delocalized.

The localized C–C bonding π orbitals of both molecules show a significantly larger degree of delocalization than the σ orbitals in the sense that they extend over more than two atomic centers with much larger magnitudes. This delocalization appears to be stronger for benzene than for linear hexatriene.

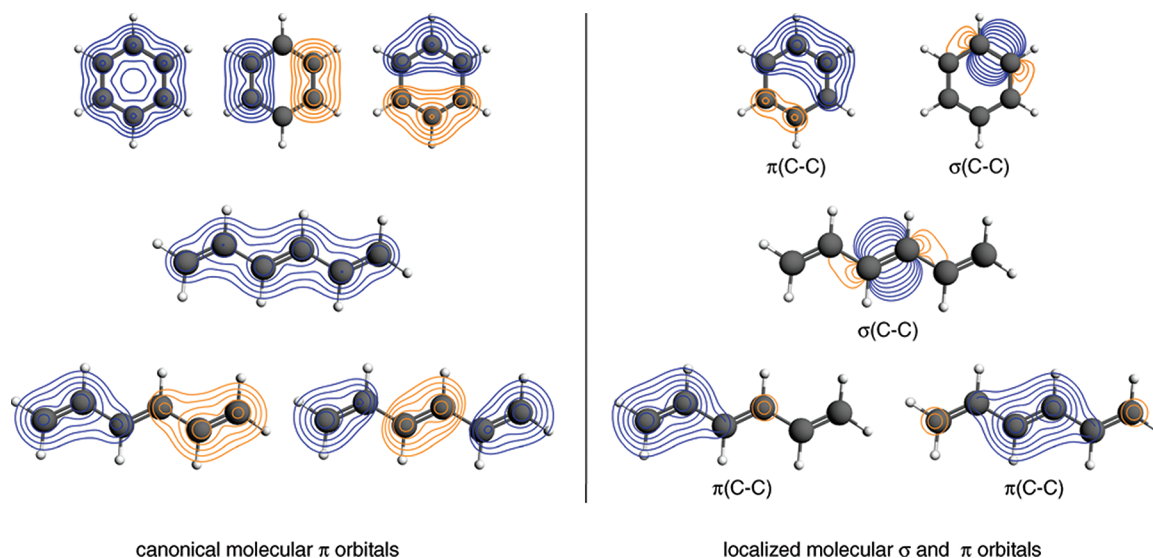


Figure 5. 2D contour plots of selected canonical and localized molecular orbitals for benzene and linear hexatriene (B3LYP/DZP//BP/DZP). For Benzene, the calculation generated three equivalent localized $\pi(\text{C}-\text{C})$ orbitals and six equivalent $\sigma(\text{C}-\text{C})$. Contour values have logarithmic spacing, 10 contours from 0.03 to 1.0 atomic units. σ orbitals plotted in the symmetry planes of the molecules, π orbitals ca. 0.5 Å above the planes.

Degrees of localization can also be quantified. There are a number of theoretical measures for doing so, and different criteria may yield somewhat different answers. Therefore, one should be careful not to overinterpret minor variations. On the basis of the localization measures provided by the Weinhold procedure used here,⁴⁸ the central $\pi(\text{C}-\text{C})$ localized orbital in hexatriene is less well localized than the two terminal ones, in agreement with the visual impression of the contour plots. For benzene, the numerical criteria of the Weinhold procedure indicate that its localized orbitals are less well localized than those of hexatriene. The differences are not visible in the canonical orbitals which are delocalized by construction. To summarize: the results from the orbital localizations show that hexatriene and benzene exhibit a significant degree of delocalization. Which one of them is more strongly delocalized may depend on the criterion used to define 'delocalization'. Irrespective of differences between the chosen criteria, quantum calculations provide ways to assess if a system is delocalized, but typically not by comparing sets of canonical orbitals. An indication for delocalization is if the orbitals of a system cannot be localized well.

5. CONCLUDING REMARKS

Orbitals are ubiquitous in chemistry. Many college students acquire in their first years certain qualitative concepts about orbitals such as 'orbitals contain electrons', 'molecular orbital theory describes the electronic structure accurately but Lewis structures are related to valence bond theories', ' π electrons and π orbitals are interchangeable terms', 'molecules have fixed orbital energy "ladders" from which the total energy is calculated by adding one-electron energies', 'unoccupied orbitals are properties of a molecule', 'orbital isosurfaces are the same as orbitals', 'STM images display actual orbitals', or 'delocalized MOs always indicate electron delocalization'. Such concepts are misleading at best, and often incorrect, but relatively easy to avoid. Math is not required in order to avoid the misconceptions listed in Sections 2 to 4. It is recommended that in introductory courses, if orbitals must be mentioned, clarifications are provided if the textbook does not mention them explicitly. Without the clarifications, some of the misconceptions are just too intuitive and,

once internalized, may cause leaning impediments in more specialized courses. In closing, the author wishes to emphasize that it would likely be counterproductive, for instance, to abandon the notion of orbital occupation. However, it would be helpful if occupation, when first mentioned, is explained as a word that researchers and instructors use frequently but that it has a somewhat different meaning than what the word suggests. One can then indicate that more of the truth will be revealed in later stages of the curriculum.

■ ASSOCIATED CONTENT

Supporting Information

Additional information about orbital theory. This material is available via the Internet at <http://pubs.acs.org>.

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(4) In a nutshell, among a variety of suitable answers would be the following: (a) orbital energy = eigenvalue of the Fock operator. Not an observable (approximately observable in some cases, see Koopmans' theorem). (b) The author forgot about the nuclear–nuclear repulsion. The author calculates the total energy from the sum of orbital energies, but in ab-initio methods this sum double counts the electron–electron repulsion. The author confuses electrons and orbitals. (c) The sketch should indicate that the orbital energies change when the occupations are changed.

(5) It would not be appropriate to single out an excellent textbook for communicating what the author of the present article perceives as common misconceptions about orbitals. The reader is therefore asked to tolerate that a reference is not provided.

(6) Sometimes, graphical representations of localized molecular orbitals are shown and presented as a valence bond approach.

(7) There is potential for interesting discussions arising from this approach. Which is the 'right' Lewis formula? Is it the one that the chemist would draw intuitively, or the one drawn based on information extracted from quantum theory? For systems with traditional bonding, the results agree amazingly often.

(8) The concept of 'aromaticity'⁹ is deliberately avoided in the context of discussing electron delocalization in this article. The reader is referred to the May 2001 (issue 5) volume 101 of *Chemical Reviews*.

(9) Schleyer, P. v. R. Introduction: Aromaticity. *Chem. Rev.* **2001**, *101*, 1115–1118.

(10) In Kohn–Sham DFT, the claim is that the set of orbitals give the exact electron density and the exact energy, but in practice, the exact energy density functional is not known. However, Kohn–Sham DFT calculations include the effects from electron correlation in an approximate sense.

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(20) Exceptions to this statement are rare. With the elusive exact energy density functional, the Kohn–Sham DFT energy of the highest molecular orbital would be exactly the negative of the ionization potential (IP), the latter being an observable quantity.

(21) Schwarz, W. H. E. Measuring orbitals: Provocation or reality? *Angew. Chem., Int. Ed.* **2006**, *45*, 1508–1517.

(22) If one is pedantic, it is only admissible to say 'π orbital' for linear systems with C_{∞v} or D_{∞h} symmetry where σ, π, δ, φ, ... are proper labels for the symmetry species. We follow the usual convention of identifying π orbitals by their antisymmetry with respect to some actual or approximate global or local plane of symmetry in general molecules that are not necessarily linear, and even only approximately planar in the vicinity of the 'π'-bond. Likewise, a σ orbital is identified by an approximate or actual local cylindrical symmetry.

(23) The idea behind this concept is that the resulting energy is as close to the true energy, by virtue of the variational principle.

(24) The important role of the kinetic energy in chemical bonding has been uncovered long ago^{25,26} but it is often ignored in introductory courses when the nature of the covalent chemical bond is discussed. Moving electronic charge into a shared covalent region of space would raise the potential energy of the bound system. Therefore, the energy rises unless—elsewhere—electronic charge moves into regions with a more strongly attractive potential during a reorganization process. This happens, for example, in H₂ where the covalent bond formation goes along with a contraction of the system perpendicular to the bond direction. This has implications regarding the size of the 'atoms in the molecule'. This contraction in the end causes the overall more attractive potential and lower total energy. The kinetic energy plays a crucial role in all this.

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(35) Some authors see the main value of orbitals in their use as a one particle basis set.¹² Yet, in Hartree–Fock/density functional theory the orbitals are generated to approximate the wave function/density. Ostrovsky pointed out³⁶ that the '[...] same object of a theory cannot simultaneously serve as a basis and as an approximation'.

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