Letter

Comments on "Is It Time To Retire the Hybrid Atomic Orbital?"

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ABSTRACT: A recent contribution to this *Journal* advocates the retirement of hybrid atomic orbitals based on premises such as "significant experimental evidence and theoretical ... indicate that hybrid orbitals do not exist and do not appropriately describe molecular bonding" and the like. Critical analysis, which includes a detailed examination of the photoelectron spectrum of methane, reveals these premises to be ill founded and inconsistent with modern electronic structure analyses. Placed in a modern context, the hybrid orbital concept helps to familiarize students with the methods of working chemists, foster construction of a deeper, more interconnected understanding of chemistry and its connection to the laws of nature, and provides a secure foundation for more advanced chemistry classes.

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In this *Journal*, Grushow recently advocated the "retirement" of the hybrid orbital concept and its removal from the chemistry curriculum.[1] The author's logical structure rests on a number of unsupported premises (P), representative examples of which can be quoted or paraphrased as follows:

- (P1) "significant experimental evidence and theoretical advances...indicate that hybrid orbitals do not exist and do not appropriately describe molecular bonding";
- (P2) "evidence indicates that hybrid atomic orbitals are inappropriate models for the description of electronic energies and electron density within a molecule";
- (P3) "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";
- (P4) "the bonding electrons in methane (or most any other molecule for that matter) simply cannot be properly characterized using a localized electron model".

The ill-founded perception that localized bond descriptions fail to accurately represent electron density distributions persists despite numerous refutations. For example, the "never-ending rivalry" of valence bond (VB) versus molecular orbital (MO) theory has been examined thoroughly, and entertainingly, through the dialogue of Hoffmann, Shaik, and Hiberty.[2] More quantitatively, the book *Valency and Bonding*[3] demonstrates that the strictly localized natural bond orbital (NBO) hybrid orbital formulation of methane *quantitatively* describes the best computed electron density distribution, as represented by one-particle density matrices, with accuracies exceeding 99.95%. Similarly complete descriptions apply to most other simple molecules. Some molecules, such as aromatic and hypervalent species, are easily identified a priori as requiring multiple Lewis structures. With addition of a few simple resonance structures,[4] the description of total density again rises to the near-complete level, as foreseen by Pauling.

It is no surprise that localized orbital descriptions accurately portray electron density distributions. Localized molecular orbitals, such as natural localized molecular orbitals (NLMOs),[5] retain the unmistakably localized hybrid orbital character of their parent NBOs, with barely perceptible "delocalization tails" that reflect subtle adaptations to the specific molecular environment. In describing the overall electron density distribution, NLMOs are *wholly equivalent* to delocalized canonical molecular orbitals (CMOs). (Of course, any *particular* member of the CMO set will differ in shape, energy, and density contribution from any member of the NLMO set, but either set may be chosen according to personal preference to describe the *exact* total electron density distribution of the MO wave function.) There is no basis for favoring delocalized over localized orbitals from the viewpoint of electron density distributions.[6]

Similar remarks apply to other physical observables. Because the density matrices for NLMOs and CMOs are related by unitary transformation, any computed physical properties of the many-electron determinantal wave function are *identical*, despite superficial differences in orbital "localization". This means that delocalized and localized MO treatments must yield identical total dipole moments, total energies, and total energy differences, such as those needed to predict photoelectron spectra (PES) or other ionization and excitation phenomena.[7]

These facts undermine all of the aforementioned premises.[8] Nonetheless, these premises seem to be remarkably widespread and persistent in the chemical education literature, even as computational chemistry methods gain increased prominence in the undergraduate curriculum.[9] Let us therefore examine these unfounded characterizations, and the utility of hybrid orbital descriptions, in the context of Grushow's statement (P4) and accompanying discussion of methane photoionization.

■ METHANE PHOTOIONIZATION

The four C−H bonds of methane are equivalent. Pictured below (Figure 1) are pairs of CMOs, NLMOs, and NBOs
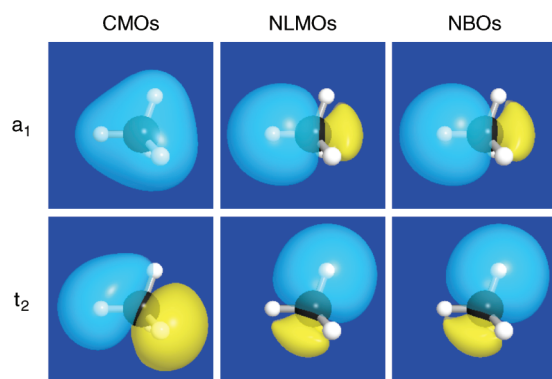
Figure 1. CMOs (left), NLMOs (center), and NBOs (right) of CH_4 showing delocalized CMOs of a_1 (upper) and t_2 (lower) symmetry and localized NLMOs/NBOs for two of the four equivalent CH bonds.

resulting from a density functional theory calculation (B3LYP/ 6-311++G**) at the optimized geometry. In each description, the valence space comprises four filled orbitals (only two of which are shown). Whereas the CMOs have two distinct symmetries and energies (nondegenerate a_1 and triply degenerate t_2), all of the NBOs have the same shape and energy, merely differing in spatial orientation. The same is true of the NLMOs. Visually, the NBOs and NLMOs are indistinguishable. So why does excitation of the valence electrons of CH_4 give rise to two distinct band envelopes (in roughly 3:1 splitting pattern[10]) in the PES?

Despite the simplistic assumptions of early PES enthusiasts (critically discussed by Heilbronner[11]), the photoelectron spectrum does *not* measure the CMO orbital energies of the neutral precursor. Rather, it reports energy differences between the ground state of the neutral molecule and the ground and excited states of the ionized molecule. Thus, we must consider the orbital structure of *both* the neutral and ionized molecules to realistically describe the PES. Ionization is a major perturbation, and there is no guarantee that orbital shapes, energies, or orderings of the neutral precursor closely resemble those of the cation, or that the orbitals of the cation excited states resemble those of the ground state.

With these principles of PES in hand, we can now see how the localized hybrid orbital model accommodates the observation of two bands in the methane PES. Starting from the $(2s)^2(2p)^2$ valence electron configuration of a free-space carbon atom, the perturbation provided by electron-pair bond formation to four incoming H atoms drives "uncoupling" of the two electrons in the 2s atomic orbital to the promoted $(2s)^1(2p)^3$ configuration. Hybridization (s–p orbital mixing) of this configuration yields the $(h_1)^1(h_2)^1(h_3)^1(h_4)^1$ configuration, in which the h_i represent variationally optimal sp^3 hybrids oriented toward the H atoms (see ref 3, pp 57–60; 94–96; 105–112). The best set of four electron-pair bonds occurs with a tetrahedral arrangement of hydrogens about the carbon.

Instantaneous removal of an electron from methane leaves a partially cationic carbon atom in the presence of a tetrahedral arrangement of partially cationic hydrogen atoms (with "partial" C, H charges dictated by the relative polarity of each CH bond). Because the symmetrically distributed $1s_H$ valence orbitals of H atoms can contribute no energetic differences to this process, we can focus attention on the distinct $2s_C$, $2p_C$ orbital contributions of the central C atom, which offer two distinct energetic pathways to ionization. Formal ionization at C can lead to a low-energy $(2s_C)^1(2p_C)^2$ or high-energy $(2p_C)^3$

configuration (because $2s_C < 2p_C$ in energy), roughly split in 3:1 intensity ratio (because the vacated 2p can be chosen as $2p_x$, $2p_y$, or $2p_z$, whereas 2s is unique).

Thus, methane is qualitatively expected to exhibit two overall peaks in the PES, because there are two underlying atomic valence orbitals from which ionization can occur. These give rise to ground and excited states of CH_4^+ cation with quite different effective hybridizations (sp^2 vs pure p). After the instantaneous "vertical" ionization event, these states will spontaneously undergo "adiabatic" geometric relaxation to distinct molecular shapes (more planar vs more pyramidal, as might be anticipated from their distinct hybrid compositions). All of this is qualitatively consistent with the analysis of Potts et al.[12] as cited by Grushow, as well as with the related discussion of Shaik and Hiberty.[13] Similarly, consideration of *both* the ionized and neutral states, the effective atomic configurations, and hybridization enable the qualitative features of PES to be understood for all simple molecules that are discussed in general chemistry.

■ SHOULD WE CONTINUE TO TEACH HYBRID ORBITALS? IF SO, WHEN?

The question of how much quantum mechanical and orbital-based reasoning should be introduced prior to physical chemistry courses challenges all general chemistry instructors. Similar concerns apply to reaction kinetics, thermodynamics, spectroscopy, and other traditional "advanced" subjects. Ultimately, it is the teachers (not textbook authors) who resolve such issues by choosing to neglect certain sections of the textbooks. One unavoidable consequence is that textbooks tend to grow in size, incorporating numerous "advanced topics" so that instructors have the flexibility to teach individual courses from a common source.

Our preceding discussion shows the arguments for the retirement of hybrid orbitals to be based on false premises. But why would an instructor choose to include hybrid orbitals and other orbital-based reasoning in general chemistry? We believe that the answer—as for other key topics of the chemistry curriculum—lies in the need to provide a deeper, more interconnected, and authentic learning experience for the students. For example, there could be no question that the periodic table is a cornerstone of modern chemistry, essential to even the most casual survey course. Although early notions of periodicity evolved from patterns of empirical data, the full structure and deeper origins of the periodic table awaited development of quantum mechanics and orbital-based notions of atomic electronic structure. By introducing atomic orbital concepts to general chemistry courses, students begin to experience the periodic table at a cognitive level beyond empirical classification, leading to recognition of its profound connection to deeper principles of physics. Orbital concepts are not essential to teach students how to *use* the periodic table. However, instructors choose to include atomic orbital concepts in general chemistry because it provokes higher-level thinking and introduces students to the understanding of working chemists.

Similar reasoning underpins the introduction of hybridization concepts to the description of chemical bonding. As Grushow notes, one could easily apply Lewis structure and VSEPR concepts to teach elementary skills in predicting molecular shapes (at least for simple main-group species), if this were the only course objective. But this is merely pattern recognition (four bonds with no lone pairs gives tetrahedral, four bonds

with two lone pairs gives square planar, and the like). Properly taught, localized hybrid and bond orbital concepts provide the essential glue that links elementary atomic orbital and Lewis structure concepts with molecular shape (including the subtleties expressed by Bent's rule[14]) as well as associated dielectric, spectroscopic, and reactivity properties, paving the way for their eventual unification and comprehension in deeper quantum mechanical principles. Contrary to Grushow's assertions P1−P4, hybrid orbital concepts do *not* violate our best current understanding of experimentally measurable properties or the underlying quantum mechanical theory of electronic structure. Rather, they serve as highly visualizable and transferable "building blocks" of electronic structure that allow students to begin developing accurate intuition in "doing quantum mechanics with pictures",[15] long before the mathematics of the Schrödinger equation is confronted.

■ SUMMARY

We believe that timely and accurate introduction of hybridization and localized bonding concepts in general chemisty serves to

- familiarize students with the methods and thinking of practicing chemists;
- foster construction of a denser, more interconnected conceptual map of chemistry and its relationship to deeper laws of nature;
- provide a secure foundation for the more detailed explorations of molecular electronic structure, spectroscopy, and chemical reactivity to be encountered in more advance organic, inorganic, and physical chemistry classes.

These are powerful instructional "degrees of freedom" for teachers of lower-level chemistry, helping students to gain their first intuitive glimpses of what lies on the forward path to professionalism (rather than mnemonic rationalizations that must be "unlearned" at the next level[16]). Why would we remove such qualities from our textbooks and curriculum?

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(6) Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: Cambridge, London, 2005; p 563ff. http://www.chem.wisc.edu/~nbo5/tut_cmo.htm (accessed Feb 2012). As illustrated in these references, there are actually many advantages in *avoiding* the superfluous canonical delocalization.

(7) Of course, at the more superficial Koopmans-theorem level, the individual orbital energies of NBOs or NLMOs provide different estimates of ionization energies than those of CMOs, but the former (although still crude) are actually *superior* to CMO-based counterparts in many Koopmans-style rationalizations of PES phenomena (Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: Cambridge, London, 2005; p 119−125).

(8) Grushow's two relevant literature citations (Purser, G. H. *J. Chem. Educ.* **1999**, *76*, 1013−1018; Galbraith, J. M. *J. Chem. Educ.,* **2007**, *84*, 783−787) are misleading in this context. The Purser article is based on numerous factual errors and misrepresentations that are discussed in a subsequent article (Weinhold, F. *J. Chem. Educ.* **2005**, *82* 526−527). The Gailbraith article essentially concurs with our viewpoint (stating that "the 'failures' of VB are really just due to oversimplification") and adopts VB-type computational methods to confirm that antiquated "d-orbital participation" models of main-group hypervalency are incorrect, in essential agreement with previous NBO-based and other studies (Kutzelnigg, W. *Angew. Chem., Int. Ed.* **1984**, *23*, 272; Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1986**, *108*, 3586; Magnusson, E. *J. Am. Chem. Soc.* **1990**, *112*, 7940; Suidan, L.; Badenhoop, J. K.; Glendening, E. D.; Weinhold, F. *J. Chem. Educ.* **1995**, *72*, 583).

(9) See, e.g., Nahum, T. L.; Mamlok-Naaman, R; Hofstein, A; Kronik, L. *J. Chem. Educ.* **2008**, *85*, 1680. Note that the current overemphasis on delocalized models is partially due to the fact that electronic structure programs commonly present SCF solutions in the CMO form that is most convenient for numerically solving SCF equations, rather than in the unitarily equivalent localized form. However, many such packages now include NBO software [http://www.chem.wisc.edu/~nbo5 (accessed Feb 2112)] that can "undo" canonical delocalization and present the solutions in the intuitive, transferable NBO/NLMO form that corresponds directly to localized bonding models.

(10) For high-level SAC-CI/6-311++G** calculations in the tetrahedral vertical geometry of the parent neutral, the "3-fold degenerate" low-energy manifold exhibits a 2:1 subsplitting pattern (14.064, 14.064, 14.074 eV) relative to the nondegenerate higher-energy level (23.131 eV).

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