Are Molecular Orbitals Delocalized?

Donald G. Truhlar*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States

ABSTRACT: In contrast to statements in a recent article in this *Journal*, the bonding electrons in methane *can* be properly described in terms of localized electrons, and photoelectron spectroscopy does *not* indicate otherwise. There is no good reason to abandon the description of the chemical bonds of methane in terms of localized bonds formed by covalent linking of hybrid orbitals.

KEYWORDS: *First-Year Undergraduate/General, Upper-Division Undergraduate, Physical Chemistry, Misconceptions/Discrepant Events, Covalent Bonding, Lewis Structures, MO Theory, Quantum Chemistry, VSEPR Theory, Valence Bond Theory*

In a recent article in this *Journal*, Grushow[1] makes several good points about the value of valence shell electron pair repulsion (VSEPR) theory[2] and the lack of predictive power of simple forms of hybrid orbital thinking, especially in inorganic chemistry. But unfortunately, the article is marred by two serious errors. Grushow writes that "the bonding electrons in methane (or most any other molecule for that matter) simply cannot be properly characterized using a localized electron model." No reference is cited, but Grushow seems to come to this conclusion based on the fact that "photoelectron spectroscopic evidence indicates that hybrid atomic orbitals are inappropriate models for the description of electronic energies and electron density within a molecule." These quoted claims are incorrect. Grushow concludes that "the hybrid atomic orbital model does more harm than good" because it "serves to reinforce the notion" of a "localized bonding model", which is disparaged as in the first quotation. The purpose of the present article is to explain the correctness of localized bonding models.

To understand the validity of localized electron models, we must first remember that orbitals are theoretical mathematical objects used to construct many-electron wave functions in the form of configuration states, often just called configurations. In the simplest case, configuration state functions are permutationally antisymmetrized products of spin orbitals, but one should always remember that real wave functions must be built from lists of configuration states, each making a partial contribution to the total wave function: "Configurations are not Mother Nature's true energy states."[3] The need for more than one configuration in an accurate description of the electron distribution is sometimes called configuration interaction (although it is sometimes pointed out that a better name would be configuration mixing). Whereas a single configuration has an independent-particle interpretation, a superposition of interacting configurations leads to correlated motion of the electrons such that the probability of finding a pair of electrons at a specified pair of points in space cannot be predicted from a single set of one-electron probability densities obtained from orbitals each containing one or two electrons. In many cases, though, there is a single configuration whose weight in the configuration sum is much greater than all the others combined. If and only if we are willing to use the single-configuration approximation can we use the model of electrons in singly and doubly occupied molecular orbitals. Thus, any discussion of the nature of molecular orbitals, such as whether they are localized or not, must be carried out in the context of a particular approximation scheme that defines the molecular orbital approximation being used. Historically this was achieved by the Hartree–Fock self-consistent-field approximation in which the antisymmetrized product of spin orbitals is conveniently written as a determinant (a "Slater determinant") in which the various spin orbitals correspond to the individual columns of the determinant,[4] and the orbitals are then found by applying the variational principle to this approximate determinantal wave function.

Using the properties of determinants, one may show that exactly the same variationally best many-electron wave function can be obtained from more than one set of orbitals.[5,6] Furthermore, "two sets of orbitals have been found to be of particular significance. The first set, called molecular orbitals, each have a symmetry determined by the nuclear framework and are generally spread throughout the molecule.... If an electron is removed from a molecule, it should be regarded as removed from a molecular orbital. The other set of orbitals, called equivalent orbitals, give rise to more localized descriptions of charge corresponding to the various bonds or lone pairs of the molecule."[5] In modern nomenclature, the former delocalized orbitals are sometimes called the canonical orbitals, but for present purposes, we can call them delocalized orbitals; the "equivalent orbitals" are often called localized orbitals. The key point though is that the two descriptions, in terms of delocalized orbitals or in terms of localized ones, lead to the same total wave function and are therefore equally valid. Both lead to the same electron density and the same variationally optimized energy. It is wrong to think that the delocalized ones are more correct.

Although Grushow described various ways that one could misuse the localized-orbital concept, that does not mean that the localized-orbital concept does not have valid and proper uses. For example, even before the widespread use of VSEPR

theory, for which localized orbitals provide a foundation, Lennard-Jones and Pople[5] used localized orbitals to explain the factors, including electrostatics, underlying the tetrahedral shape of methane. In fact, they pointed out that in a certain sense the localized-orbital description provides a more satisfactory conceptual picture in classical terms because the exchange contribution to the energy, "which cannot be so easily interpreted"[5] as the classical electrostatic energy, plays a smaller role in the localized-orbital model. Furthermore, the localized orbitals of methane (or any C—H bond in an alkane) are most clearly understood in valence bond language involving the covalent interaction of an sp^3 orbital on carbon with an s orbital on hydrogen.[7] Lone pair orbitals may also be approximately described as hybrids of s and p orbitals.[8] Localized orbitals are also useful for both analysis and computations at higher levels of theory than Hartree—Fock self-consistent field theory; for example, they are also useful for discussing some aspects of electron correlation.[9,10]

Why then are the photoelectron experiments best interpreted in terms of delocalized orbitals? This is a result of Koopmans' theorem. Koopmans[11] showed that if we ionize a molecule with N electrons and form the best possible description of the $N - 1$ orbitals of the cation from linear combinations of the N orbitals obtained in a Hartree—Fock description of the original molecule, the resulting cation orbitals can be taken as $N - 1$ of the canonical delocalized orbitals of the original molecule. Having done this, one could then, if desired or useful, transform[6] the delocalized orbitals of the cation to localized orbitals for the cation. Thus, the preference for using the localized orbitals in photoelectron spectroscopy is not telling us anything about the best orbitals for describing the electron density of either the initial neutral molecule or final cation, but rather is telling us something about the relationship between the two sets of densities.[12] Even if one includes configuration interaction, the difference between the electron distributions in the N-electron and $(N - 1)$-electron cases is a one-electron distribution, and it may be written as the absolute square of an "orbital", which is sometimes called[13] a Dyson orbital. The essential point is that the delocalized Hartree—Fock orbitals of the initial system are a better approximation to the Dyson orbital than are the localized Hartree—Fock orbitals of either the initial or final system of the ionization process; nevertheless, at the Hartree—Fock level of theory, the two kinds of orbital models give identical wave functions for either the initial or the final system considered on its own.

As a result of arguments including these errors, Grushow advocates that hybrid orbitals be removed from the curriculum because he says that they are like phlogiston, which does not exist. However, hybrid orbitals are not analogous to phlogiston, and they will probably never disappear from the toolkit of the professional quantum chemist because they are mathematically correct basis functions that are very convenient for deriving useful analytic approximations to molecular orbitals. For example, they are widely used in modern fragment molecular orbital methods.[14−16] Furthermore, the analysis of the atomic orbital contribution to molecular orbitals in terms of hybrid orbital character (percentage of s and p character) is useful for understanding bonding,[17] kinetic isotope effects,[18] X-ray crystallography,[19] X-ray absorption,[20] NMR,[21,22] and many other aspects of chemistry. One does not want to abandon this useful qualitative tool of analysis, even as quantum chemists are working to develop deeper, more predictive (and more complicated) tools. I emphasize that localized-orbital models and nonlocalized-orbital models are both applicable to any given molecule, and they each have uses for which they are best suited.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: truhlar@umn.edu.

■ REFERENCES

(1) Grushow, A. *J. Chem. Educ.* **2011**, *88*, 860−862.
(2) Gillespie, R. J. *J. Chem. Educ.* **1970**, *47*, 18−23.
(3) Simons, J.; Nichols, J. *Quantum Mechanics in Chemistry*; Oxford University Press: New York, 1997; p 189.
(4) Simons, J.; Nichols, J. *Quantum Mechanics in Chemistry*; Oxford University Press: New York, 1997; p 408.
(5) Lennard-Jones, J.; Pople, J. A. *Discuss. Faraday Soc.* **1951**, *10*, 9−18.
(6) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457−465.
(7) Coulson, C. A. *Trans. Faraday Soc.* **1942**, *38*, 433−444.
(8) Radom, L.; Hehre, W. J.; Pople, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 289−306.
(9) Pulay, P. *Chem. Phys. Lett.* **1983**, *100*, 151−154.
(10) Upton, T. H. *J. Phys. Chem. A* **1983**, *87*, 3865−3872.
(11) Koopmans, T. *Physica* **1933**, *1*, 104−113.
(12) Pauling, L. *J. Chem. Educ.* **1992**, *69*, 519−521.
(13) Duffy, P.; Chong, D. P.; Casida, M. E.; Salahub, D. R. *Phys. Rev. A* **1994**, *50*, 4707−4728.
(14) Federov, D. G.; Jensen, J. H.; Deka, R. C.; Kitaura, K. *J. Phys. Chem. A* **2008**, *112*, 11808−11816.
(15) Pu, J.; Gao, J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 632−650.
(16) Toth, G.; Gereben, O.; Náray-Szabo, G. *J. Mol. Struct. (THEOCHEM)* **1994**, *313*, 165−172.
(17) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 767−773.
(18) Pu, J.; Ma, S.; Garcia-Viloca, M.; Gao, J.; Truhlar, D. G.; Kohen, A. *J. Am. Chem. Soc.* **2005**, *127*, 14879−14886.
(19) Mugesh, G.; Panda, A.; Singh, H. B.; Butcher, R. J. *Chem.—Eur. J.* **1999**, *5*, 1411−1421.
(20) Cavalleri, M.; Ogasawasa, H.; Pettersson, L. G. M; Nilsson, A. *Chem. Phys. Lett.* **2002**, *364*, 363.
(21) Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 1471−1476.
(22) Meier, M. S.; Spielmann, H. P.; Robert, G.; Bergosh, R. G.; Haddon., R. C. *J. Am. Chem. Soc.* **2002**, *124*, 8090−8094.