

There Are No Such Things as Orbitals—Act Two!

Jack Simons

University of Utah, Salt Lake City, UT 84112

In a recent article in the *Journal of Chemical Education*¹ Ogilvie states "There Are No Such Things as Orbitals!" and goes on to criticize the teaching of orbital concepts (e.g., hybridization, electronegativity, sigma and pi bonds, hyperconjugation, HOMO-LUMO, inductive and resonance effects) in our curricula.

In that article, Ogilvie distinguishes between what he calls quantum laws (e.g., quantities such as energy and various angular momenta exist in discrete quantized states under certain conditions) that are subject to experimental verification and quantum theories or models (e.g., orbitals, configurations, term symbols, wave functions) that scientists have invented as devices for solving equations (e.g., the Schrödinger equation) that purport to describe the behavior of atoms and molecules. He directs his attack not at the laws but only at the models or theories. For example, by noting that the solutions of the molecular orbital (MO) approach to electronic structure and the valence bond (VB) approach are identical (when carried to completion), he concludes that the concepts and constructs of the MO and VB theories have no ultimate meaning (i.e., are not real). Relative to chemical education, he concludes "Quantum chemistry" or the qualitative ("hand waving") explanations of molecular structure and reactions based on orbitals and such ilk are not science (i.e., are nonsense) and should consequently be completely discarded."

I wish to offer a somewhat different perspective on these subjects. I prefer to do so by stressing the fundamental differences between the point of view put forth by Ogilvie and that to which I subscribe, rather than by pointing out where I differ with Ogilvie in each of his numerous examples of problems that arise in using orbital concepts.

I agree with some of what Ogilvie says, and I concur, in particular, with his view that orbitals are not real. However, as the following remarks indicate, I am of the opinion that models, including the orbital concept and its derivatives, will continue to play important roles in chemistry and chemical education because they provide useful frameworks in terms of which to organize patterns that are observed in experimental data. If accepted as such, and not as "real" entities, models and their constructs can be useful and not confusing or threatening.

My point of view on models and on the theory of electronic structure in particular can be summarized in the following three remarks and accompanying observations:

1. Experimental data and the molecules, atoms, and substances we subject to scrutiny constitute the "real" things² in chemistry. All quantities derived from our data through the application of models, theories, and their associated equations are not "real".

Applied to MO and VB theories, this means that orbitals, hybridization, screening, electronic configurations (e.g., $1s^2 2s^2 2p^3$), and term symbols are not real. Applied to molecular vibrational/rotational spectroscopy, it means that force constants, equilibrium bond lengths (R_e) and angles, vibrational frequencies (ω_e), anharmonicity ($\omega_e x_e$), Coriolis coupling constants, as well as the potential energy surfaces on which these motions are thought to occur are also not real. Applied to chemical kinetics, it means that the phenomenological rate constant (k) and the activation energy (ΔE^\ddagger) are not real.

2. Models, equations, and theories are constructs of our imaginations designed to aid us in organizing in a systematic manner the

trends that appear in our data. The quantities we extract from the application of a model to our data are, in some sense, no more than "fitting parameters".

3. The value of any particular model or theory is judged by how accurately, reliably, and compactly it can be used to organize known data, and whether the parameters obtained by applying the model to one or more sets of data can be used to make reasonably accurate predictions of data for materials that have not yet been subjected to our experiment.

In my opinion, it is with respect to the accuracy of its predictions that Ogilvie could reasonably have criticized quantum theory as applied to electronic structures of atoms, molecules, and materials. For example, in comparison with the theoretical framework used to analyze data from vibrational/rotational spectroscopy, modern electronic structure models lack accuracy. The expressions used to fit the line positions, spacings, and intensities of microwave and infrared spectral features as functions of the quantum numbers ν and J provide a very accurate, reliable, and compact framework in terms of which to fit the experimental data. Moreover, experience indicates that the parameters so obtained can be used to predict accurately spectra for molecules that have not been subjected to experiment.³ However, the parameters (e.g., R_e , ω_e , $\omega_e x_e$, etc.) obtained by such models are, in principle, no more or less "real" than those obtained from electronic theories applied to electronic experimental data.

The fact is that some models are more useful than others because they provide a more accurate and predictive representation of the experimental data. On this basis, the foundations of vibrational/rotational spectroscopy may be viewed as superior to quantum theory of electronic states. Even the most sophisticated and modern theories of electronic structure do not provide as accurate and reliable a description of the experimental observations as the more mature and long-studied theories of vibrational/rotational spectroscopy. On this basis, it is proper to question whether the constructs that arise in orbital theories (e.g., orbitals, screening, HOMO-LUMO interactions, back bonding, etc.) are as meaningful as the analogous constructs (e.g., R_e , ω_e , $\omega_e x_e$, etc.) of vibrational/rotational spectroscopy. However, I

¹ Ogilvie, J. F. *J. Chem. Educ.* **1990**, *67*, 280.

² One can, of course, pursue things further and ask whether even these quantities are real. I do not intend to enter into such a philosophical discussion here; I choose to define as real things that most (perhaps all) chemists would agree can be directly measured in the laboratory (e.g., a photon energy or wavelength, the attenuation of a light beam, an angle of scattering of a light beam, the enthalpy given off by a reaction in a calorimeter).

³ In applying such spectroscopic energy-level formulas, one usually must make assumptions about the equilibrium structure of the molecule under study. For some families of molecules (e.g., highly fluxional molecules and "floppy" Van der Waals complexes), the observed rotational/vibrational energy level patterns are not well-represented by the conventional equations. For this reason, such molecular families pose new challenges to the spectroscopist; a new "starting point" model is needed to more accurately and compactly represent their energy level patterns. In this sense, the analysis of "floppy" molecule vibrational/rotational energies is in the same situation as atomic and molecular electronic structure theory.

