

Can Orbitals Really Be Observed in Scanning Tunneling Microscopy Experiments?

A fundamental concept in quantum mechanics is the Heisenberg Uncertainty Principle.¹ For the purpose of this note, the main point is that a wave function, *any* wave function, cannot be thought of as a trajectory or as an observable in the same way that it is possible to consider a trajectory in classical mechanics. Rather, one can speak only of probabilities of finding particles (e.g., electrons) in particular volume elements. In view of the Heisenberg Uncertainty Principle, an important fundamental postulate (the Born postulate)² of quantum mechanics is that the probability of finding an electron in a volume element dV is $\Psi^*\Psi dV$, where Ψ is a wave function that describes the electron and Ψ^* is the complex conjugate of Ψ . The wave function amplitude $\Psi^*\Psi$ is interpreted as the probability density. All observable atomic or molecular properties are determined by the probability and a corresponding quantum mechanical operator, *not* by the wave function itself. Wave functions, even *exact* wave functions, are not observables.

The exact wave function is not obtainable for any but the simplest systems, such as the particle in the box or the harmonic oscillator. To obtain an approximate wave function for an atomic or molecular species, that is, an approximate solution to the electronic Schrodinger equation (within the Born–Oppenheimer approximation), one often introduces the concept of one-electron functions (i.e., orbitals) such that the approximate wave function is taken to be an antisymmetrized product of these orbitals. This so-called “mean field” approximation is embedded both in Hartree–Fock (HF) theory and in the most commonly used implementations of density functional theory (DFT). It is important to stress here that these orbitals (called molecular orbitals in HF theory and Kohn–Sham (KS) orbitals in DFT) are merely mathematical constructs that are used to obtain a route to an approximate solution to the Schrodinger equation. Furthermore, because an arbitrary unitary transformation of a wave function does not alter its amplitude (probability density) or consequently, any observable properties, an MO basis used to build the wave function is not unique. For example, the two very different sets of canonical and localized MOs can form bases to build wave functions of the same density, which represent the same electronic state of the system. Therefore, MOs are not unique and are not observable.

Unfortunately, many authors have claimed to image MOs, particularly the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In particular, these include claims to have observed the HOMO and LUMO of fullerene (2000),³ nitrogen (2004),⁴ pentacene (2005),^{5,6} Co^{II} tetraphenylporphyrin (2008),⁷ polyaromatic hydrocarbons,⁸ water (2014),⁹ and 3,4,9,10-perylenetetracarboxylic acid dianhydride (2017).¹⁰ Scanning tunneling microscopy (STM) experiments seem to be the most common tool used to “probe” frontier orbitals. A recent Perspective¹¹ in *Nature Chemistry* claimed that STM images of a molecule chemically/physically absorbed on a substrate are images of

(frontier) orbitals that are coupled with the electronic state of the matrix. When the coupling to the matrix is eliminated (e.g., by inserting ultrathin insulating NaCl films), the author claimed that the STM images become the images of “native”⁶ (frontier) MOs. On the basis of the foregoing discussion, this cannot be true. Orbitals are not observables.

The origin of the misinterpretation of STM images as orbitals can be understood as follows. When a bias voltage is applied to a tip positioned very close to a material surface, electron tunneling can occur. The variation of the tunneling current can be visualized as the STM image. The tunneling current at a particular space point is proportional to the density of states (DOS) of the material at that point, also called the local DOS. The DOS at a particular energy level results from the coupling of the electronic state at that energy level to perturbation sources (e.g., electronic states of adjacent molecules, external fields). The DOS at an energy level of an unperturbed state (e.g., an isolated molecule) is small and proportional to the degeneracy order at that energy level. In the STM technique, a local potential applied to the tip serves as the perturbation; therefore, the DOS is nonzero. In many molecular systems, a high DOS occurs at about the Fermi level of energy, which is usually between the first ionization and electron affinity energies. These energy levels can be *roughly approximated* by the HOMO and LUMO energies. Unfortunately, several authors have made the incorrect leap to conclude that they are actually observing the HOMO and LUMO themselves.

Claims regarding the observation of orbitals have been made even earlier than those mentioned above. In 1999, Zuo et al.¹² attributed an X-ray image to be a d-orbital of copper in Cu₂O. This paper received some much-needed attention from, for example, Scerri¹³ and Mulder,¹⁴ both of whom explained in some detail that orbitals are *not* observable. The papers by Scerri and by Mulder are important and should be read carefully by those who assert that orbitals can be observed in experiments. Unfortunately, these two papers have been ignored by several authors.

To summarize, (i) any property of a system is only fully represented by the total density; (ii) orbitals are simply mathematical constructs used to build the (approximate) wave function and then the density; (iii) orbitals can therefore not be associated directly with an observable molecular property; (iv) orbitals are nonunique, because the energy is invariant to any unitary transformation among the (HF or KS) orbitals within a given subspace (e.g., doubly occupied space).

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Published: July 6, 2017

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ACKNOWLEDGMENTS

The authors thank Professor James Evans and Dr. Da Jiang Liu for helpful discussions and the U.S. Air Force Office of Scientific Research (FA9550-14-1-0306) for support.

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