

Molecular orbitals: Physical reality or mathematical construct?

Molecular orbital framework is of central importance in chemistry. Often used by chemists and physicists to gain insight into molecular properties, Hartree–Fock or Kohn–Sham orbitals are obtained from rather crude treatments and, strictly speaking, are not observables. Yet, quantum mechanics offers a route for connecting general many-electron wavefunctions with reduced quantities—density matrices and orbitals—that give rise to observable properties. Such mapping makes possible, in principle, reconstruction of these objects from sufficiently detailed experimental data. This lecture will discuss Dyson orbitals and various types of natural transition orbitals and illustrate their role in modeling and interpreting different types of spectroscopic measurements.

A.I. Krylov, [From orbitals to observables and back](#), J. Chem. Phys. 153, 080901 (2020).