Abstract Submitted
for the DAMOP16 Meeting of
The American Physical Society

The atom in a molecule: Implications for molecular structure and properties[1] PETER LANGHOFF, Department of Chemistry and Biochemistry, UCSD, La Jolla, CA, JEFFREY MILLS, JERRY BOATZ, Air Force Research Laboratory, Edwards AFB, CA — The apparent impossibility of meaningful assignments of indistinguishable electrons to particular atomic nuclei in a molecule seemingly precludes quantum-mechanical definition of fragment atomic Hamiltonian operators. Structural symmetry, conformations, and isomers, as well as the electronic energies and properties of constituent atoms are accordingly perceived as ill defined. Here we provide assignments of electrons to atoms in molecules and define their energies and properties. A separable Hilbert space in the form of orthonormal (Eisenschitz-London) outer-products of atomic eigenstates facilitates assignments of electrons to particular atomic nuclei and also provides support for totally antisymmetric solutions of the Schrödinger equation. Self-adjoint atomic operators within a molecule are shown to have Hermitian matrix representatives and physically significant expectation values in molecular eigenstates. Nuanced descriptions of molecular structures and properties emerge naturally from this representation in the absence of additional subjective conditions, including the interplay between atomic promotion and interaction energies, atomic hybridization and charge apportionment, and atomic-state entanglements upon dissociation, attributes revealed by illustrative calculations.

[1]Work support in part by grants from AFRL, NRC, ASEE, NSF

Peter Langhoff
Department of Chemistry and Biochemistry, UCSD, La Jolla, CA

Date submitted: 23 Jan 2016 Electronic form version 1.4