

*To be presented at:
55th Sanibel Symposium; St. Simons Island, Georgia; 15-21 February 2015*

**Insights into the Electronic Structure of Molecules
from Generalized Valence Bond Theory**

Thom H. Dunning, Jr.

Northwest Institute for Advanced Computing, Pacific Northwest National Laboratory & University of Washington; Department of Chemistry, University of Washington, Seattle, Washington 98195; and Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Chemists today use molecular orbital (MO) theory as the basis for reasoning about the electronic structure of molecules and its impact on chemical phenomena. However, the restrictions associated with the Hartree-Fock (HF) wavefunction, although computationally convenient, make it difficult to understand the cause of some chemical phenomena. Generalized Valence Bond (GVB) theory lifts these restrictions and offers alternate explanations for many phenomena that elude HF/MO theory. The GVB wave function is more accurate than the Hartree-Fock wavefunction, including a major portion of the non-dynamical correlation effects present in a valence “ N electrons in N orbitals” complete active space self-consistent field (CASSCF) wave function. Unlike wave functions with multiple spatial configurations, the GVB wave function is easily interpreted using concepts familiar to most chemists. We will discuss a number of examples that illustrate the power of GVB theory, e.g., the nature of the bonding in C_2 as well as in hypervalent molecules such as SF_4 , the isomers of $F(NX)$ with $X = (O,S)$, and the transition states for inversion in $F_nPH_{(3-n)}$.