Quantum Chemistry Beyond Atomic Orbitals and Slater Determinants

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Atomic orbitals and Slater determinants have supported the development of accurate quantum chemical theory since 1930s. They both are the pillars of the well-established "technology" of quantum chemistry that is used to rationalize and guide many experimental studies of today. However, augmenting and/or dismantling both of these concepts may be necessary for truly predictive electronic structure methods.

First, I will describe our work on the explicitly correlated (R12) electronic structure methods that go beyond purely orbital approximation and describe the correlation of pairs of electrons directly in terms of the interelectronic distances. The R12 methods attain higher precision (smaller basis set error) than the standard wave function methods by the virtue of a more efficient description of the Coulomb correlation at short interelectronic distances. Our focus will be primarily on the development of R12 methods for modeling multiple electronic states.

In the second part I will discuss methods that do not use atomic orbitals. Atomic basis sets are ubiquitous in electronic structure studies of molecules and are becoming popular for solids. In search for more universal and robust numerical representations we are exploring adaptive spectral-element basis sets that in principle allow to compute wave functions with guaranteed high precision. Our focus will be on computing two-electron correlated wave functions in such bases. To make such computations feasible it is essential to use low-rank (separated) representations for both operators and functions. We will present pilot MP2 computations with such an approach.

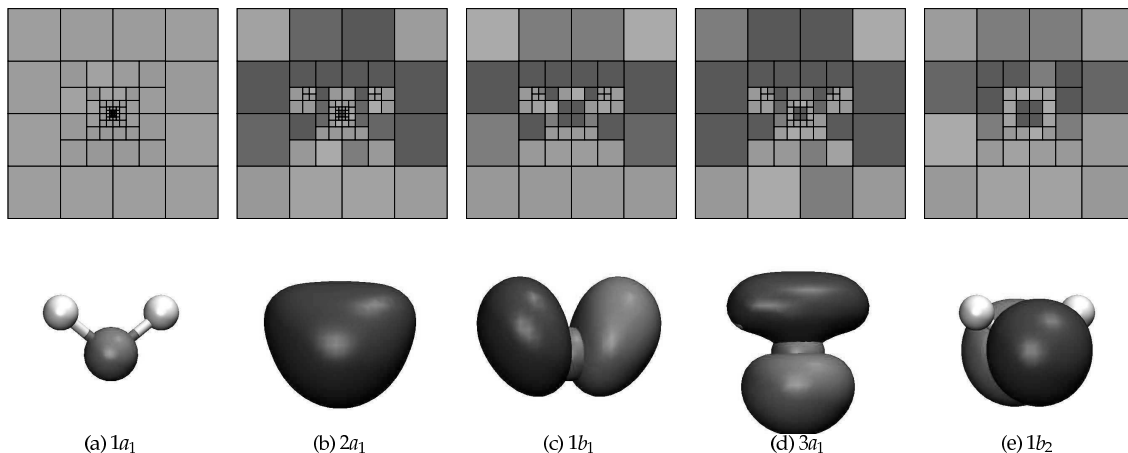(a) $1a_1$ (b) $2a_1$ (c) $1b_1$ (d) $3a_1$ (e) $1b_2$

Figure 1: Multiresolution structure of the orbitals of the water molecule. The darkest volume elements have the highest separation ranks.