

Orbital Concepts, Propagator Methods and Novel Chemical Bonding in Anions

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Molecular orbital concepts dominate qualitative reasoning about chemical bonding and computational methods for calculating observables. This trend began with the pioneering works of Hückel, Hund and Mulliken and continues to this day with the search for effective, one-electron potentials employed in density-functional theory. Because one-electron equations can be made formally exact in electron propagator theory, it is possible to rigorously relate qualitative, orbital concepts to systematically improvable treatments of electron correlation. Recently developed approximations in *ab initio* electron propagator theory are especially efficient and accurate in calculating electron affinities of molecules and electron detachment energies of anions. This approach involves an energy-dependent, non-local, one-electron operator whose eigenvalues equal electron binding energies that include orbital-relaxation and electron-correlation effects and whose eigenfunctions are Dyson orbitals. Numerical tests of the P3+, NR2 and BDT methods demonstrate their computational and conceptual advantages over other approaches. In addition to providing accurate predictions on various spectral probes of valence-bound anions, these methods also generate precise data on negatively charged species that would not be bound except for strong electron correlation. Examples include diffuse and valence excited states of fullerides, double-Rydberg anions and related species with metal atoms.