

Electrostatic vs. Covalency Conceptions of Hydrogen Bonding

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Natural bond orbital (NBO) analysis rests on a fundamentally different “natural” conception of atomic orbitals (NAOs) in the molecular environment, leading to profound disagreements with alternative analysis methods on the importance of “electrostatic” vs. “covalency” effects in the conception, force-field modeling, and pedagogy of hydrogen bonding. We describe a recently characterized class of “anti-electrostatic” H-bonds (AEHB) between closed-shell ions of *like* charge that cast fresh light on such disputes. AEHB species are found to exhibit robust kinetic stability and all familiar experimental and theoretical signatures of H-bonding, despite what must be overwhelming *opposition* by classical Coulombic and “dipole-dipole” forces as depicted in textbook expositions and empirical force-field simulations of H-bonding. We outline NBO-based analysis of AEHB species in resonance-theoretic “charge transfer” terms and show how the hydrogen bonding phenomenon relates to general Lewis-structural and resonance concepts in the broader quantum theory of chemical bonding.