Kinetic energy and chemical binding

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The H_2^+ molecule, containing only one electron, is an ideal system for understanding what happens when a chemical bond forms. The three important factors in forming this bond, namely the sharing of that electron, the polarization of atomic orbitals, and the contraction of the atomic orbitals are not complicated by many-body electron correlations.

Revisiting our old analysis[1] using converged basis sets[2,3] confirms its correctness. The changes from a hypothetical system "H plus a proton located at the correct H_2^+ bond distance" to the exact wavefunction of H_2^+ will be analyzed in terms of these three changes. The analysis uses the variational principle, and also the virial theorem, since the true H_2^+ function must minimize the total energy E=T+V and the ratio |V/T| must be 2. The results emphasize the importance of *kinetic energy* changes in causing bond formation. The conventional wisdom that increased electron density at the center of a bond causes a lowering of *potential energy* is demonstrably false; rather, the ultimate origin of H_2^+'s lower potential energy is contraction towards both nuclei.

The insight gained from the study of H_2^+ will be shown to apply to other diatomics. Consideration of H_2 introduces e-e repulsions. New results will be presented for cases such as Be_2, B_2, C_2, N_2, O_2, and F_2, which add the complication of inner shells, as well as multiple bonds, non-singlet states, avoided crossings, or prominent dispersion interactions.

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