Comments on the ground and excited states of the H2 molecule and on its representation.

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Abstract. First Part. The first ten $^1\Sigma_g^+$ states of the H_2 molecule are computed with full configuration interaction both from Hartree-Fock molecular orbitals and Heitler-London atomic orbitals and correlated by a comprehensive analysis. The basis sets utilized are extended and optimized Slater type functions, STO, and standard Gaussian functions, GTO. Preliminary computations and analyses are added for states 11 to 13. The full CI computations cover the inter-nuclear distances from R=0.01 to R=10000 bohr. The computed energies compare well with the accurate computations by L. Wolniewicz and collaborators, limited to for the first five states.

We focus on the characterization of the orbitals in the wave functions, on the electronic density evolution from the united atom to dissociation, on quantitative decomposition of the total energy into covalent and ionic components and on detailed analyses of energy contributions to the total state energy from selected STO and GTO sub-sets. These analyses lead to CI computations on related systems, like the H$^-$ negative ion interacting with a proton and the H$^+$H$^-$ ion pair systems, and on the atomic ground and excited states for He, H$^-$ performed to characterize the united atom and the dissociation products [1] .

Second part. From the above computations it is clear the need to represent the full inter-nuclear distance range from the united atom to dissociation. The traditional proposal of Molecular Orbitals fails at large inter-nuclear distances and requires very extended expansion of Configuration Interactions type to yield the correct energy. The Heitler London Atomic Orbital traditional proposal provides correct dissociation products but poor binding energies and therefore CI expansions are again required. In the last few years we have experimented with a variational combination of MO and AO wave functions, the Hartree-Fock-Heitler-London method, aiming to compute the molecular extra correlation energy, thus ensuring correct binding energies and dissociation products with short CI type expansion of non orthogonal orbitals [2, 3].

We present the Chemical Orbitals, a new type of one electron functions composed of atomic functions for the united atom and for the dissociation products and of molecular type functions [4]. The total energy for the H_2 molecule with a single configuration of Chemical Orbitals ensures correct dissociation products and has recovered part of the traditional correlation energy yielding a binding of 99.77 kcal/mol. With four configurations of chemical orbitals the computed binding energy is 108.10 kcal/mol and 108.8 kcal/mol with 11 configurations, to be compared to 109.1 kcal/mol obtained with the same basis set and

1040 configurations in a traditional CI expansions and to 109.48 kcal/mol the exact value obtained by W. Kołos with James-Coolidge type expansion in elliptical coordinates.

[1] G. Corongiu, E. Clementi (to be submitted)
[2] E. Clementi and G. Corongiu, Theochem, 2009, in press
[3] E. Clementi, and G. Corongiu, *Theor. Chem. Acc.* **2007**, *107*, 214.
[4] E. Clementi and G. Corongiu, *Int. J. Quantum Chem.,* **2008**, DOI:10.1002.