New Journal of Physics
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Deutsche Physikalische Gesellschaft DPG | IOP Institute of Physics

H_2 and $(H_2)_2$ molecules with an *ab initio* optimization of wave functions in correlated state: electron–proton couplings and intermolecular microscopic parameters

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Received 19 August 2014, revised 4 November 2014
Accepted for publication 12 November 2014
Published 8 December 2014
New Journal of Physics **16** (2014) 123022
doi:10.1088/1367-2630/16/12/123022

Abstract

The hydrogen molecules H_2 and $(H_2)_2$ are analyzed with electronic correlations taken into account between the $1s$ electrons in an exact manner. The optimal single-particle Slater orbitals are evaluated in the correlated state of H_2 by combining their variational determination with the diagonalization of the full Hamiltonian in the second-quantization language. All electron–ion coupling constants are determined explicitly and their relative importance is discussed. Sizable zero-point motion amplitude and the corresponding energy are then evaluated by taking into account the anharmonic contributions up to the ninth order in the relative displacement of the ions from their static equilibrium value. The applicability of the model to solid molecular hydrogen is briefly analyzed by calculating intermolecular microscopic parameters for the $2 \times H_2$ rectangular configuration, as well its ground state energy.