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Progress in calculating the PES of H_3^+ MICHELE PAVANELLO, Rutgers University, ALEXANDER ALIJAH, Université de Reims, LUDWIK ADAMOWICZ, University of Arizona — The most accurate electronic structure calculations are performed using wave-function expansions in terms of basis functions explicitly dependent on the interelectron distances. In our recent work we use such basis functions to calculate a highly accurate potential energy surface (PES) for the H_3^+ ion. The functions are explicitly correlated Gaussians which include interelectron distances in the exponent. Key to obtaining the high accuracy in the calculations has been the use of the analytical energy gradient determined with respect to the Gaussian exponential parameters in the minimization of the Rayleigh-Ritz variational energy functional. The effective elimination of linear dependencies between the basis functions, as well as the automatic adjustment of the positions of the Gaussian centers to the changing molecular geometry of the system, are key to the success of the computational procedure. After adiabatic and relativistic corrections are added to the PES and with an effective accounting of the non-adiabatic effects in the calculation of the rotational/vibrational states, the experimental H_3^+ rovibrational spectrum is reproduced at the 0.1 cm^{-1} accuracy level up to $16,600 \text{ cm}^{-1}$ above the ground state.

Michele Pavanello
Rutgers University

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