Ultra-precise computations for molecular paradigms

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I report on recent developments and applications about the coupled quantum mechanical motion of the electrons and the atomic nuclei through a variational [1] and also a perturbative [2] approach. For the applications, the underlying Schrödinger equation is solved using a symmetry-adapted, explicitly correlated Gaussian ansatz. The variational, pre-Born–Oppenheimer, approach has been extended towards (a) the solution of H_3^+ as an explicit five-particle problem [3], and (b) tightly converged electronically excited, rovibronic states of the H_2 molecule which appear as resonances in the full electron-nucleus problem [4]. Concerning the perturbative route to small non-adiabatic effects, we have formulated the second- (and third-)order effective Hamiltonian for the quantum nuclear motion over coupled electronic states containing diagonal and off-diagonal non-adiabatic mass-correction terms [2]. The general curvilinear expression for the non-adiabatic kinetic energy (mass) correction has been formulated [5] and its numerical properties have been studied for selected examples [6]. The non-adiabatic correction to the nuclear mass usually amounts to ca. the mass of the electrons, but for special examples non-trivial deviations arise. For example, in the outer-well of the $H\bar{H}$ $^1\Sigma_g^+$ electronic state of H_2, the dressed, vibrating proton is lighter than the proton itself, which accounts for part of the discrepancy of experiment and theory [7]. In order to achieve quantitative agreement between the computations and high-resolution spectroscopy experiments, it is necessary to account also for relativistic and radiative effects, for which we evaluate perturbative corrections for the non-relativistic result. Our recently computed pre-Born–Oppenheimer term values for the rotationally excited EF $^1\Sigma_g^+$ states of H_2 ($N = 0, 1, \ldots, 5$) [4], appended with relativistic, leading- and higher-order radiative corrections, are in a 0.001 ± 0.005 cm^{-1} agreement with experiment [8]. Further improvement of the theoretical uncertainty should reveal fine details of higher-order radiative corrections and the finite size of the proton.

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