Energy levels of the hydrogen molecule
from relativistic nonadiabatic calculations

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The theoretically derived energy of a molecular rovibrational level is composed of several additive components: nonrelativistic, relativistic, quantum electrodynamic, etc. For a light molecule, like hydrogen or its isotopologue, this energy can be well described in the framework of the nonrelativistic quantum electrodynamic theory (NRQED) using the following expansion in powers of the fine structure constant

$$E(\alpha) = \sum_{i=2}^{\infty} \alpha^i E^{(i)}. \tag{1}$$

The accuracy of the theoretically predicted energy is limited mainly by its least accurate component. In recent years, we have developed a variational method of solving the Schrödinger equation which treats the hydrogen molecule as a four-particle system without separation of nuclear and electronic motions [1–5]. As a result, the uncertainty of the dominating, nonrelativistic component of the energy, $E^{(2)}$, has reached the level of $10^{-7} - 10^{-8}\,\mathrm{cm}^{-1}$ (< 3 kHz). A typical procedure of decomposing the energy into the clamped nuclei, adiabatic, and nonadiabatic components can hardly enable such an accuracy.

In this communication, we report on extending this nonadiabatic method to the relativistic correction term, $E^{(4)}$. The four-body exponential wave function is applied to evaluate the expectation value of the Breit-Pauli Hamiltonian. The main obstacle encountered in this approach is the need for a whole class of integrals resulting from combining relativistic operators with exponential basis functions. Such integrals

$$\int dV \, \frac{e^{-t\,r_{AB}}\, e^{-u(\zeta_1+\zeta_2)}}{r_{AB}^p\, r_{12}^p\, r_{1A}^p\, r_{1B}^p\, r_{2A}^p\, r_{2B}^p} \, R^{n_0}\, r_{12}^{n_1}\, \eta_1^{n_2}\, \eta_2^{n_3}\, \zeta_1^{n_4}\, \zeta_2^{n_5}, \tag{2}$$

where one of the integer powers $p = 2$ and the remaining $p = 1$, have been successfully evaluated, and the preliminary results of the relativistic correction will be reported. The convergence analysis shows that the numerical uncertainty of this correction is of the order of $10^{-7}\,\mathrm{cm}^{-1}$. As in the case of the nonrelativistic component, the relativistic term uncertainty is small enough to enable its elimination from the overall uncertainty budget. An essential feature of the newly developed method is its applicability to an arbitrarily high rotational angular momentum without significant loss in accuracy. With the new relativistic results, augmented by QED corrections, the achieved accuracy is limited limited only by the uncertainty of the quantum electrodynamic effects, $E^{(n)}$, $n \geq 5$.

Several recent measurements [6–12] have indicated a systematic discrepancy between the most accurate theoretical and experimental data. A confrontation of the selected rovibrational transition energies will be made. Possible explanations of this observation will be discussed, setting hints for further theory development.

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