High precision calculations for excited states of the hydrogen molecule

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We performed high-precision nonrelativistic calculations for 12 excited states of the hydrogen molecule. The explicitly correlated exponential wave functions were used, which, unlike popular Gauss-type functions, do have correct asymptotic behavior in large and small interparticle distances, which is crucial for further calculations of relativistic and QED corrections. Following the Born–Oppenheimer approach, nuclei positions were treated as a fixed parameter $R = r_{AB}$ and varied from $0.1a_0$ to $20a_0$. For R up to about $9a_0$, the James–Coolidge basis set was used:

$$\phi_{n_0 \ldots n_4} = e^{-\alpha(r_{1A}+r_{1B})} e^{-\beta(r_{2A}+r_{2B})} r_{12}^{n_0} (r_{1A}-r_{1B})^{n_1} (r_{2A}-r_{2B})^{n_2} (r_{1A}+r_{1B})^{n_3} (r_{2A}+r_{2B})^{n_4}$$

where $1, 2$ – electrons, A, B – nuclei. In this case, all necessary integrals have been derived in close analytical form [1]. However, this basis set does not reproduce the dissociation limit correctly. Thus, for large R values, the more general Kołos-Wolniewicz basis set was used:

$$\begin{aligned} \phi_{n_0 \ldots n_4} &= e^{-y\,(r_{1A}-r_{1B})-x\,(r_{2A}-r_{2B})-u\,(r_{1A}+r_{1B})-w\,(r_{2A}+r_{2B})} \\ &\quad \times r_{12}^{n_0}\,(r_{1A}-r_{1B})^{n_1} (r_{2A}-r_{2B})^{n_2}\,(r_{1A}+r_{1B})^{n_3}\,(r_{2A}+r_{2B})^{n_4}\, r^{-n_0-n_1-n_2-n_3-n_4-3} \end{aligned}$$

In this case, the integrals were calculated by Taylor expansion in R, which we found numerically stable and efficient.

Our results have relative accuracy varying from about 10^{-10} to about 10^{-16}, which exceeds the best previous results of this kind [2,3] by several orders of magnitude. This opens a window for high-precision theoretical predictions for excited states of molecular hydrogen.

References

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