Long-range asymptotic behaviour of the exchange energy in the hydrogen molecule

MICHAL SILKOWSKI, KRZYSZTOF PACHUCKI, University of Warsaw — The exchange energy is of fundamental importance for the understanding of interatomic interactions. Its long-range behavior in H₂ was investigated in the early days of quantum mechanics¹. Those results were met with criticism² and asymptotically correct form was derived by Herring and Flicker³. Despite further work by many authors⁴,⁵, long-range asymptotics of exchange energy in H₂ still raises controversy.

We present high-precision variational calculations of energy splitting between the lowest hydrogen states performed with our H2SOLV⁶ package, which utilizes explicitly correlated exponential basis⁷. Due to correct asymptotic behavior of our basis, we claim that our numerical results resolve this controversy.

¹W. Heitler and F. London, Z. Physik 44, 455 (1927)
²C. Herring, Rev. Mod. Phys. 34, 631 (1962)
³C. Herring and M. Flicker, Phys. Rev. 134, A362 (1964)