Erratum: Asymptotic exchange energies for H_2 [Phys. Rev. A 86, 052525 (2012)]

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The aim of the paper was to derive an analytical approximation to the exchange energy of two interacting hydrogen atoms, and the expression obtained was in the form

$$(E_+ - E_-) = -KR^3\exp(-2R)\left[1 + O\left(\frac{1}{R}\right)\right] = O(R^3\exp(-2R)), \tag{1}$$

where R is the interatomic distance. However, the value of K that was given is incorrect. Although this does not change the basic result, the corrected version and some details of the calculation are given below. Since it is an asymptotic result, it will only be useful for very large R, and the numerical fitting for lower values of R will generally be better [1]. The error has arisen from two sources, one of which is the calculated result (1) is ascribed to $(E_+ - E_-)/2$ in error rather than the total exchange error, but the calculated values are also in error. From Eq. (38) in the original paper, we have the equation for $(E_+ - E_-)$,

$$(\pi)^2\frac{R^4}{2}\int_{u=0}\psi_A\frac{\partial\psi_A}{\partial u}G(p_1, p_2, v)dp_1dp_2dv, \tag{2}$$

where

$$G(p_1, p_2, v) = \sqrt{\left(p_1^2 - v^2\right)\left(p_2^2 - v^2\right)}(1 - v^2), \tag{3}$$

and up to terms of $O(\frac{1}{R})$,

$$\psi_A = \frac{1}{\pi}\exp[-\alpha R(p_1 - 1)]\exp[-\alpha R(p_2 - 1)]\exp(-2\alpha R)\exp(-2\alpha Ru)f(r_{12}). \tag{4}$$

In order to evaluate the leading term in R, we need to use the expression for α in (A6) of the original paper,

$$\alpha = 0.5 + \frac{0.5}{R} + O\left(\frac{1}{R^2}\right), \tag{5}$$

where we use the leading term in (5) for all terms except the term $\exp(-2\alpha R)$, where we need the first two terms in (5) to obtain $\exp(-R)\exp(-1)$. As shown in the original paper, the leading term is obtained by evaluating the derivative of ψ_A with $f = 1$ and using $p_1 = p_2 = 1$ in G. Consequently, we obtain the leading term of the exchange energy as

$$-\frac{R^5}{2}\exp(-2R)\exp(-2)\int_{u=0}\exp[-R(p_1 - 1)]\exp[-R(p_2 - 1)](1 - v^2)^2dp_1dp_2dv. \tag{6}$$

The integrals evaluate to

$$\frac{1}{R^2}\int_{-1}^{1}(1 - v^2)^2dv, \tag{7}$$

so that the explicit form of (1) is

$$(E_+ - E_-) = -0.072\,1788R^3\exp(-2R)\left[1 + O\left(\frac{1}{R}\right)\right]. \tag{8}$$

The numerical coefficient is substantially lower in magnitude than the original, but the main result that the exchange in energy is $O(R^3\exp(-2R))$ is unchanged.

[1] N. G. de Bruijn, *Asymptotic Methods in Analysis* (Dover, New York, 1981), p. 18 and 19.

