PHYSICAL REVIEW A VOLUME 48, NUMBER 6 DECEMBER 1993

COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Elastic scattering of hydrogen atoms at low temperatures"

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(Received 5 March 1993)

In a recent paper Jamieson, Dalgarno, and Yukich [Phys. Rev. A **46**, 6956 (1992)] discuss the elastic scattering of two hydrogen atoms at very low collision energies. They use as an input to their numerical calculations the potential-energy curve of the $b\ ^3\Sigma_u^+$ state obtained from a configuration-interaction (CI) calculation and report a triplet scattering length that is much larger than found previously. We show that the difference is a consequence of the neglect of a systematic shift in the $b\ ^3\Sigma_u^+$ curve. Furthermore, we show that by taking the systematic shift into account, the scattering length of the CI potential reduces to a value of $(1.2\pm0.2)a_0$, which is in agreement with previous results.

PACS number(s): 34.40.+n, 67.65.+z, 34.20.Cf

Jamieson, Dalgarno, and Yukich [1] have recently argued that the potential-energy curve of the (lowest triplet) $b\ ^3\Sigma_u^+$ state of H_2 needs to be improved. They arrive at this conclusion by investigating the uncertainties in the scattering length calculated with the triplet potential recently obtained by Frye, Lie, and Clementi [2]. Previously, the scattering length was obtained with the triplet curve of Kolos and Wolniewicz [3]. In particular, Jamieson, Dalgarno, and Yukich claim that using the potential of Frye, Lie, and Clementi gives a triplet scattering length of $1.91a_0$ instead of the $1.34a_0$ found by a number of other authors [4,5] using the Kolos and Wolniewicz potential. However, we show in this Comment that the large value of the scattering length found by these authors is due to the neglect of a systematic shift in the triplet potential. Moreover, the uncertainties in the triplet potential by Frye, Lie, and Clementi are less severe than suggested by Jamieson, Dalgarno, and Yukich. Taking the shift into account leads to a scattering length, which is in agreement with $1.34a_0$.

The configuration-interaction method used by Frye, Lie, and Clementi is a method designed to solve the atomic and molecular electronic properties of any given molecule, whereas the approach used by Kolos and Wolniewicz is only applicable to diatomic molecules as it takes advantage of the molecular symmetries. Consequently, the approach of Kolos and Wolniewicz is the natural way to obtain electronic properties of H_2 and it indeed turns out that the requirements on computer storage and available CPU time are less stringent due to the much faster convergence in terms of the number of basis functions. In fact, the configuration-interaction results of Frye, Lie, and Clementi are the first calculations with comparable accuracy. However, Frye, Lie, and Clementi report that a trade-off in terms of computer storage and accuracy was still needed and that due to the remaining deficiency in the basis set the value of the energy at which a H atom in the $1s$ state ionizes is 0.11 cm^{-1} off. For the molecule this implies that the potential energy when two $1s$ atoms are infinitely far apart is 0.22 cm^{-1} too high and equals in atomic units $-0.999\,998\,99$ hartree (see Table II of Ref. [2]). Nevertheless, Frye, Lie, and Clementi conclude that *relative* to their dissociation limit the potential-energy curve is nearly equal to the Kolos and Wolniewicz curve at least at internuclear distances larger than $6a_0$ and somewhat worse at distances between $3a_0$ and $6a_0$. For even smaller distances the differences are more profound, but due to the repulsive nature of the potential this radial region does not contribute significantly to any scattering quantity at the low collision energies considered. Beyond the internuclear separation of $12a_0$ neither Frye, Lie, and Clementi nor Kolos and Wolniewicz have calculated the triplet potential and the H+H potential-energy curve should be fitted to a multipole expansion [6].

In this Comment we incorporate the above-mentioned shift into the configuration-interaction potential, in contrast with Jamieson, Dalgarno, and Yukich as can be inferred from Table VI of their paper. At first sight this looks like a minor change but at the internuclear distance of $12a_0$, for example, this leads to dramatic changes in the potential. At this distance Kolos and Wolniewicz give -2.516×10^{-6} hartree, Frye, Lie, and Clementi, with a correct dissociation limit, give -2.78×10^{-6} hartree, while Jamieson, Dalgarno, and Yukich use -1.77×10^{-6} hartree. The multipole expansion at the same distance gives -2.528×10^{-6} hartree. Hence, the Kolos and Wolniewicz potential has negligible connection problems whereas both potentials constructed from the configuration-interaction calculation show an unacceptable discontinuity. As a consequence, Jamieson, Dalgarno, and Yukich use a spline interpolation between $12a_0$ and $15a_0$ to obtain a smooth transition between the two radial regions. At these distances we adopt a similar procedure for the shifted potential of Frye, Lie, and Clementi. Note, however, that the discontinuity of the latter potential is less severe.

We calculated the triplet scattering length of these three potential curves by solving the radial Schrödinger equation of the nuclear motion at low collision energies. The Schrödinger equation is numerically integrated using the methods applied extensively in our group to obtain decay rates of a gas of spin-polarized hydrogen [7] or cesium [8] and spin-exchange frequency shifts in the hydrogen maser [5]. Note that, contrary to the description by Jamieson, Dalgarno, and Yukich (see Table V of Ref. [1]), the calculations in Ref. [5] are based on the Kolos-Wolniewicz potential. From the wave function at large internuclear separations a phase shift can be deduced and subsequently, using the effective-range theory, the scattering length can be found.

The calculations of the scattering length using the Kolos and Wolniewicz triplet curve and the potential curve by Jamieson, Dalgarno, and Yukich give a result of $1.34a_0$ and $1.91a_0$, respectively, while the scattering length found for the Frye, Lie and Clementi potential is $1.2a_0$. The latter value is slightly lower than the scattering length of the Kolos and Wolniewicz potential. However, there are two sources of uncertainty with this potential. For the integration of the Schrödinger equation the potential curve is needed for every internuclear separation. In order to obtain these values below $12a_0$ an interpolation with B splines of degree 3 between the fourteen values given by Frye, Lie, and Clementi is used. It turns out that applying other reasonable interpolation methods leads to considerable shift in the position and energy of the minimum of the triplet potential curve. This is due to an insufficient number of points close to the potential minimum. Applying different interpolation methods indicates an uncertainty of the scattering length of $0.1a_0$.

A more fundamental uncertainty according to Frye, Lie, and Clementi is due to the deficiency in the basis set of the configuration-interaction calculation. In order to incorporate the shifted dissociation limit in the numerical evaluation of the scattering length the shift is assumed independent of distance. Again, according to Frye, Lie, and Clementi, this seems unrealistic and below $12a_0$ can locally lead to changes in the potential of the order of 10^{-7} hartree as estimated on the basis of a comparison with the multipole expansion. Note that between $12a_0$ and $15a_0$ there are corrections as well, since the potential is found by a spline interpolation connecting the configuration-interaction potential with the multipole expansion. These changes are sufficient to put another $0.1a_0$ uncertainty on the scattering length.

In conclusion, the uncertainties in the collisional quantities obtained with the potential-energy curve of the $b\,^3\Sigma_u^+$ electronic state of H_2 as calculated with the configuration-interaction method are less severe than suggested by Jamieson, Dalgarno, and Yukich. Furthermore, the calculations are in agreement with calculations incorporating the Kolos and Wolniewicz potential.

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