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Collisions of ground-state hydrogen atoms

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We derive an expression for the diffusion cross section of identical atoms and use it in a report of diffusion, viscosity, total, spin-change, frequency-shift, and broadening cross sections in hydrogen, calculated with improved interaction potentials. We also report some total cross sections for spin-polarized hydrogen.

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In a previous study, various cross sections for the elastic scattering of ground-state hydrogen atoms at low temperatures were calculated with the best interaction potentials available at the time [1]. To evaluate the effects of the improvements that were contained in the potentials, cross sections were compared with values that had been calculated earlier, with necessarily older potentials, by Allison and Smith [2]. More precise potentials have become available since our earlier calculations [1] and we present updated values for various elastic cross sections at several temperatures.

The calculated scattering length describing very low energy collisions of H$(1s)$ and H$(1s)$ atoms interacting via the $X\,{}^1\Sigma_g^+$ molecular potential varies by about 33% when the nuclear reduced mass is replaced by the atomic mass [3]; we examine the influence of the mass on the calculated cross sections.

Allison and Smith [2] calculated transport cross sections effective in diffusion, viscosity, and thermal conductivity. Because the interchange of two identical atoms does not alter the atom densities, different definitions have been used for self-diffusion cross sections [4,5]. We adopt the definition in which the treatment of the collisions is fully symmetric [5]. The resulting formulas are the same as those of Allison and Smith [2], Jamieson *et al.* [1], and Celiberto *et al.* [4] for viscosity and of Krstić and Schultz [5] for diffusion.

The wave function for a pair of identical atoms in relative motion with asymptotic wave vector **k** separated by displacement vector **R** is, for large R [6],

$$\Psi(R)\sim\exp(i\mathbf{k}\cdot\mathbf{R})\pm\exp(-i\mathbf{k}\cdot\mathbf{R})+[f(\theta,\phi)\pm f(\pi-\theta,\phi)][\exp(ikR)/R], \tag{1}$$

where $[f(\theta,\phi)\pm f(\pi-\theta,\phi)]$ is the amplitude for scattering into the solid angle $\Omega=(\theta,\phi)$ and the $\pm$ signs are such that the total wave function, including electronic and nuclear spin parts, is antisymmetric with respect to interchange of either the electrons or the nuclei. The nuclei are protons which, like the electrons, are fermions, hence the antisymmetry. We discuss the scattering amplitude and the sign in more detail below.

The pair of atoms that separate asymptotically to H$(1s)$ $+$H$(1s)$ interact via the $X\,{}^1\Sigma_g^+$ and $b\,{}^3\Sigma_u^+$ electronic states of molecular hydrogen. These states are already antisymmetrized with respect to interchange of the electrons and have statistical weights of $\frac{1}{4}$ and $\frac{3}{4}$, respectively. The nuclear *spin* states comprise a singlet which is antisymmetric and a triplet which is symmetric with respect to interchange of the nuclei; their statistical weights are $\frac{1}{4}$ and $\frac{3}{4}$, respectively. Thus we must consider four states, namely the two electronic states, $X\,{}^1\Sigma_g^+$ and $b\,{}^3\Sigma_u^+$, combined with each nuclear state. To ensure that the overall wave function is antisymmetric with respect to interchange of the nuclei, the singlet and triplet nuclear spin states must be associated with spatial wave functions that are symmetric and antisymmetric, respectively, with respect to interchange of the nuclei. We can interchange the nuclei by rotating the atom pair through an angle π. However, by doing so we rotate the electrons. We can restore them to their original positions by a reflection through the midpoint of the internuclear distance and a further reflection in a plane perpendicular to the original rotation. The midpoint reflection changes the sign of the ungerade state but leaves the gerade state unchanged. The plane reflection leaves both electronic states unchanged because of their Σ^+ symmetry (there is a sign change for Σ^- symmetry) [7].

The partial wave expansion of the asymptotic wave function $\Psi(R)$ in Eq. (1) is, for a central potential,

$$\Psi(R)\sim\sum_l (2l+1)\left(i^l j_l(kR)+\frac{1}{k}\exp(i\eta_l)\sin(\eta_l)\times\frac{\exp(ikR)}{R}\right)[P_l(\cos\theta)\pm P_l(\cos\overline{\pi-\theta})], \tag{2}$$

where j_l and P_l denote the regular spherical Bessel function of order l and the Legendre polynomial of degree l, respectively. By substituting $P_l(\cos\overline{\pi-\theta})=(-1)^l P_l(\cos\theta)$ into Eq. (2), we see that only terms with even l, which do not change sign under rotation, contribute if the positive sign is chosen in Eq. (1) and only terms with odd l, which do change sign under the rotation, contribute if the negative sign is chosen. Taking cognizance of the reflections, we achieve the required symmetries of the collision system by choosing the positive sign when l is even and the singlet nuclear state is combined with the electronic gerade state or the triplet nuclear state is combined with the electronic ungerade state and the negative

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TABLE I. Signs and molecular species.

Electronic state	Nuclear state	l odd	l even	l odd	l even
${}^1\Sigma_g^+$	Singlet	$-$	$+$		Para
${}^1\Sigma_g^+$	Triplet	$+$	$-$	Ortho	
${}^3\Sigma_u^+$	Singlet	$+$	$-$	Para	
${}^3\Sigma_u^+$	Triplet	$-$	$+$		Ortho

sign otherwise. The signs are closely related to the division of hydrogen molecules into orthohydrogen and parahydrogen; orthohydrogen is the species with the greater statistical weight [8]. Each species contains states whose rotational quantum numbers are either even or odd. The signs and species are summarized in Table I.

The incident wave, $\exp(i\mathbf{k}\cdot\mathbf{R})\pm\exp(-i\mathbf{k}\cdot\mathbf{R})$, may be written as $2\cos\mathbf{k}\cdot\mathbf{R}$ or $2i\sin\mathbf{k}\cdot\mathbf{R}$, both of which yield an average probability of 2, corresponding to either particle being the incident particle, with wave function $\exp(i\mathbf{k}\cdot\mathbf{R})$, say, or the target particle with wave function $\exp(-i\mathbf{k}\cdot\mathbf{R})$ [9]. The flux of incident particles, $\hbar k/\mu$, where μ is the reduced mass for the collision, must therefore be multiplied by 2 to yield the rate of collisions. The probability current calculated from the spherical wave part of the wave function in Eq. (1) measures the probability that either atom is scattered into the solid angle (θ,ϕ). We define the differential cross section as the ratio of this current to the rate of collisions so that it is given by one-half of the square of the modulus of the coefficient of $\exp(ikR)/R$.

On substituting the partial wave expansion in $[f(\theta,\phi)\pm f(\pi-\theta,\phi)]$, we obtain twice the sums over even values of l for the positive sign and twice the sums over odd values of l for the negative sign. The differential cross section is

$$\frac{d\sigma}{d\Omega}=\tfrac{1}{4}A_S(\theta,\phi)+\tfrac{3}{4}A_T(\theta,\phi), \tag{3}$$

where $A_S(\theta,\phi)$ and $A_T(\theta,\phi)$ are the differential cross sections for scattering *via* the electronic $X\,{}^1\Sigma_g^+$ and $b\,{}^3\Sigma_u^+$ states, respectively. Singlet and triplet nuclear spin states contribute to each of these differential cross sections. We find, from Eq. (1) with the signs now determined,

$$\begin{aligned}A_S(\theta,\phi)={}&\frac{1}{4}\,\frac{2}{k^2}\Big|\sum_{l\ \mathrm{even}}(2l+1)P_l(\cos\theta)\exp(i\eta_l^S)\sin(\eta_l^S)\Big|^2\\&+\frac{3}{4}\,\frac{2}{k^2}\Big|\sum_{l\ \mathrm{odd}}(2l+1)\\&\times P_l(\cos\theta)\exp(i\eta_l^S)\sin(\eta_l^S)\Big|^2,\\A_T(\theta,\phi)={}&\frac{1}{4}\,\frac{2}{k^2}\Big|\sum_{l\ \mathrm{odd}}(2l+1)P_l(\cos\theta)\exp(i\eta_l^T)\sin(\eta_l^T)\Big|^2\\&+\frac{3}{4}\,\frac{2}{k^2}\Big|\sum_{l\ \mathrm{even}}(2l+1)\\&\times P_l(\cos\theta)\exp(i\eta_l^T)\sin(\eta_l^T)\Big|^2,\end{aligned} \tag{4}$$

where η_l^S and η_l^T are the phase-shifts for the lth partial waves scattered via the $X\,{}^1\Sigma_g^+$ and $b\,{}^3\Sigma_u^+$ state potentials, respectively. The first term of each right-hand side is the contribution from the nuclear singlet state and the second term is the contribution from the nuclear triplet state. The total cross section is

$$\begin{aligned}\sigma_{\mathrm{Total}}={}&\int\frac{d\sigma}{d\Omega}d\Omega=(4\pi/k^2)\sum_{l\ \mathrm{odd}}(2l+1)\tfrac{3}{8}\sin^2(\eta_l^S)\\&+(4\pi/k^2)\sum_{l\ \mathrm{even}}(2l+1)\tfrac{1}{8}\sin^2(\eta_l^S)\\&+(4\pi/k^2)\sum_{l\ \mathrm{even}}(2l+1)\tfrac{9}{8}\sin^2(\eta_l^T)\\&+(4\pi/k^2)\sum_{l\ \mathrm{odd}}(2l+1)\tfrac{3}{8}\sin^2(\eta_l^T);\end{aligned} \tag{5}$$

the formulation that takes account of symmetry makes this cross section twice that used by Jamieson *et al.* [1].

The diffusion cross section is [9]

$$\sigma_D=\int(d\sigma/d\Omega)(1-\cos\theta)d\Omega. \tag{6}$$

The breakdown into sums over odd l and even l only, indicated in Eq. (4), implies that the part of the integrand with the factor $\cos\theta$ is odd in $\cos\theta$; hence, with our definition,

$$\sigma_D=\sigma_{\mathrm{Total}}, \tag{7}$$

which agrees with the formula given by Krstić and Schultz [5].

We adopted Born-Oppenheimer potentials corrected where possible for adiabatic, relativistic, and radiative effects. The Born-Oppenheimer potentials were constructed from the *ab initio* values of Frye *et al.* [10], Kolos and Rychlewski [11], and Wolniewicz [12,13]; at long range we used multipole expansions with the coefficients of Yan *et al.* [14] and the exchange expression of Herring and Flicker [15]. Adiabatic corrections were taken from the results of Wolniewicz [12] matched to the long-range expression, $V_{\mathrm{ad}}(R)$, of Dalgarno and McCarroll [16],

$$V_{\mathrm{ad}}(R)=-\frac{1}{2\mu}\{V_{\mathrm{BO}}(R)+R[dV_{\mathrm{BO}}(R)/dR]\}, \tag{8}$$

where μ is the reduced mass measured in electron mass units and $V_{\mathrm{BO}}(R)$ is the Born-Oppenheimer potential. We used the relativistic and radiative corrections of Wolniewicz [12], available only for the $X\,{}^1\Sigma_g^+$ potential, at short to medium range and ignored them at long range where the adiabatic correction (8) is more important. The adopted potentials are improved over those used previously [1] by having superior *ab initio* values, more complete adiabatic, relativistic, and radiative corrections, and more accurate asymptotic continuations to large nuclear separations.

We calculated the phase shifts by solving the differential equations for the scattering numerically by Numerov's method and fitting the solutions asymptotically to the usual linear combination of spherical Bessel functions. We evaluated the spin-change rates and viscosity cross sections from the formulas of Dalgarno and Smith [17,18] and Allison and Smith [2], respectively, and we used Eqs. (5) and (7) for the total and diffusion cross sections. We evaluated the shift and broadening cross sections, which are important in the study of hydrogen masers, in the elastic [17] or *degenerate internal states* (DIS) approximation [19]; the appropriate phase-shift

TABLE II. Cross sections (10^{-16} cm^2).

	Total		Diffusion		Viscosity	
Temp. (K)	Nucl. mass	Atom. mass	Nucl. mass	Atom. mass	Nucl. mass	Atom. mass
1.0	32.1	32.0	79.1	78.8	195.0	194.0
2.0	42.6	42.5	99.8	99.5	231.0	230.0
4.0	51.0	50.9	111.0	111.0	222.0	223.0
6.0	55.0	54.4	113.0	113.0	206.0	206.0
8.0	55.3	55.1	127.0	135.0	201.0	198.0

TABLE IV. Shift and broadening cross sections (10^{-17} cm^2).

	λ_0		σ_1		σ_2	
Temp. (K)	Nucl. mass	Atom. mass	Nucl. mass	Atom. mass	Nucl. mass	Atom. mass
0.5	-86.2	-103.0	3.15	4.44	0.004	0.018
1.0	-50.5	-61.2	2.35	3.30	0.009	0.040
2.0	-23.0	-29.9	1.65	2.24	0.029	0.072
4.0	0.620	-4.36	0.932	1.18	0.515	0.578
6.0	14.2	9.8	-2.24	-2.23	4.01	4.21
8.0	24.1	19.9	-8.77	-9.07	11.6	11.4

formulas are quoted in Ref. [1]. The weights for temperature averaging are listed in Table I of Ref. [1]; we performed the averaging by generalized Gauss-Laguerre quadrature [20].

The $X\,^1\Sigma_g^+$ potential supports a quasibound state for $l=5$ at 1.277×10^{-4} hartree for the nuclear reduced mass and at 1.247×10^{-4} hartree for the atomic reduced mass. As the energy is increased, the phase shift of a partial wave decreases through an amount π for each bound state in accordance with Levinson's theorem, and the contributions to the various cross sections oscillate. The oscillations have a neglible effect on most of our calculated temperature-averaged cross sections because of the exponential damping, but, for the $l=5$ partial wave, interference between the shape resonance and the onset of the oscillations broadens the influence of the resonance. For temperatures of 6 K and 8 K, we calculated the contribution from this shape resonance by Simpson's rule.

There is no unique choice of the value of the reduced mass, which plausibly can range from the reduced mass of the two protons, as in conventional Born-Oppenheimer calculations, to the reduced mass of two hydrogen atoms. Arguments have been presented that indicate that diabatic corrections can be partially incorporated by selecting the atomic reduced mass [24]. We explore the sensitivity of the cross sections to the choice of reduced mass. The calculations, made with the reduced nuclear and atomic masses, are shown in Tables II–IV.

The total, diffusion, and viscosity cross sections are not unduly sensitive to the reduced mass. In Table V we compare the new results with those of Allison and Smith [2]. The increasing difference with temperature is expected because of the differing cross-section formulas, as is the similarity at low temperatures, where *s*-wave scattering dominates; the formula used by Allison and Smith becomes identical to formula (5) when only *s* waves are taken into account. The difference in the viscosity cross sections, remaining steady at about 5% over the table, is attributable to the improved potentials. In this comparison, we adopted the nuclear reduced mass to ensure consistency with the calculations of Allison and Smith.

The influence of the reduced mass on the spin-change rates is quite marked at lower temperatures because the cross sections at small energies depend on the square of the differences of the (electronic) singlet and triplet phase shifts, which in turn depend on the differences of the scattering lengths, and these are very sensitive to the reduced mass [3].

The shift cross sections λ_0 are also sensitive to the reduced mass. As functions of energy, the singlet and triplet *s*-wave phase shifts cross, leading to cancellation. The energy of the crossing depends strongly on the scattering lengths and so is sensitive to the reduced mass. The broadening cross sections σ_1 also owe their sensitivity to the cancellation of the *s*-wave phase shifts; close to the energy of complete cancellation, the *p*- and *d*-wave contributions, which are small at low energies, become more important and there is further cancellation because the terms alternate in sign. The broadening cross sections σ_2 are much smaller than σ_1 at low temperatures because they vanish rapidly as the energy approaches zero.

Measurements of these cross sections have been made at a temperature of 0.5 K by Hayden *et al.* [21]. They found a value of $-21.7\pm2.8\times10^{-16}$ cm^2 for λ_0 compared with our values of -8.62×10^{-16} cm^2 with the nuclear reduced mass and -10.3×10^{-16} cm^2 with the atomic reduced mass; Kokkelmans and Verhaar [22] obtained a value of -11.9×10^{-16} cm^2 from a calculation which included the hyperfine interaction. Hayden *et al.* also measured the combined cross section $\frac{1}{2}\sigma_1+\sigma_2$, which is dominated by σ_2 at 0.5 K, as $38.5\pm3\times10^{-18}$ cm^2 compared with our values of 15.8×10^{-18} cm^2 with the nuclear reduced mass and 22.4×10^{-18} cm^2 with the atomic reduced mass. Kokkelmans and Verhaar obtained 26.3×10^{-18} cm^2. Their values (calculated with the atomic reduced mass [23]) and our elastic

TABLE III. Rate coefficients $\mathcal{R}(1-0)$ for spin change (10^{-14} cm^3 s^{-1}).

Temp. (K)	Nucl. mass	Atom. mass
1.0	6.10	8.75
2.0	6.28	8.94
4.0	12.7	14.9
6.0	62.1	65.3
8.0	188.0	191.0

TABLE V. Cross sections (10^{-16} cm^2).

	Diffusion		Viscosity	
Temp. (K)	Present	Reference [2]	Present	Reference [2]
1.0	79.1	89.8	195.0	187.0
2.0	99.8	97.0	231.0	221.0
4.0	111.0	90.6	222.0	213.0
6.0	113.0	84.2	206.0	197.0
8.0	127.0	80.5	201.0	192.0

TABLE VI. Total cross sections for spin-polarized atoms (10^{-16} cm^2).

Temp. (K)	Nucl. mass	Atom. mass
1.0	51.0	51.0
2.0	67.6	67.5
4.0	77.1	77.1
6.0	75.2	75.1
8.0	70.5	70.5

approximation values appear to underestimate the magnitudes of these cross sections. The reduced mass influences the calculated cross sections considerably but neither its effect nor the hyperfine interaction is sufficient to account for the discrepancies between the calculated and experimental values.

In this derivation of the total cross section we assumed that the nuclear and electronic spins of each atom are not correlated and we took the spin wave function to be a product of the separate nuclear and electronic spin wave functions. Exploration of the properties of ultra-cold trapped *spin-polarized* hydrogen atoms currently attracts much interest (e.g., [25]); the topic is reviewed by Julienne *et al.* [26], Walker and Feng [27], and Weiner *et al.* [28,29]. The nuclear and electronic spins of spin-polarized atoms *are* correlated. The atoms are bosons and the formulas for the cross sections must be modified because the spin wave function cannot be taken as a product. The analysis is simpler; the total wave function is symmetric with respect to interchange of the atoms (bosons) and the spin wave function is symmetric (because of the polarization), which implies that the spatial wave function is also symmetric. Hence only partial waves with even angular momentum quantum numbers l contribute to the total cross section and, furthermore, the atoms interact only through the ${}^3\Sigma_u^+$ molecular state. The total cross section for spin-polarized hydrogen atoms is

$$\sigma_{\text{Total}}=(8\pi/k^2)\sum_{l\text{ even}}(2l+1)\sin^2(\eta_l^T). \tag{9}$$

We present some calculated total cross sections in Table VI. At low temperatures they are larger than those for unpolarized hydrogen because the triplet scattering length is much larger than the singlet. They have only a weak dependence on reduced mass in accordance with the mass dependence of the triplet scattering length.

To conclude, we have shown that the strong influence of diabatic corrections on the H(1s)-H(1s) singlet scattering length carries over to the spin-change, shift, and broadening properties but not to the transport cross sections for viscosity and self-diffusion. Theoretical values of the shift and broadening cross sections at 0.5 K do not agree with experiment. The low-temperature total cross sections are increased when the atoms are spin-polarized.

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[1] M.J. Jamieson *et al.*, Phys. Rev. A **46**, 6956 (1992).
[2] A.C. Allison and F.J. Smith, At. Data **3**, 317 (1971).
[3] C.J. Williams and P.S. Julienne, Phys. Rev. A **47**, 1524 (1993).
[4] R. Celiberto *et al.*, Phys. Rev. A **58**, 2106 (1998).
[5] P.S. Krstić and D.R. Schultz, At. Plasma-Mater. Interaction Data Fusion **8**, 1 (1999).
[6] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics Non-Relativistic Theory* (Pergamon, London, 1958).
[7] P.W. Atkins and R.S. Friedman, *Molecular Quantum Mechanics* (Oxford University Press, Oxford, 1997).
[8] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).
[9] N.F. Mott and H.S.W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, Oxford, 1965).
[10] D. Frye *et al.*, J. Chem. Phys. **91**, 2366 (1989).
[11] W. Kolos and J. Rychlewski, J. Mol. Spectrosc. **143**, 237 (1990).
[12] L. Wolniewicz, J. Chem. Phys. **99**, 1851 (1993).
[13] L. Wolniewicz (private communication).
[14] Z.C. Yan, J.F. Babb, A. Dalgarno, and G.W.F. Drake, Phys. Rev. A **54**, 2824 (1996).
[15] C. Herring and M. Flicker, Phys. Rev. **134**, 362 (1964).
[16] A. Dalgarno and R. McCarroll, Proc. R. Soc. London, Ser. A **237**, 383 (1956).
[17] A. Dalgarno, Proc. R. Soc. London, Ser. A **262**, 132 (1961).
[18] F.J. Smith, Planet. Space Sci. **14**, 929 (1966).
[19] J.M.V.A. Koelman *et al.*, Phys. Rev. A **38**, 3535 (1988).
[20] Z. Kopal, *Numerical Analysis* (Chapman and Hall, London, 1961).
[21] M.E. Hayden *et al.*, Phys. Rev. A **53**, 1589 (1996).
[22] S.J.J.M.F. Kokkelmans and B.J. Verhaar, Phys. Rev. A **56**, 4038 (1997).
[23] B.J. Verhaar *et al.*, Phys. Rev. A **35**, 3825 (1987).
[24] P.R. Bunker and R.E. Moss, Mol. Phys. **33**, 417 (1977); P.R. Bunker *et al.*, *ibid.* **33**, 425 (1977).
[25] D.G. Fried *et al.*, Phys. Rev. Lett. **81**, 3811 (1998).
[26] P.S. Julienne *et al.*, Adv. At., Mol., Opt. Phys. **30**, 141 (1993).
[27] T. Walker and P. Feng, Adv. At., Mol., Opt. Phys. **34**, 125 (1994).
[28] J. Weiner, Adv. At., Mol., Opt. Phys. **35**, 45 (1995).
[29] J. Weiner *et al.*, Rev. Mod. Phys. **71**, 1 (1999).