

Comparing these expressions with Table V, it is found that two of the "sum rules" valid for non-identical atoms, Eqs. (4.21a) and (4.21c), do *not* hold in this case. All the other relations, Eqs. (4.20a), (4.20b), (4.21b), (4.21d), and (4.22), still are valid.

ACKNOWLEDGMENT

The author takes pleasure in thanking Professor E. Wichmann for many profitable discussions of this and related problems. He is also indebted to H. Gibbs for comparisons of some of the results in Sec. IV with his own work.

Effect of Hydrogen-Hydrogen Exchange Collisions

P. L. BENDER

Joint Institute for Laboratory Astrophysics, Boulder, Colorado

(Received 23 July 1963)

Exchange collisions between ground-state hydrogen atoms are considered. The density matrix after collision is calculated for pairs of atoms which initially had the same density matrix. The result is applied to the hydrogen maser with the assumption that only exchange collisions and the escape of atoms from the storage bulb influence the linewidth for the field-independent hyperfine transition. Under normal operating conditions a frequency shift of roughly 5% of the exchange collision contribution to the linewidth is predicted.

1. INTRODUCTION

THE effect of exchange collisions between ground-state hydrogen atoms has been treated by a number of authors.¹⁻⁶ In particular, Wittke and Dicke considered a case where departures from thermal equilibrium were small and the only nonzero off-diagonal elements of the density matrix for the ground-state sublevels were those corresponding to the magnetic field-independent ($F=1, M_F=0$) \rightarrow ($F=0, M_F=0$) component of the hyperfine transition. The nuclear spins and all magnetic interaction energies can be neglected during collisions and the electron wave functions for the two colliding atoms can be combined to form triplet and singlet states. The effect of a collision is to multiply the triplet and singlet parts of the wave function by $e^{-i\Delta_T\tau}$ and $e^{-i\Delta_S}$ respectively. Δ_T is the integral of (E_T/\hbar) over the time of the collision, where E_T is the triplet state hydrogen-hydrogen interaction energy, and Δ_S is defined similarly. Wittke and Dicke made the approximation that only "strong" collisions were important, where "strong" collisions are those in which the relative phase shift $\Delta = \Delta_T - \Delta_S$ is large enough so that the relative phase after the collision can be considered random.

In the present paper the approximations of strong collisions and of small departures from equilibrium are removed. The effect on the density matrix of a single hydrogen-hydrogen collision for each atom in the

sample is given in Sec. 2. The resulting effect on operation of the hydrogen maser⁷ is discussed in Sec. 3. The expected frequency shift is estimated in Sec. 4 using straight-line paths with the triplet and singlet interaction potentials of Dalgarno and Lynn.^{4,8} A shift in the field-independent hyperfine transition of up to 5% of the exchange collision contribution to the linewidth is predicted.

2. EFFECT OF A SINGLE COLLISION WITH ARBITRARY PHASE SHIFT

The initial 4×4 density matrix⁹ ρ^i for the magnetic sublevels of ground-state hydrogen atoms is written in the F, M_F representation:

$$\rho^i = \begin{array}{c|cccc} & \begin{array}{c} F, M_F \\ \hline 1, 1 \\ 1, 0 \\ 1, -1 \\ 0, 0 \end{array} & \begin{array}{c} 1, 1 \\ 1, 0 \\ 1, -1 \\ 0, 0 \end{array} & \begin{array}{c} 1, 0 \\ 1, -1 \\ 0, 0 \end{array} & \begin{array}{c} 1, -1 \\ 0, 0 \end{array} & \begin{array}{c} 0, 0 \end{array} \\ \hline & & a & e^* & f^* & h^* \\ & & e & b & g^* & j^* \\ & & f & g & c & k^* \\ & & h & j & k & d \end{array} \quad (1)$$

The 16×16 density matrix σ^i for a pair of colliding atoms just before collision in the $F_1 M_{F_1} F_2 M_{F_2}$ representation is the direct product of ρ^i with itself. σ^i is transformed by a unitary transformation Γ to a representation $S M_S I M_I$ where the two electron spins and

¹ J. P. Wittke and R. H. Dicke, Phys. Rev. **103**, 620 (1956).

² J. P. Wittke, Thesis, Princeton University, 1955 (unpublished).

³ E. M. Purcell and G. B. Field, Ap. J. **124**, 542 (1956).

⁴ A. Dalgarno, Proc. Roy. Soc. (London) **A262**, 132 (1961).

⁵ A. F. Hildebrandt, F. B. Booth, and C. A. Barth, J. Chem. Phys. **31**, 273 (1959).

⁶ R. M. Mazo, J. Chem. Phys. **34**, 169 (1961).

⁷ D. Kleppner, H. M. Goldenberg, and N. F. Ramsey, Phys. Rev. **126**, 603 (1962).

⁸ A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London) **A69**, 821 (1956).

⁹ U. Fano, Rev. Mod. Phys. **29**, 74 (1957); see also C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), Chap. 5.

TABLE I. Representation transformation matrix $\Gamma = \langle SM_{S1}M_{F1} | F_1M_{F1}F_2M_{F2} \rangle$.

$\begin{matrix} F_1M_{F1}, \\ F_2M_{F2} \\ \hline SM_{S1}M_{F1} \end{matrix}$	11, 11	11, 10	11, 1-1	11, 00	10, 11	10, 10	10, 1-1	10, 00	1-1, 11	1-1, 10	1-1, 1-1	1-1, 00	00, 11	00, 10	00, 1-1	00, 00
11, 11	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
11, 10	0	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0	0	0	0	$\frac{1}{2}$	0	0	0
11, 1-1	0	0	0	0	0	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0	0	0	0	$\frac{1}{2}$	0	$\frac{1}{2}$
11, 00	0	$\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0	0	$-\frac{1}{2}$	0	0	0
10, 11	0	$\frac{1}{2}$	0	$-\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0	0	0	0	$-\frac{1}{2}$	0	0	0
10, 10	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0	0	0	0	0	$-\frac{1}{2}$
10, 1-1	0	0	0	0	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0
10, 00	0	0	$\frac{1}{2}$	0	0	0	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	$-\frac{1}{2}$	0	0
1-1, 11	0	0	0	0	0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	0	0	0	$-\frac{1}{2}$	0	$\frac{1}{2}$
1-1, 10	0	0	0	0	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	$-\frac{1}{2}$	0
1-1, 1-1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0
1-1, 00	0	0	0	0	0	0	$\frac{1}{2}$	0	0	$-\frac{1}{2}$	0	$\frac{1}{2}$	0	0	$-\frac{1}{2}$	0
00, 11	0	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0	0	$\frac{1}{2}$	0	0	0
00, 10	0	0	$\frac{1}{2}$	0	0	0	0	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	$\frac{1}{2}$	0	0
00, 1-1	0	0	0	0	0	0	$\frac{1}{2}$	0	0	$-\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	$\frac{1}{2}$	0
00, 00	0	0	$\frac{1}{2}$	0	0	$-\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0	0	0	0	0	$\frac{1}{2}$

the two nuclear spins are coupled:

$$\sigma^{ci} = \Gamma \sigma^i \Gamma^* \quad (2)$$

The matrix Γ (see Wittke,² Appendix 2) is reproduced in Table I.

The effect of a collision yielding a phase shift Δ between the parts of the density matrix corresponding to triplet and singlet electron states can be given by a unitary transformation A :

$$\sigma^{cf} = A \sigma^{ci} A^* \quad (3)$$

A is diagonal and has unit diagonal elements except for the elements connecting $S=0, M_S=0$ states, which are

$e^{i\Delta}$. We can also write A as follows:

$$A = I - (x/4)B, \quad (4)$$

where $x = (1 - e^{i\Delta})$, B has all elements zero except the last four diagonal elements which are 4, and I is the identity matrix. Transforming back to the $F_1M_{F1}F_2M_{F2}$ representation,

$$\sigma^f = \Gamma^* A \Gamma \sigma^i \Gamma^* A^* \Gamma = \left[I - \left(\frac{x}{4} \right) C \right] \sigma^i \left[I - \left(\frac{x^*}{4} \right) C^* \right], \quad (5)$$

$$\sigma^f = \sigma^i + \frac{1}{16} |x|^2 C \sigma^i C^* - \frac{1}{4} [x C \sigma^i + x^* \sigma^i C^*],$$

where $C = \Gamma^* B \Gamma$ is given in Table II. Since $C^* = C$ and

TABLE II. Matrix $C = \Gamma^* B \Gamma$.

$\begin{matrix} F_1M_{F1}, \\ F_2M_{F2} \\ \hline F_1M_{F1}, F_2M_{F2} \end{matrix}$	11, 11	11, 10	11, 1-1	11, 00	10, 11	10, 10	10, 1-1	10, 00	1-1, 11	1-1, 10	1-1, 1-1	1-1, 00	00, 11	00, 10	00, 1-1	00, 00
11, 11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
11, 10	0	+1	0	-1	-1	0	0	0	0	0	0	0	+1	0	0	0
11, 1-1	0	0	+2	0	0	-1	0	-1	0	0	0	0	0	+1	0	+1
11, 00	0	-1	0	+1	+1	0	0	0	0	0	0	0	-1	0	0	0
10, 11	0	-1	0	+1	+1	0	0	0	0	0	0	0	-1	0	0	0
10, 10	0	0	-1	0	0	+1	0	0	-1	0	0	0	0	0	0	-1
10, 1-1	0	0	0	0	0	0	+1	0	0	-1	0	-1	0	0	+1	0
10, 00	0	0	-1	0	0	0	0	+1	+1	0	0	0	0	-1	0	0
1-1, 11	0	0	0	0	0	-1	0	+1	+2	0	0	0	0	-1	0	+1
1-1, 10	0	0	0	0	0	0	-1	0	0	+1	0	+1	0	0	-1	0
1-1, 1-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-1, 00	0	0	0	0	0	0	-1	0	0	+1	0	+1	0	0	-1	0
00, 11	0	+1	0	-1	-1	0	0	0	0	0	0	0	+1	0	0	0
00, 10	0	0	+1	0	0	0	0	-1	-1	0	0	0	0	+1	0	0
00, 1-1	0	0	0	0	0	0	+1	0	0	-1	0	-1	0	0	+1	0
00, 00	0	0	+1	0	0	-1	0	0	+1	0	0	0	0	0	0	+1

TABLE III. Density matrix elements after collision with another hydrogen atom having the same initial density matrix.

$\rho_{11}^f = a - \frac{1}{4}(1 - \cos\Delta) \{2ac - \frac{1}{2}(b+d)^2 + j ^2\} - \frac{1}{4}i(\sin\Delta) \{eg^* - ge^*\}$
$\rho_{22}^f = b - \frac{1}{4}(1 - \cos\Delta) \{2b - a(1-a) - c(1-c) - \frac{1}{2}(b+d)^2 - j ^2 - (e ^2 + g ^2 - h ^2 - k ^2) - (eg^* + ge^*)\} - \frac{1}{4}i(\sin\Delta) \{-2(eg^* - ge^*)\}$
$\rho_{33}^f = c - \frac{1}{4}(1 - \cos\Delta) \{2ac - \frac{1}{2}(b+d)^2 + j ^2\} - \frac{1}{4}i(\sin\Delta) \{eg^* - ge^*\}$
$\rho_{44}^f = d - \frac{1}{4}(1 - \cos\Delta) \{2d - a(1-a) - c(1-c) - \frac{1}{2}(b+d)^2 - j ^2 + (e ^2 + g ^2 - h ^2 - k ^2) + (eg^* + ge^*)\}$
$\rho_{21}^f = e - \frac{1}{4}(1 - \cos\Delta) \{e(b+d+2c) - g(b+d+2a) + jk^* - hj^*\} - \frac{1}{4}i(\sin\Delta) \{e(c-b) + g(a-b) + f(e^* + g^*)\}$
$\rho_{31}^f = f - \frac{1}{4}(1 - \cos\Delta) \{2f - (e^* + g^*) - 2hk^*\} - \frac{1}{4}i(\sin\Delta) \{2f(c-a) + (e^2 - g^2)\}$
$\rho_{32}^f = g - \frac{1}{4}(1 - \cos\Delta) \{g(b+d+2a) - e(b+d+2c) + hj^* - jk^*\} - \frac{1}{4}i(\sin\Delta) \{e(b-c) + g(b-a) - f(e^* + g^*)\}$
$\rho_{41}^f = h - \frac{1}{4}(1 - \cos\Delta) \{h(b+d+2c) - j(e+g)\} - \frac{1}{4}i(\sin\Delta) \{h(c-d) + fk - gj\}$
$\rho_{42}^f = j - \frac{1}{4}(1 - \cos\Delta) \{j - k(e+g) - h(e^* + g^*)\} - \frac{1}{4}i(\sin\Delta) \{j(b-d) - ek - hg^*\}$
$\rho_{43}^f = k - \frac{1}{4}(1 - \cos\Delta) \{k(b+d+2a) - j(e^* + g^*)\} - \frac{1}{4}i(\sin\Delta) \{k(a-d) + hf^* - je^*\}$

$$|x|^2 = 2(1 - \cos\Delta),$$

$$\sigma^f = \sigma^i - \frac{1}{4}(1 - \cos\Delta) (C\sigma^i + \sigma^i C - \frac{1}{2}C\sigma^i C) - \frac{1}{4}i(\sin\Delta) (\sigma^i C - C\sigma^i). \quad (6)$$

Ignoring the correlation between the atoms which have just collided, the elements of the final 4×4 density matrix ρ^{ft} for all atoms in the sample which underwent collisions at time t are given by a partial contraction of σ^f with respect to F and M_F for one of the two atoms:

$$\rho^{ft}(F_2 M_{F_2}, F_2' M_{F_2}') = \sum_{F_1 M_{F_1}, F_1' M_{F_1}'} \delta(F_1 F_1') \delta(M_{F_1} M_{F_1}') \times \sigma^f(F_1 M_{F_1}, F_2 M_{F_2}, F_1' M_{F_1}', F_2' M_{F_2}'). \quad (7)$$

We now average over the times at which collisions occur and call the resulting final density matrix ρ^f . Each density matrix element has associated with it a frequency corresponding to the energy difference of the two states connected by that element. If an element of ρ^{ft} contains an element of σ^i having a frequency different by an amount large compared with the reciprocal of the averaging time, then the contribution to ρ^f will be zero. Thus we can break up σ^i into terms having different frequency dependences,

$$\sigma^i = \sigma^i(0) + \sigma^i(\omega_1) + \sigma^i(\omega_2) + \dots \quad (8)$$

and only the contribution of $\sigma^i(\omega_n)$ to the corresponding elements of $\sigma^f(\omega_n)$ and thereby $\rho^f(\omega_n)$ should be included.

With the above prescription and Eqs. (6) and (7), we can now calculate ρ^f in terms of ρ^i . We assume the low field case where the two Zeeman frequencies are equal but all other frequencies are quite different. The results for ρ^f are given in Table III. The phase shift in ρ_{42}^f is particularly significant, since this corresponds to a small frequency shift in the magnetic-field-independent hyperfine component whose frequency ω_H can be measured precisely in the hydrogen maser.

3. APPLICATION TO THE HYDROGEN MASER

The rate of change of the density matrix for hydrogen atoms in a hydrogen maser⁷ can be written as the sum

of three terms:

$$\left(\frac{d\rho}{dt}\right) = \left(\frac{d\rho}{dt}\right)_{\text{flow}} + \left(\frac{d\rho}{dt}\right)_{\text{exchange}} + \left(\frac{d\rho}{dt}\right)_{\text{radiation}}. \quad (9)$$

Here the flow term corresponds to atoms entering and leaving the storage bulb, the exchange term represents exchange collisions between hydrogen atoms, and the radiation term involves the effects of a microwave field capable of producing transitions between the (1,0) and (0,0) states. The effect of the energy separation between the levels is included in the radiation term. Possible line broadening and frequency shifts due to collisions with the walls or anything else except exchange collisions with hydrogen atoms are not included and we assume that the only off-diagonal elements of the density matrix are those corresponding to the desired hyperfine transition component.

We take the flow term with the same ordering of states as in Eq. (1) to be

$$\left(\frac{d\rho}{dt}\right)_{\text{flow}} = r \begin{vmatrix} \frac{1}{2} & & \\ & \frac{1}{2} & \\ & & 0 \end{vmatrix} - r\rho, \quad (10)$$

where r corresponds to the rate at which hydrogen atoms flow into and out of the storage bulb. We have assumed that only atoms in the (1,1) and (1,0) states are passed by the state selector. Here $(1/r)$ is the mean time that atoms spend in the bulb.

The exchange term is given approximately by:

$$\left(\frac{d\rho}{dt}\right)_{\text{exchange}} = -2\pi n \bar{v}_{\text{rel}} \left[\int_0^\infty \{\rho - \rho'[\Delta(R)]\} R dR \right], \quad (11)$$

where n is the number of hydrogen atoms per cm^3 and \bar{v}_{rel} is the mean relative velocity. $\rho'[\Delta(R)]$ is the density matrix for an atom after an exchange collision with impact parameter R and relative velocity \bar{v}_{rel} with another atom also having the initial density matrix ρ . The elements of $(\rho - \rho'[\Delta])$ in terms of the elements of ρ may be obtained from Table III.

The nonzero elements of the radiation term can most easily be obtained from the equations of time-dependent perturbation theory for an undisturbed atom:

$$\begin{aligned} \dot{a}_2 &= -i(\omega_0/2)a_2 - i\beta e^{-i\omega t}a_4, \\ \dot{a}_4 &= i(\omega_0/2)a_4 - i\beta e^{i\omega t}a_2. \end{aligned} \quad (12)$$

a_2 and a_4 correspond to the (1,0) and (0,0) levels, respectively, and ω_0 is the unperturbed transition frequency between these two levels. The nonzero matrix elements of the term in the Hamiltonian giving the effect of an oscillating magnetic field near this transition frequency are taken to be

$$H_{42} = \hbar\beta e^{-i\omega t}, \quad H_{24} = H_{42}^*, \quad (13)$$

where β is real. The oppositely rotating terms in the matrix elements have been omitted since they are unimportant for weak oscillating fields. The results are

$$\begin{aligned} (d/dt)(a_4a_2^*) &= \dot{a}_4a_2^* + a_4\dot{a}_2^* = i\omega_0a_4a_2^* \\ &\quad - i\beta(|a_2|^2 - |a_4|^2)e^{i\omega t}, \end{aligned} \quad (14)$$

$$(d/dt)|a_2|^2 = -(d/dt)|a_4|^2 = 2\beta \operatorname{Im}(a_4a_2^*e^{-i\omega t}).$$

This gives for the density matrix:

$$(d/dt)(\rho_{42})_{\text{rad}} = i\omega_0\rho_{42} - i\beta(\rho_{22} - \rho_{44})e^{i\omega t}, \quad (15)$$

$$\begin{aligned} (d/dt)(\rho_{22})_{\text{rad}} &= -(d/dt)(\rho_{44})_{\text{rad}} \\ &= 2\beta \operatorname{Im}(\rho_{42}e^{-i\omega t}). \end{aligned} \quad (16)$$

From Eq. (9) and Table III we have:

$$\begin{aligned} d(\rho_{42})/dt &= -r\rho_{42} - \frac{1}{4}\{U + iV(\rho_{22} - \rho_{44})\}\rho_{42} \\ &\quad + i\omega_0\rho_{42} - i\beta(\rho_{22} - \rho_{44})e^{i\omega t}, \end{aligned} \quad (17)$$

$$\begin{aligned} d(\rho_{22} - \rho_{44})/dt &= \frac{1}{2}r - (\rho_{22} - \rho_{44})r - \frac{1}{2}U(\rho_{22} - \rho_{44}) \\ &\quad + 4\beta \operatorname{Im}(\rho_{42}e^{-i\omega t}), \end{aligned} \quad (18)$$

where

$$U = 2\pi n\bar{v}_{\text{rel}} \int_0^\infty [1 - \cos\Delta(R)]RdR, \quad (19)$$

$$V = 2\pi n\bar{v}_{\text{rel}} \int_0^\infty [\sin\Delta(R)]RdR.$$

These equations have a quasistationary solution obtained by setting

$$(d/dt)(\rho_{mm}) = 0, \quad \rho_{42} = \delta e^{i\omega t}. \quad (20)$$

This solution is:

$$\delta = -i\beta(\rho_{22} - \rho_{44})/[K + i(\omega - \omega')], \quad (21)$$

$$\begin{aligned} (\rho_{22} - \rho_{44}) &= \{2 + (U/r) \\ &\quad + (8\beta^2 K/r)/[K^2 + (\omega - \omega')^2]\}^{-1}, \end{aligned} \quad (22)$$

where

$$K = r + \frac{1}{4}U, \quad (23)$$

$$\omega' = \omega_0 - \frac{1}{4}(\rho_{22} - \rho_{44})V. \quad (24)$$

The rate of emission per atom is given by

$$\begin{aligned} \frac{d}{dt}(\rho_{22})_{\text{rad}} &= \frac{2\beta^2 K}{\{[K^2 + (\omega - \omega')^2][2 + (U/r)] + (8\beta^2 K/r)\}}. \end{aligned} \quad (25)$$

From the above expression the stimulated emission is maximum for $\omega = \omega'$. The frequency shift due to exchange collisions is thus given by Eq. (24). At low power levels the full linewidth at half-power is

$$\Delta\omega = 2K. \quad (26)$$

The ratio of the frequency shift to the part of the linewidth due to exchange collisions is then

$$\frac{1}{4}(V/U)[1 + (U/2r)]^{-1}. \quad (27)$$

Alternately, the ratio of the frequency shift to the limiting linewidth for low hydrogen density is

$$\frac{1}{8}(V/U)[(U/2r)]/[1 + (U/2r)]. \quad (28)$$

4. ESTIMATE OF PARAMETERS FOR HYDROGEN-HYDROGEN COLLISIONS

Given initially that the electron spin for atom 1 is $+\frac{1}{2}$ and for atom 2 is $-\frac{1}{2}$, the exchange cross section σ_{ex} is associated with the probability that if we make a measurement at a later time we will find $-\frac{1}{2}$ for the electron spin of atom 1. In this paper we use the term "exchange collision" more generally to mean an encounter in which an appreciable phase shift between the triplet and singlet parts of the electron wave function occurs, even though the electron spin is not measured after the encounter and therefore we cannot say whether exchange actually occurred. In fact, measuring the electron spin shortly after the encounter would force the phase difference to be a multiple of π and would thereby remove the possibility of obtaining a frequency shift.

The most recent work on the triplet and singlet potentials is that of Dalgarno and Lynn.^{4,8} The difference between the triplet and singlet energies can be adequately represented from $4a_0$ to $12a_0$ by⁴

$$\delta(r) = 6.87r^2e^{-kr}, \quad (29)$$

where r is the distance between the atoms in units of a_0 , $k = 1.974$, and δ is in rydbergs. Integrating $[R_\infty c\hbar\delta(r)/\hbar]$ over a straight-line path with impact parameter R to obtain the triplet phase shift minus the singlet phase shift:

$$\begin{aligned} \Delta(R) &= (6.87)(4\pi a_0 c R_\infty / v_{\text{rel}}) \\ &\quad \times \int_0^\infty (x^2 + R^2)e^{-k(x^2 + R^2)^{1/2}} dx. \end{aligned} \quad (30)$$

Expanding $(x^2+R^2)^{1/2}$ gives:

$$\begin{aligned} & \int_0^\infty (x^2+R^2)e^{-k(x^2+R^2)^{1/2}} dx \\ &= R^2 e^{-kR} \int_0^\infty e^{-(kx^2/2R)} \left[1 + \frac{x^2}{R^2} + \left(\frac{kR}{8}\right) \frac{x^4}{R^4} \right. \\ & \quad \left. - \left(\frac{kR}{16}\right) \frac{x^6}{R^6} + \dots \right] dx \\ &= (\pi R/2k)^{1/2} R^2 e^{-kR} \left[1 + (kR)^{-1} + \frac{3}{8}(kR)^{-1} \right. \\ & \quad \left. - \frac{5}{16}(kR)^{-2} + \dots \right]. \quad (31) \end{aligned}$$

Since $kR \sim 13$ when $\Delta(R) \sim 1$, we keep only the first term. Setting $v_{\text{rel}} = \sqrt{2}\bar{v}$, where \bar{v} is the mean speed, we have:

$$\Delta(R) \simeq KR^{5/2} e^{-kR}, \quad (32)$$

with

$$K = (13.74)\pi^{3/2} (a_0 c R_\infty / \bar{v}) k^{-1/2}. \quad (33)$$

At 300°K , $\bar{v} = 2.51 \times 10^5$ cm/sec and $K = 3.78 \times 10^3$. This gives $\Delta \simeq 1$ at $R = 6.55$, and Δ ranges approximately from 0.003 at $R = 10$ to 45 at $R = 4$.

Using Eq. (32) for $\Delta(R)$, we find:

$$\begin{aligned} [V/n\bar{v}_{\text{rel}}] &= 2\pi a_0^2 \int_0^\infty R(\sin\Delta) dR \\ &\simeq 2\pi a_0^2 \int_0^\infty \frac{R}{[k - (2.5/R)]} \left(\frac{\sin\Delta}{\Delta} \right) d\Delta. \quad (34) \end{aligned}$$

By numerical integration up to $\Delta(4)$, using the fact that the first factor under the integral is slowly varying, and ignoring the remainder of the integral:

$$[V/n\bar{v}_{\text{rel}}] \simeq 13\pi a_0^2. \quad (35)$$

Similarly, ignoring $\cos\Delta$ for R up to 4 and making the transformation of Eq. (34) for the rest of the interval,

$$[U/n\bar{v}_{\text{rel}}] \simeq 48\pi a_0^2 = 42 \times 10^{-16} \text{ cm}^2. \quad (36)$$

Thus the straight-line path approximation gives $(V/U) \sim 0.27$.

Since $(1/2)[U/n\bar{v}_{\text{rel}}]$ is the exchange cross section, Eq. (36) is equivalent to $\sigma_{\text{ex}} \simeq 21 \times 10^{-16} \text{ cm}^2$, in agreement with Dalgarno's result.⁴ Wittke and Dicke¹ found $\sigma_{\text{ex}} = 23 \times 10^{-16} \text{ cm}^2$ using somewhat different potentials and assuming that the phase-shift difference is random if the singlet part of the wave function experiences a close collision by overcoming the centrifugal potential barrier and is zero otherwise. Purcell and Field³ made essentially the same assumption as Wittke and Dicke and found a strong collision cross section at 300°K which can be converted to $\sigma_{\text{ex}} \simeq 22 \times 10^{-16} \text{ cm}^2$. Mazo⁶ used the experimental linewidth data of Hildebrandt, Booth, and Barth⁵ to obtain an experimental exchange cross section at 325°K of $\sigma_{\text{ex}} = 28.5 \times 10^{-16} \text{ cm}^2$. Since the assumptions of Wittke and Dicke, of Purcell and Field, and of Dalgarno all may tend to underestimate the cross section, there is no significant indication that the potentials are inadequate. A complete treatment of the exchange line broadening and frequency shift can be obtained from the method of Baranger.^{10,11} For the present purposes we will use the straight-line path value of V and a value of U deduced from the experimental exchange cross section to give an estimated value of 0.2 for (V/U) .

5. CONCLUSION

From Secs. 3 and 4 the estimated maximum frequency shift as a function of hydrogen density for the $(1,0) \rightarrow (0,0)$ transition is about 1% of the linewidth and should thus be observable. Under normal hydrogen maser operating conditions, where the exchange broadening is considerably less than the transit time broadening, the shift will be roughly 5% of that part of the linewidth due exchange broadening. While the shift is small, it is of interest both because of the high potential long term stability of hydrogen masers and because of the information the shift can give us about the interaction potentials. The size of the shift is related to the logarithmic derivative of the potential difference curve near the strong collision radius. Similar shifts occur for magnetic-field-dependent transitions, but these would be much harder to observe. The ratio of shift to exchange broadening may be even larger for alkali atoms than for hydrogen.

¹⁰ M. Baranger, Phys. Rev. **112**, 855 (1958).

¹¹ P. L. Bender (to be published).