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Discrepancies in experiments with cold hydrogen atoms

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Recent experiments with atomic clocks and hydrogen gas samples have shown discrepancies between theory and experiment. There are serious disagreements with respect to four different parameters: two different frequency shift parameters and a line broadening cross section relating to the H maser, and a longitudinal relaxation rate observed in a hydrogen gas sample. We study the changes in the short-range singlet and triplet potentials that would be needed to eliminate the above discrepancies. We find that no such changes can remove all four discrepancies simultaneously. In addition, we investigate a possible role of spin-dipole interactions, which have been neglected in previous calculations.
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I. INTRODUCTION

The cesium frequency standard is the most accurate existing atomic clock, and the hydrogen maser the most stable atomic clock over time periods of $1-10^5$ seconds [1]. In the last ten years a substantial further improvement has been accomplished for both instruments by means of versions operating with cold atoms. Modern laser-cooling methods have made it possible to build a cesium atomic fountain clock with an unprecedented accuracy [2]. Using cryogenic cooling by means of superfluid ^{4}He, a version of the H maser has been constructed, operating with increased stability at about 0.5 K [3].

These cold atomic clocks have revealed new limits to accuracy and stability, that stand in the way to achieving the full benefits envisaged for the new low-temperature versions. The most important restriction turns out to come from collisions between atoms which shift the frequency of the atomic oscillators. It has been pointed out [4] that this shift has a finite $T=0$ quantum limit, despite the reduction expected intuitively on the basis of the elastic collision rate, decreasing according to $T^{1/2}$. In view of this the collisional frequency shift is the only known frequency shift in the Cs fountain that cannot be reduced by a further lowering of the temperature [5].

In the case of the conventional H maser it was already known that spin-exchange H+H collisions broaden and shift the atomic hyperfine transition, displayed in Fig. 1, thereby coupling fluctuations in the atomic density to the maser oscillation frequency ω_m. An essential element in the development of the present state-of-the-art H masers was the idea of spin-exchange tuning, by which ω_m is made insensitive to changes in the atomic density by choosing a particular detuning of the maser microwave cavity [6]. This method makes use of the fact that the spin-exchange-induced frequency shift is proportional to the population inversion of the masing hyperfine states in the cavity (see Fig. 2), while the cavity-pulling shift shows the same proportionality, thus providing for the possibility to make these two shifts cancel.

About ten years ago, a study of the H-atom spin-exchange process by our group [7] showed that, with a proper inclusion of hyperfine interactions, the frequency shifts actually depend in a more complicated way on the occupations of the various hyperfine states of the colliding atoms. As a consequence, the spin-exchange tuning procedure is not as efficient as it was once thought to be, in particular at low temperatures, where atomic collision energies are comparable to the hyperfine interaction energy. Two experiments have since then confirmed our theoretical prediction, one at room temperature in a conventional H maser [8], and the other at 0.5 K in a low-temperature H maser [3]. In both cases a frequency shift beyond that predicted by the original theories of spin-exchange was observed and interpreted as being a direct consequence of hyperfine precessions during spin-exchange collisions (hyperfine-induced (HI) frequency shift).

There are growing indications, however, of serious disagreements between experiment and theory, not only with respect to the HI shift but in total to three different quantities relating to the H maser [3,8,9]. Another recent experiment [10] shows that the disagreement is not restricted to the H maser: It also shows up in the longitudinal relaxation rate $(1/T_1)_{\rm coll}$ due to collisions, observed in an electron-spin-

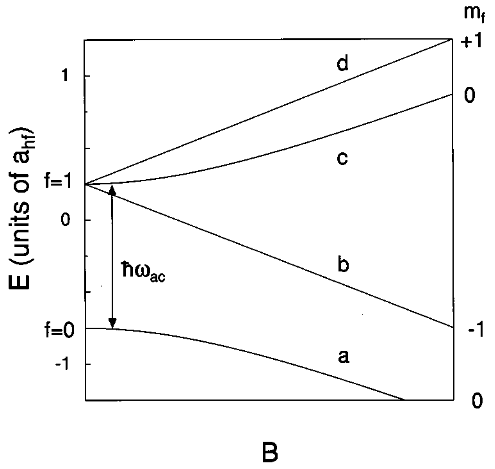

FIG. 1. Four hyperfine states of the atomic hydrogen electronic ground state, labeled $|a\rangle$, $|b\rangle$, $|c\rangle$, and $|d\rangle$ in order of increasing energy. The a-c transition is field independent in first order, and is used for both the maser and relaxation experiments.

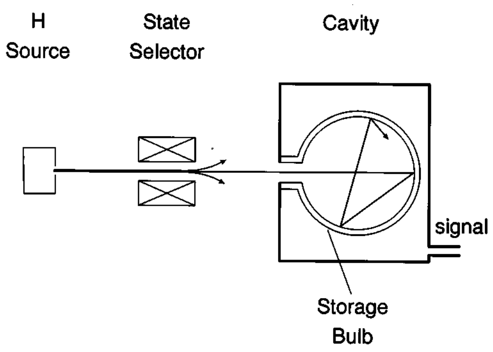

FIG. 2. Schematic representation of the hydrogen maser. The high-field seeking states a and b are removed by the state selector, thus creating a c-a population inversion

resonance measurement on an atomic hydrogen gas sample at $T=1.23$ K. An important reason to take these discrepancies seriously is the believed preciseness of the knowledge of the hydrogen atom interactions. The long-range singlet (S) and triplet (T) interaction potentials between two hydrogen atoms are accurately described by

$$V_{S,T}(r)=-C_6/r^6-C_8/r^8-C_{10}/r^{10}+V_{\text{exch}}, \tag{1}$$

with the dispersion coefficients taken from Yan *et al.* [11] and the exchange part from Smirnov and Chibisov [12]. The short-range interactions (see Fig. 3) are believed to be precisely described by calculations in the literature, including adiabatic, radiative, and relativistic corrections [13]. In addition to the above interactions, the effective two-atom Hamiltonian contains a sum of atomic hyperfine interactions:

$$\begin{aligned} V_{\text{hf}}&=\frac{a_{\text{hf}}}{\hbar^2}(s_1\cdot i_1+s_2\cdot i_2)\\ &=\frac{1}{2}\frac{a_{\text{hf}}}{\hbar^2}(s_1+s_2)\cdot(i_1+i_2)+\frac{1}{2}\frac{a_{\text{hf}}}{\hbar^2}(s_1-s_2)\cdot(i_1-i_2)\\ &\equiv V_{\text{hf}}^{+}+V_{\text{hf}}^{-}, \end{aligned} \tag{2}$$

of which the part V_{hf}^{-}, antisymmetric in the electronic-spin operators, couples the singlet and triplet subspaces. Here a_{hf} denotes the hyperfine constant.

In principle the discrepancies might point to effects not yet included in the present description of the maser and the electron spin resonance experiment, with possible fundamental consequences. In the case of the Cs fountain clock, there is less strong evidence for a disagreement: It is surprising that an analysis [14] some years ago on the basis of the best interaction potentials available at that time could only explain the experimental frequency shifts by assuming the existence of resonances both in the singlet and triplet subspaces very close to threshold. It may well be that this strong requirement is also a signature of a new process that is not yet accounted for in the present theoretical description.

We have investigated whether a suitable modification of the singlet and triplet H+H interaction potentials makes it possible to eliminate all discrepancies at the same time. The strategy is to focus first on the disagreement in the atomic hydrogen experiments, in which case any interaction already included and any interaction not yet included can be calculated from first principles. It seems likely that a change in the description of the hydrogen system will have implications also for the Cs atomic clock. We also discuss a possible role of the magnetic dipole interaction between the electron spins of the colliding atoms.

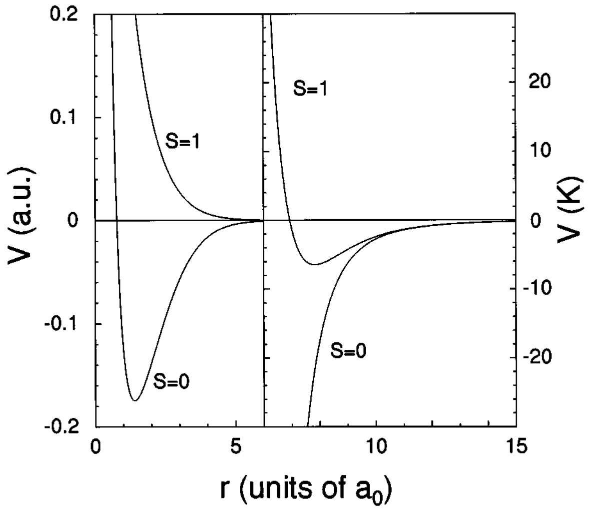

FIG. 3. Singlet ($S=0$) and triplet ($S=1$) potentials of ground-state hydrogen.

In Sec. II we give a brief description of the measured quantities as well as the discrepancies. In Sec. III we explore a possibility to remove the $1/T_1$ discrepancy by relaxing some of the assumptions in Ref. [10]. In Sec. IV this is followed by a description of our main approach and its results. Finally, in Sec. V we discuss the relevance of the magnetic spin-dipole interaction in relation to the discrepancies. Some conclusions are given in Sec. VI.

II. BRIEF DESCRIPTION OF MEASURED QUANTITIES AND DISCREPANCIES

A. Frequency shifts

The four hyperfine states of the atomic hydrogen electronic ground state are in order of increasing energy labeled as $|a\rangle$, $|b\rangle$, $|c\rangle$, and $|d\rangle$ (see Fig. 1). The hydrogen maser, schematically represented in Fig. 2, operates on the a-c transition which is field independent in first order.

Using the quantum Boltzmann equation, the frequency shift $\delta\omega$ and line broadening Γ due to spin-exchange collisions can be shown [7] to have the form

$$i\delta\omega-\Gamma=n\sum_{j}\rho_{jj}\langle v(i\lambda_j-\sigma_j)\rangle\equiv n\sum_{j}\rho_{jj}\langle v\rangle(i\overline{\lambda_j}-\overline{\sigma_j}). \tag{3}$$

The hydrogen atom density is denoted by n, the relative collision velocity by v and the single-atom spin-density matrix by ρ. The $\langle\ \rangle$ brackets denote thermal averaging over a Maxwell-Boltzmann distribution. The cross sections λ_j and σ_j ($j=a,b,c,d$), characterizing the partial frequency shift and broadening due to collisions of a coherent $a+c$ state with atoms in state j (partial density $n\rho_{jj}$), are expressed in elastic S-matrix elements by

$$i\lambda_j-\sigma_j=(1+\delta_{aj})(1+\delta_{cj})\,\frac{\pi}{k^2}\sum_l\,(2l+1)$$
$$\times[S^l_{\{aj\},\{aj\}}S^{l*}_{\{cj\},\{cj\}}-1]. \tag{4}$$

The brackets { } denote symmetrization (antisymmetrization) of the spin states for relative orbital angular momentum l even (odd). The coefficients $\overline{\lambda_j}$ and $\overline{\sigma_j}$ describe explicitly how $\delta\omega$ and Γ depend on the partial occupancies ρ_{jj} of the four single-atom hyperfine states. They can be calculated by thermally averaging the quantities $v\lambda_j$ and $v\sigma_j$, which in turn are given by the quadratic expressions (4) in terms of collisional S-matrix elements. All of these elastic S-matrix elements are to be calculated for a common value of the relative wave number k in the entrance channel, which varies over the above-mentioned Maxwell-Boltzmann distribution.

Rewriting the frequency shift and line broadening as

$$\delta\omega=n\langle v\rangle[(\rho_{cc}-\rho_{aa})\overline{\lambda_0}+(\rho_{cc}+\rho_{aa})\overline{\lambda_1}+\overline{\lambda_2}], \tag{5}$$

$$\Gamma=n\langle v\rangle[(\rho_{cc}-\rho_{aa})\overline{\sigma_0}+(\rho_{cc}+\rho_{aa})\overline{\sigma_1}+\overline{\sigma_2}], \tag{6}$$

we note that the $\overline{\lambda_1}$ and $\overline{\lambda_2}$ contributions vanish according to theoretical treatments of spin-exchange collisions [6,15,16] that ignore hyperfine interactions during collisions (the degenerate-internal-states approximation). Crampton [17] showed that for a certain detuning of the cavity the remaining $(\rho_{cc}-\rho_{aa})$-dependent frequency shift, described by the parameter λ_0, can be canceled by cavity pulling, which has been a major factor in stabilizing conventional room temperature H masers. In 1975 Crampton and Wang [18] took into account the atomic hyperfine precession during collisions in a semiclassical straight-path approximation, and found an additional ρ-independent $\overline{\lambda_2}$ term. They confirmed the presence of such a term experimentally in a room-temperature hydrogen maser. Its smallness makes it relatively unimportant for the stability of conventional hydrogen masers.

In the case of the sub-Kelvin hydrogen maser, however, the role of the hyperfine-induced $\overline{\lambda_1}$ and $\overline{\lambda_2}$ terms is of much greater importance. Hayden, Hürlimann, and Hardy reviewed the situation in their recent paper [9]. In the same paper they confirmed the existence of a HI frequency shift in their experiment, proportional to $(\rho_{aa}+\rho_{cc})\overline{\lambda_1}+\overline{\lambda_2}=\frac{1}{2}\overline{\lambda_1}+\overline{\lambda_2}$. They found its sign to be different from the theoretical prediction, however. In addition, the value of $\overline{\lambda_0}$ was almost twice the theoretical value.

Finally, in the same experiment an ingenious method to measure the linear combination $(\rho_{aa}+\rho_{cc})\overline{\sigma_1}+\overline{\sigma_2}=\frac{1}{2}\overline{\sigma_1}+\overline{\sigma_2}$ of broadening cross sections was applied. This result, too, showed a discrepancy with the theoretical value calculated by our group. Table I summarizes the experimental and theoretical values for the three above quantities. It also shows a result from an experiment by Walsworth *et al.* [8] for the room-temperature maser, which also appears to show a discrepancy with theory. We should note, however, that the theoretical calculation of the $\overline{\lambda}$ and $\overline{\sigma}$ cross sections at room temperature involves a thermal average over a range of collision energies containing a huge number of resonances. Due to the complications involved in such a calculation, we consider the evidence for a discrepancy between theory and experiment to be less direct than in the cryogenic case. Therefore, in the following we will focus on the cryogenic data.

TABLE I. Parameters showing discrepancies.

Quantity	Theory (cm^2)	Experiment (cm^2)	Ref.
$\overline{\lambda_0}$	-1.19×10^{-15}	$(-2.17\pm0.28)\times10^{-15}$	[9]
$\frac{1}{2}\overline{\lambda_1}+\overline{\lambda_2}$	-2.04×10^{-18}	$(2.2^{+0.5}_{-1.0})\times10^{-18}$	[9]
$\frac{1}{2}\overline{\sigma_1}+\overline{\sigma_2}$	26.3×10^{-18}	$(38.5\pm3)\times10^{-18}$	[9]
$\overline{\lambda_1}$	3.0×10^{-19}	-1.8×10^{-18}	[8]
$\overline{\sigma_{T_1}}$	37×10^{-18}	$(51\pm2)\times10^{-18}$	[10]

B. Longitudinal relaxation time

In a recent paper [10] the evidence for a discrepancy with theory was considerably extended by means of experimental data that do not involve the complications of a (recirculating) cryogenic hydrogen maser. Applying pulsed hyperfine magnetic resonance techniques to a gas of hydrogen atoms at a temperature of 1.23 K in a magnetic field of 60 G, it was possible to determine the longitudinal relaxation time T_1 for the a-c transition. Essentially, starting with equilibrium populations of the a, b, c, and d levels, an initial π pulse inverted the a and c populations. The return to equilibrium was monitored by means of a $\pi/2$ pulse with a variable delay time and an observation of the subsequent free induction decay.

For the analysis the authors used rate equations, which we reformulate here in a more rigorous form to exclude already a few of the possibilities for an explanation of the T_1 discrepancy. Our starting point is again the quantum Boltzmann equation. The time evolution of a partial density is then found to be given by [7,19]

$$\frac{d}{dt}n_\alpha=\sum_\beta\sum_{\{\alpha'\beta'\}}(1+\delta_{\alpha\beta})(G_{\alpha'\beta'\to\alpha\beta}n_{\alpha'}n_{\beta'}$$
$$-G_{\alpha\beta\to\alpha'\beta'}n_\alpha n_\beta), \tag{7}$$

with rate constants

$$G_{\alpha\beta\to\alpha'\beta'}=\left\langle\frac{2\pi\hbar}{mk}\sum_l\,(2l+1)\right.$$
$$\left.\times|S^l_{\{\alpha'\beta'\},\{\alpha\beta\}}-\delta_{\{\alpha'\beta'\},\{\alpha\beta\}}|^2\right\rangle, \tag{8}$$

where the slow relaxation due to the dipolar spin-spin interaction is neglected.

For an analysis of their experiment Hayden and Hardy introduce the approximate equalities $G_{aa\to bd}\approx G_{cc\to bd}$, $G_{\alpha\beta\to\gamma\delta}\approx G_{\gamma\delta\to\alpha\beta}$, and $n_a+n_c\approx n/2$, referring to the large value of k_BT compared to the internal energy intervals. Equation (7) then reduces to the simple form

$$\frac{d}{dt}(n_a-n_c)=-(2G_{cc\to aa}+G_{bd\to aa})n(n_a-n_c). \tag{9}$$

This equation leads to the expression

$$\frac{1}{T_1}=(2G_{cc\rightarrow aa}+G_{bd\rightarrow aa})n\equiv n\langle v\rangle\overline{\sigma_{T_1}} \tag{10}$$

for the longitudinal relaxation time.

The experimental result $\overline{\sigma_{T_1}}=(51\pm 2)\times 10^{-18}$ cm^2 is in disagreement with the theoretical value 37×10^{-18} cm^2 following from calculated rate constants $G_{\alpha\beta\rightarrow\gamma\delta}$ [19]. Both values are included in Table I. A recalculation using the most recent potentials [13] in the framework of the present paper, confirmed all theoretical values in this table, changes relative to the old values being at most of order 1%.

III. COMPARISON WITH MORE RIGOROUS EXPRESSION FOR LONGITUDINAL RELAXATION TIME

In a first attempt to eliminate discrepancies, we consider separately the longitudinal relaxation time. The objective is also to compare the experimental $\overline{\sigma_{T_1}}$ with a more rigorous theoretical expression, relaxing the above-mentioned simplifying assumptions of Ref. [10] and using the rigorous rate equations (7) as a starting point. One of the effects included in such an approach is that the nonequilibrium populations of the a and c levels induced by the π pulse may affect subsequently the b and d populations via the collision processes included in Eq. (7), which in turn might influence the relaxation of n_a-n_c.

Linearizing the set of equations (7) around equilibrium $(n_\alpha=n_\alpha^0)$, it reduces to the form

$$\frac{d(n_\alpha-n_\alpha^0)}{dt}=-n\langle v\rangle\sum_\beta M_{\alpha\beta}(n_\beta-n_\beta^0), \tag{11}$$

with the hyperfine states arranged in the order $\alpha=a$, b, c, and d. The coefficients $M_{\alpha\beta}$ stand for linear combinations of Gn^0 products with an overall factor $n\langle v\rangle$ splitted off. Each of the $M_{\alpha\beta}$ elements is a function of temperature T and magnetic field B.

We calculate the eigenvectors and eigenvalues of the 4×4 matrix M. Two of the eigenvalues turn out to be 0, corresponding to the linear relations

$$\sum_\alpha M_{\alpha\beta}=0, \tag{12}$$

$$M_{b\beta}-M_{d\beta}=0, \tag{13}$$

among the rows of M. Relation (12) is connected with conservation of the total density $n_a+n_b+n_c+n_d$, relation (13) with conservation of n_b-n_d, i.e., of the total spin magnetic quantum number m_F. Note that in exchange collisions the spin and orbital magnetic quantum numbers are separately conserved. As a consequence, we end up with two nontrivial rate equations associated with the two remaining eigenvalues describing the combined decay of n_a-n_c and $(n_a+n_c)-(n_b+n_d)$ to their equilibrium values. The initial condition at $t=0$ right after the π pulse, is a superposition of the two eigenvectors with $(n_a+n_c)-(n_b+n_d)$ equal to its equilibrium value. In principle, at times $t>0$ we thus obtain two decaying exponentials combining to a time-dependent solution with both n_a-n_c and $(n_a+n_c)-(n_b+n_d)$ different from their equilibrium values. The time dependence of the quantities

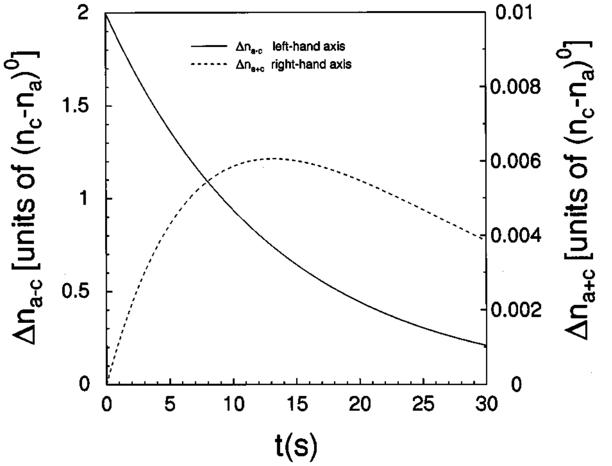

FIG. 4. Time-dependent relaxation of n_a-n_c and $n_a+n_c-(n_b+n_d)$ to their equilibrium values, due to two slightly different relaxation eigenvalues. Experimental circumstances: Temperature $T=1.23$ K, $B=60$ G, and hydrogen density $n=8.9\times 10^{10}$ cm^{-3}.

$$\Delta n_{a-c}\equiv(n_a-n_c)-(n_a-n_c)^0, \tag{14}$$

$$\Delta n_{a+c}\equiv[(n_a+n_c)-(n_b+n_d)]-[(n_a+n_c)-(n_b+n_d)]^0, \tag{15}$$

calculated for the experimental values of n, T, and B, is presented in Fig. 4. It turns out, however, that the difference of the eigenvalues is only about 2%. In addition, their average is equal to the theoretical value 37×10^{-18} cm^2 for $\overline{\sigma_{T_1}}$ quoted above as following from the simplifying assumptions of Ref. [10].

Consistent with these results we find that n_b and n_d as well as n_a+n_c to good approximation retain their equilibrium values, the deviations reaching a maximum of order 1% after a time of about 13 s, whereas n_a-n_c behaves approximately according to the simplified equation (10), the deviations again being of order 1%. We therefore continue our investigation of the T_1 discrepancy on the basis of Eq. (10).

IV. MODIFICATION OF POTENTIALS

In this section we explore the possibility to resolve the discrepancies by modifying the interaction potentials, in particular in the range of interatomic distances up to about $7a_0$ where the atomic electron clouds overlap leading to a strongly attractive singlet and a strongly repulsive triplet potential (see Fig. 2). As we will show, the effect of changes in a potential in this radial range can be studied in a model-independent way, i.e., irrespective of the precise nature of the modification, following an approach in the spirit of the accumulated-phase method [20,21]. This method has been highly successful in analyzing cold collisions among ground-state alkali atoms. The idea is to account for a possible change of an interaction potential by modifying the boundary condition for the radial wave function at the boundary r_0 of the radial range considered. In this range the singlet and triplet electronic states are so far apart in energy compared with the hyperfine coupling V_{hf} that the $S=0$ and 1 channels are still uncoupled. The new boundary condition then determines the solution of Schrödinger's equation in the further radial range $r > r_0$, and especially the interference of the singlet and triplet channels under the influence of V_{hf}. The change of the boundary condition simply summarizes the effect of the change of the potentials, wherever it occurs inside r_0. The actual modification of the boundary condition can be effected by an adjustment of the local phase ϕ of the radial wave function $F(r)$ as in Refs. [20,21] or by a change of the logarithmic derivative F'/F. We prefer the latter possibility, so that we can deal with a real-valued quantity only: The phase ϕ would be imaginary inside the classical turning point for the triplet potential near $7a_0$.

Note that the actual position of r_0 is unimportant, as long it is not too far out: A modified F'/F at r_0 not only simulates a changed interaction inside r_0, but also one outside r_0 where the $S=0$ and 1 subspaces are still sufficiently decoupled. As a matter of fact, by a modification of F'/F at r_0, one can also effect an arbitrary change at larger r. The actual value used for r_0 is $4a_0$.

Note also that F'/F, like ϕ, is in principle a function of energy E and relative angular momentum l in the collision. In the small E and l range involved in cold collisions, however, this variation is negligible, since r_0 is sufficiently far from the turning points both in the classically inaccessible range for the triplet channel and the classically accessible range for the singlet potential.

The problem we thus face is to determine the theoretical dependence of the quantities λ_0, $\frac{1}{2}\lambda_1+\lambda_2$, $\frac{1}{2}\overline{\sigma_1}+\overline{\sigma_2}$, and $\overline{\sigma_{T_1}}$ on the singlet and triplet increments

$$\Delta_S=\Delta(F_S'/F_S)_{r_0}, \quad \Delta_T=\Delta(F_T'/F_T)_{r_0}, \tag{16}$$

to see if there exist reasonable Δ_S and Δ_T values for which all four discrepancies can be eliminated simultaneously.

Figure 5 shows the changes Δ_S and Δ_T of logarithmic derivatives needed to bring the theoretical values of the observables to within twice the standard deviations from the experimental values. To compress the ranges of large Δ values where the actual differences of the radial wave functions is small, we have chosen to plot Δ_S and Δ_T in a nonlinear way: We calculate the corresponding phase changes $\Delta\phi_S$ and $\Delta\phi_T$ at the deepest points of the two potentials, and vary these quantities linearly along the axis. Note that $\Delta\phi_S$ will have to be small relative to π to avoid disagreement with experimental data for the singlet H_2 rovibrational states. The total $\Delta\phi_S$ range included in the figure is certainly larger than that allowed by these experimental data. The total $\Delta\phi_T$ range studied is also larger than it can conceivably be: It runs from a very small negative value -2.2×10^{-4}, hardly distinguishable from the abscissa, where $\Delta_T=+\infty$, to the value $=1.34$, indicated by a horizontal dashed line, where the triplet potential is so deep that a triplet state becomes bound. Positive values for $\Delta\phi_T$ exceeding 1.34 are excluded because none of the many experiments on spin-polarized atomic hydrogen has indicated the existence of a triplet bound state. Negative values extending beyond -2.2×10^{-4} are not allowed because the corresponding value for Δ_T is the maximum possible value $+\infty$ for this correction of the logarithmic derivative of the radial wave function. To give an impression of the degree to which the quantities $\Delta\phi_S$ and $\Delta\phi_T$ have converged, we note that the changes of these phase differences in going from the old to the new H+H potentials [13] are at most of order 0.001 rad.

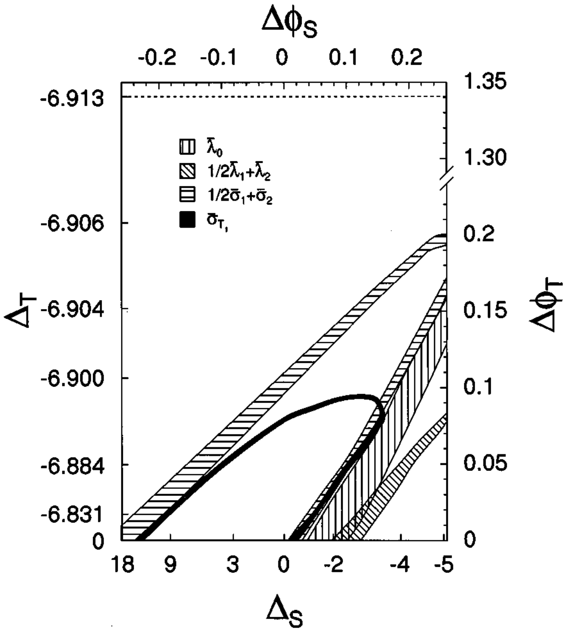

FIG. 5. Parameter regions in the Δ_S,Δ_T (or, equivalently, $\Delta\phi_S,\Delta\phi_T$) plane, where discrepancies in observables λ_0, $\frac{1}{2}\lambda_1+\lambda_2$, $\frac{1}{2}\overline{\sigma_1}+\overline{\sigma_2}$, and $\overline{\sigma_{T_1}}$ are eliminated.

Even between these unrealistically wide limits no overlap region for all observables simultaneously is found. The only overlap that occurs is between the pair of λ quantities and between the pair of $\overline{\sigma}$ quantities. We conclude that the option of better singlet and triplet potentials for internuclear distances where the electron clouds overlap strongly is not a viable solution for the existing discrepancies.

V. INFLUENCE OF MAGNETIC DIPOLE INTERACTION

In our previous calculations [7] we have neglected the magnetic dipole interaction between the spin magnetic moments (electron and proton) of the two atoms, in view of the general dominance of electric vs magnetic interactions. This dominance is illustrated, e.g., by the fact that dipolar relaxation rates are typically three orders of magnitude smaller than spin-exchange rates [19]. We point out, however, that interference between the two kinds of amplitude, which are absent in these rates, could give rise to more important contributions. Moreover, the hyperfine-induced $\frac{1}{2}\lambda_1+\lambda_2$ cross section is by itself a small effect relative to λ_0, so that the dipole interaction might in principle resolve the discrepancy in the measured hyperfine-induced frequency shift. This is what we are going to investigate in this section. We restrict ourselves to the electron-electron part of the interatomic dipole interaction, the electron-proton and proton-proton parts being much weaker.

On the basis of the structure of the $|a\rangle$ and $|c\rangle$ states the $\langle a|\mathbf{s}_i|a\rangle$ and $\langle c|\mathbf{s}_i|c\rangle$ matrix elements are zero for $B=0$, and negligible for the weak experimental field. We conclude that no direct dipolar transitions are possible in collisions where only $|a\rangle$ or $|c\rangle$ states are involved.

For small values of the collisional quantum number l the central interaction is also involved. The combination of these two interactions can result in a ‘‘two-step’’ process, where the dipolar interaction is involved in a transition from $|a\rangle$ to $|a\rangle$ or $|c\rangle$ to $|c\rangle$, via a central interaction step between $|a\rangle$ and $|c\rangle$. Considering the quantum Boltzmann equation including the dipole interaction, the frequency shift and broadening cross sections are given by

$$i\lambda_a-\sigma_a=\frac{2\pi}{k^2}\sum_{l'm'}\sum_{lm}\left[S^{l'm',lm}_{\{aa\},\{aa\}}S^{l'm',lm*}_{\{ac\},\{ac\}}-1\right],$$

$$i\lambda_c-\sigma_c=\frac{2\pi}{k^2}\sum_{l'm'}\sum_{lm}\left[S^{l'm',lm}_{\{ac\},\{ac\}}S^{l'm',lm*}_{\{cc\},\{cc\}}-1\right], \qquad (17)$$

$$\begin{aligned} i\lambda_b-\sigma_b&=i\lambda_d-\sigma_d\\ &=\frac{\pi}{k^2}\sum_{l'm'}\sum_{lm}2S^{l'm',lm}_{\{ab\},\{ad\}}S^{l'm',lm*}_{\{cb\},\{cd\}}\\ &\quad+\left[S^{l'm',lm}_{\{ad\},\{ad\}}S^{l'm',lm*}_{\{cd\},\{cd\}}-1\right].\end{aligned}$$

In comparison with expressions (4) there are some differences. First, in this case also inelastic S-matrix elements contribute. Second, the angular momentum quantum numbers l' and l are not necessarily identical: Due to the selection rules of the dipole interaction we have $l'=l-2$, $l'=l$, or $l'=l+2$, with the exception of $l'=l=0$. In view of the experimental temperatures of order 1 K, we restrict ourselves to s and d partial waves. For the cross sections in Eq. (17) with subscripts b or $dp\rightarrow p$, transitions are not forbidden by Bose symmetry. They are not included in the following, but are expected to contribute with similar orders of magnitude.

To begin with we note that $S^{20,00}_{\{aa\},\{aa\}}=S^{00,20}_{\{aa\},\{aa\}}=0$, because of angular momentum conservation: The total two-atom spin is zero in both the initial and final states, so that l has to be conserved. We divide the λ contributions additional to the expressions (4) in three categories. First, the ‘‘dipolar’’ transitions taking place only if the dipole interaction takes part, i.e., contributions to λ_d from $\{ad\}\rightarrow\{ab\}$ and $\{cd\}\rightarrow\{cb\}$ transitions. Second, interference contributions due to dipolar corrections to central elastic processes that could already take place via the central interaction, i.e., $\{ad\}\rightarrow\{ad\}$ and $\{cd\}\rightarrow\{cd\}$ contributions to λ_d. Third, contributions to λ_c with the same character, i.e., involving $\{ca\}\rightarrow\{ca\}$ and $\{cc\}\rightarrow\{cc\}$ processes. The first two will give a frequency shift proportional to n_b or n_d, the last one proportional to n_c (a contribution proportional to n_a is absent in view of the above argument).

In Table II we give results for these additional contributions, calculated for a collision energy of 0.5 K. Clearly, comparing with the discrepancies in Table I, we see that these values are far too small to be of any significance. They are even smaller than could be expected on the basis of the dipolar decay rates. The reason is essentially, as on analysis of the S-matrix elements shows, that the matrix elements $S^{20,00}_{\{c\alpha\},\{c\beta\}}$ and $S^{20,00}_{\{a\alpha\},\{a\beta\}}$ are nearly equal, so that the corresponding contribution to the frequency shifts vanishes. We conclude that the inclusion of the magnetic dipole interaction does not resolve the $\frac{1}{2}\lambda_1+\lambda_2$ discrepancy.

TABLE II. Contributions to frequency shift cross sections from magnetic dipole interaction, subdivided into three categories.

λ_c elastic	λ_d elastic	λ_d inelastic
-1.03×10^{-23} cm^2	-1.19×10^{-25} cm^2	-1.03×10^{-24} cm^2

VI. CONCLUSIONS

We have reviewed four types of discrepancies between experiment and existing theory, connected with cold atomic hydrogen gas samples. Three are associated with the sub-Kelvin hydrogen maser, one with a pulsed hyperfine magnetic resonance experiment. The discovery of the latter discrepancy in recent work has been of great importance, since it thereby becomes more probable that the resolution of the inconsistencies has to be found in the theoretical description of the cold H+H collisions. This contrasts with the earlier discrepancies, all three relating to the hydrogen maser, which could have been ascribed to an incomplete description of this setup. We have investigated two issues in connection with the inconsistencies.

First, we have studied the possibility that an additional term in the collisional Hamiltonian, operating at small internuclear distances in the region of strongly overlapping electron clouds, is overlooked in present descriptions of cold atomic collisions. We have shown that no such additional terms can eliminate all four discrepancies at the same time, without leading to other inconsistencies, such as the introduction of triplet H_2 bound states.

Second, we have investigated the possibility that the magnetic dipole forces operating between the electron spins, left out in existing theoretical descriptions of the above experiments, might lead to significant changes of the predictions. We have found that the additional contributions from this source fall short by orders of magnitude.

The growing importance of cold collisions in a number of present basic developments (Bose-Einstein condensation, atom lasers, atomic-fountain clocks) underlines the need to spend further effort to finding a solution for the discrepancies. Also in this connection, atomic hydrogen can play a role as a model system, its relative simplicity offering the possibility to reveal aspects in which the existing cold collision theory is incomplete. Recent progress in describing cold collisions of Rb atoms [22,23] makes it possible to turn to this atom species as a possible second example where discrepancies might be detected in precision experiments. In this connection envisaged experiments with a Rb atomic-fountain clock [24] would be especially interesting.

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