

## Cold-collision properties derived from frequency shifts in a cesium fountain

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We interpret recently measured collisional frequency shifts in a cesium atomic fountain using coupled-channel theory and a simple picture of hyperfine-coupled long-range molecular states. We predict the existence of  $\text{Cs}_2$  singlet and triplet states very close to threshold with an associated strong influence on ultracold collisions and large negative values for the  $\text{Cs}+\text{Cs}$  scattering lengths. Our results are important for future precision experiments using Cs fountains, and may also have important consequences for attempts to realize a Bose condensate in an ultracold atomic Cs vapor.

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The advances of techniques for using lasers to trap and manipulate atoms have, in the past few years, made it possible to cool atoms to temperatures near absolute zero and to examine unusual quantum states of matter under these circumstances. One of the most spectacular possibilities now within sight is the observation of Bose-Einstein condensation (BEC) in a weakly interacting vapor of atoms, which is predicted to take place at such low temperatures and high densities that the atomic de Broglie wavelength becomes comparable to the average distance between the atoms. Some groups are trying to achieve this phase transition in atomic hydrogen gas in a magnetic trap [1,2]. Others are attempting the same in a laser-cooled sample of alkali-metal atoms such as Cs [3] and Li [4].

Collisions between atoms play a crucial role in this endeavor. In two recent papers [5], the conditions for BEC of a cold Cs vapor were examined using the properties of  $\text{Cs}+\text{Cs}$  ground-state collisions. Due to insufficient knowledge of the interatomic potentials it was only possible to reach rough conclusions. This situation has changed drastically with a recent cesium-fountain clock experiment in which two of the present authors measured large frequency shifts due to ultracold collisions of Cs atoms during their ballistic flight in the atomic fountain [6]. While these frequency shifts will be largely eliminated in future clocks [6], here we use the measured shifts to obtain information on the interaction potentials relevant for BEC. We find strong evidence for the existence of singlet and triplet states close to the continuum with an associated large influence on ultracold collisions. The frequency shifts enable us to analyze collisions at the coldest temperatures ( $T \simeq 1.5 \mu\text{K}$ ) at which atomic collisions have ever been studied. We find the zero-energy elastic cross section for triplet scattering to be between  $10^5$  and  $10^7 \text{ \AA}^2$ .

Our conclusions are also important for ongoing attempts to improve the accuracy and stability of the cesium-fountain clock [6,7] and for future precision experiments using Cs fountains or ultracold trapped Cs.

Examples of the latter include precision atom interferometry experiments where phase changes due to atom-atom interactions are important [8] and experiments that are being planned to measure the possible electric dipole moment of the electron due to violation of the fundamental  $P$  (space inversion) and  $T$  (time inversion) symmetry [9].

The basic theoretical picture for our analysis is the theory of long-range molecules [10], according to which  $\text{Cs}_2$   $S=0$  and  $S=1$  bound states close to the continuum threshold have exceptional properties, related to the fact that the system spends most of its time near and even beyond its outer classical turning point. Of course, the low-energy resonance states have an even longer range. As a consequence, the energy splittings of all these states are determined by the dominating  $C_n$  dispersion coefficient at long range, while an additional parameter determines the absolute energy values: the generally nonintegral effective vibrational quantum number  $v_D$  at dissociation [10] or the scattering length  $a = -\lim_{k \rightarrow 0} \delta_0(k)/k$ , where  $\delta_0(k)$  is the  $s$ -wave phase shift and  $k$  the wave number. Including the hyperfine coupling between the various  $(SI)F$  states, where  $I$  and  $F$  denote the combined nuclear and total spin of the two-atom system, extends this long-range molecular picture to a multichannel version. Its validity is based on the fact that the atomic hyperfine interaction  $V_{\text{hf}}$ , although strong for Cs, is very weak relative to the depth of the singlet and triplet potentials. As a consequence, it mixes only the long-range molecular states at energies from threshold of the order of the hyperfine splitting. In principle, this mixing could be calculated by correcting the energies of the  $(SI)F$  states for the  $(\mathbf{S}_1 + \mathbf{S}_2) \cdot (\mathbf{I}_1 + \mathbf{I}_2)$  part of the total hyperfine interaction, which conserves  $S$  and  $I$ , and subsequently including the singlet-triplet coupling due to the  $(\mathbf{S}_1 - \mathbf{S}_2) \cdot (\mathbf{I}_1 - \mathbf{I}_2)$  part. Equivalently, one may start from an  $(F_1 F_2)F$  basis valid at asymptotic distances, which incorporates the average singlet-triplet potential, and subsequently include the exchange interaction  $V_{\text{ex}}$

defined as  $(V_T - V_S)/2$ . This mixing problem is dealt with rigorously by the coupled-channel method, which is used here.

The composition of the resulting multichannel states is sensitive to the relative phases of the admixed singlet and triplet wave functions in the radial regions where they are significantly coupled by the hyperfine interaction. Since the hyperfine mixing is small in the inner region due to the grossly different depths of the singlet and triplet potentials  $V_S$  and  $V_T$ , we do not need the detailed form of these potentials in that region. Instead, only accumulated phases  $\phi_S$  and  $\phi_T$  of the radial wave function at a boundary radius  $r_0$  are needed to determine the close-to-continuum collision characteristics. Fortunately, this connects precisely with the restricted existing knowledge of  $V_T$ . Knowledge of  $V_S$  is available over the whole range via a thorough analysis by Weickenmeier *et al.* [11]. Its exchange part is determined as a separate contribution outside  $15.6a_0$ . This allows us to choose  $r_0 = 15.6a_0$  and to obtain  $V_T = V_S + 2V_{ex}$  for  $r > r_0$  by inverting the exchange part of  $V_S$  (see Fig. 1).

An *ab initio* theoretical  $V_T$  [12], slightly adjusted to make its value and derivative continuous at  $r_0$ , is used for  $r < r_0$ . In addition, it was adapted so that  $\phi_T$  has the close-to-continuum energy derivative given by an analysis of measured hyperfine splittings of the  $\nu = 137$  and 138 rovibrational singlet levels with  $l = 15, 17, 45, 49$ , and 55 [13,14]. These splittings are caused by the hyperfine coupling with nearby triplet levels and thus contain the “fingerprint” of the triplet spectrum, which is also sensitive to the phase  $\phi_T(E, l)$  for each of the levels. From calculations for a range of triplet potentials, the phase  $\phi_T$  turns out to be very nearly a linear function of both  $E$  and  $l(l+1)$  in the  $E$  and  $l$  intervals ranging from the  $l=0$  states near  $E=0$  to the above rovibrational levels. Comparing the data in Ref. [14] to theoretical hyperfine splittings obtained with a bound-state version of our con-

tinuum coupled-channel code, it was possible to determine  $\partial\phi_T/\partial E|_{E=l=0}$  and  $\partial\phi_T/\partial[l(l+1)]_{E=l=0}$  for our continuum analysis. Superposed on both  $V_T$  and  $V_S$ , we introduce small changes left of  $r_0$  to change the phases  $\phi_T$  and  $\phi_S$  as a boundary condition for the solution in the interval  $r > r_0$ . As expected, the final results for the collision quantities turn out to be independent of the detailed shape of these potential adjustments.

In the framework of the picture of hyperfine-coupled long-range molecular states, three parameters should be sufficient to describe the near-threshold coupled-channel problem both for bound and continuum states:  $\phi_S$ ,  $\phi_T$ , and  $\Delta C_6$ . The latter parameter represents the deviation with respect to the  $C_6$  value of Ref. [11]. The first two parameters correspond to  $v_{DS}$  and  $v_{DT}$ , and also to  $a_S$  and  $a_T$ .

Three measured frequency shifts are used to determine  $v_{DS}$ ,  $v_{DT}$  (mod 1) and to a lesser extent  $C_6$ . The first two, which were reported in Ref. [6], are the frequency shift  $\Delta\nu_{3m}$  for atoms initially distributed evenly in the  $F=3$   $m_F$  states [so that the partial densities  $n(F=3, m_F=0) = n(F=4, m_F=0) = \frac{1}{14}$  and  $n(F=3, m_F \neq 0) = \frac{1}{7}$ ], and  $(\Delta\nu_{30} + \Delta\nu_{40})/2$ , where the atoms were initially prepared in only the  $F=3, m_F=0$  state. The third, the differential frequency shift  $(\Delta\nu_{40} - \Delta\nu_{30})/(\frac{1}{2}\Delta\nu_{40} + \frac{1}{2}\Delta\nu_{30})$ , is measured by preparing the atoms in the  $F=3, m_F=0$  state and varying the  $F=4, m_F=0$  population after the first microwave pulse. Here, by driving  $0.27\pi$  and  $0.76\pi$  pulses instead of two  $\pi/2$  pulses, we measure  $(\Delta\nu_{40} - \Delta\nu_{30})/(\frac{1}{2}\Delta\nu_{40} + \frac{1}{2}\Delta\nu_{30}) = -0.1 \pm 0.2$ , so that the cross sections are nearly equal for atoms in the  $F=3$  and  $F=4, m_F=0$  states.

The theoretical frequency shifts are normalized to a density of  $10^9 \text{ cm}^{-3}$  and are calculated using the coupled-channel method as in two previous papers [5]. Here, only elastic collisions need be considered. After an inelastic collision where one atom changes hyperfine state, the atomic velocities are so high that the atoms escape from the fountain. For collisions where  $F, m_F=0 \rightarrow F, m_F \neq 0$ , the microwave coherence is destroyed so no effect is observed. The  $s$ -wave energy-dependent frequency shifts are obtained by calculating collision quantities for two energies and then using a complex effective-range expansion to calculate the values at other energies. They are subsequently thermally and time averaged, taking into account the time-dependent temperature and density of the atomic cloud in the fountain [6]. Due to Bose symmetry, the  $p$ -wave contribution to  $\Delta\nu_{30}$  and  $\Delta\nu_{40}$  vanishes. Its contribution to  $\Delta\nu_{3m}$  is also negligible unless there is a  $p$ -wave resonance. To calculate the  $p$ -wave contribution we used the value of  $\phi_T$  for  $l=1$ , following from the above hyperfine-splitting analysis. In the parameter region required for the description of  $\Delta\nu_{30}$  and  $\Delta\nu_{40}$ , there are no  $p$ -wave resonances. The contribution of the  $d$  and higher partial waves turns out to be negligible.

As an example of our results, we show in Fig. 2 the shifts  $(\Delta\nu_{30} + \Delta\nu_{40})/2$  and  $\Delta\nu_{3m}$  as a function of  $v_{DT}$  for  $v_{DS} = -0.08$  [see parameter region (1) below] and  $C_6$  equal to the value for the unadapted  $V_S$  potential of Ref.

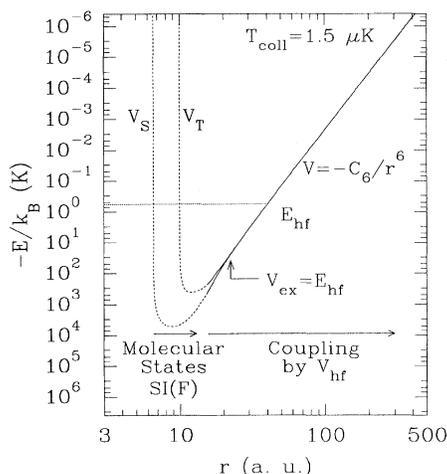


FIG. 1. Singlet and triplet interactions. The coupling of the  $(SI)F$  states by  $V_{hf}$  starts beyond  $r_0$ , where the atomic hyperfine splitting  $E_{hf}$  becomes comparable to  $V_{ex}$  and is most effective at large  $r$ , where the atoms spend most of their time. For comparison of orders of magnitude,  $E_{hf}$  and the collision energy ( $\approx k_B T$ ) are indicated.

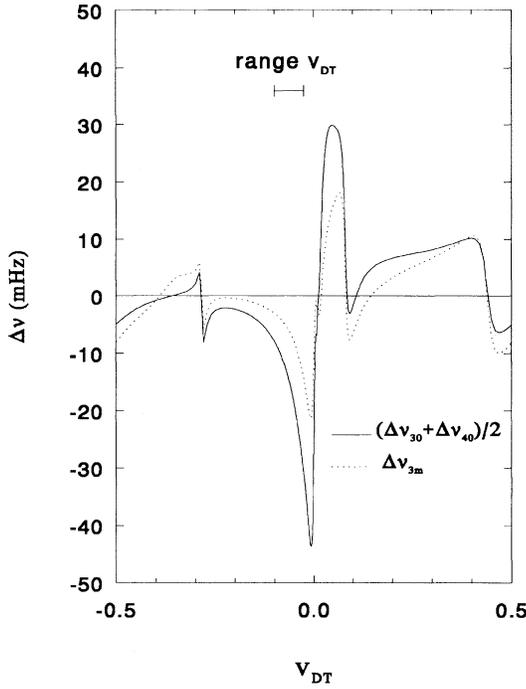


FIG. 2. Frequency shifts  $(\Delta v_{30} + \Delta v_{40})/2$  and  $\Delta v_{3m}$  due to collisions of atoms making a clock transition with other atoms for  $v_{DS} = -0.08$  (density normalized to  $10^9 \text{ cm}^{-3}$ ). The corresponding experimental numbers are  $-15.8$  and  $-4.8$  mHz. The theoretical range according to parameter region (1) is indicated.

[11]. The resonance behavior is due to the passage of a number of states through the  $(F_1 F_2) = (33)$ , (34), and (44) reaction thresholds for the  $S$ -matrix elements determining the shifts.

The three measured frequency shifts were compared to the theory using a least-squares fit to determine optimal nonintegral vibrational quantum numbers  $v_{DT}$  and  $v_{DS}$  for values of  $\Delta C_6$  within the 3% uncertainty interval indicated in Ref. [11]. We find a least-squares minimum in the  $v_{DS}, v_{DT}$  plane for a singlet and a triplet level close to the continuum threshold. The location of the minimum, almost independent of  $C_6$ , is

$$v_{DS} = -0.080_{-0.045}^{+0.050}, v_{DT} = -0.040_{-0.060}^{+0.015}. \quad (1)$$

We note that the differences between experimental data and theoretical predictions increase dramatically on the positive sides of both error bars, so that the  $v_{DS}$  and  $v_{DT}$  values are most certainly negative. In accordance with the picture of long-range molecules we find a minimum in  $\chi^2$  at the same position and with nearly the same shape when the exchange potential was changed by  $\pm 10\%$  from that in Ref. [11].

Besides this rather narrow  $C_6$ -independent minimum, we find a few other local minima for particular  $C_6$  values, which are even sharper. Although some of these have total  $\chi^2$  values comparable to that of the above solution, we

can exclude them because of too large deviations from the individual frequency shifts and by a comparison with the  $|3, -3\rangle + |3, -3\rangle$  elastic cross-section data determined in Ref. [3] from cross-dimensional heating in a magnetic trap. The latter comparison uses only the low-temperature data, since it happens that a strong  $d$ -wave resonance dominates the (decreasing)  $s$ -wave cross section at the higher temperatures. This makes the comparison with the experiment difficult, since its analysis was based on an angle- and energy-independent elastic cross section. For the parameter region (1), we find agreement almost within the experimental error bars for the three lowest energy points of Ref. [3].

We thus find strong evidence for the existence of almost bound  $s$ -wave singlet and triplet states. For  $l \neq 0$  partial waves, a negative  $v_D$  value near 0 implies low-energy resonances in the continuum part of the singlet and triplet spectrum. For  $l = 0$ , however, increasing a negative  $v_D$  continuously through 0 causes a bound state to approach  $E = 0$  and then to recede again along the negative-energy axis, corresponding to a so-called virtual (antibound) state.

The value of  $v_{DT}$  also yields a large negative value for the triplet scattering length of  $-200a_0$  to  $-1100a_0$  (and consequently a large zero-energy cross section of  $10^5$  to  $10^7 \text{ \AA}^2$ ). This may have consequences for the possibilities of realizing Bose condensation in a dilute Cs gas sample of atoms in the doubly polarized  $|4, +4\rangle$  hyperfine state, since a positive value of the triplet scattering length is needed for the stability of the Bose condensate [15]. Our results indicate that it may be impossible to study Bose condensation in such a gas. For the case of doubly polarized  $^7\text{Li}$ , a negative value of  $a$  was already reported [16]. Alternatively, for Cs, the  $|3, -3\rangle$  state is also low-field seeking for weak fields. This choice is attractive since loss mechanisms due to dipolar relaxation and second-order electron spin-orbit coupling are suppressed [3,5]. Our calculations also show that the scattering length for this state is negative, at least for magnetic fields below where the first resonance occurs. The present accuracy in the determination of  $v_{DS}$  and  $v_{DT}$  only allows a rough prediction of this field value: calculations for the  $|3, -3\rangle + |3, -3\rangle$  channel in the parameter region (1) show that it is between 0.0040 and 0.1400 T.

With the above results it becomes possible additionally to predict the behavior of many other continuum quantities. In particular, we predict values for all unmeasured frequency-shift and line-broadening cross sections for the  $|3, 0\rangle - |4, 0\rangle$  clock transition, including their magnetic field dependence. Measurements of these remaining partial frequency shifts for the Cs clock transition, and improvements in the accuracy of the already measured shifts, will lead to narrower error limits for the three parameters of our theory. We are also able to predict collisional shifts for the  $|F, +m_F\rangle - |F, -m_F\rangle$  transitions, which are crucial to devising a suitable strategy for measurements of the electric dipole moment of the electron in a cesium fountain or trap. Theoretical work along this line is in progress [9].

*Note added in proof.* After the submission of this manuscript a paper by Gribakin and Flambaum appeared

which also discusses the sign of the Cs-Cs triplet scattering length [G. F. Gribakin and V. V. Flambaum, *Phys. Rev. A* **48**, 546 (1993)]. Contrary to our result, they find evidence for a positive sign on the basis of the same experimental elastic cross section used in our analysis, but interpreting the  $|3, -3\rangle + |3, -3\rangle$  channel as a pure triplet system with  $l=0$ . Without this approximation and including also the fountain frequency shifts, we find

agreement with experiment for a negative value of  $a_T$  (and  $a_S$ ).

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