

Relativistic *ab initio* treatment of the second-order spin-orbit splitting of the $a^3\Sigma_u^+$ potential of rubidium and cesium dimers

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We have calculated the splitting between the 0_u^- and 1_u components of the $a^3\Sigma_u^+$ state of Rb_2 and Cs_2 using a relativistic *ab initio* configuration-interaction valence bond method. This so-called second-order spin-orbit splitting is entirely due to relativistic correlations within the molecule. Our *ab initio* nonperturbative splitting is 5 and 2 times larger than perturbative splittings at the inner turning point of the $a^3\Sigma_u^+$ potential for Rb_2 and Cs_2 , respectively. In addition, close-coupled nuclear dynamics calculations that estimate the effect of this splitting on experimentally accessible quantities are presented. The splitting affects the collisional loss rate of magnetically trapped ultracold Rb and Cs atoms and the spectroscopic determination of the vibrational structure of Rb_2 and Cs_2 dimers. Agreement with the experimental collisional loss rates of Cs is found.

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Over the past few years reaching quantum degeneracy in dilute fermionic and bosonic alkali-metal gases has generated an increased interest in understanding the interactions between two such atoms. Quantum degeneracy for bosons with positive scattering lengths implies a phase transition into a Bose-Einstein condensate [1]. On the road to degeneracy these ultracold dilute gases are kept in magnetic traps and are rapidly cooled by forced evaporation. For this process to be successful rethermalization rates must be much larger than inelastic loss rates. Both rates are determined by interactions between the atoms. For the bosonic alkalis that have been condensed this ratio has been favorable. So far unacceptably large inelastic losses for cesium have prevented it from condensing [2–4]. Quantitative theoretical estimates of the loss rates for the heaviest alkali-metal gases have been unavailable. It is the purpose of this paper to calculate from first principles the molecular origin of this two-body loss for Rb and Cs and present its effect on ultracold colliding atoms.

The origin of the collisional loss is due to relativistic effects in the electronic Hamiltonian that lead to a splitting of the nonrelativistic $a^3\Sigma_u^+$ electronic state into a 0_u^- and 1_u component, where $\Omega=0(1)$ is the projection of the total electronic angular momentum of the two atoms on the internuclear axis. The splitting has two contributions. The first contribution is the second-order spin-orbit interaction which entirely depends on the existence of valence electronic correlation in the dimer and therefore decreases exponentially with increasing internuclear separation R . The second contribution is due to the magnetic spin-dipole–spin-dipole interaction. This effect is a “direct” relativistic interaction proportional to $1/R^3$ [5]. The latter is believed to be the dominant relativistic effect for the lighter alkali-metal dimers up to potassium. The second-order spin-orbit effect, however, becomes important for the heavier alkali-metal dimers. This splitting has not been well characterized and new calculations are presented in the current paper.

Accurate data for the second-order spin-orbit splitting are interesting for both experiment and theory. There are several experiments that are affected by the relativistic splitting. A first class of experiments is sensitive to atom loss via ultra-

cold collisions [2–4]. Spectroscopically measuring the relativistic splitting of the weakly bound states of two interacting 2S atoms is another example [6,7]. A third experiment is the spin depolarization of room-temperature doubly polarized rubidium and cesium atoms [8].

In this paper we calculate the second-order spin-orbit splitting and subsequently use it to obtain experimental observables. For a precise value of the second-order spin-orbit splitting we need to implement a fully relativistic electronic structure formalism. We opted for an *ab initio* valence bond method where correlation is included by a configuration interaction expansion [9,10]. The nuclear motion is solved for by a coupled channel calculation [5] which uses the second-order spin-orbit splitting obtained from the valence bond method.

The previous estimate of the relativistic second-order spin-orbit splitting in Rb_2 and Cs_2 applies second-order perturbation theory [11] based on nonrelativistic wave functions and energies obtained with an effective core potential method [12]. As first-order perturbation in the relativistic spin-orbit interaction does not lift the degeneracy between the $\Omega=0$ and 1 components of the $a^3\Sigma_u^+$ state, second-order perturbation theory is needed. Reference [11] only includes contributions from the lowest $^1\Pi_u$ and $^3\Pi_u$ excited states. Consequently, the values presented in Ref. [11] are believed to be a lower bound on the splitting. Indeed, recent experiments [8] show that their value for Cs_2 is too small.

Our relativistic valence bond method is able to calculate the second-order spin-orbit splitting nonperturbatively. Briefly, the valence bond (VB) method approximates the exact electronic molecular wave function as a linear combination of basis functions that are antisymmetrized products of two atomic determinants. Each atomic determinant is constructed from orbitals that are localized and centered at the *same* nucleus. The linear combination of basis functions that describe eigenstates of the electronic Hamiltonian is obtained by the configuration interaction (CI) method. The electronic Hamiltonian contains the sum of Dirac operators for each electron and all repulsive electron-electron, attractive electron-nucleus, and repulsive nucleus-nucleus Coulomb in-

teractions. For the VB method CI implies solving for a generalized eigenvalue problem, since the basis forms a set of nonorthogonal Slater determinants.

The localized atomic orbitals are realistic orbitals obtained from solving the Dirac-Fock (DF) equations numerically. These four-component DF spinors are optimized for a specific atom and display the correct physical behavior near a nucleus and asymptotic behavior at large distances. These orbitals will be denoted by $(nl)_j$ where n is the main quantum number and $l(j)$ is the mechanical (total) angular momentum of the electron. Relativistic two-center integrals are evaluated with a modified Löwdin's reexpansion procedure [13].

Core electrons occupy the closed shells $1s_{1/2}^2$, $2s_{1/2}^2$, $2p_{1/2}^2$, $2p_{3/2}^4$, . . . up to $4s_{1/2}^2$ for the Rb atom and similarly $1s_{1/2}^2$, . . . up to $5s_{1/2}^2$ for the Cs atom. The superscript denotes the number of electrons in the shell and the subscript j is sometimes omitted in the text to simplify the notation. In the calculation, however, nl_j orbitals with different j are obtained separately and treated accordingly. The core orbitals do not contribute significantly to the formation of the molecule. Excitations out of these closed shells are therefore not included. Nevertheless, these orbitals do define a fully relativistic all-electron core potential for the valence electrons.

Occupied valence electrons are located in the $4p_{1/2}^2$, $4p_{3/2}^4$, and $5s_{1/2}$ shells for the Rb atom and $5p_{1/2}^2$, $5p_{3/2}^4$, and $6s_{1/2}$ shells for the Cs atom. These electrons play an important role in the formation of the ground electronic state of the rubidium and cesium dimer. In spite of the fact that the $4p^6$ shell in Rb and $5p^6$ shell in Cs are closed, electrons in these shells are called valence electrons as excitations will be allowed. This will ensure a proper treatment of "core polarization."

In addition to the two kinds of orbitals, discussed above, unoccupied valence orbitals are needed to increase the flexibility of the molecular wave function. The Dirac-Fock $5p_j$ orbital for the Rb atom and $6p_j$ orbital for the Cs atom are used to describe the first excited states, which are the most influential for the second-order spin-orbit splitting of the $a^3\Sigma_u^+$ potential. More highly excited DF orbitals, however, are very diffuse and are therefore not very efficient in giving correlation since the overlap with the occupied valence orbitals is small. In the calculation compact Sturmian orbitals [14] replace these highly excited orbitals. The Sturmian orbitals are self-consistent solutions of the Dirac-Fock-Sturm equations, at the valence electron energy. The complete set of Sturmian functions is discrete and is chosen to have a spatial extent and asymptotic behavior similar to the occupied $5s_{1/2}$ for Rb and $6s_{1/2}$ for Cs valence orbitals. Consequently, these functions are efficient in describing a correlation with occupied valence electrons. We label Sturmian orbitals nl_j , where $n-1$ is the number of nodes in the radial direction of the major component of the relativistic orbital and l and j are defined as before.

Atomic configurations are formed from core and valence orbitals and uniquely labeled by the occupied and unoccupied valence orbitals. For example, the main configuration of the ground state of the Rb atom is $4p_{1/2}^2 4p_{3/2}^4 5s_{1/2}$

($=4p^6 5s$), while for the Cs atom it is $5p^6 6s$. The inner core shells are the same for all configurations and are not needed to label a configuration.

In addition to the main configuration the calculation of the CI ground state wave function has to include other molecular configurations created by excitation of one or two electrons from $4p^6 5s$ for Rb and $5p^6 6s$ for Cs into higher excited orbitals. We allow excitations up to $n=7$ for Rb and $n=8$ for Cs, for $l=0-3$. The convergence of the CI expansion can only be checked by increasing the number of configurations in a systematic way. This is achieved by adding atomic orbitals out of which the atomic and thus molecular determinants are constructed. Our best basis set has on the order of 20 000 determinants.

We have chosen our basis of molecular configurations based on a calculation of the long-range dispersion coefficients of Rb_2 and Cs_2 . The C_6 dipole-dipole coefficients are known from other means [15] and must be reproduced in our calculation. Notice that at large internuclear separations the exchange interaction between orbitals located at different atomic centers does not contribute to the dispersion.

The dispersion coefficients are obtained by fitting the calculated long-range potential to $V(R) = V_\infty - C_6/R^6 - C_8/R^8$, where V_∞ is the value of the potential at $R=\infty$ and C_8 is dipole-quadrupole dispersion coefficient. The interaction potentials are calculated using a basis set that has all possible excitations from the ground configurations up to the $7d$ orbitals for Rb_2 and up to the $8d$ orbitals for Cs_2 . The potentials have the lowest total electronic energy of all bases tested. The total energies of less accurate bases converge to that of the former. The calculations give a C_6 coefficient of 4680(50) a.u. for Rb_2 and 6860(60) a.u. for Cs_2 . Moreover, we find $C_8 = 526(30) \times 10^3$ a.u. and $C_8 = 1000(300) \times 10^3$ a.u. for Rb_2 and Cs_2 , respectively. The fit is limited to internuclear separations $R \geq 32a_0$ and $34a_0$ for Rb_2 and Cs_2 , respectively. Here, $1 a_0 = 0.0529177$ nm and 1 a.u. of energy is $4.35974381 \times 10^{-18}$ J. The uncertainties are obtained from comparing the long-range coefficients of the two best bases. Our values of C_6 are in good agreement with $C_6 = 4691(23)$ a.u. and $6851(74)$ a.u. for Rb_2 and Cs_2 published by Derevianko *et al.* [15]. The dipole-quadrupole dispersion coefficients compare well with those obtained by Ref. [16].

The second-order spin-orbit splitting is calculated using all orbitals that are needed to obtain the best value for the long-range coefficient C_6 . Exchange interactions and covalent and ionic configurations are included since these contributions are crucial for the potentials at short internuclear separations. The size of the matrices that need to be diagonalized is too large to handle computationally and we are forced to limit the number of determinants. The selection of determinants is based on a perturbative estimate of the effect of excited configurations on the main configuration. If this effect is below a threshold value, the corresponding excited configuration is omitted from the CI calculation.

Figure 1 shows the second-order spin-orbit splitting $V(1_u^-) - V(0_u^-)$ of the ground configuration of Rb_2 and Cs_2 as a function of internuclear separation. These splittings are obtained by including excited orbitals up to the $7d$ orbitals for Rb_2 and $8d$ for Cs_2 and allowing single-electron excitations

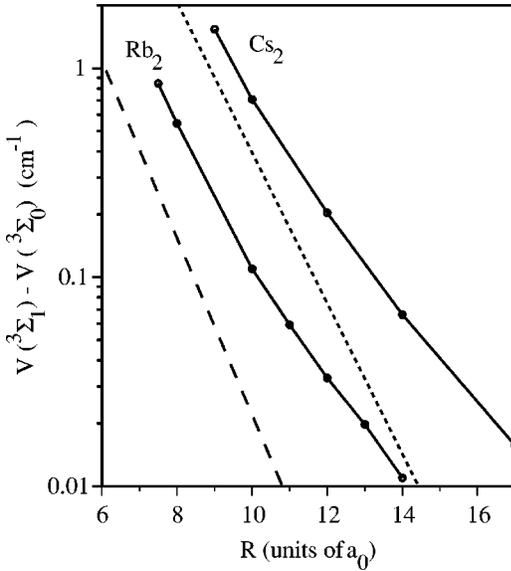


FIG. 1. The second-order spin-orbit splitting for Rb_2 and Cs_2 as a function of internuclear separation. The dashed (dotted) line shows the Rb_2 (Cs_2) spin-orbit splitting of Ref. [11].

from the $4p^6$ shell. The accuracy of the splitting is estimated at 15% by comparing to calculations which include fewer excited orbitals and that have an increased number of selected determinants.

Both *ab initio* curves in Fig. 1 are nearly exponential. Comparison with the perturbation theory of Ref. [11] shows that in both cases the slope and size of the *ab initio* second-order spin-orbit splitting are significantly larger. For the inner turning point of the $a^3\Sigma_u^+$ potential, which is approximately at $10a_0$ for both dimers, the second-order spin-orbit splitting is about 5 and 2 times larger for Rb_2 and Cs_2 , respectively.

The relativistic *ab initio* valence bond calculation finds the energetically lowest 0_u^- and 1_u Born-Oppenheimer potentials. The difference between the two potentials provides the second-order spin-orbit splitting. A nonrelativistic $a^3\Sigma_u^+$ potential of Rb_2 and Cs_2 is known from Ref. [12]. Our 0_u^- and 1_u potentials are about 15% deeper for both dimers. For Rb_2 our potentials have a steeper inner wall which leads to an inner turning point of the zero-energy collision that occurs at a $\approx 0.2a_0$ larger internuclear separation of $R = 9.85a_0$. For Cs_2 no such discrepancy between the inner turning points exists. In our calculation there is a $0.1a_0$ uncertainty in this inner turning point again based on calculations with fewer excited orbitals. The accuracy of both theoretical approaches is lower than required for spectroscopic and ultracold scattering experiments. Small modification of the Born-Oppenheimer potentials needs to be introduced to reproduce the scattering lengths for $^{87}\text{Rb} + ^{87}\text{Rb}$ [17] and $\text{Cs} + \text{Cs}$ collisions [18].

For a connection with experimental observables we calculate the effect of our second-order spin-orbit splitting on inelastic collision rates of Rb_2 and Cs_2 and weakly bound rovibrational levels of Rb_2 . The quoted uncertainties for these observables are based on a 15% uncertainty in the

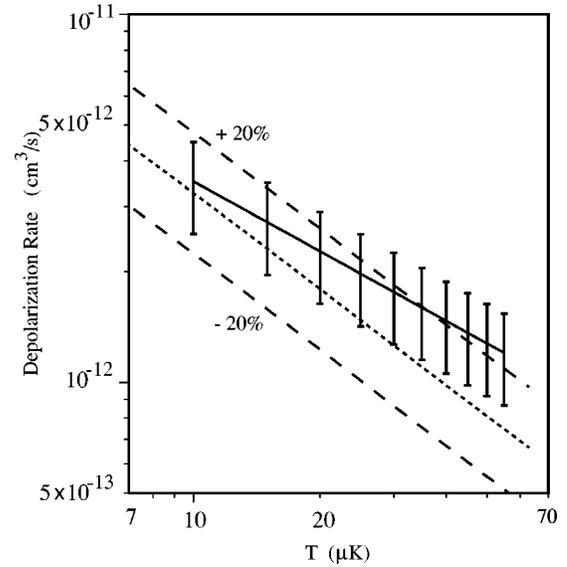


FIG. 2. The depolarization rate of a doubly polarized cesium gas as a function of temperature. The curve with error bars shows the experimental measurements of Ref. [2]. The dotted line is theoretical depolarization rate using a second-order spin-orbit splitting as shown in Fig. 1. The two dashed lines show the rate with the second-order spin-orbit splitting increased by $\pm 20\%$. These changes reflect our uncertainty in calculating the second-order spin-orbit splitting.

strength of the second-order spin-orbit splitting and a 10% uncertainty due to an uncertainty of the inner turning point of the $a^3\Sigma_u^+$ potential.

Collisional rates and binding energies of vibrational levels are calculated based on a Hamiltonian containing the $X^1\Sigma_g^+$ and $a^3\Sigma_u^+$ Born-Oppenheimer potentials, the second-order spin-orbit splitting, the nuclear kinetic energy operator, the hyperfine contact and Zeeman interaction for each atom, and the nuclear rotation [5,11]. The spin-spin dipole interaction is incorporated by adding α^2/R^3 and $-(1/2)\alpha^2/R^3$ to the 0_u^- and 1_u potentials, respectively [11], and is of opposite sign compared to the second-order spin-orbit splitting. The parameter α is the fine structure constant.

Figure 2 shows the experimental (solid line) and theoretical (dashed and dotted lines) depolarization rate of a gas of double-polarized Cs atoms as a function of temperature. The depolarization rate is defined as twice the inelastic rate coefficient since two atoms are lost for each collision. No external magnetic field is present in the theory. Magnetic field strength up to 1 mT will change depolarization rate less than 1%. Depolarization of a double-polarized gas is due to the relativistic splittings between the 0_u^- and 1_u potentials. Figure 2 shows a comparison of the depolarization rates when the second-order spin-orbit splitting as shown in Fig. 1 is used and when the size of this splitting is increased by 20%. The difference between the two calculations approximately reflects our uncertainty in the second-order spin-orbit splitting. For the temperatures shown in Fig. 2 the effect of the uncertainty of the scattering lengths and dispersion coefficients [18] on the depolarization rate is small compared to that of the second-order spin orbit splitting. Consequently the

theoretical and experimental depolarization rates of Ref. [2] agree within their error bars. We do not believe that the slope difference in Fig. 1 is significant.

The depolarization rate for a zero-temperature Rb gas lies between 2×10^{-16} cm³/s and 1×10^{-15} cm³/s. This is rather small and therefore hard to observe experimentally. Other processes such as loss through collisions with background gases will limit the lifetime of a double-polarized Rb gas.

Finally, we predict the splitting of a weakly bound d -wave rotational levels of Rb₂ caused by the second-order spin-orbit splitting and the spin-spin dipole interaction. In principle these small splittings could be measured by Raman spectroscopy in a Bose condensate. Prospects for such a measurement [7] are good based on a recent observation [6] of a weakly bound s -wave vibrational level to kHz accuracy. No splittings due to weak relativistic spin dependent interactions are present for an s -wave level.

In Ref. [6] the observed s -wave level is bound by approximately -0.636 GHz below the lowest hyperfine dissociation limit and can be labeled by $m = -2$, where m is the projection of the summed electronic and nuclear spin along the magnetic field direction. A magnetic field of 0.6 mT is present. Close to this s -wave level lies the second-last $m = -2$ d -wave vibrational level. The second-order spin orbit

splitting and the spin-spin dipole interaction for this d -wave line lift the degeneracy with the projection μ of the nuclear mechanical angular momentum along the magnetic field direction. For the 0.6 mT magnetic field our prediction for the splitting between the $|\mu| = 2$ and 0 d -wave levels is 110(20) kHz.

In summary we have used a nonperturbative relativistic valence bond method to describe the electronic structure of Rb₂ and Cs₂. The second-order spin-orbit splitting of their ground triplet potential is entirely due to relativistic correlation and therefore requires extensive correlation interaction calculations. We show that the splitting is significantly larger than that estimated from a perturbative electronic structure calculation. The long-range dispersion coefficients have been calculated and found to be in agreement with Ref. [15]. Moreover, based on our second-order spin-orbit splitting we find that inelastic rate coefficients for ultracold double polarized Cs atoms is in good agreement with experimental measurements. We also predict splittings due to the second-order spin-orbit splitting of weakly bound Rb₂ rovibrational levels.

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