Relativistic *ab-initio* electronic structure calculation of the splitting between the 0_u^+ and 1_u ($a^3\Sigma_u$) potentials of the rubidium and cesium dimer

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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 the Rb_2 and Cs_2 dimers using a relativistic *ab initio* configuration interaction valence bond method. This splitting is the so-called second-order spin-orbit splitting and is entirely due to relativistic molecular correlations. The valence bond molecular configurations are constructed from atomic Dirac-Fock and Sturmian orbitals. We have compared our calculations with a perturbative calculation based on nonrelativistic electronic structure wavefunctions [1]. Our nonperturbative splitting for Rb_2 at the inner turning point of the $a^3\Sigma_u^+$ potential is approximately a factor of five larger while for Cs_2 at the corresponding inner turning point it is twice as large. This splitting affects the collisional loss rate of magnetically trapped ultra-cold Rb and Cs atoms, the depolarization of room-temperature polarized atoms [2] and the spectroscopic determination of the vibrational structure of Rb_2 [3] and Cs_2 dimers. We also performed close-coupled nuclear dynamics calculations to estimate these experimentally accessible quantities and find that in addition to the size of the splitting the location of the $a^3\Sigma_u^+$ at the inner turning point is crucially important.

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