Rydberg molecule-induced remote spin-flips

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We have performed high resolution photoassociation spectroscopy of rubidium ultra long-range Rydberg molecules in the vicinity of the $25P$ state. Due to the hyperfine interaction in the ground state perturber atom, the emerging mixed singlet-triplet potentials contain contributions from both hyperfine states. We show that this can be used to induce remote spin-flips in the perturber atom upon excitation of a Rydberg molecule. When furthermore the spin-orbit splitting of the Rydberg state is comparable to the hyperfine splitting in the ground state, the orbital angular momentum of the Rydberg electron is entangled with the nuclear spin of the perturber atom. Our results open new possibilities for the implementation of spin-dependent interactions for ultracold atoms in bulk systems and in optical lattices.

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Implementing tunable short-range interactions in ultracold quantum gases has proven to be key to study quantum phase transitions [1] and strongly interacting many-body systems [2, 3]. The most commonly used techniques are magnetic Feshbach resonances [4] and confinement-induced effective interactions [5, 6]. Long-range interactions beyond the pure contact interaction are more challenging to achieve. Possible realizations include second order tunneling [7], cavity-mediated interactions [8], magnetic dipolar interactions in high spin atomic species [9, 11] and electric dipolar interactions between heteronuclear molecules [12]. Exciting atoms to Rydberg states is another way to induce long-range interactions, as evidenced by the demonstration of the Rydberg blockade [13, 16] and anti-blockade [17, 18]. Recently, these concepts were transferred to the realm of ultracold quantum gases [19]. First experimental results with off-resonant excitation schemes show that for short times, coherent interactions between ground state atoms can be generated [20]. In most such "Rydberg dressing" schemes the interaction is based on admixing Rydberg excitations to two particles, resulting in energy shifts which scale quadratically with the driving laser intensity. This narrows the parameter window for coherent effects drastically [20, 21].

The discovery of Rydberg macrodimers [22, 23] and Rydberg molecules [24] has opened up an increasing field of research, combining ultracold chemistry with many-body physics and low energy electron scattering. Rydberg molecules are bound by the contact interaction between the Rydberg electron and a ground state perturber atom. The large extension of the Rydberg electron wave function (50 – 1000 nm) makes it possible to induce long-range interactions between two spatially separated (remote) ground state atoms that otherwise interact solely through contact interaction on a typical length scale of 5 nm in the case of rubidium. In contrast to the usual Rydberg dressing of single species gases [21], only one excitation is required, thus leading to a more favorable first order process, which scales linearly with the laser intensity.

For alkali atoms, one can distinguish three different types of molecules: ultra-long range Rydberg molecules [23, 25], trilobite molecules [26] and butterfly molecules [27, 29]. While sharing a similar binding mechanism, they differ in the degree of perturbation, which is imposed by the ground state perturber to the Rydberg electron wave function. Here, we change the perspective and study the effect of the binding mechanism on the perturber atom. In agreement with theoretical predictions we experimentally confirm the presence of spin-flip processes in the ground state perturber upon excitation of ultra long-range Rydberg molecules. We can also excite particular Rydberg states, where the Rydberg orbital angular momentum is strongly entangled with the nuclear spin of the perturber atom. For the $25P$ state of rubidium, both effects are active over a distance of up to 50 nm between the two atoms. As we use a single photon excitation scheme to excite the molecules, we avoid spontaneous scattering from an intermediate level. Our technique is therefore suited to induce coherent and dissipative interactions in ultracold atomic gases. This includes the realization of optical Feshbach resonances [30] involving Rydberg molecules and spin-dependent dissipative processes.

Based on Fermi’s original idea of s-wave scattering by a quasi free electron [31], the interaction of a ground state perturber atom at a distance $R$ inside the Rydberg wave function is described by a zero range pseudo-potential $V_s(R) = 2\pi A_s(k_R)\delta(r - R)$ with a scattering length $A_s$ that depends on the classical electron momentum $k_R = \sqrt{\frac{2}{\hbar^2} - \frac{1}{m^2}}$. Due to shape resonances appearing in the low energy scattering of electrons and alkali atoms, it is crucial to extend the pseudo-potential to also include the p-wave scattering process [32]. Taking further into account the different scattering length for singlet and triplet scattering and the hyperfine structure in the perturber atom, the Hamiltonian for the molecular system

\[ H = \sum_i (\frac{p_i^2}{2m} + V_i(r_i)) + \sum_{ij} V_{ij}(r_{ij}) \]
FIG. 1. (Color online). (a) The contact interaction between the Rydberg electron $e^-$ and the ground state atom Rb leads to a spin-dependent interaction over distances up to 50 nm in the $25P$ state. (b) The angular momentum coupling scheme shows how the spin-spin interaction (SS) couples the fine structure (FS) of the Rydberg atoms with the hyperfine structure (HFS) of the perturber. The color of the arrows corresponds to the colors used in a). (c) Transition scheme. When the sample is in the $F = 2$ ground state only the atomic transitions to states adiabatically connecting to $F = 2$ states are possible (red arrows). Due to the hyperfine mixing of the molecular interaction (see text), also transitions to molecular states in the $F = 1$ spectrum are possible (purple arrows).

in Born-Oppenheimer approximation reads \[ \hat{H} = \hat{H}_0 + 2\pi \alpha - \epsilon \langle \mbox{spin flip} \rangle + 6\pi \left[ a_p^S(k_R)\hat{\boldsymbol{I}}^S + a_p^T(k_R)\hat{\boldsymbol{I}}^T \right] \delta^{(3)}(\vec{r} - \vec{R}) + A \hat{S}_2 \cdot \hat{I}_2. \] (1)

Here, $\hat{H}_0$ is the atomic Hamiltonian of the Rydberg atom including the fine structure, $a_p^S(a_p^T)$ are the $s$-wave scattering lengths for singlet (triplet) scattering and $a_p^S(a_p^T)$ the $p$-wave scattering lengths for singlet (triplet) scattering. The projector on the triplet subspace can be expressed in terms of the spin $\hat{S}_1$ of the Rydberg electron and the spin $\hat{S}_2$ of the perturber and is given by $\hat{\boldsymbol{I}}^T = \hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 + 3/4$. The singlet projector is $\hat{\boldsymbol{I}}^S = 1 - \hat{\boldsymbol{I}}^T$.

The hyperfine coupling in the perturber is described by the hyperfine constant $A = 3.4 \text{ GHz}$ (for $^{87}\text{Rb}$) and the coupling between the electronic spin $\hat{\boldsymbol{S}}_2$ and the nuclear spin $\hat{\boldsymbol{I}}_2$ of the perturber. Fig. 1 shows the different angular momentum couplings that occur in the Rydberg molecules.

In order to calculate the Born-Oppenheimer potential energy curves (PEC), we have carried out a full diagonalization of the Hamiltonian \[ \hat{H} \] and the resulting eigenenergies as a function of the internuclear distance $R$ are shown in Fig. 2a. The corresponding excitation scheme including the initial state of the two atoms is shown in Fig. 2b. As a consequence of the hyperfine interaction in the perturber atom, the singlet- and triplet states are mixed and the Hilbert space can no longer be separated into the according subspaces. The emerging eigenenergies therefore feature one pure triplet potential energy curve (blue lines in Fig. 2a) and one of mixed singlet-triplet character (orange lines) \[ \Phi_{\text{ent}} = a \left| 25P_{1/2} \right\rangle \left\langle F = 2 \right| + b \left| 25P_{3/2} \right\rangle \left\langle F = 1 \right| \] (3) with $a, b \approx 0.1 \ldots 0.8$, which entangle the fine structure state of the Rydberg atom with the hyperfine state of the perturber. They are distinct from the spin-flip regime by the much stronger mixing. We denote this regime as the "entanglement" regime.

In order to experimentally prove the existence of hyperfine mixing in Rydberg molecules, we photoassoci-
generate ultra-long range Rydberg molecules in the vicinity of the 25P state from a Bose-Einstein condensate (BEC) of 87Rb. The experimental apparatus is described in detail in reference [36]. In brief, a BEC of 10^5 atoms and a temperature of 100 nK is prepared in a crossed YAG optical dipole trap by forced evaporation to final trapping frequencies of 2π × 67 Hz in all three directions. Due to a small magnetic field gradient present during evaporation, the BEC is spin polarized in the 5S_1/2, F = 1, m_F = +1 ground state. Using microwave radiation the spin state of the atoms can be transferred to the fully stretched F = 2, m_F = +2 state with a Landau-Zener sweep at a fidelity of close to 100%. The photoassociation of Rydberg molecules is achieved by a frequency doubled cw dye laser at a wavelength of 297 nm and a laser linewidth below 700kHz. Once produced, the Rydberg molecules can decay into ions either by photoionization, leading to a Rb⁺ atomic ion, or by associative ionization, leading to a Rb₂⁺ molecular ion [37, 38]. The experimental sequence consists of 1000 excitation pulses (1 µs) with subsequent continuous ion detection (200 µs). Due to the different mass the atomic and molecular ions have different time of flights (TOF) to the ion detector. From the decay of the signal, we can additionally extract the lifetime of the produced molecules. We have performed photoassociation spectroscopy with a resolution of 1 MHz, spanning more than 10 GHz.

The full spectrum for a BEC in the F = 2 state is shown in Fig. 2, along with the relevant parts of the spectrum for a BEC in the F = 1 state in Fig. 2. The most prominent features in each spectrum are the two bare atomic transitions, which can only appear for those states that match the hyperfine state of the prepared BEC. As discussed above this does no longer hold for the molecular states. Instead, some of the molecular lines of the 25P₃/₂; F = 1 spectrum appear also on the blue side of the 25P₁/₂; F = 2 state in the F = 2 spectrum (Fig. 2c). As those lines can only originate
from the mixed type potential, we compare in Fig. 3 the lines in the $F = 2$ spectrum to the calculated energies of the lowest bound states in each well of the mixed type potential adiabatically connecting to the $25P_{3/2}; F = 1$ state (green bars). The three highest energy lines can not be attributed to a ground state in any of the wells and are probably higher excited states. The residual six observed lines coincide with the predicted bound state energies within 10%. Even stronger evidence for those resonances originating from the hyperfine mixing in the $25P_{3/2}; F = 1$ potential curve arises from the direct comparison of both spectra (Fig. 3). Except for the line close to $-200 \text{MHz}$ it is possible to attribute each line in the $F = 2$ spectrum to a corresponding line in the $F = 1$ spectrum. This not only provides strong evidence for the discussed hyperfine mixing but also allows us to identify which peaks in the $F = 1$ spectrum belong to the mixed potential and which, by exclusion, belong to the triplet potential. The comparable magnitude of the three interactions which couple the different angular momenta (Fig. 1b) leads to the before mentioned entanglement between the orbital degree of freedom of the Rydberg electron and the nuclear spin of the ground state atom. Since the interaction between two such molecular entangled states depends on the fine structure state of the Rydberg atom this can be used to entangle the spin of ground state atoms over the typical length scale of Rydberg-Rydberg interactions.

In contrast to the strong lines in the entanglement regime it is more challenging to observe the hyperfine mixing in the spin-flip regime. Due to the high signal-to-noise ratio provided by the ion signal we are nevertheless able to see a molecular line at $-14.8 \text{GHz}$ in the $F = 2$ spectrum (Fig. 2b), which, in comparison with the calculated PECs, can only be attributed to the $25P_{1/2}; F = 1$ state (highlighted region in Fig. 2b). Since the observed line differs only by $32 \text{MHz}$ from the expected energy of the lowest bound state in the well at $692a_0$ of the $25P_{1/2}; F = 1$ mixed potential, we assume the admixture of the $F = 2$ state to be on the order of $e^2 = 0.04\%$. The detection of bound states at higher internuclear distances is hindered by the small hyperfine mixing. At closer distances on the other hand the reduced probability to find a pair of atoms decreases and pushes the line strength below our detection limit. It should be noted that the observed molecular line has the lowest energy of all possible transitions depicted in Fig. 1 and thus the presence of $F = 1$ atoms in the initial sample can not explain the observed signal. We have thus experimentally shown a spin-flip of the ground state perturber upon photoassociation of a Rydberg molecule over a distance of $35 \text{nm}$ between the two atoms.

Due the high particle density and the presence of collective modes in the BEC, many-body effects beyond the two-particle picture might influence the observed spin-flip mechanism. However, the possibility to spectroscopically address a well-defined molecular state allows us to selectively photoassociate only atom pairs that don’t have any additional ground state atom inside the Rydberg wave function. Furthermore, bound states of two or more perturber atoms are strongly suppressed due to the geometric constraints imposed by the p-state wave function. Also, the molecular formation process can hardly excite collective modes in the BEC as the size of the molecules is much smaller than the healing length $\xi = 230 \text{nm}$.

When the separation between the two atoms in the molecular state is much smaller than the typical inter-particle distance in a quantum gas or in an optical lattice, the resulting interaction might still be classified as ”short-range”. It can then be used to modify the contact interaction between the atoms. In fact, optical Feshbach resonances are based on the coupling of a free two-particle scattering state to a molecular bound state with a photoassociation laser. Due to intrinsic losses, molecular states with long lifetimes and minimal off-resonant scattering from the bare atomic resonance are mandatory to apply this concept. Experiments have so far been performed on different atomic species, most promising results have been obtained for ytterbium and strontium. The latter features a molecular decay rate.
of $\gamma/2\pi = 14\text{kHz}$ [30]. While a shift in the scattering length could be demonstrated successfully, losses still pose a serious challenge. With the presented spin-flip mechanism, Rydberg molecules can overcome these limitations, due to the absence of scattering from a bare atomic resonance. Since furthermore the decay rates of $\gamma/2\pi = 10 - 30\text{kHz}$ (extracted from the time of flight spectra in Fig 2) are compatible, we speculate that the coupling to spin-flipped Rydberg molecules is in principle suited to implement optical Feshbach resonances without scattering from a nearby bare atomic resonance.

For the resonant excitation of Rydberg molecules, non-unitary time evolution occurs. Upon excitation, spontaneous decay of the Rydberg molecules and associative ionization [37] lead to the loss of one or both atoms. However, these losses occur only for the addressed combination of hyperfine states (Fig. 1). In an optical lattice with a two component quantum gas, one could therefore induce losses in doubly occupied sites with a specific spin composition. The phase space dynamics can then drive the system in a correlated spin state, which is decoupled from the loss process.

In conclusion, we have performed high resolution photoassociation spectroscopy of p-state Rydberg molecules and have demonstrated spin-flip collisions in Rydberg molecules. In our case these spin-flip processes happen for an interatomic distance of about 35 nm. We also resolve molecular states, which feature strong entanglement between the orbital angular momentum of the Rydberg electron and the nuclear spin of the ground state perturber atom. Our results point at the possible realization of optical Feshbach resonances employing Rydberg molecules and provide new means to induce unitary and non-unitary interactions in ultracold quantum gases. This approach works for all atomic species or mixtures which support Rydberg molecules.

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