Intercombination Effects in Resonant Energy Transfer

C L Vaillant, R M Potvliege, and M P A Jones

Department of Physics, Joint Quantum Centre (JQC) Durham-Newcastle, Durham University, South Road, Durham DH1 3LE, United Kingdom

We investigate the effect of intercombination transitions in excitation hopping processes such as those found in Förster resonance energy transfer. Taking strontium Rydberg states as our model system, the breakdown of $LS$-coupling leads to weakly allowed transitions between Rydberg states of different spin quantum number. We show that the long-range interactions between two Rydberg atoms can be affected by these weakly allowed spin transitions, and the effect is greatest when there is a near-degeneracy between the initial state and a state with a different spin quantum number. We also consider a case of four atoms in a spin chain, and show that a spin impurity can resonantly hop along the chain. By engineering the many-body energy levels of the spin-chain, the breakdown of $LS$ coupling due to inter-electronic effects in individual atoms can be mapped onto a spatial separation of the total spin and the total orbital angular momentum along the spin chain.

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The non-radiative exchange of energy due to dipole-dipole interactions plays a crucial role in biology, both in naturally occurring processes such as photosynthesis [1], but also as a tool for probing intra and inter-molecular distances [2]. The usual requirements for efficient energy transfer are an electric dipole-dipole interaction between donor and acceptor molecules, and a near degeneracy between the initial and final states that ensures the process is always resonant [2]. Resonant energy transfer has also been extensively studied in atomic physics, where these conditions are easily met. For example, dipole-dipole interactions in dense, optically excited samples can lead to cooperative Lamb shifts [3, 4]. By using Rydberg states, rather than low-lying electronic states, the strength of the interaction can be increased by many orders of magnitude, leading to energy exchange over macroscopic distances [5–12].

Resonant energy transfer is usually assumed to be mediated only by electric dipole interactions. Accordingly, it is usually assumed, in agreement with the dipole selection rules, that only states with the same value of the total electron spin quantum number $S$ are coupled by these interactions. However, in atomic and molecular systems with more than one valence electron, $S$ is at best an approximately good quantum number owing to inter-electronic interactions. Transitions between energy levels labelled as singlet and triplet therefore become weakly allowed, resulting in so-called intercombination lines. A canonical example is found in the group II elements such as Sr, where intercombination transitions are used as precision frequency standards [15–18].

In this letter, we examine the impact of spin mixing on long-range interactions, considering first the effect of intercombination transitions on non-resonant van der Waals-type interactions, and second the effect of spin mixing on resonant hopping processes. As a model system we consider the $5snd$ Rydberg states of strontium. Ultra-cold Rydberg gases of divalent atoms are of growing interest in atomic physics [15–20], and as well as systems where the precise details of the electronic wave function are known [21–20], they provide a route to precise control of the inter-particle spacing via optical lattices or tweezer arrays [27–31]. Since strontium has two valence electrons, two Rydberg series with total angular momentum $J = 2$ exist, one labelled as the singlet and one as a triplet. Early theoretical and experimental work showed that these energy eigenstates do not have a well defined spin due to their interaction with doubly excited “perturbers” of mixed singlet/triplet character [21–22, 32]. These perturbers are coupled to the Rydberg states by inter-electronic interactions, resulting in a breakdown of $LS$ coupling, which in turn affects the long-range inter-atomic interactions; the situation is depicted pictorially in Fig. 1(a). We find that, for two interacting strontium atoms, the $2 \times n \ 2D_2$ states are close in energy to the $(n - 2) \ 2F_3 + (n - 3) \ 2F'_3$ states near $n = 30$ (as shown in Fig. 1(b)), which, combined with the spin-mixing in the Rydberg series, allows near-resonant transfer between two-atom states. For the case of four atoms, we find that a spin impurity (a 28 $1F_3$ atom) in a chain of 30 $2D_2$ atoms can hop resonantly from site to site, showing a spin-forbidden propagation along the chain (as shown in Fig. 1(c)).

Although here we consider only specific cases, we anticipate that similar effects may be important elsewhere, given the ubiquity of spin mixing effects and the increased probability of degeneracy in molecular systems with broad energy bands. Important examples could include Förster coupled quantum dots, where intercombination effects have previously been considered [33], and excitonic energy transfer in organic light emitting devices [34].

We begin by considering two atoms in $5snd \ 3D_2$ states. Theoretically, this situation is most easily treated using multi-channel quantum defect theory, which provides a wave function for each single-atom energy eigenstate in...
the spin-forbidden channel, i.e. where the spin labels of

the initial and final states are different. Thus, although
the spin mixing, and hence the coupling, is weak, this
spin-forbidden process can become important.

More concretely, to describe the long-range interac-
tions, we consider each atomic energy eigenstate state,
Ψ, to be a sum over the MQDT channel states, φk, such
that Ψ = ∑k Akekφk (where ek is a function describing the
angular, spin and remnant core state wave functions
[21]). Using these state vectors, the long-range interac-
tions can be calculated either perturbatively (which cor-
corresponds to calculating a C6 coefficient [35]; details of
the calculation are supplied in the supplementary ma-
terial) or non-perturbatively (by diagonalizing an effec-
tive Hamiltonian matrix in a basis of pair states [35]).
The values of the coefficients Ak, as well as numerical
dipole matrix elements, are provided in [21]. Through-
out this paper, we only consider atoms that are initially
in the stretched state (J = |Mf|), with the internuclear
axes of the interacting atoms being aligned with the z-
axis. Stretched states do not have any degeneracies in
Mf, thereby reducing the number of states that need to be considered (even allowing for the fact that
the dipole-dipole interaction couples stretched states to
non-stretched states).

The results of the C6 calculations (where the dipole-
dipole interaction is given by C6R−6) are shown in
Fig. 2 along with the contribution from “spin-allowed”
(i.e. singlet-singlet, triplet-triplet) and “spin-forbidden”
(singlet-triplet) intermediate pair states. Large contribu-
tions from singlet-triplet pair states are found in both
series around n = 16 where the effect of the 4d6s 1D2 and
3D2 perturbers is at its maximum [22, 35]. The overall
C6 coefficients for states in this region differ significantly
from predictions based on single-channel quantum defect
calculations for Rydberg states below n = 30. Above
n = 30, however, all effects from perturbers are found
to contribute less than 2% of the overall C6, thus vali-
dating the use of a one-electron treatment for high-lying
Rydberg states of strontium [20, 35, 36].

Also visible in Fig. 2 is a large singlet-triplet contribu-
tion for 3D2 states close to n = 30. This arises due to the
Förster resonance in the 2×n3D2 → (n−2)1F3+(n−3)3F3
channel shown in Fig. 1(b). The uncertainties in the
energy levels used to calculate the C6 coefficients [35]
are large enough that the location of the Förster reso-
nance can change by one value of n, however the reso-
nance is always present to within the error of these energy
level measurements [22, 35, 37]. The small Förster
defect in this channel means that second-order pertur-
bation theory is no longer valid, and we turn to a non-perturbative calculation. Fig. 3 shows the non-
perturbative Born-Oppenheimer potential curves in the
vicinity of the 30 3D2 + 30 3D2 asymptote, which has a
spin-forbidden avoided crossing at relatively large dis-
tances with the 28 1F3 + 27 3F3 asymptotic pair state.
Without the mixing between the triplet and singlet se-
ries, the avoided crossing would not exist. Because of the small defect, the interaction between these pair states is stronger than could be expected in view of the smallness of the singlet-triplet mixing in these Rydberg states.

As another illustration of the impact of this intercombination Förster resonance on resonant energy transfer, we now examine the propagation of a singlet “impurity” in a short chain of four equally spaced atoms. Denoting the 30 \( ^3D_2 \), 28 \( ^1F_3 \), 27 \( ^3F_3 \), and 28 \( ^3F_3 \) states by \( |0\rangle, |1\rangle, |2\rangle, \) and \( |3\rangle \), respectively, we numerically calculate the time evolution of the system at time \( t \) after the \( |1000\rangle \) state is prepared. Restricting the dynamics of each atom to these four states is justified by the fact that the \( C_6 \) coefficient of the \( 2 \times 30 \ ^3D_2 \) is dominated by the Förster-resonant 28 \( ^1F_3 \) + 27 \( ^3F_3 \) and the non-resonant 28 \( ^3F_3 \) + 27 \( ^3F_3 \) pair states. All other pair states contribute less than 15% to the \( C_6 \) coefficient of the \( 2 \times 30 \ ^3D_2 \) state and are far enough away in energy to be neglected. Fig. 3 shows the consequence of only choosing the four single atom states, 30 \( ^3D_2 \), 28 \( ^1F_3 \), 27 \( ^3F_3 \), and 28 \( ^3F_3 \); the potential curve for the 30 \( ^3D_2 \) + 30 \( ^3D_2 \) asymptote is shown to be well reproduced. We include all values of \( M_\parallel \) that contribute.

Fig. 3(c) shows the evolution of the average value of the spin quantum number, \( \bar{S}_p = \sum_i S_p^{(i)} c^{(i)}(a,t) \) for a lattice spacing of 2 \( \mu m \) (a spacing that can be engineered using two crossed 1550 nm laser beams \[19, 38\]). Here \( p \) refers to the lattice site, the index \( i \) runs over all the 4\(^4\) uncoupled 4-atom states \( |q_1 q_2 q_3 q_4\rangle \) \( (q_p = 0,\ldots,3, p = 1,\ldots,4) \), \( S_p^{(i)} \) is the spin quantum number of the atomic state \( q_p \) in the uncoupled 4-atom state \( i \), and \( c^{(i)}(a,t) \) is the amplitude of this uncoupled 4-atom state in the state of the dipole-coupled chain at time \( t \). The spin can be seen to propagate along the chain of atoms and back, although there is additional state transfer due to competing second-order interactions. The calculation shown in Fig. 3(c) includes the interactions between all the atoms, not just nearest-neighbour interactions. Nevertheless, a clear propagation of a spin singlet state through the chain can be seen, a phenomenon that can only occur due to spin-mixing.

For the parameters of Fig. 3(c), the dynamics arise primarily from the spin-forbidden dipole-dipole coupling between the \( |1000\rangle, |0100\rangle, |0010\rangle \) and \( |0001\rangle \) states. The spin-forbidden Förster resonance between the \( |00\rangle \) and \( |12\rangle \) or \( |21\rangle \) pair states also has an impact on the dynamics of this spin chain. For instance, the potential energy curves shown in Fig. 3(a) (red lines) exhibit an avoided crossing between states of predominantly \( |1000\rangle \) and \( |1120\rangle \) character (these states are linear combinations of several unperturbed states due to the interactions). As a result, the average value of the total angular momentum quantum number at each site, \( \bar{J}_p = \sum_i J_p^{(i)} |c^{(i)}(a,t)|^2 \), may vary differently with \( t \) and \( p \) than the average value of the spin quantum number, \( \bar{S}_p \), as shown in Fig. 3(b)–(d). The key feature is that, due to the interactions, the
inter-electronic effects responsible for the breakdown of LS coupling within each atom are now manifested spatially in the collective state of the spin chain. Moving from $a = 2 \ \mu m$ to $a = 1.3 \ \mu m$ would reduce the energy gap between the $|1\rangle$ and $|2\rangle$ states, making it similar in magnitude to the $F$ spin chain. The triplet $\mu s$ much longer than the time scales of the dynamics of the states are 2 $\mu s$.

The natural lifetimes of the 30 $D_2$ states, which we obtain using MQDT, is the finite lifetime of the Rydberg states concerned, which we show to mostly be the case for very high values of the quantum numbers (as defined in the main text) for the spin chain with $a = 2.0 \ \mu m$. (b) Spin chain for $t = 0 \ ns$. (c) Spin chain without the microwave field, at $t = 62 \ ns$. (d) Spin chain with the microwave field, also at $t = 62 \ ns$.

FIG. 4. (color online) (a) Energy of the $|1000\rangle$ state (solid lines) and the $|1120\rangle$ state (dashed lines) for a spin chain of four atoms equally separated by a distance $a$ from their nearest neighbours. Black lines: results with the microwave field acting, giving a light shift of 165 MHz. Red lines: results without a microwave field. Sub-figures (b) to (d) show the average values of the quantum numbers (as defined in the main text) for the spin chain with $a = 2.0 \ \mu m$. (b) Spin chain for $t = 0 \ ns$. (c) Spin chain without the microwave field, at $t = 62 \ ns$. (d) Spin chain with the microwave field, also at $t = 62 \ ns$.

We turn to the feasibility of observing this effect in a lattice of ultra-cold strontium atoms. The first issue that must be considered is the finite lifetime of the Rydberg states concerned, which we obtain using MQDT. The natural lifetimes of the 30 $D_2$ and 28 $F_3$ states are 2.3 $\mu s$ and 6.9 $\mu s$ respectively [21, 39], which are much longer than the time scales of the dynamics of the spin chain. The triplet $F$ state lifetimes are unknown, but can be expected to be similar in magnitude to the 30 $D_2$ and 28 $F_3$ states. The required lattice spacings are larger than the state-of-the-art Rydberg lattices that have already been demonstrated [40, 41], making the preparation of these spin chains feasible with current technology. In order to image the dynamics, short microwave pulses could be used to state-selectively transfer the population to other Rydberg states that do not interact resonantly, thus “freezing” the dynamics. Spatial resolution could then be obtained by using spatially and spectrascopically resolved fluorescence detection.

In conclusion, we have shown that intercombination transitions in Sr Rydberg atoms not only lead to a breakdown of LS coupling but also allow dipole-forbidden excitation hopping along a chain of atoms via resonant long-range dipole-dipole interactions. Until now, these $S$-changing transitions have been considered negligible, which we show to mostly be the case for very high values of the principal quantum number $n$. Even at high $n$, though, we find that intercombination Förster resonances can have a substantial impact on the long-range interactions. The intercombination Förster resonance also gives rise to a collective breakdown of LS coupling in a spin chain, leading to spatially separated dynamics between the average spin and total angular momentum quantum numbers. Although we use Sr Rydberg states as an example, we expect that other systems with singlet-triplet mixing may show similar effects.
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