Switching exciton pulses through conical intersections

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Exciton pulses transport excitation and entanglement adiabatically through Rydberg aggregates, assemblies of highly excited light atoms, which are set into directed motion by resonant dipole-dipole interaction. Here, we demonstrate the coherent splitting of such pulses as well as the spatial segregation of electronic excitation and atomic motion. Both mechanisms exploit local non-adiabatic effects at a conical intersection, turning them from a decoherence source into an asset. The intersection provides a sensitive knob controlling the propagation direction and coherence properties of exciton pulses.

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Introduction: Frenkel Excitons [1], in which excitation energy of an interacting quantum system is coherently shared among several constituents, are a fundamental ingredient of photosynthetic light harvesting [2]. Recently, they have become accessible in ultracold Rydberg gases, due to strong long-range dipole-dipole interactions [3–7] and large lifetimes of atomic Rydberg states [8, 9]. Assemblies of several regularly placed and Rydberg excited cold atoms – flexible Rydberg aggregates – provide insight into new concepts such as adiabatic guiding of an exciton through atomic chains as an exciton pulse [10–12]. Such a pulse is initiated by a displacement of one atom in the regular chain. The displacement simultaneously localizes the exciton on the atom pair with the smallest separation and initiates the pulse, i.e., the motion of the exciton. Subsequent binary collisions propagate the exciton pulse and the associated entanglement through the chain.

That this propagation along a chain of atoms preserves the exciton with high fidelity [11] is remarkable, since the transport appears quite fragile requiring a lossless locking in of electronic excitation transfer and atomic motion. For this reason it is a priori unclear if one can guide and control the exciton pulse along other atomic arrangements but the linear chain. Any two-dimensional setup of atoms will eventually lead to the formation of a conical intersection [13] which might compromise adiabaticity known to be an important prerequisite of exciton transport.

In the following, we will show how an exciton pulse can be coherently split through a conical intersection (CI) [13, 14] that arises between two excitonic Born-Oppenheimer (BO) surfaces of the system. The junction between two atomic chains that gives rise to the conical intersection can be functionalized in two ways, as a beamsplitter or a switch, sending the pulse split in both directions on the second chain or in only the one preselected.

T-shaped aggregates: The junction is created with two chains of Rydberg atoms in a T-shape configuration (FIG. 1a), with the required one-dimensional (1D) confinement generated optically [15, 16]. Specifically, we will use 2N Rydberg atoms with mass \( M = 11000 \) a.u. and principal quantum number \( \nu = 44 \). We assume that \( N \) of these atoms are constrained on the \( x \)-axis, and the other \( N \) on the \( y \)-axis, such that all atoms can only move freely in one dimension. We start with one Rydberg atom in

\[ \text{FIG. 1: (color online) (a) Orthogonal atom chains with one Rydberg dimer each and (b-d) energy surfaces as well as exciton states of the trimer sub-unit. Atoms 0 and 1 initially share an excitation, due to which atom 1 reaches the conical intersection \( x_{\text{CI}} \). (b) The repulsive surface \( U_{\text{rep}} \) (red) and middle surface \( U_{\text{mid}} \) (green) of the trimer sub-unit (atom 1, 2 and 3) near the CI. (c,d) Forces on atom 2 (solid lines) and atom 3 (dashed lines), for the repulsive surface (red,c) and middle surface (green,d). The insets show atomic positions, excitation distribution \( d_n \), see text) and forces for the indicated values of \( x \).
\]
an angular momentum p-state, while the rest are in s-states. For such scenarios, the electronic wavefunction $|\psi_{el}(R)\rangle$ of the whole system can be expanded in the single excitation basis $|\psi_{el}(R)\rangle = \sum_{n=1}^{2N} c_n(t)|\pi_n\rangle$, where $|\pi_n\rangle = |s...p...s\rangle$ is the state with the k-th atom in the p-state $^{10,12}$. The full dynamics is ruled by the Hamiltonian

$$\hat{H} = \sum_{n,m=1}^{2N} \left( -\frac{\delta_{nm}\hbar^2}{2M} \nabla^2_{R_n} + \hat{V}_{dd}(R_{mn}) + \hat{V}_{vdW}(R_{mn}) \right),$$

where $R_{mn} = |R_m - R_n|$, the distance between atoms $m$ and $n$.

The long-range Rydberg-Rydberg interactions $^8$ are described with two explicit contributions $V_{dd}$ and $V_{vdW}$, a resonant dipole-dipole and a van-der-Waals term, respectively. $V_{dd}$ couples excitations $|\pi_n\rangle$ on different atoms $n$ through

$$\hat{V}_{dd}(R_{mn}) = -\frac{\mu^2(1 - \delta_{nm})}{R_{mn}^3}|\pi_m\rangle\langle\pi_n|,$$

where $\mu = d_{p,1;x,0}/\sqrt{5}$ is the scaled radial matrix element and $R = (R_1,...,R_n)^T$ groups all atomic coordinates. We sketch in $^17$ how this isotropic interaction can be realized using a magnetic field and selected total angular momentum states. The non-resonant Van-der-Waals interaction

$$\hat{V}_{vdW}(R_{mn}) = -\frac{C_6}{2R_{mn}^6}I,$$

ensures for $C_6 < 0$ repulsive behavior at very short distances regardless of the electronic state. Therefore, $I$ denotes a unit matrix in the electronic space. As previously shown $^{10,13}$, the joint motional and quantum state dynamics can be well understood from the eigenstates $|\phi_n(R)\rangle$ of the electronic Hamiltonian $\hat{H}_{el}(R) = \sum_{n,m}[V_{dd} + V_{vdW}]$. These eigenstates and the corresponding eigenenergies $U_k(R)$ depend parametrically on $R$ and are referred to as Frenkel excitons $^1$ and Born-Oppenheimer surfaces (BO surfaces), respectively. The total wavefunction including atomic motion can be written as $|\Psi(R)\rangle = \sum_n \phi_n(R)|\pi_n(R)\rangle$. To solve the coupled electronic and motional dynamics, we employ Tully’s fewest switching algorithm $^{17,20}$, a quantum-classical method that is well established for our type of problem $^{11,12}$.

Two perpendicular dimers: To realize a T-shape chain, a minimum of two dimers is required, see FIG. 1a. The atoms have a Gaussian distribution about their initial location $R_0$, with width $\sigma_x$, arising from initial confinement in micro-traps or optical lattice sites. The bars in FIG. 1a visualize the excitation amplitude of the exciton on the repulsive BO surface $|\phi_{rep}(R_0)\rangle$. For each atom the length of the bar shows $d_n = (\langle \pi_n | \phi_{rep}(R_0) \rangle)$, red for positive and blue for negative values. As one can see, initially the single p-excitation in the system is shared among atom 0 and 1. On the BO-surface $k$, the force on atom $n$ is given by $F_{nk} = -\nabla_{R_n} U_k(R)$. Due to the initial repulsive force $F_{n,rep}$ (blue arrows) atom 1 moves and eventually reaches the position $x_{CI}$, where the atoms 1-3 form a planar trimer. The two highest BO surfaces of this trimer conically intersect when the three atoms form an equilateral triangle, as shown in FIG. 1b and studied in detail in $^{13}$. In the following we will call these surfaces the repulsive (red) and middle (green) surface, respectively.

Exciton splitting: Initialized on the repulsive surface of the global (double dimer) system, the exciton pulse is transferred to the vertical chain via the conical intersection onto these two electronic surfaces – the repulsive and the middle one – dependent on the position of atom 1 relative to atom 2 and 3 in the y-direction when it enters the trimer configuration (see parameter $p$ in FIG. 1b). Viewed from the perspective of the trimer subsystem only, the exciton pulse enters on the middle surface, where the excitation amplitude (blue bar) matches the initial excitation distribution, see insets of FIG. 1c,d. If atom 1 arrives right in the middle between atoms 2 and 3, the atomic trimer passes through the degenerate point of the CI leading to significant transfer of exciton amplitude to the repulsive surface (FIG. 1d). If this is not the case, an asymmetric trimer configuration is realized for which non-adiabatic transitions due to the CI are much weaker and the system remains on the middle trimer surface leading to the situation of FIG. 1d with quite different forces on atom 2 and 3. This has profound consequences on the atomic motion: Amplitude on the repulsive surface leads to a symmetric repulsion of atoms 2 and 3 of the vertical chain, creating the outer pulses in the density shown in FIG. 2a. A representative quantum-classical trajectory is shown as white dotted line, with $p = 0.98$. On the other hand, amplitude on the middle surface has the effect of a very asymmetric atomic motion in $y$, with that atom on the y-axis remaining almost at rest which has initially the smaller distance to the location of the dimer on the x-axis. This type of motion is responsible for the inner and central features in FIG. 2b, with a representative trajectory shown white dashed with $p = 0.82$. One can also recognize the variant of the motion, where the other vertical atom remains at rest.

Since the nuclear wave packet of the exciton pulse will have a distribution of positions of atoms 1, 2 and 3, there will be in general a splitting of the exciton when it has passed the conical intersection with the electronic excitation propagating on the repulsive as well as the middle surface. In fact, about 50% of the initial amplitude has been transferred from the middle to the repulsive surface after 3\textmu s under the initial conditions for our exciton pulse leading to the dynamics of FIG. 2a.
Hence, not only does the exciton split into two parts traveling with the atoms in opposite directions in the y-chain, we have a further coherent splitting of electronic excitation into the middle and repulsive electronic surface: The total initial wave function was \( |\Psi_{\text{ini}}(R)\rangle = \phi_0(R)|\varphi_{\text{rep}}(R)\rangle \), where \( \phi_0(R) \) describes the initial, harmonically trapped, spatial ground state. After the evolution shown in FIG. 2, the wave function reads \( |\Psi_{\text{fin}}(R)\rangle = \phi_{\text{rep}}(R)|\varphi_{\text{rep}}(R)\rangle + \phi_{\text{mid}}(R)|\varphi_{\text{mid}}(R)\rangle \).

This final state \( |\Psi_{\text{fin}}(R)\rangle \) entangles the atomic configuration and its electronic state which can be quantified through the purity of the reduced electronic density matrix. It is obtained by averaging over the atomic position as described in [11, 12, 17]. The purity drops from one to 1/2 when the exciton is split, as shown in FIG. 2, reflecting a transition from a pure to a mixed state. For the total (pure) system state, this implies a transition from a separable to an entangled state.

**Exciton switch:** The minimal T-shape system consisting of two dimers discussed so far primarily serves the purpose to elucidate the central element for exciton pulse control, namely the junction between perpendicular atomic chains. Ultimately, we would like to interface the two dimers in FIG. 1 with longer atomic chains that can support exciton pulses as described in [11]. Such a pulse travels to the junction to become coherently split as just described, with the resulting exciton pulses on the vertical chain depending on how the conical intersection of the trimer at the junction was passed. Since the relative strength of the exciton pulse on the middle and repulsive surface of the trimer depends on the atomic positions and momenta near the conical intersection, we can control the exciton pulse propagation on the vertical chain, for example via the position of the horizontal chain relative to the vertical one. We demonstrate this effect with \( N = 4 \) atoms per chain, allowing for a vertical offset \( \Delta y \) of the horizontal chain from the center of the vertical chain, and a variable separation \( a_2 \) of the two central atoms in the second chain, see sketch in FIG. 3.

With small variations of the two control parameters \( \Delta y, a_2 \), qualitatively very different scenarios can be realized as illustrated in FIG. 3 and quantified in FIG. 4. In scenario (a), the spacing \( a_2 \) is so large that the trimer subunit discussed before does not form [22]. Since atom 3 approaches 5 closest (see FIG. 4), the exciton-pulse travels in the downwards direction. To switch it upwards we would use \( \Delta y \to -\Delta y \). We characterize the relevant entanglement transport using \( E_{ij} \), the bi-partite entanglement \([11, 12, 17]\) during the last collision of the two terminal atoms \( i, j \) on the vertical chain, i.e., \( (i, j) = (6, 7) \) upwards and \( (i, j) = (4, 5) \) downwards. The last collision happens, whenever atom 4 (atom 7) reaches position \( r_{\text{coll}} \), indicated in FIG. 3 by horizontal white lines for the downwards (upwards) direction. Our results in FIG. 4 reveal that entanglement was transported only downwards with high fidelity, demonstrating successful control of the direction of exciton-pulse propagation without loosing coherence.

In scenario (b) we segregate mechanical and electronic degrees of freedom of the exciton-pulse, by choosing \( a_2 \) small enough such that a trimer subunit forms at the junction. Since an offset \( \Delta y \) is kept, the nuclear wave packet, however, misses the conical intersection and remains on the middle trimer surface. As discussed before,
the excitation and momentum then reside on the vertical atom farther away from the horizontal chain, hence the relationship between offset \( \Delta y \) and pulse propagation direction is reversed compared to scenario (a). More importantly, the middle trimer surface does not connect to a global surface allowing coherent exciton pulse transport: At the first collision within the vertical chain (between atoms 4 and 5 in FIG. 3), the excitation evades those atoms and delocalizes on the remnant lower chain. Momentum is henceforth transported upwards by vander-Waals collisions only such that the original exciton pulse with entangled atom and electron dynamics has been ripped apart.

Finally, in scenario (c) \( \Delta y = 0 \) and the wave packet fully traverses the conical intersection at the junction. Here, the trimer subunit operates as described in the first part of the article. The wave packet is split onto both, the repulsive and middle trimer surface. As discussed for scenario (b), the middle trimer surface does not give rise to exciton-pulse propagation. On the repulsive surface, one gets symmetric (up-down) propagation of two pulses as expected. However, the entanglement transport in both directions is much weaker than in scenario (a) which is due to the fact that the atoms still share only a single p-excitation. Subsequent non-adiabatic effects allow a strong coherent pulse only in a single direction. Even within this symmetric scenario, the relative importance of the middle and repulsive surface can be tuned via the effective size of the conical intersection \[23\], determined by atomic velocities and separation (energy splittings).

![FIG. 4: Geometry and entanglement switching for the three scenarios of FIG. 3. Atom numbering and control parameters \( \Delta y \) are defined in the sketch on the left. Entanglement \( E_{ij} \) is defined in 17.](image)

**Conclusions:** We have seen how an exciton pulse can be coherently split through non-adiabatic dynamics at a conical intersection in a flexible Rydberg aggregate. Our results turn a junction between two Rydberg atom chains into a switch. The switch can control if and how exciton pulses continue to propagate in the system. Similar physics may be of interest for research on artificial light harvesting systems \[24\], where exciton transport and control is quintessential for energy efficiency. The atomic junction introduced here also provides a tool to directly examine the many-body dynamics near conical intersections in the laboratory.

The exciton splitting predicted could be experimentally monitored using high resolution Rydberg atom detection schemes \[25\] which are in addition state selective. Applied to our system, they allow a direct visualisation of many-body wave packet dynamics near a conical intersection. The essential modular subunit of an atomic trimer exhibiting a CI can be envisaged as a building block for networks of exciton carrying atomic chains or a device for controlling the energy flow in molecular aggregates.

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**Supplemental material: Exciton splitting through conical intersections:**

This supplemental material provides additional details regarding the employed quantum-classical algorithm, the Rydberg trimer subunit, our purity and entanglement measure and the realisation of isotropic dipole-dipole interactions.

**Propagation:** For larger number of atoms, solving the time dependent Schrödinger equation for our problem is not feasible in a reasonable time. However a quantum-classical propagation method, Tully’s fewest switching algorithm \[18–20\], gives results in good agreement with the full propagation of the Schrödinger equation \[11, 12, 21\]. In Tully’s fewest switching algorithm the positions of the atoms \( \mathbf{R} \) are treated classically while their electronic state is described quantum mechanically. To retain further quantum properties two features are added. First, the atoms are randomly placed according to the Wigner distribution of the initial nuclear wavefunction and also receive a corresponding random initial velocity. In the end of the simulation, all observables have to be averaged over the whole set of realizations. Second, non-adiabatic processes are added as follows: During the propagation of a single realization, the mechanical potential felt by the atoms corresponds to a single eigenenergy of the electronic Hamiltonian. During adiabatic processes the system remains on a single energy surface during the propagation. Tully’s algorithm allows for jumps to other energy surfaces during the propagation. The probability for a jump from surface \( n \) to surface \( m \), is proportional to the non-adiabatic coupling vector

\[
\mathbf{d}_{mn}(\mathbf{R}) = \langle \varphi_m(\mathbf{R}) | \nabla_{\mathbf{R}} | \varphi_n(\mathbf{R}) \rangle.
\]

The sequence of propagation is as follows: The positions and velocities of the atoms are randomly determined. The electronic Hamiltonian is diagonalized and we use one eigenenergy \( U_k \) of our choice as potential for the atoms. The atoms are propagated one time step via Newton’s equation

\[
M \ddot{\mathbf{R}} = -\nabla_{\mathbf{R}} U_k(\mathbf{R}).
\]

The new positions lead to new eigenstates and -energies and to new diabatic and adiabatic coefficients. We prop-
agate the diabatic coefficients via

$$i\hbar \dot{c}_k(t) = -\mu^2 \sum_{l \neq k}^{2N} \frac{c_l(t)}{|R_k - R_l|^3}$$

(6)

To close the loop, the nuclei will be propagated via \[5\] again.

We imagine the atoms were confined in individual harmonic traps, before these are released to let all atoms move. This motivates Gaussian probability distributions of the atomic positions and momenta. We label the standard deviation in position of atoms on chain \(i\) by \(\sigma_{\chi_i}\). The velocity probability distribution then has a standard deviation in position of atoms on chain \(i\) as

$$\sigma_{\chi_i} = \hbar/\langle M\sigma_{\chi_i} \rangle.$$  

The trimer: “Trimer” refers to an assembly of three Rydberg atoms. Since main features of the systems we studied can be understood by considering only three atoms, we provide here full details in addition to the features discussed in the main text. The configurations of the trimer which are most relevant here are shown in FIG. 5. We call the overall length scale \(u\). The geometry of the trimer around the equilateral triangle configuration is described by the distance \(x\) between atom 1 and the other two atoms and the parameter

$$p := \frac{2}{l} \left| \langle \mathbf{R}_2, \mathbf{e}_y \rangle \right| \frac{|\mathbf{R}_2 - \mathbf{R}_3|}{},$$

(7)

which we call the asymmetry parameter, since it controls the degree of symmetry with respect to the isosceles triangle. The biggest and smallest eigenenergies are globally repulsive or attractive, respectively \[10, 13\]. We label them \(U_{\text{rep}}\) and \(U_{\text{att}}\) and the corresponding eigenstates \(|\varphi_{\text{rep}}\rangle\) and \(|\varphi_{\text{att}}\rangle\). We call these repulsive and attractive surface and eigenstate, respectively. There is another eigenenergy energetically between them. We label it \(U_{\text{mid}}\) and the corresponding eigenstates \(|\varphi_{\text{mid}}\rangle\). We call it middle surface and eigenstate.

Symmetric case \(p = 1\). The middle and repulsive eigenenergies have the value \(\mu^2 u^{-3}\), when they cross. This happens, when \(x = x_{C1} := \sqrt{3}/2 u\), i.e. at the equilateral triangle configuration. It is well known that this is a conical intersection \[13, 28, 29\]. FIG. 6 (a) shows the eigenenergies as a function of the horizontal distance \(x\). The middle eigenenergy stays constant for \(x < x_{C1}\) as it arises solely from the interaction energy of atom 2 and 3. When atom 1 is far away from the other two, the middle and attractive energies are vanishing, whereas when the system realizes a linear trimer \((x = 0)\), the repulsive and attractive energy values are extremal.

Asymmetric case \(p \neq 1\). There is no crossing of eigenvalues for \(p \neq 1\). FIG. 6 (b) shows the energy separation between the repulsive and the middle state over the horizontal distance \(x\) of the atoms for different asymmetry parameters \(p\). With increasing asymmetry, the smallest energy splitting increases, as does the value of \(x\) where the splitting is smallest. From now on we call atomic configurations asymmetric, when they correspond to values of \(p \ll 1\) and symmetric, when \(p \approx 1\).

![FIG. 5: Sketch of a trimer near a configuration with CI. Atom 1 is confined on a horizontal line and atom 2 and 3 on a vertical line. The parameter \(p\) adjusts the distance of atom 2 and 3 from the horizontal line and for \(p \neq 1\) results in nonequilateral triangle configurations. All distances are expressed in units of \(u\), the distance between atom 2 and 3.](image)

![FIG. 6: Eigenenergy spectra for the trimer. (a) Eigenenergies over horizontal distance \(x\) for the symmetric case \(p = 1\). The repulsive (blue line) and middle eigenenergy (green line) cross at \(x = \sqrt{3}/2 u\). (b) Energy spacing between repulsive and middle eigenenergy for different asymmetry parameters, \(p = 1\) (solid), \(p = 0.88\) (dashed), \(p = 0.76\) (dashed dotted). The minimal energy spacing (black dots) is shifted to bigger \(x\) for higher asymmetry, which is well described by the analytical result Eq. (12) (grey line).](image)
ton of the Configuration shown in FIG. 5 is given by
\[
\hat{H}_{el}(\chi) = -\mu^2 \begin{bmatrix}
0 & s_1^{-3}(\chi) & s_2^{-3}(\chi) \\
s_1^{-3}(\chi) & 0 & s_1^{-3}(\chi) \\
s_2^{-3}(\chi) & s_1^{-3}(\chi) & 0
\end{bmatrix}.
\] (8)

We use degenerate perturbation theory to estimate the energy gap near the CI. To do so we first Taylor expand the electronic Hamiltonian around the CI configuration up to second order in \(\chi\):
\[
\hat{H}_{el}^{\text{2nd}}(\chi) \approx \hat{H}_{el}^{\text{CI}} + \hat{H}_{el}^{\text{PT}}(\chi),
\] (9)
where \(\hat{H}_{el}^{\text{CI}}\) is the electronic Hamiltonian at the CI configuration and \(\hat{H}_{el}^{\text{PT}}(\chi)\) is the perturbation. We define the perturbation matrix
\[
S_{el}(\chi)_{\alpha\beta} := \langle \varphi_{\alpha}^{(0)} | \hat{H}_{el}^{\text{PT}}(\chi) | \varphi_{\beta}^{(0)} \rangle.
\] (10)
The eigenenergies \(E_1^{(1)}(\chi), E_2^{(1)}(\chi)\) of \(S_{el}(\chi)\) are the first order corrections to the energy and lift the degeneracy. Thus the energy gap is given by \(\Delta E_{\text{el}}(\chi) = |E_1^{(1)}(\chi) - E_2^{(1)}(\chi)|\) to first order. Consistently expanding this expression to second order around \(\chi_0\), we get
\[
\Delta E_{\text{el}}^{\text{2nd}}(\chi) \approx \sqrt{12 \Delta x^2 + (1 - p)^2 \left(3 - \frac{31\sqrt{3} \Delta x}{2} + \frac{1061 \Delta x^2}{8}\right)}
\] (11)
for \(p \lesssim 1\). The asymmetry of the configuration is measured by \(1 - p\). For every small given asymmetry, there is a \(\Delta x_{\text{min}}\) where the energy gap becomes minimal:
\[
\Delta x_{\text{min}} \approx 1.12 \cdot (1 - p)^2
\] (12)
\[
\Delta E_{\text{el}}^{\text{2nd}}(p) \approx \sqrt{3} \cdot (1 - p)
\]
Thus the horizontal distance between atom 1 and the other atoms has to be bigger compared to the CI configuration, to achieve a minimal energy gap as evident in FIG. 6.

**Entanglement measure:** As described in more detail, the quantum mechanical electronic density matrix \(\hat{\sigma} = \sum_{n,m} \sigma_{nm} |\pi_n\rangle \langle \pi_m|\) is represented by
\[
\sigma_{nm} = c_n^* c_m,
\] (13)
in a quantum-classical framework, where \(\sum\) denotes the trajectory average. The purity \(P = \text{Tr}[\hat{\sigma}^2]\) quantifies to which extent the reduced electronic state is mixed \((P = 0)\) or pure \((P = 1)\).

We can further obtain a reduced density matrix for just two atoms
\[
\hat{\beta}_{ab} = \text{Tr}_{(a,b)} [\hat{\sigma}].
\] (14)
by performing the trace \(\text{Tr}_{(a,b)} [\cdots]\) over the electronic states for all atoms other than \(a, b\). For a single p-excitation in the system, this takes the form
\[
\hat{\beta}_{ab} = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & \sigma_{aa} & \sigma_{ba} & 0 \\
0 & \sigma_{ab}^* & \sigma_{aa} & 0 \\
0 & 0 & 0 & \sum_{c \notin \{a,b\}} \sigma_{cc}
\end{pmatrix}.
\] (15)
The density matrix \(\hat{\beta}_{ab}\) may describe mixed versions of entangled states, the entanglement of which is often quantified using \(E_{ab}\), the “entanglement of formation” [30][31]. It is obtained through the concurrence \(C_{ab} = 2|\sigma_{ab}|\), with the further definitions \(H(x) = -[x \log_2 x + (1 - x) \log_2 (1 - x)]\) and \(E(x) = H(1/2 + \sqrt{1 - x^2})/2\) as \(E_{ab} = E(C_{ab})\).

Fig. 4 of the main article then shows the bi-partite entanglement of formation for the two last atoms on the vertical chain, in the respective direction as indicated.

**Isotropic dipole-dipole interactions:** In all simulations we used a single excitation basis and assumed the dipole-dipole interaction to be isotropic, only dependent on the internuclear distance between two atoms, which we denote here with \(r\). If spin-orbit interaction is neglected, this situation is achieved by choosing the quantization axis \(\hat{z}\) perpendicular to our internuclear distance vectors and considering the magnetic quantum number \(m = 0\) manifold, which decouples from the others [12].

For the simulations of Fig. 2 the principal quantum number was \(\nu = 44\), which yields a finestructure-splitting of \(\Delta E_{FS} = 7.7\) MHz. The energy splitting due to dipole-dipole interactions is \(\Delta E_{dd} = 243.8\) MHz.

Nevertheless there are two reasons why we can not neglect the spin-orbit interaction. First to neglect spin-orbit interaction also during Rydberg excitation of the atoms, Rabi-frequencies have to vastly exceed \(\Delta E_{FS}\), which is technically challenging. And second, even if we could neglect spin-orbit interaction during excitation, we obtain an isotropic dipole-dipole interaction with the opposite sign than used in the main article [12].

In the following, we illustrate how it is nevertheless possible to obtain a simple state space and interaction as employed in the main article by applying an external magnetic field.

Including spin, we denote the two different \(l = 0\) states with \(|s_{m_s}\rangle\) and the \(l = 1\) states with \(|p_{j,m_j}\rangle\). The subscripts of the \(|s\rangle\) states label the spin magnetic quantum number \(m_s\) and for the \(p\) states, the total angular momentum quantum number \(j\) and its projection on the quantization axis \(m_j\) are indicated.

We then diagonalize the combined Hamiltonian \(\hat{H}_{dd+B}\), which consists of the dipole-dipole interaction \(\hat{V}\) and the paramagnetic Zeeman term, in the spin-orbit basis \(\{|s_{m_s}p_{j,m_j}\rangle, |p_{j,m_j,s_{m_s}}\rangle\}\) with \(m_s \in \{-1/2, 3/2\}, j \in \{1, 1/2, 3/2\}, m_j \in \{-j, -j + 1, \ldots, j - 1, j\}\). We assume intermediate magnetic field strengths, such that we can neglect the diamagnetic contribution of the magnetic field. The combined Hamiltonian reads:
\[
\hat{H}_{dd+B} := -\mu_B \hat{B}_z \sum_{k=1}^2 \left(j_z^{(k)} + \hat{S}_z^{(k)}\right).
\] (16)

The matrix elements of the dipole-dipole interaction in the spin-orbit basis can be expressed through the spinless
basis as
\[
\langle s_m, P_{j_2, m_2} | V | p_{j_1', m_1'} s'_m \rangle = \sum_{m_{j_2}, m_{j_1}' = -1}^{1} C_{p}^{j_2}(m_{j_2} m'_{m_2} | j_2 m_2) C_{p}^{j_1'}(m_{j_1}' m_1' | j_1 m_1') \times \langle s p m_{j_2} | V | p m_{j_1}' s' \rangle,
\]
(17)
where \( C_{p}^{j}(m_j m_j' | j m) \) denotes the Clebsch-Gordan coefficient. The magnetic field adds the following elements to the interaction matrix:
\[
\langle s_m, P_{j_1, m_1} | \sum_{k=1}^{2} (\hat{J}_{z}^{(k)} + \hat{S}_{z}^{(k)}) | s_m, P_{j_2, m_2} \rangle = \begin{cases} 2m_s + g_{p}^0 m_j & : j_1 = j_2 \\ -\frac{1}{2} \sqrt{\frac{3}{4} - m_{j}^2} & : j_1 \neq j_2, \end{cases}
\]
(18)
where \( g_{p}^0 \) denotes the Landé-factor of the p states. For a principal quantum number \( \nu = 44 \) and a field strength of 200 G, we find a subspace spanned by \( | s_{1}; p_{3/2, 3/2} \rangle \) and \( | p_{3/2, 3/2, 1} \rangle \), that decouples from all other states with a probability of 80.6\%. The magnetic field shifts both states about \( \Delta E_B = 1027.4 \text{ MHz} \). Shifting the zero point energy to \( E_{p_{3/2}} + E_{s_{1/2}} + 3\mu_B B_z \), we end up with the effective Hamiltonian
\[
\hat{H}_{\text{eff}} = \left(-\frac{d_{44,1:44,0}^2}{6R^5} - \frac{d_{44,1:44,0}^2}{6R^5} \right),
\]
(19)
where \( d_{44,1:44,0} = 1732 \text{ au} \) is the radial dipole matrix element between an s and p state for \( \nu = 44 \). This yields the parameter \( \mu = d_{44,1:44,0}/\sqrt{6} \), quoted in the main text.

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