Quantum mechanical calculation of Rydberg–Rydberg autoionization rates

Martin Kiffner1,2,5, Davide Ceresoli3, Wenhui Li1,4 and Dieter Jaksch2,1

1 Centre for Quantum Technologies, National University of Singapore, 3 Science Drive 2, 117543 Singapore
2 Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, UK
3 Istituto di Scienze e Tecnologie Molecolari CNR, via Golgi 19, 20133 Milano, Italy
4 Department of Physics, National University of Singapore, 117542, Singapore

E-mail: martin.kiffner@physics.ox.ac.uk

Received 6 May 2016, revised 23 June 2016
Accepted for publication 1 July 2016
Published 6 October 2016

Abstract
We present quantum mechanical calculations of autoionization rates for two rubidium Rydberg atoms with weakly overlapping electron clouds. We neglect exchange effects and consider tensor products of independent atom states forming an approximate basis of the two-electron state space. We consider large sets of two-atom states with randomly chosen quantum numbers and find that the charge overlap between the two Rydberg electrons allows one to characterise the magnitude of the autoionization rates. If the electron clouds overlap by more than one percent, the autoionization rates increase approximately exponentially with the charge overlap. This finding is independent of the energy of the initial state.

Keywords: Rydberg atoms, auger decay, interatomic Coulombic decay, autoionization

1. Introduction

Exciting ultracold atoms to Rydberg states [1] with large principal quantum number \( n \) furnishes the atoms with extremely exaggerated properties. For example, the size, interaction strength and polarizability increases by several orders of magnitude as compared to ground state atoms. This feature allows one to study fundamental physical phenomena on completely new time and length scales and magnifies physical effects such that they become experimentally accessible. For example, dipole–dipole interactions between ground state atoms are typically weak, but they are strong and long-ranged between Rydberg atoms such that \( \mu \text{m} \)-sized molecules consisting of two [2–9] and three [10–12] atoms become possible. Moreover, dipole–dipole interactions between Rydberg atoms give rise to the blockade effect [13, 14] and crystals of spatially ordered Rydberg excitations that were experimentally observed in [15]. The modification of the quantum dynamics of Rydberg electrons due to their dipole–dipole interaction has been demonstrated in a recent experiment by Takei et al [16] via ultrafast pump-probe laser techniques.

In systems of dipole–dipole interacting Rydberg atoms the interatomic spacing is typically large compared to the size of the Rydberg electron orbital. A fascinating prospect for future studies is the investigation of Rydberg systems with overlapping electron clouds. In this regime the exaggerated properties of Rydberg atoms would allow one to study the rich physics of electron–electron interactions on much more accessible time and length scales compared to conventional solid state systems. More specifically, the size of the valence electron orbital increases like \( R_0 = 4n^2a_0 \) where \( a_0 \) is the Bohr radius and will thus reach the typical separation between atoms in optical lattices or tweezers for \( n \geq 35 \). Overlapping electron clouds could give rise to delocalized electrons and correlated quantum many-body states via the strong Coulomb interaction between the electrons. However, these coherent processes compete with autoionization and radiative decay processes enabled by the large number of empty orbitals below the Rydberg state.

The first step in investigating the regime of Rydberg atoms with overlapping electron clouds is to characterize the time scales of the occurring physical processes. While
with weakly overlapping electron clouds, we here present a simplified model and consider two-atom states $|\psi_M\rangle$ with weakly overlapping electron clouds as shown in figure 1. We assume that $|\psi_M\rangle$ is a tensor product of two generally different independent-atom orbitals and neglect exchange effects. In order to account for the fact that these states are not eigenstates of the system, we consider large sets of states $|\psi_M\rangle$ with different quantum numbers that could serve as an approximate basis of the true two-electron eigenstate. We evaluate the autoionization rate of the states $|\psi_M\rangle$ quantum mechanically and show that the charge overlap between the two atoms allows one to characterize the magnitude of the autoionization rates. In the regime of very small charge overlap between the Rydberg orbitals, the autoionization rates are small and depend on the energy of the initial state. Moreover, the full interaction Hamiltonian can be approximated by its multipole expansion. On the contrary, above a certain threshold the multipole expansion becomes invalid and the autoionization rates increase approximately exponentially with the charge overlap.

Note that the autoionization mechanism between two Rydberg atoms considered here is related to autoionization processes in crystals and clusters that have been termed interatomic auger decay [23] and more recently interatomic Coulombic decay (ICD) [24–27]. In particular, the strong enhancement of autoionization rates through the overlap between electron orbitals in clusters was reported in [25], and ICD processes between several excited atoms in a cluster were studied in [26, 27].

This paper is organized as follows. The system of interest and our model are described in section 2. We briefly outline the calculation of the autoionization rates in section 3 and defer more technical details to appendix. In order to account for many different initial states $|\psi_M\rangle$ we randomly select these states as described in section 4. Finally, the autoionization rates of the randomly selected states are presented in section 5 and a conclusion of our work is given in section 6.

2. The system

We consider two Rydberg atoms as shown in figure 1(a), where each atom is comprised of a singly-charged core and one valence electron. We assume that the atoms are so cold that their positions do not change during the decay process. Atom A is located at $R = R e_z$, where $e_z$ is the unit vector in $z$ direction and $R$ is the atomic separation. The total Hamiltonian of the two-atom system is $H = H_0 + V$, where $H_0 = H_0^{(A)} + H_0^{(B)}$ and $H_0^{(X)}$ is the Hamiltonian of Rydberg atom $X$. All interactions between atom A and atom B are described by

$$V = \frac{q^2}{4\pi\varepsilon_0} \left( \frac{1}{R} + \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} - \frac{1}{|\hat{\mathbf{r}}_2|} - \frac{1}{|R - \hat{\mathbf{r}}_1|} \right),$$

where $q$ is the elementary charge and $\hat{\mathbf{r}}_i$ the operator associated with the position of electron $i$. The first term in equation (1) accounts for the repulsion of the two ion cores, the second is the electron–electron interaction and the third (fourth) term describes the interaction of electron 2 (1) with ion core A (B). The eigenstates of $H_0$ are

$$|\psi_M\rangle = |\psi_A, \psi_B\rangle,$$

where $|\psi_A\rangle$ and $|\psi_B\rangle$ are independent-atom Rydberg wavefunctions centered at the origin and $R$, respectively

$$\psi_A(\mathbf{r}) = \psi_{n_A m_A}(\mathbf{r}), \quad \psi_B(\mathbf{r}) = \psi_{n_B m_B}(\mathbf{r} - R).$$
We ignore the fine structure such that the wavefunctions \( \psi_{nlm}(r) \) are characterized by the principal quantum number \( n \), the orbital angular momentum quantum number \( l \) and the azimuthal quantum number \( m \). We generate the functions \( \psi_{nlm} \) with energy \( E_{nl} = -1/[n - \delta_n(l)]^2 \) via the Numerov method, where \( \delta_n(l) \) is the quantum defect [1, 28]. We choose Rubidium 85 atoms which are a popular choice in recent Rydberg experiments and obtain the energies \( E_{nl} \) (and hence the quantum defects) for \( n \leq 11 \) from spectroscopic data reported in [29]. For \( n = 11 \), the non-zero quantum defects are \( \delta_{11}(0) = 3.134, \delta_{11}(1) = 2.652 \) and \( \delta_{11}(2) = 1.341 \) which is consistent with the quantum defects provided in [30]. We ignore the weak dependence of \( \delta_n(l) \) on the principal quantum number for \( n > 11 \). Note that we order the quantum numbers in \( |\psi_m \rangle \) such that \( E_{nl} > E_{n' m'} \) by convention since the state obtained by interchanging \( A \) and \( B \) has the same autoionization rate.

An example for \( |\psi_M \rangle \) is shown in figure 1(c), where the size of the electron cloud of atom \( A \) (\( B \)) is indicated by a sphere of radius \( R_A \) (\( R_B \)), where \( R_A \) (\( R_B \)) is the classical outer turning point

\[
R_A = n^2 + n^2 \alpha^2 - \ell (\ell + 1),
\]

\( n^* = [n - \delta_n(l)] \) is the effective quantum number and \( \alpha \in \{A, B\} \). In order to quantify the overlap between the wavefunctions \( |\psi_A \rangle \) and \( |\psi_B \rangle \), we consider the amount of charge due to \( |\psi_A \rangle \) inside the sphere \( V_B \) with radius \( R_B \) around atom \( B \)

\[
\delta q_A(V_B) = q \int_{V_B} |\psi_A|^2 d^3r.
\]

Similarly

\[
\delta q_B(V_A) = q \int_{V_A} |\psi_B|^2 d^3r
\]

is the amount of charge due to \( |\psi_B \rangle \) inside the sphere \( V_A \) with radius \( R_A \) around atom \( A \). A measure for the differential overlap between \( |\psi_A \rangle \) and \( |\psi_B \rangle \) is then given by \( \delta q/Q \), where \( Q = 2q \) is the total electron charge and

\[
\delta q = \delta q_A(V_B) + \delta q_B(V_A).
\]

In the following we will consider only states with small overlap such that \( \delta q/Q \ll 1 \).

Note that the physical wavefunction of the two-electron system should include spin degrees of freedom and be completely antisymmetric with respect to electron exchange. However, we find that the simplified state in equation (2) results in a good approximation of the autoionization rate for weakly overlapping electron clouds as explained in section 3.

### 3. Autoionization rates

Next we outline the calculation of the autoionization rate for state \( |\psi_M \rangle \) in equation (2). To this end, we consider the process shown in figure 1(b) where atom \( B \) makes a transition to a lower bound state \( |\psi_n \rangle \equiv |\psi_{nlm} \rangle (r - R) \) with energy \( E_B \equiv E_{nlm} \), and the other electron is ejected into the continuum. We model the wavefunction of the ejected electron with mass \( m_e \) by energy-normalized Coulomb waves \( |\psi_{Em} \rangle \) [31, 32] with angular momentum \( l \), magnetic quantum number \( m \) and energy \( E \) obeying the generalized normalization relation

\[
\langle \psi_{Em}|\psi_{Em} \rangle = (E - E') \delta_{ll'} \delta_{mm'}.
\]

The Coulomb waves are numerically generated by following the procedure described in [1]. We calculate the autoionization rate using Fermi’s golden rule [33] and to first order in the interaction \( V \). The decay rate \( \Gamma_M^b \) for the process shown in figure 1(b) is thus given by

\[
\Gamma_M^b = \frac{2\pi}{\hbar} \sum_{l=-\infty}^{l=\infty} \sum_{m=-l}^{m=l} |\langle \psi_{Em}|V|\psi_M \rangle|^2,
\]

where the energy \( E_B = E_M - E_0 \) of the Coulomb wave is fixed by energy conservation between the initial and final states and

\[
E_M = \langle \psi_M|H|\psi_M \rangle
\]

is the expectation value of the total Hamiltonian \( H \) in the initial state \( |\psi_M \rangle \). Note that \( E_M \) differs by at most 2% from the unperturbed value \( E_M|H|\psi_M \rangle = E_{nl} + E_{nl}\) for all states considered in section 4. This is consistent with the wavefunctions comprising the initial state being only weakly perturbed by the electron–electron interaction in the overlap region.

A more rigorous calculation with a fully antisymmetric initial state would result in two Coulomb matrix elements in equation (9) that are termed the direct and the exchange term [34]. The single matrix element in equation (9) corresponds to the direct term, and the exchange term is absent since our initial state \( |\psi_M \rangle \) in equation (2) is a simple product state. The exchange term depends on the overlap between the single-electron orbitals and decreases exponentially with increasing distance \( R \) [25]. Since we are considering only weakly overlapping electron clouds we expect that exchange effects are small and hence the expression in equation (9) should be a good approximation for the autoionization rate.

The decay rate \( \Gamma_M^b \) in equation (9) accounts for all processes where atom \( B \) makes a transition into the bound state \( |\psi_B \rangle \) and atom \( A \) is ionized. In addition, we consider also the autoionization process with rate \( \Gamma_M^b \) where atom \( A \) makes a transition to \( |\psi_A \rangle \) and atom \( B \) is ionized. The full decay rate is then obtained by adding \( \Gamma_M^b \) and \( \Gamma_M^b \) and summing over all bound states

\[
\Gamma_M = \sum_{M = 0}^{M = 0} \Gamma_M^b + \Gamma_M^b.
\]

We numerically evaluate equation (11) by restricting the sum over bound states to those with \( n_A + n_B \geq 0.5(n_A + n_B) \). This is justified since the contribution of lower-lying bound states is negligible. The evaluation of the matrix element in equation (11) is described in detail in appendix. In short, we expand all involved wavefunctions and the interaction Hamiltonian \( V \) in equation (1) in terms of spherical harmonics and limit the integration region to the volume where \( |\psi_{A,B} \rangle \) both take on non-negligible values. We restrict the maximum
angular momentum in the expansion of the wavefunctions to \( l = 1000 \), and all terms in the expansion of \( V \) leading to an exchange of angular momentum \( \Delta l > 15 \) between the electrons due to the Coulomb interaction are neglected. With these choices the numerical expense of calculating one value of \( \Gamma_M \) still takes up to 20 h on a 16 core Intel E5-2640v3 compute node. We estimate that the numerical uncertainty in \( \Gamma_M \) due to these approximations is approximately 10% for initial states with \( \delta q/Q > 10^{-4} \), while we achieve full convergence for states with \( \delta q/Q \leq 10^{-4} \).

### 4. Selection of random states

The two-atom states in equation (2) are independent-atom states and thus not eigenstates of the total Hamiltonian \( H \). For sufficiently small atomic separations \( R \), the interaction \( V \) couples many states \( |\psi_M\rangle \) with different quantum numbers \( a > 4 \). Typically contains several \( Q \) that form the set \( \mathcal{M}_i \), we choose one atomic separation \( R \) and denote this selection process each set \( \mathcal{M}_i \) and \( \mathcal{M}_j \) that do not obey equation (12) are disregarded. After this pre-selection process each set \( \mathcal{M}_i \) typically contains several hundred manifolds, and we randomly select 100 manifolds in \( \mathcal{M}_J \) that form the set \( \mathcal{S}_i \). Since the total magnetic quantum number is conserved by the interaction Hamiltonian \( V \), we confine our analysis to the \( M = 0 \) subspace and assign each \( n_{A1}n_{B1} \) manifold in \( \mathcal{S}_i \), a random magnetic quantum number \( m_A \) with \( m_B = -m_A \). The distribution of the chosen states with respect to the principal quantum numbers \( n_A \) and \( n_B \) is shown in figure 2 for all four sets. It follows that each set contains a broad distribution of principal quantum numbers where the variation in both \( n_A \) and \( n_B \) is larger than five.

### 5. Results and discussion

The results for the autoionization rate \( \Gamma_M \) of the randomly chosen states in all sets \( \mathcal{S}_J \) are shown in figure 3 as a function of the overlap \( \delta q/Q \), see equation (7). There are two qualitatively different regions I and II divided by the dashed line at \( \delta q/Q = 10^{-4} \). In region I the decay rates appear to be independent of the overlap. On the contrary, the decay rates increase sharply with \( \delta q/Q \) in region II. In order to understand the physical reason for these two regions we perform reference calculations where we replace the interaction Hamiltonian \( V \) by its multipole expansion \( V_{ME} \) [36] including dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions. We find that the autoionization rates calculated with \( V_{ME} \) differ by at most 10% from the values obtained with \( V \) for all states with \( \delta q/Q \leq 10^{-3} \). We thus conclude that the multipole expansion of the interaction Hamiltonian holds if the overlap between the Rydberg orbitals is less than \( 10^{-4} \). On the other hand, the results obtained by \( V_{ME} \) and \( V \) differ greatly in region II. While all autoionization rates obtained by \( V_{ME} \) are smaller than \( 3 \times 10^9 \) s\(^{-1} \), those calculated with \( V \) can be several orders of magnitude larger for \( \delta q/Q \geq 10^{-2} \). This dramatic increase in the

![Figure 2](image-url) Distribution of the principal quantum numbers \( n_A \) and \( n_B \) in the randomly chosen sets of states \( \mathcal{S}_J \). (a) Red squares correspond to set \( \mathcal{S}_1 \), (b) green squares show set \( \mathcal{S}_2 \), (c) blue triangles are for set \( \mathcal{S}_3 \), (d) black diamonds correspond to set \( \mathcal{S}_4 \).

![Figure 3](image-url) Log–log plot of the autoionization rates \( \Gamma_M \) of the randomly chosen states \( \mathcal{S}_J \) as a function of \( \delta q/Q \). Red dots correspond to \( \mathcal{S}_1 \), green squares show \( \mathcal{S}_2 \), blue triangles are for \( \mathcal{S}_3 \) and black diamonds correspond to \( \mathcal{S}_4 \). There are two regions I and II where the autoionization rates behave qualitatively different as a function of the overlap.
autoionization rates with the overlap is consistent with the findings in [25]. It can be explained physically by noting that the full interaction Hamiltonian $V$ allows for direct electron-electron interactions in the region where the charge densities overlap, whereas the leading term in $V_{\text{ME}}$ is the dipole–dipole interaction.

In the following we analyze the autoionization rates in regions I and II in more detail. First, we focus on region I and plot all autoionization rates $\Gamma_M$ with $\delta q/Q \lesssim 10^{-4}$ as a function of the energy $E_M$ of the initial state $|\psi_M\rangle$ as shown in figure 4(a). Within each set $S_i$, the autoionization rates show no evident energy dependence. The spread in $\Gamma_M$ is roughly the same for each set $S_i$ and spans about two orders of magnitude. However, the lower and upper bounds of each set $S_i$ depend on energy such that the mean decay rates $\langle \Gamma_M \rangle$ become gradually smaller by moving from set $S_1$ to $S_4$, where $\langle \Gamma_M \rangle$ is obtained by averaging over all decay rates $\Gamma_M$ in $S_i$ with $\delta q/Q \lesssim 10^{-4}$. This is illustrated by the dashed line in figure 4(a) interpolating the four mean decay rates $\langle \Gamma_M \rangle$,

$$\langle \Gamma_M \rangle = \kappa (|E_M|/\text{Ry})^\gamma,$$

where $\kappa = 2.51 \times 10^{12} \text{s}^{-1}$, $\gamma = 3.52$ and Ry is the Rydberg constant. The dominant contribution to the autoionization rate in the multipole regime is the dipole–dipole interaction term such that $\Gamma_M' \propto d_b^2 d_i^2 R^{-6}$ [19], where $d_b$ is the dipole matrix element between $|\psi_R\rangle$ and $|\psi_b\rangle$, and $d_i$ is the dipole matrix element between $|\psi_b\rangle$ and a Coulomb wave. The average principal quantum number $n$ of the involved Rydberg states increases from set $S_1$ to set $S_4$, and hence we expect the involved dipole matrix elements to increase on average with $n^2$ [37]. However, all states in a given set $S_i$ are evaluated at a given atomic separation $R$, (see section 4) with $R_i \approx R_A + R_B \propto n^2$ (see equation (12)). It follows that $\Gamma_M' \propto n^{-4}$, and hence we expect the full autoionization rate to decrease with increasing energy of the two-atom state. On the other hand, the large spread in $\Gamma_M$ within each set $S_i$ can be explained with the strong dependence of the transition dipole matrix elements on the quantum numbers of the initial and bound states.

Second, we analyze the steep increase of $\Gamma_M$ in region II. A log-linear plot of the autoionization rates $\Gamma_M$ in region II is shown in figure 4(b) as a function of $\delta q/Q$. We find that $\Gamma_M$ increases approximately exponentially for $\delta q/Q \gtrsim 10^{-2}$. This is illustrated by the dashed line in figure 4(b) given by

$$\Gamma_M = \Gamma_0 10^{\alpha \delta q/Q},$$

where the parameters $\Gamma_0 = 3.31 \times 10^7 \text{s}^{-1}$ and $\alpha = 15.28$ are obtained by fitting the data points from all sets $S_i$ with $\delta q/Q \gtrsim 10^{-2}$ to equation (14). The spread of the decay rates around the dashed line is roughly three orders of magnitude for $\delta q/Q \lesssim 0.15$, and reduces to two orders of magnitude for $\delta q/Q > 0.15$. In particular, the autoionization rates are apparently independent of the energy of the initial state if the overlap exceeds several percent.

Finally, we note that the overlap of a given state $|\psi_M\rangle$ is correlated with the symmetry of the energy distribution between the two atoms. More specifically, we consider the symmetry parameter

$$S = 2 \frac{E_{\text{M1}}}{E_M},$$

where $E_{\text{M1}}$ is the independent-atom energy of state $|\psi_1\rangle$ and $E_M$ is defined in equation (10). A value of $S = 1$ corresponds to a completely symmetric distribution of energy $E_M$ between atoms $A$ and $B$, and $S$ decreases monotonically with reduced symmetry. Figure 5 shows a log-linear plot of $S$ for all sets of states $S_i$ as a function of $\delta q/Q$, demonstrating that symmetry and overlap are clearly correlated. This result is relevant for systems similar to the experimental setup reported in [22], where a gas of cold atoms was excited to $n\text{dnd}$ states by short laser pulses. This initial state is perfectly symmetric with $S = 1$. However, the interatomic distance of some of the atom pairs in the gas will be so small that the dipole–dipole interaction couples the initial state to near-resonant two-atom states with $S < 1$. It follows that even if the autoionization rate of the initial $n\text{dnd}$ state is small for atomic pairs with
$\delta q/Q < 10^{-4}$, some of the two-atom states involved in the dipole–dipole cascades may autoionize much faster because they have $S < 1$ and hence their overlap can be significantly larger than for the initial state. A more quantitative analysis of this point can be achieved by a simulation of the full quantum dynamics starting from an experimentally achievable initial state and including all coherent couplings between two-atom states and their autoionization rates. Such an investigation would be an interesting prospect for future studies.

6. Conclusion

In this paper we present quantum mechanical calculations for autoionization rates of two nearby Rydberg atoms. We consider sets of randomly chosen two-atom states and calculate the autoionization rates in lowest order perturbation theory. Since the electron clouds overlap only slightly, we neglect exchange corrections to the autoionization rate. We find that the autoionization rates can be classified via the charge overlap between the two states. If the overlap is less than $10^{-4}$, the multipole expansion of the interaction Hamiltonian holds and the autoionization rates are relatively small. In particular, they decrease on average with increasing energy of the two-atom state and can be smaller or comparable to dipole transition rates between near-resonant two-atom states. It follows that the quantum dynamics in this regime will exhibit a rich interplay between coherent transitions and autoionization. However, we find that the autoionization rates increase dramatically beyond the dipole–dipole regime where overlap effects become significant. Our results show that this regime begins where the overlap exceeds $10^{-4}$, and an approximately exponential increase sets in if the overlap is larger than 1%. Our calculations were carried out for the specific example of Rubidium atoms. However, our classification of the autoionization rates in terms of the charge overlap makes no reference to the quantum numbers of the initial states or specific properties of Rubidium atoms. We thus expect that our findings hold for other alkali-metal atoms as well. While we had to restrict our calculations to relatively small principal quantum numbers due to technical reasons, we anticipate that qualitatively similar results should hold for higher principal quantum numbers as well. Extending our current calculations to this regime is subject to further investigation. Other possible extensions of our work include the calculation of the correct two-electron eigenstates via full configuration interaction methods [49], and the application of the complex rotation method [50] in order to find the energies and widths of the two-electron resonances.

In summary, Rydberg atoms with slightly overlapping electron clouds offer fascinating possibilities for future theoretical and experimental studies at the boundary between ultracold atom and molecular physics. In particular, ultrafast pump-probe laser techniques [16] allow one to resolve processes that are much faster than the autoionization rate even if the electron clouds overlap by a few percent. In this way autoionization and coherent processes in correlated Rydberg electron clouds could be measured with unprecedented temporal and spatial resolution. Such experiments would represent a paradigm shift from mimicking electron-electron interactions with ultracold atoms [38–43] to actually realizing them.

Acknowledgments

We thank the National Research Foundation and the Ministry of Education of Singapore for support. The authors would like to acknowledge the use of the University of Oxford Advanced Research Computing (ARC) facility in carrying out this work (http://dx.doi.org/10.5281/zenodo.22558). The research leading to these results has received funding from the European Research Council under the European Unions Seventh Framework Programme (FP7/2007-2013)/ERC Grant Agreement no. 319286 Q-MAC.

Appendix. Evaluation of the Coulomb matrix element

Here we outline the evaluation of the matrix element

$$M = \langle \psi_{l_{lm}}^E, \psi_{il}^A | V | \psi_{il}^A, \psi_{il}^B \rangle$$

(A1)

entering the autoionization rate in equation (9). The operator $V$ in equation (1) is a sum of Coulomb interactions $1/|r - r'|$ which we expand as

$$\frac{1}{|r - r'|} = \sum_{l=0}^{\infty} \frac{4\pi}{2l + 1} r_c^l Y_l^m(\theta', \phi') Y_l^m(\theta, \phi),$$

(A2)

where $r_c = \min(r, r')$ and $r_c = \max(r, r')$. We truncate the sum over angular momenta $l$ in equation (A2) and omit all terms with $l > 15$. Here $l$ corresponds to $\Delta l$ in the main text and determines the amount of angular momentum that the Coulomb interaction can transfer between the electrons. In order to evaluate the matrix element $M$ we expand all wavefunctions in terms of spherical harmonics [44]. Since we place atom $A$ at the origin, the expansion of $|\psi_{il}^A\rangle$ and $|\psi_{lm}^E\rangle$...
comprise only a single term
\[ \psi_{\alpha}(r) = R_{\alpha}(r)Y_{l\alpha}^m(\theta, \phi), \quad (A3a) \]
\[ \psi_{\beta}^{*}(r) = C_{\beta}(r)Y_{l\beta}^m(\theta, \phi). \quad (A3b) \]
The wavefunctions \( \psi_{\alpha}(r) \) and \( \psi_{\beta}(r) \) in equation (A1) are centered at atom B. They are both of the form
\[ \psi_{\beta}(r, \theta, \phi) = \sum_{l_{\beta}=0}^{L_{\beta}} \sum_{m_{\beta}=-l_{\beta}}^{l_{\beta}} Q_{l_{\beta}}^{m_{\beta}}(r)Y_{l_{\beta}}^{m_{\beta}}(\theta, \phi), \quad (A5) \]
where we expressed \( r \) in terms of spherical coordinates \( (r, \theta, \phi) \). We set \( L_{\beta}=1000 \), and the function \( Q_{l_{\beta}}^{m_{\beta}}(r) \) can be found using the orthonormality of \( Y_{l_{\beta}}^{m_{\beta}} \),
\[ Q_{l_{\beta}}^{m_{\beta}}(r) = \int d\theta d\phi \sin \theta \psi_{\beta}(r, \theta, \phi) Y_{l_{\beta}}^{m_{\beta}}(\theta, \phi). \quad (A6) \]
We represent all radial functions on a grid with up to 14000 points. The integration region in equation (A6) is restricted to the solid angle where \( \psi_{\beta}(r) \) takes on non-negligible values, and the integral is carried out using the trapezoidal rule [45]. With the expansions in equations (A2), (A3a) and (A5) the evaluation of the matrix element \( M \) can be reduced to a double integral over the radial variables and the remaining integrals reduce to Gaunt coefficients [46]. The radial integrals are evaluated with the trapezoidal rule [45], and the Gaunt coefficients are defined as
\[ G_{l_1 l_2 m_1}^{m_2 m_3} = (-1)^{m_1} \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)}} \left| l_1, l_2; 0, 0|l_3, 0 \right| l_1, l_2; m_1, m_2|l_3, -m_3 \right). \quad (A7) \]

The evaluation of Clebsch–Gordan coefficients [46] \( \left| l_1, l_2; m_1, m_2|l_3, m_3 \right) \) involves the calculation of factorials which can be numerically unstable for large values of \( l_1, l_2 \) and \( l_3 \) if floating point numbers are used. In order to circumvent this problem, we generate a library of all non-zero Gaunt coefficients with \( l_1, l_2 \leq 1000 \) and \( l_1 \leq 15 \) with the software package MATHEMATICA [47]. The calculation of \( \Gamma_{\alpha} \) is implemented in MATLAB [48].

References

[1] Gallagher T F 1994 Rydberg Atoms (Cambridge: Cambridge University Press)
[2] Boisseau C, Simbotin I and Cotè R 2002 Phys. Rev. Lett. 88 133004
[3] Schwettmann A, Crawford J, Overstreet K R and Shaffer J P 2006 Phys. Rev. A 74 020701
[4] Schwettmann A, Overstreet K R, Tallant J and Shaffer J P 2007 J. Mod. Opt 54 2551
[5] Overstreet K R, Schwettmann A, Tallant J, Booth D and Shaffer J P 2009 Nat. Phys. 5 581
[6] Samboy N, Stanojevic J and Cote R 2011 Phys. Rev. A 83 050505
[7] Samboy N and Cote R 2011 J. Phys. B: At. Mol. Opt. Phys. 44 184006
[8] Kiffner M, Park H, Li W and Gallagher T F 2012 Phys. Rev. A 86 031401
[9] Kiffner M, Li W and Jaksh D 2013 Phys. Rev. Lett. 110 170402
[10] Samboy N and Coté R 2013 Phys. Rev. A 87 032512
[11] Kiffner M, Li W and Jaksh D 2013 Phys. Rev. Lett. 111 233003
[12] Kiffner M, Huo M, Li W and Jaksh D 2014 Phys. Rev. A 89 052717
[13] Urban E, Johnson T A, Henage T, Isenhower L, Yavuz D D, Walker T G and Saffman M 2009 Nat. Phys. 5 110
[14] Gaëtan A, Miroshnychenko Y, an A Chotia T W, Viteau M, Comparat D, Pillet P, Browaeys A and Grangier P 2009 Nat. Phys. 5 115
[15] Schauß P, Cheneau M, Endres M, Fukuhara T, Hild S, Omaran A, Pohl T, Gross C, Kuhner S and Bloch I 2012 Nature 491 87
[16] Takei N, Sommer C, Genes C, Puppillo G, Goto H, Koyasu K, Chiba H, Weidmüller M and Öhmoni K 2015 arXiv:1504.03635v1
[17] Beterov I I, Ryabtsev I I, Tyryakov D B and Entin V M 2009 Phys. Rev. A 79 052504
[18] Hahn Y 2000 J. Phys. B: At. Mol. Opt. Phys. 33 L655
[19] Amthor T, Denskat J, Giese C, Bezegh N N, Ekers A, Cederbaum L S and Weidmüller M 2009 Eur. Phys. J. D 53 329
[20] Robicheaux F 2005 J. Phys. B: At. Mol. Opt. Phys. 38 S333
[21] Robicheaux F, Goforth M M and Phillips A M 2014 Phys. Rev. A 90 022712
[22] Tanner P J, Han J, Shuman E S and Gallagher T F 2008 Phys. Rev. Lett. 100 043002
[23] Mathew J A D and Komninos Y 1975 Surf. Sci. 53 716
[24] Cederbaum L S, Zobeley J and Tarantelli F 1997 Phys. Rev. Lett. 79 4778
[25] Averbukh V, Müller I B and Cederbaum L S 2004 Phys. Rev. Lett. 93 263002
[26] Kuleff A I, Gokhberg K, Kopelke S and Cederbaum L S 2010 Phys. Rev. Lett. 105 043004
[27] Ovcharenko Y et al 2014 Phys. Rev. Lett. 112 073401
[28] Zimmerman M L, Littman M G, Kash M M and Kleppner D 1979 Phys. Rev. A 20 2251
[29] Luna F, Cavalcanti G H, Coutinho L and Trigueiros A G 2002 Phys. Rev. Lett. 89 031401
[30] Li W, Mourachko I, Noel M W and Gallagher T F 2003 Phys. Rev. A 67 052502
[31] Friedrich H 2006 Theoretical Atomic Physics (Berlin: Springer)
[32] Spencer W P, Vaidyathanathan A G, Kleppner D and Ducov T W 1982 Phys. Rev. A 26 1490
[33] Cohen-Tannoudji C, Dupont-Roc J and Grynberg G 1998 Atom-Photon Interactions (New York, NY: Wiley)
[34] Feibelman P J, McGuire E J and Pandey K C 1977 Phys. Rev. B 15 2202
[35] Cabral J S et al 2011 J. Phys. B: At. Mol. Opt. Phys. 44 184007
[36] Flannery M R, Vricello D and Ostrovsky V N 2005 J. Phys. B: At. Mol. Opt. Phys. 38 S279
[37] Walker T G and Saffman M 2008 Phys. Rev. A 77 032723
[38] Jördens R, Strohmaier N, Gnter K, Morris H and Esslinger T 2012 Nature 455 204
[39] Palmer R N and Jaksh D 2006 Phys. Rev. Lett. 96 180407
[40] Cooper N R and Dalibard J 2013 Phys. Rev. Lett. 110 185301
[41] Bloch I, Dalibard J and Zwerger W 2008 Rev. Mod. Phys. 80 885
[42] Simon J, Bakr W S, Ma R, Tai M E, Preiss P M and Greiner M 2011 Nature 472 307
[43] Sanner C, Su E J, Huang W, Kesheht A, Gillen J and Ketterle W 2012 Phys. Rev. Lett. 108 240404
[44] Cohen-Tannoudji C, Diu B and Laloë F 1977 Quantum Mechanics vol I (London: Wiley)
[45] Abramowitz M and Stegun I A (ed) 1972 Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables (New York: Dover) 9th printing
[46] Cohen-Tannoudji C, Diu B and Laloë F 1977 Quantum Mechanics vol II (London: Wiley)
[47] Wolfram Research Inc. Mathematica Version 10.1 (Irvine, Champaign, Illinois: Wolfram Research, Inc.)
[48] MATLAB 2014 Version 8.4.0 (R2014b) (Massachusetts: The MathWorks Inc. Natick)
[49] Olsen J, Roos B O, Jørgensen P and Jensen H J A 1988 J. Chem. Phys. 89 2185
[50] Ho Y K 1983 Phys. Rep. 99 1