Dipole-dipole interaction between cold Rydberg atoms

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Theoretical background

Calculations of Rydberg wavefunctions and Stark shifts enable us to choose a suitable resonant dipole-dipole transition for our experiments: 41d + 49s ↔ 42p + 49p is resonant at a field of only \( \sim 0.4 \text{ V/cm} \) and the relevant transition dipole moments are of the order of \( \sim 1000 \text{ a.u.} \). Both the calculation of the wavefunctions as well as the Stark shift are covered extensively in this chapter. Simulations of dipoles distributed over two parallel elongated volumes show that the short-time energy transfer probability scales like \( P \propto t^2/d^5 \), with \( d \) the distance between the volumes. In a simulation of excitation diffusion in a randomly organized system we observe localization resulting from the dipole blockade effect.
2.1 Introduction

This chapter describes the theoretical background and the calculations we have performed. They both provide us with physical insight as well as the necessary experimental parameters. The main goal was to find a suitable set of states for dipole-dipole interaction among Rydberg states. We aimed for a strong interaction, allowing us to measure at large atomic distances. To find resonant interactions, one needs to know the exact energies of the atoms as a function of electric field, for which the wavefunctions of the atoms should be known. The calculation of the Rydberg atom wavefunctions are described in section 2.2. The potential for the electron is not exactly known, but by making use of the experimentally known binding energies an approximate wavefunction can be obtained. We present two methods, one numerical and one analytical solution of the Schrödinger equation. The following section, section 2.3, deals with the Stark effect: the shift of atomic energy levels in an electric field. The Stark shift can be calculated by means of perturbation theory; in contrast to the situation with lower excited states, this perturbation couples many states and the calculation involves quite large matrices.

In section 2.4 dipole-dipole interactions are explained. Here we also pick a suitable resonant transition, that we will use in our experiments. The transition of our preference is 41d+49s ↔ 42p+49p. For this transition we calculated the resonance fields (0.3807 V/cm and 0.4112 V/cm) and the transition dipole moments of both involved atomic transitions 41d ↔ 42p and 49s ↔ 49p. Both dipole moments are about 1000 \(a_0e\), leading to a dipole-dipole interaction strength of \(V_{dd} = 2\pi 35\) kHz at a particle distance of 40 \(\mu m\).

<table>
<thead>
<tr>
<th>Name</th>
<th>Origin</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>length</td>
<td>Bohr radius (a_0)</td>
<td>0.529 177 208 59(36) (\cdot 10^{-10}) m</td>
</tr>
<tr>
<td>time</td>
<td>(h/E_h)</td>
<td>2.418 884 326 505(16) (\cdot 10^{-17}) s</td>
</tr>
<tr>
<td>mass</td>
<td>electron mass (m_e)</td>
<td>9.109 382 15(45) (\cdot 10^{-31}) kg</td>
</tr>
<tr>
<td>energy</td>
<td>Hartree energy (E_h = \frac{e^2}{4\pi\epsilon_0})</td>
<td>4.359 743 94(22) (\cdot 10^{-18}) J</td>
</tr>
<tr>
<td>charge</td>
<td>elementary charge (e)</td>
<td>1.602 176 487(40) (\cdot 10^{-19}) C</td>
</tr>
<tr>
<td>electric dipole moment</td>
<td>(a_0e)</td>
<td>8.478 352 81(21) (\cdot 10^{-30}) C m</td>
</tr>
<tr>
<td>electric field</td>
<td>(E_h/a_0e)</td>
<td>5.142 206 32(13) (\cdot 10^9) V/cm</td>
</tr>
<tr>
<td>magnetic dipole moment</td>
<td>(2\mu_B = \hbar e/m_e)</td>
<td>1.854 801 830(46) (\cdot 10^{-27}) J/G</td>
</tr>
<tr>
<td>magnetic field</td>
<td>(\hbar/a_0^2)</td>
<td>2.350 517 382(59) (\cdot 10^9) G</td>
</tr>
</tbody>
</table>

The last section 2.5 presents some simulations with dipole-dipole interacting atoms. In the experiments described in this thesis, we don’t have two single Rydberg atoms, but two very thin and long cylinder-like volumes with tens of Rydberg atoms. Straightforward two-particle simulations predict the experimental data from chapter 5 quite well. Furthermore we analytically derive a scaling law for the transition probability for short times as a function of distance \(d^2 P \sim t^2/d^5\). Another simulation we performed describes excitation diffusion through dipole-dipole interaction. This simulation compares the diffusion in an ordered lattice of particles to a randomly organized particle configuration, where the latter
Table 2.2: Energy conversions used in this thesis. The full precision and uncertainty can be found in [68].

<table>
<thead>
<tr>
<th></th>
<th>MHz</th>
<th>cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MHz</td>
<td>1 MHz</td>
<td>3.335 641·10⁻⁵ cm⁻¹</td>
</tr>
<tr>
<td>1 cm⁻¹</td>
<td>2.997 925·10⁴ MHz</td>
<td>1 cm⁻¹</td>
</tr>
<tr>
<td>1 eV</td>
<td>2.417 989·5·10⁸ MHz</td>
<td>8.065 545·10³ cm⁻¹</td>
</tr>
<tr>
<td>1 a.u.</td>
<td>6.579 683·920·7·10⁹ MHz</td>
<td>2.194 746·313·7·10⁵ cm⁻¹</td>
</tr>
<tr>
<td>1 J</td>
<td>1.509 190·5·10²⁷ MHz</td>
<td>5.034 117·10²² cm⁻¹</td>
</tr>
</tbody>
</table>

Table 2.2: continued

<table>
<thead>
<tr>
<th></th>
<th>eV</th>
<th>a.u.</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MHz</td>
<td>4.135 667·10⁻⁹ eV</td>
<td>1.519 829·846·0·10⁻¹⁰ a.u.</td>
<td>6.626 069·10⁻²⁸ J</td>
</tr>
<tr>
<td>1 cm⁻¹</td>
<td>1.239 841·9·10⁻¹ eV</td>
<td>4.556 335·252·8·10⁻⁶ a.u.</td>
<td>1.986 446·10⁻²³ J</td>
</tr>
<tr>
<td>1 eV</td>
<td>1 eV</td>
<td>3.674 932·5·10⁻² a.u.</td>
<td>1.602 176·5·10⁻¹⁹ J</td>
</tr>
<tr>
<td>1 a.u.</td>
<td>27.211 384 eV</td>
<td>1 a.u.</td>
<td>4.359 744·10⁻¹⁸ J</td>
</tr>
<tr>
<td>1 J</td>
<td>6.241 510·10¹⁸ eV</td>
<td>2.293 713·10¹⁷ a.u.</td>
<td>1 J</td>
</tr>
</tbody>
</table>

case shows an interesting result: a localization effect which is due to a dipole-blockade mechanism.

In this thesis atomic units are used unless stated otherwise. Atomic units form a convenient system of units in atomic physics; all quantities are measured relative to the properties of atomic hydrogen. In practice it means that the values for the electron charge, the electron mass, the reduced Planck constant are all set to unity as well as 1/4πε₀ and 2µ_B. This leads to a significant simplification of all relevant equations.

In table 2.1 the conversion factors from atomic units to SI units are given for a selection of quantities relevant in this thesis. Values are taken from the ‘2006 CODATA recommended values’ as published in [68].

The energy unit Joule is usually impractical for atomic physics. Apart from atomic units we often use MHz or cm⁻¹, also eV are common. In table 2.2 some energy conversions are given.

2.2 Rydberg wavefunctions

Alkali atoms are effectively one-electron atoms, just as hydrogen. Especially when the electron of the atom is in a highly excited state, or Rydberg state, there are many similarities. For rubidium in its ground state we have a nucleus of charge +37, and the first 36 electrons around it form a very stable configuration around the nucleus, as in the noble gas krypton, where all electron shells up to 4p are filled. The last electron is on his own in a new shell, the 5s state. When the atom is (laser) excited to a Rydberg state, this single electron is moved to a shell with a much higher principal quantum number n. Already in the 5s ground state, but especially in the higher excited states, we can consider the inner part of the atom as a point particle with charge +1, equivalent with the hydrogen nucleus. Therefore we will first discuss the hydrogen wavefunctions, which can be cal-
culated exactly (subsection 2.2.1). Then we will make some small adjustments for the wavefunctions that enter the core region of the atom: the low angular momentum states. These wavefunctions are not exact and we will discuss two different methods to calculate these wavefunctions, an analytical and a numerical method (resp. subsections 2.2.2 and 2.2.3). The last part of this section describes how the expectation values of powers of the electron position are obtained (subsection 2.2.4). The general expression for these expectation values enables us to calculate the interaction with a static electric or magnetic field as well as with electromagnetic radiation. Especially the interaction with an electric field is important, because this leads to an energy shift of the states resulting in multiple resonances of the dipole-dipole interaction. The expectation values will also be necessary to calculate the interaction strength between two Rydberg atoms.

2.2.1 Hydrogen wavefunctions

The potential for the electron is the Coulomb potential \( V = -1/r \) due to the attraction to the nucleus. To compute the wavefunctions one needs to solve the time-independent Schrödinger equation

\[
-\frac{1}{2}\nabla^2 \psi(r) - \frac{1}{r} \psi(r) = E \psi(r).
\]  

(2.1)

Given the spherically symmetric potential, we can use spherical coordinates and separate the Schrödinger equation in a radial and an angular part:

\[
\psi(r) = R(r)Y_{\ell m}(\theta, \phi).
\]

(2.2)

The spherical harmonics \( Y_{\ell m}(\theta, \phi) \) are independent of the exact potential as long as it is spherically symmetric. The solution of the angular part of the Schrödinger equation is given by [12]

\[
Y_{\ell m}(\theta, \phi) = \sqrt{\frac{(2\ell + 1)(\ell - m)!}{4\pi (\ell + m)!}} P^m_\ell(\cos \theta) e^{im\phi},
\]

(2.3)

with \( P^m_\ell \) the associated Legendre function [2]. From boundary conditions for \( \theta \) and \( \phi \) follows \( \ell \geq 0 \) and \( |m| \leq \ell \). \( \ell \) is the orbital angular momentum quantum number and \( m \) is the magnetic quantum number.

For the radial part of the Schrödinger equation it is practical to rewrite \( u(r) = rR(r) \) and we obtain

\[
\left( -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell + 1)}{2r^2} - \frac{1}{r} \right) u(r) = Eu(r).
\]

(2.4)

The solutions [12] are in the form of an exponent of \( r \), a power of \( r \) and a generalized Laguerre polynomial \( L^b_n(r) \) [2]

\[
R_{n\ell}(r) = \sqrt{\left(\frac{2}{n}\right)^\ell \frac{(n - \ell - 1)!}{2n(n + \ell)!}} e^{-r^2/n} \frac{2r^\ell}{n} L_n^{2\ell+1} \left(\frac{2r}{n}\right).
\]

(2.5)

\*Note that Bethe and Salpeter [12] use a different definition of the generalized Laguerre polynomial. We use here the Abramowitz and Stegun [2] definition, resulting in a slightly different expression for \( R_{n\ell} \).
2.2 Rydberg wavefunctions

and the energy is

$$E_n = -\frac{1}{2n^2},$$

(2.6)

with $n$ the principal quantum number. The orbital angular momentum quantum number $\ell$ can not get larger than $n - 1$, or $0 \leq \ell \leq n - 1$. The $n^{-2}$ dependence of the binding energy (Eq. 2.6) was first noted in the 1880’s by Johann Balmer and Johannes Rydberg and further developed by Niels Bohr in 1913 [105]. The associated wavenumber of a photon that just ionizes the atom is given by the Rydberg constant $R_y$. It is equivalent to half an atomic unit of energy (in units of cm$^{-1}$), given in table 2.2. So the binding energy can also be written as $E_n = -R_y/n^2$.

2.2.2 Analytical wavefunctions for alkali atoms

The adjustments for alkali atoms heavier than hydrogen lie in the low angular momentum states. Of all states, these low-$\ell$ states have the largest probability near the core of the atom, and here, the nucleus is not fully screened by the core electrons. Also electron-electron interaction is largest close to the core. The potential near the core is not exactly known, but gives rise to a change in energy, which is known experimentally. Already noted by Rydberg, the binding energy Eq. 2.6 is modified by replacing $n$ by $n^* = n - \delta_n\ell_j$

$$E_{n\ell_j} = -\frac{1}{2(n - \delta_n\ell_j)^2};$$

(2.7)

$\delta_n\ell_j$ is called the quantum defect. It depends mainly on $\ell$, but the spin orbit coupling gives rise to a small dependence on $j$; the number changes only slightly with $n$. The quantum defects we use in our calculations are based on measurements in 2003 and 2006 [60, 38, 3]. They are given by

$$\delta_n\ell_j = \delta_0 + \frac{\delta_2}{(n - \delta_0)^2},$$

(2.8)

where $\delta_0$ and $\delta_2$ depend on $\ell$ and $j$. The experimentally obtained values for $\delta_0$ and $\delta_2$ for $^{85}\text{Rb}$ are given in table 2.3.

<table>
<thead>
<tr>
<th>State</th>
<th>$\delta_0$</th>
<th>$\delta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n^1s_{1/2}$</td>
<td>3.1311804(10)</td>
<td>0.1784(6)</td>
</tr>
<tr>
<td>$n^1p_{1/2}$</td>
<td>2.6548849(10)</td>
<td>0.2900(6)</td>
</tr>
<tr>
<td>$n^1p_{3/2}$</td>
<td>2.6416737(10)</td>
<td>0.2950(7)</td>
</tr>
<tr>
<td>$n^3d_{3/2}$</td>
<td>1.34809171(40)</td>
<td>-0.60286(26)</td>
</tr>
<tr>
<td>$n^5d_{3/2}$</td>
<td>1.34646572(30)</td>
<td>-0.59600(18)</td>
</tr>
<tr>
<td>$n^5f_{5/2}$</td>
<td>0.0165192(9)</td>
<td>-0.085(9)</td>
</tr>
<tr>
<td>$n^7f_{7/2}$</td>
<td>0.0165437(7)</td>
<td>-0.086(7)</td>
</tr>
<tr>
<td>$n^7g_{7/2}$</td>
<td>0.00405(6)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3: The $^{85}\text{Rb}$ quantum defects $\delta_{n\ell_j} = \delta_0 + \delta_2/(n - \delta_0)^2$ from [60, 38, 3].

The radial wavefunction is also modified by replacing $n$ by $n^*$ in equation 2.5. However, the Laguerre polynomials need an integer bottom index. Therefore, we also replace
Theoretical background

by \( \ell' = \ell - \delta_{n\ell j} + I(\ell) \) \([10, 54]\). This modifies the radial potential in such a way that the binding energy is an exact solution of the Schrödinger equation again. In this approach the modification of the potential is proportional to the centrifugal potential, keeping the changes localized near the core. \( I(\ell) \) is an integer fixing the number of radial nodes, for which we have the restrictions \( \delta_{n\ell j} - \ell - \frac{1}{2} < I(\ell) \leq n_{\text{min}} - \ell - 1 \) with \( n_{\text{min}} \) the principal quantum number of the ground state. For rubidium we use for \( I(\ell) \) the nearest integer below or equal to \( \delta_{n\ell j} \), which gives the best agreement between the calculated and experimentally known value for the lifetime of the \( 5s - 5p \) transition. We have

\[
R_{n\ell'}(r) = \sqrt{\left(\frac{2}{n'}\right)^3 \frac{(n' - \ell' - 1)!}{2n'(n' + \ell')!}} e^{-r/n'} \left(\frac{2r}{n'}\right)^{\ell'} L_{n' - \ell' - 1}^{2\ell' + 1} \left(\frac{2r}{n'}\right). \tag{2.9}
\]

The angular part of the wavefunction is equal to the one for hydrogen (Eq. 2.3), i.e. not \( \ell' \), but just \( \ell \) should be used. We have depicted the radial wavefunctions of \( n = 9 \) in figure 2.1. Note that the number of radial zero-crossings is given by \( n' - \ell' - 1 \). Furthermore it is visible that for higher \( \ell \) the wavefunction starts further away from the core, due to the centrifugal part of the potential (the second term in equation 2.4).

2.2.3 Numerical calculation of the radial wavefunctions

A numerical method to calculate the radial wavefunctions of heavy alkali atoms is described by Zimmerman et al. \([109]\). Here the Numerov method is used to numerically solve the radial Schrödinger equation (Eq. 2.4). Numerov’s method is a numerical method to solve second-order differential equations, where the first-order term does not appear, like we have here. Zimmerman’s method uses a logarithmic scaling for \( r \), which is most efficient, because the wavefunction oscillates more and more when going inward. The very inner part of the potential and of the wavefunction are unknown, but the wavefunction can be calculated using the semi-empirically known energy (Eq. 2.7) and simply the hydrogen potential – the Coulomb potential and the centrifugal barrier, respectively the third and the second term in equation 2.4. The calculation is started from the outside and uses the fact that the outer part of the wavefunction (beyond the classical outer turning point \( r_{\text{out}} = 2n^2 \)) decreases exponentially. The starting point for the calculation is at \( r_s = 2n(n + 15) \) and from there the wavefunction is calculated step-by-step by going inwards with a logarithmic step size of \( h = 0.001 \) until the classical inner turning point \( r_{\text{in}} = n' \left(n' - \sqrt{(n')^2 - (\ell + 1/2)^2}\right) \) is reached.

Specifically, with \( x = \ln r \) and \( X = \sqrt{r} R \) the radial Schrödinger equation (Eq. 2.4) becomes

\[
d^2X \over dx^2 = g(x)X, \tag{2.10}
\]

where

\[
g(x) = 2e^{2x} \left( -\frac{1}{e^x} + \frac{1}{2(n')^2} \right) + (\ell + \frac{1}{2})^2 \tag{2.11}
\]

\(^{†}\text{In [54] the quantum defect depends on } \ell \text{ only, such that a complete orthonormal set of wavefunctions is obtained, however, we prefer to use the } n- \text{ and } j-\text{dependent version for a better match of the energy.}\)
2.2 Rydberg wavefunctions

Figure 2.1: The radial wavefunctions of \( n = 9 \) for rubidium-85. We have plotted \( rR_n^\ell \) (Eq. 2.9) versus the radius in units of the Bohr radius \( a_0 \), such that we get the total wavefunction for the whole spherical surface with radius \( r \). The insets show a small part of the analytical wavefunction together with the numerically calculated wavefunction in red, where for small \( \ell \) a small phase difference is visible.

and the Numerov algorithm is

\[
X_{i+1} = \frac{(10T_i + 2)X_i + (T_{i-1} - 1)X_{i-1}}{1 - T_{i+1}},
\]

where we used \( T_i = (\hbar^2/12)g_i \). The index \( i \) is the number of the step \( x_i = \ln r_s - ih \). The normalization constant \( N \) is obtained by

\[
N^2\hbar \sum_i X_i^2 r_i^2 = 1.
\]

The resulting wavefunctions \( \Xi = NX \) resemble the analytical wavefunctions quite well, especially for higher \( \ell \) states. In figure 2.1 a small phase difference is visible between the
The symbol \( \sum \) summations in the Appell function in 2.17 we use radial wavefunctions the expectation value becomes a simple summation. We separate this integral in an angular and a radial part. For the numerically calculated several eigenfunctions \( \psi \) initial state, to another state, the final state \( \psi_f \). Here we discuss the expectation values of powers of the electron position.

\[
\langle \psi_f | r^l | \psi_i \rangle = \int \psi^*_f(r) r^l \psi_i(r) \, dr.
\] (2.14)

We separate this integral in an angular and a radial part. For the numerically calculated radial wavefunctions the expectation value becomes a simple summation:\footnote{Note that \( \sum_j R_i^j r_j^{2+d} \Delta r_j \) can be rewritten as \( h \sum_j \Xi_j \Xi'_{j} r_j^{2+d} \)}

\[
X_{n\ell,n'\ell'} = \langle n'\ell' | r^d | n\ell \rangle = \hbar \sum_j \Xi_j \Xi'_{j} r_j^{2+d},
\] (2.15)

where the accents refer to the final state. For the analytical wavefunction we get for the radial part

\[
R_{i,f} = \langle n_f\ell_f | r^d | n_i\ell_i \rangle = \int R_{n_f\ell_f} r^{d+2} R_{n_i\ell_i} \, dr.
\] (2.16)

Inspired by [54, 74] we have worked out this integral as

\[
\frac{1}{2^{1+d}} \sqrt{\frac{(n^*_i-\ell^*_i-1)!(n^*_j-\ell^*_j-1)!}{(n^*_i+\ell^*_i)!(n^*_j+\ell^*_j)!}} \left(\frac{2}{n^*_i+n^*_j}\right)^{\ell^*_i+\ell^*_j+3+d} \left(\frac{n^*_i+n^*_j\ell^*_i}{n^*_i-\ell^*_i-1}\right)^{\ell^*_i+1+d} \left(\frac{n^*_j+n^*_j\ell^*_j}{n^*_j-\ell^*_j-1}\right) (\ell^*_i+\ell^*_j+2+d)! F_2\left(\ell^*_i+\ell^*_j+3+d;\begin{array}{c}
-n^*_i+n^*_i+1,-n^*_j+n^*_j+1; 2\ell^*_i+2,2\ell^*_j+2; \\
n^*_i+n^*_j, n^*_i+n^*_j
\end{array}\right),
\] (2.17)

where \( F_2 \) is the Appell hypergeometric function of the second kind [29]

\[
F_2(\alpha;\beta;\beta';\gamma;\gamma';x,y) = \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \left(\frac{\alpha}{p+q}\right)_{p+q} \left(\frac{\beta}{p}\right)_p \left(\frac{\beta'}{q}\right)_q x^p y^q.
\] (2.18)

The symbol \( (\alpha)_p = \Gamma(\alpha+p)/\Gamma(\alpha) \) is the Pochhammer symbol. For the upper limit of the summations in the Appell function in 2.17 we use \( p = n^*_i-\ell^*_i-1 \) and \( q = n^*_j-\ell^*_j-1 \) (the factors \( (\beta)_p \) and \( (\beta')_q \) are zero for larger \( p \) and \( q \)). This result is in fact a generalization of
the Gordon formula [12] and this Appell hypergeometric function is a generalization of
the hypergeometric function.

The angular part of equation 2.14 is given by [27]

\[ A_{i,f} = \sqrt{\frac{4\pi}{3}} \int_0^\infty \sin(\theta) d\theta \int_0^{2\pi} d\phi \ Y_{\ell_f m_f}(\theta, \phi) Y_{1 q}(\theta, \phi) Y_{\ell_i m_i}(\theta, \phi). \] (2.19)

Note that \( Y_{1 q}(\theta, \phi) \) originates from the conversion to Cartesian coordinates

\[ \sqrt{\frac{4\pi}{3}} Y_{10}(\theta, \phi) = \cos \theta = \hat{z}, \] (2.20)

\[ \sqrt{\frac{4\pi}{3}} Y_{1 \pm 1}(\theta, \phi) = \mp e^{\pm i \phi} \sin \theta \sqrt{\frac{2}{2}} = \mp \hat{x} \pm i \hat{y}. \] (2.21)

In other words \( q \) is related to the polarization of the external electromagnetic wave; \( q = \pm 1 \)
for circularly polarized radiation and \( q = 0 \) for linearly polarized radiation. This light can
be either light that pumps the transition, or light that is spontaneously emitted from the
atom that makes the transition from the initial to the final state. The integral Eq. 2.19 can
be written in terms of a Wigner 3j-symbol

\[ A_{i,f} = (-1)^{\ell_f m_f} \sqrt{\max(\ell_i, \ell_f)} \begin{pmatrix} \ell_f & m_f & \ell_i \\ -m_f & q & m_i \end{pmatrix}; \] (2.22)

this Wigner 3j-symbol is zero unless \( \Delta \ell = \ell_f - \ell_i = 0, \pm 1 \) and \( \Delta m = m_f - m_i = q \).

Due to spin-orbit interaction we get a splitting of the \( \ell \) states into states with the new
quantum number \( j \), which denotes the total electronic angular momentum. Possible values
for \( j \) run from \( \ell - s \) to \( \ell + s \) in steps of 1. The angular part of the wavefunction becomes

\[ |\ell_j m_j \rangle = \sum_i C_i Y_{\ell_i m_i}(\theta, \phi), \] (2.23)

with \( C_i \) the Clebsch-Gordan coefficients. The angular integral, now including the spin-
orbit interaction, can be worked out as follows

\[ \mathcal{A}_{i,f} = (-1)^{\ell_f - m_f + 1/2} \sqrt{\max(\ell_i, \ell_f)} \sqrt{(2j_i + 1)(2j_f + 1)} \begin{pmatrix} \ell_f & j_f & s \\ j_i & \ell_i & 1 \end{pmatrix} \begin{pmatrix} j_i & 1 & j_f \\ m_i & q & -m_f \end{pmatrix}, \] (2.24)

where \( m_i \) and \( m_f \) refer now to the value of \( m_j \) of the initial, respectively final state. Equiv-
ally we have \( \Delta j = 0, \pm 1 \) and \( \Delta m = q \) from the Wigner 3j-symbol. The array between
the curly braces is the Wigner or Racah 6j-symbol. This 6j-symbol is nonzero for \( \Delta \ell = 0, \pm 1 \).

As a test case of both methods we calculate the spontaneous emission rate of the 5p
state. The spontaneous emission rate is given in a.u. by [64]

\[ \Gamma_{i,f} = \frac{4}{3} \alpha^3 (\Delta E_{i,f})^3 |\langle \psi_f | r | \psi_i \rangle|^2, \] (2.25)

where \( \alpha \) is the fine structure constant. The final state is in this case the ground state 5s.
For \( \Delta E_{i,f} \) we use \( 1/\lambda \) with the known wavelength of the transition; \( \lambda = 780 \) nm for the
5P<sub>3/2</sub> state and λ = 795 nm for 5P<sub>1/2</sub>. The angular integral A<sub>5p,5s</sub> (Eq. 2.22) is 1/\sqrt{3} for all three possibilities of the magnetic quantum number m<sub>ℓ</sub> of the 5p state\(^6\). For the radial part we can compare the analytical version \(R_{5p,5s}\) (Eq. 2.17) with the numerical one \(X_{5p,5s}\) (Eq. 2.15). As a result we get for the 5P<sub>1/2</sub> state a lifetime of \(τ_{1/2} = 1/Γ_{5p,5s} = 30.9\) ns if we use the analytical calculation and \(τ_{1/2} = 26.1\) ns if we use the Numerov method. For the 5P<sub>3/2</sub> state we get \(τ_{3/2} = 29.7\) ns analytically and \(τ_{3/2} = 24.8\) ns numerically. All numbers are a few nanoseconds off from the experimentally known values \(τ_{1/2} = 27.70(4)\) \(τ_{3/2} = 26.24(4)\) \[99\]. The difference is due to the different phase of the radial wavefunctions, visible in figure 2.1, as already mentioned at the end of subsection 2.2.3. For high lying Rydberg states, the difference becomes much smaller; we will see in table 2.5 that the difference in the transition dipole moments is only about 0.6% for \(n\) between 40 and 50. This is because the high-\(n\) states are much less influenced by the – unknown – properties of the core region.

In the next section, section 2.3, we use the expectation value of \(z\) to calculate the energy levels in the presence of an externally applied electric field in the \(z\)-direction. In section 2.4 we calculate the transition dipole moments \(a_0e⟨\psi_f|r|\psi_i⟩\), which are the subjects in the resonant dipole-dipole interaction.

### 2.3 Rydberg atoms in a static electric field

In Rydberg experiments the coupling with an electrical field is usually important, because it is very strong. Due to this coupling the energy levels shift, which is called the Stark effect. This shift enables for resonances in dipole-dipole interactions. First we will give a general description of the Stark effect (subsection 2.3.1). The energy shift in rubidium can be calculated with perturbation theory (subsections 2.3.2 and 2.3.3). In the last subsection we describe an experiment we performed, which maps out a part of a Stark map, making use of dipole-dipole interacting atoms (subsection 2.3.4).

#### 2.3.1 The Stark effect

The coupling with the external field occurs for dipoles. A dipole \(μ\) in an external electric field \(F\) has an interaction potential of

\[
V_{\text{dip}} = -μ ⋅ F = -μ_z F,
\]

where we have chosen the field to be in the \(z\)-direction. The dipole moment of an atom \(μ\) is in fact the expectation value of \(r\) times the charge of the electron \(−e\), or, if \(r\) is in atomic units, \(μ = −a_0e⟨r⟩\) and \(μ_z = −a_0e⟨z⟩\), with \(a_0\) the Bohr radius. For pure angular momentum states the expectation value of \(r\) is always zero. However, states with a well defined angular momentum are not stable in an electric field. The atomic states are coupled to each other by means of transition dipole moments. The transition dipole

\(^6\)Note that if \(A_{5p,5s}\) (Eq. 2.24) is used, the total spontaneous emission rate is the sum over both \(Γ_{i,f}\)’s for the two possible \(m_\ell\) states of the 5s state. This gives the same result.
moments are given by $\mu_{1,2} = -a_0 e \langle \psi_1 | r | \psi_2 \rangle$. This second-order coupling (the second-order Stark effect) gives rise to a quadratic behavior of the energy levels.

$$\Delta E = -\frac{1}{2} \alpha F^2,$$

with $\alpha$ the polarizability. This polarizability can be calculated with perturbation theory described in the next subsection.

For states that are degenerate at zero field, the Stark effect will cause a splitting of the states. The energy shift of these states is linear, in other words, these states have a permanent dipole moment. In hydrogen this is the case for all angular momentum states with the same principal quantum number $n$ and in alkali’s for all higher angular momentum states with equal $n$. For the case of hydrogen it is convenient to replace the angular momentum quantum number $\ell$ by the parabolic quantum number $k$, which originates from the conversion to a parabolic coordinate system. The state $|nkm\rangle$ can be expressed as a linear superposition of $|n\ell m\rangle$ states [72, 43]

$$|nkm\rangle = \sum_{\ell} C_{k\ell} |n\ell m\rangle,$$

with the Clebsch-Gordan coefficient being

$$C_{k\ell} = (-1)^m \sqrt{2\ell + 1} \begin{pmatrix} \frac{1}{2} (n - 1) & \frac{1}{2} (n - 1) & \ell \\ \frac{1}{2} (m + k) & \frac{1}{2} (m - k) & m \end{pmatrix}.$$  

The number $k$ runs from $n - |m| - 1$ to $-n + |m| + 1$ in steps of 2. The Stark shift of such a state in a field is given by [12]

$$\Delta E = \frac{3}{2} nkF.$$  

So the quantum number $k$ is directly related to the permanent dipole moment $\mu = -\frac{3}{2} nk$ (in a.u.). In the heavier alkali atoms we will see the same linear effect in the high angular momentum states which are degenerate at zero field. However, there is no simple expression in terms of the quantum number $k$. So for the case of heavier alkali’s it is most practical to use perturbation theory to calculate the energies in an electrical field.

### 2.3.2 Perturbation theory

Perturbation theory provides us with an approximate method to calculate a complicated quantum system in terms of a simpler one. The solution of the unperturbed Schrödinger equation is already known, namely we have the unperturbed energies $E_1, E_2, \ldots, E_N$ and the unperturbed wavefunctions $\psi_1, \psi_2, \ldots, \psi_N$ from section 2.2. We use these energies and wavefunctions and then we simply add the perturbation $H'$ to the unperturbed Hamiltonian $H_0$ (from Eq. 2.1)

$$H = H_0 + H' = \begin{pmatrix} E_1 & 0 & \cdots & 0 \\ 0 & E_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E_N \end{pmatrix} + \begin{pmatrix} H'_{11} & H'_{12} & \cdots & H'_{1N} \\ H'_{21} & H'_{22} & \cdots & H'_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{N1} & H'_{N2} & \cdots & H'_{NN} \end{pmatrix}.$$  

(2.31)
The matrix elements of the perturbation are $H'_{ij} = \langle \psi_i | H' | \psi_j \rangle$. The elements on the diagonal are the first-order perturbations, the off-diagonal matrix elements are the second-order perturbations. With this Hamiltonian we can calculate the energies of the perturbed states $\mathbf{E}'$ and the new wavefunctions $\mathbf{\Psi}'$ in terms of the old ones $\mathbf{\Psi}$. We have the Schrödinger equation $H \psi = \mathbf{E} \psi$ and we can solve it by diagonalizing the Hamiltonian. $\mathbf{E}'$ is the set of eigenvalues and $\mathbf{\Psi}'$ is the set of eigenfunctions, obtained from the matrix product of $\mathbf{C}$, the set of eigenvectors, and $\mathbf{\Psi}$, the set of the original wavefunctions. Specifically, we have

$$
\begin{pmatrix}
E_1 + H'_{11} & H'_{12} & \ldots & H'_{1N} \\
H'_{21} & E_2 + H'_{22} & \ldots & H'_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
H'_{N1} & H'_{N2} & \ldots & E_N + H'_{NN}
\end{pmatrix}
\begin{pmatrix}
\psi'_1 \\
\psi'_2 \\
\vdots \\
\psi'_N
\end{pmatrix}
= 
\begin{pmatrix}
E'_1 & 0 & \ldots & 0 \\
0 & E'_2 & \ldots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \ldots & E'_N
\end{pmatrix}
\begin{pmatrix}
\psi'_1 \\
\psi'_2 \\
\vdots \\
\psi'_N
\end{pmatrix}
$$

(2.32)

and

$$
\mathbf{\Psi}' = \mathbf{C} \mathbf{\Psi} = 
\begin{pmatrix}
c_{11} \psi_1 + c_{12} \psi_2 + \ldots + c_{1N} \psi_N \\
c_{21} \psi_1 + c_{22} \psi_2 + \ldots + c_{2N} \psi_N \\
\vdots & \vdots & \ddots & \vdots \\
c_{N1} \psi_1 + c_{N2} \psi_2 + \ldots + c_{NN} \psi_N
\end{pmatrix}.
$$

(2.33)

### 2.3.3 Calculation of a Stark map

For the calculation of the energy of rubidium Rydberg levels in an external electric field the perturbation is $H' = zF$. The zero-field energies $E_1, E_2, \ldots, E_N$ are given by equation 2.7. All terms $H'_{ij}$ on the diagonal in the second matrix of equation 2.31 are zero, since we use the angular momentum wavefunctions to start with – from either subsection 2.2.2 or 2.2.3. The off-diagonal matrix elements are

$$
H'_{ij} = F \langle \psi_i | z | \psi_j \rangle.
$$

(2.34)

The angular part of this integral is given by Eq. 2.24 with $q = 0$ (see Eq. 2.20). So we have only non-zero values for $\Delta m = 0$. Therefore, we only have to use states with the same value for $m$ in our calculation (in this case we work with $m_j$). Furthermore we have the selection rule $\Delta \ell = \pm 1$. At equation 2.24 we mentioned that $\Delta \ell = 0, \pm 1$, but parity considerations require odd $\Delta \ell$ for electric dipole transitions.

We need to work with quite a lot of states. For one principal quantum number $n$ and $m_j = 1/2$ we have $2n-1$ states – there are $n$ different $\ell$ states and each one is split in two $j$-sublevels, except for the $s$ state, which is not split. Secondly, coupling occurs between states several $n$-manifolds apart; we usually work with two or three manifolds above and below the state we’re interested in. For larger $\Delta n$ the coupling strengths become negligible. For example, if we’re interested in a state in the $n = 40$ manifold, we have a Hamiltonian of approximately $550 \times 550$ elements. Fortunately, most elements are zero, due to the selection rule $\Delta \ell = \pm 1$, which saves calculation time.

In figure 2.2 we depicted the result of such a calculation, a so-called Stark map. Depicted are the binding energies versus electric field around $n = 21$. Clearly visible are the fan-like structures of high angular momentum states for each $n$-manifold, due to the linear Stark effect. Note that these states are no longer pure angular momentum states, but they
are strongly mixed, like the $k$-states in hydrogen. The three lowest angular momentum states, $s$, $p$ and $d$, are clearly visible, due to their large quantum defect. These states experience a purely quadratic and therefore weak Stark shift until they come close to other states. The point where two fan-like structures – or manifolds – of subsequent $n$ start to cross each other is given by the Inglis-Teller limit. It can easily be shown using the shift of the hydrogen $k$-states that this occurs at a field of approximately

$$F_{IT} = \frac{1}{3n^5}.$$  \hspace{1cm} (2.35)

When the external field is as strong as the Coulomb field from the core, the atom will be able to ionize. This occurs for a potential of $V_{\text{ion}} = -2 \sqrt{F}$, depicted as a blue line in figure 2.2. With a binding energy of $-1/2n^2$ we obtain an ionization field of

$$F_{\text{ion}} = \frac{1}{16n^4}.$$  \hspace{1cm} (2.36)

This is called the classical ionization limit. In quantum mechanics, states with positive $k$-values can live beyond this limit, when the $k$-states are not coupled (as in hydrogen) [35]. However, for rubidium, these $k$-states are coupled and they all have short lifetimes.

If the Stark map is examined closely, no two lines will be found that cross each other. Due to the coupling between all states the crossings are avoided crossings. This is however only true for a static field. If the field would be swept quickly over such a crossing the two levels now do cross each other and the coupling is "ignored". This is called the
diabatic case, opposed to the adiabatic case, where the eigenenergies are followed and the crossing is an avoided crossing, which occurs for a slow sweep of the field. This has implications for the method of State-selective Field Ionization (SFI), which uses the $n$ dependence of the ionization field $F_{\text{ion}}$ (Eq. 2.36) to detect the state of the atoms (see chapter 3, section 3.5). In this method the field is swept and the different $n$-states are detected subsequently when they ionize. Due to the (a)diabaticity, the exact ionization field depends on the sweep speed, which is examined in [9]. More about diabaticity and adiabaticity is explained in chapter 7, subsection 7.2.5.

2.3.4 Measurement of dipole-transitions to the manifold states

As an illustration of the Stark map we have performed a measurement, which shows the structure of the Stark-manifold, as first performed by [21]. In our setup we cannot resolve the energy of the manifold states with our laser, however, we can resolve the s- and d-states, especially at zero field, since they are the only allowed laser transitions (section 3.3.3). We make use of the resonant two atom transitions in rubidium like

$$nd + nd \leftrightarrow (n-2)m + (n+2)p,$$  
(2.37a)

$$nd + nd \leftrightarrow (n-1)m + (n+1)p,$$  
(2.37b)

where the $m$ refers to the manifold states. Both transitions are already close to resonant at zero field and if we scan the electric field, we see quite a number of manifold states. With these transitions we can now partly resolve the manifold states, after having created the d-states with our laser. The transitions are caused by dipole-dipole interaction, which is explained in the next section (section 2.4).

In the experiment we excite about 50 laser-cooled atoms up to the 32d-state, using one dye-laser beam (see chapter 3). We studied the process

$$32d + 32d \leftrightarrow 34p + 30m$$  
(2.38)

as a function of an externally applied static electric field. We let the atoms interact for 3 $\mu$s in this field and afterward we detected the atoms, resolving the 34p state from the 32d state. In figure 2.3 we have depicted the fraction of 34p atoms (a fraction of the total number of atoms) versus the applied electric field.

In the experiment we observe multiple peaks, which correspond well to the resonances shown in the upper panel of the figure. This gives us the trust that our Stark map calculation is accurate. The upper panel is constructed from a Stark map for $m_J = \frac{1}{2}$ and shows the binding energy of the manifold states as well as the difference of the binding energies of the other involved states $E_{32d} + E_{32d} - E_{34p}$, such that a resonance occurs of two lines cross. In reality more values of $m_J$ can occur, which we did not take into account in the upper panel for clarity reasons.

In the calculation in the lower panel, we did take into account all relevant $m_J$ values; with the limitation of $\Delta m_J = 0, \pm 1$ for each atom we obtain about 5000 resonances between 0 and 4 V/cm. The theoretical spectrum shown in the figure is a sum of Lorentzian peaks as given in equations 2.53 and 2.54. For the interaction strength, which determines the height and/or width of the peak, we used $V = |\mu_A| |\mu_B|/R^3$. This is a simplified form of the
2.3 Rydberg atoms in a static electric field

dipole-dipole interaction, without angular dependence (section 2.4). $\mu_A$ is the transition dipole moment between 32d and 34p with the relevant $j$ and $m_j$ and $\mu_A$ is the transition dipole moment between 32d and the relevant $n = 30$ manifold state. To obtain a peak width that fits the measurement we used a distance of $R = 1.2 \, \mu$m. Secondly we adjusted the height of the total spectrum.

Despite all the simplifications in our model, the theoretical spectrum matches the measurement remarkably well in the lower panel of figure. The distance of 1.2 $\mu$m seems rather small; a more realistic number for the average inter-particle distance would probably lie between 5 and 10 $\mu$m. Due to the $1/R^3$ dependence of the interaction, the smaller distances will make a much stronger contribution. However, probably other broadening effects in the experiment play the largest role, like stray fields etc. (see section 3.4); the average particle distance is therefore strongly underestimated. The height of the total spectrum was adjusted by factor of 0.002, which is sensible since it is not correct to simply add up all 5000 peaks.

The experiment presented in figure 2.3 is a repetition of a measurement from [21], but the calculation we performed is much simpler. Secondly, we do now understand the peak at 0.4 V/cm, which is the resonance $32d+32d \rightarrow 34p + 30g$; at the time of [21] (2004) the g-quantum defect was not accurately known yet, it was measured in 2006 [3].

**Figure 2.3:** Upper panel: Energy levels of the $n = 30$ manifold in blue and the difference energy $E_{32d} + E_{32d} - E_{34p}$ in red for all possible combinations of $j$. These are only the $m_j = 1/2$ levels; in reality more $m_j$ values are involved. The resonances are depicted as circles. Lower panel: Measurement of the 34p fraction versus the static electric field (blue), with a theoretical calculation in red.
2.4 Dipole-dipole interactions between Rydberg atoms

Dipole-dipole interactions are one of the most important interactions between atoms or molecules. The Van der Waals forces are dipole-dipole interactions of induced dipoles; two atoms or molecules induce a dipole moment to each other and these dipoles will attract. Here we will discuss resonant dipole-dipole interactions. Two dipolar atoms (or molecules) can, next to attracting or repelling each other, exchange state – and transfer energy – through dipole-dipole interaction. This resonant energy transfer is sometimes called Förster Resonance Energy Transfer (FRET) [47], which occurs for example between molecules in biological systems [95, 39, 28, 59]. Dipole-dipole interaction can also occur between magnetic dipoles [55], but here we limit ourselves to electric dipoles.

For two atomic dipoles, schematically depicted in figure 2.4, we can construct the Hamiltonian from all six Coulomb interactions between both electrons and both cores. We assume that the distance between the cores $R$ is much larger than both distances from the core to its electron, $r_1$ and $r_2$, and the cores are fixed in space

$$H = H_A + H_B + V_{dd},$$

$$V_{dd} = \frac{1}{R} - \frac{1}{|R + r_B|} - \frac{1}{|R - r_A|} + \frac{1}{|R + r_B - r_A|} \approx \frac{r_A \cdot r_B - 3(r_A \cdot \hat{R})(r_B \cdot \hat{R})}{R^3},$$

(2.39)

where the Coulomb interactions between the core and its electron are contained in $H_A$ and $H_B$ and the interaction between the atoms is contained in $V_{dd}$, the dipole-dipole interaction potential.

![Figure 2.4: Two atomic dipoles A and B schematically depicted as a red core, charge +1, and a blue electron.](image)

We use perturbation theory (subsection 2.3.2) to calculate the properties of the two atom system. The full quantum method would be to use the dipole-dipole interaction $V_{dd}$ as an operator, operating on the combined wavefunction of the two atoms and the matrix elements of the perturbation would be $\langle \psi'_A, \psi'_B | V_{dd} | \psi_A, \psi_B \rangle$. This method is described in [81] and can take into account multi-body interactions. Here we describe a simpler, semi-classical method, providing a basic understanding of the dynamics. This simplification is well justified for the low densities we have. We use the operator $r$ to calculate the dipole
2.4 Dipole-dipole interactions between Rydberg atoms

matrix elements $\mu$ per atom

\[ \mu_A = \langle \psi_A' | r | \psi_A \rangle, \quad (2.40a) \]

\[ \mu_B = \langle \psi_B' | r | \psi_B \rangle. \quad (2.40b) \]

Then we calculate the dipole-dipole interaction with

\[ V_{dd} = \mu_A \cdot \mu_B - \frac{3(\mu_A \cdot \hat{R})(\mu_B \cdot \hat{R})}{R^3}. \quad (2.41) \]

So $V_{dd}$ is now simply a number, instead of an operator.

The $\mu$’s in equation 2.41 could be either permanent dipoles or transition dipoles; from first- respectively second-order perturbation theory (subsection 2.3.2). In other words, a dipole is a permanent dipole if $\psi'$ is equal to $\psi$ in equation 2.40, for different initial and final wavefunctions we have transition dipoles. Large permanent dipoles are for example the $k$-states in hydrogen – or the equivalent manifold states in heavier alkali’s.

In this thesis we will mainly deal with transition dipoles, which can be transitions between any two states with $\Delta \ell = \pm 1$. These transition dipoles can be interpreted as oscillating dipoles. The atom is in a coherent superposition of e.g. the s- and p-state and the sum of these wavefunctions will have a dipole moment, while the separate pure angular momentum states do not. Due to the energy- and therefore phase-difference between these wavefunctions, the dipole moment will change direction with a frequency corresponding to this energy difference. Two of these oscillating dipoles can just as well dipole-interact. For both the permanent dipole as well as the transition dipole, $\mu$ scales like $n^2$, which results in a scaling law for the dipole-dipole interaction: $V_{dd} \sim n^4/R^3$.

### 2.4.1 A suitable dipole-dipole transition

In this section we describe how we have chosen a suitable dipole-dipole transition to use in our experiments, which was critical for the success of this work. We wanted our dipoles to be strong enough to be able to work at large distances. At the same time, there are some practical limitations, which have to do with laser excitation and detection, but also we want to avoid other interfering processes. At the end of the section we will give some properties of the chosen states.

Our original idea to study dipole-dipole interactions in a position resolved manner was to make use of two states with a maximum permanent dipole, which would exchange state. Like the following

\[ 60 (k = -59) + 61 (k = -60) \leftrightarrow 61 (k = -60) + 60 (k = -59), \quad (2.42) \]

as is described in [81]. We could call the $n = 60$ state the $|0\rangle$ qubit and the $n = 61$ state the $|0\rangle$-qubit. In rubidium there is no such thing as a $k = -60$ or $k = -59$ state, but we can use the lowest manifold state. We can produce this state by exciting with the laser to the $d$-state and subsequently ramping the electric field to just beneath the Inglis-Teller limit (see figure 2.2 and equation 2.35). To measure a process like this a position resolved detection system is needed. We have developed such a detection method (chapter 4), but
it is unfortunately not as easy to operate as we hoped. Secondly, we could not confirm that we were really producing the lowest manifold state.

We have chosen a different approach, which involves four different states, such that it does not need the position resolved detection technique.

\[ n_1 \ell_1 + n_2 \ell_2 \leftrightarrow n_3 \ell_3 + n_4 \ell_4. \]

(2.43)

Now we can probe the interaction by just using state-selective field ionization (SFI), which can distinguish the four states. A process like \( n_1 d + n_2 d \rightarrow n_3 p + n_4 m \), comparable to the measurement described in subsection 2.3.4, is not practical, because there are so many resonances. Furthermore, the processes from equation 2.37 between two \( nd \) atoms of the same kind occur, which severely disturbs the signal. For this reason, we search for interactions between \( s-, p- \) and \( d-\) states only.

One possible candidate is the transition \( 25s + 33s \leftrightarrow 24p + 34p \), as investigated in [7], with an interaction strength of \( V_{dd} \approx 1.5 \text{ kHz} \) at \( 20 \mu\text{m} \). However, we prefer a stronger interaction, enabling us to work at larger distances, which will be achieved if \( n \) is increased (\( V_{dd} \approx n^4/R^3 \)). Up to \( n = 50 \) we can clearly distinguish subsequent \( n \)-states using SFI. We considered transitions between \( n = 40 \) and \( 50 \) that had the smallest energy difference at zero field (the energy difference between the left- and right hand side of equation 2.43). Secondly we have to check if there existed an actual resonance for the transition and if the transition dipole moments were large enough.

In rubidium, the process \( 41d + 49s \leftrightarrow 42p + 49p \) seemed most suitable. Note that this type of transition can still be written in the form of two qubits, just as for the transition of equation 2.42, despite the fact that there are now four states involved. Atom A starts in the \( 41d \) state, or the \( |1\rangle \) state and changes to the lower lying \( 42p \) state, the \( |0\rangle \) state, while atom B starts in \( 49s \), \( |0\rangle \), and is excited to \( 49p \), \( |1\rangle \). The fact that \( |0\rangle \) and \( |1\rangle \) have a different meaning for each atom is not important, as long as the energy difference is equal. In figure 2.5 we have depicted the difference energies for the transitions of both atoms.
2.4 Dipole-dipole interactions between Rydberg atoms

Figure 2.6: The two-atom energy levels of the $|41d, 49s\rangle$ and $|42p, 49p\rangle$ system. The red line depicts the $|42p_{3/2}, 49p_{3/2}\rangle$ state, where we use the quantum numbers $n\ell jm$. Green is $|42p_{1/2}, 49p_{1/2}\rangle$. The blue solid line represents the $|41d_{3/2}, 49s_{1/2}\rangle$ state and the blue dashed line is the $|41d_{3/2}, 49s_{1/2}\rangle$ state. The last one is not excited by the laser in our experiment and therefore does not play a role. The inset shows the avoided crossings due to the dipole-dipole coupling between the atoms, zoomed in around the two relevant resonances $F_1$ and $F_2$.

Around 0.4 V/cm there is a group of four resonances. The specific transition including the quantum number $j$ for these resonances is

$$41d_{3/2} + 49s_{1/2} \leftrightarrow 42p_{1/2} + 49p_{3/2}. \quad (2.44)$$

In figure 2.6 we zoomed in around these resonances and in this case we depicted the sum of the binding energies of the two atoms, either in the $|41d_{3/2}, 49s_{1/2}\rangle$ state or the $|42p_{1/2}, 49p_{3/2}\rangle$ state. Both states split up in two, for the different $|m_j\rangle$ values. However, the initial state that is excited by the laser is only the $|41d_{3/2}, 49s_{1/2}\rangle$ state (the quantum numbers here are $n\ell jm$). This is because the laser is linearly polarized and we have $\Delta m_j = 0$ starting for both atoms from the $|5s_{1/2}\rangle$ state. Therefore we have in the experiment only two resonances that play a role; they occur at fields of $F_1 = 0.3807$ V/cm and $F_2 = 0.4112$ V/cm.

All involved states have a purely quadratic Stark shift. We fitted the energy levels from the Stark map with a parabola and obtained all polarizabilities $\alpha$ (see Eq. 2.27). The fact that energy levels shift in a field means that they are not pure $\ell$ states anymore, but they are mixed states. The amplitudes of the states that are mixed-in can be read off in the eigenstates when diagonalizing the Hamiltonian for the Stark map. At 0.4 V/cm the mixing is still very small, all involved states still have an population of 0.998 or higher in the original $\ell$ state. This mixing in of other states also leads to a permanent dipole moment, which is equal to the slope of the line in the Stark map. We have summarized
Table 2.4: The polarizability $\alpha$ of each involved state and the permanent dipole moment $\mu_{\text{perm}}$ at 0.4 V/cm (both in MHz/(V/cm) as well as atomic units) for all relevant states of the process given in Eq. 2.44. These values $\mu_{\text{perm}}$ are in fact the local derivative of the binding energy, or the slope in figure 2.6, i.e. $\mu_{\text{perm}} = 2\alpha F$. The indices in the first column refer to $j$ and $|m_j|$.

both the polarizability as well as the permanent dipole moment at 0.4 V/cm in table 2.4. The resulting permanent dipole moments are not very large, at least, compared to the transition dipole moments, which we will give below. We assume we can ignore effects due to the permanent dipole moment.

Table 2.5: The size and the polarization of the various transition dipole moments $\mu_{\text{tr}}$ in the process 2.44 and the resonance where the transition occurs. Note that here the sign of $m_j$ does matter, so the indices refer now to $j$ and $m_j$. We have given only initial $m_j$ values of 1/2; the initial $m_j$ values of -1/2 give equivalent values for the transition dipole moments. The errors are an estimate of the accuracy, based on the difference between the analytical and the numerical calculation.

The transition dipole moments are calculated with the numerical and the analytical method described in subsection 2.2.4. The results are given in table 2.5. Both dipoles are of the order of 1000 a.u., equal to ~2500 D (debye). These numbers are enormous when compared to ground-state molecules or atoms; also, they are an order of magnitude larger than for the 25s+33s interaction, where we have dipole moments of only ~60 and ~200 a.u. Secondly, note that the error of the calculation, i.e. half the difference between the numerical and the analytical method, is only 0.3%. If we calculate the dipole-dipole interaction strength (Eq. 2.41) for both transitions linearly polarized and both dipoles parallel to the distance vector $R$ we get $V_{\text{dd}} = 2\pi 35$ kHz for a distance of 40 $\mu$m. This means that the energy is transferred from one atom to the other and back in 14.5 $\mu$s, in other words the Rabi oscillation period of each atom is 14.5 $\mu$s. The radiation that drives the Rabi oscillation is a photon which is emitted by the 41d atom and absorbed by the 49s atom. The photon energy can be read off from figure 2.5: 1.1 cm$^{-1}$, corresponding to a wavelength of $\lambda = 0.91$ cm and a frequency of 32.8 GHz. This wavelength is much larger than the typical separation between the atoms, tens of microns, so it is a near-field interaction.
The energy transfer period of 14.5 $\mu$s is shorter than the natural lifetime of the states as well as the black-body transition lifetime (see subsection 3.4.3). This leads to the conclusion that the interaction is strong enough for this particular transition, even at the enormous distance of 40 $\mu$m; which is a distance we should be able to control and measure.

2.5 Simulations

In order to understand what would happen in the experimental setup and to tune the experimental parameters for observable results, we have performed several simulations. We will start with a simple 2-body calculation in subsection 2.5.1. We will compare two situations, namely one, where both particles are fixed in space, and the other, where again both particles are fixed in space, but one on a random location within a cigar-shaped ellipsoid at some distance $d$ from the other particle. The latter, averaged over lots of realizations, should represent the real experiment we are doing. In some limiting cases, the calculation can be done analytically.

In subsection 2.5.2 we describe a many-body simulation with one atom in state A among many atoms in state B, where the atoms are either arranged in a random way, like a “frozen” gas or in an ordered way, like a crystal. The calculations predict a localization effect for the randomly organized system. Unfortunately we have no experimental verification of the effect.

2.5.1 Dipoles distributed over long cylinders

In general a coupled two-level system can be described by the Hamiltonian

$$H = \begin{pmatrix} -\frac{\delta}{2} & V \\ V & \frac{\delta}{2} \end{pmatrix},$$

(2.45)

where $V$ is the interaction between the unperturbed states and $\delta$ is the unperturbed energy difference between the two states. The detuning $\delta$, for example, vary as a function of field. If we diagonalize $H$ we obtain for the eigenenergies an avoided crossing at $\delta=0$ with a width $2V$. The amplitude of both states evolve in time as follows

$$\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \left( \begin{pmatrix} c_1(0) \\ c_2(0) \end{pmatrix} e^{-iE_t/\hbar} \right) \Psi,$$

(2.46)

where $\Psi$ is the matrix containing the eigenvectors of $H$ and $E$ is the vector containing the eigenvalues of $H$. Starting with 100% probability in the first state the probability of the second state becomes

$$P_2(t) = |c_2(t)|^2 = \frac{4V^2}{4V^2 + \delta^2} \sin^2 \left( \frac{1}{2} \sqrt{4V^2 + \delta^2} t \right)$$

(2.47)

and $P_1(t) = 1 - P_2(t)$. This oscillation of the probability is called a Rabi oscillation.
In our experiments the two states are the two two-atom states \(|41d, 49s\rangle\) and \(|42p, 49p\rangle\) or \(|ds\rangle\) and \(|pp'\rangle\) for short. \(V\) is the dipole-dipole interaction. For two single atoms the dipole-dipole interaction is (see also Eq. 2.41)

\[ V = \gamma \frac{\mu_A \mu_B}{R^3}, \tag{2.48} \]

where \(\mu_A\) and \(\mu_B\) are the transition dipole strengths \(|\langle 42p| r |41d\rangle|\) and \(|\langle 49p| r |49s\rangle|\) and \(\gamma\) is a factor between -2 and 1, determined by the angles between the dipoles and the distance vector \(R\) between the atoms. At resonance \((\delta = 0)\) the \(|pp'\rangle\) probability becomes

\[ P_{pp'} = \sin \left( \frac{\gamma \mu_A \mu_B}{R^3} t \right)^2 \approx \gamma^2 \mu_A^2 \mu_B^2 \frac{t^2}{R^6}, \tag{2.49} \]

where the approximation is valid for small \(Vt\). So, for small \(Vt\), \(P_{pp'}\) scales with \(t^2/R^6\).

In the experiment multiple atoms are distributed over long cylinders. The way we calculate the \(|pp'\rangle\) probability of the system is by having one atom in a cylinder, with its center on \((x, y, z) = (0, d, 0)\) and one atom on position \((0, 0, 0)\). Interactions within one cylinder could play a role, but here we do not take them into account. We use for the dipole-dipole interaction

\[ V = \gamma(x, y, z) \frac{\mu_A \mu_B}{(x^2 + (y + d)^2 + z^2)^{3/2}}, \tag{2.50} \]

where \(\gamma(x, y, z)\) contains the angular dependence. The cylinder is oriented along the \(z\)-axis with line density \(\lambda\) and radius \(\rho\). We can integrate the short-time probability \(P_{pp'} = V^2 t^2\) to get the total probability \(P_{\text{cycl}}\) for the system. In reality the cylinders are about 500 \(\mu m\) long and have a radius of about 8 \(\mu m\). The distance \(d\) between the cylinders is typically varied from 0 to 80 \(\mu m\). Therefore, using infinitely long cylinders is well justified, but the radius of the cylinders should be taken into account. In cylinder coordinates we get

\[ P_{\text{cycl}} = \frac{\lambda \mu_A^2 \mu_B^2}{\pi \rho^2} \int_{-\infty}^{\infty} \int_{-\pi}^{\pi} \int_{0}^{\infty} \frac{\gamma(x, y, z)^2}{(r^2 \sin^2 \theta + (d + r \cos \theta)^2 + z^2)^3} r \, dr \, d\theta \, dz \]

\[ = \frac{\lambda \mu_A^2 \mu_B^2}{d^3} \gamma'(\eta)^2 \frac{(\eta - 1)^2 K \left( \frac{4\eta}{(\eta+1)} \right) - \left( 7\eta^2 + 1 \right) E \left( \frac{4\eta}{(\eta+1)} \right)}{12 (\eta - 1)^3 (\eta + \eta^2)^2} r^2, \tag{2.51} \]

where we have replaced \(\rho/d\) with \(\eta\) and \(\gamma'(\eta)\) is now the angular dependence factor. \(K(m)\) and \(E(m)\) are the complete elliptic integrals of the first and second kind. We do not know what \(\gamma'(\eta)\) is, but for \(\eta \to 0\) we can do the integration that does include the angular dependence. For dipoles oriented in the \(y\)-direction we have

\[ P_{\text{lin}} = \lambda \mu_A^2 \mu_B^2 \int_{-\infty}^{\infty} \frac{1 - 3d^2/(d^2 + z^2)^2}{(d^2 + z^2)^3} r^2 \, dz = \frac{123 \pi}{128} \frac{\lambda \mu_A^2 \mu_B^2}{d^3} r^2, \tag{2.52} \]

which means that \(|\gamma'(0)| \approx 1.6\) for dipoles in the \(y\)-direction. So for interaction between atoms on lines, the probability scales like \(r^2/d^3\) for small \(Vt\). So this probability drops
not as strongly with the distance as for the case of two point particles, where we have \( P \sim t^2/R^6 \).

For a calculation of the \(|pp'\rangle\) probability for large \( Vt \), the behavior becomes oscillatory and analytical integrations are no longer possible; we need to perform numerical simulations of the system. For this we used a three-state system, equivalent with the \( 49s+41d\rightarrow 49p+42p \) system, with two avoided crossings 4 MHz apart (see Fig. 2.6). In figures 2.7, 2.8 and 2.9 we compared the cylinder configuration to a simple two particle system.

![Figure 2.7](image)

**Figure 2.7:** a) The excited state probability as a function of detuning for one point particle and one particle distributed over a cylinder at 20 \( \mu m \) distance. The red line is a sum of two Lorentzians with width 2\( V \), but for the calculation of \( V \) we used a distance of 25 \( \mu m \). b) The same for two particles at 20 \( \mu m \) distance. The red Lorentzian here is plotted for 20 \( \mu m \).

We randomly placed one particle in an elongated ellipsoid, Gaussian in 3D with a half length of 200 \( \mu m \) and a radius of 8 \( \mu m \) (both numbers are \( 1/\sqrt{e} \) half widths or \( \sigma \)) at some distance of a probe particle. For the interaction strength we used equation 2.50 with \( \gamma(x, y, z)\mu_A\mu_B = 4000 \text{ MHz} \cdot \mu m^3 \). We evaluated the \(|pp'\rangle\) probability by diagonalizing the Hamiltonian for 10000 random cases.

For the first simulation we had the probe particle at 20 \( \mu m \) distance from the elongated ellipsoid and we determined the average \(|pp'\rangle\) probability after 10 \( \mu s \) for various detunings (e.g. various static field values). We multiplied the total probability by 3 because this gives a more realistic picture; this is justified because in the real experiment there are a few tens of atoms in each volume instead of one (however the probability does not scale linearly with the density). The result is shown in figure 2.7a. We also performed the same calculation for two particles at a fixed distance of 20 \( \mu m \), shown in figure 2.7b. Here we observe an oscillating function underneath a Lorentzian envelope with a half width of \( 2V=2 \times 4000/20^3 \text{ MHz} \), as is expected from equation 2.47. In figure 2.7a the oscillations are almost averaged out, because of all the different occurring distances and therefore different interaction strengths. Surprisingly, the oscillations have not disappeared completely. Another difference is that the Lorentzian envelope is narrower, we plotted here one with a width of \( 2 \times 4000/25^3 \text{ MHz} \). Apparently, due to the low filling of the cylinder, the effective distance is 25 \( \mu m \). This also gives rise to the lower probability of \( \sim 0.3 \) at resonance.
Figure 2.8: a) The excited state probability as a function of distance for one point particle and one particle distributed over a thin, long cylinder. In the inset of a) a log-log-plot of the data together with a a plot of equations 2.51 in green and 2.52 in red, showing that the simulation data indeed match the $d^{-5}$ scaling for large $d$. b) The excited state probability as a function of distance for two particles.

The Lorentzian line shape can be deduced from equation 2.47. For varying $V$, the oscillations average out and a Lorentzian remains. For large $Vt$ – we call the transition saturated – $\sin^2$ averages to $\frac{1}{2}$ and we have

$$P_2 \approx \frac{1}{2} \frac{4V^2}{4V^2 + \delta^2}.$$  

(2.53)

This probability as a function of detuning resembles a peak with a height of $\frac{1}{2}$ and a half width of $2V$. In the case of small $Vt$ the equation becomes $P_2 \approx V^2t^2 \text{sinc}^2 \frac{1}{2} \delta t$; this is roughly similar to the Lorentzian shape

$$P_2 \approx \frac{4}{4 + \delta^2 t^2} V^2 t^2.$$  

(2.54)

This peak has a half width of $2/t$ and a height of $V^2 t^2$.

For figure 2.8a and 2.8b we kept the detuning at one of the resonances and varied the distance between the probe particle and the cylinder resp. the other particle. The $|pp'\rangle$ probability is plotted after 10 $\mu$s. In figure 2.8a we multiplied the probability by 3. Again we see oscillations in figure 2.8b. In the center it is actually oscillating very rapidly, which is why we have left the center part out. In figure 2.8a the oscillations seem to have damped out completely. In the inset in figure 2.8a we made a comparison to the simplifications 2.52 and 2.51, which both fit quite well for larger distances.

In figure 2.9 we depicted the evolution of the $|pp'\rangle$ probability at resonance for several distances. Again for a particle and a cylinder (a), where we multiplied the probability with 3 and for just two particles (b). Also here the oscillations are not visible for the case of the cylinder. For large distances or short times the quadratic behavior of the probability is visible. If we wouldn’t have multiplied with three, the simulated probabilities all go to 0.5 for infinite times as expected. In the inset of figure 2.9a we depicted a double logarithmic plot of the transfer rate $1/\tau$, defined as $P(\tau) = 0.05$, again together with equations 2.52 and 2.51, showing that the $d^{-5/2}$ scaling of this parameter indeed fits.
2.5 Simulations

Figure 2.9: a) The excited state probability as a function of time for one point particle and one ellipsoid of particles at a distance of 20 (red), 30 (green), 40 (blue), 50 (orange), 60 (purple), 70 (black) and 80 µm (brown). In b) the same for two particles at the same range of distances. In the inset of a) a log-log-plot the rate $1/\tau$, defined as $P(\tau) = 0.05$, i.e. the dotted line in the main figure, together with a plot of equations 2.51 (green) and 2.52 (red).

Despite the fact that we used a strongly simplified calculation we could still predict the behavior of our system quite well. Qualitatively, but also quantitatively the calculations are not far off from the experimental data presented in chapter 5. Moreover, these simple calculations, especially the ones in analytical form gives us an intuitive understanding of the system. It appears that, for particles distributed over two cylinders oscillations will not appear in the experimental data, because each pair will have a different interaction strength, and hence a different oscillation frequency. Therefore it is not directly possible to measure if the interactions are coherent or not. In chapter 5 results of more extensive simulations are depicted, performed by J. V. Hernández and F. Robicheaux. Here the angular dependence, as well as many body interactions are taken into account.

2.5.2 Frustrated diffusion

In this section we study the difference between a random organization of dipoles compared to a lattice-like organization in the propagation of an excitation by dipole-dipole interaction. We placed one atom in the excited state (e.g. the 41d state) in the center of a 100 µm cube and 124 lower state atoms (e.g. in the 49s state) around it. In one case the 124 lower state atoms are distributed randomly, while in the other case they are distributed in a lattice with unit cell of 20 µm. The excited state can diffuse now over the cube through dipole-dipole interaction.

The system consists of 125 different basis states, namely the excited atom being one of the 125 atoms. All states have the same unperturbed energy and two of such states are coupled through the dipole-dipole interaction between the two atoms that exchange the excitation. We diagonalize the Hamiltonian and calculate the evolution of the system in time, as like equation 2.46 (in this case we have amplitudes $c_1, c_2, \ldots, c_{125}$). In figure 2.10 we depicted the excited state probability versus position $z$ (the direction of the dipoles), averaged over times between $t = 40–110 \mu$s, to eliminate the oscillations. For the case of
Theoretical background

**Figure 2.10:** The diffusion of an excited state in a 3D-volume with atoms in a lower state. We compare two configurations, which are illustrated on the right hand side, a random organization of atoms in blue and an ordered or lattice-like organization in red. The green filled circle represents the atom that is in the excited state at \( t = 0 \). In the main figure, the blue line depicts the excited state probability in the \( z \)-direction for the randomly organized situation, the red line is for the case of the ordered situation. Note that the vertical scale is logarithmic.

In the random gas the probability is averaged over 1000 realizations.

**Figure 2.11:** The excited state probability as a function of time for the particles arranged on a 20×40 µm rectangle as depicted in the inset. In figure a) one particle is missing and the excited state probability is only weakly transferred to the green particle on the right hand side. In figure b) the excitation is transferred to the right hand side, due to the more regular structure of the arrangement of the particles.

In the ordered lattice case the excited state diffuses virtually homogeneously over the whole cube, with a bit more probability in the center. In the randomly distributed case however, the excited state is strongly localized in the center. This is due to the fact that the energy transfer is dipole-blockaded: atoms at small distances are shifted in energy and can not resonantly transfer energy to further lying atoms.

This effect is more clearly illustrated in figures 2.11a and 2.11b. Here a similar simulation is performed with only a few atoms in a 20×40 µm rectangle. The excited state starts on the atom in the lower left corner (depicted in red). In the three-atom case the
energy is hardly transferred to the atom on the right hand side. This is because the two atoms on the left hand side have shifted energy levels due to the strong dipole-dipole interaction. This makes the interaction with the right-hand side particle no longer resonant and blockade occurs. In the four atom case, figure b, the excited state does reach the right hand side of the rectangle, because on the right hand side the energy levels are just as much shifted as on the left side, making the transfer resonant again. In a randomly distributed gas asymmetric situations like the three atom configuration in figure 2.11a occur very often, resulting in a localization of the excitation in the area where it started.

This blockade effect can actually be used when just one atom per volume is desired. If the volumes are small enough and the laser power is tuned such that it excites 0, 1 or 2 atoms per volume, e.g. like a Poisson distribution, then only in the 1 atom per volume case the dipole-dipole interaction signal between the volumes is significant. When there is more than one atom per volume, the interaction within a volume induces a level shift, making the interaction between volumes non-resonant. The term ”dipole blockade” is mainly used for the effect that with a narrow bandwidth laser the number of excited Rydberg atoms in a certain volume is limited. In this case the ground state atoms that surround one Rydberg atom can no longer be excited, because this Rydberg atom shifts the Rydberg levels of the other atoms due to the dipole-dipole interaction. This makes the laser excitation no longer resonant.

The fact that no diffusion occurs in a randomly ordered system is rather interesting and unexpected and is a similar effect as Anderson localization [5]. In [70] the claim is made that diffusion does occur, but it is not mentioned how far it extends. Secondly, the transition the authors use is essentially different – a three-state system like $ns + ns \rightarrow np + (n-1)p$. In our experiments we have not been able to proof this localization effect.

2.6 Summary

We have presented two methods to calculate the Rydberg wavefunctions, a numerical and an analytical method. There are only small differences between the results of both methods, assuring us that both type of calculations are accurate enough for our purposes. The wavefunctions form the basis for the calculation of e.g. the Stark shift or the (transition) dipole moments. The structure of the Stark map is demonstrated in a measurement of dipole-dipole interaction resonances. We used the Stark map calculation and the calculation of the transition dipole moments to find a suitable resonant dipole-dipole transition for the experiments in this thesis. We have chosen the transition $41d + 49s \leftrightarrow 42p + 49p$ which is resonant at a field of only ~0.4 V/cm. The relevant transition dipole moments are of the order of ~1000 a.u., resulting in a Rabi oscillation period of 14.5 µs for a distance of 40 µm. Simulations of dipole interacting atoms distributed over elongated volumes provide us insight in their behavior in a realistic experimental setup. It appears that for dipoles distributed over two thin parallel lines separated by the distance $d$, the short-time transition probability scales like $P \propto \hat{r}^2/d^6$. A simulation of excitation diffusion through dipole-dipole interaction shows a localization effect for randomly organized systems, due to the dipole blockade effect.