Rubidium Rydberg macrodimers

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Abstract

We explore long-range interactions between two atoms excited into high principal quantum number \( n \) Rydberg states, and present calculated potential energy curves for various symmetries of doubly excited \( ns \) and \( np \) rubidium atoms. We show that the potential curves for these symmetries exhibit deep (\( \sim \) GHz) potential wells, which can support very extended (\( \sim \mu \text{m} \)) bound vibrational states (macrodimers). We present \( n \)-scaling relations for both the depth \( D_g \) of the wells and the equilibrium separations \( R_e \) of these macrodimers, and explore their response to small electric fields and stability with respect to predissociation. Finally, we present a scheme to form and study these macrodimers via photoassociation, and show how one can probe the various \( \ell \)-character of the potential wells.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Rydberg atoms have long been studied because of their peculiar properties such as long lifetimes, large cross sections and very large polarizabilities [1]. These exaggerated properties lead to strong interactions between the Rydberg atoms, which have been experimentally detected in recent years [2, 3]. Such strong Rydberg–Rydberg interactions have fueled growing interest in the field of quantum computing, and over the past decade, their application for quantum information processing, such as fast quantum gates [4, 5] or quantum random walks [6], has been proposed. Also of particular interest is the excitation blockade effect [7], where one Rydberg atom actually prevents the excitation of other nearby atoms in an ultracold sample [8–12]. This phenomenon was recently observed in microtraps [13, 14] and a C-NOT gate was implemented using the behaviour [15].

Another active area of research with Rydberg atoms is the predicted existence of long-range ‘exotic molecules’. In one scenario, one atom remains in its ground state, while another atom is excited to a Rydberg state. The most famous examples of this type of interaction are the trilobite and butterfly states, so-called because of the resemblance of their respective wavefunctions to these creatures. The theoretical framework for such interactions was first proposed in [16], but were not observed until more recently in [17]. The second type of long-range interaction is predicted to occur when both atoms are excited to Rydberg atoms. In [18], it was first predicted that weakly bound macrodimers could be formed from the induced van der Waals interactions of two such excited atoms. However, more recent work [19] has shown that larger, more stable macrodimers can be formed from the strong mixing between \( \ell \)-characters of various Rydberg states. Recent measurements have shown signatures of such macrodimers in spectra of cesium Rydberg samples [20].

In this paper, we present long-range potential energy curves corresponding to the interaction between pairs of rubidium atoms excited to \( ns \) and \( np \) Rydberg states. In general, Rydberg–Rydberg interactions will only mix states that share the same molecular symmetry [21, 22]. Thus, only common symmetries between the excited Rydberg molecular state and the state to which it is most strongly coupled are relevant. For rubidium, the doubly excited \( ns \) atom pair is most strongly coupled to the \( np + (n+1)p \) asymptote, while the doubly excited \( np \) atom pair is most strongly coupled to the \( ns + (n+1)s \) asymptote. Since all \( ss' \) states have \( m_j = \pm \frac{1}{2} \), the only common symmetries with any \( pp' \) state are \( \Omega \equiv |m_{j_1} + m_{j_2}| = 0, 1 \). In this manner, we find that the relevant symmetries for the doubly excited \( ns \) and \( np \) asymptotes are \( 0^+ \), \( 0^- \) and \( 1^- \). We analyse all three cases for both pairs and show that potential wells exist for all of them. We also describe in detail properties of the bound levels within each well.

The paper is organized as follows: in section 2, we review how to build the basis states used to compute the potential energy curves at long range, and describe the existence of potential wells for certain asymptotes. In section 3, we investigate the effects of small external electric fields on the
potential curves, and in section 4, we discuss the scaling of the wells with principal quantum number \( n \). Finally, in section 5, we calculate bound levels supported in those wells, and estimate their lifetimes. We also outline how photoassociation could be used to form and probe macromolecules. This is followed by the concluding remarks in section 6.

2. Molecular curves

2.1. Basis curves

In this section, we review the general theory for calculating the interaction potential curves. These curves are calculated by diagonalizing the interaction Hamiltonian in the Hund’s case (c) basis set, which is appropriate when the spin–orbit coupling becomes significant and the fine structure cannot be ignored, as is the case here.

We first consider two free Rydberg atoms in states \( |a⟩ \equiv |n, \ell, j, m⟩ \) and \( |a'⟩ \equiv |n', \ell', j', m'⟩ \), where \( n \) is the principal quantum number, \( \ell \) the orbital angular momentum and \( m \) the projection of the total angular momentum \( \vec{j} = \vec{\ell} + \vec{s} \) onto a quantization axis (chosen in the \( z \)-direction for convenience). The long-range Hund’s case (c) basis states are constructed as follows:

\[
|a; a'; Ω⟩_{g,u}/|0⟩_{g,u}/ \sim |a⟩_{1}|a⟩_{2} - p(−1)^{ℓ+ℓ'}|a'⟩_{1}|a⟩_{2},
\]

where \( Ω = m + m' \) is the projection of the total angular momentum on the molecular axis and is conserved. The quantum number \( p \) describes the symmetry property under inversion and is \( 1(−1) \) for \( g (u) \) states.

For \( Ω = 0 \), we need to additionally account for the reflection through a plane containing the internuclear axis. Such a reflection will either leave the wavefunction unaffected or it will change the sign of the wavefunction. We distinguish between symmetric and antisymmetric states under the reflection operator \( \hat{σ}_z \) as follows:

\[
|0^±⟩_{g,u}/ = \frac{1 ± \hat{σ}_z}{\sqrt{2}}|0⟩_{g,u}/,
\]

where \( \hat{σ}_z \) behaves according to the following rules \[ 23, 24 \]:

\[
\hat{σ}_z|L⟩ = (−1)^{L} |L⟩ - \Lambda
\]

\[
\hat{σ}_z|S, M⟩ = (−1)^{S−M} |S, −M⟩.
\]

2.2. Long-range interactions

The interaction matrix we consider consists of both the long-range Rydberg–Rydberg interaction and the atomic fine structure. Here, ‘long-range’ refers to the case where no electron exchange takes place, i.e. the electronic clouds about both nuclei do not overlap. This occurs when the distance \( R \) between the two nuclei is greater than the LeRoy radius \[ 26 \]:

\[
R_{LR} = 2 |⟨n_1ε_1|r^2|n_1ε_1⟩|^{1/2} + |⟨n_2ε_2|r^2|n_2ε_2⟩|^{1/2} |.
\]

When the distance between the two atoms is larger than \( R_{LR} \), the interaction between them is described by the residual Coulomb potential between two non-overlapping charge distributions \[ 27 \], which can be truncated to give only the dipole–dipole (\( V_d \)) and quadrupole–quadrupole (\( V_q \)) terms. For two atoms lying along the \( z \)-axis, the \( V_d \) and \( V_q \) terms can be simplified to give \[ 28 \]:

\[
V_L(R) = −(−1)^{ℓ} 2\pi e^4 |r|^2 \sum_{m} B_{L}^{m} Y_{L}^{m} (\hat{r}_1) Y_{L}^{−m} (\hat{r}_2).
\]

Here, \( L = 1 (2) \) for dipolar (quadrupolar) interactions, \( B_{L}^{m} \equiv Ω^{L−m} \) is the binomial coefficient, \( \hat{r}_i \) is the position of electron \( i \) from its centre, and \( \hat{L} = 2L + 1 \).

Because the molecular basis states are linear combinations of the atomic states determined through symmetry considerations, each matrix element will actually be a sum of multiple interactions, i.e.

\[
⟨a; a'; Ω⟩_{g,u}/|V_L|b; b'; Ω⟩_{g,u}/ = ⟨a|a'|V_L|b⟩|b⟩ - p_a(−1)^{ℓ+ℓ'}|a⟩|V_L|b⟩|b⟩ - p_b(−1)^{ℓ+ℓ'}⟨a|a'|V_L|b⟩|b⟩ + p_a p_b(−1)^{ℓ+ℓ'}⟨a|a'|V_L|b⟩|b⟩,
\]

where \( |a; a'⟩ \equiv |a⟩|a⟩_{2} \) and so on. An analytical expression for the long-range interactions is obtained using angular momentum algebra in terms of \( 3j \) and \( 6j \) symbols:

\[
\langle 1; 2|V_L(R)|3; 4 \rangle = (−1)^{L−1} 2\pi e^4 |r|^2 \sum_{M} B_{L}^{m} Y_{L}^{m} (\hat{r}_1) Y_{L}^{−m} (\hat{r}_2)\frac{R_{L2}^{L} R_{L4}^{L}}{R_{L2}^{L+1}}.
\]

References \[ 22 \] and \[ 25 \] give the technical details for determining which states comprise the basis of the \( np + np \) rubidium asymptote. Although the procedure to find the basis states for different molecular asymptotes, such as \( ns + ns \), \( np + np \), or \( nd + nd \), is the same, the states making up these basis sets, in general, will be different. We do not review the procedure for building the basis sets here, but we note that all relevant (i.e. strongly coupled) molecular asymptotes within the vicinity of the asymptotic doubly excited Rydberg state being considered are included in each respective basis set. We again note here that because doubly excited \( ns (np) \) rubidium atoms are most strongly coupled to \( pp' (ss') \) states and because only common symmetries of such Rydberg states are allowed to mix, the relevant symmetries for the \( ns + ns \) and \( np + np \) asymptotic Rydberg states that we consider are \( P'_{s} \), \( 0'_s \) and \( 1_s \). As an example, table 1 lists the basis set for the \( 0'_s \) symmetry near the Rb 70p + 70p molecular asymptote.
with $E_i$ given by $-\frac{1}{2n_i^2 - \delta_i^2}$, where $n_i$ is the principal quantum number and $\delta_i$ is the quantum defect (values given in [29] and [30]). Since $\Delta \ell = 0$ dipole transitions are forbidden, only the $L = 2$ term of equation (8) will contribute in (9).

Figure 1 shows the results of diagonalization for the $0^+_g$, $0^-_u$ and $1^-_u$ symmetries of the $70s + 70s$ and $70p + 70p$ asymptotes with no background electric field. In all of these plots, the energies are measured from the ionization threshold of rubidium. We see that all three symmetries feature large potential wells and for the remainder of this paper, we focus our attention on the formation properties of bound states within these wells and analyse the stability of these macrodimers. We note here that we also explored the potential curves near the $nd + nd$ asymptotes, but no wells were found; hence, we do not display those curves here.

### 3. Electric field dependence

Production and/or detection of macrodimers will rely on external electric fields. In addition, since experiments cannot completely shield the atoms from undesired stray fields, it is important to study their effect on our calculated curves.

Strictly speaking, applying an external electric field $\vec{F}$ breaks the $D_{\infty h}$ symmetry of homonuclear dimers, and consequently, the basis states defined by (1) would no longer be valid. In principle, one then needs to diagonalize the interaction matrix in a basis set containing every possible Stark state, as was done in [31]. However, since the effects of such an electric field should be adiabatic, we assume that the $D_{\infty h}$ symmetry is still approximately valid for small electric fields.

We consider the effects of such an electric field as a perturbation to the original Hamiltonian. In general, an applied electric field will define a quantization axis; the molecular axes of our macrodimers will then be at some random angle to this quantization axis. In that case, one needs to transform the molecular-fixed frame back into the laboratory-fixed frame [32]. To simplify our calculations, we assume that the two Rydberg atoms are first confined in an optical lattice, such that the quantization axes of the macrodimer and the electric field coincide (see figure 2). Such one-dimensional optical lattices have already been used to experimentally excite Rydberg atoms from small Bose–Einstein condensates located at individual sites [33]. We envision a similar one-dimensional optical lattice with the distance between adjacent (or subsequent) sites adjusted to
Table 1. Asymptotic $0^1_s$ molecular states included in the Rb $70p + 70p$ basis set, which diagonalize the interaction Hamiltonian (see the text). The basis states have been symmetrized with respect to the reflection operator (2) and each $|a_i; a_2; 0_j\rangle$ state is defined by equation (1).

\[
\begin{align*}
|a_1; a_2\rangle &= \sum_i b_{i,1}(F)|a_i; a_2\rangle, \\
|a_1; a_2\rangle &= \sum_{ij} b_{1,i}(F)b_{2,j}(F)|a_{i1}; a_{i2}\rangle.
\end{align*}
\]

We then use this basis to redefine the properly symmetrized dressed molecular basis given in table 1 and to diagonalize the Rydberg–Rydberg interaction matrix.

In figure 4, we illustrate the effect of $F$ on the curves near $70p + 70p$ of the $0^1_s$ symmetry in a side-by-side comparison of the curves for $F = 0$ and $0.3 \text{ V cm}^{-1}$.

Figure 3. Atomic Rydberg energies versus the electric field for Rb with $|n1\rangle = 0$ near $n = 69$: the curves labelled by $n = 69$ include states with $\ell \geq 3$.

The atomic Stark states were computed using the method described in [18, 34] and the interaction curves for the 'pseudosymmetry' were obtained by diagonalization of the Rydberg–Rydberg interaction matrix in the dressed molecular basis set (11). We find some minor differences: the Stark effect is most notable in the shifting of the potential curves, especially the asymptotic energies. However, the relative shapes of the curves are only slightly changed and most importantly, the large potential well is robust against small electric fields.
Figure 4. $0^+_g$ molecular curves for Rb 70p + 70p: (a) $F = 0$ and (b) 0.3 V cm$^{-1}$. The states involved in the well correlated to 69s + 72s are identified (see section 5). The zero energy is set at the 70p$^{3/2}$ + 70p$^{3/2}$ asymptote in both plots.

Figure 5. (a) Isolated avoided crossing in the $0^−_u$ symmetry curves of doubly excited $ns$ atoms, which results in the potential well correlated to the 69p$^{1/2}$ + 70p$^{1/2}$ asymptote. We assume that the interactions at the crossing are mostly dipolar in nature (see the text) and label the well depth $D_e$ and the equilibrium separation $R_e$ at the avoided crossing. We also demonstrate that at long range the curves behave as $\sim 1/R^6$, but in the $R$-range of the avoided crossing, they behave as $\sim 1/R^3$. (b) Scaling relations for the well depth $D_e$ versus $n$ for the $0^−_u$ symmetry of $ns+ns$ (top) and $np+np$ (bottom). (c) Scaling relations for the equilibrium separation $R_e$ versus $n$ for the same curves as in (b).

4. Scaling

We focus our attention on the wells correlated to the $(n-1)s+(n+2)s$ asymptote near $np_{3/2} + np_{3/2}$, and those correlated to $(n-1)p_{1/2} + np_{1/2}$ near $ns + ns$ for $F = 0$. We calculated the curves for a large range of $n$ and found that the wells follow simple $n$-scaling behaviour (see figure 5). As will be discussed in section 5, the wells are produced by the mixing of several states with different $\ell$-character. The exact mixing takes place mainly via dipole and quadrupole interactions, and occurs between nearby $n$-states: hence the wells depend on the combination of the multipole interaction between states and the proximity (in energy) of those states.
To derive simple \( n \)-scaling behaviour for both the depth \( D_n \) and equilibrium separation \( R_n \), we assume that the dipole–
dipole coupling is the dominant interaction between states, and that the wells are formed as a result of an avoided
crossing between the two potential curves (see figure 5(a)). As mentioned above, the real situation is much more complex,
but these assumptions allow for a simple treatment.

The energy difference \( \Delta E_{\alpha\beta} = E_\alpha - E_\beta \) is defined by the
difference between the asymptotes of the two crossing states, \( \alpha \) and \( \beta \). Here, \( \alpha = n_\alpha s + n_\beta p \) with energy \( 2E_\alpha = -\left( v_{\alpha 3}^2 + v_{\beta 3}^2 \right) \),
and \( \beta = n_\beta p + n_\alpha s \) with energy \( 2E_\beta = -\left( v_{\beta 3}^2 + v_{\alpha 3}^2 \right) \). In both
energy terms, \( v_{\gamma i} = n_\gamma - \delta_\gamma \) includes the principal quantum number \( n \) and quantum defect \( \delta \) of the appropriate atomic state \( \gamma \) of atom \( i \). Assuming that the relevant atomic states in a
given asymptote are separated by \( \Delta n \) of the order unity, we can expand the energies as
\[
2E_\alpha = -2\frac{\Delta n_\alpha}{v_{\alpha 3}^3} \quad \text{and} \quad 2E_\beta = -2\frac{\Delta n_\beta}{v_{\beta 3}^3}, \tag{12}
\]
so that
\[
\Delta E_{\alpha\beta} \simeq \left[ \frac{\Delta n_\alpha}{v_{\alpha 3}^3} + \frac{\Delta n_\beta}{v_{\beta 3}^3} \right] \simeq \frac{\Delta n_\alpha}{v_{\alpha 3}^3} \left( 1 - \frac{\Delta n_\beta}{\Delta n_\alpha} \left( 1 - \frac{3\Delta n_\alpha}{v_{\alpha 3}} \right) \right),
\tag{13}
\]
where we assume \( v_{\gamma i} \simeq v_{\gamma 1} + \Delta v \) with \( \Delta v \) of order 1, and \( A = (\Delta n_\alpha - \Delta n_\beta) \) and \( B = 3\Delta v/\Delta n_\alpha \). In the cases leading
to our wells, \( \Delta n_\alpha \simeq \Delta n_\beta \) so that the leading dependence is
\( \Delta E_{\alpha\beta} \propto n^{-3/3} \).

From the sketch depicted in figure 5(a), assuming leading
dipole–dipole interactions, the equilibrium separation \( R_n \)
occursthe ‘intersection’ of two attractive and repulsive curves separated by \( \Delta E_{\alpha\beta} \), i.e. \( \Delta E_{\alpha\beta} \equiv C_\alpha/R_n^{3} \simeq +C_\beta/R_n^{3} \),
which lead to \( R_n \approx \left[ (C_\beta + C_\alpha)/\Delta E_{\alpha\beta} \right]^{1/3} \). Our assumption
that the two crossing curves behave as \( \sim 1/R^3 \) is valid in the
region of the intersection; at larger values of \( R \), however (\( R \gtrsim 80 000 \mu_0 \)), the curves behave more like \( \sim 1/R^6 \) (see figure 5).
From the scaling \( C_\alpha + C_\beta \propto n^4 \) and \( \Delta E_{\alpha\beta} \propto n^{-4} \), we obtain
\( R_n \propto n^{8/3} \). As for the dissociation energy \( D_n \), it is simply
given by \( \Delta E_{\alpha\beta} \equiv C_\alpha/R_n^{3} \approx D_n \) which scales as \( \Delta E_{\alpha\beta} \), i.e. \( D_n \propto n^{-4} \). Figure 5(b) shows a plot of \( D_n \) versus \( n \) for the \( 0^+ \)
symmetry of the \( ns + ns \) and \( np + np \) asymptotes, indicating that \( D_n \) indeed scales more like \( n^{-3} \) than purely \( n^{-4} \). For the same wells, figure 5(c) shows that \( R_n \) follows the predicted \( n^{8/3} \) scaling. In the interest of space, we do not show plots for all of the symmetries highlighted in figure 1, but we note that we find the same approximate scaling for all other symmetries.

Although the analytical derivations above give good
agreements with numerically determined values of \( D_n \) and \( R_n \),
the slight discrepancies, especially with the \( np + np \) plots,
reflect the more complex nature of the interactions. For example,
quadrupole coupling is present in our calculations
(although its effect is generally small). We also point out that
in the three \( np + np \) cases, the formation of each well is not
clearly given by an avoided crossing of two curves, but rather
by several interacting curves (see section 5). Nonetheless,
the good agreement depicted in figure 5 indicates that these more
complicated interactions act only as small corrections.

### Table 2. Energies of the six deepest bound levels (measured from
the bottom of the well) and corresponding classical turning points
for the \( 0^+, 0^− \) and \( \lambda \) symmetries near doubly excited \( ns \) and \( np \) Rydberg
atoms near \( n = 70 \).

| Asymptote | Symmetry | \( v \) | Energy (MHz) | \( R_1 \) (au) | \( R_2 \) (au) |
|-----------|----------|-------|-------------|-------------|-------------|
| \( ns + ns \) | \( 0^+ \) | 0 | 1.035 | 46 137 | 46 538 |
| 1 | 3.121 | 45 985 | 46 688 |
| 2 | 5.353 | 45 870 | 46 800 |
| 3 | 7.477 | 45 880 | 46 888 |
| 4 | 9.567 | 45 702 | 46 963 |
| 5 | 11.645 | 45 630 | 47 032 |
| \( ns + ns \) | \( 0^− \) | 0 | 1.034 | 45 072 | 45 488 |
| 1 | 3.161 | 44 913 | 45 650 |
| 2 | 5.262 | 44 803 | 45 761 |
| 3 | 7.331 | 44 716 | 45 854 |
| 4 | 9.368 | 44 639 | 45 934 |
| 5 | 11.392 | 44 569 | 46 008 |
| \( np + np \) | \( 0^+ \) | 0 | 0.831 | 40 228 | 40 679 |
| 1 | 2.499 | 40 068 | 40 849 |
| 2 | 4.166 | 39 959 | 40 970 |
| 3 | 5.824 | 39 870 | 41 068 |
| 4 | 7.477 | 39 795 | 41 154 |
| 5 | 9.125 | 39 728 | 41 233 |
| \( np + np \) | \( 0^− \) | 0 | 0.800 | 39 753 | 40 212 |
| 1 | 2.414 | 39 590 | 40 381 |
| 2 | 4.023 | 39 479 | 40 509 |
| 3 | 5.631 | 38 390 | 40 610 |
| 4 | 7.234 | 39 312 | 40 699 |
| 5 | 8.832 | 39 244 | 40 778 |
| \( np + np \) | \( \lambda \) | 0 | 0.708 | 36 907 | 37 361 |
| 1 | 2.212 | 36 752 | 37 535 |
| 2 | 3.721 | 36 632 | 37 635 |
| 3 | 5.219 | 36 545 | 37 780 |
| 4 | 6.734 | 36 467 | 37 870 |
| 5 | 8.238 | 36 399 | 37 954 |

### 5. Forming macrodimers

#### 5.1. Energy levels and lifetimes

The wells identified in figure 1 support many bound levels.
We list the lowest levels for each well in table 2, together
with the corresponding classical inner and outer turning points.
For those wells around the \( n \sim 70 \) asymptotes, the deepest
energy levels are separated by about 1–2 MHz, corresponding
to oscillation periods of a few \( \mu s \), rapid enough to allow for
several oscillations during the lifetime of the Rydberg atoms
(roughly a few hundred \( \mu s \) for \( n = 70 \)). These energy
splittings also allow for detection through spectroscopic
means. As illustrated by the values of the turning points
in table 2, the bound levels are very extended, leading to
macrodimers of a few \( \mu m \) in size.

As described in section 2, the molecular curves are a
direct result of the \( \ell \)-mixing occurring between the electronic
basis states (1): each molecular electronic state \( | \psi_i (R) \rangle \)
(corresponding to the potential curve \( U_i (R) \)) is expanded onto
the electronic basis states, the amount of mixing varying with $R$: \[ |\chi_\ell(R)\rangle = \sum_j c_j^{(\ell)}(R)|j\rangle, \]
where $c_j^{(\ell)}(R)$ are the eigenvectors after diagonalization for each separation $R$ and $|j\rangle$ the electronic basis states (1).

In [19], we showed that the potential well corresponding to the 69s + 72s asymptote of the $0^+_g$ symmetry curves near Rb $np + np$ was composed of five nearby asymptotes. We do not review the detailed treatment here, but highlight the significant asymptotes in figure 6(a) (left panel). We note that the composition of this well is due to the strong dipole mixing of the electronic basis states, the amount of mixing varying with the nuclear distance $R$. For both panels, we highlight the molecular curves corresponding to the five electronic states that contribute the most to the formation of the well versus the nuclear distance $R$. Inset: zoom of the inner region.

![Figure 6](image-url)

**Figure 6.** (a) $0^+_g$ symmetry curves of the rubidium 70p + 70p molecular asymptote (left panel), and the 70s + 70s molecular asymptote; both plots are zeroed at the ionization level of rubidium. For both panels, we highlight the molecular curves corresponding to the five electronic states contributing the most to the formation of the well (see the text). (b) Composition of the 69s + 72s well (left panel) and of the 69p$_{1/2}$ + 69p$_{1/2}$ well (right panel): probabilities $|c_j(R)|^2$ of the electronic states that contribute the most to the formation of the well versus the nuclear distance $R$. Inset: zoom of the inner region.

The insignificant contributions of the states below the potential wells in both cases indicate little chance of predissociation to these lower asymptotes, and hence the macrodimers should be long-lived (limited only by the lifetime of the Rydberg atoms). In [19], we showed that the nonadiabatic coupling between the 69s + 72s curve and the curves immediately below was very small, leading to metastable macrodimers. For the wells near the $ns + ns$ asymptotes, we reach the same conclusion, i.e. metastable macrodimers with lifetime limited by that of the Rydberg atoms.

### 5.2. Photoassociation

Exciting two ground state atoms into a bound level via photoassociation (PA) will allow us to probe the different electronic characters mentioned in section 5.1. In the following treatment, we describe a PA scheme for the formation of macrodimers bound by the highlighted well of $0^+_g$ symmetry of the $np + np$ asymptote (see figure 6(a), left panel). We assume that the ground state atoms are first excited to intermediate Rydberg states (treated as the ‘ground’ states) so that the coupling to higher Rydberg states is enhanced. Since the bound states of this particular well have electronic character that is mostly $|ns; n's\rangle$ and $|np; n'p\rangle$, we assumed two possible ‘ground’ states making transitions to different $\ell$-character in the well: 40p$_{3/2} + 40p_{3/2}$ to the ss’ components and 41s + 41s to the pp’ components. For simplicity, we choose intermediate states near $n \sim 40$ (see the inset of figure 7) because the electronic potential curves of these states are asymptotically flat in the $R$ region of the potential well that we wish to populate (see [19]); this greatly simplifies the calculations for the PA rates. However, our calculations can
The resonant frequency of the 70p3 molecular Rydberg macrodimers is spectroscopically determined by red-detuning the excitation lasers from the 69s+72s asymptote.

The macrodimers we predict could be realized and identified from a flat radial ground state distribution. The results of the PA formation mechanism for the case of doubly excited p atoms. The macrodimers we predict could be realized and identified spectroscopically by red-detuning the excitation lasers from the resonant frequency of the 70p3 molecular Rydberg state.

Using expression (14) for the ground state, we can rewrite (15) as

\[ K_v \propto I_1 I_2 \int_0^\infty dR e^{\epsilon g R} \sum_j |d_1 d_2|_j^2 |\chi_g(R)|^2, \]

where \( I_1 \) and \( I_2 \) are the intensities of lasers 1 and 2, \( |\phi_v(R)| \) and \( |\chi_g(R)| \) are the radial and electronic wavefunctions of the ground state, respectively, and \( \epsilon_g \) is independent of \( R \) (corresponding to a flat curve), we can rewrite (15) as

\[ K_v \propto I_1 I_2 \left| \int_0^\infty dR e^{\epsilon g R} \sum_j |d_1 d_2|_j^2 |\chi_g(R)|^2 \right|^2, \]

where \( d_1 = \langle n_1 \ell_1 | e | n_2 \ell_2 \rangle \) and \( d_2 = \langle n'_1 \ell'_1 | e | n'_2 \ell'_2 \rangle \) are the electronic dipole moments between electronic states \( |a_v; a'_v \rangle \) and \( |a_j; a'_j \rangle \) for atoms 1 and 2, respectively.

In figure 8, we present PA rate calculations for bound levels in the potential well correlated to the 69s+72s asymptote from a flat radial ground state distribution. The results of the PA rate against the detuning \( \Delta \) from the atomic 70p3/2 levels are shown in figure 8(a). Since the general expression for the PA rate \( (16) \) is proportional to the dipole moments and the laser intensities, our calculated rates are given in arbitrary units set to a maximum of 1 (for the strongest rate starting from 41s+41s). In fact, once a pair of atoms has been excited to the ‘ground’ state with fixed laser intensities, the PA rate plotted in figure 8 represents the probability of forming a macrodimer; the transition from the 5s Rb atoms to the intermediate ‘ground’ state atoms can easily be saturated so that the PA process always starts with a pair of 40p3/2+40p3/2 or 41s+41s.

We consider these PA rates to those obtained if the ground state radial wavefunction \( \phi_g(R) \) is assumed to be a Gaussian centred on \( R_c \) with a standard deviation of 14 500 \( a_0 \) (roughly half the FWHM of the potential well) in figure 8(b). The choice of a Gaussian approximates the wavefunction obtained by thermally averaging harmonic oscillator wavefunctions over a harmonic trapping potential (e.g. in an optical lattice) for both ‘ground’ state atoms. In those plots, the PA rates starting from both atoms in 40p3/2 are shown in red (dark grey) and from 41s in turquoise (light grey), respectively. The rapid oscillation between large rates for an even bound level \( (v = 0, 2, 4, \ldots \) and small rates for odd levels \( (v = 1, 3, 5, \ldots \) gives the apparent envelope of the PA signal. This behaviour is due to the oscillatory nature of the radial wavefunctions inside the well \( \phi_g(R) \): the integral in equation (16) will be near zero for odd wavefunctions. We highlight this for the Gaussian \( \psi_g(R) \) distribution of 40p3/2+40p3/2 in figure 8(c) and 41s+41s in figure 8(d), where we show a zoom of the deepest levels \( v \) (on a log scale).

We see in plots (a) and (b) of figure 8 that the signature of a macrodimer would manifest itself by the appearance of a signal starting at \( \Delta \sim −0.93 \) GHz red-detuned from the 70p3/2 atomic level, and ending abruptly at \( \sim −1.36 \) GHz. The shape of the signals indicate that the rates can reveal details of the \( \ell \)-mixing inside the potential well; for example, both plots show that the \( K_v \) mimic the probabilities \( c_j(R)^2 \) shown in figure 8(b). The progressive decrease of the 41s signal beginning at \( −1.36 \) GHz, followed by sharp increases between \( −1.22 \) and \( −1.16 \) GHz corresponds to the slow decreases of the pp’ components between \( R \sim 40,000–50,000 \) and \( \sim 33,000–35,000 \) a0. For the 40p3/2 signal, the major feature common to both (a) and (b) is the significant drop in the \( K_v \) at \( −1.13 \) and \( −1.09 \) GHz, which mirrors the decrease in the ss’ states between \( R \sim 52,000–55,000 \) a0 in figure 8(b). As noted in [19], this range of frequency with the noticeable drop in the PA rate could serve as a switch to excite or not excite a macrodimer, depending on the ‘ground’ state being used. We also note that in both cases, the signals for the 40p3/2+40p3/2 ‘ground’ state are higher overall across the \( R \) regime of the well, with a few exceptions. This indicates that despite the presence of the pp’ character, this well is still largely composed of the ss’ character.

As expected, the Gaussian ground state distribution shares many qualitative features with the constant ground state distribution. We considered both ground state distributions having populations in the \( R \) range of \( \sim 30,000–70,000 \) a0. Normalizing both ground state distributions over this range...
Figure 8. PA rate versus the detuning $\Delta$ from the 70$p_{3/2}$ atomic state for (a) a constant radial ground state distribution and (b) a Gaussian radial ground state distribution—both on linear scales set to a maximum of 1. The $|41s; 41s\rangle$ state populates the pp character in the well (turquoise/light grey), and the $|40p_{3/2}; 40p_{3/2}\rangle$ the ss (red/dark grey). Plots (c) and (d) show the rates for the deepest levels of the Gaussian distribution on a logarithmic scale (see the text).

yielded slightly larger signal rates in the deepest part of the well for the Gaussian, corresponding to its peak. However, the major difference between figures 8(a) and (b) is noticeable in both the 40$p_{3/2} + 40p_{3/2}$ and the 41$s + 41s$ rate signals between $\Delta \sim -1.09$ and $-0.85$ GHz. Whereas the uniform distribution shows a steady 41$s + 41s$ signal and a steady increase of the 40$p_{3/2} + 40p_{3/2}$ signal, the Gaussian distribution shows both signals rapidly decreasing. As we chose to centre the Gaussian at the minimum of the well, the decrease in both signals obviously corresponds to the decreasing probability of the Gaussian distribution in this $R$ regime (i.e. the tails). If one wanted to take advantage of the large, isolated 69$s72$s character at higher $R$, this could easily be accomplished by recentring the Gaussian appropriately.

6. Conclusion

We have presented long-range interaction potential curves for the $0^+_u$, $0^-_u$ and $1_u$ symmetries of doubly excited $ns$ and $np$ Rydberg atoms and have demonstrated the existence of potential wells between these excited atoms. These wells are very deep and very extended, due to the strong $\ell$-mixing between the various electronic Rydberg states. These wells are robust against small electric fields and support several bound vibrational levels, separated by a few MHz, which could be detected in spectroscopy experiments. The macrodimers corresponding to these bound vibrational levels are stable with respect to predissociation and have lifetimes limited only by the Rydberg atoms themselves. These macrodimers could be realized through population of the vibrational energy levels by photoassociation, resulting in a detectable signal that could be used to probe the various $\ell$-characters of the potential well.

In conclusion, we note that the detection of such extended dimers could facilitate studies in a variety of areas. For example, the effect of retardation on the interaction at very large separation, which becomes important if the photon time-of-flight between the atoms is comparable to the classical orbital period of a Rydberg electron around its core [18], could potentially be probed experimentally. Another example relates to chemistry of molecules with high internal energy: a third atom approaching a macrodimer could quench its internal state to lower levels, or could potentially react with the molecule at very large distances and create a new product such as trilobite or butterfly Rydberg molecules [16]. Finally, as mentioned in the introduction, Rydberg atoms are being investigated intensively for quantum information processing, e.g. using the blockade mechanism [7], and the possibility of frequency ranges where the PA rate is strong or weak due to the $\ell$-character mixing could potentially be used as a quantum mechanical switch. These few examples illustrate some possible applications of macrodimers.

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