Ultralong-range Rydberg molecules in combined electric and magnetic fields

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Abstract
We investigate the impact of combined electric and magnetic fields on the structure of ultralong-range polar Rydberg molecules. Our focus is hereby on the parallel as well as the crossed field configuration, taking into account both the s-wave and p-wave interactions of the Rydberg electron and the neutral ground state atom. We show the strong impact of the p-wave interaction on the ultralong-range molecular states for a pure B-field configuration. In the presence of external fields, the angular degrees of freedom acquire vibrational character, and we encounter two- and three-dimensional oscillatory adiabatic potential energy surfaces for the parallel and crossed field configuration, respectively. The equilibrium configurations of local potential wells can be controlled via the external field parameters for both field configurations depending on the specific degree of electronic excitation. This allows us to tune the molecular alignment and orientation. The resulting electric dipole moment is in the order of several kDebye, and the rovibrational level spacings are in the range of 2–250 MHz. Both properties are analyzed with varying field strengths.

Keywords: ultralong-range Rydberg molecules, molecules in external fields, ultracold molecular physics, ultracold Rydberg physics

(Some figures may appear in colour only in the online journal)

1. Introduction

The preparation and control of ultracold atomic and molecular systems offer a unique platform for a detailed understanding and analysis of fundamental quantum processes. The external degrees of freedom can be accessed by designing and switching almost arbitrarily shaped traps [1–3], which are created by external electric, magnetic, or electromagnetic fields. Furthermore, interatomic interaction strength can be tuned via magnetic or optical Feshbach resonances [4–9]. A prominent new species is the weakly bound ultralong-range diatomic molecules composed of a ground state and a Rydberg atom. Theoretically predicted more than a decade ago [10], they have been recently discovered experimentally [11]. The molecular Born-Oppenheimer potential energy surfaces, which are responsible for the diatomic binding, show for these species an unusually strong oscillatory behavior providing a large number of local potential minima. This structure can be understood intuitively as the interaction of a neutral ground state atom with the Rydberg atom, which can be modeled as a low-energy scattering potential between the quasi-free Rydberg electron and the ground state atom. In a first approximation, this so-called s-wave Fermi pseudopotential ansatz [12, 13] leads to diatomic molecular species with unique features like internuclear distances in the order of the Rydberg atom. For the considered quantum numbers $n \approx 30–50$, the vibrational binding energies are in the MHz and GHz regimes, depending on the type of states. More specifically, low-angular momentum non polar states and large angular momentum polar states, so-called trilobites, have been predicted [10]. They possess electric dipole moments in the range of 1 Debye (low-ℓ) up to 1 kDebye (high-ℓ) in the polar case. The large electric dipole moment of the latter makes them accessible for external field
manipulation, which opens the possibility for the control of the molecular degrees of freedom. For instance, the selective excitation of stationary molecular D-states in external magnetic fields was demonstrated recently to possess an extraordinary degree of alignment or antialignment with respect to the magnetic field axis [14]. The impact of either magnetic or electric fields on ultralong-range molecules has been studied in previous works [15, 16]. It has been shown that in the presence of an external field, the angular degree of freedom between the field and the internuclear axis acquires a vibrational character, resulting in two-dimensional adiabatic potential energy surfaces (PES). A pure magnetic field yields innomolecular states oriented perpendicular to the molecular axis and leads, with increasing field strength, to a monotonic lowering of the magnitude of the electric dipole moment [15]. However, a pure electric field forces the molecule into a parallel-oriented configuration with an electric dipole of growing magnitude for increasing electric field strength [16]. By combining electric and magnetic fields in a crossed field configuration, the existence and properties of so-called giant dipole ultralong-range molecules had been analyzed [17], which correspond to the situation of a magnetic field dominating over the Coulomb interaction.

In the present work, we explore the impact of combined electric and magnetic fields, more specifically, the cases of parallel and crossed (perpendicular) fields on the structure and dynamics of high-\(\ell\) ultralong-range diatomic rubidium molecules. Our analysis goes beyond the s-wave approximation, taking into account the next-order p-wave term in the Fermi-pseudopotential [13, 18, 19]. Already for the case of a magnetic field only we demonstrate the strong impact of the p-wave contribution. Due to p-wave interactions, the potential wells providing the weakly bound trilobate states vanish beyond a critical magnetic field strength, and consequently, no bound states exist anymore. For combined electric and magnetic fields, the topology of the PES strongly depend on the specific field configuration and the applied field strengths. The resulting PES show a strong oscillatory behavior with depths up to hundreds of MHz, and we find rovibrational bound states with level spacings in the MHz regime. By tuning the field parameters separately, we can control the molecular orientation for the parallel configuration from a perpendicular to an antiparallel molecular configuration with respect to the magnetic field. For the crossed field configuration, the alignment can be tuned from an aligned to an antialigned molecular state. For both field configurations, we present an analysis of the electric dipole moment.

In detail, we proceed as follows. In section 2 we present the molecular Hamiltonian and a discussion of the underlying interactions. Sections 3 and 4 contain the methodology and our results of the pure magnetic field configuration, respectively. In section 5 we analyze the impact of the combined fields on the topology of the PES for the parallel as well as the crossed field configuration. Their rovibrational spectra are addressed in section 6. A detailed study of the alignment and orientation, as well as the corresponding electric dipole moment, are provided in sections 7 and 8, respectively. Finally, section 9 contains our conclusions.

2. Molecular Hamiltonian and interactions

We consider a highly excited Rydberg atom interacting with a ground state neutral atom (the ‘perturber’ atom) in combined static and homogeneous electric and magnetic fields. Throughout this work, we focus on the \(^{87}\)Rb atom. The Hamiltonian treating of the rubidium ionic core and the neutral perturber as point particles is given by (if not stated otherwise, atomic units will be used throughout):

\[
H = \frac{p^2}{2M} + H_3 + V_{n,e}(\mathbf{r}, \mathbf{R}),
\]

\[
H_3 = H_0 + \mathbf{E} \cdot \mathbf{r} + \frac{1}{2} \mathbf{B} \cdot \mathbf{L} + \frac{1}{8} (\mathbf{B} \times \mathbf{r})^2,
\]

\[
H_0 = \frac{p^2}{2} + V_I(r),
\]

where \((M, \mathbf{P}, \mathbf{R})\) denote the atomic rubidium mass and the relative momentum and position of the ground state \(^{87}\)Rb atom with respect to the ionic core. The tuple \((m_e, \mathbf{p}, \mathbf{r})\) indicates the corresponding quantities for the Rydberg electron. The electronic Hamiltonian \(H_0\) consists of the field-free Hamiltonian \(H_0\) and the usual Stark, Zeeman, and diamagnetic terms of an electron in static external \(E, B\)-fields. \(V_I(r)\) is the \(\ell\)-dependent one-body pseudopotential felt by the Rydberg electron when interacting with the ionic core [20]. For low-lying angular momentum states, the electron penetrates the finite ionic \(R^n\)-core. This leads to an angular momentum-dependent interaction potential \(V_I(r)\) due to polarization and scattering effects [21]. In this work, we choose the direction of the magnetic field to coincide with the \(z\)-axis of the coordinate system, i.e., \(\mathbf{B} = Be_z\). Finally, we model the interatomic potential \(V_{n,e}\) for the low-energy scattering between the Rydberg electron and the neutral perturber as a so-called Fermi-pseudopotential

\[
V_{n,e}(\mathbf{r}, \mathbf{R}) = 2\pi A_3[k(R)] \delta (\mathbf{r} - \mathbf{R})
+ 6\pi A_{3/2}[k(R)] \mathbf{V} \delta (\mathbf{r} - \mathbf{R}) \mathbf{V}. \tag{2}
\]

In our setup, we consider the triplet scattering \((S = 1)\) of the electron from the spin-\(\frac{1}{2}\) ground state alkali atom. Suppression of singlet scattering events can be achieved by an appropriate preparation of the initial atomic gas. In equation (2) the quantities \(A_3[k(R)] = -\tan (\delta_0(k))/k\) and \(A_{3/2}[k] = -\tan (\delta_1(k))/k^3\) denote the energy-dependent triplet \(s\)- and \(p\)-wave scattering lengths, respectively. They are evaluated from the corresponding phase shifts \(\delta_l(k), \ l = 0, 1\). The kinetic energy \(E_{\text{kin}} = k^2/2\) of the valence electron at the collision point with the neutral perturber can be taken according to \(k^2/2 = 1/R - 1/2n^2\), which represents a semiclassical approximation.

3. Methodology

In order to solve the eigenvalue problem associated with the Hamiltonian (1), we adopt an adiabatic ansatz for the electronic and heavy particle dynamics. We write the total wave function as \(\Psi(\mathbf{r}, \mathbf{R}) = \psi(\mathbf{r}; \mathbf{R}) \phi(\mathbf{R})\) and obtain within the
adiabatic approximation

\[
\begin{align*}
    [H_0 + E \cdot r + \frac{1}{2} B \cdot L + \frac{1}{8} (B \times r)^2 + V_{ne}(r, R)]\psi_i(r, R) = & \epsilon_i(R)\psi_i(r, R), \\
    \left(\frac{\mathbf{P}^2}{M} + \epsilon_i(R)\right)\phi_{il}(R) = & E_{il}\phi_{il}(R),
\end{align*}
\]

where \(\psi_i\) describes the electronic molecular wave function for a given relative position \(R\), and \(\epsilon_i\) determines the vibrational state of the molecule. To calculate the potential energy surface \(\epsilon_i(R)\), we expand \(\psi_i(r; R)\) in the eigenbasis of \(H_0\), i.e.,

\[
\psi_i(r; R) = \sum_{nlm} C_{nlm}^{\psi_i}(R) \chi_{nlm}(r) \text{with } H_0 \chi_{nlm}(r) = \epsilon_{nlm} \chi_{nlm}(r),
\]

\(\chi_{nlm}(r) \equiv (l|m\ell\ell m) = R_\ell(r) Y_{j\ell}(\theta, \phi)\). For \(l \geq l_{\text{min}} = 3\) we neglect all quantum defects, i.e., \(H_0\) is identical to the hydrogen problem. Finally, we have to solve the following eigenvalue problem:

\[
\begin{align*}
    \left[\epsilon_{nl} - \epsilon_i(R) + mB^2/2\right] C_{nlm} + & \sum_{n' l' m'} C_{n'l'm'}^{nlm} \langle nlm|E_r \cos \Omega \rangle \\
    + & \frac{B^2}{8} r^2 \sin^2(\theta)|n'l'm'\rangle + \langle nlm|V_{ne}(r, R)|n'l'm'\rangle = 0, \quad \text{(5)}
\end{align*}
\]

with

\[
\cos(\Omega) = \sin(\theta_E) \cos(\phi_E - \phi) + \cos(\theta_E) \cos(\theta).
\]

The angles \((\theta_E, \phi_E)\) specify the direction of the electric field (see figure 1). Without loss of generality, one can choose \(\phi_E = 0\). In this work, we analyze the parallel \((\theta_E = 0)\) and perpendicular \((\theta_E = \pi/2)\) field configuration. To study the different configurations, we use standard numerical techniques for the diagonalization of the resulting hermitian matrices. Throughout this work we focus on the high-\(\ell\) \(n = 35\) manifold; for other \(n\)-quantum numbers, the underlying physical processes remain similar. In case of zero electric field, this high-\(\ell\) manifold provides the trilobite states [10]. To ensure convergence, we vary the number of basis states finally achieving a relative accuracy of \(10^{-3}\) for the energy. For the \(n = 35\) trilobite manifold we used, in addition to the degenerate \(n = 35, l \geq 3\) manifold, a basis set that includes the 38s, 37d, 36p quantum defect split states due to their energetic closeness. This basis set contains 1225 states in total.

From equations (3) and (4) we already deduce some symmetry properties of the states \(\psi, \phi\), and the energies \(\epsilon\) for the different field configurations. If \(P_{R, E}\) denotes the general-ized parity operator that transforms \((r, R, E) \rightarrow (-r, -R, -E)\) we have \([H, P_{R, E}] = [V_{ne}(r, R), P_{R, E}] = 0\). This means that the states \(\psi, \phi\) are parity (anti)symmetric and the PES fulfill \(\epsilon_{\parallel, \perp} (R; E) = \epsilon_{\parallel, \perp}(-R; -E)\), where \((\parallel, \perp)\) denote the PES in case of parallel and perpendicular fields, respectively. In addition, if \(\theta_E = 0\) (parallel configuration), the PES possess an azimuthal symmetry, e.g., \(\epsilon_{\parallel, \perp}(R, \theta) = \epsilon_{\parallel, \perp}(R, \theta)\) and the vector defining the internuclear axis can, without loss of generality, be chosen to lie in the \(x\)-\(z\)-plane. In contrast, if \(\theta_E = \pi/2\) (perpendicular configuration), the PES depend on the azimuthal coordinate \(\phi\) as well and possess only reflection symmetries with respect to the \(x\)-\(y\)-plane and the \(x\)-\(z\)-plane, i.e., \(\epsilon_{\parallel, \perp}(R, \pi - \theta, \phi) = \epsilon_{\parallel, \perp}(R, \theta, \phi)\) and \(\epsilon_{\parallel, \perp}(R, \theta, 2\pi - \phi) = \epsilon_{\parallel, \perp}(R, \theta, \phi)\). In this work, the energy offset of all PES is the dissociation limit of the atomic states \(\text{Rb}_{5s} + \text{Rb}\) \((n = 35, l \geq 3)\).

4. \(p\)-wave interaction effects in a magnetic field

Before we study the combined field configurations, let us analyze the system for zero electric field \((E = 0)\). In [15] this has been done considering only the \(s\)-wave scattering for the electron-perturber interaction. In contrast to this, we include here the \(p\)-wave interaction as well.

Figure 2 shows a one-dimensional cut through the \(s\) - and \(p\)-wave dominated PES (black lines) in comparison with the purely \(s\)-wave dominated potential curves (blue lines) for a magnetic field strength \(B = 20\) G (dashed lines) and \(100\) G (solid lines). The specific cut is taken along the \(\theta = \pi/2\) direction. As discussed in [15] in the case of a pure \(s\)-wave scattering potential, the field-dependent terms represent a perturbation with respect to the field-free molecular Hamiltonian, and the considered potential curve is just the known trilobite potential curve [10] shifted by the Zeeman splitting. The resulting PES provide, beside a global minimum between \(R = 1400a_0\) and \(1500a_0\), a number of local minima, which are taken on for the \(\theta = \pi/2\) configuration for which the internuclear axis is perpendicular to the applied field. This behavior is clearly visible in figure 2 for the blue curves, which represent the purely \(s\)-wave dominated potential curves. However, including the \(p\)-wave scattering term changes the situation substantially. As discussed in detail in [16], in the field-free case, additional potential curves arise.
causing an avoided crossing in the vicinity of the global minimum of the s-wave trilobite curve.

As shown in figure 2 for \( \theta = \pi/2 \), we are faced with two additional potential curves. For \( B = 20 \) G (dashed, black curves), the avoided crossings in the region \( R = 1400a_0 - 1600a_0 \) known from the field-free case are still visible. With a decreasing energetically order, we first have an oscillating potential curve with a potential minimum at approximately \(-7.44 \) GHz for \( R = 1312a_0 \) that strongly increases for \( R \geq 1400a_0 \). Because it arises from the additional p-wave interaction, we denote this PES as p-wave PES. Second, we find a monotonically increasing potential curve ranging from \( R = 1400a_0 \) to \( 1500a_0 \). In this work, this PES is not of interest because it does not exhibit any potential minima and therefore contains no bound states. The third and energetically lowest potential curve is the one providing the ultralong-range molecules ('trilobite states') from [10] in the field-free case. This curve does not possess a global minimum any more. It monotonically increases until \( R \approx 1450a_0 \) and thereafter possesses an oscillatory behavior with local potential wells of depths in the hundred MHz regime. We observe that for increasing radial distance \( R \), the s-wave character becomes more and more dominant. This curve provides metastable bound states. We denote this potential surface as the s-wave PES. In the field-free case this surface is, at least in a certain region, strongly p-wave interaction affected [16].

Finally, the effect of an increasing field strength on the p-wave dominated potential curves can be seen in figure 2 as well. We present the p-wave dominated potential energy curves for a magnetic field strength of \( B = 100 \) G (solid black curves). An obvious consequence is that the s- and p-wave PES have moved up and down in energy, respectively, while the energetically intermediate curve is still monotonically increasing, but now in the enlarged spatial region \( 1400a_0 \leq R \leq 1600a_0 \). This behavior can be understood by applying perturbation theory. For \( 0 \leq B \leq 50 \) G the PES are well reproduced by the expression

\[
\epsilon^{(s,p)}(R; B) = \epsilon_0^{(s,p)}(R) + \frac{B}{2} \langle s, p; R \mid L_z \mid s, p; R \rangle + \frac{B^2}{4} \sum_{n \neq (s,p)} \left| \langle n; R \mid L_z \mid s, p; R \rangle \right|^2,
\]

where \( \langle n; R \mid L_z \mid s, p; R \rangle \) denote the field-free adiabatic electronic eigenstates and eigenenergies. The diamagnetic term in (1) can be neglected here. Obviously, the term of \( O(B^2) \) potentially becomes relevant in the region of avoided crossings of the field-free curves which are localized around \( R \approx 1450a_0 \) [16]. For increasing magnetic field strength the term proportional to \( B^2 \) in (6) becomes dominant in spatial regions beyond the point of the field-free avoided crossings \( (R \approx 1450a_0) \). This causes the PES to separate energetically in the way as it can be seen in figure 2 for the field strength \( B = 20 \) G and \( B = 100 \) G. Besides the energetic separation a second consequence of the p-wave interaction is the disappearance of the local potential wells in case of the s-wave curve with increasing magnetic field strength.

Indeed for \( B = 20 \) G and \( R \geq 1450a_0 \) we find four local potential wells with depths of the order of hundreds of MHz whereas for \( B = 100 \) G no local potential wells are present. Instead the s-wave PES monotonically increases and possesses two plateaus at radial positions where the former two outermost potential wells had been localized. Therefore in case of a pure magnetic field and beyond a critical field strength of \( B_{cr} = 100 \) G the s-wave curve does not provide any bound states for the \( \theta = \pi/2 \) configuration.

In figure 3(a) the complete two-dimensional s-wave PES is shown as a function of \((R, \theta)\) for \( B = 40 \) G for radial distances \( 1600a_0 \leq R \leq 2250a_0 \). We observe a \( \theta \rightarrow \pi - \theta \) reflection symmetric potential surface with local potential minima at \( R_{eq} = 1728a_0, 1918a_0, 2159a_0 \) and \( \theta_{eq} = \pi/2 \).

In figure 3(b) the complete two-dimensional p-wave PES is shown as a function of \((R, \theta)\) for \( B = 40 \) G for radial distances \( 1000a_0 \leq R \leq 1500a_0 \). We observe a potential surface with the global equilibrium positions at \( R_{eq} = 1432a_0, \theta_{eq} = 0, \pi \). This p-wave PES provides bound rovibrational states. The region around \( R = 1500a_0, \theta = \pi/2 \) is strongly affected by the level repulsion of the s- and p-wave PES as it has been described above. In figure 3(a) and 3(b) we see also that in this region the s- and p-wave PES strongly decreases and increases, respectively.

However, for \( R = 1500a_0 \) and \( \theta \) approaching \( \pi \) or \( 0 \) respectively, the effect of the s- and p-wave level repulsion decreases for the s- and p-wave PES. For \( \theta = 0 \), this effect vanishes completely, which is due to the fact that the Hamiltonian (3) then separates into a \( m = 0 \) and \( m = 1 \) block. The considered s- and p-wave curves arise due to the diagonalization of the \( m = 0 \) subspace of the electronic problem (3). If we neglect the diamagnetic term in (3) the Zeeman interaction term does not couple the s- and p-wave curves because \( L_z \langle m, l, 0 \rangle = 0 \), \( \forall n, l \). Because of this, the
the level repulsion with respect to the s-wave PES. We can tune the topology of the PES between the pure electric and magnetic field limits. To be specific, we choose $B = 60 \text{ G}$ and vary the electric field strength $E = 0 - 100 \text{ V/cm}$. Figure 4(a) presents the s-wave PES for $B = 60 \text{ G}$, $E = 20 \text{ V/cm}$. We observe three local potential minima, which we label $(I_1)$, $(I_2)$ and $(II_0)$. In case of $E = 0$ we find these potential wells along the perpendicular configuration ($\theta = \pi/2$) with the radial minima position at $R_{I_1} = 1728\alpha_0$, $R_{II_0} = 1918\alpha_0$, and $R_{II_0} = 2159\alpha_0$, respectively (see figure 3(a)). For $R \approx 1600\alpha_0$ the s-wave potential well decreases monotonically for decreasing $R$, which is caused by the level repulsion described in section 4. For finite electric field strengths the topology of the s-wave PES changes in the sense that the angular positions of minima of the potential wells $(I_1)$ are shifted to higher $\theta \in [\pi/2, \pi]$ values. This is clearly visible in figure 4(a). This effect is simply explained by the fact that the electric field forces the electron density to align in its negative $z$-direction, which is reflected in a deeper Born-Oppenheimer potential in this region. The radial positions $R_{I_1} - R_{II_0}$ of the minima are less
strongly affected. With increasing electric field, they are transferred to the final values 1750a₀ (R_{II}), 1940a₀ (R_{III}), and 2175a₀ (R_{III}) for \( E \geq 80 \frac{V}{m} \). Furthermore, we see that the larger the radial position \( R \) of the considered potential well from the ionic core, the larger the angular distance from \( \theta = \pi/2 \). This feature can be understood in a semiclassical picture where we compare the Lorentz force \( F_L \) with the electrostatic force \( F_E \) on the electron. Since \( F_L \sim \beta a_0 E \sim \sqrt{1/R - \frac{1}{2}m^2} \), the Lorentz force decreases with \( R \) while \( F_E \sim E \) remains constant. Therefore, the electron density further away from the ionic rubidium core is more strongly affected by the electric field. In general, the depth of the potential wells (I₁–III₃) strongly varies with the corresponding parameter values. In case of a dominant magnetic field (\( B \geq 80 \text{ G}, E \leq 60 \frac{V}{m} \)) the wells possess depths up to 100 MHz. For a dominant electric field (\( B \leq 40 \text{ G}, E \geq 40 \frac{V}{m} \)) their depths are 200–300 MHz.

In figure 4(b) we present the p-wave PES curve for \( B = 60 \text{ G}, E = 20 \frac{V}{m} \). It possesses a global equilibrium position at \( R = 1432a_0, \theta = \pi/2 \) denoted by IV₈. As described in section 4 in case of a pure magnetic field, the p-wave PES possesses a \( \theta \rightarrow \pi - \theta \) symmetry (see figure 3). A finite electric field along the z-axis breaks this symmetry and tends, as mentioned earlier, to enhance the electron density in the negative z-direction. As a consequence, we find in case of the p-wave PES the potential minimum at \( \theta = \pi \) (figure 4(b)). The depth of this potential well is approximately 300 MHz and remains roughly constant for all considered field strengths.

5.2. Perpendicular field configuration

Figure 5(a) shows the three-dimensional s-wave PES for the crossed field configuration \( B = 100 \text{ G}, E = 60 \frac{V}{m} \) as a function of \((R, \theta, \phi)\). Because of the \( \theta \rightarrow \pi - \theta \) and \( \phi \rightarrow 2\pi - \phi \) symmetries (see section 3), we present the potential surface in the range of \( 0 \leq \theta \leq \pi/2 \) and \( 0 \leq \phi \leq \pi \). We clearly see an oscillating structure with local potential minima aligned into the negative x-direction (\( \theta = \pi/2, \phi = \pi \)). This feature can be understood in a semiclassical picture where the electric field simply deforms the azimuthally symmetric PES for a finite magnetic field strength in the sense that it forces the electron density to align along the negative x-direction. Due to this, we obtain molecular states with a well-defined orientation antiparallel to the electric field. In contrast to the parallel field configuration, the orientation of these molecular states cannot be tuned by varying the electric and magnetic field strengths. In the considered parameter range, tuning the field parameters just changes the depth of the local potential minima at \( \theta = \pi/2, \phi = \pi \).

This feature is shown in detail in figure 5(b), which presents one-dimensional potential cuts for the crossed field configuration. We have fixed the magnetic field strength to \( B = B_a = 100 \text{ G} \) and varied the electric field from \( E = 0 - 100 \frac{V}{m} \) in steps of \( 20 \frac{V}{m} \). As already discussed in section 4 for \( E = 0 \), we obtain no potential local wells, i.e., no bound states are provided for this magnetic field strength. With increasing electric field strength, we again obtain local potential wells at the minima positions \( R_{I} = 1728a_0, R_{II} = 1918a_0, \) and \( R_{III} = 2159a_0 \), respectively. Obviously, these values are very close to those obtained for the parallel field configuration (see previous subsection). Similar to the parallel field configuration, we label the wells/plateaus with \((I_{L}), (II_{L}), \) and \((III_{L})\). The radial equilibrium positions increase with increasing electric field strength up to \( 1750a_0 \) \((R_{I})\), \( 1940a_0 \) \((R_{II})\), and \( 2175a_0 \) \((R_{III})\). As we observe in figure 5(b) the well \((III_{L})\) is affected most by the increasing electric field in the sense that its depth increases from 0 up to 140 MHz. Similarly, the depths of the well \((II_{L})\) and \((I_{L})\) increase up to 100 MHz \((II_{L})\) and 40 MHz \((I_{L})\), respectively. We therefore conclude that the electric field counterbalances
the effect of the p-wave interaction and leads to bound states where otherwise none would have existed. This result is reminiscent of an effect already observed for the pure electric field configuration where the electric field stabilizes bound molecular states of the s-wave PES [16] as well. For dominant electric fields in the considered field regime, the depths of the potential wells increase up to a value of approximately 300 MHz.

In figure 6 we present a two-dimensional cut defined by $\phi = \pi$ through the p-wave PES for the crossed field configuration for $B = 100$ G, $E = 60 \frac{V}{m}$. As with the p-wave PES in the parallel field configuration, we concentrate on the potential well providing the global equilibrium position. This well is labeled IV_L. The radial equilibrium position is again given by $R = 1432 \text{a}_0$ for $\theta = 0, \pi$. In case of a pure electric field, the single existing potential minimum is localized at $R = 1432 \text{a}_0$, $\theta = \pi/2$, $\phi = \pi$, which is shown in the inset of figure 6. By increasing the magnetic field strength, the angular equilibrium position is shifted from $\theta_{eq} = \pi/2$ to $\theta_{eq} = \pi/2 \pm \delta$, $\delta \in (0, \pi/2]$. This means the topology of the p-wave PES changes from a single well to a double well PES. For all applied field strengths, the depth of the well IV_L remains around 300 MHz.

In table 1 we summarize the topological properties for both field configurations in the limit of dominant electric and magnetic field strengths.

### Table 1. Topological properties of the s- and p-wave PES for both field configurations for dominant magnetic ($B \gg E$) and electric ($B \ll E$) fields.

| | $I_3$ | $I_{41}$ | $I_{42}$ | $I_{43}$ |
|---|---|---|---|---|
| $B \gg E$ | 1728$\text{a}_0$, $\pi/2$ | 1918$\text{a}_0$, $\pi/2$ | 2159$\text{a}_0$, $\pi/2$ | 1432$\text{a}_0$, $(0, \pi)$ |
| $B \ll E$ | 1750$\text{a}_0$, $\pi$ | 1940$\text{a}_0$, $\pi$ | 2175$\text{a}_0$, $\pi$ | 1432$\text{a}_0$, $\pi$ |

6. Rovibrational states

To analyze the rovibrational states for the parallel field configurations, we introduce cylindrical coordinates $(\rho, Z, \varphi)$ for the parametrization $|\psi(\rho, Z)\rangle$. We have $[H_{rv}, L_z] = 0$, which means the azimuthal quantum number $m$ is a good quantum number. With this, we write the rovibrational wave function $\psi(\rho, Z, \varphi) = \sum_{m} \left| e_{m}(\rho, Z) \right\rangle \exp (i m \varphi)$, $m \in \mathbb{Z}$, $\nu \in \mathbb{N}_0$, which transforms the Hamiltonian (4) into

$$H_{rv} = -\frac{1}{M} \left( \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} \right) + \frac{m^2}{4} + \frac{1}{4} \frac{\partial^2}{\partial Z^2} + \epsilon_{\varphi}(\rho, Z).$$

We solve the corresponding Schrödinger equation, focusing on $m = 0$ using a fourth-order finite difference method for electric field strengths in the range 0, 20, ..., 80 $\frac{V}{m}$ and $B = 60$ G.
In figure 7 we present the ground state probability densities of the local potential well (III₀) in cylindrical coordinates (ρ, Z). We label the densities according to the applied field strengths E with a, b, c. For instance, (III₀,c) indicates the probability density of the ground state in the well (III₀) with an applied electric field strength of $E = 40 \sqrt{V / m}$. As described in section 5 with increasing electric field strength, the wells move from the $\theta = \pi/2$ configuration to the $\theta = \pi$ direction. This feature is clearly reflected in the position of the ground state probability densities. For field strengths beyond $E = 40 \sqrt{V / m}$ the position of the minimum of the well remains close to $\theta = \pi$; as a result, there are no qualitative changes of the corresponding ground state rovibrational probability densities. The latter can be characterized by their radial $\Delta R$ and angular extension $\Delta \theta$. Typical values observed are of the order of $\Delta R = 80a_0$ and $\Delta \theta = 250a_0$ (III₀,a) up to $650a_0$ (III₀,b). We see that with increasing electric field strength from $E = 0$ to $20 \sqrt{V / m}$ the angular extension of the rovibrational probability densities in (III₀,a) and (III₀,b) increase as well. For higher field strengths, the potential well (III₀) approaches $\theta = \pi$ and the angular extension of the probability density decreases again. This is clearly visible for (III₀,c) in figure 7 and is caused by the potential term $-\frac{1}{4}\alpha_{\phi,\phi}$.

In the inset (i) of figure 7 we present the first five eigenenergies of the rovibrational states for the potential well (III₀) of the s-wave PES, relative to the minimum of the potential well. The level spacing decreases to 2 MHz for $E = 20 \sqrt{V / m}$, which can be explained by the minor decrease of the angular confinement. With increasing E beyond a field strength of $40 \sqrt{V / m}$ the potential gets affected by the centrifugal term in equation (7) and the angular confinement increases. This leads to a larger level spacing up to 10 MHz as can be seen in the inset (i) of figure 7.

For the p-wave PES the level spacing is of the order of 10–30 MHz (see inset (ii) of figure 7). In case of the low-lying states, it hardly varies with increasing field strength; only the higher excited states are affected in the sense that their level spacing increases from 5 to 10 MHz. This can be explained by the fact that enhancing the electric field strength increases the angular confinement, which more strongly affects the higher excited states than the energetically low-lying ones.

In case of the crossed field configuration, we have $[H_{\text{p},Y}, P_i] = [H_{\text{p},Y}, P_2] = 0$ where $P_i$: $Y \to -Y$ and $P_2$: $Z \to -Z$. Due to these symmetry properties, the wave functions $F(\rho, Z, \phi)$ now obey $F(\rho, -Z, \phi) = \pm F(\rho, Z, \phi)$ and $F(\rho, Z, 2\pi - \phi) = \pm F(\rho, Z, \phi)$. To estimate the rovibrational level spacings we use the fact that the exact potential energy surfaces can be expanded around their equilibrium positions $(R_{\text{eq}}, \theta_{\text{eq}}, \pi)$ as

$$
eq_{\perp}(R, \theta, \phi) \approx \epsilon_{\perp}(R_{\text{eq}}, \theta_{\text{eq}}, \pi) + \frac{1}{4}M\omega_{\phi}^2(R - R_{\text{eq}})^2$$
$$+ \frac{1}{4}M\omega_{\theta}^2R_{\text{eq}}^2(\theta - \theta_{\text{eq}})^2$$
$$+ \frac{1}{4}M\omega_{\pi}^2R_{\text{eq}}^2(\phi - \pi)^2$$

where $\Delta V$, $\omega_i$, and $\omega_R$ are the energy difference to the potential minimum and the fitted values for the semi-axis of the underlying ellipsoid. For the specific setup we find level spacings of $\omega_R = 130$ MHz ($I_\perp$) and 140 MHz ($III_\perp$) and $150$ MHz ($II_\perp$). This means each potential well only provides up to one radial excitation. For the angular degrees of freedom we get $\omega_\phi \approx 5$ MHz for all three potential wells. In case of the $I_{\perp}$ potential well for the p-wave PES, we obtain level spacings of the order of $\omega_\phi \approx 200$ MHz in the radial and $\omega_\theta \approx 5–20$ MHz, $\omega_\phi = 5$ MHz in the angular degrees of freedom.

We remark that for both field configurations and s- as well as p-wave PES the radial as well as the angular level spacing strongly depends on the applied fields. The general level structure implies a single radial excitation (130–250 MHz) with several angular excitations (5–30 MHz) on top. For both field configurations the states in the wells ($I_{\perp}$–$III_\perp$) and ($I_{\perp}$–$III_\perp$) of the s-wave PES possess a finite lifetime due to a tunneling out of the local potential wells. These
lifetimes strongly depend on the considered field strengths, and we get maximal lifetimes in the order of microseconds.

7. Molecular alignment and orientation

In section 5 we presented the possibility of varying the topology of the molecular PES via tuning of the electric and magnetic fields. Obviously, this provides the possibility to control the molecular orientation and alignment.

To quantify the orientation and alignment in case of the parallel field configuration, we have to analyze the expectation value \(\langle \cos(\theta) \rangle_{\phi} \) and the variance \(\Delta \cos(\theta) = \sqrt{\langle \cos^2(\theta) \rangle_{\phi} - \langle \cos(\theta) \rangle_{\phi}^2} \). The expectation values \(\langle \cdot \rangle_{\phi} \) are taken with respect to the rovibrational state \(\phi(R)\) for the ground states in the potential wells (I\(_h\)), (II\(_h\)), and (III\(_h\)). The closer the absolute value of \(\langle \cos(\theta) \rangle_{\phi}\) to one, the stronger is the alignment of the state into the \(z\)-direction and the closer \(\Delta \cos(\theta)\) is to zero, the stronger is the alignment of the state.

We consider the ground state probability densities in the single wells to be strongly localized such that we can approximate the expectation values according to \(\langle \cos(\theta) \rangle_{\phi} \approx \cos(\theta_{eq})\) and \(\langle \cos(\theta)^2 \rangle_{\phi} \approx \cos^2(\theta_{eq})\) where \(\theta_{eq}\) denotes the angular equilibrium position of the underlying potential well (see figure 7). In this approximation we get the variance \(\Delta \cos(\theta) \approx 0\), which means that the degree of alignment is perfect.

In figure 9(a) we present the dependence of \(\cos(\theta_{eq})\) of the ground state of the potential well (II\(_h\)) on the applied field. The inset in this figure shows the same analysis but for the (I\(_h\)) well. We see that for pure magnetic and pure electric fields, the state is oriented in a perpendicular (red region) and antiparallel (blue region) configuration, respectively. For both potential wells we find a crossover regime (yellow region) between the two configurations. We see that for fixed magnetic field strength the antiparallel configuration for the well (II\(_h\)) is achieved for lower electric field strengths than for (I\(_h\)). This can be explained by the fact that the electric field strongly affects the states in the well (II\(_h\)) as compared to (I\(_h\)) (see section 5). In case of the crossed field configuration, the rovibrational Hamiltonian (7) possesses a \(P_2\) reflection symmetry, i.e., we get \(\langle \cos(\theta) \rangle_{\phi} = 0\). In this case the molecular alignment is quantified by \(\langle \cos^2(\theta) \rangle_{\phi} \approx \cos^2(\theta_{eq})\), \(\theta_{eq} \in [0, \pi/2]\) for ground rovibrational states. For the \(s\)-wave PES we have molecular states with a well-defined perpendicular configuration of the internuclear axis with respect to the \(z\)-axis. Here we have \(\cos^2(\theta_{eq}) = 0\), which means they are antialigned with respect to the \(z\)-axis. For the \(p\)-wave PES and finite magnetic field strength, we have potential surfaces with a double-well character. In this case the rovibrational states are delocalized over the double wells.

In figure 9(b) we present the field-dependent alignment of the ground states in the corresponding IV\(_h\) potential well. We see that for pure electric and magnetic field configuration we have perfectly (anti)aligned molecular states. Similar to the molecular orientation for the parallel field configuration, we find a crossover regime (yellow region) where the alignment changes from antialigned (blue region) to aligned states (red region).

8. Electric dipole moment

Due to the impact on the molecular configuration, the electric dipole moment can be readily tuned by changing the field strengths and specific field configuration. Let us analyze the absolute value of the dipole moments along the internuclear axis in the following:

\[
D_{al} = \left| \langle \phi(r; R_{eq}; B, E) | n \cdot \mathbf{r} | \psi(r; R_{eq}; B, E) \rangle \right|. \tag{10}
\]

where \(n\) denotes the unit vector along the internuclear axis.
In figure 10 we show the electric dipole moment for the s-wave PES for the parallel field configuration as a function of B and E. We observe that with increasing B the dipole moment decreases, while it increases with increasing E. This can be understood by the fact that in the absence of any contact interaction and B ≠ 0, E = 0 the reflection operations P_r ⊗ P_z and P_z are exact symmetries of the Hamiltonian (3). In the presence of the neutral perturber and B = 0, E = 0 the mixing of degenerate Rydberg states leads to an electric dipole given by the empirical approximation $D_{el} \approx R_{eq} - \frac{e^2}{2}$ for a purely s-wave interaction dominated PES. However, with as the magnetic field increases, the magnetic field terms become dominant and the corresponding symmetry properties get imprinted in the quantum states [15].

For a pure strong magnetic field case, the s-wave PES is approximately dominated by the (35, 34, −34) hydrogen state, which explains the decrease of the electric dipole moment. In case of an increasing electric field, the electron cloud is more aligned into the negative field direction, which causes the increase of $D_{el}$.

Next we perform some (semi)analytical analysis to estimate the electric dipole moment. First we check the validity of the empirical approximation for finite electric and magnetic field strengths. As discussed in section 5 for the considered field regimes, the radial positions of the potential wells is only affected by the external fields (see table 1) to a minor extent. Therefore, we estimate the electric dipole moment as $R_{eq} - \frac{e}{2}$ where $R_{eq}$ denotes the mean value of the minimal and maximal radial positions for a considered potential well for varying field strength. For instance, $R_{eq}$, $l_i = 1728a_0$ for $B = 80 G$, $E = 0$, and $R_{eq}$, $l_i = 1750a_0$ for $B = 0 G$, $E = 80 V/m$ which gives $R_{eq}$, $l_i = (1728a_0 + 1750a_0)/2 = 1739a_0$ and an approximate dipole moment of $D_{el} \approx 2.85$ kDebye. This corresponds to a relative deviation of 5% compared to the exact result, which means that in the considered parameter regime, this simple estimate is quite accurate.

As discussed in section 5 in case of the p-wave PES its equilibrium position remains constant ($R_{eq} = 1432a_0$, $\theta_{eq} = \pi$) with respect to a variation of the field strengths. In particular, in section 4 we have shown that the corresponding electronic eigenvector $|\psi_r(r; R_{eq}; B, E)\rangle$ is independent of the applied magnetic field. Due to this, we can reduce the analysis of the dipole moment of the p-wave state to an arbitrary value of B, which we choose to be $B = 0 G$. In figure 10(b) we show the electric dipole moment for the p-wave PES for $B = 0 G$ as a function of E. With increasing electric field strength $D_{el}$ grows quadratically. To verify this, we present a corresponding semi-analytical result for the electric dipole moment where we expanded the state $|\psi_r(r; R_{eq}; B = 0, E)\rangle$ in a perturbative series up to the $O(E^2)$:

$$|\psi_r(r; R_{eq}; 0, E)\rangle = |\psi_0(r; R_{eq})\rangle + E \sum_{n\neq 0} C_n^{(1)} |\psi_n(r; R_{eq})\rangle + E^2 \sum_{n\neq 0} C_n^{(2)} |\psi_n(r; R_{eq})\rangle. \tag{11}$$

In this expansion $|\psi_n(r; R_{eq})\rangle$ indicate the field-free electronic states and $C_n^{(1, 2)}$ are the expansion coefficients given by standard perturbation theory [22]. Inserting this ansatz into (10) and keeping terms up to $O(E)$ and $O(E^2)$, we obtain the linear term (red) and quadratic term (green) approximations according to figure 10(b). We see that the exact data (blue line and crosses) are well approximated by the quadratic approximation. The empirical approximation gives a result of $D_{el} = 2.08$ kDebye, which deviates from the obtained data by 10%. The larger deviation compared to the s-wave state can be explained by the fact that the empirical approximation is originally derived for s-wave interactions in the absence of any fields. Although we expect the p-wave state to possess a strong s-wave character far away from the region of avoided crossings ($R < 1450a_0$) for the region of the localized potential well ($R_{eq} = 1432a_0$), the p-wave character still provides a substantial contribution, which explains the less accurate result for the resulting electric dipole moment.
Table 2. Minimal ($D_{el,min}$) and maximal ($D_{el,max}$) electric dipole moment for the potential wells (I$_1$–III$_1$). The minimal (maximal) values are taken for $B = 80$ G, $E = 0$ m (B = 0 G, E = 80 $\frac{1}{m}$) For comparison, we present the empirical approximation $\bar{R}_{el} = \frac{n_e^2}{\pi}$.

|      | $D_{el,min}$ | $D_{el,max}$ | $\bar{R}_{el} - \frac{n_e^2}{\pi}$ |
|------|--------------|--------------|----------------------------------|
| I$_1$ | 2.69         | 2.94         | 2.86                             |
| II$_1$| 3.25         | 3.39         | 3.34                             |
| III$_1$| 3.92         | 3.98         | 3.95                             |

For the crossed field configuration, the electric dipole moments of the s-wave PES potential wells (I$_1$–III$_1$) show a qualitatively similar behavior as their counterparts (I$_0$–III$_0$) in case of the parallel configuration. For all potential wells we find a decreasing dipole moment for increasing magnetic field strength and an increase of $D_{el}$ for an increasing electric field strength. In table 2 we present the minimal ($D_{el,min}$) and maximal ($D_{el,max}$) value of the electric dipole moment (10) for the wells (I$_1$–III$_1$). As for the parallel field configuration, we compare these results with the empirical approximation $\bar{R}_{el} = \frac{n_e^2}{\pi}$. With a maximal deviation of 1–5% the exact results are reproduced satisfactorily.

9. Conclusions

The recent experimental progress in preparing, detecting, and probing the properties of non-polar ultralong-range Rydberg molecules [11, 14, 23–25] has opened the doorway for a variety of possibilities to create novel species where atoms, molecules, and even mesoscopic quantum systems are bound to Rydberg atoms. Therefore, the understanding and control of the properties of these hybrid Rydberg systems are of essential importance. Due to the high sensitivity of the weakly bound Rydberg electron, the primary choice to obtain electronic as well as rovibrational control is the application of external fields.

In this work we have explored the effect of combined electric and magnetic fields on the polar high angular momentum molecular states for a parallel as well as a crossed field configuration. Taking into account both s- and p-wave interactions, it turns out that for a pure magnetic field configuration strong level repulsion causes the potential wells that provide the triborate states in the field-free case [10] to vanish. For this PES beyond a critical field strength of around 100 G, no bound states are provided anymore. For finite field strengths the angular degrees of freedom are converted from rotational to vibrational degrees of freedom, thereby rendering the field-free potential energy curve into a two- and three-dimensional energy surface for parallel and crossed field configurations, respectively. We obtain oscillatory potential curves with localization in the radial and angular degrees of freedom with depths up to hundreds of MHz providing a rich topology depending on the specific degree of electronic excitation and field configuration. The resulting rovibrational level spacings are in the order of several MHz.

The parallel as well as the crossed field configuration provide unique ways to control the topology of the adiabatic potential energy surfaces. This directly leads to the possibility of controlling molecular orientation and alignment for the parallel and crossed field configuration, respectively. For instance, for parallel fields, the molecular orientation can be tuned from a perpendicular to an antiparallel configuration by varying applied field strengths. In case of crossed fields, the molecular alignment can be changed between an aligned and anti-aligned configuration with respect to the magnetic field. In addition, the topological control of the PES provides the possibility of directly controlling the electric dipole moment as well. Apart from numerical results, we have also provided an empirical estimate and perturbative analysis of the electric dipole moment.

The plethora of interesting effects of high-$l$ ultralong-range Rydberg molecules in external fields keeps this particular species a promising candidate for future investigations. Because of its high sensitivity to small field strengths, it is worth studying the dependence of molecular properties like electric and magnetic polarizabilities and susceptibilities. In case of Rydberg atoms, these quantities strongly depend on the Rydberg excitation.

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