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LETTER TO THE EDITOR

Ultra-long-range Rydberg molecules exposed to a magnetic field

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Abstract

We investigate the impact of an external magnetic field on ultra-long-range and ultracold Rydberg molecules. The Born–Oppenheimer potential surfaces are analysed and discussed for different values of the magnetic field strength. The magnetic field provides an angular confinement turning a rotational degree of freedom into a vibrational one. We explore the vibrational dynamics and observe a pronounced transition in the level spacing from a linear splitting via an irregular regime to a 2D harmonic oscillator-like behaviour. Scaling arguments for the dependence of the potential energy surfaces on the field strengths are provided. The occurrence of a monotonic lowering of the magnitude of the electric dipole moment with increasing magnetic field strength is shown.

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

1. Introduction

The ease and accuracy with which ultracold Rydberg atoms are being created by using tunable lasers these days [1–7] promise their eventual control and manipulation with external electric and magnetic fields. The main appeal of trapped Rydberg systems is their translational immobility which makes them available for long time interrogation. Rydberg atoms can develop large permanent electric dipole moments—stemming from the near degeneracy of states with different orbital angular momenta—and, as such are quite amenable to control by external electric fields. In crossed electric and magnetic fields so-called decentred giant dipole states [8, 9] emerge due to the presence of an outer potential well, which prevents the Rydberg electron and the atomic core from approaching each other, with implications for the stability

of matter–antimatter systems in such field configurations: the potential barrier between the particle and antiparticle permits decentred matter–antimatter atoms to exist up to many years [10]. Also, very recently the possibility of trapping ultracold Rydberg atoms in the quantum regime of a coupled centre of mass state has been reported [11].

Rydberg molecules can likewise be manipulated with external magnetic fields [12, 13]. Recently the existence of novel classes of ultra-long-range and ultracold Rydberg molecules among the ultracold Rydberg gas in a magneto-optical trap has been predicted [14–16]. Such Rydberg molecules were given exotic monikers as trilobite and butterfly molecules, due to whether the Rydberg electron collision with the perturbed ground state atom was in the regime of strictly s-wave scattering or p-wave scattering.

In this work, we study the effect of a magnetic field on the structure and dynamics of ultracold, ultra-long-range Rydberg molecules. Section 2 provides the formulation of the problem. Here we briefly discuss the underlying interactions and model the Born–Oppenheimer (BO) Hamiltonian. In section 3 we analyse the structure of the BO potential energy surfaces (PES) with respect to changes of the magnetic field strength. Moreover, we present the energy spectrum accounting for the newly emerging vibrational modes and present an analysis of the electric dipole moment. Section 4 contains our conclusions. Atomic units will be used throughout this paper unless otherwise stated.

2. Interactions and molecular Hamiltonian

In the framework of the Born–Oppenheimer approximation the interatomic potential energy for the collision between a Rydberg atom and a ground state atom, in the absence of any external field, is constructed, as in [14, 17] from the contact interaction of the Rydberg electron with the ground state atom involving the so-called Fermi pseudopotential

$$V(\mathbf{r}, \mathbf{R}) = 2\pi A_T[k(R)]\delta(\mathbf{r} - \mathbf{R}).$$
(1)

Here **r** and **R** are, respectively, the relative position of the Rydberg electron with respect to its parent ion and the relative position of the ion to the ground neutral atom. We consider here the triplet (S = 1) scattering of the electron from the spin-1/2 alkali metal ground state atom. Suppression of singlet scattering can be ensured by appropriately preparing the initial ultracold atomic gas. In a magnetic trap, for instance, the selection of hyperfine substates with maximum projection quantum number ensures the parallel alignment of the spins of the individual valence electrons. In such scenario mainly triplet scattering is expected to occur.

The momentum-dependent triplet scattering length $A_T[k] \equiv -\tan \delta_0^T(k)/k$ is evaluated from the corresponding s-wave phase shift $\delta_0^T(k)$. The trilobite molecular states are formed from a sum over the nearly degenerate manifold of orbital angular momentum states with $l \ge l_{\min}$, as

$$E(R) = -\frac{1}{2n^2} + 2\pi A_T[k(R)] \sum_{l=l_{\min}}^{n-1} \frac{2l+1}{4\pi} R_{nl}(R)^2,$$
(2)

where $R_{nl}(R)$ are the hydrogenic radial wavefunctions with the quantum numbers, *n* and *l*. l_{\min} refers to the smallest angular momentum quantum number at which, for a given *n*, the quantum defects of the Rydberg energies are negligible. The linear momentum of the Rydberg electron at the colliding point with the neutral perturber can be approximated according to $\frac{1}{2}k^2 = \frac{1}{R} - \frac{1}{2n^2}$. Beyond the classical turning point, the zero-energy scattering length for the ³S symmetry ($A_T[0] = -16.05$ au) [18] for e⁻-Rb(5s) is used. Letter to the Editor

The total non-relativistic BO Hamiltonian in the presence of a magnetic field of arbitrary strength is then given by

$$H = \frac{1}{2}\mathbf{p}^2 + V(\mathbf{r}) + \frac{1}{2}\mathbf{B}\cdot\mathbf{L} + \frac{1}{8}[\mathbf{B}\times\mathbf{r}]^2 + 2\pi A_T[k(R)]\delta(\mathbf{r}-\mathbf{R}),$$
(3)

where the first term is the field-free kinetic energy of the electron and $V(\mathbf{r})$ is the effective one-body potential felt by the valence electron when interacting with the ionic core. **L** is the electronic orbital angular momentum in the molecular-fixed frame and **B** is the magnetic field vector. The direction of the magnetic field is assumed to coincide with the *z*-axis of the coordinate system. Due to rotational invariance, the vector **R** defining the internuclear axis, can, without loss of generality, be chosen to lie in the *x*-*z*-plane. With these conventions and employing spherical coordinates the Hamiltonian (3) becomes

$$H = \frac{1}{2}\mathbf{p}^{2} + V(\mathbf{r}) + \frac{1}{2}BL_{z} + \frac{1}{8}B^{2}r^{2}\sin^{2}\theta + \frac{1}{r^{2}}A_{T}[k(R)]\delta(r-R)\delta(\cos\theta - \sin\beta)\delta(\phi)$$
(4)

with *R* and $\alpha = \frac{\pi}{2} - \beta$ being the radial coordinate and the polar angle of the position of the perturbing ground state atom, respectively. In the absence of the magnetic field, the PES depend exclusively on the internuclear distance *R*. However, when a field is present, the BO surfaces depend on both the internuclear axis and the angle of inclination α between the field vector and the internuclear axis. The Schrödinger equation reads

$$H|\kappa; R, \beta\rangle = E_{\kappa}(R, \beta)|\kappa; R, \beta\rangle, \tag{5}$$

where $|\kappa; R, \beta\rangle$ is the κ th electronic state depending parametrically on R and β . One can easily show the electronic Hamiltonian to obey $P_x H(\beta) P_x = H(-\beta)$, where P_x represents the corresponding reflection operator. Hence, the BO surfaces $E_{\kappa}(R, \beta)$ do not depend on the sign of β and thus need to be calculated for $\frac{\pi}{2} \leq \beta \leq \pi$ only.

3. Results and discussion

3.1. Born–Oppenheimer potential energy surfaces

In figure 1, we present intersections of the PES for $\beta = 0$, i.e. for the perpendicular configuration of the internuclear and magnetic field axis. The dissociation limits correspond to the atomic states Rb(5s) + Rb(n = 35, $l \ge 3$). For the magnetic field strengths of interest, the principal quantum number n is a 'good' quantum number, i.e. there is no significant mixing between adjacent *n*-manifolds. The magnetic field induces a splitting of both l and m states. The linear splitting of the manifold of states belonging to different magnetic quantum numbers m is clearly visible in figure 1 for R > 1600. As the magnetic field strength increases, the BO curves shift to lower energies. The critical field B_c is then defined to be the value at which the lowest Zeeman level matches in energy the bottom of the lowest field-free potential. In the present case, this field is at about $B_c \sim 2 \times 10^{-7}$, which corresponds to 470 G. For fields stronger than 470 G, the oscillations of the lowest BO curve damp out. At equilibrium separations of the BO potentials due to s-wave scattering, the contribution from the p-wave phase shift [15, 16] is more than one order of magnitude smaller and is ignored here.

In figure 2, the energetically lowest PES for four different values of the field strength is displayed as a function of R and β . In the absence of an external field, the BO surface would be independent of β as seen in equation (2). For a finite field strength, this spherical symmetry is broken which is seen in the top-left panel of figure 2. For all field strengths the potential minimum is taken on by the perpendicular configuration $\beta = 0$. This is partly because in the perpendicular configuration, due to availability of many nearly degenerate *l* states, there is a strong mixing of L_z and hence a general energy lowering. The magnetic field therefore turns a rotational degree of freedom β to a vibrational one. As the field strength increases,



Figure 1. Intersections of the PES through the plane defined by $\beta = 0$, i.e. for the perpendicular configuration. For small values of *B* the Zeeman splitting of the degenerate *m*-levels is already visible in the upper part of the figure and only a single oscillatory BO curve is split away. With increasing Zeeman splitting the level structure is altered. Finally, the oscillations in the lowermost BO curve vanish at a critical field strength B_c which, in the present case, is approximately 2×10^{-7} (470 G).

a stronger confinement of the angular motion is achieved. Finally, for $B > B_c$ we find a non-oscillatory BO surface whose appearance is almost independent of the specific value of B. Here the magnetic interaction dominates. This is nicely seen in figure 3 where the competition between the contact and external field interactions is shown as a function of the magnetic field. For values below B_c , the molecular interaction dominates and the value of the minimum of the PES is smaller than the value of the lowest possible Zeeman energy $E_{1z} = -\frac{B}{2}(n-1)$. For field strengths larger than 2×10^{-7} , the Zeeman energy entirely dominates and the bottom of the PES is almost solely determined by the Zeeman interaction. The critical field strength scales as $B_c \propto n^{-5}$. Comparing the contributions of the Zeeman E_{zee} and the diamagnetic term E_{dm} in the Hamiltonian (4) one finds the ratio to be $E_{dm}/E_{zee} \propto Bn^3$. The critical field strength scales as $B_c \propto n^{-5}$, resulting in $E_{dm}/E_{zee} \propto n^{-2}$. Thus the contribution of the diamagnetic term can be safely neglected even far beyond B_c , where the oscillatory PES are already destroyed.

Significantly beyond B_c , the contact interaction of the electron with the ground state atom can be treated as a perturbation on the Zeeman energy levels. The corresponding BO surfaces can then be calculated via first-order perturbation theory from the unperturbed atomic states $|n, l, m\rangle$. Considering only the energetically lowest surface (l = -m = n - 1) one finds

$$E_{-n+1}(R,\beta) = E(n,B) + \langle n, n-1, -n+1 | 2\pi A_T[k(R)] \delta(\mathbf{r} - \mathbf{R}) | n, n-1, -n+1 \rangle$$

$$= -\frac{1}{2n^2} - \frac{B}{2}(n-1) + \frac{2A_T[k(R)]}{n^{2n+2}[(n-1)!]^2} e^{-\frac{2R}{n}} R^{2n-2} \cos^{2n-2} \beta.$$
(6)

Letter to the Editor



Figure 2. A two-dimensional plot of the energetically lowest PES for four different values of the magnetic field strength. An increase of *B* goes along with a stronger confinement of the angular motion. Beyond the critical field strength B_c the oscillations vanish and only a single potential well remains whose appearance does not change significantly even if *B* is further increased.



Figure 3. Competition between the contact and the magnetic field interaction. Shown is the value of the minimum of the energetically lowest PES of the Hamiltonian (4) (solid blue curve). For $B > B_c$ the magnetic interaction dominates the spectrum of the Hamiltonian. The minimal energy decreases linearly with increasing field strength as this is expected for the lowermost Zeeman level whose energy is determined through $E_{lz} = -\frac{B}{2}(n-1)$ (dashed red curve).

Thus for $B > B_c$ the lowest PES exhibits only a single confining well whose position and shape are independent of the specific value of *B*. The corresponding minimum is approximately located at $\beta = 0$ and R = n(n - 1).



Figure 4. Shown are the 11 energetically lowest vibrational energies as a function of the field strength. Three different regimes can be distinguished: For $B < 5 \times 10^{-8}$ a linear increase of the level spacing is observed followed by an irregular region that is caused by the radial deformation of the oscillating BO surface. Beyond B_c the level structure resembles that of an isotropic two-dimensional harmonic oscillator.

3.2. Vibrational dynamics

The vibrational spectrum is given by the stationary Schrödinger equation belonging to the Hamiltonian

$$H = \frac{\mathbf{P}^2}{M} + E(R,\beta) \tag{7}$$

with *M* being the mass of a single atom. In figure 4, we provide the 11 lowest vibrational states living in the lowest PES for various values of the field strength. In order to yield a normalized view of the spectrum the energy of the minimum of the energetically lowest BO surface has been subtracted. For $B < 5 \times 10^{-8}$, the distance between adjacent energy levels increases approximately linearly with *B*. This a direct consequence of the increasing angular confinement. In the successive region $(5 \times 10^{-8} < B < B_c)$ the entire spectrum undergoes a restructuring. Here, not only the angular confinement but also the radial shape and therefore the oscillatory character of the BO surface is altered by the magnetic field. Depending upon the actual value of *B*, the vibrational states occupy different radial wells, which results in an irregular level structure with a number of approximate degeneracies. By increasing *B* further beyond B_c , the spectrum assumes a most simple shape. The arrangement of the vibrational energy levels is reminiscent of those of an isotropic harmonic oscillator. In this regime the lowest BO surface is well approximated by the potential (6), which for small displacements from its minimum is well approximated by a harmonic well.

3.3. Electric dipole moment

In [14] the authors reported on the unprecedented large electric dipole moments of the ultralong-range Rydberg molecules. The zero-field permanent dipole moment for the trilobite states scales as $D = R - \frac{1}{2n^2}$. This unique feature persists even after the application of an external magnetic field. Figure 5 displays the expectation value of the component of the electric dipole moment being aligned with the internuclear axis, i.e. $D_{IA} = z \sin \beta - x \cos \beta$. The data presented are for the vibrational ground state only, but higher excited states exhibit a qualitatively similar behaviour. $\langle D_{IA} \rangle$ shows a monotonic decrease with increasing field strength. In the absence of the contact interaction, the reflection operations $P_x \otimes P_y$ and P_z are exact symmetries of the Hamiltonian (4) and therefore the expectation values of all



Figure 5. Expectation value of the electric dipole moment: the component D_{IA} , along the internuclear axis, is displayed. The monotonic decrease of $\langle D_{IA} \rangle$ originates from the particular symmetry properties of the magnetic field which become more and more manifest as the field strength increases.

Cartesian coordinates would vanish. In the presence of the perturbing atom and for B = 0 the mixing of the nearly degenerate Rydberg states that are not split away by quantum defects leads to a huge electric dipole moment of the molecular eigenstates. However, with increasing magnitude of *B*, the magnetic field terms become dominant, which also means that their corresponding symmetry properties get 'imprinted' in the quantum states. In this particular case, the above-mentioned reflection symmetries become more and more established resulting in a gradual decrease of $\langle D_{IA} \rangle$.

4. Conclusions

We have presented an investigation on the behaviour and the properties of ultra-long-range Rydberg molecules exposed to a homogeneous magnetic field. By studying the BO surfaces, we have found the magnetic field to create an angular confinement for the molecular motion thereby turning a rotational degree of freedom into a vibrational one. For small field strengths, the energetically lowest BO surfaces still exhibit an oscillatory behaviour as already observed in the field-free case. However, beyond the critical magnetic field strength B_c , these oscillations vanish and are instead replaced by a single potential well whose shape barely changes with a further increasing field strength. In this regime, perturbation theory can be successfully applied in order to describe the energetically lowest BO surface.

We studied the vibrational motion of the ultra-long-range molecules. Here three regimes of the energy spectrum can be distinguished. For weak fields, one finds the spacing of adjacent energy levels to increase approximately linearly with the field strength, followed by an irregular region as B is increased. Beyond the critical field strength, the spectrum then is similar to that of a two-dimensional isotropic harmonic oscillator and almost independent of the specific value of B. The electric dipole moment of the molecular states has been shown to decrease monotonically with the field strength. This is caused by the symmetry properties of the magnetic field interactions which become increasingly dominant.

Our findings indicate that external magnetic fields can be used for the alignment and angular localization of ultra-long-range Rydberg molecules at ultracold temperatures. Moreover, they allow for tuning the internal properties of these molecules such as the strength of the electric dipole moment. This is of potential use for establishing a controllable dipole– dipole interaction between two of such molecules. This, together with the capability to address them individually, gives rise for a number of potential applications including the design of quantum gates.

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