Spin mixing in Cs ultralong-range Rydberg molecules: a case study

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We calculate vibrational spectra of ultralong-range Cs(32p) Rydberg molecules which form in an ultracold gas of Cs atoms. We account for the partial-wave scattering of the Rydberg electrons from the ground Cs perturber atoms by including the full set of spin-resolved $^{1,3}S_J$ and $^{1,3}P_J$ scattering phase shifts, and allow for the mixing of singlet ($S = 0$) and triplet ($S = 1$) spin states through Rydberg electron spin-orbit and ground electron hyperfine interactions. Excellent agreement with observed data in Saßmannshausen et al. [Phys. Rev. Lett. 113, 133201(2015)] in line positions and profiles is obtained. We also determine the spin-dependent permanent electric dipole moments for these molecules. This is the first such calculation of ultralong-range Rydberg molecules in which all of the relativistic contributions are accounted for.

I. INTRODUCTION

Rydberg atoms are weakly bound systems which can simultaneously exhibit quantum and classical behavior [1, 2]. This quantum to classical evolution is at the heart of the Bohr-Sommerfeld quantization. Rydberg spectroscopy is a useful technique for probing many of the subtle properties of an atomic or molecular core, for measuring the Rydberg constant, and probing interactions in the surrounding gas or plasma. The interaction and collision of a Rydberg atom with the neutral and ionic species in the gas broadens and shifts the atomic lines, through which much can be learned about the scattering properties of the gas. The seminal measurements of Amaldi and Segré [3] confirmed that the classical macroscopic polarization of the dielectric medium was insufficient to describe the Rydberg line shifts and that the scattering of Rydberg electrons from the perturber gas atoms would have to be accounted for. This led Fermi to develop a zero-range scattering theory, now called the Fermi pseudopotential (or contact potential) method [4].

Fermi realized that the low-energy scattering of a Rydberg electron from a perturber gas atom can be effectively described by a short-range elastic scattering interaction; this model has had much subsequent success in determining low-energy electron-atom scattering lengths of many other species [3]. The form of zero-energy scattering of an s-wave electron from a perturber is then,

\[ H_s(\vec{r}, \vec{R}) = 2\pi a_s(0)\delta^{(3)}(\vec{r} - \vec{R}) \]  

(1)

where $\vec{r}$ is the electronic coordinate, measured from the Rydberg core, $\vec{R}$ is the vector connecting the Rydberg nucleus to the perturber atom nucleus, and $a_s(0)$ is the zero-energy s-wave scattering length.

The delta-function contact interaction formalism can be extended to higher scattering angular momenta; an analytical form for p-wave scattering was derived by Omont [6], as

\[ H_p(\vec{r}, \vec{R}) = 6\pi a_p^3(k)\delta^{(3)}(\vec{r} - \vec{R})\vec{n} \cdot \vec{\nabla} \]  

(2)

where $a_p(k)$ is the k-dependent p-wave scattering length

\[ a_{\ell_{sc}+1}^{2\ell_{sc}+1}(k) = -\frac{\tan \delta_{\ell_{sc}}(k)}{k^{2\ell_{sc}+1}}. \]  

(3)

Here $\ell_{sc}$ is the orbital angular momentum about the perturber atom and $\ell_{sc} = 0, 1$ denote s- and p-wave scattering of the electron from the perturber atom, respectively.

The Born-Oppenheimer (BO) potential curves, as eigenstates of the Hamiltonian with $H_s$ and $H_p$ contributions, are highly oscillatory in internuclear distance $R$ due to the admixture of Rydberg electron wave functions with high principal quantum numbers $n$. It was realized in [7, 8] that those multi-well BO potentials can support bound vibrational levels when $a_s(0) < 0$ as is the case for all alkali-metal atoms.

Such exotic molecular Rydberg states were realized in magnetic and dipole traps, first in an ultracold gas of Rb atoms [9], where such Rydberg molecules have $^3\Sigma Rb_2(ns)$ spherical symmetry. It was confirmed that, even though such molecules were homonuclear, the mixing of Rb(ns) levels with Rb$(n - 3, l > 2)$ hydrogenic manifolds, produces appreciable permanent electric dipole moments in these molecular species [10]. The prediction for Rydberg molecules with kilo-Debye dipole moments (trilobite molecules) were realized with ultracold Cs atoms [11, 12] in which the Cs$(n - 4, l > 2)$ degenerate manifolds are energetically much closer to Cs(ns) levels, hence providing for much stronger mixing of opposite parity electronic states. More recently, butterfly molecules (Rydberg molecules stemming from the presence of p-wave resonances) were predicted [8, 13, 14] and
confirmed [15]. In increasingly dense gases, additional molecular lines stemming from the formation of trimers, tetramers, pentamers, etc. have been observed [16–18].

The above scattering formalism is spin-independent, i.e. while the scattering phase shifts depend separately on the total spin of electrons, the scattering amplitudes add up incoherently. For Rydberg excitation in a gas of alkali-metal atoms, the total spin channels are $S = |s_r + s_g| = 0, 1$ for singlet and triplet scattering, respectively, with $s_r$ and $s_g$ the Rydberg electron and the perturber ground electron spins.

In this work we will account for all of the relevant and relativistic effects in Rydberg perturber atom scattering. We include all of the fine structure resolved s- and p-wave scattering Hamiltonians, the Rydberg electron spin-orbit, and the ground electron hyperfine interactions. From the resulting BO potentials we not only predict the spatial structure and energies of the Rydberg molecules but can also reproduce the spectral line profiles in the recent experiment [19] as shown in Fig. 1.

II. HAMILTONIAN

The total Hamiltonian with all spin degrees of freedom included is,

$$H = H_0 + H_{p,T} \cdot P_T + H_{p,S} \cdot P_S +$$

$$H_{s,s} \cdot P_T + H_{p,S} \cdot P_S + H_{so} + H_{hf}$$

where $H_0$ is the Hamiltonian for the unperturbed Rydberg atom, and $H_{(s,p),T}$ and $H_{(s,p),S}$ are the (s-wave, p-wave) scattering Hamiltonians for triplet and singlet spin configurations, respectively. The operators $P_T = s_r \cdot s_g + 3/4$ and $P_S = 1 - P_T$ are the triplet and singlet projection operators for the total electronic spin.

It was first pointed out by Anderson et al. [20] that the ground state hyperfine interaction can mix singlet and triplet spin configurations. The hyperfine Hamiltonian is $H_{hf} = A_{hf} \cdot s_g \cdot P_T$, where $i_g$ is the nuclear spin and $A_{hf}$ is the hyperfine interaction; in Cs, the focus of this work, $A_{hf} = 2298.1579425$ MHz, and $i_g = 7/2$. Anderson et al. demonstrated this in Rb, where they observed bound vibrational levels due to mixing of singlet and triplet spins, even though the singlet zero energy scattering length for Rb is known to be small and positive. This is particularly important as, in magneto-optical and magnetic traps, spin alignment dictates that the interactions occur via the triplet scattering channel.

The spin-orbit interaction for the Rydberg electron, $H_{so} = A_{so} \cdot s_r$, where $L_r$ is the orbital momentum and $A_{so}$ is the spin-orbit strength for $l_r \neq 0$ levels. Anderson et al. neglected this term, because it scales as $n^{-3}$. For intermediate $n$, however, the spin-orbit splitting will be comparable to the hyperfine splitting. The details of the matrix elements of $H_{so}$ and the terms for Cs(up) states will follow below.

Recent studies have explored the extent to which spin effects are necessary to properly predict, \textit{ab initio}, the vibrational spectra of these molecules, largely concluding that fine, hyperfine, and p-wave effects can have significant effects on these spectra [19, 20]. To date, no study has incorporated all of the interaction terms (s-wave, p-wave, spin-orbit, and hyperfine) on the vibrational spectra of Cs Rydberg molecules. Due to the large hyperfine shift in $^{133}\text{Cs}$, and the existence of several p-wave resonances at intermediate energies, these contributions can be significant in Cs. The current results are employed here to interpret the observations by Saßmannshausen et al. [19].

III. HAMILTONIAN MATRIX ELEMENTS

The matrix elements of the unperturbed Rydberg Hamiltonian ($H_0$) are calculated from the solutions $\phi_{nl,m_r}(\vec{r})$ to the equation $H_0 \phi_{nl,m_r}(\vec{r}) =$
Cs atom levels are used as follows: the quantum defects \( \mu_r \) for Cs atom levels are used as follows:

| \( l_r \) | \( \mu_r \) |
|---|---|
| 0 | 4.05739 |
| 1 | 3.57564 |
| 2 | 2.471396 |
| 3 | 0.0334998 |
| 4 | 0.00705658 |
| \( \geq 5 \) | 0 |

We use the spherical coordinate system centered at the Rydberg core, as portrayed in Fig. 2. The Rydberg orbitals forming our truncated basis set are comprised of \( \{ns,(n+1)s, np, (n-1)d, (n-3)d, (n-4)l \} \), \( n \geq 3 \), \( (n-4)l \geq 3 \), for \( n=1,2 \). The asymptotic form for the radial wave function is given by

\[
F_{nl}(r) \propto r^l e^{-\frac{r}{\mu_r}} F_1 \left( l_r - n + 1 + \mu_r, 2 + 2l_r, \frac{2r}{n - \mu_r} \right)
\]

where \( F_1 \) is the confluent hypergeometric function. For \( \mu = 0 \), this reduces to the usual hydrogenic solution:

\[
F_{nl}(r) = \sqrt{\frac{2}{n}} \left( \frac{n - l_r - 1}{2n(n + l_r)} \right)! \frac{(2l_r + 1)}{2} \left( \frac{2r}{n} \right)^{l_r} L_n^{(\alpha)} \left( \frac{2r}{n} \right)
\]

where \( L_n^{(\alpha)} \) is the generalized Laguerre polynomial. For non-integer quantum defects, the wave functions \( F_{nl} = 1 \) diverge at origin. To remedy this problem, they are matched to numerically calculated wave functions at small- \( r \) [21].

**Spin-dependent s-wave interaction.**— The Hamiltonian matrix elements describing s-wave scattering between basis functions \( \phi_i \) and \( \phi_j \) are,

\[
\langle \phi_i | H_s | \phi_j \rangle = 2\pi \sum_S a_S^\ell (k) \langle \delta_\ell^3 (R - \bar{r}) | \phi_j \rangle
\]

where \( | \phi_i \rangle \) is shorthand for the basis element \( | nl_{r_i} m_{s_{r_i}} s_{g_i} m_{s_{g_i}} \rangle \), and \( m_S = m_{s_r} + m_{s_g} \) is the total spin projection along the internuclear axis. The s-wave scattering length \( a_S^\ell (k) \) has been generalized to accommodate the \( (S = 0,1) \) singlet and triplet scattering lengths.

**Spin-dependent p-wave interaction.**— Additional caution is necessary when dealing with the p-wave electron-atom scattering, which depends on the total electronic spin \( S = s_r + s_g \) and angular momentum \( J = l_{sc} + S \) centered on the perturber atom. The triplet \( (S = 1) \) p-wave scattering phase shift in Cs exhibits a relatively large splitting for \( J = 0,1,2 \). This is in contrast to previous studies in Rb where the triplet p-wave scattering length is treated as a single resonance. The resulting Cs p-wave scattering interaction operator thus takes the form

\[
\hat{H}_p = 6\pi \sum_{J = 0,1,2} \delta_{J0,1,2} \langle \delta_\ell^3 (R - \bar{r}) \nabla \cdot \nabla | J_m_J; S_m_S \rangle \langle J_m_J; S_m_S | J_m_J; m_S \rangle
\]

where \( S = 0,1 \) and \( m_J \) is the projection of \( J \) along the internuclear axis. In the uncoupled basis \( | nl_{r} m_{s_r} ; S_m_S \rangle \), where \( | nl_{r} m_{s_r} \rangle \) is a Rydberg orbital and \( | S_m_S \rangle \) is the total spin state of the two electrons, matrix elements of this interaction take on the form

\[
\langle \phi_i | \hat{H}_p | \phi_j \rangle = \langle \delta_\ell^3 (R - \bar{r}) \nabla \cdot \nabla | \psi_i \rangle \langle \delta_\ell^3 (R - \bar{r}) \nabla \cdot \nabla | \psi_j \rangle
\]

with the effective scattering volume as

\[
\langle \delta_\ell^3 (k) \rangle = \sum_{J = 0,1,2} \left( \langle \ell_{sc} = 1 \rangle m_{\ell_{sc}}, (S = 1) m_S | J_{m_J} \rangle \langle J_{m_J} | m_S \rangle \langle \ell_{sc} = 1 \rangle m_{\ell_{sc}}, (S = 0) m_S | J_{m_J} \rangle \langle J_{m_J} | m_S \rangle \langle \ell_{sc} = 1 \rangle m_{\ell_{sc}}, (S = 0) m_S | J_{m_J} \rangle \langle J_{m_J} | m_S \rangle \right)
\]

where \( \langle \ell_{sc}, S_m_S | J_{m_J} \rangle \) is a Clebsch-Gordan coefficient coupling the orbital angular momentum of the Rydberg electron to the combined total spin of the ground state atom and Rydberg electron. Note that \( m_{\ell_{sc}} = m_{\ell} \), since angular momentum projections are invariant under translation along the axis of projection. Because of the projection onto the p-wave relative angular momentum states, only Rydberg states with spatial angular momentum projection \( m_{\ell} = 0 \) or \( \pm 1 \) contribute to the interaction.

The spatial integral in Eq. 9 can be evaluated as
\[ \langle \phi_i | \delta^{(3)}(\mathbf{R} - \mathbf{r}) \mathbf{\nabla} \cdot \mathbf{\nabla} | \phi_j \rangle = \lim_{\mathbf{r} \to \mathbf{R}^2} \frac{2i + 1}{4\pi} \delta_{m_i,0} \frac{\partial F_{n_i,l_i}(r = R)}{\partial r} \frac{\partial F_{n_j,l_j}(r = R)}{\partial r} + \delta_{|m_i|} |F_{n_i,l_i}(r = R)F_{n_j,l_j}(r = R)\rangle \int d(cos \theta) d\phi \nabla Y_{l_i,m_i}^* (\theta, \phi) \cdot \nabla Y_{l_j,m_j} (\theta, \phi) \delta_{m_i,m_j}, \quad (11) \]

where \( Y_{lm}(\theta, \phi) \) is a spherical harmonic, \( F_{nl}(r) \) is the radial part of the Rydberg wave function, and we suppress the subindex \( r \) on \( (l, m) \) for notational convenience. It should be noted that the radial derivatives only act on wave functions with \( m_l = 0 \) while the angular derivatives \( \nabla Y_{l,m} \) are only non-zero for states with \( m_l = \pm 1 \).

**S- and P-wave scattering phase shifts.**— In order to fully characterize the electron-perturber interaction, the s- and p-wave scattering lengths must be determined. In the case of \( a_s^{j=0,1,2,3}=1 \) and \( a_p^{j=0,1,2,3} \), these are derived by solving the scattering equation including the polarization potential \( V_{-C_s} = -\alpha/2r^4 \) where \( \alpha = 402.2 \) \( a_0^3 \) is the polarizability of the ground state Cs atom. We extract the phase shift by enforcing a hard wall boundary condition at short range \( (r_0 \lesssim 3 \text{ a.u.}) \) on the polarization potential.

For \( a_s^{S=1,0} \), we adjust the hard wall to reproduce experimentally known zero-energy scattering lengths. For \( a_p^{j=0,1,2,3}=1 \), the position of the hard wall by is chosen so as to enforce a resonance in the scattering phase shift, i.e. \( \delta E = \pi/2 \), at a resonant energy \( E \) consistent with experimental measurements. While it is unlikely that this simple procedure captures all of the details of the p-wave electron-atom scattering process, the effects of the p-wave interaction on the molecular potentials are largely captured by the position and width of the \( ^3P_l \) scattering resonances. Specifically, we set the position of the \( ^3P_1 \) to 8 meV, as observed [22]. The \( ^3P_0 \) and \( ^3P_2 \) resonance positions are set to respectively be 3.8 meV below and 7.2 meV above the \( ^3P_1 \) resonance position in accordance with [23]. The energy-dependent phase shifts for \( S=0 \), and 1 spin scattering in s-wave and p-wave are shown in Fig 3.

**Rydberg spin-orbit matrix elements.**— The Rydberg electron spin-orbit Hamiltonian has the form \( H_{so} = A_{so}(n, l_r) \mathbf{L} \cdot \mathbf{s}_r \), whose coefficients for Cs(np) states have been measured in [25]. The matrix elements are

\[ \langle \phi_i | H_{so} | \phi_j \rangle = A_{so}(n, l_r) \mathbf{L} \cdot \mathbf{s}_r \quad (12) \]

where, for \( l_r = 1, 2, 3 \) [25]

\[ A_{so}(n, l_r) = \left( l_r + \frac{1}{2} \right)^{-1} \left[ A(l_r)(n - \epsilon(n, l_r))^{-3} + B(l_r)(n - \epsilon(n, l_r))^{-5} + C(l_r)B(l_r)(n - \epsilon(n, l_r))^{-7} \right] \quad (13) \]

\[ A(l_r) = 2.139258 \times 10^{-2} \]

\[ B(l_r) = -5.67 \times -5.67 \times 10^{-2} \]

\[ C(l_r) = 3.98 \times 0.00 \]

\[ \epsilon(n, l_r) = \epsilon^*(l_r) + a(l_r)(n - \epsilon)^2 \]

**FIG. 3.** The \( ^1S_0, ^3S \) electron- Cs(6s) phase shifts as a function of the electron scattering momentum are reproduced here. The \( ^1P_1 \) phase shift was obtained from a calculation by U. Thumm [24]. The \( ^3S_0 \) and \( ^3P_{j=0,1,2} \) resonant phase shifts are obtained by matching a short distance boundary condition to experimental measurements of scattering resonances [21, 22].

where \( \epsilon(n, l_r) = \epsilon^*(l_r) + a(l_r)(n - \epsilon)^2 \)

The \( l_r \)-dependent parameters \( A, B, C, \epsilon, a \) are

| \( A(l_r) \) (MHz) | \( l_r = 1 \) | \( l_r = 2 \) | \( l_r = 3 \) |
|------------------|-------------|-------------|-------------|
| 2.139258e8       | 6.02183e7   | -9.796e5    |

| \( B(l_r) \) (MHz) | \( l_r = 1 \) | \( l_r = 2 \) | \( l_r = 3 \) |
|------------------|-------------|-------------|-------------|
| -5.67e7          | -5.67e7     | 1.22e7      |

| \( C(l_r) \) (MHz) | \( l_r = 1 \) | \( l_r = 2 \) | \( l_r = 3 \) |
|------------------|-------------|-------------|-------------|
| 3.98e8           | 0.00        | -3.376e7    |

where \( \epsilon(n, l_r) = \epsilon^*(l_r) + a(l_r)(n - \epsilon)^2 \)

\[ a \]

\[ 0.3727 \]

\[ 0.0612 \]

\[ -0.191 \]

while for \( l_r \geq 4 \), \( A_{so}(n, l_r) \) takes on its hydrogenic values:

\[ A_{so}(n, l_r) = \frac{\mu_0}{4\pi} g_l \mu_B^2 \frac{1}{n^3 l_r(l_r + \frac{1}{2})(l_r + 1)} \quad (14) \]

where \( g_l \) is the Landé g-factor, \( \mu_0 \) is the vacuum permeability, and \( \mu_B \) is the Bohr magneton.

In the uncoupled angular momentum basis, the operator \( \mathbf{L} \cdot \mathbf{s}_r \) has the representation [26]

\[ \mathbf{L} \cdot \mathbf{s}_r = l_z s_r + \frac{1}{2} l_r s_+ + \frac{1}{2} l_r s_- \quad (15) \]
They are

\[
\langle l_r \cdot s_r \rangle = \begin{cases} 
    m_l m_s & \text{if } l_i = l_j, s_i = s_j, \\
    m_l = m_i, m_s = m_s_j + 1, & \text{if } l_i = l_j, s_i = s_j, \\
    \frac{1}{2} \sqrt{\left(l_i(l_i + 1) - l_{z,i}(l_{z,i} + 1)\right)} \cdot \sqrt{\left(s_i(s_i + 1) - s_{z,i}(s_{z,i} + 1)\right)} & \text{if } l_i = l_j, s_i = s_j, \\
    m_l = m_i - 1, & m_s_i = m_s_j + 1,
\end{cases}
\]

Through the ladder terms, the spin-orbit coupling will therefore couple \( \Sigma \) and \( \Pi \)-states, as well as singlet (S=0) and triplet (S=1) states.

**Ground hyperfine matrix elements.**— The ground electron hyperfine interaction Hamiltonian matrix elements are calculated as

\[
s_g \cdot i_g = s_{z,i} i_{z,g} + \frac{1}{2} s_x i_{-g} + \frac{1}{2} s_y i_{+g}
\]

where \((s, i)_{\pm, g}\) are the ladder operators for the perturber valence electronic and nuclear spins.

We chose to demonstrate the utility of our method toward calculation of the vibrational spectrum of \( \text{Cs}(6s_{1/2})-\text{Cs}(32p_{1/2}) \) Rydberg molecules [19]. For this particular Rydberg excitation, the fine-structure splitting \( \Delta E_{32p_{1/2}-32p_{3/2}} \) is nearly degenerate with the ground state hyperfine splitting, \( \Delta E_{hf} \approx 9.2 \) GHz.

For \(^{133}\text{Cs}\) with \( i_g = 7/2 \), therefore, our full basis, including angular momentum degrees of freedom, is

\[
\{32s, 33s, 32p, 31d, n \mid 29, 3 \leq l_i \leq 28, n = 28, 3 \leq l_r \leq 27 \} \times \{ -m_l \leq m_{l_i} \leq l_i \} \times \{ m_{s_n} = \pm \frac{1}{2} \} \times \{ m_{s_{p_i}} = \pm \frac{1}{2} \} \times \{ m_{s_g} = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2} \}.
\]

We truncate this basis such that no basis element has \(|m_{l_i}| > 2\) The total number of basis states included in our calculation is 8480.

The projection of the total angular momentum, \( K \) onto \( R \), \( m_K = m_{l_i} + m_{s_n} + m_{s_{p_i}} + m_{s_g} \) is a good quantum number, so that the basis set diagonalization need only be performed in blocks of 1060, 1008, 851, 638, 422, 209, and 52 elements, for \( |m_K| = \frac{1}{2}, \frac{3}{2} \) \( \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}, \frac{13}{2} \), respectively.

**IV. RESULTS AND DISCUSSIONS**

In Fig. 4, we show the full set of BO potential energy curves which result from the diagonalization of Eq. 4 with the basis functions defined in Sec. III. This landscape of Rydberg potential energies reveals the influence of the three \( 3P_j \) resonances. Due to the different widths of J-resonances, see Fig. 3, the avoided crossings of molecular potentials in \( R \) occur at different locations with the various unperturbed Rydberg manifolds. For example, near the 31d Rydberg level, the \( 3P_1 \) resonance crosses before the narrow 3P_0 resonance.

While in Fig. 4 the potential energy curves are shown for all possible projections \( m_K \), in Fig. 5 we show in detail the BO potentials for \( m_K = 1/2 \). In the outer region, there are two distinct sets of curves; the lower set corresponds to the potential curves dissociating to the \( \text{Cs}(6s_{1/2}) - \text{Cs}(32p_{1/2}) \) \( F = 4 \) threshold, and the upper set of curves dissociate to the \( \text{Cs}(6s_{1/2}) - \text{Cs}(32p_{3/2}) \) \( F = 3 \) threshold. The \( F = 3 \) and \( F = 4 \) thresholds are within \( \sim 100 \) MHz of each other because in excitation of \( \text{Cs}(32p) \), the Rydberg SO and the ground HF splittings are nearly degenerate. Within each set, the lowest curve refers to a predominantly triplet potential energy curve and the upper curve refers to the more mixed singlet/triplet potential. Generally, in the outer
region, defined by internuclear distances $R$ greater than all the p-wave resonance crossings, the predominantly triplet curve will have greater than 90% triplet character — the singlet mixing enters mainly through the $^1\Pi$ molecular symmetry — while the mixed curve will have between 60% and 70% triplet character. There will also be other non-binding potential energy curves (up to two more in a given $m_K$ block) which largely have $\Pi$ character. We stress that all of these molecular potentials are admixtures of $\Sigma$ and $\Pi$ symmetry states; $\Delta$ contributions are in principle also present, but not of significance here. On the scale of Fig. 5 the relativistic $^3P_0$ scattering resonances manifest themselves as sharp vertical lines.

We calculate the bound vibrational wave functions in the Born-Oppenheimer approximation using the previously calculated potential energy curves. The resulting Rydberg molecular binding energies are indicated by the thin blue lines in the rightmost pane of each figure, together with the absorption spectra measured in [19]. It is evident from the comparison that many of the spectral features in the experiment are reproduced in Fig. 5, which demonstrates that the experiment resolves different $m_K$ vibrational lines.

The BO potential energy curves correlating to the Cs($6s$) - Cs($32p_{3/2}$) $F=3$ and 4 asymptotes for $m_K = \frac{3}{2}$, $m_K = \frac{5}{2}$, $m_K = \frac{7}{2}$, and $m_K = \frac{9}{2}$, are shown in Fig. 6. The corresponding molecular bound states lead to additional spectral features that can be identified by comparing the vibrational energies to the observed spectral features. For $m_K = \frac{9}{2}$, the $F = 4$ potential energy curves are not binding, and for the $F = 3$ potential energy curves, there is no contribution from the $^3P_0$ scattering resonance, and hence the absence of any sharp avoided crossings.

**Spin weighting.** To accurately calculate the transition rates in photoassociation of trapped gas atoms into Rydberg molecules, we must take into account the electronic transition dipoles, as well as both the nuclear Franck-Condon and spin-overlap integrals. We assume that the atom pairs, which will bind into a Rydberg molecule, are initially in states $|6s(F_0 = F), 6s(F_0 = F)\rangle$, i.e. the ground state atoms are in the same hyperfine state $F$ when optically pumped [19], and $F_0(F_0)$ refers to the hyperfine state of the ground state atom which will be Rydberg excited (will remain in the ground state). This initial state will be mixed uniformly and incoherently about $m_F, m_F \in \{-F, \cdots, F\}$. For a given initial $m_F, m_F$, the oscillator strength between two electronic states at internuclear distance $R$ is proportional to

$$
\langle 6s(F_0, m_{F_0}), 6s(F_0, m_{F_0}) | \vec{d} | \psi \rangle
$$

where $|\psi\rangle = \sum_i a_i |\phi_i\rangle$ are the calculated electronic eigenstates, and $\vec{d}$ is the electric dipole operator.

The overlap integral in Eq. 20 then becomes

$$
O(R; m_{F_0}, m_{F_0}) = \langle 6s \cdots | \vec{d} | \psi(R) \rangle \langle F_0, m_{F_0}, m_{F_0} | \psi(R) \rangle.
$$

We neglect in $\langle 6s \cdots | \vec{d} | \psi \rangle$ the contributions to $|\psi\rangle$ other than the 32p state.

For experimentally realized temperatures, the wave function of the ground state atom pair is constant on the
FIG. 6. The BO potential energy curves correlating to the Cs(6s) - Cs(32p3/2) F=3 (right) and F=4 (left and bottom) asymptotes, for $m_K = \frac{3}{2}$, $m_K = \frac{1}{2}$, $m_K = \frac{7}{2}$, $m_K = \frac{9}{2}$ (top to bottom). For $m_K = \frac{9}{2}$, the F=4 potential energy curves are not binding, being primarily of Π molecular symmetry.
scale of the Rydberg molecule wave function. Therefore the vibrational Franck-Condon factors take the form,

\[ FC_\nu(m_{F_{ro}}, m_{F_{ro}}) \propto \int dR R^2 \psi_\nu(R)O(R; m_{F_{ro}}, m_{F_{ro}}) \]  

(22)

for a given vibrational state \( \psi_\nu(R) \).

The overall Rydberg molecule formation rate is an incoherent sum over these Franck-Condon factors

\[ \Gamma_\nu \sim \sum_{m_{F_{ro}}} \sum_{m_{F_{ro}}} |FC_\nu(m_{F_{ro}}, m_{F_{ro}})|^2 G_L, \]  

(23)

where \( G_L \) accounts for the laser profile. The calculated absorption line profiles are compared with the observed spectra in Fig. 1, where a Gaussian laser line profile \( G_L \) of width 5 MHz was used [19]. The agreement with the measured spectra (dashed lines) is excellent. In this comparison the zero-energy triplet s-wave scattering length was adjusted by 5%, i.e. \( a_s^2(0) = -20.71 \ a_0 \).

**Electric dipole moments.**— Our approach also allows for the prediction of electric dipole moments of Rydberg molecules. For the electronic wave functions the transition and permanent electric dipole moments are

\[ \langle \psi | \hat{d} | \psi \rangle = \sum_i \sum_j \langle \phi_i | \hat{d} | \phi_j \rangle a_i a_j, \]  

(24)

Because of the mixing of the opposite parity \((n-1)\) and \((n-3)\) states with \( np \) states in Cs, the Rydberg molecule obtains a permanent electric dipole moment (PEDM) [10, 12]. We note however that the dominant electronic transition is between the 32p and 31d atomic states whose dipole moment is \( \langle 32p | \hat{d} | 31d \rangle = 1583 \ \text{D} \); we neglect therefore all other contributions to the dipole moments. Thus, the spin-dependent dipole moments are

\[ d^S = \int dR \psi^*_\nu(R) \psi_\nu(R) d^S(R). \]  

(26)

The PEDMs are calculated for the predominantly triplet \( d^T \) and mixed \( d^{T+T} \) \( \nu = 0 \) vibrational levels for each \( m_K \) value. For the \( m_K = \frac{1}{2} \) potential dissociating to the \( J=3/2, F=3(F=4) \) threshold the dipole moments are \( d^T_0 = 9.8(8.5) \ \text{D} \) and \( d^{T+T}_0 = 3.7(3.7) \ \text{D} \). For \( m_K = \frac{3}{2} \), \( d^T_0 = 9.1(8.6) \ \text{D} \) and \( d^{T+T}_0 = 1.7(3.2) \ \text{D} \), while for \( m_K = \frac{5}{2} \), \( d^T_0 = 7.8(8.2) \ \text{D} \) and \( d^{T+T}_0 = 2.3(3.6) \ \text{D} \), respectively.

**V. OUTLOOK**

The level of spectroscopic precision of current experiments on Rydberg molecules combined with spin resolution allow for the determinative evaluation of such fundamental properties as the scattering length and energies of scattering resonances of electron-neutral atom collisions. The spin-dependence of the Rydberg molecular potentials opens the possibility to control the spin state of the molecules and to realize paradigm spin models in an entirely new regime. Our method can be readily extended to study such phenomena as spin and angular momentum alignment in high angular momentum Rydberg molecules such as Cs(nd).

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[1] T. F. Gallagher, *Rydberg Atoms* (Cambridge University Press, 2005).
[2] A. Buchleitner, D. Delande, and J. Zakrzewski, *Physics Reports* 368, 409 (2002).
[3] E. Amaldi and E. Segrè, *Il Nuovo Cimento* 11, 145 (1934).
[4] E. Fermi, *Il Nuovo Cimento* 11, 157 (1934).
[5] D. C. Thompson, E. Kammermayer, B. P. Stoicheff, and E. Weinberger, *Physical Review A* 36, 2134 (1987).
[6] A. Omont, *Journal de Physique* 38, 1343 (1977).
[7] C. H. Greene, A. S. Dickinson, and H. R. Sadeghpour, *Physical Review Letters* 85, 2458 (2000).
[8] E. L. Hamilton, C. H. Greene, and H. R. Sadeghpour, *Journal of Physics B: Atomic, Molecular and Optical*
Physics 35, L199 (2002).
[9] V. Bendkowsky, B. Butscher, J. Nipper, J. P. Shaffer, R. Löw, and T. Pfau, Nature 458, 1005 (2009).
[10] W. Li, T. Pohl, J. M. Rost, S. T. Rittenhouse, H. R. Sadeghpour, J. Nipper, B. Butscher, J. B. Balewski, V. Bendkowsky, R. Löw, and T. Pfau, Science 334, 1110 (2011).
[11] J. Tallant, S. T. Rittenhouse, D. Booth, H. R. Sadeghpour, and J. P. Shaffer, Physical Review Letters 109, 173202 (2012).
[12] D. Booth, S. T. Rittenhouse, J. Yang, H. R. Sadeghpour, and J. P. Shaffer, Science 348, 99 (2015).
[13] A. A. Khuskivadze, M. I. Chibisov, and I. I. Fabrikant, Physical Review A 66, 042709 (2002).
[14] M. I. Chibisov, A. A. Khuskivadze, and I. I. Fabrikant, Journal of Physics B: Atomic, Molecular and Optical Physics 35, L193 (2002).
[15] T. Niederprüm, O. Thomas, T. Eichert, C. Lippe, J. Pérez-Ríos, C. H. Greene, and H. Ott, arXiv:1602.08400 (2016).
[16] A. Gaj, A. T. Krupp, J. B. Balewski, R. Löw, S. Hofferberth, and T. Pfau, Nature Communications 5 (2014).
[17] M. Schlagmüller, T. C. Liebisch, H. Nguyen, G. Lochead, F. Engel, F. Böttcher, K. M. Westphal, K. S. Kleinbach, R. Löw, S. Hofferberth, T. Pfau, J. Pérez-Ríos, and C. H. Greene, Phys. Rev. Lett. 116, 053001 (2016).
[18] R. Schmidt, H. R. Sadeghpour, and E. Demler, Physical Review Letters 116 (2016).
[19] H. Sakmannshausen, F. Merkt, and J. Deiglmayr, Physical Review Letters 114, 133201 (2015).
[20] D. A. Anderson, S. A. Miller, and G. Raithel, Physical Review A 90, 062518 (2014).
[21] M. Marinescu, H. R. Sadeghpour, and A. Dalgarno, Physical Review A 49, 982 (1994).
[22] M. Scheer, J. Thogersen, R. C. Bilodeau, C. A. Brodie, H. K. Haugen, H. H. Andersen, P. Kristensen, and T. Andersen, Physical Review Letters 80, 684 (1998).
[23] U. Thumm and D. W. Norcross, Physical Review Letters 67, 3495 (1991).
[24] U. Thumm, private communication.
[25] P. Goy, J. M. Raimond, G. Vitrant, and S. Haroche, Physical Review A 26, 2733 (1982).
[26] J. J. Sakurai and J. Napolitano, Modern Quantum Mechanics (Addison-Wesley, 2011).