Photoassociation of rotating ultra-long range Rydberg molecules

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Abstract
We discuss the rotational structure of ultra-long range Rydberg molecules and their angular nuclear wave function. Expressing the complete molecular wave function in a laboratory fixed frame, we derive the transition matrix elements for the photoassociation of free ground state atoms. The coupling strength depends on the angular momentum coupling in the Rydberg molecule, which differs for the various types of Rydberg molecules. This work explains the different steps to calculate the wave functions and the transition matrix elements in a way, that they can be transferred to other Rydberg molecules involving different atomic species or molecular coupling cases.

Keywords: photoassociation, Rydberg molecules, rotational spectra

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

1. Introduction

Since their first theoretical description [1] and experimental discovery [2], Rydberg molecules have been of great interest in theoretical as well as experimental studies. Rydberg molecules are formed by the low-energy scattering between an electron in a Rydberg state and a perturber atom in an electronic ground state. They have been investigated for a manifold of different excited states as well as for different atomic species [2–4]. Polyatomic states, with more than one perturber atom, have been found [5]. Also more exotic molecules, such as the trilobite and butterfly molecules with up to several kilodebye permanent electric dipole moment, have been produced in experiments [3, 6]. Coherent control of the molecular states has been demonstrated [7] and recently Rydberg molecules have been used as an optical Feshbach resonance to tune the interactions in a many-body system [8, 9].

The scattering interaction between the electron in a Rydberg state and the perturber atom is typically described by a Fermi type pseudo-potential taking into account S- and P-wave scattering. The calculation of the Born–Oppenheimer potentials in a molecular fixed frame is a well established task and has been described in numerous works [10–14]. A complete description of the molecular wave function in a laboratory fixed frame and the calculation of transition matrix elements for photoassociation to different rotational states is missing so far. This is, in principle, a well established procedure for conventional molecules and there exists extensive literature, which covers the description of rotational molecular states as well as the photoassociation at ultracold temperatures [15–20]. However, Rydberg molecules feature several aspects, which deserve a closer discussion. Especially, we aim to explain the procedure in a comprehensive way, such that it can be easily adapted to other Rydberg molecules and atomic species. We will here concentrate on the class of ultra-long range Rydberg molecules, but most arguments are also valid for butterfly and trilobite molecules.

The outline of this article is as follows: in section 2, the calculation of the Born–Oppenheimer potentials and the description of diatomic Rydberg molecules is briefly revised. We will discuss the different angular momentum couplings and introduce the full molecular wave function in a laboratory fixed frame. In section 3, the wave function of two free ground state atoms shall be introduced and transformed into the same basis as the Rydberg molecule. In section 4 we
will then calculate the transition matrix elements for one and two-photon transitions and, finally, we discuss the implications for the excited rotational states in section 5.

Before starting let us first introduce the coordinate system used throughout this work (see figure 1(a)). We will consider two atoms with one of them being excited to a Rydberg state. The coordinate of the excited electron with respect to its positively charged nucleus will be labeled with \( \mathbf{r}' \) and the separation between the two nuclei with \( \mathbf{R} \). In a molecular fixed frame we will choose the \( z \)-axis to coincide with the symmetry axis of the system, therefore only having to consider the absolute value \( R \).

To distinguish the electronic coordinate in the two systems we will overline it in the molecular frame. Thus \( \mathbf{\bar{r}}' \) is the electric coordinate in the molecular frame and \( \mathbf{\bar{R}} \) in the laboratory fixed frame. To transform the coordinate systems into each other we will use the three Euler angles \( \alpha, \beta \) and \( \gamma \) in \( z-y-z \) convention. The first two Euler angles may be identified as the usual coordinates \( \Phi(=\alpha) \) and \( \Theta(=\beta) \) in spherical coordinates, while the third coordinate corresponds to a rotation around the symmetry axis. While this may be ambiguous for a diatomic molecule we will nevertheless keep it for the sake of generality. As we will often use Wigner-D matrices in this work to transform from one frame to the other and to describe rotational states it should be noted that we will stick to the convention used by Rose et al [21].

2. Rydberg molecules

Diatomic Rydberg molecules are typically described in a molecular fixed frame by a set of quantum numbers including all involved spins except the nuclear spin of the Rydberg atom, which is neglected due to the small hyperfine interaction in Rydberg atoms. In an atomic basis, the quantum numbers are therefore \( |n_1l_1j_1m_{J_1}\rangle \otimes |n_2l_2j_2m_{J_2}l_2m_{I_2}\rangle \) with the index 1 indicating the atom excited to the Rydberg state and 2 the bound perturber atom. We have dropped \( s_1 = s_2 = 1/2 \) for simplicity. The bars indicate, that the atomic basis states are taken with respect to the internuclear axis.

The electronic Hamiltonian in Born–Oppenheimer approximation is then written as [12]:

\[
\hat{H}(\mathbf{r}', \mathbf{R}) = -\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}}^2 + V_C(\mathbf{r}) + V_{\Omega_1}
+ \sum_{i=S,T} 2\pi A_i'(k) \delta^3(\mathbf{r}' - \mathbf{R}) \mathbf{\hat{p}}_i
+ \sum_{i=S,T} 6\pi A_i''(k) \delta^3(\mathbf{r}' - \mathbf{R}) \mathbf{\nabla} \cdot \mathbf{\hat{p}}_i
+ A_{\Omega_2} S_2 \cdot \mathbf{\hat{I}}_2. \tag{1}
\]

Here, the first three terms correspond to the kinetic energy of the Rydberg electron, its Coulomb interaction with the ionic core and its fine structure. The next two terms are the S- and P-wave interaction for singlet and triplet scattering of the Rydberg electron and the perturber atom, with \( A_i'(k) \) the energy dependent S- and P-wave scattering length and \( \mathbf{\hat{p}}_i \) the singlet/triplet projector for \( i = S/T \), respectively. The last term corresponds to the hyperfine interaction in the perturber atom.

The solution of the corresponding Schrödinger equation to equation (1) leads to Born–Oppenheimer potential curves \( U_{BO}(R) \) and electronic eigenstates \( |\Psi_{\text{mol}}(R)\rangle \), which parametrically depend on the internuclear distance. The calculation of the potentials and eigenstates has been described in detail elsewhere [10–14]. Here, we will assume that \( U_{BO}(R) \) and

\[
|\Psi_{\text{mol}}(R)\rangle = \sum_i c_i(R) \times |[m_1l_1j_1m_{J_1}\rangle \otimes [n_2l_2j_2m_{J_2}l_2m_{I_2}\rangle]_i \rangle \tag{2}
\]

are known in the molecular fixed frame. The coefficients \( c_i \) depend on \( R \) and express the electronic configuration in the atomic basis, fulfilling the normalization condition \( \sum |c_i(R)|^2 = 1 \). Note that the index \( i \) runs over all atomic basis states.

In the same notation as in [12] in figure 1(b) the potential curves around the \( (25P_{3/2} + 5S_{1/2}, \ F = 2) \) manifold in \( ^{87}\text{Rb} \) are depicted. The composition of the different potential curves is rather complex and depends on the relative strength of the fine structure, hyperfine structure and scattering interaction. In the present example, three potential curves occur. In this article we will discuss states in the so-called deep and shallow potential, as in most cases both of them support bound molecular states and are the appropriate description in all species having a hyperfine structure in the perturber atom exceeding the scattering interaction.

The rotational energy of Rydberg molecules is typically smaller than any of the other energy scales, as the rotational constant \( B = \hbar^2/2I \) is very small for states with large bond length \( d (B = \hbar \times 46 \text{ kHz for } ^{85}\text{Rb} \text{ with } d = 950 \text{ a}_0) \). Therefore, the angular momentum coupling for most Rydberg molecules can be best described either in a Hund’s case (a) or (c) depending on the size of the fine structure splitting, hyperfine structure splitting and scattering interaction [12]. In

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**Figure 1.** (a) Coordinate system used throughout this work. Atom 1 is excited to a Rydberg state and atom 2 is bound to a molecular state by the scattering interaction with the electron in the Rydberg state. (b) Born–Oppenheimer potential curves \( U_{BO}(R) \) for \(^{87}\text{Rb} \) around the \((25P_{3/2} + 5S_{1/2}, \ F = 2) \) manifold. Each potential type is degenerate with different \( \Omega \) quantum numbers. The vibrational ground state in each well and the corresponding radial wave function \( \Phi(R) \) for the so-called deep potential are depicted in blue.
To form a treatment of non-adiabatic effects could be done in the usual way. We will discuss in section 5 how to handle this. In this work, we will base our description on a Hund’s case (c), for which the fine structure splitting and the hyperfine structure splitting dominate the scattering interaction. This is also the most intuitive choice for the chosen basis to solve equation (1). Note that because the basis states for each Hund’s case are complete, the overall result does not depend on the chosen basis and we could base our description on any one.

In Hund’s case (c), the two electronic angular momenta and the nuclear spin of atom 2 are coupled to the angular momentum $\vec{K} = J_1 + J_2 + I_2$, with projection $\Omega$ onto the internuclear axis (see figure 2). This projection is then coupled with the nuclear orbital angular momentum $\vec{N}$ to form the total angular momentum $\vec{J} = \vec{N} + \vec{e}_r$. As the rotational constant $B$ is small for Rydberg molecules, we can neglect variations of the centrifugal barrier over the extent of a bound molecular state. The rotational energy of a molecular state in a Hund’s case (c) including adiabatic corrections is then given as [16]

$$E_{\text{rot}} = B(J(J + 1) - \Omega^2 + \langle \Phi_{\text{mol}} | \hat{K}_r^2 + \hat{K}_d^2 | \Phi_{\text{mol}} \rangle).$$

(3)

It should be noted that $K$ is not a good quantum number even for a Hund’s case (c) molecule. However, as ultra-long range Rydberg molecules typically only weakly admix states with different values $l$, $K$ is a quasi good quantum number and we can evaluate the remaining expectation value,

$$\langle \Phi_{\text{mol}} | \hat{K}_r^2 + \hat{K}_d^2 | \Phi_{\text{mol}} \rangle \approx K(K + 1) - \Omega^2.$$  

(4)

To completely characterize a molecular state we use $|X, \nu, J, m_J, \Omega\rangle$, where we have summarized all electronic quantum numbers (except $\Omega$) into one single label $X$. The different vibrational states, characterized by $\nu$, are obtained by solving the nuclear Schrödinger equation in Born–Oppenheimer approximation:

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + U_{\text{BO}}^{X,\Omega}(R) \right) \Phi_{\nu}^{X,\Omega}(R) = E_{\text{mol}} \Phi_{\nu}^{X,\Omega}(R),$$

(5)

where $\mu$ is the reduced mass of the two nuclei. We will assume that this equation is solved either numerically or in some analytic way to obtain the molecular energy $E_{\text{mol}}$ and the radial nuclear wave function $\Phi_{\nu}^{X,\Omega}(R)$. Note that $E_{\text{mol}}$ does not include the rotational energy equation (3) yet. In our treatment we neglect any non-adiabatic couplings, which could lead to a mixing of the different $\Omega$ states. For a proper inclusion of this effect, one would have to include the relativistic spin–orbit coupling in the P-wave scattering channel at the same time [13, 14]. This leads to a splitting of states with different $\Omega$. A treatment of non-adiabatic effects could then be done in the usual way.

Altogether, the wave function of a diatomic Rydberg molecule can be written as [16, 21]:

$$\Psi_{\text{mol}} = \frac{1}{R} \Phi_{\nu}^{X,\Omega}(R) \mathcal{H}_{\mu,\Omega}(\alpha, \beta, \gamma) \Phi_{\text{mol}}^{J,\Omega}(R, \vec{F}),$$

(6)

where $\mathcal{H}_{\mu,\Omega} = \frac{\sqrt{2J + 1}}{\sqrt{8\pi\mu}} D^J_{\mu,\Omega}$ are normalized Wigner-D matrices describing the orientation of the molecular axis in the laboratory frame, and $\Phi_{\text{mol}}^{J,\Omega}(R, \vec{F})$ describes the electronic part of the molecular wave function. Note that the possible values of the total angular momentum $J$ are restricted by the conditions $J \geq \Omega$ and the usual $J \geq m_J$. We will use this expression later on to calculate transition matrix elements for the photoassociation of two ground state atoms.

3. Initial state

In ultracold gases, the initial state for photoassociation usually corresponds to two free ground state atoms undergoing an S-wave collision. The formulas discussed above are not easily adapted for this case as an internuclear axis cannot be defined for spherical symmetry. In a molecular language, such a situation is best described in the often neglected Hund’s case (e). Therefore, in order to calculate transition matrix elements, we have to transform the wave function of the two free ground state atoms into a molecular frame.
To this purpose, we assume that both atoms are initially prepared in a hyperfine ground state $|n_i, j_i, f_i, m_f_i\rangle$ ($s_i = 1/2$ as before) where $i = 1, 2$ labels the two atoms. In a typical experiment this initial state will be prepared with respect to the laboratory frame and we therefore do not overline the magnetic quantum numbers. As in a Rydberg molecule the hyperfine interaction in the excited atom can be neglected, we separate the nuclear spin of one atom from our description

$$|X_i f_i m_f_i\rangle = \sum_{m_i,m_{j_{1}}} C^{i}_{m_{i}m_{j_{1}}}|X_i j_{i} m_{j_{i}}\rangle |I_{3} m_{f_{i}}\rangle,$$

where $C^{i}_{m_{i}m_{j_{1}}}$ is a Clebsch–Gordon coefficient and we have summarized the remaining quantum numbers in $I_f$ and $X_i$ for the hyperfine and fine structure case, respectively. Note that this procedure is quite special and only occurs in Rydberg molecules. We then couple the fine structure state of atom 1 with the hyperfine state of atom 2 to the total angular momentum $K = \hat{J} + \hat{F}$:

$$|X_1 f_1 m_{f_1}\rangle |Y_2 f_2 m_{f_2}\rangle = \sum_{m_{f_1},m_{f_2}} C^{i}_{m_{i}m_{j_{1}}} C^{1}_{m_{1}m_{f_1}} |X_1 j_1 m_{j_1}\rangle |Y_2 j_2 m_{j_2}\rangle \times |Y_2 f_2 K m_{k}\rangle |I_{3} m_{f_{1}}\rangle |I_{3} m_{f_{2}}\rangle$$

with $m_{k} = m_{j_1} + m_{j_2}$ the projection quantum number along the laboratory fixed z-axis. We transform this coupled state into a molecular fixed frame using [21]:

$$|X_1 Y_2 j_1 f_1 K m_{k}\rangle = \sum_{\Omega} D^{\\Omega}_{m_{k}m_{f_1}}(\alpha, \beta, \gamma) |X_1 Y_2 j_1 f_2 K \Omega\rangle.$$

So far we have not yet included the rotational state of the two nuclei. While for most ultracold experiments usually only S-wave scattering has to be considered, for Rydberg molecules higher partial waves might be of relevance because of the long bond length in Rydberg molecules. As a reference, for $r = 2000\ a_0$ the P-wave centrifugal barrier for $^{87}$Rb is only 1 $\mu$K high. Therefore, in the temperature range of a typical experiment this initial state will be prepared with respect to the laboratory frame and we therefore do not overline the magnetic quantum numbers. As in a Rydberg molecule the nuclear spin wave function of atom 1 and describe the ground state as:

$$\Psi_g = \frac{1}{R} F_g (\mathbf{R}) \sum_{m_y,m_z} \sqrt{\frac{2N + 1}{8\pi^{2}}} \times C^{i}_{m_{i}m_{j_{1}}} C^{1}_{m_{1}m_{f_1}} C^{K}_{m_{k}m_{f_2}} c^{K,N,I}_{\Omega_{\Omega_2}}(\mathbf{r}) \chi_{l,m_{l_n}}.$$

Here, $\Psi_g^{i,j_{i},f_{i},K^{i,j_{i},f_{i}}}(\mathbf{r})$ is the wave function corresponding to the state in equation (9) and $\chi_{l,m_{l_n}}$ the nuclear spin wave function of atom 1. An atomic pair scattering in a single channel characterized by $|N, m_{N}\rangle$ thus corresponds to a sum over different angular momenta $\mathbf{J}$ and different angular projections $\Omega$. It should also be noted, that $m_j$ has no well defined value in above description. Only $m_{f_1} + m_{f_2}$ as the total angular momentum projection number has a fixed value.

To simplify from here on, we will assume that the two atoms are in fully stretched states colliding in an s-wave ($N = 0$). For this case, all Clebsch–Gordon coefficients in equation (11) are equal to one. Additionally, we will drop the remaining nuclear spin wave function of atom 1 and describe the ground state as:

$$\Psi_g = \frac{1}{R} F_g (\mathbf{R}) \sum_{\Omega_{\Omega_2}} \sqrt{\frac{1}{8\pi^{2}}} D^{\\Omega}_{m_{k}m_{f_1}}(\alpha, \beta, \gamma) \Phi^{K^{i,j_{i},f_{i}}}(\mathbf{r}),$$

where $X$ denotes all electronic quantum numbers except of $\Omega$. Note that the electronic wave function $\Phi^{K^{i,j_{i},f_{i}}}(\mathbf{r})$ does not depend on $R$. Equation (12) will be our starting point to calculate transition matrix elements for photoassociation of molecular Rydberg states.

### 4. Transition matrix elements

To calculate the transition matrix elements to different molecular states we first consider a single photon transition, where the polarization of the photon is given in the laboratory fixed frame. The dipole operators, which have to be evaluated, are therefore $q_{\parallel}$ with $q = 0, \pm 1$ for $\pi, \sigma^{\pm}$ transitions, respectively. As we have expressed the electronic wave functions in a molecular fixed frame, we also have to transform the dipole operator accordingly [21]

$$\hat{d}_{q} = \sum_{\parallel} D^{l_{q_{\parallel}}}_{m_{q_{\parallel}}}(\mathbf{r})$$

where $\hat{d}_{q}$ is the dipole operator in the molecular fixed frame. In the following, we assume that only atom 1 can be excited and evaluate $d_{q_{\parallel}} \otimes \mathbf{I}_2$. If both atoms are in the same initial state and can be excited, one has to evaluate $d_{q_{\parallel}} \otimes \mathbf{I}_2 + \mathbf{I}_1 \otimes \hat{d}_{q_{\perp}}$, in order to account for the correct symmetry of the system. An excitation will then couple to a superposition of atom 1 excited and atom 2 bound in its Rydberg electron wave function and vice versa. In total this leads to an additional factor of $\sqrt{2}$ which can be taken into account by hand if necessary.
Priming all quantum numbers associated with the molecular state, the transition matrix element is given as:

\[
\langle \Psi_{\text{mol}} \mid \hat{d}_{q1} \otimes I_2 \mid \Psi_{\xi} \rangle = \frac{\sqrt{2J' + 1}}{8\pi^2} \int dR \int d\alpha \sin \beta d\beta d\gamma \\
\times F_{\xi}^{\nu',\Omega',q}(R) F_{\xi}(R) \\
\times \sum_{\sigma,\Omega} \langle D_{\nu',\Omega'}^{\sigma}(\alpha, \beta, \gamma) D_{\nu,\sigma}^{\nu}(\alpha, \beta, \gamma) \rangle \\
\times \langle \Psi_{\text{mol}}(R, \vec{r}) \mid d_{q1} \otimes I_2 \mid \Psi_{\xi}(\vec{r}) \rangle. \tag{14}
\]

For ultra-long range molecules the parametric dependency on \( R \) of the excited electronic state is very weak. We can therefore use the Franck–Condon principle approximating \( \Phi_{\text{mol}}^{X,Y}(R, \vec{r}) \approx \Phi_{\text{mol}}^{X,Y}(\vec{r}) \) and split equation (14) into three separate parts. In this way, we only have to take care of the summations over \( \Omega \) and \( \sigma \) later on.

The first term is a Franck–Condon integral for the radial wave function

\[
\int dR \overline{F}_{\nu'}^{X,Y,\Omega,\sigma}(R) F_{\xi}(R). \tag{15}
\]

As we have assumed that the molecular wave function and the ground state wave function are known, the integral can be calculated straightforward, as has been done in various other works \([22, 23]\). They are subject to the usual selection rules of an atomic transition \( \Delta l_i = 0, \pm 1, \Delta m_f = 0, \pm 1 \), while maintaining the quantum numbers in atom 2, \( \Delta n_2 = \Delta l_2 = \Delta m_2 = 0 \).

With this formalism at hand, equation (14) can be evaluated to get the transition matrix elements and the corresponding Rabi frequencies to excite a particular molecular Rydberg state.

Before discussing the implications on the excited nuclear wave functions and their orientation in space, we want to briefly discuss how to handle the experimentally more common two-photon transitions and the implications of the neglected hyperfine interaction in atom 1.

For a two-photon transition the scheme is not more complicated than discussed so far. We can simply replace the initial state with the intermediate state \( \ket{g} \), where \( i \) denotes the intermediate level of atom 1 and evaluate equation (14) to get the transition matrix element \( d_{\text{mol}} \). Because for typical experiments the detuning from the intermediate state \( \Delta \) is larger than its hyperfine splitting in most cases a description of \( \ket{i} \) in a fine structure picture will be sufficient.

The total coupling strength is then \( \propto d_{\text{lower}} d_{\text{mol}}/(2\Delta) \) where \( d_{\text{lower}} \) is the transition matrix element for the lower transition \([24]\).

Neglecting the hyperfine interaction in the Rydberg atom is a good approximation in the case of Rydberg states with \( l > 0 \) as for these the hyperfine interaction is smaller than the rotational energy. For S-states however the hyperfine interaction will exceed in most cases the rotational energy \((v_{\text{rot}} \approx 33 \text{ GHz}/(n^3)^3 \text{ in } ^8\text{Rb} [25])\). The correct coupling would therefore require to include the hyperfine interaction before adding the nuclear rotation. This will lead to some changes in the above description, which should be straightforward to include.

5. Rotational states of Rydberg molecules

To discuss the angular nuclear wave function of Rydberg molecules, we have to give up the generality we have tried to keep so far. In the following, we will give a few selected examples, which capture the most relevant aspects of the photoassociation process. We will discuss molecular states in \(^8\text{Rb}\) bound in the outermost well of the molecular deep and shallow potentials. The eigenvectors \(X^{\Omega}(\vec{r})\) are retrieved from a full numerical diagonalization of equation (1) at the minimum of the potential well. To further simplify the treatment, we will assume that the two atoms are colliding in an S-wave.
To check the numerical procedure for consistency, we have verified that in the limit of vanishing molecular interaction, the formalism leads to a spherical nuclear wave function in the excited state. It should also be noted that despite using some fixed main quantum numbers \( n \) and \( n' \) for the ground, intermediate and excited state, the principle arguments will be valid for any main quantum number. Calculated transition matrix elements from equation (14) will be given in reference to the equivalent atomic transition, however, excluding the Franck–Condon factor equation (15).

Let us first discuss the often used excitation from a fully stretched ground state \([5S_{1/2}, F = 2, m_F = +2, 5S_{1/2}, F = 2, m_F = +2]\) to a molecular S-state via two photons using a \( \sigma^+ \) transition for the lower and a \( \sigma^- \) transition for the upper transition. In this case, the intermediate state is a pure fine structure state \([6P_{3/2}, m_J = 3/2, 5S_{1/2}, F = 2, m_F = +2]\) and corresponds in our framework to a total angular momentum of \( J = 7/2 \) and a projection of the angular momentum onto the laboratory fixed \( z \)-axis of \( m_J = 7/2 \). The only possible excitation for the second step is a \( \sigma^- \) transition to states in the deep potential connected to the \((26S_{1/2} + 5S_{1/2}), F = 2)\) manifold with \( J' = 5/2 \) and \( m_J = 5/2 \).

As already mentioned earlier an ultra-long range S-state molecule is best described in a Hund’s case (b). In this description due to the vanishing spin–orbit interaction the spin states completely decouple from the molecular axis. The rotational energy is thus not given by equation (3) but rather by

\[
E_{\text{rot}} = B[P(P + 1) - \Lambda^2 + \{\Phi_{\text{mol}}|l_z^2 + l_\sigma^2|\Phi_{\text{mol}}\}] ,
\]

where \( P = \Lambda^2 + N \) and \( \Lambda \) is the projection of the orbital angular momentum of the electron \( l_z \) onto the molecular axis and equals zero for S-state molecules. The remaining expectation value can be evaluated in a similar way as in equation (4) and also equals zero.

In the upper part of figure 3 this case is depicted. As the different \( \Omega' \) states in a Hund’s case (c) description are degenerate, the excited molecular state is a superposition of all of them, resulting in a spherically symmetric nuclear wave function \( \sum_{\Omega} D_{\Omega}^{J'}(\alpha, \beta, 0)^2 = 1 \). Note that this is only true as long as any residual spin–orbit coupling is weaker than the rotational energy. If this is not the case, the spins can be coupled to the internuclear axis. For S-state molecules, this can have two reasons: first, we know from the diagonalization of equation (1) that even for molecular states with large bond length the scattering interaction mixes high-\( l \) states with non vanishing spin–orbit coupling into the potential curves. Second, relativistic effects in the triplet P-wave scattering [13, 14], which are not included in this work, will also lead to a coupling to the molecular axis. If these couplings introduce a larger energy scale than the rotational constant, the molecule should be rather described in Hund’s case (c), as depicted in the lower part of figure 3. Then, the resonance splits into three individual lines each with equal \( |\Omega'\rangle \) and the coupling leads to non-spherical angular nuclear wave functions \( |D_{\Omega^*}^{J'}(\alpha, \beta, 0)^2 + |D_{\Omega^*}^{J'}(\alpha, \beta, 0)^2| \). We expect that in most cases an intermediate situation between Hund’s case (b) and (c) is realized. However, irrespective of the coupling scheme within the molecule, the total transition rate summed over all rotational states is equal to the atomic one (excluding the Franck–Condon Factor). S-state Rydberg molecules can also be excited with a \( \pi-\pi \) transition, however the transition matrix elements are then reduced by the additional Clebsch–Gordan coefficients for the two atomic transitions.

There is also an intuitive explanation within our framework why transitions to the corresponding \emph{shallow} potential are not accessible for the \( \sigma^+-\sigma^- \) excitation scheme. As the initial state is described by an S-wave \((N = 0)\) the intermediate state has the quantum numbers \( J = K = 7/2 \). However from the numerical calculation of the excited potential, we know that it has a total electronic angular momentum of \( K = 3/2 \). Thus, upon excitation, two quanta of electronic angular momentum have to be annihilated in the second absorption process. As the light field in dipole approximation can only carry away one quantum of angular momentum, the other one has to be transferred to the rotation of the molecule. Such a process is strongly suppressed or even absent due to the decoupling of the spin from the internuclear axis.

Another important photoassociation scheme is the single photon transition to P-state Rydberg molecules. Because
of the fine structure in the Rydberg state, a much richer molecular spectrum arises. Now, the spin–orbit interaction strongly couples the electronic spin to the internuclear axis. Exciting from a fully stretched ground state as before, \( |5S_{1/2}, F = 2, m_F = +2, 5S_{1/2}, F = 2, m_F = +2 \rangle \), several rotational states in the deep potential, connected to the \((25P_{3/2} + 5S_{1/2}, F = 2)\) manifold, can be excited. In figure 4 the molecular spectrum for a \( \sigma^+ \) and a \( \pi \) transition are shown. As the initial state can be described through the quantum numbers \( J = 5/2, m_J = 5/2 \), the excited state is either \( m_J = 7/2 \) or \( m_J = 5/2 \) respectively. In contrast to the previous example the coupling to different \( \Omega \) states is not of equal strength but rather depends on the individual state. Additionally for a \( \pi \) transition \( J' = 5/2 \) as well as \( J' = 7/2 \) states have similar coupling strengths leading to rather complex excitation spectra. For narrow laser linewidth, this rotational structure should be observable in an experiment.

In figure 5 we show the molecular spectrum for a \( \sigma \) transition from the \((5S_{1/2}, F = 1, m_F = +1, 5S_{1/2}, F = 1, m_F = +1)\) to the deep and shallow potentials of the \((25P_{3/2} + 5S_{1/2}, F = 1)\) manifold. Again, a large variety of rotational states can be excited. Surprisingly, we also find molecules with a spherical shape of the angular nuclear wave function, which one might not expect for a pure Hund’s case (c) coupling. This can be explained as follows. As already discussed before, different \( |\Omega \rangle \) states now split due to the rotational energy. In addition, we know from the properties of the Wigner-D matrix that \( \sum_{\Omega'} |D_{m_J'\Omega'}|^2 = 1 \). Spherically symmetric molecules are therefore possible, if \( \Omega' = \pm 1/2 \) and \( J' = 1/2 \). In the present example, this is the case for the deep potential and the shallow potential connected to an \( F = 1 \) ground state manifold. In both cases, we have \( K' = 1/2 \) and the lowest lying molecular state has a spherically symmetric nuclear wave function with \( J = 1/2 \) and \( |\Omega'\rangle = 1/2 \). This is rather uninformative as the underlying electronic wave function is off course non spherically symmetric due to the coupling of the electronic orbital wave function to the internuclear axis.

6. Conclusion

To conclude, we have presented a complete treatment of ultralong range molecular Rydberg states including rotation in a laboratory fixed frame. We have calculated transition matrix elements for the photoassociation of Rydberg molecules and discussed the implications for the excited spectra and angular nuclear wave functions for selected transitions. Our results can be easily transferred to other Rydberg systems like triblode or butterfly molecules and atomic species.

The formalism described in this work is not limited to this kind of application. In a similar way transitions between different molecular states can be calculated and even interactions between molecular states can be investigated. As the description is rather generic it should be straightforward to adapt it for cases including spin dependent scattering interactions not discussed here [13, 14] or generalizing it further, fully including the hyperfine interaction of the Rydberg state.
With state of the art experiments the presented features should be measurable in typical spectroscopic experiments in ultracold systems from a Bose–Einstein condensate or an ultracold system with comparable temperature.

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