Spatial imaging of the movement of bound atoms to reveal the Rydberg molecular bond via electromagnetically induced transparency

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Abstract – We propose an approach to detect individual Rydberg molecules, where each molecule consists of two atoms lying in different Rydberg states. The scheme exploits the different movements of atoms and molecules in the presence of external forces to differentiate atoms and molecules. The forces acting on the two atoms in the molecule are different. We consider the most ideal situation, that is, the external force is exerted only on one of the two Rydberg atoms in the molecule. The movement of Rydberg atoms that are not affected by the external force depends on whether they are bound to the Rydberg atoms affected by the force. Therefore, bound Rydberg atoms can be distinguished from free Rydberg atoms. By non-destructively resolving the locations of Rydberg atoms through detecting the absorption events with the probe field or the fluorescence signal, the scheme can be utilized to detect the positions of Rydberg molecules, and also the bond force in the Rydberg molecule.

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Introduction. – The motions and forces of individual molecules can reveal their fundamental properties. They can be measured by utilizing the single-molecule force spectroscopy techniques [1–7]. The forces associated with such measurements are usually on the order of $10^{-3}$–$10^{3}$ pN in the lengthscale of several nanometers [6]. Among the molecules, Rydberg molecules can be formed due to the interaction between the Rydberg electron and the ground-state atoms [8–13]. The long-range interaction between two Rydberg atoms can also be utilized to create Rydberg molecules [14–25]. Here the Rydberg atoms are atoms where at least one electron is in a highly excited state [26]. The most common technique for detecting the Rydberg molecules is the ionization of Rydberg atoms, which breaks the Rydberg molecular bonds to measure the Rydberg molecule [13,18]. The spatial distributions of Rydberg atoms can be measured non-destructively by Rydberg electromagnetically induced transparency (EIT) [27,28]. Based on the work of non-destructive measurement of individual Rydberg atoms, we find that it is possible to measure the spatial positions of individual Rydberg molecules and the molecular bond strengths.

We consider a Rydberg molecule consisting of two Rydberg atoms [24]. For the system, there exists a stable energy minimum. It is surrounded by a region of attraction extending to some distance, beyond which the potential becomes vanishing or repulsive. This binding potential results from avoided crossings, which are caused by the long-range dipole-dipole interaction between two atoms lying in different Rydberg states [24]. When the inter-atomic distance is larger than the region of attraction, the Rydberg molecular bond can be considered broken. The main idea is that the forces acting on the two atoms in the molecule are different. So the two atoms, and the two-atom molecule will produce different movement distances, through which one can distinguish the free atoms and the Rydberg molecules. We consider the most ideal situation, that is, applying the force on one of the two atoms. The force with a moderate strength drags one of the two atoms in the molecule, which can make the other atom move due to the binding between the two atoms. In the presence of an external force, the Rydberg molecules and free atoms move to different distances, which can be measured by detecting surrounding probe atoms. We would like to remark that it is also a good idea to consider the applied
field to be red detuned for the atomic transition involving the state of one atom, and blue detuned for the atomic transition involving the state of the other atom. The two atoms will move along two opposite directions. For the measurement, our scheme only requires imaging for two times. The first one is performed after the creation of the Rydberg molecules. It records the original locations of the molecules. The second one is performed after dragging the Rydberg molecules for about 10 μs, which records the final locations of the molecules. Here the EIT can be utilized for the measurement, because the interaction destroys the condition of the EIT, so the probe atoms will be scattered by the photons. Since the photons in the probe light are scattered, the Rydberg atoms or molecules can be measured by detecting the probe light. Since the probe atoms scatter the photons, the probe atoms may decay to the ground state, and it is possible to reach another ground state that is different from the ground state initially prepared. By using the fluorescence to measure these probe atoms in the different ground state, one can also observe the Rydberg atoms or molecules. So in the same experiment, there are two ways to detect the Rydberg atoms or molecules. They are achieved by measuring the probe light, or measuring the probe atoms in the different ground state. So the fluorescence imaging can help to better detect the Rydberg atoms or molecules. Our analysis shows that the time for Rydberg molecule creation, evolution, and imaging is within the lifetime of the Rydberg molecules.

The system and the Hamiltonian. – The Rydberg molecule under consideration consists of two atoms lying in different Rydberg states ns and np [24]. Here we label the atomic energy level as nlj. For Rydberg atoms, as shown in fig. 1(a), the principal quantum number n >> 1. l = s, p labels the orbital angular momentum of the excited valence electron. j is the total angular momentum. The ns level is separated from the np3/2 level by an energy difference equal to ℏωp, while the np1/2 level is separated from the np3/2 level by the fine-structure splitting energy ℏ|Δ|. For Rb atoms, ωp is much larger than Δ [29]. Our scheme starts with a dilute gas of cold Rb atoms prepared in the ground state 5s [12,17]. The atoms are excited to the Rydberg state ns via the two-photon transition. It is followed by microwave radiations to excite a pair of ns atoms to the ns-np molecule [24]. We propose to measure these Rydberg molecules by detecting the strength of the probe field in an Rydberg EIT transition of the surrounding probe atoms [28]. Here a Rydberg molecule can cause energy shifts of the Rydberg states in the surrounding atoms. This results in the breaking of the EIT condition, and therefore the creation of one spot in the probe-field absorption image. We find a method for enhancing the imaging of Rydberg molecules inspired by ref. [30]. The probe atoms scattered by the probe field may decay into another ground state different from their ground state initially prepared. By detecting the fluorescence signal of the surrounding atoms, the Rydberg molecules can be measured. The unbound ns and np atoms can also cause energy shifts of the Rydberg states of the surrounding atoms, therefore they will also be imaged. To distinguish the Rydberg molecules from the unbound ns and np atoms, we propose to switch on a detuned laser beam with an homogeneous intensity to drag the ns atoms. By imaging the Rydberg molecules before and after the evolution, we can identify unmoved objects, moved objects, and objects moved for a double distance. They correspond to the np atoms, the ns-np molecules and the ns atoms, respectively. The double-distance movement of ns atoms is due to the fact that the molecule mass is twice the single-atom mass. We find that the rupture force of Rydberg molecular bond, which is on the order of 1000 pN in the lengthscale of several micrometers, should be detectable by utilizing our scheme.

The Hamiltonian describing two Rydberg atoms is

$$H_{2\text{atoms}} = (\hat{p}_i^2 + \hat{p}_j^2)/(2m) + H_0(R_1, R_2),$$

where $\hat{p}_i$ is the momentum of the i-th atom and m is the mass of a single atom. The Hamiltonian of two Rydberg
The molecular potential. – Some software packages can be utilized to compute the interatomic potentials [31,32]. In the ns-np subspace consisting of two Rydberg atoms, one atom is lying in the ns state and the other atom is lying in the np state. By utilizing the Born-Oppenheimer approximation to calculate the internal eigenstates, the molecular potential has been revealed [20,22,24]. It has been verified through the semiclassical calculations that the atomic motion in the potential remains adiabatic [22]. The reason is that the eigenstate corresponding to the potential, i.e., the bound state, is energetically well separated from other eigenstates, and the velocity of atoms in the potential is sufficiently small [22]. When |R| ≥ r0, other two-atom states cause a negligible van der Waals shift, since their energy distance from the np-manifold is large compared to the energy of h/|Δ|. Here R is the interatomic distance. r0 is a characteristic length as defined in appendix A. In fig. 1(b), we display a molecular potential, with the minimum value appearing around Rf ≃ 1.7r0. The potential depth is on the order of 100 MHz for n = 40 Rydberg atoms. An electric field can induce a Stark shift δ, where |δ| ≪ |Δ|. It allows one to align the Rydberg molecule in the electric-field direction [24].

Our scheme starts with a dilute gas of Rb atoms lying in the ground state [12,17]. We expect to create some Rydberg molecules with a low density with certain probabilities [12,17]. The populations of Rydberg atoms and molecules should be small but allow the experiments in a realistic time scale, and the effect of the ground-state atoms should be negligible [12,17]. For two atoms close to each other, the transition from one Rydberg excitation to two Rydberg excitations is shifted by the dipole-dipole interaction between two atoms. This forms an energy band. Due to the known interatomic distance in the molecule, i.e., the known blockade energy, one can utilize a laser with a different frequency to excite the second Rydberg atom. Moreover, the ns-ns state is not the ultimate state. We can directly utilize a microwave to excite the second atom to the np state. The frequency of the microwave is determined by taking into account the blockade effect. This is given by the energy difference of the ns and np states, the blockade energy due to the interaction between two ns atoms, and the binding energy of the molecule due to the interaction between the ns and np atoms. At the temperature of 300 μK, the decay rate is approximately 25 kHz for 85 Rb atoms lying in the n = 40 Rydberg states. The vibrational frequencies of the molecular motion are about 2π × 0.4 MHz, and the rotational frequencies are about 2π × 0.1 kHz [24]. The equilibrium distance is given by Rp = 1.55 μm. A necessary condition for measuring the Rydberg molecules is that their kinetic energy is smaller than the potential depth, which corresponds to a temperature ~ 4.8 mK (100 MHz) [24].

Measuring the locations of Rydberg molecules by utilizing the EIT. – Our scheme utilizes the Rydberg EIT. The probe beam Ωp and the control beam Ωc are resonant to the transitions of g ↔ e and e ↔ ns, respectively (see fig. 1(a) and appendix B). Here the g and e states denote the ground and excited states, respectively. We assume that the e state decays with the same decay rate into the g state and another ground state g′. The g′ state is decoupled from the EIT lasers, and is measurable with the fluorescence. When the probe atom is far from the region around a Rydberg atom or molecule, the imaginary part of the susceptibility Im[χ] (i.e., the absorption rate, see appendix B) and the g′-state population of the probe atom are zero. When the probe atom is in the vicinity of a Rydberg atom or molecule, the ns state of the probe atom is shifted due to the dipole-dipole interaction, leading to a finite Im[χ] and g′-state population.

We consider one molecule consisting of two atoms positioned at ρ = 0, z = ±Rp/2, and one probe atom with a varying spatial position, as shown in fig. 2(a). Im[χ] is zero when the probe atom is far from the region around the molecule. Within a radius of Rc ≃ 3 μm in the vicinity of the molecule, the value of Im[χ] becomes nonzero. We would like to remark that, several lines appear in this region corresponding to Im[χ] significantly smaller than 1. This is due to the existence of degenerate states. They are degenerate to the state in which the probe atom in the ns state is far from the molecule. However, these lines are very thin. In the calculation, we set Ωp = 2π × 1 MHz and Ωc = 2π × 10 MHz. The decay rates from the e and ns states are Γp = 2π × 6 MHz and Γc = 2π × 25 kHz, respectively.
The $g'$-state population is plotted in fig. 2(b) by numerically solving the master equation. Here the EIT lasers are set to remain switched on for 2 µs. We plot the $g'$-state population for $z = 0$ only in (b), since the distribution of $g'$-state population in the $z$-$p$ plane has a similar shape as the shape of $\text{Im}[\chi]$ in (a). When the population of $ns$ atoms is small, i.e., $\rho_{2D}R_{12}^2/|\Omega|^2 \ll 1$, the results for single probe atom can be applied to an ensemble of probe atoms. Here $\rho_{2D}$ is the density of atoms in 2D. Taking into account the atomic density fluctuation, we simulate a spatially resolved fluorescence image, as shown in fig. 2(c). We set $\rho_{2D} = 1 \mu m^{-2}$. Each pixel has a region of $(0.5 \mu m)^2$. As illustrated in fig. 2(c), the location of a molecule is surrounded by the green spots, with each spot representing one $g'$ atom. There are approximately 20 spots on average surrounding the molecule.

Moreover, the atomic motion in the potential remains adiabatic. The reason is that the eigenstate corresponding to the potential is energetically well separated from other eigenstates. The center-of-mass motion of two atoms is decoupled from the internal atomic state. So only the relative motion needs to be considered. The frequencies of vibrations and rotations are $< 1$ MHz. In the presence of the external force, the frequency of the relative motion is also $< 1$ MHz (as shown in fig. 3(b)). They are much smaller than the minimum energy separation ($\sim 100$ MHz) between the bound state and the other eigenstates. In this case, the internal state evolves adiabatically, where the system stays in an eigenstate adiabatically connected to the initial bound state.

**Switching on an external force to distinguish the Rydberg molecules from free atoms.** – To distinguish Rydberg molecules from Rydberg atoms, we exert an energy slope of approximately $0.08$ GHz/µm on $ns$ atoms to drag the molecules for a resolvable distance $9 \mu m$. This energy slope can be achieved by an off-resonant atomic transition involving the $ns$ state. Here the detuning is $20$ GHz, the Rabi frequency increases linearly from 0 to $8$ GHz in the lengthscale of $10 \mu m$. Under these parameters, the depopulation of the $ns$ state occurs with a probability of $4\%$. One candidate is a transition between $n$ and $n'$ Rydberg states driven by a microwave field. The strength of the electric field to drive an atomic transition is $E = \hbar \Omega /d$, where $\Omega$ is the Rabi frequency, and $d$ is the dipole moment of the atomic transition [33]. For $\Omega = 8$ GHz and $n, n' \sim 40$, the electric-field strength is $E \sim 1$ V/cm [34]. The laser power is $S = E^2 /Z_0$, where $Z_0 = 377 \Omega$ is the impedance of free space. So the laser power corresponding to the electric field of $1$ V/cm is approximately $26$ W/m². The strength of the electric field for the ionization is on the order of $\sim 100$ V/cm [12,17]. Therefore, the electric-field strength $E$ for dragging is two orders of magnitude smaller than the electric-field strength for the ionization. Moreover, the field strength corresponding to the applied force is approximately equal to the field utilized in the alignment of the Rydberg molecular state. It is a weak electric field on the order of $1$ V/cm, such that the mixing of states with the opposite parity is negligible [24]. The energy of the $np$ level may also be shifted, however, the magnitude of the shift could be much smaller. When $n'$ is significantly smaller than $n$, the energy splittings in the $n'$ levels are much larger than those in the $n$ levels. According to the selection rule, the detunings of atomic transitions involving the $np$ state are determined by the energy splittings in the $n'$ level: there are only atomic transitions of $np \leftrightarrow n's$ and $np \leftrightarrow n'd$. Therefore, the detunings for atomic transitions involving the $np$ state could be much larger than the detunings involving the $ns$ state.

In the presence of the external force, the dissociation process is a competition between the dragging and potential forces. The systems stays in an eigenstate adiabatically connected to the initial bound state. We label the molecular bound state as $\psi(R_1, R_2)$. Under the Born-Oppenheimer approximation, the motion of two atoms is described with a classical Hamiltonian as $H_{2\text{atom}}(R_1, R_2) = (p_1^2 + p_2^2)/(2m) + H_0(R_1, R_2)$, where $H_0(R_1, R_2) = \langle \psi(R_1, R_2) | H_0(R_1, R_2) | \psi(R_1, R_2) \rangle$. The external force dragging the $i$-th atom is denoted as $U_i = u(R_i) \sum_{j} |ns, j_{z} \rangle \langle ns, j_{z}|$. Here, $u(R_i)$ is the energy shift of the $ns$ state of the $i$-th atom. $j_{z}$ is the projection of the total angular momentum onto the $z$-axis. In the Hamiltonian mechanics, the time evolution of the classical system is described by Hamilton’s equations $d\mathbf{p}_i/dt = -\nabla_{R_i} H_0(R_1, R_2)$ and $dR_i/dt = \mathbf{p}_i/m$.

The dragging force is applied by a linear energy shift $u = \alpha z$. We consider the case that the molecule is aligned along the direction of the applied force because in this case, the molecular bond can be broken apart with the minimum force strength. Two atoms are initially located at $x = y = 0$, $z = \pm R_0/2$. The positions of two atoms as a function of the time are plotted in fig. 3(a). The solid line corresponds to the case of a small energy shift.
with $\alpha = 0.08 \text{ hGHz}/\mu\text{m} \simeq 5 \times 10^{-7} \text{ pN}$, where two atoms move together by $9 \mu\text{m}$ in $10 \mu\text{s}$. For a larger force with $\alpha = 0.12 \text{ hGHz}/\mu\text{m}$ (dashed line), two atoms begin to drift away from each other, indicating that the Rydberg molecular bond is broken apart. For a small $\alpha$, there is an oscillatory behaviour of the relative displacement of two binding atoms, as shown in fig. 3(b). When $\alpha$ exceeds $0.1 \text{ hGHz}/\mu\text{m}$, the relative displacement of two atoms becomes larger and larger, without the oscillation. This shows that the Rydberg molecular bond is broken apart. We would like to remark that, as shown in fig. 3(b), the frequency of the relative motion in the presence of the applied force is $< 1 \text{ MHz}$. We calculate the overlap between the initial bound state and the $\psi(\mathbf{R}_1, \mathbf{R}_2)$ state, which is the state in a system with an applied force with $\alpha = 0.08 \text{ hGHz}/\mu\text{m}$. The overlap is larger than 98%. Therefore, the internal state stays in an eigenstate adiabatically connected to the initial bound eigenstate with a high probability. Once the molecule is projected onto other states, two atoms will be separated up, which is measurable.

The interaction between the probe atoms is the van der Waals interaction $V \approx -\hbar C_6/R^6$. For the probe atoms lying in the 40s level, $C_6 = 2\pi \times 1 \text{ GHz} \mu\text{m}^6$ [35]. The critical radius is defined as when the interaction energy exceeds the width of the EIT window [36]. This gives the critical radius as $R_c' = (2C_6\Gamma_p/\Omega_q^2)^{1/6} \approx 2 \mu\text{m}$, at which the imaginary part of the susceptibility decreases to half its maximum [27]. For the probe atoms, we can choose an EIT involved $n'$s level with $1 \ll n' < 40$ to shorten the radius $R_c'$. The interaction coefficient $C_6$ will decrease, as the leading term of $C_6$ is proportional to $n^{11}$ [35]. A large signal-to-noise ratio requires the condition $\rho_{2D} < \Omega_q^2/(\pi \epsilon_0 R_c^6 \Omega_p^2)$, above which the contrast of the image decreases [27]. Our scheme uses a 2D gas with a density $\rho_{2D} = 1 \mu\text{m}^{-2}$. The radius is $R_c' = 2 \mu\text{m}$. The Rabi frequency is $\Omega_p^2/\Omega_q^2 = 100$. This distance is short enough for creating the Rydberg molecules, and the condition for a large signal-to-noise is satisfied. In ref. [28], the time for imaging the Rydberg atoms is $2 - 20 \mu\text{s}$. This is within the timescale of the lifetime of the Rydberg molecule considered in our scheme. We find that, the number of the probe atoms in the $g'$ state surrounding one molecule in our scheme is approximately equal to the amplification factor of one Rydberg atom in ref. [28]. Here the amplification factor of one Rydberg atom is related to the optical depth [28].

### Conclusion

In summary, we have proposed a scheme to non-destructively measure the Rydberg molecules. With an applied dragging force, the Rydberg molecules are distinguished from the free atoms by the distinct features in the non-destructive imaging via the Rydberg EIT. Our scheme utilizes a new method to enhance the EIT imaging protocol by not only directly measuring the absorption of the probe field, but also measuring the states of the probe atoms via the fluorescence signal. We have shown that the Rydberg molecular bond can remain unbroken in the presence of an applied force, when the strength of the force is within a range. The imaging is performed on the surrounding atoms, which allows a non-destructive measurement for the Rydberg molecules. The rupture force of the Rydberg molecular bond can be measured by increasing the applied force. This scheme provides a way to study the Rydberg molecular bond more visually. The scheme can be utilized to reveal the dynamics involved in the Rydberg molecular bond and the movement of the atoms. These are different from other standard methods based on the ionization, which provides information about the spectra. This scheme allows a non-destructive measurement of the Rydberg molecular position with an accuracy at the micrometer scale, and can measure the time-dependent changes. The measurement gives the dynamic process of the light-induced reaction of the Rydberg molecular bond in the real time and in the real space, which can be utilized as a tool for studying the dynamics of the system.

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### Appendix A: the Hamiltonian and the Rydberg molecular potential

- The Hamiltonian describing the $i$-th Rydberg atom is

$$
H_i = \hbar \omega_0 \sum_{j_i = -3/2}^{3/2} |np_{3/2}, j_z\rangle \langle np_{3/2}, j_z| + \hbar (\omega_0 + \Delta) \sum_{j_z = -1/2}^{1/2} |np_{1/2}, j_z\rangle \langle np_{1/2}, j_z|.
$$

Here $\omega_0$ is the resonance frequency of the ns $\leftrightarrow np_{3/2}$ atomic transition. $\hbar |\Delta|$ is the energy difference between the $np_{1/2}$ state and the $np_{3/2}$ state. The $i$-th atom and the $j$-th atom locate at $\mathbf{R}_i$ and $\mathbf{R}_j$, respectively. Their dipole-dipole interaction is [37]

$$
V_{ij} = \frac{1}{4\pi\varepsilon_0 R^3} \left\{ \mathbf{d}^{(i)} \cdot \mathbf{d}^{(j)} - 3(\mathbf{d}^{(i)} \cdot \mathbf{R})(\mathbf{d}^{(j)} \cdot \mathbf{R}) \right\}.
$$

Here $\varepsilon_0$ is the dielectric constant. $\mathbf{d}^{(i)}$ is the electric-dipole-moment operator of the $i$-th atom. $\mathbf{R} = \mathbf{R}_i - \mathbf{R}_j$, $R = |\mathbf{R}|$, and $\mathbf{R}/R$ is the unit vector. For the individual atoms, the matrix elements of the electric-dipole-moment operator $\mathbf{d}$ are evaluated via the Wigner-Eckert theorem [34,38]. The reduced dipole matrix element is defined as $D = e\langle np|\mathbf{r}|ns\rangle/\sqrt{3}$. For alkali-metal atoms with $n \geq 40$, we have $\langle np|\mathbf{r}|ns\rangle \approx n^2 a_0$, where $a_0$ is the Bohr radius [34]. The characteristic strength of the dipole-dipole interaction is given by $h\Omega = |D|^2/(4\pi\varepsilon_0 R^3)$. 

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The characteristic length scale $r_0$, corresponding to the occurrence of the bound states, can be obtained by equating $\Omega$ with $|\Delta|$. This gives $r_0 = [(D^2/(4\pi\epsilon_0\hbar|\Delta|))]^{1/3}$. For the $^{85}$Rb with $n = 40$, the energy difference is $\Delta \approx 2\pi \times 1$ GHz, which yields $r_0 \approx 1 \mu m$ [24].

**Appendix B: The susceptibility.** – The Hamiltonian describing the interaction between a probe atom and EIT lasers is

\[
H_{\text{EIT}} = \hbar \sum_{j_x=-1/2}^{1/2} \left[ |\Delta_p| \langle e, j_x | e, j_x \rangle \right. \\
+ (\Delta_p + \Delta_c) |ns, j_x \rangle \langle ns, j_x | \\
+ \frac{\Omega_p}{2} |\langle e, j_x | g, j_x | + \text{H.c.} \rangle \\
\left. + \frac{\Omega_c}{2} |\langle ns, j_x | e, j_x | + \text{H.c.} \rangle \right],
\]

where $g$ and $e$ represent the ground and excited states, respectively. The Rabi frequency of the probe field $\Omega_p$ and the Rabi frequency of the control field $\Omega_c$ drive the $g \leftrightarrow e$ and $e \leftrightarrow ns$ atomic transitions with the detunings $\Delta_p$ and $\Delta_c$, respectively. $\Gamma_p$ and $\Gamma_c$ are the spontaneous decay rates of the $e$ and $ns$ states, respectively.

In the limit of the weak Rabi frequency of the probe field, $\Omega_p \ll \Omega_c$. For the system with small populations in the $e$ and $ns$ states, the susceptibility corresponding to the atomic transition driven by the probe field is [27,36,39]

\[
\chi = \frac{i\Gamma_p}{\Gamma_p - i\Delta_p + \sum_k \Omega_k^2 F_k^2 (\Gamma_c - i\Delta_k)^{-1}},
\]

where the summation over $k$ accounts for the effect of the multiple energy levels $|\psi_k\rangle$ of the three-Rydberg-atom states [39]. We label the $k$-th eigenenergy and the $k$-th eigenstate of the three Rydberg atoms as $E_k$ and $|\psi_k\rangle$, respectively. $F_k$ is defined as $F_k = \sum_{j_x=-1/2}^{1/2} |\langle ns, j_x | m | \psi_k \rangle|^2$. Here the state $|ns, j_x, m\rangle$ represents that the probe atom is in the $|ns, j_x, m\rangle$ state, and the other two atoms are in the molecular state. $E_0$ is the energy corresponding to the $|ns, j_x, m\rangle$ state when the probe atom is far away from the molecule. The detuning $\Delta_k$ is $\Delta_k = \Delta_p + \Delta_c + E_k - E_0$.

**REFERENCES**

[1] Weiss S., Science, **283** (1999) 1676.
[2] Gross L., Mohr F., Moll N., Liljeroth P. and Meyer G., Science, **325** (2009) 1110.
[3] Gross L., Mohr F., Moll N., Liljeroth P. and Meyer G., Nat. Chem., **2** (2010) 821.
[4] Ullmann J., Deglmaier J., Repp M., Wester R. and Weidemüller M., Chem. Rev., **112** (2012) 4890.
[5] de Oteyza D. G. et al., Science, **340** (2013) 1343.
[6] Neuman K. C. and Nagy A., Nat. Methods, **5** (2008) 491.
[7] Walter N. G., Huang C.-Y., Manzo A. J. and Sobhy M. A., Nat. Methods, **5** (2008) 475.
[8] Greene C. H., Dickinson A. S. andSadeghpour H. R., Phys. Rev. Lett., **85** (2000) 2458.
[9] Liu I. C. H., Stanojevic J. and Rost J. M., Phys. Rev. Lett., **102** (2009) 173001.
[10] Bendkowsky V. et al., Phys. Rev. Lett., **105** (2010) 163201.
[11] Li W. et al., Science, **334** (2011) 1110.
[12] Bendkowsky V., Butscher B., Shaffer J. N. J., Löw R. and Pfau T., Nature, **458** (2009) 1005.
[13] Kruipp A. T. et al., Phys. Rev. Lett., **112** (2014) 143008.
[14] Boisseau C., Simiotin I. and Côté R., Phys. Rev. Lett., **88** (2002) 133004.
[15] Schawtettman A., Crawford J., Overstreet K. R. and Shaffer J. P., Phys. Rev. A, **74** (2006) 020701(R).
[16] Schawtettman A., Overstreet K. R., Tallant J. and Shaffer J. P., J. Mod. Opt., **54** (2007) 2551.
[17] Overstreet K. R., Schawtettman A., Tallant J., Booth D. and Shaffer J. P., Nat. Phys., **5** (2009) 581.
[18] Samboy N., Stanojevic J. and Côté R., Phys. Rev. A, **83** (2011) 050501(R).
[19] Samboy N. and Côté R., J. Phys. B, **44** (2011) 184006.
[20] Kiffner M., Park H., Li W. and Gallagher T. F., Phys. Rev. A, **86** (2012) 031401(R).
[21] Tallant J., Rittenhouse S. T., Booth D., Sadeghpour H. R. and Shaffer J. P., Phys. Rev. Lett., **109** (2012) 173202.
[22] Kiffner M., Li W. and Jaksch D., Phys. Rev. Lett., **110** (2013) 170402.
[23] Kiffner M., Li W. and Jaksch D., J. Phys. B, **46** (2013) 134008.
[24] Kiffner M., Huo M., Li W. and Jaksch D., Phys. Rev. A, **89** (2014) 052717.
[25] Petrovyansk and Molmer K., Phys. Rev. Lett., **113** (2014) 123003.
[26] Gallagher T. F., Rydberg Atoms (Cambridge University Press, Cambridge, England) 1994.
[27] Günther G., Robert-de-Saint-Vincent M., Scheppe H., Hofmann C. S., Whillock S. and Weidemüller M., Phys. Rev. Lett., **108** (2012) 013002.
[28] Günter G. et al., Science, **342** (2013) 954.
[29] Li W., Mourachko I., Noel M. W. and Gallagher T. F., Phys. Rev. A, **67** (2003) 052502.
[30] Olmos B., Li W., Hofferberth S. and Lesanovsky I., Phys. Rev. A, **84** (2011) 041607(R).
[31] Sibalić N., Pritchard J. D., Adams C. S. and Weatherill K. J., arXiv:1612.05529, to be published in Comput. Phys. Commn. (2017).
[32] Weber S. et al., J. Phys. B: At. Mol. Opt. Phys., **50** (2017) 133001.
[33] Anderson D. A. et al., Phys. Rev. Appl., **5** (2016) 034003.
[34] Walker T. G. and Saffman M., Phys. Rev. A, **77** (2008) 032723.
[35] Singer K., Stanojevic J., Weidemüller M. and Côté R., J. Phys. B, **38** (2005) S295.
[36] Sevinc¸li S., Henkel N., Ates C. and Pohl T., Phys. Rev. Lett., **107** (2011) 153001.
[37] Cohen-Tannoudji C., Dupont-Roc J. and Grynberg G., Atom-Photon Interactions: Basic Processes and Applications (Wiley-VCH) 1998.
[38] Edmonds A. R., Angular Momentum in Quantum Mechanics (Princeton University Press) 1960.
[39] Badger S. D., Hughes I. G. and Adams C. S., J. Phys. B, **34** (2001) L749.