Quantum-classical model for the formation of Rydberg molecules

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(Received 27 January 2012; published 30 July 2012)

A fascinating aspect of Rydberg atoms is their ability to form huge but very weakly bound molecules with a ground-state atom, only held together by a scattering process between the latter and the Rydberg electron. Beyond the usual way of creating such molecules by laser excitation from two ground-state atoms with a distance of less than the Rydberg radius, we demonstrate that Rydberg molecules can also be formed by capturing a ground-state atom which is initially located outside the range of the Rydberg atom when it comes in contact with it. To demonstrate this effect, we investigate the scattering process between the Rydberg electron and the ground-state atom within a quantum-classical framework. In this picture, the capture results from a dissipative finite-mass correction term in the classical equations of motion. We show that, and under which conditions the capturing takes place.

DOI: 10.1103/PhysRevA.86.012713 PACS number(s): 34.50.Cx, 34.20.Cf

I. INTRODUCTION

Highly excited Rydberg atoms have long been the focus of numerous theoretical and experimental investigations [1–8], which exploit, e.g., their large spatial extensions, which give rise to huge polarizabilities and strong interactions, or their long lifetimes. In 2000, Greene *et al.* [3] predicted that Rydberg atoms can form very weakly bound molecules with ground-state atoms. This was experimentally confirmed in 2009 by Bendkowsky *et al.* [1] in a cold dilute gas of rubidium atoms, and the results well agree with a simple quantum-mechanical model developed by Greene *et al.* [3].

Rydberg molecules are created by laser excitation of one ground-state atom in a two-photon process using detuned lasers. The resulting Rydberg atom can then form a molecule with another ground-state atom, which, at the time of laser excitation, is within a distance from the nucleus of the Rydberg atom smaller than the extension of the wave function of the Rydberg electron. In this way, the creation of excited dimers and Rydberg trimers is also possible [2,8]. The experiments reported in Ref. [8] also show the yet unexplained formation of $Rb_2{}^+$ in the photoassociation spectra without any detuning of the lasers, i.e., at resonance of the Rydberg atom.

In this paper, we pursue a quantum-classical approach to understand the mechanism by which Rydberg molecules are formed. In such a picture we will demonstrate how ground-state atoms which are initially located at distances from the Rydberg atom larger than its extension can be captured by the latter *after* its excitation. This will lead to the interpretation that a Rydberg molecule is formed in the sense of a chemical reaction in which two reactants, the Rydberg and the ground-state atom, interact to form the reaction product, i.e., the Rydberg molecule. As is well known chemical reactions cannot take place between two single particles because energy and momentum cannot be conserved simultaneously. A reaction, however, can occur in the formation of a Rydberg molecule because the Rydberg electron plays the role of a third particle which can, within the natural linewidth of the Rydberg state, absorb kinetic energy from the ground-state atom.

Our paper is organized as follows: First, we give a brief review and discussion of Greene's quantum-mechanical model before we introduce our quantum-classical treatment. The latter is based on classically describing the motion of the Rydberg electron in the $1/r$ potential, locally approximating it as a superposition of plane waves at the position of the ground-state atom, and quantum mechanically describing the scattering process. As a result, we can derive an expression for the force acting on the ground-state atom which includes a dissipative finite-mass correction term in the classical equations of motion. Finally, we compare the results obtained for the models with and without the correction term, and determine under which conditions the capturing of a ground-state atom, i.e., the formation of a molecule, can occur.

II. THEORY

As a framework for the theoretical description of the dynamics one could use quantum molecular dynamics [9] classically describing the motion of the nuclei of the molecule under the influence of the electron. However, in the case of Rydberg molecules, the dynamics of the Rydberg electron is predominantly determined by the nucleus of the Rydberg atom since the latter is positively charged, and the ground-state atom is a neutral particle which only acts as a small perturber. Thus, the wave function of the Rydberg electron is known for given quantum numbers and an appropriate description of the interaction between the Rydberg electron and the ground-state atom in a quantum-classical picture is therefore possible by *locally* approximating the known Rydberg wave function by a superposition of plane waves, each representing one corresponding classical Kepler ellipse of the Rydberg electron. The following two sections review the quantum-mechanical description of Rydberg atoms and introduce the quantum-classical treatment of the scattering process.

A. Molecular potential of Rydberg molecules

In the quantum-mechanical model of Greene *et al.* [3] the interaction between the Rydberg electron and the ground-state atom is described using a Fermi-type pseudopotential [10]

$$V(\boldsymbol{r},\boldsymbol{R}) = 2\pi a_s(k)\delta(\boldsymbol{r}-\boldsymbol{R}), \tag{1}$$

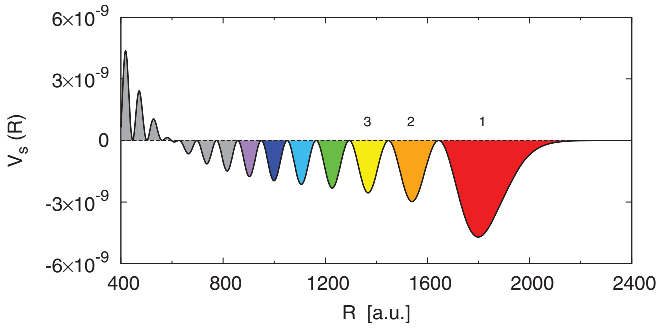

FIG. 1. (Color online) Molecular potential of a rubidium Rydberg molecule as a function of the internuclear distance for a negative scattering length $a_0 = -16.05$ and a polarizability $\alpha = 319$ in Eq. (2), calculated from Eq. (3) for quantum numbers $n = 31$, $l = 0$, $m = 0$. The numbers count the minima starting from the outermost one and the assignment of colors to the different potential wells will be the same in Fig. 4.

where $\boldsymbol{r}$ and $\boldsymbol{R}$ denote the positions of the Rydberg electron and the ground-state atom, respectively, and the function $a_s(k)$ is the s-wave scattering length, which depends on the wave vector k of the Rydberg electron. In a first-order approximation, it can be expressed in the form [11]

$$a_s(k) = a_{s,0} + \frac{\pi}{3}\alpha k + O(k^2). \quad (2)$$

Here $a_{s,0} = -16.05$ a.u. is the zero-energy scattering length and $\alpha = 319$ is the polarizability of the target [1,2,12]. Within a mean-field approximation this contact interaction leads to the molecular potential

$$V_s(\boldsymbol{R}) = 2\pi a_s(k)|\psi_{\mathrm{Ry}}(\boldsymbol{R})|^2, \quad (3)$$

where $\psi_{\mathrm{Ry}}(\boldsymbol{R})$ is the value of the wave function of the Rydberg electron at the position $\boldsymbol{R}$ of the ground-state atom. If $a_s(k) < 0$ the interaction is attractive. Figure 1 shows the molecular potential (3) for a particular set of quantum numbers.

In the potential shown in Fig. 1 and used in Refs. [1,3] only s-wave scattering is taken into account. A more realistic potential is obtained when also p-wave scattering is taken into account by the additional term

$$V_p(\boldsymbol{R}) = 6\pi a_p^3 \left|\nabla\psi_{\mathrm{Ry}}(\boldsymbol{R})\right|^2 \quad (4)$$

with $a_p = -21.15$ a.u. [2] so that the molecular potential is given by

$$V(\boldsymbol{R}) = \begin{cases} V_s(\boldsymbol{R}), & \text{pure } s\text{-wave scattering} \\ V_s(\boldsymbol{R}) + V_p(\boldsymbol{R}), & \text{with } p\text{-wave scattering} \end{cases} \quad (5)$$

As will be shown in Sec. III the occurrence of the quasiclassical formation of Rydberg molecules does not depend on whether or not p-wave scattering is considered.

By construction, Eq. (5) associates a *fixed* position $\boldsymbol{R}$ of the ground-state atom with the potential energy $V(\boldsymbol{R})$. If one considers a single scattering event of the Rydberg electron with the ground-state atom this is physically equivalent to the assumption that the center of mass of the two scattering partners lies exactly at the center of the ground-state atom, i.e., $m_e/m_{\mathrm{Rb}} = 0$. Moreover, Eq. (5) only takes into account the mean density distribution of the Rydberg electron and thus neglects dynamical effects of the scattering process.

B. Scattering process within the quantum-classical framework

The assumption $m_e/m_{\mathrm{Rb}} = 0$ is, of course, never strictly fulfilled, and, e.g., for rubidium atoms, which we consider throughout this paper, we have $m_e/m_{\mathrm{Rb}} \approx 6 \times 10^{-6}$. Thus the description of the electron rubidium scattering in the framework of Eq. (5) is not complete. To take into account dynamical effects of single scattering events, we will describe these in a quantum-classical way. In the classical equations of motion, by which we describe the dynamics of the heavy ground-state atom, this treatment will lead to a small but nonvanishing dissipative correction term in the order of the ratio of the masses of the two scattering partners, $O(m_e/m_{\mathrm{Rb}})$. In spite of its smallness it can have drastic effects on the dynamics of the rubidium atoms, as we will demonstrate in Sec. III.

Our quantum-classical model is based on the following assumptions: We describe the Rydberg atom as hydrogenlike with one Rydberg electron and a core with charge $+e$. Because of the high excitation of the Rydberg atom ($n \gg 1$), correspondence principle allows us to treat the motion of the Rydberg electron in terms of the classical trajectories, namely, Kepler ellipses, and we quantize the latters' angular momentum L and their energy E semiclassically according to

$$L = l + \frac{1}{2}, \quad E = \frac{\boldsymbol{p}^2}{2} - \frac{1}{r} = -\frac{1}{2n^2}, \quad (6)$$

where $n = 1,2,3,\ldots$ and $l = 0,1,2,\ldots$ are the principal and angular momentum quantum numbers, respectively, $\boldsymbol{p}$ is the momentum of the Rydberg electron, and $r = |\boldsymbol{r}|$ is its distance from the core. Note that the continuous set of Kepler ellipses fulfilling these conditions only differ from each other by a rotation of the ellipses around the azimuthal quantization axis.

Since the interaction between the Rydberg electron and the ground-state atom is of contactlike type, within this quantum-classical framework these two will only interact if the Kepler ellipses hit the latter (see Fig. 2), i.e., if the orbit includes the

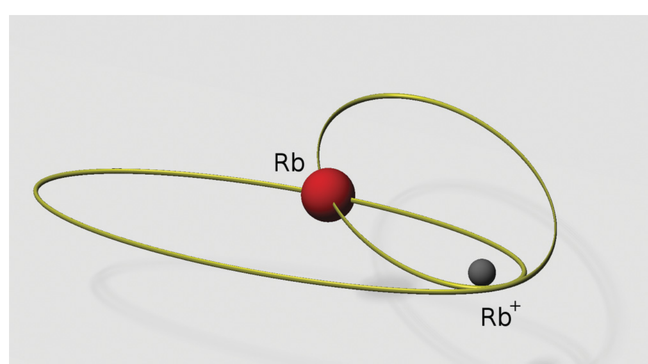

FIG. 2. (Color online) Schematic drawing of the quantum-classical model for the interaction between the Rydberg electron, orbiting the Rb^+ core (small gray sphere), and the Rb ground-state atom (big red sphere). For the magnetic quantum number $m = 0$ considered here, there are only two Kepler orbits on which the Rydberg electron can hit the ground-state atom and each is traversed in clockwise and counterclockwise directions.

position $\boldsymbol{R}$ of the ground-state atom. It can be easily shown that out of the infinite set of equivalent Kepler ellipses with given quantum numbers n,l,m only *four* ellipses fulfill this additional condition (see also Ref. [13]). In experiments only molecules with the Rydberg atom in an s-state have been formed so far, therefore we will also restrict ourselves to the angular momentum quantum numbers $l = m = 0$. In this case always two of the four possible ellipses coincide, and we are left with only two Kepler orbits that can intersect with the ground-state atom, each of which is traversed in clockwise and counterclockwise directions. Thus the momenta $\boldsymbol{p}^{(i)}$ of the Rydberg electron on the ith Kepler ellipse at the point of intersection are opposite to each other:

$$\boldsymbol{p}^{(1)} = -\boldsymbol{p}^{(2)}, \quad \boldsymbol{p}^{(3)} = -\boldsymbol{p}^{(4)} \tag{7}$$

for $m = 0$. Their values can be easily calculated for each point on the orbit and, in particular, at the point of intersection, i.e., the position of the ground-state atom.

To describe the process of the Rydberg electron orbiting on a Kepler ellipse being s-wave scattered at the ground-state atom we make use of the fact that the extension of the highly excited Rydberg atom is, by far, larger than that of the ground-state atom. Thus, we can assume the Coulomb potential $V_{\mathrm{C}}(\boldsymbol{r})$ of the Rydberg atom's nucleus to be constant in a small vicinity of the ground-state atom, i.e., $V_{\mathrm{C}}(\boldsymbol{r}) \approx$ const. for $\boldsymbol{r} \approx \boldsymbol{R}$, further allowing us to approximate the Rydberg electron on the ith Kepler ellipse by a plane wave $\psi_{\mathrm{pw}}^{(i)}(\boldsymbol{r}) = A^{(i)} \exp(i\,\boldsymbol{p}^{(i)}\boldsymbol{r})$. The *local* approximation of the total wave function is consequently a superposition of four plane waves, corresponding to the four ellipses,

$$\psi_{\mathrm{Ry}}(\boldsymbol{r}) \approx \sum_{i=1}^{4} \psi_{\mathrm{pw}}^{(i)}(\boldsymbol{r}) = \sum_{i=1}^{4} A^{(i)} \exp(i\,\boldsymbol{p}^{(i)}\boldsymbol{r}), \tag{8}$$

which establishes the key link between the classical picture of the interaction and the quantum-mechanical description of the scattering process: The momenta are identical to those of the electron on the Kepler orbit at the point of collision, and the amplitudes $A^{(i)}$ are determined by fitting the wave function to the exact quantum-mechanical Rydberg wave function. For $m = 0$ this wave function is real valued and cylindrically symmetric, $\psi_{\mathrm{Ry}} = \psi_{\mathrm{Ry}}(\rho,z)$, which implies that the complex amplitudes $A^{(i)}$ come in complex conjugate pairs, $A^{(1)} = A^{*(2)}$ and $A^{(3)} = A^{*(4)}$. We are therefore left with four unknowns, the real and imaginary parts of $A^{(1)}$ and $A^{(3)}$. To determine these we require that at the intersection point the values of the wave functions and their first derivatives coincide:

$$\psi_{\mathrm{pw}}|_{\boldsymbol{r}=\boldsymbol{R}} = \psi_{\mathrm{Ry}}|_{\boldsymbol{r}=\boldsymbol{R}}, \tag{9a}$$

$$\partial_\rho \psi_{\mathrm{pw}}|_{\boldsymbol{r}=\boldsymbol{R}} = \partial_\rho \psi_{\mathrm{Ry}}|_{\boldsymbol{r}=\boldsymbol{R}}, \tag{9b}$$

$$\partial_z \psi_{\mathrm{pw}}|_{\boldsymbol{r}=\boldsymbol{R}} = \partial_z \psi_{\mathrm{Ry}}|_{\boldsymbol{r}=\boldsymbol{R}}. \tag{9c}$$

Requiring also the identity of the second derivatives would provide three more equations but render the total set of equations overdetermined. To obtain a fourth equation we therefore only require that the sum of the moduli squared of the deviations of the second derivatives of the quantum-classical and the Rydberg wave function be a minimum

$$\left[\partial_\rho^2(\psi_{\mathrm{pw}} - \psi_{\mathrm{Ry}})|_{\boldsymbol{r}=\boldsymbol{R}}\right]^2 + \left[\partial_z^2(\psi_{\mathrm{pw}} - \psi_{\mathrm{Ry}})|_{\boldsymbol{r}=\boldsymbol{R}}\right]^2 + \left[\partial_\rho\partial_z(\psi_{\mathrm{pw}} - \psi_{\mathrm{Ry}})|_{\boldsymbol{r}=\boldsymbol{R}}\right]^2 = \min. \tag{10}$$

This leads to the best possible approximation of the Rydberg wave function by the four plane waves $\psi_{\mathrm{pw}}^{(i)}$.

To describe the scattering process in the quantum-classical picture, we first consider scattering of a *single* electron with a ground-state atom in the latter's rest frame. The incoming Rydberg electron on the ith Kepler ellipse, described by the plane wave $\psi_{\mathrm{pw}}^{(i)}$ with momentum $\boldsymbol{p}_{\mathrm{in}}^{(i)} = m_e \boldsymbol{v}_e^{(i)} = \hbar \boldsymbol{k}^{(i)}$, is scattered to an outgoing wave

$$\psi_{\mathrm{out}}^{(i)} \sim \frac{\exp\left(i p_{\mathrm{out}}^{(i)} |\boldsymbol{r} - \boldsymbol{R}|\right)}{|\boldsymbol{r} - \boldsymbol{R}|}(f_s + f_p \cos\theta + \cdots), \tag{11}$$

where f_l are the scattering amplitudes that are related to the scattering phase shifts δ_l by $f_l = k^{-1}(2l+1)e^{i\delta_l}\sin\delta_l$.

The wave number of the Rydberg electron is given by $k = \sqrt{2/R - 1/n^2}$ so that we obtain $k \lesssim 0.025$ for typical values $n = 31$ and $R \gtrsim 1200$ (see below). For rubidium, scattering in this region is therefore dominated by the s-wave so that δ_p and contributions from higher partial waves can be neglected in the scattering process.

Because of the spherically symmetric angle distribution the total momentum of the outgoing s-wave is $\boldsymbol{p}_{\mathrm{out}}^{(i)} = 0$ so that the Rydberg electron transfers a momentum of $\Delta \boldsymbol{P}_{\mathrm{Rb}}^{(i)} = m_e \boldsymbol{v}_e^{(i)}$ to the target, i.e., the rubidium ground-state atom. A number of $N^{(i)}$ colliding electrons consequently lead to a momentum transfer of

$$\Delta \boldsymbol{P}_{\mathrm{Rb}}^{(i)} = N^{(i)} m_e \boldsymbol{v}_e^{(i)}, \tag{12}$$

and if the scattering events occur in a time Δt this corresponds to a classical force

$$\boldsymbol{F}_{\mathrm{Rb}}^{(i)} = \Delta \boldsymbol{P}_{\mathrm{Rb}}^{(i)} \big/ \Delta t \tag{13}$$

acting on the ground-state atom. We now proceed from single but continuous scattering processes to a current density

$$\boldsymbol{j}_e^{(i)} = n_e^{(i)} \boldsymbol{v}_e^{(i)} = \frac{N^{(i)}}{\sigma\,\Delta t}\,\hat{\boldsymbol{e}}_{\boldsymbol{v}_e^{(i)}}, \tag{14}$$

where $n_e^{(i)} = |A^{(i)}|^2$ is the electron density on the ith Kepler ellipse, $\sigma = 4\pi a_s^2(k)$ is the scattering cross section, and $\hat{\boldsymbol{e}}_{\boldsymbol{v}_e^{(i)}}$ is the unit vector in the direction of $\boldsymbol{v}_e^{(i)}$. Similar to the discussion above, including p-wave scattering does not change the total scattering cross section σ significantly in the important region $R \gtrsim 1200$ a.u. Combining Eqs. (12)–(14) we end up with

$$\boldsymbol{F}_{\mathrm{Rb}}^{(i)} = n_e^{(i)} m_e \sigma \left|\boldsymbol{v}_e^{(i)}\right|^2 \hat{\boldsymbol{e}}_{\boldsymbol{v}_e^{(i)}}. \tag{15}$$

We now switch to the laboratory frame, where the ground-state atom, in general, moves with a velocity $\boldsymbol{v}_{\mathrm{Rb}} \neq 0$ relative to the ionic core of the Rydberg atom and, without loss of generality, assume the latter to be at rest. The transformation to the laboratory frame then results in the formal substitution $\boldsymbol{v}_e \to \boldsymbol{v}_e - \boldsymbol{v}_{\mathrm{Rb}}$ in Eq. (15), which leads to

$$\boldsymbol{F}_{\mathrm{Rb}} = \sum_{i=1}^{4} \boldsymbol{F}_{\mathrm{Rb}}^{(i)}, \tag{16a}$$

$$\boldsymbol{F}_{\mathrm{Rb}}^{(i)} = n_e^{(i)} m_e \sigma \left|\boldsymbol{v}_e^{(i)} - \boldsymbol{v}_{\mathrm{Rb}}\right|^2 \hat{\boldsymbol{e}}_{(\boldsymbol{v}_e^{(i)} - \boldsymbol{v}_{\mathrm{Rb}})}. \tag{16b}$$

Note that by locally describing the four Kepler ellipses as *independent* plane waves we lose all interference terms and thus the nodal structure of the Rydberg wave function.

Therefore Eqs. (16) cannot catch the mean electron density distribution. Moreover, since $\boldsymbol{F}_{\mathrm{Rb}}^{(i)} \sim n_e^{(i)}$ with the electron density $n_e^{(i)} = |\psi_{\mathrm{pw}}^{(i)}(\boldsymbol{r})|^2$, any phase-factor corrections which may occur when transforming from the ground-state atom's rest frame to the laboratory frame will cancel out.

For a simple discussion of the effect of the forces acting on the ground-state atom described by Eqs. (16) imagine the interaction with only the two coinciding Kepler ellipses $i = 1,2$ (the same holds, of course, for $i = 3,4$) and the case where at the collision the ground-state atom and the Rydberg electron fly in the same direction, $\hat{\boldsymbol{e}}_{\boldsymbol{v}_{\mathrm{Rb}}} = \hat{\boldsymbol{e}}_{\boldsymbol{v}_e^{(1)}}$. Since Eq. (7) then implies $\hat{\boldsymbol{e}}_{\boldsymbol{v}_e^{(2)}} = -\hat{\boldsymbol{e}}_{\boldsymbol{v}_e^{(1)}}$, we obtain a net force on the ground-state atom

$$\boldsymbol{F}_{\mathrm{Rb}} = \boldsymbol{F}_{\mathrm{Rb}}^{(1)} + \boldsymbol{F}_{\mathrm{Rb}}^{(2)} = -4 m_e \sigma n_e^{(1,2)} v_e^{(1,2)} v_{\mathrm{Rb}} \hat{\boldsymbol{e}}_{\boldsymbol{v}_{\mathrm{Rb}}}, \tag{17}$$

which for any value of the modulus of its velocity $v_{\mathrm{Rb}} > 0$ is directed opposite to its direction of flight, i.e., the ground-state atom is decelerated. Note that in Eq. (17) one contribution to the force is always accelerating (here the one with $\hat{\boldsymbol{e}}_{\boldsymbol{v}_{\mathrm{Rb}}} = \hat{\boldsymbol{e}}_{\boldsymbol{v}_e^{(1)}}$) and the other one is decelerating (here the one with $\hat{\boldsymbol{e}}_{\boldsymbol{v}_{\mathrm{Rb}}} = -\hat{\boldsymbol{e}}_{\boldsymbol{v}_e^{(2)}}$), whereas the latter dominates since $|\boldsymbol{v}_e^{(1)} - \boldsymbol{v}_{\mathrm{Rb}}| < |\boldsymbol{v}_e^{(2)} - \boldsymbol{v}_{\mathrm{Rb}}|$. The discussion can be generalized to the case of arbitrary flight directions $\hat{\boldsymbol{e}}_{\boldsymbol{v}_{\mathrm{Rb}}}$, and there always occurs a deceleration of the ground-state atom as a net effect.

Taking into account both the potential Eq. (5) resulting from the mean electron density distribution and the dissipative correction terms due to the dynamical effects, Eqs. (16), one can write down the classical equations of motion for the dynamics of the ground-state atom under the influence of the Rydberg atom:

$$\frac{d^2\boldsymbol{R}}{dt^2} = -\frac{1}{m_{\mathrm{Rb}}}\nabla V(\boldsymbol{R}) + \frac{m_e}{m_{\mathrm{Rb}}}\sigma \sum_{i=1}^{4} n_e^{(i)} \left|\boldsymbol{v}_e^{(i)} - \boldsymbol{v}_{\mathrm{Rb}}\right|^2 \hat{\boldsymbol{e}}_{\boldsymbol{v}_e^{(i)} - \boldsymbol{v}_{\mathrm{Rb}}}. \tag{18}$$

The second term is on the order of $m_e/m_{\mathrm{Rb}} \approx 6 \times 10^{-6}$ and therefore small, but as will be shown below, can have drastic effects on the motion of the ground-state atom. Note that in the limit $m_e/m_{\mathrm{Rb}} \to 0$ we recover the original model of Greene *et al.* [3].

III. RESULTS AND DISCUSSION

We obtain the following results solving the differential equation (18) for initial values $\boldsymbol{R}$ and $\boldsymbol{v}_{\mathrm{Rb}}$. The physical parameters are chosen in such a way that they cover the experiment in Ref. [1], in which ^{87}Rb atoms have been excited to Rydberg s-states $n' \geqslant 34$. Including quantum defect corrections of $\delta = 3$ for rubidium [14], we therefore use quantum numbers $n = n' - \delta = 31$, $l = 0$, and $m = 0$.

Since we assume the Rydberg atom to be in the spherically symmetrical s-state, there are only three quantities which determine the dynamics of the ground-state atom, namely, the absolute value of the initial velocity of the ground-state atom, v_{Rb}, the initial internuclear distance R_0, and the angle ϕ between the direction of the initial velocity and the line connecting the ground-state atom and the center of the Rydberg atom, $\cos\phi = \boldsymbol{v}_{\mathrm{Rb}}\boldsymbol{R}/(v_{\mathrm{Rb}}R)$. Throughout this section we choose $R_0 = 2500$ a.u. which is outside the range of the Rydberg electron including the tail of the Fermi pseudopotential. In the following Sec. III A we first present the results for the quasiclassical model using s-wave scattering. The modifications obtained by including p-wave scattering are discussed in Sec. III B. An interpretation of the model beyond the quasiclassical approach is outlined in Sec. III C.

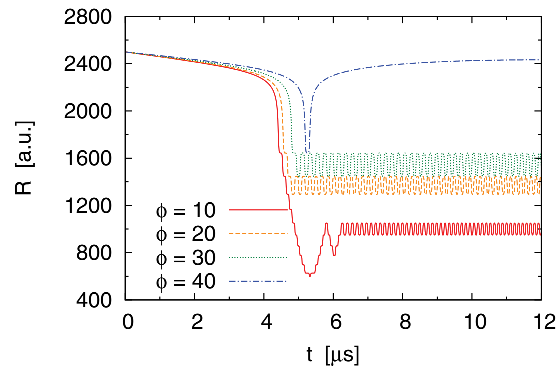

FIG. 3. (Color online) Internuclear distance between the Rydberg and the ground-state atom in dependence of time for different angles ϕ between the initial direction of the motion of the ground-state atom and the connecting line to the nucleus of the Rydberg atom. The initial velocity is set to $v_{\mathrm{Rb}} = 10^{-9}$ a.u. For all angles shown the ground-state atom will be captured but the selection of a specific local minimum strongly depends on the initial value of ϕ.

A. Model with s-wave scattering

To demonstrate the effect of the finite-mass correction term in Eq. (18) we discuss the trajectories of the ground-state atom obtained with the correction. Figure 3 shows the internuclear distance between the Rydberg and the ground-state atom for initial values $v_{\mathrm{Rb}} = 10^{-9}$ a.u. and various angles between $\phi = 10^\circ$ and $\phi = 40^\circ$.

If only the conservative potential is taken into account, the ground-state atom approaches the Rydberg atom, reaches some minimum distance, and then leaves it again. Taking into account the finite-mass correction term, the ground-state atom initially shows a similar behavior, but on its way out from the Rydberg atom, it begins to oscillate, e.g., around a distance of $R \approx 1500$ a.u. for the orbit launched with $\phi = 30^\circ$ in Fig. 3, and no longer leaves the Rydberg atom. The physical meaning is that the ground-state atom has been captured in one of the potential wells, i.e., the total energy of the ground-state atom has decreased below zero and it cannot leave the Rydberg atom anymore:

$$E_{\mathrm{g.a.}} = \frac{m_{\mathrm{Rb}}}{2}\boldsymbol{v}_{\mathrm{Rb}}^2 + V(\boldsymbol{R}) < 0. \tag{19}$$

We emphasize that the formation of the molecule occurs *after* the excitation of the Rydberg atom and not, as usual, by excitation with a detuned laser.

In the example with $\phi = 10^\circ$ shown in Fig. 3 the ground-state atom enters the vicinity of the Rydberg atom at $t \approx 3\ \mu$s. The total energy $E_{\mathrm{g.a.}}$ of the ground state atom becomes negative at $t \approx 6\ \mu$s, which means that the Rydberg molecule is formed within $\sim 3\ \mu$s. Note that this time is significantly smaller than the lifetime of the Rydberg molecule of $\sim$15 μs [1].

Since the system of the ionic Rydberg core, the Rydberg electron, and the ground-state atom is closed, an important issue of the process described here is conservation of energy. In order to observe a deceleration of the ground-state atom, its initial kinetic energy has to be transferred to its scattering partner, i.e., the Rydberg electron. To satisfy Eq. (19) for the initial velocity $v_{\mathrm{Rb}} = 10^{-9}$ a.u., in total, a kinetic energy of $E_{\mathrm{kin}} =$ 525 Hz has to be absorbed. However, this amount of energy is small compared to the level spacing between the quantum state considered and a neighboring one, so that the excitation of a higher quantum state would be highly off resonant and thus, quantum mechanically forbidden. Nevertheless, the process remains allowed due to the very exotic conditions in the ultracold Rydberg gas: The quantum state n of the Rydberg electron is not sharp, but has a natural linewidth of $\Gamma/2\pi \approx 10.5$ kHz resulting from the 15 μs lifetime of the Rydberg molecule. The extremely small amount of kinetic energy therefore will *not* be deposited into an excitation of a higher quantum state but is absorbed *at resonance* within the linewidth of the same state.

After the point of capturing, the classical computations show a further decrease of the ground-state atom's energy, which is, within the lifetime of the Rydberg molecule, however, small compared to the depth of the potential and thus the molecule will have dissociated long before reaching binding energies of the quantized stationary vibrational states of the molecule. In addition, the latter has to be excluded because of physical reasons, since the required amount of energy cannot be deposited in the excitation of the Rydberg electron within the natural linewidth of the Rydberg state.

Moreover, we find a crucial dependence of the minimum of the potential in which the ground-state atom is captured on the initial angle ϕ (see Fig. 3 for some exemplary trajectories). In fact, for each potential well there is a corresponding range of angles ϕ leading to the formation of a molecule with an internuclear distance associated to the particular well.

To generally determine for which initial conditions the ground-state atom will be captured by the Rydberg atom, we calculate collisions for angles ϕ between 0° and 90° and initial velocities v_{Rb} from 10^{-9} to 10^{-8} a.u. corresponding to kinetic energies of about 525 Hz to 52.5 kHz. As a reference for the velocity we take the mean velocity $\bar{v} \approx 1.3 \times 10^{-8}$ a.u. of an ideal gas at the temperature of $T = 3.5$ μK at which the experiment of Bendkowsky *et al.* [1] was performed, i.e., this range of velocity corresponds to "slow" ground-state atoms.

Figure 4(a) shows the domains of initial values ϕ and v_{Rb} where capture occurs. The numbers indicate in which of the local potential minima the ground-state atom is captured. It can be seen from Fig. 4(a) that it strongly depends on the initial conditions whether or not the ground-state atom is captured. For slow atoms there is a broad range of angles ϕ in which a molecule is formed while this range quickly shrinks with increasing velocity of the ground-state atom. The areas with branches reaching to $v_{\mathrm{Rb}} \gtrsim 10^{-8}$ a.u. correspond to situations where the ground-state atom is directly captured when approaching the Rydberg atom. For small angles $\phi \lesssim 20^\circ$ and

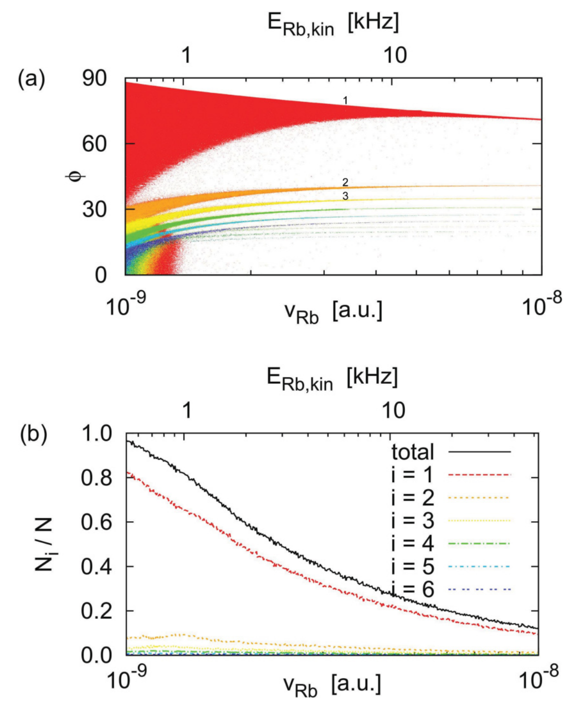

FIG. 4. (Color online) (a) Result of the dynamics calculations of the ground-state atom for initial values $R_0 = 2500$ a.u., $v_{\mathrm{Rb}} = 10^{-9}$ to $v_{\mathrm{Rb}} = 10^{-8}$, and angles ϕ from 0° to 90°. Each single point represents a set of initial conditions (v_{Rb},ϕ) and the numbers indicate in which minimum of the potential the ground-state atom will come to rest (numbers and colors refer to Fig. 1). White means that there is no capturing, i.e., the ground-state atom will again leave the Rydberg atom. (b) Fraction N_i/N of the N_i ground-state atoms that are captured in the ith potential minimum out of a total of N atoms as a function of their velocity v_{Rb}. The solid line shows the total fraction of captured ground-state atoms.

velocities $v_{\mathrm{Rb}} \lesssim 1.5 \times 10^{-9}$ a.u. we also find situations where the ground-state atom is captured on its way out from the Rydberg atom after a reflection at some minimum internuclear distance. For $v_{\mathrm{Rb}} \lesssim 10^{-9}$ a.u. (not shown) almost all angles ϕ lead to capture. However, initial velocities of $v_{\mathrm{Rb}} \gtrsim 0.5\bar{v}$ corresponding to energies above the natural linewidth of the Rydberg molecule would lead to off-resonant absorption and are thus forbidden.

To compute probabilities with which a ground-state atom of the velocity v_{Rb} is captured in the ith potential minimum, we regard a uniform current of N ground-state atoms and a diameter of at least the extension of the Rydberg atom interacting with it. Considering that the different angles then occur with a weighting factor of $4\pi\ \sin^2\phi$, integrating over the cross section of this current and dividing by all N ground-state atoms yields the probability of being captured in the ith minimum. This fraction N_i/N is shown in Fig. 4(b) (numbers i again correspond to those in Fig. 1). As can be seen, the predominant part will be captured in the outermost minimum ($i = 1$), in which the vibrational ground state of the Rydberg molecule is also located (see Refs. [1,3]). Capturing in other minima also happens, but by far more rarely.

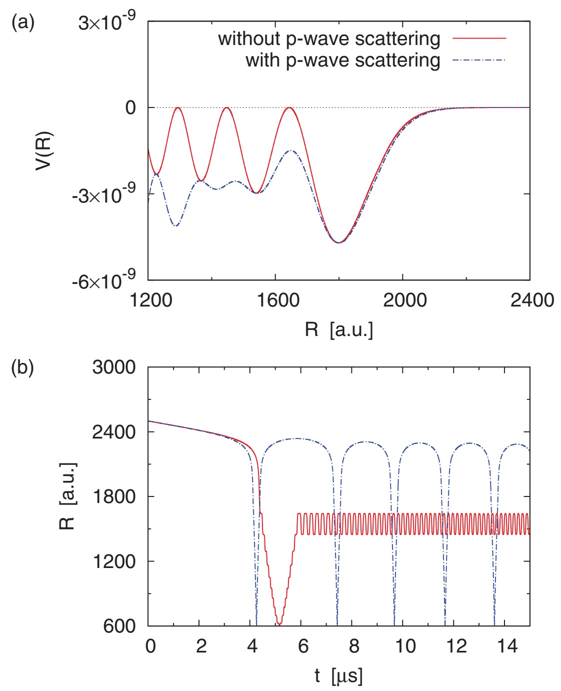

FIG. 5. (Color online) (a) Comparison of the molecular potential $V(\boldsymbol{r})$ with (solid line) and without (dashed-dotted line) p-wave scattering. (b) Comparison of two trajectories of the ground-state atom in the influence of the Rydberg atom for the same initial conditions with (dashed-dotted line) and without (solid line) p-wave scattering. The detailed dynamics changes significantly; the fact that the ground-state atom is captured, however, is not affected.

B. Extended model including *p*-wave scattering

The potential (5) entering the equation of motion (18) is significantly modified near the Rydberg core when p-wave scattering [2,15] is also taken into account by the additional term given in Eq. (4). The main effect for the calculations performed in this paper is the fact that the single potential wells are no more separated by some internuclear separation R with $V(R) = 0$ [see Fig. 5(a)]. For a particle with $E \lesssim 0$ one is therefore no more able to distinguish the different regions of capturing which, in the quantum-classical model, is expressed by the fact that the reversal points of the ground-state atom's trajectory are shifted within the interaction region: The outer reversal point will then in general be determined by the exponential tail of the wave function ($R \sim 2400$) and the inner one is given by the molecular potential together with the centrifugal barrier for noncentral collisions. However, also with p-wave scattering the potential remains conservative so that the dissipative interaction described by the second term in Eq. (18) is not affected.

To illustrate the effects of p-wave scattering, Fig. 5(b) shows a comparison of two trajectories of a slow ground-state atom, one of which is obtained by taking account of p-wave scattering (dashed-dotted line) in the potential (5) and the other trajectory (solid line) by neglecting this effect. In the first case the ground-state atom is no more captured in a particular well, however, the point *that* the ground-state atom is captured remains valid since in both cases we have $V(R) \to 0$ for $R \to \infty$ which precludes a ground-state atom with $E < 0$ to escape from the Rydberg atom.

C. Beyond the quantum-classical approach

In the quasiclassical model the motion of the heavy ground-state atom is described as purely classical. Nevertheless, the question arises, what is the quantum state of the ground-state atom when it has been decelerated to energy $E < 0$? The atom can no longer be in a pure continuum state, however, the density of states at $E \lesssim 0$ is small and the energy gap to the highest vibrational bound state is still rather large. The atom must therefore be in a nonstationary superposition of eigenstates with an admixture of one or more vibrational bound states. As explained above, the Rydberg state of the electron must absorb the transferred energy (within the natural linewidth of the state), and thus is slightly detuned. This somehow unstable configuration may now develop in one of the following directions.

On the one hand, the detuning of the Rydberg state may just lead to a decrease of its lifetime. Reduced lifetimes of Rydberg molecules in vibrational ground and excited states have already been measured experimentally [8] but the mechanism for that reduction has not yet been clarified. The dissipative finite-mass correction term which couples the Rydberg state and the motion of the ground-state atom may thus provide a physical interpretation for the reduced lifetimes of Rydberg molecules.

On the other hand, the admixture of lower vibrational states to the quantum dynamics of the ground-state atom may enable the ground-state atom to jump into the next lower stationary vibrational state by photon emission with a much higher probability than is to be expected for *spontaneous* emission, which is negligibly small due to the small energy differences between the states. The detailed investigation of such a process, which would require the treatment within quantum electrodynamics, however, goes far beyond the scope of this paper.

IV. CONCLUSION AND OUTLOOK

Investigating the interaction between a Rydberg electron and a ground-state atom in Rydberg excited gases within a quantum-classical framework, we were able to derive a dissipative finite-mass correction term to the classical equations of motion describing the dynamics of a ground-state atom interacting with a Rydberg atom. Considering this correction term of order $O(m_e/m_{\mathrm{Rb}})$ we have shown that a free ground-state atom can, for suitable initial conditions, be captured by the Rydberg atom and thus form a Rydberg molecule. According to our calculations, this process takes place for slow ground-state atoms, and does not depend on whether or not p-wave scattering is considered in the molecular potential. However, the classical paths with and without p-wave scattering differ: While with pure s-wave scattering capturing is most likely in the outermost potential minimum, there is no capturing in a particular well when p-wave scattering is included.

In the experiment of Butscher *et al.* [8] molecular Rb_2^+ ions have been detected in the photoassociation spectra at resonance of the Rydberg atom, i.e., without any detuning of the lasers. The formation of Rydberg molecules with the quantum-classical model introduced in this paper and a subsequent ionization process may provide a first hint towards a physical explanation of that observation, however, further investigations are necessary to get a deeper understanding of the dynamics of ultralong-range Rydberg molecules.

ACKNOWLEDGMENTS

This work was supported by Deutsche Forschungsgemeinschaft. A. J. is grateful for support from the Landesgraduiertenförderung of the Land Baden-Württemberg. We also thank T. Pfau and his group for fruitful discussions.

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