Ultra-Long-Range Rydberg Trimers with a Repulsive Two-Body Interaction

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A Rydberg and a ground-state atom can form ultra-long-range diatomic molecules provided the interaction between the ground-state atom and the Rydberg electron is attractive [C. H. Greene *et al.*, Phys. Rev. Lett. **85**, 2458 (2000)]. A repulsive interaction does not support bound states. However, as we will show, adding a second ground-state atom, a long-range bound triatomic molecule becomes possible.

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With the advent of ultracold atomic physics, new forms of atomic systems become possible. The trilobite, arguably one of the most exotic molecules, is a Rydberg atom bound to a ground-state atom by its polarization potential. The existence of this extremely-long-range molecule was proposed, along with its name, by Greene *et al.* [1]. Following this line of argument, previously unexplained satellite peaks in thermal spectra of molecules could be traced to the formation of such long-range molecules [2]. The idea of long-range cold molecules generated considerable interest [2–6], which will increase even more through the recent experimental proof that ultracold trilobites exist [7]. The basis of the molecular bond in such systems is a negative scattering length leading to an attractive atom-Rydberg atom potential, which is in addition modulated by the electronic Rydberg wave function. An extension of the trilobite to polyatomic Rydberg molecules involving several ground-state atoms and one Rydberg atom was investigated in [8]. There it was found that certain geometric arrangements have adiabatic molecular potentials, which are many times deeper than in the diatomic case making clear that a large variety of molecular Rydberg systems can exist in an ultracold environment, with the possibility for a novel kind of chemistry with weakly bound systems.

Here we will show that the building principles of long-range molecular binding in the ultracold regime allow the formation of a triatomic molecule even if the interaction between the Rydberg atom and each of the two ground-state atoms is repulsive (positive scattering length). We will concentrate on neon as an example which has a positive scattering length. The Rydberg neon trimer is a molecule formed out of three linearly aligned neon atoms where the one in the middle is Rydberg excited. We will use atomic units unless stated otherwise.

Since the Rydberg wave function does not vary over the extension of a ground-state electronic wave function, the interaction can be described by a Fermi pseudopotential [9], which amounts to a contact interaction

$$V_F(\mathbf{r}; \mathbf{r}_1) = L_1 \delta(\mathbf{r} - \mathbf{r}_1), \tag{1}$$

where $\mathbf{r}$ is the coordinate of the Rydberg electron and $\mathbf{r}_1$ is the position of the ground-state atom A measured from the Rydberg atom. Furthermore, $L_1 = -2\pi \tan\delta_0/k(r_1)$ is the *energy-dependent* scattering length of the collision system $e^- + A$ containing the s-wave phase shift δ_0 and the local momentum $k(r_1)$ of the Rydberg electron, related to the distance r_1 through the energy conservation $k(r_1)^2/2 = -1/2n^2 + 1/R$. In the low-energy limit, the modified effective range theory [10] expresses L_1 analytically in terms of the zero-energy scattering length L_0 and the polarizability of the atom α,

$$\frac{L_1}{2\pi} = L_0 + \frac{\pi}{3}\alpha k(r_1). \tag{2}$$

For impact energy larger than 0.003 eV in the $e^- + $ Ne system, *ab initio* phase shift data [11] allow one to connect the scattering length of Eq. (2) to higher energies accurately, using the values $\alpha = 2.613$ a.u. and $L_0 = 0.2218$ a.u. from Ref. [11].

For N ground-state atoms at positions $\mathbf{r}_i$, the full electronic Hamiltonian reads

$$h_N = H_c(r) + \sum_{i=1}^{N} L_i \delta(\mathbf{r} - \mathbf{r}_i), \tag{3}$$

where $H_c = p^2/2 + V_c(r)$ is the hydrogenic Rydberg Hamiltonian with Coulomb interaction $V_c(r)$ of the Rydberg electron and its mother ion. For N_d degenerate levels ($N_d \geq N$) of H_c, the eigenenergies of h_N may be obtained by diagonalizing the interaction $\Sigma_i V_F(\mathbf{r}; \mathbf{r}_i)$ within a degenerate manifold of hydrogenic eigenfunctions Φ_{nlm} of principal quantum number n. It is straightforward to show that the resulting interaction matrix $\hat{V}_F$ has $N_d - N$ eigenvalues equal to zero. The remaining N nontrivial eigenvalues of $\hat{V}_F$ can be obtained by diagonalizing the interaction $\Sigma_i V_F(\mathbf{r}; \mathbf{r}_i)$ in the basis of the $i = 1, \ldots, N$ states

$$\psi_n(\mathbf{r}; \mathbf{r}_i) = \sum_{l \geq l_{\min}, m} \Phi_{nlm}^*(\mathbf{r}_i)\Phi_{nlm}(\mathbf{r}), \tag{4}$$

which are neither orthogonal nor normalized. Low-l states may have different energies due to large quantum defects, so they need to be excluded from the basis formed with states of Coulomb energy $-1/2n^2$.

In the case of a dimer, $\psi_n(\mathbf{r}; \mathbf{r}_1)$ given by Eq. (4) is an eigenstate of h_2. Making use of the addition theorem for spherical harmonics ($\hat{\mathbf{x}}$ is a unit vector) [12], we reduce $\psi_n(\mathbf{r}; \mathbf{r}_1)$ to

$$\psi_n(\mathbf{r}; \mathbf{r}_1) = \sum_{l \geq l_{\min}} \phi_{nl}(r_1)\phi_{nl}(r)\frac{2l+1}{4\pi}P_l(\hat{\mathbf{r}}_1\hat{\mathbf{r}}), \quad (5)$$

with the radial hydrogenic eigenfunctions ϕ_{nl}. It is convenient to specify the overlap integral $S_{ij} \equiv \langle \psi_n(\mathbf{r}; \mathbf{r}_i) | \psi_n(\mathbf{r}; \mathbf{r}_j) \rangle_{\mathbf{r}}$ which yields

$$S_{ij} = \sum_l \phi_{nl}(r_i)\phi_{nl}(r_j)\frac{2l+1}{4\pi}P_l(\hat{\mathbf{r}}_i\hat{\mathbf{r}}_j). \quad (6)$$

Clearly, the normalized dimer eigenfunction reads $\Psi_n(\mathbf{r}; \mathbf{r}_1) = \psi_n(\mathbf{r}; \mathbf{r}_1)/S_{11}^{1/2}$. The relation Eq. (6) allows one to write the dimer energy $E_2(r_1) = \langle \Psi_n | h_2(r_1) | \Psi_n \rangle + 1/2n^2$ in the compact form

$$E_2(r_1) = L_1 S_{11}, \quad (7)$$

which is shown for the neon Rydberg dimer Ne + Ne* as the dash-dotted line in Fig. 1. Clearly, $E_2(r_1)$ does not support bound states.

However, we will show that adding another neon ground-state atom allows for long-range bound states of the neon trimer with Hamiltonian

$$h_3 = H_c(r) + L_1 \delta(\mathbf{r} - \mathbf{r}_1) + L_2 \delta(\mathbf{r} - \mathbf{r}_2), \quad (8)$$

where $L_i > 0$. To accommodate for gerade (+) or ungerade (−) symmetry (since the two neon atoms 1 and 2 are identical), the superpositions $\Psi_\pm$ of states $\Psi_n(\mathbf{r}; \mathbf{r}_i) = \psi_n(\mathbf{r}; \mathbf{r}_i)/S_{ii}^{1/2}$ are used as basis functions

$$\Psi_\pm(\mathbf{r}; \mathbf{r}_1, \mathbf{r}_2) = [\Psi_n(\mathbf{r}; \mathbf{r}_1) \pm \Psi_n(\mathbf{r}; \mathbf{r}_2)]/\sqrt{N_\pm}, \quad (9)$$

where $N_\pm$ are the normalization factors

$$N_\pm = 2 \pm 2\frac{S_{12}}{\sqrt{S_{11}S_{22}}}. \quad (10)$$
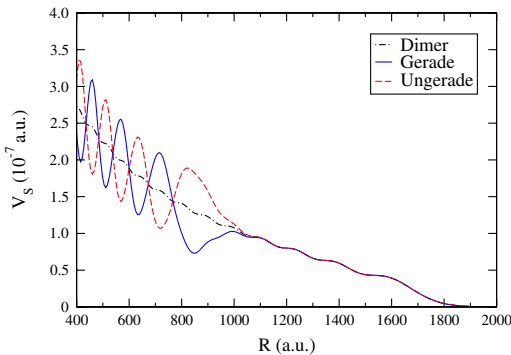

FIG. 1 (color online). The adiabatic potential Eq. (7) with $r_1 = R$ for the ($n = 30$) neon Rydberg dimer (dash-dotted black line) and the symmetric stretch cuts Eq. (15) of trimer in solid blue line (+) and dashed red line (−).

In this set of basis functions, the Hamiltonian h_3 forms a 2×2 matrix with diagonal terms $E_{\mathrm{dia}}^\pm = \langle \Psi_\pm | h_3 | \Psi_\pm \rangle + 1/2n^2$ of the simple form

$$E_{\mathrm{dia}}^\pm(\mathbf{r}_1, \mathbf{r}_2) = \frac{L_1 S_{11} + L_2 S_{22}}{4}N_\pm, \quad (11)$$

and the off-diagonal terms $E_{\mathrm{off}} = \langle \Psi_\pm | h_3 | \Psi_\mp \rangle$

$$E_{\mathrm{off}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{L_1 S_{11} - L_2 S_{22}}{4}\sqrt{N_+ N_-}. \quad (12)$$

The adiabatic potentials are the eigenvalues of this 2×2 potential matrix and have the following analytical form

$$E^{u\,(d)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{L_1 S_{11} + L_2 S_{22}}{2}$$
$$\pm \frac{\sqrt{(L_1 S_{11} - L_2 S_{22})^2 + 4L_1 L_2 S_{12}^2}}{2}. \quad (13)$$

A symmetric cut through this potential for $\mathbf{r}_2 = -\mathbf{r}_1 \equiv \mathbf{R}$ is shown in Fig. 1. Since $E_{\mathrm{off}}(\mathbf{r}_1, -\mathbf{r}_1) = 0$, the symmetric cut has the appealing analytical form

$$E^{u\,(d)}(\mathbf{r}_1, -\mathbf{r}_1) = E_{\mathrm{dia}}^\pm(\mathbf{r}_1, -\mathbf{r}_1) = 2L_1 S_\pm, \quad (14)$$

where $S_\pm = [\psi_n(\mathbf{r}_1; \mathbf{r}_1) \pm \psi_n(\mathbf{r}_1; -\mathbf{r}_1)]/2$. Hence, depending on gerade (ungerade) symmetry only even (odd) components l in the sum of Eq. (5) contribute. The symmetry induced separation of basis functions with even and odd l results in a more pronounced undulation of the corresponding potentials (as can be seen in Fig. 1), since there is less interference from wave functions with different nodal structure.

To determine if the neon Rydberg trimer can support long-range bound states we make a normal mode analysis on the electronic surface from Eq. (13), to which the outermost minimum belongs. To this end it is useful to define symmetry adopted Jacobi coordinates for the nuclear motion,

$$\mathbf{r}_A = (\mathbf{r}_1 + \mathbf{r}_2)/2, \qquad \mathbf{R} = (\mathbf{r}_1 - \mathbf{r}_2)/2. \quad (15)$$

In these coordinates, the nuclear Hamiltonian for total angular momentum $L = 0$ is given by

$$H = \frac{1}{4}\frac{P^2}{m} + \frac{3}{4}\frac{p_A^2}{m} + E^{u\,(d)}(\mathbf{r}_A + R\hat{\mathbf{z}}, \mathbf{r}_A - R\hat{\mathbf{z}}), \quad (16)$$

where m is the mass of a neon atom, and we have chosen the coordinates such that $\mathbf{R} = R\hat{\mathbf{z}}$ along the body fixed z axis. We may reexpress the potential energy surface as $E^{u\,(d)} = \mathcal{E}^{u(d)}(R, z, \rho)$.

In the following, we quantize the trimer with $n = 30$ in a separable approximation closely related to the normal mode analysis for molecules. With the condition $d\mathcal{E}^d/dR = d\mathcal{E}^d/d\rho = d\mathcal{E}^d/dz = 0$ we determine the equilibrium points $(R, \rho, z) = (R_i, 0, 0)$ of the potential. Figure 1 reveals many minima in the symmetric stretch (SS) coordinate R; we will quantize the outermost mini-

mum at $R_0 = 850$ a.u. As can be seen in the same figure, tunneling of the quantized states in the R coordinate depends sensitively on the form of the potential. Hence, instead of a formal harmonic normal mode expansion about the equilibrium point, we simply split the potential in several contributions, leaving only one coordinate as a variable in each term while fixing the others at their equilibrium values. This allows for an explicit numerical solution in each degree of freedom under the total potential

$$\mathcal{E}^0(R, z, \rho) = V_S(R) + V_A(z) + V_B(\rho) - 2V_0, \quad (17)$$

with

$$\begin{aligned} V_0 &= \mathcal{E}^d(R_0, 0, 0) \\ V_A(z) &= \mathcal{E}^d(R_0, 0, z) \\ V_S(R) &= E^+_{\text{dia}}(R\hat{\mathbf{z}}, -R\hat{\mathbf{z}}) \\ V_B(\rho) &= E^+_{\text{dia}}(\rho\hat{\mathbf{x}} + R_0\hat{\mathbf{z}}, \rho\hat{\mathbf{x}} - R_0\hat{\mathbf{z}}). \end{aligned} \quad (18)$$

The potentials V_S, V_B, and V_A are computed and shown in Figs. 1–3, respectively. The modes correspond to molecular types of normal mode vibrations along the SS (in R), the bending (in ρ), and the asymmetric stretch (AS) (in z) with the product wave function

$$\Psi^0(R, z, \rho) = \chi(R)\phi(z)\xi(\rho), \quad (19)$$

where

$$\left(-\frac{1}{4m}\frac{d^2}{dR^2} + V_S(R)\right)\chi(R) = E_S\chi(R), \quad (20)$$

and similarly for the other coordinates.

The quantized bending motion has a zero-point energy at $E_B = 1.04 \times 10^{-7}$ a.u. as shown in Fig. 2. The SS potential shown in Fig. 1 supports a ground state with energy $E_S = 8.11 \times 10^{-8}$ a.u. and an excited state. Both of them are, in principle, resonances which decay through tunneling in the separable approximation. However, the ground state is practically stable. Last, we come to the AS which has near equilibrium ($z = 0$) the form of an inverted oscillator (Fig. 3). From its maximum at $z = 0$ the curve falls to the left and to the right into deep but narrow wells, which are the familiar $Ne_2{}^+$ electronic ground-state potentials, to which the asymptotic polarization potential $-\alpha/2r_i^4$ of the Rydberg excited level smoothly connects. For even shorter distances, the *ab initio* data for the $Ne_2{}^+$ potential from Ref. [13] are used. The potential landscape is similar to that of triatomic *ABA* molecules for which so-called hyperspherical resonances exist [14]. The corresponding quasibound resonant eigenfunctions are highly excited with many nodes along the AS, and the resonant energy E_A almost touches the top of the barrier, i.e., the equilibrium point $E_A \approx V_0 = 7.30 \times 10^{-8}$ a.u.. To a good approximation the lifetime of the resonance can be estimated from the curvature k_A of the potential at V_0, $\tau_A \approx 2\pi\omega_A^{-1} = 2\pi\sqrt{\mu_A/k_A} =$
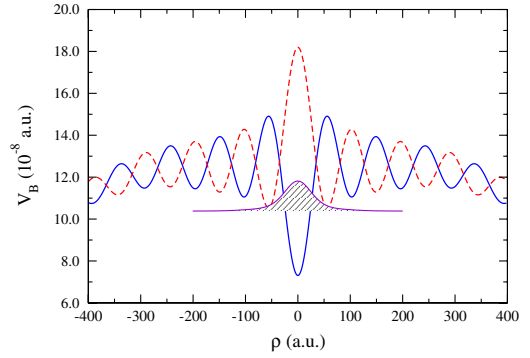

FIG. 2 (color online). The adiabatic potential $V_B(\rho)$ [see Eq. (18)] at the outermost equilibrium point R_0 as a function of the bending coordinate ρ for the ($n = 30$) neon Rydberg trimer. The solid blue line and the dashed red line correspond to E^+_{dia} and E^-_{dia} in Eq. (11), respectively. The shaded area shows the quantized state.

57 ns with $\mu_A = 2m/3$. Intuitively, this curvature determines the time scale on which probability density "slides down" the inverted oscillator potential towards the dimer diatomic decay channel. To summarize, the total ground-state energy of the long-range neon trimer measured from the Rydberg energy $-1/2n^2$ (which is the energy of the three-body system in the separated-atom limit $r_{1/2} \to \infty$) is given by

$$E_0 = E_S + E_A + 2E_B - 3V_0 = 1.43 \times 10^{-7} \text{ a.u.} \quad (21)$$

This means a blueshift of 940 MHz from the Rydberg excitation line and the lifetime is limited by the decay of the AS mode to about $\tau \approx 57$ ns. Because of the cylindrical symmetry of the collinear trimer in equilibrium, the bending motion in (ρ, ϕ) is doubly degenerate, hence it contributes $2E_B$.

For $n = 30$, the bending can be neglected due to the localized motion about $\rho = 0$ and the long bond length. Figure 4 gives an overview of the dynamics of the trimer in
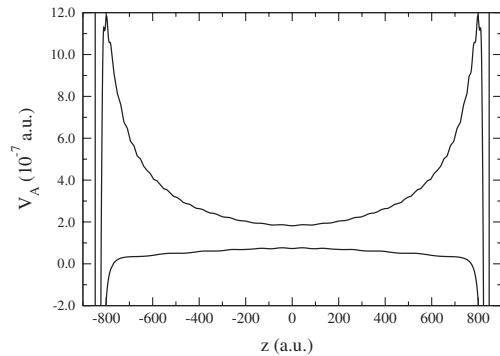

FIG. 3. The adiabatic potential $V_A(z)$ [see Eq. (18)] at the outermost equilibrium point R_0 as a function of the asymmetric stretch coordinate z for the ($n = 30$) neon Rydberg trimer as well as the corresponding potential for the $\mathcal{E}^u$ potential (upper curve).
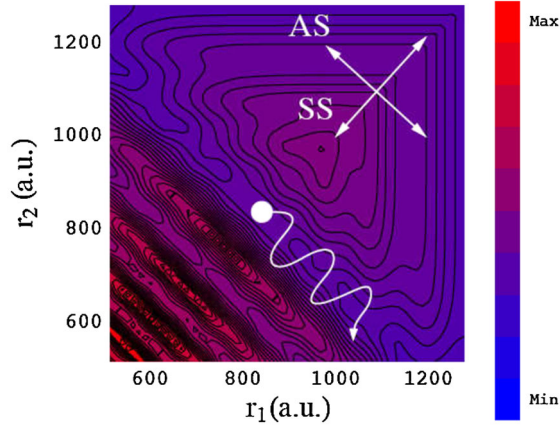
FIG. 4 (color online).   The contour plot for the lower adiabatic potential surface of the neon Rydberg trimer in collinear configuration. The directions of the symmetric (SS) and asymmetric stretch (AS) modes are indicated. The white dot represents the system at the equilibrium point (850, 0, 0), whose subsequent decay with the combined SS motion in the AS direction is represented by the curly arrow.

the plane of the SS and AS coordinate (in collinear geometry with $\rho = 0$). The system rolls down from the top of the saddle point through a potential valley into the two-body region.

The lifetime of the loosely bound Rydberg trimer can be optimized by varying the Rydberg excitation n: Higher n leads to shallower potentials which increases the lifetime in the AS but decreases it in the SS and the bending due to a stronger tunneling. Hence, there exists some n with maximum lifetime τ. To determine its value, we first obtained a general expression for the curvature of the saddle in the AS, which gives an estimate for the decaying time $\tau_A = n^4\sqrt{2\pi^3 \mu_A/L_0}$. This is obtained by approximating the shape of the saddle with a parabola of height $L_0/\pi n^4$ and width $2n^2$. We then numerically calculate the tunneling times τ_S and τ_B in the SS and the bending by solving the corresponding Schrödinger equations and matching the asymptotic phases, for increasing n at the outermost minimum until the tunneling in the bending becomes too large. For Ne$_3$*, it was found that this optimal value occurs at about $n = 55$, where the overall lifetime is as large as $\tau = (1/\tau_S + 2/\tau_B + 1/\tau_A)^{-1} = 0.46 \ \mu$s.

One may question the validity of the adiabatic approximation in the presence of a series of conical intersections as obvious from the crossings in the diagonal part of the Hamiltonian matrix Eq. (14) and Fig. 1. However, the vibrational ground-state wave function χ_0 is strongly localized about R_0, suppressing the effect of coupling even at the closest conical intersection. Future work will consider the effect of a series of conical sections in a situation where they are dynamically active, i.e., not sitting on a decaying background potential which renders the adiabatic wave function exponentially small under a larger barrier at the location of the intersections.

To summarize, we have demonstrated that a Rydberg atom may form with two ground-state atoms an ultra-long-range molecule with finite but long lifetime despite positive scattering length of the Rydberg electron-ground-state-atom interaction. With respect to the long-range ultracold dynamics, this binding is akin to the Borromean systems where three particles form a bound (ground) state though each pair of particles does not have a bound state [15]. The three-body system considered here enjoys binding forces with similar characteristics, namely, neither the corresponding diatomic molecule with a Rydberg and a ground-state atom nor a pair of ultracold ground-state Ne atoms has a long-range bound state. In contrast to a traditional Borromean system, the atoms of the Rydberg long-range trimer are additionally subject to the usual (short-range) molecular binding, which is responsible for the formation of diatomic molecules.

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