Rydberg Borromean Trimmers

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(Dated: July 13, 2008, version 1.6)

A Rydberg and a ground-state atom can form ultralong 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 bound trimeric molecule becomes possible constituting a Borromean Rydberg system.

PACS numbers: 36.40.Gk, 31.15.Qg, 36.40.Wa

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 ground-state atom bound to a Rydberg atom by the polarization potential of the latter. The existence of this extremely long range molecule was proposed, along with its name, by Greene et al. [1]. This idea generated considerable interest [2-6], although a clear experimental verification has not yet been achieved so far but may be possible within a BEC making use of its density orders of magnitude larger compared to an ultracold gas [7]. Moreover, previously unexplained satellite peaks in thermal spectra of molecules could be traced to the formation of such long molecules [8]. 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 wavefunction. 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.

However, a Rydberg molecule can even form with a positive scattering length, i.e., repulsive interaction, as we will show in the following. While a diatomic molecule is indeed not possible under repulsive interaction, a triatomic molecule can be formed which we call Borromean. The name comes from a similar phenomenon in nuclear physics [9]. The essence of a Borromean system is the existence of a three-body bound state although none of the two-body subsystems are bound. For the origin of “Borromean rings” see [10].

In the following, we will show that the building principles of such ultralong range molecules allow the formation of a Borromean trimer using neon as an example. This is a molecule formed out of three linearly aligned neon atoms where the one in the middle is Rydberg excited. The mutual interaction of two neon atoms is repulsive and none of the atomic pairs has a bound state. Nevertheless, the triatomic system can have a bound state. We will use atomic units unless stated otherwise.

Since the Rydberg wavefunction does not vary over the extension of a ground-state electronic wavefunction, the interaction can be described by a Fermi-pseudopotential [11], which amounts to a contact interaction

\[ V_F(\mathbf{r}; \mathbf{r}_1) = L_1 \delta(\mathbf{r} - \mathbf{r}_1), \]

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 \( \delta_0 \) 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 [12] expresses \( L_1 \) analytically in terms of the zero-energy scattering length \( L_0 \) and the polarizability of the atom \( \alpha \),

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

For impact energy larger than 0.003 eV in the \( e^- + \text{Ne} \) system, \textit{ab initio} phase shift data [13] allow one to connect the scattering length of Eq. (2) to higher energies accurately, using the values \( L_0 = 2.613 \) a.u. and \( \alpha = 0.2218 \) a.u. from [14].

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

\[ \hat{h}_N = \frac{p^2}{2} + V_c(\mathbf{r}) + \sum_{i=1}^{N} L_i \delta(\mathbf{r} - \mathbf{r}_i), \]

where \( V_c(\mathbf{r}) \) is the Coulomb interaction of the Rydberg electron with its mother ion. The eigenenergy of a dimer \( \hat{h}_2 \) may be obtained by diagonalizing the interaction \( V_F \) within a degenerate manifold of hydrogenic eigenfunctions \( \Phi_{nlm} \) of principal quantum number \( n \). This leads to the (unnormalized) solution

\[ \psi_n(\mathbf{r}; \mathbf{r}_1) = \sum_{l \geq l_{\text{min}}, m} \Phi_{nlm}^*(\mathbf{r}_1) \Phi_{nlm}(\mathbf{r}). \]

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 \(-1/2n^2\).
The repulsive interaction $V_{\text{dd}}$ for the $(n = 30)$ neon Rydberg dimer (dash-dotted black) and the symmetric stretch cuts Eq. (14) of trimer in solid blue (+) and dashed red (−).

Making use of the addition theorem for spherical harmonics ($\hat{x}$ is a unit vector) [14], we reduce Eq. (4) to

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

with the radial hydrogenic eigenfunctions $\phi_{nl}$. It is convenient to specify the overlap integral $N_{12} \equiv \langle \psi_n(\mathbf{r}; \mathbf{r}_1) | \psi_n(\mathbf{r}; \mathbf{r}_2) \rangle$, which yields

$$
N_{12} = \sum_l \phi_{nl}(r_2)\phi_{nl}(r_1) \frac{2l + 1}{4\pi} P_l(\hat{r}_2 \hat{r}_1). \quad (6)
$$

Clearly, the normalized eigenfunction Eq. (4) reads

$$
\Psi_n(\mathbf{r}; \mathbf{r}_1) = \psi_n(\mathbf{r}; \mathbf{r}_1)/N_{11}^{1/2}. \quad (7)
$$

The relation Eq. (6) allows one to write the dimer energy $E_2(r_1) = \langle \Psi_n | h_3 | \Psi_n \rangle + 1/2n^2$ in the compact form

$$
E_2(r_1) = L_1 N_{11}. \quad (8)
$$

The repulsive interaction $V_{\text{dd}}$ for the neon Rydberg dimer Ne+Ne* $E_2$ is shown as a dash-dotted line in Fig. 1. Clearly, this system does not have bound states.

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

$$
h_3 = \frac{p^2}{2} + V_{\text{c}}(r) + L_1 \delta(r - r_1) + L_2 \delta(r - r_2), \quad (9)
$$

where $L_i > 0$. The following basis functions are defined which are symmetry-adapted linear combinations of dimer eigenfunctions with gerade/ungerade ($\pm$) symmetry (since the two neon atoms 1 and 2 are identical),

$$
\Psi_{\pm}(\mathbf{r}; \mathbf{r}_1, \mathbf{r}_2) = [\Psi_n(\mathbf{r}; \mathbf{r}_1) \pm \Psi_n(\mathbf{r}; \mathbf{r}_2)]/N_{1\pm}^{1/2}, \quad (10)
$$

with the normalization factors

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

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

$$
E_{\text{dia}}^{\pm}(\mathbf{r}_1, \mathbf{r}_2) = \frac{L_1 N_{11} + L_2 N_{22}}{4} N_{\pm}. \quad (12)
$$

The off-diagonal terms $E_{\text{off}} = \langle \Psi_{\pm} | h_3 | \Psi_{\mp} \rangle + 1/2n^2$ read

$$
E_{\text{off}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{L_1 N_{11} + L_2 N_{22}}{4} \sqrt{N_{\pm}N_{\mp}}. \quad (13)
$$

A symmetric cut through this potential for $\mathbf{r}_2 = -\mathbf{r}_1 = \mathbf{R}$ is shown in Fig. 1. This cut has the appealing analytical form

$$
E_{\text{dia}}^{\pm}(\mathbf{r}_1, -\mathbf{r}_1) = 2L_1 N_{11}. \quad (14)
$$

Hence, depending on gerade/ungerade symmetry only even/odd components $l$ in the sum of Eq. (16) 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 wavefunctions with different nodal structure. For the full solution the $2 \times 2$ potential matrix can be diagonalized whose eigenvalues give the adiabatic potentials in the analytical form

$$
E^{u/d}(\mathbf{r}_1, \mathbf{r}_2) = \frac{L_1 N_{11} + L_2 N_{22}}{2} \pm \sqrt{(L_1 N_{11} - L_2 N_{22})^2 + 4L_1 L_2 N_{12}^2}/2. \quad (15)
$$

To determine if the neon Rydberg trimer can support bound states we make a normal mode analysis on the electronic surface from Eq. (15), to which the outermost minimum belongs. To this end it is useful to define symmetry adopted Jacobi coordinates for the nuclear motion,

$$
\mathbf{r}_A = \frac{(\mathbf{r}_1 + \mathbf{r}_2)}{2}, \quad \mathbf{R} = \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{2}. \quad (16)
$$

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

$$
H = \frac{1}{4m} \frac{p^2}{2} + \frac{3}{4m} \frac{\mathbf{p}_A^2}{2} + E^{u/d}(\mathbf{r}_A + \mathbf{R}, \mathbf{r}_A - \mathbf{R}), \quad (17)
$$

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

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 $dE^{u/d}/dR = dE^{u/d}/d\rho = dE^{u/d}/dz = 0$ 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 minimum at $R_0 = 850 \text{ au}$. As can be seen on 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

$$\mathcal{E}^0(R, z, \rho) = V_S(R) + V_A(z) + V_B(\rho) - 2V_0, \quad (18)$$

with

$$V_0 = \mathcal{E}^\text{d}(R_0, 0, 0)$$

$$V_A(z) = \mathcal{E}^\text{d}(R_0, 0, z)$$

$$V_S(R) = E_d^+ (R\hat{z}, -R\hat{z})$$

$$V_B(\rho) = E_d^+ (\rho\hat{\rho} + R_0\hat{z}, \rho\hat{\rho} - R_0\hat{z}).$$

The modes correspond to molecular types of normal mode vibrations along the SS (in $R$), the bending (in $\rho$) and the asymmetric stretch (AS) (in $z$) with the product wavefunction

$$\Psi^0(R, z, \rho) = \chi(R) \phi(z) \xi(\rho), \quad (20)$$

where

$$\left( -\frac{1}{4m} \frac{d^2}{dR^2} + V_S(R) \right) \chi(R) = E_S \chi(R) \quad (21)$$

and similarly for the other coordinates.

The quantized bending motion has a zero-point energy at $E_B = 1.04 \times 10^{-7} \text{ au}$ as shown in Fig. 3. The SS potential shown in Fig. 1 supports a ground state with energy $E_S = 8.11 \times 10^{-8} \text{ au}$ 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). The downward-bent curve falls on the left and right into deep but narrow wells, which are the normal $\text{Ne}_2^+$ electronic ground-state potentials, to which the asymptotic polarization potential $-\alpha/2r_1^2$ of the Rydberg excited level is smoothly connected. For even shorter distances, the $ab\text{ initio}$ data for the $\text{Ne}_2^+$ potential from Ref. [15] are used. The potential landscape is similar to those of triatomic ABA molecules for which so called hyperspherical resonances exist [16]. 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 $E_A \approx V_0 = 7.30 \times 10^{-8} \text{ au}$. To a good approximation the lifetime of the resonance can be estimated by the curvature $k_A$ of the potential at $V_0$, $\tau_A \approx 2\pi\omega_A^{-1} = 2\pi\sqrt{\mu_A/k_A} = 57 \text{ ns}$ 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 Borromean trimer measured from the Rydberg energy $-1/2\hbar^2$ is given by

$$E_0 = E_S + E_A + 2E_B - 3V_0 = 1.43 \times 10^{-7} \text{ au}. \quad (22)$$

This means a blue shift of 940 MHz from the Rydberg excitation line and the lifetime is limited by the decay of the AS mode to about $\tau \approx 57 \text{ ns}$. Due to the cylindrical symmetry of the collinear trimer in equilibrium, the bending motion in $(\rho, \phi)$ is doubly degenerate, hence it contributes $2E_B$. 

FIG. 2: The adiabatic potential $V_B(\rho)$ (see Eq. 19) at the outermost equilibrium point $R_0$ as a function of the bending coordinate $\rho$ for the $(n = 30)$ neon Rydberg trimer. The solid blue and the dashed red correspond to $E_d^+$ and $E_d^-$ in Eq. 12 respectively. The shaded area shows the quantized state.

FIG. 3: The adiabatic potential $V_A(z)$ (see Eq. 19) 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 $\mathcal{E}^0$ potential (upper curve).
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 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 Rydberg Borromean trimer can be optimized by varying the Rydberg excitation $n$: Higher $n$ leads to shallower potentials which enlarges the lifetime in the AS but shortens it in the SS and the bending due to a stronger tunneling. Hence, there exists some $n$ with the maximum $\tau$. 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 $\tau_A = n^4 \sqrt{2\pi^2 L_A}/L_0$. 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 $\tau_S$ and $\tau_B$ in the SS and the bending by solving the corresponding Schrödinger equations and matching the asymptotic phases, for increasing $n$ at the outer-most 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 $\tau = (1/\tau_S + 2/\tau_B + 1/\tau_A)^{-1} = 0.46\mu s$.

We note in passing that a similar analysis of the Rydberg trimer under negative scattering length for $^{87}$Rb produces a bound state, red shifted by -12.7 GHz with respect to the Rydberg line, with the corresponding potential minimum $V_0 = -14.3$ GHz at $(865, 0, 0)$.

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 wavefunction $\chi_0$ 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 wavefunction 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 ultralong range Borromean molecule with finite but long lifetime for positive scattering length of the Rydberg electron-ground-state-atom interaction. We call it Borromean since the corresponding diatomic molecule Rydberg and ground-state atom, do not have a bound state or long lived resonance.

We thank Fédéric Merkt for drawing our attention to the problem of the repulsive Rydberg dimer. ICHL thanks the International Max Planck Research School “Dynamical Processes in Atoms, Molecules and Solids” for financial support.

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