

Ultracold Long-Range Rydberg Molecules with Complex Multichannel Spectra

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A generalized class of ultralong-range Rydberg molecules is predicted which consist of a multichannel Rydberg atom whose outermost electron creates a chemical bond with a distant ground state atom. Such multichannel Rydberg molecules exhibit favorable properties for laser excitation, because states exist where the quantum defect varies strongly with the principal quantum number. The resulting occurrence of near degeneracies with states of high orbital angular momentum promotes the admixture of low l into the high l deeply bound “trilobite” molecule states, thereby circumventing the usual difficulty posed by electric dipole selection rules. Such states also can exhibit multiscale binding possibilities that could present novel options for quantum manipulation.

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Ultralong-range Rydberg molecules were predicted some time ago for the simplest atoms in the periodic table, consisting of one ground state atom and one Rydberg atom having just one valence electron outside of a closed-shell core [1–5]. These unusual long-range Rydberg molecules have since been observed experimentally, in a number of experiments that have focused primarily on penetrating Rydberg states of low orbital angular momentum. Very recently, experimental evidence [6] of a true long-range trilobite molecule has been found, consisting of an ns Rydberg state of Cs with a large admixture of high angular momentum states that hybridize to form an electronic wave function with a huge kilodebye electric dipole moment.

The simplest type of such excited-ground state molecules has thus been confirmed, and the theoretical description has been generalized to include hyperfine interactions and the coupling of electronic singlet and triplet states [7]. Moreover, other interesting generalizations have been developed, such as the binding of multiple ground state atoms [8,9], the behavior of long-range Rydberg molecules subjected to an external electric field [10–12], and even the behavior of a single Rydberg alkali atom excited in a Bose-Einstein condensate [13].

While an alkali atom Rydberg gas provides a simple and easily controlled system for the excitation of novel molecular states, in fact Rydberg atoms throughout the rest of the periodic table are far richer and more complex, as they consist primarily of perturbed, multichannel Rydberg spectra [14–17]. The present Letter demonstrates some of the opportunities provided by this richer class of multichannel Rydberg atoms that can bind one or more ground state atoms. One finding in particular is that the existence of doubly excited perturbors, which are states with two excited electrons that couple to and shift the usual Rydberg series of a single excited electron, can be used in the alkaline earth atoms to directly excite long-range trilobite molecules with their exceptionally large electric

dipole moments. Another possibility raised by the existence of doubly excited perturbors is that energy eigenfunctions exist whose multichannel character exhibits two very different length scales.

This Letter focuses on the $4snd\ ^1D_2$ levels in calcium, where perturbations from the doubly excited states $3d4d$ and $3d5s\ ^1D_2$ cause the $4snd$ singlet quantum defect to vary rapidly in the vicinity of these perturbing levels [18]. Figure 1 depicts the strong n dependence of the nd quantum defects. Calcium is chosen because the d -wave quantum defects pass through unity as the principal quantum number n increases between $n \sim 20 \pm 2$; the nd state is therefore highly degenerate with high angular momentum states in the $n - 1$ manifold. This accidental degeneracy strongly couples these states together, allowing for direct two-photon excitation of trilobite molecules, circumventing the usual challenges of exciting high angular

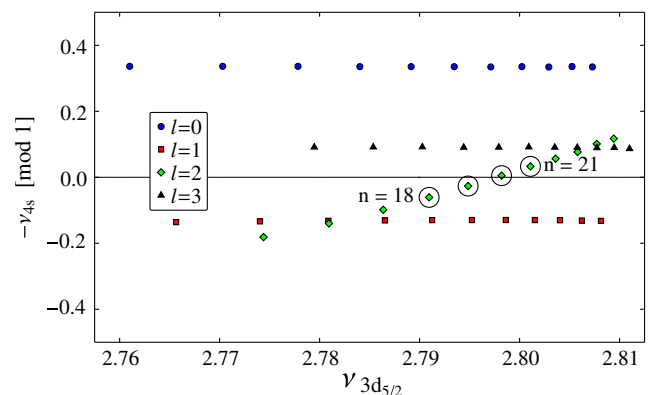


FIG. 1 (color online). A Lu-Fano plot [19] highlighting the effects of level perturbors on the quantum defects of the nd states of Ca [20], in contrast to the energy-independent behavior of the quantum defects for s , p , and f states. The quantum number n rises from 15 to 24 from left to right. This Letter investigates the circled states.

momentum states which typically require electric fields to break dipole selection rules or else an additional microwave photon after a two-photon process [1]. This removes the experimental obstacles in creating and studying these exotic long-range molecules. The interaction responsible for molecular binding between the calcium Rydberg atom and a nearby ground state calcium atom is due to the scattering of the nearly free Rydberg electron off of the ground state atom. This is simply and accurately described by the Fermi pseudopotential [2]

$$V(\vec{r}, \vec{R}) = 2\pi a_s [k(R)] \delta^3(\vec{r} - R\hat{z}) + 6\pi a_p [k(R)] \delta^3(\vec{r} - R\hat{z}) \vec{\nabla}_{\vec{r}} \cdot \vec{\nabla}_{\vec{r}}, \quad (1)$$

where the energy-dependent s -wave scattering length and p -wave scattering volume are, respectively, $a_s[k(R)] = -\tan \delta_0/k(R)$ and $a_p[k(R)] = -\tan \delta_1/[k(R)]^3$. These implicitly depend on the internuclear separation R through the semiclassical kinetic energy $\frac{1}{2}k(R)^2 = E_{nl} + (1/R)$. The internuclear axis points in the $\hat{z}$ direction. The energy-dependent phase shift data used to calculate these scattering properties were calculated by Ref. [21]. Both earlier [5] and recent [22] work has emphasized that diagonalization using this delta-function pseudopotential is formally nonconvergent, but comparison with more complicated Green function or Kirchhoff integral methods [11,23] shows that nevertheless the models agree to first order. Quantitative accuracy with experimental data within the pseudopotential model can be achieved by fitting the scattering lengths to observed spectra [24].

Two characteristics of the phase shifts differentiate this interaction in calcium from those previously studied in the alkalis. Since calcium does not possess the p -wave shape resonance that significantly modifies the potential curves of the alkali dimers [21,25], the potential wells due to the interaction given by Eq. (1) at all but very small internuclear distances are determined almost entirely by s -wave electron-atom scattering properties. The second contrast is that the p -wave phase shift is negative except at very low energies, so the scattering volume is positive over nearly the entire range of internuclear distances. These two differences eliminate the strongly attractive p -wave interactions present in the alkalis that support “butterfly”-type bound states [26], and instead the p -wave interaction produces a weakly repulsive potential. Bound states could possibly form in this repulsive potential in the presence of a second perturber [27].

Adiabatic potential energy curves for $18 \leq n \leq 21$ calculated by basis set diagonalization are presented in Fig. 2(a). As n increases the $(n+1)d$ state sweeps downwards through the n manifold, and for $n=19, 20$ in particular it is strongly mixed into the trilobite state. This systematic change of quantum defects with energy, caused by familiar level perturbations in multichannel

spectroscopy [14], is ubiquitous in the heavier alkaline earth metal atoms and in most other atoms in the periodic table. Reference [1] predicts two classes of long-range Rb molecules: low-angular momentum states (class a) that have been observed experimentally to admix a fractional amount of trilobite character giving them non-negligible permanent electric dipole moments [28], and (class b) the trilobite molecules themselves, consisting of an admixture of high angular momentum states. The states shown here in Ca have a level of mixing intermediate between these two regimes, akin to the recent results in Cs [6]. Figures 2(b) and 2(c) display the electronic wave functions, demonstrating the change in character from primarily g and “trilobite” states in $n=18, 19$ to primarily d and trilobite character in $n=20$, and a mix of these three major contributions in $n=21$.

The molecular vibrational levels seen in the potential well inset are approximately spaced at 1 GHz. Many vibrational bound states are supported in these wells, which range from 30 to 60 GHz deep. These molecules should therefore be somewhat more tightly bound than those predicted for rubidium [1,23]. The permanent electric dipole moments associated with these molecules are many hundreds of debye allowing for the possibility of delicate manipulation of these molecules with electric and magnetic fields [29,30]. The stability of these states is limited by blackbody radiation [17], with an estimated lifetime of a few μ s [31].

A second example of the rich physics provided by two-electron systems is predicted by exploiting the complex channel interactions due to the fine-structure splitting to create long-range molecules that display two distinct length scales. In silicon the $3p^2P_{1/2}^o$ and $3p^2P_{3/2}^o$ ionization thresholds are separated by $\Delta E = 287.84 \text{ cm}^{-1}$. Nonperturbative interactions between Rydberg series in different channels converging to these two thresholds require the framework of multichannel quantum defect theory (MQDT) to describe the bound states of the atom. Silicon has been studied in this framework both from a semiempirical standpoint [32] and through nearly *ab initio* R -matrix calculations [14,33,34]. Only the salient details of the semiempirical approach will be described here, since the references contain thorough descriptions [14,35–38]. The elements of a diagonal short-range reaction matrix in LS coupling, $K_{ii'}^{(LS)} = \delta_{ii'} \tan \pi \mu_i$, are treated as fit parameters by matching experimental quantum defects μ_i with MQDT predictions. The advantage of the K -matrix formulation is that these elements have slow energy dependence in the short-range region near the core since asymptotic boundary conditions have not yet been enforced. The i' th linearly independent wave function outside of this region is

$$\Psi_{i'} = \mathcal{A} \sum_i \Phi_i(\Omega) [f_i(r) \delta_{ii'} - g_i(r) K_{ii'}^{(LS)}], \quad (2)$$

where i labels different channels, $\Phi_i(\Omega)$ contains the wave function of the atomic core and all spin and orbital angular

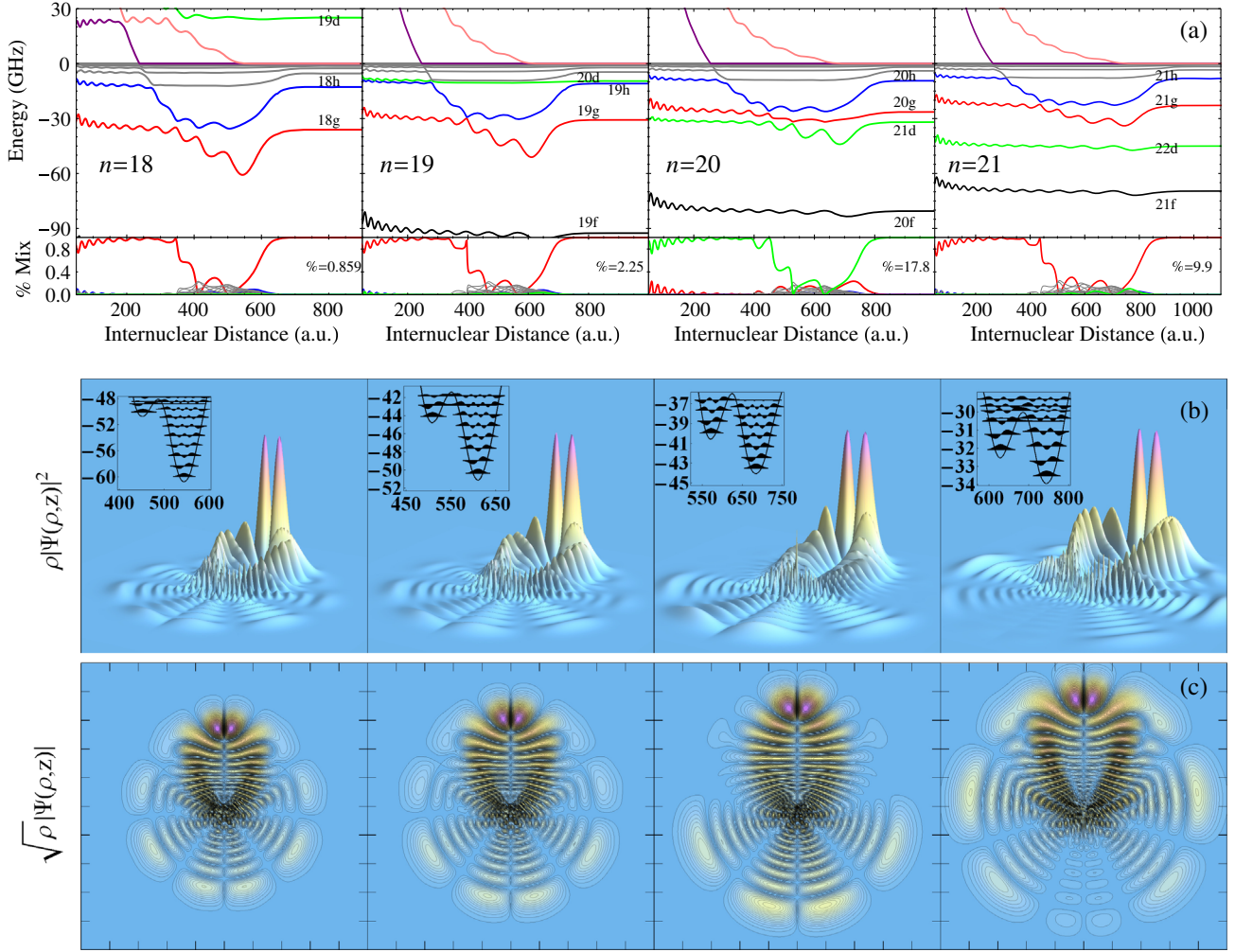


FIG. 2 (color online). (a) Potential curves for $\Omega = 0$ states, with n increasing from 18–21 from left to right. The energy scale is relative to $-(1/2n^2)$. The $(n+1)d$ state descends through the degenerate manifold with increasing n . The expansion coefficients are plotted with the same color scheme, showing the locations of the trilobite states (large mixing of high angular momentum states) and importantly the amount of $(n+1)d$ mixing in the trilobite state. The percentage labeled gives the percent contribution of the d state in the trilobites plotted in panels (b) and (c). (b) Electron probability densities $\rho|\Psi(\rho, z)|^2$ in cylindrical coordinates over a region in the $(\rho, z, 0)$ plane spanning $(-1000, 1000)$. These characteristic trilobite-shaped wave functions are in the deepest minimum of the potential wells, shown in the inset along with the lowest vibrational states (in GHz, as a function of internuclear distance) of the Rydberg molecule. The Rydberg core lies under the small peaks in the middle of each panel; the ground state atom is located in between the tallest peaks of the wave function at $z \sim 600 \rightarrow 800a_0$. (c) Contour plots of the probability amplitudes, showing the transition from primarily g -wave character outside of the trilobite wave function in $n = 18, 19$ to d -wave character in 20 and a mix of d and g in 21. In all panels the abscissa is ρ and runs in steps of 200 a.u. from -1000 to 1000 ; the ordinate is z and runs over the same range.

momentum degrees of freedom of the Rydberg electron, and (f, g) are the regular and irregular solutions to the Schrödinger equation with a Coulomb potential outside of the atomic core [37]. An antisymmetrization operator is denoted here as $\mathcal{A}$. The atomic core and Rydberg electron orbital angular momenta are referred to, respectively, as l_c and l_e . LS coupling, which couples the orbital and spin angular momenta separately and is described by the ket $[(l_c l_e) L(\frac{1}{2} \frac{1}{2}) S] J M_J$ is accurate for low-lying states where the electron is near the core and exchange effects dominate [37]. This coupling scheme breaks down at long range where the electron accumulates radial phase at rates strongly

dependent on the atomic core's total angular momentum [14]. Here a “geometric” orthogonal frame transformation matrix U_{ij} , given by standard angular momentum algebra, is used to transform into the more appropriate jj -coupling scheme represented by the ket $[(l_c \frac{1}{2}) J_c (l_e \frac{1}{2}) J_e] J M_J$ [39]. The jj -coupled K matrix is $K_{ii'}^{(jj)} = \sum_{jj'} U_{ij} K_{jj'}^{(LS)} U_{j'i'}^T$. Imposition of boundary conditions at long-range requires that

$$(\delta_{ii'} \sin \beta_i + \cos \beta_i K_{ii'}^{(jj)}) B_{i'} = 0; \quad \beta_i = \pi(\nu_i - l_i). \quad (3)$$

Ensuring a vanishing determinant constrains the allowed values of $n - \mu_i = \nu_i$ to take on discrete values, and the

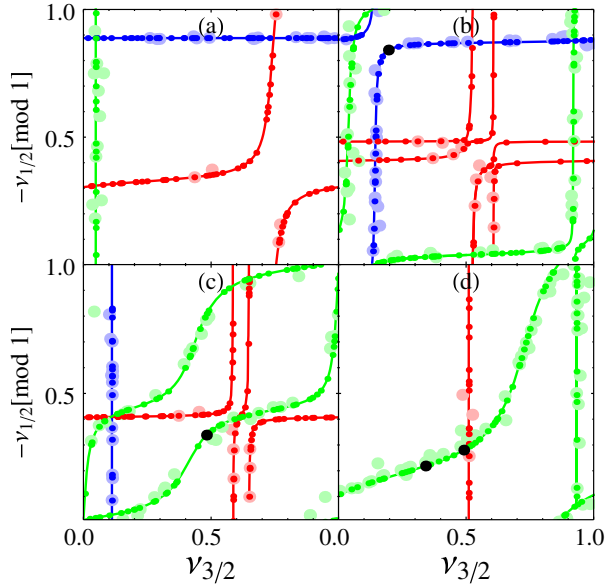


FIG. 3 (color online). Lu-Fano plots for (a) $J = 0$, (b) $J = 1$, (c) $J = 2$, and (d) $J = 3$ symmetries. Blue points are $l_e \approx 0$ odd parity; red are $l_e \approx 1$ even parity, and green are $l_e \approx 2$ odd parity. Larger points represent experimental levels; smaller points theoretically predicted. Black points mark the states in Fig. 4.

eigenvector B_i can be matched at long range to an expansion in renormalized Whittaker functions $W(r, \nu_i, l_i)$ that exponentially decay at long range (Ref. [14], Eq. 2.53):

$$\Psi_{i'} = \mathcal{A} \sum_i \left[-\frac{B_i}{\cos \beta_i} \right] \Phi_i(\Omega) W_i(r, \nu_i, l_i). \quad (4)$$

The critical parameters in this expression are the mixing coefficients $B_i / \cos(\pi \beta_i)$, which determine the weighting of each channel eigenfunction in the energy eigenstate. These coefficients, as well as the bound state energies, were determined here by fitting the quantum defects μ_i and a set of orthogonal rotation matrices to high-lying experimental levels. Spectroscopic data for $l_e = 0, 2$ odd parity and $l_e = 1$ even parity states with $J = 0-3$ were fitted this way, with results (Fig. 3) that compare favorably with R -matrix methods [33,34]. Most high-lying experimental energies were fitted to within 0.5 cm^{-1} , but the results for $l_e = 1$ are very uncertain due to a dearth of experimental values available for fitting. The model's accuracy can be seen by comparing the larger points on Fig. 3 with the theoretical points.

After the spectrum of a Rydberg Si atom is calculated, its interaction via the Fermi pseudopotential with a Ca ground state atom is studied. This heteronuclear dimer was chosen in contrast to the homonuclear Si^*-Si dimer because silicon's scattering information is poorly known. A very dilute Si gas within a much denser Ca gas is envisioned. Figure 4 displays potential curves and vibrational spectra for low angular momentum states, similar to class (a) from Ref. [1].

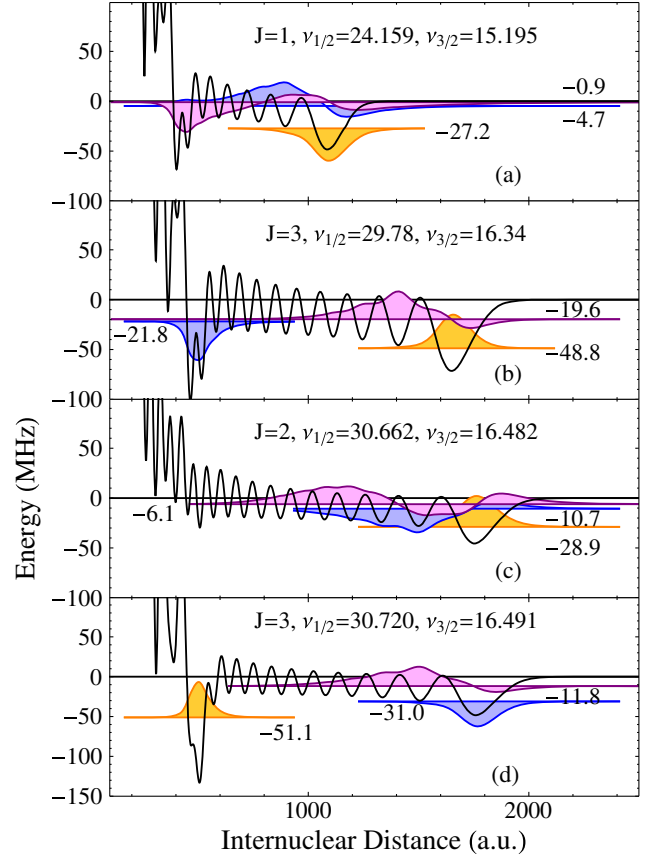


FIG. 4 (color online). Panels (a) through (d) display adiabatic potential curves, bound state energies, and molecular vibrational wave functions (in color) for several $M_J = 0$, low- J levels of the Si^*-Ca Rydberg molecule. The quantum numbers are labeled in each panel. The binding energies (in MHz) labeling each bound state are listed relative to the asymptotic atomic energy, which can be obtained from $E = E_1 - 1/2\nu_{1/2}^2 = E_2 - 1/2\nu_{3/2}^2$. We estimate an uncertainty of 0.5 MHz in these values.

Those states exhibiting the multiscale binding behavior predicted here must lie on rapidly varying portions of the Lu-Fano plot; hence, the $J = 3$, $l_e \approx 2$ states most consistently display deep separated wells. Panels (b) and (d) of Fig. 4 show two typical potential curves for this symmetry, while Fig. 4(a) shows one of the few $J = 1$, $l_e \approx 0$ states to display two deep and highly separated wells. Panel (c) demonstrates that a locally varying Lu-Fano plot is a necessary but insufficient condition for multiscale binding, as the angular momentum components $\Phi_i(\Omega)$ in Eq. (4) also contribute to the amount of mixing between channels. Specifically, the angular momentum state must have a substantial $m_{l_e} = 0$ component, since this is the only nonzero contribution for $M_J = 0$. The increasing well separation is due to the spatial scaling of each single-channel wave function with ν_i^2 . The potential curves are typically separated from neighboring curves by several hundred MHz or more. The ability of these potentials to support bound states is enhanced by the relatively

large spin-orbit splitting and high molecular reduced mass.

These two scenarios illustrate the rich effects of the physics of long-range multichannel molecules formed by divalent atoms. Interactions with doubly excited states in Ca allow for direct excitation of trilobite molecules through low- l channels, providing a new method for experimental realization of these molecules through direct excitation. This is a major reduction in experimental challenges, and together with recent efforts with Sr [40,41] suggests that the alkaline atoms will be fertile fields of progress in ultralong-range molecular studies. In the Si*-Ca molecules predicted here, the multichannel description of the Rydberg structure predicts far richer low angular momentum potential energy curves than those studied in the alkalis, which formed bound states essentially only in the outermost well. Electric or magnetic field dependence of silicon's MQDT spectrum and of the positions of avoided crossings in Si*-Ca states could be investigated to further explore possibilities for manipulation and control [42]. Additionally, a STIRAP technique could be used to transition between vibrational states, provided favorable Franck-Condon overlaps exist.

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