

Avoided Crossings in the Interaction of a Xe Rydberg Atom with a Metal Surface[†]

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We investigate the interaction of a xenon Rydberg atom with a metal surface in the presence of an applied electric field. The xenon atom is modeled using a pseudo potential that accounts for the experimentally observed quantum defects. We show that several of the xenon levels exhibit avoided crossings as the atom approaches the surface. We propose that adiabatic and nonadiabatic transitions at such avoided crossings might help explain recent experimental observations involving the scattering of state-selected xenon Rydberg atoms at a metal surface.

I. Introduction

The study of charge-transfer processes in atom–surface scattering can provide important information about the lifetimes of excited states at surfaces.^{1,2} Much theoretical effort has been devoted to the development of accurate microscopic models to describe charge-transfer processes. The first theoretical approaches employed perturbation theory and used simplified model Hamiltonians that neglected many-electron interactions.^{3–5} These early approaches proved very successful in interpreting experimental data^{6–8} and laid the foundation for the development of more quantitative charge transfer theories based on the time-dependent Anderson model and of nonperturbative approaches for the calculation of energy shifts and broadening of atomic resonances near metal surfaces.^{9–14} These approaches have been very successful in interpreting experimental data and it is fair to state that, at this time, charge transfer in atom–surface scattering is a relatively well understood phenomenon.

However, the quantitative agreement between theory and experiment stems from a combination of relatively complex dynamical theory (time-dependent Anderson models) and quite challenging nonperturbative calculations of atomic level shifts and widths outside a surface. Both of these components of the theory involve a number of simplifications and assumptions, and it is thus of interest to study a system where calculations can be performed with a minimum of approximations. An example of such a system is the ionization of Rydberg atoms, i.e., atoms in which one electron is excited to a state of large principal quantum number n , at a metal surface. This system possesses a number of characteristics that make it an ideal testing ground for detailed quantitative comparisons between theory and experiment. First, the large physical size and weak binding energy of Rydberg atoms means that ionization will occur at large atom–surface separations where the lateral corrugation of the surface is unimportant and can be neglected. Second, for a Rydberg atom at a large distance from a surface, the potential energy of the excited electron is to a large extent determined by classical effects, i.e., by the Coulomb interaction within the atom and by classical image interactions with the metal surface. Thus, the potential for the excited electron can be constructed without having to introduce any significant approximations. A third advantage of the Rydberg atom system

is that the kinetic energy of the incident Rydberg atoms can be made very small. This feature enables an almost exact solution of the dynamical part of the charge-transfer problem (the time-dependent Anderson model).

A novel approach for the experimental determination of the ionization distances for Rydberg atoms impinging on a flat metal surface was developed a few years ago.¹⁵ In this method, a beam of thermal-energy Rydberg atoms is directed at near grazing incidence onto the surface in the presence of an applied external electric field. As the atom approaches the surface the ionization probability increases exponentially. At some distance Z_1 , the excited electron tunnels into the surface whereupon the resulting ion is attracted toward the surface by its image charge. The magnitude of this “harpooning force” is $F_1 = (1/2Z_1)^2$ au. In the absence of any applied electric field, the ion will be rapidly accelerated toward the surface where it will be neutralized by an Auger process. This can be prevented by the application of an external field. Because the initial image charge field experienced by the ion, and thus the external field required to counteract it, depends on the distance from the surface at which ionization occurred, the ionization distance can be inferred from measurements of the surface ionization signal, i.e., the signal of Xe^+ ions that escape the surface, as a function of applied field.

Recently, this approach has been used to study the ionization of xenon Rydberg atoms at a flat Au(111) surface. The Rydberg atoms were created near the surface, in the presence of a small DC field allowing selective excitation of “red” and “blue” Stark states, i.e., Stark state that are shifted down or up in energy, respectively. The polarization of the exciting laser was selected to produce only $m = 0$ states. Initial experiments were undertaken using the lowest-energy, red-most state in each $\text{Xe}(m = 0)$ Stark manifold, which, for the experimental conditions selected,¹⁶ corresponded to states that were initially oriented toward the surface. [This orientation is governed by the direction of the applied field, the red-most (blue-most) Stark states being antiparallel (parallel) to the field.] These measurements yielded ionization distances that were in excellent agreement with predictions based on hydrogenic theory.¹⁶ To achieve this agreement, it was necessary to include the effects of the applied electric field on the broadening of the Rydberg levels and to correct for the kinetic energy of the incident atoms.^{17,18} These red-most states are found to be strongly oriented toward the surface.

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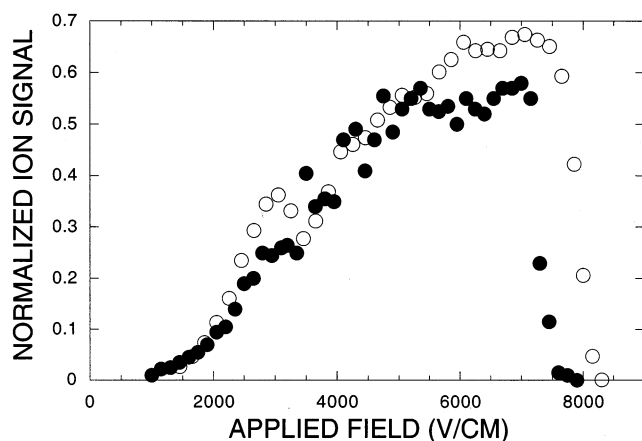


Figure 1. Applied field dependence of the surface ion signals measured when atoms initially prepared in the blue-most (solid circles) and red-most (open circles) states in the Xe($n = 15$) Stark manifold are incident on a near atomically flat Au(111) surface. The data are normalized to the initial number of Rydberg atoms created, which was determined by field ionization.

Subsequent experiments, however, have shown that atoms initially prepared in the highest energy, blue-most state in each Xe(n) Stark manifold ionize at similar atom–surface separations to the corresponding red-most Stark state, despite the fact that the blue-most Stark states are initially oriented toward vacuum. This is illustrated in Figure 1, which shows the applied field dependence of the Xe⁺ surface ion signal observed when atoms initially prepared in the red-most and blue-most states in the Xe($n = 15$) manifold are incident at $\theta = 4^\circ$ on a nearly atomically flat Au(111) surface. The threshold fields for ion collection are the same for both states pointing to ionization at similar atom–surface separations. This observation is in marked contrast to the predictions of hydrogenic theory which suggests that states oriented toward vacuum should ionize much closer to the surface than states oriented toward the surface, resulting in much higher threshold fields. Hydrogenic theory, however, suggested a possible explanation for this discrepancy because it showed that, as the surface is approached, surface-induced perturbations lead to energy level shifts that can cause a series of crossings between the outermost states in neighboring Stark manifolds before ionization occurs.¹⁹ If such crossings are traversed adiabatically, an initial Stark state will alternatively assume the character of red and blue Stark states, i.e., its electron probability density will oscillate between being oriented toward the surface and toward vacuum. The electron probability densities associated with the extreme red and blue members of adjacent Stark manifold would then, on average, be similar leading to ionization at similar atom–surface separations.

Here, we examine this picture by studying the interaction of Xe Rydberg atoms with a metal surface in the presence of an applied electric field. The energy shifts and widths of the Rydberg levels are calculated as a function of atom–surface separation and applied electric field using an atomic pseudopotential. The results show the presence of avoided crossings that might explain the experimental observations.

II. Theory

The energies ϵ_R and widths Γ of the electronic states of a xenon Rydberg atom near a metal surface can be calculated by using the complex scaling method to solve the Schrödinger equation appropriate to an electron interacting with a Xe⁺ core and a metal surface. A detailed review of this method and the potential used to describe the surface can be found elsewhere.^{12,20}

The interaction between the excited electron and the Xe⁺ core is a complex many body problem that cannot be solved exactly. In a previous investigation of the interaction of a xenon Rydberg atom with a metal surface in the absence of an external electric field, three different pseudopotentials were developed.²¹ The use of these pseudopotentials, however, turned out to require very large basis sets when the external electric field is included. This complication makes extensive investigations of the energy shifts and broadening of the atomic levels as a function of atom–surface separation and as a function of applied field very time-consuming. For this reason, it was necessary to develop a pseudopotential, that enables a faster solution using a smaller basis set.

To describe the xenon Rydberg atom, we have developed an angular-momentum dependent pseudopotential $V^{PS}(r)$ of the form

$$V^{PS}(r) = \left(\sum_l V_l^{PS}(r) |l\rangle \langle l| \right) - \frac{1}{r} \quad (1)$$

where r is the radial coordinate, specifying the distance of the electron from the core. For $V_l^{PS}(r)$ we use the expression developed by Bardsley.²² The angular-momentum dependent pseudopotentials have the form

$$V_l^{PS}(r) = A_l r^p e^{(-\xi r^q)} - \frac{\alpha_d}{2(r^2 + d^2)^2} - \frac{\alpha_q}{2(r^2 + d^2)^3} \quad (2)$$

For the dipole and quadrupole polarizabilities we choose $\alpha_d = 4.044$ au and $\alpha_q = 14.235$ au.²³ The cutoff distance d was set to 1.0 au. The parameter ξ was set to 0.01. The coefficients A_l were determined by fitting the calculated atomic energy levels to the experimentally determined quantum defects of Xe Rydberg atoms.^{24–26} The best fit was for $A_0 = -1.2151$ au, $A_1 = -0.08849$ au, $A_2 = -0.5931$ au, and $A_3 = -0.0109$. The remaining A_l were set to 0. The parameters p and q are chosen to be 0.0 and 2.0, respectively. This is consistent with previous implementations²⁰ of this pseudopotential, which has been used to describe alkali systems.

The wave functions were expanded in a basis consisting of generalized Laguerre polynomials and spherical harmonics²⁰

$$\phi_{nlm} = e^{-\lambda r/2} r^l L_n^{2l+2}(\lambda r) Y_{lm}(\Omega) \quad (3)$$

where λ is a parameter that can be used to optimize the basis. In the present calculations $\lambda = 0.25$ au. For each quantum number l , we include $n(l)$ radial functions specified by a vector $(n(0), n(1), \dots, n(l_{\max}))$, where there are $n(0)$ $l = 0$ radial functions, $n(1)$ $l = 1$ radial functions etc. A value of 18 was used for l_{\max} and $\vec{n} = (60, 60, 60, 50, 40, 40, 30, 30, 30, 25, 25, 20, 20, 20, 20, 20, 20, 10)$. The total number of basis functions used in the calculations presented in this paper was 600. No significant changes resulted when including more basis functions.

III. Results

Figure 2 shows, for zero applied electric field, the $m = 0$ states of xenon as a function of atom–surface separation Z for an energy range that encompasses the $n = 15$ levels. Several individual s, p, and d states are labeled separately, with the remaining states in each n manifold labeled on the right. It is interesting to note that the 15s and 15p states lie well below the $n = 12$ manifold and that the 19s and 19p states lie just above the $n = 15$ manifold. The shifts and broadening of the

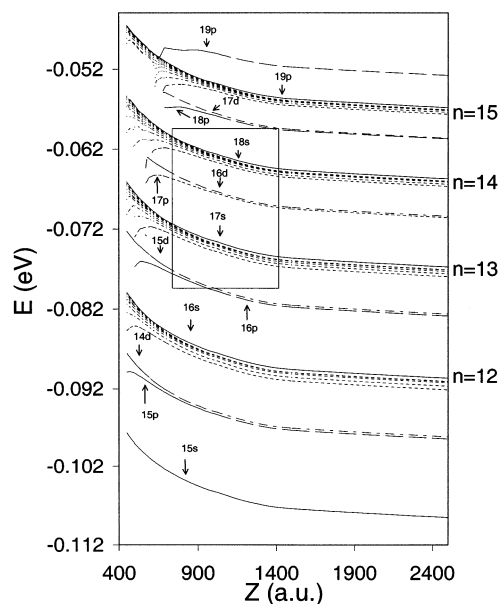


Figure 2. Calculated energy shifts for xenon Rydberg states as a function of atom-surface separation Z in the absence of an applied electric field. The solid lines indicate the $l = 0$ states, the long dashed lines $l = 1$ states, and the short dashed lines $l = 2$ states. The dotted lines show the $l > 2$ states.

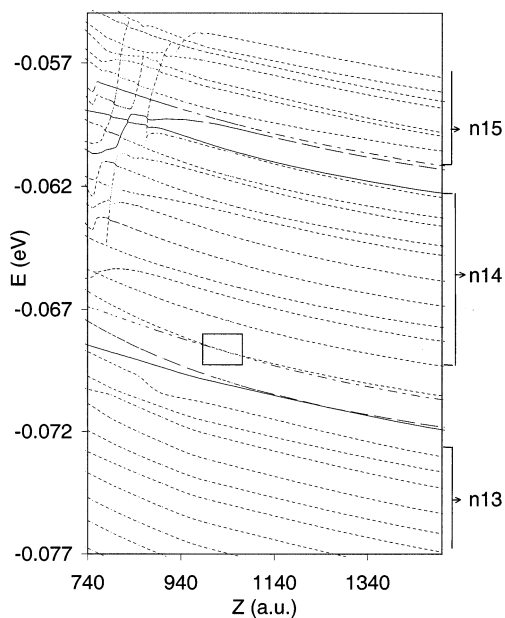


Figure 3. Calculated energy shifts for xenon Rydberg states as a function of atom-surface separation Z for the region indicated by the box in Figure 2 and an applied electric field $E = 1.0 \times 10^{-6}$ au.

individual levels are similar to those predicted for hydrogenic levels, which have been discussed elsewhere.¹⁷ The large quantum defects for Xe, however, increase the complexity of the system and, near the surface, states from several n manifolds begin to overlap.

The presence of an applied electric field results in Stark energy level shifts that broaden the n manifolds. The effect of this is apparent in Figure 3, which shows, on an expanded scale, that part of the energy level diagram indicated by the box drawn in Figure 2 when a field $E = 1.0 \times 10^{-6}$ au is applied. The presence of this field leads to increased interactions between neighboring n -manifolds and many level crossings are observed at relatively large atom-surface separations. Here, we focus on the region contained within the small box shown in Figure

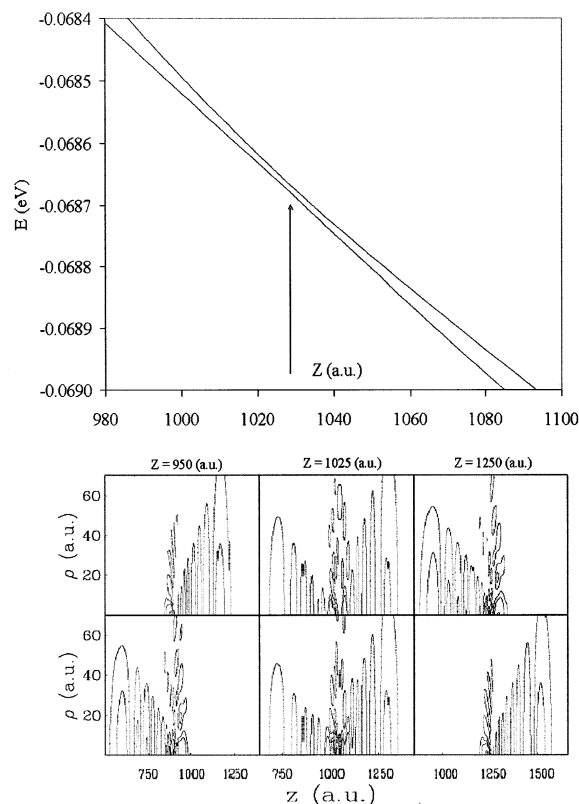


Figure 4. Upper: expanded view of the avoided crossing indicated by the box in Figure 3. Lower: contour plots of the electron probability densities of the two states associated with the avoided crossing. The three upper panels are for the upper level and the three lower panels are for the lower level. The contour plots are evaluated for atom-surface separations of $Z = 950$, 1025 , and 1250 au and ρ denotes the perpendicular distance from a surface normal drawn through the atom.

3. A blow up of this region is presented in Figure 4 and clearly demonstrates that the levels exhibit an avoided crossing. The lower part of Figure 4 contains contour plots showing the electron probability densities associated with these two Stark levels for three atom-surface separations in the vicinity of the avoided crossing. Outside the crossing, for $Z = 1250$ au, the upper level is oriented toward the surface while the lower level is oriented toward the vacuum. Near the center of the avoided crossing, at $Z = 1025$ au, the two levels are strongly mixed and have no specific orientation with respect to the surface. Inside the avoided crossing, at $Z = 950$ au, the orientation of the wave functions is reversed.

The sensitivity of the avoided crossings to the size of the applied field is illustrated in Figure 5 which shows the avoided crossing just discussed for three different applied field strengths, $E = 0.99 \times 10^{-6}$, 1.0×10^{-6} , and 1.1×10^{-6} au. These fields are of a similar magnitude as the fields used in the experiment. The scale of the figure makes it difficult to see the energy level separation at the avoided crossings. However, their presence shows up clearly in the widths of the two levels, which are also included in Figure 5. The width of each level changes by more than 2 orders of magnitude as the avoided crossing is traversed. Figure 5 also shows that small changes in applied electric field can lead to marked changes in the position of avoided crossings. Indeed, the positions of all avoided crossings are governed by the size of the applied field.

The atom-surface separation at which an incident Rydberg atom will ionize depends critically on the component of its velocity perpendicular to the surface. In the limit of very low atomic velocities, ionization should occur far from the surface

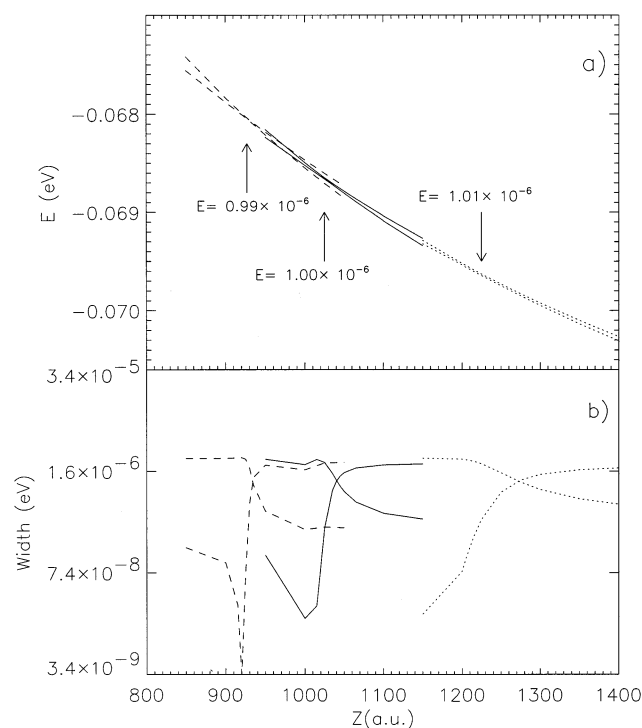


Figure 5. Applied field dependence of the avoided crossing between the two levels highlighted in Figure 3. (a) Energy levels as a function of atom-surface separation; (b) the width of the levels.

and before any avoided crossings have been reached. In this limit, sizable differences in ionization distances for Rydberg atoms initially prepared in surface-oriented and vacuum-oriented states are to be expected. For larger atomic velocities, ionization will occur closer to the surface where the effects of avoided crossings become important. If these are all traversed adiabatically, the electron probability densities associated with incident states will oscillate between being oriented toward the surface and toward vacuum, leading to ionization at similar atom-surface separations. Furthermore, because the ionization rate increases exponentially with the degree of overlap between the surface and the electronic wave function, ionization should occur at atom-surface separations characteristic of the most strongly surface-oriented states, i.e., the red-most Stark states.

More work is clearly needed to explain the experimental data shown in Figure 1. However the present calculations suggest that a number of level crossings will occur as an atom approaches the surface. The probability for a nonadiabatic transition at an avoided crossing can in principle be calculated using the complex scaling method. The complexity of this problem decreases markedly with decreasing principal quantum number n and work is currently in progress trying to identify an experimentally accessible regime that would enable a detailed comparison between theory and experiment. Clearly, however, the study of Rydberg atom/surface interactions promises to reveal a rich variety of dynamical behaviors including electron tunneling and non-adiabatic transitions.

IV. Conclusions

A pseudo potential for the description of xenon Rydberg atoms has been developed. Using this pseudopotential and the complex scaling method, the energy shifts and broadening of xenon Rydberg levels outside a metal surface in the presence of an applied electric field have been calculated. The results reveal the presence of avoided crossings between states in neighboring n -manifolds which, for large applied fields, occur at relatively large atom-surface separations. The character of individual atomic states can change markedly as such crossings are traversed and we propose that such behavior might explain why the experimentally measured ionization distances for xenon Rydberg atoms initially prepared in states oriented toward and away from the surface are found to be similar.

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