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Atomic triply excited double Rydberg states of lanthanum investigated by selective laser excitation

W. Sun,[1] P. Xue,[1] X. P. Xie,[1] W. Huang,[1,2] C. B. Xu,[1] Z. P. Zhong,[3] and X. Y. Xu[1,4]
[1]*Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China*
[2]*Department of Physics, Wesleyan University, Middletown, Connecticut 06459*
[3]*Department of Physics, Graduate School at Beijing, University of Science and Technology of China, Academia Sinica, Beijing 100039, People's Republic of China*
[4]*Hainan University, Haikou, Hainan 570228, People's Republic of China*
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The atomic triply excited double Rydberg states (TEDRS) of La have been studied both experimentally and theoretically. It is revealed that in such an asymmetric four-body system where three electrons have very different orbital energies, the electronic correlations can be understood by means of decomposing into different dielectronic correlations that play different roles time-dependently. The correlations depend strongly on the relative excited orbital energies of three valence electrons. Our theoretical approach based on a semiclassical model is able to interpret the two observed patterns of La^+ ion distributions among high Rydberg states resulted from the decay of TEDRS.

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Electronic correlations play important roles in many processes in excited states of nonhydrogenlike atoms. It is expected that the electronic correlations could be understood by means of ''decomposing'' into pairs of dielectronic correlations. In the simplest case where only one pair of dielectronic correlation dominates, such as in the doubly excited states in He and alkaline-earth-metal atoms (the ''three-body problem''), various theoretical models have been set up, which were developed either from the independent electron model (e.g., [1–3]) or the fully correlated model (e.g., [4,5]). These models have been successfully used to interpret various phenomena in the excitation and autoionization processes observed in experiment. It remains a challenge to examine or apply the schemes in those three-body models (i.e., to ''compose'' the dielectronic correlations) for other complex cases where two or more pairs of dielectronic correlations produce significant effects.

The simplest problem for the complex cases is the ''four-body'' problem, such as the triply excited states of atoms with three-valence electrons. Compared to the He spectrum, a very different structure has been observed in the excitation spectrum of the triply excited states of Li in experiment. It indicates the importance of the interactions among the dielectronic correlations. Up to now, very few results (using charge exchange or synchrotron radiation excitation) for the four-body system had been obtained in experiment [6,7] due to the lack of efficient excitation technique.

In this Rapid Communication, we report a study on triply excited double Rydberg states (TEDRS) $5d_{5/2}NLnl$ in La. In TEDRS, which is an asymmetric four-body system, two electrons are excited to Rydberg orbits ($NL,nl,N^*\simeq 14$–$27, n^*\simeq 46$–50; the asterisk denotes the effective quantum number in this paper) and a third one to a low excited orbit ($5d_{5/2}$). In experiment, the excitation spectrum is obtained by using efficient stepwise laser excitation combined with a sequential electric-field ionization method. The decay process is studied by measuring La^+ ion distributions among high Rydberg states resulting from the autoionization of TEDRS. We have found two different distribution patterns that depend strongly on the relative orbital energies of the three excited electrons in TEDRS. In theory, a semiclassical approach is used to simulate the decay process. It is revealed that for such an asymmetric four-body system, the effects of the complicated electronic correlations can be understood by studying the individual decomposed dielectronic correlation. The different dielectronic correlations are found to play different roles time-dependently. Our calculated results are in good agreement with the observed distribution patterns.

The experimental method used here is developed from that of atomic double Rydberg states [8,9]. In summary, La atoms in the ground state in a diffusive beam are excited by two dye lasers to $5d^2(^3F_2)nl$ [10], which are further excited by another three dye lasers (delayed by 30 ns) to TEDRS $5d_{5/2}NLnl$ via two intermediate resonant states $5d6p(^3F_1)nl$ and $5d6d(^1P_1)nl$. All five dye lasers are pumped by an XeCl excimer laser (pulse width is 20 ns, duty cycle is 10 Hz). The excitation scheme is shown in Fig. 1.

A La atom in TEDRS will autoionize quickly after the excitation. There are one or two possible decay paths. One will produce La^+ ion (usually in bound Rydberg state) and an electron. And if the excited energy of the TEDRS is above the double escape threshold of La, there is another possible path that will produce La^{2+} ion and two electrons. For the TEDRS we study, the latter has very little or no probability and will be neglected (see discussion later). For the former, the La^+ ion in bound Rydberg state will be field-ionized to La^{2+} ion and detected by a special designed time-of-flight system using a technique of sequential ionization by a pulsed and a constant electric field, which can filter out the large background La^+ ions produced in other processes.

Figure 2(a) shows a typical observed excitation spectrum of La TEDRS. The spectrum of the autoionizing ionic Rydberg states La^+ $5d_{5/2}NL$ excited from $5d6d(^1P_1)$ is also shown in Fig. 2(b) [11,12]. It can be seen in Fig. 2 that there are some similar structures in two spectra. This phenomenon can be understood by means of the model used for a similar process in the excitation of atomic double Rydberg states [1,8]. Briefly, the last step of the excitation is the excitation of the inner electrons in the presence of the outmost electron (nl). The outmost electron, for which the interaction with the

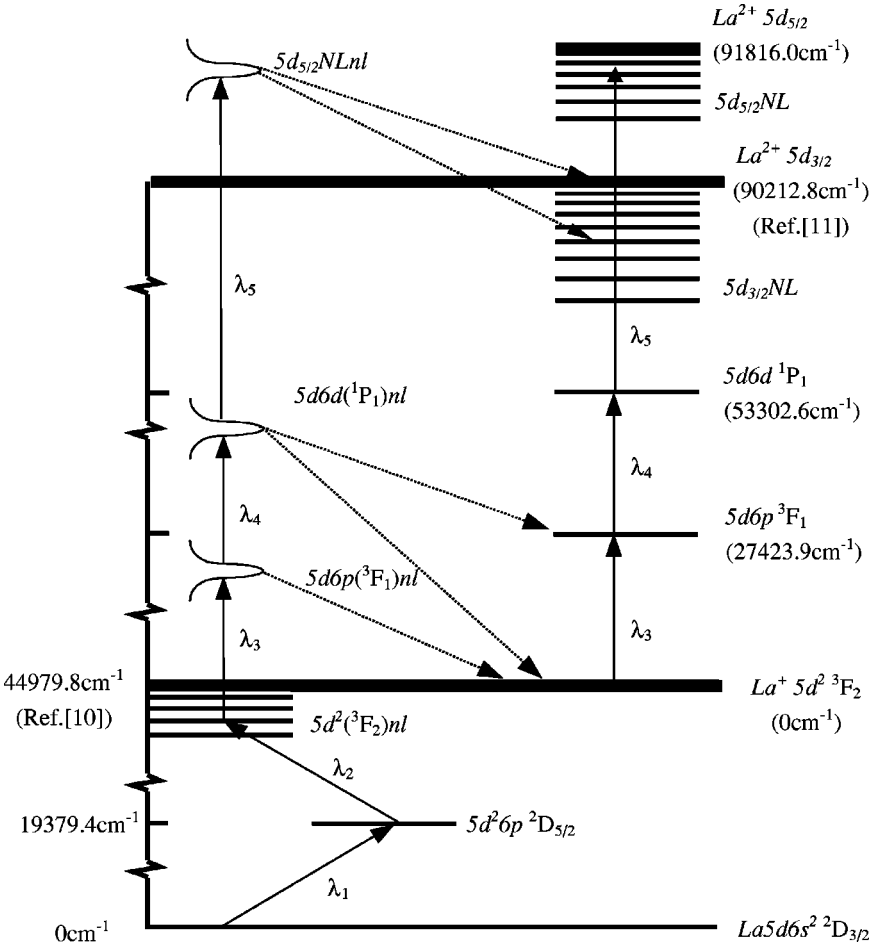

FIG. 1. Laser excitation scheme of La triply excited double Rydberg states (TEDRS). The left part shows the excitation channel for TEDRS. The right part shows the parallel excitation process of La^+ autoionizing Rydberg states. The dot lines represent the autoionization processes. The energy unit used in the figure is cm^{-1}.

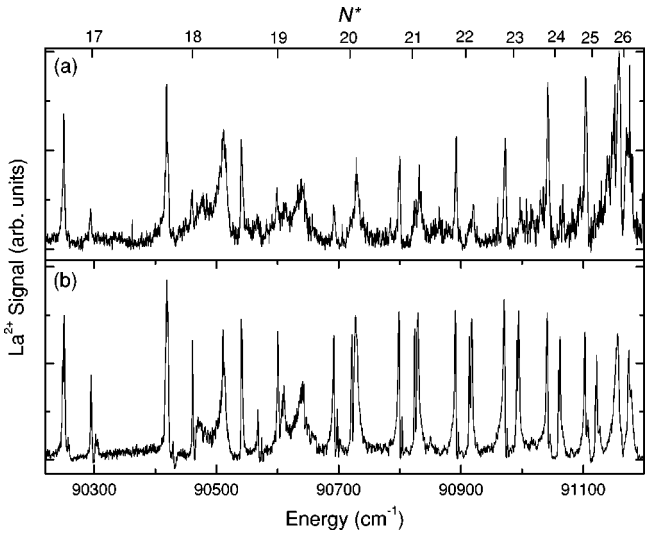

FIG. 2. (a) Typical observed excitation spectrum of La TEDRS $5d_{5/2}NLnl$ ($n^*=46.6$), obtained by scanning the frequency of the final laser λ_5 in Fig. 1 and recording the signals of La^{2+} ions produced by the field ionization of the TEDRS-decayed products La^+ Rydberg ions. (b) Spectrum of La^+ autoionizing Rydberg states $5d_{5/2}NL$ excited from $5d6d(^1P_1)$ [11]. The abscissa is the total energy imposed by the last three dye lasers.

laser field can be neglected (because it is in a highly excited orbit), produces an effect like the stark effect of an electric field. In the other aspect, the spectrum of TEDRS looks more complicated than that of double Rydberg states [in Fig. 2(a) there are several embedding TEDRS perturbers (e.g., around $N^*=18$, 19 and presumably 26) with the core electron in an orbit higher than $5d_{5/2}$], indicating the nontrivial influences of the interactions among the dielectronic correlations. The complicated interactions will be discussed in further detail in later investigation of the decay process of TEDRS. A recent approach based on the semiclassical closed orbit theory has been able to interpret quantitatively the excitation structure of double Rydberg states [5]. The spectrum in Fig. 2(a) provides a first example in triply excited states that can be used to test the closed orbit theory.

In order to learn more electronic correlation effects in TEDRS, we have studied the dynamic process of TEDRS after the excitation. The measured and calculated probabilities are shown in Figs. 3 and 4 for TEDRS-decayed La^+ ions having a binding energy smaller than $Z^2/(2N'^*{}^2)$ (atomic units, $Z=2$, N'^* stands for the effective quantum number of the TEDRS-decayed La^+ Rydberg states). TEDRS are below and above the double escape threshold of La in Figs. 3 and 4, respectively. It will be seen in later discussions that the distribution pattern in Fig. 3 is very different from that in Fig. 4. In theory, an approach developed from the ''breathing sphere'' model [3] is used to simulate the dynamic process in TEDRS, as described below.

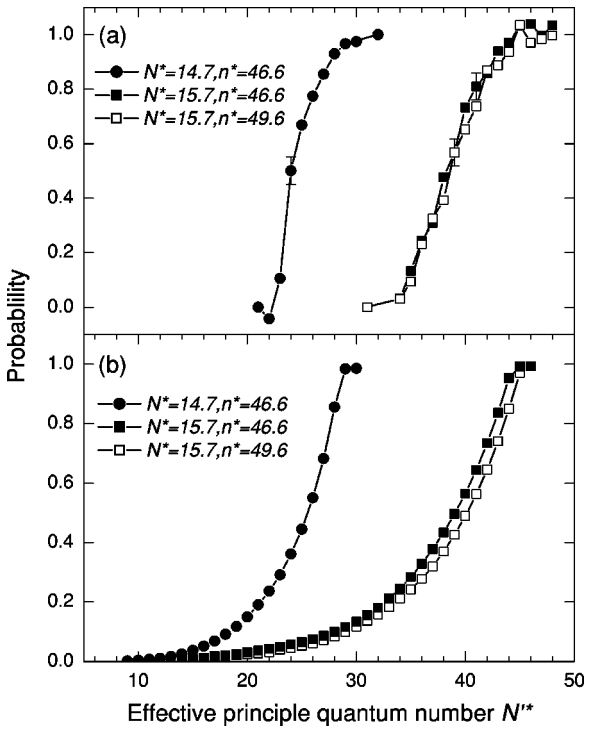

FIG. 3. (a) Measured and (b) calculated probabilities of the decayed La^+ ions having a binding energy smaller than $4/(2N'^*)^2$ (a.u.) for TEDRS $5d_{5/2}NLnl$ below La double escape threshold. Due to the limitation in technique, the measurements in (a) do not include the probabilities to the lowest La^+ ionic Rydberg states (with binding energies below that of the leftmost point in each curve. The leftmost points of the curves with ■ and □ points overlap.), which however, does not influence our discussions. For details see text. Note that the distribution is *sensitive* to N^* and *insensitive* to n^*.

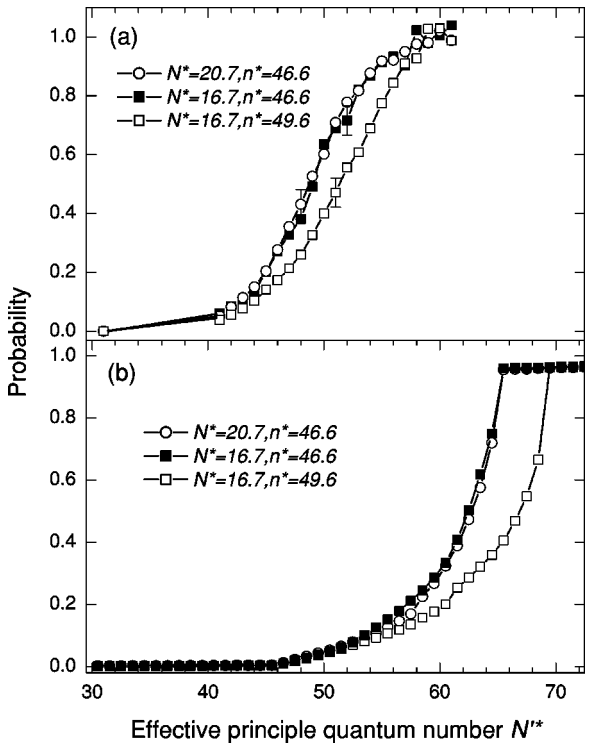

FIG. 4. Similar to Fig. 3, but for TEDRS $5d_{5/2}NLnl$ above La double escape threshold. Note that in reverse to Fig. 3, the distribution is *insensitive* to N^* and *sensitive* to n^*.

In our theoretical approach, after the excitation, the outer two Rydberg electrons are treated as two one-dimensional radial wave packets that will propagate along the classical trajectories if they do not meet each other. The interaction between the third excited electron (in a valence orbit) and any of the Rydberg electrons is neglected unless a Rydberg electron is close to the valence orbit. The exchange effects are also neglected. Our method is not intended to achieve accurate description for the complex details of TEDRS, but rather to understand the important features in the autoionization of TEDRS.

Using the above approximation, the complex electronic correlations in the TEDRS can be decomposed into individual pairs of the electronic correlation. For each important stage in the autoionization process of the TEDRS, only one pair of electronic correlation is needed to account. The case where both Rydberg electrons are very close to the valence orbit has very little probability and can be neglected. When both Rydberg electrons are far from the valence orbit, only the correlation between the Rydberg electrons is accounted by using the ''breathing sphere'' model. In that case, the correlation takes place when the two wave packets penetrate each other, and the Rydberg electrons will exchange their potentials and their kinetic energies remain unchanged. When one of the Rydberg electrons is close to the valence orbit, only the correlation between the incoming Rydberg electron and the valence electron is accounted. Near the valence orbit, a Rydberg electron has some probability to exchange energy with the third electron (in the valence orbit). This probability ($\sim 1/14$) can be estimated using the linewidth of the autoionizing Rydberg states of La^+ [13]. In our system, it will de-excite the third (valence) electron (which could be excited again by another such event) and increase the energy of the Rydberg electron.

The calculated probabilities corresponding to the measured ones are shown in Figs. 3(b) and 4(b). The calculated results are normalized for all possible decay processes, while the measured results are normalized within a limit range due to the limitations (e.g., the collection efficiency of the ion and the maximum field strength for field ionization) in the technique of sequential field ionization [8,9]. The range of the binding energy for a measurable TEDRS-decayed La^+ ion in our experiment is $4/(2N'^{*2})$ (a.u.) with N'^* between the end points in each curve in Figs. 3(a) and 4(a). Therefore distributions below the leftmost and above the rightmost points of the curves are not included in our measurements. Note that in Fig. 3(a), the real distributions vanish above the rightmost points because an escape electron has a positive orbital energy. By comparing the measurements and the calculations, it can be seen that most of the TEDRS will decay into the measurable region.

In Fig. 3 where the TEDRS are below the double escape threshold of La, the calculated results are in good agreement with the measurements. In our theoretical simulation, we have found that the autoionization is dominated by a process where the middle electron (NL) exchanges and gains energy *first* from the innermost electron (the low excited valence

one), and then interacts with the outermost electron (nl) that leads to the ejection of one free electron (the autoionization). It can be seen in Fig. 3 that the distribution is nearly independent of n^*, the orbital energy of the outermost electron. On the other hand, it depends strongly on N^*, the orbital energy of the middle electron. This phenomenon is because as a result of the interaction between the outer two electrons, the autoionization that depends strongly on their instant kinetic energies takes place in a region closed to the orbit of the middle electron where the kinetic energies are sensitive to N^* and insensitive to n^*.

In Fig. 4 where the TEDRS are above the double escape threshold of La, the calculated results have similar distributions as the measurements, except that the calculated results shift to higher N'^*. It is found that the autoionization is dominated by the same process in Fig. 3. However, in reverse to Fig. 3, it can be seen that the distribution is insensitive to N^* and sensitive to n^*. That is because after the middle electron gains energy from the low excited valence electron, it will have a positive orbital energy and tend to escape after interacting with the outermost electron. Therefore after the autoionization, the outermost electron most likely remains in an ionic bound Rydberg orbit, where the orbital energy is sensitive to that of the outermost (decided by n^*) and insensitive to that of the middle electron (decided by N^*) before autoionization. This process is similar to the postcollision interaction [14] except that the outmost here is bound at the beginning. It is also found in calculation that the double escape process where both of two outermost electrons escape has very little probability although allowed by the energy requirement, which is presumably due to the difficult fine energy balance required between the two electrons.

The shifting between calculation and measurement in Fig. 4 is because the one-dimension approximation [3] used in our calculation. Briefly, in the real three-dimensional process, after the middle electron gains energy from the valence electron, it has a positive orbital energy. Then it may move *towards* or *backwards* the outermost electron. Due to repulsive force between electrons, the electron (most likely the middle) tends to escape more along the ''backward'' orbit for which the remained outermost electron will go to a lower ionic Rydberg orbit compared to that in the one-dimension model. Therefore the measured distributions are lower than the calculated results. It should be noted that the similar effect for Fig. 3 does not produce much difference between calculation and measurement, which could be due to the more complicated interaction between the outer two electrons therein.

It is worth mentioning that there is a process which, while having little probability for the measured TEDRS here, can become significant when the orbit of the middle electron is close to that of the outermost electron. In this process, the autoionization will occur without gaining energy from the excited electron near the valence orbit, and if the resulted ion is in an unbound state, it will continue to autoionize and produce a La^{2+} ion (a sequential double escape process).

In conclusion, we have studied the electronic correlations in La TEDRS, an atomic asymmetric four-body system. The correlation effects can be understood by means of decomposing the electronic correlations into dielectronic correlations.

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