Propensity Rule for Novel Selective Double Photoexcitation of Helium Atoms in Strong Static Electric Fields

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We studied the double photoexcitation spectra of helium in a strong dc electric field and compared the results with the recent experimental data of Harries *et al.* [Phys. Rev. Lett. **90**, 133002 (2003)]. We derived the propensity rules based on the crossing or noncrossing of energies in the Stark map to predict the selective subset of doubly excited states that are preferentially populated in such experiments. It is shown that the propensity rule is a consequence of the ubiquitous correlation properties of doubly excited states in general.

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In a recent paper [1], Harries *et al.* reported the double photoexcitation spectra of helium atoms in a strong dc electric field. In the absence of electric field, two prominent $^1P^0$ resonances were observed for photon energies spanning from 64.8 to 65.15 eV. These two resonances are the well-understood $n = 6$ and $n = 7$ states of the "+" Rydberg series below the He^+ ($N = 2$) threshold. In a dc field, many new resonances appeared. In particular, at 84.4 kV/cm, about six and nine new resonances were found near each field-free resonance, respectively. The new resonances near the $n = 6$ state have been compared to the calculations by Chung *et al.* [2], but resonances near the $n = 7$ state were not interpreted. Furthermore, many more resonances were predicted by the calculation of Chung *et al.*, but only a few have been observed in the experiment. In this Letter we propose a propensity rule which predicts the new prominent resonances induced by the static electric field in double photoexcitation. The rule governs how each pair of energy levels in a Stark map be treated as crossing or noncrossing, based on the correlation properties of doubly excited states in the absence of electric field. We also perform *ab initio* calculations to verify the results predicted by the propensity rule.

The new experiment of Harries *et al.* [1] continues the long history of surprises involving the doubly excited states of helium. For photon energies near 60 eV, the helium spectra were already studied by Madden and Codling [3] in 1963 when synchrotron radiation first became available. Based on the shell model, it was expected that three $^1P^0$ Rydberg series, $2snp$, $2pns$, and $2pnd$, would be observed converging to the He^+ ($N = 2$) threshold with nearly equal strength. On the contrary, the experiment found only one prominent series accompanied by a very weak one. The third series was not seen. This experiment prompted Cooper *et al.* [4] to declare the complete failure of shell model in describing doubly excited states. They suggested that the observed dominant series be more appropriately expressed as $2snp + 2pns$, the weak one as $2snp - 2pns$, while the third unobserved series as $2pnd$. These three series, now often called "+", "−" and "pd" series, respectively, emphasize the correlation properties of the two excited electrons which are not present in the shell model. In the ensuing years the correlation properties of doubly excited states have been investigated by different equivalent theoretical models [5–9] and cumulated with a new set of quantum numbers (K, T, A) [6] (or their equivalents) for describing all the doubly excited states. In the meanwhile, this part of the helium spectra continued to draw the interest of the experimentalists with the arrival of each new generation of synchrotron radiation. The first observation of the $2pnd$ series was not achieved until 1992 [10]. In recent years, new features of these states have been obtained through the observation of the yield of metastable atoms and vacuum ultraviolet fluorescence [11,12]. Despite these studies, the majority of doubly excited states which cannot be excited by photons directly remain unexplored. The experiment of Harries *et al.* [1] offers an opportunity to probe a large new set of doubly excited states, and the propensity rule proposed in this Letter is to guide the interpretation of such experiments in the future.

Experimental and theoretical studies of atoms in a strong electric field often are limited to singly excited Rydberg states. For doubly excited states, the only systematic studies were carried out by Halka *et al.* [13] using the unique relativistic H^- ion beam at Los Alamos in the late 1980s and the early 1990s. However, the number of doubly excited states in H^- below each detachment threshold is small. With the many more states available in He the experiment by Harries *et al.* [1] provides many new opportunities, but it also posts a new challenge since many new Stark induced resonances have to be interpreted.

To study double photoexcitation of He in an electric field, we used the hyperspherical close-coupling method (HSCC) to calculate the energy and the oscillator strength of each resonance, from the field-free limit to

the maximum field of 84.4 kV/cm used by Harries *et al.* [1]. The HSCC method has been applied previously to calculate photoabsorption spectra of He [14]. Briefly, one replaces the two distances r_1 and r_2 of the electrons from the nucleus by a hyperradius R and a hyperangle α, $R = \sqrt{r_1^2 + r_2^2}$, and $\alpha = \arctan r_1/r_2$. In the absence of electric field we solved the two-electron Hamiltonian with R as an adiabatic parameter. The nonadiabatic coupling between the potential curves is treated by the smooth-variable-discretization method [15]. Thus for each total orbital and spin angular momentum, L and S, and parity π, a set of adiabatic hyperspherical potential curves is first obtained. An example of such curves for $^1P^0$ states below the He^+ ($N = 2$) threshold is shown in Fig. 1.

The three curves in Fig. 1 are often labeled as $+$, $-$, and pd, but they can be designated by the more general $(K, T,)^A = (0, 1)^+$, $(1, 0)^-$, and $(-1, 0)^0$ quantum numbers as well, or simply as "a," "b," and "c" for the present purpose, as was used by Harries *et al.*[1]. For the energies and widths of doubly excited states, they are obtained by solving the coupled hyperradial equations. For simplicity and the purpose of this work the hyperradial equations are solved using pseudospectral basis functions [16]; thus only the energies and wave functions of doubly excited states are obtained. To avoid possible confusion with pseudostates we varied the discretization parameters and checked the normalization of each state within a box ($R = 60$ a.u.). In the presence of electric fields, the electric dipole operator couples $^1P^0$ curves with adiabatic potential curves from other symmetries. Since we are focusing on doubly excited states near the $n = 6$ and $n = 7$ states, we include field-free $^1S^e$, $^1P^0$, $^1D^e$, $^1F^0$, $^1G^e$, $^1H^0$, $^1I^e$, and $^1J^0$ potential curves in the coupled equations to obtain the resulting Stark induced resonances. To improve accuracy actually the potential curves converging to the $N = 1$ and $N = 3$ limits of He^+ are also included in the calculation. Using this method, all the Stark induced resonances are obtained simultaneously in a single diagonalization. For a different electric field, only the set of coupled hyperradial equations has to be solved one more time. By taking the dipole matrix elements of the eigenfunctions with the ground state of He, the oscillator strength of each state is also calculated.

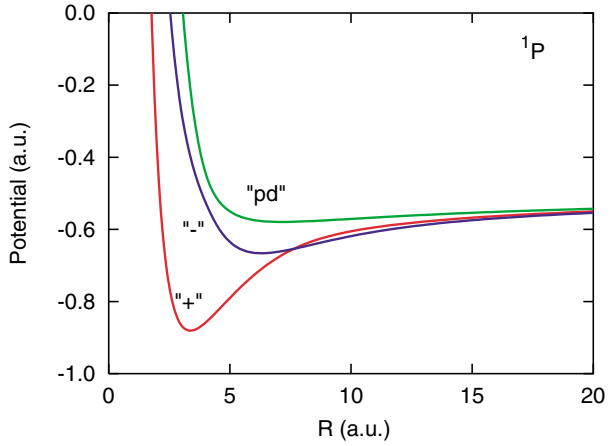

FIG. 1 (color online). Hyperspherical potential curves for He $^1P^0$ states converging to the $N = 2$ threshold of He^+.

In Fig. 2 we display the photoabsorption spectra of He obtained by Harries *et al.* [1] at a field strength of 84.4 kV/cm. The calculated position and oscillator strength (measured by the length of the bar) for each resonance are shown below the experimental data. There is a general agreement. To understand the Stark induced spectra, we also calculated the position and oscillator strength of the $^1P^0$ resonances when there is no electric field. These resonances are labeled in the figure, and their relative oscillator strengths are 1.000 ($6a$), 0.677 ($7a$), 0.573 ($8a$), 0.015 ($7b$), 0.012 ($8b$), 0.003 ($6c$), and 0.001 ($7c$). In the energy region shown, we focus the analysis on the two groups of states near $6a$ and $7a$. For the low-energy group, the new resonances appear to draw their strength from the $6a$ state. The "original" $6a$ state is still quite recognizable, with a Stark shift calculated to be 5.1 meV, as compared to the experimental 5.3 ± 0.5 meV. For the high-energy group, the new resonances draw the strength mostly from the $7a$ state, but the Stark mixing is so strong there that the $7a$ state is no longer readily recognizable. (Note that in making the comparison with experiment, we shifted our calculated energies by 0.03 eV throughout.)

Despite the general agreement between our calculations and the experimental spectra, there remains a larger issue. Near the $6a$ state, we expect to have 17 states that can be induced by the electric field, but only about 6 or 7 were seen in the photoexcitation spectra. It is important to be able to understand what kind of states are induced in an electric field and to be able to follow their positions as the

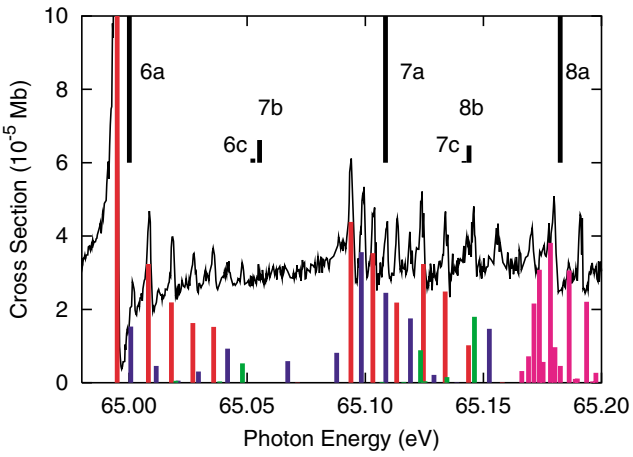

FIG. 2 (color online). Comparison of calculated spectra of He in the presence of a dc electric field at 84.4 kV/cm with the experimental data of Harries *et al.* [1]. The red (dark gray), blue (dark), and green (light gray) bars indicate these states evolved from the a,b, and c field-free states, respectively, following the present propensity rule. The length of each bar measures the relative oscillator strength. The field-free $^1P^0$ resonances are also indicated at the top of the figure.

the electric field is varied. For this purpose we study the Stark map of doubly excited states, i.e., their positions versus the electric field.

In Fig. 3 the Stark map near the $6a$ state is shown from 64.99 to 65.07 eV for field strength up to 100 kV/cm. The spectra measured by Harries *et al.* [1] are also shown for a few fields, where each spectra is vertically shifted. The calculated energy and oscillator strength at each experimental field strength are indicated by vertical bars, where the length of the bar indicates the relative strength (except for the original $6a$ state which has been scaled down by a factor of 10). The Stark map is color coded. At zero field, each state can be identified as $6a\,^1S^e$, $6b\,^1D^e, \ldots$, etc. Within the states considered here, there is no ambiguity to call them $6a(S)$, $6b(D), \ldots$, etc. We use red (dark gray) lines for a states, blue (dark) lines for b states, and green (light gray) lines for c states. Thus, in the zero-field limit, for the red (dark gray) lines, in the order of increasing energies are $6a(P, F, H, G, D)$ and $7a(S)$; for the blue (dark) lines, $6b(G, F, H, I, S)$ and $7b(P)$; and for the green (light gray) lines $6c(G, F, D, P)$. The $6b(D)$ lies below $6a(P)$ and is outside the range plotted. As the electric field is turned on, the wave functions from these states will mix and the new resonances will be shifted. We want to construct a "correlation" diagram such that the level shifts can be easily understood and new strong photoabsorption peaks identified.

In Fig. 3 the correlation diagram for the Stark map was constructed following this rule: Stark induced states originating from the same group do not cross, while those originating from different groups are allowed to cross. This is the propensity rule for constructing the Stark map for doubly excited states of helium. Since the Stark induced states derive their oscillator strength from the $6a(P)$ state (recall that the field-free $6c$ and $7b$ states have little oscillator strength), the rule implies that only those states evolved from the field-free a states are preferentially populated. This is the propensity rule for selective double photoexcitation of helium in an electric field. Among the a states, of course, those which have smaller energy separations with respect to the $6a(P)$ state are expected to draw more oscillator strength. By perusing the calculated oscillator strengths and the experimental data, in particular, at 84.4 kV/cm, one can clearly see that all the major peaks are associated with the red (dark gray) curves, or evolved from the field-free a states. The only "minor" peak which does not belong to the a group is a b state which is closest to the $6a(P)$ state at zero field. Note that its strength is still weaker than those states from the a group.

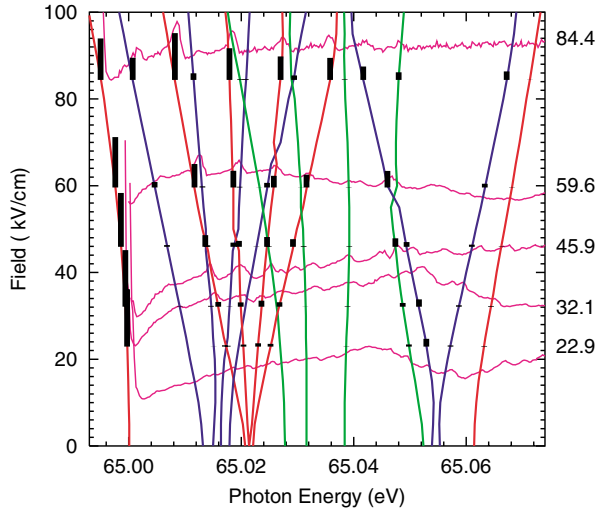

FIG. 3 (color online). Stark map around the $6a\,^1P^0$ state. The correlation diagram is constructed from the present calculated energies at different fields following the proposed propensity rule. The purple curves are from the experimental data of Harries *et al.* [1]. The calculated oscillator strength for the prominent states are shown by gray bars. For details, see the text.

The existence of propensity rules is not unexpected. According to the independent electron model, there are three Rydberg series for each L (and fixed spin and parity) considered here, called $2snL$, $2pn(L-1)$, and $2pn(L+1)$. Because of electron-electron interaction, these states are mixed and the eigenstates are reclassified into a, b, and c groups in general, as indicated above. For higher L, we can associate the a group with the $2snL$ series, the b with $2pn(L-1)$, and the c with $2pn(L+1)$ approximately. Recall that a, b, and c are short-hand notations for the collection of correlation quantum numbers K, T, and A, where these quantum numbers come from the approximate dynamic symmetry in helium atom [5]. The dc electric field operator will couple pairs of states which have similar correlation quantum numbers but with L differing by one unit. Thus all the a states from different L's tend to couple to each other by the electric field, and they are observed in photoaborption when helium is placed in a dc electric field; their energies follow the noncrossing rule. Because of the approximate dynamic symmetry, on the other hand, states from the b and c groups do not couple with states from the a group, and they can cross with the a states. This forms the basis of our proposed noncrossing rule for states originating from the same group, and crossing for states originating from different groups. This propensity rule was used to construct the Stark map in Fig. 3 and then to interpret the observed and calculated spectra. Note that a Stark map was presented in Fig. 4 of Harries *et al.* [1], but they followed the noncrossing rule from earlier theoretical calculations such that no simple interpretation of the observed spectra was possible.

We next apply the propensity rule to obtain the Stark map, Fig. 4, for states induced by the static electric field near the zero-field $7a(P)$ state. Comparing to the states examined in Fig. 3, we expect three more resonances in the field-free limit. The evolution of the spectra for this group of states was not available in Harries *et al.* [1]. Nevertheless, we have generated the Stark map from our calculation and compared the calculated results at

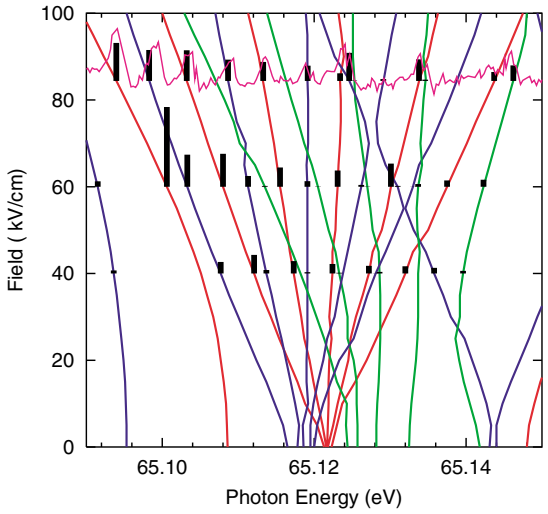

FIG. 4 (color online). Stark map around the $7a\,^1P^0$ state. Others are the same as Fig. 3.

84.4 kV/cm with the experimental data. In Fig. 2, the experimental data show that there are many more peaks near the $7a(P)$ state at this field strength compared to the induced states near the $6a(P)$ state. The Stark shifted $7a(P)$ state is no longer easily identified without the calculation since most of the field induced states have nearly identical strength. Thus we are dealing with a region where the Stark field strength is not small. The Stark map for $n = 7$ shown in Fig. 4, constructed with the propensity rule, is very similar to the map shown for $n = 6$ in Fig. 3. The relative positions of the field-free states are similar also except that one more state appears for each group, a, b, and c. Note that all the red (dark gray) curves are connected to one of the peaks at 84.4 kV/cm. However, a few additional peaks are clearly visible at 84.4 kV/cm as well. These peaks are adiabatically connected to the b states in the field-free limit. In other words, at this field strength which is considered to be large for the $n = 7$ states, several b states which lie near the $7a(P)$ state can also be excited since their energy positions at zero field are very close to the $7a(P)$ state and thus can be excited as well when the field strength is large. We note, however, as confirmed from our theoretical calculations, these b states are not populated significantly at lower fields; see Fig. 4. In other words, we can expect only a small violation of the propensity rule when the field strength is large. By comparing Figs. 3 and 4, we notice the similarity between the two Stark maps.

We next return to discuss other smaller features in Fig. 3 starting from the four field-free states near 65.06 eV. These four states are $6c(P)$, $6b(S)$, $7b(P)$, and $7a(S)$. At low fields, their strengths come mostly from the field-free $7b(P)$ state. At higher fields, the sum of their oscillator strength increases, indicating that these states begin to interact with the states from the $n = 7$ manifold and gaining additional contributions from the $7a(P)$ state. The same can be said about the four equivalent states, $7c(P)$, $7b(S)$, $8b(P)$, and $8a(S)$, near 65.14 eV in Fig. 4. There the contribution from the $n = 8$ manifold is even more evident. Still, in this energy region, the prediction from the propensity rule is mostly correct.

In summary, we have proposed a propensity rule for constructing a Stark map for determining the doubly excited states that are expected to be predominantly excited for a helium atom in a static electric field. The propensity rule was derived based on the correlation properties of doubly excited states in the field-free limit. The propensity rule has been used to interpret the observed prominent peaks from Harries *et al.* [1], but it should be applicable to guide the interpretation of future experiments on double photoexcitation of helium in an electric field from which non-$^1P^0$ doubly excited states can be probed with high precision.

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