Autodetachment of Doubly Excited States in Nonhydrogenic Negative Ions

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(Received 14 February 2000)

A semiclassical model is developed to describe the two-electron dynamics of the process of autodetachment. A formula derived for the partial width of a doubly excited state represents a product of an amplitude and phase factors. An anomalous width behavior is predicted for states near a threshold when the orbital angular momentum of the outer electron is high. Oscillations of the phase factor, as a function of energy, determine the functional behavior of relative widths in the region farther from threshold for a given series of states.

PACS numbers: 32.10.–f, 31.50.+w, 32.80.Dz

Recent experiments on photodetachment from negative ions revealed rich spectra of bound states that exist in these atomic systems above the first detachment thresholds. These states are doubly excited because the outer electron in such a state is bound to an excited atom. Depending on the excitation level, doubly excited states are embedded in one or more continua and thus rapidly decay via the process of autodetachment. These bound states manifest themselves as resonances in photodetachment cross sections. In earlier studies, strong resonances were found in Rb^- and Cs^- below the first excited states thresholds [1]. Later work on He^- [2], Li^- [3,4], Na^- [5], and K^- [6] revealed series of doubly excited states bound to higher lying thresholds. Resonance structures, associated with doubly excited states, were also observed in the cross section of electron scattering on neutral targets [7].

The nature of binding forces in atomic systems determines the properties of their atomic spectra, such as the energies and widths of bound states. This binding is fundamentally different in a nonhydrogenic negative ion compared to atoms, positive ions, or H^-. In atoms and positive ions the valence electron moves in a long range field of the Coulomb potential. A spectrum of bound states in these systems represents infinite series of states converging on corresponding ionization thresholds. This convergence follows the Rydberg formula near a threshold. The negative ion H^- is a special case. Here the outer electron moves in the field of a permanent dipole associated with the H atom in an excited state. This potential supports an infinite series of states exponentially converging on a corresponding detachment threshold [8]. Widths of these states exponentially decrease to zero at the threshold. In the case of a nonhydrogenic negative ion considered in the present work, the outer electron moves in the field of a dipole potential induced by the outer electron in the parent atom. The range of this type of potential is much shorter in comparison with the Coulomb and permanent dipole potentials. As a consequence, it can support only a finite number of states. Description of properties of states bound by an induced dipole potential represents an interesting fundamental problem.

A general feature of doubly excited states in negative ions is the weakness of their binding to a parent atomic state. Consequently, the outer electron in such a state moves essentially in the asymptotic region, where its density distribution is well separated from the density distribution of the atomic electrons. The effect of electron interactions is, thus, reduced to the polarization of the residual atom by the outer electron. The corresponding asymptotic potential has the form $-\alpha/2r^4$, where α is the dipole polarizability of the parent atomic state. The asymptotic approximation allows one to develop analytical methods in order to describe the properties of doubly excited states. Such a method, based on a semiclassical consideration, was presented in Ref. [2]. A semiclassical formula derived in this work predicts relative energies of a series of doubly excited states converging on a given threshold. It was shown that this convergence is of a polynomial character. This formula was successful in describing the energy spectra of negative ions observed in recent experiments [2,5,6]. In the present work we develop a semiclassical method to describe the dynamics of autodetachment process.

Let us first consider autodetachment into a single final state of the residual atom. Since the outer electron moves at large distances from the core, the initial doubly excited state can be represented by a product of wave functions of the inner and outer electrons, $\psi_1(\mathbf{r}_a)$ and $\psi_i(\mathbf{r})$, respectively. The outer electron is bound by a polarization potential, and the energy E of the bound state is negative relative to the corresponding initial atomic state threshold (see Fig. 1). In the final state, the outer electron is in the continuum associated with the lower atomic state. The kinetic energy of the outer electron is defined according to the energy conservation rule: $k^2/2 = E_1 - E_2 + E$, where E_1 and E_2 are energies of the initial and final states of the residual atom, respectively. The final state can be represented by a product of the continuum wave function of the outer electron $\psi_f(\mathbf{r})$ and the wave function of the relaxed atomic electron $\psi_2(\mathbf{r}_a)$. The transition from the initial state to the final state occurs due to the Coulomb interaction between electrons. The width of an autodetaching state is determined by the transition probability

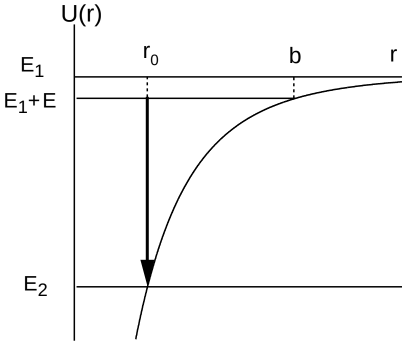

FIG. 1. The polarization potential curve. E_1 and E_2 denote the energy levels of the initial and final states of the residual atom. E is the energy of the outer electron in the initial bound state. The autodetachment transition, indicated by the arrow, occurs at the distance r_0 where the kinetic energy of the bound electron corresponds to the kinetic energy of the outgoing electron.

per unit time, and can be expressed in terms of the matrix element of the energy of interaction (atomic units are used throughout):

$$\Gamma = 2\pi \int \left| \langle \psi_2 \psi_f | \frac{1}{|\mathbf{r} - \mathbf{r}_a|} | \psi_1 \psi_i \rangle \right|^2 \times \delta\left(\frac{k^2}{2} + E_2 - E_1 - E\right) \frac{d^3\mathbf{k}}{(2\pi)^3} . \qquad (1)$$

We describe the initial state of the outer electron $|\psi_i\rangle$ semiclassically. In the classically allowed region, $r < b$, the corresponding radial wave function has the form

$$R_i(r) = \frac{C(E)}{r\sqrt{p(r)}} \cos\left(-\int_b^r p(x)\,dx - \frac{\pi}{4}\right), \qquad (2)$$

where $p(r)$ is the electron momentum in a field of the superposition of a polarization potential and an orbital potential associated with the angular momentum l_i of the weakly bound electron, and $C(E)$ is the normalization coefficient that depends on the energy of the bound state.

The effective range of the atomic potential that the outer electron experiences in the final state is short because the inner electron is relaxed. It will be seen below that small distances r do not contribute to the integral of the matrix element. Thus, as an approximation, we describe the final state of the outer electron asymptotically. The corresponding radial wave function of the l_f-wave component of the continuum state $|\psi_f\rangle$ has the asymptotic form

$$R_f(r) \sim \frac{1}{kr} \sin\left(kr - \frac{l_f}{2}\pi + \delta_{l_f}\right), \qquad (3)$$

where δ_{l_f} is the phase shift. The continuum spectrum is normalized on the $k/2\pi$ scale, as it should be in accordance with Eq. (1).

The integral of the matrix element in Eq. (1) can be separated in the radial and angular coordinates by expanding the interaction term $1/|\mathbf{r} - \mathbf{r}_a|$ into a series of Legendre polynomials. Integrating over the angular coordinates and the momentum space $d^3\mathbf{k}$, we obtain

$$\Gamma = \frac{4C^2(E)}{k} \sum_{l_f} \left[\sum_l Q_{l_f l} \int \int R_1(r_a) R_2(r_a) r_a^2 \frac{r_<^l}{r_>^{l+1}} \frac{1}{\sqrt{p(r)}} \cos\left(-\int_b^r p(x)\,dx - \frac{\pi}{4}\right) \times \sin\left(kr - \frac{l_f}{2}\pi + \delta_{l_f}\right) dr\, dr_a \right]^2 , \qquad (4)$$

where $R_1(r_a)$ and $R_2(r_a)$ are radial wave functions of the $|\psi_1\rangle$ and $|\psi_2\rangle$ atomic states, respectively, $r_<$ and $r_>$ denote the smaller and greater of the magnitudes of r and r_a, l is the multipole order in the expansion series of Legendre polynomials, and $Q_{l_f l}$ is the result of integration over the angular coordinates.

In the following we focus our consideration on the integral over the radial coordinate r. The integrand of Eq. (4) contains a product of two oscillating functions. Using the trigonometric relation $2\sin\beta\cos\gamma = \sin(\beta - \gamma) + \sin(\beta + \gamma)$ and taking into account only the term where the oscillation frequencies are subtracted, we obtain the following expression for the radial integral over r:

$$\mathrm{Im}\frac{1}{2} \int \frac{r_<^l}{r_>^{l+1}} \frac{1}{\sqrt{p}} e^{i(kr - \int_b^r p\,dx - \frac{l_f}{2}\pi + \delta_{l_f} - \frac{\pi}{4})}\, dr . \qquad (5)$$

This integral can be analytically evaluated using the method of steepest descents. For the sake of simplicity, the integrand function is written only for the classically allowed region. Its continuation in the classically forbidden region is an exponentially decreasing function and, thus, the contribution to the matrix element from the forbidden region can be neglected. The contribution from small distances $r \to 0$ is also negligible. Here the integrand function oscillates with an infinitely high frequency and has an infinitely small amplitude. Thus, the main contribution to the integral of Eq. (5) comes from the saddle point r_0 which is determined by the condition

$$p(r_0) = k . \qquad (6)$$

This condition has a clear physical meaning. The radial motion of the outer electron in the initial state is bound between the turning point b and the origin. Its kinetic energy varies from zero at the turning point to an infinitely high value at the origin. At the point r_0 defined by Eq. (6), the kinetic energy is equal to the kinetic energy of the outer electron in the final state. At this point the inner electron makes the relaxation transition into the lower state, and the outer electron continues moving as a free electron with the corresponding kinetic energy.

Evaluating the integral of Eq. (5) by the use of the method of steepest descents and substituting the result obtained into Eq. (4), we find

$$\Gamma = \pi \frac{C^2(E)\alpha^{1/4}}{k[2(E_1 - E_2)]^{5/4}} \sum_{l_f} \sin^2(\Delta\Phi_{l_f}) J_{l_f}^2, \qquad (7)$$

where

$$J_{l_f} = \sum_l Q_{l_f l} \left(\int_0^{r_0} \frac{r^{l+2}}{r_0^{l+1}} R_1 R_2 \, dr + \int_{r_0}^{\infty} \frac{r_0^l}{r^{l-1}} R_1 R_2 \, dr \right)$$

and

$$\Delta\Phi_{l_f} = k r_0 - \int_b^{r_0} p(x)\, dx - \frac{l_f}{2}\pi + \delta_{l_f}. \qquad (8)$$

In Eq. (7) we use an approximative expression for the saddle point $r_0 = [\alpha/2(E_1 - E_2)]^{1/4}$, where the orbital term is omitted. In the inner region the orbital term is small in comparison with the polarization potential term, and it can be neglected if the inequality $[2\alpha(E_1 - E_2)]^{1/2} \gg l_i(l_i + 1)$ is satisfied. This inequality is valid for all experimentally measured doubly excited states. The sine function in Eq. (7) represents a phase factor. One should recall here that the semiclassical phase over half a period of the bound motion is quantized and is equal to $(n + 1/2)\pi$, where n is an integer number. Then, the phase factor can be represented as a cosine function of the phase difference $\Delta\phi$ between the semiclassical phase of the bound motion in the initial state and the asymptotic phase of the free motion in the final state, both calculated at the transition point r_0. The phase factor acquires its maximum value when the phase difference is zero.

The coefficient $C^2(E)$ and the phase $\Delta\Phi_{l_f}$ can be analytically expressed in terms of elliptic integrals. Here we present only a formula for $C^2(E)$ which will be used below:

$$C^2(E) = \frac{[l_i(l_i + 1)\eta]^{3/2}}{2\alpha} K'^{-1}\left(\sqrt{\frac{\eta - 1}{2\eta}} \right), \qquad (9)$$

where $K(x)$ is a complete elliptic integral of the first kind, the prime denotes differentiation over the function argument, and $\eta = \sqrt{1 + 8E\alpha/[l_i(l_i + 1)]^2}$.

In the following analysis we let E be a variable parameter. Consider the limit of small energies $|E| \ll E_1 - E_2$, which corresponds to upper doubly excited states lying close to the parent atomic state. In this limit, the phase difference $\Delta\phi$ at the transition point r_0 is nearly independent of the energy E and, therefore, the phase $\Delta\Phi_{l_f}$ differs by π for two neighbor states, as it should be according to the semiclassical quantization rule. The phase factor, as a function of E, makes one oscillation between energies of two bound states, but it acquires the same value at each of these energies. Then, for a given series of doubly excited states, the behavior of the width of a state as a function of the energy is determined basically by the coefficient $C^2(E)$. If the orbital momentum of the outer electron in the initial state is zero, $l_i = 0$, from Eqs. (7) and (9) we find that $\Gamma \sim E^{3/4}$. In this case the width can be infinitely small when the energy approaches the threshold $E = 0$. If $l_i \neq 0$, the width has a finite value at the threshold. Moreover, the coefficient $C^2(E)$ as a function of E has a minimum below the threshold, as can be seen from Fig. 2 where a reduced coefficient $C_r = \alpha C^2(E)/[l_i(l_i + 1)]^{3/2}$ is plotted versus a reduced energy $E_r = \alpha|E|/[l_i(l_i + 1)]^2$. Thus, if the value of the initial orbital momentum l_i is large, the last state, the one that is the closest to the threshold, does not need to be the narrowest in a given series of doubly excited states. The following paper reports on the observation of this anomalous width behavior [6].

So far we have considered autodetachment into a single final state of the residual atom. When more than one channel is open, the total width of a doubly excited state represents a sum over partial widths. One can see from Eq. (7), however, that the amplitude factor of the partial width decreases with an increase in the energy separation between the initial and final atomic states. In the limit of small energies, $|E| \ll E_1 - E_2$, the amplitude factor contains a multiplier which decreases as $(E_1 - E_2)^{-7/4}$. As an approximation, in the following analysis of experimental data we will consider only the partial width for autodetachment into the closest atomic state.

Widths of series of doubly excited states were measured in alkali negative ions below the Li($6p$), Na($4d$), and K($5f$) thresholds [4–6]. In these experiments, states of ^1P symmetry were populated by photoexcitation from the ground state of a negative ion. The closest atomic states accessible to autodetachment are the Li($6s$), Na($5s$), and K($7s$) states, respectively. Since in all cases the final atomic state is an s state, the angular momentum of the outgoing electron is equal to 1. Thus, in the closest channel approximation the sum over l_f in Eq. (7) contains only one term with $l_f = 1$. The values of J_{l_f} and δ_{l_f} are not dependent on the energy E. We do not calculate these parameters here but use them as fit parameters. A comparison of experimental data with theoretical predictions is shown in Fig. 3, where widths are plotted versus the absolute values of energies of bound states. It should be understood that the energy scale represents the variable parameter E, which acquires values of energies of states at

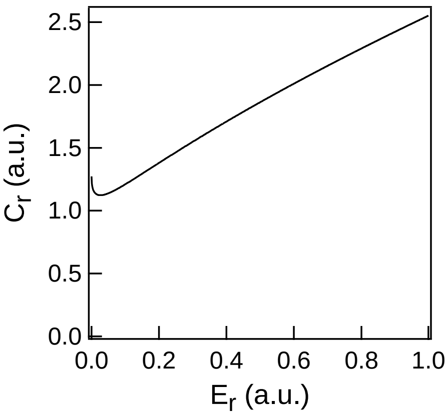

FIG. 2. The dependence of the reduced coefficient C_r on the reduced energy E_r in the region close to the threshold $E = 0$.

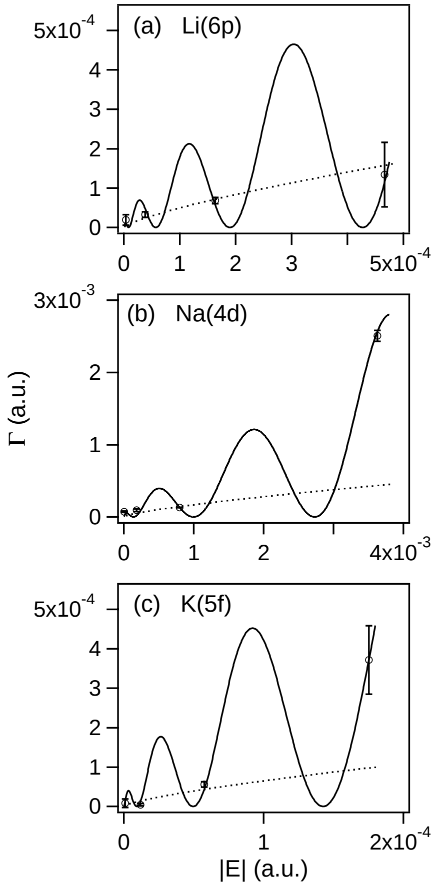

FIG. 3. Widths of doubly excited states versus the absolute values of their energies for a given series of states in (a) Li$^-$, (b) Na$^-$, and (c) K$^-$. Circles represent experimental data. Fits of experimental data to Eqs. (7) and (9) are shown by the solid and dotted curves, respectively.

a discrete number of points on this scale. The dotted curve represents the energy dependence of the normalizing coefficient $C^2(E)$ calculated from Eq. (9). Figure 3 shows that the experimental data can be well described by this smooth curve in the region of small energies. However, a strong deviation from the smooth behavior can be seen in the region farther from threshold. The solid curve represents calculations with the phase factor taken into account [Eq. (7)]. This curve makes one oscillation between energies of the two states, when these states are close to the threshold. It oscillates more frequently in the region farther from threshold. This is because the phase difference $\Delta\phi$ becomes strongly dependent on the energy E in this region. Thus, the oscillations in the phase factor are important in the description of the width behavior over the entire spectrum of a given series of states.

In conclusion, the semiclassical model shows that the autodetachment transition occurs in the region where the kinetic energy of the weakly bound electron corresponds to the kinetic energy of the outgoing electron. The partial width of a doubly excited state can be described by a product of an amplitude and phase factors. The phase factor reflects phase matching between the semiclassical phase of the outer electron in the initial state and the phase of the continuum wave of the outgoing electron. This factor is nearly constant at small energies below the threshold, where the functional behavior of widths can be described by the amplitude factor determined by the wave function normalization coefficient. It is predicted that in the case where the outer electron has a high angular momentum, the widths can have an anomalous behavior near the threshold. The semiclassical model describes reasonably well the experimental data on widths in the closest channel approximation. Further investigations are required in order to reveal the role of correlation effects in the process of autodetachment.

I acknowledge support from the Royal Swedish Academy of Sciences and the Deutsche Forschungsgemeinschaft (SFB 276, TP C14).

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