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What happens to two-electron resonances when their energy approaches the break-up threshold?

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Abstract. – Using semiclassical S-matrix theory in a simulated electron-hydrogen scattering experiment and converged quantum calculations for the widths of high-lying resonances in H^- we show that resonance formation (or the lifetime of resonances) below the fragmentation threshold $E = 0$ and ionization above threshold have the same energy dependence $|E|^{1.127}$ for $|E| \to 0$. Hence, series of resonances which have been characterized by approximate quantum numbers will disappear towards threshold.

The dynamics of three charged particles is a fundamental problem, exactly solvable neither in classical nor in quantum mechanics. With increasing computer power, the resonance spectra of two-electron atoms can be now calculated numerically without approximations for high excitations of both electrons [1], [2]. The theoretical spectra show good agreement with photoabsorption spectra from recent experiments that have generated and resolved isolated resonances in doubly excited helium and H^- to high precision [3], [4]. Theoretical and experimental attempts are now devoted to probe the region very close to the break-up threshold with high resolution. The task is complicated by the fact that at energies reached by experiment and theory entire resonance series are perturbed by members of other series [2] and it is not obvious whether the concept of isolated resonances is adequate for the dynamics in the threshold [5].

In this letter we predict that in an experiment probing the spectrum in the limit $E \to 0^-$ multiple series of isolated resonances will generally disappear for two reasons: Firstly, the probability of exciting a resonance from an initial state with finite spatial extension (a typical situation in photoabsorption or a scattering experiment) vanishes towards threshold. Secondly, for $E \to 0^-$ the average width of resonances decreases slower than the number of resonances increases. Hence, resonances which had been isolated for lower energies will strongly overlap and most of them disappear in the background signal.

Since the discovery of (low-lying) two-electron resonances [6] and the experimental confirmation [7] of the previously predicted anomalous threshold law for two-electron escape close to $E = 0$ [8] there has been a continuing interest in the connection between resonant ($E < 0$)

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and escaping ($E > 0$) two-electron states [9]-[13]. Recently this connection has been demonstrated *qualitatively* on the basis of classical S-matrix theory [14]. Here, we further elucidate this connection and present *quantitative* consequences for the relation between two–electron resonances and two-electron escape.

The energy dependence of the cross-section for resonance formation ($E < 0$) and for two-electron escape ($E > 0$) is obtained from a simulated electron-hydrogen scattering process where it is possible to cover the energy range from negative energies through threshold to positive energies (by tuning the energy of the projectile) with the same theoretical description, a (semi)-classical S-matrix approach [14]. We will show that the global cross-section for resonance formation below threshold is related to the widths of resonances which we have determined quantum mechanically by complex scaling [2]. Expanded to leading order about the threshold energy $E = 0$, the widths of certain two-electron resonances and the two-electron escape cross-section have the same energy dependence.

The (semi)-classical S-matrix description of total cross-sections for electron-hydrogen scattering near threshold is facilitated by approximations which enter naturally through the classical dynamics and which have been described elsewhere [15]:

i) For $|E| \to 0$ the classical dynamics for all fixed total angular momenta L collapses to the same effective Hamiltonian. Hence for the relative total cross-section it is sufficient to calculate the $L = 0$ case.

ii) The interelectronic angle of $\Theta_{12} = \pi$ is a fixed point of the classical equations of motion. For global features like the total cross-section, the dynamics at this fixed point give a sufficiently accurate picture of the scattering process. In the "one-dimensional world" (only one coordinate, the distance to the nucleus, r_i, describes electron i) the cross-section reduces to a probability and is directly proportional to the S-matrix.

iii) We are only interested in the region very close to threshold ($|E| < 1$ eV) where a purely classical calculation is justified (see [16]).

The classical probability for inelastic scattering of an electron from hydrogen in its $1s$ ground state is given by [14]

$$P_{\epsilon,\epsilon'}(E) = \sum_i \frac{\mathcal{P}(\epsilon,\epsilon',E)_i}{R} \equiv R^{-1} \sum_i \left| \frac{\partial \epsilon}{\partial r_i'} \right|_{\epsilon'}^{-1}, \tag{1}$$

where R is the normalization constant resulting from the preservation of probability and $\mathcal{P}(\epsilon,\epsilon',E)_i$ is the contribution from the i-th trajectory. The sum runs over all trajectories i that take the projectile from energy $\epsilon' = E - E_{1s}$ to ϵ during the collision. These trajectories differ by their starting point r_i' of the projectile while the target electron is always started at the same (but otherwise arbitrary) point on its orbit. As can be seen from fig. 1 *a*), the function $\epsilon(r')$ is monotonic so that only a *single* trajectory contributes to a final ϵ. Then the total ionization cross-section, defined as

$$P_{\epsilon'}(E) = \int_0^E P_{\epsilon,\epsilon'}(E) \mathrm{d}\epsilon = \frac{\Delta r'(2^+)}{R}, \tag{2}$$

becomes proportional to the interval of initial conditions $\Delta r'(j)$ for which ionization happens (fig. 1 *a*)). This is the case for interval $j = 2^+$ where $0 < \epsilon < E$ leaves a positive energy for the second electron as well. If after the collision $\epsilon < 0$ (interval 1^+) then the projectile has become bound in exchange for the target electron. Interval 3^+ describes, with $\epsilon > E$, an excitation process (the target electron is still bound after the collision). The normalization is given by the sum of all processes that can happen, $R = \sum_{j=1}^{3} \Delta r'(j^+)$. The intervals j^+ indicate initial conditions for positive energies while the respective intervals for $E < 0$ are labelled j^-.

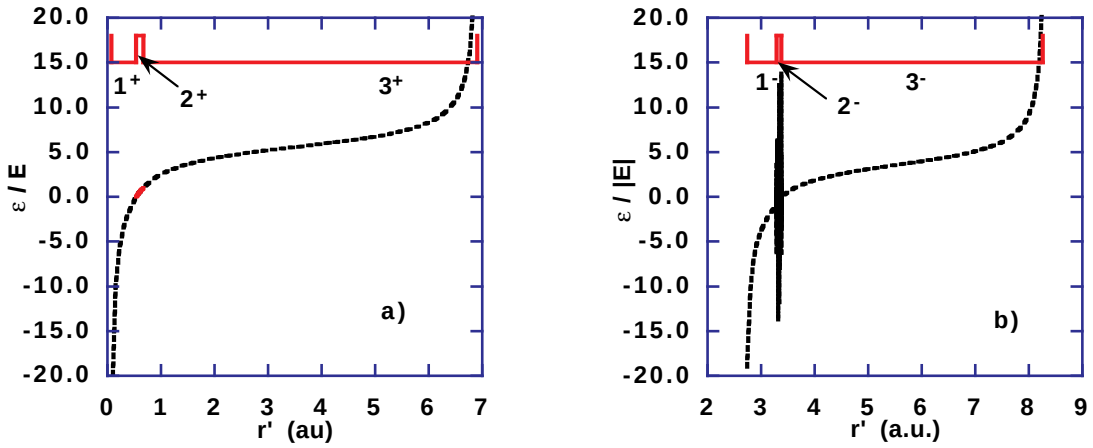

Fig. 1. – Energy dependence $\epsilon/|E|$ of the projectile on its initial position 1000 a.u. $+ r'$, normalized to the total energy $|E|$. The inverse derivative of this function enters eq. (1), see text. The intervals 1 and 3 stand for exchange and excitation, respectively. Part *a*) is for a total energy of 0.1 a.u. with interval 2^+ marking the ionization events. Part *b*) is for a total energy of -0.1 a.u. with interval 2^- for chaotic scattering.

Below the ionization threshold ($E < 0$, fig. 1 *b*)) the intervals for exchange (1^-) and for direct excitation (3^-) are very similar to the corresponding intervals for $E > 0$ (fig. 1 *a*)). The interval 2^-, however, is characterized by chaotic scattering [17] replacing ionization (as in 2^+) which is energetically not possible for negative energies. Chaos is generated by trajectories along which both electrons bounce many times into the nucleus. Thereby, they suffer a time delay compared to electrons following "direct" trajectories from the intervals 1 and 3. The time delay is the signature of a resonance [18]. Hence, what had been ionization above threshold, described by a regular behaviour of interval 2^+, becomes resonance formation below threshold, characterized by the irregular scattering in the corresponding interval 2^-. Although it might seem hopeless to deal with a fractal object like the interval 2^- in fig. 1 *b*), we can form the analogy to the total ionization cross-section. Instead of integrating all contributions from interval 2^+ over all electron energies ϵ as we did in eq. (2), we integrate now over all contributions from the interval 2^-. What we will obtain is the probability for resonance scattering, that is, the probability that the electron suffered a time delay in the scattering event and, for a short time, an (excited) 3-body complex had been formed. For each ϵ there is not only one but an infinite set of trajectories $\{i\}$ contributing to the sum of eq. (1). However, to each index i there belongs a continuous branch of trajectories with all energies ϵ. This branch yields, upon integration over ϵ, a small subinterval $\delta_i(r')$. The sum over i then recovers the entire interval $\Delta r'(2^-) = \sum_i \delta_i$ of chaotic scattering, which replaces $\Delta r'(2^+)$ in eq. (2). Thus, the probability for resonance formation below threshold is in exact analogy with the total ionization cross-section (eq. (2)) above threshold. Together the probabilities represent 3-body events where both electrons have to participate in the scattering process simultaneously. Experimentally such events have been detected by measuring extremely slow ("zero kinetic energy", $\epsilon \approx 0$) electrons produced in electron-atom collisions [10] or in photoionization [13]. Assuming that the energy distribution of the electron $\mathrm{d}\sigma/\mathrm{d}\epsilon$ is almost flat for energies $E \approx 0$ [10], [16] the probability for three-body events, as discussed above, is related to the slow-electron spectrum through

$$\sigma_{\epsilon=0}(E) \approx \sigma_{\pm} \frac{P(E)}{E}. \tag{3}$$

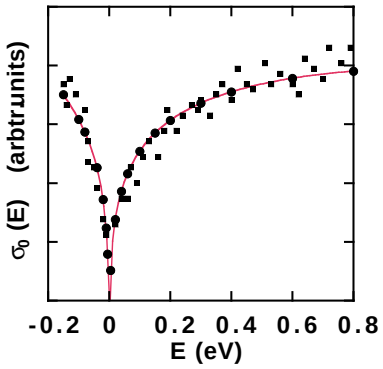

Fig. 2.

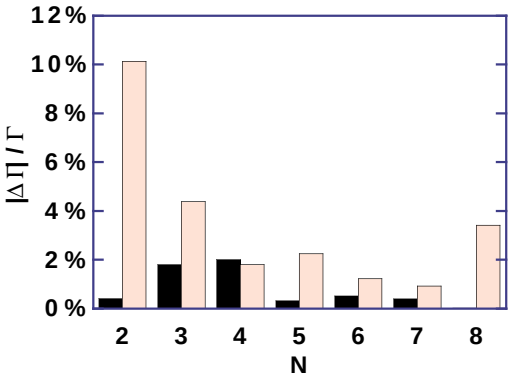

Fig. 3.

Fig. 2. – Cross-section for the production of slow electrons following electron impact on atoms close to the fragmentation threshold. The black squares are experimental data for a He($1s^2$) target [10]. The black circles are the theory for a hydrogen target H($1s$). The solid line is a fit of the theory according to eq. (4).

Fig. 3. – Relative error of the fit (eq. (4)) for ${}^1S^e$ saddle resonances in H^- shown with black stacks. For comparison the error for a fit with a linear exponent $\alpha = 1$ is shown with grey stacks.

The constant of proportionality $\sigma_\pm$ is expected to be different for negative and positive energies E. The actual ratio σ_-/σ_+ depends on experimental parameters (such as pressure in the gas cell) and is not yet fully understood [13]. However, in the present context, we are more interested in the *energy dependence* determined by $P(E)$. The cross-section (3) calculated with $P(E)$ from (2) is shown in fig. 2 with black points. The spectrum has been normalized to the experimental data from [10] (open squares) separately for $E > 0$ (σ_+) and $E < 0$ (σ_-). The solid line is a parameterization of the theoretical cross-section with the function

$$\sigma_0(E) = \sigma_\pm |E|^{\alpha-1}(1 + a|E|^{\frac{1}{2}} + bE), \tag{4}$$

where $\alpha = 1.127$. For $E > 0$ eq. (4) reflects the "classical" result [8], [16] that the total ionization cross-section close to threshold is proportional to the 1.127-th power of E. Noting from fig. 2 and eq. (4) that this holds also below threshold, we can conclude that $|E|^{1.127}$ originates in the 3-body amplitude of the S-matrix and should be independent of the process through which it was activated. The residual dynamics depends on the initial state and the excitation as a whole (by photon or particle impact etc.) However, the residual part varies slowly with energy. This includes slow electrons from direct excitation. Hence, we can take these contributions into account with a Taylor expansion about $E = 0$ in eq. (3) represented by the energy-independent parameters a and b. Since a and b depend on the actual threshold process, they are not universal like the threshold exponent α.

One might suspect that the good agreement between experiment and theory below threshold is misleading: The absence of structure in the cross-section could be a consequence of the finite energy resolution on the experimental side and an artifact of the classical treatment on the theoretical side.

To clarify the situation, we have determined highly excited resonant states in H^- quantum-mechanically by complex scaling [2]. The widths, formulated as transition matrix elements with an S-matrix [19], contain the same 3-body amplitude as the cross-section for ionization/resonant scattering. Hence, we expect an energy dependence $|E|^\alpha$ for widths of states which approach, in the limit $E \to 0^-$, a similar geometrical configuration to that given by

the classical fixed point with $\theta = \pi$. Such states are well known and often referred to in the literature as *Wannier* resonances, *saddle* resonances or *intrashell* resonances. The last name indicates that these resonances are characterized by approximately equal principal quantum numbers $n_1 = n_2 \equiv N$ of both electrons.

We have calculated the widths Γ_N and positions E_N for the saddle resonances $2 \leq N \leq 8$ in H^-. In fig. 3 we show the relative error for the fit of Γ_N/E_N with eq. (4). To demonstrate the sensitivity on the exponent $\alpha = 1.127$, we also give the fit with a linear exponent $\alpha = 1$ which reproduces the quantum-mechanical widths not very well.

Thus, the picture of the threshold dynamics for $E \to 0^-$ obtained classically is quantum-mechanically confirmed. In particular, the energy dependence of the widths $\Gamma \propto |E|^{1.127}$ implies that these resonances will strongly overlap because their spacing $E_N - E_{N-1} \propto N^{-3} \propto |E|^{1.5}$ decreases faster towards $E = 0$ than their widths. Indeed, the $N = 8$ resonance was the highest saddle resonance isolated enough so that a converged complex energy could be obtained. The experimental spectrum in fig. 2 does not exhibit isolated resonances for the displayed energy range of $E \geq -0.15$ eV. Although not conclusive due to the experimental energy resolution, this observation is nevertheless consistent with our quantum calculation because the $N = 8$ resonance lies at $E = -0.28$ eV.

On the other side, a quasi-regular part of the spectrum will prevail towards threshold although the energy intervals it occupies become smaller and smaller compared to the intervals the irregular spectrum covers. The surviving regular spectrum consists of configurations where $n_1 \gg n_2 \gg 1$, that is where electron one is very far outside the already highly excited core with the second electron. Such a configuration implies little interaction between the two electrons. The resulting long lifetime of these asymmetric resonances makes them difficult to observe experimentally.

To summarize, we have formulated threshold dynamics in a two-electron system below and above $E = 0$ in the framework of a (semi)-classical S-matrix theory. The results, consistent with early experimental observations and our quantum-mechanical calculations below threshold, imply drastic consequences for the high-precision experiments currently being prepared in the limit $E \to 0^-$: We predict that the spectrum of isolated resonances that can be related to approximate constants of motion [20] will disappear for $E \to 0^-$. Furthermore, we have discovered that the energy dependence of the widths for saddle resonances, which have been related to the Wannier ionization mechanism for a long time, is indeed given by the Wannier power law for $|E| \to 0$. Different power laws $|E|^\alpha$ have been predicted [11] for the width which neither agree among themselves nor with our result, apart from a recent prediction of an approximately linear behaviour $\alpha \approx 1$ for helium [21]. A detailed comparison is beyond the scope of this letter, even more, since the quantities which have been discussed respectively (partial cross-section for excitation, intensity at resonance, total width etc.) are slightly different.

We are still far from having solved the threshold problem, however, we believe that the present results will provide a new direction in the formulation of questions concerning threshold ionization. For instance, it is necessary to understand *how* the complicated spectrum of multiple Rydberg and dipole-like series of resonances disappears with $E \to 0^-$. It is conceivable [21] that in a small energy range a global fluctuation pattern like that of Ericson fluctuations, known from nuclear physics [22], replaces the resonance structure before the cross-section becomes smooth very close to $E = 0$.

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