Dynamic Characteristics of Excited Atomic Systems

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Abstract. The dynamics of excited atom interactions with other atoms, which often lead to associative ionization, is largely governed by stochastic diffusion of the valence electron through Rydberg states prior to the ionization. Such processes are associated with random changes of the energy state of the highly excited electron, and they are likely to influence the nuclear dynamics, especially at subthermal collision energies. Possibilities of manipulation of the chaotic dynamics of Rydberg states require a detailed exploration. For an electron in a given Rydberg state moving in a microwave field, which can be generated via interaction with another atom or molecule, there exists critical field strength, above which motion of the electron in the energy space is chaotic. Recently a way to block the dynamic chaos regime was shown, if a given Rydberg state is located somewhat above the middle between the two other states with the orbital quantum number differing by one, whereby level shifts can be controlled by employing Stark/Zeeman shifts in external DC electric/magnetic fields. The stochastic effects in collisions involving Rydberg particles, in which the initial and final reaction channels are connected via intermediate highly excited collision complexes with multiple crossings of energy levels, can be treated using the dynamic chaos approach (Chirikov criterion, Standard and Keppler mapping of time evolution of the Rydberg electron, solution of the Fokker-Plank- and Langevin-type of equations, etc.). Such approach to obtaining dynamics characteristics is a natural choice, since the treatment of Rydberg electron dynamics as a kind of diffusion process allowing one to bypass the multi-level-crossing problem, which can hardly be solved by conventional quantum chemistry methods.

1. Introduction
As demonstrated by the results of research on the subject of Rydberg atoms (both theoretical and experimental), when the principal quantum number value \( n \) of a selectively excited atom increases, an optical electron in the terms of the quasi-classical approximation of quantum mechanics begins to show its trajectory instability (see, e.g., [1]). In addition to that the evolution of quasi-molecular collision complexes during the time of one collision leads to multiple quasi-crossings of the initial term with neighboring terms and therefore to migrating excitation across the grid of crossing energy terms with the distance between them \( \Delta W \approx n^{-3} \) [2]. Within the framework of today’s ideas of the determinancy and chaos in the physics of atomic collisions this allowed speaking about the manifestation of the effect of the deterministic (having a cause) dynamic chaos in chemi-ionization processes in case of thermal and subthermal collisions involving Rydberg atoms (RA) with values of \( n > 5 \) [3]. In recent research on Rydberg atoms cooled to temperature of \( 3 \cdot 10^{-4} \) K [4], [5], where many-particle long-range dipole-dipole interaction was considered to be the main ionization channel, marked
instability of the plasma of cold atoms has been observed. It is highly probable that manifestations of deterministic chaos in the ensemble of frozen RA are also observed. On the one hand this circumstance limits the selectivity of processes in magneto-optical traps, operation of computer logic based on dipole-dipole interaction involving Rydberg atoms. On the other hand, however, the possibility arises to control to a certain extent the parameters of excited media.

Poincaré in the late 19th century [6] was the first to suggest the mathematical basis of the theory of chaos in the world around in his works that demonstrated the existence of “integrable” and “nonintegrable” systems of equations. As integrable the systems were understood with smooth response to a weak disturbance when the possibility of analytical solution remains, e.g. Newton and Lagrange trajectories. In the most general case the system of motion equations cannot be considered to be absolutely integrable, as it is impossible to exclude absolutely the probability of a strong disturbance leading to the failure of the solution stability.

The reason for this instability, which eventually leads to global chaos, is related to the appearance of dynamic resonances. Within the framework of KAM theory (Kolmogorov, Arnold, Moser) [7] this leads to Hamilton indeterminancy of solutions with respect to the operator's own solutions. In other words, it leads to stochasticity effects of both trajectory calculations within the framework of quasi-classics and the approximate nature of solutions of Shrödinger equations. Physical literature often gives physical arguments in addition to mathematical ones in order to interpret the nature of chaos in specific phenomena.

A recent survey [8] has summarized to a certain extent the research on the subject of Rydberg condensed matter. This research started in 1990 with the publication of the results of experiments that analyzed the mass composition of heavy particles in a thermionic converter of thermal energy into electrical energy in alkali-metal vapors [9]. Later it was suggested to include ultracold Rydberg plasma into the category of Rydberg matter [8].

In all above examples, we deal with many-particle systems in a field of a long-range potential.

2. Rydberg atom.
The use of the name "Rydberg atoms" in literature began in the late 19th century after Rydberg’s pioneer work on spectroscopy of highly excited atoms was published.

Below the parameters of an excited hydrogen atom within the framework of Bohr-Sommerfeld quasi-classical model are given depending on the values of the principal quantum number.

1. Radius of the outer (optical) electron orbit
\[ r \approx n^2 \]
2. Excited atom lifetime
\[ \tau \approx n^3 \]
3. Binding energy of an optical electron (energy threshold for RA photo-ionization)
\[ E \approx n^2 \]
4. Distance between adjacent levels
\[ \Delta W \approx n^{-3} \]
5. Average speed of an optical electron rotation in orbit
\[ v \approx n^{-1} \]
6. Polarizability
\[ \alpha \approx n^7 \]
7. Dipole moment
\[ |d| \approx n^2 \]
8. Energy of interaction with an electric field of E intensity
\[ W_E \approx n^2 E \]
9. Energy of interaction with a magnetic field of H induction
\[ W_B \approx \alpha^2 n^4 B^2 \]
10. RA interaction with a black body radiation – experimental volume walls at temperature T.
\[ W_T \approx \alpha^2 T^2 \]

Due to the latter circumstance, for \( n < 40 \) most chemi-ionization experiments usually record charged particles via associative ionization channel with molecular ions formation. On the other hand, there is a known diagnostics of RA concentration based on their ionization by wall radiation.

The active phase of experimental and theoretical research on RA began with Fermi’s work, who suggested considering a hydrogen RA as a system consisting of an ionic core and an optical electron loosely-bound to it.

Further development of the theory of ionization processes involving RA was driven by chemi-ionization studies and the emergence of a theoretical model of a dipole resonance mechanism [11].
within which in general experimental and theoretical results are currently compared (see Fig. 1). In its turn, the analysis of the first results of chemi-ionization of hydrogen-like atoms of alkali metals led its authors [2] to the idea of collisional diffusion ionization of RA as a manifestation of the dynamic chaos effect during a single collision RA + A.

**Figure 1** A microwave electric field generated in a collisional Rydberg quasi-molecule (PA + A). d is the dipole moment of subsystem (A− + A) with the interparticle distance R, ΔR is the exchange splitting of molecular ion term A2+. RA geometry is according to Fermi.

**Figure 2** Nonlinear dynamic resonance. Within the framework of quantum mechanics, they correspond to the case of m-photon resonances; Δε is the oscillation of RE energy that illustrates the initial stage of global chaos.

3. **Stochastic dynamics of a hydrogen atom in an external microwave field**

Within the framework of quantum mechanics, the condition of multi-photon resonance when total energy of photons coincides with the energy distance between the atomic terms corresponds to the effective mechanism of mixing two fixed atomic states. In classical mechanics, the emergence of an additional stationary member in the potential of a disturbing field – the effect of a dynamic nonlinear
resonance – corresponds to the concept of resonance. The condition of resonance overlapping, known in literature as Chirikov criterion [12] (see Fig. 2), leads to realization of K-system. It should be noted that the calculation of the effects of dynamic chaos in real situations is possible only when the numerical algorithms used are stable over large time spans. Moreover, standard numerical integration methods are unacceptable, since an error of such calculations grows exponentially over time. Paper [13] proposed a method which makes it possible to calculate correctly the conditions of dynamic chaos in atomic systems in steady-state and alternating electric and magnetic fields. Figure 3 illustrates a Rydberg electron (RE) reaching ionization limit in the conditions of global dynamic chaos. Distinctly irregular movement of RE in the energy space of bound states is evident. The lower limit of stochasticity is due to large distances between levels for \( n < n_{\text{min}} \). It is the deterministic motion area of RE.

For the development of diffusion ionization of a Rydberg electron (RE), the finite time is needed that depends on the chaotic diffusion coefficient value, which is proportional to the values of the principal quantum number of degree three. This implies that the diffusion ionization of RA during one atom-atom collision is primarily realized within the range of slow collisions.

\[ E(t) \text{[a.u.]} ]
\[ t \text{[a.u.]} ]

**Figure 3** RA stochastic ionization development.

4. **Specific features of RE stochastic diffusion under the conditions of double Stark resonance or Förster resonance**

Large values of dipole moments for transitions between Rydberg states of an excited atom give rise to optical nonlinear effects in relatively weak electric fields. One of the manifestations of these effects include the case of Förster resonance [14], that occurs when level \( \ell \) of a series is strictly in the middle between the two levels of \( (\ell - 1) \) or \( (\ell + 1) \) series. This configuration corresponds to a two-photon resonance for the transition \( \{\ell + 1, n\} \rightarrow \{\ell, n\} \rightarrow \{\ell(n-1)\} \) for \{s,p\} and \{p,d\} series of hydrogen-like alkali atoms for the values of electrical fields of the order of 1 V cm\(^{-1}\), but is absent in a hydrogen atom (see Figure 4). Incidentally, hence the term "double Stark resonance" originated.
Figure 4 The scheme of terms of a highly excited atom, corresponding to the emergence of double Stark resonance (Förster resonance) for s-p series \( \ell + 1, n \rightarrow \ell, n \rightarrow \ell + 1, n - 1 \).

Literature considers the effect of double Stark resonance as an effective method for manipulating atoms in laser fields. This method has good prospects in solving practical problems of quantum information science. This is primarily due to the possibility of blocking dipole transitions that are directly related to the dynamics of global chaos, because the scheme of terms corresponding to the case of Förster resonance is completely analogous to the case of a three-dimensional quantum oscillator, in which only "short" transitions to adjacent levels are allowed. Thus, for RA the role of "long" transitions with large variations of \( \Delta W \) is small, while near transitions are blocked. This situation will negatively affect the processes of stochastic diffusion development.

Figure 5 Time required for RA diffusion ionization as a function of Sommerfeld parameter. \(<N>\) is the number of cycles of RE motion along the trajectory required for a RE to go into a continuum.

Figure 5 from [15,16,17] shows the dependence of the diffuse ionization time required for RE to achieve ionization limit in the conditions of global chaos for different values of Sommerfeld parameter \( \alpha \), which characterizes the difference value between the spectrum of a hydrogen-like atom and a hydrogen atom (\( \alpha = 0 \)). Maximum dependence at \( \alpha = 2,81 \) corresponds to the case of two-photon Stark resonance for s-p series at a fixed value of the initial effective quantum number \( n_{\text{ef}} = 30 \) and the
microwave electric field intensity that is several times higher than its threshold value \( F_\varepsilon \approx F_c \approx n^{-5} \omega^{-1/3} \),

where \( \omega \) has the value of the order of the RE rotation speed in the Keplerian orbit, \( \omega \approx n^{-5} \omega^{-1/3} \), i.e. it is assumed that the effect of a field on a RE is of resonant nature.

It can be seen that the maximum dependence, which corresponds to the maximum suppressing of the stochastic diffusion effect, corresponds to the value \( \alpha = 2.81 \), i.e. to the case of Förster resonance for s-p series of alkali atoms. The features of radiation kinetics caused by Förster resonance in the system of RA terms are directly related to the probabilities of spontaneous transitions between them, and therefore to the lifetimes of highly excited atoms. Figure 6 shows the total probability of radiative transitions in RA for a fixed \( n = 30 \). Apparently, in the vicinity of the two-photon Stark resonance (\( \alpha = 2.81 \)) the probability of radiative transitions decreases by more than an order of magnitude, and hence the lifetime of RA increases.

![Figure 6](image)

**Figure 6** The total probability of spontaneous transitions from the fixed state nS (n=30) depending on the Sommerfeld parameter value. Position of the minimum on the curve corresponds to the manifestation of the Förster resonance effect (atomic units).

5. Conclusion

The study of the emission spectra of celestial bodies forms the basis of today’s astrophysics. For the typical parameters of the ionized atmospheres of planets and cooling stars (dwarfs) the manifestations of dynamic chaos can be controlled by external electric and magnetic fields. Thus, astrophysical literature has not yet explained the cause of an anomaly in the infrared spectrum of "white dwarfs" for the RA values of n of the order of 10. It should be noted that this range of n values corresponds to the maximum values of chemi-ionization processes in thermal and subthermal atomic collisions. In terrestrial conditions, RA chaotic diffusion processes in a single collision should influence the stability effectiveness of operation of computer logistics devices.

The material given in the report suggests that the processes of collisional dynamics of Rydberg atoms are beginning to be considered within the framework of a dynamic chaos model of the parameters of an excited atom. Contrary to a traditional (deterministic) approach, chaotic diffusion
develops during a single atom-atom collision. To understand these processes and their nature, as well as to ascertain their specific mechanisms is crucial for the models of laser-guided physicochemical reactions and parameters of excited atoms ensembles.

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