Rydberg Wave Packets in External Static Fields

Recent developments in the theoretical description of the dynamics of atomic Rydberg wave packets in static external fields are discussed. Classical path representations of the relevant atomic transition amplitudes clearly exhibit the connection between quantum and classical mechanics.

Key Words: *Rydberg wave packets, non-integrable electronic dynamics*

The recent development of short and intense laser pulses in the (sub)picosecond regime has renewed interest in coherent laser-excitation processes of atoms and molecules. Typically in these processes a large number of energy-eigenstates are excited coherently, thus preparing a quantum state whose probability distribution is non-stationary and (at least) partially localized with respect to the classically accessible range. Such *wave packets* are of particular interest as they provide a bridge between quantum mechanics and the classical concept of a particle-trajectory. Studying their time-evolution provides real-time observations of atomic or molecular dynamics.[1,2]

A coherent superposition of Rydberg states, i.e., bound energy-eigenstates of a valence electron close to a photoionization threshold, represents a localized electronic wave packet.[2] As laser-induced excitation of a large number of Rydberg states from an energetically low-lying bound atomic state can only prepare a superposition of energy-eigenstates with low values of the angular

Comments At. Mol. Phys.
1991, Vol. 26, No. 1, pp. 47–57
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momentum, the resulting wave packet is only localized with respect to the radial electronic coordinate.[3] Because of the infinite level density of Rydberg states at a photoionization threshold, such *radial Rydberg wave packets* always arise in multiphoton processes, which involve highly excited Rydberg states as intermediate resonances. In order to localize also the angular coordinates of the excited electron a superposition of energy-eigenstates with high values of the angular momentum is needed. This may be achieved, for example, by additional external fields which mix in high angular momentum components. Recent studies[4–8] indicate that in the future it might even become possible to prepare *ideal Kepler wave packets* which represent localized electronic states evolving along a Kepler ellipse with minimum quantum fluctuations.

In this article we discuss recent theoretical work on the dynamics of radial Rydberg wave packets in external static fields.[2] Basic physical principles involved in their generation and detection are summarized in Section 1. In Section 2 we outline basic ideas for the theoretical description of their dynamics in static external fields and present the case of a static magnetic field as an example.

1. RADIAL RYDBERG WAVE PACKETS: GENERATION AND DETECTION

The basic physical principles which lead to generation of radial Rydberg wave packets in atoms can easily be understood[2] by considering the simple example of one-photon excitation of Rydberg states with mean principal quantum number $\bar{n} >> 1$ starting from an energetically low-lying bound state $|i\rangle$. If the exciting laser pulse is so short that its Fourier-limited width, $2\pi/\tau$, is much larger than the mean distance between adjacent Rydberg states, $\Delta\bar{\epsilon}_n = (\bar{n})^{-3}$, many Rydberg states are excited coherently. (We use Hartree atomic units, $m_e = \hbar = e = 1$.) As the classical orbit time of a Rydberg electron is given by $T_{\epsilon_n} = 2\pi(-2\epsilon_n)^{-3/2}$, this implies $\tau << T_{\bar{\epsilon}_n}$ and the laser-induced excitation process is *localized in time*. Typically, the initial state, $|i\rangle$, extends only a few Bohr radii around the atomic nucleus. This distance is small in comparison with characteristic extensions of highly excited Rydberg states of low angular momenta so that such an excitation process is also *localized in*

space. This localization in space and time implies the generation of a Rydberg wave packet. However, due to radiative selection rules, only a few angular momentum eigenstates are excited so that this wave packet is only localized with respect to the radial coordinate. The angular coordinates of the electron are still delocalized. Figure 1 shows the time evolution of the radial probability distribution of such a radial Rydberg wave packet. Typically, we observe a narrowing of the wave packet as it approaches the outer turning point of its orbit and its (local) velocity slows down.

The time evolution of a Rydberg wave packet may be probed by any process which is also localized in space and time. A two-photon Raman process with two time-delayed short laser pulses is an example. Thereby a first short laser pulse generates a Rydberg wave packet and a second short laser pulse probes its dynamics by inducing a transition to some energetically low-lying bound state, $|f\rangle$. As the initial excitation and final recombination process are

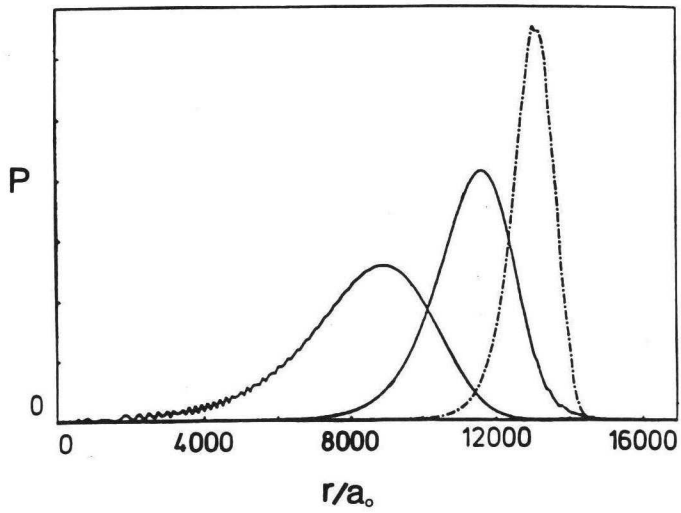

FIGURE 1 Radial probability distribution, $P = |r\psi(r, t)|^2$ (in arbitrary units), of a hydrogenic radial Rydberg wave packet. (a_0 is the Bohr radius.) A short Gaussian laser pulse, $\tau = 8$ ps, induces $s \rightarrow p$ transitions around mean principal quantum number $\bar{n} = 85$ ($T_{\epsilon_{\bar{n}}} = 94$ ps). P is shown at times $t = (1/9)T_{\epsilon_{\bar{n}}}$, $(2/9)T_{\epsilon_{\bar{n}}}$, $(3/9)T_{\epsilon_{\bar{n}}}$ after the excitation process.

both localized in a region of a few Bohr radii around the atomic nucleus, the final-state (or Raman transition) probability is large whenever the time delay between pump and probe pulse is a multiple of the mean classical orbit time of the excited Rydberg states. It can be shown that in the optical frequency regime, laser-induced transitions from highly excited Rydberg states to continuum states well above threshold are also localized inside a *reaction zone* which typically extends only a few Bohr radii around the atomic nucleus.[9] Therefore, the time evolution of a radial Rydberg wave packet may also be probed by ionization from the excited Rydberg states as has been demonstrated by recent experiments.[10,11]

Recent studies[12] show that a radial Rydberg wave packet may also be generated by a long and intense laser pulse as long as the laser-induced excitation process itself is localized in space and time. In the optical frequency regime this may be achieved by a long laser pulse which is so intense that the initial state, $|i\rangle$, is depleted on a time scale short in comparison with the orbit times of the excited Rydberg states. In this case the localization of the excitation process in time is due to the fact that the effective interaction time is determined by the time the generated wave packet spends inside the reaction zone and this time is short in comparison with the classical orbit times of the excited Rydberg states. Furthermore, even excitation by incoherent and long laser pulses leads to the generation of a Rydberg wave packet as long as the coherence time of the pulses is small in comparison with the orbit times of the Rydberg states.[13]

2. DYNAMICS OF RYDBERG WAVE PACKETS IN STATIC EXTERNAL FIELDS

In the case of an isolated atom the dynamics of a Rydberg wave packet at large distances from the atomic nucleus is determined by the $(1/r)$-Coulomb potential of the charged ionic core and the corresponding classical motion is completely integrable. In the presence of an additional external static field, this situation changes drastically. Even if the external field is weak, highly excited Rydberg states are strongly modified at large distances from the atomic nucleus and, typically, the corresponding classical motion may no

longer be integrable and exhibits complicated phase-space structure. Usually quantum spectra of such a strongly perturbed Rydberg atom are very complicated and difficult to interpret in conventional quantum mechanical terms.[14–17] Studies on the time evolution of a Rydberg wave packet in such a quantum system offer a complimentary view as they directly yield real-time observation of the electronic dynamics and thus help to reveal the connection between quantum and classical dynamics.[18,19]

2.1. Theoretical Aspects

In the theoretical description of the dynamics of radial Rydberg wave packets in static external fields, *classical path representations* of the relevant atomic transition amplitudes play an important role as they clearly exhibit the connection between quantum and classical mechanics. Such classical path representations may be derived with the help of methods of Multichannel Quantum Defect Theory (MQDT)[20,21] and semiclassical methods.[22]

In order to put the problem into perspective, let us consider the quantity of central importance in the description of resonant absorption and emission of laser photons, namely the two-photon transition amplitude,[2]

$$T_{fi}(\epsilon) = \langle f|\boldsymbol{\mu}\boldsymbol{\epsilon}_2^*|F_\epsilon\rangle, \tag{1}$$

where $|F_\epsilon\rangle$ is a solution of the inhomogeneous Schrödinger equation

$$[\epsilon - H_A + i0]|F_\epsilon\rangle = \boldsymbol{\mu}\boldsymbol{\epsilon}_1|i\rangle \tag{2}$$

and $\epsilon \sim \epsilon_i + \omega_1$. Initial and final states of the corresponding atomic transition are denoted $|i\rangle$ and $|f\rangle$ with energies ϵ_i and ϵ_f; $(\omega_1, \boldsymbol{\epsilon}_1)$ and $(\omega_2, \boldsymbol{\epsilon}_2)$ are the laser frequencies and polarizations and $\boldsymbol{\mu}$ is the atomic dipole operator. This transition amplitude is related to the corresponding two-photon Raman transition probability, P_{fi}, which has been discussed in Section 1, by

$$P_{fi} = |(1/2\pi)\int_{-\infty}^{\infty} d\epsilon \tilde{\mathscr{E}}_2^*(\epsilon - \epsilon_f - \omega_2)\,\tilde{\mathscr{E}}_1(\epsilon - \epsilon_i - \omega_1)T_{fi}(\epsilon)e^{-i\epsilon(t_2-t_1)}|^2 \tag{3}$$

with $\tilde{\mathscr{E}}_k(\Delta) = \int_{-\infty}^{\infty} dt\,\mathscr{E}_k(t)e^{i\Delta(t-t_k)}$ $(k = 1, 2)$ denoting the Fourier

transforms of the laser pulse-shapes, $\mathcal{E}_k(t)$, which are centered around times t_k. According to Eqs. (1) and (2), $T_{fi}(\epsilon)$ may be evaluated in two steps: In a first step we solve Eq. (2) and in a second step we evaluate the overlap-integral of Eq. (1). Because $|f\rangle$ is an energetically low-lying bound state, the energy dependence of $T_{fi}(\epsilon)$ is determined by the energy dependence of $|F_\epsilon\rangle$ at distances close to the atomic nucleus.

The solution of Eq. (2) is facilitated by noting that as far as the dynamics of a highly excited Rydberg electron is concerned, we may distinguish three characteristic spatial regimes:

- The atom–laser interaction and electron-correlation effects are localized inside a *reaction zone* which typically extends only a few Bohr radii around the atomic nucleus.
- In the surrounding *Coulomb zone* the electronic dynamics is dominantly influenced by the $(1/r)$-Coulomb potential of the positively charged ionic core.
- At sufficiently large distances from the ionic core, i.e., for $r \geq a$, the external static potential finally becomes at least as important as the Coulomb potential. Generally, the Hamiltonian which describes the dynamics of the Rydberg electron in this *asymptotic zone* is not separable and the corresponding classical dynamics may even be nonintegrable.

Inside the Coulomb zone we may find a general (local) solution of the inhomogeneous Schrödinger equation which is regular at the origin with the help of methods of Multichannel Quantum Defect Theory.[20,21] In the Coulomb and asymptotic zone we may solve the Schrödinger equation semiclassically[22] because in the case of highly excited Rydberg states and weak external fields, i.e., $a \gg 1$, the corresponding classical actions are large. Matching the semiclassical solution to the MQDT-solution inside the Coulomb zone, we finally obtain a global solution of the inhomogeneous Schrödinger equation.[2,23] According to this matching procedure, inside the reaction and Coulomb zone $|F_\epsilon\rangle$ is determined by contributions from all classical trajectories which leave and return again to the Coulomb zone with purely radial momenta. This way we obtain a *classical path representation* in which the two-photon transition amplitude is expressed as a sum of contributions of all closed orbits.

In particular, we may distinguish two limiting cases[2]:

1. All trajectories return again simultaneously and therefore their contributions interfere constructively. Because of rotational symmetry of the Coulomb problem, this happens in the absence of any external field. It reflects the complete integrability of the corresponding classical dynamics. Under these conditions the classical path representation reduces to the results of MQDT.

2. In general, a static external field breaks this rotational symmetry and only *isolated closed trajectories* leave and return again to the Coulomb zone with pure radial momenta. In this case only trajectories in their immediate neighborhood contribute significantly to $T_{fi}(\epsilon)$. If the classically accessible region of configuration space is compact, as in the case of bound states, the appearance of isolated periodic orbits is a characteristic feature of nonintegrable Hamiltonian dynamics. As an example let us consider the classical path representation in a case where all closed orbits are isolated. Explicitly it is given by[2,23,24]

$$T_{fi}(\epsilon) = T_{fi}^{(s)}(\epsilon) + 2i\pi \sum_{m} \sum_{j,M_j} d_m^{(+)}(\Theta_j, \varphi_j) \sqrt{(2\pi)^2 / \left| \frac{dp_\Omega^{(M_j)}}{d\Omega_0} \right|}$$

$$\times e^{i\left\{M_j[S_j(\epsilon) - \mu_j \pi/2] + \sin\left(\frac{\partial(p\Theta, p\varphi)}{\partial(\Theta, \varphi)}\right)\pi/4\right\}} d_m^{(-)}(\Theta_{j0}, \varphi_{j0}). \qquad (4)$$

The M_j-th term of the sum represents the contribution of the M-th revolution of the excited electron along the isolated closed orbit j which is characterized by initial and final angles $(\Theta_{j0}, \varphi_{j0})$ and (Θ_j, φ_j). The corresponding probability amplitude is determined by

- the photoionization and recombination dipole matrix elements $d_m^{(-)}(\Theta_{j0}, \varphi_{j0}) = \Sigma_l \mathcal{D}_{lm}^{(-)} Y_l^m(\Theta_{j0}, \varphi_{j0})\ (-1)^l$ and $d_m^{(+)}(\Theta_j, \varphi_j) = \Sigma_l \mathcal{D}_{lm}^{(+)} Y_l^m(\Theta_j, \varphi_j)^*\ (-1)^l$, which characterize the atom–laser interaction inside the reaction zone, and
- the classical action, $S_j(\epsilon)$, the Morse index, μ_j, and the cross-section, $dp_\Omega^{(M_j)}/d\Omega_0$, which characterize the classical motion of the excited Rydberg electron.

Ω_0 and $p_\Omega^{(M_j)}$ indicate the initial solid angle in configuration space

and the final angle in momentum space of trajectories in the immediate neighborhood of the isolated closed orbit, j, after M revolutions. $T_{fi}^{(s)}(\epsilon)$ is a smooth function of energy and describes the "direct" two-photon transition which takes place inside the reaction zone. In the absence of any closed orbits it is the only contribution to the two-photon transition amplitude. Inserting Eq. (4) into Eq. (3) we notice that the Raman transition probability is large whenever the time delay between pump and probe pulse, $t_2 - t_1$, is a multiple of one of the mean orbit times, $T_j(\epsilon) = 2\pi\, dS_j/d\epsilon\,|_{\epsilon=\epsilon_i+\omega_1}$. According to Eq. (4) the amplitudes of the recombination peaks reflect the stability properties of the corresponding isolated orbits.

2.2. Dynamics in a Static Magnetic Field

As an example let us consider the dynamics of a radial Rydberg wave packet in a weak static magnetic field.[19] In the presence of a static magnetic field, $\mathbf{B} = B\mathbf{e}_z$, the dynamics of a highly excited Rydberg electron is strongly modified at distances $r \geq a = (B/2)^{-2/3}$ at which the diamagnetic interaction potential, $V_{\text{dia}}(\mathbf{x}) = (1/8)B^2(x^2 + y^2)$ becomes comparable to the Coulomb potential of the ionic core.[17] (The paramagnetic interaction term may be absorbed in energy shifts of the photoionization threshold.) As the magnetic unit of field strength is given by $B_0 = 2.35 \times 10^5$ T, the classically accessible region is large for magnetic field strengths of the order of a few T or less and electron energies close to the photoionization threshold. Therefore, typical values of the classical actions are large and classical path representations for atomic transition amplitudes may be derived along the lines indicated in Section 2.1. As the classical dynamics of a highly excited Rydberg electron in the Coulomb and asymptotic zone is not integrable, we expect the appearance of isolated closed orbits. However, due to cylindrical symmetry of the corresponding Hamiltonian around the magnetic field axis, these closed orbits are not completely isolated but appear in one-parameter families. Within one of these isolated families all trajectories return again to the Coulomb zone simultaneously and therefore interfere constructively.

Preparing a radial electronic Rydberg wave packet, for example, by a short laser pulse, we may observe the time evolution of an

excited electron. As soon as the wave packet leaves the Coulomb zone it is broken up under the influence of the Coulomb and diamagnetic interaction potential. Different parts of the original wave packet evolve along the various families of isolated orbits and return again to the reaction zone at different times where they may be probed, for example, by a second short laser pulse. The probability with which one of these parts returns again to the reaction zone depends on the stability properties of the corresponding family of closed orbits. Figure 2 shows the corresponding two-photon Raman transition probability as a function of the time delay between pump and probe pulse in units of $(\Gamma_0\tau)^2$ as obtained from Eqs. (3) and (4). Γ_0 is the zero-magnetic field excitation rate at threshold. A sodium atom is excited by a short laser pulse with pulse duration $\tau = 7.6$ ps from an initial s-state. Pump and probe pulse have identical Gaussian pulse forms and are linearly polar-

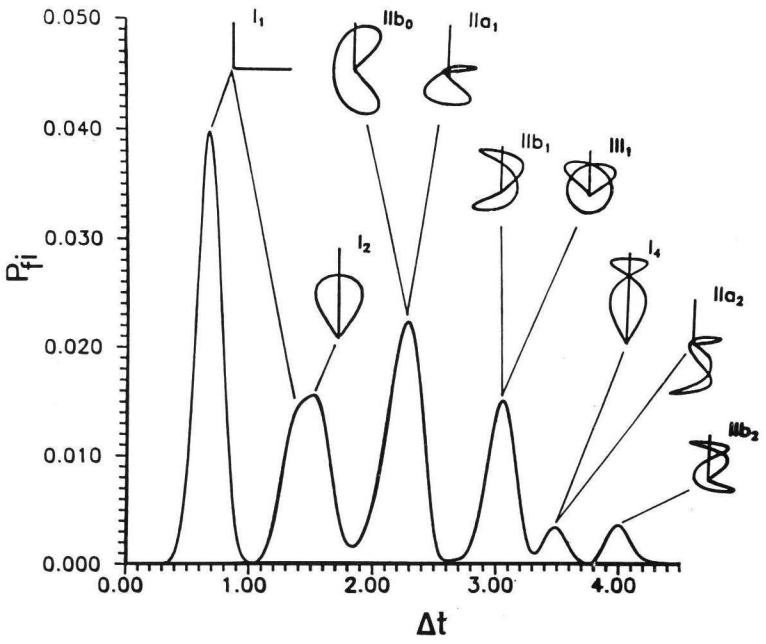

FIGURE 2 Raman transition probability, P_{fi}, as a function of time delay, $\Delta t = (t_2 - t_1)/T$, between both laser pulses with $T = 2\pi/B = 7.6$ ps.

ized perpendicular to the static magnetic field of field strength $B = 0.47$ T. The pulse durations are less than the orbit time of the fastest closed orbit, I_1, so that the laser-induced excitation process is localized in space and time. The recombination peaks in Fig. 2 correspond to repeated returns of various fractions of the generated electronic wave packet to the reaction zone where they are detected by the second short laser pulse. On top of each recombination peak the form of one of the closed orbits of the corresponding family is shown with the vertical line indicating the magnetic field axis.

So far experimental studies on electronic wave packets have concentrated on basic dynamical aspects of radial and angular wave packets in pure Coulomb systems and their results are in good agreement with theoretical predictions.[2] Though much experimental effort has been spent recently to obtain high resolution quantum spectra of Rydberg states in external static fields,[14–16] no direct real-time observation of the corresponding dynamics of an electronic Rydberg wave packet exists so far. In molecular physics time resolved studies of wave packet dynamics have already become a valuable tool for studying various molecular phenomena.[1] Hopefully, in the near future this approach may also yield interesting insight into electronic dynamics in atoms.

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