Coherent control of high-n Rydberg lifetimes using wavepacket technology

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Abstract

We describe a simple, experimentally feasible scheme for enhancing lifetimes of high-n Rydberg states. We propose a new control scheme, based upon a 'wavepacket technology' which uses time-dependent, crossed electric and magnetic fields. Model (hydrogenic) calculations illustrating the control over l and m quantum numbers are presented and experimental parameters are suggested. The effects of core multipole moments on the decay of the target state (high l, high m) are discussed. Coherent lifetime enhancement should be applicable to small signal zero-kinetic-energy (ZEKE) photoelectron spectroscopy experiments and to Rydberg photofragment translational energy spectroscopy.

1. Introduction

Wavepackets, being coherent sums of quantum states created by short, phase-controlled optical pulses, belong to both the classical and quantum worlds and as such are useful for investigating fundamental aspects of quantum mechanics, such as the correspondence principle limit [1]. The free evolution of wavepackets reflects directly the dynamical evolution of the system and wavepacket methods are now widely used to study fast processes in both gas [2] and condensed phase [3] chemistry. Recently, we suggested that wavepacket techniques and methods of analysis should be considered together as a general and flexible 'technology' to be applied to a variety of practical problems [4] such as, for example, isotope separation. In this Letter, we suggest a method for enhancing lifetimes of high-n molecular Rydberg states (observed in zero-kinetic-energy (ZEKE) photoelectron spectroscopy) based upon the preparation and subsequent control of coherent superpositions of Rydberg states as another example of 'wavepacket technology'.

The technique of ZEKE photoelectron spectroscopy derives from the observation that the lifetimes of high-n Rydberg states are much longer than expected from extrapolations [5] based on n^3. This is because, in ZEKE experiments, the lifetime is enhanced by changes to the angular momentum quantum numbers l and m of the Rydberg electron. The changes to l can arise from the stray dc electric fields in the apparatus which spoil spherical symmetry [6,7]. Since the decay rate of Rydberg states is determined by close range interactions with the core, their lifetime is relatively short for low l and becomes very long for high l. Hence, l mixing induced by a dc field leads to a dilution of the fast decaying components and the observation of longer lifetimes [8]. Mixing over all l can lead to a lifetime enhancement of order n. A further dilution of the fast decaying state results from the field effects of nearby ions [9] which change both l and m due to the

spoiling of both spherical and cylindrical symmetry [6,10]. Mixing over all m engenders a further lifetime enhancement, also of order n. In sum, ion-Rydberg collisions and stray fields can cause incoherent 'diffusion' of Rydberg population over all l and m, leading to a lifetime enhancement [6] of order n^2. In this paper we propose a *coherent* scheme using applied fields which may allow one to obtain much greater lifetime enhancement.

Two recent studies considered the combined effects of static electric and magnetic fields on Rydberg states. One study showed that crossed dc electric and magnetic fields may also enhance lifetimes beyond simple l mixing due to the combined Stark and Zeeman mixing, again spoiling both the l and m quantum numbers [11]. A second study was of quasi-bound Rydberg wavepackets in parallel electric and magnetic fields, showing a stabilization effect due to the diamagnetic interaction [12]. The purpose of this communication is to show that using coherent evolution of Rydberg wavepackets in *time-dependent* electric and magnetic fields one can achieve lifetime enhancement much better than n^2. Coherent control schemes [13] attract much attention due to their ability to control ionization (and dissociation) in both molecules [14] and solids [15]. In the case of a dc electric field, coherent angular momentum evolution of a single n-manifold prepared in a low-l state may be calculated accurately [16]. Spatially separated crossed electric and magnetic fields have been used to produce circular or elliptic oriented Rydberg atoms [17–19]; the thermal drift carrying the atoms between the different field regions. However, this method would not work for the case of fast decaying molecular Rydberg states.

The idea of coherent Rydberg lifetime enhancement is simple: a pulsed electric field is applied during the Rydberg preparation, leading to wavepacket evolution in l (i.e. revival structure). At a characteristic time, this field turns off leaving the Rydberg wavepacket at high l. However, due to the stray electric fields (mV/cm) in the apparatus, even an ideal high-l hydrogenic state is not stable [20]. Furthermore, this scheme actually applies an external dc electric field (which dominates all stray fields) in order to maintain overall cylindrical symmetry, for reasons discussed below. Therefore, in order to prevent the decay of the Rydberg wavepacket (through

its return to low l), we must also achieve high m. In our scheme, this is accomplished by applying a time-dependent magnetic field. We present a method which coherently transfers Rydberg population to high l, high m, avoiding the incoherent 'diffusion' of Rydberg population equally over all l and m, and could thereby yield lifetime enhancements much greater than n^2.

This scheme of Rydberg wavepacket control models only the hydrogenic case. For other atoms and for molecules, the effects of the core multipoles on the state distributions must be considered. Molecules, furthermore, have intramolecular predissociation channels which lead to an overall loss of Rydberg population. This predissociative loss is related to the low-l Rydberg states which have significant overlap with the core valence states. The high-l states do not overlap with the core (i.e. non-penetrating) and, in order to decay, must first evolve into low-l states via interseries mixing induced by the core multipoles. Recent interesting theoretical studies have shown the effects of core multipoles on interseries mixing in and of rotational autoionization from non-pentrating high-n Rydberg states [21–23]. These studies showed that the timescale for wavepacket evolution due to the core multipoles is much longer than the rapid evolution induced by applied electric and magnetic fields in the case considered here. Therefore, while the applied fields are on, the wavepacket evolution of the non-penetrating states – those with $l > 3$ – can be treated well using hydrogenic functions (due to their negliglible quantum defects). It is clear, however, that the initial wavepacket evolution will be partly non-hydrogenic due to both the non-zero quantum defects and the fast decay of the low-l states which lead to a loss of population near $t = 0$ of the evolution. Thus, we consider here only those Rydberg states which have survived evolution out to at least $l = 3$. We note that discussions of Rydberg lifetime enhancement due to ion collisions or stray fields also consider only those states which have survived any fast initial intramolecular decay. The eventual slow decay of the target (high-l, high-m) state due to core multipoles is discussed in a later section.

In contrast with previous work on the creation of circular Rydberg states in atoms, it is the higher values of n and the fast decay of the low-l states

which are of concern in this study. When combined with the technical restrictions imposed on the parameters of electric and magnetic field pulses, the creation of circular states presents new problems. Devising a scheme which is efficient yet practical is another purpose of this communication.

The applications of coherent Rydberg lifetime enhancement can be seen in several areas. For example, in ZEKE experiments which produce very few ions (e.g. VUV laser or synchrotron experiments), it could be advantageous to 'capture' decaying Rydberg states, using the coherent enhancement scheme in order to improve the signal-to-noise ratio. A particularly interesting application of this scheme could be in the area of photofragment translational energy spectroscopy [24]. In this technique, photofragment product state distributions can be determined by measuring the angle-resolved time-of-flight of a given product to a detector [25]. A major advance in the resolution of this method was obtained through the use of hydrogen Rydberg atom preparation and measurement [26]. In this technique, a product hydrogen atom is excited to a high Rydberg state (typically about $n = 70$) which has a long lifetime. The time-of-flight is then measured with very high (rotational) resolution by field ionization at a distant detector. The success of the method is based upon the survival of the hydrogen Rydberg atom during its long (e.g. 100 μs) time-of-flight. This technique has very recently been extended to oxygen atoms and even NO molecules [27]. This method could allow for the extension of the recently developed technique of correlated-product-states distribution measurements [28] to other systems.

2. Model

We illustrate the proposed scheme in Fig. 1. A molecular beam introduces molecules to the interaction region of a spectrometer. Either photofragments from a pump laser step or the molecules themselves are prepared as high-n Rydberg states by the probe laser. The application of an electric field during Rydberg preparation leads to a wavepacket in Stark states [12]. In terms of angular momentum states, this wavepacket evolves periodically from the initially prepared low-l to the high-l states. If the
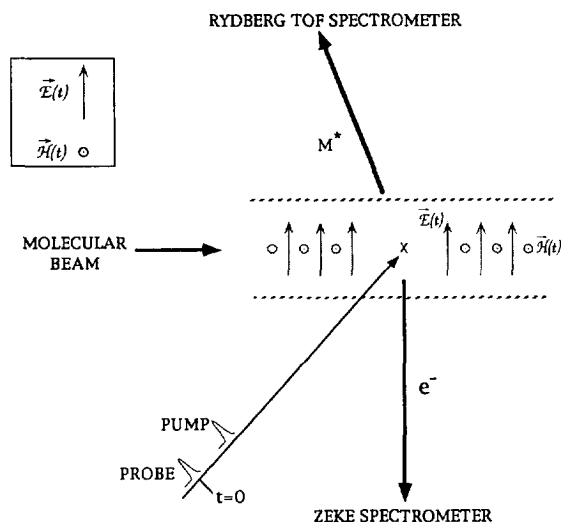

Fig. 1. An illustration of the Rydberg lifetime enhancement scheme. Molecules (or photofragments produced by a pump laser) are introduced by a beam and are coherently prepared as a high-n Rydberg wavepacket by the probe laser. Using crossed, time-separated electric and magnetic fields, $\mathscr{E}(t)$ and $\mathscr{H}(t)$, the l- and m-state distribution may be coherently mapped onto high-l, high-m states (which are stable against decay).

electric field pulse is turned off at one-half the l-recursion time, when the wavepacket has reached the high-l turning point, the wavepacket will be 'trapped' in high-l states. Due to the presence of electric fields (and core multipoles), however, this state will not be stable (i.e. it will *eventually* return to low l). We therefore apply a crossed magnetic field pulse exactly when the wavepacket is in high-l states, causing a coherent periodic evolution in the Zeeman states. This m-wavepacket is initially at low m and evolves towards high m according to the level structure induced by the applied magnetic field. The m-wavepacket recursion times are also well defined. We turn off the pulsed magnetic field at a time when the wavepacket reaches the high-m turning point, trapping the wavepacket at high l, high m. We note two important points for this discussion: (1) due to the applied cylindrical symmetry, any further evolution in m is most likely due to small stray magnetic fields and weak interaction of the circular states with the core and, hence, very slow; (2) since l can never be less than m, even though a dc field is present, the decay of the wavepacket is determined by the evolution of m. Such a high-l, high-m state is expected to

be quite stable against decay [11]. For the purposes of illustrating the coherent control scheme for enhancement of Rydberg lifetimes, we consider a system with principal quantum number n about 70. Atomic units are used throughout unless indicated otherwise.

2.1. Evolution in a pulsed electric field

Although the idea of using pulsed, crossed electric and magnetic fields is quite simple, its practical implementation in the case of high Rydberg states is not immediate. At the first step of the scheme – evolution in a pulsed electric field – constraints are placed both by the molecular system and, more importantly, by reasonable parameters for the electric field pulses and stray electric fields.

In a quantum system, an upper limit to the applied electric field strength is determined by field ionization: $E < 1/16n^4$. Furthermore, although not strictly necessary, we would like to avoid significant overlap of Stark manifolds with different n, since it will make l evolution unnecessarily more complex and also effectively transfer population between different n (in non-hydrogenic systems). Thus, if the requirements were dictated only by our quantum system, an optimum field would be the one for which the width of the Stark manifold is on the order of $1/n^3$. That is to say, we are at or just below the Inglis–Teller limit. In such a field, the distance between neighbouring Stark sublevels is $1/n^4$ and the recursion

time of the l-wavepacket is nT_n, where $T_n = 2\pi n^3$ is the Kepler period. In our example of $n = 70$ this time is about 3 ns.

As soon as l reaches large values, the field must be turned off. An experimentally reasonable turn-off time is, say, 10 ns, longer than the recursion time in our example. Furthermore, after the electric field is turned off, the Rydberg states will continue to evolve in the stray fields, which can have arbitrary directions, leading to uncontrollable changes [6] in both l and m.

The coherent control scheme is shown in Fig. 2. In this scheme $\mathscr{E}(t)$ falls linearly over a period $\tau_E = 20$ ns to a *residual field strength* E_{res}, which should dominate any stray fields present in the apparatus, ensuring both well-defined evolution of l and a fixed space quantization axis. A relatively short *probe* pulse prepares the high-n Rydberg states *at the falling edge* of $\mathscr{E}(t)$, so that the strong electric field is turned off in few nanoseconds. (In the case of photodissociation studies, a pump laser could excite a parent molecule that emits a product atom or molecule which would be subsequently prepared as a high-n Rydberg state by the probe pulse.) The mathematical conditions dictating the choice of E_s and τ_E are discussed below.

The energy levels (atomic units) of a hydrogenic system in an electric field $\mathscr{E}$ are $E_{nk} = -1/2n^2 + 3/2\mathscr{E}nk$, with the distance between neighbour Stark sublevels being $\Omega_E = 3\mathscr{E}n$. We note that the wavepacket is prepared in fields at or just below the
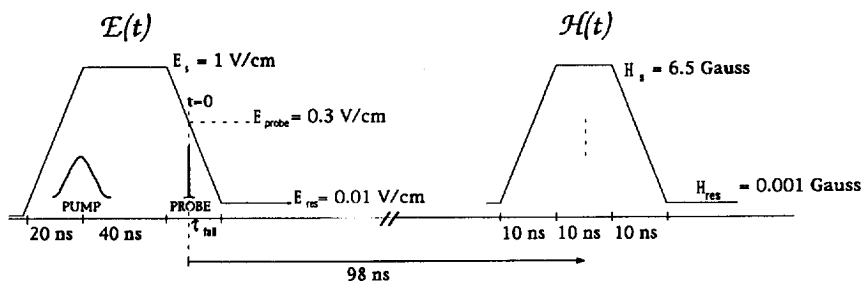

Fig. 2. A wavepacket technology scheme for applying pulsed crossed electric and magnetic field pulses $\mathscr{E}(t)$ and $\mathscr{H}(t)$. The electric field has a maximum strength of $E_s = 1$ V/cm and falls to a residual field strength of $E_{\mathrm{res}} = 0.01$ V/cm in a time $\tau_E \approx 20$ ns. A probe laser pulse creates a Rydberg wavepacket at a specific time (defined to be $t = 0$) during the fall of the pulse. (For photodissociation experiments producing product states to be observed by Rydberg detection, a photodissociation laser pulse is shown preceding the probe laser pulse.) The electric pulse $\mathscr{E}(t)$ is used to control the Rydberg wavepacket l-state evolution. The crossed magnetic pulse $\mathscr{H}(t)$ is used to control the wavepacket m-state evolution. The magnetic field strength and duration are chosen such that the mean m-value cycles before leaving the Rydberg wavepacket at high m at the end of the pulse.

Inglis–Teller limit and, as discussed above, we can reasonably approximate its subsequent evolution in the field as hydrogenic. Coherent preparation of these levels leads to wavepacket oscillation with a frequency Ω_E. In terms of the angular momentum states, the wavepacket evolves [11] according to: $\langle l^2 \rangle \approx n^2 \sin^2(\Omega_E t/2)$. If the pulse falls off linearly, then:

$$\langle l^2 \rangle \approx n^2 \sin^2 \left(\int_0^{\tau_E} \Omega_E(t')\ dt'/2 \right). \tag{1}$$

At the end of the electrical pulse, we would like $\langle l^2 \rangle$ to reach a sufficiently large value, say $\langle l^2 \rangle \approx n^2/2$. In this case, we have:

$$\int_0^{\tau_E} \Omega_E(t')\ dt' \approx \pi/2. \tag{2}$$

For a pulse fall-time of τ_E and a maximum electric field strength of E_s, Eq. (2) yields the following condition for E_{probe}, the value of the electric field at the time of the probe laser:

$$E_{\mathrm{probe}} = \left[(\pi/3)\, E_s/n\tau_E \right]^{1/2}. \tag{3}$$

For experimental simplicity, the fall-time of the pulse τ_E should be on the order of 10^1 ns. The time τ_0 for the increase of the angular momenta in the field, $\tau_0 = \tau_E(E_{\mathrm{probe}}/E_s)$, is then on the order of few nanoseconds – i.e. l increases quickly. Since we do not want the Stark manifolds to overlap at the moment of excitation (i.e. at or just below the Inglis–Teller limit), we also require $3n^2 E_{\mathrm{probe}} < n^{-3}$. This condition must be satisfied simultaneously with Eq. (3), and with τ_E on the order of 10^1 ns. These requirements are met, for $n = 70$, with $E_s = 1$ V/cm, $\tau_E = 20$ ns, and $E_{\mathrm{probe}} = 0.31$ V/cm, as shown in Fig. 2. This corresponds to $3n^2 E_{\mathrm{probe}} \approx 0.3\ n^{-3}$ so that the Stark manifolds do not overlap while at the same time the evolution of l is sufficiently fast: in $\tau_0 = 6.1$ ns the average l becomes $\langle l^2 \rangle^{1/2} \approx 50$.

After the electric field reaches its residual value, we enter the stage of slow evolution of l. As l is now sufficiently large, we may treat the evolution in the field as hydrogenic. The applied residual field E_{res} dominates the stray fields in the apparatus and determines further evolution of the angular momentum. We assume that stray fields can be reduced to the order of 1 mV/cm and therefore we choose $E_{\mathrm{res}} = 0.01$ V/cm. The evolution of the Rydberg state is $\langle l^2 \rangle \approx n^2 \sin^2(\Omega_{\mathrm{res}} t/2 + \phi_0)$, where ϕ_0 is
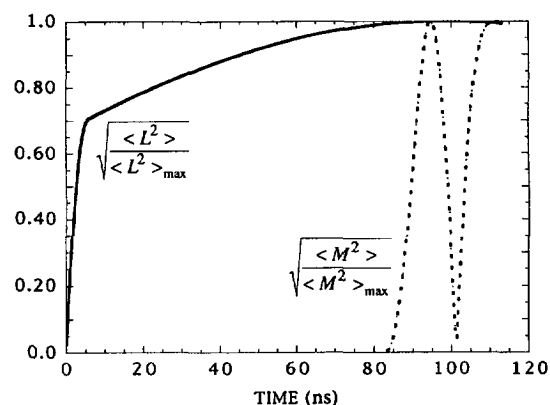

Fig. 3. The evolution of $\langle l^2 \rangle$ and $\langle m^2 \rangle$ is plotted as a fraction of their maximal value and shown as a function of time. The angular momenta, evolving due to the pulsed electric field $\mathscr{E}(t)$, increase very quickly during the electric field pulse and then much more slowly in the residual field, finally achieving their maximal value at a time near 100 ns. Around this characteristic (half the wavepacket revival) time, a magnetic field pulse $\mathscr{H}(t)$ is applied, causing adiabatic evolution of the magnetic quantum numbers. For our choice of $\mathscr{H}(t)$, the m-values cycle twice before achieving a maximal value at the end of the magnetic pulse.

the phase accumulated during the previous (stronger field) evolution and $\Omega_{\mathrm{res}} = 3nE_{\mathrm{res}}$. As discussed above, $\phi_0 = \pi/4$.

The evolution of the angular momenta in the pulsed and residual electric fields is shown in Fig. 3. The time zero is defined by the firing of the probe laser. The angular momentum $\langle l^2 \rangle^{1/2}$ is shown to increase rapidly from zero during the pulse E_s and then to evolve much more slowly in the residual field E_{res}, finally reaching the maximal value at a time $\tau_0 + \tau_{E,\mathrm{res}} \approx \pi/4\Omega_{\mathrm{res}} + \tau_0$, which is close to 98 ns in Fig. 3. The angular momenta, of course, will eventually return to low l due to the periodic evolution of l in the field E_{res}. In order to avoid this, we implement a pulsed, crossed magnetic field, as discussed below.

2.2. Evolution in a pulsed magnetic field

The evolution in l near its maximum value is very slow (Fig. 3). This allows us to apply a pulsed magnetic field, shown as $\mathscr{H}(t)$ in Fig. 2, appearing close to the time $\tau_{E,\mathrm{res}}$, in order to quickly increase m-quantum numbers for a period during which l is almost stationary. As discussed below, we will choose a magnetic pulse duration of about 40 ns.

There are several requirements for the magnetic field pulse. The first requirement is that the Zeeman frequency $\Omega_H = \mathscr{H}/2c$ should greatly exceed the Stark frequency in the residual field Ω_{res}:

$$\Omega_H \gg \Omega_{res}. \tag{4}$$

This allows for clean, simple evolution of m while l changes adiabatically. Although not strictly necessary, for the sake of simple m evolution, we will require that the Zeeman splitting should not mix adjacent n-manifolds:

$$n\Omega_H \leqslant n^{-3}. \tag{5}$$

Other constraints are that the magnetic field pulse should be fast enough to neglect changes in l during the pulse yet slow enough for technical simplicity and, furthermore, that the pulsed magnetic field dominates the stray magnetic field of the earth (about 500 mG, which may easily be reduced, if necessary, to less than 1 mG).

As long as $\Omega_H \gg \Omega_{res}$, one can derive the following simple equation for the evolution of the m-quantum numbers:

$$\langle m^2 \rangle = l^2 \, \sin^2\left(\int_{t_i}^{t_f} \Omega_H(t') \, dt' \right). \tag{6}$$

Here the m-averaging is actually for fixed l^2, but since for $l \gg 1$, Ω_H is l independent, the formula is correct for variable l as long as this variation is adiabatically slow compared to m evolution. The independence of Ω_H from l also allows us to immediately perform averaging over l in Eq. (7), below, which leads to substituting l^2 with $\langle l^2 \rangle$. If we choose $\Omega_H \approx 10\Omega_{res}$, then for $E_{res} = 0.01$ V/cm, as discussed above, we estimate that a magnetic field strength of at least $\mathscr{H} \approx 4.7$ G is required. This type of field is readily obtained in the lab with conventional coils and pulsed power supplies. Under these conditions, the timescale for changing m-quantum numbers from an initial value of zero to the maximal value is $\pi/2\Omega_H \approx 0.1\tau_{E,res} \approx 9.2$ ns, a reasonable duration in terms of experimental feasibility. In order that $\langle m^2 \rangle$ is maximal at the end of the magnetic pulse, $\mathscr{H}(t) = \mathscr{H}$, $f(t)$ must satisfy the equation:

$$\Omega_H \int_{t_i}^{t_f} f(t') \, dt' = (\pi/2)(2q - 1), \tag{7}$$

where $q = 1, 2, \ldots$ We note that for $l \gg 1$, Ω_H is independent of n, l. Therefore, although there may be many l-states in the wavepacket, for each l the magnetic quantum numbers will evolve in a synchronized manner, reaching maxima and minima at the same times.

A typical magnetic pulse which may be used is shown in Fig. 2. We assume rise and fall times of 10 ns and take the peak value $\mathscr{H} = 6.5$ G. The evolution of $\langle m^2 \rangle$ in the pulse $\mathscr{H}(t)$ is shown in Fig. 3. Our choice of the peak value of the magnetic field corresponds to the case $q = 2$. The case of a single maximum ($q = 1$) is also easily realizable with common pulsed power supplies. For $q = 2$, the mean m-quantum number oscillates from zero to the maximal value in about 10 ns and returns to the maximal value for a second time as the magnetic pulse turns off. This essentially 'traps' the wavepacket at high m. The subsequent evolution of the Rydberg wavepacket in the residual fields is discussed in the following section.

3. Discussion and conclusion

We have presented a scheme for the enhancement of Rydberg lifetimes based on the coherent evolution of Rydberg wavepackets in time-dependent crossed electric and magnetic fields. The target of the control scheme is a high-l, high-m wavepacket, which is quite stable against decay. Our simplified calculations are based upon the control of a single n-manifold ($n = 70$) prepared with a transform-limited pulse. These conditions are seldom met in most laboratory ZEKE experiments. However, we note that this scheme has tremendous flexibility in terms of the experimental parameters available to optimize Rydberg lifetimes in real experiments. The experimental control parameters are: (1) strength of the electric field at the time of Rydberg preparation; (2) timing of the probe laser pulse with respect to the pulsed electric field; (3) strength of the residual electric field; (4) timing of the magnetic field pulse; (5) strength of the magnetic field pulse; (6) duration of the magnetic field pulse. In practice, one would vary these parameters in order to maximize the desired Rydberg signal.

An accurate quantitative estimate of the lifetime enhancement which can be obtained with the pro-

posed scheme requires large scale calculations on a specific molecule. However, several qualitative remarks are easily made. We have used a hydrogenic treatment of the wavepacket dynamics in the field: this ignores the effects of core multipoles on the level spacings (i.e. non-zero quantum defects) and intramolecular predissociation. We argued in Section 1 that, while the fields are on, the evolution due to the applied fields is faster than the evolution induced by core multipoles. Therefore, following an initial loss of population due to fast predissociative decay or autoionization of some low-l states, the subsequent wavepacket evolution of states with, say, $l > 3$, should be roughly hydrogenic. We consider, below, decay mechanisms of the high-l, high-m target states prepared with our scheme.

The high-l states are not directly coupled to predissociation or autoionization channels and therefore must decay first to low-l states through interseries mixing and this should be the rate limiting step. Bixon and Jortner [23], using the near threshold Bessel approximation, have determined dipolar and multipolar interseries coupling matrix elements and presented their scaling power laws. Remacle and Levine [21], using exact calculations, have determined dipolar interseries coupling matrix elements and also have included the effects of an applied static electric field. Generally speaking, the multipolar matrix elements for the decay of l decrease very strongly as l increases (e.g. according to Bixon and Jortner, as l^{-5} to l^{-9}, depending upon the interaction). There is a bottleneck for the multipolar decay of high-l states. Remacle and Levine [21] and Remacle, Levine and Baronov [22] have shown that for the case of dipolar coupling, the decrease in the coupling matrix elements, out to about $l/n = 0.5$, is actually much slower.

In our control scenario, total M_{total} ($= m_{Ry} + m_{core}$) is conserved due to the applied cylindrical symmetry from the field E_{res} (see Fig. 2) and, therefore, for decay to occur, the Rydberg electron can only exchange its m with that of the core. Recall that although the field E_{res} mixes rapidly the available l, l can never be less than m_{Ry} and so the decay of the wavepacket is governed by the decay of m_{Ry}. For couplings which can preserve the core state (e.g. quadrupolar), the exchange of m is limited by the relatively low angular momentum of the core (low as

compared with the high-l Rydberg state): the core quickly "runs out" of m, providing a bottleneck for the decay. Any further decay must therefore involve couplings which increase the core angular momentum. However, the energy gaps associated with core rotational states very quickly exceed the coupling strengths of the high-l states and again a bottleneck is reached. We expect that a prepared Rydberg wavepacket with high M_{total} should exhibit very long lifetimes, limited finally by small perturbations such as black body radiation.

We hope that these ideas will inspire experimentalists to apply pulsed fields in the laboratory in order to enhance Rydberg lifetimes. The technical implementation of such schemes is simple and allows for experimental control of important parameters required for l, m-state control. Such lifetime enhancements could not only improve small signal ZEKE experiments but may also allow the formation of very long lived atomic and molecular Rydberg states for photofragment Rydberg time-of-flight studies of photodissociation dynamics.

The present work provides another example of 'wavepacket technology', here applied to the problem of Rydberg lifetime enhancement. We envisage numerous other applications and we expect the current efforts of several groups on the controlled shaping of ultrashort laser pulses [29–33] to provide working tools for this new 'wavepacket technology' which emerges at the classical–quantum border.

Acknowledgement

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