A Quantitative Model for the Dynamics of High Rydberg States of Molecules: 
The Iterated Map and its Kinetic Limit

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An iterated map which mimics the dynamics of a high Rydberg electron revolving around an anisotropic ionic core is described. The map specifies the change in the quantum numbers of the electron due to its passage near to the rotating core. Attention is centered on the limiting case of physical interest where the rotation of the core is faster than the orbital motion of the electron. While the map does provide for a very efficient way to numerically simulate the motion, its main advantage is in that it delineates the various dimensionless coupling parameters that govern the dynamics. To make contact with many experiments, external electrical and magnetic fields are included in the Hamiltonian. The stretch of the kinetic time axis due to the presence of external fields is discussed. The full map can be further approximated by a one-dimensional map which captures the essence of the dynamics. The primary aspects having to do with the three-dimensional character of the actual motion are incorporated in the magnitude of the dimensionless coupling parameters. A simple but realistic limit of the one-dimensional map is discussed which can be considered as the electron undergoing diffusion in its energy. The mean first passage time out of the detection window and the branching fractions for ionization vs. stabilization of the electron are computed in the diffusion approximation. As is experimentally observed, the lifetime of the high Rydberg states exhibits a maximal value when plotted vs. the energy.

1. Introduction

The physical picture underlying the theoretical developments discussed in this paper is a simple one: The orbital motion of a very high n Rydberg electron is slower than the motion of the atoms in the ionic molecular core about which the electron revolves. In the frequency domain this means that the spacings of adjacent Rydberg states are closer then those in the rovibrational spectrum of the core. Under such circumstances, it is the sluggish electron which is being perturbed by the faster nuclear motions. One can thus expect that a simple description of the dynamics will be that of a 'Brownian motion' of the electron, which is being buffeted by the core. Such a picture has indeed been used to interpret delayed ionization in large molecules [1, 2].

The orbital period (2πn²) in au’s of high Rydberg states is so long because the Coulomb potential has an extremely long-range tail [1]. During much of its orbit the electron is thus far from the core and it is only once per orbit, during the rapid transversal of the region of closest approach, that the coupling, due to the electrical anisotropy of the core [3-8], is effective. Our [7, 8] classical trajectory calculations clearly exhibit this very localized interaction region. Another point from these computations is that the electron core coupling is not very strong. A natural measure of the strength of the coupling in classical mechanics is the fractional change in the principal action (the classical analog of the quantum number n) of the electron per passage near the core. At the high n's of interest to us, and for realistic molecular parameters, this fractional change is at most of the order of a few percent. Yet, because n is high, the absolute change in the classical action is of the order of or more. It follows that one can use classical dynamics to reliably estimate the changes in n by measuring classical actions in units of h.

The first technical step in this paper is the conversion of a mechanical (i.e., Hamiltonian) description of the dynamics to a map [10-15]. This is based on the change, per revolution, in n being accurately given by first-order perturbation theory, i.e., on the change being small compared to n itself. The other ingredient needed for this conversion is the use of classical action-angle variables [9, 10]. When measured in units of h, classical action variables mimic quantum numbers. In the present context, this means more than just the convenience of a quasiclassical correspondence. It means that, for much of the time, the classical actions are not changing. Such changes that do take place occur only during the brief and far apart time intervals when the electron is near to the core. In our trajectory computations, we use this to advantage by integrating the equations of motion for these variables. Here, this enables us to compute the change in the action variables per orbit. The corresponding angle variables, and particularly the angle variable conjugate to the classical n, are rapidly varying even in the absence of coupling. Hence the change in the angle variables can be well approximated by their motion in the absence of coupling.

The present results differ in an essential way from those derived for a hydrogen atom in a microwave electromagnetic field [10-14] in that the field acts on the electron...
throughout its orbit (and more so when the electron is further away from the core), whereas the coupling to the molecular dipole is only effective when the electron is in the vicinity of its point of closest approach. In addition to the coupling to the dipole, our map allows for the presence of both electrical and magnetic fields.

In the second technical step of this paper, we introduce a 'random phase approximation' in which the change in \( \sin \phi \), per revolution around the core is, de facto, a random number in the interval \( \pm 1 \). With this approximation, the mapping can be immediately reduced to a Langevin-like (or, equivalently, Fokker-Planck like [16]) description of the changes in \( n \). It will, however, turn out that the simplest (i.e., Brownian-like) description is in terms of the energy of the Rydberg state rather than in terms of its principal quantum number, \( n \). The one disadvantage of our use of the random-phase approximation is that we give up a phase-space description\(^2\). The map is only in the quantum numbers (or, more correctly, in the classical actions). Since our primary concern is not with the development of classically chaotic behavior, and since, in any case, we do wish to average over the initial values of the angle variables so as to mimic a quantum initial state, we regard our approach as not only simpler but as preferable.

The experiments that motivated the present study were time-resolved monitoring of the population of high molecular Rydberg states \([17 - 19]\) by ZEKE (Zero Electron Kinetic Energy) spectroscopy \([20, 21]\). The primary observation is that of an essentially exponential decay with a sub \( \mu \)s decay constant, and of a smaller and longer living component. The shorter lifetime has an unexpected, bell shaped, frequency dependence \([17]\), which is shown for two different, initially internally cold, molecules in Fig. 1. All details of the experiment are as in Ref. 17 and will not be repeated here.

Several technical points about the experiments are relevant to the comparison with the present theoretical results. First is the nature of the detection. What is determined by the delayed pulse ionization employed in ZEKE spectroscopy is the total number of Rydberg states whose energy lies in a specified range, sometimes called 'the detection window'. The lower limit of the range is determined by the amplitude of the delayed ionization field. In the experiments shown in Fig. 1, this lower limit corresponds to about \(-11\) cm\(^{-1}\) or to \( n = 90 \). The energy corresponding to the upper end of the detection range is, in principle, zero so that all states with \( n \geq 90 \) are detected. In practice, the upper end is somewhat below zero because the very highest Rydberg states will be ionized by stray DC fields. By an experiment \([22]\) where an external DC field is imposed, one can estimate that the magnitude of the stray DC field is such that the upper end of the detection window is \( \approx -1\) cm\(^{-1}\). Another point is that, due to the need to remove promptly produced electrons, the detection begins only 100 ns or so later than the initial excitation. Finally, as noted in connection with Fig. 1, most of the experiments were for cold aromatic molecules so that the rotational excitation of the core is quite low. In this paper we take it that the frequency of the photon is such that the total energy of the molecule is above the threshold for ionization.

Using the diffusion equation for the energy of the Rydberg state, we obtain very simple analytical expressions for the lifetime as a function of the excitation energy of the initial state and for the rates of exit out of the two ends of the detection window (the so called) up and down processes \([17]\). While the diffusion equation is too simplistic a limit to provide a quantitative fit to the experimental results, it does capture the essence of the phenomena. In particular,

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Footnote:

\(^2\) Using both action and angle variables, one can define a so-called 'canonical' map \([10]\). This will conserve the volume in phase space. A map which uses only action variables is not canonical.

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**Fig. 1**

The measured lifetime (in ns; see Ref. 17 for further details) of the high Rydberg states of (a) Perylene and (b) DCA (DiChloroAnthracene) vs. the energy of the state in cm\(^{-1}\). The continuous curve is a fit to the analytical result for the lifetime in the random phase approximation (Eq. (3.12)). This simple limit is not quantitative but is seen to capture the essence. The kinetics of these cold aromatic molecules can be experimentally monitored only after a 100 ns delay and no information is currently available on earlier times. The kinetics exhibit an essentially exponential decay of the number of Rydberg states in the detection window plus a smaller (<10%) and longer living component \([17, 18]\). The lifetime shown is for the major component.
it identifies the maximum in the lifetime vs. frequency plot, cf. Fig. 1, as due to the competition between the down and up processes. The full mapping cannot be quite so easily solved. However, as a computational scheme, it runs orders of magnitude faster than the full Hamiltonian dynamics and provides a realistic numerical approximation.

Sect. 2 of this paper introduces the conversion from Hamiltonian dynamics to a map for a simple limit, that of a one-dimensional motion of the electron, a case which contains much of the essential physics of the coupling to the core. Not covered in the one-dimensional case is the role of an external DC field which induces an oscillation of the plane of rotation of the electron or the role of a magnetic field. When the electrical and magnetic fields are not parallel, the motion is unavoidably three-dimensional, even in the limit when the diamagnetic term of the magnetic field is neglected [9]. The general case (see, e.g., [23]) is even more complex. However, in the first order of perturbation theory the different couplings are additive, so that a map can still be obtained. This general case is outlined in Sect. 3. The short summary is that a semiquantitative account of the full three-dimensional case is provided by the one-dimensional example of Sect. 2, with suitable modifications.

2. The Map for the One-Dimensional Case

The map specifies the change in the value of the quantum numbers of the electron upon one revolution around the core. Given the current value and the change, one computes the value after the next round. The dynamical history is thus equivalent to the iteration of the map. The map is computed by the approximation that, unlike the angle variables, whose unperturbed change is rapid, the action variables do not appreciably change during one revolution and hence their change can be computed by first-order perturbation theory. A fancier way of stating this is to say that the change is computed using the exact equations of motion but with the action variables constrained to their current value. (This value is, of course, updated for computing the next value of the change). The conversion of a Hamiltonian system to a map is extensively discussed in Refs. 10, 11 and 15, and the application to the Coulomb problem has also received attention [12-15].

What makes the map an approximation is that the change is computed for a finite time step, but using the starting values of the quantum numbers. Hence, if the change in the quantum numbers is due to a single ‘kick’ by the potential, the map can be an exact representation of the dynamics. Hamiltonians which represent ‘kicks’ and their corresponding maps have indeed been discussed [10, 11, 15]. In the present problem, and in the absence of external fields [7], the quantum numbers of the Rydberg electron are indeed constant, apart from the rather brief passage near the core. The electron is not kicked in a mathematical sense, but, at the high n’s of interest, the time during which it is coupled to the core is very short compared to its orbital period. Fig. 2 contrasts the time dependence of the force on the electron due to the dipole of the core and due to an electrical field, oscillating at the same frequency as the dipole. Clearly, the dipolar coupling to the core can be realistically treated by a conversion to a map.

There is another reason why the map is very well suited to our purpose. It is that the fractional change in the quantum numbers of the electron, per revolution, is small [7]. We will however introduce one approximation, which is not essential, but which simplifies the results and reduces the number of variables (the ‘dimension’) of the map. We take the rotation of the core (period $2\pi/\omega$) to be fast compared with the orbital period $(2\pi n^3)$ of the electron. The ratio, $\chi = \omega n^3$, of the orbital to core rotation periods will be a key parameter, and we shall work in the limit $\chi > 1$. The approximation is known as the classical-path one; namely, we solve for the motion of the electron revolving around the freely rotating dipole. Typically, it is the electron that is faster, and one solves for the motion of the rotor induced by the free motion of the electron. Here, consistent with our so called ‘inverse Born-Oppenheimer’ limit [18, 19] it is the other way round. It is the slow electron which is perturbed by the faster rotation of the core.

A. The One-Dimensional Map

In this section we consider in detail the limit of a one-dimensional motion of the electron. The three-dimensional
case is discussed in Sect. 3. The Hamiltonian, in atomic units, is

\[ H = B j^2 + \left( p^2 / 2 \right) - (1/2) \right) + d \cos (\alpha_j) / r^2 = B j^2 - (1/2) n^2 \]

\[ + d \cos (\omega t) / r^2 , \]  

(2.1)

where \( r \) and \( p \) are the Cartesian coordinate and momentum of the electron, with the core being at the origin; \( d \) is the dipole moment of the core; \( \alpha_j \) is the angle variable conjugate to the angular momentum of the rotating core \( j \), so that the dipolar coupling term, \( d \cdot r / r^3 \) is written, for a one-dimensional motion of the electron, as in (2.1). In the classical path approximation, this angle changes linearly with time, \( \alpha_j = \omega t \). Since \( j \) is a constant of the motion in the classical path approximation, we can neglect all terms in (2.1) involving only \( j \), i.e., \( B j^2 \). \( n \) is the classical action of the electron in units of \( \hbar \). The angle variable conjugate to \( n \) is \( \alpha_n \) and, as usual, \( \alpha_n = u \), known as eccentric anomaly, by

\[ \alpha_n = u - \sin u \, , \]

(2.2)

where the zero of \( u \) is taken at the inner turning point. \( u \) will serve as a scaled time variable. The orbit is parametrized as

\[ r = n^2 (1 - \cos u) \]

(3.3)

and, since when \( n \) is constant, \( \omega t = \omega n^2 \alpha_n + \phi \) or \( \omega t = \omega n^3 (u - \sin u) + \phi \), we have

\[ \partial \alpha / \partial u = n^3 (1 - \cos u) \]

\[ \partial \alpha / \partial \alpha_n = 1 / (1 - \cos u) \, . \]

(2.4)

With these results, the one-dimensional map can be readily obtained. From Hamilton’s equations of motion, we obtain by integrating over one period (\( \tau \))

\[ \Delta n = - \int \frac{\partial H}{\partial \alpha_n} dt = 2 d n^{-3} \int_{-\pi}^{\pi} \cos (\chi (u - \sin u) + \phi) \]

\[ \cdot n^2 \sin u du = (2 d / n) \int_{-\pi}^{\pi} \frac{\cos (\chi (u - \sin u)) \cos \phi}{(1 - \cos u)^3} \sin u du \]

\[ \cdot \sin u du - (2 d / n) \int_{-\pi}^{\pi} \frac{\sin (\chi (u - \sin u)) \sin \phi}{(1 - \cos u)^3} \sin u du \, . \]

(2.5)

where \( \phi \) is the phase of the angle between the rotor and the electron at \( t = 0 \), cf. Eq. (2.1). The first integral in (2.5) vanishes (symmetry properties). The integration over \( u \) in the second integral in (2.5) can be done by parts, and leads to an explicit expression for the change in \( n \) in one revolution

\[ \Delta n = \int \frac{J_x (\chi) \sin \phi}{(1 - \cos u)^3} \sin u du \, . \]

(2.6)

Here \( J_x (\chi) \) is the derivative of the Bessel function \(^3\) of the first kind \([24] \) (\( \chi \) is approximated by the nearest integer and \( \varepsilon = 1 \) in the one-dimensional case)

\[ J_x (\chi) = \int_{-\pi}^{\pi} \cos (\chi (u - \sin u)) du \]

\[ J_x (\chi) = \int_{-\pi}^{\pi} \sin u \sin (\chi (u - \sin u)) du \, . \]

(2.7)

As we will have several occasions to point out, the Bessel function, whose argument \( \chi \) is the ratio of the rotation frequency of the dipole to that of the electron, determines the resonance between these two motions and hence the propensity for energy transfer. Since typically \( \chi > 1 \), one can use the asymptotic form \([12, 24] \)

\[ J_x (\chi) = \frac{2^{2/3}}{\chi^{2/3}} A_i (0) = \frac{0.41}{\chi^{2/3}} \, , \]

(2.8)

where \( A_i \) is the derivative of the Airy function \([24] \), leading to:

\[ \Delta n = 2.6 d \omega^{4/3} n^3 \sin \phi \, , \quad \chi > 1 \, . \]

(2.9)

If \( k \) is the index of the orbit, (2.6) leads to the following iteration scheme for the principal quantum number

\[ n_{k+1} = n_k + 2.6 d \omega^{4/3} n_k^3 \sin \phi \, . \]

(2.10)

Eq. (2.10) is not quite a map because we have, so far, not specified the change, per orbit, in the phase \( \phi \). We will use only the zero’th order change to determine the current value of \( \phi \) since the first-order correction is quite small, by comparison,

\[ \phi_{k+1} = \phi_k + 2 \pi \omega n_k^3 \sin \phi = \phi_k + 2 \pi \chi_k \, . \]

(2.11)

For many purposes it is sufficient to invoke a ‘random-phase’ approximation which consists in replacing \( \sin \phi \) by a random number in the range \( \pm 1 \). In this approximation, the current value of the phase is not needed.

### B. Implications of the One-Dimensional Limit

The result (2.9) has the following immediate implications: i. Per revolution around the core, the change in the energy of the Rydberg state, \( \Delta E = \Delta (-1/2 n^2) = \Delta n / n^3 \) is independent of the energy of the state. While this is strictly true only in the random-phase approximation, it is a very useful limit. Specifically, it implies (cf. Sect. 2.C below) that on a coarse grained time axis (i.e., when the index \( k \) of the orbit can be regarded as a continuous variable), the

\[ J_x (\chi) = d J_x (x) / dx \text{ at } x = \chi \, . \]

The discussion assumes that \( \chi \) is an integer. If it is not, the integration by parts in (2.5) must be done with more care and \( J_x \) is the Anger function \([24] \).
energy of the state undergoes a diffusive process. ii. Per revolution, the change in energy (or in n) increases with the frequency of the rotor. When \( \chi > 1 \), the increase scales as \( \omega^{2/3} \). The result is not immediately expected because when \( \chi > 1 \), the rotor and the electron cannot achieve a 1:1 resonance. Indeed, it is constructive to contrast this behavior with what is found if the electron is perturbed not by the anisotropic field of the rotor but by an electromagnetic field [12-15]. In this case, the perturbation term in the Hamiltonian, cf. Eq. (2.1) is \( F r \cos \omega t \), where \( F \) is the amplitude of the field. In this case, the term proportional to \((1 - \cos \omega t)^{-3}\) in Eq. (2.5) is absent. (The two integrands are compared in Fig. 2). The result for the change in \( n \) is, in this case \([11-15]\),

\[
\Delta n = 2 \pi F n^{3} J_{3/2}^{\prime}(\chi).
\]

Using (2.7), the asymptotic value of the change in \( n \), for large \( \omega \), scales as \( n^{3/2} \omega^{-2/3} \). The reason for this intuitively more obvious behavior stems from the nature of the coupling. As a periodic function, the distance \( r \) of the electron from the core can be expanded in a Fourier series in the angle variable \( a_n \).

\[
r = \sum_{s=0}^{\infty} r_{s} \cos sa_{n} \quad (2.13)
\]

The explicit form of the coefficients \( r_{s} \) is known \([9]\), \( r_{s} = n^{2} J_{s}(s)/s \). What is of importance to us is the asymptotic form of \( r_{s} \) for high \( s \), \( r_{s} \approx 0.41 n^{2} s^{-5/3} \). Using (2.13), the perturbation due to the oscillating field can be represented as a series of terms of the type \( \cos (s a_{n} \pm \omega t) \) where the angle variable is itself, cf. (2.4), time dependent. The terms with the plus sign always vary rapidly. The terms with the minus sign can be stationary when \( s a_{n} = \omega \), where the dot designates the time derivative. This, of course, is an \( s:1 \) resonance and occurs when \( \chi = s \). At or near a resonance the coupling will be quite effective. As a general result \([11]\), one expects higher order Fourier coefficients to be smaller, and hence the coupling will decrease with increasing order, \( s = \omega n^{3} \), of the resonance. For this reason one expects the coupling to decrease with increasing \( \omega \). These expectations are borne out by the explicit results for an electromagnetic field of frequency \( \omega \), cf. Eq. (2.12). The strength of the \( n^{3} \)th resonance at high \( \chi = s \) is, using \( s = \omega n^{3} \), \( r_{s} \approx n^{-3} \omega^{-5/3} \). When the perturbation is due to the rotation of the dipole, the behavior is different. Even though the dipole rotates faster than the electron, \( s > 1 \), the change in \( n \) increases with increasing \( \omega \).

It appears very reasonable to expect that the coupling will be most effective if the rotation of the core is such that at every passage of the electron near to it, it will be oriented so as to exert a maximal torque. Indeed, the change in \( n \) is proportional to \( \sin \phi \), cf. Eq. (2.6), where, cf. (2.1), \( \phi \) is the phase angle between the electron and the core at the point of closest approach. As for the case of the electromagnetic field, the resonance condition is determined by the frequency matching between the orbital motion \( r(t) \) and the rotation, \( \cos \omega t \). What is different is the magnitude of the coupling, which in the case of the dipolar core, increases with \( \omega \). The increase is as \( d \omega^{2} = d \chi^{2} \omega^{6} \). The origin of this dependence can be directly traced to the \( r^{-2} \) dependence of the electron-dipole coupling, which requires two integrations by parts to bring (2.5) to the form (2.6).

The unexpected increase of the coupling with the faster rotation of the core is not an artifact of the conversion to a map. The same behavior is exhibited by computing classical trajectories for the Hamiltonian (2.1). Yet one can wonder if this increase is truly valid however large \( \omega \) can become. The answer is no, because, at some point, \( \omega \) (or rather, \( \chi \)) is large enough that the dipole returns a second time to a favorable position for delivering a kick while the electron is still in the region of close approach to the core. At that point, the conversion to a map breaks down as the core no longer delivers a single kick per revolution of the electron. The time spent in the vicinity of the core scales as \( n^{2} \) (or, in the more realistic case of three-dimensional motion as \( n^{2}(l+1/2) \) where \( l \) is the orbital angular momentum of the electron). Hence, an upper limit of validity of our map is at \( \chi < n \).

The region of validity \( 1 < \chi < n \) is ample for our purpose because the rotational frequencies of most molecules, except diatomic hydrides, do not reach \( n^{-2} \) au's. (1 au = \( 2 \text{Ry} = 2.195 \times 10^{9} \text{cm}^{-1} \), where \( \text{Ry} \) is the Rydberg constant). That is not the case for the vibrational modes, whose frequencies can be as high as \( n^{-1} \) au's, or even higher. The increase of the coupling with the frequency of rotation should not, without due care, be extrapolated to discuss the role of vibrations.

The primary observation in time-resolved ZEKE experiments is of the scaling with the initial value of \( n \). In the one-dimensional case, Eq. (2.9), the change in \( n \) per revolution scales with \( n^{3} \), and this will hold also in three-dimensions but will be modified if an electrical DC field or a magnetic field is present, cf. Sect. 3 below. To determine the kinetics, we need, however, not only the change in \( n \) for a given classical trajectory, but an ensemble average over the initial phase, because the phase is not selected by an experiment \(^4\).

C. The Brownian Motion Limit

The transformation from a map to a kinetic equation for the actions is not trivial; analytical considerations and numerical experiments show that even a simple map can, because of the dependence on initial conditions, give rise to quite complex evolution in action space. In particular, the

\(^4\) In quantum mechanics there is, of course, an uncertainty relation for the action variable and its conjugate angle. If we select a sharp value for the action variable, we must uniformly sample over the angle variable. It is possible to prepare 'coherent' initial state where there is some uncertainty in the initial actions so that the angle variables are more localized.
kinetic description for a hydrogen atom in a microwave field has received much attention [10, 15, 25]. We will, however, center attention on the ‘random phase’ limit, familiar to scattering theorists [26, 27], which considerably simplifies the discussion. In this limit, which is well justified by numerical results [7], the phase \( \phi \) varies so much between one revolution and another that \( \sin \phi \) can be regarded as a random variable. The analytical justification is that, even in zeroth order (cf. Eq. (2.11)), in the \( \chi > 1 \) regime the phase change is indeed large. The map which consists of Eqs. (2.10) and (2.11) is so simple that it can be iterated on a programmable handheld calculator. It is even simpler in the random-phase approximation:

\[
E_{k+1} = E_k + \kappa \cdot \text{random} \; ,
\]

where \( \kappa \) is a random number in the range \(-1 \) to \(1\), \( \kappa = 2.6d \omega^{4/3} \) and \( E \) is the electron energy where \( E = -1/(2n^2) \). It is instructive to generate trajectories using this map. Despite its simplicity, it captures the essence of the dynamics. When plotted (Fig. 3) against time rather than the orbit index \( k \), the trajectories mimic rather well the results of full dynamical computations [7].

In the random-phase approximation it follows from (2.14) or from (2.9) that

\[
\langle \Delta E \rangle = \langle \Delta n/n^3 \rangle = 0 \; ,
\]

where the brackets denote an ensemble average for one revolution. The ensemble-averaged motion is thus diffusive, without a drift term. The diffusion coefficient, \( D \), is determined by the magnitude of the second moment [16].

For one orbital period (= \( \tau \)) and in the random phase approximation, where the phases of different trajectories are uncorrelated and \( \langle \sin^2 \phi \rangle = 1/2 \), one obtains from (2.9)

\[
\langle (\Delta E)^2 \rangle = \langle (\Delta n)^2/n^6 \rangle = D \; ,
\]

where

\[
D = \kappa^2/2 = 3.4d^2 \omega^{8/3} \; .
\]

Eq. (2.17) is the central result of this section. It will be modified when external fields are present and for higher-dimensional motion. But the changes will only be quantitative. The essential physics is already contained in (2.17): Due to the coupling to the core, the energy of the Rydberg electron undergoes a diffusive motion.

There is an implicit assumption in our discussion. It is that the modulus, \( \kappa n^3 \), of the change in \( n \) per revolution does not suffice to kick the electron to the continuum already in the first round. Of course, even if it does, ionization will not necessarily occur because the actual kick of any particular trajectory is given by \( \kappa n^3 \sin \phi \) and the phase factor can be below unity or even negative. Even so, prompt ionization is possible whenever \( \kappa > - E \) or \( 2\kappa n^2 > 1 \), where \( E \) is the initial energy of the Rydberg state. The condition for possible prompt ionization is

\[
n > \frac{1}{\sqrt{2\kappa}} \; .
\]

The larger is \( \kappa \), \( \kappa = 2.6d \omega^{4/3} \), the wider is the range of initial phases which allow for prompt ionization. For the realistic values \( d = 1 \) au and \( \omega = 1 \times 10^{-5} \) au, (2.18) gives that the onset of prompt ionization is \( n > 1000 \). In the random phase approximation, the fraction of states which undergo prompt ionization can be as high as 1/2. However, since for realistic conditions \( |\Delta n|/n < 1 \) and \( \Delta n/n = \kappa n^3 \sin \phi \), the fraction of states that do promptly ionize is small.

The condition (2.18) for prompt ionization is physically reasonable as \( \kappa \) is the maximal energy that the dipole can deliver in one kick, cf. (2.14). On the other hand, all states can ionize because the total energy is above the ionization threshold.

D. The Kinetic Description

Given that the initial energy \( E_0 \) of the electron is sharply defined, its subsequent distribution at the time \( t \) can be readily written down in the diffusion approximation

\[
P(E, t | E_0, 0) = (4\pi D t)^{-1/2} \exp (- (E - E_0)^2/4D t) \; ,
\]

where \( D \) is the previously derived energy diffusion coefficient, Eq. (2.17). As \( t\to 0 \), (2.19) becomes localized about \( E_0 \). Hence, with this distribution one can discuss the kinetics of the disappearance of states from the ZEKE detection window, following a well defined initial excitation.
energy. Firstly, note that since the detection window spans a finite range of energies about $E_0$, there will typically be a finite induction time before any significant loss of population can be detected. The only exception is if $E_0$ is so low compared to the coupling strength that prompt ionization is possible. Otherwise (Fig. 4), the very steep decline of the wings of Gaussian function (2.19) means that there is a fairly well defined induction time, of the order of $E_0^2/D$, prior to ionization. This is a simple illustration of the more general result of delayed ionization [1, 2]. Since the only degree of freedom we include here is the rotation of the core, the delay is not large. Using (2.17) for $D$, and an initial $n$ of 100, the delay is 0.4 ps for $d = 1$ au and $\omega = 1 \times 10^{-5}$ au. This is typically shorter than the ~100 ns minimal delay time at which detection can start in the time-resolved experiments [17 – 19].

The decay of the population within the detection window is not simply exponential. It can, however, be characterized by the mean first passage time $T(E_0)$ out of the detection window, for a given initial energy. Using the general formalism for one-dimensional Fokker-Planck Eqs. [16], one finds

$$T(E_0) = (E_1 - E_0)(E_0 - E_1)/(2D),$$

where $E_1$ and $E_2$ are the upper and lower ends of the detection window. The experimental results (Fig. 1) do not have quite the simple parabolic dependence on $E_0$ predicted by (2.20). On the other hand, there are too many simplifying assumptions in this derivation to expect a quantitative fit: for example the assumption that the detection window has sharp upper and lower boundaries. Both ends of the window are determined by the onset of field-induced ionization, and one knows [28], that the onset is not a sharp function of the energy of the state.

Fitting Eq. (2.20) to the lifetime vs. $E_0$ plot of the type shown in Fig. 1, results in values of $E_1$ and $E_2$ which are physically realistic. In particular, the energy span of the detection window is found to be of the expected order of 10 cm$^{-1}$.

The interpretation of the shape of the lifetime vs. excitation frequency, as given by (2.20), is in accord with our original suggestion [17]: As the frequency increases, the lifetime first increases because the exit down takes longer, until the point where the exits up and down are equally fast. Beyond that point, the main exit is up, with a rate that increases with $E_0$ so that the lifetime decreases. It is also possible to compute the two exit probabilities [16]:

$$\Pi_1 = (E_0 - E_1)/(E_1 - E_2), \quad \Pi_2 = (E_1 - E_0)/(E_1 - E_2)$$

(2.21)

$$k_1 = 2D/(E_1 - E_0)(E_1 - E_1), \quad k_2 = 2D/(E_0 - E_1)(E_1 - E_1).$$

(2.22)

Fig. 5 shows a comparison of the branching ratios given by (2.21) with results of (three dimensional) trajectory computations [7].

The trajectory computations clearly demonstrate that beyond an early induction time, the up and down processes compete for the same population [8]. The rates for the up and down exits can therefore be computed as $\Pi_1/T$. From (2.21), it is seen that $k_1$ decreases with increasing initial $n$,
with an opposite behavior for \( k_1 \). The two rates are equal midway through the detection window. While a quantitative comparison with experimental results [18] for the two rates is not really warranted, the dependence on the initial \( n \) is well recovered (Fig. 6).

![Graph showing rates for up and down exits from the detection window vs. initial value of the principal quantum number \( n_0 \).](image)

**Fig. 6**

The rates for up and down exits from the detection window vs. the initial value of the principal quantum number \( n_0 \), computed in the diffusion approximation (Eq. (2.22)). The detection window spans the range 90 to 300 in \( n \).

### E. The Onset of Kinetic Behavior

The literature of nonlinear mechanics (e.g., [10–15]) is rather concerned with the question of the onset of diffusive-like behavior in Hamiltonian systems. Why do we take it for granted? The empirical answer is that we have the evidence from trajectory simulations [7, 8, 22] of the Hamiltonian dynamics that for realistic molecular parameters one is in the diffusive regime. The more theoretical answer is that, as shown in Sect. 2.C, the random phase limit is synonymous with a diffusive behavior. In the literature of nonlinear mechanics one typically finds different criteria, the most common one being ‘overlap of resonances’ [10–15]. A map based on the multi-channel quantum defect theory [30] has been discussed in detail in this connection [31]. In this approach, the strength of the coupling is measured by the dependence of the quantum defect on the projection of the electron orbital angular momentum \( l \) on the molecular axis. It has therefore no one-dimensional version.

### 3. The Map in Three Dimensions, Including External Fields

Allowance for the three-dimensional motion of the electron necessarily makes for a more elaborate map: there are two additional quantum numbers for the electron, its orbital angular momentum \( l \) and the projection \( m_l \). These will change not only due to the coupling to the core but also due to the presence of external fields, and it is because of the latter that a three-dimensional description is unavoidable. On the other hand, it will turn out that the changes in \( n \) can be described by a one-dimensional map provided the time axis is ‘stretched’. We have already discussed this stretching of time, from a Hamiltonian point of view, as induced by a DC field [8, 22]. (The Hamiltonian approach in the case of an external magnetic field will be presented in detail elsewhere.) The physics of this ‘stretch’ is very straightforward. A DC field induces a Stark splitting of the energies \( n^2 \) degenerate components of the Rydberg state. In the time domain, this frequency splitting is equivalent to an oscillation in the magnitude of the orbital angular momentum \( l \). Indeed, a forerunner of the idea of a map is the computation reported by Born (cf. Sect. 38 of [9]) of the change in \( l \) per revolution of the electron around the core. (Born includes also a magnetic field, but only the term linear in the field. Unfortunately, at high \( n \)'s one cannot neglect the term which is second order in the magnetic field strength, see equation (3.8) below). The magnitude of \( l \) determines how close the electron gets to the core. (For most of the range of \( l \) values the distance of closest approach is well approximated by \( l(l+1)/2 \). Hence, if \( l \) is large, the electron is isolated from the core, a point recently emphasized as a possible route to long-term stability of high Rydberg states [32–34]. In the presence of a DC field, the magnitude of \( l \) oscillates, with the Stark frequency \( 3nF \) [8]. However, while \( l \) is large, the coupling to the core is ineffective. The presence of the field reduces the number of revolutions during which the electron gets near to the core. This is even more so if a magnetic field is also present. The reason is that the magnetic field changes \( m_l \) (which is conserved for an electrical field in a fixed space direction) and \( l \geq m_l \).

Fig. 7 is an illustration, for a two-dimensional motion, of the time stretch due to a DC field, as computed by the map discussed below. It is seen that \( n \) changes only during those time windows when \( l \) is small. It is simple to show [8] that these ‘windows of opportunity’ span the fraction \( l_0/n \) of any time interval, where the coupling to the core is effective for \( l \leq l_0 \). We also note that there is an onset of the time stretch, determined by the magnitude of the quantum defect [8]. If a magnetic field is also present, the ‘window’ in time shrinks further because \( l \) and \( m_l \) must be simultaneously below \( l_0 \). Further details on the time stretch for combined electrical/magnetic field, and, in particular, on the dependence on the orientation of the two fields, will be provided elsewhere [29]. Suffice it here to say that a magnetic field can significantly enhance the stretch of the time axis.

### A. The Three-Dimensional Map

The new feature in two or three dimensions is that the iteration on \( n \) is coupled to the iteration on \( l \) and, in three dimensions, also on \( m_l \). In other words, all three quantum numbers of the electron need to be simultaneously advanced from one revolution to the next. In general, this can only be implemented numerically, and it provides an efficient algorithm for simulating the motion. However, since at higher
The origin of the 'time stretch' as illustrated directly for the map. Shown are the values of the quantum numbers $(n, l)$ (the angular momentum of the electron) vs. time, for a two-dimensional motion, computed using the map, in the presence of a DC electrical field of $0.1 \text{ V/cm}$ where $d = 10$ and $\omega = 1.11 \times 10^{-3} \text{ au}$. In the presence of the field the magnitude of $l$ executes a periodic variation. Note how $n$ can change only when $l$ is low in absolute value. The reason is, of course, that when $l$ is not near zero, the electron cannot get near to the core, and it is only when it is near to the core that the dipolar coupling is effective (cf. Fig. 2). It follows that the kinetic time 'slows down'. The decay time of the electron is thereby 'stretched' [8, 22]

\[ \Delta n = 2\pi d \omega^2 n^3 \sin \alpha_m \]

\[ \Delta l = 2\pi d \omega^2 n^2 \sin \alpha_m \]

\[ \Delta m = 2\pi d \omega^2 n^2 \sin \alpha_m \]

Here, as before, $\chi = \omega n^3$ is taken to be equal to the nearest integer number, $\varepsilon$ is the eccentricity of the orbit, $c^2 = 1 - l^2/n^2$, the angle variables are identified by the conjugate action variable as a subscript. $m$ is $m_j$, $\phi$ is the phase angle between the position vector $r$ of the electron and the dipole and $\beta$ measures the tilt angle, $\cos \beta = m/l$. The Bessel function [24] is defined by the integral representation (Eq. (2.7)).

There are corresponding changes in $n$, $l$, and $m$, due to the $y$ and $z$ components of the coupling. The contribution of the $y$ component has the same structure as (3.3) except for the changes in the angle variables required by a rotation of $\pi/2$ around the $z$ axis.

\[ \Delta n = 2\pi d \omega^2 n^5 \sin \alpha_m \]

\[ \Delta l = 2\pi d \omega^2 n^2 \sin \alpha_m \]

The angle variable conjugate to $m_j$ is still present in the effective Hamiltonian because the dipole need not rotate in the plane of the orbit of the electron. The changes in $n$, $l$ and $m_j$ per one revolution around the core for the coupling with the $x$ component of the position of the electron are found to be
\[ \Delta m = 2\pi d\omega n^2 \cos \alpha_m \]
\[ - J'_x(\varepsilon \chi) \cos \alpha_i \cos \alpha_m \sin \phi \cos \beta + \\
+ (l/n \varepsilon) J_x(\varepsilon \chi) \sin \alpha_i \cos \alpha_m \cos \phi \cos \beta + \\
+ (l/n \varepsilon) J_x(\varepsilon \chi) \sin \alpha_i \sin \alpha_m \sin \phi + \\
+ J'_x(\varepsilon \chi) \cos \alpha_i \sin \alpha_m \cos \phi \]

(3.4)

The \( z \) component of the coupling leads to
\[ \Delta n = 2\pi d\omega^2 n^2 \sin \beta \]
\[ + J'_x(\varepsilon \chi) \cos \alpha_i \sin \phi + \\
- (l/n \varepsilon) J_x(\varepsilon \chi) \sin \alpha_i \cos \phi \]

(3.5)

\[ \Delta l = 2\pi d\omega n^2 \sin \beta \]
\[ - J'_x(\varepsilon \chi) \sin \alpha_i \cos \phi + \\
+ (l/n \varepsilon) J_x(\varepsilon \chi) \cos \alpha_i \sin \phi \]

\[ m \text{ does not change due to the } z \text{ component because } z \text{ does not depend on } \alpha_m. \]

These equations can be iterated using a map for the changes in the action and angle variables. A simpler procedure is to use an approximate map describing the zeroth order evolution of the angle \( \beta \) and a first order evolution for the others (in zeroth order the other angle variables do not change). In Eq. (3.6) we neglect the dependence of \( \varepsilon \) on \( l \) (\( \partial \varepsilon/\partial l = 1 \cdot n^{-2} \cdot e^{-1} \)), since its contribution is an order of magnitude smaller than the terms retained in (3.6)

\[ \Delta \phi = 2\pi \omega n^3 \]

\[ \Delta \alpha_i = -2\pi d\omega n^2 \]
\[ + (m/l^2) J'_x(\varepsilon \chi) \cos \alpha_i \cos \alpha_m \sin \phi \sin \alpha_m + \\
+ (l/n \varepsilon) J_x(\varepsilon \chi) \sin \alpha_i \sin \alpha_m \sin \phi \cos \alpha_m + \\
- (l/n \varepsilon) J_x(\varepsilon \chi) \cos \alpha_i \cos \alpha_m \phi \cos \alpha_m + \\
+ (m^2/l^3) J'_x(\varepsilon \chi) \cos \alpha_i \cos \phi/\sin \beta + \\
+ (1/n \varepsilon) J_x(\varepsilon \chi) \sin \alpha_i \sin \phi \sin \beta \]

\[ \Delta \alpha_m = -2\pi d\omega n^2 \]
\[ - (1/l) J'_x(\varepsilon \chi) \cos \alpha_i \cos \alpha_m \sin \phi \sin \alpha_m + \\
+ (l/n \varepsilon) J_x(\varepsilon \chi) \sin \alpha_i \cos \alpha_m \phi \sin \alpha_m + \\
- (1/l) J_x(\varepsilon \chi) \cos \alpha_i \sin \alpha_m \sin \phi \cos \alpha_m + \\
- (l/n \varepsilon) J_x(\varepsilon \chi) \sin \alpha_i \sin \alpha_m \cos \phi \cos \alpha_m + \\
+ (m/l^2) J'_x(\varepsilon \chi) \cos \alpha_i \cos \phi/\sin \beta + \\
+ (l/n \varepsilon) J_x(\varepsilon \chi) \sin \alpha_i \sin \phi/\sin \beta \]

(3.6)

It is simplest to use the random-phase approximation for \( \phi \).

Eqs. (3.3)–(3.6) show that up to a factor of \( \chi = \omega n^3 \), the coupling terms for the changes in \( n \) and \( l \) are the same. Figs. 8 and 9 show the magnitude of the coupling terms in

\[ \text{Fig. 8} \]
The coupling terms in the three-dimensional map (Eqs. (3.3)–(3.6)) vs. the rotation frequency \( \omega \) of core. The Bessel functions are defined in the text (Eq. (2.7)). \( \chi \) is the ratio of the core to the electron rotation frequencies \( \chi = \omega n^3 \) and \( \varepsilon \) is the eccentricity of the orbit of the electron. Computed for \( n = 100 \) and \( l = 3 \). The curves are the results of a fit to the \( \omega \) dependence as given by the asymptotic form of the Bessel function. Squares: an \( \omega^{5/3} \) dependence; circles: an \( \omega^{5/3} \) dependence. Note how the additional coupling term that is due to the three-dimensional character of the motion is significantly smaller than the term which is also present in the one-dimensional case.

\[ \text{Fig. 9} \]
Same as Fig. 8 but plotted vs. the quantum number \( n \). \( l = 3, \omega = 4.410^{-5} \text{ au} \). The symbols are a fit to the asymptotic \( n^3 \) dependence

(3.3)–(3.6) plotted vs. \( \omega \) and \( n \) respectively. The first observation is that the derivative, \( J'_x \), of the Bessel function dominates the other term. As discussed in connection with Eq. (2.7), the Bessel function plays the role of the resonance function \([35]\) for the energy transfer from the rotating dipole to the electron. It can therefore be expected to appear in both the one- and three-dimensional versions of the theory. In the three-dimensional case the argument of the Bessel function is not \( \chi \) but \( \varepsilon \chi \), where \( \varepsilon \) is the eccentricity
of the orbit. However, as we already argued, the coupling will, in any case, be confined to lower \( l \) values for which \( \varepsilon \approx 1 \). The three-dimensional map can therefore be approximated by a one-dimensional one.

The second observation about Figs. 8 and 9 is that the change in \( l \) is smaller than the change in \( n \), for realistic values of the parameters. A coupling to the rotating anisotropic core does not suffice to change \( l \) in a marked way, just as is observed in the exact trajectory computations [7].

The cutout of the coupling with increasing distance of closest approach of the electron to the core leads to the results shown in Fig. 10, where the coupling constant is shown vs. \( l \) at two values of \( n \). The steep drop of the coupling, roughly as \( l^{-2} \), is very evident.

\[ \Delta l = -3\pi F n^5 \varepsilon (\sin \alpha_i \cos a_m \cos \beta + \cos \alpha_i \sin a_m) \]
\[ \Delta m = -3\pi F n^5 \varepsilon (\cos \alpha_i \sin a_m \cos \beta + \sin \alpha_i \sin a_m) \] (3.7)

The trajectory shown in Fig. 7 used the result (3.7) but for a two-dimensional motion for which \( m/l = \cos \beta = 0 \). The time intervals during which \( l \) is large so that \( n \) is unchanging are clearly evident in the plot. In general, (3.7) is consistent with the expectation [22] that at the high \( n \)'s of interest, and for fields of realistic strength, \( l \) varies faster as compared to \( n \).

For a magnetic field \( \beta \) in the \( z \) direction, where the coupling is \( Bm + (B^2/8)(r^2 - z^2) \)
\[ \Delta l = -(5/8)\pi B^2 n^7 \varepsilon^2 \sin^2 \beta \sin 2\alpha_i \]
\[ \Delta m = 0 \] (3.8)

C. The One-Dimensional Limit

In the absence of external fields, when \( l \) is essentially unchanged, the similarity between the three- and one-dimensional results is evident. In the presence of the DC field \( l \) changes faster than \( n \). During those revolutions when \( l \) is large, \( n \) will not change. Hence the diffusion constant in the presence of a field is lowered by the fraction of revolutions during which \( l \) is smaller than \( l_0 \). Since at low \( l \) the change in \( l \) is practically independent of \( l \), this fraction is \( l_0/n \), just as for the Hamiltonian problem [8]. When a magnetic field is also present, \( l \) is bounded from below by the value of \( m_i \).

From (3.7) one sees that in the random-phase approximation \( m_i \) is below \( l_0 \) for the fraction \( l_0/n \) of the time. The combined stretch is of the order of \((l_0/n)^{-2}\). The superposition of (not codirected) electrical and magnetic fields can thus induce a significant stretching of the kinetic time axis. In a forthcoming study [29] we shall show that this is also the case for the Hamiltonian approach.

D. The Time Stretched Kinetics

In the presence of a DC electrical field, the kinetic time scale slows down by \( l_0/n \). Eqs. (2.15) and (2.16) are therefore modified to
\[ \langle \Delta n/n^3 \rangle = 0 \quad \langle \Delta n^2/n^6 \rangle = (l_0/n)D \] (3.9)

Since the change in \( n \) per revolution is small, one can rewrite the variance as
\[ \langle \Delta n^2/n^6 \rangle = l_0 D = D' \] (3.10)

Thus, in the presence of a DC electrical field, it is the variable \( X, X = -(2/3)n^{-3/2} \), and not the energy \( E, E = -(1/2)n^{-2} \), that undergoes a pure diffusion
\[ \langle \Delta X^2 \rangle = D' \] (3.11)

with a diffusion coefficient \( D', D' = l_0 D \) defined in (3.10). To every value of \( n \) one can therefore assign a value of \( X \)
to define a detection window also along the $X$ axis. The resulting first passage time out of this detection window is, cf. (2.20),

$$T(X_0) = (X_0 - X_f)(X_i - X_0)/(2D').$$

(3.12)

This is the functional form that was used in Fig. 1 and is compared to the first passage time in the absence of a field, Eq. (2.20), in Fig. 11. While the diffusion coefficient $D'$ is larger than $D$ by an order of magnitude, the variable $X$ is larger than the energy $E$ by even a greater factor so that the exit out of the detection window is indeed slower in the presence of a field.

![Graph](image-url)

**Fig. 11**

The first passage time out of the detection window, plotted (in units of the same diffusion constant $D$, Eq. (2.17)), vs. the initial energy of the Rydberg state, in the absence (upper panel) and the presence (lower panel) of an electrical field. (Eqs. (2.20) and (3.12) respectively, with $l_0 = 10$). Note how the time stretch extends the lifetime

4. **Concluding Remarks**

The essence of the dynamics of a high Rydberg electron, coupled to a rotating molecular core can be captured by a simple map. The additional perturbations caused by the presence of external electrical and magnetic fields can also be discussed. In particular, the concept of a ‘time stretch’, due to such fields, can be derived from the map. The simplicity of the results is due to the rotation of the core being faster than the orbital motion of the electron and to the use of the random phase approximation. The map provides useful insights such as the increase of the strength of the coupling with increasing rotation of the core. Explicit analytical results are derived for the first passage time of the electron out of the detection window and for the fraction of Rydberg states that ionize.

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**References**
