Transition State Theory without Time-Reversal Symmetry: Chaotic Ionization of the Hydrogen Atom

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We present the first application of transition state theory to a system that evolves from an initial to a final state without time-reversal symmetry. The problem studied is the chaotic ionization of a hydrogen atom in crossed electric and magnetic fields. The stable manifolds of the transition state reveal a fractal tiling which connects the geometrical properties of the tiling to the ionization rate, leading to a theoretical explanation for the computational and experimental observation of "prompt" and "delayed" electrons in this problem.

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Transition state theory (TST), introduced by Eyring and Polanyi [1,2] in 1931 as an early attempt to determine absolute reaction rates, is too often considered the domain of the chemist or chemical physicist. However, the transition state (TS) is actually a general property of dynamical systems which involve an evolution from "reactants" to "products." Such processes include, but are by no means limited to, the ionization of atoms, the dissociation or reaction of molecules, and even the escape of an asteroid from its orbit. Conventional TST [3,4] postulates the existence of a minimal set of states that all reactive trajectories must pass through and which are never encountered by any nonreactive trajectories. Thus, the TS is a hypersurface of no return. While, as noted, TST has been used mainly in chemical physics, it also offers considerable advantages in other problems, especially those whose dynamics are nonlinear or chaotic, that involve some form of progression from an initial to a final state.

In the particular problem studied in this Letter, one encounters new challenges not usually found in chemical problems. The resolution of these challenges has important ramifications for the problem at hand, which is of great experimental interest, namely, the ionization of a hydrogen atom in crossed electric and magnetic fields [5,6]. However, our findings go well beyond this particular system which we have chosen, in part, because it allows us to illustrate the key concepts with clarity. The specific peculiarity of the problem we solve is that it is not time-reversal symmetric [7].

In the experiments on the hydrogen atom in crossed electric and magnetic fields, the electric field is present intentionally so as to break the symmetry and thus to unleash the full complexity of the dynamics. This, and similar systems, have confounded conventional treatments of ionization dynamics mainly because the Lorentz force leads to chaotic scattering [6,8,9] which was detected through its quantum signature, Ericsson fluctuations [8]. In a previous paper, we have presented a computational study of this system and a number of novel features were identified [10]. In particular, we found that phase space is divided into three parts: a regular part, an "open" region from which electrons ionize promptly, and a boundary region between the two from which "delayed" electrons ionize only after repeated encounters with the core region [11,12]. This behavior has recently been observed experimentally [6].

In this Letter, we present the solution of this problem using the transition state, and, in the process, extend the theory of the TS itself. Combining TST with modern methods of nonlinear dynamics [13] enables us to use the dynamics to partition phase space. This partitioning is a fractal tiling [14] whose geometrical properties determine the rate of ionization. More generally, our approach also provides an excellent way to picture the scattering dynamics in a large class of experimentally important problems ranging from neutron stars and plasmas to excitonic systems [10].

Our strategy is first to find the TS in the absence of time-reversal symmetry and then use its stable and unstable manifolds [13] to provide information about the progress of the transformation from reactants to products. The resulting TS is shown to be a boundary in phase rather than configuration space and can be used to investigate the fractal structure of the dynamics [15] which in turn determines the rate of ionization.

Theory.—In conventional systems with time-reversal symmetry, the TS is constructed using a potential energy surface [3,4]: One finds the periodic orbits that connect the branches of the equipotentials. Their projections in coordinate space, the so-called periodic orbit dividing surfaces (PODS), partition the coordinate space, and the PODS with minimum flux across it is the TS. The equipotentials are time-reversal symmetry lines, i.e., the time development of the dynamical variables satisfy

$$\begin{aligned} \mathbf{q}(-t + t_0) &= \mathbf{q}(t + t_0), \\ \dot{\mathbf{q}}(-t + t_0) &= -\dot{\mathbf{q}}(t + t_0), \end{aligned} \tag{1}$$

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where the trajectory touches the equipotential at time t_0. Clearly, this prescription fails in the presence of velocity-dependent forces where it is not possible to define a potential energy. Yet lines with analogous properties to the equipotentials can be found, as we are about to show. The TS is once again the projection of an unstable periodic orbit that connects the "time-reversal symmetry lines" (see below). Its stable and unstable manifolds partition phase space [13,15,16]. The volume interior to the stable manifold corresponds to states that eventually ionize, while that of exterior corresponds to states that remain bound for all time. The intersections of this manifold with a Poincaré surface of section yield a fractal tiling [14] of the surface of section; geometrical properties of this tiling are directly related to the rate of ionization.

In the following, we will first identify the time-reversal symmetry lines, then we will present the associated PODS, and finally outline the analysis of the fractal partitioning of phase space yielding the ionization rate.

The Hamiltonian (in atomic units) in Cartesian coordinates for the planar hydrogen atom in crossed electric and magnetic fields is

$$H = \frac{1}{2}(p_x^2 + p_y^2) - \frac{1}{r} + \left[\frac{\omega_c}{2}(xp_y - yp_x) + \frac{{\omega_c}^2}{8}(x^2 + y^2) - \mathcal{E}x\right], \tag{2}$$

where $r = \sqrt{x^2 + y^2}$, ω_c is the cyclotron frequency, and $\mathcal{E}$ is the electric field strength. This model is known to capture the dynamics of the most detailed experiments to date [5]. The terms in the brackets are the paramagnetic term, the diamagnetic term, and the electric field interaction, respectively. The paramagnetic term gives rise to the velocity-dependent forces. This Hamiltonian has a single critical point that is usually called the Stark saddle point [10].

The Coulomb singularity can be eliminated by regularization [10] in semiparabolic coordinates (u, v) [which are defined by $x = (u^2 - v^2)/2$ and $y = uv$] and the resulting Hamiltonian becomes

$$K = \frac{2}{\Omega} = \frac{1}{2}(p_u^2 + p_v^2) + \frac{1}{2}(u^2 + v^2) + \left[\frac{1}{4\Omega^2}(u^2 + v^2)(up_v - vp_u) + \frac{1}{32\Omega^4}(u^2 + v^2)^3 - \frac{\varepsilon}{2\Omega^3}(u^4 - v^4)\right]. \tag{3}$$

where $\Omega = \omega_c^{-1/3}\sqrt{-2H}$ and $\varepsilon = \omega_c^{-4/3}\mathcal{E}$. The equations of motion can be transformed into a form which is symmetric with respect to time reversal by the simple expedient of switching the identity of the momentum and coordinate of one of the pairs of conjugate variables [17] through the canonical transformation

$$v = P_w, \qquad P_v = -w. \tag{4}$$

We choose to exchange the identity of (v, P_v) as opposed to (u, P_u) because the system ionizes in the u direction, and thus we wish to retain u as one of our dynamical variables. In this set of coordinates, the time-reversal symmetry lines are obtained by setting the velocities ($\dot{u} = \dot{w} = 0$) equal to zero, which results in

$$w^2 - \frac{u^3}{2\Omega^2}w + \left(\frac{u^6}{16\Omega^4} - \frac{\varepsilon u^4}{\Omega^3} + u^2 - \frac{4}{\Omega}\right) = 0. \tag{5}$$

Using these curves in place of the equipotentials enables us to construct the TS's.

Periodic orbits.—There are four periodic orbits that connect the two branches of the time-reversal symmetry lines. The projections of these orbits into the (u, v) space are shown in Fig. 1(a), and the projections into (u, w) space [or, equivalently, (u, P_v) space] appear in Fig. 1(b). The values of the parameters used in these calculations are scaled energy $(\omega_c^{-2/3}H) = -1.52$, corresponding to $\Omega = \sqrt{3.04}$ and $\varepsilon = 0.6$. The two orbits in the center, labeled (iii) and (iv), are, respectively, the uphill and downhill periodic orbits associated with the Stark effect. The two outer orbits, labeled (i) and (ii), lie above the Stark saddle and correspond to the TS. In Fig. 2, we show the projections of the outer orbits in the original variables: Observe that in the original coordinate space, Fig. 2(a), the periodic orbit corresponding to the TS does not encounter the boundaries of the classically allowed region; however, when projected into the (x, P_y) phase plane, it does touch the time-reversal symmetry lines, clearly demonstrating that it is a PODS. The two TS's

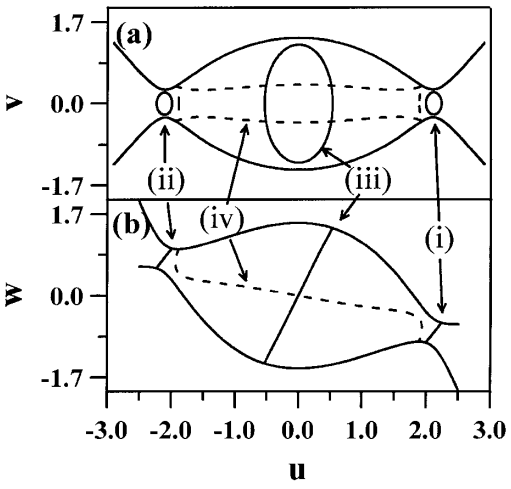

FIG. 1. The PODS that touch both time-reversal symmetry lines at a field strength $\varepsilon = 0.6$ well above the ionization threshold ($\Omega = \sqrt{3.04}$). Shown in (a) are the projections of these orbits into the (u, v) space and in (b) into the (u, P_v) space.

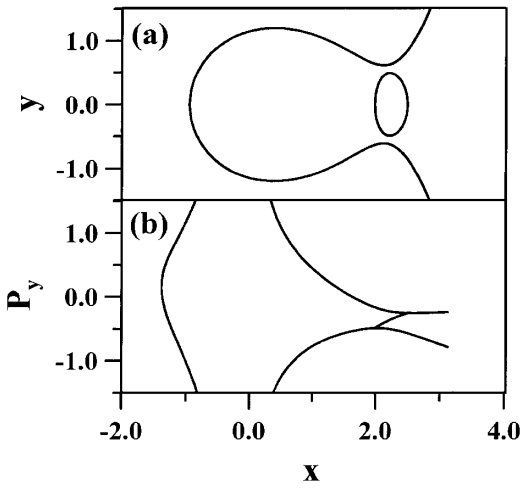

FIG. 2. The PODS that corresponds to the transition state. In (a) this orbit is shown in the original Cartesian space (x, y) and in (b) in the (x, P_y) space. $(\varepsilon = 0.60, \Omega = \sqrt{3.04})$.

seen in Fig. 1 represent a single TS in Fig. 2 because of doubling of phase space during the regularization of the Hamiltonian. Again, because of this doubling the electron can ionize to the left or to the right. Ionization to the right requires an odd number of periods, ionization to the left an even number.

Next, we construct the stable manifolds of the PODS and examine their intersections with a conveniently chosen Poincaré surface of section, which for our purposes is constructed using the central periodic orbit [labeled (iii) in Fig. 1]. For electric field strengths well below the ionization threshold, the surfaces of section are characteristic of two coupled oscillators. With increasing electric field strength, but still below the ionization threshold, one observes the onset of chaotic behavior. This gives rise to a chaotic sea in an annulus around the periodic orbit labeled (iv) in Fig. 1. When the field strength is just above the ionization threshold, the chaotic sea is drained by the ionization. Typically, an ionizing classical trajectory intersects the surface of section many times, behavior characteristic of chaotic ionization. At field strengths well above the ionization threshold, one sees the onset of "prompt" ionization, i.e., electrons ionizing without orbiting about the nucleus. The following discussion focuses on the chaotic ionization processes.

The unstable periodic orbits identified as PODS possess stable and unstable manifolds of codimension-1 (like a line on a surface) and thus partition the classical phase space [13]. The volumes interior to the stable manifold correspond to states that will ionize sometime in the future, while those exterior to the manifold will remain bound for all time. The partitioning of phase space by the unstable manifold is similar: Those states within the unstable manifold correspond to the capture of the electron at some time in the past, while those exterior to the manifold have been bound for all previous times. The trajectories that lie outside both the stable and unstable manifolds are bound in both the infinite future and the past.

Ionization mechanism.—In order to investigate the dynamics of chaotic ionization, we examine the intersections of the stable manifolds with the Poincaré surface of section. The partitioning of the surface of section by the stable manifolds, which is shown in Fig. 3, is a fractal tiling [15]. If we follow the stable manifold of the transition state on the right backwards in time until it intersects the surface of section, we obtain a closed curve. The interior of this curve is a tile and is labeled (1) in Fig. 3. It represents all states that will ionize within the next period [18]. Following the stable manifold of the transition state on the left backwards in time until it intersects the surface of section yields a second tile that is wrapped around the first tile. This tile is labeled (2). It corresponds to all states that will ionize in two periods. Following the two manifolds backwards in time until their second intersection with the surface of section yields two more tiles, which are labeled (3) and (4). The states associated with the tile labeled (3) will pass through the tile labeled (1) in two periods and then will ionize during the third period. Similarly, the states represented by the tile labeled (4) will pass through tile (2) in two periods and will then ionize during the fourth period. Repeating this swirling and stretching exercise *ad infinitum* we obtain a fractal tiling of the surface of section; the states interior to each tile will ionize in a specific number of periods. The fractal boundary between the totally regular parts of phase space and the regions of phase space that ionize promptly explains the existence of prompt and delayed ionizing electrons [6].

The area of the nth tile, α_n, is proportional to the number of states that will ionize during the nth period. If, in the limit $n \to \infty$, the areas of the tiles obey a scaling

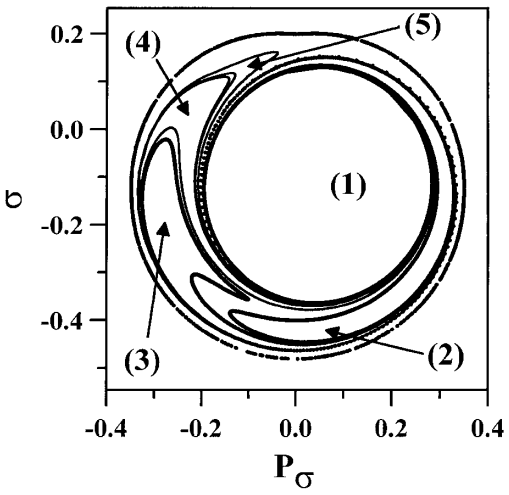

FIG. 3. The tiling of the periodic orbit surface of section for an electric field strength of $\varepsilon = 0.60$ $(\Omega = \sqrt{3.04})$.

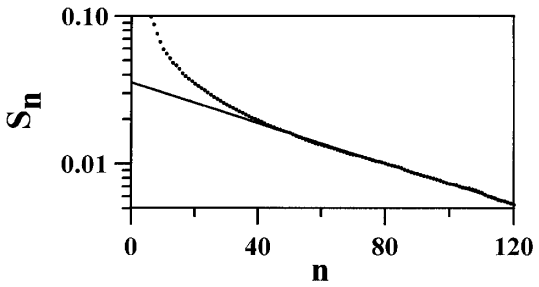

FIG. 4. The survival probabilities for an electric field strength $\varepsilon = 0.60$ ($\Omega = \sqrt{3.04}$).

law of the form $\alpha_{n+1} = \eta\alpha_n$, where η is the scaling parameter, then this scaling parameter is related to the classical rate of ionization. In the long time limit, the number of states ionizing during each period will be an exponential function of the number of periods, that is,

$$F_n \propto e^{-nk}, \tag{6}$$

where k is the classical rate of ionization. Making use of the scaling relation, the number of states ionizing during the nth period will be proportional to η^n and thus the classical rate of ionization is given by

$$k = -\ln\eta\,. \tag{7}$$

Shown in Fig. 4 is the survival probability, that is, the number of states that have not ionized after n periods. After an induction period, the survival probability behaves exponentially, verifying our expectations concerning the scaling law. This clearly establishes the connection between the fractal geometry imposed upon phase space by the dynamics.

We have shown by construction that there is a TS in the planar crossed fields problem, which, when viewed as a PODS, reveals the mechanism of chaotic scattering that characterizes these systems. Its stable manifolds are used to partition the surface of section into a fractal tiling. The properties of this tiling provide the connection between the fractal geometry and the physical observables: Specifically, the states associated with a particular tile will ionize after a specific number of periods and the areas of the tiles obey a simple scaling law, leading to the connection between the geometrical properties of the tiling and the ionization rate. This analysis clearly establishes the utility of TST in the analysis of chaotic ionization in the presences of velocity-dependent forces.

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