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Charge transfer in the Rydberg Hydrogen atom metal surface interaction: A Transition State Approach

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Abstract

We study the classical dynamics of a hydrogen atom near a metallic surface in the presence of a uniform electric field. By continuation of families of periodic orbits and surfaces of section we show that, due to the electric field, the atom falls into a Stark regime through two pitchfork bifurcations. The charge transfer is studiedy using the Dynamical Transition State Theory. Indeed, we obtain analytically the geometrical structures that in phase space regulate the ionization of the atom and we calculate efficiently the ionization probability as a function of the electric field strength.

The Problem

- A Rydberg hydrogen atom perturbed by a metal surface located at $z=-d$, and by a static electric field $\vec{F}=F\,\widehat{z}$, can be described by the 2-dof Hamiltonian ($P_\phi=0$) [1]:

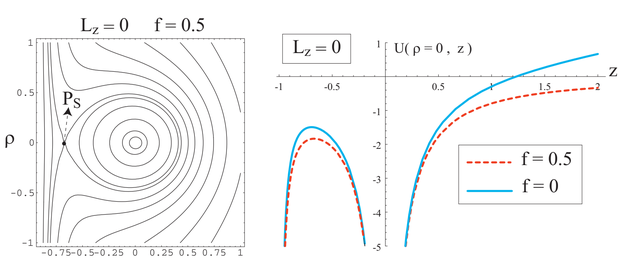
$$H=\frac{P_r^2+P_z^2}{2}-\frac{1}{\sqrt{\rho^2+z^2}}+\frac{1}{\sqrt{\rho^2+(2d+z)^2}}-\frac{1}{4(d+z)}+Fz,$$

- Scaling as $\mathbf{r}'=\mathbf{r}/d$, $\mathbf{P}'=d^{1/2}\mathbf{P}$ we get (dropping primes):

$$\mathcal{H}=\frac{P_r^2+P_z^2}{2}-\frac{1}{\sqrt{\rho^2+z^2}}+\frac{1}{\sqrt{\rho^2+(2+z)^2}}-\frac{1}{4(1+z)}+fz,$$

where $\mathcal{H}=H\,d$ and $f=F\,d^2$ is the scaled electric field.

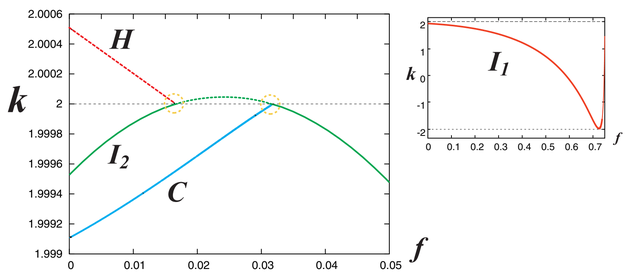
- Escape channel through the saddle point $P_s=(0,z_s<0)$.

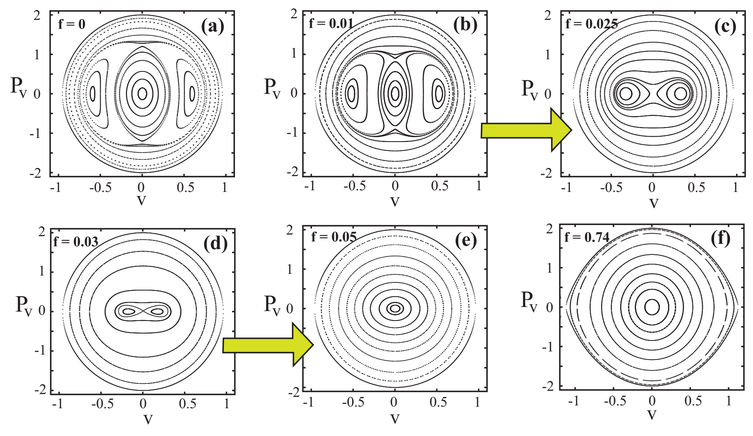


Phase space evolution:Stark regime

- We use numerical continuation of families of periodic orbits ($P.O.s$) and surfaces of section (SOS).

- Evolution of the stability parameter k and the $SOS's$ as a function of f: There are two pitchfork bifurcations.





- After bifurcations, a **Stark-like regime** prevails because the electric field polarizes the atom along the z-axis [2].

Dynamical Transition State Theory

- There exist in phase-space of a minimal set of states, the Transition State (TS), that all reactive trajectories cross.

- Dynamical Transition State Theory ($DTST$): Algorithmic procedure to determine analytically the geometrical objects that separate "reactants" from "products [3].

- Around P_s, a sequence of canonical transformations between the old $(x_1,..,x_n,p_{x_1},..,p_{x_n})$ and the new $(q_1,..,q_n,p_1,..,p_n)$ coordinates lead $\mathcal{H}$ to normal form $\mathcal{K}$.

- As a function of the new n integrals $(J_1,...,J_{n-1},I)$, $\mathcal{K}=\mathcal{K}(J_1,...,J_{n-1},I)$, $J_i=(q_i^2+p_i^2)/2$, $I=(q_n^2-p_n^2)/2$,

- The manifold $q_n=p_n=0$ defines a $(2n-3)$ normally hyperbolic invariant manifold ($NHIM$)that acts like a higher-dimensional saddle point [4].

- The $(2n-2)$-sphere obtained by setting $q_n=0$ in $\mathcal{K}$ is the TS. The $NHIM$ is the limit ("equator") of the TS.

- The TS is locally a surface of no return.

- The $NHIM$ is unstable: It has stable $\mathcal{W}^s$ and unstable $\mathcal{W}^u$ manifolds which act like multidimensional separatrices.

- The $(2n-2)$-spherical cylinders $\mathcal{W}^s$ and $\mathcal{W}^u$ are given by setting, respectively, $p_n=\pm q_n$ in $\mathcal{K}$.

- $\mathcal{W}^s$ and $\mathcal{W}^u$ bound a region in the $(2n-1)$-dimensional energy surface $\mathcal{K}$ that is divided into two components by the TS. All reacting trajectories start in one component, cross the TS and enter the other component.

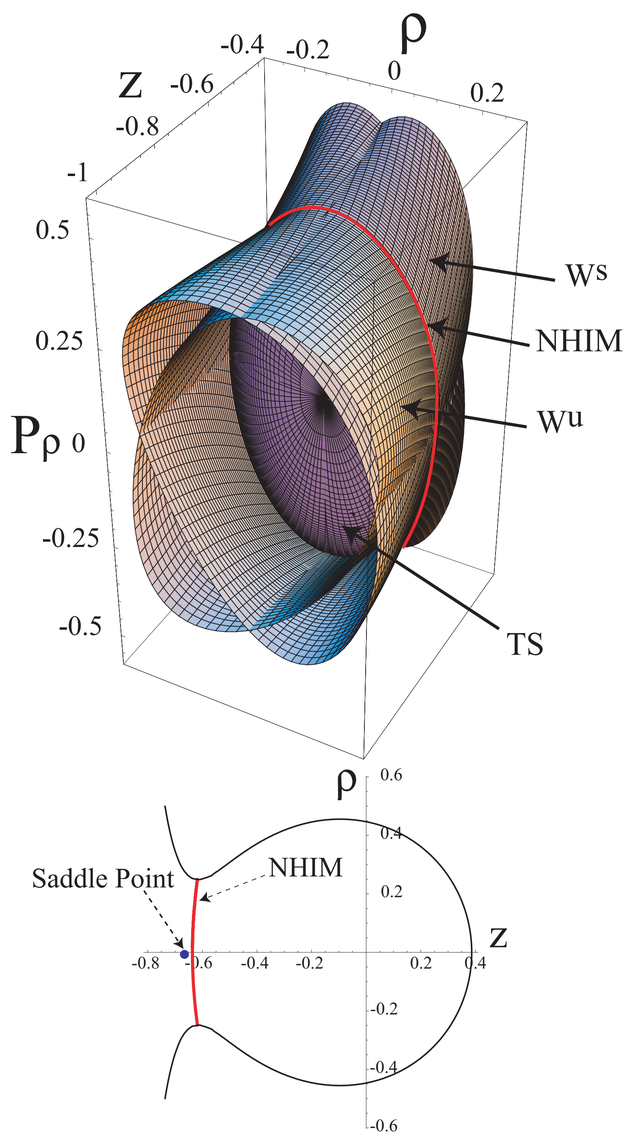
Charge transfer: $DTST$ approach

- To ionize, the electron must to overcome a potential energy barrier P_s and this process resembles a chemical reaction.

- We compute the normal form $\mathcal{K}$ up to the order N:
$\mathcal{K}=\mathcal{K}(J,\mathcal{I}),\quad J=(P_{\rho_N}^2+\rho_N^2)/2,\quad \mathcal{I}=(P_{z_N}^2-z_N^2)/2,$

- The $NHIM$, the TS, $\mathcal{W}^s$ and $\mathcal{W}^u$ are obtained by setting in $\mathcal{K}$, respectively, $J=0$, $z_N=0$ and $P_{z_N}=\pm z_N$.

- $\mathcal{H}$ is a 2-dof system $\Rightarrow$ The $NHIM$ is a $P.O.$.



Ionization Probability P_∞

- For a given energy, P_∞ is the fraction of the total bound initial conditions that lead to escape trajectories:

$$P_\infty=\frac{V_e}{V_o},$$

$V_e\equiv$ Phase-space volume of escape trajectories
$V_0\equiv$ Total phase-space volume

- Mean passage time of the initial conditions on the TS [5]:

$$<t>=\frac{\int_{TS} t\;d\rho_N\;dP_{\rho_N}}{\int_{TS} d\rho_N\;dP_{\rho_N}},$$

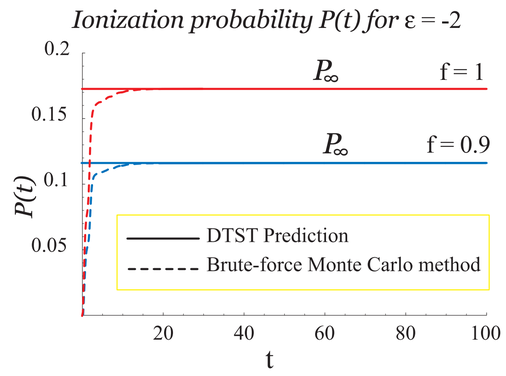
- By using the Spectral Theorem [6]:$V_e=\int_{TS} t\;d\rho_N\;dP_{\rho_N}$.

- The flux ϕ_{TS} through the TS is the action of the $NHIM$:

$$\phi_{TS}=\int_{TS} d\rho_N\;dP_{\rho_N}=\oint_{NHIM} d\rho_N\;dP_{\rho_N},$$

$$V_e=<t>\int_{TS} d\rho_N\;dP_{\rho_N}=<t>\;\phi_{TS}.$$

- This method is much more efficient than the standard brute–force Monte Carlo sampling method.



Acknowledgments

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