Chaotic Ionization of the Rydberg Hydrogen Atom Through Its Dynamic Reactivity Profiles

Pratim Kumar Chattaraj, Utpal Sarkar and Debesh Ranjan Roy

Abstract- The quantum signature of chaos in hydrogen atom has been studied using dynamical profiles of various reactivity parameters like chemical potential, hardness, polarizability, phase volume and electrophilicity index. Pertinent time dependent Schrödinger equation is solved in gaining insights into the ground (n=1) and excited state (n=25) dynamics of hydrogen. Hardness and phase volume show marked difference for these two states. It appears that smaller hardness and larger phase volume signal chaotic dynamics. Other quantities also lend additional support.

Keywords- Chaotic ionization, Rydberg atoms, Density functional theory (DFT), Chemical reactivity parameters, Quantum chaos, Maximum hardness principle, Minimum polarizability principle, Electrophilicity.

I. INTRODUCTION

In recent times the experimental [1] and theoretical [2] studies of highly excited hydrogen atoms by intense oscillating electromagnetic fields have generated great interest, opening the way to study collisions, photoionization, electron-core interaction etc. Sanders and Jenson [3] provide the classical theory of this exotic phenomenon. Hydrogen atom in an oscillating electric field is a periodically perturbed nonlinear oscillator. The equations of motion can become chaotic for a suitable strength of the perturbing force. We have presented a study of chaotic ionization using time dependence of various reactivity indices.

There are many reactivity parameters in density functional theory (DFT) [4] with the help of which the structure, reactivity and dynamics of a many-electron system can be described. Diagnostics used for this study include electronegativity [5], hardness [6], time dependent polarizability [7], phase volume [8,9] and electrophilicity index [9]. The electronegativity and hardness of an N-electron system with total energy E can be written, within density functional frame work, as

\[ \chi = -\mu = -\left( \frac{\partial E}{\partial N} \right)_{\nu(\vec{r})} \]  

and

\[ \eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_{\nu(\vec{r})} = \frac{1}{2} \left( \frac{\partial \mu}{\partial N} \right)_{\nu(\vec{r})} \]  

where \( \mu \) and \( \nu(\vec{r}) \) are chemical potential and external potential respectively. Hardness can be equivalently described [10] as

\[ \eta = \frac{1}{N} \int \eta(\vec{r},\vec{r}') f(\vec{r}') \rho(\vec{r}) d\vec{r} d\vec{r}' \]  

where \( f(\vec{r}) \) is the Fukui function [11] and the hardness kernel is given by [10]

\[ \eta(\vec{r},\vec{r}') = \frac{1}{2} \left( \frac{\delta^2 F[\rho]}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \right) \]  

F[\rho] being the Hohenberg- kohn universal functional of DFT [4].

To obtain the local fukui function [11], we use

\[ f(\vec{r}) = \frac{s(\vec{r})}{\int s(\vec{r}) d\vec{r}} \]  

where \( s(\vec{r}) \) is the local softness as prescribed by Fuentealba [12]

\[ s(\vec{r}) = \frac{\delta^2}{\delta \rho(\vec{r})^2} \frac{\delta(\vec{r} - \vec{r}')}{2\eta(\vec{r},\vec{r}')} \]  

For a many-electron system F[\rho] may be taken as

\[ F[\rho] = \frac{1}{2} \rho(\vec{r},\vec{t}) \nabla \chi(\vec{r},\vec{t}) \]  

\[ + T[\rho] + \frac{1}{2} \int \rho(\vec{r},\vec{t}) \nabla \chi(\vec{r},\vec{t})^2 d\vec{r} + T[\rho] + \frac{1}{2} \int \rho(\vec{r},\vec{t}) \nabla \chi(\vec{r},\vec{t}) d\vec{r} d\vec{r}' \]  

where the first term represents the macroscopic kinetic energy, the last term represents the exchange-correlation energy and T[\rho] is the intrinsic kinetic energy given by [7]

\[ T[\rho] = T_0[\rho] + T_w[\rho] - a(N) \lambda \int \frac{\rho(\vec{r},\vec{t})}{1 + \rho(\vec{r},\vec{t})^{1/3}} d\vec{r} \]  

where \( T_0[\rho] \) is the Thomas-Fermi functional [4], \( T_w[\rho] \) is the Weizsäcker functional [4], \( \lambda \) is a constant [7] and a(N) is an N-dependent parameter [7].

To calculate \( \eta(\vec{r},\vec{r}') \) the following local form of \( F[\rho] \) is used [7]

\[ F_{local}[\rho] = T_{local}[\rho] + E_{xc}[\rho] \]  

where the local kinetic energy [7,13] \( T_{local}[\rho] \) is taken as

\[ T_{local}[\rho] = \frac{1}{m} \left( 3\pi^2 \right)^{1/3} \int \rho^{1/3}(\vec{r}) d\vec{r} + \frac{1}{4\pi} \left( 3\pi^2 \right)^{1/3} \int \frac{\rho^{4/3}}{1 + \rho^{1/3}} d\vec{r} \]  

Pratim Kumar Chattaraj, Utpal Sarkar and Debesh Ranjan Roy are with the Department of Chemistry, I.I.T. Kharagpur-721302, India. (e-mail Address: pkc@chem.iitkgp.ernet.in, utpal@chem.iitkgp.ernet.in and debesh@chem.iitkgp.ernet.in)
and $E_{xc}^{local}[\rho]$ is given by

$$ E_{xc}^{local}[\rho] = -\frac{3}{4\pi} \int \rho^{1/3} d\mathbf{r} + \int \frac{\rho}{r \omega_{\infty}} d\mathbf{r} - \int \frac{\rho}{9.81 \times 21.437 \rho^{1/3}} d\mathbf{r} \quad [10b] $$

The $z$-component of the time-dependent dipole polarizability tensor is used to define the polarizability as

$$ \alpha(t) = \frac{|D_{z}(t)|}{\epsilon_0} \quad [11] $$

where $D_{z}(t)$ is the $z$-component of the electronic part of the induced dipole moment and $\epsilon_0$ is the maximum amplitude of the external field.

The phase volume or uncertainty product $[8,14]$ is defined as

$$ V_{\rho\phi} = \left\{ \left( p_{\rho} - \left< p_{\rho} \right> \right)^{2} \left( p_{\phi} - \left< p_{\phi} \right> \right)^{2} \left( \phi - \left< \phi \right> \right)^{2} \left( \rho - \left< \rho \right> \right)^{2} \left( \phi - \left< \phi \right> \right)^{2} \right\}^{1/2} \quad [12] $$

This quantity is an important diagnostic of the quantum signature of classical chaos $[8]$.

The electrophilicity index (W) is defined as $[9]

$$ W = \frac{\omega_{\infty}}{\eta} \quad [13] $$

which is a measure of the propensity to absorb electrons.

The Sanderson’s principle $[15]$ states that “electronegativity of all atoms in a molecule are equal” and the statement of maximum hardness principle (MHP) $[16]$ is “there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible”. On the other hand, the minimum polarizability principle (MPP) $[7]$ states that “the natural direction of evolution of any system is toward a state of minimum polarizability”. Chattaraj and Sengupta $[14]$ have shown that when a system goes from a regular to a chaotic region, the hardness value often decreases. In order to understand the chaotic dynamics in the quantum domain we study the interaction of the H-atom in two different electronic states ($n=1,25$). Theoretical background is presented in section II and section III contains the results and discussions. Section IV presents some concluding remarks.

II. THE PHYSICAL PROBLEM AND THE METHOD OF SOLUTION

In the present work we study the time evolution of $\psi_{1S}$ and $\psi_{25s}$ wave function of the hydrogen atom placed in an external electric field. The time dependent Schrödinger equation in cylindrical polar coordinates ($\rho, z, \phi$) is

$$ \left[ -\frac{1}{2} \nabla^{2} + V(\mathbf{r}, t) \right] \psi(\mathbf{r}, t) = i \frac{\partial \psi(\mathbf{r}, t)}{\partial t} \quad [14] $$

where the potential $V(\mathbf{r})$ is given by

$$ V(\mathbf{r}) = -\frac{1}{\mathbf{r}} + V_{ext}(\mathbf{r}, t) \quad [15] $$

Here $V_{ext}(\mathbf{r}, t)$, is the external potential for the electric field polarized in the $z$-direction can be written as

$$ V_{ext}(\mathbf{r}, t) = \epsilon \sin(\omega t) Z \quad [16] $$

To have a slow oscillation during and after the laser field being switched on, $\epsilon$ is written in terms of the maximum amplitude $\epsilon_0$ and the switch on time $t'$ as

$$ \epsilon = \epsilon_0 \frac{t}{t'} \quad [17a] $$

$$ = \epsilon_0 \quad \text{otherwise} \quad [17b] $$

The time dependent Schrödinger equation (TDSE) is solved numerically by using alternating direction implicit method $[17]$. As the electron density is varying along $\rho$ axis, we make the transformation

$$ y = \tilde{\rho} \psi \quad [18] $$

$$ \tilde{\rho} = \rho^2 \quad [19] $$

Equation (14) takes the following form in the transformed variables after the analytical integration is carried out $0 \leq \phi \leq 2\pi$,

$$ \left\{\frac{\partial y}{\partial x} \frac{\partial y}{\partial x} - \frac{\partial^2 y}{\partial x^2} - \frac{\partial^2 y}{\partial z^2} \right\} - \left( \frac{1}{\epsilon^2} - 2 \nu \right) y = 2 i \frac{\partial y}{\partial t} \quad [20] $$

The numerical solution proceeds with $\psi_{1S}$ and $\psi_{25s}$. The resulting tridiagonal matrix is solved using Thomas algorithm. Mesh size adopted here are $\Delta t = 0.4$ au and $\Delta x = 0.01$ au.

The initial and boundary condition associated with this problem are

$$ y(x, z) \text{ is known for } \forall \ x, z \text{ at } t=0 \quad [21a] $$

$$ y(0, z) = 0 = y(\infty, z) \text{ for } \forall \ z, t \quad [21b] $$

$$ y(x, z=0) = 0 \quad \forall \ x, t \quad [21c] $$

The numerical scheme is stable $[18]$ because of the presence of $i = \sqrt{-1}$. We have verified the conservation of the norm and energy (in zero field case) as well. Calculations are done in double precision. The parameters are taken as $\epsilon_0 = 0.1$, $t=14$ and $\omega = 4\pi$ (all are in atomic units).

Figure 1. Time evolution of the external electric field.
III. RESULTS AND DISCUSSION

The time dependence of different quantities are presented in figures 1–6. Red color represents excited state and blue color represents ground state. Figure 1 presents the time dependence of external electric field. Figure 2 depicts the behavior of chemical potential ($\mu$). Chemical potential has higher value in the ground state as compared to the excited state.

![Figure 2](image2.png)

Figure 2. Time evolution of chemical potential in the presence of the external electric field. Excited State (---), Ground State (--), intensity=0.1 au, $\omega=4\pi$, $t^* = \frac{4\pi}{\omega}$.

![Figure 3](image3.png)

Figure 3. Time evolution of chemical hardness in the presence of the external electric field. Excited State (---), Ground State (--), intensity=0.1 au, $\omega=4\pi$, $t^* = \frac{4\pi}{\omega}$.

The time evolution of chemical hardness ($\eta$) is presented in figure 3. Chemical hardness is larger in the ground state than in the excited as would have been expected from MHP [16]. It is clear from the figure that there is an oscillation in the $\eta$ profile which is neither in-phase nor steady through out.

The time dependent polarizability $\alpha(t)$ is given in figure 4. The $\alpha(t)$ value of ground state is less than the excited state which is in conformity with the MPP [7]. The $\alpha(t)$ oscillations are not in-phase with that of the external field. Figure 5 depicts the dynamics of phase volume (uncertainty product), $V_p$. The phase volume has smaller value in the ground state than that of the excited state. The phase volume is slowing increasing in the ground whereas in the excited state it is rapidly increasing. In both the cases phase volume is oscillating neither in-phase nor out-of phase.

![Figure 4](image4.png)

Figure 4. Time evolution of time dependent polarizability in the presence of the external electric field. Excited State (---), Ground State (--), intensity=0.1 au, $\omega=4\pi$, $t^* = \frac{4\pi}{\omega}$.

![Figure 5](image5.png)

Figure 5. Time evolution of phase volume in the presence of the external electric field. Excited State (---), Ground State (--), intensity=0.1 au, $\omega=4\pi$, $t^* = \frac{4\pi}{\omega}$.

![Figure 6](image6.png)

Figure 6. Time evolution of electrophilicity index in the presence of the external electric field. Excited State (---), Ground State (--), intensity=0.1 au, $\omega=4\pi$, $t^* = \frac{4\pi}{\omega}$.
Since the electron density is more compact in the ground state than in the excited state, the corresponding uncertainty product is expected to be small in ground state than that of the excited state. Large phase volume for the excited state discards the chaotic behavior owing to larger quantum fluctuations in the less compact electron cloud in the phase space in comparison to the ground state.

The time dependence of electrophilicity index (W) is presented in figure 6. The excited state electrophilicity index is larger in magnitude in comparison to the ground state. In the present study we found that the profiles of $\mu$ mirror the profile of W because electronegativity and electrophilicity ought to follow similar trends.

IV. CONCLUDING REMARKS

Dynamics of hydrogen atom in its ground state and excited state in the presence of intense laser field have been studied in terms of the time evolution of the hardness, polarizability, uncertainty product and electrophilicity. A large value of uncertainty product in the excited state implies a possible chaotic dynamics where as a larger hardness value in the ground state is expected to characterize a regular behavior. In the ground state atom is harder, less polarizable with smaller phase volume, chemical potential and electrophilicity index than the excited state.

ACKNOWLEDGMENTS

Financial assistance from CSIR, New Delhi is gratefully acknowledged.

REFERENCES


