

Chemical Reactivity Dynamics and Quantum Chaos in Highly Excited Hydrogen Atoms in an External Field: A Quantum Potential Approach

P. K. Chattaraj* and **B. Maiti**

Department of Chemistry, Indian Institute of Technology, Kharagpur, 721302, India

E-mail: pkc@chem.iitkgp.ernet.in

* Corresponding author.

Received: 13 August 2001 / Accepted: 7 January 2002 / Published: 25 April 2002

Abstract: Dynamical behavior of chemical reactivity indices like electronegativity, hardness, polarizability, electrophilicity and nucleophilicity indices is studied within a quantum fluid density functional framework for the interactions of a hydrogen atom in its ground electronic state ($n = 1$) and an excited electronic state ($n = 20$) with monochromatic and bichromatic laser pulses. Time dependent analogues of various electronic structure principles like the principles of electronegativity equalization, maximum hardness, minimum polarizability and maximum entropy have been found to be operative. Insights into the variation of intensities of the generated higher order harmonics on the color of the external laser field are obtained. The quantum signature of chaos in hydrogen atom has been studied using a quantum theory of motion and quantum fluid dynamics. A hydrogen atom in the electronic ground state ($n = 1$) and in an excited electronic state ($n = 20$) behaves differently when placed in external oscillating monochromatic and bichromatic electric fields. Temporal evolutions of Shannon entropy, quantum Lyapunov exponent and Kolmogorov – Sinai entropy defined in terms of the distance between two initially close Bohmian trajectories for these two cases show marked differences. It appears that a larger uncertainty product and a smaller hardness value signal a chaotic behavior.

Keywords: Chemical reactivity, Electronegativity, Hardness, Hydrogen atom, Quantum theory of motion(QTM), Quantum chaos, Quantum fluid dynamics(QFD), Chaotic dynamics.

I. Introduction

The chaotic ionization of hydrogen atoms [1-3] in highly excited states by microwave fields has become an important area of research for both experimentalists [1-7] and theoreticians [4]. In 1974 Bayfield and Koch [8] first studied the chaotic ionization of hydrogen atoms which has been considered to be very important in atomic theory [1,2,4,5,9-28]. Sanders and Jensen [4] have studied the chaotic ionization of hydrogen and helium using classical mechanics [4]. When the hydrogen atom is promoted to a highly excited state it gets ionized in case the field intensity is above some threshold value and the ionization probability depends on the field intensity [4,6,7]. Standard diagnostics used for the present study include electronegativity (χ), hardness (η), polarizability (α), phase – volume (V_{ps}), electrophilicity index (W), nucleophilicity index ($1/W$), Shannon entropy (S), quantum Lyapunov exponent (Λ) and Kolmogorov – Sinai entropy (H) defined in terms of the distance between two initially close Bohmian trajectories. In this paper we have generated the higher – order harmonics [3,29,30]. The response of the atom when it interacts with the external field vis-à-vis the variation of its reactivity is an important area of research. Electronegativity (χ) [31] and hardness (η) [32] are two cardinal indices of chemical reactivity. Pauling [33] introduced the concept of electronegativity as the power of an atom in a molecule to attract electrons to itself. The concept of hardness was given by Pearson [34] in his hard – soft acid – base (HSAB) principle which states that, “hard likes hard and soft likes soft”. These popular qualitative chemical reactivity concepts have been quantified in density functional theory (DFT) [35]. Another important hardness – related principle is the maximum hardness principle (MHP) [36,37], which states that, “there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible”. The quantitative definitions for electronegativity [38] and hardness [39] for an N – electron system with total energy E can respectively be given as

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \quad (1)$$

and

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})} . \quad (2)$$

In eqs. (1) and (2) μ and $v(\vec{r})$ are chemical potential (Lagrange multiplier associated with the normalization constraint of DFT [34,36]) and external potential respectively. An equivalent expression [40,41] for hardness is

$$\eta = \frac{1}{N} \iint \eta(\vec{r}, \vec{r}') f(\vec{r}') \rho(\vec{r}) d\vec{r} d\vec{r}' \quad (3)$$

where $f(\vec{r})$ is the Fukui function [40] and $\eta(\vec{r}, \vec{r}')$ is the hardness kernel given by [40]

$$\eta(\vec{r}, \vec{r}') = \frac{1}{2} \frac{\delta^2 F[\rho]}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \quad (4)$$

where $F(\rho)$ is the Hohenberg - Kohn universal functional of DFT [35].

The complete characterization of an N – particle system acted on by an external potential $v(\vec{r})$ requires only N and $v(\vec{r})$. The response of the system subjected to a change in N at fixed $v(\vec{r})$ is given by χ and η while the linear response function [34] measures the response of the system when $v(\vec{r})$ is varied at constant N . If the system is kept under the influence of the weak electric field, polarizability (α) takes care of the corresponding response. During molecule formation the electronegativities of the pertinent atoms get equalized [42,43]. A stable configuration or a favorable process is generally associated with maximum hardness [36,37], minimum polarizability [44-47] and maximum entropy [48] values. The conditions for maximum hardness and entropy and minimum polarizability complement the usual minimum energy criterion for stability.

Recently Parr et. al. [49] have defined the electrophilicity index (W) as

$$W = \frac{\mu^2}{2\eta} \quad (5)$$

We also study the behavior of $(1/W)$, a valid candidate for the nucleophilicity index. Note that the quantity $(1-W)$ will also serve the purpose of a nucleophilicity index. It has also been shown recently [50] that the uncertainty product or the phase space volume (V_{ps}) is a measure of quantum fluctuations and hence has bearing in the studies of quantum domain behavior of classically chaotic systems.

It has been already demonstrated [51] that in case we focus our attention to a specific atom / molecule taking part in a chemical reaction the whole procedure can be simulated by the interaction of an atom / molecule with an external field of the strength of the order of the “chemical reaction field”. A molecular reaction dynamics can be envisaged [44] by monitoring the time evolution of the electronegativity of a specific atom from its isolated atom value to the equalized molecular electronegativity value as well as by studying the dynamic profiles of hardness and entropy and how they get maximized and that of the minimization of polarizability during the course of the chemical reaction. In the present work we study the interaction of a hydrogen atom in its ground electronic state and an excited electronic state with laser fields of different colors. The effect of the frequency of the external laser field on the overall reactivity of the atom in its various electronic states vis-à-vis the validity of the associated electronic structure principles in a dynamical context as well as the intensities of the generated higher order harmonics [52] would be understood in this study.

Dynamics of these reactivity parameters (η and α) have been studied [44,46,53] in the contexts of various time dependent processes. Whether η and α can provide some insight into the quantum domain behavior of a classically chaotic system is yet to be analyzed. Hydrogen atoms and molecules in an oscillating electric field have been considered to be “veritable gold mines for exploring the quantum aspects of chaos” [54]. Depending on the frequency and the field intensity, hydrogen [54,55] atoms in the presence of an external field have been shown to exhibit regular / chaotic dynamics. Both quantum fluid dynamics (QFD) [56,57] and quantum theory of motion (QTM) [58,59] have provided quantum signatures of chaos in hydrogen atoms. In QFD [56] the overall motion of the system under

consideration is mapped onto that of a “probability fluid” having density $\rho(\vec{r}, t)$ and current density $j(\vec{r}, t)$ under the influence of the external classical potential augmented by a quantum potential [55-59] and $\rho(\vec{r}, t)$ and $\chi(\vec{r}, t)$ ($j = \rho \nabla \chi$) are respectively obtained [55-59] from the amplitude and the phase of the wave function. In QTM [58], the wave motion is governed by the solution to the time dependent Schrödinger equation (TDSE) and the particle motion is followed by solving the pertinent Newton’s equation of motion with forces originating from both classical and quantum potentials. Important insight into the chaotic dynamics has been obtained [57] through ρ vs $-\chi$ plots which can be considered to be “canonically conjugate”. In QTM it is obtained [59] in terms of the distance between two initially close Bohmian trajectories and the associated Kolmogorov – Sinai entropy.

In the present paper we monitor the possible regular / chaotic dynamics through the time evolution of various reactivity indices of a hydrogen atom in the ground and highly excited electronic states in the presence of one – color and two – color laser pulses. The theoretical background of the present work is provided in section II. Section III presents the numerical details, and the results and discussions are given in section IV. Finally, section V contains some concluding remarks.

II. Theoretical Background

Classical interpretation of quantum mechanics is as old as the quantum mechanics itself. In the Madelung representation [55] the time – dependent Schrödinger equation for a single particle moving under potential $V(\vec{r})$ (in au), viz.

$$\left[-\frac{1}{2} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}, t) = i \frac{\partial \psi(\vec{r}, t)}{\partial t}, \quad i = \sqrt{-1} \quad (6)$$

is transformed into two fluid dynamical equations. Substituting the following polar form of the wave function

$$\psi(\vec{r}, t) = \rho^{1/2}(\vec{r}, t) \exp(i\chi(\vec{r}, t)) \quad (7)$$

in eq. (6) and separating the real and the imaginary parts, one obtains an equation of continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot j = 0 \quad (8a)$$

and an Euler – type equation of motion

$$\frac{\partial v}{\partial t} + (v \cdot \nabla) v = -\nabla (V + V_{qu}). \quad (8b)$$

In eqs (8) the charge density, $\rho(\vec{r}, t)$ and current density, $j(\vec{r}, t)$ is

$$j(\vec{r}, t) = \rho(\vec{r}, t) v(\vec{r}, t) \quad (9a)$$

where the velocity $v(\vec{r}, t)$ can be defined in terms of the phase of the wave function as

$$v(\vec{r}, t) = \dot{\vec{r}} = \nabla \chi(\vec{r}, t) \quad (9b)$$

The quantity V_{qu} appearing in eq. (8b) is called the quantum potential or Bohm potential of hidden variable theory [60] and defined as

$$V_{qu} = -\frac{1}{2} \frac{\nabla^2 \rho^{1/2}}{\rho^{1/2}} \quad (9c)$$

Therefore, in this quantum fluid dynamics [55] the overall motion of the system under consideration can be thought of as a motion of a “probability fluid” having density $\rho(\vec{r}, t)$ and velocity $v(\vec{r}, t)$ under the influence of the external classical potential augmented by a quantum potential, V_{qu} .

For the ground state of a many – particle system, $\rho(\vec{r}, t)$ contains all information [35]. In a time – dependent situation also the time – dependent density functional theory [52] asserts that any physical observable can be expressed as a functional of $\rho(\vec{r}, t)$ and $j(\vec{r}, t)$ and thus allows us to formulate the dynamics in terms of “classical – like” 3D quantities. Although Madelung transformation in terms of $\rho(\vec{r}, t)$ and $j(\vec{r}, t)$ is not straightforward in a many particle situation, we can make use of the time dependent density functional theory in constructing two fluid – dynamical equations in 3D – space. The formalism is termed as quantum fluid density functional theory [61] which has been applied in understanding ion – atom collisions [61-63], atom – field interactions [64,65] and electronegativity [51,66], hardness [66-68] and entropy dynamics [68] in a chemical reaction.

Quantum potential plays a crucial role in the quantum theory of motion [58] as well. In this representation of quantum mechanics developed by de Broglie [69] and Bohm [70], the overall motion of the system is understood in terms of the motion of a particle experiencing forces originating from the classical and quantum potentials. The Newton’s equation of motion for this particle guided by a wave (represented by $\psi(\vec{r}, t)$), a solution to eq. (6) can be written as

$$\left(\frac{\partial}{\partial t} + \dot{\vec{r}} \cdot \nabla \right) (\dot{\vec{r}}) = -\nabla(V + V_{qu}) \Big|_{\vec{r}=\vec{r}(t)} \quad (9d)$$

At a particular instant the solution to the time dependent Schrödinger equation (6) fixes the velocity of the particle (cf. eq. 9b) and, hence, for a given initial position the particle motion can be studied through the solution $\vec{r}(t)$ to the eq. (9b).

Theories based on quantum potential idea have been applied in solving various physico – chemical problems [58, 71-83]. Because of the presence of nonlinearity and also the “classical language”, these theories have been found [57-59, 81-85] to be helpful in understanding the quantum domain behavior of classically chaotic systems which is described as quantum chaology by Berry [86]. The quantum theory of motion, however, allows one to study the quantum chaos in a system without any resort to its classical domain dynamics [58].

The time – dependent Schrödinger equation (in a u.) for the present problem is

$$\left[-\frac{1}{2} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}, t) = i \frac{\partial \psi(\vec{r}, t)}{\partial t} \quad (10a)$$

where the potential $V(\vec{r}, t)$ is given by

$$V(\vec{r}, t) = -\frac{1}{r} + v_{ext}(\vec{r}, t) . \quad (10b)$$

In eq. (10b) the external potential for the monochromatic and bichromatic laser pulses may be written as

$$v_{ext}(\vec{r}, t) = \varepsilon_1 z, \text{ for monochromatic pulse} \tag{10c}$$

$$= \varepsilon_2 z, \text{ for bichromatic pulse} \tag{10d}$$

where

$$\varepsilon_1 = \varepsilon \cos(\omega_0 t) \tag{10e}$$

and

$$\varepsilon_2 = 0.5\varepsilon[\cos(\omega_0 t) + \cos(\omega_1 t)] \tag{10f}$$

To have slow oscillations during and after the source being switched on, ε is written in terms of the maximum amplitude ε_0 and the switch – on time t' as

$$\varepsilon = \varepsilon_0 t / t' \quad \text{for } 0 \leq t \leq t' \tag{10g}$$

$$= \varepsilon_0 \quad \text{otherwise.} \tag{10h}$$

It may be noted that for a many – electron problem one may either solve the associated TDSE or the corresponding generalized nonlinear Schrödinger equation within a quantum fluid density functional framework [46,53,55,63-66,69,89], the latter being three dimensional even in the case of a many – electron system. To construct the hardness kernel (eq 4), we need the Hohenberg – Kohn universal functional $F[\rho]$. For a many – electron system $F[\rho]$ may be taken as [53]

$$F[\rho] = \frac{1}{2} \int \rho(\vec{r}, t) |\nabla \chi(\vec{r}, t)|^2 d\vec{r} + T[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}, t) \rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[\rho] \tag{11a}$$

where the first term is the macroscopic kinetic energy, the last term is the exchange – correlation energy, and $T[\rho]$ is the intrinsic kinetic energy given by [53]

$$T[\rho] = T_0[\rho] + T_w[\rho] - a(N)\lambda \int \frac{\rho^{4/3} / \vec{r}}{1 + \frac{\vec{r} \rho^{1/3}}{0.043}} d\vec{r} \tag{11b}$$

where $T_0[\rho]$ is the Thomas – Fermi functional [88], $T_w[\rho]$ is the Weizsäcker functional [88], λ is a constant [53], $a(N)$ is an N – dependent parameter [53].

For obtaining the global hardness η (eq. 3) we also require the Fukui function $f(\vec{r})$. We employ the following local formula for $f(\vec{r})$,

$$f(\vec{r}) = \frac{s(\vec{r})}{\int s(\vec{r}) d\vec{r}} \tag{11c}$$

where the local softness $s(\vec{r})$ is given as follows as prescribed by Fuentealba [89]

$$s(\vec{r}) = \frac{\delta(\vec{r} - \vec{r}')}{2\eta(\vec{r}, \vec{r}')} \tag{11d}$$

For calculating $\eta(\vec{r}, \vec{r}')$ of the above equation the following local form for $F[\rho]$ is used [53]:

$$F[\rho] = T^{local}[\rho] + V_{ee}^{local}[\rho] \tag{11e}$$

where the local kinetic energy [90] and the electron – electron repulsion energy [91] may be taken as [53]

$$T^{local}[\rho] = T_0[\rho] + \frac{3}{4\pi} (3\pi^2)^{1/2} \int \frac{\rho^{4/3} / \bar{r}}{1 + \frac{\bar{r}\rho^{1/3}}{0.043}} d\bar{r} \tag{11f}$$

and

$$V_{ee}^{local}[\rho] = 0.7937(N - 1)^{2/3} \int \rho^{4/3} d\bar{r}. \tag{11g}$$

Note that the above treatment is applicable to many – electron systems and all electron – electron interaction terms would be absent in the case of a hydrogen atom.

To follow the polarizability dynamics the dynamic polarizability is defined as [44,53]

$$\alpha(t) = |D_{ind}^z(t)| / |\mathfrak{S}_z(t)| \tag{12a}$$

where $D_{ind}^z(t)$ is the electronic part of the induced dipole moment given as

$$D_{ind}^z(t) = \int z\rho(\bar{r},t)d\bar{r} \tag{12b}$$

and $\mathfrak{S}_z(t)$ is the z - component of the external field.

The phase space volume or the uncertainty product V_{ps} has been shown [92] to be an important diagnostic of the quantum signature of classical chaos [92] as related to the compactness of the electron cloud [93]. For the present problem it may be defined as

$$V_{ps} = \left\{ \langle (\mathbf{p}_{\tilde{\rho}} - \langle \mathbf{p}_{\tilde{\rho}} \rangle)^2 \rangle \langle (\mathbf{p}_z - \langle \mathbf{p}_z \rangle)^2 \rangle \langle (\tilde{\rho} - \langle \tilde{\rho} \rangle)^2 \rangle \langle (\mathbf{z} - \langle \mathbf{z} \rangle)^2 \rangle \right\}^{1/2}. \tag{13}$$

A sharp increase in $V_{ps}(t)$ implies a chaotic motion [92] since it is a measure of the associated quantum fluctuations [92].

To generate the harmonic spectrum the induced dipole moment, $D_{ind}^z(t)$ is Fourier transformed to obtain $d(\omega)$. It has been shown [94] that the absolute square of the Fourier transform, $|d(\omega)|^2$ is roughly proportional to the experimental harmonic distribution.

The Shannon entropy is given by

$$S = -k \int \rho \ln(\rho) d\bar{r}, \tag{14}$$

where k is the Boltzmann constant.

We can generate the “quantum trajectory” of a particle for a given initial position from equation (9b). Now, we are in a position to analyze the sensitive dependence on initial condition, a characteristic of a chaotic system. Equation (9b) is solved with two different initial positions of the particle, $(\tilde{\rho}, z)$ and $(\tilde{\rho} + d\tilde{\rho}, z + dz)$, $d\tilde{\rho} = 0$ $dz = 0.01$. Initial momentum of the particle is taken as

zero in all cases. We study the time evolution of phase space distance (D) for the corresponding quantum trajectories defined as [56,59,82,83]

$$D(t) = \left[(\tilde{p}_1(t) - \tilde{p}_2(t))^2 + (z_1(t) - z_2(t))^2 + (p_{\tilde{p}_1}(t) - p_{\tilde{p}_2}(t))^2 + (p_{z_1}(t) - p_{z_2}(t))^2 \right]^{1/2}, \quad (15a)$$

where $(\tilde{p}, p_{\tilde{p}}, z, p_z)$ refers to a point in phase space.

We also calculate the associated Kolmogorov – Sinai entropy as defined [82,83] below

$$H = \sum_{\Lambda_+ > 0} \Lambda_+, \quad (15b)$$

where the Lyapunov exponent is given by [82,83]

$$\Lambda = \lim_{\substack{D(0) \rightarrow 0 \\ t \rightarrow \infty}} \frac{1}{t} \ln [D(t) / D(0)] \quad (15c)$$

According to the Hamilton – Jacobi formulation of quantum mechanics, a positive KS entropy is associated with a chaotic quantum dynamics [59,87].

III. Numerical Solution

The TDSE (eq. 10a) is solved numerically in cylindrical polar coordinates $(\tilde{\rho}, \tilde{\phi}, z)$, as an initial boundary value problem using an alternating direction implicit method [95]. The solution procedure begins with the ψ_{1s} and ψ_{20s} analytical wave functions of the hydrogen atom. Since the electron density varies rapidly near the nucleus and relatively slowly elsewhere, we transform the variables as follows

$$y = \tilde{\rho}\phi \quad (16a)$$

and

$$\tilde{\rho} = x^2. \quad (16b)$$

Eq. (10a) takes the following form in the transformed variables once an analytical integration is carried out over $0 \leq \tilde{\phi} \leq 2\pi$,

$$\left\{ \left(\frac{3}{4x^3} \right) \frac{\partial y}{\partial x} - \left(\frac{1}{4x^2} \right) \frac{\partial^2 y}{\partial x^2} - \frac{\partial^2 y}{\partial z^2} \right\} - \left(\frac{1}{x^4} - 2\nu_{eff} \right) y = 2i \frac{\partial y}{\partial t}. \quad (17)$$

The resulting tridiagonal matrix equation is solved using a Thomas algorithm. The mesh sizes adopted here are $\Delta x = \Delta z = 0.4$ au and $\Delta t = 0.01$ au, ensuring the stability of the forward – time – central – space type numerical scheme adopted here.

The initial and boundary conditions associated with this problem are

$$y(x,z) \text{ is known for } \forall x,z \text{ at } t = 0 \quad (18a)$$

$$y(0,z) = 0 = y(\infty, z) \quad \forall z,t \quad (18b)$$

$$y(x, \pm\infty) = 0 \quad \forall x,t. \quad (18c)$$

The numerical scheme is stable [96] due to the presence of $i = \sqrt{-1}$. As a further check of the numerical accuracy, we have verified the conservation of norm and energy (in zero field cases). The wave function is moved forward to the end of the simulation and then taken back to its initial position by reversing the time direction, where the original profile is reproduced well within the tolerance limit of the present calculation. We have also solved eq. (9b) using a second order Runge – Kutta method to generate the “quantum trajectories” of a given initial position. The field parameters are in atomic units unless otherwise specified.

IV. Results and Discussions

The time evolution of different reactivity parameters are depicted in Figures 1 – 12. All quantities are in atomic units. Unless otherwise specified, in all figures a and b refer to the ground state ($n=1$) and excited state ($n=20$) of the hydrogen atom, respectively, and a red colored solid line and blue colored solid line respectively signify monochromatic and bichromatic pulses.

Figure 1 presents the time dependence of the external field with different frequencies and the same amplitude.

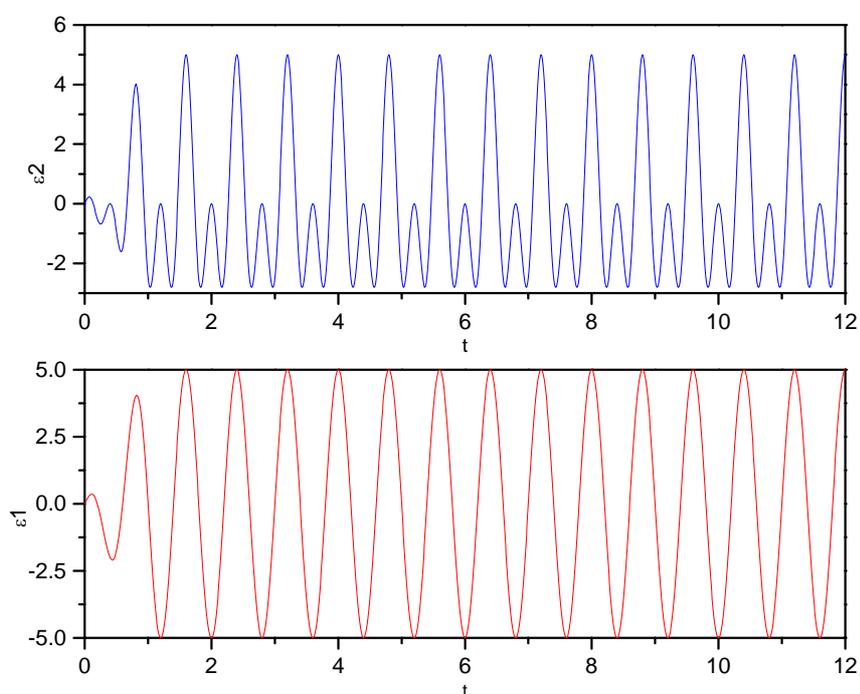


Figure 1: Time evolution of the external electric field: ϵ_1 (—) monochromatic pulse, ϵ_2 (—) bichromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

Temporal evolution of the chemical potential is depicted in Figure 2. It exhibits characteristic oscillations. The oscillations in μ is not in phase with the external field. It is important to note that the amplitude of μ - oscillations becomes very large for both the electronic states and both monochromatic and bichromatic pulses.

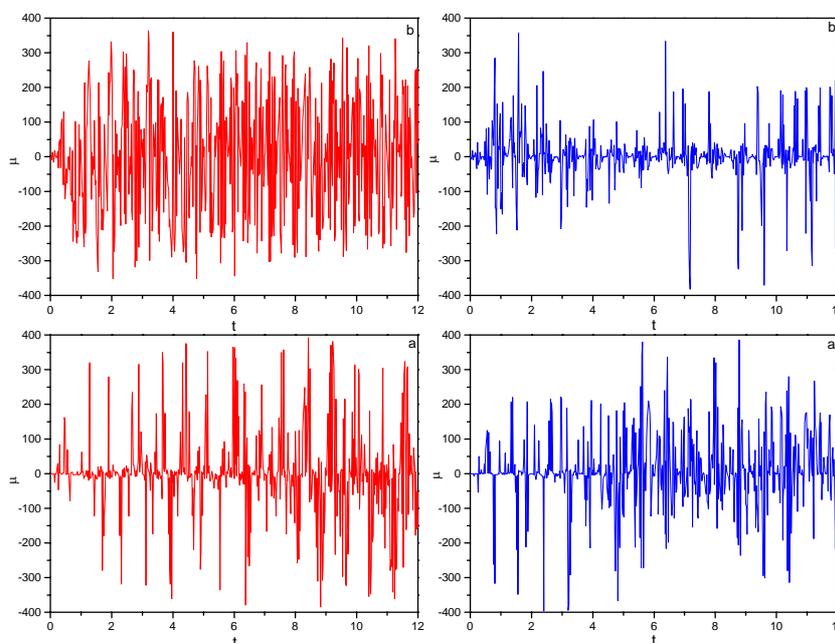


Figure 2: Time evolution of chemical potential (μ) when a hydrogen atom is subjected to external electric fields: a – Ground state; b – Excited state. (—) Monochromatic pulse, (—) bichromatic pulse. Field parameters: $\varepsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

Chemical hardness (η) is presented in Figure 3. For both one and two – color cases η is much larger for $n=1$ state than that of the $n=20$ state for the whole time range. This may be considered to be a dynamical variant of the MHP. Hardness oscillates in time in all the cases. However, the oscillation is neither in phase nor out of phase with respect to the oscillations in the external one – and two – color fields. It is expected because of the fact that as soon as the laser is switched on, there starts a tug – of – war between the atomic nucleus and the external field to govern the electron – density distribution. The nucleus tries to make the density distribution spherically symmetric owing to the central nature of the nuclear coulomb field while the cylindrical symmetry of the applied electric field tries to create an oscillating dipole that emits radiation including higher harmonics. Overall density oscillation becomes nonlinear due to the interplay of two different types of effects. Hardness for the $n=1$ state decreases (for both one – and two - color situations) and attains a more or less steady value at the end of the simulation, which is still large in comparison to the corresponding value for the $n=20$ state. For both

one- and two-color situations, η values relative to the corresponding values in absence of the field (not shown) are much larger for the $n=1$ state. It appears that a relatively smaller η value signals a possible chaotic dynamics.

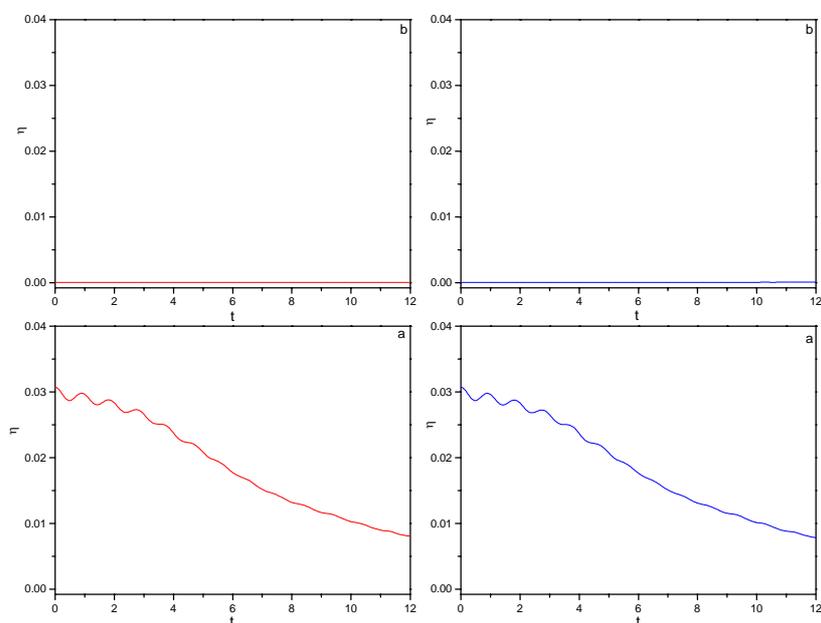


Figure 3: Time evolution of hardness (η) when a hydrogen atom is subjected to external electric fields: a – Ground state; b – Excited state. (—) Monochromatic pulse, (—) bichromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

Polarizability values as they evolve in the course of time are presented in Figure 4. It oscillates with a frequency that is double that of the external field. The extrema in the external field corresponding to the minima in α and the latter blows up when the field is zero. Here also if we compare the respective minimum α values (α_{\min}) for the two electronic states, α_{\min} for the ground state is smaller than that of the excited state which is conspicuous for the bichromatic pulse. This is in conformity with minimum polarizability principle (MPP). The MPP reveals itself in a time-dependent situation.

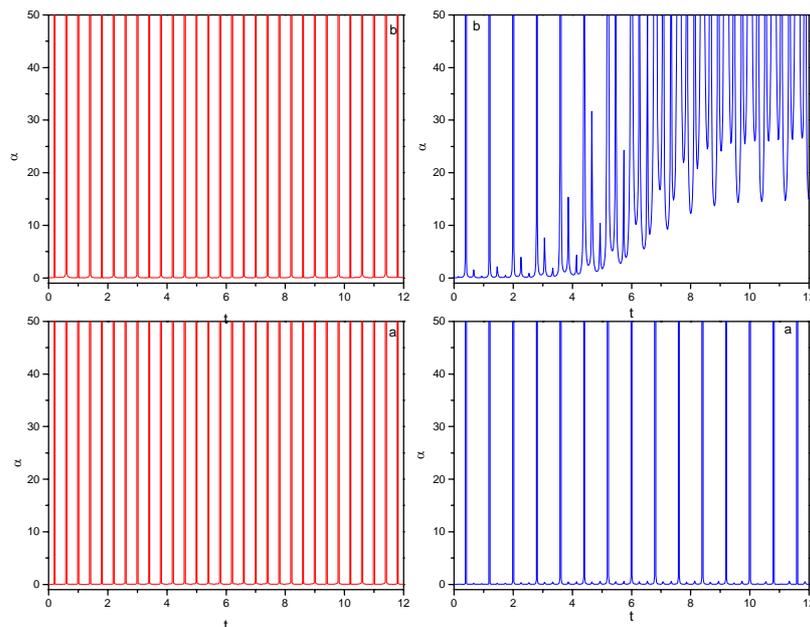


Figure 4: Time evolution of polarizability (α) when a hydrogen atom is subjected to external electric fields: a – Ground state; b – Excited state. (—) Monochromatic pulse, (—) bichromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

Figure 5 depicts the dynamics of the uncertainty product (phase volume). As in the cases of μ and η , V_{ps} also oscillates neither in phase nor out of phase with the external field. The magnitude of V_{ps} retains its initial ($t=0$) small value for the $n=1$ state whereas for the $n=20$ state it increases quickly to a very large value. Since V_{ps} measures the quantum fluctuations, a chaotic trajectory is generally associated with large V_{ps} values [92]. “..... large increases in V_{ps} can be expected to accompany a chaotic trajectory. Conversely, small to moderate increases in V_{ps} can be evidence that given quantum mechanical trajectory should be regarded a nonchaotic [92a]”. In general, the electrons are “tightly bound” and hence the distribution is “less diffuse” for the $n=1$ state and “loosely bound” for the $n=20$ state and the system is expected to be harder and less polarizable for the ground state [32,34,46,53,88,93]. Again, the electron density being more compact in the ground state, the corresponding uncertainty product is expected [93] to be small. Once the external field is switched on, the ground state density would be distributed over a larger volume and consequently there would be a decrease in η and increase in α and V_{ps} of the system. Since a smaller η value is accompanied with a large V_{ps} value and vice versa and V_{ps} is known [92] to bear the signature of the classical chaos in the corresponding quantum domain behavior, hardness can as well be considered to be a diagnostic of the chaotic dynamics in a quantum system.

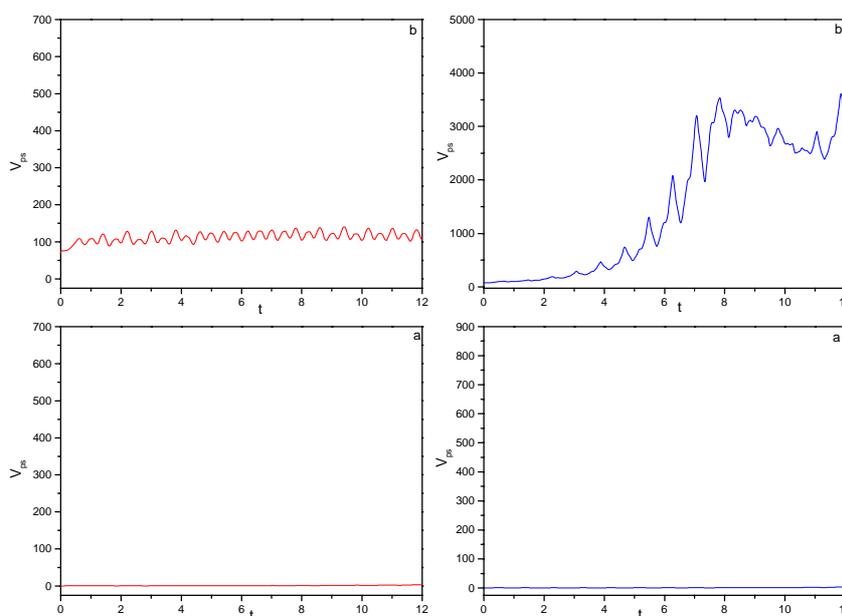


Figure 5: Time evolution of phase volume (V_{ps}) when a hydrogen atom is subjected to external electric fields: a – Ground state; b – Excited state. (—) Monochromatic pulse, (—) bichromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

Figures 6 and 7 depict respectively the dynamical profiles of electrophilicity and nucleophilicity indices respectively. Both W and $1/W$ show oscillations characteristic of the resultant field of two competing ones for both the electronic states and for the one- and two-color pulses.

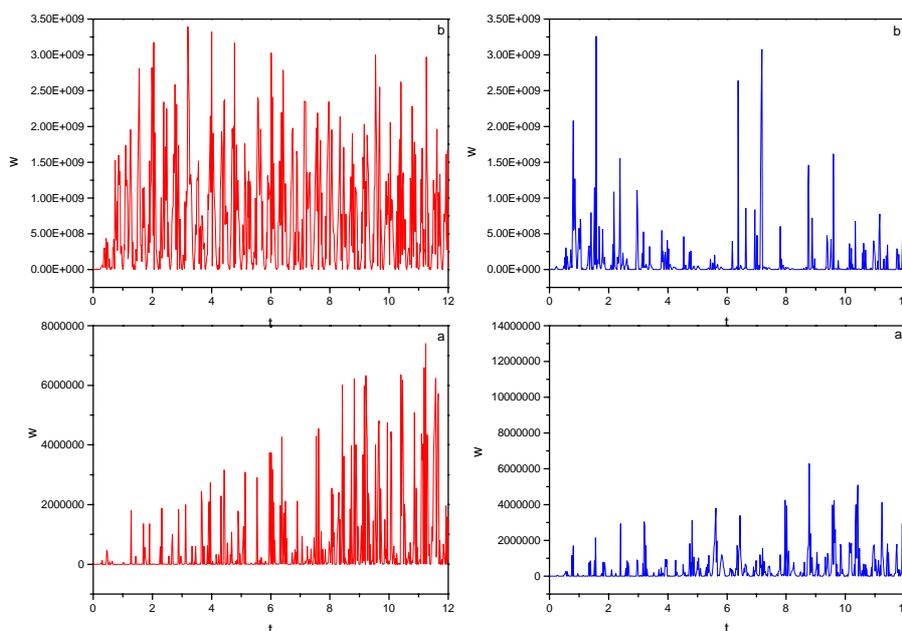


Figure 6: Time evolution of electrophilicity index (W) when a hydrogen atom is subjected to external electric fields: a – Ground state; b – Excited state. (—) Monochromatic pulse, (—) bichromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

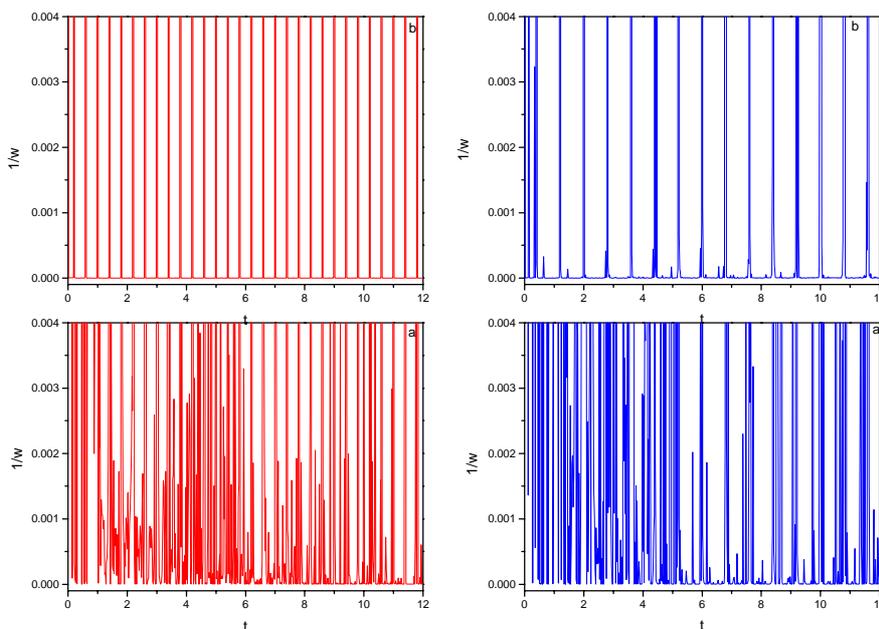


Figure 7: Time evolution of nucleophilicity index ($1/W$) when a hydrogen atom is subjected to external electric fields: a – Ground state; b – Excited state. (—) Monochromatic pulse, (—) bichromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

The harmonic spectra are presented in Figure 8. The overall domain of the spectra and their envelopes look like those reported by Erhard and Gross [52]. We found that the harmonics generated by the monochromatic and bichromatic pulses look similar and those generated from the former is less intense than those resulted from the latter [52].

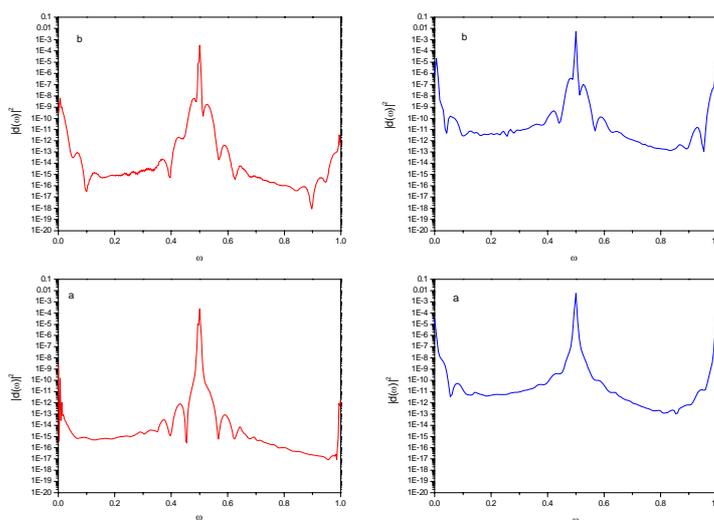


Figure 8: $|d(\omega)|^2$ vs ω plot when a hydrogen atom is subjected to external electric fields: a – Ground state; b – Excited state. (—) Monochromatic pulse, (—) bichromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

Figure 9 depicts the phase ($p_{\tilde{\rho}}$ vs $\tilde{\rho}$ and p_z vs z) of cases a and b for monochromatic laser pulse, The fraction of the total phase space visited by the Bohmian trajectories is much more for the excited state. These plots reflect that the case a is for regular motion whereas the case b is for chaotic motion.

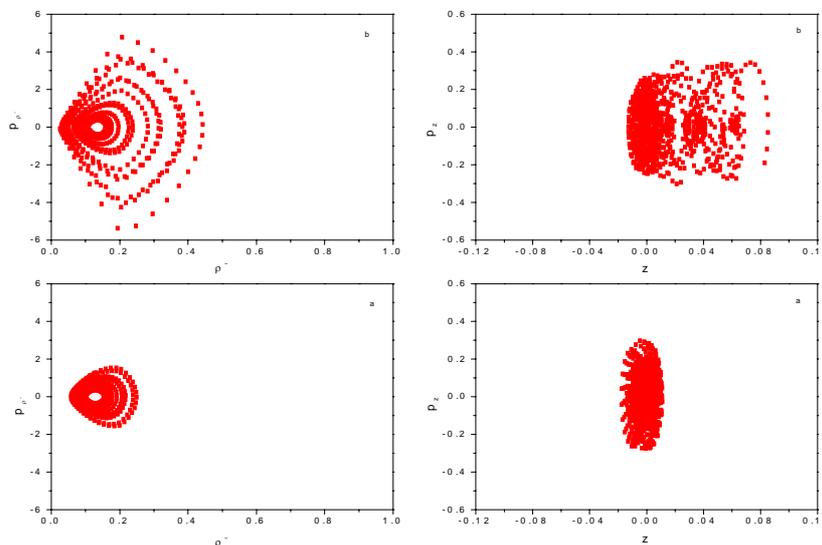


Figure 9: Phase space trajectories when a hydrogen atom is subjected to external electric field: a – Ground state; b – Excited state. (.....) Monochromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

Figure 10 depicts the phase ($p_{\tilde{\rho}}$ vs $\tilde{\rho}$ and p_z vs z) plots case a and b for bichromatic laser pulse. These plots also reflect that the case a is for regular motion whereas the case b is for chaotic motion.

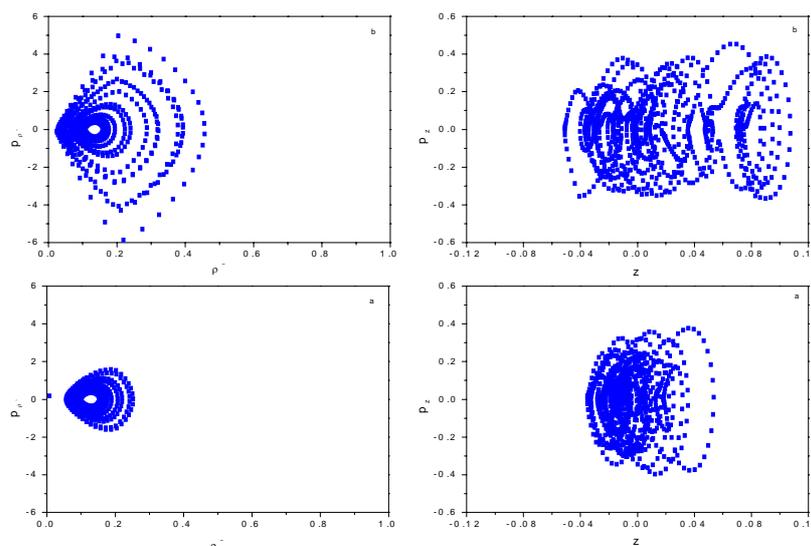


Figure 10: Phase space trajectories when a hydrogen atom is subjected to external electric field: a – Ground state; b – Excited state. (.....) Bichromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

Figure 11 depicts the Kolmogorov – Sinai (KS) entropy for both ground ($n=1$) and excited ($n=20$) states for monochromatic and bichromatic laser pulses. For both monochromatic and bichromatic laser pulses the KS entropy (H) retains its initial very small value for $n=1$. For $n=20$ case H remains small initially and then increases rapidly to a high positive value. The small H value in the former case vis – á – vis the very large H value in the latter provides unmistakable signature of chaos in the highly excited state of the hydrogen atom in presence of an external electric field.

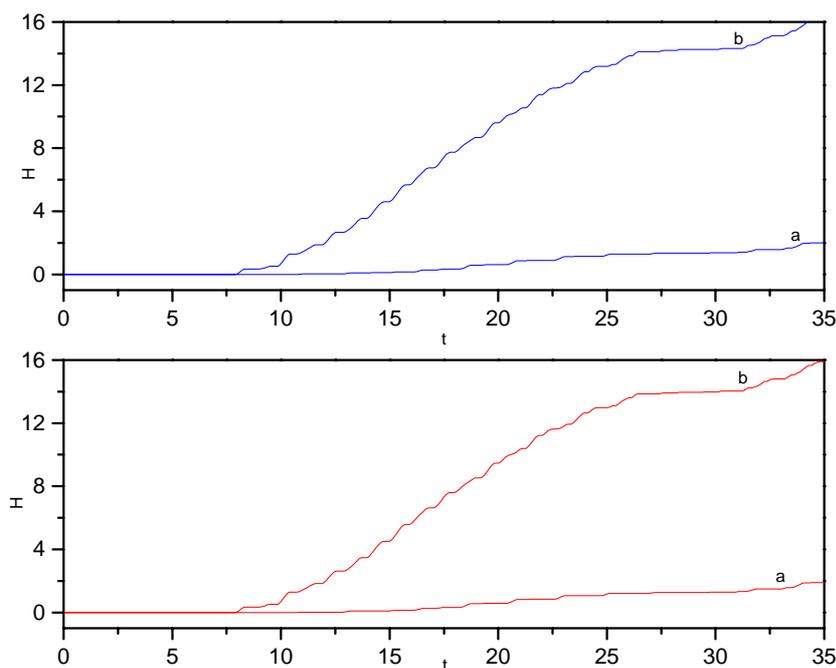


Figure 11: Time evolution of KS entropy (H) when a hydrogen atom is subjected to external electric fields: a – Ground state; b – Excited state. (—) Monochromatic pulse, (—) bichromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

Shannon entropy has been shown in Figure 12. In the figure a and b refer to the ground and $n=20$ states of the hydrogen atom respectively. It increases in the ground state and decreases in the excited state for both the laser pulses, a possible signature of the maximum entropy principle vis – á – vis chaotic ionization from the highly excited state.

It is important to note that the calculations have been carried out up to 3500 au with no change in the qualitative trends. Plots are truncated at a much smaller time steps for easy visualization.

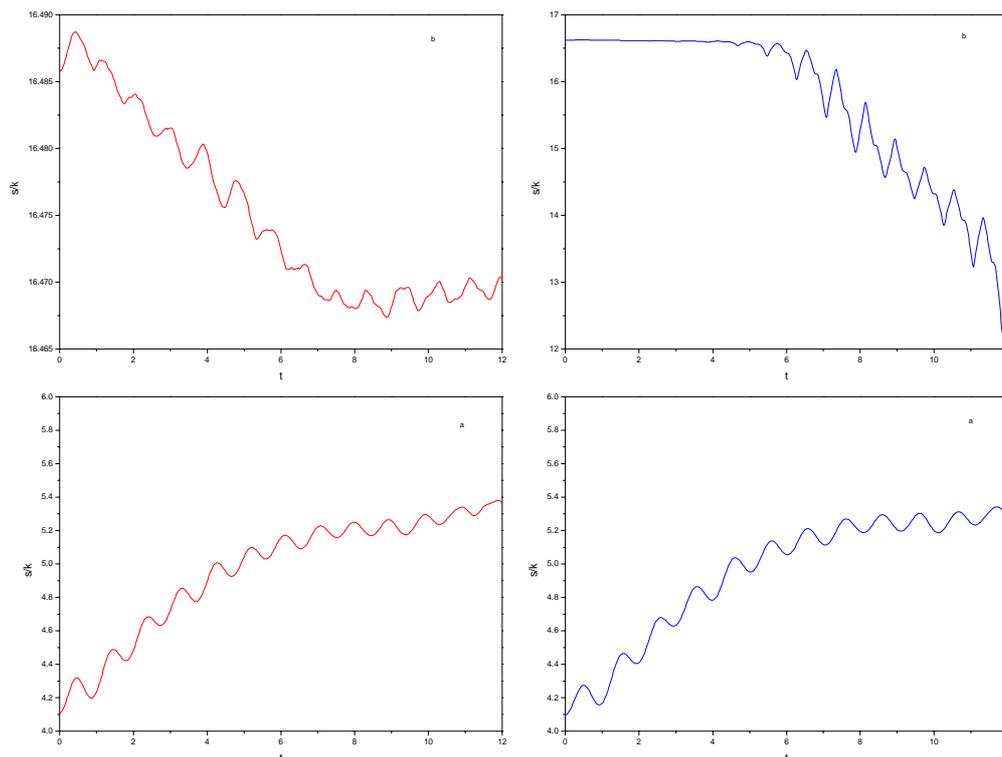


Figure 12: Time evolution of S/k , where S is the Shannon entropy and k is the Boltzmann constant when a hydrogen atom is subjected to external electric fields: a – Ground state; b – Excited state. (—) Monochromatic pulse, (—) bichromatic pulse. Field parameters: $\epsilon_0 = 5.0$; $\omega_0 = 2.5\pi$, $\omega_1 = 2\omega_0$.

V. Concluding Remarks

Quantum potential based theories are adopted to study the reactivity dynamics and chaos of a hydrogen atom in its ground and excited electronic states interacting with z – polarized laser pulses of different colors. Dynamical variants of the principles of electronegativity equalization, maximum hardness, minimum polarizability and maximum entropy manifest themselves. A tug – of – war between the spherically symmetric nuclear coulomb field and cylindrically symmetric external electric field to govern the electron density distribution is delineated through the dynamical profiles of various reactivity indices like electronegativity, hardness, polarzability, electrophilicity, nucleophilicity and phase volume for the external field and in different electronic states. Harmonic spectra of the higher order harmonics included in the radiation emitted by the resulting oscillating dipole have been analyzed. Temporal evolution of Bohmian trajectory, KS entropy and Shannon entropy has easily differentiated the regular and chaotic behavior of hydrogen atom respectively in ground and excited states in presence of an oscillating electric field. For both the laser pulses the increase in the uncertainty product for the excited state is very large, which implies a possible chaotic dynamics. A large hardness value, on the other hand, is expected to characterize a regular behavior.

Acknowledgment

We thank CSIR, New Delhi for financial assistance and Mr. U. Sarkar for help in computation.

References and Notes

1. Jensen, R. V.; Susskind, S. M.; Sanders, M. M. *Phys. Rep.* **1991**, *201*, 1-56.
2. Koch, P. M.; van Leeuwen, K. A. H. *Phys. Rep.* **1995**, *255*, 289 – 403.
3. *Atoms in Intense Laser Fields*; Gavrilu, M. Ed.; Academic Press: Boston, 1992.
4. Sanders, M. M.; Jensen, R. V.; *Am. J. Phys.* **1996**, *64*, 21-31; **1996**, *64*, 1013.
5. Mariani, D. R.; *The Ionisation of Hydrogen and Helium Atoms by Static and Microwave ionization of highly excited hydrogen atoms: Experimental and theory, in the physics of phase space*, edited by Y. S. Kim and W. W. Zachary; Springer, New York, 1987, pp. 106-113.
6. Mariani, D. R.; van de Water, W.; Koch, P. M.; Bergeman, T. *Phys. Rev. Lett.* **1983**, *50*, 1261.
7. van de Water, W.; Yoakum, S.; van Leeuwen, K. A. H.; Sauer, B. E.; Moorman, L.; Galvez, E. J.; Mariani, D. R.; Koch, P. M. *Phys. Rev. A.* **1990**, *42*, 573.
8. Bayfield, J. E.; Koch, P. M. *Phys. Rev. Lett.* **1974**, *33*, 258-261.
9. Koch, P. M.; van Leeuwen, K. A. H.; Rath, O.; Richards, D.; Jensen, R. V. *Microwave ionization of highly excited hydrogen atoms: Experiment and theory, in the physics of phase space*, edited by Y. S. Kim and W. W. Zachary; Springer, New York, 1987, pp. 106-113.
10. van Leeuwen, K. A. H.; Oppen, G. V.; Renwick, S.; Bowlin, J. B.; Koch, P. M.; Jensen, R. V.; Rath, O.; Richards, D.; Leopold, J. G. *Phys. Rev. Lett.* **1985**, *55*, 2231-2234.
11. Galvez, E. J.; Sauer, B. B.; Moorman, L.; Koch, P. M.; Richards, D. *Phys. Rev. Lett.* **1988**, *61*, 2011-2014.
12. Leopold, J. G.; Richards, D. J. *Phys. B At. Mol. Phys.* **1989**, *24*, 1209-1240.
13. Sanders, M. M. *Chaotic Ionisation of One and Two Electron Atom. Ph. D. thesis*, Yale University, New Haven, CT, 1991.
14. Bayfield, J. E. *Am. Sci.* **1983**, *71*, 375-383.
15. Leopold, J. G.; Percival, I. C. *J. Phys. B At. Mol. Phys.* **1979**, *12*, 709-721.
16. Rath, O.; Richards, D. *J. Phys. B* (submitted).
17. Born, M. *The Mechanics of the Atom; Frederick Ungar*, New York, 1960.
18. Leopold, J. G. and Richards, D. J. *Phys. B. At. Mol. Phys.* **1986**, *19*, 1125.
19. Jensen, R. V. *Phys. Rev. Lett.* **1982**, *49*, 1365-1368.
20. Jensen, R. V. *Phys. Rev. A.* **1982**, *30*, 386-397.
21. Schwieters, C. D.; Delos, J. B. *Phys. Rev. A* **1995**, *51*, 1030-1041.
22. Shepelyansky, D. L. *Chaotic Behavior in Quantum System: Theory and Application; Plenum*, New York, 1985, pp. 187 – 197.
23. Lichtenberg, A. J.; Liebergman, M. A. *Regular and Stochastic Motion*, Springer, New York, 1983.

24. Casati, G.; Chirikov, B. V.; Shepelyansky, D. L. *Phys. Rev. Lett.* **1984**, *53*, 2525 – 2528.
25. Casati, G.; Guarneri, L.; Shepelyansky, D. L. *IEEE J. Quantum Electron.* **1988**, *QE – 24*, 1420 – 1444.
26. Jensen, R. V. *Phys. Scr.* **1987**, *35*, 668 – 673.
27. Landau, L. D.; Lifshitz, E. M. *Mechanics, Course of Theoretical Physics*; Pergamon: New York, 1976; Vol. 1.; 3rd ed.
28. Goldstein, H. *Classical Mechanics. Addison – Wesley, Reading, MA*, **1980**, 2nd ed.
29. McPherson, A.; Gibson, G.; Jara, H.; Johann, U.; Luk, T. S.; McIntyre, I. A.; Boyer, K.; Rhodes, C. K. *J. Opt. Soc. Am.* **1987**, *B4*, 595.
30. *Super – Intense Laser – Atom Physics*; Piraux, B.; L’Huillier, A., Rzazewski, K. Eds.; NATO ASI Series B316; Plenum Press: New York, 1993.
31. *Electronegativity: Struct. Bonding*; Sen, K. D.; Jorgenson, C. K. Eds.; Springer–Verlag: Berlin, 1987, Vol. 66.
32. *Chemical Hardness: Struct. Bonding*; Sen, K. D; Mingos, D. M. P.; Eds.; Springer–Verlag: Berlin, 1987; Vol. 66.
33. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
34. Pearson, R. G. *Coord. Chem. Rev.* **1990**, *100*, 403; *Hard and Soft Acids and Bases*; Dowden, Hutchinson and Ross: Stroudsburg, PA, 1973.
35. Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864; Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133; Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press; Oxford, 1989; *Annu. Rev. Phys. Chem.* **1995**, *46*, 701; Chattaraj, P. K. *J. Indian. Chem. Soc.* **1992**, *69*, 173; Kohn, W.; Becke, A. D.; Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974.
36. Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561; *Acc. Chem. Res.* **1993**, *26*, 250; *J. Chem. Educ.* **1999**, *76*, 267.
37. Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1854; Chattaraj, P. K.; Liu, G. H.; Parr, R. G. *Chem. Phys. Lett.* **1995**, *237*, 171; Pearson, R. G. *Chemtracts Inorg. Chem.* **1991**, *3*, 317; Liu, S.; Parr, R. G. *J. Chem. Phys.* **1997**, *106*, 5578; Chattaraj, P. K. *Proc. Indian Natl. Sci. Acad. Part A* **1996**, *62*, 513; Pearson, R. G. *Chemical Hardness: Application from Molecules to Solid*; Wiley–VCH Verlag GMBH: Weinheim, 1997; Ayers, P. W.; Parr, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 2010.
38. Parr, R. G.; Donnelly, D. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.
39. Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.
40. Berkowitz, M.; Ghosh, S. K.; Parr, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6811; Ghosh, S. K.; Berkowitz, M. *J. Chem. Phys.* **1985**, *83*, 2976.
41. Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.
42. Sanderson, R. T. *Science* **1951**, *114*, 670; *Science* **1955**, *121*, 207; *J. Chem. Educ.* **1954**, *31*, 238; Chattaraj, P. K.; Maiti, B.; *J. Chem. Educ.* **2001**, *78*, 811 – 813.

43. Politzer, P.; Weinstein, H. *J. Chem. Phys.* **1979**, *70*, 3680; Parr, R. G.; Bartolotti, L. J. *J. Am. Chem. Soc.* **1982**, *104*, 3081; Nalewajski, R. F. *J. Phys. Chem.* **1985**, *89*, 2831; Mortier, W. J.; Ghosh, S. K.; Shankar, S. *J. Am. Chem. Soc.* **1986**, *108*, 4315.
44. Chattaraj, P. K.; Sengupta, S. *J. Phys. Chem.* **1996**, *100*, 16126.
45. Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1996**, *100*, 12296.
46. Chattaraj, P. K.; Sengupta, S. *J. Phys. Chem. A* **1997**, *101*, 7893.
47. Chattaraj, P. K.; Poddar, A. *J. Phys. Chem. A* **1998**, *102*, 9944; **1999**, *103*, 1274; Chattaraj, P. K.; Fuentealba, P.; Gomez, B.; Contreas, R. *J. Am. Chem. Soc.* **2000**, *122*, 348; Fuentealba P.; Simon – Manso, Y.; Chattaraj, P. K. *J. Phys. Chem. A* **2000**, *104*, 3185; Chattaraj, P. K.; Fuentealba, P.; Jaque, P.; Toro – Labbe, A. *J. Phys. Chem. A* **1999**, *103*, 9307; Chattaraj, P. K.; Maiti, B. *J. Phys. Chem. A* **2001**, *105*, 169 – 183.
48. Jaynes, E. T. *In Statistical Physics*; Ford, K. W., Ed.; Brandeis Lectures, Vol – 3; Benjamin: New York, 1963. Levine, R. D.; Bernstein, R. B. *In Dynamics of Molecular Collisions*; Miller, W. H., Ed.; Plenum Press: New York, 1976; Gadre, S. R.; Bendale, R. D. *Curr. Sci.* **1985**, *54*, 970.
49. Parr, R. G.; Szentpaly, L. v.; Liu, S. *J. Am. Chem. Soc.* **1999**, *121*, 1922.
50. Chattaraj, P. K.; Sengupta, S.; *J. Phys. Chem. A* **1999**, *103*, 6122.
51. Chattaraj, P. K.; Nath, S. *Int. J. Quantum Chem.* **1994**, *49*, 705.
52. Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997; Dhara, A. K.; Ghosh, S. K. *Phys. Rev. A* **1987**, *35*, 442; Erhard, S.; Gross, E. K. U. *In Multiphoton Processes* 1996; Lambropoulos, P.; Walther, H. Eds.; IOP Publishing: London, 1997; pp. 37 – 45 and reference therein.
53. Chattaraj, P. K.; Sengupta, S.; Poddar, A. *Int. J. Quantum Chem.* **1998**, *69*, 279; *In Nonlinear Dynamics and Computational Physics*; Sheorey, V. B. Ed.; Narosa: New Delhi, 1999; pp. 45 – 53.
54. Lakshmanan, M.; Ganeshan, K. *Curr. Sci.* **1995**, *68*, 38.
55. Casati, G.; Chirikov, B. V.; Guarneri, I; Shepelyansky, D. L. *Phys. Rep.* **1987**, *154*, 77; Hasegawa, H.; Robnik, M.; Wunner, G. *Prog. Theo. Phys. Suppl.* **1989**, *98*, 198; Ganeshan, K.; Lakshmanan, M. *Phys. Rev. A* **1990**, *42*, 3940. Howard, J. E.; Farelly, D. *Phys. Lett. A* **1993**, *178*, 62; Delande, D.; Gay, J. C. *Phys. Rev. Lett.* **1987**, *59*, 1809; Delande, D. *Chaos and Quantum Physics*; Elsevier: Amsterdam, 1991; Friedrich, H.; Wintgen, D. *Phys. Rep.* **1989**, *183*, 37; Holle, A.; Weibusch, G.; Main, J.; Hager, B.; Rottke, H.; Welge, K. H. *Phys. Rev. Lett.* **1986**, *56*, 2594; Holle, A.; Marini Rottke, H.; Welge, K. H. *Phys. Rev. Lett.* **1986**, *56*, 2594; Holle, A.; Marini, J.; Weibusch, G.; Rottke, H.; Welge, K. H. *Phys. Rev. Lett.* **1988**, *61*, 161.
56. Madelung, E. *Z. Phys.* **1926**, *40*, 322; Ghosh, S. K.; Deb, B. M. *Phys. Rep.* **1982**, *92*, 1 – 44.
57. Chattaraj, P. K.; Sengupta, S. *Phys. Lett. A* **1993**, *181*, 225; *Ind. J. Pure Appl. Phys.* **1996**, *34*, 518; Chattaraj, P. K. *Ind. J. Pure Appl. Phys.* **1994**, *32*, 101.
58. Holland, P. R. *The Quantum Theory of Motion*; Cambridge University Press: Cambridge, U. K., 1993.
59. Sengupta, S.; Chattaraj, P. K. *Phys. Lett. A* **1996**, *215*, 119; Chattaraj, P. K.; Sengupta, S. *Curr. Sci.* **1996**, *71*, 134; Chattaraj, P. K.; Sengupta, S. *J. Phys. Chem. A* **1999**, *103*, 6122 – 6126.

60. Belinfante, F. J. *A Survey of Hidden Variable Theories*, Pergamon Press, New York, 1973.
61. Deb, B. M.; Chattaraj, P. K. *Phys. Rev. A* **1989**, *39*, 1696 – 1713.
62. Deb, B. M.; Chattaraj, P. K. *Chem. Phys. Lett.* **1988**, *148*, 550 – 556.
63. Deb, B. M.; Chattaraj, P. K.; Mishra, S. *Phys. Rev. A* **1991**, *43*, 1248 – 1257.
64. Chattaraj, P. K. *Int. J. Quant. Chem.* **1992**, *41*, 845 – 859.
65. Deb, B. M.; Dey, B. K. *Int. J. Quant. Chem.* **1995**, *56*
66. Nath, S.; Chattaraj, P. K. *Pramana*, **1995**, *45*, 65 – 73.
67. Chattaraj, P. K.; Nath, S. *Chem. Phys. Lett.* **1994**, *217*, 342 – 348.
68. Chattaraj, P. K.; Nath, S. *Proc. Indian. Acad. Sci. (Ch. Sci.)* **1994**, *106*, 229 – 249.
69. de Broglie, L. *Nonlinear Wave Mechanics: A Causal Interpretation*, Elsevier, Amsterdam, 1993.
70. Bohm, D. *Phys. Rev.* **1952**, *85*, 166 – 179, 180 – 193.
71. Gutzwiller, M. C. *Chaos in Classical and Quantum Mechanics*, Springer, Berlin, 1990.
72. Eckhardt, B. *Phys. Rep.* **1988**, *103*, 205 – 297.
73. Jensen, R. V. *Nature*, **1992**, *355*, 311 – 317; **1995**, *373*, 16 and references therein.
74. Dewdney, C.; Hiley, B. J. *Found. Phys.* **1982**, *12*, 27 – 48.
75. Takabayasi, T. *Prog. Theor. Phys.* **1952**, *8*, 143 – 182; **1953**, *9*, 187 – 222; **1955**, *14*, 283 – 302.
76. Kan, K. K.; Griffin, J. *Phys. Rev. C* **1977**, *15*, 1126 – 1157.
77. Weiner, J. H.; Partom, Y. *Phys. Rev.* **1969**, *187*, 1134 – 1147; Weiner J. H.; Askar, A. *J. Chem. Phys.* **1972**, *54*, 3534 – 3541.
78. McCullough, E. A.; Wyatt, R. E. *J. Chem. Phys.* **1971**, *54*, 3534 – 3541.
79. Hirschfelder, J. O.; Christoph, A. C.; Palke, W. E. *J. Chem. Phys.* **1974**, *61*, 5435 – 5455; Hirschfelder, J. O.; Tang, K. T. *J. Chem. Phys.* **1976**, *64*, 760 – 785; **1976**, *65*, 470 – 486.
80. Skodje, R. T.; Rohrs, H. W.; VanBuskirk, J. *Phys. Rev. A* **1989**, *40*, 2894 – 2916.
81. Parmenter, R. H.; Valentine, R. W. *Phys. Lett. A* **1995**, *201*, 1 – 8.
82. Schwengelbeck, U.; Faisal, F. H. M. *Phys. Lett. A* **1995**, *199*, 281 – 286.
83. Faisal, F. H. M.; Schwengelbeck, U. *Phys. Lett. A* **1995**, *207*, 31 – 36.
84. Misner, C. W.; Thorne, K. S.; Wheeler, J. A. *Gravitation*; W. H. Freeman and Company: San Francisco, 1973.
85. McDonald, S. W.; Kaufman, A. N. *Phys. Rev. Lett.* **1979**, *42*, 1189 – 1191.
86. Berry, M. V. *Proc. R. Soc. A, London*, **1987**, *413*, 183 – 198.
87. Chattaraj, P. K. in *Symmetries and Singularity Structures: Intregability and Chaos in Nonlinear Dynamical Systems*: Lakshmanan, M; Daniel, M, Eds.; Springer-Verlag; Berlin, 1990; pp. 172–182.
88. Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U. K. 1989.
89. Fuentealba, P. *J. Chem. Phys.* **1995**, *103*, 6571
90. Ghosh, S. K.; Deb, B. M. *J. Phys. B* **1994**, *27*, 381.
91. Parr, R. G. *J. Phys. Chem.* **1988**, *92*, 3060.

92. (a) Feit, M. D.; Fleck, J. A., Jr. *J. Chem. Phys.* **1984**, *80*, 2578; (b) Choudhury, S.; Gangopadhyay, G.; Ray, D. S. *Ind. J. Phys. B* **1995**, *69*, 507; (c) Graham, R.; Hohnerbach, M. *Phys. Rev. A* **1991**, *43*, 3966; (d) *Idem. Phys. Rev. Lett.* **1990**, *64*, 637.
93. Pearson, R. G. *Chemical Hardness: Applications from Molecules to Solids*; Wiley – VCH Verlag GMBH; Weinheim, 1997; pp. 116 – 119.
94. L'Huillier, A.; Lompre, L. A.; Mainfray, G.; Manus, C. *In Atoms in Intense Laser Fields*; Gavrila, M. Ed.; Academic Press; Boston, 1992, pp. 139.
95. Ames, W. F. *Numerical Methods for Partial Differential Equations*; Academic: New York, 1977, pp. 252.
96. Chattaraj, P. K.; Rao, K. S.; Deb, B. M. *J. Comput. Phys.* **1987**, *72*, 504.