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Quantum chaos in Rydberg atoms: A quantum potential approach

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The quantum signature of chaos in Rydberg atoms 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 an external oscillating electric field. Temporal evolutions of Shannon entropy, density correlation, phase space distance function of Bohmian trajectories and associated Kolmogorov-Sinai entropy for these two cases show marked differences.

CLASSICAL interpretation of quantum mechanics is as old as the quantum mechanics itself. In the Madelung representation¹ the time-dependent Schrödinger equation for a single particle of mass m moving under potential $V(r)$, viz.

$$[-(\hbar^2/2m)\nabla^2 + V(r)]\Psi(r, t) = i\hbar\partial\Psi/\partial t \quad (1)$$

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

$$\Psi(r, t) = R(r, t) \exp(iS(r, t)/\hbar) \quad (2)$$

in eq. (1) and separating the real and the imaginary parts, one obtains an equation of continuity

$$\partial\rho/\partial t + \nabla \cdot j = 0, \quad (3a)$$

and an Euler-type equation of motion

$$\partial v/\partial t + (v \cdot \nabla)v = -(1/m)\nabla(V + V_{qu}). \quad (3b)$$

In eqs (3) the charge density, $\rho(r, t)$ and current density, $j(r, t)$ are

$$\rho(r, t) = [R(r, t)]^2 \quad (4a)$$

and

$$j(r, t) = \rho(r, t)v(r, t). \quad (4b)$$

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

$$v(r, t) = (1/m)\nabla S(r, t). \quad (4c)$$

The quantity V_{qu} appearing in eq. (3b) is called the quantum potential or Bohm potential of hidden variable theory² and defined as

$$V_{qu} = -(\hbar^2/2m)\nabla^2 R/R. \quad (5)$$

Therefore, in this quantum fluid dynamics¹ the overall motion of the system under consideration can be thought of as the motion of a 'probability fluid' having density $\rho(r, t)$ and velocity $v(r, t)$ under the influence of the external classical potential augmented by a quantum potential, V_{qu} .

For the ground state of a many-particle system, $\rho(r, t)$ contains all information³. In a time-dependent situation

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also the time-dependent density functional theory^{4,5} asserts that any physical observable can be expressed as a functional of $\rho(r, t)$ and $j(r, t)$ and thus allows us to formulate the dynamics in terms of 'classical-like' 3D quantities. Although Madlung transformation in terms of $\rho(r, t)$ and $j(r, t)$ 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. This formalism is termed as quantum fluid density functional theory⁶ which has been applied in understanding ion-atom collisions⁶⁻⁸, atom-field interactions^{9,10} and electronegativity^{11,12}, hardness¹²⁻¹⁴ and entropy dynamics¹⁴ in a chemical reaction.

Quantum potential plays a crucial role in the quantum theory of motion¹⁵ as well. In this representation of quantum mechanics developed by de Broglie¹⁶ and Bohm¹⁷, 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 $\Psi(r, t)$, a solution to eq. (1)) can be written as

$$(\partial/\partial t + \dot{r} \cdot \nabla)(m \dot{r}) = -\nabla(V + V_{qu})|_{r=r(t)} \quad (6)$$

At a particular instant the solution to the time dependent Schrödinger equation (1) fixes the velocity of the particle (cf. eq. 4c) and, hence, for a given initial position the particle motion can be studied through the solution $r(t)$ to the equation

$$v(r, t) = \dot{r} = (1/m)\nabla S(r, t)|_{r=r(t)} \quad (4c)$$

Theories based on quantum potential idea have been applied in solving various physico-chemical problems^{15,18-32}. Because of the presence of nonlinearity and also the 'classical language', these theories have been found^{15,21,22,30,32-34} to be helpful in understanding the quantum domain behaviour of a classically chaotic system which is described as quantum chaology by Berry³⁵. The quantum theory of motion, however, allows one to study the quantum chaos in a system without any resort to its classical domain dynamics¹⁵.

We adopt here a quantum potential approach to study the chaotic dynamics of a typical quantum system, viz. a Rydberg atom in an oscillating electric field. Of late, these systems have been considered to be 'veritable gold mines for exploring the quantum aspects of chaos'³⁶. It has also been discussed³⁷ that depending on the frequency and field intensity, hydrogen atom exhibits order to chaos transition when placed in an external oscillating field. Since hydrogen atom is one of the simplest possible solvable quantum mechanical systems and its classical mechanical counterpart, a Keplerian system, is known to exhibit chaotic dynamics³⁸ in presence of external field, we try to investigate the possible quantum signature of chaos in an electronically excited hydrogen

atom in presence of an external field. Both theoretical³⁹ and experimental⁴⁰ studies have been carried out on this system to understand the chaotic behaviour associated with quadratic Zeeman effect. For a beautiful review on this subject see ref. 36. In the present work we study the time evolution of Ψ_{1s} and Ψ_{20s} wave functions of hydrogen atom placed in an external oscillating electric field with $\omega = 5\pi$ and for both $F = 0$ and $F = 5$. We apply the quantum theory of motion in gaining insights into the possible chaotic dynamics in electronically excited hydrogen atom subjected to an external electric field^{36,37}.

The time-dependent Schrödinger equation (in a.u.) for the present problem in cylindrical polar coordinate system $(\tilde{\rho}, z, \phi)$ is

$$[-\nabla^2/2 + V]\Psi = i\partial\Psi/\partial t \quad (7a)$$

where the potential V is given by

$$V = -1/r + Fz\cos\omega t. \quad (7b)$$

Making use of the following transformations

$$y = \tilde{\rho}\Psi. \quad (8a)$$

$$\tilde{\rho} = x^2 \quad (8b)$$

and integrating over $0 \leq \phi \leq 2\pi$, eqs (7) turn out to be

$$\begin{aligned} & [3/4x^3\partial y/\partial x - 1/4x^2\partial^2 y/\partial x^2 - \partial^2 y/\partial z^2] \\ & - [1/x^4 - 2V]y = 2i\partial y/\partial t. \end{aligned} \quad (9)$$

The above equation is solved as an initial boundary value problem using an alternating direction implicit method⁴¹. The resulting tridiagonal matrix equation is solved using Thomas algorithm. The mesh sizes adopted here are $\Delta x = \Delta z = 0.4$ a.u. and $\Delta t = 0.01$ a.u., ensuring stability of the forward-time-central-space type numerical scheme used here. Note that each alternating direction implicit cycle corresponds to $2\Delta t$ and atomic units of length and time are 0.5292×10^{-10} m and 2.4189×10^{-17} sec respectively.

The initial and boundary conditions associated with this problem are:

$$\text{at } t = 0, y(x, z) \text{ is known for } \forall x, z, \quad (10a)$$

$$y(0, z) = 0 = y(\infty, z) \quad \forall z, t, \quad (10b)$$

$$y(x, \mp \infty) = 0 \quad \forall x, t. \quad (10c)$$

The numerical scheme is stable⁴² due to the presence of $i = \sqrt{-1}$. As a further check of numerical accuracy we have verified the conservation of norm and energy (in zero field cases). The wave function is moved forward up to the end of simulation ($N\Delta t = 7$ a.u.) and then taken back to its initial position where the original profile is reproduced well within the tolerance limit of the present calculation. We could not, however, perform the long time simulation because of our inadequate computational facilities.

The dynamical quantities calculated in the present work are as follows:

a) Shannon entropy given by

$$S = -k \int \rho \ln(\rho) dr,$$

where k is the Boltzmann constant.

b) Density correlation function defined as

$$C = \int \rho^{1/2}(r, 0) \rho^{1/2}(r, t) dr.$$

We have also solved eq. (4c) using a second order Runge-Kutta method to generate the 'quantum trajectory' of a particle for a given initial position. Now, we are in a position to analyse the sensitive dependence on initial condition, a characteristic of a chaotic system. We can change the initial condition in two ways: i) by shifting the wave function slightly and ii) shifting the initial position of the particle slightly. In the first case the time-dependent Schrödinger equation is solved with both $\Psi(r, t=0)$ and $\Psi(r + \Delta, t=0)$ as inputs, $\Delta = 0.01$ while the second case deals with the solution of eq. (4c) with two different initial positions of the particle, $(\bar{\rho}, z)$ and $(\bar{\rho} + d\bar{\rho}, z + dz)$, $d\bar{\rho} = 0$ $dz = 0.01$. 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^{21,31,32}

$$D(t) = ((x_1(t) - x_2(t))^2 + (p_{x_1}(t) - p_{x_2}(t))^2 + (y_1(t) - y_2(t))^2 + (p_{y_1}(t) - p_{y_2}(t))^2)^{1/2}, \quad (11a)$$

where (x, p_x, y, p_y) refers to a point in phase space.

We also calculate the associated Kolmogorov-Sinai entropy as defined^{31,32} below

$$H = \sum_{\Lambda_+ > 0} \Lambda_+, \quad (11b)$$

where the Lyapunov exponent is given by^{31,32}

$$\Lambda = \lim_{t \rightarrow \infty} \frac{1}{t} \ln(D(t)/D(0)). \quad (11c)$$

'Quantum dynamics is chaotic if in a given region of phase space the flow of trajectories, according to the Hamilton-Jacobi formulation of quantum mechanics, has positive KS entropy'³¹. The efficacy of this definition has already been tested in the cases of a quantum Henon-Heiles oscillator²¹, the quantum standard map³¹ and Weigert's quantum cat map³². For the sake of brevity unless otherwise specified, we present the time evolution of all quantities calculated for the non-zero field relative to the corresponding zero field counterpart. The Kolmogorov-Sinai entropy is calculated using this relative distance. In all plots the temporal variation is expressed in terms of the corresponding numerical integration step number, N .

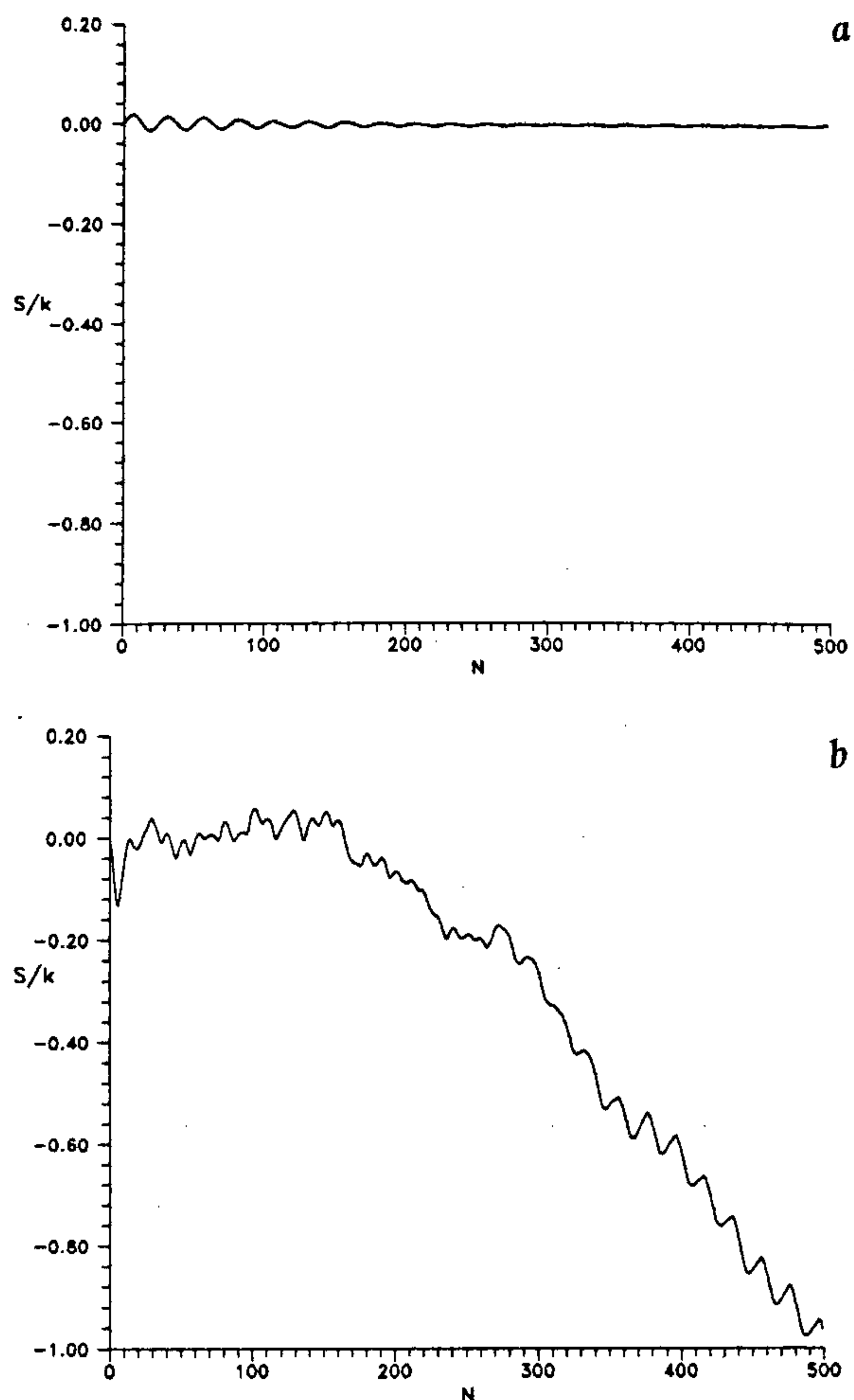


Figure 1a, b. Time evolution of S/k , where S is the Shannon entropy and k is the Boltzmann constant, for Rydberg atom in external field: (a) $n = 1$ (b) $n = 20$.

Shannon entropy and density correlation function have been shown in Figures 1a, b and 2a, b respectively. In both the figures a and b refer to the ground state and $n = 20$ state of the hydrogen atom respectively. As is clear in these figures, the applied field causes drastic change in the dynamics of Ψ_{20s} state of H-atom whereas it hardly has any effect for the ground state. In Figures 1a and 2a we see that entropy and density correlation values for $n = 1$ state do not change when the external field is applied whereas those quantities for $n = 20$ state exhibit (Figures 1b and 2b) significant changes on application of the field of same strength as in the previous case ($n = 1$).

Figures 3a, b depict the time evolution of D and H respectively for the shifted wavepacket case. For clarity we also present the behaviour of D for the non-zero field case (Figure 3c). The distance remains the same (in fact

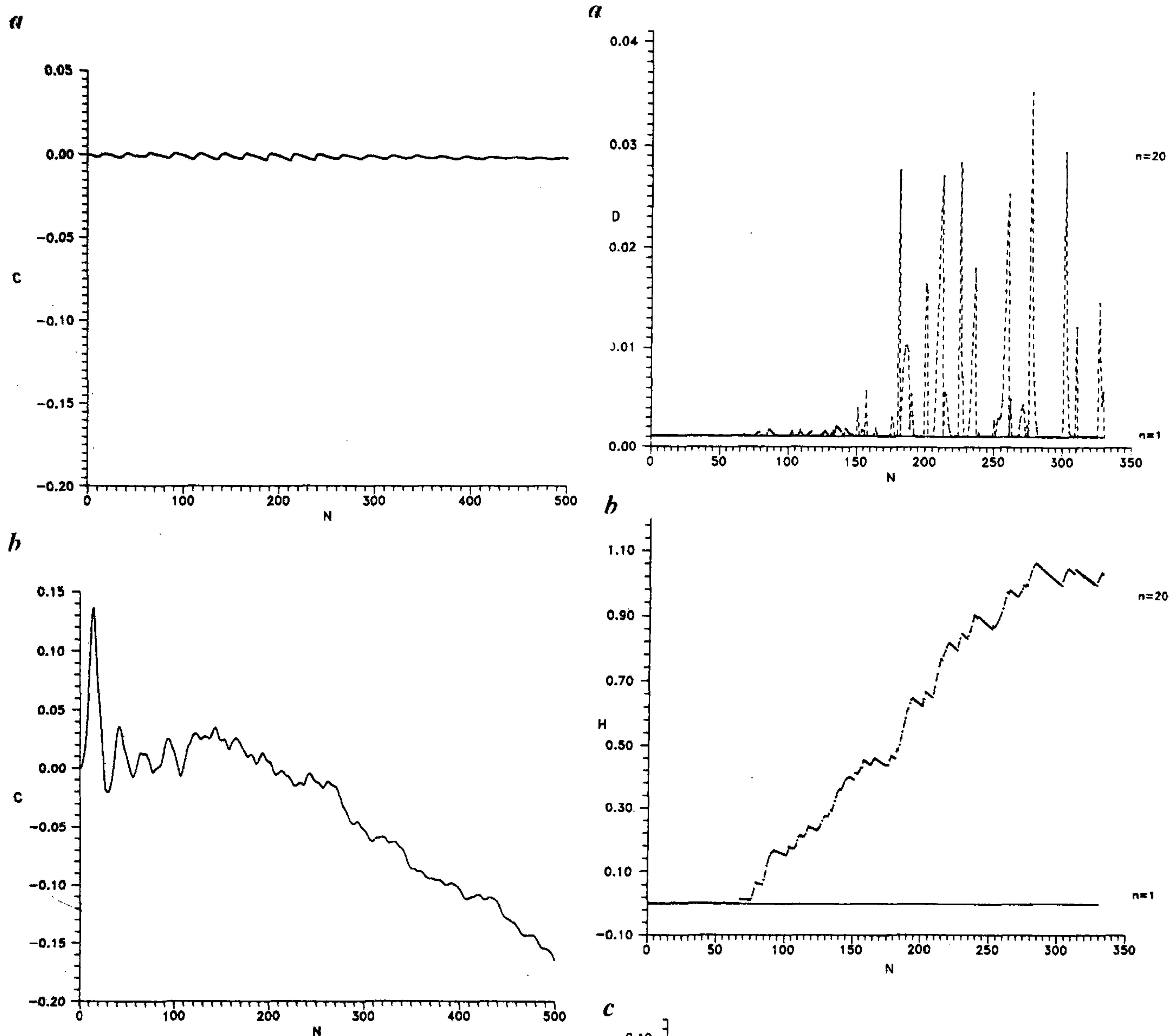


Figure 2a, b. Time evolution of density correlation function C for Rydberg atom in external field: (a) $n = 1$, (b) $n = 20$.

decreases at times) for $n = 1$ but oscillates for $n = 20$, becoming very large sometimes. Although we could simulate only up to $N\Delta t = 7$ a.u., it is clear from Figure 3b that H remains practically constant at zero value for $n = 1$ while it increases rapidly to a positive value for the $n = 20$ case, reflecting discernible chaotic dynamics through sensitive dependence on initial conditions. Two initially ($t = 0$) nearby 'Bohmian trajectories' remain close in course of time for the $n = 1$ case while they diverge for the $n = 20$ case. In these figures, it is discernible that there is a time scale after which the 'chaotic' behaviour sets in. However, it needs a thorough study whether this time is related to the break-time of Chirikov and Casati³⁷. The authors are grateful to the referee for pointing this out. Corresponding D and H

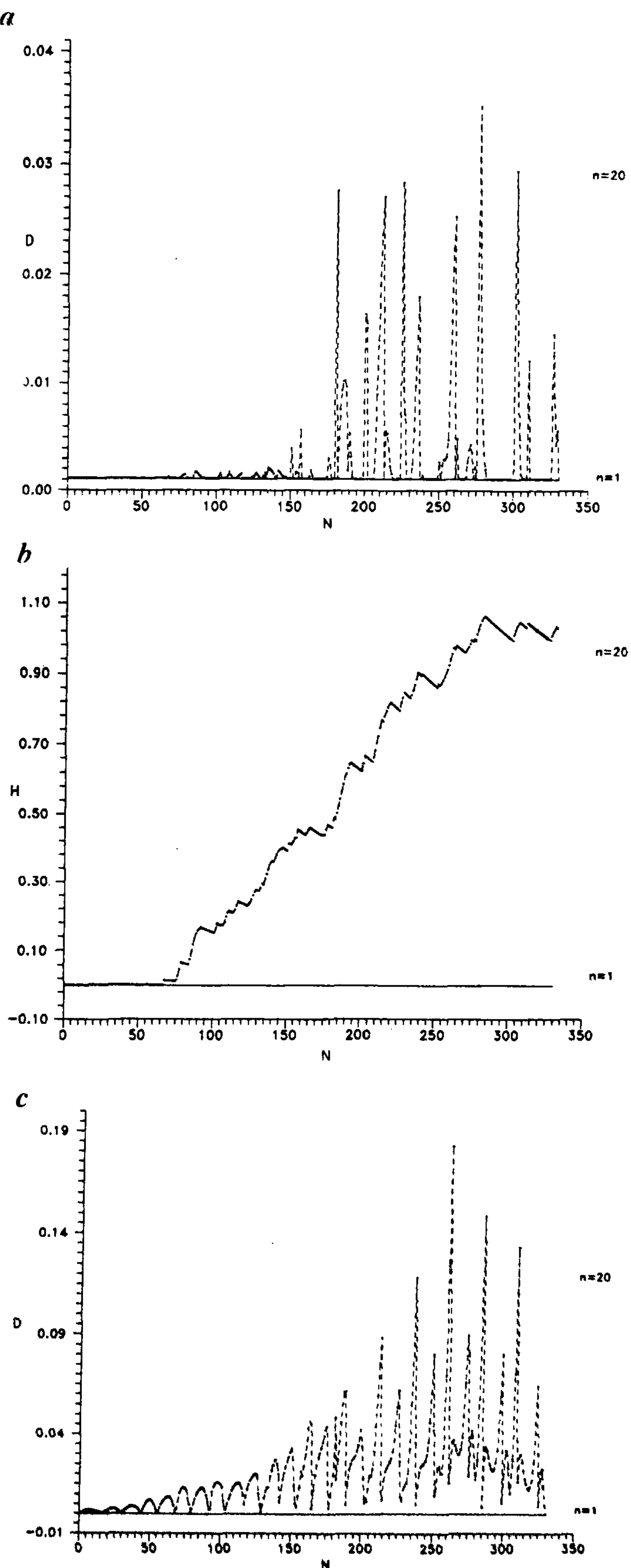


Figure 3a-c. Time evolution of phase space distance function D and KS entropy H in shifted wave function case (see text for details) for Rydberg atoms in external field: (a) D for nonzero field relative to zero field, (b) H associated with D in Figure 3a, (c) D in nonzero field.

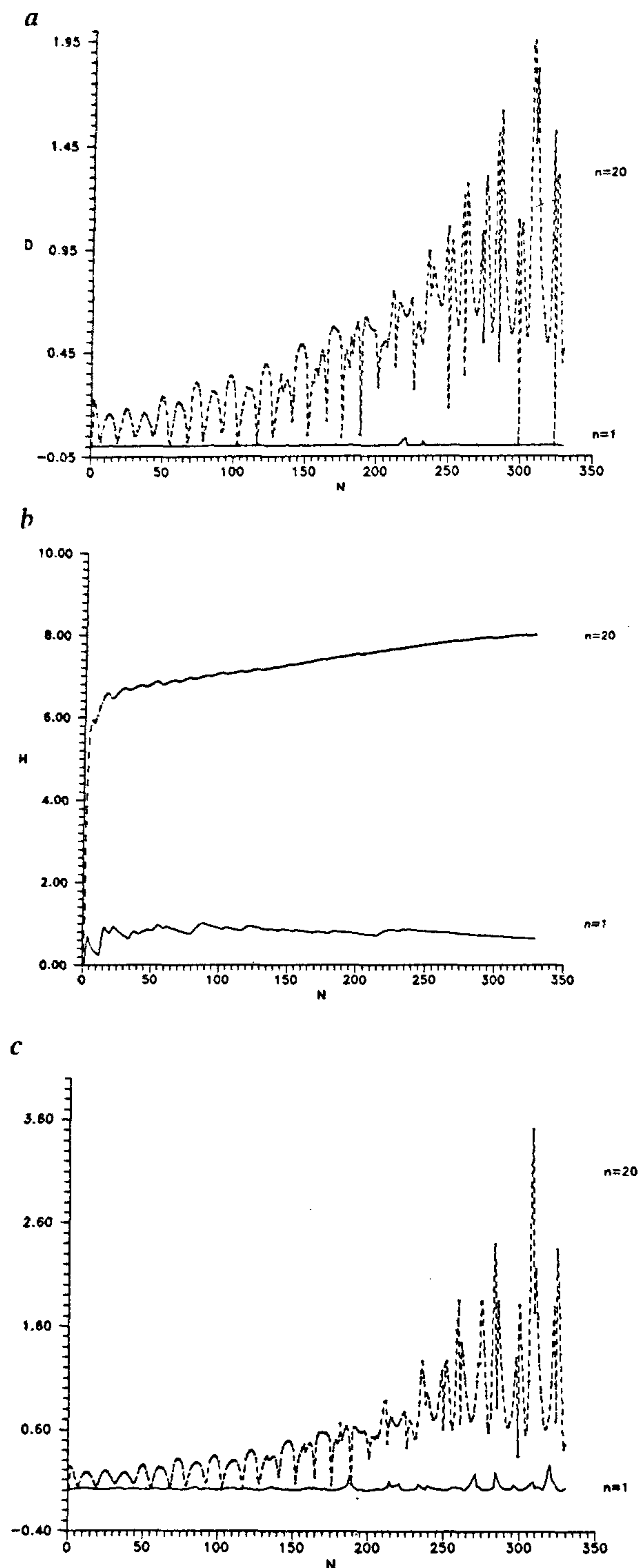


Figure 4a-c. Time evolution of phase space distance function D and KS entropy H in shifted particle position case (see text for details) for Rydberg atoms in external field: **a**, D for nonzero field relative to zero field; **b**, H associated with D in Figure 4a; **c**, D in nonzero field.

plots for shifted particle case are presented in Figures 4a-c. As before, Figure 4c is for the non-zero field case. Like the shifted wavepacket case, here also D remains more or less constant for $n=1$ and increases to a large value for $n=20$. The Kolmogorov-Sinai entropy initially oscillates around zero and then gradually approaches zero for $n=1$. For $n=20$ case H increases rapidly to a high positive value and then increases slowly via feeble oscillation. The negative slope in the former case *vis-à-vis* the positive slope in the latter, towards the end of the simulation, provides unmistakable signature of chaos in Rydberg atom in presence of external electric field. We have also studied (not shown here) the time evolutions of S , C , D and H for $n=5$ and $n=10$ states and also by using $F=2$. In general, for a given n , a higher value of F causes greater variations in the temporal profiles of these quantities. On the other hand, for a given F , a state with larger n value suffers more in comparison to little or no effect on a state with smaller n value. Since it requires too much of computer time we could not pinpoint the critical F value, for a given n , to exhibit the onset of chaos. In a nutshell F and n are considered to be two parameters of the present problem whose continuous variations and the associated dynamics are not studied. We have also obtained more or less similar results (not shown here) when a hydrogen atom in various electronic states experiences the time-dependent external Coulomb field due to a proton approaching for a head-on collision. It is important to note that the present short time simulation is inadequate in getting insights into the long-time asymptotic behaviour and hence one cannot infer with certainty about the final state and ionisation of the system as well as quantal suppression of chaos³⁷, if any.

In summary, we have shown that the quantum potential theories are helpful in studying the chaotic dynamics of a typical quantum system. Temporal evolution of Shannon entropy and correlation function has easily differentiated the regular and chaotic behaviour of hydrogen atom respectively in ground state and in a Rydberg state in presence of an oscillating electric field. Sensitive dependence on initial conditions is understood through time variation of phase space distance and the associated Kolmogorov-Sinai entropy. Further studies related to variations in n , F , ω , the atom, the nature of the external field, the time limit, etc. are in progress.

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Reduced uptake based zinc resistance in *Azospirillum brasilense* sp7

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Zinc resistant *Azospirillum brasilense* sp7 exhibited a low affinity for the metal. A zinc-sensitized, streptomycin-resistant variant and a sensitive mutant of the parent strain showed an increased affinity for zinc. Both the affinity for, and uptake of the metal were in the order of parent strain < sensitised variant < sensitive mutant, suggesting reduced uptake as the mechanism of resistance to zinc. Neither magnesium nor manganese could bestow any protection against zinc toxicity in the sensitive mutant, suggesting a specific pathway for the entry of the metal.

THE presence and buildup of metal pollutants in the soil affects the soil microflora, which encompass the beneficial microorganisms, like the biological nitrogen fixers or BNFs. It has been reported that the total output of BNFs could be reduced in the presence of a metal ion¹. One such nitrogen fixer is the gram negative *Azospirillum brasilense* sp7, which has gained importance owing to its non-obligate association with grasses. This bacterium expressed a high level (10 mM) tolerance to zinc (Zn) which was constitutively expressed². Continuing to work with the same strain (referred to as the parent strain hereafter), the mechanism of Zn resistance has been studied in the bacterium and is presented in this paper.

The minimal nutrient medium (MM) and culture conditions for *A. brasilense* sp7 were as mentioned earlier². A streptomycin-resistant variant, MS12, was derived with a reduced maximum tolerable concentration¹ (MTC) of Zn of 2 mM. This mutation seems to be of a multifold importance in azospirilla.

A. brasilense sp7 has been known to be recalcitrant to mutagen treatments. For the members of the Azotobac-