Dynamics of atomic hydrogen in a generalized van der Waals potential

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The classical dynamics of a hydrogen atom in a generalized van der Waals potential is investigated. In order to carry out the analytical and numerical investigations for a range of parametric values, we removed the singularity of the problem using Levi-Civita regularization and converted the problem into that of two coupled sextic anharmonic oscillators. We identify the integrable choices of the oscillator system using the Painlevé singularity analysis, and the associated second integrals of motion are derived using the extended Lie transformations. Numerical investigations are carried out for other nonintegrable regions and we observe chaos-order-chaos type of transition regions when one of the system parameters is varied.

I. INTRODUCTION

van der Waals forces[1] play an important role in solid-state physics and physical chemistry, particularly considering the interactions involving no valence electrons. If we consider a single hydrogen atom kept a distance d from a perfectly conducting wall, then the dipole interaction energy between the atom and the wall is

$$W=-\frac{e^2}{8d^3}(x^2+y^2+2z^2)\ . \tag{1}$$

This is the instantaneous van der Waals potential.[1]

If we generalize[2] the instantaneous van der Waals potential as

$$V=\gamma(x^2+y^2+\beta^2z^2)\ , \tag{2}$$

where γ and β are constants, Eq. (2) is called the generalized van der Waals interaction. The Hamiltonian of the hydrogen atom in such a generalized potential (in the nonrelativistic limit) is then

$$H=\frac{p^2}{2}-\frac{1}{r}+\gamma(x^2+y^2+\beta^2z^2)\ . \tag{3}$$

Here we use atomic units, $e=\hbar=m_e=1$. Hamiltonian (3) represents many systems such as (i) the quadratic Zeeman problem[3] ($\beta=0$, $\gamma\neq0$), (ii) the spherical quadratic Zeeman problem[4] ($\beta=1$, $\gamma\neq0$), (iii) the instantaneous van der Waals potential[2,5] problem ($\beta=\sqrt{2}$, $\gamma\neq0$), and (iv) the standard hydrogen-atom problem or Kepler problem[6] ($\beta=0$, $\gamma=0$).

Considering the system (3), a large body of information is now available for nonzero values of the γ and $\beta=0$ case.[7] However, the hydrogen-atom problem involving the generalized van der Waals force is yet to be studied in detail both classically and quantum mechanically. In this paper we are interested in understanding the classical dynamics of the system (3) for nonzero values of γ and β. Using a singularity structure and symmetry analysis, we identify the integrable limits of (3). For nonintegrable regimes we carry out a numerical analysis to bring out the chaos-order-chaos transitions.

The plan of the paper is as follows: In Sec. II we bring out the connection existing between the perturbed hydrogen-atom problem (3) and the coupled nonlinear oscillators. In Sec. III we explain how the Painlevé singularity analysis can be used to locate integrable cases of the oscillator Hamiltonian. We discuss the Lie symmetry approach to find out the associated second integrals of motion or the integrable cases in Sec. IV. Finally, Sec. V contains our numerical results of nonintegrable regions and discussions about the system.

II. CONNECTION BETWEEN PERTURBED HYDROGEN ATOM AND THE COUPLED NONLINEAR OSCILLATORS

System (3) possesses cylindrical symmetry. If we introduce the cylindrical coordinates (namely, $x=\rho\cos\phi$, $y=\rho\sin\phi$, and $z=z$) in Eq. (3), we have

$$H=\tfrac{1}{2}(p_\rho^2+p_z^2)+\frac{p_\phi^2}{2\rho^2}+\gamma(\rho^2+\beta^2z^2)-\frac{1}{(\rho^2+z^2)^{1/2}}\ , \tag{4}$$

where p_ρ, p_ϕ, and p_z are the canonical momenta conjugate to the coordinates ρ, ϕ, and z, respectively.

Equation (4) is a three degrees of freedom Hamiltonian system in which ϕ is a cyclic variable and so the corresponding canonically conjugate momenta p_ϕ is conserved. Since p_ϕ is the z component of the angular momentum, it can be quantized as

$$p_\phi=m\hbar\ , \tag{5}$$

where m is the magnetic quantum number. In this analysis the Coulomb singularity $r=0$ poses considerable difficulties as in the case of the quadratic Zeeman problem.[8] Consequently, we will have to deal with the $m\neq0$ and $m=0$ cases separately.

A. $m\neq0$ case

In the original Hamiltonian (3) in Cartsian coordinates, there is a singularity at $r=0$, which necessitates an infinitesimally small step size for numerical integration of

the corresponding equations of motion. This can be circumvented to a large extent in the cylindrical polar coordinates, as the singularity at $r=0$ can be compensated by the centrifugal term $(p_\phi^2/2\rho^2)$ in Eq. (4) and hence there is no difficulty in carrying out the numerical calculations using Eq. (4).

B. $m=0$ case

If we consider the $m=0$ case in Eq. (4), there is a singularity at $\rho^2+z^2=0$ and there is no centrifugal term to compensate this singularity. So, one has to introduce appropriate coordinate transformations to remove this singularity. For this purpose, one can use the well-known Levi-Civita regularization[8,9] using "squared-parabolic" coordinates

$$\rho=uv \ , \tag{6a}$$

$$z=\frac{u^2-v^2}{2} \ , \tag{6b}$$

with the rescaled time variable

$$\tau=\int^t [u^2(t')+v^2(t')]^{-1/2}dt' \ . \tag{6c}$$

Hereafter we will designate τ as t itself. Then Eq. (4) can be rewritten as

$$\overline{H}=2=\tfrac{1}{2}(p_u^2+p_v^2)-E(u^2+v^2)+A(u^6+v^6) +B(u^4v^2+u^2v^4) \ , \tag{7}$$

where

$$A=(\gamma\beta^2)/4, \quad B=[\gamma-(\gamma\beta^2)/4] \ .$$

Here, the true energy E occurs as a parameter and the physical trajectories evolve in an effective potential whose pseudoenergy is always equal to 2. Also there is no singularity problem here and hence one can integrate numerically the Hamilton's equation of motion of (7), namely,

$$\dot{u}=p_u \ , \tag{8a}$$

$$\dot{v}=p_v \ , \tag{8b}$$

$$\dot{p}_u=-(-2Eu+6Au^5+4Bu^3v^2+2Buv^4) \ , \tag{8c}$$

$$\dot{p}_v=-(-2Ev+6Av^5+2Bu^4v+4Bu^2v^3) \ , \tag{8d}$$

without any difficulty and also one can apply certain analytical techniques to investigate the integrability of Eqs. (8a)–(8d).

III. PAINLEVÉ ANALYSIS AND IDENTIFICATION OF REGULAR REGIMES FOR THE $m=0$ CASE

To analyze whether the system (7) is integrable for any parametric choice, it is useful to analyze the singularity structure aspects of equations of motion of Eq. (7). Such singularity analysis or the so-called Painlevé analysis is found to be most useful in the case of polynomial oscillators.[10]

The Painlevé analysis essentially consists of a local analysis of the structure of the solution of the equation of motion in the neighborhood of a movable singularity in the complex time plane and identifying the conditions under which it is free from movable critical singularities, especially of the logarithmic branch-point type or certain complex branch-point and irrational types (so-called densed branching). For this purpose, one considers locally the solution in the form of a Laurent series in a deleted neighborhood of the movable singular point t_0. Now the problem reduces to the following three steps: (a) determination of the leading-order behaviors of the Laurent expansion of the solution of the equation of motion (8), (b) determination of the resonances or the powers at which arbitrary constants can enter into the Laurent expansion, and (c) verifying that a sufficient number of arbitrary constants exist in the Laurent series solution without the introduction of movable critical points.

To analyze the system (8), we consider a set of two coupled sextic anharmonic oscillators defined by the Hamiltonian

$$H=\tfrac{1}{2}(p_x^2+p_y^2)+\omega_1x^2+\omega_2y^2+\alpha x^6+\beta y^6 +\delta_1x^4y^2+\delta_2x^2y^4 \ , \tag{9}$$

where ω_1, ω_2, α, β, δ_1, and δ_2 are parameters. The associated equations of motion are

$$\frac{d^2x}{dt^2}+2\omega_1x+6\alpha x^5+4\delta_1x^3y^2+2\delta_2xy^4=0 \ , \tag{10a}$$

$$\frac{d^2y}{dt^2}+2\omega_2y+6\beta y^5+2\delta_1x^4y+4\delta_2x^2y^3=0 \ . \tag{10b}$$

We will discuss the three steps of the Painlevé analysis separately.

A. Leading-order behaviors

We assume that the leading-order behavior of the solutions $x(t)$ and $y(t)$ of Eqs. (10a)–(10b) in a sufficiently small neighborhood of the movable singularity t_0 is

$$x(t)\simeq a_0\tau^p, \quad y(t)\simeq b_0\tau^q, \quad \tau=t-t_0\to 0 \ . \tag{11}$$

To determine p, q, a_0, and b_0, we use (11) in Eqs. (10a)–(10b) and obtain a pair of leading-order equations,

$$a_0p(p-1)\tau^{p-2}+6\alpha a_0^5\tau^{5p}+4\delta_1a_0^3b_0^2\tau^{3p+2q} +2\delta_2a_0b_0^4\tau^{p+4q}=0 \ , \tag{12a}$$

$$b_0q(q-1)\tau^{q-2}+6\beta b_0^5\tau^{5q}+2\delta_1a_0^4b_0\tau^{4p+q} +4\delta_2a_0^2b_0^3\tau^{2p+3q}=0 \ . \tag{12b}$$

Considering Eqs. (12a)–(12b), we can identify the following different distinct sets of solutions.

Case (1).

$$p=q=-\tfrac{1}{2} \ ,$$

$$3\alpha a_0^4+2\delta_1a_0^2b_0^2+\delta_2b_0^4=-\tfrac{3}{8} \ , \tag{13}$$

$$3\beta b_0^4+\delta_1a_0^4+2\delta_2a_0^2b_0^2=-\tfrac{3}{8} \ .$$

Case 2(a).

$$p=-\tfrac{1}{2},\quad q=\tfrac{1}{2}+\tfrac{1}{2}\left[1+\frac{\delta_1}{\alpha}\right]^{1/2}\geq\tfrac{1}{2}\ . \tag{14a}$$

Case 2(b).

$$p=-\tfrac{1}{2},\quad q=\tfrac{1}{2}-\tfrac{1}{2}\left[1+\frac{\delta_1}{\alpha}\right]^{1/2}>-\tfrac{1}{2}\ , \tag{14b}$$

where the leading-order coefficients are given by

$$a_0^4=-\frac{1}{8\alpha},\quad b_0=\text{arbitrary}\ . \tag{14c}$$

[Note: We do not consider in the following the cases in which the roles of p and q are interchanged as distinct as they can be trivially obtained from Eq. (14).]

B. Resonances

For finding the resonances, that is, the powers at which the arbitrary constants may enter into the Laurent series expansion as $\tau\to 0$, we substitute

$$x(t)\simeq a_0\tau^p+\Omega_1\tau^{p+r},\quad y(t)=b_0\tau^q+\Omega_2\tau^{q+r},\quad \tau\to 0 \tag{15}$$

into the equations of motion (10a)–(10b). Retaining the leading-order terms and solving the system of linear algebraic equations, we get the following resonances.

Case (1).

$$\begin{aligned} &r=-1,\ 3,\ 1\pm(1-4\chi_0)^{1/2}\ ,\\ &\chi_0=2[(\delta_2-\delta_1)a_0^2+(3\beta-\delta_2)b_0^2]b_0^2\ . \end{aligned} \tag{16}$$

Case (2).

$$r=-1,\ 0,\ (1-2q),\ 3\ .$$

If we allow for the possibility of square-root-type branch points corresponding to weak Painlevé property,[11] we obtain the following possibilities for resonances:

Case 1(i).

$$(\delta_2-\delta_1)a_0^2b_0^2+(3\beta-\delta_2)b_0^4=\tfrac{3}{32},\quad r=-1,\ \tfrac{1}{2},\ \tfrac{3}{2},\ 3\ . \tag{17a}$$

Case 1(ii).

$$(\delta_2-\delta_1)a_0^2b_0^2+(3\beta-\delta_2)b_0^4=0,\quad r=-1,\ 0,\ 2,\ 3\ . \tag{17b}$$

Case (2b).

$$4\delta_1=5\alpha,\quad q=-\tfrac{1}{4},\quad r=-1,\ 0,\ \tfrac{3}{2},\ 3\ . \tag{18}$$

C. Evaluation of arbitrary constants

For evaluating the arbitrary constants of the solution $x(t)$ and $y(t)$ of Eqs. (10a)–(10b) associated with the resonance sets (17a)–(17b) and (18), we have to substitute

$$x(t)=\sum_{k=0}^{6}a_k\tau^{(1/2)k+p},\quad y(t)=\sum_{k=0}^{6}b_k\tau^{(1/2)k+q} \tag{19}$$

into Eqs. (10a)–(10b) and then check that no dense branches need to be introduced. Then we get the following parametric restrictions.

Case 1(i).

$$\omega_1=\omega_2,\quad \alpha=\beta,\quad \delta_1=\delta_2=15\alpha\ .$$

Case 1(ii).

$$\omega_1=\omega_2,\quad \alpha=\beta,\quad \delta_1=\delta_2=3\alpha\ .$$

Case (2b).

$$\omega_1=4\omega_2,\quad \alpha=64\beta,\quad \delta_1=80\beta,\quad \delta_2=24\beta\ .$$

Finally, there is also the trivial case $\delta_1=\delta_2=0$, corresponding to two independent decoupled sextic oscillators. For our oscillator Hamiltonian (7), $\omega_1=\omega_2=-E$, $\alpha=\beta=A$, and $\delta_1=\delta_2=B$. For these choices only the fol-

TABLE I. Properties of the hydrogen atom in a generalized van der Waals potential problem for various parametric values.

Cases	Parametric restrictions of the oscillator problem	Parametric restrictions in the van der Waals problem	Second integral of motion of the oscillator problem	Remarks
1	A=arbitrary $B=0$	$\beta=2$ γ=arbitrary	Two uncoupled sextic oscillators	Oscillator system decouples
2	A=arbitrary $B=3A$	$\beta=1$ γ=arbitrary	$I_2=(up_v-vp_u)^2$	Circularly symmetric
3	A=arbitrary $B=15A$	$\beta=\frac{1}{2}$ γ=arbitrary	$I_2=p_up_v-2Euv$ $+6A(u^4+v^4)uv$ $+20Au^3v^3$	Solvable in terms of Jacobian elliptic *fn*

lowing parametric restrictions are valid: (i) $B=15A$, (ii) $B=3A$, (iii) $B=0$, and (iv) the trivial case, $A=0$, $B=0$. From Eq. (7) we know that $A=\gamma\beta^2/4$ and $B=\gamma-\gamma\beta^2/4$. Thus $B=0$ corresponds to $\beta=2$, $B=3A$ corresponds to $\beta=1$, and $B=15A$ corresponds to $\beta=\frac{1}{2}$ of the original Hamiltonian (3). Interestingly, Alhassid *et al.*[2] have pointed out the existence of quantum dynamical symmetries exactly for these three cases of the original van der Waals problem. So one can conclude that the integrability of the classical system may be the reason for the existence of dynamical symmetries of the van der Waals problem.[12] Our results are tabulated in Table I.

IV. GENERALIZED LIE SYMMETRIES OF THE TWO COUPLED SEXTIC ANHARMONIC OSCILLATOR AND THE ASSOCIATED SECOND INTEGRALS OF MOTION

Let us verify the integrability of the Painlevé cases isolated in the above section and also find the associated second integral of motion using generalized Lie symmetries. The integrals of motion of finite-dimensional Lagrangian systems can be related to the infinitesimal symmetries under extended Lie transformations involving velocity-dependent terms.[13] We consider the two coupled sextic anharmonic oscillator system (10) and show the existence of nontrivial generalized Lie symmetries for specific sets of parametric values.

The Euler-Lagrange equations of motion of Eq. (9) are

$$\ddot{x}=\frac{\partial L}{\partial x}=\alpha_1(x,y)$$
$$=-(2\omega_1 x+6\alpha x^5+4\delta_1 x^3y^2+2\delta_2 xy^4)\ , \tag{20a}$$
$$\ddot{y}=\frac{\partial L}{\partial y}=\alpha_2(x,y)$$
$$=-(2\omega_2 y+6\beta y^5+2\delta_1 x^4y+4\delta_2 x^2y^3)\ . \tag{20b}$$

We consider the following time-dependent infinitesimal transformations:

$$x\to X=x+\varepsilon\eta_1(x,y,\dot{x},\dot{y},t)\ , \tag{21a}$$
$$y\to Y=y+\varepsilon\eta_2(x,y,\dot{x},\dot{y},t)\ , \tag{21b}$$
$$t\to T=t+\varepsilon\xi(x,y,\dot{x},\dot{y},t)\ , \tag{21c}$$
$$\dot{x}\to\dot{X}=\dot{x}+\varepsilon(\dot{\eta}_1-\dot{\xi}\dot{x})\ , \tag{21d}$$
$$\dot{y}\to\dot{Y}=\dot{y}+\varepsilon(\dot{\eta}_2-\dot{\xi}\dot{y}),\quad \varepsilon\ll 1 \tag{21e}$$

where

$$\dot{\eta}_i=\left[\frac{\partial}{\partial t}+\frac{\partial}{\partial x}\dot{x}+\frac{\partial}{\partial y}\dot{y}+\frac{\partial}{\partial\dot{x}}\alpha_1+\frac{\partial}{\partial\dot{y}}\alpha_2\right]\eta_i,\quad i=1,2 \tag{21f}$$

$$\dot{\xi}=\left[\frac{\partial}{\partial t}+\frac{\partial}{\partial x}\dot{x}+\frac{\partial}{\partial y}\dot{y}+\frac{\partial}{\partial\dot{x}}\alpha_1+\frac{\partial}{\partial\dot{y}}\alpha_2\right]\xi\ . \tag{21g}$$

For Eqs. (20a)–(20b) to be invariant under these transformations, the following invariance conditions should hold:

$$\ddot{\eta}_1-\dot{x}\ddot{\xi}-2\dot{\xi}\alpha_1=E(\alpha_1)\ , \tag{22a}$$
$$\ddot{\eta}_2-\dot{y}\ddot{\xi}-2\dot{\xi}\alpha_2=E(\alpha_2)\ , \tag{22b}$$

where E is the infinitesimal generator of the transformation

$$E=\xi\left[\frac{\partial}{\partial t}\right]+\eta_1\left[\frac{\partial}{\partial x}\right]+\eta_2\left[\frac{\partial}{\partial y}\right]$$
$$+(\dot{\eta}_1-\dot{\xi}\dot{x})\left[\frac{\partial}{\partial\dot{x}}\right]+(\dot{\eta}_2-\dot{\xi}\dot{y})\left[\frac{\partial}{\partial\dot{y}}\right]\ . \tag{23}$$

Now we have two equations, Eqs. (22a) and (22b), with three unknowns η_1, η_2, and ξ. So one has to assume a specific form for η_1, η_2, and ξ. We assume the following specific forms for η_1, η_2, and ξ:

$$\eta_1=b_1+b_2\dot{x}+b_3\dot{y}\ , \tag{24a}$$
$$\eta_2=c_1+c_2\dot{x}+c_3\dot{y}\ , \tag{24b}$$
$$\xi=0\ , \tag{24c}$$

where b_i's and c_i's are functions of (x,y) only. Substituting (24a)–(24c) in (22a) and (22b) and equating the coefficients of various powers of $\dot{x}^m\dot{y}^n$, we get the following set of overdetermined partial differential equations:

$$b_{1xx}=0\ , \tag{25a}$$
$$b_{1xy}=0\ , \tag{25b}$$
$$b_{1yy}=0\ , \tag{25c}$$
$$b_{2xx}=0\ , \tag{25d}$$
$$2b_{2xy}+b_{3xx}=0\ , \tag{25e}$$
$$b_{2yy}+2b_{3xy}=0\ , \tag{25f}$$
$$b_{3yy}=0\ , \tag{25g}$$
$$c_{1xx}=0\ , \tag{26a}$$
$$c_{1xy}=0\ , \tag{26b}$$
$$c_{1yy}=0\ , \tag{26c}$$
$$c_{2xx}=0\ , \tag{26d}$$
$$2c_{2xy}+c_{3xx}=0\ , \tag{26e}$$
$$c_{2yy}+2c_{3xy}=0\ , \tag{26f}$$
$$c_{3yy}=0\ . \tag{26g}$$

Solving (25a)–(25g) we get

$$b_1=b_{10}x+b_{11}y+b_{12}\ , \tag{27a}$$
$$b_2=b_{20}y^2+b_{21}xy+b_{22}x+b_{23}y+b_{24}\ , \tag{27b}$$
$$b_3=-b_{21}x^2-b_{20}xy+b_{30}x+b_{31}y+b_{32}\ , \tag{27c}$$

where b_{10}, b_{11}, b_{12}, b_{20}, b_{21}, b_{22}, b_{23}, b_{24}, b_{30}, b_{31}, and b_{32} are constants. Similarly, by solving (26a)–(26g), we get

$$c_1=c_{10}x+c_{11}y+c_{12}\ , \tag{28a}$$
$$c_2=c_{20}y^2+c_{21}xy+c_{22}x+c_{23}y+c_{24}\ , \tag{28b}$$

TABLE II. The symmetries and second integral of motion of the oscillator system (9).

Number	Parameters	Symmetries	Second integral
(1)	$\omega_1=\omega_2,\ \alpha=\beta,\ \delta_1=\delta_2=3\alpha$	$\eta_1=2y(\dot{x}y-x\dot{y})$ $\eta_2=2x(x\dot{y}-y\dot{x})$	$(x\dot{y}-y\dot{x})^2$
(2)	$\omega_1=\omega_2,\ \alpha=\beta,\ \delta_1=\delta_2=15\alpha$	$\eta_1=k\dot{y}$ $\eta_2=k\dot{x}$	$\dot{x}\dot{y}+2\omega_1xy+6\alpha x^5y$ $+6\alpha xy^5+20\alpha x^3y^3$
(3)	$\omega_1=4\omega_2,\ \alpha=64\beta,$ $\delta_1=80\beta,\ \delta_2=24\beta$	$\eta_1=y\dot{y}$ $\eta_2=y\dot{x}-2x\dot{y}$	$(y\dot{x}-x\dot{y})\dot{y}$ $+2(\omega_2+3\beta y^4$ $+16\beta x^4+16\beta x^2y^2)xy^2$

$$c_3=-c_{21}x^2-c_{20}xy+c_{30}x+c_{31}y+c_{32}\ , \tag{28c}$$

where b's and c's are constants.

In addition, we have

$$3\alpha_1b_{2x}+b_3\alpha_{2x}+2\alpha_2b_{3x}+\alpha_2b_{2y}=c_2\alpha_{1y}\ , \tag{29a}$$

$$b_2\alpha_{1y}+2\alpha_1b_{2y}+b_3\alpha_{2y}+3\alpha_2b_{3y}+\alpha_1b_{3x}=b_3\alpha_{1x}+c_3\alpha_{1y}\ , \tag{29b}$$

$$\alpha_1b_{1x}+\alpha_2b_{1y}=b_1\alpha_{1x}+c_1\alpha_{1y}\ , \tag{29c}$$

$$c_2\alpha_{1x}+3\alpha_1c_{2x}+c_3\alpha_{2x}+2\alpha_2c_{3x}+\alpha_2c_{2y}=b_2\alpha_{2x}+c_2\alpha_{2y}\ , \tag{29d}$$

$$c_2\alpha_{1y}+2\alpha_1c_{2y}+3\alpha_2c_{3y}+\alpha_1c_{3x}=b_3\alpha_{2x}\ , \tag{29e}$$

$$\alpha_1c_{1x}+\alpha_2c_{1y}=b_1\alpha_{2x}+c_1\alpha_{2y}\ . \tag{29f}$$

By using Eqs. (27a)–(27c), Eqs. (28a)–(28c) along with the equations of motion (20a) and (20b) in Eqs. (29a)–(29f), we get a system of six algebraic equations. By equating various powers of x^my^n, $m,n=0,1,\ldots,6$, independently to zero, we get consistency conditions only for certain parametric choices which are exactly the same cases identified through the Painlevé analysis in Sec. III. These parametric choices along with the associated dynamical symmetries are given in Table II. To prove the integrability, we derive the corresponding integrals of motion using Noether's theorem[14] as

$$I=(\xi\dot{x}-\eta_1)\frac{\partial L}{\partial\dot{x}}+(\xi\dot{y}-\eta_2)\frac{\partial L}{\partial\dot{y}}-\xi L+f\ , \tag{30}$$

where f is a function of (x,y,t) and it can be found using[13]

TABLE III. The four one-dimensional Lyapunov exponents of the oscillator system (7).

Parameters	λ_1	λ_2	λ_3	λ_4	$\sum_i\lambda_i$	Inference	Constants of motion
$A=\frac{1}{6}$ $B=-0.1$	0.51	0	0	−0.51	0	Chaos	Total energy
$A=\frac{1}{6}$ $B=0$	0	0	0	0	0	Integrable (regular)	Total energy System decouples
$A=\frac{1}{6}$ $B=0.25$	0.14	0	0	−0.14	0	Chaos	Total energy
$A=\frac{1}{6}$ $B=0.5$	0	0	0	0	0	Integrable (regular)	Total energy $I_2=(up_v-vp_u)^2$
$A=\frac{1}{6}$ $B=1$	0.12	0	0	−0.12	0	Chaos	Total energy
$A=\frac{1}{6}$ $B=2.5$	0	0	0	0	0	Integrable (regular)	Total energy $I_2=p_up_v-2Euv$ $+6A(u^4+v^4)uv$ $+20Au^3v^3$
$A=\frac{1}{6}$ $B=5$	0.7	0	0	−0.7	0	Chaos	Total energy

$$E(L)+\dot{\xi}L=\dot{f}\ . \tag{31}$$

For our analysis, we substitute η_1, η_2, and ξ in Eq. (31) and we find f. Using this f in Eq. (30), we get the required second integral of motion. For the sextic Hamiltonian system (7) only cases (1) and (2) of Table II survive, while the third case is $\omega_1=\omega_2$, $\delta_1=\delta_2=0$ for which the system (7) decouples into two independent sextic oscillators.

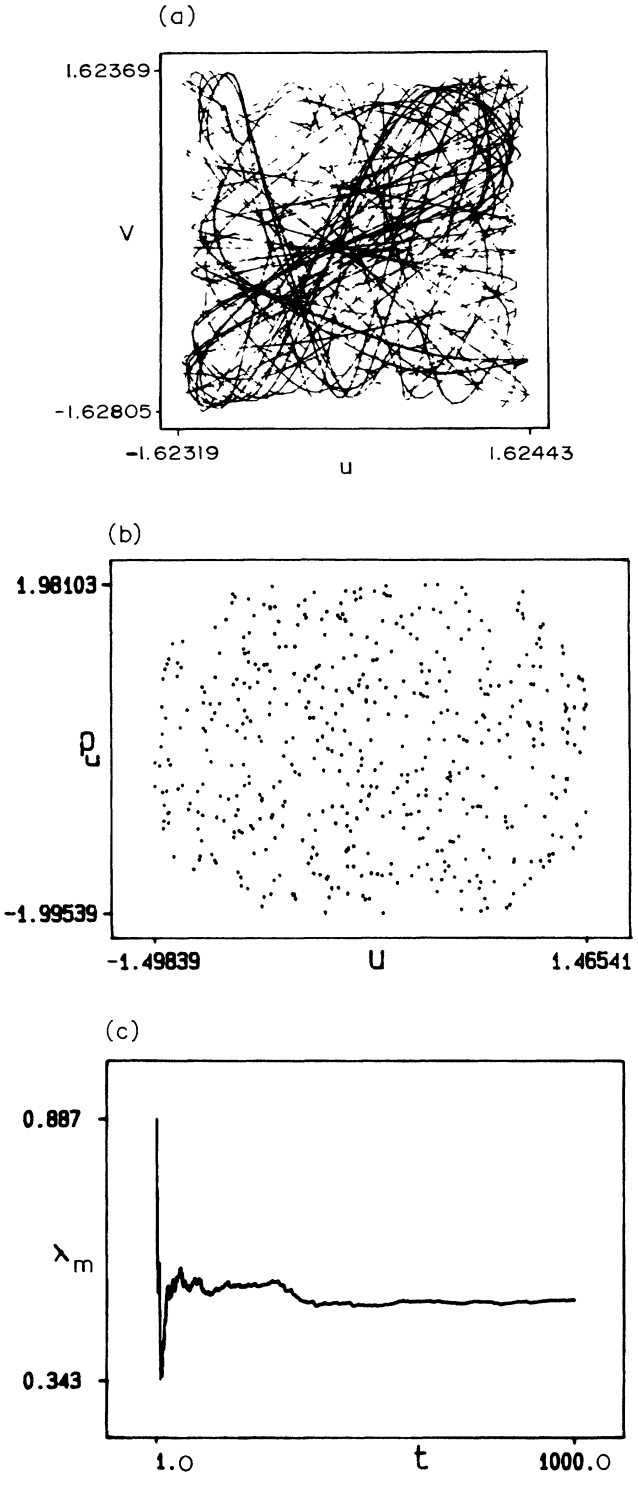

FIG. 1. For the oscillator Hamiltonian (7) with $A=\frac{1}{6}$, $B=-0.1$: (a) trajectory plot, (b) Poincaré surface of section ($v=0$, $p_v>0$), and (c) variation of the maximal Lyapunov exponent.

V. NUMERICAL INVESTIGATIONS OF NONINTEGRABLE REGIONS AND DISCUSSIONS

In Secs. III and IV we identified the integrable regions and their associated second integrals of motion. In order to understand the dynamics of various other regions, we carried out a detailed numerical investigation of Eqs. (8a)–(8d). We have now a system of four first-order ordinary differential equations which can be solved numerically for a fixed negative energy value E of the original system (3). For our computation we have used $E=-1.0\times10^{-8}$. As $E=0$ is the threshold value for the bound states in the case of the hydrogen-atom problem, we have chosen this high value for E in order to capture the onset of chaos easily. Then we solved Eqs. (8a)–(8d) using the Runge-Kutta-Gill fourth-order method and obtained (i) the trajectory plot, (ii) the Poincaré surface of section, and (iii) the spectrum of one-dimensional Lyapunov exponents.

In the case of the trajectory plot we integrated Eqs. (8a)–(8d) for 25 000 times with an optimum time step value. For the Poincaré surface of section plot we integrated Eqs. (8a)–(8d) for 500 points and projected out of the phase space the $v=0$, $p_v>0$ plane and plotted u versus its momentum p_u. To calculate the one-dimensional Lyapunov exponents and the maximum Lyapunov exponent we integrated Eqs. (8a)–(8d) along with their variational equations.[15] From our Painlevé-analysis, it is clear that Eqs. (8a)–(8d) are integrable for three different choices of B, namely, $B=0$, $B=3A$, and $B=15A$. Fixing $A=\frac{1}{6}$ for numerical calculations, Eqs. (8a)–(8d) become integrable for $B=0$, $B=0.5$, and $B=2.5$. In our numerical analysis, B was varied in the region $(-0.1,5.0)$. In each case the trajectory plot, the Poincaré surface of section plot, and a spectrum of one-dimensional Lyapunov exponents were obtained for a grid of initial conditions. The results for typical values of B are tabulated in Table III. Figures 1–3 are sample plots of our numerical investigations corresponding to a single initial condition [except Fig. 2(b)]. Of course, our studies were repeated for a grid of initial conditions in each of the cases, before coming to conclusions.

Figure 1(a) represents the trajectory plot (u versus v) of Eqs. (8a)–(8d) for $B=-0.1$. It possesses a complicated structure. The surface of section plot consists of randomly distributed points [Fig. 1(b)]. The variation of maximum Lyapunov exponent with respect to time is shown in Fig. 1(c). It settles down to a positive value of 0.51. Repeating this for various initial conditions and various negative values of B, we conclude that the system becomes chaotic for negative values of B.

As noted already, for $B=0$ the system (7) decouples into two independent sextic oscillators and hence be-

comes separable. The trajectory plot [Fig. 2(a)], Poincaré surface of section [Fig. 2(b)], and the maximum Lyapunov exponent [Fig. 2(c)] are in conformity with the integrable nature of the system.

For $B=0.25$ the trajectory plot [Fig. 3(a)] shows a fairly complicated behavior. The corresponding Poincaré surface of section [Fig. 3(b)] contains randomly distributed points occupying only some regions of phase space.

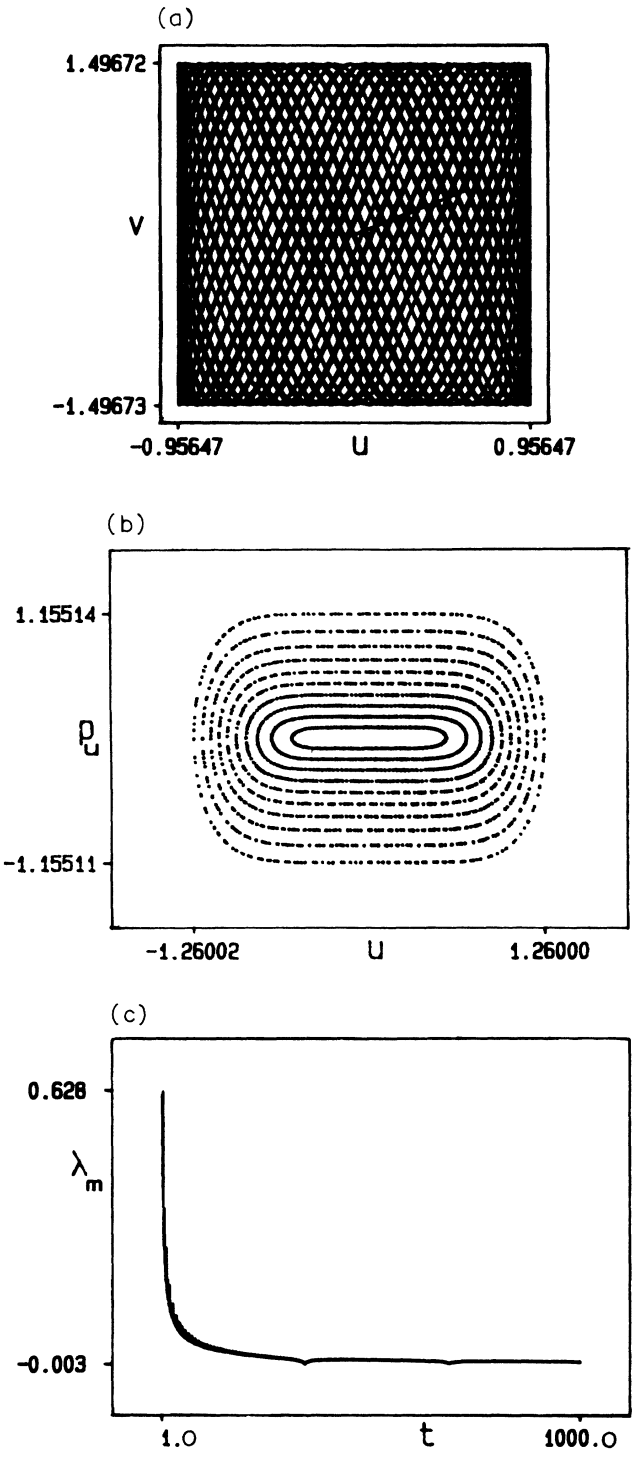

FIG. 2. For the oscillator Hamiltonian (7) with $A=\frac{1}{6}$, $B=0.0$: (a) trajectory plot, (b) Poincaré surface of section ($v=0$, $p_v>0$), and (c) variation of the maximal Lyapunov exponent.

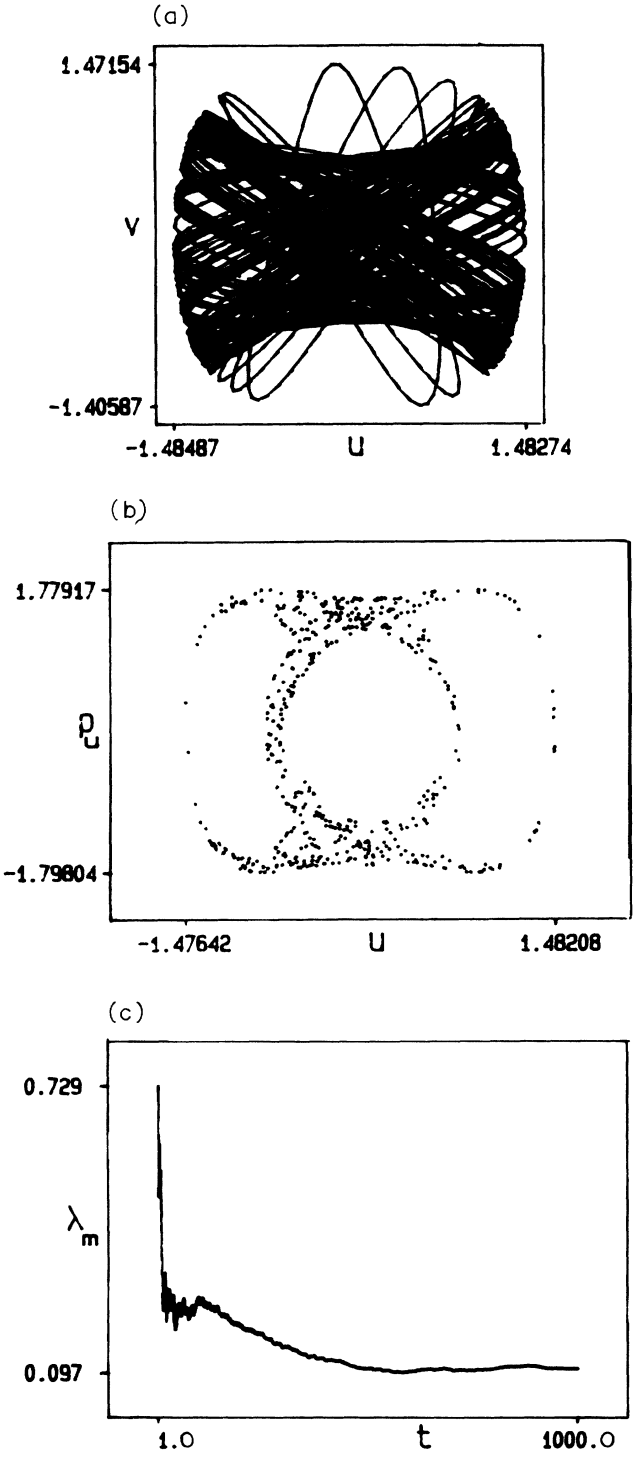

FIG. 3. For the oscillator Hamiltonian (7) with $A=\frac{1}{6}$, $B=0.25$: (a) trajectory plot, (b) Poincaré surface of section ($v=0$, $p_v>0$), and (c) variation of the maximal Lyapunov exponent.

The maximum Lyapunov exponent [Fig. 3(c)] settles down to a small positive value of 0.14. This has been confirmed for various initial conditions. Hence we conclude that for $B=0.25$ the system shows chaotic behavior but the fraction of phase-space volume occupied by the chaotic trajectory is small.

Similarly, we carried our numerical investigations for other values of B lying around the integrable regions. From our detailed study we found that for $B=0.0$, 0.5, and 2.5, we have only regular behavior as expected corresponding to the integrable cases identified in Secs. III and IV. For $B=-0.1$, 0.25, 1.0, and 5.0, we observed chaotic behavior. In the cases of $B=-0.1$ and $B=5.0$, chaotic trajectories filled a large fraction of phase-space volume. In the cases of $B=0.25$ and $B=1.0$, we observed chaotic trajectories filling a small fraction of phase-space volume. This is due to the fact that these two choices lie in between the integrable values—that is, the $B=0.25$ case lies in between the $B=0.0$ and $B=0.5$ integrable cases. Similarly, the $B=1.0$ case lies in between the $B=0.5$ and $B=2.5$ integrable cases.

For the $m\neq 0$ case, we integrated the original Hamiltonian (4) itself directly for different values of energy, m, γ, and β, and also for various initial conditions. Here we failed to identify any chaotic region in our computation. However, it needs further investigation.[16]

We conclude that by varying the value of B from negative to positive values one can observe chaos-order-chaos-type transition regions. As the value of B can be related with the γ and β values of the original system, we can say that there are chaos-order-chaos regions in the perturbed hydrogen-atom problem. It is to be recalled that in the usual quadratic Zeeman problem ($\beta=0$), if we increase the value of γ, then there is a smooth transition from regular motion to chaos.[17] In the anisotropic Kepler problem, when we vary the anisotropy parameter, the system makes an abrupt transition from regular behavior to chaos.[9] However, if we include β and vary it, we observe a chaos-order-chaos transition phenomenon which seems not to be observed in any of the other perturbed hydrogen-atom problems so far.

In addition, instead of fixing the value of γ and varying β, we fixed the value of β^2 as 2 (instantaneous van der Waals potential) and varied the value of γ gradually to a higher value. As in the quadratic Zeeman problem case, the system makes a transition from regular behavior to chaos but the fraction of phase-space volume occupied by the chaotic trajectories is found to be small even for a large value of γ. The hydrogen-atom problem in a generalized van der Waals potential is an interesting system for the study of quantum chaos.[18] The results of it will be published separately.[16]

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