Semiclassical quantization of the hydrogen atom in a generalized van der Waals potential

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(Received 15 July 1991)

A semiclassical quantization of the hydrogen atom in a generalized van der Waals potential is carried out using the Kustaanheimo-Stiefel transformation and Birkhoff-Gustavson normal-form procedure, employed by Kuwata, Harada, and Hasegawa [J. Phys. A **23**, 3227 (1990)] for the diamagnetic Kepler problem. We derive here the generalized approximate Solov'ev constant of motion. By using appropriate action-angle variables in the normal Hamiltonian, we derive four canonically equivalent action integrals that take an especially simple form for the three classically integrable cases and provide exact quantum numbers. For near-integrable cases the semiclassical spectrum can be generated by integrating the appropriate action integrals numerically.

PACS number(s): 34.30.+h, 03.65.Sq, 12.15.−y, 32.60.+i

I. INTRODUCTION

The Hamiltonian of the hydrogen atom in a generalized van der Waals potential [1] (in atomic units $e=\hbar=m_e=1$) can be written in the form

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

where γ and β are constants. The special cases of it include (i) the quadratic Zeeman effect [2] ($\gamma\neq0$, $\beta=0$), (ii) the spherical quadratic Zeeman problem [3] ($\gamma\neq0$, $\beta=1$), (iii) the instantaneous van der Waals potential [1,4] ($\gamma\neq0$, $\beta=\sqrt{2}$), and (iv) the standard hydrogen-atom problem [5] ($\gamma=0$, $\beta=0$). The classical dynamics of (1) shows a rich variety of nonlinear phenomena [6]. Also the problem can be converted into that of a system of two-coupled sextic anharmonic oscillators using a Levi-Civita regularization. Using the Painlevé singularity analysis and Lie symmetry invariance analysis, it has been shown [7] that the system (for the vanishing magnetic quantum-number case) is integrable for the three choices $\beta=\frac{1}{2}$, 1, and 2 in the Hamiltonian (1). For these three cases existence of dynamical symmetries has been pointed out [1] earlier by Alhassid, Hinds, and Meschede. However, the problem is yet to be investigated semiclassically for the entire β parameter range. In this paper we are interested in the semiclassical behavior of the system.

Using the Kustaanheimo-Stiefel transformation and Birkhoff-Gustavson normal-form procedure employed by Kuwata, Harada, and Hasegawa [8] recently for the diamagnetic Kepler problem, we derive here the generalized approximate Solov'ev constant of motion for the system (1). By introducing appropriate action-angle variables into the normal Hamiltonian, we obtain four canonically equivalent action integrals which take an especially simple form for the three classically integrable cases and thereby obtain the exact quantum numbers for the three integrable cases mentioned above. For the near-integrable regions any one of the four action integrals may be evaluated numerically to obtain the semiclassical spectrum.

The plan of the paper is as follows. In Sec. II we briefly discuss the connection existing between the perturbed hydrogen-atom problem and the four-coupled anharmonic oscillators by extending the method of Kuwata, Harada, and Hasegawa [8] to system (1). In Sec. III we write the Hamiltonian in its normal form using the Birkhoff-Gustavson procedure and also derive the generalized Solov'ev constant of motion for system (1). After introducing appropriate action-angle variables for the vanishing magnetic quantum-number case in Sec. IV, we derive exact quantum numbers for the three classically integrable cases by evaluating the action integrals explicitly. For the near-integrable cases appropriate action integrals are evaluated numerically to generate the quantized values of the Solov'ev constant of motion and the method of obtaining the semiclassical spectrum is briefly discussed in Sec. V.

II. CONNECTION BETWEEN THE PERTURBED HYDROGEN ATOM AND THE FOUR-COUPLED ANHARMONIC OSCILLATORS

Using the well-known Kustaanheimo-Stiefel (KS) transformation [9], the hydrogen atom in a generalized van der Waals potential can be transformed into that of a system of four-coupled sextic oscillators as in the case of the diamagnetic Kepler problem [8] studied by Kuwata, Harada, and Hasegawa. Considering the column matrices

$$X=\begin{bmatrix}x_1\\x_2\\x_3\\0\end{bmatrix},\quad P_X=\begin{bmatrix}p_{x_1}\\p_{x_2}\\p_{x_3}\\0\end{bmatrix},\qquad U=\begin{bmatrix}u_1\\u_2\\u_3\\u_4\end{bmatrix},\quad P_U=\begin{bmatrix}p_{u_1}\\p_{u_2}\\p_{u_3}\\p_{u_4}\end{bmatrix}, \tag{2}$$

where x_1,x_2,x_3 and p_{x_1},p_{x_2},p_{x_3} are, respectively, the coordinates and momenta on $\mathbb{R}^3$ and u_1,u_2,u_3,u_4 and $p_{u_1},p_{u_2},p_{u_3},p_{u_4}$ are, respectively, the local coordinates and conjugate momenta on $\mathbb{R}^4$, the KS transformation is given by the matrix equation [9]

$$X=TU\ , \tag{3}$$

where

$$T=\begin{bmatrix} u_1 & -u_2 & -u_3 & u_4 \\ u_2 & u_1 & -u_4 & -u_3 \\ u_3 & u_4 & u_1 & u_2 \\ u_4 & -u_3 & u_2 & -u_1 \end{bmatrix} \tag{4}$$

so that in component form we have the transformations

$$x_1=u_1^2-u_2^2-u_3^2+u_4^2\ , \tag{5}$$

$$x_2=2(u_1u_2-u_3u_4)\ , \tag{6}$$

$$x_3=2(u_1u_3+u_2u_4)\ , \tag{7}$$

along with the constraint

$$u_1p_{u_4}-u_4p_{u_1}+u_3p_{u_2}-u_2p_{u_3}=0\ . \tag{8}$$

Then

$$P_X=(\tfrac{1}{2})U^{-2}TP_U=\left[\frac{1}{2r}\right]TP_U\ , \qquad U^2=u_1^2+u_2^2+u_3^2+u_4^2\ , \tag{9}$$

where $r^2=x^2+y^2+z^2$.

Denoting $x_1=z$, $x_2=x$, and $x_3=y$ in the Hamiltonian (1), the above KS transformation gives rise to the new Hamiltonian

$$\begin{aligned} H'=\left[\frac{1}{8r}\right]P_U^2-\left[\frac{1}{U^2}\right]&+4\gamma(u_1^2+u_4^2)(u_2^2+u_3^2) \\ &+\gamma\beta^2(u_1^4+u_2^4+u_3^4+u_4^4-2u_1^2u_2^2-2u_1^2u_3^2+2u_1^2u_4^2 \\ &\qquad+2u_2^2u_3^2-2u_2^2u_4^2-2u_3^2u_4^2)\ , \end{aligned} \tag{10}$$

where $P_U^2=p_{u_1}^2+p_{u_2}^2+p_{u_3}^2+p_{u_4}^2$. Redefining the time variable t in terms of s as

$$\left[\frac{dt}{ds}\right]^2=4r=4U^2\ , \tag{11}$$

we can effect the Levi-Civita regularization [10] and remove the singularity at $U=0$ and obtain a modified Hamiltonian

$$\begin{aligned}\bar{H}=(\tfrac{1}{2})(P_U^2+\omega^2U^2)&+8\gamma(2-\beta^2)U^2[(u_1^2+u_4^2)(u_2^2+u_3^2)] \\ &+4\gamma\beta^2U^2[(u_1^2+u_4^2)^2+(u_2^2+u_3^2)^2]=4\ ,\end{aligned} \tag{12}$$

where

$$\omega^2=-8E,\quad E=-\left[\frac{1}{2n^2}\right]\ , \tag{13}$$

where E is the energy of the unperturbed hydrogen atom. Hamiltonian (12) represents a system of four-coupled sextic oscillators. For the $\beta=0$ case, it reduces to the case of the diamagnetic Kepler problem studied by Kuwata, Harada, and Hasegawa [8].

Having transformed the Hamiltonian (1) into the oscillator system Hamiltonian (12), we may carryout a semiclassical, EBK type of torus quantization of the form [11]

$$I_k=\oint_{\mathscr{C}_k}p_k\cdot dq_k=2\pi\hbar\left[n_k+\frac{\alpha_k}{4}\right],\quad k=1,2,3,4 \tag{14}$$

where $\mathscr{C}_k$ is the topologically independent contour on an invariant torus, n_k and α_k are the corresponding quantum numbers and the Maslov indices, respectively. If an explicit transformation to action-angle variables is possible, then the energy levels can be determined by the condition

$$E=H(I_1,I_2,I_3,I_4)\ . \tag{15}$$

Such a torus quantization can be more effectively performed if the oscillator Hamiltonian (12) is reexpressed into its normal form, wherein the Hamiltonian is a function of the harmonic-oscillator terms only.

A simple way to achieve the normal Hamiltonian is to use the Birkhoff-Gustavson normal-form procedure [12,13]. For this purpose one can introduce the complex variables

$$Z_j=\frac{1}{\sqrt{2\omega}}(\omega u_j+ip_{u_j})\ \text{ and }\ Z_j^*=\frac{1}{\sqrt{2\omega}}(\omega u_j-ip_{u_j})\ ,\qquad j=1,2,3,4 \tag{16}$$

so that the Hamiltonian (12) can be rewritten as

$$\begin{aligned}\bar{H}=4=\omega\sum_{j=1}^{4}|Z_j|^2+\frac{4\gamma}{\omega^3}&[\{2(2-\beta^2)[|Z_1|^2+|Z_4|^2+\mathrm{Re}(Z_1^2+Z_4^2)][|Z_2|^2+|\dot{Z}_3|^2+\mathrm{Re}(Z_2^{*2}+Z_3^{*2})]\} \\ &+(\beta^2\{(|Z_1|^2+|Z_4|^2)^2+[\mathrm{Re}(Z_1^2+Z_4^2)]^2+2(|Z_1|^2+|Z_4|^2)\mathrm{Re}(Z_1^2+Z_4^2) \\ &+(|Z_2|^2+|Z_3|^2)^2+[\mathrm{Re}(Z_2^{*2}+Z_3^{*2})]^2 \\ &+2(|Z_2|^2+|Z_3|^2)\mathrm{Re}(Z_2^{*2}+Z_3^{*2})\})]\left[\sum_{j=1}^{4}|Z_j|^2+\mathrm{Re}(Z_j^2)\right] \\ =H^{(2)}+H^{(6)}\ ,\end{aligned} \tag{17}$$

where $H^{(2)}=\omega\sum_{j=1}^{4}|Z_j|^2$ is the unperturbed part and the perturbed part $H^{(6)}$ is the remainder of the terms in the Hamiltonian (17) proportional to γ. We will normalize this Hamiltonian (17) using the Birkhoff-Gustavson procedure in the next section.

III. THE NORMAL FORM

The Birkhoff-Gustavson algorithm [12,13] for writing the Hamiltonian in its normal form makes use of successive canonical transformations. Following the standard procedure [13], the sixth-order (sextant) normal form of the perturbed Hamiltonian $H_{\rm NF}^{(6)}$ is given by

$$\begin{aligned}\overline{H}_{\rm NF}^{(6)}=\frac{4\gamma}{\omega^3}\{(|Z_1|^2+|Z_4|^2)[(2-\beta^2)|Z_2^2+Z_3^2|^2+\beta^2|Z_1^2+Z_4^2|^2]+(|Z_2|^2+|Z_3|^2)[(2-\beta^2)|Z_1^2+Z_4^2|^2+\beta^2|Z_2^2+Z_3^2|^2]\}\\ +\frac{2\gamma}{\omega^3}\left[\sum_{j=1}^{4}|Z_j|^2\right]\{4(2-\beta^2)[(|Z_1|^2+|Z_4|^2)(|Z_2|^2+|Z_3|^2)+\mathrm{Re}(Z_1^2+Z_4^2)(Z_2^{*2}+Z_3^{*2})]\\ +2\beta^2[(|Z_1|^2+|Z_4|^2)^2+(|Z_2|^2+|Z_3|^2)^2+\mathrm{Re}(Z_1^2+Z_4^2)(Z_2^{*2}+Z_3^{*2})]\\ +\beta^2(|Z_2^2+Z_3^2|^2+|Z_1^2+Z_4^2|^2)\}\ ,\end{aligned} \tag{18}$$

where the constraint (8) has been utilized as and when necessary. It is straightforward to check the normal-form condition $D\overline{H}_{\rm NF}^{(6)}=0$, where

$$D=-i\omega\sum_{j=1}^{4}\left[Z_j\frac{\partial}{\partial Z_j}-Z_j^*\frac{\partial}{\partial Z_j^*}\right].$$

This expression (18) may be considerably simplified [8] when reexpressed in terms of the orbital angular-momentum vector $\mathbf{L}=\mathbf{r}\times\mathbf{p}$ and the Runge-Lenz vector $\mathbf{A}=[(\mathbf{p}\times\mathbf{L})-\mathbf{r}/|\mathbf{r}|]$ of the unperturbed hydrogen atom satisfying the condition

$$A^2=\left[1-\frac{\omega^2}{4}L^2\right]. \tag{19}$$

Equation (18) simplifies to

$$\overline{H}_{\rm NF}^{(6)}=\frac{32\gamma}{\omega^3}\left[\sum_{j=1}^{4}|Z_j|^2\left[\frac{1+\Lambda+\beta^2}{\omega^2}+\tfrac{1}{4}(1-\beta^2)L_z^2\right]\right]. \tag{20}$$

Here

$$\Lambda=(4-\beta^2)A^2+5(\beta^2-1)A_z^2 \tag{21}$$

is the generalized Runge-Lenz hyperboloid or generalized Solov'ev constant [1] which generalizes the result $\Lambda=4A^2-5A_z^2$ found by Solov'ev [14] for the diamagnetic Kepler problem, namely the $\beta=0$ case. In terms of the real variables, u_i, p_{u_i}, $i=1,2,3,4$, the full normal-form Hamiltonian becomes

$$\begin{aligned}\overline{H}_{\rm NF}&=\overline{H}_{\rm NF}^{(2)}+\overline{H}_{\rm NF}^{(6)}\\ &=\tfrac{1}{2}(P_U^2+\omega^2U^2)\\ &\quad\times\left[1+\frac{32\gamma}{\omega^6}\left[1+\beta^2+\Lambda+\frac{\omega^2}{4}(1-\beta^2)L_z^2\right]\right].\end{aligned} \tag{22}$$

The original Hamiltonian (1) is related to the oscillator normal Hamiltonian $\overline{H}_{\rm NF}$ through the relation [13]

$$\begin{aligned}H_{\rm NF}&=-\tfrac{1}{2}(\overline{H}_{\rm NF})^{-2}=-\tfrac{1}{2}(\overline{H}_{\rm NF}^{(2)})^{-2}\left[1+\frac{32\gamma}{\omega^6}\left[1+\beta^2+\Lambda+\frac{\omega^2}{4}(1-\beta^2)L_z^2\right]\right]^{-2}\\ &\cong-\frac{1}{2n^2}+\frac{\gamma n^4}{2}\left[1+\beta^2+\Lambda+\frac{\omega^2}{4}(1-\beta^2)L_z^2\right].\end{aligned} \tag{23}$$

Next we wish to introduce action-angle variables into the normal Hamiltonian (23) and construct explicit action integrals for quantization. As the Hamiltonian (23) is a four-degrees-of-freedom system, one has to naturally introduce four sets of action-angle variables which in general is a difficult task to achieve. For simplicity we consider the special case in which the z component of the angular momentum $L_z=m=0$ so that the Hamiltonian (23) can be reduced to a two-degrees-of-freedom system. Quantization for this special case will be discussed in Sec. V.

IV. ACTION INTEGRALS FOR THE VANISHING MAGNETIC QUANTUM-NUMBER CASE

As in the case of the diamagnetic Kepler problem [8], we consider the polar form for Z_j, namely

$$Z_j=\sqrt{I_j}e^{i\phi_j},\quad j=1,2,3,4 \tag{24}$$

where I_j's can be identified as actions and ϕ_j's as angle variables. For the $m=0$ case, the constraint (8) implies $\phi_1=\phi_4$ and $\phi_2=\phi_3$. For this case, we have

$$\tfrac{1}{2}[(p_{u_1}^2+p_{u_4}^2)+\omega^2(u_1^2+u_4^2)]=\omega(|Z_1|^2+|Z_4|^2)$$
$$=\omega(I_1+I_4)\ , \tag{25}$$
$$\tfrac{1}{2}[(p_{u_2}^2+p_{u_3}^2)+\omega^2(u_2^2+u_3^2)]=\omega(|Z_2|^2+|Z_3|^2)$$
$$=\omega(I_2+I_3). \tag{26}$$

Therefore the two two-dimensional oscillators consisting of (u_1,u_4) and (u_2,u_3) become effectively one dimensional. Hence for the $L_z=0$ case, one can introduce new variables defined as $\xi^2=u_1^2+u_4^2$, $\eta^2=u_2^2+u_3^2$, $p_\xi^2=p_{u_1}^2+p_{u_4}^2$, and $p_\eta^2=p_{u_2}^2+p_{u_3}^2$. The Hamiltonian (12) in terms of these new variables (for the $L_z=0$ case) becomes

$$\hat{H}=\tfrac{1}{2}(p_\xi^2+\omega^2\xi^2)+\tfrac{1}{2}(p_\eta^2+\omega^2\eta^2)+4\gamma\beta^2(\xi^6+\eta^6)$$
$$+4\gamma(4-\beta^2)(\xi^2\eta^4+\xi^4\eta^2)=4\ . \tag{27}$$

This Hamiltonian is analogous to the two-coupled sextic anharmonic oscillators discussed in Ref. [7]. Let (I_ξ,ϕ_ξ) and (I_η,ϕ_η) be the action-angle variables associated with the ξ and η oscillators so that the normal Hamiltonian (22) becomes

$$\bar{H}_{\rm NF}=\omega(I_\xi+I_\eta)\left[1+\frac{32\gamma}{\omega^6}(1+\beta^2+\Lambda)\right]\ . \tag{28}$$

In terms of these action-angle variables, the generalized Solov'ev constant (21) becomes

$$\Lambda=\tfrac{1}{4}\{\omega^2 I_\xi I_\eta[5(1-\beta^2)-(4-\beta^2)\sin^2(\phi_\xi-\phi_\eta)]$$
$$+20\beta^2\}-(1+\beta^2)\ . \tag{29}$$

Using Eqs. (13), (25), and (26) we have

$$n=\frac{2}{\omega}=\tfrac{1}{2}(I_\xi+I_\eta)\ . \tag{30}$$

By introducing the variables I and ϕ, which are related to the action-angle variables, as

$$I=\tfrac{1}{2}(I_\eta-I_\xi),\quad \phi=(\phi_\xi-\phi_\eta)\ , \tag{31}$$

the Solov'ev approximate constant (29) becomes

$$\Lambda=\frac{1-4\beta^2}{n^2k^2}[(n^2-I^2)(1-k'^2\sin^2\phi)]+4\beta^2-1\ , \tag{32}$$

where

$$k'^2=\frac{4-\beta^2}{5(1-\beta^2)},\quad k^2=1-k'^2\ . \tag{33}$$

Here we have one pair of action-angle variables (I,ϕ) only while the other action "n" is cyclic.

Now we note that the quantity k^2 in Eq. (33), unlike the case of the diamagnetic Kepler problem [8] ($\beta=0$), where it takes a fixed value $k^2=\frac{1}{5}$, can vary as shown in Fig. 1(a). There is a discontinuity at $\beta=1$. The variation of k^2 as a function of β is shown in Fig. 1(a). For the sake of simplicity, the β parameter region can be divided into four distinct regimes. They are (i) $0\le\beta\le0.5$, (ii) $0.5<\beta\le1$, (iii) $1\le\beta<2$, and (iv) $\beta\ge2$.

We introduce k_i^2, $i=1,2,3,4$ in the above-mentioned four regions such that in region (i), we have

$$0\le k_1^2=k^2=\left[\frac{1-4\beta^2}{5(1-\beta^2)}\right]\le1\quad\text{for } \tfrac{1}{2}\ge\beta\ge0\ .$$

Similarly for the regions (ii) and (iii), we have

$$0\le k_2^2=\left[\frac{1}{k'^2}\right]=\left[\frac{5(1-\beta^2)}{(4-\beta^2)}\right]\le1\quad\text{for } 1\ge\beta>\tfrac{1}{2}\ ,$$

$$0\le k_3^2=\left[\frac{1}{k^2}\right]=\left[\frac{5(1-\beta^2)}{(1-4\beta^2)}\right]\le1\quad\text{for } 2>\beta\ge1\ ,$$

and in region (iv), we have

$$0\le k_4^2=k'^2=\left[\frac{(4-\beta^2)}{5(1-\beta^2)}\right]\le1\quad\text{for } \beta\ge2\ .$$

Now the four k_i^2, $i=1,2,3,4$ can be identified with the modulus square of the standard elliptic integrals [15]. The variation of k_i^2, $i=1,2,3,4$ with respect to β, is

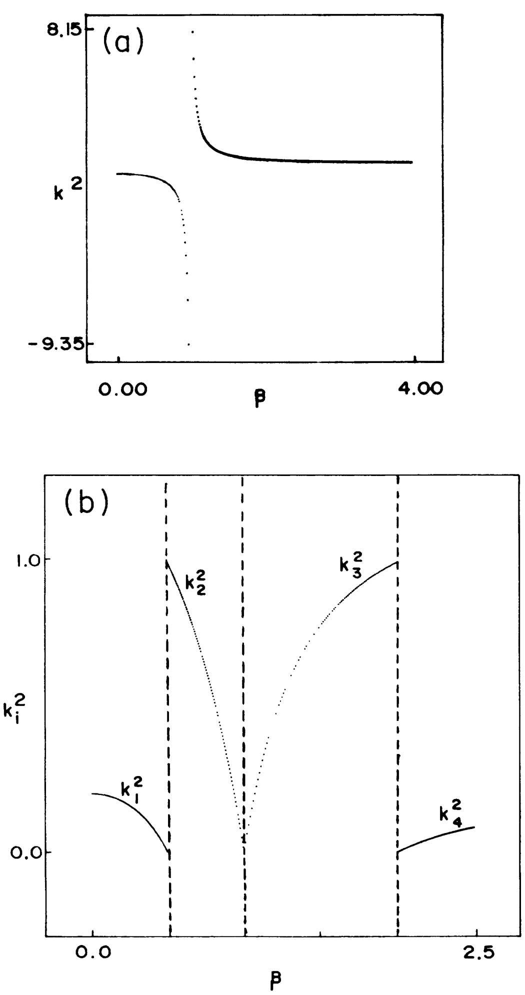

FIG. 1. (a) Variation of k^2 for $0\le\beta\le4$. (b) Variation of k_i^2, $i=1,2,3,4$ for the $0\le\beta\le2.5$ range.

shown in Fig. 1(b). Thus to cover the whole β-parameter range it is convenient to define appropriate action integrals in each of the regions that are functions of k_i^2, $i=1,2,3,4$ separately. These turn out to be the canonically equivalent action integrals obtained by Kuwata, Harada, and Hasegawa [8], but each one convenient for a particular range of the parameter β. These canonically equivalent action-angle variables are as follows:

$$\text{(i)}\ (I,\phi)\ , \tag{34a}$$

$$\text{(ii)}\ (P_1,\vartheta)\ \text{where}\ P_1^2=(n^2-I^2)\cos^2\phi \quad \text{and}\ I^2=(n^2-P_1^2)\cos^2\vartheta\ , \tag{34b}$$

$$\text{(iii)}\ (P_2,\psi)\ \text{where}\ P_2^2=(n^2-I^2)\sin^2\phi \quad \text{and}\ I^2=(n^2-P_2^2)\cos^2\psi\ . \tag{34c}$$

Correspondingly we have the following action integrals for different β regions.

(i) *Region I.* $0.5 \ge \beta \ge 0.0$. Using Eqs. (32) and (34b) we get

$$S^{(1)}(\Lambda)=\frac{1}{2\pi}\oint P_1(\vartheta)d\vartheta = \frac{n}{2\pi}\oint\left[1-\frac{\{(1-k_1^2)-(k_1^2\Lambda')\}}{(1-k_1^2\sin^2\vartheta)}\right]^{1/2}d\vartheta\ , \tag{35}$$

where

$$\Lambda'=\Lambda/(1-4\beta^2)\ . \tag{36}$$

(ii) *Region II.* $1\ge\beta>\frac{1}{2}$. Using Eqs. (32) and (34c) we get

$$S^{(2)}(\Lambda)=\frac{1}{2\pi}\oint P_2(\psi)d\psi = \frac{n}{2\pi}\oint\left[1+\frac{\Lambda'(1-k_2^2)}{(1-k_2^2\cos^2\psi)}\right]^{1/2}d\psi\ . \tag{37}$$

(iii) *Region III.* $2>\beta\ge 1$. Using Eqs. (32) and (34c) we get

$$S^{(3)}(\Lambda)=\frac{1}{2\pi}\oint P_2(\psi)d\psi = \frac{n}{2\pi}\oint\left[1+\frac{\Lambda'}{(1-k_3^2\sin^2\psi)}\right]^{1/2}d\psi\ . \tag{38}$$

(iv) *Region IV.* $\beta\ge 2$. From Eq. (32) we get

$$S^{(4)}(\Lambda)=\frac{1}{2\pi}\oint I(\phi)d\phi = \frac{n}{2\pi}\oint\left[1-\frac{(1-k_4^2)(1+\Lambda')}{(1-k_4^2\sin^2\phi)}\right]^{1/2}d\phi\ . \tag{39}$$

V. SEMICLASSICAL QUANTIZATION FOR THE CLASSICALLY INTEGRABLE CASES AND NEAR-INTEGRABLE REGIONS

A. Integrable cases

The quantity n introduced in the preceding section corresponds to the total energy and it can be identified as the principal quantum number and can be quantized in the usual sense. For an arbitrary value of the parameter β, one has to choose the appropriate action integrals [Eqs. (35)–(39)] given above and solve the corresponding elliptic integral numerically [16] to find the associated second quantum number for Λ. However, for the three special values of β, namely $\beta=\frac{1}{2}$, 1, and 2, which correspond to the classically integrable cases, the action integrals assume simple form and hence can be evaluated trivially, and thereby the associated quantum numbers can be obtained explicitly. The three cases of special interest are as follows.

Case (i). $\beta=\frac{1}{2}$. *Region I.* Here $k_1^2=0$. Therefore the action integral (35) becomes

$$S^{(1)}(\Lambda)=\frac{n}{2\pi}\oint(\Lambda/\tfrac{15}{4})^{1/2}d\vartheta = (n_1+\tfrac{1}{2})\ . \tag{40}$$

Here the Maslov index is taken to be 2 since the associated classical trajectories are of boxlike [17] nature as in Fig. 2(a). Equation (40) implies $n^2\Lambda=\frac{15}{4}(n_1+\frac{1}{2})^2$. Using this in Eq. (23), we get the expression for the energy-level shift as

$$\Delta E_{n,n_1}=\frac{\gamma n^2}{2}[\tfrac{5}{4}n^2+\tfrac{15}{4}(n_1+\tfrac{1}{2})^2]\ . \tag{41}$$

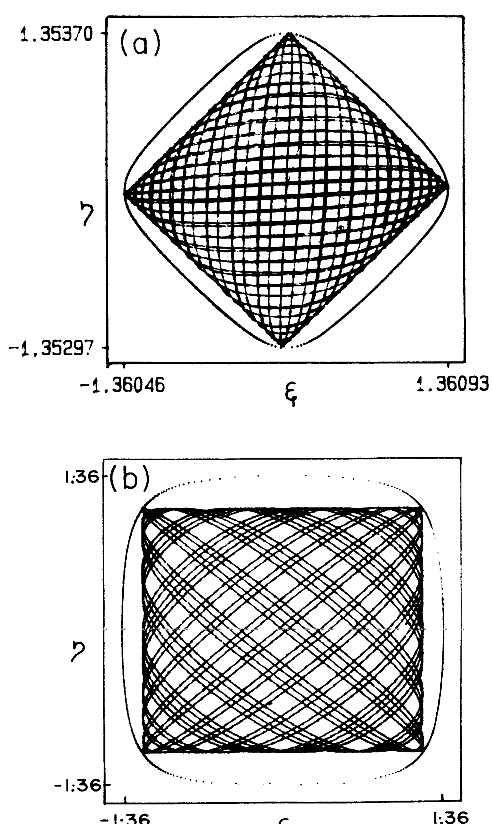

FIG. 2. (a) Trajectory plot for the Hamiltonian (27) along with the energy surface for the $\beta=0.5$ case. (b) Same as in (a) but for the $\beta=2$ case.

TABLE I. Results of Hamiltonian (27) for various integrable parametric values.

β	k_1^2	k_2^2	k_3^2	k_4^2	Action integral	Quantum operator [1]	Quantum number	Classical constant of motion [7]	Energy shift
$\frac{1}{2}$	0	1	∞	1	$S^1(\Lambda)$	$(A_x^2+A_y^2)$	$\eta(\eta+1)$	$\left[p_\xi p_\eta+5\gamma\beta^2\xi^3\eta^3 -2E\xi\eta+\left[\frac{6\gamma\beta^2}{4}\right](\xi^4+\eta^4)\xi\eta\right]$	$\frac{\gamma n^2}{2}[\frac{5}{4}n^2+\frac{15}{4}(n_1+\frac{1}{2})^2]$
1	∞	0	0	∞	$S^{2,3}(\Lambda)$	L^2	$1(1+1)$	$(\xi p_\eta-\eta p_\xi)^2$	$\frac{\gamma n^2}{2}[5n^2-3(n_2+\frac{1}{2})^2]$
2	1	∞	1	0	$S^4(\Lambda)$	A_z	m'	System decouples into two Sextic oscillators	$\frac{\gamma n^2}{2}[5n^2+15(n_3+\frac{1}{2})^2]$

Case (ii). $\beta=1$. (Region II or region III). Here $k_2^2=0$ and $k_3^2=0$. For this choice both the action integrals (37) and (38) degenerate into the same expression. Correspondingly we get

$$S^{(2)}(\Lambda)=S^{(3)}(\Lambda)=\frac{n}{2\pi}\oint\left[1-\frac{\Lambda}{3}\right]^{1/2}d\psi=(n_2+\tfrac{1}{2})\ . \tag{42}$$

Again the Maslov index is chosen as 2 because for the $\beta=1$ case, our oscillator Hamiltonian (27) decouples. Equation (42) implies $n^2\Lambda=3n^2-3(n_2+\frac{1}{2})^2$. Using this expression in Eq. (23), we obtain the energy-level shift as

$$\Delta E_{n,n_2}=\frac{\gamma n^2}{2}[5n^2-3(n_2+\tfrac{1}{2})^2]\ . \tag{43}$$

Case (iii). $\beta=2$. (Region IV). Here $k_4^2=0$. Hence the action integral (39) becomes

$$S^{(4)}(\Lambda)=\frac{n}{2\pi}\oint\left[\frac{\Lambda}{15}\right]^{1/2}d\phi\ ,$$

which can be quantized using the EBK quantization rule as

$$\frac{n}{2\pi}\oint\left[\frac{\Lambda}{15}\right]^{1/2}d\phi=(n_3+\tfrac{1}{2})\ , \tag{44}$$

where n_3 is an integer. For this choice also the Maslov index is 2 because of the existence of box-type trajectory [17] [Fig. 2(b)]. From Eq. (44), we have

$$n^2\Lambda=15(n_3+\tfrac{1}{2})^2\ . \tag{45}$$

Using this in Eq. (23), the shift in energy becomes as

$$\Delta E_{n,n_3}=\frac{\gamma n^2}{2}[5n^2+15(n_3+\tfrac{1}{2})^2]\ . \tag{46}$$

If we designate the quantum numbers $(n_1+\frac{1}{2})^2$ as $\eta(\eta+1)$, $(n_2+\frac{1}{2})^2$ as $1(1+1)$, and $(n_3+\frac{1}{2})$ as m' then our expressions for the energy-level shift for $\beta=\frac{1}{2}$, 1, and 2 cases are analogous to those obtained by Alhassid, Hinds, and Meschede [1] (of course for the $m=0$ case),

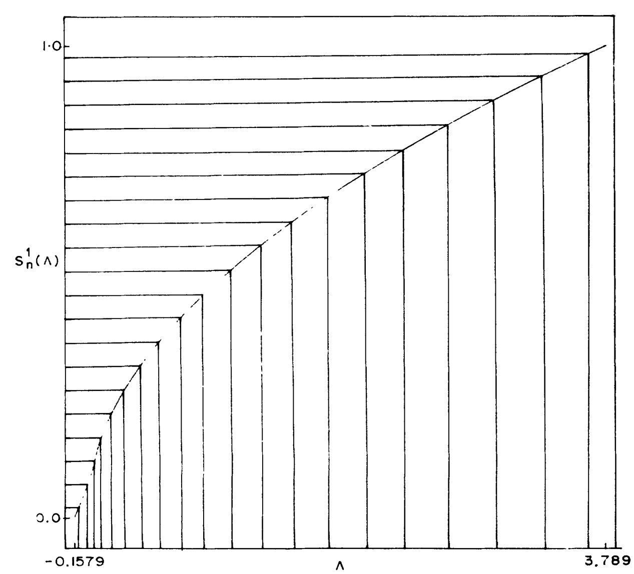

FIG. 3. Normalized action integral plotted against Λ for $\beta=0.4588$ case.

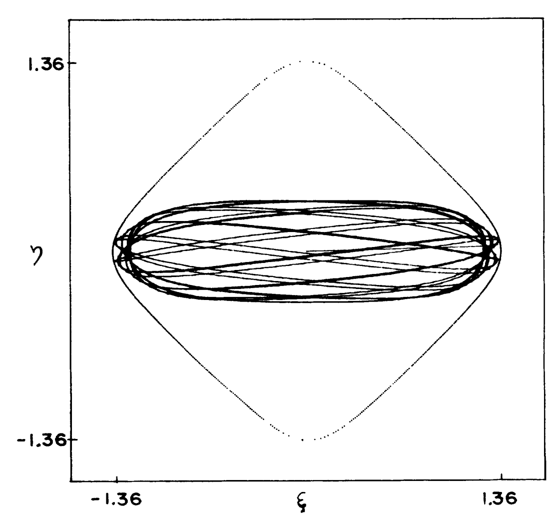

FIG. 4. Sample trajectory plot for the Hamiltonian (27) along with the energy surface for the $\beta=0.4588$ case.

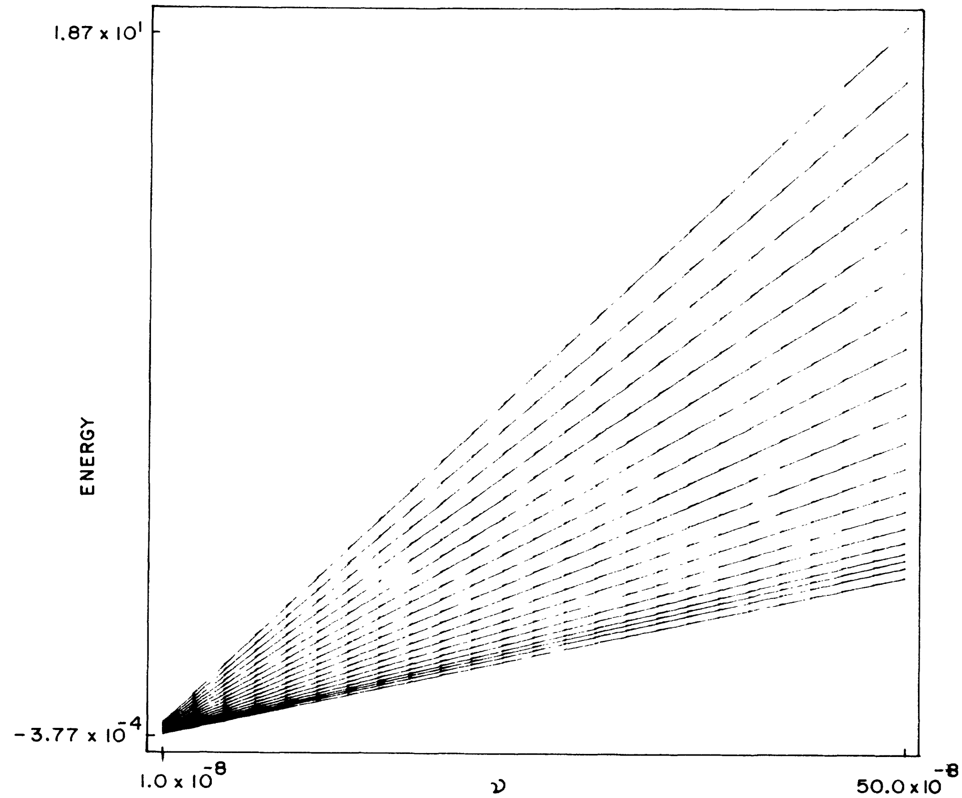

FIG. 5. Semiclassical spectrum generated using Eq. (23) for the $\beta=0.4588$ case ($n=20$).

using dynamical symmetry-group analysis. Additional constant factors in their expression are due to the form of the Casimir invariant chosen. We have used $n^2A^2=n^2-L^2$ rather than $L^2+A^2=n^2-1$. We have summarized our results in Table I.

B. Near-integrable regions

In order to understand the nonintegrable but near-integrable regions of β, one has to choose the appropriate action integral among (35)–(39), depending upon the β value, and integrate it numerically. For example, we choose $\beta^2=\frac{4}{19}$ which corresponds to $\beta=0.4588$ that lies near the integrable choice $\beta=0.5$. The corresponding classical dynamics is discussed in Ref. [7]. For this choice of β, we choose the action integral in the form (35). For the hydrogen atom in a generalized van der Waals potential problem, the generalized Solov'ev constant Λ on a unit sphere can vary between $4\beta^2-1$ and $(4-\beta^2)$. (We recall that for the diamagnetic Kepler problem Λ varies from -1 to 4.) For $\beta=0.4588$, Λ can vary from $-(\frac{3}{19})$ to $(\frac{72}{19})$. Here $k_1^2=0.04$. We have the normalized action integral (35) quantized as

$$S_n^1(\Lambda)=\frac{2}{\pi}\int_0^{\vartheta_1}\left[1-\left[\frac{(0.96)-(0.04\Lambda')}{(1-0.04\sin^2\vartheta)}\right]\right]^{1/2}d\vartheta$$
$$=\frac{1}{n}\left[n_1+\frac{\alpha}{4}\right], \qquad (47)$$

where

$$\vartheta_1=\begin{cases}\sin^{-1}\sqrt{(1+\Lambda')} & \text{for} -(\frac{3}{19})\le\Lambda<0\\ \frac{\pi}{2} & \text{for } 0\le\Lambda\le(\frac{72}{19}).\end{cases}$$

We integrated the integral in Eq. (47) using the Gaussian quadrature integration method [18] for different Λ values ranging from $-\frac{3}{19}$ to $\frac{72}{19}$ and obtained the quantized values of Λ. Figure 3 is a plot of the normalized action-integral value against the Λ value for the $n=20$ manifold. For the β value chosen, the classical trajectory touches the energy surface at four caustic points as indicated in Fig. 4, which implies a value of $\alpha=2$. For a given n manifold, n_1 can vary from $0,1,\ldots,(n-1)$. Using these in Eq. (23) we can generate the semiclassical spectrum for different γ values. One such spectrum generated for $\beta=0.4588$ case is shown in Fig. 5.

ACKNOWLEDGMENTS

This work forms part of a Council of Scientific and Industrial Research (CSIR) project of M.L. One of us (K.G.) express his sincere gratitude to CSIR for providing financial support.

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