Electronic structure of Rydberg atoms in parallel electric and magnetic fields

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The structure of the eigenstates of a hydrogen atom in parallel uniform electric and magnetic fields is investigated using high-order classical perturbation theory. The Kustaanheimo-Stiefel transformation is first used to convert the problem into an anharmonically perturbed four-dimensional isotropic oscillator. A canonical transformation to a set of extended "Lissajous" action-angle variables is then introduced that considerably simplifies the perturbation expansion, leading to a simple and compelling classification scheme for the eigenstates. Extended Lissajous action-angle variables allow the construction of rotational energy surfaces, which provide a compact geometrical picture that captures important details of the energy-level structure of the system.

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I. INTRODUCTION

Atoms placed in relatively weak external fields react by reorganizing their energy-level structure according to the new set of exact or approximate symmetries which may be imposed by the external perturbation. A case in point is the quadratic Zeeman effect (QZE) in Rydberg atoms [1–6], which has become a unique laboratory for the study of chaos and nonintegrability in quantum systems [7–12]. As well as experimental studies there have been many quantum studies of Rydberg atoms in external fields using high-order quantum perturbation theory [13–24] or accurate numerical methods [25–34]. Not surprisingly, in view of the large number of studies devoted to this problem (only a fraction of which have been cited), a plethora of experimental and computational data exists. In order to interpret and consolidate these data and provide new insights into any order underlying them, classical and semiclassical methods have been used successfully to identify new quantum numbers and provide qualitative descriptions of the evolution of the energy levels as a function of field strength [35–54]. When an external electric field is added to the magnetic field the level structure becomes even more complex (notwithstanding field ionization) and again guidance from classical and semiclassical methods becomes indispensable. One of the earliest calculations using high-order quantum perturbation theory for this problem was by Johnson, Scheibner, and Farrelly [24] who invoked Canterbury approximants to resum the divergent perturbation expansion [55]. In any case, the essence of a classical study is to build an accurate and concise physical picture which captures the overall systematic trends contained in quantum or experimental data. Accordingly, the major objective of this account is to develop a comprehensive classical theory of the electronic structure of hydrogenic Rydberg states in external parallel electric and magnetic fields in the regime where the diamagnetic term in the Hamiltonian is important [the Stark–quadratic-Zeeman effect (SQZE)] [35,42–47]. This approach, based on the determination of apt action-angle variables and high-order classical perturbation theory, is exploited to develop a compact geometrical picture which affords considerable insight into the global behavior of the system as a function of field strengths and quantum numbers.

The SQZE has been studied experimentally rather thoroughly in alkali-metal atoms but no experimental results evidently exist for the hydrogen atom itself. Studies by Cacciani, and co-workers [42–46] indicate that deviations from pure hydrogenic behavior in alkali-metal atoms can mask effects that are implied by lowest-order perturbation theory. In this paper high-order classical perturbation theory is performed in both of the external fields for the hydrogen atom with the aims of understanding the robustness of low-order results, developing a classification of the eigenstates and of encouraging experimental studies of the hydrogen atom itself. An interesting result is the finding that the fields mix at and beyond third order in the combined fields, which implies that the

level structure will be much more complicated than that assigned on the basis of low-order perturbation theory.

The determination of action-angle variables reflecting the actual dynamics of a system is a prominent and persistent problem in treating resonant (degenerate) classical systems like the QZE and the SQZE. This issue has preoccupied celestial mechanicians and astronomers for more than a century [35,56,57]. Several previous classical and semiclassical studies of the QZE and the SQZE have relied on the intuition of astronomers by using the Delaunay elements, which are often appropriate for perturbed Kepler problems [37,38,47,53,54,56]. In order to make a connection with quantum mechanics, however, it is necessary that the set of action-angle variables used be physically motivated. The Delaunay elements, while convenient for application of classical perturbation theory, do not necessarily prove to be the best variables in which to understand the level structure. For example, they may lead to singular quantization formulas [3,49,53]. The problem of determining good action-angle variables is solved for the SQZE by a new transformation to uniformly valid action-angle variables based on the Kustaanheimo-Stiefel (KS) transformation [58–61] and insights gleaned from a group theoretical perspective [62–70]. The final issue of import is the interpretation of classical perturbation expansions containing numerous complicated terms. The key is visualization [35,71]. Using the device of a rotational energy surface [72–77] (RES), the global features contained in the perturbation expansion are revealed at once in a simple and geometrically pleasing fashion.

The article is organized as follows; Sec. II is devoted to a description of classical perturbation theory as applied to the SQZE Hamiltonian. The coordinates of Kustaanheimo and Stiefel are used throughout [58–61]. Next a canonical transformation to action-angle variables is produced which collapses the $\sim 10^5$ terms in the original expansion to around 100. Much experimental effort has been directed to the $m=0$ case which emerges as a special case of the present treatment (the azimuthal quantum number m is preserved as an exact quantum number in the SQZE). In Sec. III an alterative derivation of the $m=0$ case is presented which has the advantage of providing a nontrivial check of the more general case while shedding considerable light on the symmetries present in the SQZE. Construction of the RES's is described in Sec. IV where results are presented. The paper concludes with a brief discussion in Sec. V.

II. CLASSICAL PERTURBATION THEORY

In Cartesian coordinates and atomic units $m_e=e=\hbar=1$ the Hamiltonian for the SQZE with the fields parallel and along the z axis is [24,35,42–47]

$$H=E=\tfrac{1}{2}(P_x^2+P_y^2+P_z^2)+\frac{\gamma}{2}L_z+\frac{\gamma^2}{8}(x^2+y^2)-\frac{1}{r}-Fz \tag{1}$$

where E is energy and

$$L_z=xP_y-yP_x=m\hbar\ , \tag{2}$$

and the electric and magnetic field strengths are F and γ, respectively. In atomic units the unit of electric field is 5.14×10^9 V/cm and the unit of magnetic field is 2.35×10^5 T (1 T$=10^4$ G). An approximate constant of motion for the QZE found by Solov'ev [39,40] and Herrick [41] is given by [48]

$$\Lambda=4\,\mathbf{A}^2-5\,\mathbf{A}_z^2 \tag{3}$$

where

$$\mathbf{A}=\frac{1}{(-2H_0)^{1/2}}\left[\mathbf{p}\times\mathbf{L}-\frac{\mathbf{r}}{r}\right] \tag{4}$$

is the modified Runge-Lenz vector [78] and $H_0=E_0$ is the unperturbed Kepler energy. For the SQZE the corresponding constant of motion is the following [42–47]:

$$\Lambda_\beta=4\,\mathbf{A}^2-5\,\mathbf{A}_z^2-10\beta A_z \tag{5}$$

where

$$\beta=12F/(5n^2\gamma^2)\ . \tag{6}$$

Λ_β is the lowest vanishing term in the perturbation expansion and at this order the fields obviously do not mix. In order to go to higher order in both fields the methods of classical secular perturbation theory will be used [79–89]; these provide an integrable approximation to the original Hamiltonian often called the normal form. This method provides a straightforward way of calculating high-order expansions for mixed perturbations with the aid of symbolic algebraic manipulation programs like MATHEMATICA or SMP [35,71].

As noted, in the case of perturbed Kepler systems it is common to work in terms of the Delaunay elements which include the principal action n, the angular momentum, and its z component, together with their conjugate angles. The angular momentum is not conserved in either the QZE or the SQZE which suggests that a different choice of action-angle variables than the Delaunay elements might be preferable. It turns out that perturbation expansions in the Delaunay elements are unsatisfactory for the QZE and SQZE in the limit $m=0$ because they lead to singular quantization rules at the separatrix [3,49,53]. This problem has been studied for the $m=0$ case by Grozdanov and Rakovic [90] and Farrelly and Krantzman [49]. Rather than work in terms of the Delaunay elements, classical perturbation theory is performed in the Kustaanheimo-Stiefel coordinates which allow the perturbation expansion to be readily converted into an expression in terms of a set of particularly apt action-angle variables. These elements are here called extended Lissajous (or simply Lissajous) action-angle variables because they can be viewed as being a generalization of the variables introduced by Deprit [54(b)]. They readily account for the Lissajous figures generated from an isotropic harmonic oscillator Hamiltonian in two (or more) dimensions and emerge naturally from the KS transformation. The KS transformation was originally designed to regularize the effect of the potential energy singularity on the classical dynamics in the vicinity of the origin. It allows the unperturbed Hamiltonian and any perturbation to be written in terms of the canonical coor-

dinates and momenta of an isotropic four-dimensional harmonic oscillator. For the SQZE the Hamiltonian is first converted into a perturbed four-dimensional oscillator using the KS transformation, the normal form is then constructed, followed by a transformation to action-angle variables.

The KS transformation starts by relating the original coordinates to a set of coordinates in a four dimensional space using [59,61]

$$\mathbf{r}=\mathbf{T}\mathbf{u} \tag{7}$$

where

$$\mathbf{T}=\begin{bmatrix} u_1 & -u_2 & -u_3 & u_4 \\ u_2 & u_1 & -u_4 & -u_3 \\ u_3 & u_4 & u_1 & u_2 \\ u_4 & -u_3 & u_2 & -u_1 \end{bmatrix} \tag{8}$$

and $\mathbf{u}={}^t(u_1,u_2,u_3,u_4)$, $\mathbf{r}={}^t(x_1,x_2,x_3,0)$, and $\mathbf{T}$ satisfies the orthogonality relation (superscript t means transpose),

$$\mathbf{T}{}^t\mathbf{T}={}^t\mathbf{T}\mathbf{T}=|\mathbf{u}|^2 . \tag{9}$$

In Eq. (9),

$$|\mathbf{u}|^2=u_1^2+u_2^2+u_3^2+u_4^2 . \tag{10}$$

The two sets of coordinates are related explicitly by

$$x_1=z=u_1^2-u_2^2-u_3^2+u_4^2 , \tag{11}$$

$$x_2=y=2(u_1u_2-u_3u_4) , \tag{12}$$

$$x_2=x=2(u_1u_3+u_2u_4) . \tag{13}$$

The dynamical variables can be related by using the momenta $\mathbf{P_u}$ which are conjugate to $\mathbf{u}$,

$$\mathbf{P_u}={}^t(P_1,P_2,P_3,P_4) \tag{14}$$

for which the following constraint holds:

$$u_1P_4-u_4P_1+u_3P_2-u_2P_3=0 \tag{15}$$

where

$$\sum_{i=1}^{3} P_{x_i}dx_i=\sum_{i=1}^{4} P_i du_i . \tag{16}$$

Thus

$$\mathbf{P_x}=\frac{1}{2r}\mathbf{T}\mathbf{P_u} \tag{17}$$

where

$$\mathbf{P_x}={}^t(P_{x_1},P_{x_2},P_{x_3},0) . \tag{18}$$

In view of Eq. (15) the system is subject to the restriction

$$P_\phi=m=u_1P_4-u_4P_1=-u_3P_2+u_2P_3 , \tag{19}$$

enforcement of which converts the SQZE Hamiltonian into

$$H=\frac{1}{8r}\mathbf{P}_u^2-\frac{1}{|u|^2}+\frac{\gamma}{2}m+\frac{\gamma^2}{2}(u_1^2+u_4^2)(u_2^2+u_3^2) -F(u_1^2-u_2^2-u_3^2+u_4^2) . \tag{20}$$

This Hamiltonian, in turn, can be converted into a system of four coupled anharmonic oscillators by making the transformation to a new time variable s (regularization),

$$\frac{dt}{ds}=4r=4|\mathbf{u}|^2 . \tag{21}$$

Multiplying through by $4r$ gives the Hamiltonian

$$K=4=\tfrac{1}{2}(\mathbf{P}_u^2+\omega^2|\mathbf{u}|^2)+2\gamma^2|\mathbf{u}|^2(u_1^2+u_4^2)(u_2^2+u_3^2) -4F|\mathbf{u}|^2(u_1^2-u_2^2-u_3^2+u_4^2) \tag{22}$$

where

$$\omega^2=4\gamma m-8E . \tag{23}$$

Scaling the coordinates and momenta yields

$$K=\frac{4}{\omega}=\tfrac{1}{2}(\mathbf{P}_u^2+|\mathbf{u}|^2)+2\frac{\gamma^2}{\omega^4}|\mathbf{u}|^2(u_1^2+u_4^2)(u_2^2+u_3^2) -\frac{4F}{\omega^3}|\mathbf{u}|^2(u_1^2-u_2^2-u_3^2+u_4^2) . \tag{24}$$

The normal form was obtained in these coordinates using the symbolic manipulation program MATHEMATICA as implemented on a Macintosh IIci personal computer [91]. The raw expansion, a tenth-order polynomial in coordinates and momenta, contained approximately 100 000 terms through fourth order in each field. Previous [92] analysis of the QZE suggests that a considerable simplification of this expression might be achieved by performing the following sequence of transformations.

First, a transformation to new coordinates and momenta is made, equivalent to a rotation in phase space,

$$\begin{aligned} u_1&=\frac{(q_1+p_4)}{\sqrt{2}}, & P_1&=\frac{(q_4-p_1)}{\sqrt{2}} , \\ u_2&=\frac{(q_3+p_2)}{\sqrt{2}}, & P_2&=\frac{(q_2-p_3)}{\sqrt{2}} , \\ u_3&=\frac{(q_2+p_3)}{\sqrt{2}}, & P_3&=\frac{(q_3-p_2)}{\sqrt{2}} , \\ u_4&=\frac{(q_4+p_1)}{\sqrt{2}}, & P_4&=\frac{(q_1-p_4)}{\sqrt{2}} . \end{aligned} \tag{25}$$

Next a transformation to action-angle variables is desired: Based on previous studies of resonant systems a transformation is sought which will convert the normal form into an expression containing the action variables n and A_z and the angle conjugate to A_z, namely, ϕ_{A_z} [35,87,92]. A solitary angle is expected to persist because the problem is resonant [62]. The initial transformation is

$$q_i=(2I_i)^{1/2}\sin\phi_i, \quad p_i=(2I_i)^{1/2}\cos\phi_i \tag{26}$$

where $i=1,2,3,4$. Two further transformations are then performed in order to eliminate all but one angle; first,

$$I_1=\frac{(I_a+I_b)}{2},\quad \phi_1=\phi_a+\phi_b\ ,$$
$$I_2=\frac{(I_a-I_b)}{2},\quad \phi_2=\phi_a-\phi_b\ ,$$
$$I_3=\frac{(I_c+I_d)}{2},\quad \phi_3=\phi_c+\phi_d\ ,$$
$$I_4=\frac{(I_c-I_d)}{2},\quad \phi_4=\phi_c-\phi_d\ . \tag{27}$$

The constraint (19) requires that $I_a=I_c=n$. The final transformation to the Lissajous action-angle variables is

$$I_b=m+A_z,\quad \phi_b=\frac{(\phi_m+\phi_{A_z})}{2}\ ,$$
$$I_d=m-A_z,\quad \phi_d=\frac{(\phi_m-\phi_{A_z})}{2}\ . \tag{28}$$

This converts the normal form $K_m^{\rm NF}$ into the following expression:

$$K_m^{\rm NF}=\frac{4}{\omega}=2n-\frac{A_0}{\omega^3}F+\frac{A_1}{\omega^6}F^2+\frac{A_2}{\omega^9}F^3+\frac{A_3}{\omega^{12}}F^4+\frac{A_4}{\omega^4}\gamma^2+\frac{A_5}{\omega^7}\gamma^2F+\frac{A_6}{\omega^{10}}\gamma^2F^2+\frac{A_7}{\omega^8}\gamma^4\ , \tag{29}$$

where the coefficients are given explicitly in terms of the Lissajous variables in Table I. Alternatively, the normal form (29) may be inverted to yield the energy directly,

$$E=-\frac{1}{2n^2}-\frac{A_0F}{16}+\frac{\gamma m}{2}+\gamma^2\frac{nA_4}{32}+F^2\left[\frac{3n^2A_0^2}{512}+\frac{n^3A_1}{128}\right]+F\gamma^2\left[\frac{-n^3A_0A_4}{128}+\frac{n^4A_5}{256}\right]$$
$$+F^3\left[\frac{-5n^4A_0^3}{4096}-\frac{3n^5A_0A_1}{1024}+\frac{n^6A_2}{1024}\right]+F^2\gamma^2\left[\frac{21n^5A_0^2A_4}{8192}+\frac{7n^6A_1A_4}{4096}-\frac{7n^6A_0A_5}{4096}+\frac{n^7A_6}{2048}\right]$$
$$+F^4\left[\frac{21n^6A_0^4}{65536}+\frac{9n^7A_0^2A_1}{8192}+\frac{9n^8A_1^2}{32768}-\frac{9n^8A_0A_2}{16384}+\frac{n^9A_3}{8192}\right]+\gamma^4\left[\frac{5n^4A_4^2}{2048}+\frac{n^5A_7}{512}\right]\ . \tag{30}$$

TABLE I. Coefficients occurring in the expansions (29) and (30). The quantity $X=\{[n^2-(m+A_z)^2][n^2-(m-A_z)^2]\}^{1/2}$.

$$A_0=24nA_z$$
$$A_1=72nm^2-136n^3-408nA_z^2$$
$$A_2=-12\,000nA_z^3+4128nm^2A_z-12\,000n^3A_z$$
$$A_3=-427\,560A_z^4+71\,280n^2m^2-7272nm^4-855\,120n^3A_z^2+213\,840nm^2A_z^2-85\,512n^5$$
$$A_4=-6nA_z^2-2nm^2+6n^3-4nX+8nX\cos^2\phi_{A_z}$$
$$A_5=-272nA_z^3+272n^3A_z-168nXA_z+336nXA_z\cos^2\phi_{A_z}$$
$$A_6=-13\,156nA_z^4-3320n^3m^2+140nm^4-2776n^3X+8312n^3A_z^2+512n^5\cos^2\phi_{A_z}-512n^5\cos^4\phi_{A_z}$$
$$-7704nXA_z^2+512nA_z^4\cos^2\phi_{A_z}-512nA_z^4\cos^4\phi_{A_z}+664nm^2X+3032nm^2A_z^2-1024n^3m^2\cos^2\phi_{A_z}$$
$$+1024n^3m^2\cos^4\phi_{A_z}+512nm^4\cos^2\phi_{A_z}-512m^4n\cos^4\phi_{A_z}+5552n^3X\cos^2\phi_{A_z}-1024n^3A_z^2\cos^2\phi_{A_z}$$
$$+1024n^3A_z^2\cos^4\phi_{A_z}+15\,408nA_z^2\cos^2\phi_{A_z}-1328nm^2\cos^2\phi_{A_z}-1024nm^2A_z^2\cos^2\phi_{A_z}$$
$$+4844n^5+1024nm^2A_z^2\cos^4\phi_{A_z}$$
$$A_7=\frac{-347nA_z^4}{6}+\frac{253n^3m^2}{3}-\frac{115nm^4}{6}+\frac{286n^3X}{3}+159nA_z^2$$
$$+72n^5\cos^2\phi_{A_z}-72n^5\cos^4\phi_{A_z}-\frac{154nXA_z^2}{3}+72nA_z^4\cos^2\phi_{A_z}-72nA_z^4\cos^4\phi_{A_z}$$
$$-\frac{46nm^2X}{3}+29nm^2A_z^2-144n^3m^2\cos^2\phi_{A_z}+144n^3m^2\cos^4\phi_{A_z}$$
$$+72nm^4\cos^2\phi_{A_z}-72nm^4\cos^4\phi_{A_z}-\frac{572n^3X\cos^2\phi_{A_z}}{3}-144n^3A_z^2\cos^4\phi_{A_z}$$
$$+144n^3A_z^2\cos^4\phi_{A_z}+\frac{308nA_z^2X\cos^2\phi_{A_z}}{3}+\frac{92nm^2X\cos^2\phi_{A_z}}{3}$$
$$-144n^2m^2A_z^2\cos^2\phi_{A_z}+144nm^2A_z^2\cos^4\phi_{A_z}-\frac{607n^5}{6}$$

This expression agrees with previous low-order results in the limits that either field is zero and with the low-order results of Cacciani, and co-workers [43–45]. The approximate constant of motion Λ_β is given explicitly by the following expression:

$$n^2\Lambda_\beta=2\{[n^2-(m+A_z)^2][n^2-(m-A_z)^2]\}^{1/2}\cos 2\phi_{A_z} -3A_z^2-2m^2+2n^2-10\beta A_z \ . \tag{31}$$

This completes the derivation of the normal form and its transformation to action-angle variables for arbitrary values of m. In the next section the particular case $m=0$ is considered.

III. NORMALIZATION WHEN $m=0$ AND LOW-FIELD LIMITS

Although a special case of the theory developed in the preceding section, the problem with $m=0$ merits consideration in its own right [35,88–97]. This case has mainly been studied in the parabolic coordinates originally applied by Edmonds and Pullen [93] to the QZE and followed shortly thereafter by Reinhardt and Farrelly [48] who not only generated the normal form for the QZE in these variables but provided the first convincing graphical demonstration that a good approximate invariant exists. Robnik and Schrüfer [88] subsequently expanded the QZE to sixth order in the magnetic field in these variables. For the SQZE parabolic coordinates are especially useful because the pure Stark effect in hydrogen is separable in this coordinate system [90,98]. In fact, the separation constant is essentially A_z itself [78]. A second advantage of considering the SQZE system in these coordinates is that it provides an alternative derivation of the normal form which provides a nontrivial and independent check of the expansion (31).

The Hamiltonian (1) is first written in cylindrical coordinates and it is assumed immediately that $m=0$,

$$H=E=\tfrac{1}{2}(P_\rho^2+P_z^2)+\frac{\gamma^2}{8}\rho^2-\frac{1}{r}-Fz \tag{32}$$

where

$$\rho^2=x^2+y^2 \ . \tag{33}$$

Using semiparabolic coordinates [88,96],

$$\rho=uv, \quad z=\tfrac{1}{2}(u^2-v^2), \quad r=\tfrac{1}{2}(u^2+v^2) \tag{34}$$

and performing the Levi-Civita regularization [93,97],

$$\frac{dt}{ds}=2r \tag{35}$$

together with the following rescaling of the coordinates and momenta:

$$u\rightarrow\frac{u}{\sqrt{\Omega}}, \quad v\rightarrow\frac{v}{\sqrt{\Omega}}, \quad P_u\rightarrow\sqrt{\Omega}P_u, \quad P_v\rightarrow\sqrt{\Omega}P_v \ , \tag{36}$$

where $\Omega=\sqrt{-2E}$ gives

$$\frac{2}{\Omega}=\tfrac{1}{2}(P_u^2+P_v^2)+\tfrac{1}{2}(u^2+v^2) +\frac{\gamma^2}{8\Omega^4}(u^2+v^2)(u^2v^2)-\frac{F}{2\Omega^3}(u^4-v^4) \ . \tag{37}$$

Normalization is effected in this set of coordinates after which a transformation to action-angle variables is performed. Again, the raw normal form in terms of the parabolic coordinates and momenta contained many thousands of terms. The transformation to action-angle variables in this case proceeds by exploiting the exact SU(2) symmetry of the unperturbed problem, i.e., the two-dimensional harmonic oscillator. The unperturbed four-dimensional oscillator K_0 [obtained by eliminating the perturbation in Eq. (24)] may be written in terms of the actions I_i, $i=1,2,3,4$ of Eq. (27),

$$K_0=\frac{2}{\Omega}=I_1+I_2+I_3+I_4 \ . \tag{38}$$

Setting $m=0$ in Eq. (28) reveals that in this limit $I_b=-I_d=A_z$ which collapses Eq. (38) into a two-dimensional harmonic oscillator [compare Eq. (37)].

The normal form may be written entirely in terms of the oscillator action-angle variables, and through fourth order in each field it becomes

$$K_{m=0}^{\mathrm{NF}}=\frac{2}{\Omega}=2n-\frac{B_0}{\Omega^3}F+\frac{B_1}{\Omega^6}F^3+\frac{B_2}{\Omega^9}F^2+\frac{B_3}{\Omega^{12}}F^4 +\frac{B_4}{\Omega^4}\gamma^2+\frac{B_5}{\Omega^7}\gamma^2F+\frac{B_6}{\Omega^{10}}\gamma^2F^2+\frac{B_7}{\Omega^8}\gamma^4 \ . \tag{39}$$

The coefficients are given in Table II. This expression agrees with Eq. (29) when m is set to zero in that expression. The normal form (39) can be inverted to give the energy directly,

$$E_{m=0}=-\frac{1}{2n^2}-\frac{B_0F}{2}+\gamma^2\frac{nB_4}{2}+F^2\left[\frac{3n^2B_0^2}{8}+\frac{n^3B_1}{2}\right]+F\gamma^2\left[-n^3B_0B_4+\frac{n^4B_5}{2}\right] +F^3\left[\frac{-5n^4B_0^3}{8}-\frac{3n^5B_0B_1}{2}+\frac{n^6B_2}{2}\right]+F^2\gamma^2\left[\frac{21n^5B_0^2B_4}{8}+\frac{7n^6B_1B_4}{4}-\frac{7n^6B_0B_5}{4}+\frac{n^7B_6}{2}\right] +F^4\left[\frac{21n^6B_0^4}{16}+\frac{9n^7B_0^2B_1}{2}+\frac{9n^8B_1^2}{8}-\frac{9n^8B_0B_2}{4}+\frac{n^9B_3}{2}\right]+\gamma^4\left[\frac{5n^4B_4^2}{8}+\frac{n^5B_7}{2}\right] \tag{40}$$

TABLE II. Coefficients occurring in the expansions (39) and (40).

$$B_0 = 3nA_z$$

$$B_1 = -\frac{51nA_z^2}{8} - \frac{17n^3}{8}$$

$$B_2 = -\frac{375nA_z^3}{16} - \frac{375n^3A_z}{16}$$

$$B_3 = -\frac{53\,445nA_z^4}{512} - \frac{53\,445n^3A_z^2}{256} - \frac{10\,689n^5}{512}$$

$$B_4 = -\frac{nA_z^2}{8} + \frac{n^3}{8} - \frac{nA_z^2\cos^2\phi_{A_z}}{2} + \frac{n^3\cos^2\phi_{A_z}}{2}$$

$$B_5 = -\frac{13nA_z^3}{16} + \frac{13n^3A_z}{16} - \frac{21nA_z^3\cos^2\phi_{A_z}}{8} + \frac{21n^3A_z\cos^2\phi_{A_z}}{8}$$

$$B_6 = -\frac{1363nA_z^4}{256} + \frac{423n^3A_z^2}{128} + \frac{517n^5}{256} - \frac{931nA_z^4\cos^2\phi_{A_z}}{64} + \frac{69n^3A_z^2\cos^2\phi_{A_z}}{8} + \frac{379n^5\cos^2\phi_{A_z}}{64} - \frac{nA_z^4\cos^4\phi_{A_z}}{2} + n^3A_z^2\cos^2\phi_{A_z} - \frac{n^5\cos^4\phi_{A_z}}{2}$$

$$B_7 = \frac{-13nA_z^4}{512} + \frac{37n^3A_z^2}{768} - \frac{35n^5}{1536} - \frac{23nA_z^4\cos^2\phi_{A_z}}{192} + \frac{7n^3A_z^2\cos^2\phi_{A_z}}{12} - \frac{89n^5\cos^2\phi_{A_z}}{192} - \frac{9nA_z^4\cos^4\phi_{A_z}}{32} + \frac{9n^3A_z^2\cos^4\phi_{A_z}}{16} - \frac{9n^5\cos^4\phi_{A_z}}{32}$$

which agrees with Eq. (30) when m is set to zero there.

Various low-field limits can be examined to provide further checks of the results and agreement was obtained with previous results in the various limits [13,99,100]. When the magnetic field is absent the energy expression (40) agrees with the second-order quantum result given by Landau and Lifshitz [98] (apart from a constant, unimportant in the limit of large n) in terms of the parabolic quantum numbers n_1 and n_2. The connection with the parabolic quantum numbers is made via the relation

$$n_1 - n_2 = A_z \ . \tag{41}$$

Ignoring terms which are higher order than quadratic in γ and in the limit $F=0$ Eq. (29) reduces to the correct limit [61],

$$E = -\frac{1}{2n^2} + \frac{\gamma^2 n^4}{16}[1+\Lambda+(m/n)^2] \ . \tag{42}$$

IV. ENERGY-LEVEL CLASSIFICATION AND ROTATIONAL ENERGY SURFACES

The expression for the energy developed in terms of action-angle variables in Eq. (30) provides a convenient vantage point from which to scrutinize the energy-level structure. To begin with it is illuminating to consider only Eq. (31) which expresses the approximate invariant Λ_β in terms of the new set of Lissajous action-angle variables. This expression leads to an immediate classification of the eigenstates. It is worthwhile to review briefly the situation for the QZE where the corresponding quantity to Λ_β is simply Λ as defined in Eq. (3).

Λ takes values in the range $(-n^2, 4n^2)$ and the two extremal values correspond to different limiting types of classical motion with a separatrix occurring at $\Lambda=0$. Trajectories with $\Lambda>0$ have the full symmetry of the potential and are usually labeled rotational. As Λ approaches its maximum value the trajectories become localized along the ρ axis (in cylindrical coordinates) and correspond to the ridge states of Fano and co-workers [101,102] and Rau [103,104] which give rise to the $3/2\hbar\omega$ quasi-Landau resonances [1,35,101–108]. The second class of trajectories with $\Lambda<0$ are vibrational in character and occur in degenerate pairs. This leads to splittings in the eigenvalue spectrum due to tunneling. The separatrix between the rotational and vibrational types of trajectory occurs at $\Lambda=0$ and is clearly visible in Poincaré surfaces of section [3]. For the vibrational states A_z itself is a fairly good constant of motion making the problem in this limit similar to the Stark effect in hydrogen. In the Hamiltonian (1) the quantum number m appears as a parameter and the dynamics must therefore be examined at each value of m. It is of particular interest to note that, based on first-order classical perturbation theory, the dynamics can be divided into two broad categories depending upon the ratio m/n [53,54]. If $m/n < 1/\sqrt{5}$ both vibrational and rotational trajectories exist while if $m/n > 1/\sqrt{5}$ only rotational trajectories occur. The separatrix disappears when $m/n = 1/\sqrt{5}$. This phenomenon has important consequences for quantization; when $m/n < 1/\sqrt{5}$ (the separatrix exists) a quantization formula is needed which goes smoothly from the

regime where $\Lambda < 0$ to that where $\Lambda > 0$. When only rotational motion exists then a different quantization formula is needed to treat the single class of rotational states. In this case quantization formulas based on classical perturbation theory performed in the Delaunay elements give good agreement. However, such formulas are singular at the separatrix and technically invalid in the limit $m=0$ [53]. They perform best when $m/n > 1/\sqrt{5}$, i.e., for the rotational states.

Stated somewhat differently, Herrick [41] (see also Alhassid, Hinds, and Meschede [63] and Kalnins, Miller, and Winternitz [64]) has shown that the QZE can be viewed as falling between two exact dynamical symmetry limits: $O(4) \supset O(3)_\lambda \supset O(2)$ and $O(4) \supset O(2) \otimes O(2)$ [The subscript λ in $O(3)_\lambda$ indicates that the generators of the Lie algebra are those of a nonstandard angular momentum having components (A_x, A_y, L_z)]. As the value of m increases the fomer dynamical chain becomes more appropriate. By contrast, in the pure Stark limit the latter symmetry chain is more fitted. Therefore an interesting competition between the two symmetry chains is expected to take place as m and F are both varied.

The general situation is somewhat similar in the SQZE to that in the QZE. If the electric field is gradually turned on then the energy-level classification scheme is expected to evolve smoothly from the QZE limit. In some ways the problem is simpler than the QZE because increasing the electric field leads to A_z being a better invariant or quantum number (it is exact in the pure Stark limit). For the $m=0$ case and based on low-order perturbation theory Cacciani *et al.* [43–45] have shown that three classes of state exist, labeled I, II (vibrational), and III (rotational). The effect of the electric field is to break the degeneracy of the vibrational states in the QZE giving rise to two distinct classes of vibrational state. If the electric field continues to be increased, first one class of vibrational state vanishes (at $\beta=0.2$) followed shortly afterwards by the rotational states (at $\beta=1.0$), leaving

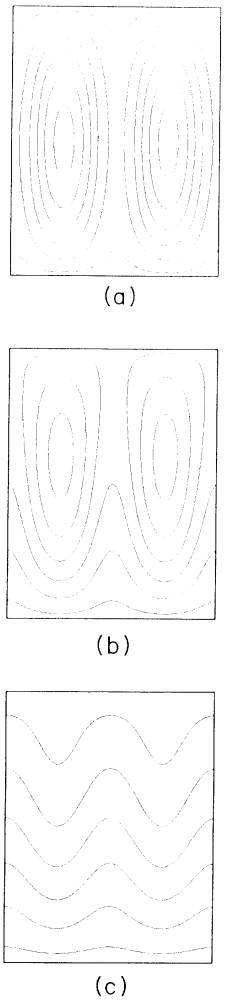

FIG. 1. Level curves of Λ_β as A_z and ϕ_{A_z} are varied with $m=0$ and $n=30$. In each case the abscissa, ϕ_{A_z}, ranges between $-\pi$ and π and the ordinate, A_z, ranges from the most negative to the most positive value which it can take. The actual values are immaterial. The vibrational states of the SQZE are the rotating states in the rotor picture while the SQZE rotational states are localized in the two wells. In (a) $\beta=0$, in (b) $\beta=0.2$, and in (c) $\beta=1.0$.

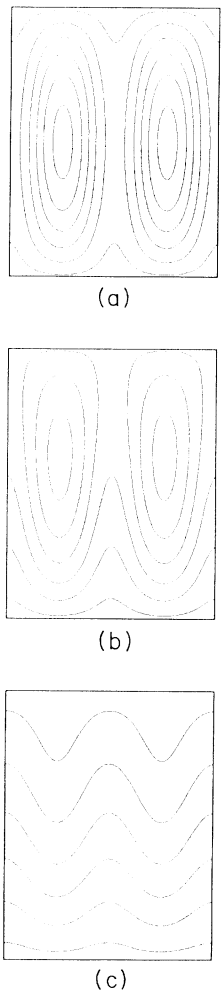

FIG. 2. Same as Fig. 1 but $m=1$.

only a single class of vibrational states in the Stark limit. By examining level curves of Λ_β in the action-angle variables of Eq. (31) this sequence of events is plainly evident in Fig. 1. This figure merits explanation. When $m=0$ and the electric field is small or absent [Fig. 1(a)] phase space resembles that of a twofold hindered roter. A curious feature of the KS transformation and the passage to the action-angle variables of eq. (31) is that the librational states of the rotor which lie in the wells correspond to rotational states of the original Hamiltonian (1). Conversely, the original vibrational states have been mapped onto rotational states of the rotor. The two sets of SQZE vibrational states are the rotating states of the rotor which appear at the top and bottom of Fig. 1(a). This might seem puzzling: however, the original vibrational trajectories are localized in disjoint regions of phase space and the transformation to regularized coordinates is thus expected to map these trajectories into localized states of the oscillator. Local modes in the oscillator picture are those best conserving the rotor action [109], i.e., the rotational states of the rotor (which almost conserve A_z). The oscillator normal mode states in the wells become the QZE ridge (rotational) states of Fano and Rau and co-workers [101–108] as Λ approaches its maximum value. The stability of these states against "falling" off of the ridge can be understood by noting that they exist at the bottom of a well in action-angle space. This picture assumes that the higher-order terms in the normal form are negligible compared to those which are second order in the magnetic field. This has been verified numerically in this limit. As the fields are increased the higher-order terms become more important and begin to distort this picture. The present analysis is restricted to the case that only second-order terms need be retained. Following the sequence in Fig. 1; when $\beta=0.2$ one class of vibrational states has just vanished, leaving only vibrators and rotators. If higher-order terms in the normal form are included, then, in fact, both classes of vibrational state persist at these field strengths. The parameter β is only strictly useful if the lowest-order perturbation result is valid. When higher-order terms are important then the topology of phase space depends upon F and γ independently rather than just through the ratio β. In Fig. 1(c) $\beta=1.0$ and the rotational states have gone.

Waterland, Delos, and Du [47] found that for nonzero m there are apparently up to five classes of states; three

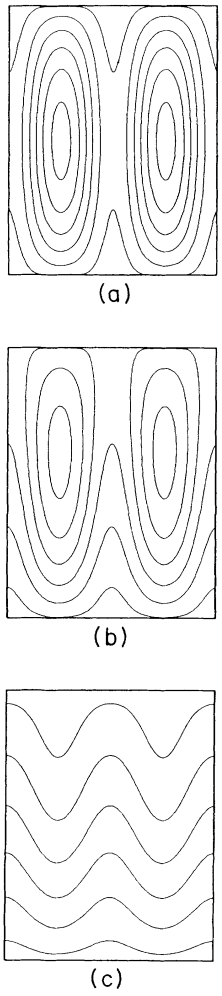

FIG. 3. Same as Fig. 1 but $m=4$.

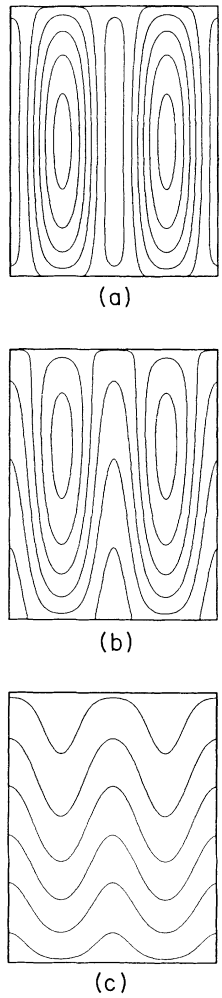

FIG. 4. Same as Fig. 1 but $m=n/\sqrt{5}$.

vibrational and two rotational. They examined the case $n=30$ and $m=1$. This conclusion was based on examination of the analogs of Figs. 1–4 in the Delaunay actions but note that some of the separatrices they observed may have arisen because of the nonanalyticity of the perturbation expansion in certain limits. The present choice of action-angle variables allows a uniform categorization of states previously thought distinct. Examination of level curves of Λ_β in the current action variables for the case $n=30$ and $m=1$ reveals that for $m=1$ the picture is essentially the same as $m=0$; namely, two classes of vibrators and a single class of rotational states. This is portrayed in Fig. 2 which is qualitatively similar to Fig. 1. Examination of a much wider range of β values than actually shown here leaves these conclusions unchanged. Admittedly, for nonzero m values some of the vibrational states become localized between the ever expanding rotators at low F. These, nevertheless, maintain true vibrational character and may have been labeled as rotational in Ref. [47]. Waterland, Delos, and Du [47] did note that there was very little difference between some of their rotational and vibrational states. In any case, the comparative simplicity of the phase portraits in Figs. 1–4 seems to indicate the advantage of working with the Lissajous action-angle variables. The best zero-order action variable in either the Zeeman or Stark limits is A_z rather than the Delaunay element corresponding to the angular momentum.

In the pure QZE, as m is increased the volume of phase space supporting vibrational states shrinks until $m/n=1/\sqrt{5}$ when the vibrational states, along with the separatrix, have vanished altogether, leaving only rotational states. By contrast, in the SQZE it is the rotational states which finally vanish leaving only vibrational states. It is therefore of considerable interest to examine the SQZE in this regime in order to look for a competition between the symmetries of the various classes of states. For the moderate value of $m=4$ in Fig. 3(a) it is already apparent that the rotational states are starting to dominate. This expansion is curtailed, however, as the electric field grows. Already in Fig. 3(b) the vibrational states are growing in and the rotational states are totally absent in Fig. 3(c). The situation is more complex when $m/n=1/\sqrt{5}$ in Fig. 4. For $\beta=0$ the rotational states are the only states present. As β is increased the vibrational states again start to grow; however, in Fig. 4(b) the QZE vibrational states are mapped onto two kinds of "rotor" states; freely rotating states and states trapped in two wells which have appeared. Phase space no longer legitimately can be thought of as a hindered rotor, resembling more the intrinsic kind of resonance found in molecules like formaldehyde [35,110,111] or coupled spin systems [112]. As the electric field continues to be increased the normal Stark limit is achieved. It would be of considerable theoretical and experimental interest to study in great detail the regime corresponding to Fig. 4(b).

Alternatively, the level structure may be understood by taking advantage of the connection between the QZE, the SQZE, and the asymmetric top [35,76,77]. The normal form Eq. (39) and the energy (40) can both be written entirely in terms of the components of a generalized angular momentum $\mathbf{J}$ with components (J_1,J_2,J_3) through the mapping,

$$\begin{aligned} J^2&=|\mathbf{J}|^2=\frac{n^2}{4}\ , \\ J_1&=\frac{A_z}{2}\ , \\ J_2&=(J^2-J_1^2)^{1/2}\sin\theta_z\ , \\ J_3&=(J^2-J_1^2)^{1/2}\cos\theta_z\ , \end{aligned} \tag{43}$$

where

$$\theta_z=2\phi_{A_Z}\ . \tag{44}$$

In terms of these variables the lowest-order SQZE energy for $m=0$ is given by

$$E=-\frac{1}{2n^2}+\frac{\gamma^2 n}{2}B_4-\frac{F}{2}B_0 \tag{45}$$

with

$$B_0=3nJ_1 \tag{46}$$

and

$$B_4=\frac{n}{8}(J_2^2+5J_3^2)\ . \tag{47}$$

This gives for the energy

$$E=-\frac{1}{2n^2}+\frac{\gamma^2 n^2}{16}(J_2^2+5J_3^2)-\frac{3nF}{2}J_1\ . \tag{48}$$

An interesting way to examine the structure of phase space is thus to use the idea of a RES in which the energy of a system is plotted as a function of the direction of the angular momentum vector $\mathbf{J}$ [35,72–76]. The unperturbed Kepler energy which dominates the energy expansion has been subtracted in order to bring out further the rich structure of the perturbation. The components of angular momentum are interpreted as Cartesian coordinates of a position vector whose length is equal to the total energy which is plotted radially outwards. Figure 5 is a collage that shows RES's as the electric field is progressively increased from zero for $m=0$. Figure 5(a) is the pure QZE and the separatrix is clearly visible. The vibrational states are localized in the dimples of the RES. As β is increased the separatrix vanishes and one class of vibrational states disappears (localized in the dimple of the RES which is not visible in Fig. 5). The vibrational states in the visible dimple in Fig. 5 start to take over phase space until in Fig. 5(c) the rotational states (localized around the lobes of the RES) have been displaced altogether. Figures 5(a)–5(c) should be compared to Fig. 1.

It is also possible to construct RES's for nonzero m numerically by means of the following mapping:

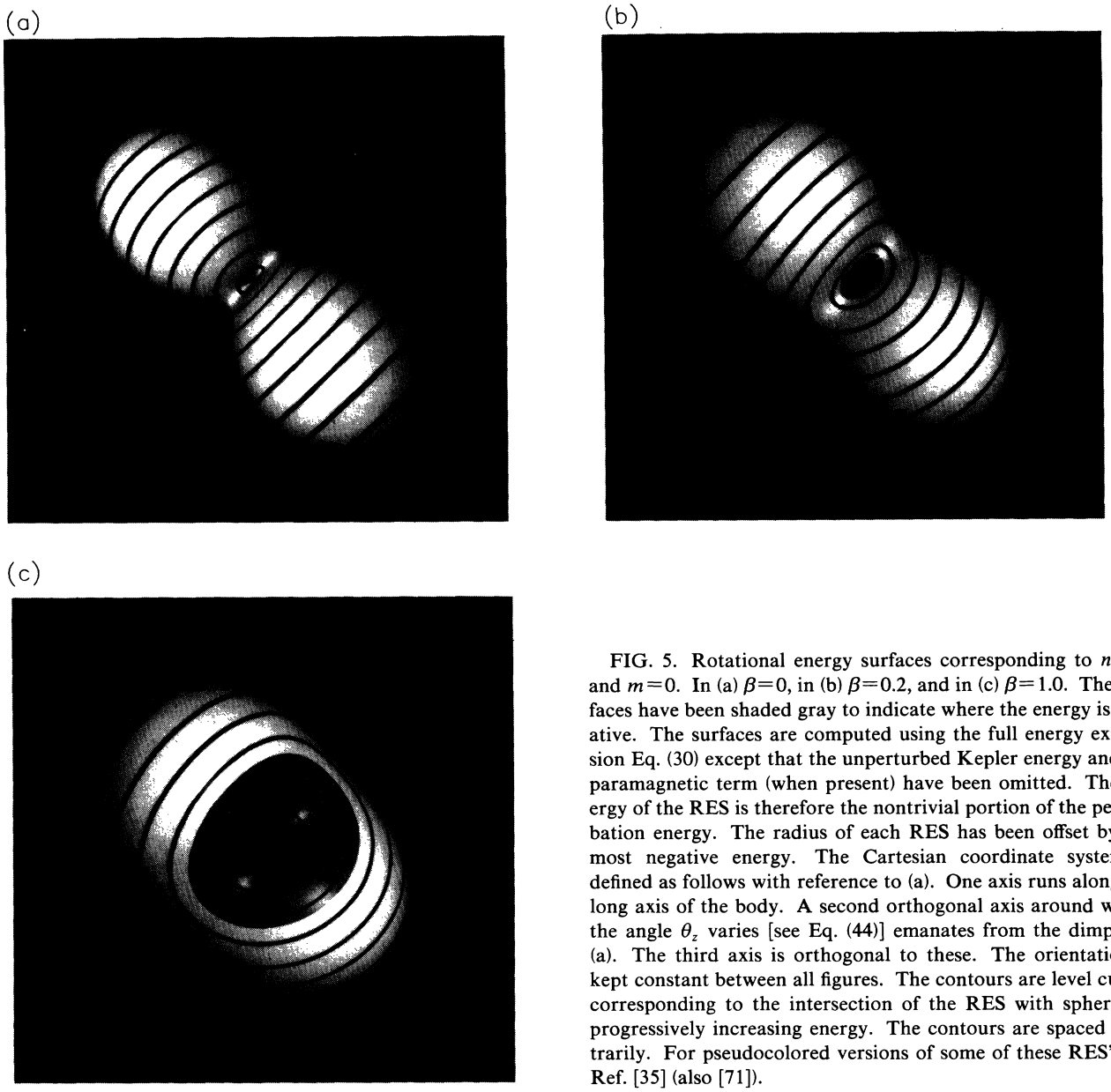

FIG. 5. Rotational energy surfaces corresponding to $n=30$ and $m=0$. In (a) $\beta=0$, in (b) $\beta=0.2$, and in (c) $\beta=1.0$. The surfaces have been shaded gray to indicate where the energy is negative. The surfaces are computed using the full energy expression Eq. (30) except that the unperturbed Kepler energy and the paramagnetic term (when present) have been omitted. The energy of the RES is therefore the nontrivial portion of the perturbation energy. The radius of each RES has been offset by the most negative energy. The Cartesian coordinate system is defined as follows with reference to (a). One axis runs along the long axis of the body. A second orthogonal axis around which the angle θ_z varies [see Eq. (44)] emanates from the dimple in (a). The third axis is orthogonal to these. The orientation is kept constant between all figures. The contours are level curves corresponding to the intersection of the RES with spheres of progressively increasing energy. The contours are spaced arbitrarily. For pseudocolored versions of some of these RES's see Ref. [35] (also [71]).

$$
\begin{aligned}
J^2=|\mathbf{J}|^2&=\frac{(n-|m|)^2}{4}\ ,\\
J_1&=\frac{A_z}{2}\ ,\\
J_2&=(J^2-J_1^2)^{1/2}\sin\theta_z\ ,\\
J_3&=(J^2-J_1^2)^{1/2}\cos\theta_z\ ,
\end{aligned}
\tag{49}
$$

where

$$
|A_z|\le|(n-|m|)|\ . \tag{50}
$$

As in the $m=0$ case the unperturbed energy (together with the paramagnetic term) has been subtracted from the energy. Figures 6 and 7 are montages corresponding to Figs. 3 and 4 although calculated including the high-order terms. The trends in Figs. 6 and 7 when m is different from zero are qualitatively the same as when $m=0$ and reveal the smooth transition from the pure QZE to the pure Stark limit. When $m=n/\sqrt{5}$ (see Fig. 7) the competition between the two dynamical symmetry chains is apparent for small to intermediate values of β. As β is increased, again the usual Stark limit is achieved. In Fig. 8, $m=29$ and the figure shows the RES in the extreme that m and n are very close in value. The approaches described here can also be extended to study the hydrogen atom interacting with a circularly polarized microwave field [113].

CONCLUSIONS

A comprehensive classical treatment of the SQZE has been presented. The combination of high-order classical

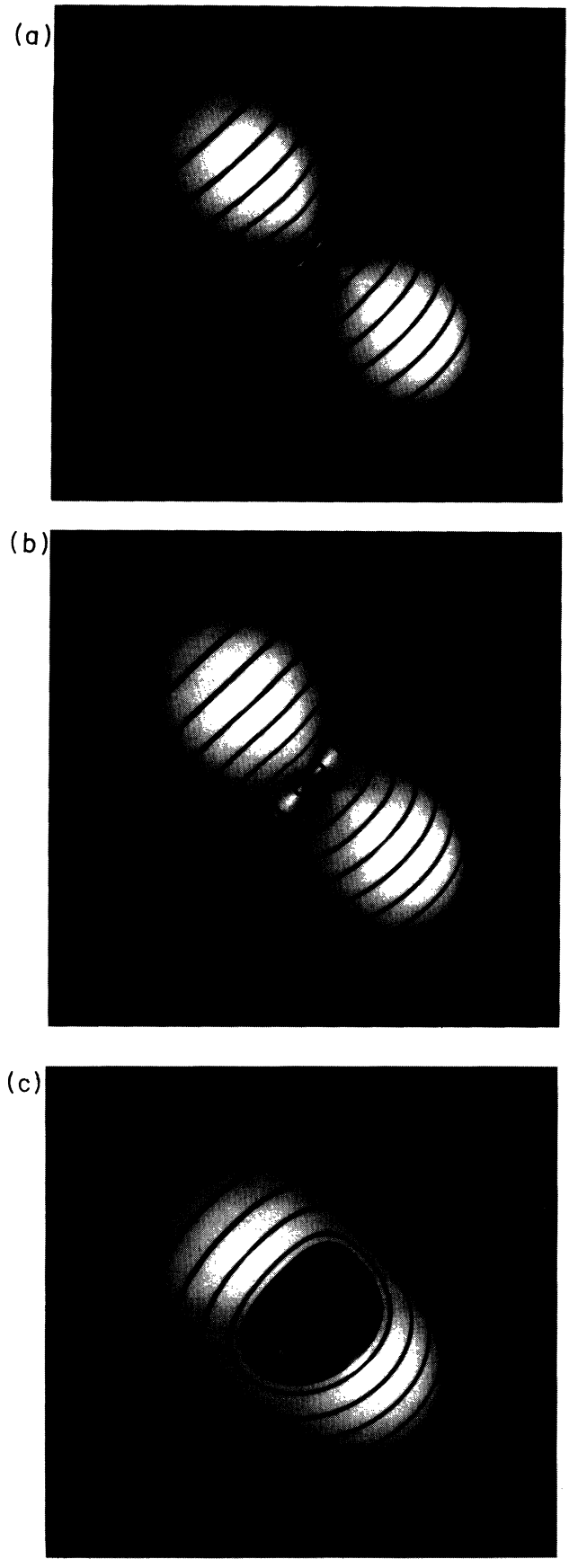

FIG. 6. Same as Fig. 5 but $m=4$.

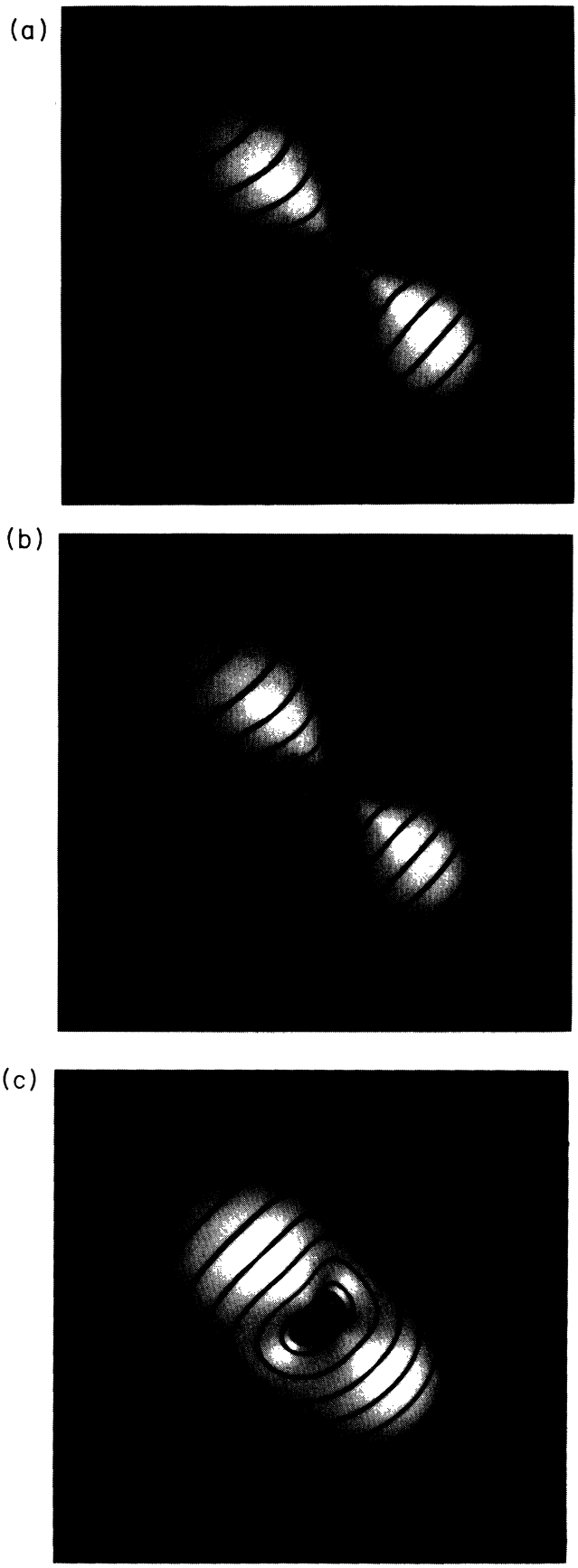

FIG. 7. Same as Fig. 5 but $m=n/\sqrt{5}$.

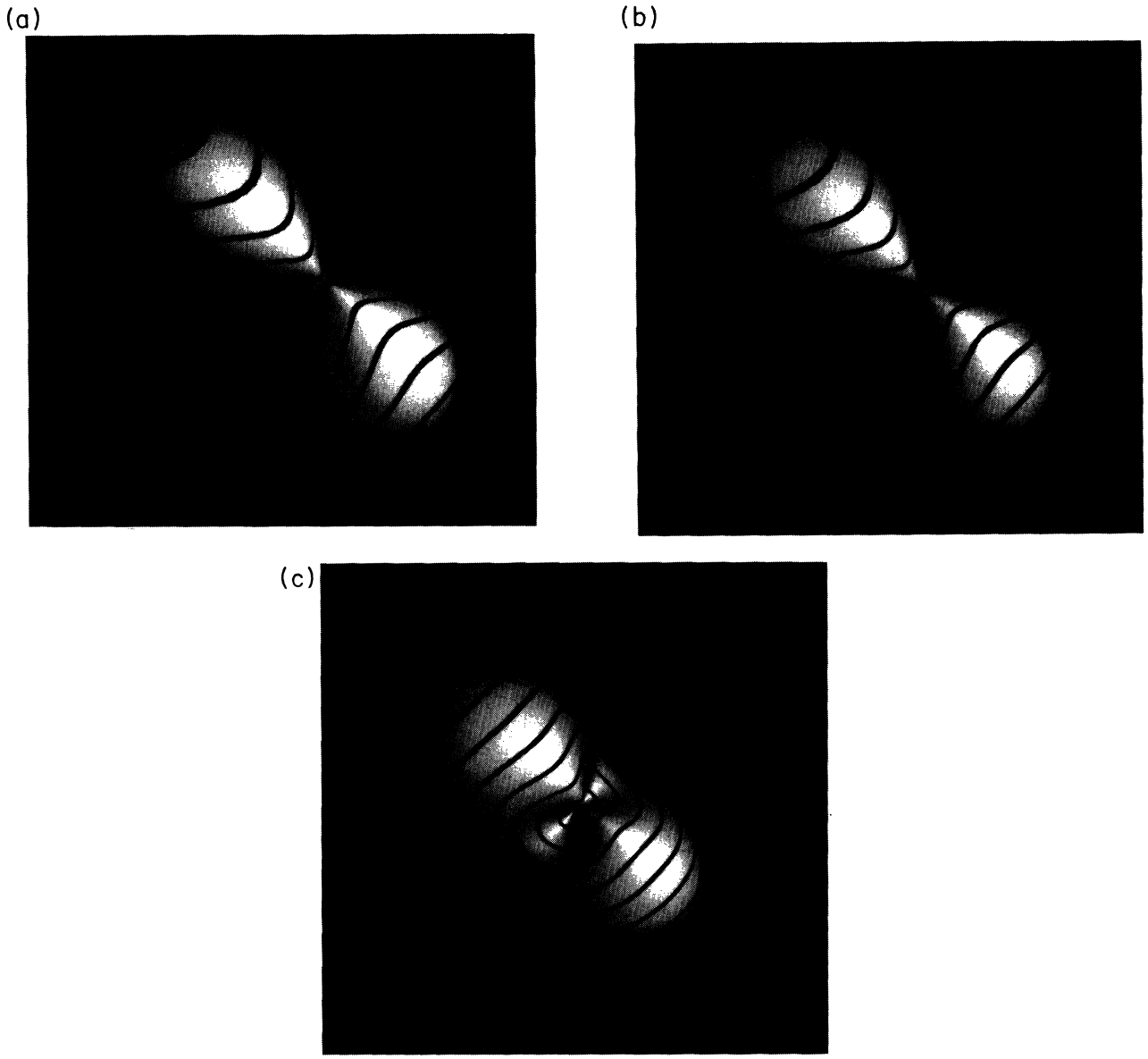

FIG. 8. Same as Fig. 5 but $m = 29$.

perturbation theory with a theoretically sound choice of action-angle variables provided a simple and compelling picture of the changes in the eigenstate structure as the magnetic and electric fields were varied, in tandem with changes in the quantum number m. The device of a RES, constructed using the Lissajous action-angle variables, provides a simple and compact geometrical picture of the energy-level structure of the SQZE. While quantization of this system was not discussed, a comprehensive and numerically accurate approach to semiclassical quantization of the QZE has been presented elsewhere [92]. Past attempts to quantize this type of system have encountered singularities associated with the classical separatrix. In this paper uniformly valid action-angle variables were introduced which will allow the development of a singularity-free uniform quantization scheme. Extension of this approach to quantization of very high-order classical perturbation expansions is straightforward, and is expected to rival quantum methods in the low field limits.

Note added in proof. We thank Dr. A. Deprit for informing us of Ref. [54(b)], which contains technical details of the Lissajous transformation.

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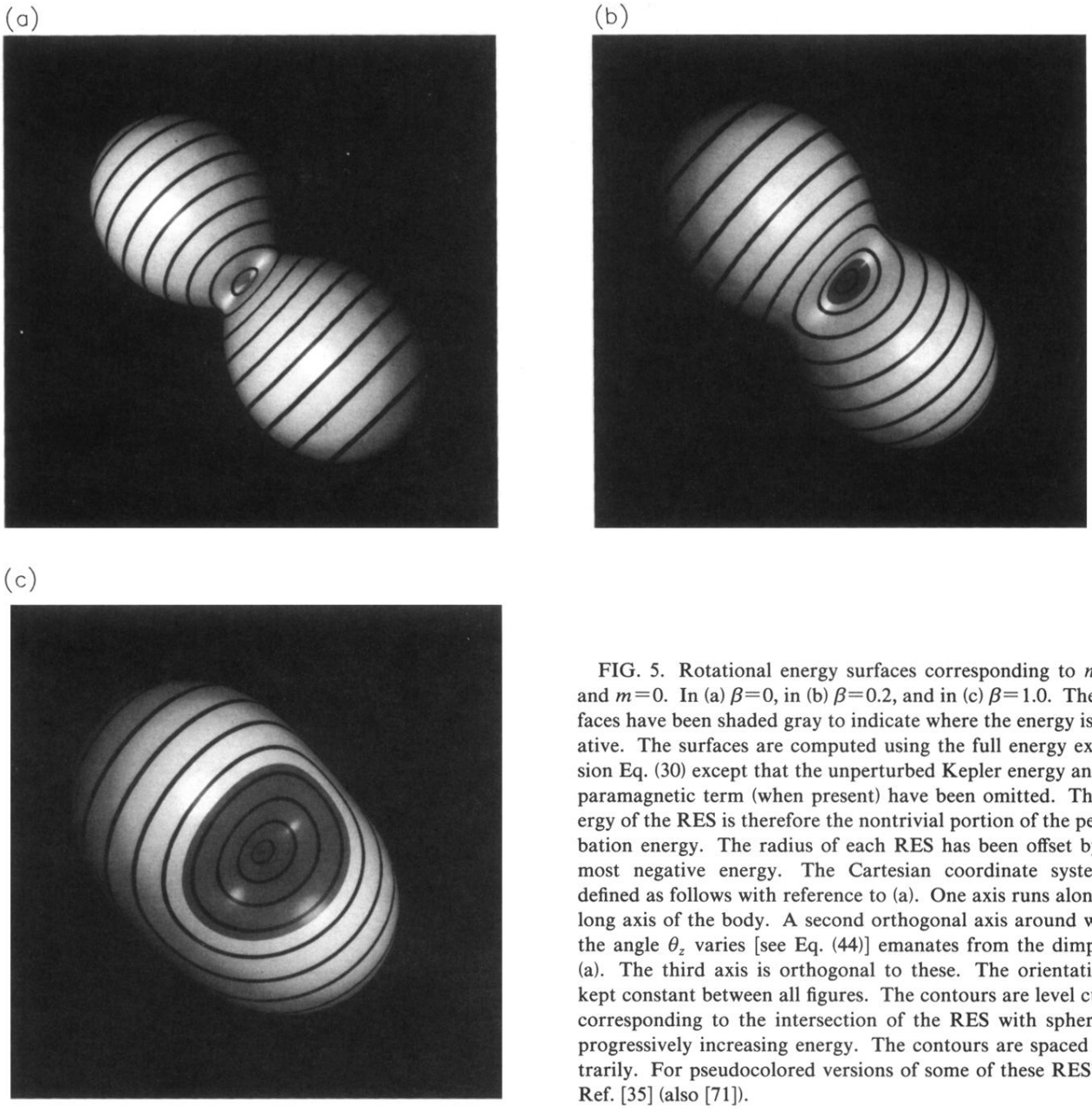

FIG. 5. Rotational energy surfaces corresponding to $n=30$ and $m=0$. In (a) $\beta=0$, in (b) $\beta=0.2$, and in (c) $\beta=1.0$. The surfaces have been shaded gray to indicate where the energy is negative. The surfaces are computed using the full energy expression Eq. (30) except that the unperturbed Kepler energy and the paramagnetic term (when present) have been omitted. The energy of the RES is therefore the nontrivial portion of the perturbation energy. The radius of each RES has been offset by the most negative energy. The Cartesian coordinate system is defined as follows with reference to (a). One axis runs along the long axis of the body. A second orthogonal axis around which the angle θ_z varies [see Eq. (44)] emanates from the dimple in (a). The third axis is orthogonal to these. The orientation is kept constant between all figures. The contours are level curves corresponding to the intersection of the RES with spheres of progressively increasing energy. The contours are spaced arbitrarily. For pseudocolored versions of some of these RES's see Ref. [35] (also [71]).

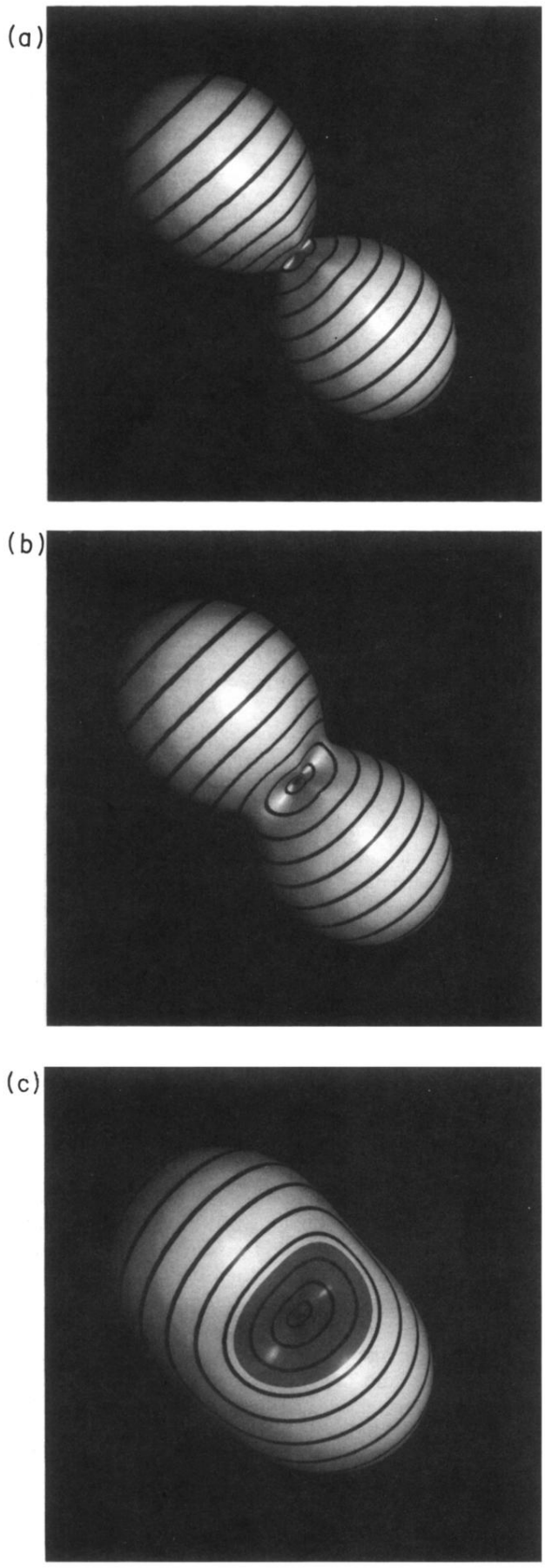

FIG. 6. Same as Fig. 5 but $m = 4$.

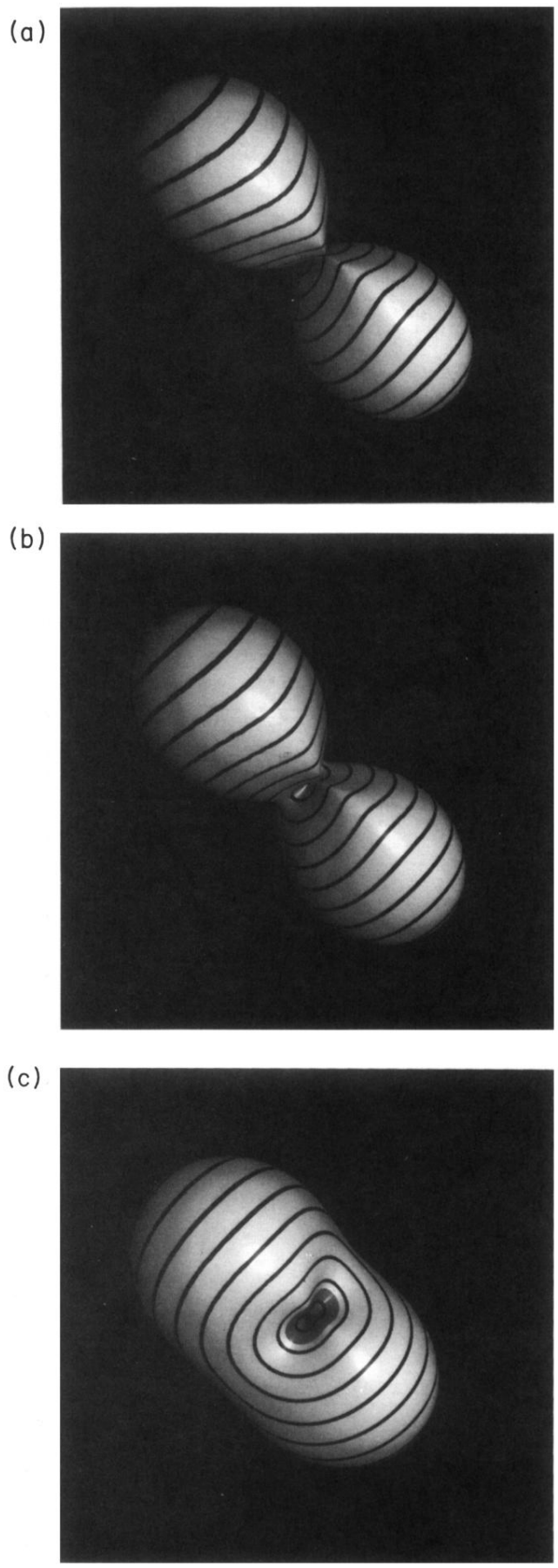

FIG. 7. Same as Fig. 5 but $m = n/\sqrt{5}$.

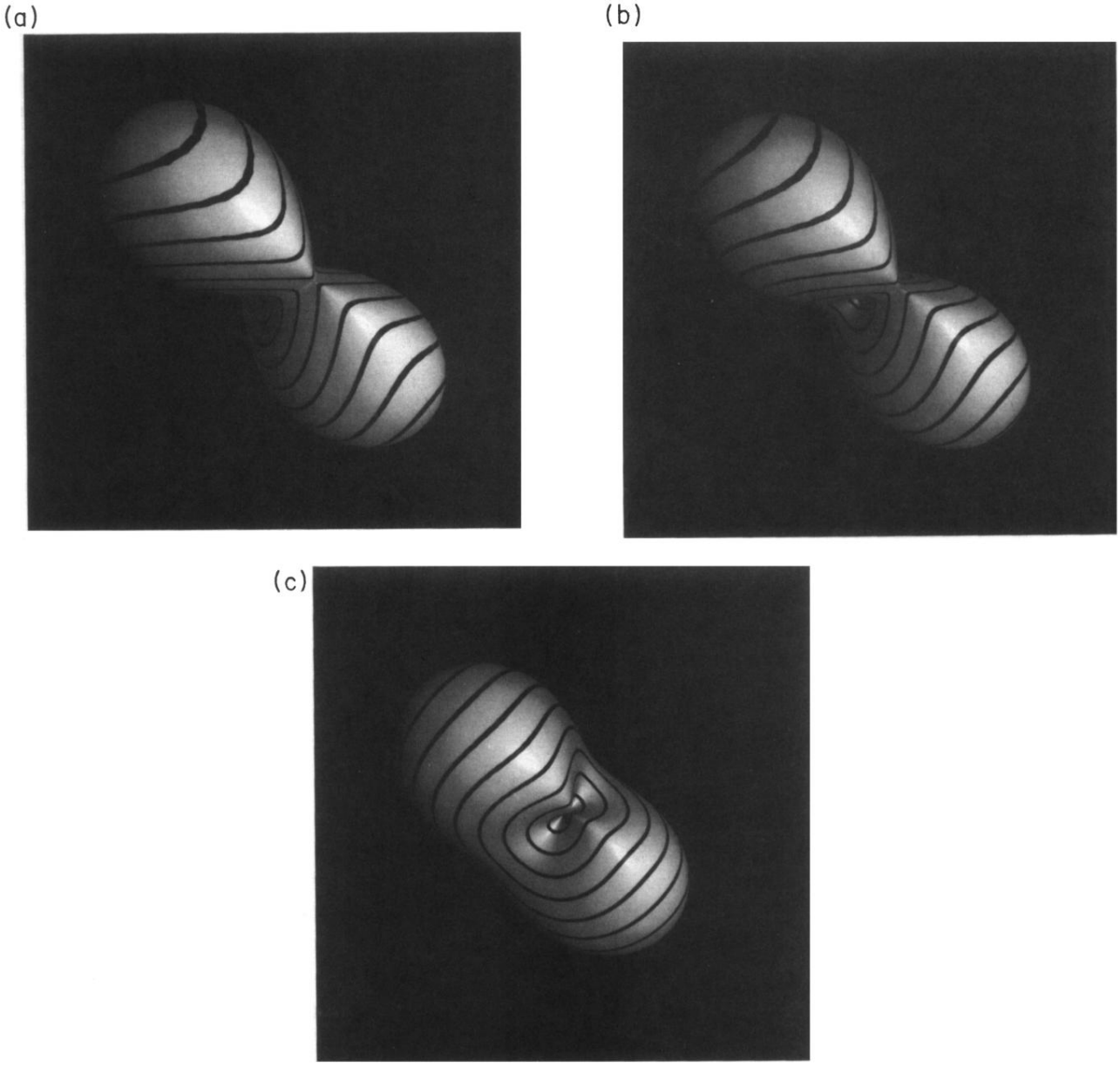

FIG. 8. Same as Fig. 5 but $m = 29$.