PHYSICAL REVIEW A VOLUME 59, NUMBER 1 JANUARY 1999

Nonlinear dynamical behavior of a hydrogen molecular ion and similar three-body Coulomb systems

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(Received 23 June 1997; revised manuscript received 31 July 1998)

We investigate the classical dynamical stability of a hydrogen molecular ion beyond the Born-Oppenheimer approximation. We study both the coplanar and collinear arrangements. Results show that invariant structures exist in phase space, including a quasiperiodic zone surrounding the antisymmetric stretching periodic orbit. Outside this zone, bound chaotic orbits exist which correspond to a hybrid motion between two types of motion, quite different from the normal quasiperiodic or chaotic motion. We extend the dynamical stability study to several other three-body Coulomb systems, similar to the hydrogen molecular ion, and present results of primitive semiclassical quantization of the quasiperiodic zone of the collinear hydrogen molecular ion. These semiclassical results suggest that the ground electronic state of the hydrogen molecular ion is stable. [S1050-2947(99)05301-9]

PACS number(s): 31.15.Gy, 05.45.Gg, 45.05.+x

I. INTRODUCTION

Classical stability of the hydrogen molecular ion ($H_2{}^+$) is an interesting problem to investigate, because of its similarity to the gravitational three-body systems. The difference in $H_2{}^+$ is that the force between protons is repulsive. Furthermore, classical stability of $H_2{}^+$ has other physical implications, it represents in some sense classical manifestation of chemical bonding. Pauli [1] had studied the stability of the $H_2{}^+$ in his Ph.D. dissertation, under the supervision of Sommerfeld, using the then newly invented quantum theory of Bohr. His conclusion that $H_2{}^+$ was only metastable with an equilibrium distance of 5.5 bohrs, instead of the observed 2.0 bohrs of a stable $H_2{}^+$, together with the similar failure of helium, contributed to the downfall of Bohr's old quantum theory. Strand and Reinhardt [2] studied the dynamics of the $H_2{}^+$ system under the Born-Oppenheimer approximation (BOA) and following Pauli they classified the electronic motion into $P1$,$P2$,$P3$ types. (More details are given in Sec. III.) They also showed that semiclassical quantization of the quasiperiodic behavior with the uniform approximation yields reasonable eigenenergies for the system. More general classification of three-body Coulomb systems with nuclei of arbitrary charges within BOA has recently been carried out by Abramov *et al.* [3] and they emphasize the semiclassical relation between branch points of the separated equations and the electronic transitions. Duan *et al.* [4] have, on the other hand, systematically investigated the periodic orbits of the two-centered $H_2{}^+$ system within BOA and showed that quantization using periodic orbits also yields reasonable energies of the system.

In the BOA limit the mass of the protons is assumed to be infinite, thus their positions are fixed, and the electron moves under the influence of their Coulomb attraction. The above-cited papers showed that the classical equations in this limit are separable, thus integrable, and the phase space consists entirely of quasiperiodic behavior and an infinite number of periodic orbits exist [1–4]. In analogy to the gravitational three-body problem, we expect interesting dynamical behavior to show up, if we go beyond BOA. Mueller *et al.* [5] have recently reexamined the classical stability problem of $H_2{}^+$ beyond BOA and found the approximate adiabatic invariant of the system. Sohlberg *et al.* [6], on the other hand, have carried out primitive semiclassical quantization of the $H_2{}^+$ system. However, up to now the classical dynamical behavior of $H_2{}^+$ beyond BOA has not been fully explored.

The objective of the present paper is to gain more global understanding of the classical dynamical behavior of three-body Coulomb systems. We are interested in finding out more about their phase space structures, whether chaos exists, and how the dynamical behavior of $H_2{}^+$ differs from that of He. The organization of the present article is as follows. We describe in Sec. II the regularized coordinate system in which the $H_2{}^+$ problem is solved. We study the dynamics of the coplanar $H_2{}^+$ system and present the lifetime and Poincaré surface of section results in Sec. III. We also investigate the stability of the collinear $H_2{}^+$ system and present the results in Sec. IV. Extension to other similar three-body Coulomb systems is also included in the same section. In Sec. V we discuss some of the results of primitive semiclassical quantization of the torus in the phase space of the collinear $H_2{}^+$ system. This is followed by a summary and discussion section.

II. DESCRIPTION OF THE SYSTEM IN REGULARIZED COORDINATES

To study the classical dynamics of $H_2{}^+$ beyond the Born-Oppenheimer approximation (non-BOA), we can use the Jacobi coordinates, r, R, and θ, for a three-body system, where R denotes the interproton distance, r the distance from the electron to the center of mass of the two protons, and θ the angle between r and R. However, there exist two difficulties in a treatment using this set of coordinates: the presence of two very different time scales, one associated with the elec-

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tronic motion and the other the nuclear motion, and the singularities of two- and three-body collisions. One way to overcome partially the time scale problem is to transform to the $\mathbf{r}_{13}=\mathbf{r}_1-\mathbf{r}_3$ and $\mathbf{r}_{23}=\mathbf{r}_2-\mathbf{r}_3$ coordinates [7], where $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$ are the position vectors for the two protons and the electron, respectively. The Hamiltonian in the center-of-mass system then becomes

$$H=\frac{P_{13}^2}{2\mu_{13}}+\frac{P_{23}^2}{2\mu_{23}}+\frac{\mathbf{P}_{13}\cdot\mathbf{P}_{23}}{m_3}+\frac{Z_1Z_3}{r_{13}}+\frac{Z_2Z_3}{r_{23}}+\frac{Z_1Z_2}{r_{12}}=-1, \tag{1}$$

where μ_{ij} denotes reduced mass of particles i and j, $\mathbf{P}_{ij}$ the conjugate momentum of $\mathbf{r}_{ij}$, and Z_i and m_i are the charge and mass of particle i. Since the potential of a three-body Coulomb system is homogeneous, the dynamics is scale invariant with respect to the total energy, which is taken to be -1 for an energy below the three-body breakup threshold $(E=0)$. The problem of the two-body Coulomb singularities can be removed by transforming canonically to the regularized coordinates using, for example, the Kustaanheimo-Stiefel transformation, one of the regularization transformations used in celestial mechanics. The regularized Hamiltonian for a planar configuration (i.e., all $z_{ij}=0$) then becomes

$$\begin{aligned}\mathcal{H}=0=&\frac{R_2^2\mathbf{p}_1^2}{8\mu_{13}}+\frac{R_1^2\mathbf{p}_2^2}{8\mu_{23}}\\&+\frac{(\mathbf{R}_1\cdot\mathbf{R}_2)(\mathbf{p}_1\cdot\mathbf{p}_2)-(\mathbf{R}_1\times\mathbf{R}_2)(\mathbf{p}_1\times\mathbf{p}_2)}{4m_3}+Z_1Z_3R_2^2\\&+Z_2Z_3R_1^2+R_1^2R_2^2\left(1+\frac{Z_1Z_2}{R_{12}^2}\right),\end{aligned} \tag{2}$$

where the regularized coordinates $Q_i's$ are related to the x,y components of r_{j3} through $x_{13}=Q_1^2-Q_2^2, y_{13}=2Q_1Q_2$ and $x_{23}=Q_3^2-Q_4^2, y_{23}=2Q_3Q_4$, and it follows $r_{13}=R_1^2=Q_1^2+Q_2^2$ and $r_{23}=R_2^2=Q_3^2+Q_4^2$. We also define $R_{12}^2=r_{12}, \mathbf{R_1}=(Q_1,Q_2), \mathbf{R_2}=(Q_3,Q_4), p_1=(P_1,P_2), \mathbf{p}_2=(P_3,P_4)$, and the time t is transformed into τ according to $dt=r_{13}r_{23}d\tau$. For other details of the transformation, we refer to [7,8]. We investigate the dynamics of three-body Coulomb systems by integrating the eight Hamilton equations of motion in Q_i and P_i using the fourth-order variable-step Runge-Kutta and the Bulirsch-Stoer methods [9] and report the results in the following sections.

III. DYNAMICS OF THE COPLANAR SYSTEM

We have investigated the coplanar system of $H_2{}^+$, which is a system of three degrees of freedom and the Poincaré surface of section (PSOS) is three dimensional. Since it is time consuming to explore the entire five-dimensional initial-value parameter space, we restrict our dynamical exploration using the following initial configurations: Starting with all three particles on a straight line, we assume that the interproton distance is R_0 and the electron is at x_{b0} distance away from the proton B (the right-hand-side proton). The initial momenta of protons, p_1 and p_2, are perpendicular to the interproton axis and their magnitudes determined from the total angular momentum L (set to zero), and the total energy $(E=-1)$. The $L=0$ manifold investigated here is only a submanifold of the invariant planar configuraion. With this initial configuration the free parameters to vary are R_0 and x_{b0}/R_0, the latter can be varied between -0.5 (negative, when the electron is between protons) and infinity. We investigate the dynamics of the $H_2{}^+$ system and present the results in the initial-value parameter space of R_0 and x_{b0}/R_0 in Fig. 1. In Fig. 1(a), the gray scale represents the lifetime T of $H_2{}^+$ during which the molecule is considered stable. The lifetime is defined by the time at which the overall change of R during T, ΔR, first becomes greater than a certain large value (here taken to be 20 in scaled units) [10]. It can be seen in Fig. 1(a) that there exist two large regions in the R_0-x_{b0}/R_0 parameter space in which $H_2{}^+$ is mostly stable up to the time limit of integration (5000 in the scaled regularized time). These regions are gray with instability islands embedded in the larger R_0 zones and the white regions are classically forbidden. Another way to present the results is to plot ΔR in gray scale, as done in Fig. 1(b), in which unstable regions correspond to large overall change of R, i.e., ΔR. This figure reveals more structures in the stable regions, for example, a light-colored band appears in the lower part of the right-hand-side region, which seems to be the most stable region.

To show what types of motion contribute to the stability of the $H_2{}^+$ molecule, we plot several trajectories corresponding to points in the stable regions of Fig. 1(b). Before discussing our findings, we first review the three types of motions allowed in the $H_2{}^+$ molecule within the BOA [1,2]. Following the notation of Strand and Reinhardt [2], the three types are $P1$, $P2$, and $P3$. For a $P1$ type of motion the electron is restricted to move between two ellipses with the two protons located at their foci and cannot cross between the protons. For a $P2$ type of motion, on the other hand, the electron moves inside a single ellipse and can and does cross the interproton axis. For a $P3$ type of motion, the electron is confined to move inside an ellipse and a hyperbola, thus the electron moves around a single proton and does not cross the vertical bisector of the interproton axis. One may ask which among these three types of motion is stable and contributes to chemical bonding, when the protons are free to move. The $P1$ type of motion becomes unstable, as already pointed out by Pauli, because of the Coulomb repulsion between protons and the fact that the electron spends little time between the protons. The other two types of motion can be stable [5], as illustrated in Fig. 2. In Figs. 2(a) and 2(b) we plot a $P2$ trajectory in which the electron goes around both protons which roughly move in the neighborhood of $x=+0.5$ or -0.5 and $y=0$. This trajectory originates at a point near the tip of the light-colored stability band discussed above. A stable $P3$ orbit is shown in Figs. 2(c) and 2(d), in which the electron moves around only one proton which stays near $x=1$. Besides orbits of the $P2$ or $P3$ type, we have also found stable orbits in which the trajectory continuously alternates between the $P2$ and $P3$ types of behavior, as discussed in the recent works of Mueller *et al.* and Duan *et al.* [5,4]. We present such an example in Figs. 2(e) and 2(f), which shows clearly that the electron moves alternately around both nuclei and around just one. We shall call this type of motion the

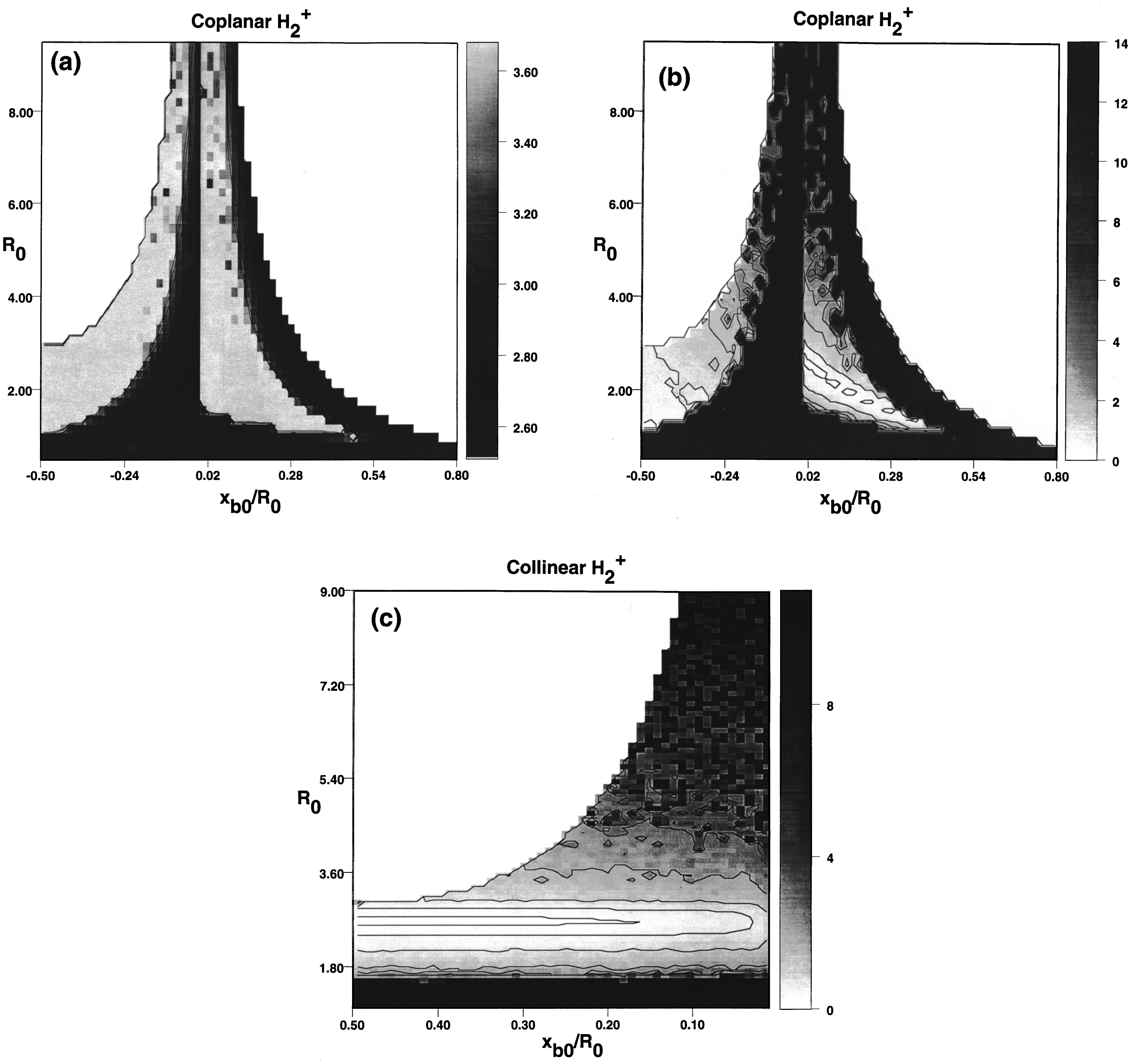

FIG. 1. Dynamical stability of the H_2^+ system beyond BOA. (a) Lifetime in gray scale plotted as a function of the initial values of variables R_0 and x_{b0}/R_0 in the coplanar case. The lifetime is defined by the time when the overall change in $R_0, \Delta R$, is greater than 20 in scaled units. Logarithm of lifetime is used in grade scale. (b) Same as (a) except the gray scale represents ΔR and a contour of ΔR is plotted on top. (c) Same as in (b), but for the collinear H_2^+ system. All quantities are in atomic units with E set to -1.

$P2/P3$ hybrid orbit. Among the three types of stable motion discussed above, the $P2$ and $P2/P3$ orbits are common in the stability zone, but a stable $P3$ orbit is a rare event and occurs usually near the stability boundary. This can be understood because a breakup reaction, $H_2^+ \rightarrow H + H^+$, takes place via a $P3$ type of motion.

IV. THE COLLINEAR H_2^+ AND OTHER SIMILAR SYSTEMS

A collinear study of a full three-dimensional system often provides valuable information about the original system. A well-known example is the bound-state study [7] and scattering study [11,12] of collinear systems of atomic helium. Based on this experience we expect a collinear investigation of a H_2^+ ion to provide us with useful information. Such an investigation will be described in this section.

Unlike a coplanar system, the Poincaré surface of section of a collinear system is only two dimensional. This fact facilitates the numerical search for all possible dynamical behavior in phase space. Furthermore, the dynamical behavior of the collinear system seems to resemble that of the coplanar system, as revealed by comparing Fig. 1(b) with Fig. 1(c). The latter is obtained by restricting all three particles to move on a straight line with the electron located between the nuclei. We see some similarities between Fig. 1(c) and Fig. 1(b). For example, in both cases there exist regions with small R_0 in which ΔR remains small over the course of

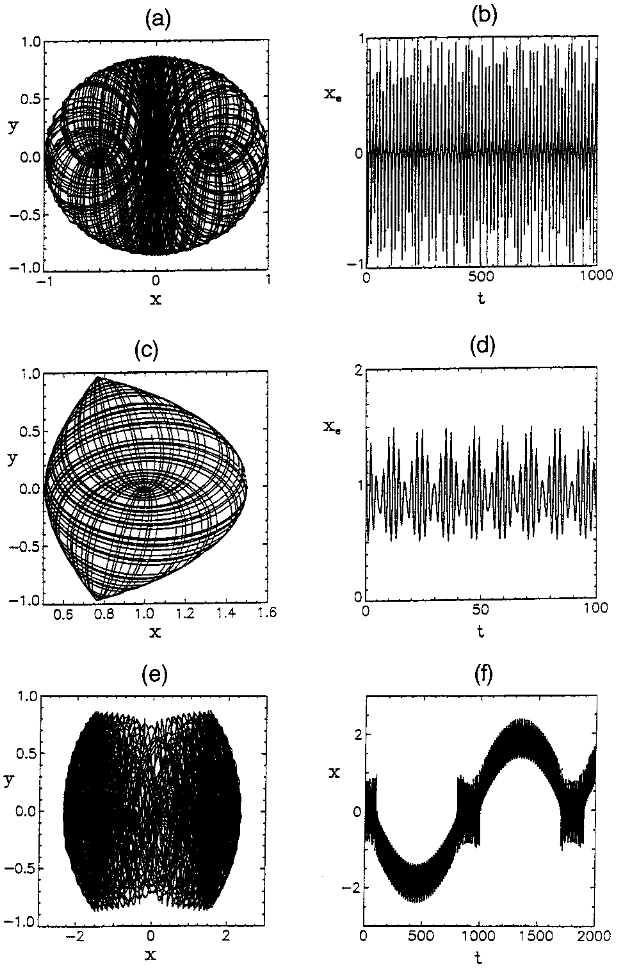

FIG. 2. Representative electron and proton trajectories of a non-BOA coplanar $H_2{}^+$ system, plotted in a Cartesian coordinate system with the origin located at the center of mass of the two protons. (a) A $P2$ type of trajectory originated at $R_0=1$ and $x_{b0}=0.4964$. (b) Time evolution of the x component of the electron trajectory plotted in (a). (c) A $P3$ type of trajectory originated at $R_0=2$ and $x_{b0}=0.5038$. (d) Time evolution of the x component of the electron trajectory plotted in (c). (e) A $P2/P3$ hybrid trajectory originated at $R_0=1$ and $x_{b0}=0.3196$. (f) Time evolution of the x component of the electron trajectory plotted in (e).

integration. On the other hand, for the large R_0 region, the value of ΔR seems to fluctuate rapidly with respect to the initial values of R_0 or x_{b0}. To reveal the dynamical information contained in Fig. 1(c), we plot in Fig. 3 a PSOS obtained by recording the R and P_R values of trajectories every time when the electron collides with proton A. As shown in Fig. 3, the PSOS consists of a stable Kolmogorov-Arnold-Moser (KAM) zone, surrounded by another stable but irregular region, which is itself surrounded by an unstable region, in which the $H_2{}^+$ ion flies apart. The fact that the KAM zone is quasiperiodic and the surrounding region is chaotic is consistent with the results obtained in a Lyapunov exponent calculation. The periodic orbit in the middle of the KAM zone turns out to be the antisymmetric stretching orbit, which is stable here, in contrast to that of atomic helium. The antisymmetric stretching periodic orbit corresponds to a periodic orbit in which the electron bounces between two protons.

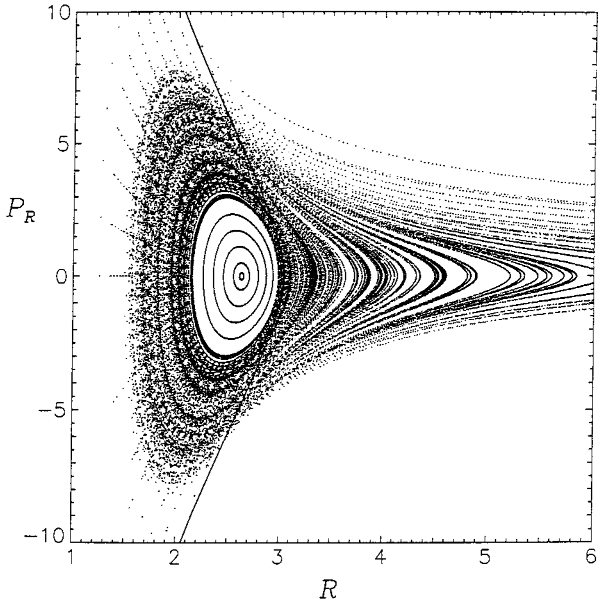

FIG. 3. Poincaré surfaces of section (PSOS) of the collinear $H_2{}^+$ system. The solid curve separates the $P2$ and $P3$ types of motion.

To find out what types of orbits exist in the stable regions, we plot in Fig. 4 two trajectories, one from the KAM zone and another from the irregular region of Fig. 3. The trajectory taken from inside the KAM zone corresponds to a $P2$ trajectory, as exemplified by Figs. 4(c) and 4(d). In this case, the electron bounces rapidly between two protons, while the latter vibrate slowly relative to each other, making a breath-

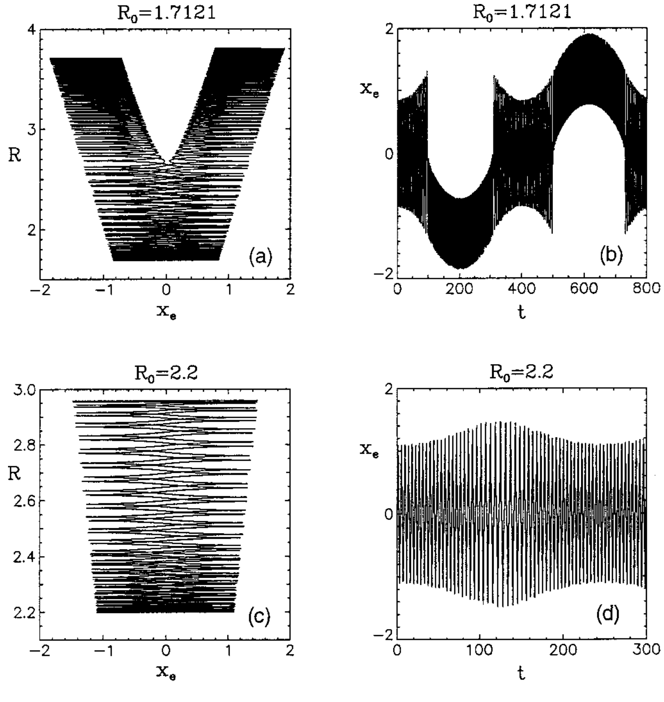

FIG. 4. Representative trajectories of collinear $H_2{}^+$, where x_e is the electronic coordinate measured from the midpoint of R. (a) A $P2$ trajectory originated at $R_0=1.712$ and $x_{b0}=0$. (b) Time evolution of the x component of the electron trajectory plotted in (a). (c) A $P2/P3$ trajectory originated at $R_0=2.2$ and $x_{b0}=0$. (d) Time evolution of the x component of the electron trajectory plotted in (c).

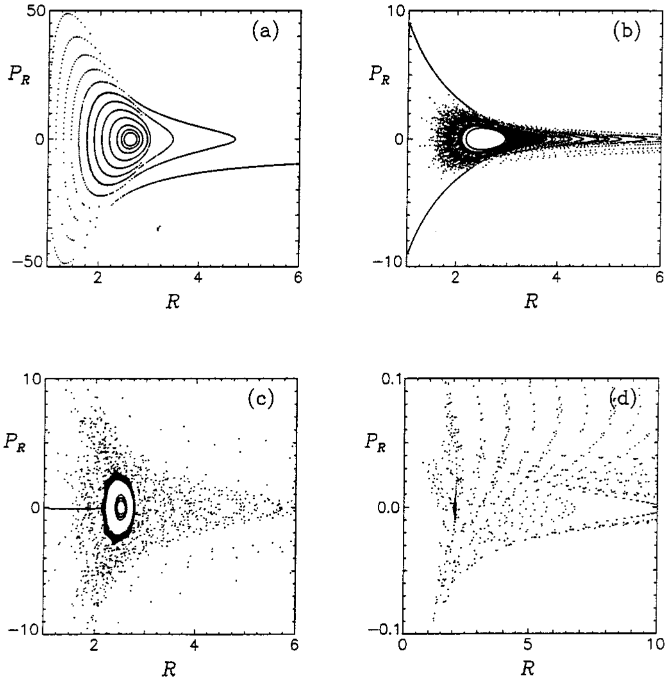

FIG. 5. Poincaré surfaces of section (PSOS) of other collinear three-body Coulomb systems. (a) A model system with the proton to electron mass ratio set to 18 360. (b) A model system with the proton to electron mass ratio set to 183.6. (c) The $P\mu^-P$ system. The horizontal solid line comes from the initial conditions of the trajectories. (d) The $e^+e^-e^+$ system.

ing type of motion. We show in Figs. 4(a) and 4(b) a trajectory from the bound irregular region, which corresponds to a one-dimensional equivalence of the $P2/P3$ hybrid motion. This type of motion is interesting, for when the interproton distance is small, the potential barrier between two protons remains low and the electron bounces between two protons, but when the interproton distance becomes large, the interproton barrier rises and the electron bounces between a proton and the interproton barrier. Thus the barrier height increases with the interproton distance. This motion therefore represents a strong correlation between the nuclear and electronic motions and cannot be described adequately using a theory based on BOA, ignoring proton motion.

Other remarkable features of the $P2/P3$ hybrid motion follow. Because the $P2/P3$ hybrid motion is aperiodic, but still bound, it represents a different type of chemical bonding from a $P2$ orbit. The fact that the net change of the interproton distance of a hybrid motion is much larger than that of a $P2$ type of motion suggests that it may also represent a classical manifestation of a nonadiabatic electronic transition. Finally, we note that the transition from the regular to chaotic motion as shown in Fig. 3 appears to be sudden and the correlation between the electron and nuclear motions is very similar to that between the light and heavy atoms in a heavy-light-heavy triatomic system [13].

It is advantageous to consider all three-body Coulomb systems in a unified picture, for this helps alleviate the difficulty caused by very different time scales existing in H_2^+. We present in Figs. 5(a)–5(d) the PSOS of four other three-body Coulomb systems. If we make the proton mass ten times greater than its natural mass [Fig. 5(a)], the chaotic or $P2/P3$ hybrid domain disappears, all bound motions are regular, and the dynamical behavior approaches the BOA limit. On the other hand, if we decrease the proton mass by a factor of 10 [Fig. 5(b)] so that the mass ratio is close to that of a $\mu^+e\mu^+$ system (~ 200), both the KAM zone and the bound aperiodic domain become smaller than those of the H_2^+ system. Furthermore, the PSOS for a $P\mu^-P$ system (mass ratio $= 8.9$) also has a smaller KAM zone as shown in Fig. 3(c). Here it seems that, unlike Figs. 3 and 5(b), the transition from the regular to chaos behavior takes place via an ordinary Birkhoff-Poincaré bifurcation. Finally, for the $e^+e^-e^+$ system (unit mass ratio) shown in Fig. 5(d) the KAM zone shrinks to a very small size, but nonzero, thus the antisymmetric stretching periodic orbit of this system is still stable. In contrast, those of the $\mu^-P\mu^-$ system and the atomic helium are unstable. Experimental verifications of these predictions and identification of the $P2/P3$ hybrid type of motion are important [14].

V. RESULTS OF PRIMITIVE SEMICLASSICAL QUANTIZATION OF COLLINEAR H_2^+ MOTION

The KAM zone found in the Poincaré surface of section of the collinear H_2^+ is large enough to support several bound states. The immediate question that one may ask is whether one can apply the Einstein-Brillouin-Keller (EBK) quantization rules [15,16] to this KAM zone to obtain reasonable vibrational-electronic or vibronic energies of the H_2^+ system in one calculation step. This is in contrast with the traditional methods based on BOA, in which one must first obtain the electronic potential energy curves, before calculating the vibrational energy levels supported by them.

In this section we shall apply a semiclassical procedure due to Miller [17] and expanded by Wintgen and co-workers [18–20] to the quantization of collinear H_2^+. Wintgen *et al.* derived a triple-Rydberg formula of the form

$$E_{nkl} = -\frac{S^2}{[n+\frac{1}{2}+(l+\frac{1}{2})\gamma_R+(2k+1)\gamma_\Theta]^2}, \tag{3}$$

where the semiclassical quantum numbers n,k,l reflect the approximate separability of the associated wave functions in local coordinates parallel and perpendicular to the periodic orbit [18]. In the present system, n denotes the nodal excitations along the antisymmetric periodic orbit (electron bounces between two protons), l counts the excitations along the symmetric stretch orbit (molecular vibration), and k counts excitations of the bending motion perpendicular to the molecular axis. There exist 2 degenerate bending modes, which contribute a factor of two in the formula. In formula (3) γ_R and γ_Θ are the winding numbers for radial and angular motion transverse to the collinear antisymmetric stretch periodic orbit. At $E = -1$, we obtain numerically $S = 1.603\,573$ for the scaled action of this periodic orbit and by integrating the monodromy matrix along the periodic orbit, we obtain $\gamma_R = 0.035\,03$ and $\gamma_\Theta = 0.3937$, which are energy independent.

As shown by Wintgen and Richter [18], formula (3) is equivalent to torus quantization, but with a Gutzwiller approximation imposed on it, that is, the the action functionals and the winding numbers are replaced by their values at the periodic orbits. Because of this approximation, the energy

TABLE I. Energies for $H_2{}^+$ in atomic units with reference to the double ionization and dissociation threshold. The label $n=1$ has been identified with the ground electronic state, $X\,^2\Sigma_g=1s\sigma_g$, $n=2$ identified with the first excited electronic state, $^2\Sigma_u=2p\sigma_u$, and $n=3$ identified with the $^2\Pi_u=2p\pi_u$. The label $l=1$ has been identified with the vibrational quantum number v.

n	l	k	QM (3D)	EBK(1) [a]	EBK(2) [b]	QM(1D) [c]
1	0	0	$-0.597\,139\,1$ [d]	-0.704	-0.51	-0.8227
1	1	0	$-0.587\,155\,7$ [d]	-0.679		-0.8079
2	0	0	$-0.499\,743\,5$ [e]	-0.303	-0.49	-0.5139
3	0	0	$-0.133\,841\,9$ [f]	-0.168		-0.1905
3	1	0	$-0.132\,689\,8$ [f]	-0.165		-0.1885

[a] Present EBK results with the Gutzwiller approximation, Eq. (3).

[b] Sohlberg *et al.* [6].

[c] Quantum mechanical (QM) results obtained by Duan *et al.* for a collinear system within BOA [25].

[d] Moss [21].

[e] Peek [23].

[f] Taylor *et al.* [24], results are for the $N=1$ rotational state.

values obtained using the energy-scaling relation, namely, formula (3), are only valid for low l and k values, i.e., for the lowest vibrational quantum numbers. (The $v=1$ values listed in Table I are for reference purpose only.) The energy values obtained using formula (3) are listed in Table I, with the ''exact'' quantum mechanical values [21–24].

We see in Table I that the predicted binding energy of the $X\,^2\Sigma_g$ state of $H_2{}^+$ is about 100% greater than the exact value. This is in contrast with the result obtained by Sohlberg *et al.* [6], who quantize three-mode tori using the surface-of-section technique [15]. Their binding energy is about 90% smaller than the exact value. They attribute the large error to electron tunneling through the potential barrier which rises as two protons recede from each other [4,6]. This tunneling effect is certainly missing in a primitive semiclassical quantization treatment. Our results of previous sections suggest another possible contributing factor, that is, we actually have a mixed, instead of integrable, system in which the $P2$ KAM zone is surrounded by the $P2/P3$ intermittent chaos. One may then ask how we account for the fact that the collinear calculation predicts a more tightly bound ground state for $H_2{}^+$. This may be due to the fact that in a collinear configuration the electron is restricted to move between the two protons at all times, and thus contributes more effectively to the binding than a coplanar or three-dimensional (3D) configuration. An evidence of this restricting effect is provided by the quantum mechanical solution of the collinear system [25] (within BOA). The latter yields the strongest binding among all results listed. Furthermore, the results of Strand and Reinhardt [2] using primitive semiclassical quantization reveal that the ground electronic state (within BOA) also shows stronger binding for $R\leqslant 1.25$ bohrs. Incidentally, the equilibrium distance of 1D quantum calculations agrees with the location of the antisymmetric periodic unit of Fig. 3 ($R\sim 2.6$ bohr).

Both collinear and coplanar (or three-mode) semiclassical calculations predict chemical bonding in the ground electronic state, but this is not the case for the first excited state ($2p\sigma_u$), which is a very weakly bound van der Waals state [14]. As pointed out by Sohlberg *et al.* the stability of this state is entirely due to electron tunneling, thus it is not surprising that methods based on primitive semiclassical quantization cannot predict its stability. On the other hand, in the language of the previous sections, a $2p\sigma_u$ state would correspond to a stable $P3$ periodic orbit, which is clearly absent in the collinear case as revealed by Fig. 3. A search of its existence in the coplanar case is so far inconclusive, thus we cannot rule out the possibility that stable $P3$ islands exist in the 2D and 3D cases. As to the collinear quantum calculation the result of the $2p\sigma_u$ state again shows stronger binding than the 3D quantum result. Finally, for the $2p\pi_u$ state, all theoretical results listed in Table I predict that it is stable (with reference to -0.125 a.u.) and the relative error in the result of formula (3) becomes to some extent more reasonable.

Before leaving this section we note that what makes the study of the collinear configuration possible at all is the regularization procedure, as disussed in Sec. II. By using it we obtain a clear phase space structure for the hydrogen molecular ion. Regularization should improve the accuracy of trajectory calculations in higher-dimensional space too, a problem mentioned by Sohlberg *et al.* [6] in their study.

VI. SUMMARY AND DISCUSSIONS

The purpose of the present article is to study the correlated classical motion between the electron and the protons, which is an ingredient missing in the BOA approximation. Within BOA, $H_2{}^+$ is separable, thus integrable. It is interesting to find out what types of dynamical behavior will show up when we go beyond the adiabatic approximation. We have found that the periodic orbits of antisymmetric stretching vibration of $H_2{}^+$ and of a wide class of three-body Coulomb systems are stable. In the phase space of such systems, this periodic orbit is surrounded by a KAM zone, which is further surrounded by a region of bound aperiodic orbits, called $P2/P3$ hybrid orbits.

Other remarkable features of the $P2/P3$ hybrid motion follow. Because the $P2/P3$ hybrid motion is aperiodic, but still bound, it represents a different type of chemical bonding from a $P2$ orbit. The fact that the net change of the interproton distance of a hybrid motion is much larger than that of a $P2$ type of motion suggests that it may also represent a classical manifestation of a nonadiabatic electronic transition. Finally, we note that the transition from the regular to chaotic motion as shown in Fig. 3 appears to be sudden and the correlation between the electron and nuclear motions is very similar to that between the light and heavy atoms in a heavy-light-heavy triatomic system [13].

This last connection can be far reaching, for it implies that we can generalize the current formulation to the studies of hydrogen bonds. In such a model, instead of an electron, a proton moves between two negative centers to induce bonding. This formulation is capable of explaining both the normal type and the short-strong or symmetric type of hydrogen bonds, discussed in recent literature [26].

The semiclassical vibronic energies obtained by the EBK procedure in the last section are not in satisfactory agreement with the quantum results. The same is true for the three-mode results of Sohlberg *et al.* Together they bring out the importance of including electron tunneling in semiclassical quantization of the hydrogen molecular ion [2]. Such a treatment is yet to be carried out beyond the Born-Oppenheimer approximation, but it is important for the undestanding of chemical bonding. Unlike the BOA counterpart [2] where consideration of 1D tunneling suffices, the main challenge that we are faced with is tunneling in higher-dimensional space. For this purpose it is easier to start with a collinear system, where tunneling through only a two-dimensional potential need be considered. For such a potential trajectories in complex coordinate space have been used [27].

Finally, we should mention that, even in the current situation, it seems interesting that part of the chemical bonding can come from classical contributions, as revealed by the stable phase space structures discussed in the present article and by the results of Sohlberg *et al.* [6].

ACKNOWLEDGMENTS

We thank Professor Greg Ezra for useful discussions. The work was supported by the National Science Foundation under Grant No. PHY9408879, and the National Natural Science Foundation of China.

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