Hydrogen Molecule as a Classical Restricted Four-Body Problem

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Bohr was the first to use an orbit to describe the chemical bond of the hydrogen molecule. In this Letter the hydrogen molecule was studied classically as an extension of the helium atom. Various types of symmetric orbits like Bohr's and Langmuir's orbits for the helium atom were found and their stability indexes computed. The importance of these orbits in the semiclassical quantization of the hydrogen molecule is presented. [S0031-9007(96)01753-X]

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Before quantum mechanics, physics had only classical mechanics to describe nature. With the advent of the so-called old quantum theory, which was an initial attempt at quantum mechanics with a classical intuitive view, several important problems were solved. The failure of the old quantum theory to describe very important problems in atomic and molecular physics, e.g., the helium atom (three body problem) [1] was provoked by a lack of knowledge such as the inability to deal with conjugate points along classical trajectories and of periodic orbits when the classical dynamics are nonintegrable. In the same way that the helium atom (He) [1,2] and the positive hydrogen molecule-ion (H_2^+) [3,4] gave rise to difficulties in the old quantum theory, so did the hydrogen molecule (H_2) [5]. Starting from stability mechanical principles, Bohr was the first to try to apply the quantization rules for H_2 [5].

With the full development of quantum mechanics, the semiclassical description becomes outdated. Quantum mechanics was able to show its great predictive power in spite of some lack of intuitive view. In addition, quantum mechanical calculations were shown to be cumbersome and elaborate in the studies of three(or more)-body systems, for instance. Quantum mechanics seldom permits understanding of the structure of its solutions unless some more direct and intuitive approaches can be found. One of these intuitive procedures is the direct use of classical mechanics with proper allowance for the necessary modifications that are required by quantum mechanics. Classical mechanics can help to uncover local integrals of motion or adiabatic coordinates [6]. The best way to achieve this goal starts with finding at least one periodic orbit in the purely classical problem, and then imposing the appropriate quantization condition (semiclassical approach), which depends on the stability character of this classical orbit. The recent success of the application of the "correct" semiclassical procedures in He [2,6] allowed important discoveries in the field of atomic physics [6,7]. The extension of these studies to molecular physics seems natural through the study of H_2. One of the most important fields dealing with the structure of the matter is chemistry, where the chemical bond plays the crucial rule. And H_2, even more so than H_2^+, contains the basic ingredients for understanding the chemical bond.

A classical study of H_2 systems begins with an extension of the He [6–8], i.e., as a three-body (restricted four-body) problem where the nuclear charge in H_2 is distributed in two points (two coupled Kepler problems of two centers).

The objective of this Letter is to present for the first time the Bohr and Langmuir orbits for two central force problems. In the sequence the stability indexes of the respective orbits are computed and their behavior discussed.

In classical studies of the H_2 system, the difficulties are similar to those of He since the Hamiltonian below is singular, nonintegrable, and multidimensional:

$$H_{H_2} = \frac{1}{2}(\mathbf{P}_1^2 + \mathbf{P}_2^2) - \frac{Z_A}{|\mathbf{r}_{1A}|} - \frac{Z_B}{|\mathbf{r}_{1B}|} - \frac{Z_A}{|\mathbf{r}_{2A}|} - \frac{Z_B}{|\mathbf{r}_{2B}|} + \frac{Z_A Z_B}{R} + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|},$$

where $\mathbf{r}_i$ is the ith electron position vector, $\mathbf{P}_i$ is the conjugate momentum, $\mathbf{r}_{iC}$ is the ith electron position vector with respect to nuclei C, Z_C (= 1, for H_2) is the nuclear charge, and R is the internuclear distance, considered as a parameter. This Hamiltonian is scaled with R, similarly to H_2^+ [4]. Since the nuclei are fixed, the H_2 problem is reduced to six degrees of freedom.

This multidimensional system is essentially nonintegrable, presenting both regular and chaotic movements. In the last case, the system is relevant to chaotic studies, since experimental measurements can be directly compared to theoretical results. The chaotic behavior can be more easily studied if it is reduced to 1D, e.g., in the internuclear axis which is similar to the 1D He atom [6] (see 1D axial trajectories).

The Hamiltonian above can be given in the confocal elliptic coordinates defined by [9]: $\xi_i = (r_{iA} + r_{iB})/R$, $\eta_i = (r_{iA} - r_{iB})/R$, and φ_i, where φ is the azimuthal angle and the interelectronic separation ($|\mathbf{r}_2 - \mathbf{r}_1|$) is described in Ref. [10]. This Hamiltonian is regularized [11] in order to eliminate the difficulties of the singularities

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which appear in the numerical calculation. The regularized Hamiltonian is given by

$$\Gamma = \frac{1}{2}\frac{[\chi_2^2 + (R/2)^2\sin^2\theta_2]}{[\chi_2^2 + (R/2)^2]}P_{\chi_1}^2 + \frac{1}{2}\frac{[\chi_1^2 + (R/2)^2\sin^2\theta_1]}{[\chi_1^2 + (R/2)^2]}P_{\chi_2}^2 + \frac{1}{2}\frac{[\chi_2^2 + (R/2)^2\sin^2\theta_2]}{[\chi_1^2 + (R/2)^2][\chi_2^2 + (R/2)^2]}P_{\theta_1^2}$$
$$+ \frac{1}{2}\frac{[\chi_1^2 + (R/2)^2\sin^2\theta_1]}{[\chi_1^2 + (R/2)^2][\chi_2^2 + (R/2)^2]}P_{\theta_2}^2 + \frac{[\chi_1^2 + (R/2)^2\sin^2\theta_1][\chi_2^2 + (R/2)^2\sin^2\theta_2]}{[\chi_1^2 + (R/2)^2][\chi_2^2 + (R/2)^2]}$$
$$\times\left[-E + \frac{1}{2}\frac{P_{\varphi_1}^2}{\chi_1^2\sin^2\theta_1} + \frac{1}{2}\frac{P_{\varphi_2}^2}{\chi_2^2\sin^2\theta_2}\right]$$
$$- \frac{[\chi_2^2 + (R/2)^2\sin^2\theta_2][(Z_A + Z_B)\sqrt{\chi_1^2 + (R/2)^2} - (Z_A - Z_B)(R/2)\cos\theta_1]}{[\chi_1^2 + (R/2)^2][\chi_2^2 + (R/2)^2]}$$
$$- \frac{[\chi_1^2 + (R/2)^2\sin^2\theta_1][(Z_A + Z_B)\sqrt{\chi_2^2 + (R/2)^2} - (Z_A - Z_B)(R/2)\cos\theta_2]}{[\chi_1^2 + (R/2)^2][\chi_2^2 + (R/2)^2]}$$
$$+ \frac{[\chi_1^2 + (R/2)^2\sin^2\theta_1][\chi_2^2 + (R/2)^2\sin^2\theta_2]}{[\chi_1^2 + (R/2)^2][\chi_2^2 + (R/2)^2][R_{12}]},$$

where $R_{12} = \{\chi_1^2 + \chi_2^2 + (R/2)^2(\cos^2\theta_1 + \cos^2\theta_2) - 2\sqrt{\chi_1^2 + (R/2)^2}\sqrt{\chi_2^2 + (R/2)^2}\cos\theta_1\cos\theta_2 - 2\cos(\varphi_1 - \varphi_2)\chi_1\chi_2\sin\theta_1\sin\theta_2\}^{1/2}$, $\Gamma = [(\xi_1^2 - \eta_1^2)(\xi_2^2 - \eta_2^2)/(\xi_1^2\xi_2^2)](H_{\rm el} - E) = 0$, $\chi_i = (R/2)\sqrt{\xi_i^2 - 1}$, $P_{\chi_i} = (2/R)^2(\chi_i P_{\xi_i}/\xi_i)$, $\theta_i = \arccos\eta_i$, and $P_{\theta_i} = -\sin\theta_i P_{\eta_i}$. The $H_{\rm el}$ is the $H_{\rm H_2}$ without the internuclear repulsion ($Z_A Z_B/R$). This regularization procedure can be used in order to solve the H_2^+ system [4] or, generically, the restricted three body problem [12].

The Hamilton equations obtained from the regularized Hamiltonian are easily integrated numerically with the Runge-Kutta method of fifth order. In this way, the trajectories are obtained in 3D. It is possible to find various new orbits for the H_2 system starting from some known orbits for He [1,2]. A sketch of these orbits is presented in Fig. 1. The Langmuir's orbits are obtained from Bohr's orbits by making a Bohr-Kramers' rotation (R_S) of the orbit of the electron 1 over a plane conveniently selected. All these orbits were found and calculated by the complete regularized Hamiltonian.

The orbits that appear in Fig. 1 for the H_2 system are described below:

The BH_2a orbit was proposed by Bohr [5], who was trying to obtain the binding energy of the H_2. This orbit is shown in Fig. 2 in 3D Cartesian coordinates space given in atomic units. Bohr proposed that the valence electrons (outer electrons) were localized in a ring around the internuclear axis representing the chemical bond. This was the first physical interpretation of the chemical bond.

The stability indexes for the symmetric displacement for BH_2a and other orbits were calculated by the monodromy method [13] with effective three degrees of freedom. These indexes for BH_2a orbit appear in Fig. 3. The symmetric displacement belonging to the orbital plane is always stable [λ (Lyapunov exponent-module 2π) $= 0$ and θ (stability angle-module 2π) $\neq 0$]. The symmetric displacement normal to the orbit plane is stable for $E > -1.16$ a.u., with $R = 2.0$ a.u. Asymmetric displacements are possibly unstable for all orbits calculated in this Letter. The value $\tilde{E} = -1.11$ a.u. [$\tilde{E} = E(R/2)$] was found for the energy [$E = -(3^{3/2} - 1)^2/(2^4 n^2)$ a.u.] given by Bohr's calculation [5] with $n = 1$ and $R = 2^3/(3^2 - 3^{1/2})$ a.u. scaled to $\tilde{R} = 2$ a.u. and with the internuclear repulsion subtracted. This energy ($\tilde{E} = -1.11$ a.u.) belongs to the stable range reflecting the importance of the BH_2a orbit for the description of the ground state of H_2 by Bohr [5].

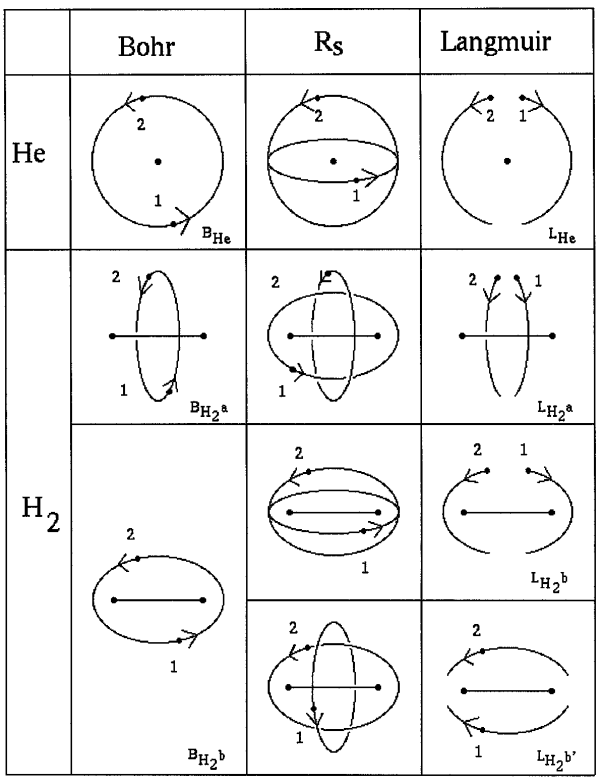

FIG. 1. Bohr's and Langmuir's orbits for the helium atom (He) and for the hydrogen molecule (H_2).

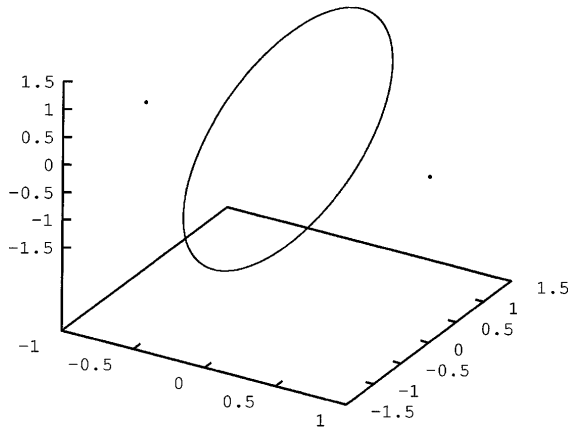

FIG. 2. The $B\mathrm{H}_2a$ orbit of the 3D hydrogen molecule with $E = -1.0$ a.u. and $R = 2.0$ a.u. The dots represent the nuclei.

The $B\mathrm{H}_2b$ orbit [sketched in Fig. 1] and the $B\mathrm{H}_2a$ orbit can be considered a generalization of the orbit proposed by Bohr for He (BHe) [Fig. 1]. The $B\mathrm{H}_2b$ orbit is stable for symmetric displacements belonging to the orbital plane.

The $L\mathrm{H}_2a$ orbit is shown in Fig. 4 in 3D Cartesian coordinates space and the $L\mathrm{H}_2b$ and $L\mathrm{H}_2b'$ orbits are sketched in Fig. 1. These orbits are generalizations of the Langmuir's orbit for the helium atom (LHe) to H_2. The stability indexes for symmetric displacement of the $L\mathrm{H}_2a$ orbit are shown in Fig. 5. The two eigenvalues show that the orbit presents stable or unstable behavior depending on the range of energy. For $-1.23 \leq E \leq -0.60$ the orbit is always stable and for $E \approx -0.36$ it is totally unstable. The stability angle for symmetric displacement is shown in Fig. 6 for $B\mathrm{H}_2b$, $L\mathrm{H}_2b$, and $L\mathrm{H}_2b'$ orbits with $\lambda = 0$. The stability angle belonging to the orbital plane for all Langmuir's orbits is always $\theta \approx 0.12$ for $E \approx 0$. This value of θ coincides with the

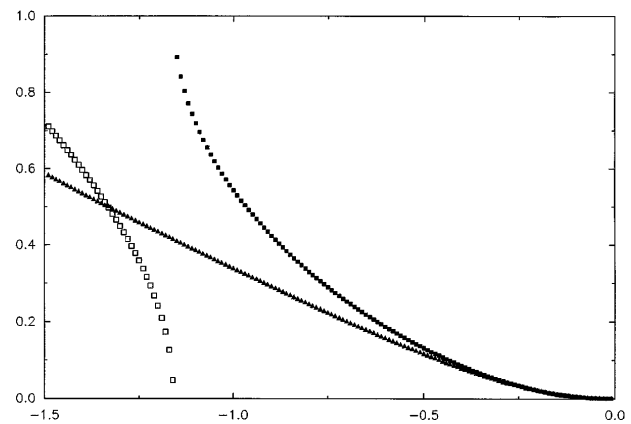

FIG. 3. Stability angle (θ) (full symbols) and Lyapunov exponent (λ) (open symbols) as a function of the electronic energy (E) in atomic units for the $B\mathrm{H}_2a$ orbit. Triangle symbols indicate symmetric displacements in the orbital plane. Square symbols indicate symmetric displacements perpendicular to the orbital plane. When θ or λ do not appear in the figure, they have null values.

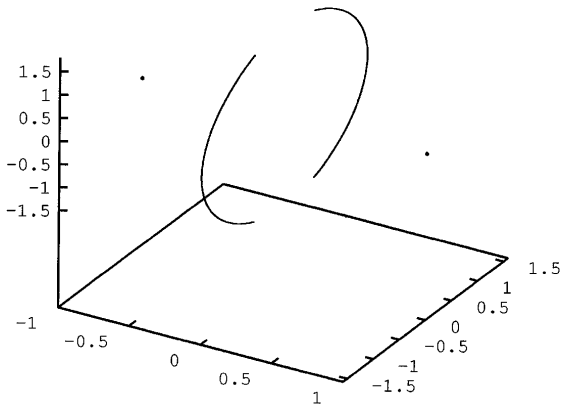

FIG. 4. The $L\mathrm{H}_2a$ orbit. Comments are the same as for Fig. 2.

corresponding Langmuir's orbit of He. The azimuthal direction is decoupled for symmetric displacements for symmetric orbits (marginally stable orbit, $\lambda = \theta = 0$) which belong to the plane that contains the nuclear axis. In addition, when the $B\mathrm{H}_2a$ and $L\mathrm{H}_2a$ orbits are stable for symmetric displacement the correlated unrestricted four-body problem can also be stable.

The semiclassical action (S) for each electron of several orbits can be estimated considering $S = 2\pi[n + \alpha/4 + \theta_1(l + 1/2) + \theta_2(m + 1/2)]$, where α is the Maslov index ($\alpha = 0$ for Bohr's orbits and $\alpha = 2$ for Langmuir's orbits), θ_1 and θ_2 are the stability angles corresponding to small symmetric librations in the orbital plane and normal to the orbital plane. Since the H_2 system is not scaled with energy (E) the relationship between E and S is calculated numerically. The rigorous EBK quantization of invariant KAM tori around Bohr's and Langmuir's orbits is not applicable to the H_2 system, since asymmetric librations are unstable. However, the semiclassical path-integral quantization of nonintegrable Hamiltonian systems [14] is applicable.

Trajectories in 1D can also be found:

(a) Pendulum trajectories (for the H_2^+ [3])—the two electrons oscillate along the middle axis (perpendicular

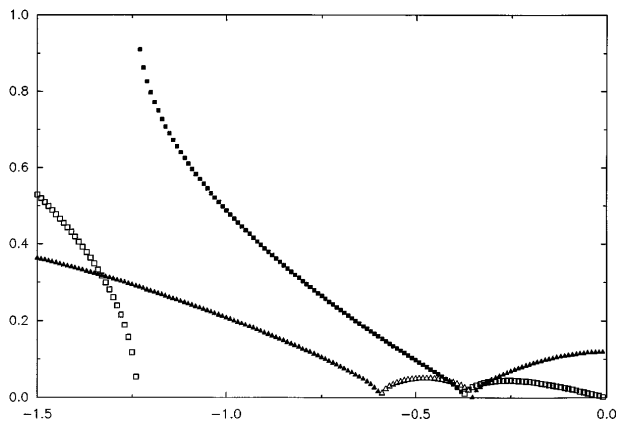

FIG. 5. θ and λ for the $L\mathrm{H}_2a$ orbit. Remaining comments are the same as for Fig. 3.

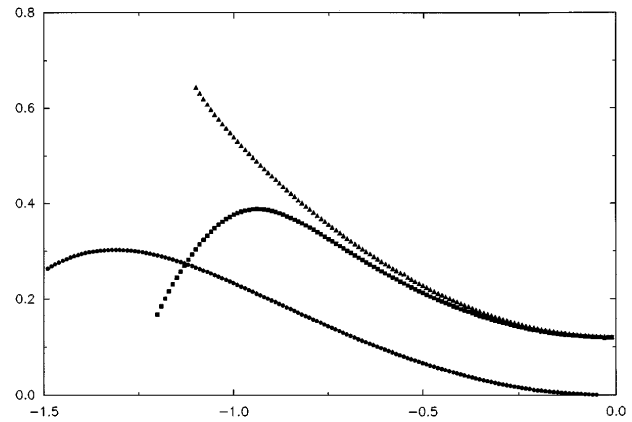

FIG. 6. θ for symmetric displacements in the orbital plane. Circle symbols indicate the $B\mathrm{H}_2b$ orbit, triangle symbols indicate the $L\mathrm{H}_2b$ orbit, and square symbols indicate the $L\mathrm{H}_2b'$ orbit. Remaining comments are the same as for Fig. 3.

to the internuclear axis) between the two protons. The oscillation may be symmetric or asymmetric (chaotic).

(b) Axial trajectories—in this case the electrons are on the internuclear axis, as in the He in 1D [6]. Four distinct combinations are possible because there are two electrons and two protons that divide the internuclear axis into three regions. An example: The two electrons can be on the right (or left) of the two protons. This case is a generalization of the "frozen planetary atom" (FPA) of He [6,7,15,16] for H_2 system. In the case of H_2 in 1D a FPA configuration can be found. The Poincaré map of this FPA configuration shows tori, which represents the intermediate case between He and the negative hydrogen ion (H^-). On the other hand, the trajectories in 2D associated with the neighborhood of a FPA orbit are destabilized by perturbations which are applied to the He Hamiltonian in order to transform it in the H_2 Hamiltonian. There are basically two types of perturbations: (a) separation of the two protons slightly by a distance δR; (b) fixing two charges $(Z - \delta q)$ and (δq) at a distance R (or δR). Calculations of the stability indexes for the H_2 system in four degrees of freedom with $R = 2$ a.u. (or for any value of R since the Hamiltonian is scaled with R) show unstable behavior of the FPA orbit.

The three other combinations in 1D (axial) show chaotic behavior that depends on the internuclear separation. These configurations are similar to the eZe configuration of He [6]. In relation to He system, the near-collinear intra shell resonances are associated with an asymmetric stretchlike motion of the electron pair rather than the symmetric stretch motion along with the Wannier ridge [17]. Similar results can be expected for the H_2 for near-collinear motion.

The rediscovery of the $B\mathrm{H}_2a$ orbit for the H_2 system shows Bohr's great physical intuition evidenced by his thoughts about mechanical stability principles and the chemical bond [18,19]. The other orbits shown in this Letter were consequences of Bohr's and Langmuir's descriptions of He. The orbits presented in this work are almost always stable for symmetric displacement and this reinforces their importance in the stability of the system and consequently in their quantization. The importance of all these orbits for the description of the doubly occupied symmetric quantum states will be considered in a future paper.

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