Classical and Semiclassical Studies of the Hydrogen Molecule

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Abstract

The hydrogen molecule contains the basic ingredients to understand the chemical bond, i.e, a pair of electrons. We show a step to understand The Correspondence Principle for chaotic system in the Chemical World.

The hydrogen molecule is studied classically as an extension of the helium atom. Several types of orbits were found for two-fixed-centers system (hydrogen molecule) starting from some known orbits for one-fixed center one (helium atom), e.g., one dimension orbits as pendulum and axial and also Bohr and Langmuir's orbits [11, 12].

The classical stability and the single quantization of some one-dimensional periodic orbits are shown. These orbits are used to make a global quantization of that molecular chaotic system. We discuss the importance of those periodic orbits in the comprehension of the nature of chemical bond.

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1 Introduction

Bohr's model for the hydrogenlike atoms gives the correct (exact) spectrum for such systems and so was an important paradigm in the development of the so-called old quantum theory. However, the extension of that model to other non-hydrogenlike atoms is non-trivial.

Similar ideas were soon applied to the helium atom (two-electron system) [1], but the old quantum theory cannot describe the helium atom in the same accuracy level of the hydrogen atom. Essentially, the inaccuracy is not an exclusive manifestation of the old quantum theory, but classical theory. A three-body system is generically a non-integrable system, it is not possible to find the necessary number of integrals of motion as for two-body system (integrable). A nonintegrable system can show several behavior patterns depending on the initial conditions, i.e., a (quasi-)regular, chaotic or mixing behaviors [2]. The regular or integrable system obeys special conditions which allows the application of the basic principles of the old quantum theory rules. However, that theory has some incorrect statements, e.g., the inability to treat the conjugated points along classical trajectories [2]. The correct version of the old quantum theory is denominated semiclassical theory.

Important applications of semiclassical theory can be seen in the studies of the connection between the classical mechanic and quantum one (correspondence principle) when the classical system is chaotic [2, 3].

The helium atom can be solved in a high degree of accuracy with quantum mechanics with "brute force." That system was studied at the end of the seventies [4] with a semiclassical theory obtaining good results. A decade before, the semiclassical theory was developed by Gutzwiller with application to the quantization of chaotic systems [2]. Meeting those conditions, in the beginning of the nineties, the helium atom was extensively studied with semiclassical theory [5, 6]. Several important results were managed for helium atom in one dimension based on classical properties of the periodic orbits.

The semiclassical theory can also be applied to molecules. Of course, the molecular systems are remarkably more difficult to understand in comparison to atoms. It is possible to make some extension of those atomic studies in order to improve the knowledge in the molecular system and principally the chemical bond.

Since Dalton's time, or even before, people try to understand the nature of the (chemical) bond among atoms or, in other words, the molecular structure. Bohr was the first to try to describe the chemical bond under a physical point-of-view of the hydrogen molecule (H_2) and other systems [7]. Bohr made an original proposal to describe the chemical bond of the hydrogen molecule. He 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. That description was made before the *ad hoc* Lewis, Langmuir and Thomson's theories [8].

The extension of such studies of the helium atom to molecular systems

seems natural through the study of H_2. A study of H_2 system begins 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). This system of two central forces can be understood as a system between the helium atom and two hydrogen atoms or ions.

The simplest molecule is the H_2^+. The molecule-ion H_2^+ in adiabatic approximation is an integrable system as the isolated hydrogen atom. Of course, the H_2^+ as a three-body system is a nonintegrable problem. W.Pauli tried to calculate the energy formation of the hydrogen molecule-ion (H_2^+) applying the (incorrect) old quantum theory (Bohr-Sommerfeld quantization) [9]. The first correct semiclassical quantization was presented at the end of the seventies [10]. However, the H_2 molecule, even more so than H_2^+, contains the basic ingredients for understanding the chemical bond, i.e., an electron pair.

The hydrogen molecule is the natural choice to start the study of the chemical systems since it is the simplest problem where the chemical aspects can be studied in full details.

The problem of the hydrogen molecule belongs in no-person's land between Chemistry and contemporary Physics. This molecule is very simple conceptually considered in the point-of-view of the present Theoretical Quantum Chemistry and very complex over first principles of the present Physic. On the other hand, we try to show that the hydrogen molecule is a capital problem in order to understand the fundamental matter structure and the quantum mechanics.

Semiclassical studies of H_2 with few types of symmetric Bohr and Langmuir's orbits in two dimension (2-D) were considered [11, 12]. Those studies of H_2 were made with few 2-D periodic orbit filling the 3-D. The full 3-D problem is generically impossible to deal with. However, if one uses chemical and physical arguments, i.e., disposition of electrons in electron-pair, symmetries, etc, some special periodic orbits can be found and an incipient quantization with few orbits can be achieved.

These semiclassical studies can be considered to understand the chemical bond. It is known that the chemical bond is formed by decreasing of kinetic energy in the chemical bond direction with accumulation of the electronic charge in the internuclear region [13]. We show with classical and semiclassical physics that the perpendicular plane to the axial direction is the most important region to describe the chemical bonding.

Here, we show a modest first step to understand "the Correspondence Principle" in chemical world that treats essentially nonlinear systems.

2   Theory and Models

H_2 is the simplest molecule in the chemical context, but it is a very complex system under some basic principles, i.e., H_2 is nonintegrable, multidimensional and singular. The hydrogen molecule may be studied in the context

of nonlinear dynamics, its complex dynamics can only be studied by nonperturbative theory.

The H_2^+ is the starting model to study the H_2 system as shown below.

1-D two-center Kepler problem - H_2^+

The Classical Hamiltonian for H_2^+ system in 1-D or two-centers Kepler problem (one electron and two protons) is given by

$$H_{H_2^+} = \frac{P^2}{2} - \frac{1}{|z - R/2|} - \frac{1}{|z + R/2|}.$$ (1)

The Hamiltonian (1) shows important numerical problems in the integration of the classical Hamilton equations since the potentials diverge on $|z| = R/2$. However, the phase space expansion technique can solve that numerical problem. The time (t) and the (quasi-)energy (E) are treated as canonical variables in that technique. We need firstly to define a Hamiltonian (Γ) identically null. Γ can be multiplied by the inverse of the singular function in Hamiltonian (1). (Such technique is the reguralization procedure used in Celestial Mechanics [14].)

The regularized Hamiltonian can be achieved as shown below.

$$\Gamma^* = P_t + H(z, P, t) = 0,$$

where $P_t = $ -E $= - H(z, P, t)$.

The new time variable (t^*) is defined as

$$dt/dt^* \equiv dq_t/dt^* = \partial\Gamma^*/\partial P_t = 1,$$

if

$$\Gamma = f(z, P, t)\Gamma^*,$$

$t^{*'}$ variable is

$$t^{*'} = f^{-1}(z)(t + cte),$$

where all divergence problem is transfered to determination of $t^{*'}$, i.e., in the divergence region $t^{*'}$ becomes slower than t.

The function $f(z)$ that regularizes the Hamiltonian (1) is

$$f(z) = |(R/2)^2 - z^2|$$ (2)

and Γ is

$$\Gamma = |(R/2)^2 - z^2|P_t + |(R/2)^2 - z^2|P^2/2 - (R, 2|z|),$$ (3)

where $(R, 2|z|)$ is the step function, i.e., for $|z| < R/2$ the function $(R, 2|z|)$ is R with $|(R/2)^2 - z^2| = [(R/2)^2 - z^2]$ and for $|z| > R/2$ it is $2|z|$ with

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$|(R/2)^2 - z^2| = [z^2 - (R/2)^2]$. The Hamiltonian (1) is separable in two regions ("outside" and "inside" of the molecule) and the regularized Hamiltonian maintains similar property.

It is necessary to make a canonical transformation in the Hamiltonian Γ in order to obtain the Hamilton equations. Such transformation changes the finite product $[(R/2)^2 - z^2]P^2$ (P diverges from $z = R/2$) to a single canonical variable.

The "outside" regions are obtained with $(|z| > R/2)$ and so

$$z^2 = (R/2)^2 + \chi^2,$$

with $(R/2) < |z| < +\infty$, and $0 < |\chi| < +\infty$.

The final reguralized Hamiltonian is

$$\Gamma' = \Gamma/z^2 = 1/2 P_\chi^2 + \frac{\chi^2 P_t}{[(R/2)^2 + \chi^2]} - \frac{2}{[(R/2)^2 + \chi^2]^{1/2}} = 0, \qquad (4)$$

where $P_\chi = \chi P/[(R/2)^2 + \chi^2]^{1/2}$ and the generating function [16] $F_3 = -P[(R/2)^2 + \chi^2]^{1/2}$.

Γ' is similar to a harmonic oscillator near the collision electron-proton ($\chi << R/2$). The hydrogen atom (one-center problem) is exactly a harmonic oscillator for similar regularization procedure [14].

The "inside" region is obtained with $(|z| < R/2)$ and the Γ is given below with $2z/R = \cos\theta$.

$$\Gamma = 1/2 P_\theta^2 + (R/2)^2 \sin^2\theta P_t - R = 0, \qquad (5)$$

where $P_\theta = -(R/2)\sin\theta P$ and $F_3 = -(R/2)P\cos\theta$. The Hamiltonian (5) is the simple pendulum equation.

That regularization procedure of two centers is similar to Thiele-Burrau regularization [14]. We consider in our regularization an angle variable ($\theta \in [0 : \pi]$) inside of the molecule and a variable $\chi \in [0 : \infty]$ outside of the molecule. The lines $\chi = $ constant are ellipses and the lines $\theta = $ constant are hyperbola in the physical Cartesian coordinates plane, similar to the confocal elliptic coordinates [15].

The regularization above is applied to the hydrogen molecule that is related to coupling of two Kepler problems of two centers.

1-D Hydrogen Molecule

The hydrogen molecule in 3-D has 6 degrees of freedom (dof) for fixed nuclei. Since the energy is a constant of movement the system can be reduced to 5 dofs. The angular moment is not a constant in general. However, the angular moment can be a constant depending on the initial conditions, e.g., for pendulum periodic orbits.

The hydrogen molecule can be studied in 1-D as the helium atom [5]. The helium atom has two configurations in 1-D named Zee (stable orbit - with two electrons (e) in the same side of the nucleus (Z)) and eZe (unstable orbits - with two electrons in each side) [5]. On the other hand, the H_2 has one pendulum and four axial configurations.

a) Pendulum trajectories - as defined by Pauli [9] for H_2^+ - two electrons belong to the middle plane perpendicular to the internuclear axis of the molecule. The electron oscillation may be symmetric stretch (SS - Wannier orbit) or asymmetric stretch (AS).

b) Axial trajectories - the electrons are in the internuclear axis. Four distinct combinations are possible because there are two electrons and two protons, which divide the internuclear axis into three regions. These four distinct combinations can be named $eZZe$, $ZeeZ$, $ZeZe$, and $ZZee$ considering the two nuclei (Z) and the two electrons (e). SS and AS periodic orbits (PO) can be found for the axial configurations.

The 3-D Hamiltonian is essential to describe the H_2 system completely. However, the 1-D approximation can be used. The difficulties of the multi-dimensional calculation are drastically reduced in 1-D model.

The dynamical of the axial trajectories does not have any other constant of movement than that of the energy. The angular moment is a constant of the movement for that of the pendulum trajectories. In the last case the whole system can be reduced to 4 dofs.

The axial and pendulum configurations (1-D) are important parts of the complete phase space for H_2 like He atom. There is no place for SS PO in 1-D for He. However, for H_2 they are possible since the triple collision is voided, except to $ZeZe$ configuration. The SS POs can have an important contribution in high dimension for He and H_2, e.g., Bohr and Langmuir orbits. Anyway, the perpendicular motion to orbit must be stable in order to permit the perpendicular harmonic oscillator quantization since the bounded systems need a certain classical stability.

The 3-D Hamiltonian and its regularization are shown in reference [12]. The 1-D Hamiltonian for H_2 is given by:

$$H_{axial} = \frac{(P_1^2 + P_2^2)}{2} - \frac{1}{|z_1 - R/2|} - \frac{1}{|z_1 + R/2|} - \frac{1}{|z_2 - R/2|} - \frac{1}{|z_2 + R/2|} + \frac{1}{|z_1 - z_2|}, \tag{6}$$

where P_i is the momentum conjugated at position z_i of the $i-$electron and R is the internuclear parameter. The variables and the parameters can be calculated for other geometries with a scaling relation as $z = \tilde{z}(R/2), t = \tilde{t}(R/2)^{3/2}, S = \tilde{S}(R/2)^{1/2}, E = \tilde{E}(2/R)$, etc, where $\tilde{O}$ is a variable or parameter obtained with $R = 2$ and z, t, S and E are the electronic coordinate, time, action and energy, respectively.

The 1-D procedure regularization added a centrifugal barrier over each nucleus that represents the true barrier in 2-D [17]. That barrier implies a

parabolic orbit ($e = 1$, where e is the eccentricity) of the electrons around the nuclei. In this case, the H$_2$ system divides the space in three regions separated by singular potentials. (A smoothed potential (without barrier) will connect the movements of electrons (with enough energy) in these three regions). The pendulum configuration is governed by a smoothed potential like to He model (see below for more details). The regularization is not necessary for pendulum configuration since $R \neq 0$ and $|z_1 - z_2| \neq 0$ for limited energy.

The Hamiltonians for $ZeeZ$, $ZeZe$, $eZZe$ and $ZZee$ configurations can be obtained from Hamiltonian (6) or from Eq (4) and Eq (5) for two-electron molecule.

The Hamiltonian for $ZeeZ$ configuration is obtained with $\chi_i = 0$ and $P_{\chi_i} = 0$ and it is

$$\Gamma_{ZeeZ} = \frac{1}{2}\frac{\sin^2\theta_2}{(R/2)^2}P_{\theta_1}^2 + \frac{1}{2}\frac{\sin^2\theta_1}{(R/2)^2}P_{\theta_2}^2 -$$

$$\frac{2\sin^2\theta_2}{(R/2)} - \frac{2\sin^2\theta_1}{(R/2)} + \sin^2\theta_1\sin^2\theta_2(P_t + \frac{1}{R_{12}}),$$

where $R_{12} = (R/2)|\cos\theta_1 - \cos\theta_2|$.

For $ZeZe$ configuration ($\chi_1 = 0, P_{\chi_1} = 0, \theta_2 = 0$ and $P_{\theta_2} = 0$) the Hamiltonian is

$$\Gamma_{ZeZe} = \frac{1}{2}\sin^2\theta_1 P_{\chi_2}^2 + \frac{1}{2}\frac{\chi_2^2}{(R/2)^2[\chi_2^2 + (R/2)^2]}P_{\theta_1}^2 -$$

$$\frac{2\chi_2^2}{(R/2)[\chi_2^2 + (R/2)^2]} - \frac{2\sin^2\theta_1}{[\chi_2^2 + (R/2)^2]^{1/2}} + \frac{\sin^2\theta_1\chi_2^2}{[\chi_2^2 + (R/2)^2]}(P_t + \frac{1}{R_{12}}),$$

where $R_{12} = [\chi_2^2 + (R/2)^2(\cos^2\theta_1 + 1) - R\sqrt{\chi_2^2 + (R/2)^2}\cos\theta_1]^{1/2}$.

For $eZZe$ configuration [$\theta_1 = \pi(\cos\theta_1 = -1), \theta_2 = 0(\cos\theta_2 = 1)$ and $P_{\theta_i} = 0$] and for $ZZee$ one ($\theta_i = 0$ and $P_{\theta_i} = 0$) the Hamiltonians are similar, differing by R_{12}

$$\Gamma_{eZZe} = \Gamma_{ZZee} = \frac{1}{2}\frac{\chi_2^2}{[\chi_2^2 + (R/2)^2]}P_{\chi_1}^2 + \frac{1}{2}\frac{\chi_1^2}{[\chi_1^2 + (R/2)^2]}P_{\chi_2}^2 -$$

$$\frac{2\chi_2^2}{[\chi_1^2 + (R/2)^2]^{1/2}[\chi_2^2 + (R/2)^2]} - \frac{2\chi_1^2}{[\chi_1^2 + (R/2)^2][\chi_2^2 + (R/2)^2]^{1/2}} +$$

$$\frac{\chi_1^2\chi_2^2}{[\chi_1^2 + (R/2)^2][\chi_2^2 + (R/2)^2]}(P_t + \frac{1}{R_{12}}),$$

where $R_{12} = \sqrt{\chi_1^2 + (R/2)^2} + \sqrt{\chi_2^2 + (R/2)^2}$ for $eZZe$ configuration and $R_{12} = |\sqrt{\chi_1^2 + (R/2)^2} - \sqrt{\chi_2^2 + (R/2)^2}|$ for $ZZee$ one.

The Hamiltonian for pendulum configuration is

$$H_{pend} = \frac{1}{2}P_{y_1}^2 + \frac{1}{2}P_{y_2}^2 - \frac{2}{\sqrt{y_1^2 + (R/2)^2}} - \frac{2}{\sqrt{y_2^2 + (R/2)^2}} + \frac{1}{[R_{12}]},$$

where $R_{12} = |y_1 - y_2|$ with $y-$axis is perpendicular to internuclear axis or $z-$axis.

The last equation is similar to He atom with smoothed potential [17, 18], where $(R/2)$ represents the smoothed parameter ($\delta = R/2$), noting that the interelectronic repulsion term is not smoothed. Therefore, the understanding of the smoothed He system can help to know the pendulum configuration behavior for H_2 molecule.

Semiclassical quantization

Integrable and quasi-integrable systems can be studied with a generalized Bohr-Sommerfeld procedure or Einstein-Brillouin-Keller (EBK) quantization [2, 3]. The EBK quantization works well if the regular dynamics dominates a system, e.g., systems with weak correlation movements.

The quantization of the action of the periodic orbits is the first step in order to apply the EBK quantization. The actions of the orbits can be calculated as

$$S = 2\pi(n + \alpha/4)$$

where α is the Maslov index where for simple rotation $\alpha = 0$ and for simple libration $\alpha = 2$. Nevertheless, it is necessary to modify the actions in more degree of freedoms as

$$S = \sum_i 2\pi[n + \alpha/4 + \theta_i(l + 1/2)]$$

where θ_i is the stability angle for i degree of freedom belongs to perpendicular displacements of the orbit. The term $(l + 1/2)$ is the properly eigenvalue of a perpendicular harmonic oscillator

The rigorous EBK quantization of invariant KAM tori around 1-D periodic orbits is not applied to the H_2 system since they are unstable and consequently the system can not be reduced to an one-periodic-orbit model. However, the semiclassical path-integral quantization of nonintegrable Hamiltonian systems [2] can be applied.

A better semiclassical description can be obtained using the Gutzwiller trace formula [2] to calculate the density of levels.

Non-integrable systems are more difficult to study. We need infinity periodic orbits (PO) to describe a complex system completely. We need to find procedures of the truncation of the sum (resummation) for practical propose in order to converge convincing results with finite PO (similarly to use a finite base in quantum calculation). Each PO can contain implicitly correlation of

the movement similarly to a correlated base (e.g., Hylleras functions) of the quantum calculation.

The extension of the quantization for most part of the non-integrable systems is unknown yet. However, the global quantization with classical periodic orbits is an alternative.

The quantization for a non-integrable system was made by Gutzwiller [2]. The semiclassical density of states (trace formula) is [19]

$$d(E) = \sum_r \frac{T_r}{\pi\hbar} \sum_{j\neq 0} \frac{\cos[j(S_r/\hbar - \alpha_r\pi/2)]}{|[det(\mathbf{M}_r^j - \mathbf{1})]^{1/2}|}. \tag{7}$$

The trace formula above sums all repetitions (j) of the primitive periodic orbits (r) with period T_r, action S_r and Maslov index α_r and $\mathbf{M_r}$ is the stability matrix. The determinant of the trace formula depends on the fixed point. In two degrees of freedom, it is given as

$$(1/2)[det(\mathbf{M}_r^j - \mathbf{1})]^{1/2} = \begin{cases} -i\sinh(j\lambda/2), & \text{hyperbolic,} \\ \cosh(j\lambda/2), & \text{inverse hyperbolic,} \\ \sin(j\pi\theta), & \text{elliptic,} \end{cases}$$

where λ is the Lyapunov exponent (real eigenvalue) and θ is the stability angle (imaginary eigenvalue), if the system has more than two degrees of freedom complex (or loxodromic) eigenvalue can be obtained. The singular spectrum is obtained with all repetitions of the (infinity) primitive orbits in the Gutzwiller formula. The spectrum is smoothed for a finite number of the repetitions, e.g., fixing a maximum period (T_{max}). The trace formula has convergence problems, i.e., the sum diverges. Several types of the resummation were developed [2, 3] in order to try convergences in the trace formula. For example, the zeta function representation of the trace formula works well for semiclassical quantization [5, 20, 21].

The Gutzwiller trace formula in product representation or Gutzwiller-Voros zeta function [5, 20] given below.

$$Z(E) = \prod_n (E - E_n) \sim \prod_{m_k} \zeta^{-1} = \prod_{m_k} \prod_p (1 - t_p^{m_k}), \tag{8}$$

where ζ^{-1} is the dynamical zeta function or simply zeta function, the weight t_p for each primitive (nonrepeating) periodic orbit (PPO) is given by

$$t_p^{m_k}(E) = (\pm 1)^{m_k} \exp[2\pi i(S(E) - \alpha/4) - \sum_k (m_k + 1/2)\chi_k(E)], \tag{9}$$

or

$$t_p^{m_k}(z) = (\pm 1)^{m_k} \exp[2\pi i(z\tilde{S}(Rez) - \alpha/4) - \sum_k (m_k + 1/2)\chi_k(Rez)], \tag{10}$$

where z is the effective quantum (complex) number with real part given by $Rez = (-E)^{-1/2}$. $\tilde{S}(Rez) = S(E)(-E)^{1/2} = S(E)/Rez$, where $S(E)$ is the action for energy E, α is Maslov index and χ_k is the stability exponent associated to eigenvalue k of the stability matrix for each PPO that depends on the energy for this non-scaled energy system. Note that the $\tilde{S}$ is not a scaled action since the H_2 is not scaled system. $\tilde{S}$ is a convenient notation well defined in the real axis. m_k gives the bending excitation, we considered $m_k = 0$.

The symmetry decomposition of the zeta function is obtained considering that the collinear hydrogen molecule has a C_2 symmetry. The symmetric subspace of the zeta function (ζ_+^{-1}) is obtained maintaining the A_1 symmetry of the C_2 group. The antisymmetric subspace of the zeta function (ζ_-^{-1}) is obtained with A_2 symmetry. The ζ_+^{-1} is correlated to symmetric quantum resonances (singlet states) and the ζ_-^{-1} with antisymmetric quantum resonances (triplet states).

The POs are classified in boundary (denoted by $+$), symmetric ($-$) and non-symmetric (NS). The zeta function gives the resonances of the PO The factorized form of the zeta function for non-desymmetrized PPO is given by [20] for each 1-D configuration

$$\zeta_+^{-1} = (1 - t_+)(1 - t_-)(1 - t_{NS}) \tag{11}$$

and

$$\zeta_-^{-1} = (1 + t_-)(1 - t_{NS}) \tag{12}$$

where t_+, t_- and t_{NS} are the weight for boundary, symmetric and non-symmetric PPOs. The zeta function in symmetry factorized form is given by

$$\zeta^{-1} = \zeta_+^{-1}\zeta_-^{-1} \tag{13}$$

Each 1-D configuration of the H_2 is described by a Eq (13). We build a new zeta function given by

$$\zeta^{-1} = \zeta_{ZeeZ}^{-1} \otimes \zeta_{eZZe}^{-1} \otimes \zeta_{ZZee}^{-1} \otimes \zeta_{pendulum}^{-1} \tag{14}$$

where the contribution for quantum resonances for each configuration is considered in a same zeta function. The zeta function (14) can be factorized, as in Eq (13), in order to obtain the respective symmetric and antisymmetric zeta functions for all configurations. The $\otimes$ operation can be direct product or direct sum depending on the approximation, i.e., if the configurations are not or are approximately independent to each other.

Quantum Methods

Several methods can be used in order to calculate the Schrödinger equation in the adiabatic approximation (fixed nuclei) for excited states of the two-electron systems [6]:

a) A Hartree-Fock calculation as an initial guess to obtain the molecular base following an electronic correlation correction with Configuration Interaction (CI) or Perturbation Theory (PT);

b) The selection of important contributions obtained via CI can be made with Feshbach projection operator in order to describe the resonance states;

c) Independent particle method with following a PT in order to correct the interelectronic repulsion term obtained via C.Neumann formula [28];

d) R matrix method;

e) Complex rotation method, etc.

Those methods can be applied suitable depending on the behavior of the system or states.

The calculation of the Schrödinger equation is not difficult to realize for quantum systems when the correspondent classical ones are integrable or quasi-integrable, i.e., one-electron systems or many-electrons ones with low degree of the correlation. An initial guess base can give an excellent numerical convergence for those systems. The difficulties in the convergence increase with correlation movement and with quantum number.

There are serious difficulties to find a good guess base for correspondent non-integrable systems since a base is a (approximative) solution of an integrable system. Because of that the numerical convergence is very hard to manage for non-integrable systems. A good strategy is to find, if exists, a particular coordinate which can describe explicitly the quasi separability of the problem. For example, the adiabatic quantum calculation of the frozen planetary atom [5].

Quantum X Semiclassical

We can summarize some important aspects of the quantum and semiclassical calculations.

Advantages of quantum calculation:

a) The quantum theory is correct;

b) It is possible to calculate any system via brute force;

c) Very known theory.

Disadvantages of the quantum calculation:

a) Difficulties to interpret the results;

b) Difficulties to treat highly excited states;

c) High computational costs.

Advantages of the semiclassical calculation:

a) Suitable on interpretation of the results;

b) Suitable to treat highly excited states;

c) Low computational costs.

Disadvantages of the semiclassical calculation:

a) The semiclassical theory is approximate with few exceptions;

b) It is hard to find the solution for generic systems;

c) Unknowing of the generic recipes to quantization of the chaotic systems.

3   Results and Discussions

Our starting point of the studies of the H_2 is to compare this two-electron molecular system to a two-electron atomic, i.e., the helium atom. The He atom was studied semiclassically [4, 5, 6, 29] and very important results are managed.

Classical studies

Firstly, we have to integrate the Hamilton equations from H_2 numerically with a variable step fourth-order Runge-Kutta method in order to obtain the periodic orbits (PO). Some those PO are shown in Fig.1 and Fig.2 for $R = 2.0$au.

The Fig.1 shows the potential energy level curves for axial configurations with a smoothed parameter $\delta = 1$ in order to avoid the divergences in level curves. Of course, we do not consider the smoothed parameter in our calculations. The abscissa and ordinate axes represent each other one electron. The protons are located at $(+1, -1)$ and $(-1, +1)$ (absolute minima of the potential energy),where all axial POs emerge, exception for $ZZee$ configuration. The saddle point is located at origin (0,0). The diagonal line $(x = y)$ is the place where the electronic repulsion is infinity. The energy of the POs increases with their size for a same configuration.

The $eZZe$ Wannier (SS) and fundamental (AS) POs in Cartesian coordinates for several values of energy ($E = -2.5$au (SS and AS), -2.0 and -1.0) are shown in the places on the potential energy curves labeled with $eZZe$ in Fig.1. The fundamental orbit is an AS PO where the period is the shortest of those orbits belonging to same AS configuration. That orbit is similar to fundamental PO of the eZe configuration of the He [5]. The $ZeeZ$ fundamental POs in Cartesian coordinates for $E = -2.41$au (SS and AS), -2.0 and -0.55 are shown in $ZeeZ$ place. The $ZeZe$ fundamental AS POs in Cartesian coordinates for $E = -3.71$au, -2.66 and -2.4 are shown in $ZeZe$ and $eZeZ$ places. Near SS POs (simultaneous double collision) for $ZeZe$ at $(+1, -1)$ and for $eZeZ$ at $(-1, +1)$ and near SS POs (triple collision) for $ZeZe$ at $(+1, +1)$ and for $eZeZ$ at $(-1, -1)$ are not considered. The molecular Frozen Planetary Configuration (FPC) [12] POs of the ZZee configuration in Cartesian coordinates for $E = -5.65$au and -4.01 are shown in $ZZee$ and $eeZZ$ places. Those POs received the molecular FPC name by analogy with Frozen Planetary Atom for He atom [5].
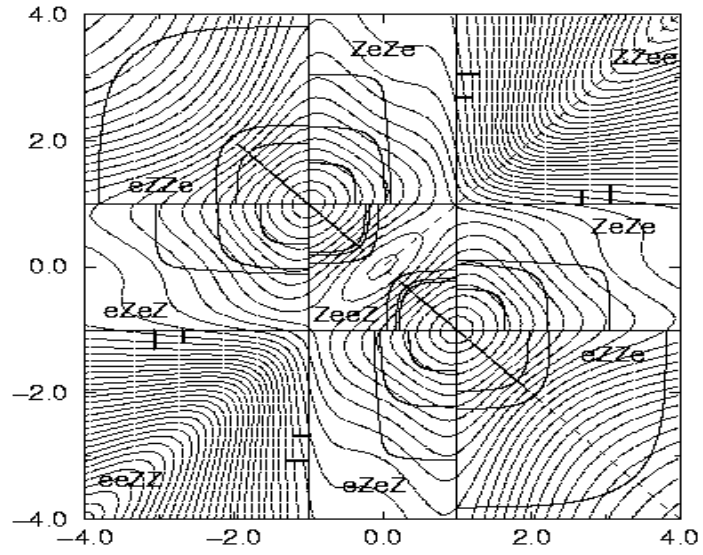
Figure 1: Potential energy level curves for axial configurations with smoothed parameter $\delta = 1$ and $R = 2$. Each axis represents one electron coordinate. The protons are located at $(+1, -1)$ and $(-1, +1)$. The Wannier and fundamental POs in Cartesian coordinates for several values of energy are put in their respective configurations. The dashed lines shows the desymmetrized region.
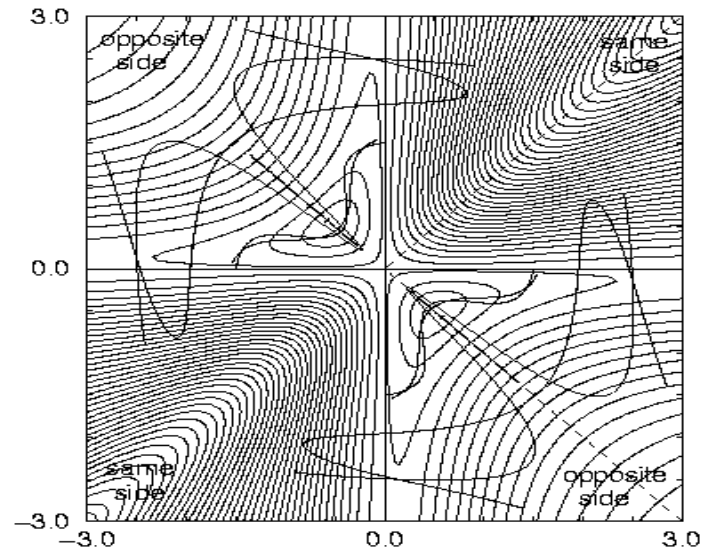
Figure 2: Potential energy level curves for pendulum configuration with smoothed parameter $\delta = 1$ and $R = 2$. Each axis represents one electron coordinate.The pendulum orbits born in $3^{-1/2}(\pm 1, \mp 1)$. The dashed lines shows the desymmetrized region.

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The Fig.2 shows the potential energy level curves for pendulum configuration. Each axis represents one electron coordinate. The potential energy level curves show two absolute minima of the energy, where all pendulum POs emerge. The diagonal line ($x = y$) is where the electronic repulsion takes place. The diagonal ($x = -y$) lines are the Wannier POs in Cartesian coordinates for $E = -2.48$au located in the *opposite side* labeled place. The pendulum fundamental POs in Cartesian coordinates for $E = -2.5979$au (near to minima), $-2.47, -2.45$ (energy bifurcation), -1.60 and -1.60 (two different orbits with similar energy) are shown in *opposite side* place for $E < -2.45$. The POs extend to *same side* for $E > -2.45$, i.e., after bifurcation. The energy of the POs increases with their size.

We calculated the stability exponent of the "fundamental" orbits of all axial and pendulum configurations. We also obtained the stability indexes of the Wannier orbit for $eZZe$, $ZeeZ$ and pendulum configurations. The stability angles and the Lyapunov exponents of the periodic orbits [2, 3] were obtained by the Monodromy method [22, 23].

Stability exponents

The He is scaled with energy, but H_2 with R parameter (internuclear distance) is not scaled with energy. It is necessary to calculate the stability index for all range of energy (E) parameter where each point can be scaled with R. (The parameters R and E can be exchanged in relation to scaling law.) The Monodromy matrix of He atom in 2-D has two trivial pairs of eigenvalues. However, H_2 molecule in 2-D has only one trivial pair of eigenvalues for axial configurations. The angular momentum is not a constant of the movement for H_2 molecule since the symmetry of that is less than of the He atom. The motion belonging to axial orbit for H_2 gives one trivial pair of eigenvalues of the monodromy matrix and other generally real ones (hyperbolic). The perpendicular motion of the 1-D orbit gives two non-trivial pairs of eigenvalues and the He atom gives one non-trivial pair of eigenvalues.

The Wannier orbits has infinity Lyapunov [5] for He atom. However, the Wannier orbit for axial and pendulum configurations have finite Lyapunov. The Wannier orbit for pendulum configuration coincides with Bohr (BH_2a) and Langmuir (LH_2a) orbits [11] for parabolic eccentricity ($e = 1$). The Wannier orbits for $ZeeZ$ and $eZZe$ configurations coincide with the 1-D projection of the BH_2b and LH_2b orbits [11]. The 1-D Wannier orbits can contain contribution of those orbits in higher dimension [12].

The effective potential of the pendulum Wannier orbit is discussed below. We can compare the H_2 system to the He atom. The symmetric potential function of the He is

$$V_{He}(z) = -7/(2z), \qquad (15)$$

where z is the module of the electronic position vector. The potential (15) is an assympthotical approximation for triple collision.

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The Wannier orbit potential of the pendulum configuration is

$$V_{H_2}(z) \approx V_{He}(y) + R^2/(2y^3). \qquad (16)$$

The potential (16) presents a minimum that stabilizes the system.

Now we discuss the stability indexes in order to initiate the classical studies of the hydrogen molecule. The stability index curves are shown in Figs.3a to 3h for all 1-D PO calculated for H_2 with $R = 2$a.u., all solid lines are the stability angles and the dashed lines are the Lyapunov exponents.

The stability indexes of the H_2 differ from He by an important symmetry property discussed ahead. The direct consequence is: the H_2 molecule has a bigger number of pairs of the non-trivial stability matrix eigenvalue [see Eq. (7)] than that for He. For example, the number of the non-trivial pairs of the eigenvalues or equivalently, stability indexes for axial configuration(s) of the He (H_2) with four dof's is two (three): one correspondent to the parallel dof to PO and one (two) perpendicular one(s). Following we discuss the stability indexes of the H_2.

The stability indexes of the Wannier and fundamental orbits of the $eZZe$ configuration are shown in Figs.3a and 3b, respectively for $-2.0 < E < -0.33$. The Fig.3a has two curves, the curves are the stability angle divided by 2π for perpendicular (stable) dof ($y-$axis). The curves are the same for $x-$axis since the system has azimuthal symmetry. The lowest curve describes a stable behavior until $E \approx -0.65$au, besides the behavior change to unstable and the curve becomes the Lyapunov divided by 2π. The Fig.3b has three curves, the lowest curve is the Lyapunov divided by 2π for parallel (unstable) dof of the PO. The other curves are the stability angle divided by 2π for perpendicular (stable) dof ($y-$axis). The lowest curve describes a stable behavior until $E \approx -0.4$au. Besides the behavior becomes unstable. The curves for $E < -2.0$ follow same behavior and the Lyapunov curves are multiplied by 10 for Figs.3a and 3b.

The eigenvalue of the stability matrix for axial dof for PO of the $ZeeZ$, $eZZe$ and $ZeZe$ configurations are real, i.e., they describe an unstable behavior similar to eZe of the He. The eigenvalues of the perpendicular dof are imaginary (elliptic) or real (hyperbolic) depending on the energy range. That behavior is different from He since the perpendicular dof is ever imaginary. The pendulum configuration shows similar behavior of the axial ones.

The stability indexes of the Wannier and fundamental orbits of the $ZeeZ$ configuration are shown in Figs.3c and 3.d, respectively for $-2.0 < E < -0.0$. The Fig.3c shows the Lyapunov and the stability angle are for perpendicular dof. The Fig.3d shows the Lyapunov curve for parallel dof as a lowest curve. The other Lyapunov and the stability angle curves are for perpendicular dof. These last stability indexes are components of a complex (loxodromic) eigenvalue. However, those indexes change to two imaginary eigenvalues (stability angles) for $E < -2.33$. The action and the period do not increase with energy for those POs since the electrons are limited by two singular potential for ZeeZ configuration. That behavior is distinct from any other 1-D PO.
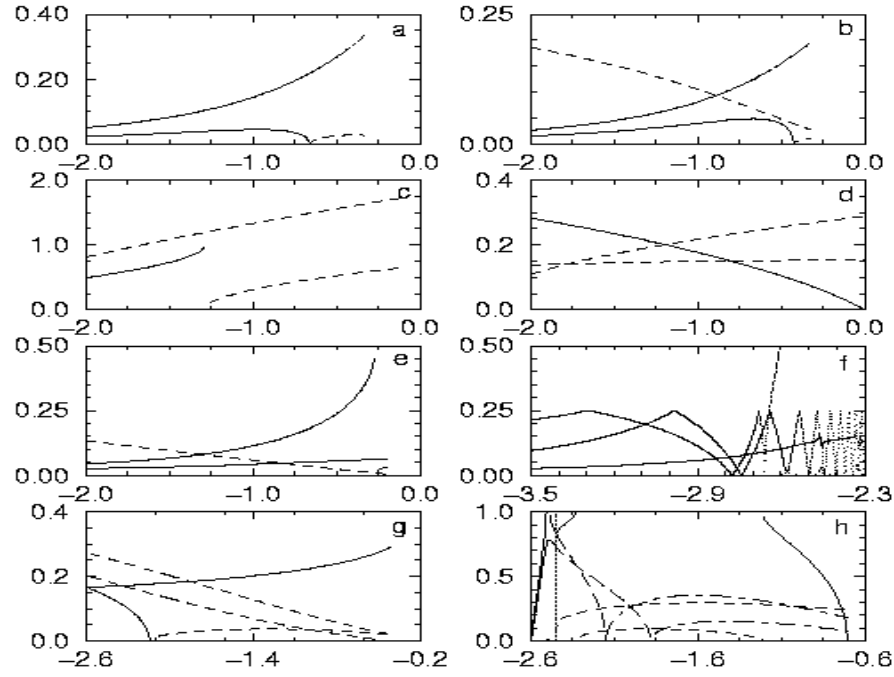
Figure 3: The stability index curves for 1-D POs with $R = 2$au as a function of electronic energy for $R = 2$: (a) Wannier-eZZe; (b) eZZe; (c) Wannier-ZeeZ; (d) ZeeZ; (e) ZZee; (f) ZeZe; (g) Wannier-pendulum, and (h) pendulum orbits (1) and (2). The continuous lines are the stability angles and the dashed ones are the Lyapunov exponents. The stability angles for second pendulum PO (2) are given by long-dashed curves and the Lyapunov exponents by dot-dashed curves for same PO in figure h. The Lyapunov curves are multiplied by 10 in figures a, b, e and h

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The stability indexes of the molecular FPC PO of the $ZZee$ configuration are shown in Fig.3e for $-2.0 < E < -0.2$. The intermediary curve is the stability angle for parallel dof. The highest curve is the stability angle for perpendicular dof and the lowest one is the Lyapunov for same perpendicular dof. The curves for $E < -2.0$ follow similar behavior. The Lyapunov curves are multiplied by 10.

The PO of the $ZZee$ configuration (molecular FPC) in 1-D is stable as FPA for He [5], but in 2-D the molecular FPC is unstable since the inner electron can not shield the farthest proton and the outer electron can be attracted by that proton unstabilizing the system. The stability index in axial direction shows stability for all range of energy, the perpendicular dof changes the stability depending on the energy range.

The stability indexes of the fundamental orbit of the $ZeZe$ configuration are shown in Fig.3f for $-3.5 < E < -2.3$. The curves are the stability angle for all dof with some oscillations between the stable and unstable behavior. That PO is totally stable for $E < -2.65$au, it is the only case since known of the non-ergodicity of H_2 system. All exponent indexes are represented by dotted lines in the Fig.3f. The stability angles are limited to 0.25, but the Lyapunov exponent is not. The highest curve belongs to the parallel dof for $E = -3.5$.

The stability indexes of Wannier orbit of the pendulum configuration are shown in Fig.3g for $-2.6 < E < -0.4$. That figure has four curves, two dashed curves are the Lyapunov for perpendicular dof in axial direction. The highest continuous curve is the stability angle for other perpendicular dof and the lowest one is the stability angle for $E < -2.17$ for increasing E is the Lyapunov for parallel dof.

The stability indexes of the two fundamental orbits of the pendulum configuration are shown in Fig.3h for $-2.6 < E < -0.7$. That figure has four curves, two curves for each PO. Similar to Wannier PO, the fundamental PO for pendulum configuration has four non-trivial stability matrix eigenvalues. However, the stability exponents (Lyapunov) for perpendicular dof in axial direction are not shown. The stability indexes are the same for the two PO with $E < -2.45$au. Those indexes become different for each PO when $E > -2.45$au. A bifurcation appears for $E \approx -2.45$au and emerge two orbits approximately with equal periods. The vertical dotted line in Fig.3h separates the energy regions "before" and "after" bifurcation (see discussions below). The four indexes oscillated between the stability angle and Lyapunov exponents. The stability angles for second PO are given by long-dashed curves and the Lyapunov exponents by dot-dashed curves. The Lyapunov curves for the two pendulum POs are multiplied by 10.

The two dofs perpendicular to the POs for 1-D pendulum configuration are not equivalent that is different from axial configuration and for 1-D He atom. The plane that contains 1-D pendulum POs and the perpendicular dof, non-parallel to internuclear axis, has rotational symmetry.

Some simple calculations can be performed in order to study the behavior of the pendulum configuration.

Pendulum configuration behavior

The absolute minimum of energy is obtained considering the electrostatic equilibrium for $y_1 = -y_2$ with energy $E = -3\sqrt{3}/R$ and $y_1 = R/(2\sqrt{3})$. Below of that energy is not classically permitted for pendulum configuration. The electrons remain fixed in the minimum. All orbits start of that minimum for pendulum configuration (see Fig.2).

The Hamiltonian of the pendulum configuration is very near to the He atom with smoothed potential [17]. The internuclear dof is always unstable, the He analogy is valid for perpendicular plane of the internuclear axis. The fundamental pendulum orbit is marginally stable (integrable) for $E = -3\sqrt{3}/R$ and stable for the range $-3\sqrt{3}/R < E < E_c$, where $E_c = -(2/R)(2 + (2^{2/3} - 1)^{3/2})$ is a critical energy. The orbit is similar to eZe configuration of the He for stable region, i.e., the electrons are in opposite side of the He with smoothed potential (internuclear axis). Note that the He orbit is stable because of the smooth parameter $(R/2)$. The fundamental PO connects the "eZe" (opposite side) configuration with "Zee" one (same side) for $E > -(2/R)(2 + (2^{2/3} - 1)^{3/2})$, in this energy the system becomes unstable for increasing energy.

The $E_c = -(2/R)(2 + (2^{2/3} - 1)^{3/2})$ is found considering the electrons remain stopped (kinetic energy is null) in, e.g., $y_1 = 0$ and $y_2 = -(R/2)(2^{2/3} - 1)^{-1/2}$, for increasing energy ($y_1 < 0$) the system connects the eZe and Zee smoothed configurations. FPC orbit is not possible for smoothed He with "Zee" configuration since "Zee" is ever connected to hyperbolic "eZe" configuration.

The Fig.3h shows the stability exponents for two pendulum orbits, which bifurcated in transition $eZe --- > eZe + Zee$ with $E = -2.45$ and $R = 2$ (see Fig.2).

Axial Wannier orbits

The axial Wannier orbits for $ZeeZ$ and $eZZe$ configurations present simultaneous binary collisions (SBC). When the two electrons collide simultaneously with the protons the regularization function Eq.(2) for two-electron system approaches from zero as square potential and the Hamiltonians Γ_{ZeeZ} and Γ_{eZZe} diverge. It is necessary to change the reguralization strategy. The treatment of the SBC is known [24]. However, we obtained the eigenvalues belonging to the perpendicular degree of freedom (dof) of the Wannier orbits for ZeeZ and eZZe configurations by an alternative simple way.

The principal argument is based on symmetry reductions:

1) The full Hamiltonian is reduced to 2 dof for an effective electron interacting with its image, i.e., $\chi_1 = -\chi_2$ and $\theta_2 = \pi - \theta_1$. The effective Hamiltonian is very easy to calculate and the stability exponents are: one trivial (energy conservation) and other non-trivial correspondent to perpendicular dof.

Following, the stability exponents are obtained with Hamiltonians with 4 dofs.

2) It was considered the coupling of the two H_2^+ systems, where the interaction term (R_{12}^{-1}) and the energy were multiplied by the factor $(f_1 + f_2)$ instead $(f_1 * f_2)$ [12], where f_i is the regularization function for electron i. The exact Hamiltonian is recovered in the limit of the symmetric stretch. The stability exponents are correct for perpendicular dof, but one eigenvalue for parallel dof is not correct.

The following approximations confirm those results.

3) The factor $(f_1 + f_2)$ was substituted by $(f_1 * f_2)^{1/2}$ and same eigenvalues for perpendicular displacement are obtained.

Those results are already confirmed with the last approximation:

4) The complete Hamiltonian in 4 dofs (without any approximations) [12] was considered. However, the neighborhoods of the Wannier orbits with dephased the collisions were the starting trajectories. The calculation with this quasi-orbit is very difficult since the neighborhoods are chosen very near to the Wannier orbit to avoid significant numerical deviation of the previous calculations. The same eigenvalues for perpendicular dof are obtained, but the non-trivial eigenvalue parallel to the internuclear axis can not be obtained satisfactorily, although it does not matter since the most important eigenvalues for semiclassical quantization are the perpendicular ones. A more elaborated calculation [24] is necessary to obtain all eigenvalues.

The instability related to the parallel dof of the internuclear axis (z-axis) is high in comparison to other axis for axial and pendulum configurations. Because of that the semiclassical quantum contribution of that dof is little. Therefore, the dynamic motion in the plane perpendicular to internuclear (bonding) axis is the most important in the semiclassical quantization (see above).

The eZe configuration is hyperbolic and the Zee one is near to integrable for He atom [5] and for H^- ion [26]. The H atom is integrable system. The H_2 molecule has a intermediary behavior between the H and He atoms, i.e., between the near integrable and hyperbolic behaviors. The correlation diagram among the configurations of the H_2 molecule with atoms is showed in Fig.4

Semiclassical studies

Single Quantization

We obtained some results of the single quantization of the 1-D orbits. We considered the following action $S(n, E; R) = 2\pi[n + \alpha/4 + (1/2) \sum_{i=1}^{N} \theta_i(E)/2\pi]$, where n is the principal quantum number, α is the Maslov indices ($\alpha = 4$ for all 1-D orbits considered), $\theta_i(E)$ is the stability angle and N is a integer number that depends on the orbit, the energy and the dof and R is a parameter. The axial configurations have degenerated (isotropic) perpendicular directions, i.e., the stability indexes are equal for the two direction perpendicular
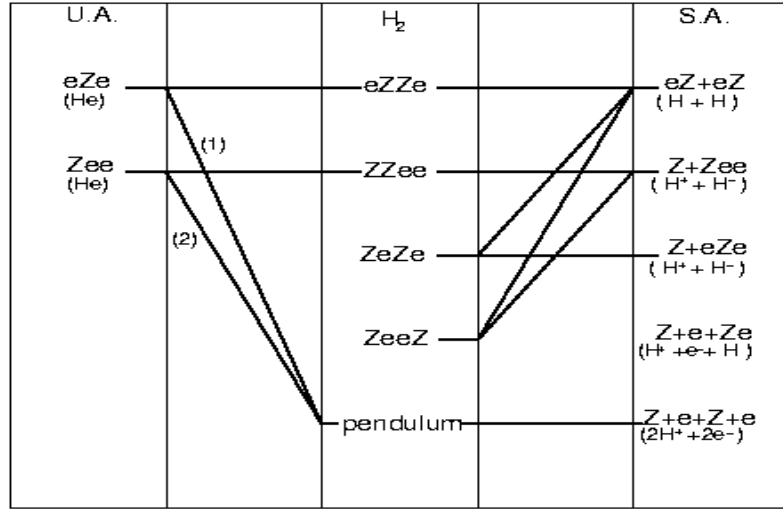
Figure 4: Correlation diagram among the configurations of the H_2 molecule with the H^+, H, H^- (separated atoms - SA), and He atoms (united atom - UA). The correlations labeled with (1) and (2) appear for $E > E_c$ for pendulum configuration and for $E < E_c$ only appears the correlation (1)

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to bonding distance. The all directions of the pendulum configuration are different.

Curves of single quantization for some 1-D orbits are shown in Fig.5. We used the scale law in order to obtain the total energy (with nuclear repulsion term) as a function of internuclear distance (R). The lower curve with circle is the ground state of the hydrogen molecule. The single quantization results are: the lines labeled with **w** are for Wannier orbits; the lines labeled with **p** are for pendulum orbits; the lines with **a1** are for $eZZe$ orbit and the lines with **a2** are for $ZeeZ$ orbit.

The single quantization does not work well to describe the hydrogen molecule for intermediary value of the bonding distance (R). Since the molecular quantum states studied are composed approximately by a linear combinations of the atomic quantum states or, in semiclassical words, by a combination of the POs of the atomic limits ($R \rightarrow 0$ and $R \rightarrow \infty$). The single quantization shows that all POs can contribute in a description of the quantum states. The $eZZe$ POs can be the most important ones as the asymmetric stretch PO of the eZe configuration of the He atom.

We show that the single quantization can not describe the first states of the H_2 system and a more elaborated theory can be used in order to account a better result. However, since the H_2 system is not a hyperbolic system as He atom, it is possible to find some stability island which are suitable for WKB quantization, e.g., for pendulum orbits around the absolute minimum of energy ($E = -3\sqrt{3}/R$, see Fig.2) and for $ZZee$ and $ZeZe$ orbits (see Figs3.e and 3.f). Those WKB quantization will be connected to particular subspectrum of the H_2 system.

Semiclassical Quantization

The density of levels was obtained from trace formula with few repetitions, i.e., fixing a maximum period (T_{max}). The T_{max} was considered as the period of the fundamental pendulum orbits (T_{pend}) since this period is longer than the others considered here. The orbits are summed several times depending on the ratio T_i/T_{pend}, where T_i is the period of the orbit considered. The ratio T_i/T_{pend} changes according to energy, since the system is not scaled to energy with R fixed. The number of the repetitions is $\text{Int}[T_i/T_{pend}]$, where $\text{Int}[X]$ is the entire part of the X.

We study the possibility to include the axial and pendulum orbits (6-dof) in the same trace formula. The axial orbits have five eigenvalue pairs different from one, the pendulum orbits have four eigenvalue pairs different from one. We considered four dof trace formula to describe simultaneously the quantization of the axial and pendulum orbits. We considered four perpendicular dofs to internuclear axis for pendulum orbits (two non-trivial different pairs of the eigenvalues) and for axial orbits (four non-trivial pairs of the eigenvalues where two pairs are distinct) in the trace formula. The two dof parallel to internuclear axis are related to unstable motions (exception to $ZZee$ PO)
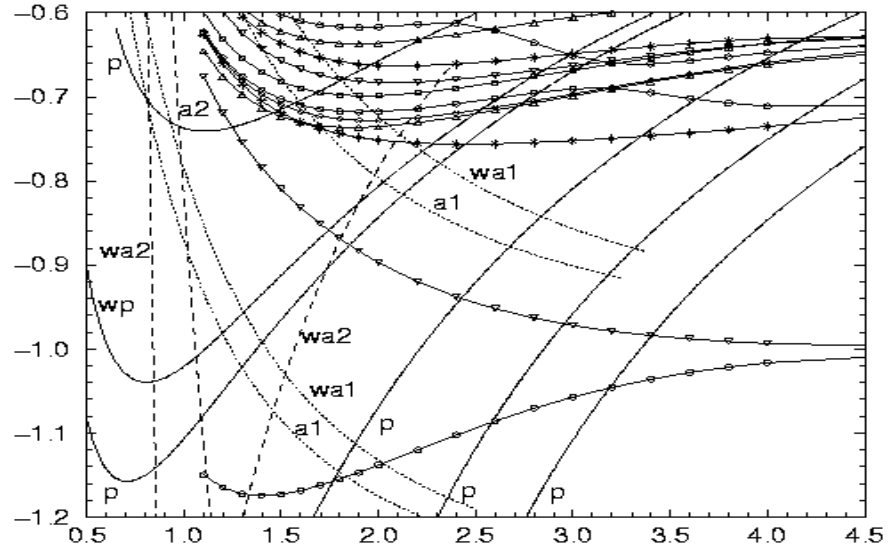
Figure 5: The total energy as a function of internuclear distance (R). The quantum states are labeled with symbols: $\circ - {}^1\Sigma_g^+$; $\bigtriangledown - {}^3\Sigma_u^-$; $* - {}^1\Sigma_u^-$; $\triangle - {}^3\Sigma_g^+$; $\diamond - {}^3\Pi_g$ and (square) ${}^1\Pi_g$. The single quantization results are: the solid line labeled with **wp** is for Wannier pendulum orbit; the solid lines labeled with **p** are for pendulum orbits; the dotted lines with **wa1** and **a1** are for $eZZe$ Wannier and fundamental orbits and the dashed lines with **wa2** and **a2** are for $ZeeZ$ Wannier and fundamental orbits, respectively

are not included in trace formula.

The related semiclassical density of states in four degrees of freedom for $R = 2$ is presented in Figs.6. In the abscissa of Figs.6 one will find $(-E_{el})^{-1/2}$ or the effective quantum number (N_{eff}) while the ordinate shows the density of levels $[d(E_{el})]$ in arbitrary unity given by a solid line. The vertical lines in these figures are the quantum eigenvalues (discussed below)and the dotted line is a non-normalized smoothed quantum spectrum. The quantum smoothed spectrum were resolved with the maximum orbital period (T_{pend}).The smoothed quantum spectrum is given by

$$d_Q(E) = (\Delta E \sqrt{2\pi})^{-1} \sum_n e^{-(E-E_n)^2/(2\Delta E^2)},$$

where E_n are the quantum eigenvalues and $\Delta E = \hbar/T_{pend} = 1/T_{pend}$. The smoothed quantum spectrum for all states is shown in Fig.6.

The spectra calculated by Gutzwiller formula, presented in Fig.6, are smoothed since they did not include many repetitions. The trace formula summed all primitive orbits, but in this calculation only the Wannier (SS) and the fundamental (AS) orbits (pendulum and $ZeeZ$ and $eZZe$ axial configurations) and the molecular FPC were included. The semiclassical calculations take into account a semi-quantitative agreement with quantum data for present degree of approximation.

The Fig.6a shows the density of levels for simple sum of the pendulum and axial orbits for $R = 2$. The Fig.6b shows the density of levels for pendulum orbits and the Fig.6c shows the density for axial orbits.

The study of the H_2 molecule is close to that for He atom. By analogy, we consider the Wannier PO (SS) and the fundamental PO (AS) as first POs of the a "symbolic dynamic", the SS PO is denoted by symbol $+$ and the AS PO is denoted by symbol $-$. The symbolic dynamic is applied to the hyperbolic systems, but the H_2 system is a mixed one and a symbolic dynamic can not describe the whole system. Some parts of the H_2 can be described as a hyperbolic system and other ones as near a integrable problem. All POs considered here show generally an unstable behavior. We do not make any geometric series expansion for trace formula and because of that, triplet states appear together with singlet states in the density of levels.

It is necessary to consider a large number of POs in order to obtain a semiclassical quantization with the trace formula and the zeta function. However, a incipient semiclassical quantization can be given only few POs. The trace formula and the zeta function were obtained for several configurations simultaneously, i.e., the axial ($ZeeZ$, $eZZe$ and $ZZee$) and pendulum configurations are convolutionated in the same trace formula and zeta function. Since the whole H_2 system in 3-D connects all configurations that convolution can be justified. For example, the Bohr and Langmuir's POs for H_2 [11] are connected to 1-D POs by eccentricity parameter. The Bohr and Langmuir's POs belong to middle plane (or to plane that contain the
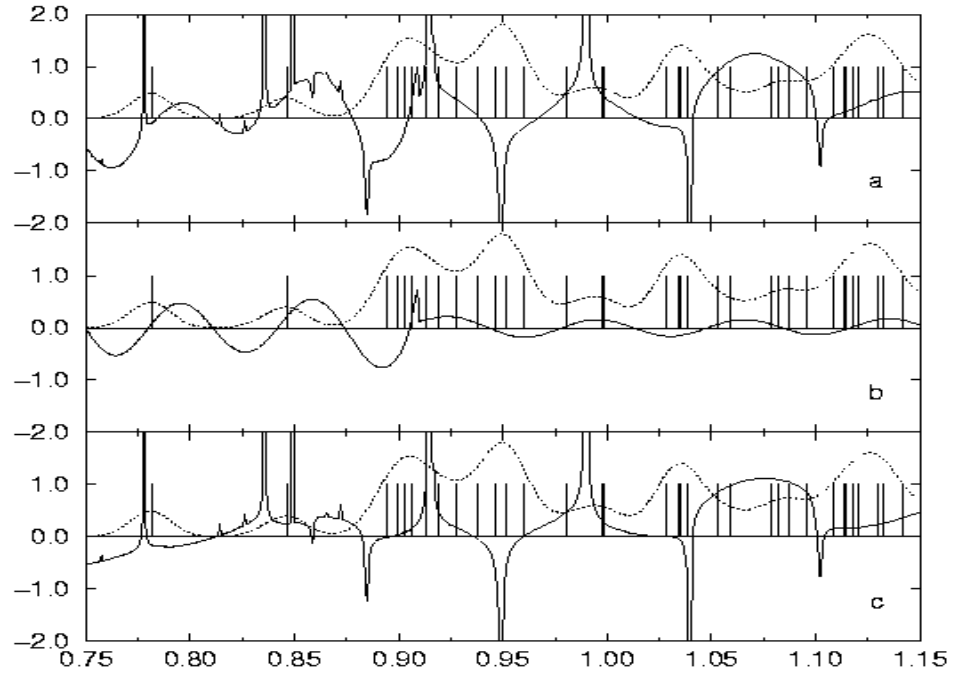
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Figure 6: Density of States in arbitrary unity as a function of effective quantum number $Rez = (-E_{el})^{-1/2}$ (solid line) with R=2 a.u., quantum spectrum (vertical lines) and smoothed quantum spectrum (dotted line). a) Density of States for the axial and the pendulum orbits; b) for the pendulum orbits only; c) for the axial ones only

internuclear axis) are reduced to pendulum (or axial) POs for high value of the eccentricity.

The H_2 molecule has several important configurations where each one contributed with infinity PO. Different from H_2, the He atom has only one configuration with infinity PO. If one can describe the H_2 molecule it is necessary to sum the PO for all configurations. There are mixes of those PO for finite R. The H_2 system is reduced to He atom for $R \rightarrow 0$ and to H^+ plus H^- [26] or to H for $R \rightarrow \infty$. We make a simple sum in trace formula, we do not consider any distinction among different topologies of the 1-D configurations.

We calculated the Density of States for ground-state (singlet) and the first triplet state with several geometries, i.e., with internuclear distance equal to 1.2, 1.6, 2.0 and 2.4au. These results are shown in Fig.7. The trace formula can be calculated for any geometry of the H_2 system. These results are shown in Fig.7 for ground and first triplet states with several internuclear distances. These results agree very well with quantum data for ground state for $R = 1.2$ and $R = 1.6$ and for other geometries and for first triplet state the agreement is reasonable. The resonance ($N_{eff} =$)0.836 in Fig.7c is not important since it appears due to the truncation process of the repetition and for slight change this peak vanishes. Those agreement is relevant if we compare with the single quantization results for ground and low excited states. The H_2 system can not be described semi-quantitatively by a single quantization procedure since all configurations contributed for those states.

We can compare the configurations of the H_2 among each other and with the configurations of the He atom. For example, the $eZZe$ configuration can describe the eZe one of the He for $R \rightarrow 0$. The eZe configuration is important to describe the atomic bounded states, but the ground state and other excited states of the bounded H_2 system need more than that. For example, the ground state of H_2 needs a bounded state between two hydrogen atoms that it is not present in He system (the alpha particle is bounded!), the H_2 is considered in adiabatic approximation. Perhaps, the $ZeeZ$ and pendular configurations play the role of an essential task to describe the ground-state.

That aspect becomes more complex the H_2 system than He and, in addition, the lost of the spherical symmetry for H_2 system divides the importance between the $ZeeZ$ and pendular configurations which does not exist in He atom.

The Fig.4 shows the correlation among the configurations for the united atom limit and separated atoms limit with molecular configurations. All axial configurations are also correlated to the $(Z + e + Ze)$ and $(Z + e + Z + e)$ separated atoms limit. An important goal can be obtained the complete correlation between the quantum states of the atomic limits with those of the molecular configurations. For example, the separated atom limit of the ground-state and first triplet state are integrate systems, i.e., two hydrogen atom in ground-state described by wavefunctions Ψ_1 and Ψ_2. The simple sum (linear combination of the atomic orbitals) of the wavefunction gives the ground-state ($\Psi_{GS} = \Psi_1 + \Psi_2$) and first triplet state ($\Psi_{FTS} = \Psi_1 - \Psi_2$). Those
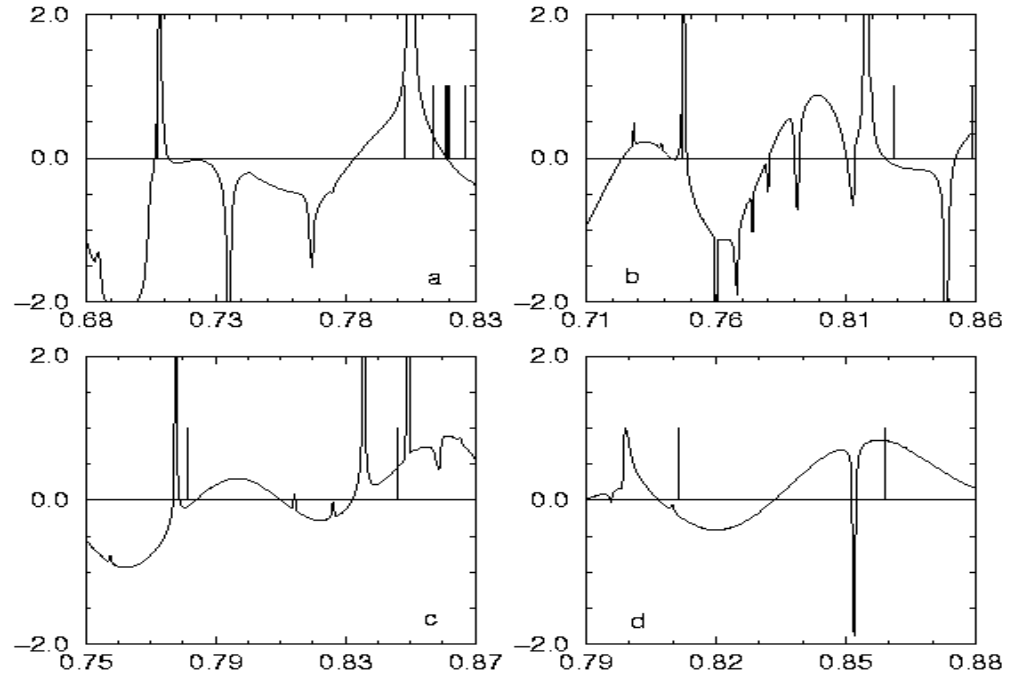
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Figure 7: Density of States in arbitrary unity for the axial and the pendulum orbits as a function of Rez (solid line) and quantum spectrum (vertical lines). a) R=1.2au; b) R=1.6; c) R=2.0 and d) R=2.4
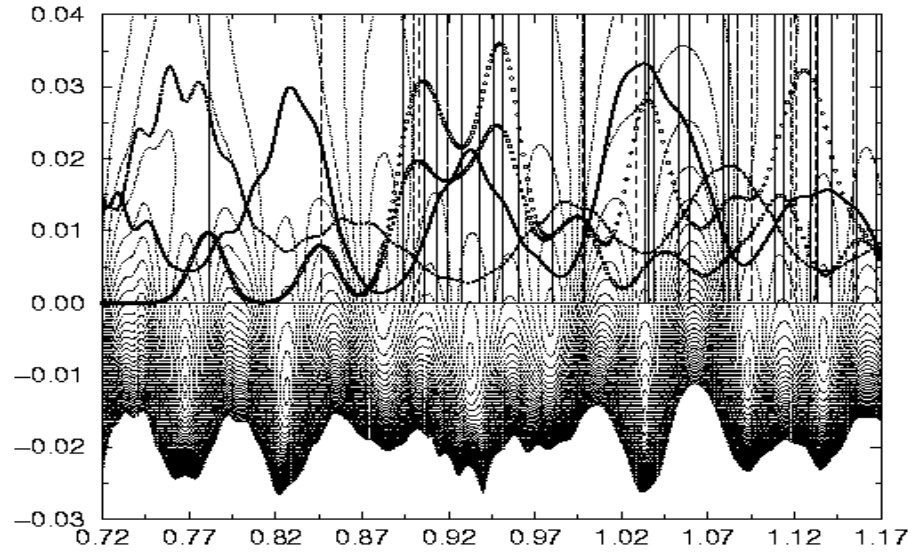
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Figure 8: Zeta function level curves for all POs as a function of the real (abscissa) and imaginary (ordinate) part of the effective quantum number-z (dotted lines) with R=2 a.u.; symmetric zeta function (ζ_+^{-1}) square module in arbitrary unity as a function of Rez (solid line); antisymmetric zeta function (ζ_-^{-1}) (dotted line); quantum spectrum for (vertical lines) singlet states (solid lines) and triplet states (dashed lines); smoothed quantum spectrum for all states (circle) and without Π and Δ states (square)
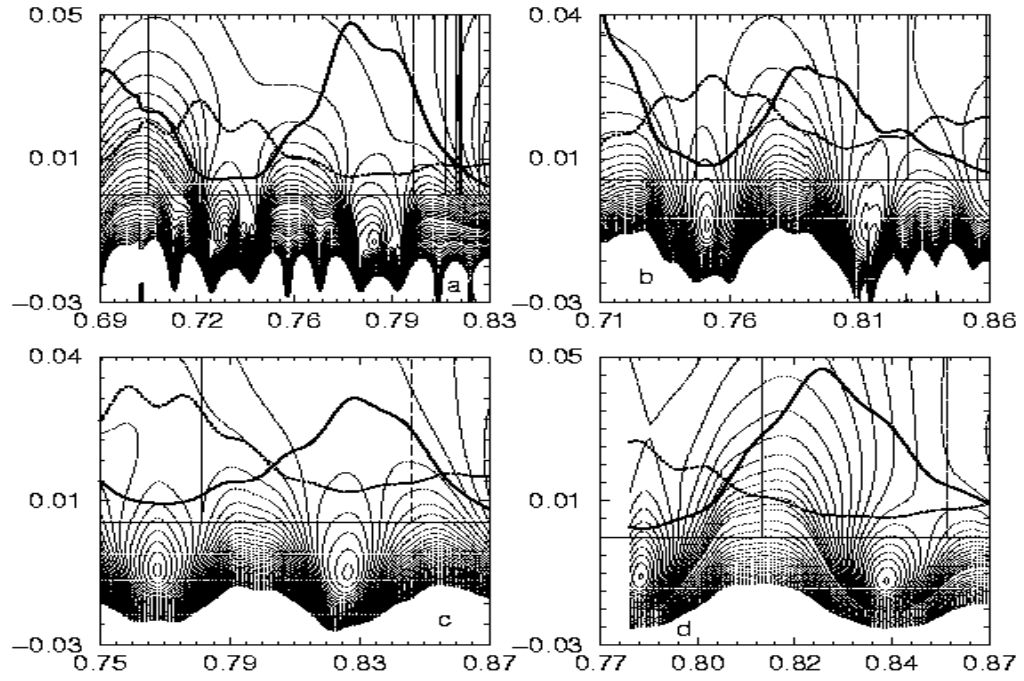
Figure 9: Zeta function level curves for all POs as a function of the real (abscissa) and imaginary (ordinate) part of the effective quantum number-z (tinny dotted lines); symmetric zeta function (ζ_+^{-1}) square module in arbitrary unity as a function of $Re z$ (solid line); antisymmetric zeta function (ζ_-^{-1}) (dotted line) and quantum spectrum (vertical lines: singlet states - solid lines, triplet states - dashed lines). a) R=1.2au; b) R=1.6; c) R=2.0 and d) R=2.4

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states coalesce to He states, i.e., for respective ground-state and the first triplet state of the He. That naïve description must be improved considering the correlation motion that is implicit in the POs, which are absent in the simple sum of the wavefunction shown above.

The agreement between the quantum spectrum and the density levels (Fig.6) is weak for whole excited states since was considered few POs. It is necessary to consider more POs with bigger period and also the stability islands. However, the ground-state and the first triplet state can be described better with these few POs.

The ground-state for low values of the internuclear distance ($R = 1.2$) is described mainly by $ZZee$ PO. That PO describes a repulsive behavior between the nuclei (the nuclear repulsion dominates) that causes the expansion of the molecule to equilibrium geometry ($R = 1.4$). The $ZeeZ$ POs dominate for increases values of $R(= 1.4 - 2.0)$, for bigger value of $R(= 2.4)$ the pendulum orbits increase their contributions. The electron attraction of the nuclei dominates for $R > 1.4$ maintaining the molecular binding.

The electrons are inside of the molecule for $R \geq 1.4$, i.e., with high contribution of the $ZeeZ$ POs, which describe the bonded state. The first triplet state is described mainly by $eZZe$ POs and few contribution of the repetitions of the $ZZee$ PO for any geometry ($1.2 \leq R \leq 2.4$). The electrons of the $eZZe$ POs are outside of the molecule that characterizes a non-bonded molecular state.

An important feature of the trace formula is: all contributions for ground state resonance are obtained by repetitions of the POs, i.e., successive excitations of the primitive PO. However, no important repetitions are made for $eZZe$ PO to describe the first triplet state.

The zeta function gives the $eZZe$ configurations as the most important to describe the (smoothed) quantum spectrum. The basic electronic structure can be described by $eZZe$ configuration as eZe configuration for He atom. However, the $eZZe$ configuration fails to describe the bonding state and other configurations must be added (see discussion above).

The zeta functions are shown in Fig.8. The zeta function level curves in complex plane for all POs with R=2 a.u. is shown in Fig.8. That zeta function is obtained from the sum of the zeta functions for each configuration. The symmetric (ζ_+^{-1}) and antisymmetric (ζ_-^{-1}) zeta functions square module in Fig.8 are given by product of the respective zeta functions for each configuration. The quantum spectrum (vertical lines: singlet states - solid lines, triplet states - dashed lines), the smoothed quantum spectrum for all states (circle) and without Π and Δ states (square) are also disposal in Fig.8. The ζ_+^{-1} gives the singlet resonances and ζ_-^{-1} gives the triplet ones. All resonances (minimum) obtained by zeta functions are correlated with peaks of the smoothed quantum spectrum.

The results for trace formula and zeta function for $R = 2.0$ are summarized in Table.I.

TABLE I. Effective quantum number for quantum (eigenvalues) and semi-classical (resonances) calculations with $R = 2.0$: SQS - smoothed quan-

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tum spectrum; SQS^* - smoothed quantum spectrum without Π and Δ states; $d(E)$ - trace formula; ζ^{-1} - resonances for ζ_+^{-1} and ζ_-^{-1}; $\zeta^{-1*} = \zeta_{ZeeZ}^{-1} + \zeta_{eZZe}^{-1} + \zeta_{ZZee}^{-1} + \zeta_{pendulum}^{-1}$

SQS	SQS^*	$d(E)$	ζ^{-1}	ζ^{-1*}
0.781	0.781	0.777	0.767	0.768
0.846	0.846	0.849	0.824	0.827
0.904	0.902	$--$	0.879	0.882
0.949	0.948	$--$	0.932	0.932
0.994	0.994	$--$	0.986	0.979
1.035	1.045	$--$	1.035	1.034
1.085	1.112	$--$	1.090	1.094
1.125	1.159	$--$	1.137	1.137

The zeta functions were calculated for several geometries and these results are shown in Fig.9. The resonances of the trace formula and the zeta function for ground state are summarized in Table.II and for first triplet state in Table.III.

TABLE II. Effective quantum number (N_{eff}) for ground state resonances for several geometries. The numbers in bracket are the total energy ($E_t = 1/R - 1/N_{eff}^2$)

R	$Quantum$	$d(E)$	ζ^{-1}
1.2	0.7074(-1.1650)	0.708(2)(-1.1605)	0.731(-1.038)
1.4	0.7277(-1.1741)	$-------$	0.742(-1.102)
1.6	0.7467(-1.1685)	0.747(0)(-1.1671)	0.752(-1.143)
2.0	0.7813(-1.1382)	0.777(3)(-1.1551)	0.769(-1.191)
2.4	0.8114(-1.1022)	0.798(8)(-1.1505)	0.780(-1.227)

TABLE III. Effective quantum number (N_{eff}) for first triplet state resonances for several geometries. The numbers in bracket are the total energy ($E_t = 1/R - 1/N_{eff}^2$)

R	$Quantum$	$d(E)$	ζ^{-1}
1.2	0.8026(-0.7191)	0.805(1)(-0.7094)	0.779(-0.815)
1.4	0.8169(-0.7842)	$-------$	0.794(-0.872)
1.6	0.8285(-0.8319)	0.818(1)(-0.8691)	0.804(-0.922)
2.0	0.8460(-0.8972)	0.849(1)(-0.8870)	0.827(-0.962)
2.4	0.8592(-0.9379)	0.857(3)(-0.9439)	0.843(-0.990)

The ground state shows a minimum in total energy for $R = 1.4$. The trace formula gives same feature, in despite of the calculation problem for $R = 1.4$ (see discussion above). The zeta function does not give the minimum and the state has a repulsive behavior as WKB calculations. The repulsive behavior of the first triplet state is obtained for all semiclassical calculations. The calculation with trace formula for $R = 1.4$ gives a different result. The effective quantum number for resonances of the ground state is $0.724(E_t = -1.195)$ and for first triplet state is $0.819(E_t = -0.775)$ in absence of the $ZZee$ and pendular POs. If those POs are included on the trace formula the resonances are destroyed for the two states.

How the $eZZe$ configuration dominates the results of the zeta function then the resonances are near to those of the WKB results for that $eZZe$ POs. The 1-D configurations are not linked to each other, only in 2-D and 3-D, and the convolution is critical to maintain the balance among the configurations. For example, if we change the contribution of the $eZZe$ configuration for half, the resonances of the ground and first triplet states shift to similar results of the trace formula. The pendulum, $ZZee$ and $ZeeZ$ configurations contribute to describe better the values of the semiclassical resonances for ground-state, giving the minimum (bounded state), and first triplet state. The trace formula indicates that the ground state is described mainly by successive excitations of some POs. It indicates that zeta function can need POs with large period to reproduce the resonances with same accuracy of the trace formula for ground state and first triplet one.

The semiclassical quantization of the H_2 molecule is remarkable complex. However, some important features can be obtained. The results of the trace formula and zeta function are complementary for few POs. The trace formula gives some sharp results, but appears frequently spurious resonances and complicated profile. The zeta function is better behaviored than trace formula, but some difficulties appear, e.g., when several configurations are considered. A better result is managed if two semiclassical methods are considered complementarity.

The semiclassical quantization considered in these studies was reduced to the perpendicular plane to the internuclear axis. Some considerations allow that reduction, the parallel motion to chemical bond is unstable and the perpendicular is stable or weakly unstable depending on the energy. That reduction can be better understood when the chemical bonding will be discussed. The main plane to describe the chemical bonding is the perpendicular one, but for non-bonding state perhaps the parallel plane can be important.

Quantum studies

The Schrödinger equation for H_2 molecule was calculated using the MELD program [27]. This program uses as initial guess a linear combination of the Cartesian Gaussian atomic bases. These atomic bases were constituted by $9s$,

$6p$, $4d$, $3f$, and $2g$ atomic function, where s, p, d, f, and g represent the usual notation of the hydrogen atom solution. The Cartesian Gaussian has the angular part described by a polynomial, e.g., for s function the polynomial is degree zero, for p is degree one, etc. The electronic structure was described at the full configuration-interaction level and having the Hartree-Fock configuration as the zero-order function. The lowest eigenvalues and eigenvectors were obtained of the configuration-interaction matrix for all symmetries for the D_{2h} point group and for singlet and triplet multiplicity. The calculations were performed in D_{2h} subgroup of the $D_{\infty h}$, because of the limitation of the program.

The quantum eigenvalues are given in Table.IV in order to compare the accuracy of the quantum and semiclassical calculations. The complete spectra of the singlet and triplet states are shown in Fig.10.

TABLE IV. Electronic energy for several states of the H_2 for different symmetries and geometries.

States	$R = 1.2$	$R = 1.4$	$R = 1.6$	$R = 2.0$	$R = 2.4$
$^1\Sigma_g^+$	-1.99807482	-1.88858658	-1.79342268	-1.63799147	-1.51896199
$^3\Sigma_u^-$	-1.55233372	-1.49839961	-1.45669112	-1.39704906	-1.35456212
$^1\Sigma_u^-$	-1.49369920	-1.41915299	-1.35496600	-1.25143196	-1.17284326
$^3\Sigma_g^+$	-1.50929781	-1.42723452	-1.35522921	-1.23551307	-1.14076781
$^3\Pi_u$	-1.48957702	-1.41139779	-1.34262235	-1.22772023	-1.13605465
$^1\Sigma_g^+$	-1.48676404	-1.40583131	-1.33492395	-1.21739177	-1.12506771
$^1\Pi_g$	-1.46419102	-1.38464740	-1.31480857	-1.19862781	-1.10669065
$^3\Sigma_u^-$	-1.43183076	-1.35736416	-1.29197876	-1.18282088	-1.09598014
$^1\Sigma_u^-$	-1.41374173	-1.33760497	-1.27141851	-1.16262421	-1.07773494
$^3\Sigma_g^+$	-1.40640301	-1.32554820	-1.25448492	-1.13605979	-1.04249061
$^1\Sigma_g^+$	-1.38661492	-1.30571704	-1.23474544	-1.11695144	-1.02912903

The quantum calculation performed considers that all states are discrete, which represent an important limitation to the calculation. Several quantum methods can be applied to calculate the H_2 system, see subsection Quantum Methods.

The difficulties of the semiclassical calculation of the H_2 molecule can be better understood with Fig.10. The numerous avoid-crossings are present for excited states. Those avoid-crossings interchange the electronic configurations among the states. If we disposal a significant numbers of the POs it will be possible to describe those complex spectra.

Correlation between the classical orbit and the shape of the probability density of the molecular orbitals can also be managed [12]. The appearance
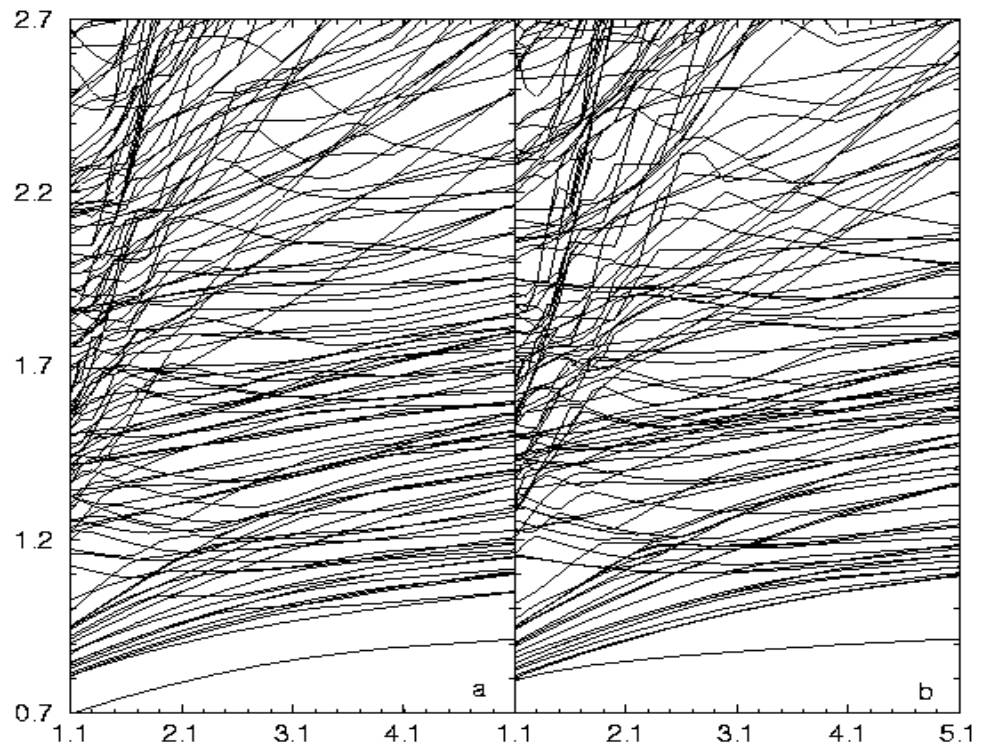
Figure 10: Effective quantum number ($N_{eff} = (-E_{el})^{-1/2}$) as a function of internuclear distance (R). a) singlet states; b) triplet states

of scars in the wavefunction can help to find specific POs. Of course, a systematic search of the POs is necessary for complete knowledge of the H_2 system.

We can also use some chemical knowledge to find some classical track in the multidimensional quantum world. Those knowledge can be the electronic distribution around the chemical bonding; electroafinity, i.e., localization of the electron around some preferential atoms; adiabatization coordinates (repulsion and attraction coordinates), chemical bonding dynamics (rate between kinetic and potential energies), etc. One can select some periodic orbits considering the molecular orbital shape of the states, e.g., σ states with Bohr orbits and π states with Langmuir orbits [12]; covalent states with $ZeeZ$ and pendulum orbits; repulsive states with $eZZe$; ionic states with $ZZee$ orbits; the profile of *scars*; etc.

The Chemical Bonding

Ruedenberg [13] showed that the chemical bond is formed by decreasing of kinetic energy in the chemical bond direction. That aspect can be better understood with classical and semiclassical physics. It is possible to infer that the perpendicular plane to the axial direction is the most important region to describe the chemical bonding since the depression of the kinetic energy provokes the accumulation of electrons around the perpendicular plane of chemical bond axis.

H_2 has basic ingredients to study the chemical bond, i.e., a pair of electrons. Perhaps, there are connections between the Rudenberg's theory and the classical mechanics of the POs.

It is possible to verify the correlation between the stability of the PO of the H_2 and the chemical bonding formation. It is known the origin of the bonding energy of the H_2 molecule is a consequence of the kinetic energy depression that happens with accumulation of the electronic charge in the internuclear region [13, 30]. It is possible to anticipate some manifestations of chemical bonding properties with 1-D orbits. The instability of the 1-D PO in the internuclear direction indicates that the motion of the electrons in that direction can not be important in the formation of the chemical bonding. Perpendicular motion to internuclear axis, that is a stable motion or weakly unstable one, can be important to formation of the chemical bonding since the electrons can orbit the nuclei in a plane perpendicular to internuclear axis. Therefore, Bohr's, Lewis', and other equivalent theories of the electron pair localization [8] can have a simple interpretation with a deep meaning in the description of the chemical bonding.

The H_2 molecule has some return points near to nuclei (centrifugal barrier) and near to average middle point of the internuclear axis (electron-electron repulsion). The average kinetic energy near to nuclei is high and near to middle point is low. The electronic charge can accumulate dynamically near to middle point because of the slow motion and consequently the electron permanence is high in average. The permanence time depends on

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the motion, on the PO and on the state (bonding or not).

We studied the behavior of the kinetic energy of the $ZeeZ$ and pendulum fundamental POs and verify that there are several regions of the electron accumulation.

A simple connection between the Bohr orbit of the H_2 and Ruedenberg's theory of the origin of the binding energy for H_2 was found [30]. That connection considers the behavior of the kinetic energy and the virial theorem for some variations over the Bohr orbit.

Shortly, Ruedenberg's work [13, 32] shows that the chemical bond formation is consequence of the depression of the kinetic energy along of the internuclear axis. The module of the total $|E_t|$, potential $|E_p|$ and kinetic $|E_k|$ energies of the molecule are bigger than those of the separated atoms with $|E_t| = |E_k| = |E_p|/2$ (virial rate). The molecule can be seen as a box with dimension along of the internuclear axis (ΔX_2) bigger than the atom (ΔX_1) and the dimension perpendicular to the internuclear axis (ΔX_2^p) smaller than the atom (ΔX_1^p). That is, $\Delta X_1 < \Delta X_2 \Rightarrow \Delta P_1 > \Delta P_2$ and $\Delta X_1^p > \Delta X_2^p \Rightarrow \Delta P_1^p < \Delta P_2^p$. How $\Delta P_1 > \Delta P_2$, it is more probable to obtain a smaller kinetic energy in the parallel direction of the chemical bond of the molecule than of the atom; conversely for perpendicular direction. It is possible to show that the smaller value of the kinetic energy causes the depression in it around the middle plane and the electrons can accumulate between the nuclei. The electron accumulation and the stable motion in the perpendicular direction of the internuclear axis are the classical ingredients of the chemical bond.

Now, we need to obtain the principal POs that describe the ground state in order to study the formation of the chemical bond.

Our semiclassical studies give us that the $eZZe$ POs contribute to describe as a quasi-classical interaction (each electron is described by an independent electronic density) [32] of the two hydrogen atom to constitute the ground state of the molecule. That $eZZe$ configuration is enough to describe the united atom limit, i.e., He atom, but it is not for the chemical bond since the $eZZe$ POs give a non-bonding behavior.

The chemical bond is obtained by quantum interference of the atomic wavefunction ($\Psi_{GS} = \Psi_1 + \Psi_2$). That interference can be mimicked by the semiclassical quantization since it describes the minimum of the energy for ground state. Bohr quantization for H_2 gave the first calculation of the chemical bond [7, 8]. The connection of that (semiclassical single) quantization with Ruedenberg's theory was made [30]. However, Bohr quantization gave a qualitative result since the H_2 molecule can not be reduced to one simple PO. The H_2 molecule is a complex system, several POs must participate of a (semi)quantitative description.

The ground state of the H_2 is described basically by $eZZe$, $ZeeZ$ and pendulum POs. The $eZZe$ POs are very important since gives the principal interaction of the charges. The $ZeeZ$ and pendulum POs give the fine adjust in order to manage the chemical bond.

The $ZeeZ$ and pendulum POs were studied classically and they showed

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similar depression of the kinetic energy obtained with quantum mechanics [13]. Probably the POs which show a depression of the kinetic energy between the nuclei are important to describe a chemical bond. The minima of the potential energy for excited states caused by avoid-crossings (see Fig.10) can be different.

The starting point of the studies of the semiclassical quantization of the H_2 [11, 12] was the Bohr orbit for H_2 [7]. Bohr extended that model (orbit) to describe other molecules. That Bohr's idea was applied to several molecules [31] and potentially the semiclassical quantization can also be applied to those systems.

In summary, some 1-D POs show an accumulation of the electronic charge between the nuclei. The stability of the perpendicular dof of the internuclear axis shows a stable or weakly unstable motion. Therefore, the electrons can accumulate preferencially in the chemical bond field.

4   Conclusions

Several studies for the H_2 molecule were shown in this paper. These studies are important for a future understanding of the connection between classical and quantum worlds ("the Correspondence Principle") to chaotic problems and of the chemical bond since the H_2 system contains the basic ingredients (two-electron binding) for that.

Some Bohr-Sommerfeld quantizations have been performed, but those calculations were not enough to describe the H_2 system. Unfortunately, that (chaotic) system is not integrable and a global semiclassical quantization must be made. Gutzwiller formula and the zeta function were calculated for 1-D periodic orbits.

We can enumerate some perspectives of this work:

a) Obtain the relation between chemical bond and classical properties of periodic orbits: the POs which show a depression of the kinetic energy between the nuclei are important to describe a chemical bond;

b) Verify the Correspondence Principle for H_2, mainly in chaotic regime;

c) Use the classical and semiclassical mechanics to help the quantum mechanic interpretation;

d) Use the semiclassical method in order to give the correct results for high excited state in substitution of the quantum numerical calculation.

Mainly, this work describes a theoretical study of the non-linear dynamics of the hydrogen molecule. We show a first step to understand "the Correspondence Principle" in the chemical world that treats essentially nonlinear systems.

Acknowledgments

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