Classical and Semiclassical Studies of the Hydrogen Molecule
Thomas Sauvaget

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Classical and Semiclassical Studies of the Hydrogen Molecule

by Thomas Sauvaget

Thesis submitted to the University of Nottingham for the degree of Doctor of Philosophy
August 2006
Abstract

The aim of this work is to account for the global shape of some Born-Oppenheimer (BO) curves of the hydrogen molecule, in particular the ground state, at the semi-classical level.

In the first two chapters we review semiclassical cycle expansion techniques which proved useful in the study of the resonant spectrum of the helium atom, another few-body Coulomb system.

Then we first study in detail the geometry of the classical phase space of the hydrogen molecule. This being done, we analyze the dynamics in three of its subspaces and compute various quantities related to their shortest periodic orbits.

We then turn to semiclassical studies. One of these subspaces is discarded on instability grounds, while the other two are used as a basis for the construction of semiclassical approximations to the ground state BO curve. We find that each of the two subspaces allow to describe one of the two asymptotic trends of the BO curve.

This allows to provide a classical underpinning to bond formation in $H_2$. 
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My Parents

&

Mr Douglas Whitelaw FRCSEd FRCS, General Surgeon; Mrs Kontouli, Anesthesist; the theatre crew; the nurses of the High Dependency Unit; the nurses and staff of the Cobham clinic; the physios; and the ambulance crew of the Luton and Dunstable Hospital.

“[… the status of the continuum hypothesis convinced me that Platonist views of mathematical ontology and truth could not be correct [...]”

Thimothy W. Gowers
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Chapter 1

Introduction

Since the advent of quantum mechanics (QM) at the beginning of the XXth century, it has been possible to predict and organize a lot of phenomena involving atoms and molecules (see e.g. [BJ03, BC03, SO96]).

There are nevertheless various aspects requiring calculations which are very intensive and time-consuming, and sometimes in fact intractable. In those cases it is thus useful to develop approximations of QM which, while being possibly less accurate, still provide enough information to obtain similar predictions and understanding but at a much reduced cost (see §1.1).

An important related topic is to understand how quantum mechanics leads to behaviours well described by classical mechanics, and more generally to study how the formalisms of these two theories are related (see §1.2).

The aim of this thesis is to address a particular problem which lies at the intersection of these two thematics, namely to describe the structure of some electronic states of the hydrogen molecule by using the so-called semiclassical approximation of QM, an approximation built from classical mechanical quantities (see §1.3).
1.1 Approximations in quantum mechanics

The aim of this chapter is to describe in some detail what is called the *semiclassical limit* of quantum mechanics, and the kind of approximation it allows in various situations. To put it into proper context we first review other exact and approximate methods used over the past decades in quantum mechanics, stressing their domain of applicability.

1.1.1 Basic setup

Suppose we are studying a simple quantum system, i.e. one which can be modelled as taking place in a finite-dimensional flat configuration space \( \mathbb{R}^N \), and which is also time-independent and of the form ‘kinetic plus potential’. \( N \) is the number of *degrees of freedom (DOF)*. The main example is that of a general \( n \)-body system\(^1\) in constant external fields. We suppose moreover that relativistic and spin effects can be neglected.

We are therefore led to study the usual *eigenvalue problem* for the corresponding (linear) Schrödinger operator \( \hat{H} \):

\[
\hat{H}\psi_k := \sum_{i=1}^{N} -\frac{\hbar^2}{2m_i} \Delta_i \psi_k + V \psi_k = E_k \psi_k
\]  

where \( E_k \) is real and the wavefunction \( \psi_k \in L^2(\mathbb{R}^N) \) is decaying to 0 at infinity.

Of course in all the following we will assume that nothing pathological happens, but without making very precise statements. For example we are assuming that \( V \) is such that \( \hat{H} \) is *self-adjoint on some domain* – and has thus indeed a real spectrum – and is bounded from below. This is for example the case if \( V \) is a *Kato potential* [HS00], i.e. if for any positive real number \( \alpha \) and all smooth \( \psi \) which decays to 0 at infinity we can find a number \( \beta = \beta(\alpha) \) such that \( \|V\psi\| \leq \) 

\(^1\)Here \( n \) is the number of bodies, so for example in the case of bodies moving in 3–dimensional space we would have \( N = 3n \).
\[ \alpha \| T \psi \| + \beta \| \psi \|, \] where \( T \) is the kinetic energy operator. In particular, \( n \)-body Coulomb potentials, on which we will focus in chapter 2, are Kato potentials.

Other quantities of interest after the discrete (real) eigenvalues are discrete (complex) resonances \( F_m = E_m - i\Gamma_m \in \mathbb{C} \). They exist when some of the coordinates of our configuration space can go to infinity (scattering process). There are various possible definitions depending on the form of \( V \) (e.g., whether it is long-range or short-range [Zwo99]), but roughly speaking resonances are isolated complex poles of some meromorphic continuation of the resolvent \((\hat{H} - s \hat{I})^{-1}\), the real poles being the eigenvalues (the parameter \( s \) being real). In the time-dependent Schrödinger equation, a time-dependent damping factor thus comes in and the decay rate of such states is given by the imaginary part \( \Gamma_m \) of the resonance.

Let us see now how to actually compute at least some eigenvalues and resonances of our \( N \)-dimensional Hamiltonian, possibly together with the eigenfunctions.

### 1.1.2 Exact solutions

The first idea coming to mind is of course to look for exact solutions, but we must be slightly more precise. Indeed we could ask, from more general to more specific, for

(a) exact but not necessarily explicit solutions;

(b) explicit solutions given by (convergent) series;

(c) explicit solutions given by a single non-elementary function;

(d) explicit solutions given by an elementary function. \(^2\)

The literature is a bit confusing on this topic since there are authors who reserve the usage of the word exactly-solvable for either of those cases.

\(^2\)i.e. not involving special functions. Recall that a theorem by Liouville, generalized by Ostrowski and later Rosenlich [Ros72], says that not all elementary functions have elementary antiderivatives, for example \( F := \int \frac{\sin(t)}{t} \) is not an elementary function.
Chapter 1: Introduction

Case (a) covers for example the situation where (say) the first $m$ eigenvalues (or all of them if the spectrum is finite) are recast into being unknown solutions of a nonlinear system of equations which is itself known explicitly. This is the case in the work of Voros [Vor05] on the 1D polynomial Schrödinger equation of any degree (where in fact in this case the full infinite spectrum is characterized). In many other areas of physics where one studies Hamiltonians not of the form (1.1), for example second-quantized operators in nuclear or condensed matter physics [DPS04], one also calls these problems exactly-solvable in such a situation.

On top of that, either our Schrödinger PDE is separable into a set $N$ uncoupled ODEs by a suitable choice of coordinates or it is not. In both cases one then may, or may not, find the spectrum and eigenfunctions explicitly. Of course this is much simpler in the separable case, where examples have been known for a long time in all four situations (a-d).

In the 1D case, it has recently been shown [BG03] that several widely used model potentials including:

\[
V_{HO}(x) := \frac{\omega^2 x^2}{2} \quad \text{(harmonic oscillator potential)} \quad (1.2)
\]
\[
V_M(x) := B^2 e^{-2ax} - B(2A + \alpha)e^{-ax} \quad \text{(Morse potential)} \quad (1.3)
\]
\[
V_{RC}(x) := -\frac{e^2}{x} + \frac{\ell(\ell + 1)}{x^2} \quad \text{(rotational-Coulomb potential)} \quad (1.4)
\]

all belong to an explicitly known family of potentials (depending on eight parameters and a level-dependent scalar) which are solvable in the strongest possible sense, namely (d).

On the other hand examples of non-separable $N$–dimensional potentials whose spectrum and eigenfunctions are known in the sense of (c) were apparently found only a few years ago [BEE+02]. These are periodic potentials related to models of some condensed matter systems, and the solutions are found through the use of a
fair amount of complex analysis.

But it remains that many systems of great interest are not solvable in any of the above senses – in particular, the $n$–body Coulomb problem of atomic and molecular physics is not – and therefore one is led to find methods of approximations which work for any potential.

1.1.3 Direct numerical solutions

The most natural potential-independent approximation one could think of is simply to solve the eigenvalue problem (1.1) numerically at some prescribed order of accuracy. In computational chemistry this is called an \textit{ab initio} method. Again there are many ways to do this.

From the traditionnal point of view of numerical analysis, one would consider (adaptive) mesh-based methods like finite differences and finite elements (FEM), but these do not have favorable scaling properties with respect to the dimension $N$ of the system. The corresponding literature is thus rather scarce, including in the Coulomb case [ZY04].

Much more successful methods are those based on the variational formulation of the problem, namely (1.1) is seen as an Euler-Lagrange equation (the stationary solution we are looking for being a minimum). The key step is then to find a suitable orthogonal basis $(\varphi_k)_{k=1}^{\infty}$ of the (huge) variational space $H^1(\mathbb{R}^N)$. Indeed, in this \textit{direct route} one wishes to use trial wavefunctions of the form 

$$
\psi_d(x_1, \ldots, x_N) = \sum_{k=1}^{d} c_k \varphi_k(x_1, \ldots, x_N).
$$

The best set of coefficients, in the case of the ground state, then corresponds to the global minimum of the $d$–dimensional Rayleigh-Ritz ratio

$$
E_{RR}(c_1, \ldots, c_d) = \frac{\langle \psi_d | \hat{H} | \psi_d \rangle}{\langle \psi_d | \psi_d \rangle}.
$$

(1.5)
For higher states the minimization must be done under the constraints of orthogonality with the lower states. Thus the basis should allow a fast evaluation of the matrix elements (integrals on two copies of the configuration space) while requiring a low number \( d \) of members (at the level of chemical accuracy) to be of any use. In practice, at least in the Coulomb case of atoms and molecules, finding such a basis is not possible even for systems of relatively small size (say, \( N = 30 \)) [LBge03].

For larger systems one therefore seeks further approximations by restricting the variational space. For example, in atomic physics the Hartree-Fock approximation assumes that the Hamiltonian can be split into \( n \) weakly interacting parts (individual electrons terms) whose interactions are neglected except from a common averaged one. Using those one-electron orbitals \( \phi_i \), the variational wavefunction then has the form of a Hartree product \( \psi_d = \prod_{i=1}^{n} \phi_i \) (or is an antisymmetric Slater determinant \( \text{det}(\phi_i) \) if one wishes to take into account the Pauli principle). So only a good basis of the smaller space \( H^1(\mathbb{R}^{\frac{N}{n}}) \) is needed. The solution is then found iteratively (due to the self-consistency constraint of the averaged electronic interaction) by solving a generalized eigenvalue problem associated to the Fock matrix, rather than minimizing the energy as in the direct method. Interactions can then be taken into account by using sums of determinants rather than a single one (configuration-interaction (CI) method). See [Pop99, SO96, LBge03] for a detailed introduction to such wavefunction-based methods. In particular, the rate of convergence of the expansion remains the most fundamental issue, see also [Kut05]. Other methods to account for correlations include the coupled-clusters one, which can be very powerful [NE05].

Yet, for even larger systems the approximately constant number \( P \) of new orbital parameters needed per added degree of freedom implies the existence of an exponential barrier \( P^N \) [Koh99], and one thus needs yet another form of approximation. In the 1960s, building on the Thomas-Fermi approximation, Kohn and
coworkers realized that the electronic density $\rho$ – which lives in $H^1(\mathbb{R}^3)$ – contains exactly the same information as the full wavefunction provided one uses a certain (unknown) functional. The impact of this Density Functional Theory (DFT) has been tremendous in the analysis of large systems, despite the use of only approximate functionals. For a more mathematically oriented approach to these and other related issues one should refer to [LBL05, KM05].

These numerical approximations are mainly aimed at computing low-lying states and in particular the ground state, the high-lying ones being out of reach except for small enough systems.

Finally, calculations of resonances (see [BC71], [Moi98] and [Lin02]) are usually done by performing a complex scaling$^3$ of the space variables. One then looks at the real spectrum of a corresponding scaled non-self-adjoint complex operator, either analytically or numerically.

### 1.1.4 Approximate asymptotic eigenfunctions

Matched asymptotic expansions are used as a method of approximation in many areas of applied mathematics. Let us take again the example of $n$–body Coulomb problems, where its use is in fact quite recent so that only some few-body systems have been considered so far.

In a series of papers [KPTT96, PTT99, Pat99, Pat00, Pat03], Patil and coworkers have used the constraints on the exact wavefunction coming from collisions of pairs of bodies (like the famous Kato cusp condition at electron-nucleus collision) and from escape at infinity. There is a prescribed behaviour in these regions, and some global approximate wavefunctions are found by matching those local expressions under some assumptions on electronic interactions and overall symmetry. We shall

---

$^3$In the mathematical literature when such scaling is valid one says that the Hamiltonian has the *dilation analyticity* property.
consider these results in more details when discussing the helium atom in chapter 2.

Since the consideration of the numerical precision of the approximate eigenvalue alone is not a very sensitive test on the quality of the corresponding approximate eigenfunction (this is the quasi-mode problem, see appendix 11 in [Arn89]), one uses the so-called local energy test. This simply means that an approximate wavefunction \( \tilde{\psi} \) of good quality must be such that the ratio of the values of the two functions \( \hat{H}\tilde{\psi} \) and \( E\tilde{\psi} \) is very close to 1 and slowly varying over the whole configuration space. It is indeed the case for the wavefunctions of Patil and coworkers.

The main issue to be surmounted in order to use this method on bigger atoms is, not surprisingly, to find explicitly some approximate but accurate multi-electron interaction terms, which is not obvious.

### 1.2 The semiclassical limit of quantum mechanics

We shall now consider in some details another kind of useful approximation; it has two main related goals: (1) to provide reliable results for the high-lying states at a reasonable cost, (2) to understand the transition from quantum to classical mechanics.

It has been developed by the three different communities of mathematicians, physicists and chemists, each with its own motivations and emphasis. It is thus a very large subject and we shall only present it in the restricted framework of our eigenvalue problem (1.1) without studying the various other situations where similar methods have been developed (recent reviews describe in particular the cases of billiard-type systems [Wir99], field theories [MG03] and quantum graphs [GS06]).
There are essentially two textbooks which taken together cover most of the material we are interested in: the enjoyable online book [CAM+05] (in its latest and now quite complete version 11.0), and the textbook [BB] which is shorter and contains some complementary topics and various examples. An overview of some early developments in this area can be found in [Gut90]. We are going to summarize the relevant theoretical ideas, and leave calculations in concrete examples from atomic physics to the next chapter. See appendix A for some background on classical mechanics; we mark any first occurrence of terms defined there with the symbol \( \bullet \).

1.2.1 Setting

Our aim is to consider the formal and singular \(^4\) limit \( \hbar \to 0 \) (which must recover classical mechanics as the commutation relations imply) and to find methods to compute the eigenvalues, and possibly the eigenfunctions, up to \( O(\hbar^2) \), at least in the cases where classical dynamics is fairly well understood (integrable\( \bullet \), and hyperbolic\( \bullet \) systems).

Other approaches relating classical and quantum mechanics have been developed, but we shall not study them. In particular, we are not interested in constructing quantum systems from classical ones as in geometric quantization (see [Got99] for a precise statement of the Gr"{u}wald-van Hove `no-go` theorem which shows the limits of this approach). We are also not going to talk about the relations between the semi-classical limit and the ideas coming from deformation quantization [DS02, CGSL\( ^+ \)05b, CGSL05a].

\(^4\) i.e. the small parameter \( \hbar \) is a factor of the highest order differential term of the Hamiltonian, namely the Laplacian, hence at \( \hbar = 0 \) there is a sudden drop of order.
1.2.2 Case of an integrable limit

Suppose that our classical limit is an integrable system with \( N \) DOF. Then there exists a well-known method, developed by Einstein, Brillouin and Keller (EBK quantization\(^5\)), which allows to locally construct in a neighborhood of a regular value \( f = (E, f_2, \ldots, f_N) \) of the energy-momentum map a lattice of approximate quantum states together with their associated eigenfunctions. Let us first deal with the original construction (we make here a synthesis of Keller’s review [Kel85], some parts of Guillemin & Sternberg’s book [GS77], Murayama’s lecture notes [Mur04], and [Gut90, CAM\(^+\)05]) and then we shall consider an alternative version with a more quantum flavor due to Littlejohn [Lit86b, Lit86a].

WKB method

Let us consider the case \( N = 1 \) succinctly to notice the change of point of view offered by the geometric reformulation of the older WKB method, which itself goes as follows. Suppose

\[
H(x, p) = \frac{p^2}{2} + V(x)
\]

(1.6)

with \( V \) satisfying \( V(x) \approx x^2 \) near \( x = 0 \) and \( \lim_{|x| \to +\infty} V(x) = +\infty \)

\[\text{Figure 1.1: Some potential } V \text{ when } N = 1\]

\(^5\)Sometimes also called torus quantization for obvious reasons. In the mathematical literature the terminology Bohr-Sommerfeld quantization (which in physics refers to the narrower ad hoc method of action quantization of the “old quantum theory” of Bohr) is employed.
At a given energy $E$, configuration space splits into three regions: $I$ and $III$ are classically forbidden while $II$ is allowed, the boundaries between these regions being the two turning points $x_1$ and $x_2$ where the momentum vanishes. In fact the momentum is a multivalued function $p = P(x)$ of the position since only the square of $p$ appears in $H$. The corresponding plot is

![Figure 1.2: The momentum is a multivalued function of the position](image)

We now solve Schrödinger’s equation order by order in $\hbar$ with the ansatz

$$\psi(x) = A(x)e^{\frac{i}{\hbar}B(x)} \quad (1.7)$$

at a regular point $x$.

At $O(\hbar^0)$ we find $0 = (B')^2 + V - E$. This is the Hamilton-Jacobi equation for $B$, the solution is hence the action

$$B(x) = S(x) = \int_{x_0}^{x} P(u)\,du + S_0 \quad (1.8)$$

where $x_0$ is a reference point. $S$ is then also a multivalued function since we must pick a branch of $P$. These two branches simply have opposite signs and we can choose the convention $P_2(x) = -P_1(x) > 0$.

At $O(\hbar^1)$ we find

$$0 = 2A'B' + AB'' = \frac{(A^2)'B' + A^2B''}{A} \quad (1.9)$$
so we must have \((A^2 B')' = 0\): this is the continuity equation for a “quantum fluid” of density \(A^2\) and momenta \(B'\). The solution is

\[
A(x) = \frac{\kappa}{\sqrt{|S'(x)|}} = \frac{\kappa}{\sqrt{|P'(x)|}}
\]

for some constant \(\kappa\).

Terms of higher order can be found recursively from here and are neglected. We hence end up with two (so-called Liouville-Green) local solutions

\[
\chi_k(x) = \frac{\kappa_k}{\sqrt{|P_k(x)|}} e^{i S_k(x)}
\]

(1.11)

corresponding to each branch \(P_k\) of \(P\) (and hence of \(S\)), and by linearity of Schrödinger’s equation we get our local approximate solution as

\[
\phi_{II}(x) = \chi_1(x) + \chi_2(x)
\]

(1.12)

with \(\kappa_1\) and \(\kappa_2\) still to be determined. Similarly

\[
\phi_I(x) = \frac{\alpha}{\sqrt{|P(x)|}} e^{\frac{1}{\pi} \int_{x_1}^{x} |P(u)| du}
\]

(1.13)

and

\[
\phi_{III}(x) = \frac{\beta}{\sqrt{|P(x)|}} e^{\frac{1}{\pi} \int_{x_2}^{x} |P(u)| du}
\]

(1.14)

These local Liouville-Green solutions blow up at the turning points since \(P_j(x_i) = 0\), so in order to construct a global wavefunction we need to match the local ones using the asymptotic properties of the exact wavefunction at \(x_1\) and \(x_2\). This is done by using a linear approximation of \(V\) near each \(x_i\), the exact solution of the corresponding Schrödinger equations being the first Airy function

\[
Ai(s) = \frac{1}{\pi} \int_0^\infty \cos(\frac{t^3}{3} + st) dt
\]

(1.15)
whose asymptotic form at large $|s|$ is known. It is then found that in the region II the wavefunction should be at the same time of the form

$$\frac{C}{\sqrt{P_2(x)}} \cos\left(\int_{x_1}^{x} P_2(u) du - \frac{\pi}{4}\right)$$

(1.16)

and

$$\pm \frac{C}{\sqrt{P_2(x)}} \cos\left(\int_{x_2}^{x} P_2(u) du + \frac{\pi}{4}\right)$$

(1.17)

where $C$ is some constant. This is equivalent to the quantization condition

$$\int_{x_1}^{x_2} P_2(u) du = (r + 2 \cdot \frac{1}{4}) \pi \hbar$$

(1.18)

(with $r \in \mathbb{N}$), an implicit equation in $E$ (from the start $E$ was a parameter in $P_j(x)$) which singles out the discrete values $E_r$ at which such global approximate wavefunctions exist. There are now definite relations between the coefficients of the three regions

$$C = \beta = \kappa_1 e^{\frac{i\pi}{4}} = \kappa_2 e^{-\frac{i\pi}{4}} = (-1)^r \alpha$$

(1.19)

**EBK quantization à la Keller-Maslov**

In order to find analogous conditions in the general case $N > 1$ Keller and Maslov introduced a crucial modification of the geometrically invariant reformulation of the ad hoc Bohr-Sommerfeld rules that Einstein had presented earlier. Multiplying by 2 the WKB quantization condition (1.18) and using the fact that the two branches of $P$ (fig. 1.1) can also be seen as forming a smooth submanifold of phase space, namely a 1–torus $\mathbb{T}_E$, we can rewrite the condition as

$$\oint_{\mathbb{T}_E} P(u) du = (r + 2 \cdot \frac{1}{4}) 2\pi \hbar$$

(1.20)

This is reminiscent of Einstein’s ad hoc action quantization condition except for the extra half-integer: a phase loss of $\frac{\pi}{2}$ is created here by each of the turning
points when going from one branch of \( P \) to the other, i.e. when comparing \( \chi_1 \) with respect to \( \chi_2 \). This last observation can be explained by using the method of stationary phase to transform smoothly \( \chi_1 \) into \( \chi_2 \). In its general formulation \(^6\) this states that from two functions \( a(u,v) \) and \( b(u,v) \) and a small parameter \( \epsilon \) we can construct a function of the variables \( u \) only by considering the oscillatory integral

\[
\varphi(u) = \int_V a(u,v)e^{i\epsilon b(u,v)}dv
\]  

(1.21)

Its asymptotic expansion in powers of \( \epsilon \) at any given value of \( u \) is

\[
\varphi(u) \sim (2\pi\epsilon)^{\frac{d}{2}} \left( \sum v_j \left( a(u,v_j^*)e^{i\epsilon b(u,v_j^*)} \right) \right) + O(\epsilon^{\frac{d}{2}+1})
\]  

(1.22)

where \( d \) is the dimension of the \( v \)-space, the \( v_j^* \) are the points where the derivatives \( \nabla_v b \) vanish (we assume there is a finite number of those points), \( G \) is the Hessian matrix of \( b \) with respect to the \( v \) variables, and \( s_j \) is the signature of \( G \) at \( (u,v_j^*) \), which is what controls the additional relative phases.

In our \( N = 1 \) case, if we set \( \epsilon = \hbar \) and define

\[
a_2(x,p)e^{\frac{i\hbar}{\epsilon}b_2(u,v)} := e^{-\frac{i\pi}{4}}\chi_2(x)
\]  

(1.23)
i.e. \( a_2(x,p) := \frac{\kappa_2}{\sqrt{|P_2(x)|}} \) and \( b_2(x,p) := S_2(x) - xp \), then doing a stationary phase with respect to \( p \), propagating smoothly until reaching the \( P_1 \) branch and going back to \( q \)-representation (see [CAM+05]) we find that indeed a phase loss of \( \frac{\pi}{2} \) has been introduced so that \( \kappa_2 = \kappa_1 e^{-i\frac{\pi}{4}} \), i.e. \( \kappa_1 e^{i\frac{\pi}{4}} = \kappa_2 e^{-i\frac{\pi}{4}} \) just like the WKB method showed.

In the case \( N > 1 \) the situation is now the following: we consider a regular value \( f \) of the energy-momentum map of our integrable \( N \)-dofs Hamiltonian

---

\(^6\)The method of stationary phase is described in details in the very informative first chapter of [GS77]. The rest of that old book, which covers also EBK quantization and other topics like geometric quantization, is written from a pure-mathematician’s point of view with very tedious general constructions and no attention to practical computational issues.
system and make the simplifying assumption that the fiber• is compact and connected: we have one torus $T_f$ in phase space. This torus provides a cover of some part $W := \Pi Q(T_f)$ of configuration space, where $\Pi Q$ is the projection on $Q$. Then $W$ can be decomposed into a union of disjoint open sets $W = \cup j W_j$ such that the number $N W_j$ of pieces of $T_f$ over any point $q \in W_j$ is constant over the whole of $W_j$, this for each $j$. The common boundaries between the $W_j$, where the projection is singular, is the caustic (set), analogous to the turning points of the $N = 1$ case. The existence of this covering shows that the momenta $p$ are multivalued functions of the positions $q$.

The problem we face is then to match these local solutions at the caustics (where again the amplitudes diverge) to get a global solution. We thus have to compare each local $\chi_j$ term to the others through the caustics, and this is done by considering each independent loop of a homotopy basis• $\{C_k\}_{k=1}^N$ of $T_f$. So we get $N$ implicit quantization conditions for $f$ as

$$\oint_{C_k} P(q) \, dq = (r_k + \mu_k \cdot \frac{1}{4}) \, 2\pi \hbar$$

where $\mu_k$ is an even integer called the Keller-Maslov index (of the loop $C_k$ on the Lagrangian manifold $T_f$ with respect to $\Pi Q$) which counts the number of times a change of branch happens along $C_k$. The reason why we need only these $N$ homotopy conditions is that the action is an homotopy invariant. This is easily shown by using the action-angle variables and Stokes’ theorem: pick two homotopic loops $C$ and $\tilde{C}$ on $T_f$. Then

$$\int_{C - \tilde{C}} P \, dq = \int A \nabla \wedge P \, dq = \int B \nabla \wedge I \, d\theta = 0$$

since the $I$ are constant.
EBK rules via wavepackets methods

There exists another method in the literature to derive the EBK rules which is due to Littlejohn. The idea is to work with the linear flows obtained by using the actions

\[ I_k = \frac{1}{2\pi} \oint_{\gamma_k} P(u) du \]  

(1.26)

as Hamiltonians. One can construct a semiclassical approximation of the associated quantum propagator

\[ V_k(\tau) = e^{-\frac{i}{\hbar} I_k} \]  

(1.27)

using the *metaplectic representation* of the linearized dynamics around the trajectories of the flow of \( I_k \), defined as follows.

Recall that there exists a 2-to-1 unitary representation of the symplectic group \( Sp(2N, \mathbb{R}) \) by a group \( Mp(2N, \mathbb{R}) \) of operators acting on Hilbert space, called the metaplectic representation [GS84]. To any symplectic matrix \( S = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \) there corresponds two operators (differering by a sign) given by

\[
\hat{M}_S \psi(x) = \pm e^{-in\frac{\pi}{4}} \frac{1}{\sqrt{|\det B|}} \left( \frac{1}{(\sqrt{2\pi})^n} \right) \int_{\mathbb{R}^N} e^{iW(x,y)} \psi(y) dy
\]

(1.28)

with

\[
W(x,y) = \frac{1}{2} (DB^{-1} x \cdot x + B^{-1} Ay \cdot y - 2B^{-T} y \cdot x)
\]

(1.29)

Littlejohn then shows that \( V_k \) can be approximated semiclassically by

\[
V_k^{sc}(\tau; z_0) = e^{\frac{i}{\hbar} (\alpha(\tau) - \tau I_k(z_0))} \hat{T}(z(\tau)) \hat{M}_S(\tau) \hat{T}^\dagger(z_0)
\]

(1.30)

where \( z(\tau) = (q(\tau), p(\tau)) \) is a trajectory of the flow of \( I_k \) and \( z_0 \) an initial condition, where

\[
\alpha(\tau) := \frac{1}{2} \int_{z_0}^{z(\tau)} (pdq - qdp)
\]

(1.31)
is a symmetrized Bohr-Sommerfeld phase, and where

\[ \hat{T}(z) := e^{i \frac{\pi}{\hbar} (p\hat{q} - q\hat{p})} \]  \hspace{1cm} (1.32)

are Weyl-Heisenberg operators (which produce phase space translations).

Since \( S(\tau) \) is itself \( 2\pi \)-periodic around a \( 2\pi \)-periodic orbit of the flow of \( I_k \), it is found that

\[ \hat{M}_S(\tau + 2\pi) = e^{-i \theta_k \pi} \hat{M}_S(\tau) \]  \hspace{1cm} (1.33)

with \( \theta_k \) the \( k \)-th Keller-Maslov index, and \( \alpha(\tau + 2\pi) = \alpha(\tau) + 2\pi I_k(z_0) \). So \( I_k(z_0) \) is an eigenvalue of \( \hat{I}_k \) only if its associated eigenstate exists, i.e. only if the Fourier transform does not vanish

\[ |r_k\rangle := \lim_{L \to +\infty} \frac{1}{2L} \int_{-L}^{L} e^{i \tau I_k(z_0)} \hat{V}_k^\infty(\tau; z_0) |0\rangle d\tau \neq 0 \]  \hspace{1cm} (1.34)

where \( |0\rangle \) is some initial state.

Then, using the periodicity properties above, this can be rewritten as

\[ |r_k\rangle = \lim_{\ell \to +\infty, \epsilon \in \mathbb{N}} \left( \sum_{j=-\ell}^{\ell} \frac{1}{2\pi(2\ell + 1)} \right) \times \int_{0+2j\pi}^{2\pi+2j\pi} e^{i(2\frac{\pi}{\hbar} I_k(z_0) - i\mu_k \frac{\pi}{2})} e^{i\alpha(\tau)} \hat{T}(z(\tau)) \hat{M}_S(\tau) |0\rangle d\tau \]  \hspace{1cm} (1.35)

and we find that an eigenstates exists only if

\[ \frac{1}{\hbar} 2\pi I_k(z_0) - \mu_k \frac{\pi}{2} = 2\pi r_k \]  \hspace{1cm} (1.36)

where \( r_k \in \mathbb{N} \), that is if

\[ I_k(z_0) = (r_k + \frac{\mu_k}{4})\hbar \]  \hspace{1cm} (1.37)

which is indeed the EBK rule for the \( k \)-th action.

In subsequent work of Littlejohn and Robbins [LR87] an algorithm was found
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to compute the Keller-Maslov indices which avoids counting caustics. Define an homotopy basis of our torus $\mathbb{T}_f$ by

$$
\Gamma_k(\vartheta_k) := \{ \vartheta_k \in [0; 2\pi] | I_p, \theta_p \text{ fixed for } p \neq k \} \quad (1.38)
$$

Assume the original flow $(q(t), p(t))$ is known explicitly (analytically or numerically) in terms of $\vartheta_k$. Then we have

$$
\mu_k = 2 \times \text{wn} \left[ \det \left( \frac{\partial q_k}{\partial \theta_p}(\vartheta_k) - i \frac{\partial p_k}{\partial \theta_p}(\vartheta_k) \right) \right] \quad (1.39)
$$

i.e. twice the winding number of a loop in $\mathbb{C}$ around the origin. Such a topological definition of the Keller-Maslov index in terms of winding numbers had been formulated by Arnold [Arn72] (who gave more general definitions in terms of Lagrangian Grassmanians, and who worked out the relation with the Morse index in the case where the loop is a trajectory of the flow).

Quantum monodromy

In many concrete examples of integrable systems, including integrable approximations of some small molecules [CDG+04], the torus bundle* over the regular values of the energy-momentum map is not trivial (there are separatrices or singular values in the image or the energy-momentum map), so that action-angle variables and hence quantum numbers are not globally defined quantities.

The main kind of such obstruction to global good quantum numbers is called quantum monodromy, since it is the quantum manifestation of the monodromy* of the classical system. Quantum monodromy can also be interpreted as the consequence of (local or non-local) defects in the quantum lattice [Zhi05]. We shall say more on these issues in the next chapter when discussing the $H_2^+$ ion.
Non-integrability issues

Many problems obviously arise as soon as the system is not integrable: in the Keller-Maslov version we get an infinity of branches of momenta. In the Littlejohn version, the flows of the $I_k$ do not commute anymore and ordering issues for the operators occur. Thus other methods must be devised for systems far from integrability.

1.2.3 Case of an hyperbolic limit

There exists such other methods in the case of classical systems possessing a dynamics which is at the opposite end of integrability, namely classical uniformly hyperbolic systems\footnote{Systems with a dense set of isolated periodic orbits.} with a dense set of isolated periodic orbits.

The main idea, the \textit{Gutzwiller trace formula (GTF)}, was first derived by Gutzwiller in the early 70s [Gut71] (for a mathematical version see [Mei92]). But to become a computationally interesting tool it needs to be rewritten into a so-called \textit{semiclassical spectral determinant} which is then computed using \textit{cycle expansion techniques}, and these were introduced only two decades later [Cvi88, CE89, CAM05]. Those ideas will be summarized below.

Recently, two sets of papers appeared which presented new derivations of the GTF: in the first one wavepackets techniques akin to those of Littlejohn above are introduced in this context [CRR99, MW01b]; in the second one properties of an index associated to periodic orbits which appears in the GTF are detailed [Mei94, Sug01, MG03]. We shall take these long bodies of work for granted here and only mention the facts of direct use for us.

There exists many different (and conflicting) notations in the literature for the quantities introduced below; we try here mainly to be self-contained and consistent with our previous ones.
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Gutzwiller trace formula

The first step is to construct a semiclassical approximation of the quantum propagator. For short times this was done by Van Vleck in 1928; then Gutzwiller made a fundamental modification by showing that extra phases at the conjugate points occur for large times. By doing a stationary phase approximation of the Feynman path integral (which is a summation over all possible paths, classical or not) one obtains the Gutzwiller-van Vleck propagator, which is equal to a sum over only the classical paths from the initial to the final point

$$K_{sc}(q, \tilde{q}, t) = \left(\frac{1}{\sqrt{2i\pi\hbar}}\right)^N \sum_{\alpha} \sqrt{\det C_{\alpha}} e^{\frac{i}{\hbar} R_{\alpha}(q, \tilde{q}, t) - im_\alpha \frac{\pi}{2}}$$

(1.40)

where $C_{\alpha(i,j)}(q, \tilde{q}, t) = -\frac{\partial^2 R}{\partial q_i \partial q_j}(q, \tilde{q}, t)$, and $R$ is Hamilton’s principal function*. The quantity $m_\alpha$ is an integer, called the Morse index, equal to the number of conjugated points along the path $\alpha$ (the duration $t$ being fixed), i.e. the number of times $\det C_\alpha$ changes of sign.

Then the object which contains the information about the eigenvalues, namely the semiclassical Green’s function (Laplace transform of the propagator) can be computed, also by stationary phase

$$G_{sc}(q, \tilde{q}, E) = G_0(q, \tilde{q}, E) + \frac{1}{i\hbar} \left(\frac{1}{\sqrt{2i\pi\hbar}}\right)^{N-1} \sum_{\alpha} \sqrt{\det D_{\alpha}} e^{\frac{i}{\hbar} S_{\alpha}(q, \tilde{q}, E) - i\mu_\alpha \frac{\pi}{2}}$$

(1.41)

where

$$D = \begin{pmatrix}
\frac{\partial^2 S_{\alpha}}{\partial q_i \partial q_j} & \frac{\partial^2 S_{\alpha}}{\partial q_i \partial E} \\
\frac{\partial^2 S_{\alpha}}{\partial q_j \partial E} & \frac{\partial^2 S_{\alpha}}{\partial q \partial E^2}
\end{pmatrix}$$

(1.42)

and $\mu_\alpha$ is an integer which counts the number of conjugated points along the path $\alpha$ (the energy $E$ being fixed), while $G_0$ is the contribution of trajectories whose action is smaller than $\hbar$.

Finally, the trace of $G_{sc}$ is evaluated by doing a stationary phase integration
with respect to the variables $q^\perp$ which are transverse to the flow. This trace selects periodic orbits (PO) among all the classical paths in the summation of (1.41), and after several steps one finds the GTF, which involves the regularized part $G_{reg}$ of $G_{sc}$ (i.e. $G_{reg}$ is what remains after removal of ultraviolet divergences)

$$\text{Tr } G_{reg}(q, \tilde{q}, E) = -i\pi d_0(E) + \frac{1}{i\hbar} \sum_{\gamma} \sum_{r=1}^{\infty} \frac{1}{r} \frac{rT_\gamma}{\sqrt{|\det(1 - M_\gamma)|}} e^{i\pi rS_\gamma - i\eta_\gamma^{(r)} \pi}$$  \quad (1.43)

The trace converges when adopting a suitable smoothing of the discrete spectrum (or, equivalently, an upper bound in periods which cuts-off very long orbits). Here $d_0(E)$ is the smooth part of the density of states: the ratio of the volume of the classical level set $\{(q, p) | H(q, p) = E\}$ by that of a quantum cell \textsuperscript{7}. What we are interested in is the other term in (1.43). Its imaginary part $d_{osc}(E)$ is a sum which provides an oscillating contribution to the density of states and the poles of $d_{osc}(E)$ are our approximations of the quantum eigenvalues (to first order in $\hbar$).

This sum is made only of classical quantities, and these are associated to the $r-$th repeat of the orbits $\gamma$, which are the primitive periodic orbits (PPO)\* of the classical dynamics. Namely, $rT_\gamma$ is the period, $rS_\gamma$ the action, $M_\gamma$ the stability matrix\*\*, and $\eta_\gamma^{(r)}$ is an integer.

This last integer is a crucial quantity which needs to be computed carefully since we are interested in phase effects. Precisely what $\eta_\gamma^{(r)}$ exactly is has been studied in depth in the literature, both from conceptual and numerical point of views, and we now discuss this.

Alternative definitions and properties of the topological index $\eta_\gamma^{(r)}$

Recall that at the beginning of the derivation it has been assumed that the dynamics is uniformly hyperbolic and that it has only isolated PO. So orbits are described by \textsuperscript{7}i.e. an $N-$dimensional parallelepiped of side length $\hbar$, where as before $N$ is the number of DOF.


a certain set of DOF and they are unstable with respect to these DOF.

Now, such instability is not the most crucial issue: the GTF is also valid in some non-hyperbolic situations, where the isolated PO are stable with respect to some of the DOF of the system\footnote{The condition that the PO are isolated is there to ensure that the quantity det(1 – $M_{r}$) does not vanish. The GTF can be modified and adapted to the more general case where orbits instead of being isolated come in families as a result of some continuous symmetries. But we will recall in chapter 2 how in this situation one is led back to the case of isolated orbits for an associated symmetry-reduced system, so that the following discussion deals with all the issues that we shall encounter in practice later on.}. The fact that the GTF can be used in various stable and unstable cases requires a careful terminology. Indeed, two different approaches have been developed to define and compute $\eta_{r}^{(r)}$, but they are not applicable in exactly the same situations. Let us review the topic gradually.

**Presentation of the two approaches.** The first approach, called henceforth A, has itself two versions, called A-KM and A-CZ. In the A-KM version, the index $\eta_{r}^{(r)}$ is seen as the Keller-Maslov index of the loop defined by a given orbit $\gamma$ on its stable/unstable manifold $W_{u,s}(\gamma)$. That manifold is indeed Lagrangian as required in the definition of such index (1.24). This point of view has been developed by Creagh, Robbins and Littlejohn [CRL90, Rob91, Rob92], based on the work of Arnold [Arn72].

On the other hand, in the A-CZ version the index $\eta_{r}^{(r)}$ is seen as a Conley-Zehnder index [CZ84]. Such identification was first made by Meinrenken [Mei94] (actually this seems not widely known to physicists), and rediscovered and analyzed in a more explicit way by Sugita [Sug01] and Muratore-Ginanneschi [MG03]. Of course both versions A-KM and A-CZ always provide the same answers, but the details of the computations are different. Moreover, in the case of an orbit which is unstable with respect to all DOF the index is a winding number, while if some DOF are stable it is a sum of winding numbers.

The second approach, called henceforth B, is more restricted in nature and goes back in its first correct version to Miller [Mil72]. It requires that the orbits possess
some stable DOF, but not all kind of stabilities can be treated. More precisely, whether it can be employed or not depends on the exact form of the numerators $\sqrt{\det(1-M\gamma)}$ in (1.43). When applicable the approach B consists in modifying these denominators to perform some phase cancelations, allowing to rewrite the GTF in a different way.

Some topological phases still appear in the resulting expression, but they are not equal to those of A. In the situations where both A and B can be used, the conceptually most pleasing expression is B since it involves indices with simpler properties, and more importantly since it is that form of the GTF which can be turned into a computationally efficient tool to compute semiclassical spectra (see below).

The instances, which we shall call ♦, where B is not applicable are when at least one of the PPO (call it $\gamma$) in the sum of the GTF is such that

- it is spectrally stable• with respect to some set of DOF
- it is spectrally unstable with respect to another set of DOF
- these stable and unstable DOF are linearly coupled along $\gamma$

and this will be shown below.

Now, two numerical methods have been developed to compute the indices appearing in A. One of them is issued from the A-KM point of view and works for systems of the type “kinetic+potential”; we shall call it in this thesis the CRL method (Creagh-Robbins-Littlejohn) [CRL90]. Another method exists and comes from considerations on the A-CZ version; it can be used for more general systems and will be called the PB method (Pletyukhov-Brack) [PB03]. In situations different from ♦, the GTF can be rewritten in its B formulation, and the indices appearing there can then be obtained from those of A. Before presenting these numerical methods as well as the general formula for the indices mentioned previously, let us consider a very simple example.
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An example. The following system was originally introduced in an A-KM setting and treated with the CRL method analytically in [BJ95]. Then later it was studied, also analytically, from the A-CZ point of view with the PB method in [PB03]. It consists of a 2 DOF oscillator with irrational frequency ratios. The Hamiltonian is

\[ H := \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\omega_x^2 x^2 + \omega_y^2 y^2) \]  

(1.44)

where \( \omega_x / \omega_y \) is irrational. In that case there are only 2 PPO: these are the oscillations along both axis (call them \( \gamma_x \) and \( \gamma_y \)), and they are stable with respect to both DOF. Their respective period and stability angle\* are found to be \( T_x = \frac{2\pi}{\omega_x} \), \( T_y = \frac{2\pi}{\omega_y} \) and \( \chi_x = 2\pi \frac{\omega_y}{\omega_x}, \chi_y = 2\pi \frac{\omega_x}{\omega_y} \).

The oscillating part of the density of states is then (up to a constant factor)

\[ d_{osc}(E) \approx \sum_{k=1}^{+\infty} \left( \frac{1}{k} \cos \left( k \frac{S_x}{\hbar} - \eta_x^{(k)} \frac{\pi}{2} \right) \right) + \sum_{\ell=1}^{+\infty} \left( \frac{1}{\ell} \cos \left( \frac{\ell \chi_y}{2} \right) \right) \]  

(1.45)

Since all PPO are stable with respect to all the DOF of the system we are not in the problematic situation ♦ mentionned above. This means we can choose to compute the \( \eta_x^{(k)} \) and \( \eta_y^{(\ell)} \) indices either as Keller-Maslov ones (A-KM case) or as Conley-Zehnder ones (A-CZ case), and also that we will be able to switch to the B formulation. We shall only compute \( \eta_x^{(k)} \) since the other can be found by permuting the letters \( x \) and \( y \) and replacing \( k \) with \( \ell \) in the resulting expressions.

A-KM case. The index is a sum of two contributions: the Morse index \( \mu_x^{(r)} \) from the semiclassical Green’s function \( G_{reg} \) and a contribution \( \nu_x^{(k)} \) from taking its trace \( TrG_{reg} \). Skipping the details, one ultimately finds

\[ \mu_x^{(k)} = 2k + \left| 2k \frac{\omega_y}{\omega_x} \right| \]  

(1.46)

\[ \nu_x^{(k)} = \frac{1}{2}(1 + (-1)^{2k \frac{\omega_y}{\omega_x}}) \]  

(1.47)
where the notation \([s] \) indicates the integer part of the real number \(s\).

A-CZ case. An explicit iteration formula exists (see details for the general case below) which reads here

\[
\eta^{(k)}_x = 1 + 2 \left\lfloor \frac{k \chi_x}{2\pi} \right\rfloor + 2km_x
\]

(1.48)

and its ingredients are, after some calculations, found to be

\[
\chi_x \equiv \frac{\chi_x}{2\pi} := \frac{\chi_x}{2\pi} - \left\lfloor \frac{\chi_x}{2\pi} \right\rfloor
\]

(1.49)

\[
= \frac{\omega_y}{\omega_x} - \left\lfloor \frac{\omega_y}{\omega_x} \right\rfloor
\]

(1.50)

and

\[
m_x = 1 + \left\lfloor \frac{\omega_y}{\omega_x} \right\rfloor
\]

(1.51)

So in both cases A-KM and A-CZ one obtains

\[
\eta^{(k)}_x = 1 + 2k + 2 \left\lfloor \frac{k \omega_y}{\omega_x} \right\rfloor
\]

(1.53)

which in particular implies that, contrarily to periods or actions for example, the indices in the A approach are not additive under iteration of the PPO. That is, for

\[ k = 2, 3, \ldots \] we have

\[
\eta^{(k)}_x \neq k\eta^{(1)}_x
\]

(1.54)

This is a general property for systems with stable DOF rather than a feature of the example. Notice also that there is no simple relation between the ingredients of
the two calculations. In particular

$$\mu^{(k)}_x - 2km_x = \begin{vmatrix} 2k \frac{\omega_y}{\omega_x} & -2k \frac{\omega_y}{\omega_x} \\ \omega_y & \omega_x \end{vmatrix}$$

(1.55)

is a non-constant, irregular, function of \( k \).

Now, to rewrite (1.45) in the B form (which is possible here as mentionned earlier) one notices that

$$| \sin \left( k \pi \frac{\omega_y}{\omega_x} \right) | = (-1)^{\lfloor k \omega_y / \omega_x \rfloor} \sin \left( k \pi \frac{\omega_y}{\omega_x} \right)$$

(1.56)

and similarly for the other determinant. On the other hand, using (1.53), the numerator is found to be

$$\cos \left( k \frac{S_x}{\hbar} - \eta^{(k)}_x \right) = \cos \left( k \frac{S_x}{\hbar} - (2k + 2) \frac{\omega_y}{\omega_x} + 1 \right)$$

(1.57)

$$= (-1)^{\lfloor k \omega_y / \omega_x \rfloor} \sin \left( k \frac{S_x}{\hbar} - 2k \frac{\pi}{2} \right)$$

(1.58)

so (1.45) becomes

$$d_{osc}(E) \approx \sum_{k=1}^{+\infty} \frac{1}{k} \sin \left( k \left( \frac{S_x}{\hbar} - \frac{\beta_x \pi}{2} \right) \right) + \sum_{\ell=1}^{+\infty} \frac{1}{\ell} \sin \left( \ell \left( \frac{S_y}{\hbar} - \frac{\beta_y \pi}{2} \right) \right)$$

(1.59)

where \( k \beta_x = 2k \) and \( \ell \beta_y = 2\ell \) are the indices of the repetitions of the two PPO in the B approach. In particular they are additive under repetition of the PPO unlike those of approach A.

**General case.** The general case is very similar to this example: when not in the \( \Diamond \) situation the stable and unstable DOF are linearly decoupled so that the iterated stability matrices are of the form

$$M^r_\gamma = \begin{pmatrix} M^r_{\gamma,S} & 0 \\ 0 & M^r_{\gamma,U} \end{pmatrix}$$

(1.60)
where the letters $S$ and $U$ refer respectively to stable and unstable parts. Hence the denominators can be decomposed into a product

$$\sqrt{|\det(1 - M^r_{\gamma})|} = \sqrt{|\det(1 - M^r_{\gamma,S})|} \sqrt{|\det(1 - M^r_{\gamma,U})|}$$

(1.61)

The unstable determinant is a real number and thus does not introduce phase issues. On the other hand, the absolute values in the stable part of the numerators can be dropped to the expense of introducing a phase just like in the example. This phase cancels exactly with the non-additive part of the A-indices, making the B-indices appear.

So, overall, one can rewrite the GTF in the form B (and thereby benefit of its simpler-behaved indices) only if one can decompose the stability matrices as in (1.60). That is, those B-indices are always well-defined but in the non-decomposable case they do not provide enough information to write down the GTF, an extra phase related to the numerator being needed.

Back to the A approach, it is Meinrenken [Mei94] who proved the equality of the index appearing in the general form of the GTF (1.43) with one introduced in 1983 by Conley and Zehnder [CZ84]. It is an intersection number for pairs of curves in $Sp(2N, \mathbb{R})$, these curves being in our case the linearized flow and the identity.

The iteration properties of such index are non-trivial, as seen in the example. The advantage of the A-CZ version over the A-KM one is that a general iteration formula for the indices can be worked out explicitly. This has first been done by Sugita [Sug01] who used discretizations of quadratic phase space path integrals and normal forms for homotopic paths in $Sp(2N, \mathbb{R})$. Then later Muratore-Ginanneschi [MG03] found the same formula with field-theoretic tools. A slightly earlier mathematical paper by Long [Lon00] also seems to contain this formula but in a more abstract setting and without mentioning the relation of this index
to the GTF.

Using as a convention the modulo $2\pi$ part $\tilde{\chi}_j \in [0; 2\pi)$ of the stability angles $\chi_j$ of the PPO, the iteration formula reads

$$\eta^{(r)} = \sum_{j=1}^{N_{\text{ell}}} \left(1 + 2\left\lfloor \frac{r \tilde{\chi}_j}{2\pi} \right\rfloor \right) + r N_{\text{inv}} + 2mr$$

where $r$ is the number of repetitions of $\gamma$, $N_{\text{ell}}$ is the number of elliptic blocks of $M^r$, $N_{\text{inv}}$ is the number of inverse-hyperbolic blocks of $M^r$, and $m$ is another integer called the Gel'fand-Lidskií index [GL58]. In particular, given our earlier discussion, we find that in systems where there are no inverse-hyperbolic DOF the B-indices are equal to $2m$, a result which we shall use in chapter 3.

**CRL method.** We now review how the Conley-Zehnder can be computed in practise, first by the CRL method. The idea is simply to follow the derivation of the trace formula, where the final index $\eta^{(r)}$ is the sum of a Morse index $\theta^{(r)}$ (from the semiclassical Green’s function) and a contribution $\nu^{(r)}$ from the evaluation of the trace.

To compute $\theta^{(r)}$ one has to count the number of times the determinant $\det(B)$ of the upper-right block of the time-dependent variational matrix $N(t) = (A(t) \quad B(t))$ vanishes from $t = 0$ to $t = rT_\gamma$, not counting the initial zero. Then $\nu^{(r)}$ is equal to the number of negative eigenvalues of a matrix $W$ computed from the monodromy matrix $M^r = N(rT_\gamma)$

$$W := B^{-1}A + DB^{-1} - B^{-1}B^{-\top}$$

**PB method.** Here one decomposes $N(t)$ into its periodic and non-periodic parts $N(t) = N_p(t)N_n(t)$, where $N_n(t) = \exp(tK)$ with $K = \ln(M^r)/(rT_\gamma)$. The
Gel’fand-Lidskii index $m$ is then given by $m = \psi(rT) - \psi(0)$, where

$$
\psi(t) = \frac{1}{2\pi} \text{Arg} \det \left( A_p(t) + iB_p(t) \right)
$$

(1.64)

The remaining terms in the iteration formula (1.62) are then taken directly from $M^r$.

**Further notations.** In order to succinctly describe various situations which occur a lot in practice (and in subsequent parts of this thesis) we find useful to introduce the following notations.

As a common requirement suppose that we have a set of isolated PPO, which we call $\Gamma$, in some phase space $M$ of dimension $2N$. There are thus $N$ DOF in total which we denote by $(q_v)^N_{v=1}$. Now suppose that some DOF are nonlinearly decoupled from the motion. Then we call the DOF of the motion the $\Gamma$—explored DOF. Up to permutations of the indices we can assume without loss of generality that these are the first $J$ DOF $(q_v)^J_{v=1}$ of the system. In particular if $\Gamma$ cannot be confined to any strict invariant subspace of $M$ then $J = N$. On the other hand $J < N$ means that some DOF are nonlinearly decoupled and these will be called the $\Gamma$—unexplored DOF.

Then we distinguish the following four situations

- type A: $J \leq N$ and the PO are unstable with respect to all the DOF
- type B: $J < N$ and the PO are unstable with respect to all the $\Gamma$—explored DOF, but stable with respect to some of the $\Gamma$—unexplored DOF
- type C: $J = N$ and all DOF are stable
- type D: $J = N$ and there are both stable and unstable DOF (and since $J = N$ these are necessarily coupled)

In particular, the example of the irrational oscillator is of type C. Indeed, there the set of PPO of the system is $\Gamma = \{\gamma_x, \gamma_y\}$, and even though each PPO is restricted
to an axis (and hence to a subspace of phase space) the overall set of \(\Gamma\)-explored DOF is the full set of DOF of the system, \(x\) and \(y\), so \(J = N\). Moreover we saw that all DOF are stable in that example.

Note also that the case ♦ which prevents rewriting the GTF in the B form is a subcase of our type D, since there exists systems where nonlinearly coupled DOF are decoupled at the linear level while the converse is never true (see §1.7 in [MR98]).

From now on we shall denote by \(\beta_\gamma\) the B-index of a PO \(\gamma\), so that its \(r\)-th repetition is equal to \(r\beta_\gamma\). On the other hand for the A-indices we will use \(\eta_\gamma\), with the repetition \(\eta_\gamma^{(r)}\) given by (1.62).

Semiclassical spectral determinants and cycle expansions

Having seen how to compute all the ingredients in the GTF we now explain how this formula can be turned into a computationally efficient tool. We shall only consider systems of type B, hence it will always be possible to rewrite the GTF in terms of B-indices.

Moreover, we assume that the dynamics in the \(\Gamma\)-explored DOF is not only unstable but in fact uniformly hyperbolic and generated by a subshift of finite type*. Finally, we also require that the number of stable and unstable DOF are the same \(N_S\) and \(N_U\) for all orbits, a situation which will suit our needs in chapters 2 and 4.

Inspired by zeta functions and spectral determinants from chaotic classical dynamical systems and thermodynamic formalism [Rue78, PP90, Bal02], one can attempt to recast the poles of the imaginary part of \(\text{Tr}G_{\text{reg}}\) into zeros of a semiclassical
Chapter 1: Introduction

spectral determinant [CE89, CAM+05]

\[
\det(\hat{H} - E)_{sc} := e^{i\pi N_{sc}(E)} \exp \left( -\sum_{\tau} \sum_{r=1}^{\infty} \frac{1}{r} \sqrt{\det(1 - M_{r,\tau}^\gamma)} \prod_j \sin \left( r \frac{\chi_j}{2} \right) \right)
\]

where we use previous notations, in particular the \( \chi_j \) are the stability angles of the PPO \( \gamma \). (In fact we could also use instead their modulo \( 2\pi \) parts \( \tilde{\chi}_j \) since now there is nothing in the above formula which requires to use specifically one form or the other.)

Here \( t_{\gamma}^{(a,b)} \) is a weight corresponding to \( a \) excitations in the stable DOF and \( b \) excitations in the unstable DOF of \( \gamma \). The multi-indices \( a = (a_1, \ldots, a_{N_S}) \) and \( b = (b_1, \ldots, b_{N_U}) \) come from the expansion of respectively the stable and unstable parts of the determinant in the numerators.

The above product is an infinite one and its zeros do not come from equating \( 1 - t_{\gamma}^{(a,b)} = 0 \) for each factor. The idea of cycle expansion [Cvi88, CE89, CAM+05] is then to expand \( \det(\hat{H} - E)_{sc} \) into a sum using a well-defined ordering. In this work we shall only require finite products over \( a \) and \( b \) (see chapter 2 and 4) and in that situation we are left to study the expansion of dynamical zeta functions \( \zeta_{(a,b)} \) defined by

\[
\zeta_{(a,b)} := \prod_\gamma (1 - t_{\gamma}^{(a,b)}) \quad (1.66)
\]

The cycle expansion for such objects is then a simple sum over the admissible symbolic codes of the dynamics. For example in the case of a complete binary
dynamics with symbols 0 and 1 we get [CAM+05] (dropping a and b for simplicity)

\[ \zeta^{-1} = 1 - t_0 - t_1 - t_{01} - t_{001} - t_{011} - t_{0001} - t_{0011} - \ldots \]
\[ + t_0 t_1 + t_0 t_{01} + t_0 t_{10} + t_0 t_{001} + t_0 t_{011} + \ldots \]
\[ - t_0 t_{01} t_1 - \ldots \]  

(1.67)

The key step is then to reorganise this into a sum over pseudocycles. These are products of weights whose codes are factors of a given larger code: for example \( t_{01} \) and \( t_0 t_1 \) are two pseudocycles for the code 01 (the first one being a true cycle). In this way one obtains

\[ \zeta^{-1} = 1 - t_0 - t_1 - [(t_{01} - t_0 t_1)] - [(t_{001} - t_0 t_{01}) + (t_{011} - t_0 t_{011})] \ldots \]  

(1.68)

where \( t_0 \) and \( t_1 \) are called fundamental terms while the terms in brackets are curvature corrections. The terms in parenthesis are small, a fact called shadowing, allowing the curvature terms to decay exponentially with increasing code length.

Using such expansions, convergence of the zeros of \( \zeta^{-1} \) to the correct eigenvalues and resonances is obtained as the number of terms, i.e. of orbits, is increased.

The idea of using symbolic dynamics to enumerate periodic orbits was already present in the work of Gutzwiller on the Anisotropic Kepler Problem [Gut77, Gut90], but not the ideas of shadowing and pseudocycles which are crucial for fast convergence.

### 1.3 Organization of the thesis

Chapter 2 is a review of the literature on few-body Coulomb problems and in particular on their semiclassical aspects, a topic which developed essentially in
the past 15 years. We then present motivations for studying the hydrogen molecule in the same spirit and the kind of complications expected.

Then in chapter 3 we present our study of the classical hydrogen molecule. First, geometric aspects are analysed; in a second part we turn to dynamical aspects and investigate the structurally most important configurations.

In chapter 4, a semiclassical quantization based on this classical dynamics is performed and discussed. In particular we show that the ground state of the molecule can be described quite accurately, shedding a new light on the bonding phenomenon.

The final chapter summarizes the main results of this work.
Chapter 2

Few-body Coulomb problems

2.1 Motivation

How useful are semiclassical techniques in practise? What kind of classical dynamics do simple atoms possess? It is the aim of this chapter to answer these questions. We shall do so by reviewing the cases of the hydrogen molecular ion and of the helium atom. Their basic properties are well-understood quantum mechanically, but we shall see that a number of issues arise for which a semiclassical treatment provides useful structural information.

In both problems three bodies are involved, the general three-body Hamiltonian being

\[
\hat{H}\psi(q) = \sum_{i=1}^{3} -\frac{\hbar^2}{2m_i} \Delta_i \psi(q) + \left( \sum_{i<j} \frac{Z_iZ_j}{r_{ij}} \right) \psi(q) \tag{2.1}
\]

and our two examples belong to the two possible families of three-body systems which have a pair of identical bodies (i.e. in such cases there is either a pair of light bodies, as in He, or a pair of heavy bodies, as in \(H_2^+\)).

Many other values of the mass and charge parameters \(m_i\) and \(Z_i\) corresponding to actual three-body systems are realized in nature. We shall not study those here, but we expect similarities with either \(He\) or \(H_2^+\) as soon as two of the bodies are approximately similar. See [ARV05] for a recent review on how the existence of
bound states depends on masses and charges in three- and four-body quantum systems, including exotic ones (i.e. involving antiparticles).

2.2 Hydrogen molecular ion

2.2.1 Setting

The system is made of two identical positively charged point-like bodies (the nuclei, $Z_a = Z_b = +1$) and a much lighter negatively charged one (the electron, $Z_e = -1$). So we have nine degrees of freedom altogether and the first step is to remove three dofs by going to the center-of-mass (CM) frame.

In fact we can remove even more dofs by adopting the Born-Oppenheimer Approximation (BOA): since the mass ratio is large $M_{\text{nucl}}/m_{\text{elec}} \approx 1836$, the nuclei are much slower than the electrons. In the BOA one assumes that the electrons form an instantaneous potential which drives the nuclei. The latter are thus considered as fixed, with a parameter $R$ measuring the distance between them.

For each value of $R$ one solves an electronic Schrödinger equation and forms effective potentials for the nuclei

$$V_s(R) = \frac{1}{R} + E_{s}^{\text{el}}(R)$$

where $E_{s}^{\text{el}}(R)$ is an eigenvalue of the electronic Hamiltonian.

The resulting nuclear Hamiltonian is

$$\hat{H}_{\text{nucl}}\phi(R) := -\frac{\hbar^2}{2\mu} \Delta(R)\phi(R) + V_s(R)\phi(R)$$

where

$$\mu = \frac{M_{\text{nucl}} \cdot M_{\text{nucl}}}{M_{\text{nucl}} + M_{\text{nucl}}} = \frac{M_{\text{nucl}}}{2}$$
is the reduced mass. This $\hat{H}_{\text{nucl}}$ then has eigenvalues which are approximations of those of the original non-BOA Hamiltonian (2.1).

We shall adopt the convention that the nuclei are placed on the $z$–axis at the distance $\pm \frac{R}{2}$ away from the origin.

### 2.2.2 Solution of the quantum problem

#### Exact solution

It was found in the early days of quantum mechanics [Bur27] that the $H_2^+$ ion in the BOA provides a system which is separable in prolate ellipsoidal coordinates

\[
\begin{align*}
\xi &= \frac{\sqrt{x^2 + y^2 + (z - \frac{R}{2})^2} + \sqrt{x^2 + y^2 + (z + \frac{R}{2})^2}}{R} \in [1; +\infty[ \quad (2.5) \\
\eta &= \frac{\sqrt{x^2 + y^2 + (z + \frac{R}{2})^2} - \sqrt{x^2 + y^2 + (z - \frac{R}{2})^2}}{R} \in [-1; 1] \quad (2.6) \\
\phi &= \arctan\left(\frac{y}{x}\right) \in [0; 2\pi[ \quad (2.7) \\
\end{align*}
\]

It has explicit solutions (so-called spheroidal functions) expressed as infinite power series, see appendix 1 in chapter 6 of [BC03], and [Fal99]. The separation of the system comes from the commutation of $\hat{H}$ with two independent operators [EH49] which in atomic units read \(^1\)

\[
\begin{align*}
\hat{L}_z &:= -i \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \\
\hat{G} &:= \hat{L}^2 + \frac{R^2}{4} \left( \frac{\partial}{\partial z} \right)^2 + Rz \left( \frac{Z_b}{\sqrt{x^2 + y^2 + (z + \frac{R}{2})^2}} - \frac{Z_a}{\sqrt{x^2 + y^2 + (z - \frac{R}{2})^2}} \right) \\
\end{align*}
\]

where $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. So one can label states locally with three quantum numbers $n$, $m$ and $g$. The geometrical symmetry group of bound states

\(^1\)The relation of this operator $\hat{G}$ with Erikson and Hill’s $\hat{\Omega}$ is $\hat{G} = \hat{\Omega} + \frac{R^2}{2} \hat{H}$.
is the 1-dimensional \(SO(2)\), while the degeneracy group of such states is the 3-dimensional \(SO(2) \otimes SO(2) \otimes O(2)\) [AM67]. Recall that for the hydrogen atom those groups are respectively the 3-dimensional \(SO(3)\) and the 6-dimensional \(SO(4)\) (see appendix B), so there is much less symmetry in \(H_2^+\) than in \(H\).

**Matched-asymptotics solution**

The explicit solutions are nevertheless quite cumbersome to use. In order to approximate them by simpler expressions, Patil [Pat00] used the constraints given by the asymptotic and coalescence properties of the exact wavefunctions (again in prolate ellipsoidal coordinates) to construct explicit approximate eigenfunctions \(\tilde{\psi}_m\) of good quality. Namely, writing

\[
\tilde{\psi}_m(\xi, \eta, \phi) = \left(\xi^2 - 1\right)^{m/2} (1 - \eta^2)^{m/2} f(\xi)g(\eta)e^{im\phi} \quad (2.11)
\]

we get conditions on \(f\) and \(g\) by considering the limits \(\{\xi \to 1\) and \(\eta \to \pm 1\}\) when the electron collides with either nuclei. Similarly by considering the asymptotic limit \(\xi \to +\infty\) the first few coefficients of an expansion of \(f\) in \(\frac{1}{\xi}\) can be determined. An approximate wavefunction of good quality is then obtained by modifying a Guillemin-Zener type one (i.e. one of the form \(\psi \sim e^{-a\xi \cosh(b\eta)}\)) so that these asymptotic conditions are fulfilled.

In the case of the ground state, which satisfies \(\hat{L}_z = 0\), we can work in the plane \((x, z)\), or equivalently \((\xi, \eta)\). Patil’s approximate wavefunction is then

\[
\varphi(\xi, \eta) = C(1 + B\xi)^\beta e^{-a\xi \cosh(A\eta)} \quad (2.12)
\]

where all the parameters depend explicitly on \(R\) and the eigenvalue \(E_\ast\) only \((E_\ast\) being found iteratively).

Recall the relation which expresses the invariance of local probability under
change of coordinates

$$|\psi(x, y, z)|^2 dx dy dz = |\tilde{\psi}(\xi, \eta, \phi)|^2 \cdot Jac(\xi, \eta, \phi)d\xi d\eta d\phi$$  \hspace{1cm} (2.13)

where $Jac(\xi, \eta, \phi)$ is the determinant of the Jacobian matrix from Cartesian to prolate ellipsoidal coordinates. We can now plot $\varphi$ back in Cartesian coordinates (instead of prolate ellipsoidal ones as is usually done). The figures show a sequence for various values of $R$ of Patil’s ground state probability densities averaged over $\phi$ (in a half $(x, z)$ plane only for better visualization). Note that we use the same scale for the $(x, z)$ coordinates throughout, while the scale for probability densities varies.

![Figure 2.1: Patil’s ground state probability density of $H^+_2$ at $R = 1.0$](image)

On these plots $Prob(x_0, z_0)$ is the probability of finding the electron on the circle $C = \{(x, y, z) \in \mathbb{R}^3 | x^2 + y^2 + z^2 = x_0^2 + z_0^2\}$ around the $z-$axis passing through $(x_0, z_0)$. As expected the probability of finding the electron on the nuclei is 0 at all $R$ (something not immediately obvious in non-cartesian plots). We moreover recover the behaviour of the ground state of the $H$ atom at small $R$ and that of two $H-$like densities at large $R$. 

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Figure 2.2: Patil’s ground state probability density of $H_2^+$ at $R = R_{eq} = 2.0$

Other topics

Even with the knowledge of such explicit solutions, either exact or approximate, one still has to answer the following important structural questions.

First, why can the system be stable in the first place? That is, what is the origin of the very shape of the BO electronic curves with these wells supporting states below the ground state energy of $H + H^+$?

Also, we saw that there are as many quantum numbers\(^2\) as degrees of freedom here, but the labelling of states provided by the triplets $(n, m, g)$ is a priori valid only locally: are these numbers in fact globally defined?

Regarding the semiclassical approximation one may ask: how accurate is it here? Is $\hbar$ small compared to the characteristic actions of this system, and what do we recover? And if a semiclassical approximation is valid, how does it compare to the quantum mechanical one in terms of computational cost?

\(^2\)Sometimes one finds the terminology “good quantum numbers” to insist on the fact that one is speaking only about numbers associated to exact symmetries of the full Hamiltonian, and neither about approximate symmetries thereof nor about numbers of the system with the interactions switched off.
2.2.3 Origin of molecular stability

Let us answer the questions raised in the previous section. Since the BO curves are all of the form

$$U(R) = \frac{1}{R} + E^\text{el}(R)$$

the problem boils down to accounting for the behaviour of the electronic eigenenergies. And since the values in the $R \to 0$ limit are those of the helium ion $He^+$ (which are lower than those of $H + H^+$) what matters is the growth rate of $E^\text{el}(R)$ for increasing values of $R$. One would like to account for this growth rate in terms of properties of the Hamiltonian of $H_2^+$.

In the case of the ground state $^2\Sigma_g^+$ curve, the textbook approach (see e.g. [Pra00]) is to consider within the LCAO approximation an electronic wavefunction of the form $\psi = \alpha \phi_a + \beta \phi_b$, where $\phi_a$ and $\phi_b$ are hydrogen 1s orbitals centered on respectively the first and second nuclei. Standard application of the

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3This is the usual molecular term symbol (here for a homonuclear diatomic molecule, i.e. of $D_{\infty h}$ symmetry): $\Sigma$ says that total angular momentum is 0; $+$ indicates invariance of the wavefunction under reflexion with respect to a plane perpendicular to the nuclear axis through its middle, while $g$ means invariance by inversion through the middle of the internuclear axis; finally the left superscript is equal to $2S + 1$, accounting for total spin.

4Linear Combination of Atomic Orbitals, see chapter 1.
variational method then leads to a bonding curve of the form

\[ E^{el}_{LCAO}(R) = E_H - \frac{j + k}{1 + s} \] (2.15)

where

\[ k := \int \phi_a \cdot \frac{1}{r_a} \cdot \phi_b = \int \phi_a \cdot \frac{1}{r_b} \cdot \phi_b \text{ exchange integral} \] (2.16)

\[ j := \int \phi_a \cdot \frac{1}{r_a} \cdot \phi_a \text{ Coulomb integral} \] (2.17)

\[ s := \int \phi_a \cdot \phi_b \text{ overlap integral} \] (2.18)

One finds that the \( E^{el}_{LCAO}(R) \) curve provides a crude but qualitatively satisfying model of the ground state. So the growth rate of the molecular ground state curve of \( H^+_I \) is in essence governed by the varying overlap of a simple coherent superposition of two individual atomic orbitals.

Let us now move on to the study of the semiclassical limit for our system, and of the range of validity of the quantum numbers.

### 2.2.4 Semiclassical limit: tunneling geometry, monodromy and bifurcations

Interestingly, the structure of the electronic BO curves can also be recovered from a semiclassical study, as was shown by Strand and Reinhardt [SR79]. In the case of \( L_z = 0 \), a given value of the two other classical integrals \( H \) and \( G \) corresponds to a certain region in phase space, which is found to be either the empty set (classically forbidden region), or one torus, or a pair of tori. These tori belong to one of three families: there are two families \( P_1 \) and \( P_2 \) of single torus and one family \( P_3 \) of tori pairs (corresponding to the electron being trapped around the first or the second nucleus), see\(^5\) fig 2.4.

\(^5\)The initial conditions we have taken here are \( R = 2, x = 0.5, z = 2, p_x = 0 \) with respectively \( p_x = 0.5, 1, 1.2 \) for the \( P_1, P_2, P_3 \) families.
A straightforward use of the EBK rules does not provide satisfactory results since it turns out that the ground state wavefunction corresponds to a tori pair. After inclusion of tunneling between those (by using uniform EBK rules which match EBK results across the potential barrier, see [SR79]) one obtains a very satisfying result (see fig. 2.5). The same method provides good results for many other states, in particular for \( L_z \neq 0 \) as well where we have this time non-planar orbits organized into two families. This semiclassical approach thus presents an alternative point of view on the binding phenomenon: we have an integrable system where the ground state wavefunction turns out to localize roughly on a pair of tori, each of them having configuration space properties reminiscent of an hydrogen atom (i.e. revolving around only one of the two nuclei).

At this point let us note that there has been some other semiclassical work on \( H_2^+ \) [DYB95, DY99]. To quantize the system, these authors use the set of periodic
orbits within the Berry-Tabor formula (which is an analog of the Gutzwiller trace formula in the case of integrable systems [BT76]) instead of tori as above. They obtain reasonable results (error less than a percent) for the ground state energy at \( R = 1 \), while the excited states are not as accurate. Unfortunately, what they do to obtain the values of the eigenenergies at other internuclear distances is to scale the ones at \( R = 1 \) using the relation \( E(R) = E_1/R \). This is an incorrect way to proceed, since this relation assumes that varying \( R \) does not change which periodic orbits to use in the Berry-Tabor formula. In fact not all periodic orbits exist at all values of \( R \) as bifurcation diagrams show. Instead, one should study the classical system at some fixed negative value of the Hamiltonian, say \( H = -1 \), and for each value of \( R \) one should find which periodic orbits exist, and compute from them the levels via the Berry-Tabor formula. In that way one should in fact probably not require as many periodic orbits as these authors have used (thousands) to obtain reasonable results for all values of \( R \). Also, one should take into account tunneling, which is
not the case in the usual Berry-Tabor approach.

**Globalization of local quantum numbers**

Now we can turn to the issue of the labelling of states by our three quantum numbers. It turns out that this labelling is not global, one cannot use $n, m, g$ continuously for all states. This was shown by Waalkens and collaborators [WJD03, WDP04] as a byproduct of their comprehensive account of the properties of the classical two-center problem from the point of view of energy-momentum maps.

They studied how the phase space of our system is foliated by tori, and this foliation has bifurcations as we vary the values of the integrals. More precisely, there is a change of caustics as $L_z \to 0$: in the system there are two families of trajectories with $L_z \neq 0$ (non-planar orbits); one of them bifurcates into two of the planar families ($P_1$ and $P_2$) in the limit of vanishing angular momentum, while the other goes smoothly to the other planar family ($P_3$). As a consequence, there is a topological obstruction called *monodromy* which prevents the action variables to exist globally. Monodromy means that there is at least one closed path in the image of the energy-momentum map whose associated torus bundle is non-trivial. For example, since there exists isolated critical points of the energy momentum map with $L_z = 0$ (corresponding to singular tori), any loop of values $(h, \ell)$ of $H$ and $L_z$ around such a point for a fixed value of $G$ provides the required path.

This topological obstruction to global actions is then transmitted to the quantum numbers: doing (uniform) EBK quantization, which we saw in chapter 1 to be an action quantization, provides a lattice of accurate approximate eigenstates, and this lattice then is not globally labelled by the quantum numbers. One says that there is *quantum monodromy*. This fact can easily be seen by moving a *quantum elementary cell* around the critical point and finding that it does not go back to itself, it is shifted. This is illustrated in fig. 2.6, where the EBK lattice is put on
top of a slice of the image of the energy-momentum map at some fixed value of $G$. The circled point is the isolated critical value mentioned above, which corresponds to a singular tori at the boundary between the planar families $P_1$ and $P_2$. In configuration space this is an orbit joining the two nuclei along the $z-$axis.

Figure 2.6: Zhilinskií diagram showing monodromy in $H_2^+$, after [WJD03] (see text)

One could detect quantum monodromy only by diagonalizing the Hamiltonian, plotting the eigenstates and figuring out whether the lattice has defects or not. But the number of states required is not known a priori and depending on the system this may mean a lot of them. The approach via the geometry of the classical system is more systematic. See [EJS04] for more details on monodromy and a worked-out example. Vû Ngọc [VuN99] has defined a more conceptual mathematical notion of quantum monodromy (using cocycles with values in affine groups).

2.2.5 Adiabatic invariant and dynamics beyond the BOA

Some work has also been done, still from a semiclassical point of view, to characterize the properties of $H_2^+$ without relying on the BOA. First, an adiabatic invariant$^6$

$^6$That is, a quantity which is approximately conserved as one varies slowly the parameters. See page 293 of [Arn89] for more details.
of order $O\left(\frac{m}{M}\right)$ has been found \[MBN95\] which allows to characterize the zones of KAM stability of the BOA problem.

Then, a primitive semiclassical quantization in 3-DOF by the Surface-Of-Section method \footnote{The basic idea is to compute approximately the actions of a torus by measuring the area of its intersection with various planes, and then EBK quantize it.} has been done \[STSN98\] and it accounts for only 10\% of bonding but with a correct sign (note that action quantization is not expected to work well here: we have a non-integrable system so the size of the KAM islands plays a crucial role for this kind of quantization). It is to be noted that some of the periodic orbits found in those works average roughly on the wavefunction’s maximum zone, with the electron classically going back and forth around both nuclei.

Finally, in \[DBY99\] a further study of parts of the full 5-dimensional $L_z = 0$ subspace were done including lifetime plots. They confirmed that one family of tori (the P1 one) is made of unstable orbits while for the other two families some orbits are stable. They also looked at collinear $H_2^+$ and found that the simplest periodic orbit (the so-called asymmetric stretch) is stable. Again orbit quantization predicts binding (i.e. correct sign) but is not at all accurate (the error is about 100\%).

To conclude on $H_2^+$, a thorough knowledge of the classical BOA system has been achieved and this has made it possible to recover many quantum results. On the other hand the full classical system is a mixed one which remains to be explored in a systematic way, for instance using so called uniform trace formulas \[Cre96,KWB04\] which take into account the loss of integrability and the fact that non-isolated periodic orbits appear when bifurcations occur.
Chapter 2: Few-body Coulomb problems

2.3 Helium atom: experiments and quantum aspects

The case of the helium atom has received a lot of attention during the past four decades, and this has been thoroughly reviewed [TRR00]. We will recall the main historical steps here and then cover the semiclassical aspects, including recent developments.

2.3.1 Experimental input and spectral structure

While the bound state spectrum could be computed and classified satisfactorily in the early years of quantum mechanics, the resonance spectrum of helium came under investigation much later. In the 1960’s a series of experiments by Madden and Coddling on this resonance spectrum revealed that it is organized in a way which is very different from the bound spectrum and triggered a lot of work, as we now explain.

First, recall that helium possesses some exact (total) quantum numbers: $L$ (angular momentum), $M$ (component of angular momentum along some reference axis), $S$ (spin), $M_S$ (spin projection on the reference axis) and $\pi$ (parity) leading to the usual spectroscopic notation $2S+1L\pi$. Very accurate numerical calculations using complex rotation for the $1S^e$ states are shown in fig 2.7. One observes three regions populated respectively by bound states (including the ground state), resonances, and complete fragmentation.

An independent-electron model would lead to series with the inner electron in a state $(N, \ell_1)$ while the other progresses as $(n \to \infty, \ell_2)$. For $S$–states we have $L = \ell_1 + \ell_2 = 0$ with $\ell_1$ having values ranging from 0 to $N - 1$, so one would expect $N$ distinct series converging to each ionization potential $I_N = -\frac{Z^2}{2N\pi}$. It is the case, as can be seen from the figure, but this is all such an independent-electron model can offer: it also predicts that the states from the different series have all
the same lifetimes, but experiments show that this is not the case. Indeed only the first series starting from the left is easily observed in each group and the others are orders of magnitude fainter. This fact has been confirmed by more recent experiments at BESSY in Berlin [DXP+91, DRK92, DSR+95, DSR+96], and later at ALS in Berkeley [SKD+96] with a much better resolution.

This implies that those resonances, so-called *doubly excited states (DES)*, are the result of a high degree of correlations between electrons. Therefore there lacks a satisfactory labelling of such states: accurate CI calculations involve many configurations with a large amount of mixing, and one does not have *a priori* knowledge of which precise configurations are involved in a given resonance. Theoretical models to quantitatively tackle those problems were built from both quantum and semiclassical point of views over many decades.
2.3.2 Quantum approaches

Three main approaches can be distinguished: the group theoretical one which
developed in the 1970s; the hyperspherical adiabatic one following it in the early
1980s; and finally the molecular orbital (MO) one of the late 1980s.

Group theoretical approach

The group theoretical treatment of the hydrogen atom is well-understood, see ap-
pendix B. What Wulfman [Wul73] and independently Sinanoğlu & Herrick [SH75]
found was an analytical method to provide the configurations which make up a
given resonance together with approximate mixing coefficients of very good qual-
ity. In fact this was done in the case of intrashell resonances, i.e. those for which the
principal number of the inner electron, \( N \), is equal to the one of the outer electron,
\( n \). For example when \( N = n = 2 \) they found that the two numerically obtained
states

\[
|^{1}S_{a}\rangle = -0.476 \, |2s^{2} \, ^{1}S\rangle + 0.880 \, |2p^{2} \, ^{1}S\rangle \\
|^{1}S_{b}\rangle = -0.880 \, |2s^{2} \, ^{1}S\rangle - 0.476 \, |2p^{2} \, ^{1}S\rangle
\]  

are very well approximated by their analytically found states

\[
|0,0 \, ^{1}S\rangle = -\frac{1}{2} \, |2s^{2} \, ^{1}S\rangle + \frac{\sqrt{3}}{2} \, |2p^{2} \, ^{1}S\rangle \\
|2,0 \, ^{1}S\rangle = -\frac{\sqrt{3}}{2} \, |2s^{2} \, ^{1}S\rangle - \frac{1}{2} \, |2p^{2} \, ^{1}S\rangle
\]

with \([P, Q]\) denoting an \( SO(4) \) irreducible representation (where \( P := u + v \geq 0 \)
and \( Q := u - v \), with \( u \) and \( v \) as in appendix B).

Here the \( SO(4) \) is not a 1-electron symmetry as in the hydrogen atom, but an
approximate 2-electron one. The idea is that introducing the operators

\[ \hat{L}^{(12)} := \hat{L}^{(1)} + \hat{L}^{(2)} \]  
\[ \hat{A}^{(12)} := \hat{A}^{(1)} - \hat{A}^{(2)} \]  

(2.23) (2.24)

(which are respectively the total angular momentum and a measure of electronic alignment in terms of Pauli-Laplace-Runge-Lenz operators) one generates an \( \mathfrak{so}(4) \) algebra, and 2-electron states within its irreps are thus labelled as \( |PQLM\rangle \). Such operators allow to approximate the electron-electron interaction as follows: one constructs a group theoretic operator \( \hat{H}_{GT} \) depending only on these operators (and those which commute with them) whose diagonalization leads to an approximate diagonalization of the true Hamiltonian. Explicitly, one finds that the Coulomb repulsion term can be approximated as

\[ \frac{1}{r_{12}} \approx \frac{1}{2} \frac{1}{\delta_1 + \delta_2 \hat{A}^{(12)}} \]  

(2.25)

with \( \delta_1 = 5.0820 + \frac{2.8507}{Z} \) and \( \delta_2 = 0.2123 - \frac{0.0434}{Z} \).

The associated approximate quantum numbers describing the behaviour of the electron pair are

\[ T := |Q| \text{ with values 0, 1... to } \min(L, N - 1) \]  
\[ K := P - n - 1 \text{ ranging from } -(N - 1), -(N - 3) \ldots \text{ to } N - 1 \]  
\[ A := \pi(-1)^{S+T} \text{ when } K > L - N \text{ and } A := 0 \text{ else.} \]  

(2.26) (2.27) (2.28)

For intrashell resonances these numbers can be related to the average value of the cosine of the interelectronic angle \( \theta_{12} \), namely (see [Her83]) it is found

\[ \langle \cos \theta_{12} \rangle = \frac{4N^2 - 3(N + K)^2 - 1}{8N^2} \]  

(2.29)
Intuitively, $K < 0$ means the electrons are on the same side of the nucleus and $K > 0$ that they are on opposite sides; $T$ measures the projection of $\vec{L}^{(12)}$ on the electron-electron axis; and $A = 1$ if the electrons both approach or go away from the nucleus, $A = -1$ if one approaches while the other goes away.

To describe other resonances apart from intrashell ones, Herrick and Kellman have used various decompositions of this $so(4)$ to produce multiplets of states. Rotor-like supermultiplets of states (the system electron-nucleus-electron is treated in the spirit of XYX molecules) are also obtained using an embedding of each 1-electron $SO(4)$ in $SU(4)$ so that 2-electron states are embedded in $SU(4) \times SU(4)$, although this is done at the expense of introducing some spurious states. Another approach without this shortcoming uses $SO(5)$ properties instead and has been sketched by Wybourne [Wyb99].

Despite these successes, the group theoretical approach has some important shortcomings. First, the new labels are valid approximate quantum numbers only as long as series do not overlap (i.e. they are for example valid for $N \leq 4$ in the case of $1^S_e$ states). For highly excited intershell states Herrick’s formula is $\langle \cos \theta_{12} \rangle \sim -\frac{K}{N}$ and comparison with ab initio results show it is valid only for the leftmost series $K = N - 1$ which corresponds to electrons on opposite sides of the nucleus [BWR95, BBL98, B99]. In fact, from a “quantum chaos” point of view the loss of these approximate quantum numbers should imply that the statistical properties of the spectrum can be described by a Random Matrix type law as opposed to Poissonian statistics at lower energy, and this has indeed been verified experimentally and numerically [PGD⁺00].

Also, and crucially, an explanation of the different widths of the various DES series is lacking in this approach. Finally there is no explicit knowledge of the special coordinates which allow for such an approximate symmetry (i.e. separability) to exist in the 2-electron dynamics. All this motivated other approaches in the study of doubly excited states.
Hyperspherical adiabatic approach

Here one forces a separation of variables by choosing bluntly the hyperadius \( R := \sqrt{r_1^2 + r_2^2} \) (i.e. the overall "size" of the atom) as a slow variable. One then has to solve numerically a non-separable 5-dimensional angular problem (three angles describing the rotation of the system and two angles related to electronic correlations: \( \alpha := \tan^{-1}\left(\frac{r_2}{r_1}\right) \) and the interelectronic angle \( \theta_{12} \)). Its solutions are adiabatic potential curves which converge to each ionization threshold \( I_N \), and so each of them carries naturally a series of states. One indeed recovers the DES quite accurately in this way. Moreover, the 2-electron densities have nicely regular patterns in \( \alpha, \theta_{12} \) coordinates.

A breakthrough then came when Lin [Lin84], by studying the correlation patterns of such 2-electron densities, succeeded in relating this hyperspherical setting to the group theoretical one, by associating to each adiabatic curve specific values of the approximate \( K, T, A \) numbers. In particular it encompassed singly excited states for which \((K, T) = (0, 0)\) and accounted for supermultiplet rotor-like structures in DES (for given \((K, T, A)\) higher values of \( L \) correspond to higher adiabatic curves). This also allowed him to find approximate photoabsorption selection (or "propensity") rules \( \Delta A = 0 \) and \( \Delta T = 1 \), as well as rules for electron-atom collisions \( \Delta N = 0, \Delta K = 1, \Delta T = 0, \Delta A = 0 \).

Still, this choice of slow variable and the origin of the observed nodal patterns of 2-electron densities need, beyond being observed numerically, to be justified.

Molecular orbital approach

In this approach [FB88], one finally answers the question of the origin of the approximate separability of the DES wavefunctions by introducing another choice of slow variable for which an associated approximately separating coordinate system is available. The idea is to choose the slow variable to be the electron-pair vector \( \vec{r}_{12} := \vec{r}_2 - \vec{r}_1 \). The motion of the electronic center of mass then separates from
electron-electron vibrations and one is led to the $H_2^+$ Hamiltonian, which as we saw above can be conveniently studied in prolate spheroidal coordinates $(\xi, \eta, \phi)$.

This means that one again obtains adiabatic potential curves, but which are now labelled by the corresponding quantum numbers $n_\xi, n_\eta, n_\phi$. In this way one gets a complete classification of DES by $(L, M, S, M_S, \pi, \eta, n_\xi, n_\eta, n_\phi)$ (with $\eta := n - N$) and an approximate nodal structure for wavefunctions in a natural way. Propensity rules result from the pronounced avoided crossings between the adiabatic curves, and the correspondance with previous approaches in terms of quantum numbers is

\begin{align*}
n_\xi & = \frac{1}{2}(N - K - 1 - T) \tag{2.30} \\
\left\lfloor \frac{n_\eta}{2} \right\rfloor & = \frac{1}{2}(N + K - 1 - T) \tag{2.31} \\
n_\phi & = T \tag{2.32} \\
(-1)^n_\eta & = A. \tag{2.33}
\end{align*}

In fact such separability is indeed only an approximate one, since as shown by Rost and coworkers [RGR+91] accurate resonance wavefunctions (computed by direct diagonalisation in Sturmian basis) exhibit a mixing between $r_{12}$ and $\eta$ motions. These authors then attempted to explain the validity of their adiabatic separation by relating it to the classical dynamics of the system. We shall now turn to these classical aspects in detail: as we shall see, semiclassical studies have provided many complementary insights about the resonances of helium.
Chapter 2: Few-body Coulomb problems

2.4 Helium atom: semiclassical aspects

The semiclassical study of the helium atom developed in the early 1990’s and continued steadily until the present time. The following is a synthesis of these results, where some emphasis has been put on aspects which will be important for our work on the hydrogen molecule.

2.4.1 Setting

We shall use the infinite mass approximation for the nucleus and employ atomic units throughout. The system is made of a body of charge \( Z \) which is fixed at the origin (the nucleus), and two identical bodies with masses and charges set to unity (the electrons) moving in \( \mathbb{R}^3 \). For the time being we shall keep \( Z \) as a parameter, and restrict to the helium case \( Z = 2 \) later on.

We have six degrees of freedom, our configuration space is \( Q = \mathbb{R}^6 \) and phase space is \( M = T^*Q \cong \mathbb{R}^{12} \). We shall note \( x_i, y_i, z_i \) and \( q_i := (x_i, y_i, z_i) \) the Cartesian coordinates of the two electrons \( (i = 1, 2) \), and \( p_{x_i}, p_{y_i}, p_{z_i} \) and \( p_i := (p_{x_i}, p_{y_i}, p_{z_i}) \) the corresponding momenta. Points of \( M \) will be noted by \( w := (q_1, q_2, p_1, p_2) \).

The Hamiltonian then reads \( H(w) = T(p) + V(q) \) with

\[
T(p) := \frac{p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2 + p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2}{2} \quad (2.34)
\]

and

\[
V(q) := \frac{1}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}} - \frac{Z}{\sqrt{x_1^2 + y_1^2 + z_1^2}} - \frac{Z}{\sqrt{x_2^2 + y_2^2 + z_2^2}} \quad (2.35)
\]

The first term in \( V \) is the electron-electron repulsion term, while the two others are the attraction of either electrons with the nucleus.
The equations of motion are then
\[
\frac{dx_i}{dt} = \frac{\partial H}{\partial p_{x_i}} = p_{x_i} ; \quad \frac{dy_i}{dt} = \frac{\partial H}{\partial p_{y_i}} = p_{y_i} ; \quad \frac{dz_i}{dt} = \frac{\partial H}{\partial p_{z_i}} = p_{z_i}
\]
(2.36)
\[
\frac{dp_{x_i}}{dt} = -\frac{\partial H}{\partial x_i} = \frac{\kappa_i (x_2 - x_1)}{((x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2)^{\frac{3}{2}}} - \frac{Z x_i}{(x_1^2 + y_1^2 + z_1^2)^{\frac{3}{2}}}
\]
(2.37)
\[
\frac{dp_{y_i}}{dt} = -\frac{\partial H}{\partial y_i} = \frac{\kappa_i (y_2 - y_1)}{((x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2)^{\frac{3}{2}}} - \frac{Z y_i}{(x_1^2 + y_1^2 + z_1^2)^{\frac{3}{2}}}
\]
(2.38)
\[
\frac{dp_{z_i}}{dt} = -\frac{\partial H}{\partial z_i} = \frac{\kappa_i (z_2 - z_1)}{((x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2)^{\frac{3}{2}}} - \frac{Z z_i}{(x_1^2 + y_1^2 + z_1^2)^{\frac{3}{2}}}
\]
(2.39)

where \(\kappa_1 = -1, \kappa_2 = 1\).

Hamiltonian systems with similar long range interactions have been studied for a long time in celestial mechanics. As far as trajectories are concerned, they have been computed essentially by numerical means. The reason is that although an explicit series solution is known for most trajectories\(^8\) of the \(N\)–body problem [Wan91] it is not useful at all since it converges extremely slowly, and there is no hope of improving its convergence (this being a consequence of the complicated geometry of the phase space of this non-integrable system). In the same fashion, classical Coulomb systems (like our helium atom) have been studied mostly numerically, guided by some considerations on the geometry of phase space.

Now, our aim is to recover semiclassically the \(^1S^e\) spectrum mentioned above, which as we saw earlier consists of bound states and of resonances whose corresponding eigenvalues have a negative real part. Hence, given the semiclassical framework of chapter 1, we shall be interested by the classical dynamics corresponding to all the negative values of the Hamiltonian. It turns out that we need only study the dynamics for one such negative value of \(H\) as we now show.

\(^8\)Except trajectories where two or more bodies collide, which form a set of zero measure [Saa81].
2.4.2 Scaling property

A great simplification of the study of the classical dynamics is possible here due to the fact that $H$ is a homogeneous function of its variables. Namely, the following scaling transformation relates the values at $E = -1$ of the positions, momenta, times and actions (marked with a tilde) to those at any other negative energy:

$$
q_i(E) = \frac{\tilde{q}_i}{-E} ; \quad p_i(E) = \sqrt{-E} \tilde{p}_i ; \quad t(E) = \frac{\tilde{t}}{(-E)^{3/2}} ; \quad S(E) = \frac{\tilde{S}}{\sqrt{-E}} \quad (2.40)
$$

In the following we thus deal exclusively with dynamics at $E = -1$, which takes place on the level set

$$
\mathcal{M}_{-1} := \{ w \in \mathcal{M} \mid H(w) = -1 \} \quad (2.41)
$$

and we drop the tilde for brevity.

In fact, the flow is not defined at all point of $\mathcal{M}_{-1}$, there are singular points which we now study.

2.4.3 Collision singularities

Collision set

From the expressions of $V$ and $H$ above it appears that these functions are defined everywhere except on the collision set

$$
\mathcal{C} := \{ w \in \mathcal{M} \mid q_1 = 0 \} \cup \{ w \in \mathcal{M} \mid q_2 = 0 \} \cup \{ w \in \mathcal{M} \mid q_1 = q_2 \} \quad (2.42)
$$

The origin in $\mathcal{O}$ is the only place where a triple collision can happen. The other points of $\mathcal{C}$ correspond to binary collisions.

Due to our energy requirement $H = -1$ we remark that the binary electron-electron collision cannot occur, since in that case the negative part of $V$ stays finite.
while the positive part blows up. On the other hand, the triple collision and the electron-nucleus binary collisions are energetically allowed.

The Hamiltonian flow corresponding to $H$ behaves very differently near a binary collision compared to a triple collision. These issues have been thoroughly studied in the context of celestial mechanics many decades ago, and the same tools can be used here.

Types of regularizations

The question one wants to answer is: can we continue the motion after a collision, and if so how is it done? That is, one wants to study the regularization of a collision singularity. Historically, there have been two different notions of regularization. Suppose that our collision trajectory\(^9\) is parametrized by a time parameter $t$ which increases from negative times until the collision happens at $t = 0$ (the system being autonomous we can always shift the time axis so that it is the case).

First was introduced what is called analytic regularization\(^{10}\) of the collision trajectory [Sun12]. In that case, one attempts to continue the trajectory $w(t)$ through the collision singularity by looking for a suitable parametrization by a modified time $\tau = f(t)$ so that the resulting orbit $\tilde{w}(\tau)$ is analytic with respect to $\tau$ in an interval containing the collision time $\tau_0 = f(0)$. If this is possible, then one uses the analytic continuation principle to conclude that the collision trajectory can be continued for positive times by its time-reversal image.

The other notion is block regularization\(^{11}\), which is a geometric idea [Eas71]. Here, one studies not only the collision orbit but also its neighborhood in phase space. Namely, one looks at maps which to a tube of trajectories near the collision orbit associate a tube of trajectories near an ejection orbit\(^{12}\). The aim is then to

---

\(^9\)An orbit which ends at a collision and which had no collision at earlier times.

\(^{10}\)Also called sometimes branch regularization, or Siegel regularization.

\(^{11}\)Also called Easton regularization.

\(^{12}\)That is, an orbit which starts at a collision (i.e. it is a collision orbit when seen backwards in time).
study the smoothness of such maps, to see if the geometry of the neighboring orbits is nice enough to enforce a smooth and unique way of gluing together the collision trajectory to the ejection trajectory at the singularity.

Types of collisions

To cover cases useful for both the helium atom and our study of the hydrogen molecule in chapter 3 we consider here Coulomb systems with up to \( n = 4 \) bodies. As far as regularization is concerned, there are only three possible collision behaviours.

**Isolated binary collisions.** The first kind of behaviour is that of an isolated binary collision at \( t = 0 \). This means that a pair of bodies collides while all the others remain separated from one another (example: a binary collision in the helium atom). In that case it is possible to regularize the collision in both the analytic and geometric senses.

The analytic regularisation is performed by using \( \tau = t^{1/3} \) to parametrize the trajectory across the singularity; this goes back to Sundman [Sun12]. The trajectory is thus continued for positive times by its time-reversal image: in configuration space this produces an elastic bounce of the two bodies.

Block regularization is also possible. For bodies moving in the plane it can be done (among various other methods) by the Levi-Civita transformation [LC20]. Suppose for simplicity that we consider the Kepler problem with one of the colliding bodies fixed at the origin while the other has coordinates \( x, y \). First, one introduces new variables \( Q_1 \) and \( Q_2 \) by

\[
\mathcal{L} : \begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix} \mapsto \begin{pmatrix} x \\ y \end{pmatrix} = \mathcal{L}(Q_1, Q_2) \begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix} = \begin{pmatrix} Q_1 & -Q_2 \\ Q_2 & Q_1 \end{pmatrix} \begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix} = \begin{pmatrix} Q_1^2 - Q_2^2 \\ 2Q_1Q_2 \end{pmatrix}
\]

\( ^{13} \)The idea was in fact found independently some years earlier by Bohlin [AKN97].
and so the distance to the collision becomes 
\[ r = \sqrt{x^2 + y^2} = Q_1^2 + Q_2^2 =: R^2 \]
(sometimes called “the squaring trick”).

The associated momentum transformation making this change of variables symplectic is then

\[
L^* : \begin{pmatrix} P_1 \\ P_2 \end{pmatrix} \mapsto \begin{pmatrix} P_x \\ P_y \end{pmatrix} = (\nabla L)^{-\top} (Q_1, Q_2) \begin{pmatrix} P_1 \\ P_2 \end{pmatrix} = \begin{pmatrix} \frac{Q_1 P_1 - Q_2 P_2}{2(Q_1^2 + Q_2^2)} \\ \frac{Q_2 P_1 + Q_1 P_2}{2(Q_1^2 + Q_2^2)} \end{pmatrix}
\]  
(2.44)

and so the Hamiltonian \( H(x, y, p_x, p_y) \) becomes \( \tilde{H}(Q_1, Q_2, P_1, P_2) \).

The second step is to rescale \(^{14}\) this Hamiltonian at the level \( E \) to get a new Hamiltonian \( \mathcal{H}(Q_1, Q_2, P_1, P_2) := R^2(\tilde{H} - E) = 0 \). This has the effect of inducing a time reparametrization. Indeed, one finds that

\[
\frac{\partial \mathcal{H}}{\partial P_i} = R^2 \frac{\partial \tilde{H}}{\partial P_i} = R^2 \frac{\partial \tilde{H}}{\partial P_i} + 2R(\tilde{H} - E) + R^2 \frac{\partial \tilde{H}}{\partial Q_i} = R^2 \frac{\partial \tilde{H}}{\partial Q_i}
\]  
(2.46)

so that defining \( d\tau := dt/R^2 \) one gets

\[
\frac{dQ_i}{d\tau} = \frac{dQ_i}{dt} \frac{dt}{d\tau} = \frac{dQ_i}{dt} \frac{\partial \tilde{H}}{\partial P_i} R^2 = \frac{\partial \mathcal{H}}{\partial P_i}
\]  
(2.47)

\[
\frac{dP_i}{d\tau} = \frac{dP_i}{dt} \frac{dt}{d\tau} = -\frac{\partial \tilde{H}}{\partial Q_i} R^2 = -\frac{\partial \mathcal{H}}{\partial Q_i}
\]  
(2.48)

and so it is only with this new time scale that we get the Hamiltonian flow of \( \mathcal{H} \).

Now this flow is no longer singular at binary collisions since the multiplication by \( R^2 \) in \( \mathcal{H} \) has killed all divergent terms, so we are done.

\(^{14}\)This kind of transformation is called a Poincaré transformation.
vicinity of the collision. On the other hand, making only a change of variable without time rescaling would not have removed the singularity.

A generalization of this method for bodies moving in $3$--dimensional space is provided by the Kustaanheimo-Stiefel map [KS65]. It replaces the three original variables $x, y, z$ not by three but by four new variables $Q_1, Q_2, Q_3, Q_4$ and one constraint. Namely one has

$$\begin{pmatrix} x \\ y \\ z \\ 0 \end{pmatrix} = \begin{pmatrix} Q_1 & -Q_2 & -Q_3 & Q_4 \\ Q_2 & Q_1 & -Q_4 & -Q_3 \\ Q_3 & Q_4 & Q_1 & Q_2 \\ Q_4 & -Q_3 & Q_2 & -Q_1 \end{pmatrix} \begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \\ Q_4 \end{pmatrix}$$

One then follows the same line of reasoning as above to obtain again a flow where binary collisions are regularized. See [Wal06] for the relation between this map and the the quaternions.

**Triple collisions.** In the three-body problem of celestial mechanics there are two kinds of triple collisions (TC), the *Euler type* for which the limiting positions of the bodies as they approach the TC is a line, and the *Lagrange type* for which it is an equilateral triangle. The reason for such a behaviour is that any orbit ending in a TC must approach one of the allowed central configurations. By definition a central configuration is a point of phase space at which for all the bodies the position vector is parallel to the acceleration vector. Since such a property is conserved for all times, central configurations are either equilibrium points or they belong to a homothetic orbit. In the Newtonian three-body problem one finds that there are two homothetic orbits, one where the bodies move on a line and one where the bodies form an equilateral triangle, hence the two types of TC. Moreover as

---

15Which is nothing else than the map found by Hopf in 1931 which provides a fibration of the $3$--sphere by circles over the $2$--sphere.
one approaches the collision, the distance $r_{ij}(t)$ between any two colliding bodies varies as $t^{2/3}$ (i.e. $r_{ij}(t) = O(t^{2/3})$) [Saa81, Saa80].

On the other hand, in the Coulomb three-body problem with masses and charges as in the helium atom, it has been shown in [PCSSY96] and independently in [SMP97] that central configurations can only happen when the three bodies are on a same line, so there is just one kind of TC. The corresponding collinear homothetic orbit is called the Wannier orbit (WO) and its geometrical and dynamical meaning within phase space will be explained below. What we can already expect from this result is that the dynamical behaviour of the classical helium atom is simpler than that of gravitational three-body systems.

A crucial feature, which is shown below to govern to a large extent the dynamics of three-body problems, is that for most values of the mass and charge parameters the triple collision is not regularizable in both senses.

In the case of gravitational systems, Siegel has shown that triple collisions cannot be analytically regularized, except for a dense set of measure zero (a countable set of curves [Sim80]) in the space of the mass parameters, in which case it is done with a rescaling of time of the form $\tau = t^{a/2b+1}$ where $a, b$ are integers determined by the kind of TC encountered.

On the other hand, the fact that triple collisions are not block regularisable was first discovered by McGehee [McG74] in the case of the collinear gravitational three-body problem. This kind of non-regularizability means that the behaviour of orbits close to a TC one is very complicated in phase space: a TC is a source of chaos in the system. What McGehee did was to introduce a change of coordinates which transforms the phase space and the flow into new ones which are not Hamiltonian anymore, but such that the TC singular point becomes an invariant collision manifold $\mathcal{T}$ (i.e. this is a blow-up of the singularity) of the new flow. This $\mathcal{T}$ forms a boundary of the new phase space and the flow on it (which is a smooth
limit of the flow on the rest of phase space) describes a fictitious dynamics at the TC which turns out to be qualitatively simple\textsuperscript{16}. So seen the other way round, the behaviour of orbits near the TC is dictated by this dynamics on $\mathcal{T}$ (by continuity of the flow).

We shall present more details below as it is a useful tool for studying Coulomb systems too, and in particular the helium atom. For the moment let us simply mention that there are two fixed points on $\mathcal{T}$ (they are hyperbolic) and that a necessary condition for non-block regularizability of the TC is that there is no heteroclinic connection within $\mathcal{T}$ between those fixed points. This is true for most masses of the three bodies, except for a countable non-dense set of curves (thus a set of measure zero) in the mass parameter space [Sim80].

For a detailed discussion of various simple examples of McGehee blow-up see [Dev81]. The method can be extended to handle triple collisions of bodies moving in $d$–dimensional space (see [Sus93] for the planar gravitational three-body problem) as well as collisions of more bodies including the case of different clusters of bodies [ElB90].

**Simultaneous binary collisions.** In chapter three we shall study the classical dynamics of the hydrogen molecule, a four-body problem. In that case another type of collision can happen: *simultaneous binary collisions* (SBC). It turns out that the behaviour of the flow near an SBC is drastically different from that of a BC.

From the point of view of analytic regularization, there is no difference: Sperling has shown that SBCs in the gravitational $N$–body problem are analytically regularizable, again with $\tau = t^{1/3}$ [Spe75].

On the other hand the block regularization is possible, but is not as smooth as in the BC case, here it is only of finite order. In particular, a simultaneous

\textsuperscript{16}It is a *gradient-like flow*, which means that there is a function which increases along all non-equilibrium solutions.
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time-rescaling $dt = r_1 r_2 d\tau$ combined with Levi-Civita change of coordinates for both electrons does not remove the SBC singularity. The behaviour of the flow near SBCs in one, two and three dimensions has been studied in great detail by ElBialy [ElB93, ElB96a, ElB96b]. Later, Martínez and Simó [MS00] have shown that the SBC block map in the collinear gravitational four-body problem is exactly $\frac{8}{3}$-Hölder, so positions and speed of the bodies across an SBC are continuous, but not the acceleration. Nearby orbits are such that one pair of bodies undergoes a BC while the other pair is infinitesimally close to a BC. The finite order of regularizability means that the colliding pair induces a kick in the accelerations of the other pair of near-colliding bodies. (Recall that a function $f$ is said to be $(k + \frac{a}{b})$–Hölder at some point $x_0$ (with $a < b$ two coprime integers) if its k-th derivative $f^{(k)}$ is at most proportional to $(x - x_0)^{a/b}$ in a neighborhood $D_{x_0}$ of $x_0$.) In short, an SBC is also a source of chaos like a TC.

Let us now resume the study of the three-body Coulomb problem, and in particular the helium atom.

2.4.4 Symmetries, integrals and reduced space

To study the geometry of the problem we use standard tools from geometric mechanics (see appendix C for a reminder). First, one observes that $V$ is invariant under the diagonal action of the group $SO(3)$

$$SO(3) \times \Omega \longrightarrow \Omega$$

$$(g_{u,\phi}, (q_1, q_2)) \mapsto (g_{u,\phi} \cdot q_1, g_{u,\phi} \cdot q_2)$$

where $g_{u,\phi}$ is a rotation of angle $\phi$ around the axis defined by the unitary vector $u \in \mathbb{R}^3$.

This action is then lifted to phase space. Therefore, according to Noether’s theorem, there are associated first integrals. Here, these are the three components
of total angular momentum

\[
L_x = \left( y_1 p_{z_1} - z_1 p_{y_1} \right) + \left( y_2 p_{z_2} - z_2 p_{y_2} \right) \tag{2.52}
\]

\[
L_y = -\left( x_1 p_{z_1} - z_1 p_{x_1} \right) - \left( x_2 p_{z_2} - z_2 p_{x_2} \right) \tag{2.53}
\]

\[
L_z = \left( x_1 p_{y_1} - y_1 p_{x_1} \right) + \left( x_2 p_{y_2} - y_2 p_{x_2} \right) \tag{2.54}
\]

So we have an energy-momentum map \( F := (H, L_x, L_y, L_z) \)

\[
F : \mathcal{M} \longrightarrow \mathbb{R}^4 \tag{2.55}
\]

\[
w \mapsto (E, \ell_x, \ell_y, \ell_z) \tag{2.56}
\]

Now, the values of angular momentum we are interested in are \( \ell_x = \ell_y = \ell_z = 0 \). Indeed, we want to compute the \( ^1S^e \) states (so zero quantum angular momentum \( \ell = 0 \)) and it has been shown by Creagh (see §6 in [Cre93]) \(^{17}\), that a trace formula using periodic orbits belonging to the reduced dynamics at zero angular momentum gives a semiclassical spectrum corresponding to zero quantum angular momentum.

Our region of interest in phase space is then the 8–dimensional\(^{18} \) level set

\[
\mathcal{N} := F^{-1}(-1, 0, 0, 0) \tag{2.57}
\]

and now we need to reduce the symmetry. Again we use methods from geometric mechanics, see appendix C.

Our action is non-free since some points of phase space have nontrivial isotropy, and so we need to do a singular reduction. More precisely, a point

\(^{17}\)See [Cas05] for a mathematical version of this type of “reduction commutes with semiclassical quantization” results, using the wavepackets techniques of [CRR99] and in the more restricted case of regular reduction for systems with a single isotropy type.

\(^{18}\)Since \( \dim(\mathcal{N}) = \dim(\mathcal{M}) - 4 \).
\[ w = (q_1, q_2, p_1, p_2) \text{ of phase space is fixed by some } g_{u,\phi} \in SO(3) \text{ iff the axis defined by } u \text{ is parallel to all the non-zero components of } w. \] The isotropy subgroups of the system are then

- \( SO(3) \) for the origin of \( Q \), which is the triple collision configuration \( q_1 = q_2 = p_1 = p_2 = 0 \)
- \( SO(2) \) for any collinear configuration of the three particles, i.e. configurations where some of the four vectors \( q_1, q_2, p_1, p_2 \) are possibly zero while the non-zero ones are all parallel with one another
- \( \{e\} \) for all the other configurations

We thus have three isotropy submanifolds in \( \mathcal{N} \)

\[
\mathcal{N}_{SO(3)} = \{ w \in \mathcal{N} \mid G_w \sim SO(3) \} = \{ (0, 0, 0, 0) \} \tag{2.58}
\]
\[
\mathcal{N}_{SO(2)} = \{ w \in \mathcal{N} \mid G_w \sim SO(2) \} = \{ w \in \mathcal{N} \mid q_1 \wedge q_2 = p_1 \wedge p_2 = q_1 \wedge p_1 = 0 \} \tag{2.59}
\]
\[
\mathcal{N}_{\{e\}} = \mathcal{N} - (\mathcal{N}_{SO(3)} \cup \mathcal{N}_{SO(2)})
\]

where we have

\[
\text{dim}(\mathcal{N}_{SO(2)}) = \text{dim}(\mathcal{N}) - \text{codim}_{SO(3)}(SO(2)) = 8 - 2 = 6 \tag{2.60}
\]
\[
\text{dim}(\mathcal{N}_{\{e\}}) = \text{dim}(\mathcal{N}) = 8 \tag{2.61}
\]
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So the resulting reduced phase space $\mathcal{N}$ is made of three strata

\[
\mathcal{N}_{SO(3)} := \mathcal{N}_{SO(3)}/SO(3) \quad (2.62)
\]

\[
\mathcal{N}_{SO(2)} := \mathcal{N}_{SO(2)}/SO(3) \quad (2.63)
\]

\[
\mathcal{N}_{\{e\}} := \mathcal{N}_{\{e\}}/SO(3) \quad (2.64)
\]

$\mathcal{N}_{SO(3)}$ is just a single point, so does not deserve further attention.

$\mathcal{N}_{SO(2)}$ is 3-dimensional since

\[
dim(\mathcal{N}_{SO(2)}) = dim(\mathcal{N}_{SO(2)}) - dim(SO(3)) = 6 - 3 = 3 \quad (2.65)
\]

and corresponds to two kinds of 2 DOF collinear configurations: one where the electrons stay on opposite sides of the nucleus (eZe configuration) and one where the electrons remain on the same side of the nucleus (Zee configuration).

![Figure 2.8: Representations of the two kinds of configurations in $\mathcal{N}_{SO(2)}$: collinear eZe (left) and collinear Zee (right).](image)

Finally $\mathcal{N}_{\{e\}}$ is 5-dimensional because

\[
dim(\mathcal{N}_{\{e\}}) = dim(\mathcal{N}_{\{e\}}) - dim(SO(3)) = 8 - 3 = 5 \quad (2.66)
\]

and consists of a 3 DOF planar configuration.

In the helium system, since all configurations have at most 3 DOF, we are in the fortunate situation of being able to plot the energetically allowed domain of configuration space, call it $\Delta_{\text{helium}}$, corresponding to all the strata of reduced phase space. We obtain the region delimited by the planes $r_1 = 0$, $r_2 = 0$, $\cos(\theta_{12}) = -1$, 

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\[ \text{He}^{++} \]

\[ r_1, r_2, \theta_{12} \]

**Figure 2.9:** Representation of the planar configuration corresponding to \( \overline{N}_{\{e\}} \).

\[ \cos(\theta_{12}) = 1 \] and the surface \( V = -1 \), where \( r_1, r_2 \) and \( \theta_{12} \) are the coordinates of the reduced configuration space.

**Figure 2.10:** The energetically allowed part of configuration space in reduced coordinates \( r_1, r_2, \cos(\theta_{12}) \) delimited by the planes and the surface (see text).

The situation is thus fairly simple: the interior of \( \Delta_{\text{helium}} \) corresponds to 3 DOF motions within the strata \( \overline{N}_{\{e\}} \). As for the 2 DOF strata \( \overline{N}_{\{SO(2)\}} \), it corresponds to motions on the two invariant planes \( \cos(\theta_{12}) = -1 \) (eZe configuration) and \( \cos(\theta_{12}) = 1 \) (Zee configuration).

At this point there are still two discrete symmetries left, the electron-exchange
symmetry $\Pi_e$ and the time-reversal symmetry $\Pi_t$, defined respectively by

\[ \Pi_e : w = (q_1, q_2, p_1, p_2) \rightarrow \Pi_e(w) = (q_2, q_1, p_2, p_1) \] (2.67)

\[ \Pi_t : w(t) \rightarrow \Pi_t(w(t)) = w(-t) \] (2.68)

and these have to be reduced in each strata of the reduced space.

We shall now study the dynamics in each of them separately, and then we will turn to the computation of the spectrum.

### 2.4.5 Collinear eZe dynamics

The study of this configuration goes back to the early 90’s [ERTW91, TSB+91, WRT92].

There are 2 DOF: the distances $r_1$ and $r_2$ of each electron to the fixed nucleus.

Given the previous discussion on energy scaling, one studies the following Hamiltonian

\[ H = \frac{p_1^2 + p_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_1 + r_2} = -1 \] (2.69)

The possible collisions are therefore two BC (nucleus-electron) and a TC (the electrons hit at the same time the nucleus). As explained above the BC can be regularized, while the TC cannot. In fig 2.11 is shown what a typical orbit looks like when the BC have been regularized.

The energetically allowed domain, which is in the $\cos(\theta_{12}) = -1$ plane as described in the previous section, extends to infinity along both axis so that we have an open system\(^{19}\). Motion is regular far in these two channels, whereas it is chaotic near the nucleus as shown by the Poincaré section defined by the condition $r_2 = 0$, i.e. the collision nuclei-electron2 (fig 2.12).

\(^{19}\)Needless to say this terminology is not to be confused with the open systems of thermodynamics...
Figure 2.11: An eZe orbit bouncing within the energetically allowed region which is delimited by the dashed curve.

Figure 2.12: The $r_2 = 0$ PSOS of eZe after [WRT92]. Coordinates are $\sqrt{r_1}$ in abcissa, against $p_{r_1}$.

The origin of such chaotic behaviour is the TC. Indeed, the TC point has stable and unstable manifolds which turn out to provide a fine partition of phase space, first reported for this system in [RGW93]. Various numerical studies of these objects have been undertaken [BYY98, San04] which suggest that the dynamics in this configuration is probably hyperbolic.
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There exist indeed a simple binary symbolic description of the orbits. To see that, recall that there are still two discrete symmetries to be reduced. One introduces the fundamental domain $\Delta_{eZ_e}$ of this configuration as being the part of the energetically allowed region which is below the diagonal $r_2 = r_1$. When an orbit reaches the diagonal it is reflected back into $\Delta_{eZ_e}$. Doing so allows to reduce the exchange symmetry $\Pi_e$, so that electron 2 is always closer to the nuclei than electron 1. In particular, only the BC $r_2 = 0$ for electron 2 remains.

The time-reversal symmetry $\Pi_t$ is in fact also reduced in the process. Indeed, a way of choosing a positive direction of time is to pick a global PSOS and to choose a direction in which orbits cross it. This direction is then declared as corresponding to positive time evolution. Here, the boundary $r_1 = r_2$ of $\Delta_{eZ_e}$ is such a global PSOS, so that one can start any orbit on it, and the condition of going only inside one of the two halves effectively defines the direction of time.

This done, one finds that the following binary code allows, on the basis of numerical evidence, to label uniquely each orbit

- add a symbol 0 if the trajectory is not reflected by the diagonal between two collisions with the nucleus
- add a symbol 1 if the trajectory is reflected by the diagonal between two collisions with the nucleus

All sequences seem to be realized, with the notable exception of the repetition 000..., which corresponds to a marginally stable orbit at infinity. Indeed from the Poincaré section it is seen that motions are regular far in the channels, so that intermittency occurs in the system.

In fig 2.13 are shown the shortest PO together with their codes. One notices that there are two kinds of PO: the ones symmetric with respect to the diagonal, and the non-symmetric ones. Note that the shortest PO, the one whose code is 1, is called asymmetric stretch orbit in the literature to underline its basic dynamical
behaviour, but of course it is a symmetric PO.

![Figure 2.13: The shortest eZe PO and their symbolic code, after [WRT92].](image)

The action, stability and topological indices of these orbits can be computed. Perturbations along the configuration axis decouple from those perpendicular to it. Moreover, one finds that motion within the axis of the configuration leads to a pair of eigenvalues $1, 1$ corresponding to conservation of energy (symmetric perturbations $\delta r_1 = \delta r_2$) and to a pair of unstable eigenvalues $\Lambda_\parallel, \Lambda_\parallel^{-1}$ (asymmetric perturbations $\delta r_1 = -\delta r_2$).
On the other hand, perturbations away from the axis of the configuration lead to a pair of eigenvalues 1, 1 corresponding to conservation of angular momentum and a pair of stable eigenvalues ("bending perturbation" along the interelectronic angle $\theta_{12}$). These perturbations are doubly degenerate due to the symmetry around the configuration axis.

Such results mean that we are in the type B situation as defined in chapter 1. This implies that one can use the B version of the GTF, and cycle expansions too. So one only needs to compute what we called the B-indices of the orbits $\beta_{\gamma}$. It is found here that there is a simple relation between those indices and the symbolic code: in the fundamental domain $\Delta_{eZe}$ the B-index is equal to twice the number of symbols of the orbit’s code.

### 2.4.6 Collinear Zee dynamics

The other collinear space is the one where both electrons remain on the same side of the nucleus. It also has 2 DOF and turns out to be near-integrable [RW90]. What happens is that the inner electron bounces back on the nucleus, creating a very flat effective potential for the outer electron. Motions are thus stable, in fact they are stable also away from the axis, implying the existence of a KAM island in all 3 DOF of the system. As a result, the motions of this configuration have been dubbed ‘frozen planet orbits’.

### 2.4.7 Planar dynamics

#### Wannier Ridge configuration

The strata $\overline{N}_{(e)}$ is described by 3 DOF and consists of planar motion. It is found that it has an invariant 2 DOF subspace, called the Wannier Ridge, which consists of symmetric planar motions $r_1 = r_2$ and $p_{r_1} = p_{r_2}$ for all times, the DOF being $r := r_1$ and $\theta_{12}$. Several studies [RGW93, AM94] have revealed that this configuration is of mixed regular-chaotic type. In fact the value of the charge $Z$ of the nuclei is the
parameter which leads to a KAM transition from integrable at \( Z \approx 1/4 \) to chaotic as \( Z \) is increased.

The boundary of the PSOS of this configuration defined by \( \theta_{12} = \pi \) is called the Wannier Orbit (WO) and consists of a simple periodic oscillation in \( r \). Such orbit is also found in the eZe configuration and it is their only common orbit (in our reduced configuration space it is the line defined by \( r_1 = r_2, \cos(\theta_{12}) = -1 \)). This orbit goes into the triple collision, but can be branch regularized. So it is an heteroclinic connection between the Triple Collision Point (TCP) and its time-reverse image the Double Escape Point (DEP) [AM94,CTL04,LTC05].

Planar periodic orbits

Apart from that subspace there are isolated PO in \( \mathcal{N}_{\{e\}} \), some of which have been studied in [GS91,GS95,Sim97,Sim03,YK93,YK98]. In particular there exists orbits, let us call them GS orbits, in which the radial part \( r_1, r_2 \) of the motion behaves approximately like the asymmetric stretch orbit of eZe while the angle \( \theta_{12} \) does some revolutions. As shown by Simonović these planar orbits look very much like Lissajous figures when plotted in the MO coordinates \( \lambda = (r_1 + r_2)/r_{12} \) and \( \mu = (r_1 - r_2)/r_{12} \) discussed in §2.3.2, providing a classical basis for such an approximate separation, see fig 2.14.

Scattering dynamics

Then there remains all the non-periodic part of the dynamics in \( \mathcal{N}_{\{e\}} \), and studies aiming to provide a comprehensive picture of this situation have been initiated in a series of papers by Choi, Lee and Tanner [CTL04,LTC05,LCT05]. We do not have the space here to describe these in details, so let us only single out one aspect.

When discussing the various types of collision singularities in §2.4.3 we mentioned that the fact that triple collisions (TC) cannot be block-regularized and that this can be seen by studying motions on a manifold \( \mathcal{J} \) which is a blow-up of
such collisions occurring in the collinear eZe configuration. Dynamics on $\mathcal{T}$ corresponds to a fictitious dynamics at the collision, or equivalently at zero energy $H = 0$, which allows to study how TC-orbits and their neighbours are related to double escape orbits (DE-orbits) and their neighbours (DE-orbits are time-reversal images of TC-orbits). One finds that on $\mathcal{T}$ there are two fixed points: the triple collision point (TCP) and the double escape point (DEP), see fig 2.15. The fact that there is no heteroclinic connection between the TCP and the DEP within $\mathcal{T}$ implies the impossibility of block-regularization.

But, as mentioned just above, there is an heteroclinic connection between the TCP and the DEP outside of $\mathcal{T}$, namely the WO. Moreover motions at zero energy within the Wannier ridge (WR) too allow to connect the TCP to the DEP (see also [AM94]). One then finds that the WO is in fact a crucial object, namely the entrance gate into the physical (i.e. $E < 0$) scattering part of the dynamics, see fig 2.16.

We now present the semiclassical spectrum associated to the classical dynamics.
Figure 2.15: The triple collision manifold $\mathcal{T}$ of the $eZe$ configuration with its two fixed points: the TCP (noted $c$) and the DEP (noted $d$), after [McG74]. The flow on $\mathcal{T}$ is gradient-like with respect to the $v$ coordinate (i.e. $v$ is monotonically increasing along all trajectories).

Figure 2.16: The conveyor belt mechanism in phase space between the TCP and the DEP, after [LTC05] (see text).

of the helium atom.
2.4.8 Semiclassical quantization

Early attempts

An early precursor of a semiclassical quantization of the classical dynamics of the helium atom in the case of equivalent electrons with zero total angular momentum (i.e. intrashell S states) is the work of Solov’ev [Sol85]. He chose an ad hoc initial configuration consisting of two non-interacting electrons revolving along Kepler ellipses around the nucleus. He then carefully applied first order degenerate perturbation theory and EBK quantized the resulting motion, obtaining a resonable approximate eigenvalue of $E = -3.05$ for the ground state (to be compared with the quantum value is $E \approx -2.9035$).

Cycle expansion results

These results are now superseeded by those of the modern semiclassical techniques described in chapter 1 as follows. The eZe configuration described above is seen to fulfill all the requirements of this approach, namely the dynamics in the $\Gamma$–explored DOF is hyperbolic while there is a decoupling between the stable and unstable DOF. We can thus apply this methodology straight away.

The orbit weights for the cycle expansion are found to be

$$t^{(a,b)}_\gamma = \frac{1}{\sqrt{|e^{\lambda_\gamma T_\gamma}|e^{a \lambda_\gamma T_\gamma}}} \exp \left[ i (s S_\gamma - \beta_\gamma \frac{\pi}{2} - 2 \cdot 2\pi (b + \frac{1}{2}) \frac{\chi_\gamma}{2\pi}) \right]$$

(2.70)

where $\chi_\gamma$ is the stability exponent of the $\theta_{12}$–bending perturbations, $\lambda_\gamma$ is the Lyapunov exponent of the unstable axial pertubations, the index $a$ corresponds to excitations of this unstable DOF whereas $b$ is the one for the stable bending pertubations. The factor two for the stable part accounts for the degeneracy of perturbations perpendicular to the configuration axis. Finally $s = \sqrt{1/(-E)}$ is an energy parameter resulting from the scaling property of the action.

The indices $a$ and $b$ have very different meanings: the study can be restricted
to \( a = 0 \) since higher values of this index only allow to refine the estimate of resonances with large imaginary parts, i.e. the very unstable ones. On the other hand, each value of \( b \) corresponds to a kind of quantized bending perturbations and allows to obtain the different series corresponding to a given ionization threshold. In particular \( b = 0 \) provides the lowest, leftmost, series of each family. Thus \( b \) is a quantum number obtained from considerations on the actual classical dynamics of the system.

Another quantum number comes from the exchange symmetry of the dynamics, so that one can factor the zeta function in a product of symmetric and antisymmetric parts

\[
\zeta^{-1}_{(b)} = \zeta^{-1}_{(b),+} \zeta^{-1}_{(b),-}
\]

(2.71)

where

\[
\zeta^{-1}_{(b),\pm} = \prod_A (1 - t_A) \prod_S (1 \mp t_S)
\]

(2.72)

with \( S \) denoting the symmetric PO and \( A \) the antisymmetric ones. Then to obtain \( ^1S^e \) states one finds the zeros of \( \zeta^{-1}_{(b),+} \).

The results obtained for bound states and resonances are reasonably accurate. To first order in the expansion (i.e. in code length) one has the condition \( 1 - t_{(0,b)} = 0 \) and this leads to an EBK-like formula

\[
E_{b,N} = -\frac{(S_1/2\pi)^2}{[b + \frac{1}{2} + 2(N + \frac{1}{2}) \frac{3\pi}{2\pi}]^2}
\]

(2.73)

where \( N \) is the principal quantum number. This formula is found to provide already quite accurate estimations of the states such that \( n = N \), i.e. the ground state and the intrashell resonances. For the ground state the result is \( E_{1,1} = -3.0970 \). Adding more terms in the expansion allows to recover also the next states in the series while improving accuracy. In fig 2.17 are shown further results for bound states. At code length 16 (which represents about 8000 PPO) one finds (ground state and a few resonances shown) the following table of values
Chapter 2: Few-body Coulomb problems

Figure 2.17: Numerical results of semiclassical cycle expansion compared to QM values; $\epsilon$ is the error in % of mean level spacing, after [ERTW91].

<table>
<thead>
<tr>
<th>$N = 1$</th>
<th>QM</th>
<th>Cyc Exp</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.903721</td>
<td>2.928251</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>2.145974</td>
<td>2.135623</td>
<td>6.9</td>
</tr>
<tr>
<td>3</td>
<td>2.061272</td>
<td>2.059238</td>
<td>4.9</td>
</tr>
<tr>
<td>4</td>
<td>2.033587</td>
<td>2.032887</td>
<td>4.1</td>
</tr>
<tr>
<td>5</td>
<td>2.021177</td>
<td>2.020860</td>
<td>3.7</td>
</tr>
<tr>
<td>6</td>
<td>2.014563</td>
<td>2.014394</td>
<td>3.4</td>
</tr>
<tr>
<td>7</td>
<td>2.010626</td>
<td>2.010525</td>
<td>3.3</td>
</tr>
<tr>
<td>8</td>
<td>2.008094</td>
<td>2.008029</td>
<td>3.2</td>
</tr>
<tr>
<td>9</td>
<td>2.006370</td>
<td>2.006326</td>
<td>3.1</td>
</tr>
<tr>
<td>10</td>
<td>2.005143</td>
<td>2.005112</td>
<td>3.0</td>
</tr>
<tr>
<td>11</td>
<td>2.004239</td>
<td>2.004216</td>
<td>3.0</td>
</tr>
<tr>
<td>12</td>
<td>2.003555</td>
<td>2.003537</td>
<td>2.9</td>
</tr>
<tr>
<td>13</td>
<td>2.003023</td>
<td>2.003001</td>
<td>2.9</td>
</tr>
<tr>
<td>$\infty$</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.17: Numerical results of semiclassical cycle expansion compared to QM values; $\epsilon$ is the error in % of mean level spacing, after [ERTW91].

<table>
<thead>
<tr>
<th>$N$</th>
<th>$n$</th>
<th>16th order</th>
<th>QM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-2.9248</td>
<td>-2.9037</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
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<tr>
<td>2</td>
<td>3</td>
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<td>-0.5899</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>-0.5429</td>
<td>-0.5449</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>-0.3503</td>
<td>-0.3535</td>
</tr>
<tr>
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<td>4</td>
<td>-0.2808</td>
<td>-0.2811</td>
</tr>
<tr>
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<td>3</td>
<td>6</td>
<td>-0.2433</td>
<td>-0.2438</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>-0.2012</td>
<td>-0.2010</td>
</tr>
<tr>
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<td>5</td>
<td>-0.1657</td>
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</tr>
<tr>
<td>4</td>
<td>6</td>
<td>-0.1507</td>
<td>-0.1508</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>-0.1426</td>
<td>-0.1426</td>
</tr>
</tbody>
</table>

Other topics

There exists many other aspects of such semiclassical studies, for which we refer to the review [TRR00]. Let us just mention that a striking feature of resonant intrashell wavefunctions is that they strongly localise along the asymmetric stretch orbit when projected onto the $\theta_{12} = \pi$ plane, with their nodal structure clearly aligned with respect to the orbit.
Also, the correspondance between spectrum and periodic orbits does works either way in practise too: by taking the Fourier transform of the numerical spectrum obtained by ab initio methods, one observes a flat signal except for strong, well-defined peaks around the actual actions of the short PO of the system (those from the eZe and Zee configurations).

2.5 Hydrogen molecule

Our aim in this thesis is to analyze the structure of the classical dynamics of the hydrogen molecule $H_2$, and then to use it to produce semiclassical results. We do so in the next two chapters, but before presenting our study we review some aspects of the physics of $H_2$.

2.5.1 Quantum aspects

The hydrogen molecule has received a lot of attention, both experimentally and theoretically, and it is impossible to summarize the whole literature. Let us instead mention a few key points, all emphasizing that $H_2$ is a vastly more complicated system than the helium atom $He$, based on recent accounts [Uba00,BC03,GMS05].

First, while the infinite mass approximation of the nucleus is virtually harmless for atoms, on the contrary the corresponding BO approximation for molecules mentioned in §2.2.1 is not quite justified for light molecules such as $H_2$, and this results in fairly large deviations from experimental data. One then has to include so-called adiabatic corrections.

Secondly, and unlike what happens for $He$, the BO curves of the doubly excited states of $H_2$ (which are purely repulsive curves, i.e. without wells) are not necessarily higher in energy than those of the singly excited states. For instance the BO curve of the $(2p\sigma_u)^2$ doubly excited state crosses those of the $n^1\Sigma_g^+$ singly excited
Figure 2.18: Lowest singly excited electronic BO curves of $^1\Sigma_g^+$ symmetry ($n = 1$ to $n = 6$, solid lines) and their diabatic versions (dashed lines), after [AE04]. One observes in particular a double-well structure for BO curves.

states (i.e. $n \geq 2$), and this has the effect of creating a double-well structure in the latter curves, see fig 2.18, as well as in those of other excited states of different symmetry. Since the ionization potential is situated at 124417.491 cm$^{-1}$ [Wol95], some long-range (i.e. large $R$) bound states are allowed to exist, for example in
the outer well of the curve named $\overline{H}$ in fig 2.18.

And then, of course, for superexcited molecules (i.e. above the electronic ground state BO curve of $H_2^+$) there are very many possible decay channels (including non-atom-like ones): $H_2^+ + e^-; H^+ + H + e^-; H^+ + H^-; H(1s) + H(2s);\ H(1s) + H(2p);...; H(2p) + H(n\ell)...$

These facts put constraints on what may or may not be achievable by semiclassical methods, as we now explain.

## 2.5.2 Semiclassical approaches

What one may hope to account for, and explain from another (hopefully fruitful) point of view, are aspects which involve structural issues, rather than very high numerical accuracy. Here are some of them.

### Double-well shape

An important structural property of the system is the double-well shape of the BO curves mentioned above. At the semiclassical level, this has been explained recently by Nakamura and Solov’ev [NS03], in a work were they presented an analytical formula for quantum defects. They treated the excited $H_2$ molecule as an $H_2^+$ core with the other electron far away. The binding energy of the highly excited electron is then approximately

$$E_{n\ell m}(R) = -\frac{2}{(n - \Delta_{lm}(R))^2} \quad (2.74)$$

where $n, l, m$ are spherical quantum numbers and $\Delta_{lm}(R)$ is the so-called quantum defect. The latter is decomposed into a sum of a constant term $\delta_l$ from the united atom limit ($R = 0$) and an $R$-dependent term $\Delta_{lm}^{TC}(R)$ from the Two Center core. Then the eigenenergy of the core electron, noted $\epsilon_{n\ell m}(R)$, is related to the quantum
defect by

\[ \Delta_{lm}^{TC}(R) = n - \frac{2}{\sqrt{-2\epsilon_{nlm}(R)}} \]  

These authors then use a uniform semiclassical approximation in the \( H_2^+ \) problem to obtain successively \( \epsilon_{nlm}(R) \), \( \Delta_{lm}^{TC}(R) \) and \( \epsilon_{nlm}(R) \) (for the latter they require non-semiclassical input, namely the ab initio \((2p\sigma_u)^2\) curve and some assumptions on states couplings, but not for the first two).

As a result, they find that the avoided crossings of the BO curves of \( H_2 \), which corresponds to branch points of their corresponding surfaces in the complex \( R \) plane, are caused by the passage through the separatrix between the P1 and P2 families as \( R \) is increased (recall fig 2.4). In dynamical terms, this means that strong quantum diabatic behaviour corresponds to classical motions where the core electron is confined near a highly unstable configuration, namely here near the PO which consists of an electron bouncing between the two nuclei (ZeZ configuration). This provides a complementary explanation to the quantum one since it appeals more to one’s physical intuition than the ab initio blunt fact that some doubly excited state curves exist low in energy.

Asymptotic behaviour of the BO curves

Another fact that one can try to account for is the asymptotic behaviour of the BO curves in the two limits \( R \to 0 \) and \( R \to +\infty \). The results of Nakamura and Solov’ev are not fully semiclassical as mentioned above, so that these limits still have to be investigated from purely classical considerations.

Bond formation

A last aspect worth studying is of course the very formation of a molecule from two separated atoms. From a quantum-mechanical point of view one can observe a clear transition already in Hartree-Fock wavefunctions (which do not take correlations into account) of the \( ^1\Sigma_g^+ \) state [Iva02]: below \( R \approx 2.3 \) the densities for each
electrons are symmetric and peaked at both nuclei, whereas for larger values of $R$ they quickly becomes concentrated around one of the nuclei and flat around the other (there is strong tunneling like in the $H_2^+$ case mentioned earlier). It would be interesting to see whether such phenomena has a classical counterpart.

Earlier works on classical dynamics

Very few works have been devoted to the (semi)classical study of the dynamics of the hydrogen molecule, a more or less complete bibliography being [LC98, LC03, Waa94], and in these works the two basic questions mentioned previously remain unanswered.

2.6 Numerical methods

In the next chapters we used for our numerical work mainly the C++ programming language [Str00], while some parts required a computer algebra system in which case we used MapLe™ [MT03] (and when needed we exported the results to C++).

The integration of differential equations has been done in most cases with an explicit Runge-Kutta method of order 8 with step-size control (and dense output\(^{20}\) of order 7) written by Hairer and Wanner [HNW93] which suited our needs well. We used its C version due to Colinge [CHW94].

When long integrations were required, namely when computing Poincaré Surfaces Of Section (PSOS), we followed the advices of Ben Leimkuhler [Lei03] and used explicit symplectic integrators of various orders, including sometimes the simple order 2 leapfrog [LR04]. These are integrators which conserve the symplectic form $\omega$, and hence many Hamiltonian properties, at each time step (up to numerical round-off errors, which have been shown to be unimportant): noting $(q_{tm}, p_{tm})$

\(^{20}\)This means that there is a function returning the value of the solution at order 7 for any value of the time parameter between the effectively computed time steps.
and \((q_{tm+1}, p_{tm+1})\) the values of the numerical solution at steps \(m\) and \(m+1\) we have for any \(m\) that \(\varpi(q_{tm}, p_{tm}) = \varpi(q_{tm+1}, p_{tm+1})\).

We used the routines from the GNU Scientific Library (GSL) [GT04] for most minimizations done in this work, in particular the vector Broyden-Fletcher-Goldfarb-Shanno (BFGS) routine (which is a version of the conjugate gradient algorithm) for multidimensional minimizations. In a few 1–dimensional cases a standard bisection method has been used.

For the linear algebra computations like the computation of the eigenvalues of the monodromy matrices, which are non-symmetric real matrices, we used the TNT and JAMA libraries [Poz04].

As for the remaining data processing required, in particular for sorting the parameter-dependent eigenvalues coming from unsorted JAMA outputs, we used our own carefully checked codes. Finally, we used GNUPLOT [WKO04] to produce figures from our numerical data.
Chapter 3

Classical dynamics of the hydrogen molecule

3.1 Introduction

The aim of this chapter is to analyze in a systematic way the structure of the classical dynamics of the hydrogen molecule in the BOA, a four-body Coulomb problem. We shall adopt atomic units throughout.

Our system depends on one parameter, the inter-nuclear distance \( R \). In the limit \( R \to 0 \) one formally obtains the helium atom. On the other hand, the limit \( R \to +\infty \) leads (among other things, see below) to two separated hydrogen atoms. Finally, one recovers the integrable \( H_2^+ \) system (§2.2.4) when one of the electrons escapes to infinity. Hence our system is related to the other few-body Coulomb problems presented earlier as specified in the following diagram.
Chapter 3: Classical dynamics of the hydrogen molecule

3.2 Setting

We have a classical Hamiltonian system consisting of two identical negatively charged bodies with unit mass and charge (the electrons) moving in the field of two fixed positively charged bodies of unit charge (the nuclei) in 3-dimensional euclidean space. Hence the system has 6 DOF in total, configuration space is $\Omega := \mathbb{R}^6$ and phase space is $\mathcal{M} := T^*\Omega = \mathbb{R}^{12}$.

The distance between the nuclei is $R$ and they are placed on the $z-$axis at a distance $\frac{R}{2}$ from the origin, see fig 3.1.

The Hamiltonian reads

$$H(w) := T(p) + V(q) \quad (3.1)$$

with

$$T(p) := \frac{p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2 + p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2}{2} \quad (3.2)$$
Figure 3.1: The classical hydrogen molecule within the BOA.

The first term in $V$ is the electron-electron repulsion term and the others are the attraction of each electron to the two nuclei. We are thus led to study the following Hamiltonian system
\begin{align*}
\frac{dx_i}{dt} &= \frac{\partial H}{\partial p_{x_i}} = p_{x_i} ; \quad \frac{dy_i}{dt} = \frac{\partial H}{\partial p_{y_i}} = p_{y_i} ; \quad \frac{dz_i}{dt} = \frac{\partial H}{\partial p_{z_i}} = p_{z_i} \\
\frac{dp_{x_i}}{dt} &= -\frac{\partial H}{\partial x_i} = -\frac{\kappa_i (x_1 - x_2)}{x_i} - \frac{(x_i^2 + y_i^2 + (z_i - \frac{R}{2})^2)^\frac{3}{2}}{x_i} \left(\frac{(x_i^2 + y_i^2 + (z_i - \frac{R}{2})^2)^\frac{3}{2}}{x_i} - \frac{(x_i^2 + y_i^2 + (z_i + \frac{R}{2})^2)^\frac{3}{2}}{x_i}\right) \\
\frac{dp_{y_i}}{dt} &= -\frac{\partial H}{\partial y_i} = -\frac{\kappa_i (y_1 - y_2)}{y_i} - \frac{y_i}{y_i} \left(\frac{(x_i^2 + y_i^2 + (z_i - \frac{R}{2})^2)^\frac{3}{2}}{y_i} - \frac{y_i}{y_i} \left(\frac{(x_i^2 + y_i^2 + (z_i + \frac{R}{2})^2)^\frac{3}{2}}{y_i}\right)\right) \\
\frac{dp_{z_i}}{dt} &= -\frac{\partial H}{\partial z_i} = -\frac{\kappa_i (z_1 - z_2)}{z_i} - \frac{z_i}{z_i} \left(\frac{(x_i^2 + y_i^2 + (z_i - \frac{R}{2})^2)^\frac{3}{2}}{z_i} - \frac{z_i}{z_i} \left(\frac{(x_i^2 + y_i^2 + (z_i + \frac{R}{2})^2)^\frac{3}{2}}{z_i}\right)\right)
\end{align*}

where \(i = 1, 2\) and \(\kappa_1 = 1, \kappa_2 = -1\).

### 3.3 Scaling property

The potential \(V\) is not an homogeneous function of \(q\) as can be seen from the electron-nuclei attraction terms. This means that to scale out the energy as in the case of the helium atom one would need to rescale also the inter-nuclear distance

\begin{align*}
q_i(E) &= \tilde{q}_i \frac{-E}{\tilde{E}} ; \quad p_i(E) = \sqrt{-E} \tilde{p}_i ; \quad R(E) = \frac{-\tilde{R}}{E} ; \quad t(E) = \sqrt{\frac{-\tilde{t}}{(E)^{3/2}}} ; \quad S(E) = \frac{-\tilde{S}}{\sqrt{-E}}
\end{align*}

We are thus instead going to study the geometry and dynamics of the \(E = -1\) level set as a function of the parameter \(R\), and we drop the tilde (which indicates
values at $E = -1$) for brevity.

## 3.4 Collision set

The potential is not defined on the collision set

\[
\mathcal{C} := \{ w \in \mathcal{M} \mid q_1 = (0, 0, -R/2) \} \cup \{ w \in \mathcal{M} \mid q_1 = (0, 0, R/2) \}
\]
\[
\cup \{ w \in \mathcal{M} \mid q_2 = (0, 0, -R/2) \} \cup \{ w \in \mathcal{M} \mid q_2 = (0, 0, R/2) \}
\]
\[
\cup \{ w \in \mathcal{M} \mid q_1 = q_2 \}
\] (3.9)

Due to our energy requirement $H = -1$ the binary electron-electron collision cannot occur, but all other collisions are energetically allowed. Binary collisions (BC) and triple collisions (TC) can happen at both nuclei, and also simultaneous binary collisions (SBC) of two pairs made of one electron and one nucleus.

In analogy with the case of the classical helium atom (§2.4), the dynamics of this classical system can thus be expected to be governed by three families of (now $R$–dependent) objects: the stable and unstable manifolds $W^s(TC_A), W^u(TC_A)$ of the triple collision with nucleus A, the stable and unstable manifolds $W^s(TC_B), W^u(TC_B)$ of the triple collision with nucleus B, and finally the stable and unstable manifolds $W^s(SBC), W^u(SBC)$ of the SBC.

## 3.5 Symmetries, integrals and reduction

### 3.5.1 Continuous symmetries

The system is rotationally invariant around the nuclear axis leading to an $SO(2)$ symmetry group. The integral associated to this action is the component of total angular momentum along the $z$–axis

\[
L_z(w) := x_1 p_{y_1} - y_1 p_{x_1} + x_2 p_{y_2} - y_2 p_{x_2}
\] (3.10)
Chapter 3: Classical dynamics of the hydrogen molecule

and so we have an energy-momentum map \( F := (H, L_z) \)

\[
F : \mathcal{M} \longrightarrow \mathbb{R}^2 \\
w \mapsto (E, \ell_z)
\] (3.11) (3.12)

We are interested in the value \((-1, 0)\) since we wish in a second part to obtain a semiclassical approximation of the \(^1\Sigma_g^+\) states of the hydrogen molecule. We are thus interested in the level set

\[
\mathcal{N} := F^{-1}(-1, 0)
\] (3.13)

and we now need to reduce the symmetry from it using methods from geometric mechanics (see appendix C for terminology and examples).

The \(SO(2)\) action is not free hence we need to do a singular reduction. Fixed points are those for which \(q_1, q_2, p_1, p_2\) are all either zero or aligned with the \(z\) axis. So the isotropy subgroups of the system are simply

\(SO(2)\) for any collinear configuration of the four particles on \(O_z\)

\(\{e\}\) for all the other configurations

We thus have two isotropy submanifolds in \(\mathcal{N}\)

\[
\mathcal{N}_{(SO(2))} = \{w = (0, 0, z_1, 0, 0, z_2, 0, 0, p_{z_1}, 0, 0, p_{z_2}) \mid H(w) = -1\} \quad (3.14)
\]

\[
\mathcal{N}_\{e\} = \mathcal{N} - \mathcal{N}_{(SO(2))} \quad (3.15)
\]

with

\[
dim(\mathcal{N}_{(SO(2))}) = 3 \quad (3.16)
\]
\[
dim(\mathcal{N}_\{e\}) = 10 \quad (3.17)
\]
Chapter 3: Classical dynamics of the hydrogen molecule

So in the end the reduced phase space of our system is made of two strata

$$\mathcal{N}_{(SO(2))} := \mathcal{N}_{(SO(2))}/SO(2)$$  \hspace{1cm} (3.18)

$$\mathcal{N}_{(e)} := \mathcal{N}_{(e)}/SO(2)$$ \hspace{1cm} (3.19)

\(\mathcal{N}_{(SO(2))}\) is 3–dimensional and corresponds to four kinds of collinear 2 DOF configurations: one where the electrons stay on opposite sides of the nucleus (eZZe configuration); one where the two electrons stay between both nuclei (ZeeZ configuration); one where the electrons remain on the same side of either nuclei (ZZee configuration); and finally one having an electron trapped between the nuclei and the other outside (ZeZe configuration).

On the other hand \(\mathcal{N}_{(e)}\) is 9–dimensional because

$$\dim(\mathcal{N}_{(e)}) = \dim(\mathcal{N}_{(e)}) - \dim(SO(2)) = 10 - 1 = 9$$ \hspace{1cm} (3.20)

and consists of 5 DOF spatial configurations.

3.5.2 Discrete symmetries

Finally, we note that our original Hamiltonian system (3.7) is invariant under two discrete symmetries:
Chapter 3: Classical dynamics of the hydrogen molecule

the electron exchange symmetry $\Pi_e : (q_1, q_2, p_1, p_2) \rightarrow (q_2, q_1, p_2, p_1)$
the time-reversal symmetry $\Pi_t : t \rightarrow -t$

and these will be reduced in each strata separately (see below).

Having worked out the geometry of our system we now turn to the study of its dynamics.

\section{Dynamics in $\overline{N}_{(SO(2))}$}

As we saw above, $\overline{N}_{(SO(2))}$ is an $R-$dependent object which is made of four parts corresponding to four different collinear configurations along the $z-$axis. The Hamiltonian reduces to

$$H_{(SO(2))}(z_1, z_2, p_{z_1}, p_{z_2}) := \frac{p_{z_1}^2 + p_{z_2}^2}{2} + \frac{1}{|z_2 - z_1|} - \frac{1}{|z_1 - \frac{R}{2}|} - \frac{1}{|z_1 + \frac{R}{2}|} - \frac{1}{|z_2 - \frac{R}{2}|} - \frac{1}{|z_2 + \frac{R}{2}|}$$

(3.21)

It is seen that the condition $H_{(SO(2))} = -1$ is allowed for all values of $R$, so that these four configurations exist for $R \in [0; +\infty)$.

Of the four collinear configurations, only the eZZe one has the helium eZe configuration as a limit when $R \rightarrow 0$. Since we saw in chapter 2 that the helium $^1S_e$ states (including the ground state) can be well approximated by semiclassical quantization of eZe dynamics, the eZZe promises to be an interesting subspace potentially describing the $^1\Sigma_g^+$ states of the hydrogen molecule.

Also, in the $R \rightarrow +\infty$ limit this eZZe space consists of two weakly interacting H atoms which are 1-dimensional and so this corresponds to two approximately isolated atoms each having zero angular momentum. This makes the eZZe configuration a good candidate to study bond formation at large values of $R$. We shall thus study this configuration in more details. On the other hand we do not expect
the three other collinear configurations to describe the ground state: the ZZee one tends to the Zee configuration of helium which does not support the ground state, while the ZeeZ and ZeZe ones do not tend to any of the helium configurations.

### 3.6.1 Dynamics of the eZZe configuration

**Setting**

First we need to reduce the two discrete symmetries left (electron exchange symmetry and the time-reversal symmetry). We factor out the first one by choosing that electron 1 is on the negative part of the $z-$axis and electron 2 on the positive part. To reduce the time-reversal symmetry a choice of a global Poincaré surface of section (PSOS) must be made, which we do later on. Then we choose a direction of crossing of the PSOS and consider only the initial conditions on the PSOS where the flow points in our chosen direction of crossing. The Hamiltonian reads

$$H_{eZZe}(z_1, z_2, p_{z_1}, p_{z_2}) := \frac{p_{z_1}^2 + p_{z_2}^2}{2} + \frac{1}{z_2 - z_1} - \frac{1}{-z_1 - R/2} - \frac{1}{-z_1 + R/2} - \frac{1}{z_2 - R/2} - \frac{1}{z_2 + R/2}$$

(3.22)

where for future reference we note

$$r_{1A} := -z_1 - \frac{R}{2} \geq 0$$  

(3.23)

$$r_{1B} := -z_1 + \frac{R}{2} \geq R$$  

(3.24)

$$r_{2A} := z_2 + \frac{R}{2} \geq R$$  

(3.25)

$$r_{2B} := z_2 - \frac{R}{2} \geq 0$$  

(3.26)

so that $r_{1A}$ and $r_{2B}$ are the two potentially vanishing electron-nucleus distances. Hence in this configuration the types of collisions which occur are two different BCs and the SBC.
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The corresponding flow is

\[
\frac{dz_1}{dt} = p_{z_1} ; \quad \frac{dz_2}{dt} = p_{z_2} \tag{3.27}
\]

\[
\frac{dp_{z_1}}{dt} = -\frac{1}{(z_2 - z_1)^2} + \frac{1}{(-z_1 + \frac{R}{2})^2} + \frac{1}{(-z_1 - \frac{R}{2})^2} \tag{3.28}
\]

\[
\frac{dp_{z_2}}{dt} = \frac{1}{(z_2 - z_1)^2} - \frac{1}{(z_2 + \frac{R}{2})^2} - \frac{1}{(z_2 - \frac{R}{2})^2} \tag{3.29}
\]

We shall study this system in analogy to the helium eZe configuration.

Collision manifold

In terms of collision manifolds we have the following situation. As mentioned above the types of collisions occurring in this system are two BCs and an SBC. We are thus interested in the Simultaneous Binary Collision Manifold (SBCM).

Following the same procedure as in [McG74] we introduce McGehee coordinates

\[
r := \sqrt{(-z_1)^2 + (z_2)^2} ; \quad \theta := \arctan \left( \frac{z_2}{-z_1} \right) ; \quad v := \sqrt{r} p_r ; \quad u := \frac{p_\theta}{\sqrt{r}} \tag{3.30}
\]

together with a new time scale \( dr := dt/r^{3/2} \) and a rescaled Hamiltonian

\[
\mathcal{H}_{eZe} := r \mathcal{H}_{eZe} \tag{3.31}
\]

\[
= \frac{u^2 + v^2}{2} - \frac{1}{r \cos \theta} - \frac{1}{r \sin \theta} + r \left( \frac{1}{r \cos \theta + R + r \sin \theta} - \frac{1}{R + r \cos \theta} + \frac{1}{R + r \sin \theta} \right) \tag{3.32}
\]

The SBCM is given by the condition \( r = 0 \), so combined with the energy relation
(3.32) we obtain

\[ \frac{u^2 + v^2}{2} - \frac{1}{\cos \theta} - \frac{1}{\sin \theta} = 0 \]  

(3.33)

from which we find that the shape of SBCM is that of a sphere with four points at infinity \((u = \pm \infty; v = 0; \theta = 0, \frac{\pi}{2})\) just like in eZe helium.

But the size of the SBCM is different from that of the TCM: at \(\theta = \frac{\pi}{4}\) we have a circle in the \(u\) and \(v\) variables of radius \(R_{eZZe} = \sqrt{4/\sqrt{2}}\), while in the eZe case there is a larger radius \(R_{eZe} = \sqrt{7/\sqrt{2}}\). It is these subtle differences in metric properties which make the SBC mildly block-regularisable, contrary to the TC. Notice also that, as expected from our presentation in §2.4.3, the SBCM is independent of the relative positions of the bodies (here the internuclear distance \(R\)) and the flow on it corresponds to two uncoupled 2-body problems.

Poincaré sections

Next we plot Poincaré sections at our fixed energy \(E = -1\) for various values of the parameter \(R\). Obviously we can expect that as \(R\) increases the electron-electron interaction weakens and the system becomes near-integrable.

We choose \(z_2 = R/2\) (the binary collision between electron 2 and nucleus A) as definition of our PSOS, with initial directions chosen to be \(p_{z_2} > 0\). Hence coordinates on the PSOS are \((z_1, p_{z_1})\), and a crossing of the PSOS occurs if at one instant \(t_a\) we have \(p_{z_2}^{(a)} < 0\) and at the next instant \(t_b = t_a + \Delta t\) we have \(p_{z_2}^{(b)} > 0\). In that case we introduce a local fictitious time variable \(\alpha := z_2\) and rewrite each component \(f_i(t) := dw_i(t)/dt\) of the flow in terms of \(\alpha\), namely \(f_i(\alpha) = [f_i(t)]/[d\alpha/dt]\). Integrating this new flow from \(\alpha_{ini} := z_2^{(a)}\) to \(\alpha_{final} := R/2\) allows to land exactly on the PSOS.

Before computing these sections, we need to regularize the BCs of each electron. Since here our electrons can only collide with one specific nucleus we simply need to regularize these two BCs. The two distances which can go to zero in \(H_{eZZe}\)
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Figure 3.3: PSOS of the eZZe configuration at $R = 2, 4$ (see text).

are

$$r_1 := -(z_1 + \frac{R}{2}) \geq 0; \quad r_2 := z_2 - \frac{R}{2} \geq 0$$

(3.34)

so we proceed with a 1–dimensional Levi-Civita regularization of both of them, taking into account the negative sign in $r_1$

$$r_1 = Q_1^2; \quad p_{z_1} = -\frac{P_1}{2Q_1}$$

(3.35)

$$r_2 = Q_2^2; \quad p_{z_2} = \frac{P_2}{2Q_2}$$

(3.36)

so that rescaling the Hamiltonian at the level $E = -1$ to get

$$\mathcal{H}_{eZZe} := Q_1^2 Q_2^2 (H_{eZZe} + 1)$$

(3.37)

we obtain a regularized flow (where $1 \leq i \neq j \leq 2$)

$$\frac{dQ_i}{d\tau} = \frac{P_i}{4}$$

(3.38)

$$\frac{dP_i}{d\tau} = 2Q_i \left(1 - Q_j^2 + \frac{Q_j^2}{Q_j^2 + R} + \frac{Q_j^2 (2Q_i^2 + R)}{(Q_i^2 + R)^2} + \frac{Q_j^2 (2Q_i^2 + Q_j^2 + R)}{(Q_i^2 + Q_j^2 + R)^2} \right)$$

(3.39)
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with a new time $dt = Q_1^2 Q_2^2 d\tau$. Although it is trajectories in such regularized coordinates which are effectively computed, we keep track at each time step of the values of the original variables to detect crossings of the PSOS.

Let us now consider the plots (fig.3.3 and fig. 3.4) of these PSOS of eZZe. First, note that for any $R$ there exists trajectories which go out to infinity and where one electron escapes as in eZe helium; we only included some in our first two figures.

![Figure 3.4: PSOS of the eZZe configuration at $R = 8, 14$ and zoom of $R = 14$ (see text).](image)

We observe that the chaotic region which exists for small $r_1$ in the eZe helium configuration (see fig 2.12) is still present in our eZZe configuration for small values of $R$ (at $R = 2, 4$ and to a lesser extend $R = 8$). As we mentionned in
§2.4.3, a collinear SBC is only block-regularizable to a very low degree, so it also induces nearby chaotic motion. On the other hand, the dynamics when $r_1$ is large and $p_{r_1}$ moderate is regular for small values of $R$, which is again similar to the situation in eZe helium.

The chaotic region then gradually shrinks at larger values of the internuclear distance ($R = 14$), while KAM-islands start to develop around some of the (now stable) periodic orbits. This illustrates that in the $R \to +\infty$ limit the system becomes near-integrable. The integrals present in that limit are those of two independent 1–dimensional hydrogen atoms, namely the two-body Hamiltonians of each pair.

Labelling and continuation of periodic orbits

Next we would like to study how the periodic orbits of the system are organized and how this depends on the parameter $R$.

Now, despite the flow of our system (3.29) being formally equal to that of eZe helium when setting $R = 0$, we know that the limit $R \to 0$ is in fact not smooth everywhere since the two collision manifolds are different. Nevertheless, this non-smoothness occurs only in the vicinity of SBC and TC orbits. In configuration space, which is the $(z_1, z_2)$ plane, such orbits are tangent to the antidiagonal $z_2 = -z_1$ at the origin. The remaining orbits on the other hand can be smoothly continued from the eZZe to the eZe configuration and vice-versa.

So for instance all the short periodic orbits of eZe helium are continuable for $R \neq 0$ since we know that they do not approach the TC singularity closely (they cross the antidiagonal far from the origin). This means that the basic structure of the set of periodic orbits is the same as that of eZe helium, in particular that we can label orbits in the same way by their sequence of binary collisions (see §2.4.5).
We thus proceed to the continuation of these orbits as a function of $R$ as follows. At some value $R = R_0$ we are given the initial condition $z_1^{(0)}$ of a chosen periodic orbit on our PSOS as well as the number $N_{ret}$ of returns to the PSOS that this orbit requires to close. Then at $R = R_1 = R_0 + \delta R$ a linear estimate is made for the initial condition $z_1^{(1)} = a \cdot z_1^{(0)} + b$ of this orbit and then we minimize the absolute value of the difference between $z_1^{(1)}$ and its $N_{ret}$-th return to the PSOS. The algorithm is initialized with initial conditions from eZe helium.

In fig 3.5 we plot as a function of $R$ the position $^1$ on the PSOS of the absolute value $|z_1^T(R)| = -z_1^T(R)$ of the initial condition of the periodic orbit with code $T$ (the asymmetric stretch orbit). In the limit $R \to 0$ we have by construction convergence to the eZe value in a continuous way. As $R$ increases we observe that the distance, call it $D_{cn}(R)$, between the position of this initial condition and that of the closest nucleus (this nucleus is located at $R/2$) decreases monotonically and converges as expected as $R \to +\infty$ towards the asymptotic value $D_{cn}^\infty = \sqrt{2}$ of two independent 1–dimensional Kepler problems (the regularized motions of those being $Q_1^\infty(\tau) = 2 \cos^2(\frac{\tau}{2})$, $Q_2^\infty(\tau) = 2 \cos^2(\frac{\tau + \pi}{2})$ of period $2\pi$).

The period and action of these periodic orbits are then computed via the regularized coordinates. For the period we integrate

$$\frac{dt}{d\tau} = Q_1^2 Q_2^2$$

and for the action since

$$S = \int_\gamma \sum_i p_i dq_i = \int_0^T \sum_i p_i^2 dt$$

---

1The numerical values of regularized initial conditions for that periodic orbit at $R = 1.0001$ for example are $Q_1^{(1)} \approx 1.1420873$, $P_1^{(1)} \approx -0.9137247$, $Q_1^{(2)} = Q_1^{(1)}$, $P_1^{(2)} = -P_1^{(2)}$ with the remaining coordinates determined by the relations mentioned earlier.
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Figure 3.5: Absolute value of initial condition $|z_1^\text{ini}| = -z_1^\text{ini}$ of the asymmetric stretch orbit of the eZZe configuration as a function of $R$ compared to position of closest nucleus.

we have $\frac{dS}{dt} = \sum_i p_i^2$ and so we integrate

$$\frac{dS}{d\tau} = \sum_i p_i^2 \frac{d\tau}{dt} = \frac{P_1^2}{Q_1^2} + \frac{P_2^2}{Q_2^2} = \frac{Q_2^2 P_1^2 + Q_1^2 P_2^2}{4}$$

(3.42)

Figure 3.6: Period and action of the asymmetric stretch orbit of the eZZe configuration as a function of $R$ together with their asymptotic limits.

For our asymmetric stretch orbit $T$ we find that its period decreases monotonically from the value of the helium eZe asymmetric stretch towards the asymptotic value $T_{H+H} = 2\pi$ as $R$ increases, while the action also decreases monotonically
from the eZe value towards its asymptotic value $S_{H+H} = 4\pi$, see fig 3.6.

Stability of periodic orbits

We now discuss the spectral stability of these periodic orbits (see appendix A for a definition) and what we require is the full spectral stability, i.e. for electrons moving in 3–dimensional physical space. In fact due to the $SO(2)$–symmetry around the $z$–axis we have that the stability in the $x_i$ DOF is the same as that in the $y_i$ DOF. So we only need to consider that the electrons move on the $z$–axis within a fixed plane containing the nuclei, say $xOz$.

Thus we introduce one extra coordinate for both electrons (respectively $x_1$ and $x_2$) and then we compute the variational flow for our 4 DOF orbits. These extra coordinates are of course equal to zero for all times along our periodic orbits but we do need to introduce them to compute the off-collinear perturbations. Hence we work with a planar Levi-Civita regularization for each of the colliding pairs, and for that we introduce new regularized variables for the two electrons $Q_{1}^{(i)}$, $Q_{2}^{(i)}$, $P_{1}^{(i)}$, $P_{2}^{(i)}$ (where $i = 1, 2$) which are such that

$$x_i = (Q_1^{(i)})^2 - (Q_2^{(i)})^2$$

(3.43)

$$z_i + \kappa_i \frac{R}{2} = 2Q_1^{(i)}Q_2^{(i)}$$

(3.44)

and

$$p_{xi} = \frac{Q_1^{(i)}P_1^{(i)} - Q_2^{(i)}P_2^{(i)}}{2((Q_1^{(i)})^2 + (Q_2^{(i)})^2)}$$

(3.45)

$$p_{zi} = \frac{Q_2^{(i)}P_1^{(i)} + Q_1^{(i)}P_2^{(i)}}{2((Q_1^{(i)})^2 + (Q_2^{(i)})^2)}$$

(3.46)

where $\kappa_1 = +1$ and $\kappa_2 = -1$. 

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The suitably regularized Hamiltonian is then

\[ H_{eZZe} := \left( (Q_1^{(1)})^2 + (Q_2^{(1)})^2 \right) \left( (Q_1^{(2)})^2 + (Q_2^{(2)})^2 \right) (H_{eZZe} + 1) \]  \hspace{1cm} (3.47)

We get the Hamiltonian flow from it – which involves expressions too long to be written down either here or in an appendix – and then we specify the regularized initial conditions so that \( x_1 = x_2 = p_{x_1} = p_{x_2} = 0 \).

From the relations above we find that \( x_1 = 0 \) implies

\[ Q_1^{(1)} = \pm \sqrt{-\left( \frac{z_1}{2} + \frac{R}{4} \right)} = -Q_2^{(1)} \]  \hspace{1cm} (3.48)

and we choose \( Q_1^{(1)} \) to be positive. Then the condition \( P_{x_1} = 0 \) combined with the previous results leads to

\[ P_1^{(1)} = -2p_{z_1} \sqrt{-\left( \frac{z_1}{2} + \frac{R}{4} \right)} = -P_2^{(1)} \]  \hspace{1cm} (3.49)

Similarly we find that initial conditions for the second electron are

\[ Q_1^{(2)} = \sqrt{\frac{z_2}{2} - \frac{R}{4}} = Q_2^{(2)} \]  \hspace{1cm} (3.50)

with

\[ P_1^{(2)} = 2p_{z_2} \sqrt{\frac{z_1}{2} - \frac{R}{4}} = P_2^{(2)} \]  \hspace{1cm} (3.51)

We can now set up the variational flow in these planar regularized coordinates. The stability and Lyapunov exponents being intrinsic properties of periodic orbits they are independent of the symplectic coordinate system used, and so the regularized variational flow also provides the stability eigenvalues we are looking for.

As we have 2 DOF for each electron we study the evolution of \( d \times d \) square
matrices $M$ where $d = 4 + 4 = 8$, and along a given periodic orbit $\gamma(t)$ we compute from $t = 0$ to $t = T_\gamma$

$$\frac{dM}{dt}(t) = J \cdot \text{Hess}(\mathcal{H}_{eZZe})(\gamma(t)) \cdot M(t)$$

with initial condition $M(0) = \text{Id}$, where $\text{Hess}(\mathcal{H}_{eZZe})$ is the Hessian matrix of $\mathcal{H}_{eZZe}$ and $J$ is the standard $d \times d$ symplectic matrix (see appendix A).

Then we are interested in the spectrum of the monodromy matrix $M(T_\gamma)$, and this spectrum is here of the form

$$\text{sp}(M) = \{1, 1, \Lambda_{\parallel,eZZe}, \Lambda_{\parallel,eZZe}^{(sym)}, \Lambda_{\perp,eZZe}^{(sym)}, \Lambda_{\perp,eZZe}^{(rot)}, \Lambda_{\perp,eZZe}^{(rot)}\}$$

where we have the following conjugated pairs of eigenvalues (see fig 3.7)

- $1, 1$ comes from the conservation of the integral $\mathcal{H}_{eZZe}$ and is related to sym-
metric perturbations along the collinear DOF

• $\Lambda_{\parallel,eZZe}, \Lambda_{\parallel,eZZe}$ describes anti-symmetric collinear perturbations

• $\Lambda_{\perp,eZZe}, \Lambda_{\perp,eZZe}$ corresponds to symmetric off-collinear perturbations

• $\Lambda_{\perp,eZZe}, \Lambda_{\perp,eZZe}$ are associated to anti-symmetric off-collinear perturbations

Recall that the spectral stability of periodic orbits of the eZe helium configuration also lead to four pairs of eigenvalues corresponding to similar perturbations (see §2.4.5). There it was found that the pair corresponding to anti-symmetric off-collinear perturbations, namely $\Lambda_{\perp,eZZe}, \Lambda_{\perp,eZZe}$, was equal to 1, 1 due to the larger rotationnal symmetry. On the other hand, anti-symmetric collinear perturbations were unstable while symmetric off-collinear ones were stable.

Let us first study the limit $R \to 0$ towards this eZe helium configuration. Our results for the asymmetric stretch orbit $\Gamma$ are as follows. We find that the pair $\Lambda_{\parallel,eZZe}, \Lambda_{\parallel,eZZe}$ does converge to the helium pair $\Lambda_{\parallel,eZe}, \Lambda_{\parallel,eZe}$, see fig 3.8. In particular, we observe that such type of collinear perturbations remain (weakly) unstable for all values of $R$.

As for the two other pairs of eigenvalues, we find that they do not converge to those of the helium eZe configuration. In fig 3.8 we plot the value of the two corresponding stability exponents. The pair $\Lambda_{\perp,eZZe}, \Lambda_{\perp,eZZe}$, which is associated to anti-symmetric off-collinear perturbations does not converge to a pair of eigenvalue 1 but remains stable. The other pair $\Lambda_{\perp,eZZe}, \Lambda_{\perp,eZZe}$, which corresponds to symmetric off-collinear perturbations becomes unstable for $R \lesssim 0.84$, and gives rise to the second Lyapunov exponent of fig 3.8. In fact in the limit $R \to 0$ it becomes very unstable, possibly infinitely so.
Figure 3.8: Top: Lyapunov exponents of the asymmetric stretch orbit of the $eZZe$ configuration as a function of $R$. In particular $\lambda_\parallel := \log \left( \Lambda_\parallel,eZZe \right) / T_e^{eZZe}$ converges to the $eZe$ value $\lambda_{eZe}$. Bottom: Stability exponents of the asymmetric stretch orbit of the $eZZe$ configuration as a function of $R$.

This non-smooth limit for the stability exponents can be explained as follows. As electron 2 approaches nuclei A, when $R$ is very small we are in fact close a TC. It is not a dynamical TC like in helium where two electrons move and approach a fixed nucleus. Here it is rather a parametric TC since it involves two fixed nuclei and a moving electron. But still, we know that we cannot expect orbits going close to a TC (be it dynamical or parametric) to behave smoothly with respect to small
perturbations and indeed this is what we are witnessing here. Fig 3.9 illustrates this, showing that only the stability properties of a motion around both nuclei can be expected to converge smoothly, not one which picks up what happens between the nuclei.

**Topological indices**

Due to this non-continuous $R \to 0$ limit for stability exponents, we can conclude that the Conley-Zenhder indices of the periodic orbits do not possess a continuous limit too, since the explicit formula (1.62) shows that for those one must take into account the number of elliptic blocks of the monodromy matrices as well as the precise values of the stability exponents.
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For example already for the initial index of the asymmetric stretch orbit we find

\[ \eta_{T}^{eZe} = N_{eZe} + 2m_{eZe} = 2 + 2m_{eZe} \]  \hspace{1cm} (3.54)

\[ \eta_{T}^{eZZe} = N_{eZZe} + 2m_{eZZe} = 1 + 2m_{eZZe} \]  \hspace{1cm} (3.55)

so that one is even and the other odd, hence necessarily different.

On the other hand, we are only interested in the B-indices of our orbits, which in our present case are equal to twice the Gel’fand-Lidskii indices \( m \). The computation of \( m \) by the PB method in the case of the \( R - \bar{T} \) orbit at \( R = 3 \) is illustrated by fig 3.10. We find \( m = 4 \), so the B-index of this orbit is equal to 8 at \( R = 3 \) (we remark that this is different from the \( eZe \) case where the index is equal to 4). This result will suffice for our semiclassical study in chapter 4.

Figure 3.10: Winding in the complex plane of \( \det P(t) = \det(A_p(t) + iB_p(t)) \) (see eq 1.64) computed along the \( R - \bar{T} \) PO at \( R=3 \). It provides a loop from which the Gel’fand-Lidskii index of the orbit is computed: here we find \( m = 4 \).
3.7 Dynamics in $\mathbb{N}_{\{e\}}$

3.7.1 Setting

The other strata of our reduced phase space is $\mathbb{N}_{\{e\}}$ and as mentioned previously consists of a 5 DOF configuration which involves spatial motion of both electrons within $\{E = -1\} \cap \{L_z = 0\}$. This configuration possesses various invariant subspaces that we now discuss.

The reduction of the continuous symmetry group $SO(2)$ mentioned in §3.5.1 is done in practise by using the six cylindrical coordinates for both electrons (respectively $(\rho_1, \theta_1, z_1)$ and $(\rho_2, \theta_2, z_2)$), so that the configuration is parametrized by the five coordinates $\rho_1, \rho_2, \theta_{12}, z_1, z_2$, where $\theta_{12} := \theta_2 - \theta_1$. The sixth variable left is the angle $\theta_{L_z} := \theta_1 + \theta_2$ which is the cyclic coordinate associated to the integral $L_z$ of $SO(2)$. We thus have a first change of variables

\[
\begin{pmatrix}
\rho_1 \\
\rho_2 \\
\theta_{12} \\
z_1 \\
z_2 \\
\theta_{L_z}
\end{pmatrix}
\rightarrow
\begin{pmatrix}
\frac{\rho_1 + \rho_2}{2} \\
\frac{\rho_1 - \rho_2}{2} \\
\frac{\theta_{12}}{2} \\
z_1 \\
z_2 \\
\frac{\theta_{L_z} + \theta_{12}}{2}
\end{pmatrix}
\rightarrow
\begin{pmatrix}
x_1 = \rho_1 \cos(\theta_1) = \rho_1 \cos\left(\frac{\theta_{L_z} - \theta_{12}}{2}\right) \\
y_1 = \rho_1 \sin(\theta_1) = \rho_1 \sin\left(\frac{\theta_{L_z} - \theta_{12}}{2}\right) \\
x_2 = \rho_2 \cos(\theta_2) = \rho_2 \cos\left(\frac{\theta_{L_z} + \theta_{12}}{2}\right) \\
y_2 = \rho_2 \sin(\theta_2) = \rho_2 \sin\left(\frac{\theta_{L_z} + \theta_{12}}{2}\right)
\end{pmatrix}
\]

where $\rho_i \in \mathbb{R}^+$ and $z_i, \theta_{12}, \theta_{L_z} \in \mathbb{R}$.

Next we need to reduce the two discrete symmetries (electron-exchange $\Pi_e$ and time-reversal $\Pi_t$, see §3.5.2) to obtain our fully reduced stata $\mathbb{N}_{\{e\}}/\{\Pi_e, \Pi_t\}$. We start with electron-exchange by introducing the following symmetrized coordinates

\[
\rho_+ := \rho_1 + \rho_2, \quad \rho_- := \rho_2 - \rho_1, \quad z_+ := z_1 + z_2, \quad z_- := z_2 - z_1
\]
so that applying $\Pi_e$ leaves $\rho_+, z_+$ and $\theta_{Lz}$ fixed while it reverses the signs of $\rho_-, z_-$ and $\theta_{12}$. To reduce $\Pi_e$ we can thus choose as a fundamental domain in configuration space the intersection of the region

$$D_{\{e\}} := \{ \rho_+ \geq 0, z_+ \geq 0, \theta_{Lz} \geq 0, \rho_- \geq 0, z_- \geq 0, \theta_{12} \geq 0 \}$$

(3.58)

with our chosen level set $N = F^{-1}(-1,0)$, namely

$$\Delta_{\{e\}} := D_{\{e\}} \cap N$$

(3.59)

This means that all trajectories are started inside this domain, and each time a trajectory hits one of the boundaries it is continued by a hard-wall reflection back into $\Delta_{\{e\}}$. In particular, the fact that $\rho_- \geq 0$ and $z_- \geq 0$ for all times means that electron 2 has been chosen as the outer electron for this $\Pi_e$-reduced dynamics.

Finally we have to reduce the time-reversal symmetry. This can be done, similarly to what we did in helium, by choosing a PSOS which is transversal to the trajectories we are interested in and then to choose a crossing direction to define positive times, and consider dynamics only for positive times. Here there is no global PSOS, but there is a very large one which will suit our needs. It is defined by $\rho_1 = \rho_2$, with positive times direction chosen as going into the $\rho_2 > \rho_1$ half. The only kind of dynamics not transversal to this PSOS consists of Wannier-type trajectories satisfying $\rho_1 = \rho_2$ for all times; we shall see below that these trajectories form small lower-dimensional invariant subspaces which can be studied independently.

This PSOS is one of the boundaries of the $\Pi_e$-fundamental domain $\Delta_{\{e\}}$. Indeed the condition $\rho_1 = \rho_2$ means $\rho_- = 0$ and our chosen direction of PSOS cross-

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2This means that electron 2 is always either further away or at a same distance to the origin than electron 1. Of course in the original non-reduced phase space the trajectories are not considered up to electron-exchange and there electron 2 will sometimes be closer to the origin than electron 1.
ings means going into the $\rho_- > 0$ part, which is exactly the hard-wall reflexion condition at the $\rho_- = 0$ boundary of $\Delta_{\{e\}}$. So the reduction of $\Pi_t$ can be done simply by starting all trajectories on the $\rho_- = 0$ boundary and going inside $\Delta_{\{e\}}$.

3.7.2 Flow

Now that we have found what the natural coordinates and the configuration space domain are, we need to find the flow. For that we need first to generate the associated momenta by a cotangent lift\(^*\) of our change of coordinates. Explicitly, we find that the physical momenta are given in terms of the new ones as

\begin{align}
p_{x_i} &= c_i(P_{\rho_+} + \kappa_i P_{\rho_-}) + \frac{2s_i(P_{\theta_{12}} + \kappa_i P_{\theta_{Lz}})}{\rho_- + \kappa_i \rho_+} \tag{3.60} \\
p_{y_i} &= s_i(P_{\rho_+} + \kappa_i P_{\rho_-}) + \frac{2c_i(P_{\theta_{12}} + \kappa_i P_{\theta_{Lz}})}{\rho_- + \kappa_i \rho_+} \tag{3.61} \\
p_{z_i} &= P_{z_+} + \kappa_i P_{z_-} \tag{3.62}
\end{align}

where $i = 1, 2$, $\kappa_1 = -1$, $\kappa_2 = 1$, $c_i := \cos\left(\frac{\theta_{Lz} + \kappa_i \theta_{12}}{2}\right)$ and $s_i := \sin\left(\frac{\theta_{Lz} + \kappa_i \theta_{12}}{2}\right)$.

The Hamiltonian (3.1) is then rewritten into a new one, say $\mathcal{H}$, and the flow in $\overline{N_{\{e\}}}/\{\Pi_e, \Pi_t\}$ is the one associated to $\mathcal{H}$. Introducing

\begin{align}
a_\pm &:= c_2 \frac{\rho_+ + \rho_-}{2} \pm c_1 \frac{\rho_+ - \rho_-}{2} \quad ; \quad b_\pm := s_2 \frac{\rho_+ + \rho_-}{2} \pm s_1 \frac{\rho_+ - \rho_-}{2} \tag{3.63}
\end{align}

we obtain the following flow

\begin{align}
\frac{d\rho_+}{dt} &= 2P_{\rho_+} \quad ; \quad \frac{d\rho_-}{dt} = 2P_{\rho_-} \quad ; \quad \frac{dz_+}{dt} = 2P_{z_+} \quad ; \quad \frac{dz_-}{dt} = 2P_{z_-} \tag{3.64}
\end{align}

\begin{align}
\frac{d\theta_{12}}{dt} &= \frac{8(P_{\theta_{12}}(\rho_+^2 + \rho_-^2) - 2P_{\theta_{Lz}} \rho_- \rho_+)}{(\rho_+^2 - \rho_-^2)^2} \quad ; \quad \frac{d\theta_{Lz}}{dt} = \frac{8(P_{\theta_{Lz}} (\rho_+^2 + \rho_-^2) - 2P_{\theta_{12}} \rho_- \rho_+)}{(\rho_+^2 - \rho_-^2)^2} \tag{3.65}
\end{align}
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\[
\frac{dP_{\rho_\pm}}{dt} = \frac{a_- (c_2 + c_1) + b_+ (s_2 + s_1)}{2(a^2 + b^2)^{3/2}} \pm \frac{4(\rho_+ - \rho_-)}{(\rho_+ - \rho_-)^2 + R^2)^{3/2}} - \frac{4(\rho_+ + \rho_-)}{(\rho_+ + \rho_-)^2 + R^2)^{3/2}}
\]

\[
\pm 8 \left( P_{\theta_{Lz}} P_{\theta_{12}} (6 \rho_+^2 \rho_+ + 2 \rho_+^3) - (P_{\theta_{Lz}}^2 + P_{\theta_{12}}^2) (3 \rho_\pm \rho_+^2 + \rho_\pm^3) \right) \quad (3.66)
\]

\[
\frac{dP_{\theta_{12}}}{dt} = \frac{a_+ b_- - a_- b_+}{2(a^2 + b^2)^{3/2}} \quad \frac{dP_{\theta_{Lz}}}{dt} = 0 \quad (3.67)
\]

\[
\frac{dP_{z_\pm}}{dt} = -\frac{\pm 2(z_+ - z_- - R)}{((\rho_+ - \rho_-)^2 + (z_+ - z_- - R)^2)^{3/2}} - \frac{\pm 2(z_+ - z_- + R)}{((\rho_+ - \rho_-)^2 + (z_+ - z_- + R)^2)^{3/2}}
\]

\[
-\frac{2(z_+ + z_- - R)}{((\rho_+ + \rho_-)^2 + (z_+ + z_- - R)^2)^{3/2}} - \frac{2(z_+ + z_- + R)}{((\rho_+ + \rho_-)^2 + (z_+ + z_- + R)^2)^{3/2}}
\]

\[
\frac{\mu_{z_\pm}}{2(\rho_+ \left( \frac{1-c_1 c_2 - s_1 s_2}{2} \right) + \rho_- \left( \frac{1+c_1 c_2 + s_1 s_2}{2} \right) + z_-^2)^{3/2}}
\]

where \( \mu_+ = 0, \mu_- = 1 \).

Note in particular that the cyclic variable \( \theta_{Lz} \), for which we choose the initial value 0, evolves along trajectories. Orbits which are periodic in our five reduced DOF \( \rho_\pm, z_\pm, \theta_{12} \) but for which \( \theta_{Lz} \) does not go back to its original value after one reduced period are called relative periodic orbits (RPO). This means that such orbits are not closed in physical space after a time equal to the reduced period (we will find examples of such orbits below). From now on, the acronym PO will always refer to orbits which are periodic both in reduced and physical space, the others being RPO.

There exists also the notion of relative equilibria (RE): fixed points of the reduced flow which corresponds in physical space to uniformly rotating orbits with angular momentum \( L_z \). But since here we are working with \( L_z = 0 \) there are no REs, any equilibrium of the reduced system is also an equilibrium in physical space.
Of course, the coordinate $P_{\theta_{12}}$ remains fixed along any orbit and its value is 0 for our system.

### 3.7.3 Fixed points

The system is $R$–dependent and it turns out that there is only one fixed point (at our $E = -1$). It occurs for $R_{eq} = 3\sqrt{3} \approx 5.19615$ and is located at

$$
\rho_+ = 3; \rho_- = 0; \theta_{12} = \pi; z_+ = 0; z_- = 0; P_{\rho_+} = 0; P_{\rho_-} = 0; P_{\theta_{12}} = 0; P_{z_+} = 0; P_{z_-} = 0.
$$

(3.69)

In physical space it consists of placing the two electrons symmetrically with respect to the origin on any line through the origin contained in the xOy plane. The electrons are then at a distance $d_{eq} = 1.5$ of the origin, see fig 3.11.

### 3.7.4 Invariant subspaces

Whenever at least one conjugated pair of components of our flow vanishes identically we obtain a lower dimensional invariant subspace corresponding to a configuration with less DOF.

#### 4 DOF subspaces

First we observe that to have $d\theta_{12}/dt = 0$, $dP_{\theta_{12}}/dt = 0$ one must have $P_{\theta_{12}} = 0$ and either $c_1s_1 = c_2s_2$ or $\rho_-^2 = \rho_+^2$. This last condition does not involve $\theta_{12}$ so is discarded, but the other does, and it implies either $\theta_{12} = 0$ or $\theta_{12} = \pi$.

In fact, we find that the remaining components of the flow are equivalent in the two cases $\theta_{12} = 0$ and $\theta_{12} = \pi$. So all orbits of our reduced phase space starting with either $\theta_{12} = 0$, $P_{\theta_{12}} = 0$ or $\theta_{12} = \pi$, $P_{\theta_{12}} = 0$ belong to the same 4 DOF...
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Figure 3.11: There are equilibria only at $R = 3\sqrt{3}$ in which case the electrons are placed symmetrically at a distance $d = 1.5$ of the origin on any line in the $xOy$ plane.

invariant subspace, call it $Z$, in which $d\theta_{12}/dt = 0$. In physical coordinates this corresponds to dynamics in invariant planes containing the $z$–axis, like the $xOz$ plane, see fig 3.12.

There are no other invariant 4 DOF subspaces, since imposing $d\chi/dt = 0$, $dP_\chi/dt = 0$ where $\chi$ is any of the four other DOF ($\rho_+, \rho_-, z_+, z_-$) leads to conditions on $\chi$, $P_\chi$ which are impossible to fulfill.

3 DOF subspaces

To find whether there exists 3 DOF subspaces we have to study two cases:

- one where the flow components of the pair $\theta_{12}$, $P_{\theta_{12}}$ vanish together with the flow components of one other DOF $\chi$, $P_\chi$ (i.e. in that case we would obtain a subspace of $Z$)
Figure 3.12: Top: representation in physical coordinates of the 4 DOF planar configuration $\mathcal{Z}$. Bottom: representation in physical coordinates of the 3 DOF outer-planar configuration $\mathcal{Z}_\perp$ (it has $L_z = 0$).

- one where the $\theta_{12}$ DOF evolves while two other DOFS $\chi$ and $\nu$ are invariant
The first case is impossible as an inspection of the expressions for the flow show, and so we conclude that there is no 3 DOF subspace within $\mathcal{Z}$.

On the other hand the second case is possible but only with the choice $\chi = z_+, \nu = z_-$, which implies $z_+ = 0$, $z_- = 0$ for all times. We call the corresponding configuration $\mathcal{Z}_\perp$; in physical space it consists of electronic motions (within $E = -1$, $L_z = 0$) which are restricted to the plane $xOy$ which is orthogonal to the $z-$axis at the origin, see fig 3.12.

2 DOF subspaces

Finally we determine all the 2 DOF subspaces. The three invariant DOF can either be:

- $\theta_{12}$ and two others, leading to subspaces of $\mathcal{Z}$

- $z_+$, $z_-$ and one other (apart from $\theta_{12}$), leading to subspaces of $\mathcal{Z}_\perp$

In the first case we find the following invariant subspaces in $\mathcal{Z}$

- $\mathcal{W}_z$ which has $\theta_{12}$, $z_+$ and $\rho_-$ invariants; in physical space this is Wannier-like motion in planes containing the $x-$axis, with axis of symmetry the $z-$axis

- $\mathcal{W}_\rho$ which has $\theta_{12}$, $z_-$ and $\rho_+$ invariants; in physical space this is Wannier-like motion in planes containing the $z-$axis, with axis of symmetry the other axis (the $x-$axis in the case of the $xOz$ plane)

- $S$ which has $\theta_{12}$, $z_+$ and $\rho_+$ invariant; in physical space it consists in motions in planes containing the $z-$axis such that the electrons are centrally symmetric with respect to the origin
Figure 3.13: Representation in physical coordinates of the two Wannier-Ridge-like 2 DOF configurations ($W_\rho$ top, $W_z$ bottom).

- $\mathcal{P}$ which has $\theta_{12}$, $z_+$ and $z_-$ invariants; in physical space it consists in motions in planes containing the $z-$axis such that the electrons are restricted to collinear motion on the other axis
In the second case we can only have $z_+, z_- \text{ and } \rho_+$ invariant. We call this configuration $\mathcal{W}_{\rho, \perp}$; in physical space it consists of Wannier-like motion in planes perpendicular to the $z-$ axis at the origin, with axis of symmetry any axis in this
plane.

![Figure 3.15](image)

Figure 3.15: Representation in physical coordinates of the outer-planar Wannier Ridge like 2 DOF configuration $W_{\rho, \perp}$.

The diagram in fig 3.16 sums up how the various subspaces of our 5 DOF fully reduced strata $N_{\{e\}}/\{\Pi_e, \Pi_I\}$ are organized.

$R-$dependence of the subspaces

The shapes of all the subspaces mentioned above change as $R$ is varied, and some of these subspaces do not exist for some ranges of $R$ values. The situation is as follows.

For any given configuration $\mathcal{K}$, the part of configuration space where motion is allowed to take place is the region

$$\Delta_{\text{allowed}}(\mathcal{K}) := \{(\rho_+; \rho_-; \theta_{12}; z_+, z_-) | V_{\mathcal{K}}(\rho_+; \rho_-; \theta_{12}; z_+, z_-) \leq -1\} \quad (3.70)$$
We find that for configurations in which the electrons have the $z_+$ and $z_-$ DOF invariant (that is, $Z_\perp$, $P$ and $W_{\rho,\perp}$) this allowed region shrinks as $R$ increases and becomes the empty set for $R > R_{eq}$, so these configurations do not exist at large $R$.

In fig 3.17 and fig 3.18 we plot in physical configuration space the contours of slices in the xOz plane of the region $V(q) \leq -1$ for $P$ and $W_{\rho,\perp}$. In the case of $Z_\perp$ we show instead in fig 3.19 how the allowed region looks like in reduced configuration space (in fact we use $\cos(\theta_{12})$ rather than $\theta_{12}$). The results in all three cases are consistent with the intuition: when $R$ is large the dynamics takes place near each nuclei and the xOy plane (which supports these three configurations) becomes too far from the nuclei to be within the classically allowed region.

In the $W_\rho$ configuration (see fig 3.20) each electron is confined to a region which at small $R$ is similar to that of the Wannier configuration in the helium atom. When $R$ increases the small forbidden central region grows bigger until at $R = R_{eq}$ the region splits into four parts. At large $R$ the two parts around a given nuclei tend to have the same shape as in the helium Wannier configuration. So
Figure 3.17: Plots on the physical xOz plane of the contour of the level set $V = -1$ of the $P$ configuration. Allowed motion takes place inside the dotted regions. From left to right, top to bottom, we have $R = 0.5, 1, 2, 4, 5$.

Any quantum state which localizes on this configuration $W_p$ at large $R$ will tunnel between these two nuclei-centered regions.

A similar scenario happens in the $S$ configuration (see fig3.21): a forbidden region which is small at small $R$ grows larger as $R$ increases until the whole region breaks into two components at $R = R_{eq}$, again implying that tunneling will occur for any quantum state localizing on this configuration at large $R$.

Finally there remains the $W_z$ configuration, which as can be seen in fig3.22, is the only one whose topology does not change drastically at $R = R_{eq}$. Like in the $W_p$ case, the classically allowed region of $W_z$ is split from the beginning into two regions whose shape is similar to that of the helium Wannier configuration. Then as $R$ increases these two regions simply gradually become spheres centered at each nuclei.
Figure 3.18: Plots on the physical xOy plane of the contour of the level set \( V = -1 \) of the \( W_{\rho,\perp} \) configuration. Allowed motion takes place inside the dotted regions. From left to right, top to bottom, we have \( R = 1, 2, 4, 5 \).

Figure 3.19: Plots in \( \rho_1, \rho_2, \cos(\theta_{12}) \) coordinates of the contour of the level set \( V = -1 \) of the \( Z_\perp \) configuration. Allowed motion takes place between the bottom plane (\( \cos(\theta_{12}) = -1 \)) and the surface. From left to right, top to bottom, we have \( R = 0.3, 1.4, 3, 4.5, 5.1 \).
Figure 3.20: Plots on the physical xOz plane of the contour of the level set $V = -1$ of the $W_\rho$ configuration. Allowed motion takes place inside the dotted regions. From left to right, top to bottom, we have $R = 0.5, 1, 2, 4, 5, 8$.

Figure 3.21: Plots on the physical xOz plane of the contour of the level set $V = -1$ of the $S$ configuration. Allowed motion takes place inside the dotted regions. From left to right, top to bottom, we have $R = 1, 2, 4, 5, 6, 8$.

Symmetry breaking at small $R$

Before studying the dynamics in some of these configurations let us examine how they are related to those of the helium atom (with $E = -1$ and $L_{tot} = 0$) in the
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Figure 3.22: Plots on the physical xOz plane of the contour of the level set $V = -1$ of the $W_z$ configuration. Allowed motion takes place inside the dotted regions. From left to right, top to bottom, we have $R = 0.5, 1, 2, 4, 5, 8$.

$R \to 0$ limit. This will allow us to determine which of our configurations, if any, converge to the helium eZe configuration (which we know to support the helium ground state).

We saw already that all three Wannier-like configurations $W_\rho$, $W_z$ and $W_{\rho,\perp}$ converge to the Wannier configuration of helium in that limit. Since the helium ground state is not localized on this configuration we shall not study these three ones further.

The $S$ and $P$ configurations are specific to the hydrogen molecule and do not converge to any of the helium configurations. For $S$ this is clear since at $R = 0$ such symmetric motions would have non-zero total angular momentum. In the case of $P$ this is less evident and can be noticed by the fact that the shape of the $V = -1$ region at small $R$ is very different from that of helium eZe. This has been missed by two authors who studied this configuration [Waa94, LC03] and therefore we shall present a detailed study of the dynamics in $P$ in the next section.
On the other hand, a part of the $Z_\perp$ configuration does converge to the helium eZe one as $R \rightarrow 0$. Indeed in that limit, the shape of the classically allowed region converges to that of the 3 DOF subspace $L_{tot} = 0$ of helium. In particular there must be orbits converging to those of each of the three subspaces eZe, Zee and WR of $L_{tot} = 0$. We shall study the dynamics in $Z_\perp$, including this limit to eZe, in details at the end of this chapter.

### 3.7.5 Dynamics in the collinear pendulum configuration

As we mentioned above, the collinear pendulum configuration $P$ exists only for $0 < R < 3\sqrt{3}$. Moreover, the shape of its energetically allowed configuration space domain does not tend, in the limit $R \rightarrow 0$, to that of the helium eZe configuration. So while we cannot expect this configuration to contribute to the semiclassical structure of the spectrum of the hydrogen molecule at small or large $R$, it still remains to be seen how its dynamics is organized at intermediate values of $R$.

#### Coordinates and flow

In this configuration, the two evolving DOF are $\rho_+$ and $\rho_-$, the three others being invariant. In order to make easier some comparisons with previous work on this configuration by other authors [Waa94, LC98, LC03], we shall use in fact another set of coordinates.

After reducing the $SO(2)$ symmetry, the electrons in this configuration can be thought of as evolving on the $x-$axis, so the two DOF are then $x_1$ and $x_2$. In order to reduce the discrete symmetries (electron-exchange $\Pi_e$ and time-reversal $\Pi_t$), we again need to introduce symmetrized coordinates and so our chosen DOF are finally $x_\pm := x_2 \pm x_1$. A suitable fundamental domain in configuration space to reduce $\Pi_e$ and $\Pi_t$ is then

$$\Delta_P := \{x_+ \geq 0; x_- \geq 0\} \cap \{V_P(x_+, x_-) \leq -1\} \quad (3.71)$$
with PSOS defined by \( \{ x_+ = 0; \ p_{x_-} > 0 \} \).

The flow in these coordinates reads

\[
\begin{align*}
\frac{dx_+}{dt} &= 2p_{x_+}; \quad \frac{dx_-}{dt} = 2p_{x_-} \tag{3.72} \\
\frac{dp_{x_+}}{dt} &= -\frac{4(x_+ - x_-)}{((x_+ - x_-)^2 + R^2)^{3/2}} - \frac{4(x_+ + x_-)}{((x_+ + x_-)^2 + R^2)^{3/2}} \tag{3.73} \\
\frac{dp_{x_-}}{dt} &= +\frac{4(x_+ - x_-)}{((x_+ - x_-)^2 + R^2)^{3/2}} - \frac{4(x_+ + x_-)}{((x_+ + x_-)^2 + R^2)^{3/2}} + \frac{1}{x_-^2} \tag{3.74}
\end{align*}
\]

For simplicity we plot in fact in figs 3.25 and 3.27 the boundary of the \( \{ V_p \leq -1 \} \) region for various values of \( R \) (together with a few key periodic orbits discussed below), the fundamental domain itself being the right half only. The domain is compact when \( R > 4 \), while it is unbounded for \( R \leq 4 \). Indeed, from the potential

\[
V_p(x_+, x_-) = \frac{1}{|x_-|} - \frac{4}{\sqrt{(x_+ - x_-)^2 + R^2}} - \frac{4}{\sqrt{(x_+ + x_-)^2 + R^2}} \tag{3.75}
\]

it is seen that 4 is the largest value of \( R \) for which an electron can still escape to infinity (i.e. \( V_p = -1 \) with either \( x_+ - x_- \rightarrow +\infty \) and \( x_+ + x_- \rightarrow 0 \), or \( x_+ + x_- \rightarrow +\infty \) and \( x_+ - x_- \rightarrow 0 \)). We shall call this the classical single ionization limit, \( R_{csi} = 4 \).

**Poincaré surfaces of section and periodic orbits**

With the previous background in mind we present in fig 3.23 and 3.24 some plots of the PSOS for various values of \( R \).

We observe a KAM transition from integrable behaviour near \( R = 3\sqrt{3} \) to chaotic behaviour as \( R \) is decreased. In all these plots, the boundary of the PSOS
corresponds to one of the two non-linear normal modes near the equilibrium, namely the symmetric stretch orbit (i.e. the two electrons oscillate in phase on the $x$–axis). The center of the initial torus foliation at $R = 5.1$ is the other non-linear normal mode, the asymmetric stretch orbit (out of phase oscillations), which is a period–1 orbit (that is, it closes after one return to the PSOS), see fig 3.25. Such a near-integrable behaviour is readily explained by the fact that at $R \approx 3\sqrt{3}$ the motion takes place in the bottom of a potential well.

As $R$ is decreased this PO undergoes bifurcations while some other PO appear. Since the dynamics is bounded for $R > 4$ we can easily monitor these changes by plotting the two components of the difference between the $r$–th iteration of the Poincaré return map and the initial condition, as a function of the PSOS coordinate $x_+$. Indeed these two functions must thus be continuous and bounded, and when they have a common zero we obtain the initial conditions of a period–$r$ orbit. In
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Figure 3.24: Plots of PSOS of the $\mathcal{P}$ configuration for various values of $R$. From left to right, top to bottom, we have $R = 4.8$, $4.6$, $4.4$, $4.0$.

Figure 3.25: Plots of asymmetric non-linear normal mode (without reducing the time-reversal symmetry $\Pi_t$) inside the energetically allowed region: left $R = 5.1$, right $R = 4.7$.

this way we can find the orbits which correspond to various KAM islands observed on the PSOS (i.e. we can continue these PO as a function of $R$ and study the related bifurcations). Although straightforward, such a study had not been undertaken in the earlier works on this configuration cited above, resulting in some incorrect claims.
What we find is that the asymmetric stretch PO stays stable until $R \approx 3.751$ (as far as these two DOF are concerned, see below). A saddle-node bifurcation occurs at $R \approx 4.92$ and creates a pair of short period-1 PO, see fig 3.26. It is one of these PO (the one which we denote by (b)) which is at the center of the smallest KAM island with $x_\sim \approx 2.4$ at $R = 4.9$ in fig 3.23. The unstable PO (c) had been previously mistakenly identified with the asymmetric non-linear normal mode [LC98], despite having been understood correctly before [Waa94].

![Figure 3.26](image)

Figure 3.26: Plots of a pair of PO which are born at $R \approx 4.92$ via a saddle-node bifurcation. They are plotted here at $R = 4.9$ inside the energetically allowed region.

The KAM scenario continues as $R$ is decreased, and in particular at $R \approx 4.12$ a short period−1 orbit is born. Since it looks like the helium asymmetric stretch we call it the pseudo asymmetric stretch. This PO had been previously either found but mistakenly identified with the asymmetric non-linear normal mode [Waa94] or not found at all [LC98,LC03]. In fact these two orbits exist and are different, see fig3.27. The center of the large KAM island at $x_\sim \approx 5.3$ for $R = 4.0$ is the pseudo asymmetric stretch, see fig 3.24.

We shall not discuss the structure of this KAM transition further as this is not our main aim, but note that a very detailed methodology for studying such bifurcations have been developed by various authors in the past decade [BHLV03].
Figure 3.27: Plots of non-linear normal mode and pseudo asymmetric stretch periodic orbits (without reducing the time-reversal symmetry $\Pi_t$). From left to right, top to bottom, we have $R = 4.1, 1.0, 0.1$. In the last plot the helium eZe asymmetric stretch orbit ($R = 0$) in its different energetically allowed region is also shown for comparison.

**Full stability of periodic orbits**

We studied the full spatial stability of these PO. In that situation the monodromy matrix has 6 pairs of eigenvalues and in fact we find that perturbations along each pair of axial DOF (i.e. $x_1, x_2, y_1, y_2, z_1, z_2$) decouple.

The $x-$block consists of a pair of eigenvalues 1 (corresponding to energy conservation) and another pair which goes from stable to unstable as $R$ is decreased. The $y-$block consists of two pairs of eigenvalues which are both unstable at intermediate $R$, while at small $R$ one of them becomes stable and the other becomes unstable. Finally the $z-$block consists of one pair of eigenvalue 1 (conservation of $L_z$) and one pair of eigenvalues which goes from stable to unstable and then stable again at very small $R$. In fig 3.28 we plot the Lyapunov exponents of all the unstable eigenvalues as a function of $R$ in the case of the pseudo asymmetric
stretch orbit.

![Lyapunov exponents as a function of $R$ of the pseudo asymmetric stretch PO (which is born at $R \approx 4.15$).](image)

The situation in the case of this collinear configuration $\mathcal{P}$ is thus markedly different from that of the $eZZe$ configuration that we presented earlier. Here, there is no limit to $eZe$ due to the difference of the shapes of the fundamental domains (even for very small $R$ the electrons here still move between the two nuclei, they do not bounce back). Furthermore, at intermediate $R$ there is no stability at all contrarily to the $eZZe$ case where off-collinear pertubations are stable. Such an instability in fact rules out the $\mathcal{P}$ configuration as a potentially relevant part of phase space in view of semiclassical studies. Thus we have not proceeded further, in particular we have not computed the Conley-Zehnder indices of these PO.

### 3.7.6 Dynamics in the $Z_\perp$ configuration

There is another configuration where in physical space the electrons stay between the nuclei for all times, it is $Z_\perp$ and involves the 3 DOF $\rho_+, \rho_-$ and $\theta_{12}$.

Recall that just like the collinear pendulum $\mathcal{P}$, the $Z_\perp$ configuration exists only
for $0 < R < 3\sqrt{3}$. Moreover, in the limit $R \to 0$ the fundamental domain and
the flow of this configuration both continuously become those of the full 3 DOF
$L_{tot} = 0$ subspace of the helium atom, including its collinear subspaces $eZ e$ and
$Z ee$. Thus we expect in particular to find PO within $\mathbb{Z}_\perp$ which are continuous
$R-$deformation of the PO of the helium $eZ e$ configuration.

On the other hand, as in the $eZ Ze$ to $eZe$ limit, the transition from $\mathbb{Z}_\perp$ to $L_{tot} = 0$
cannot be expected to be smooth around the orbits which experience a parametric
triple collision (i.e. orbits where one electron comes very close to the $z-$axis as
$R \to 0$). This is in particular the case for the $R-$deformation of all the $eZe$ orbits.

Still, it remains to be seen how the stability properties and actions of the
$\mathbb{Z}_\perp$ PO behave as $R$ increases.

Structure of the flow

The reduced flow of §3.7.2 is used, and we choose to start trajectories on the PSOS

$$G := \{ \theta_{12} = \pi \ (mod\ 2\pi) \} \quad (3.76)$$

in analogy with the $L_{tot} = 0$ configuration of helium. The associated Poincaré
return map is the 4-dimensional map

$$\Psi : G \rightarrow G$$

$$w_{g}^{(ini)} := \begin{pmatrix} \rho_{+}^{(ini)} \\ \rho_{-}^{(ini)} \\ P_{\rho+}^{(ini)} \\ P_{\rho-}^{(ini)} \end{pmatrix} \rightarrow w_{g}^{(return)} := \begin{pmatrix} \rho_{+}^{(return)} \\ \rho_{-}^{(return)} \\ P_{\rho+}^{(return)} \\ P_{\rho-}^{(return)} \end{pmatrix} \quad (3.77)$$

the fifth quantity $P_{\theta_{12}}$ (known to be positive) being determined for any point $w_{g}$ on
$G$ by the energy relation $H(w_{g}) = -1$. 

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Any PO of $\mathcal{Z}_\perp$ is equivalent to a fixed point of some $r$–th iteration of $\Psi$, or similarly to a (degenerate) global minimum of the quadratic function

$$F_r(w^{(ini)}_g) := \|w^{(ini)}_g - w^{(r)}_g\|^2$$

and it is such a minimization that we performed to find the required initial conditions.

Continuation of Wannier orbits

Orbits which satisfy furthermore $\rho^{(ini)}_- = 0$, $P^{(ini)}_\rho = 0$ and $P^{(ini)}_- = 0$ belong to the configuration $\mathcal{W}_{\rho,\perp}$, and as such they are continuations of the helium Wannier orbits. As explained previously we shall not study this configuration.

Continuation of eZe orbits

Next, we find the PO which are the $R$–deformations in $\mathcal{Z}_\perp$ of those of the helium eZe configuration. Since there are many other orbits in $\mathcal{Z}_\perp$ which are not related to eZe, let us call for simplicity these $R$–deformations the $R$–eZe PO of $\mathcal{Z}_\perp$.

Recall from chapter 2 that there are two kinds of PO in the helium eZe configuration: the symmetric ones (SPO) are those which hit the $r_- = 0$ boundary of the fundamental domain in an orthogonal way; the others are non-symmetric (NSPO). Recall also that in eZe we have $\theta_{12} = \pi$ for all times, while the PSOS is defined by the condition $r^{(ini)}_- = 0$.

This corresponds here to $\rho^{(ini)}_- = 0$, and so to continue the eZe orbits we pick a small value of $R$, say $R_{\text{min}} = 0.01$ and we determine the initial condition at $R = R_{\text{min}}$ by starting the minimization with a guess adapted from the eZe point, i.e. of the form

$$\rho^{(ini)}_+ = \rho^{(eZe)}_+ ; \rho^{(ini)}_- = 0 ; P^{(ini)}_\rho = P^{(eZe)}_\rho ; P^{(ini)}_- = P^{(eZe)}_-$$

(3.80)
where we have $P_{\rho_+}^{(\text{eZe})} = 0$ for the SPO, while it is non-zero for the NSPO. Then we slowly increase $R$ while starting each new minimization with the converged value of the previous step. In this way we are indeed able to continue all the eZe PO.

![Figure 3.29: Plots at various values of $R$ of the continuation of the helium eZe orbit called T. Left: in reduced space with $\theta_{12}^{(\text{ini})} = \pi$ and $\theta_{12}^{(\text{end})} = \pi + 2\pi$; right: in physical xOy plane. From top to bottom we have $R = 0.1, 1.5, 3.2$. In the reduced space plots we also show the projection of the trajectory on the $\rho_+, \rho_-$ plane for comparison with helium eZe.

In the case of the eZe SPO we find that the initial conditions on the PSOS of their $R$–deformations still fulfill $P_{\rho_+}^{(\text{ini})} = 0$ for any value of $R$. As a consequence, these $\mathcal{Z}_\perp$ orbits are periodic both in reduced and in physical spaces. In fig 3.29 we
plot in both spaces for various values of $R$ the $\overline{1}$ $R$–eZe PO, which is a period-1 orbit with respect to $\mathcal{G}$. In fig 3.30 we plot $\overline{01}$ (period-2) and $\overline{001}$ (period-3) in physical space.

Figure 3.30: Plots at $R = 0.1$ (top) and $R = 1.5$ (bottom) of the $R$–eZe PO called $\overline{01}$ (left) and $\overline{001}$ (right).

On the other hand, we find that the eZe NSPO become relative periodic orbits (RPO) in $\mathbb{Z}_\perp$ since for these orbits $\theta_{L_z}$ does not come back to its original value after one reduced period. In fig 3.31 we show plots in physical space of the deformation of the $\overline{011}$ eZe PO, the shortest such RPO.

The $R$–eZe orbits that we obtain are smooth as far as the configuration space paths are concerned. As for momenta, the deformations are also smooth except at the points of close approach to the origin in the limit $R \rightarrow 0$ (parametric TC) where they are discontinuous. Indeed, the momentum during such a close approach is orthogonal to the orbit axis for any $R \neq 0$, its magnitude going to infinity in the limit $R \rightarrow 0$. This is different from the situation in eZe where the momenta at the
Figure 3.31: The $R$–eZe PO called $\mathfrak{011}$, which is an RPO, plotted in physical space at $R = 0.1$ (left) and $R = 1.5$ (right). The origin also has infinite magnitude but is parallel to the orbit axis. This discontinuity of the momentum does not occur at turning points, since although it is orthogonal to the orbit axis there too, its magnitude vanishes in the limit $R \to 0$. These observations are illustrated in fig 3.32.

Figure 3.32: The $R$–deformation of an eZe orbit and the momenta at various points (see text).

Note also that the number of windings that each electron does around the origin in physical space is in direct correspondence with the number of binary collisions of each kind during one period of the corresponding eZe orbit. The reason is that the extra DOF in $Z_\perp$ compared to eZe is $\theta_{12}$. This variable increases monotonically along orbits and so it does not introduce further complexity. In particular, it preserves the validity of labelling the orbits by the list of close approaches of the electrons to the origin.
Now, in fact (in analogy with the $\mathcal{P}$ configuration) the $Z_\perp$ configuration is one where motions are regular for $R \approx R_{eq} = 3\sqrt{3}$ while they gradually become chaotic as $R$ is decreased, with some bifurcations happening in the process. In fig 3.33 we show an $R$-eZe PO which is a period doubling of the $\Gamma$ PO. We observe that its projection to the $\rho_+, \rho_-$ plane does not correspond to any eZe orbit. Such orbits are forbidden in eZe by the grammar rules of the symbolic dynamics, hence we conclude that the $Z_\perp$ orbits which converge to those of eZe can have bifurcation partners in $Z_\perp$ which themselves may not converge to an eZe orbit.

We found that the orbit of fig 3.33 is the shortest such orbit. It is period-4 with respect to our PSOS $\mathcal{G}$ and the only shortest PO in $Z_\perp$ are the three orbits plotted previously $R - \Gamma$, $R - 0\Gamma$ and $R - 00\Gamma$.

![Figure 3.33: A period doubling orbit at $R = 0.1$ of the $R - \Gamma$ PO. Left in physical space; right: projection on the $\rho_+, \rho_-$ plane of reduced space.](image)

Having determined the orbits we compute their action as a function of $R$. We find a very different $R$-dependence for these orbits compared to the continuations in the $eZZe$ configuration of the same initial helium eZe orbit, as shown in fig 3.34 for the $\Gamma$ orbit. In particular the $eZZe$ action has a very large rate of change at small $R$, in contrast with the slower variation of the $R$-eZe action. The semiclassical implications of this will be discussed in chapter 4.
Figure 3.34: Comparison between the R-dependent actions of the two continuation in eZZe and in $\mathbb{Z}_\perp$ of the eZe orbit called $\overline{\mathbb{T}}$. The two curves both converge to the same eZe limit $S_{eZe} \approx 22.9839$ at $R = 0$ but their rate of change are very different.

**Stability of $R$–eZe PO**

The $R$–dependence of the stability of these orbits is also of interest. We find a similar behaviour than in the eZZe configuration: the parametric TC leads to a non-continuous limit for some of the stability exponents, as we now explain.

First recall that the $z_+$ and $z_-$ DOF are decoupled from $\rho_+$, $\rho_-$ and $\theta_{12}$, being the very definition of $\mathbb{Z}_\perp$. We computed the variational flow for this configuration and obtained the monodromy matrices of various periodic orbits. In the case of the $R$–eZe orbit $\overline{\mathbb{T}}$ we find the following structure.

The $\rho_+$ DOF is associated to conservation of energy and leads to a pair of eigenvalues $1, 1$. On the other hand the $\rho_-$ DOF is unstable and corresponds in the limit $R \to 0$ to the asymmetric perturbations along $r_-$ of eZe. Smooth convergence of the corresponding Lyapunov exponent to the eZe value is observed. The $\theta_{12}$ DOF is stable for all values of $R$ and its stability exponent does converge to the corresponding one in eZe (i.e. the stable bending away from the collinear eZe configuration).

On the other hand, the perturbations away from $\mathbb{Z}_\perp$ do not all behave continu-
ously in the $R \to 0$ limit. More precisely, the perturbations in $z_+$ do converge to the limiting eZe behaviour, namely a neutral pair $1, 1$ corresponding to conservation of angular momentum in the $xOz$ plane. For $R \neq 0$ we find that these perturbations are stable until $R \approx 1.4$. But perturbations along $z_-$ do not converge to the stable bending of eZe. In fact, for this particular orbit such perturbations become unstable at $R \approx 0.3$ and below. We have confirmed this by computing nonlinear estimates of the resulting Lyapunov exponents which agree with our linear results. Again this behaviour is due to the parametric TC occurring when one electron comes close to the $z$ axis. We plot the stability exponents of the stable DOF of this orbit in fig 3.35. Not plotted here but worth mentioning is that the eigenvalues corresponding to perturbations in the $z_+$ and $z_-$ DOF later become loxodromic ($1.4 < R < 1.5$) with moderate instability, and then they become real and large, meaning high instability, for larger $R$ values.

![Figure 3.35: Stability exponents of the $R-T$ PO.](image)

For the second shortest PO we find a similar behaviour but with different $R$ ranges: instability of collinear perturbation with convergence to the eZe value, stability for all $R$ of $\theta_{12}$ perturbations with convergence to eZe values, instability of $z_-$ DOF when $0 < R < 0.28$, then stability for $0.28 < R < 0.82$, then loxodromy
when \(0.82 < R < 0.97\) for both this DOF and the \(z_+\) DOF, and then high instability for larger values of \(R\), see fig 3.36.

![Stability exponents of the \(R-0\) PO.](image)

Figure 3.36: Stability exponents of the \(R - \overline{01}\) PO.

**Topological indices**

Finally, the Conley-Zehnder indices of these \(\mathbb{Z}_\perp\) PO must be determined. Indeed, due to the coupling between stable and unstable DOF the B-indices of these orbits do not contain enough information for semiclassical applications. We did not complete this task since we show in the next chapter that the result obtained would anyway not be of use in our situation.

**Other families of orbits**

There exists many other periodic orbits in \(\mathbb{Z}_\perp\), in particular orbits which are continuations of Zee orbits and of other \(L_{tot} = 0\) orbits like those of Grujić and Simonović mentioned in chapter 2. We have not attempted to study those in this work since we were primarily interested in investigating the limit to the helium eZe configuration as explained earlier.
Chapter 4

Semiclassical quantization of the hydrogen molecule

We shall first study the contribution of each of the two configurations eZZe and \( \mathcal{Z}_\perp \) studied in the previous chapter, and then we shall describe how these can be combined.

4.1 Quantization of the eZZe configuration

The main issue to be resolved is that of the non-continuous limit of some of the stability exponents as \( R \to 0 \), bearing in mind that if the eZZe configuration turns out not to describe this limit, then there is no problem.

We have computed zeros of the first truncation of the symmetric semiclassical zeta function, i.e. solutions of

\[
1 - t_T^{(0,0)}(R) = 0
\]

as a function of \( R \) using the stability exponents and index found in chapter 3, and
where the weights now read

\[ \psi_{0,0}^{(0)}(R) = \frac{1}{\sqrt{|e^{\lambda_{\gamma}(R)}\chi_{\gamma}(R)|}} \exp \left[ i\left( s\gamma_{\gamma}(R) - \beta_{\gamma}(R)\frac{\pi}{2} - 2\cdot2\pi\frac{\chi(R)}{2\pi} \right) \right] \quad (4.2) \]

with \( \chi_{\gamma}(R) \) the \( R \)-dependent stability exponent of the \( \theta_{12} \)-bending perturbation (which is doubly degenerate due to the symmetry around the configuration axis, just like in eZe helium) and \( \lambda_{\gamma}(R) \) the \( R \)-dependent Lyapunov exponent of the unstable axial perturbations (compare with equation 2.70).

The lowest energy curve obtained must thus provide an approximation to the electronic part of the quantum ground state BO curve if, as we argued earlier, eZZe contributes to it. How accurate this curve actually is remains to be seen.

The results we find are shown in fig 4.1, where plot the electronic energies of our first order semiclassical approximation (upper curve) compared to the ab initio quantum results of Wolniewicz [Wol95]. A very good agreement is observed from \( R \approx 4 \) onwards, while there is a large overestimate in the intermediate \( R \) range. The result is also reasonable at the \( R = 0 \) limit, but it virtually immediately breaks
In terms of total energy we then get the curve plotted in fig 4.2. It confirms that we indeed describe part of the ground state (the $R \geq 5$ region) since the semiclassical curve is below the quantum one, hence a bonding curve too.

We thus conclude that the $R \to +\infty$ asymptotics of the ground state can be satisfactorily described with the simple eZZe asymmetric stretch orbit, while this configuration does not allow to account for correct binding energies.

A reasonable candidate for a semiclassical approximation of the small $R$ region must be a configuration where electrons stay localized between the nuclei, according to the ab initio electronic densities. Therefore, given our earlier classical study, one or both of the collinear $P$ configuration and the planar $Z_\perp$ configuration must be involved.

Nevertheless, we noted in chapter 3 that the PO in the $P$ configuration are very unstable with respect to all types of perturbations for intermediate values of $R$, therefore this configuration is ruled out. On the other hand, the PO in the $Z_\perp$
configuration are stable with respect to most DOF at intermediate $R$ and can thus be studied.

### 4.2 Quantization of the $\mathbb{Z}_\perp$ configuration

Since the present configuration should be involved in the semiclassical description of states at intermediate and small values of $R$, we expect that this time the non-continuous limit of some of the stability exponents as $R \to 0$ will be a problem for the semiclassical formalism we use, since it is based on spectral stability properties. This is the reason why we did not compute the topological indices of such PO in the previous chapter.

![Graph showing semiclassical versus quantum results](image-url)

**Figure 4.3:** Semiclassical approximation built on the $R - \mathbb{T}$ orbit of $\mathbb{Z}_\perp$ compared to the ground state quantum ab initio result of [Wol95] (small $R$ range, electronic energies).

As a first step, we have computed the zeros of the first few truncations of the corresponding zeta function using in the weights *only* the $R$–dependent actions of the $R - eZe$ orbits, and neither their true stability exponents nor true topological indices. Instead we have artificially kept these quantities at the values of the eZe configuration.
Chapter 4: Semiclassical quantization of the hydrogen molecule

The resulting curve must nevertheless show whether or not the precise $R$-dependence of the actions of the $R - eZe$ orbits corresponds to the trend of the quantum curve.

The results we find in this way are shown in fig 4.3 and 4.4. We observe, in particular in the electronic energy plot, that the slope of the semiclassical result is very similar to that of the quantum one. Moreover, as we include more orbits, the semiclassical curves do get closer to the quantum BO curve.

![Figure 4.4: Semiclassical approximations using only the actions of the $Z_\perp$ PO, this up to code length 1, 2, and 3. That is, with respectively the $R-\bar{T}$ orbit (semiclassical[1]); the $R-\bar{T}$ and $R-\bar{0}\bar{T}$ orbits (semiclassical[2]); and the $R-\bar{T}$, $R-\bar{0}\bar{T}$ and $R-\bar{0}\bar{0}\bar{T}$ orbits (semiclassical [3]) of the $Z_\perp$ configuration (full R range, total energy) compared to the ground state quantum ab initio result of [Wol95] (full $R$ range, total energies).](image)

This strongly hints that the $Z_\perp$ configuration is the part of phase space from which the ground state curve is predominantly built for small values of $R$.

We now turn to the issue of bond formation.
4.3 Bond formation mechanism

Figure 4.5: Semiclassical approximation built on the asymmetric stretch orbit of eZZe and the $R - \bar{T}$ orbit of $Z_\perp$ compared to the ground state quantum ab initio result of [Wol95] (electronic energies in function of the internuclear distance $R$).

To account for bond formation we propose the following, admittedly ad hoc, procedure. Since the two configurations eZZe and $Z_\perp$ have sets of PO which both converge to the same helium eZe set as $R \to 0$, we consider that a zeta function for the full molecule should be built with PO weights of the form

$$t_j^{\text{full}}(R) = \alpha_{eZZe}(R)t_j^{eZZe}(R) + \alpha_{Z_\perp}(R)t_j^{Z_\perp}(R)$$  \hspace{1cm} (4.3)$$

Without further information we bluntly set $\alpha_{eZZe}(R) = \alpha_{Z_\perp}(R) = \frac{1}{2}$, i.e. we assume that in the limit $R \to 0$ the two subspaces eZZe and $Z_\perp$ contribute equally to their common limit eZe, and that this still holds for other values of $R$. We then obtain for the first order truncation the curves shown in fig 4.5 and fig 4.6.

Apart from the range $2 < R < 3$, where presumably orbits from other configurations come into play, there is a good structural agreement, which is pleasing
given all the crude approximations we have made.

Figure 4.6: Semiclassical approximation built on the asymmetric stretch orbit of eZZe and the $R - \overline{1}$ orbit of $Z_\perp$ compared to the ground state quantum ab initio result of [Wol95] (total energies in function of the internuclear distance $R$).

We thus conclude that as two separated hydrogen atoms are brought together (i.e. as $R$ decreases) it is the appearance at $R = 3\sqrt{3}$ of the $Z_\perp$ subspace in another part of phase space, and then the very details of the properties of its shortest periodic orbits (more precisely the way their action depend on $R$) which leads to the deep potential well observed in the ground state BO curve of the hydrogen molecule.
Chapter 5

Conclusions

We have shown in this thesis how the classical and semiclassical techniques reviewed in the first two chapters, which have proved successful in the study of the helium atom, can be applied to a more complicated few-body Coulomb problem, namely the hydrogen molecule.

5.1 Summary of results

In the first part of our work we have described how the phase space of the classical hydrogen molecule is organized at two levels: first geometrically by studying the reduced phase space and its different strata; and then dynamically by identifying all the invariant subspaces, computing Poincaré sections, and constructing families of PO.

Then we have presented semiclassical computations in order to evaluate the accuracy of an approximation of the quantum ground state BO curve based on the dynamics in two particular subspaces (while a third one has been discarded, these choices being made on classical grounds).

The results we have obtained allow us to answer two issues raised while discussing the quantum structure of $H_2$: we have identified which classical configura-
tions contribute the most to the ground state Born-Oppenheimer curve in the two limits $R \to 0$ and $R \to +\infty$. These are respectively:

- the $Z_\perp$ configuration, a 3 DOF configuration consisting of motions within the internuclear symmetry plane;

- the eZZe configuration, a collinear 2 DOF configuration which asymptotically leads to two uncoupled $H$ atoms.

The resulting approximation is reasonably accurate as far as these two asymptotic limits are concerned, and a pronounced well in the semiclassical BO curve does appear, similarly to the quantum situation.

5.2 Future work

On the other hand the intermediate range $2 < R < 3$ is not well reproduced at all, hinting that configurations not studied in this work (notably the 2 DOF ZeeZ and the 4 DOF $Z$) may be involved.

We also have observed in the course of our work some technical issues concerning the semiclassical formalism used: the non-regularizability of parametric triple collisions in classical Coulomb systems leads to a non-continuous limit behaviour of the stability exponents of the PO, with a breakdown occurring at a relatively large finite distance of the exact limit. A probable remedy for this would be to use a uniform version of the trace formula taking into account the symmetry breaking [Cre96].

More generally, an open problem is to investigate whether or not there exists dynamical structures in the phase space of the classical hydrogen molecule which would allow to unify the enumeration of the PO of the various invariant subspaces by a single common (and finite) symbolic coding.
Appendix A

Notations for classical mechanics

In the 1960s, under the influence of many people (Thom, Smale, Kolmogorov, Arnold, Moser, Souriau, ...), a geometrization of classical mechanics, and more generally of dynamical systems started to flourish (following the earlier footsteps of Poincaré). It embraced both the finite dimensional (ODE) and infinite dimensional (PDE) cases. Since then, many other notions have been developed regarding specific classes of systems (e.g. related to integrability, uniform hyperbolicity, ...). We shall be concerned here with some finite dimensional ones.

There are many excellent textbooks – at the level of the graduate student – which now cover this material in details. Classical mechanical systems are well treated in the complementary books [Arn89], [MR98] and [AKN97]. Other topics can be found in [MR05]. Introductions to dynamical systems in general are provided by [HK03] and [Dev03] while a much more advanced treatment can be found in [KH95]. A very good source for physicists is also the online book [CAM⁺05]. We shall use this appendix to fix the notations.

An autonomous Hamiltonian mechanical system is specified by a symplectic manifold $\left( M, \omega \right)$ and a smooth numerical function $H : M \to \mathbb{R}$, the Hamiltonian. $M$ is the phase space of the system. The standard example is provided by the cotangent bundle $M = T^*\Omega$ of some configuration space $\Omega$ of dimension $N$ with canonical 2–form $\omega := \sum_j dq_j \wedge dp_j$ and with Hamiltonian of the form ‘kinetic plus potential’
Chapter A: Notations for classical mechanics

\[ H(q,p) = T(p) + V(q). \]

There is a natural vector field \( X_H \) on \( M \) given at \( w = (q,p) \) by saying that the differential of \( H \) (which is by definition acting on the tangent space to \( M \) at \( w \)) is equal to the 1–form that we get by making the interior product of that vector field \( X_H \) with the symplectic 2–form: for any vector \( \xi \in T_w M \) we have \( \varpi_w(\xi, X_H(w)) = (dH)_w(\xi) \). In coordinates this thus reads

\[
\begin{cases}
\dot{q}_j &= \frac{\partial H}{\partial p_j} \\
\dot{p}_j &= -\frac{\partial H}{\partial q_j}
\end{cases}
\]

which, introducing the \( 2N \times 2N \) matrix \( J := \begin{pmatrix} 0 & I_N \\ -I_N & 0 \end{pmatrix} \in Sp(2N) \), becomes in vector form \( \dot{w} = J \nabla H(w) \) (symplectic-gradient of \( H \)).

Hamiltonian flows have many properties. Liouville’s theorem asserts that phase space volume is conserved under time evolution. Another invariant is the Hamilton principal function (HPF) \( R(\ell) := \oint_\ell (pdq - H dt) \) associated to any closed loop in extended phase space \( (q,p,E,t) \) (i.e. it stays constant as the loop is deformed by the flow). It is this quantity which is involved in the variational principle of Lagragian mechanics (i.e. the first variation of the HPF along a classical path vanishes). One then define, by a Legendre transformation, the corresponding fixed-energy quantity called the action of a phase space loop \( S(\ell) := \oint_\ell pdq \). Finally, a more subtle result of Gromov states that in fact the areas of each of the projections of a volume on the canonical planes \( (q_j, p_j) \) are conserved (i.e. even in a large phase space Hamiltonian dynamics is still under the influence of some intrinsically 2–dimensional properties).

The phase space transformations which conserve the canonical 2–form \( \varpi \) are called canonical. To find such transformations one can use a so-called generating function \( \mathcal{F} \). In general these depend on \( 2N + 1 \) variables: \( N \) from an initial point \( \tilde{w} \), the \( N \) conjugated ones of the end point \( w \) and time. For example if \( \mathcal{F} = \mathcal{F}(\tilde{q}, q, t) \)
then the associated canonical transformation is given by

\[ \alpha_F : \begin{pmatrix} \tilde{q} \\ \tilde{p} := -\frac{\partial F}{\partial \tilde{q}} \end{pmatrix} \rightarrow \begin{pmatrix} q \\ p := \frac{\partial F}{\partial q} \end{pmatrix} \]  

and the new Hamiltonian is \( H(q, p, t) = \tilde{H}(\tilde{q}, \tilde{p}, t) - \frac{\partial F}{\partial t} \). An even simpler case, forgetting generating functions, is when one chooses a configuration space transformation \( q = \phi(\tilde{q}) \); the new momenta must then be \( p = (d\phi)_q^{-1}\tilde{p} \) to ensure canonicity. This is called the cotangent lift of the configuration space transformation \( \phi \).

As with every flow, the natural objects to look at are equilibria, periodic orbits, invariant submanifolds, and the stable and unstable manifolds of these objects. A tool of choice for the study of (un)stability issues is that of (local) Poincaré sections and their induced return map \( P_\gamma \), usually combined with the linearization of the flow along trajectories called the variational equations

\[ \frac{d\overline{M}(t)}{dt} = J\text{Hess}_H(\gamma(t)) \cdot \overline{M}(t) \]  

where \( \overline{M} \) is an \( 2N \times 2N \) matrix and \( J\text{Hess}_H(\gamma(t)) \) is the Hessian matrix of \( H \) at the point \( \gamma(t) \). In the case of a periodic orbit \( \gamma \), the matrix obtained at the end of one period \( T_\gamma \) is called the monodromy matrix \( \overline{M}(T_\gamma) \). Its submatrix corresponding to directions different from the one of the flow is called the stability matrix (it is this quantity which enters the GTF of chapter 1). A periodic orbit is said to be primitive if it is not the repetition of another shorter orbit (i.e. the period is minimal).

There are three notions of stability, best formulated in the general case. In the study of a system \( \dot{x} = F(x) \), a solution \( x_\epsilon \) is nonlinearly stable if

\[ \forall \epsilon \exists \delta \text{ such that } d(x_0, x_\epsilon) < \delta \Rightarrow d(x(t), x_\epsilon) < \epsilon \forall t \]  

i.e. finite differences don’t grow arbitrarily large. The solution \( x_\epsilon \) is linearly stable if the zero solution \( \Delta x = 0 \) of the linearized system is stable, where the linearized
system is as previously \( \frac{d}{dt}(\Delta x) = \nabla F(x_e) \cdot \Delta x \). Now if \( (\Delta x)^* \) is an eigenfunction of the linearized system for the eigenvalue \( \lambda_j \in \mathbb{C} \) then the linear perturbation is of the form \( (\Delta x)(t) = e^{t\lambda_j}(\Delta x)^* \) and we say that \( x_e \) is \textit{spectrally stable} if \( \Re(\lambda_j) \leq 0 \ \forall \ j = 1...N \). We have that nonlinear stability implies spectral stability and linear stability implies spectral stability. But the converse are not true, spectral stability does not imply nonlinear stability, and moreover spectral stability does not imply linear stability, due to the cases where there are complex eigenvalues with positive real part (for example on the unit circle).

A more algebraic tool for studying Hamiltonian systems is the \textit{Poisson bracket} of two phase space functions defined\(^1\) as \( \{F, G\} := \varpi(X_F, X_G) = \sum_j \left( \frac{\partial F}{\partial p_j} \frac{\partial G}{\partial q_j} - \frac{\partial F}{\partial q_j} \frac{\partial G}{\partial p_j} \right) \).

We have that if \( F = H \) then we get the rate of change of \( G \) along the flow of \( H \), that is \( \{H, G\} = \frac{\partial G}{\partial t} \). In particular for \( G = H \) we find \( \{H, H\} = 0 \), which means that the level sets of \( H \) are invariant submanifolds \textit{(energy is conserved)}. Functions (not identically constant) which Poisson commute with the Hamiltonian, i.e. for which \( \{H, F\} = 0 \), are called \textit{(first) integrals} and imply that the flow leaves invariant some lower dimensional submanifolds of the level sets of \( H \).

In particular if there exists \( n \) functions \( F_1 := H, F_2, \ldots, F_n \) which are \textit{functionally independent} (=the differentials \( dF_i \) are linearly independent) almost everywhere (=except on a set of measure 0) and which pairwise Poisson commute \((\{F_i, F_j\} = 0 \ \forall i, j)\) then the system is said to be \textit{integrable}. The map \( \mathcal{F} = (F_1, \ldots, F_N) \) from phase space \( M \) to \( \mathbb{R}^N \) is called the \textit{energy-momentum map}. The \textit{Arnold-Liouville-Mineur theorem} states that the regular level sets of \( \mathcal{F} \), when compact, are unions of \textit{(Lagrangian) \( N \)–tori} \( \mathbb{T}^N \). Phase space is then said to be a torus fibration over the image of the energy-momentum map, and the set of tori which make up \( \mathcal{F}^{-1}(f_1, \ldots, f_N) \) is called the \textit{fiber of} \((f_1, \ldots, f_N)\). One can \textit{locally} find so-called \textit{action-angle coordinates} in which the flow linearizes on the tori and possesses \( N \) frequencies. On the topological side, an homotopy basis for \( \mathbb{T}^N \) is any

\(^1\text{Warning: there are different sign convention used in the litterature regarding the 2– form } \varpi \text{ and thus of the Poisson brackets. What matters is to be consistent.}\)
set of $\mathcal{N}$ closed loops $c_j$ on $\mathbb{T}^N$ such that all other closed loops can be continuously deformed to a sum $\sum_{j=1}^{\mathcal{N}} c_j c_j$ where the $c_j$ are non-zero integers (such sums being defined from the flat torus version).

Of course this fibration need not be trivial, i.e. there can be singularities (that is, some fibers contain points where the $F_i$ are not independent [this corresponds geometrically for example to fixed points, pinched tori, etc.], in which case the action-angle variables are not global ones (see [CB97] for many examples treated explicitly). More precisely, to a closed path in configuration space corresponds a family of tori. The initial and final tori of this family coincide, but it may happen that the homotopy basis of the final torus, which is the result of the evolution along the path, is different from the one of the initial torus. In which case one says that the integrable system has monodromy, and this prevents the existence of global action-angle variables.

When the frequencies are rationally dependent, trajectories are periodic on the torus, while they are non-periodic ("quasi-periodic") and dense for other tori. The rational tori, also called resonant tori, are the first to break up as integrability is destroyed by a small perturbation of the Hamiltonian, the remaining (Diophantine) tori – a set of positive measure – being only deformed (KAM scenario, see also [BCFT04] for a global geometric formulation).

Another class of well-studied systems are the hyperbolic ones, in particular uniformly hyperbolic ones: given a smooth flow $\varphi : \mathbb{R} \times \mathcal{N} \to \mathcal{N}$ on a smooth manifold $\mathcal{N}$, a compact invariant subset $\mathcal{A} \subset \mathcal{N}$ is hyperbolic if there exist a Riemannian metric in an open neighborhood of $\mathcal{A}$ such that at each point $w \in \mathcal{A}$ the linearization of the flow has only contracting and expanding directions (i.e. only real eigenvalues) apart from the neutral one along the flow: all expanding eigenvalues $\Lambda_j$ of the linearization are uniformly bounded away from unity by some finite amount $|\Lambda_j| > a > 1$ for all $j$.

If $\mathcal{A} = \mathcal{M}$ (and still compact) then the flow is called Anosov. For example the
geodesic flow on a manifold of everywhere negative curvature is Anosov. Similar behaviour arises in Hamiltonian systems for example near a hyperbolic fixed point, with the creation of horseshoe-like structures. Hyperbolic systems are structurally stable, their orbit structure is robust to little deformations. A useful tool in this context are Markov partitions and the associated symbolic coding of chaotic trajectories it provides. When the coding can be done with a finite number of symbols and some grammar rules one says that the corresponding symbolic dynamics is a subshift of finite type.
Appendix B

Group theory and the hydrogen atom

Here we briefly recall (in the case of spinless bound states only) the various steps of the reasoning without detailing the calculations. This topic is treated in various complementary references [Bl66, Sin05, LL75, Wyb99, Kib04] (notations differ between authors; for clarity reasons we have chosen not to set units $\hbar$ and $e$ to one).

B.1 Geometrical group

In Cartesian coordinates $x_1$, $x_2$, $x_3$, the Hamiltonian reads

$$\hat{H} := -\frac{\hbar^2}{2\mu} \Delta - \frac{\alpha}{r} \quad (B.1)$$

with $\mu$ the reduced mass, $\alpha := Ze^2$ the charge and $r := \sqrt{x_1^2 + x_2^2 + x_3^2}$ the distance to the center of mass.

It is easily checked that angular momentum operators

$$\hat{L}_a := \epsilon_{abc} x_b \hat{P}_c = -i\hbar \epsilon_{abc} x_b \frac{\partial}{\partial x_c} \quad (B.2)$$
(where $\epsilon_{abc}$ is the usual permutation tensor and Einstein’s summation convention is implied) satisfy commutation relations

$$[[\hat{L}_a, \hat{L}_b]] = i\hbar \epsilon_{abc} \hat{L}_c$$  \hspace{1cm} (B.3)

so they span a rank one Lie algebra isomorphic to $so(3)$ whose Casimir operator is then

$$\hat{L}^2 = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2 \text{ (squared angular momentum)}$$  \hspace{1cm} (B.4)

The latter is proportional to the identity and the proportionality constant is written $\hbar^2 \ell(\ell + 1)$ for notational convenience.

Since we have $[\hat{H}, \hat{L}_a] = 0$, solutions are simultaneous eigenfunctions of three independent operators, conventionally $\hat{H}$, $\hat{L}^2$ and $\hat{L}_3$, and so there are three good quantum numbers, respectively $n$, $\ell$ and $m$, for labelling such solutions. These solutions can be found explicitly and lead to the relations $n = 1, 2, 3...$, $\ell = 0$ to $n - 1$ and $m = -\ell$ to $\ell$. The geometrical symmetry group is the real Lie group $SO(3)$ of 3-dimensional rotations, and so we expect eigenvalues of given angular momentum (i.e. for given $\ell$ and thus $n$) to have degeneracies equal to the dimensions $d_\ell = 2\ell + 1$ of the irreducible representations (irreps) of $SO(3)$ (these irreps being spanned by the angular part of the solutions, i.e. the spherical harmonics $Y_{\ell m}$).

Now in fact one finds that eigenvalues are given by

$$E = E(n) = -\frac{\beta n^2}{\hbar^2}, \text{ with } \beta = \frac{\mu Z^2 e^4}{2\hbar^2}$$  \hspace{1cm} (B.5)

so they depend only on $n$ which means there is an extra (“accidental”) degeneracy in $\ell$, i.e. the true degeneracies are $\sum_{\ell=0}^{n-1}(2\ell + 1) = n^2$. One can suspect that there is some additional (“hidden”) symmetry in the system, all the more since in the classical system Laplace and later Runge and Lenz, in order to account for the fact that the elliptic solutions do not precess, found a vector which leads to a new independent integral (the system is superintegrable). On semiclassical grounds,
this has to show up in the quantum system.

B.2 Degeneracy group

An extra amount of symmetry is indeed also present in the quantum system, as can be seen from the fact that the Hamiltonian is separable in different coordinate systems:

- the spherical one

\[
x_1 = r \cos \theta \cos \phi \; ; \; x_2 = r \cos \theta \sin \phi \; ; \; x_3 = r \sin \theta
\]  

in which the three commuting operators are \( \hat{H}, \hat{L}_2 \) and \( \hat{L}_3 \);

- the prolate spheroidal one

\[
x_1 = \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \phi \; ; \; x_2 = \sqrt{(\xi^2 - 1)(1 - \eta^2)} \sin \phi \; ; \; x_3 = \xi \eta
\]  

in which the three commuting operators are \( \hat{H}, \hat{L}_3, \hat{G} \) (with \( \xi, \eta, \phi \) and \( \hat{G} \) as in the two-centers system of §2.2.2, but where of course one the two centers has a charge set to zero, while the charged center is at the origin);

- the parabolic one

\[
x = \sqrt{\chi \xi} \cos \varphi \; ; \; y = \sqrt{\chi \xi} \sin \varphi \; ; \; z = \frac{1}{2} (\chi - \xi)
\]  

in which the three commuting operators are \( \hat{H}, \hat{L}_3, \hat{P}_3 \) (where \( \hat{P}_3 \) does not commute with \( \hat{L} \), see below).

This operator \( \hat{P}_3 \) is a component of the quantum analog of the classical Laplace-Runge-Lenz vector, and was introduced by Pauli in 1926. These Pauli-Laplace-Runge-Lenz operators are obtained by symmetrizing what one gets when using the
Bohr correspondence principle in the classical integrals, namely

\[ \hat{p}_a := \frac{1}{2\mu} \epsilon_{abc} (\hat{p}_b \hat{L}_c - \hat{L}_b \hat{p}_c) - \frac{\alpha x_a}{r} \]  

(B.9)

The following results can be checked, after sometimes tedious calculations.

First

\[ \hat{L} \cdot \hat{p} = \hat{L}_1 \hat{p}_1 + \hat{L}_2 \hat{p}_2 + \hat{L}_3 \hat{p}_3 = 0 \]  

(B.10)

Then we have the following commutation relations

\[ \left[ \hat{H}, \hat{p}_a \right] = 0 \]  

(B.11)

\[ \left[ \hat{L}_a, \hat{p}_b \right] = i\hbar \epsilon_{abc} \hat{p}_c \]  

(B.12)

\[ \left[ \hat{p}_a, \hat{p}_b \right] = \frac{2i\hbar}{\mu} \epsilon_{abc} \hat{H} \hat{L}_c \]  

(B.13)

Also, one finds the relation

\[ \hat{p}^2 = e^4 + \frac{2}{\mu} \hat{H}(\hat{L}^2 + \hbar^2) \]  

(B.14)

Introducing the rescaled operators

\[ \hat{A}_a := \sqrt{\frac{\mu}{-2E}} \hat{p}_a \text{ where } E < 0 \]  

(B.15)

and then the combinations

\[ \hat{M}_a := \frac{1}{2}(\hat{L}_a + \hat{A}_a) \]  

(B.16)

\[ \hat{N}_a := \frac{1}{2}(\hat{L}_a - \hat{A}_a) \]  

(B.17)
one finds that

\[ [\hat{M}_a, \hat{M}_b] = i\hbar \epsilon_{abc} \hat{M}_c \]  \hspace{1cm} (B.18)

\[ [\hat{N}_a, \hat{N}_b] = i\hbar \epsilon_{abc} \hat{N}_c \]  \hspace{1cm} (B.19)

\[ [\hat{M}_a, \hat{N}_b] = 0 \]  \hspace{1cm} (B.20)

This corresponds to the rank two Lie algebra \( so(3) \otimes so(3) \simeq so(4) \), whose Casimirs are

\[ \hat{\mathbf{M}}^2 = \hbar^2 u(u + 1) \]  \hspace{1cm} (B.21)

\[ \hat{\mathbf{N}}^2 = \hbar^2 v(v + 1) \]  \hspace{1cm} (B.22)

so that states are labelled by four angular momentum-like quantum numbers \( u, m_u, v \) and \( m_v \). One thus expects that only three of these numbers are independent, and using some of the relations mentioned above one finds that in fact \( \hat{\mathbf{M}}^2 = \hat{\mathbf{N}}^2 \) and thus \( u = v \), which turns out to be a half-integer. This means only special representations of \( so(4) \) occur and that states are in this framework labelled by the three good quantum numbers \( u = v, m_u \) and \( m_v \).

Further calculations using other relations mentioned above then allow to get \( E \) in terms of these, namely \( E = -\beta (2u+1)^2 \). So the principal quantum number \( n \) is related to those \( so(4) \) numbers by \( n = 2u + 1 \). The degeneracy of each eigenvalue is then equal to the remaining possibilities, i.e. the number of possible values of \( m_u \) times the number of possible values of \( m_v \), which is

\[ (2u+1)(2v+1) = (2u+1)^2 = n^2 \]  \hspace{1cm} (B.23)

So this is indeed the degeneracies sought for, and they are equal to the dimensions
of the irreps of $SO(4)$, the degeneracy group\textsuperscript{1} of the spinless bound states the hydrogen atom.

\textsuperscript{1}Some authors name it dynamical invariance group as opposed to the dynamical noninvariance group $SO(4,2)$ which encompasses both bound and scattering states. One also finds for $SO(4)$ simply dynamical group, which is not confusing as long as one clearly states that only bound states are considered.
Appendix C

Reduction theory for Hamiltonian systems

The Hamiltonian systems studied in this work are in particular invariant under some continuous groups of symmetries. This leads to conserved quantities $F_j$ via Noether's theorem, and one then has to study smaller systems where the integrals $F_j$ have some fixed values and where the symmetry has been factored out.

The mathematical technique to do this is called reduction theory. It has a long history going back to Jacobi, and in the framework of symplectic geometry to the 1970s, while the full theory is more recent [MW74, Mey73, SL91, LMS93, MW01a, CS05, IY05]. We describe in this appendix the aspects which are directly relevant for our work; any unnecessary ideas are avoided. Moreover, simple examples are used to illustrate them in details.

C.1 Setting

We consider a Hamiltonian of the form $H = T + V$, where the potential $V$ is defined on some configuration space $Q$ of dimension $N$. 
Chapter C: Reduction theory for Hamiltonian systems

C.1.1 Symmetry group and integrals

Suppose that $V$ is invariant under some compact Lie group $G$ of dimension $m$ (the examples of the 1-dimensional $SO(2)$ and 3-dimensional $SO(3)$ rotation groups are all we require in our work). We use $e$ to denote the identity element of $G$.

The associated action of $G$ on $\mathcal{Q}$ is denoted by

$$\varphi : G \times \mathcal{Q} \rightarrow \mathcal{Q} \quad (C.1)$$

$$(g, q) \mapsto \varphi_g(q)$$

and satisfies that for any $q \in \mathcal{Q}$ we have $e \cdot q = q$ and $g_2 \cdot (g_1 \cdot q) = (g_2 g_1) \cdot q$.

This action on configuration space is then lifted to phase space $\mathcal{M} = T^*\mathcal{Q}$: the action of $g \in G$ on $(q, p) \in \mathcal{M}$ is denoted by $(g \cdot q, g \cdot p)$, with the fiber part being a linear map in $p$ defined by the derivative at the point $g \cdot q$ of the map $\varphi_{g^{-1}}$, namely (see paragraph 6.3 of [MR98])

$$g \cdot p := D\varphi_{g^{-1}}(g \cdot q)p \quad (C.3)$$

It is then a theorem that this action preserves our Hamiltonian flow, i.e. we have

$$g \cdot J \nabla H(q, p) = J \nabla H(g \cdot (q, p)) \quad (C.4)$$

for any $g$ and any $(q, p)$.

Let $(\xi_j)$ be a basis of the Lie algebra $\mathfrak{g}$ of $G$. Then for every $\xi_j$ there is a vector field associated to our $G$–action on $\mathcal{M}$. Suppose this vector field is Hamiltonian, coming from a function

$$F_j : \mathcal{M} \rightarrow \mathbb{R} \quad (C.5)$$
Then the $F_j$ are independent, and Noether’s theorem says that the $F_j$ are constant along the Hamiltonian flow generated by $H$.

Having found the integrals we can now proceed to the next step, which is to study how the $G$–action is decomposing phase space.

### C.1.2 Isotropy types and invariant manifolds

For each point $w = (q, p)$ of phase space one associates a subgroup of $G$ called the isotropy group of $w$ (or sometimes stabilizer of $w$). It is defined as

$$G_w := \{ g \in G \mid g \cdot w = w \} \quad \text{(C.6)}$$

it is the subgroup of $G$ made of all the elements which leave the phase space point $w$ invariant.

The list of all the subgroups of $G$ which arise as isotropy group of at least one point $w$ is then organised into an oriented graph whose vertices are these isotropy groups, and whose edges between two vertices $A$ and $B$ are one-sided arrows: an arrow $A \to B$ indicates that $A$ is a subgroup of $B$. This graph is called the isotropy lattice of the $G$–action on $\mathcal{M}$.

Now to each isotropy group $A$ there corresponds a submanifold $\mathcal{M}_{(A)}$ of phase space, called the set of points of orbit type $A$, defined by

$$\mathcal{M}_{(A)} := \{ w \in \mathcal{M} \mid G_w \in (A) \} \quad \text{(C.7)}$$

where $(A)$ is the set of all the subgroups which are conjugated to $A$ in $G$. Such submanifolds $\mathcal{M}_{(A)}$ are invariant by the Hamiltonian flow (this is called the law of conservation of isotropy) and are thus providing a partition of phase space.

Before showing how to obtain the reduced phase space, we need to distinguish two types of $G$–actions.
C.1.3 Free and non-free actions

The action of $G$ on $M$ is said to be free if it has no fixed points: if any $g$ in $G$ different from the identity element induces a phase space transformation $\varphi_g$ which moves all the points (i.e. for any $w$ we have $g \cdot w \neq w$). In terms of isotropy groups, a free $G$–action is one for which for any $w$ its isotropy group $G_w$ is the trivial group $\{e\}$. So for a free action there is no decomposition of phase space, we only have one piece $M = M(\{e\})$.

A simple example of a free action is given by $G = SO(2)$ acting on the phase space associated to a configuration space

$$Q = \{(x, y, z) \in \mathbb{R}^3 \mid x^2 + y^2 = R, -\ell < z < \ell\}$$

(C.8)

having the shape of a tube of radius $R$ and height $2\ell$ around the $z$–axis. Any element (= a rotation) of $SO(2)$ apart from the identity indeed moves all the points of phase space, so that for each $w$ we do get $G_w = \{e\}$. The associated integral on phase space $T^*Q$ is the angular momentum along the $z$-axis $L_z = xP_y - yP_x$.

On the other hand, a non-free action is one for which at least one point $w$ of phase space has a non-trivial isotropy group. So in that case phase space is decomposed into at least two isotropy type submanifolds.

As a simple example of a non-free action, consider now the action of $SO(2)$ on the phase space associated to a sphere

$$Q = \{(x, y, z) \in \mathbb{R}^3 \mid x^2 + y^2 + z^2 = R\}$$

(C.9)

of radius $R$ around the $z$–axis. The north and south poles associated to the momenta $p = 0$ provide phase space points $(q_S, 0)$ and $(q_N, 0)$ which are fixed under any rotation, and so their isotropy group is the full group $SO(2)$. All the other points have trivial isotropy. Thus here phase space is decomposed into two isotropy
type submanifolds: $\mathcal{M}_{\text{(SO(2))}}$ which is made of two connected components $(q_S, 0)$ and $(q_N, 0)$, and $\mathcal{M}_{\{e\}} = \mathcal{M} - \mathcal{M}_{\text{(SO(2))}}$.

We now explain how the integrals and the isotropy type submanifolds are related.

### C.1.4 Energy momentum map

With the Hamiltonian $H$ and the integrals $F_j$ one forms the energy-momentum map

$$F = (F_0 = H, F_1, \ldots, F_m) : \mathcal{M} \to \mathbb{R}^{m+1} \quad (C.10)$$

For each value $f = (E, f_1, \ldots, f_m)$ of $F$, the level set $\mathcal{M}_f := F^{-1}(f)$ is thus a subset of phase space on which all integrals take some fixed value.

By definition $f$ is a regular value of $F$ if $\nabla F(w) \neq 0$ for any $w \in F^{-1}(f)$. So in that case $\mathcal{M}_f$ is a submanifold of phase space, and all its points have trivial isotropy. The other values $f$ are called singular values of $F$ and the subset $\mathcal{M}_f$ is not a submanifold, some of its points having non-trivial isotropy.

Our final aim of factoring out the symmetry from each level set $\mathcal{M}_f$ of the integrals then splits into these two regular and singular cases, which we work out next.

### C.2 Regular reduction

In the case of a free action (e.g. our tube example) we necessarily have that any value $f$ of $F$ is regular, and so the corresponding level set $\mathcal{M}_f$ is a submanifold of phase space.
Define the group orbit through the phase space point $w$ by set of points equivalent to $w$ modulo $G$, namely

$$O_w := \{ g \cdot w \text{ as } g \text{ runs through } G \} \quad \text{(C.11)}$$

These orbits are submanifolds of phase space, so they partition $\mathcal{M}$ and $\mathcal{M}_f$.

Factoring out the symmetry from $\mathcal{M}_f$ can then only mean one thing: pick a representative point in each group orbit and work only with the resulting smaller space, i.e. use the orbit space $\overline{\mathcal{M}}_f := \mathcal{M}_f/G$. This is our reduced phase space.

The main theorem [MW74, Mey73] concerning regular reduction can then be expressed by the picture in figure 1.

In words:
- the reduced space $\overline{\mathcal{M}}_f$ is a manifold;
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- on the reduced space we have a reduced Hamiltonian $\overline{H}_f$ given by

$$\overline{H}_f \circ \pi_f = H \circ i_f \quad (C.12)$$

and a reduced flow $\overline{\phi}_t$ satisfying

$$\pi_f \circ \phi_t \circ i_f = \overline{\phi}_t \circ \pi_f \quad (C.13)$$

- but the reduced phase space $\overline{M}_f$ is in general not a submanifold of phase space, it is another manifold. This is because in general $M_f$ is not a simple direct product $G \times \overline{M}_f$ (i.e. it is a priori not a trivial bundle).

C.3 Singular reduction

The other case we will need to consider is that of a non-free action (e.g. our sphere example) at a singular value $f$ of $F$, a situation analyzed more recently [SL91, LMS93, CS05].

In that case already the level set $M_f$ is this time not a submanifold of phase space, it is a non-smooth union of submanifolds

$$M_f = M_{(A)}^f \sqcup M_{(B)}^f \cdots \quad (C.14)$$

where

$$M_{(A)}^f := M_f \cap M_{(A)} \quad (C.15)$$

$$M_{(B)}^f := M_f \cap M_{(B)} \quad (C.16)$$

$$\ldots \quad (C.17)$$

$$\ldots \quad (C.18)$$

are the intersection of the level set with the various isotropy type submanifolds of $167$
the $G$–action.

So now we need to deal with each of those submanifolds separately. What happens is that on each of them we have now a free action of $G$. So for each submanifold $M^f_{(A)}$ we can use the method for free actions. We then construct our reduced space as a union of the resulting orbit spaces:

$$\overline{M}^f = \overline{M}^f_{(A)} \sqcup \overline{M}^f_{(B)} \ldots$$

(C.19)

where, as we said, $\overline{M}^f_{(A)} := M^f_{(A)} / G$ and so on. The reduced space is then not a manifold in this case. All this is summarized in the following figure.

Figure C.2: Geometry of singular reduction
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