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Influence of Relativistic Terms in the Spectra of Hydrogen Atom Highly Excited in an External Strong Magnetic Field.

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We present a numerical study for the relativistic effect of hydrogen atom in presence of a strong magnetic field. In particular we explore the manifestation of the quantum chaos taking into account the relativistic correction. We observe that as soon as the magnetic field rises any symmetry will be destroyed and the energy levels will be crossed.

Keywords: Hydrogen atom; Rydberg atom; Strong magnetic fields; Chaos.

1 Introduction

Recently the interaction of atoms or similar systems with electromagnetic fields has raised a lot of interest [1–8]. It leads to interesting quantum features such as soliton propagation [9, 10], entanglement [11], antibunching [12], squeezing [13] and bistabilty [14]. The problem of the hydrogen atom in a strong magnetic field constitutes a general physical problem which has not been completely solved yet. In the strong magnetic field, the dynamical symmetry of the hydrogen atom disappears completely [15, 17]. The most difficult region to investigate where the Coulomb and magnetic field forces are of comparable strength ($B \approx 10^7 - 10^{11}$Gauss) [18–20]. That part of the spectrum, where these conditions are met, has been called the "strong field mixing regime" [21]. To significantly disturb the hydrogen atom in its fundamental state, we must apply gigantic external magnetic fields of the order of $10^5\ T$ (a field prevailing at the surface of pulsars), and that seems to be non experimental feasible [15, 22–24]. Atomic diamagnetism was observed for the first time by Jenkins and Segré (1939) in sodium and potassium Rydberg states [17, 19, 25, 26]. Modern interest in the diamagnetism of Rydberg states originates from the experiments of Garton and Tomkins in 1969 [27]. Classically, the motion of an electron in the Coulomb field of

the proton turns chaotic when a diamagnetic interaction, called some times the quadratic Zeeman effect, of comparable strength is added [28–31].

A lot of papers neglect all relativistic terms in the interaction between the electron and nucleus, that's why no effect of the spin-orbit interaction is included [32]. In this work, we study the influence of relativistic terms to level energies. We developed a code (digital diagonalization with Maple) taking in to account the relativistic term. Our code is validated by comparing our simulations to Delande ones [15]. We find an agreement. Relativistic terms is added to see its effect on the diagrams. It is worth to mention that just recently, the free iterative complement interaction method has given a very high precision for solving the Schrdinger and Dirac equations of Hydrogen atom in a strong magnetic field [16] .

2 Atom Hydrogen in uniform magnetic field

The Dirac equation in the weakly relativistic domain [33, 34] is:

$$H = m_e c^2 + H_0 - W_{mv} + W_{SO} + W_D + ... \tag{2.1}$$

with: $m_e c^2$ is the rest-mass energy of the electron, $H_0 = \frac{P^2}{2m} + V(r)$ is the non-relativistic Hamiltonian and the following terms

$$W_{mv} = \frac{P^4}{8m_e^3 c^2}, W_{SO} = \frac{1}{2m_e^2 c^2}\frac{1}{r}\frac{dV(r)}{dr}\overrightarrow{L}.\overrightarrow{S}, W_D = \frac{\hbar^2}{8m_e^2 c^2} \triangle V(r)$$

are called fine structure terms.

All the fine structure terms are about 10^4 times smaller than the non-relativistic Hamiltonian [33].

The effect of an external magnetic field $\overrightarrow{B}$ is taken into account by replacing $\overrightarrow{P}$ by $(\overrightarrow{p} + e\overrightarrow{A})$ in the Hamiltonian. e is the electron charge and $\overrightarrow{A}$ is the vector potential of the field which satisfies $\overrightarrow{div}(\overrightarrow{A}) = 0$. Choosing $\overrightarrow{A} = \frac{\overrightarrow{B}\Lambda\overrightarrow{r}}{2}$,we have

$$\frac{P^2}{2m_e} = \frac{1}{2m_e}(\overrightarrow{p} + e\overrightarrow{A})^2 = \frac{p^2}{2m_e} + \frac{e^2}{2m_e}\overrightarrow{B}.\overrightarrow{L} + \frac{e^2\overrightarrow{A}^2}{2m_e} \tag{2.2}$$

Furthermore, by considering the spin magnetic moment $\overrightarrow{\mu} = -\frac{e}{m_e}\overrightarrow{s}$ of an electron associated with its spin angular momentum $s = \frac{\hbar}{2}$, an extra term $\frac{e}{m_e}\overrightarrow{B}.\overrightarrow{S}$ has to be added into the hamiltonian. If we take $\overrightarrow{B}$ along the $\theta = 0$ direction of polar coordinate system (r, θ, φ), then $\overrightarrow{B}\Lambda\overrightarrow{r} = Br\sin\theta$. The third term in equation (2.2) becomes:

$$\frac{e^2\overrightarrow{A}^2}{2m_e} = \frac{e^2B^2}{8m_e}r^2\sin^2(\theta) \tag{2.3}$$

Considering equations (2.2, 2.3) and the spin magnetic moment, we write the Hamiltonian of hydrogen atom in a uniform magnetic field as:

$$H = m_e c^2 + \frac{p^2}{2m_e} + \frac{e^2}{2m_e}\overrightarrow{B}.(\overrightarrow{L} + 2\overrightarrow{S}) + \frac{e^2B^2}{8m_e}r^2\sin^2(\theta) - W_{mv} + W_{SO} + W_D + ... \tag{2.4}$$

$H_p = \frac{e^2}{2m_e}\overrightarrow{B}.(\overrightarrow{L} + 2\overrightarrow{S})$ and $H_d = \frac{e^2B^2}{8m_e}r^2\sin^2(\theta)$ represent the paramagnetic and diamagnetic terms respectively. We are studding in this paper the diamagnetic term effect on highly excited hydrogen atom (Rydberg atom).

The diamagnetic term H_d (in atomic units $H_d = \frac{B^2}{8}r^2\sin^2(\theta)$) [35] is responsible for the difficult nature of the problem,by which chaos arrives. In order to make the movement chaotic, the term diamagnetic has to be of the same Hamiltonian order of value, in the absence of the magnetic field. This could be realized by using highly excited atoms to which, the Coulombian interaction is weak.

In case of small atomic size (like atom hydrogen) and weak magnetic field, the diamagnetic part of the Hamiltonian H_d has a much smaller effect on the total energy. However, since $H_d \sim r^2$ and $r \sim n^2$, H_d scales as fourth power of the principal quantum number n. When an atomic is excited to high Rydberg system states(characterized by principle quantum number $n = 10 - 300$), the effect of H_d grows quickly and hence can no longer be neglected.

3 Methods of Computation

All computed spectra presented in this paper are obtained by diagonalization of the Hamiltonian matrix in a suitable basis. The spherical Sturmian basis is used for hydrogen in a magnetic field.

3.1 Sturmian Spherical Basis

The base's choice allowing efficient calculations requires considerations of symmetry. All hydrogenoïd states of the same value M are mixed. Therefore, it's necessary to consider a dynamic group including the different states. The group $SO(2,2)$ satisfies the previous criterion.

The eigenstates bases built thanks to this group are the bases of Sturmien functions ensuring the global representation of the states' space (discreet,continuum) with a countable base at the expense of the loss of orthogonality of base's vectors.

The Sturmien base is the proper base describing the system of two oscillators equal to hydrogen atom. The Schrödinger equation is expressed with a simple algebraic form in function of generators($\overrightarrow{S}^{(\alpha)}$, $\overrightarrow{T}^{(\alpha)}$) of dynamic group $SO(2,2)$.

The Hamiltonian "oscillator" obtained coincides with his expression in the context of the classic mechanic.

$$\left(S_3^{(\alpha)} + T_3^{(\alpha)} + \frac{\gamma^2}{2(-2E)^2}(S_1^{(\alpha)} + S_3^{(\alpha)})(T_1^{(\alpha)} + T_3^{(\alpha)}) \right.$$
$$\left. (S_1^{(\alpha)} + S_3^{(\alpha)} + T_1^{(\alpha)} + T_3^{(\alpha)}) - \frac{1}{\sqrt{-2E}}\right)|\Psi\rangle = 0 \qquad (3.1)$$

with $\alpha = \frac{1}{\sqrt{-2E}}$. We can write a more general equation by taking any value of the adjustable parameter α [15, 40]. (which leads us to adjust the length scale defining the Sturmian functions, or the frequency $\frac{1}{\alpha}$ of the oscillator system). We obtain:

$$\left[A^{(\alpha)} - \alpha + (-2E\alpha^2)B^{(\alpha)} + \frac{\gamma^2\alpha^4}{2}C^{(\alpha)}\right]|\Psi\rangle = 0 \tag{3.2}$$

with :

$$A^{(\alpha)} = \frac{S_3^{(\alpha)} - S_1^{(\alpha)}}{2} + \frac{T_3^{(\alpha)} - T_1^{(\alpha)}}{2}$$
$$B^{(\alpha)} = \frac{S_3^{(\alpha)} + S_1^{(\alpha)}}{2} + \frac{T_3^{(\alpha)} + T_1^{(\alpha)}}{2}$$
$$C^{(\alpha)} = (S_3^{(\alpha)} + S_1^{(\alpha)})(T_3^{(\alpha)} + T_1^{(\alpha)})(S_3^{(\alpha)} + S_1^{(\alpha)} + T_3^{(\alpha)} + T_1^{(\alpha)})$$

$$S_3^{(\alpha)}|nlm\rangle^{(\alpha)} = \frac{n}{2}|nlm\rangle^{(\alpha)} + \frac{1}{2}\sqrt{n^2-(l+1)^2}C_M^{l+1}|nl+1m\rangle^{(\alpha)} + \frac{1}{2}\sqrt{n^2-(l)^2}C_M^{l}|nl-1m\rangle^{(\alpha)}$$

$$T_3^{(\alpha)}|nlm\rangle^{(\alpha)} = \frac{n}{2}|nlm\rangle^{(\alpha)} - \frac{1}{2}\sqrt{n^2-(l+1)^2}C_M^{l+1}|nl+1m\rangle^{(\alpha)} - \frac{1}{2}\sqrt{n^2-l^2}C_M^{l}|nl-1m\rangle^{(\alpha)}$$

$$S_1 = \frac{S_+ + S_-}{2}, \qquad T_1 = \frac{T_+ + T_-}{2}.$$

$$S_+^{(\alpha)}|nlm\rangle^{(\alpha)} = \frac{\sqrt{(n+l+1)(n-l)}}{2}|n+1lm\rangle^{(\alpha)} + \frac{\sqrt{(n+l+2)(n+l+1)}}{2} C_M^{l+1}|n+1l+1m\rangle^{(\alpha)} + \frac{\sqrt{(n-l)(n-l+1)}}{2}C_M^{l}|n+1l-1m\rangle^{(\alpha)}$$

$$T_+^{(\alpha)}|nlm\rangle^{(\alpha)} = \frac{\sqrt{(n+l+1)(n-l)}}{2}|n+1lm\rangle^{(\alpha)} - \frac{\sqrt{(n+l+2)(n+l+1)}}{2} C_M^{l+1}|n+1l+1m\rangle^{(\alpha)} - \frac{\sqrt{(n-l)(n-l+1)}}{2}C_M^{l}|n+1l-1m\rangle^{(\alpha)}$$

$$S_-^{(\alpha)}|nlm\rangle^{(\alpha)} = \frac{\sqrt{(n+l)(n-l-1)}}{2}|n-1lm\rangle^{(\alpha)} + \frac{\sqrt{(n-l-1)(n-l-2)}}{2} C_M^{l+1}|n-1l+1m\rangle^{(\alpha)} + \frac{\sqrt{(n+l)(n+l-1)}}{2}C_M^{l}|n-1l-1m\rangle^{(\alpha)}$$

$$T_{-}^{(\alpha)}\,|nlm\rangle^{(\alpha)} = \frac{\sqrt{(n+l)(n-l-1)}}{2}\,|n-1lm\rangle^{(\alpha)} - \frac{\sqrt{(n-l-1)(n-l-2)}}{2}$$
$$C_M^{l+1}\,|n-1l+1m\rangle^{(\alpha)} + \frac{\sqrt{(n+l)(n+l-1)}}{2}\,C_M^{l}\,|n-1l-1m\rangle^{(\alpha)}$$

and

$$C_M^l = \sqrt{\frac{l^2-M^2}{4l^2-1}} \tag{3.3}$$

From these relationships a simple form for the overlap matrix in the basis of Sturmian functions of common exponent ζ follows

$$E_{nl,n'l'} = \int_0^\infty S_{nl}^{\zeta}(r) S_{n'l'}^{\zeta}(r) dr.$$

This matrix takes the simple form

$$E_{nl,n'l'} = \begin{cases} \frac{n}{\zeta} & n'=n \quad l=l' \\ -\frac{1}{2}\zeta[(n+l+1)(n-l)]^{\frac{1}{2}} & n'=n+1 \quad l=l' \\ 0 & l\neq l' \end{cases}$$

It is also found that the matrix elements of the quadratic magnetic potential, namely

$$Q_{nl,n'l'} = \int_0^\infty S_{nl}^{\zeta}(r) r^2 S_{n'l'}^{\zeta}(r) dr.$$

are non-zero only for $|n-n'| = 0,1,2,3, |l-l'| = 0,2$, and in these cases take the following simple forms:

$$Q_{nl,n'l'+2} =$$

$$\begin{array}{cc}
-\frac{1}{2}\zeta^{-3}[(n-l-1)(n-l-2)(n-l-3)(n-l-4)(n-l-5)(n+l)]^{\frac{1}{2}} & n'=n-3 \\
\zeta^{-3}[(3n+2l)(n-l-1)(n-l-2)(n-l-3)(n-l-4)]^{\frac{1}{2}} & n'=n-2 \\
-\frac{5}{2}\zeta^{-3}[(3n+l)(n-l-1)(n-l-2)(n-l-3)(n+l+1)]^{\frac{1}{2}} & n'=n-1 \\
10n\zeta^{-3}[(n+l+1)(n+l+2)(n-l-1)(n-l-2)]^{\frac{1}{2}} & n'=n \\
-\frac{5}{2}\zeta^{-3}(3n-l)[(n+l+3)(n+l+2)(n+l+1)(n-l-1)]^{\frac{1}{2}} & n'=n+1 \\
\zeta^{-3}(3n-2l)[(n+l+4)(n+l+3)(n+l+2)(n+l+1)]^{\frac{1}{2}} & n'=n+2 \\
-\frac{1}{2}\zeta^{-3}(n+l+5)(n+l+4)(n+l+3)(n+l+2)(n+l+1)(n-l)]^{\frac{1}{2}} & n'=n+3
\end{array}$$

and

$$Q_{nl,n'l'} =$$

$$\begin{array}{cc}
2n\zeta^{-3}[5n^2-3l(l+1)+1] & n'=n \\
-\frac{3}{2}\zeta^{-3}[5n(n+1)-l(l+1)+2][(n+l+1)(n-l)]^{\frac{1}{2}} & n'=n+1 \\
3\zeta^{-3}(n+1)[(n+l+1)(n-l)(n+l+2)(n-l+1)]^{\frac{1}{2}} & n'=n+2 \\
-\frac{1}{2}\zeta^{-3}[(n+l+1)(n+2-l)(n-l)(n+l+3)(n+l+2)(n+1-l)]^{\frac{1}{2}} & n'=n+3
\end{array}$$

Charles W. Clark and K. T. Taylor [27] have found, that it is usually preferable to choose higher values of ζ; for instance, in calculations using $\zeta = \frac{2}{n}$, intended to determine energies near the ionization limit.

Our numerical simulations consist in diagonalizing the matrix representing the operator (3.2) in a Sturmien base. The matrix elements of generators are not α dependent.

3.2 Types of simulations realizable:

The four terms involved in the equation (3.2) depend on the parameter α so differently. By setting 3 of 4 coefficients, we obtain a general problem for eigenvalues of the form :

$$(M - \lambda N)\,|\Psi\rangle = 0$$

where M and N matrix are fixed, λ and $|\Psi\rangle$ are the eigenvalues and eigenvectors searched

3.2.1 Simulation at fixed magnetic field:

We opted for $\alpha = \alpha_0 = C^{te}$ and we fix the magnetic field. We obtain an equation in the generalized eigenvalues with :

$$\begin{aligned} M &= A^{(\alpha)} - \alpha_0 + \frac{\gamma^2 \alpha_0^4}{2} C^{(\alpha)} \\ N &= B^{(\alpha)} \\ \lambda &= -2E\alpha_0^2 \end{aligned}$$

which determines the energy levels.

3.2.2 Simulation at fixed energy:

We opted for $\alpha = \alpha_0 = C^{te}$ and we fix the energy. We obtain an equation in the generalized eigenvalues with :

$$\begin{aligned} M &= A^{(\alpha)} - \alpha_0 + (-2E\alpha_0^2) B^{(\alpha)} \\ N &= C^{(\alpha)} \\ \lambda &= \frac{\gamma^2 \alpha_0^4}{2} \end{aligned}$$

which determines the spectrum of magnetic field values corresponding to the fixed energy. ***Note***: The two types of simulations lead strictly to the same results. The choice of one or the other is dictated slowly by considerations of convenience.

3.2.3 Diagonalization algorithm and convergence criterion:

The matrix elements of generators ($\overrightarrow{S}^{(\alpha)}, \overrightarrow{T}^{(\alpha)}$) in a Sturmian basis have rules selection. The matrix eigenvalue problem generalized to solve are real symmetric matrices in strips.

To calculate the eigenvalues and eigenvectors we used our technique (digital diagonalization with Maple).

Control parameter α_0 : For each of the two types of simulations possible, have an adjustable parameter α_0 to check convergence. In fact, α_0 is related to the natural frequency of the basic oscillator (Sturmian) chosen. Exact searched values are not dependent on this parameter. At a fixed base size, the function representing the eigenvalue as a function of α_0 has a bearing more or less marked around the exact eigenvalue. A wide bearing and flat ensures that the result is converged [15].

3.3 Energy diagrams:

By using the simulation 3.2.1 at fixed magnetic field, we can draw for a large number of points diagrams $\texttt{Energy} = f(\gamma^2)$ in the fig.1, fig.2, fig.3 and fig.4. The levels are followed from their zero-field positions through the inter-l and inter-n diamagnetic mixing regimes.

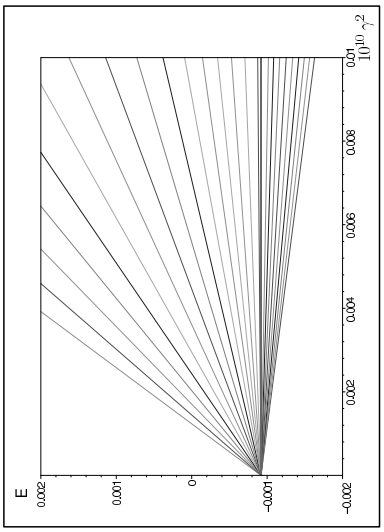

Figure 3.1: The energy spectrum of hydrogen atom highly excited $n = 33$ in strong magnetic field. [1]

Fig. 3.1 shows the diagram $\texttt{E}(\texttt{Hartree}) = f(\gamma^2)$ for Rydberg states $n = 33$ in the system with rather low field ($B < 3T$). Diamagnetism breaks the zero-field l-degeneracy of hydrogen.

In very weak field (l-system inter-mixing), the diamagnetic term completely removes the degeneracy of the levels proportional to γ^2. This is known as the l-mixing regime. We see the rovibrationnelle structure:

(a) the vibrational levels below the diamagnetic multiplet

(b) the rotational levels up the diamagnetic multiplet

(c) and to the transition between the two: the effect of the conventional separation characterized by a tightening levels.

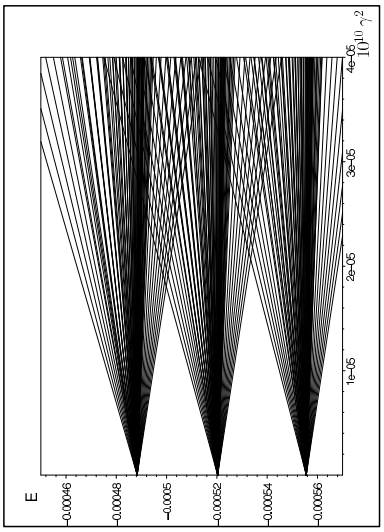

Figure 3.2: Level scheme of the hydrogen atom(corresponding to principal quantum numbers $n = 30 - 32$) in the energy [Hartree] as a function of the square of the magnetic field strength. [1]

Fig. 3.2 shows the behavior of the energy levels of the hydrogen atom originating from multiplets with principal quantum numbers between 30 and 32 in the magnetic field range $1 - 3T$. In this regime where the classical movement is regular, the energy levels intersect.

Fig. 3.3 represents the diagram $\mathsf{E} = f(\gamma^2)$ for Rydberg states $n = 30-32$ in the regime of intermediate field where the Coulomb and diamagnetic interactions are of comparable strength. A new phenomenon occurs: classically chaotic dynamics appears, it is precisely the classical movement near the separation between rotational and vibrational states which becomes chaotic for the weakest fields. In fact, these states do not possess a well defined symmetry [41]. The vibrational symmetry is destroyed. Finally, in a strong field, higher than $\beta = \dfrac{\gamma^2}{(-2E)^3} > 60$, Fig. 3.4 shows that the rotational symmetry is destroyed, the classical dynamic is totally chaotic and quantum spectrum includes only large anticrossing [42].

3.4 The effect of relativistic terms $\triangle E_l = \dfrac{\alpha^2}{2n^3 l(l+1)}$ on the diagrams.

The relativistic effects and the spin of the electron contribute to the splitting of the atomic levels. For the hydrogen atom, the relativistic effects are not great and can be taken into account within the limits of the perturbation theory. However, for heavy atoms the

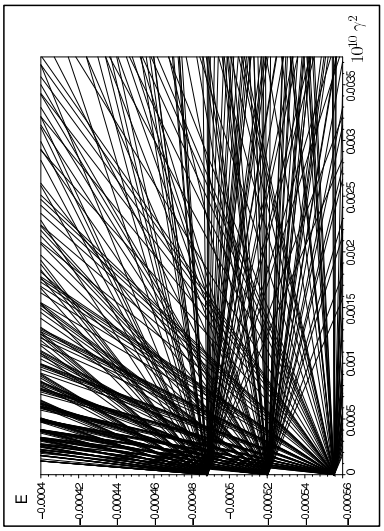

Figure 3.3: Diagram of energy levels of the hydrogen atom in strong magnetic field. Regime of intermediate magnetic field ($\beta = \frac{\gamma^2}{(-2E)^3} \simeq 2$). [1]

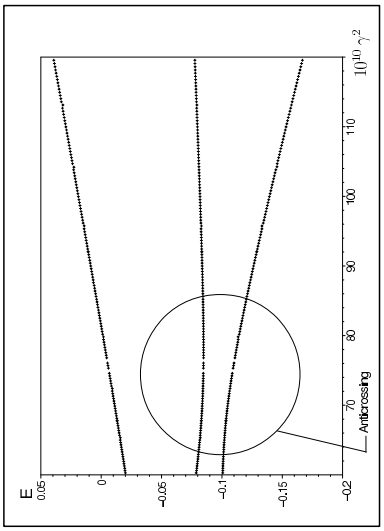

Figure 3.4: Diagram of energy levels of atomic hydrogen in strong magnetic field. Intense regime field ($B > 18\,T$).

relativistic effects are significant. The levels shift [27] due to this effect can be written as

$$\triangle E_l = \frac{\alpha^2}{2n^3 l(l+1)},$$

where $\alpha = \dfrac{1}{\hbar c} \simeq \dfrac{1}{137}$ is the fine structure constant which defines the scale of the splitting. We have realized the simulation at fixed energy for $n = 31$ by varying l from 20 to 30. We have obtained in the Fig. 3.5 the diagram of the magnetic field square γ^2 in function of orbital angular momentum l which illustrates the presence of an extremely negligible fact.

We worked with Maple, with 30 digits. We found a difference between the values, for

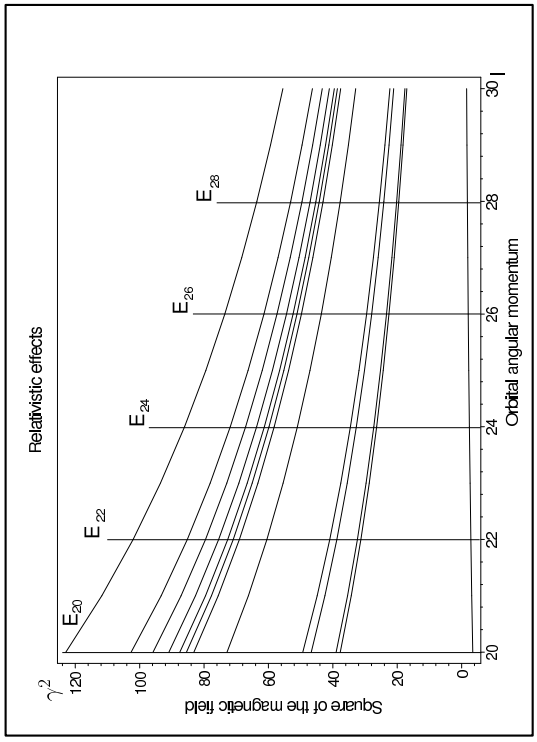

Figure 3.5: Plot of the magnetic field square as a function of $l \in \{20, 22, 24, 26, 28\}$ for energy E(Hartree): E_{20}=-0.00052029136103, E_{22}=-0.00052029136139, E_{24}=-0.00052029136167, E_{26}=-0.00052029136188, E_{28}=-0.00052029136206.

$l = 0$ and $l = 25$ start to deviate after the 20^{th} digit.

4 Conclusion

Our work is based on the study of the hydrogen atom which is excited by a magnetic field. We have numerically calculated the spectrum and the eigenstates using the diagonalization calculus developing an effective code "Digital diagonalization with Maple". The choice of state basis(sturmian basis) adopted to dynamic symmetries is essential in order not to fulfill the computer memory. We explored some quantum characteristics. More precisely, in a weak field the diamagnetic term removes the degeneracy of energy levels.

Table 3.1: digital γ^2 values respectively for $l = 0$ and $l = 25$.

$l = 0$	$l = 25$
8112. 488871519324280520367896 25	8112. 488871519324280520385971 98
10. 549744262177353566329255 7818	10. 549744262177353566328417 7593
3. 029143951175830189514105 18181	3. 029143951175830189513904 27913
1. 612211333425169598947288 97195	1. 612211333425169598947189 13517
1. 038312585403814085332013 80784	1. 038312585403814085331952 80131
. 738537746730232564534039 579702	. 738537746730232564533997 817243
. 559685417472607242089800 213308	. 559685417472607242089769 303825
. 442492199317050804030807 541345	. 442492199317050804030783 761362
. 358420161980715210789558 271207	. 358420161980715210789541 396220
. 145329892956338988582252 985358	. 145329892956338988582248 351595
. 291177146019978828877059 598414	. 291177146019978828877052 263475
. 171378671744125914435791 750787	. 171378671744125914435786 579823
. 239974276777479248254893 091822	. 239974276777479248254887 245569

As soon as the magnetic field rises any symmetry will be destroyed, the different states will integrate and the energy levels will be strengthly crossed. This effect is known as the quantum chaos. Furthermore, we studied the energy difference taking into account the relativistic effect (spin-orbit interaction). We show that the effect of spin-orbit is very low (20 order of magnitude lower) compared to non-relativistic Hamiltonian and can be neglected.

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