CHAPTER IX

MULTIDIMENSIONAL SYSTEMS: THE PROBLEM OF THE ZEEMAN EFFECT IN HYDROGEN

§.30. Importance of the problem and applications of the model.

The aim of this chapter is to present an up-to-date, general overview of a problem of current interest: the properties of matter placed in strong magnetic fields. Moreover, we shall discuss here different theoretical methods that have been developed and applied to study several phenomena appearing under the effect of external magnetic fields.

The Zeeman effect, arisen when an external magnetic field acts on an atom, is known from the beginning of this century. However, until recently, there had taken place small progress in this field regarding to what already was known since the early days of quantum mechanics /1/. This situation was mainly due to the fact that theoretical methods were suitable to explain the majority of experimental phenomena, occurring within the small range of magnetic fields attainable in the laboratory.

But there are certain phenomena, a great deal of them of recent discovery, that require to take into account much stronger magnetic fields. In order to explain these new experimental facts it is necessary to consider the theoretical problem where the interaction of electrons with the magnetic field is stronger than the Coulombic nucleus-electron interaction.

Let us summarize briefly some phenomena involving very intense effective fields. For this purpose it is convenient to consider a hydrogen-like atom with nuclear charge $Z$, placed in a magnetic field of magnetic induction $B$. The properties of the system, such as absolute energy, binding energy, expectation value of powers of coordinates, electronic transition probability and intensity, among others are obtained from the solutions of the Schrödinger equation within the context of the non-relativistic approximation, which is valid for magnetic fields lower than $10^{14}$ G /2-4/, the Hamiltonian depends trivially on the spin, and the Schrödinger equation is (see Appendix H):

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\[ H\psi_{\{n\}} = E_{\{n\}}\psi_{\{n\}} \]  

(30.1)

\[ H = -\frac{\hbar^2}{2\mu} \Delta + \frac{e}{2\mu c} \bar{B} \cdot \bar{L} + \frac{e^2}{8\mu c^2} B^2 r^2 \sin^2 \theta - \frac{Z}{D r} \]  

(30.2)

with \( \mu \) the reduced mass for the two-body (nucleus and electron) system, and \( D \) the dielectric constant of the medium (considered as a continuum) where the atom is placed.

Furthermore, \( \bar{L} \) is the electronic orbital angular momentum vector and \( \{n\} \) denotes the set of quantum numbers necessary to classify the state of eigenenergy \( E \). For the moment we are excluding any reference to the spin in the Schrödinger equation, in the approximation where such angular momentum is considered as a constant of motion.

The problem defined via Eqs. (30.1) and (30.2) is a highly nontrivial one, since no implicit or explicit expression exists for \( E_{\{n\}} \) as a function of \( B = ||\bar{B}|| \). This is due to the nonseparability property of the differential equation because of the strong coupling of variables between magnetic and coulombic terms (third and fourth terms in Eq. (30.2), respectively) /5/.

This property is clearly seen re-writing the Hamiltonian (30.2) as follows

\[ H = -\frac{\hbar^2}{2\mu} \Delta + \frac{e}{2\mu c} \bar{B} \cdot \bar{L} + \frac{e^2}{8\mu c^2} B^2 \rho^2 - \frac{Z}{D(z^2+\rho^2)^{1/2}} \]  

(30.3a)

\[ \rho^2 = x^2+y^2 = r^2-z^2 \]  

(30.3b)

where the coupling takes place in the coulombic term between variables \( \rho \) (cylindrical) and \( z \) (z-axis is coincident with the magnetic field direction).

Several characteristic phenomena with very strong associated mag-
nentic fields occur in physics and chemistry. Although we will try to
give below a self-contained presentation of the Zeeman effect, it
cannot be considered by any means as complete, due to the vast lite-
rature on the subject. An introductory summary may be seen in Refs.
/6-8/.

If we consider that (30.3) describes the effect of a magnetic field
on a hydrogen-like atom, it is evident that the external field $B$ to
be applied must be very intense for the magnetic interaction to be the
dominant effect in the ground state. For $Z=1$, both interactions are
comparable for $B=2\times 10^9$ G (Appendix H); as a comparison, typical intense
magnetic field attainable in the laboratory has a strength of $10^4$ G
(1T) /6,8/.

However, since long ago it is well known that (30.3) is an appro-
priate Hamiltonian model to describe other phenomena. For example, the
magneto-optical properties of some dopped semiconductors are determined
by the one-electron bound states appearing in the forbidden band of
the source solid, near its border. When such a system is subjected to
radiation, valence band electrons are promoted into the conduction
band, creating hole-electron pairs. Such pairs, excitons, give rise to
bound systems which are essentially hydrogen-like ones, where the hole
plays the role of nucleus. This sort of system is basically assimilable
to positronium. In simplified terms, it can be said that the properties
of a dopped semiconductor, placed in an exterior magnetic field, are
described through the Zeeman effect of excitons. However, to describe
an exciton the Hamiltonian must be properly modified, since now the
electron is not in the vacuum.

The basic changes to be introduced lie in the electronic and nuclear
mass, which have to be replaced by effective masses, as well, as the
dielectric constant, that is to say,

$$m_n \rightarrow m_n^* ; \quad m_e \rightarrow m_e^* ; \quad \mu \rightarrow \mu^* ; \quad D \rightarrow D^* . \quad (30.4)$$

For electronic absorption problems of impurities involving excitons,
the typical constant values are $D^* = 10$, where $m_n^* \gg m_e^*$, with $m_e^*$ is
two or three orders of magnitude lower than $m_e$. 
Above new definitions lead to a situation where small exterior fields will correspond to very intense local fields. This phenomenon was the first to promote the interest in the Zeeman effect for hydrogen-like atoms in very strong fields /9-13/. For example, choosing the typical case of InSb, its natural constants \( (m^*_n, m^*_e, D^*) \) are such that an exterior field of \( 2.4 \times 10^4 \text{G} \) makes up a local (real) field on an exciton of \( 3.6 \times 10^{10} \text{G} \). Accordingly, the Zeeman effect for the exciton has the features of a very intense magnetic field, i.e. one where the coulombic interaction may be considered as a perturbation in relation to the interaction of the electron in the external magnetic field. This state of affairs is exactly opposed to that verified in the classic Zeeman experiences. These previous experiences involved typical field strengths of 2-4T, and this kind of fields is weak regarding the coulombic interaction, which is only compensated by fields of about \( 10^5 \text{T} \).

It is necessary to point out the present impossibility to attain super-strong magnetic fields in the laboratory /6,8/. The reason of such difficulties is easy to understand: the pressure (in Newton/m\(^2\)) on a given material under a magnetic field \( B \) (in T) is given by

\[
\mathbf{P} = 3.9 \times 10^5 \mathbf{B}^2
\]

For example, a field of 0.5T gives rise to a pressure of around 1 atm, but for \( B = 10^3 \text{T} \) the pressure is \( 10^6 \text{ atm} \), which is the pressure at the center of the Earth. Consequently, there are no "normal" materials capable to sustain the direct application of such intense magnetic fields.

Spectra of Rydberg atoms are another important phenomena whose characteristics have to be understood by considering a very intense local field, while the applied external field is low (about 1T). The research on this subject started around 1970; these systems consist basically in atoms with an electron excited up to a very high energy level. Such electron is responsible of the most outstanding features of the atomic absorption spectra, when the atom is placed in external fields. A brief summary of the state of art on this subject can be found in Refs. /8,14/. 
The occurrence of such intense fields can be understood by considering that \( E_n \) fulfills (in an approximate fashion) a scaling relation with \( n_r \) (number of radial zeros in the wave function), such as

\[ E_{n_r} (Z,B) \approx n_r^{-2} E_0 (Z,Bn_r^3) \quad . \quad (30.6) \]

It can be seen that \((Bn_r^3)\) plays the role of the effective field acting on one electron, in a state with quantum number \( n_r \). Obviously, for a given \( B \), such a field will be more intense when \( n_r \) increases, i.e. when the electron is more excited. In fact, for a field strength of about 1T, an excited electron in a state with \( n_r \approx 50 \) "sees" a local field of about \( 10^5 \) T. This behavior of electrons in Rydberg atoms can be intuitively understood as follows: when the electron is located at excited states its expectation value \( \langle r \rangle \) increases. From a semiclassical standpoint, it follows at once that such an increase implies a decrease of the electron-nucleus coulombic interaction, so that it can be balanced or even exceeded by an external magnetic field.

Relationship (30.6) is valid for \( n_r \gg 1 \) in the hydrogen atom, although there are semiclassical arguments impelling to believe that a similar law must be valid for other Rydberg atoms (such as alkaline or alkaline-earth atoms /13,19/).

From the experimental viewpoint, the great interest on the properties of Rydberg atoms placed in magnetic fields started with the experiments of Garton and Tomkins /20/. These authors studied the absorption spectrum of Ba I (vapor) for the transition

\[ \text{(6s}^2 \text{)} \quad ^1S_0 \rightarrow \text{(6s np) } ^1P_1 \]

in a magnetic field of about \( 10^4 \) G. They observed occurrence of the so-called "quasi-Landau resonances" for the levels \( n \approx 75 \), near the ionization limit at zero field. The quasi-Landau resonances are basically equally spaced spectral lines, which, being totally different from those normal absorption spectral lines of hydrogen-like atoms, require
to consider very intense magnetic fields in order to understand their very presence. Let us remind that the Landau spectrum for an electron in a magnetic field presents bound states equally spaced in energy (Appendix H). The main qualitative features of the quasi-Landau resonances may be explained by means of simple enough semiclassical models /16-17/, semiclassical virial arguments /18/ or the 1D JWKB method /21-24/. Notwithstanding, these successful approaches, there remain yet some recently discussed /25,26/ properties that cannot be explained in a wholly satisfactory way via the simple JWKB scheme. Since the problem is not separable, the Einstein-Brillouin-Keller quantization scheme /27,28/ should be used. Ref./29/ displays a summary on the state of art of this problem, and we will turn again on this subject in the next paragraph.

Other series of relevant phenomena where very intense magnetic fields appear involved are those of astrophysical and astronomical interest appearing on the surfaces of neutron (pulsars) and white dwarf stars. At the beginning of the 70's, the experimental finding of a very intense magnetic field (of about $10^8$ G) in a white dwarf star /30/, gave strong impulse to the study of cosmic bodies where very intense fields were involved. At present, there have been detected a large number of white dwarf stars where exist very strong magnetic fields /31/. The existence of such intense fields in these objects may be understood from the fact that this sort of stars arise from the collapse of stars from the principal series, keeping constant the magnetic flux. Typically, a star like our sun, with a magnetic field of about a few hundreds of gauss, would give rise to a field of $10^8$ G if compressed to a star with the size of Earth.

On the other hand, pulsars were discovered in 1967 /32/ and they were modelled at once as neutron stars, having more intense magnetic fields than the white dwarf stars /33/. In 1973 such assumption was confirmed with the finding of a magnetic field of $5.3 \times 10^{12}$ G in the Hercules X-1 star /34/. This star emits X rays and the spectrum of this radiation has been used to measure field strength /35/. The lines of the X-ray spectrum were quickly interpreted as electron transitions in a discrete Landau spectrum, corresponding to the highly magnetised hot plasm at the star poles. It deserves to be pointed out that this sort of stars actually are binary compounds consisting of a normal star plus a neutron star. This last one produces a strong gravitational on its mate star and sucks matter from the normal star. Such matter
forms a disk around the denser star whose inner border is a plasm falling towards the neutron star (at a rate of about $10^{11}$ ton/sec), by the poles and led by its magnetic field. Nearly 10% of the matter sucked, and quickly accelerated by the intense gravity of the pulsar is transformed into X rays, which are finally seen.

The rather large field strengths of these new objects makes necessary a peculiar explanation for the spectrum of their surface plasms. In fact, they are understood on the basis that the coulombic interaction is a small perturbation with respect to the existing magnetic field, even for the atomic ground state. Therefore, the properties of this new Zeeman effect must be radically different from those corresponding to small or intermediate fields (like those appearing in the white dwarf stars or the quasi-Landau resonances). A more complete discussion on this topic may be found in Refs. /6,8,36/.

Due to the new experimental results sketched along this paragraph, we are faced with the theoretical problem of developing methods to describe the energy and other properties for different states of the hydrogen atom within the whole range of field intensities. In other words, it is necessary to know the physical properties from the coulombic up to the Landau regime.

One of the aims of this book is to develop adequate approximate analytic expressions for the energy and other physical properties. The intention is to use as illustrative examples several models, among which the Zeeman effect for hydrogen-like atoms is included. For that purpose, we will study the VFM and RSPT in a combined fashion. Before presenting the methodology, we deem appropriate to review the different theoretical models previously employed, and to discuss their usefulness range. This is the purpose of the remaining paragraphs in this chapter.
§.31. Application of non-perturbative methods

From now on we will restrict ourselves to the hydrogen atom model to present our discussions, although several conclusions to be derived are also valid for many-electron atoms. In first place, we comment below analytical as well as numerical expressions available in the literature, that approach the energy and other atomic properties in the whole range of field intensities.

Let us first consider the methods used to describe the Zeeman effect, viz. that corresponding to weak magnetic fields, compared to the coulombic field. One has the following cases:

a) Lineal Zeeman effect: The Hamiltonian (30.3) does not include the interaction terms between the field and electronic spin as well as the term associated with the spin-orbit coupling. As shown in Appendix H, the magnetic field-spin coupling term may be introduced into the Hamiltonian as

\[ H_e = H(Z, \lambda) + H_p, \quad (31.1) \]

\[ H(Z, \lambda) = -\frac{\lambda}{2} - \frac{Z}{r} + \frac{\lambda^2}{8} (x^2 + y^2) + \frac{\lambda^2}{2} \left( x^2 + y^2 + z^2 \right) \quad (31.2) \]

\[ H_p = \frac{\lambda}{2} (L_z + g_s S_z) \quad (31.3) \]

in atomic units for a hydrogen-like atom (Appendix H). Hamiltonian \( H_e \) (Eq.(31.1)) is split into two terms: \( H \) contains the impulse and coordinate operators while \( H_p \) the constants of motion (paramagnetic term). Such constants of motion are represented by the projections in the field direction (i.e. z axis) of orbital and spin angular momenta \( (L_z \) and \( S_z \), respectively). Constant \( g_s \) in Eq. (31.3) is the so-called spin g-factor.

The lineal Zeeman effect appears as a level splitting produced by the paramagnetic term \( H_p \). This typical effect of weak field can be totally described by way of RSPT up to the first order. Besides, this effect can be considered as a very weak one with respect the Russell-
Saunders spin-orbit coupling /6,37/.

b) Paschen-Back effect: This "high" field effect, regarding that discussed in a) corresponds to that case where the magnetic interaction is much stronger than the spin-orbit interaction, but much weaker than the coulombic interaction /6,37/. The hyperfine splitting in the magnetic field (due to the nuclear spin) is observed together with the Paschen-Back effect. A theoretical interpretation of the effects taking place in this range of magnetic fields can be given in a satisfactory manner by means of the Rayleigh-Ritz method, with a suitable choice of the basis set. The two most appropriate basis sets are those made up by the wave functions $\{|SLJM>\}$ and $\{|SM_{LM}>\}$, where letters denote total quantum numbers. The use of the first set makes diagonal the spin part of the Hamiltonian, while the second set diagonalizes that portion of the Hamiltonian depending linearly on the field.

c) Quadratic Zeeman effect: This effect is characterized by a field intensity that prevents neglecting the $\lambda^2$-term in the Hamiltonian with respect to the $\lambda$-term. This effect, in contrast with those two precedent ones cannot be described by means of RSPT any longer /38/. In this regime the atom starts to part off up to an appreciable degree from its original symmetry. The most employed (non-perturbative) technique to study this particular range has been the variational Rayleigh-Ritz method, after choosing suitably the set of functions adapted to the change of symmetry. Cabib et al /39/ showed that using hydrogen-like wave functions (i.e. Legendre polynomials for the angular part of the wave function), the quadratic Zeeman effect region ($\lambda=0.1$ in Eq. (31.2)) is described by an abundant mixture of different $\lambda$-functions.

This effect, called "inter-$\lambda$-mixing", has been also studied by other variational methods /40-47/. Among such variational methods one can mention:

i) Variational fitting with two or more parameters, which has proved to be useful to compute ionization energies /40/ and transition probabilities /41/ for bound states;

ii) Use of simple functions with two parameters in combination with RSPT /42/.

iii) Rayleigh-Ritz method using Laguerre polynomials as basis sets /43/;
eigenfunctions of the Hamiltonian at zero field ($\lambda=0$) /44-46/ and properly chosen functions adapted to the cylindrical symmetry. This approach has been found useful for field strengths around $\lambda=1$.

Above methods supply excellent numerical results for eigenvalues within the range corresponding to the quadratic Zeeman effect, but they do not provide simple analytical expressions.

Some further comments on variational methods are due here. The Rayleigh-Ritz method consists of expanding the wave function in a complete basis set, and then to analyse the convergence properties of the eigenvalues obtained upon diagonalizing the Hamiltonian truncated matrix, with increasing truncation order. However, the hydrogen-like basis set does not furnish a complete basis set, unless the continuum is included. Since this last step cannot be explicitly considered because the H matrix elements cannot be computed, the results are restricted to work with the lower energy states, and the condition $\lambda \leq 1$. This state of affairs can be improved up to a certain point by means of using a Sturmian basis set /48,49/, which considers in some partial way the continuum contribution.

d) Zeeman effect in the Landau regime: Here we call Landau regime to the spectrum characterized by the condition $\lambda^2 \gg \lambda$. Obviously, this effect describes a situation where the coulombic potential can be made up of the electron movement in a magnetic field. As shown in Appendix H, the Landau spectrum (limit $Z \to 0$ or $\lambda \to \infty$ in Eqs. (31.1) and (31.2)) is only quantized in directions normal to the field, and such condition describes a 2D isotropic oscillator. This regime of the spectrum is so different to that corresponding to $\lambda \to 0$, that the necessary methods to describe it with accuracy must be entirely different.

Among the non-perturbational methods we have to refer again the variational approximations. Naturally, the greater number of efficient variational methods to study the strong field region are related to the use of Landau orbitals, i.e. eigenfunctions of the 2D oscillator just cited.

One of the first studied approximations /9/ was a gaussian function like

$$\psi(\rho,z) = N \exp(-a_1^2 z^2+a_2^2 \rho^2); \ a_1>0; \ a_2>0 \ . \quad (31.4)$$
Function (31.4) is suitable to represent the ground state associated with the Hamiltonian for large magnetic field strengths. A significant and particularly important result arising from a simple function as Eq. (31.4) is that the variational energy (an extremum regarding the $a_1$ and $a_2$ parameters) predicts properly the unboundness and monotonicity of the binding energy as a function of the magnetic field:

$$\xi_0 = \frac{\lambda}{2} - E_0 = \frac{1}{2} \ln^2(\lambda) + O(\ln\lambda + \ln\ln\lambda); \ m = 0, \lambda \gg 1 \quad (31.5)$$

The binding energy has a similar behavior for all the states fulfilling the condition (see Appendix I)

$$m = - \ell \quad (31.6)$$

These are called tight-bound states. As we shall see in the next paragraphs, property (31.5) (which is intrinsic to the Schrödinger differential equation) is a rather difficult one to be described properly.

Though other authors have used variational functions similar to (31.4) /50/, the Rayleigh-Ritz method Landau orbitals functions /17,51-56/ has proved to be more efficient to study several properties. Among such properties, one can mention eigenvalues, transition probabilities, quantum defects for highly excited states and oscillator strengths. Besides, the Rayleigh-Ritz method with a basis set of 3D isotropic oscillator /45,57/ was applied to study the hydrogen atom under super-strong magnetic field.

The so-called adiabatic approximation is a method closely related to the last one and it has shown to be suitable for this sort of applications. The method was formerly developed by Schiff and Snyder /58/ to explain the Jenkins and Segre experiences on atoms in very intense magnetic fields /59/. Basically the method consists of approaching the wave function as a product of two functions, one of them describing the motion in the field direction and the other the motion along a perpendicular axis. Notice that such a separability only occurs strictly in the limit of large field. Accordingly, it is relevant to describe the Zeeman effect in the Landau regime.
On account of the adiabatic approximation, the function describing the
temperature along the Z-direction may be obtained through a 1D Schrödinger
equation with an effective potential. The first term of such potential
($\lambda \rightleftharpoons \omega$) is a sort of 1D coulombic potential in each subspace of $m$. The
expression for effective Hamiltonian in $z$ is (Appendix I)

$$H(z) = \langle \psi_m(x,y) | H \psi_m(x,y) \rangle \approx \frac{1}{2} \lambda \left\{ -\frac{1}{2} \frac{d^2}{dz^2} - \lambda \right\}^{1/2} \frac{c_m}{|z| + q_m}$$

(31.7)

where $\psi_m(x,y)$ is a function belonging to the fundamental band of
Landau states, and $c_m, q_m$ are constants depending only on $m$. The problem
posed by Eq. (31.7) has received considerable attention in the
standard literature /17,58,60-68/ and it is known that the ground
state of $H(z)$ (i.e. $m = 0$) behaves as Eq. (31.5).

The adiabatic approximation has been used by several authors to
study many properties of the hydrogen atom in superstrong fields:
eigenvalues of the first levels /69-71/ and their dependence with the
nuclear mass /72,73/; eigenvalues, local values of wavefunctions,
oscillator strengths, sum rules, transition intensities and probabilities /71,74/.
Besides, it has been studied the effect on the results
of using one or more configurations built from the Landau spectrum
/71-75/.

The adiabatic approximation together with the expansion in Landau
orbitals gives excellent results for the high and intermediate field
regimes. The combination of these techniques plus the expansion in
appropriate hydrogen-like eigenfunctions to analyse the quadratic Zeeman
effect have led to the most accurate numerical results for the eigen-
values in the whole range of magnetic field intensities /74-77/.

All the methods mentioned before yield results of good accuracy,
but they are exclusively numerical. In other words, these methods do
not provide approximatst analytical expressions for eigenvalues and
other physical properties, except for some suitable fitting of the
numerical results /76/. However, even these pseudo-analytic expres-
sions do not describe properly the intermediate field regime /75,76/.

In the next sections we will see how the VFM allows one to obtain
a possible solution to the question of linking between the coulombic and Landau regimes. The necessary numerical comparisons will be made with the very accurate data presented by Wunner et al. /74-77/.

A final reference regarding non-perturbational approximations for the Zeeman effect of hydrogen-like atoms is the numerical resolution of the Schrödinger equation /39/ and the application of the finite-difference method /78/.

We briefly saw in §.30 that the semiclassical methods are of special relevance to report the properties of matter placed in very intense magnetic fields. Thus, the quasi-Landau resonances for Rydberg atoms (and other properties corresponding to highly excited levels) can be explained in a simple way by means of semiclassical methods in their several alternatives. Among these we can mention the Bohr atomic model and the Bohr-Sommerfeld quantization rules (Chapter II) /16,17/, the use of the Landau quantization condition /79/, the Bohr-Pauli-Landau model (Thomas-Fermi atomic model) /80/, 1D and 2D first order JWKB method /15,21-24,81,82/. Some of these approximation have recently been discussed in a comparative fashion /83/. The EBK quantization theory is more recent /27,28/ and has been applied to discuss classical orbits for the problem with Lorentz and coulombic forces acting on the same particle /84,85/. From a rigorous perspective, this last model should be used since the reference problem is not separable. Noteworthy, this semiclassical scheme has allowed the interpretation of some peculiarities in the experimental results for quasi-Landau resonances /25/ that cannot be explained via the JWKB method.

In the remaining part of this paragraph we summarily discuss the semiclassical Bohr model /6,16,17/. This simple model will be useful to illustrate some results of conceptual importance, regarding the Zeeman effect. Our treatment is different from the usual one, and corrects some mistakes that appear in the standard literature about the employment of the model.

Let us consider a hydrogen-like atom with nuclear charge Z whose electron moves on a plane surface. The classical Hamiltonian function is

\[ H = \frac{p^2}{2m} - \frac{Ze^2}{Dr}; \quad p = mv, \]

(31.8)
where \( m, e \) and \( \mathbf{v} \) are the electron mass, charge and velocity, respectively. \( D \) corresponds to the dielectric constant for the medium. We restrict the analysis to circular orbits, so that

\[
\frac{dr}{dt} = \dot{r} = 0 \tag{31.9}
\]

Upon introducing a magnetic field with intensity \( B \equiv |\mathbf{B}| \), the semiclassical method yields the orbit's radius and the electron velocity \( \mathbf{v} \) under Lorentz and Coulomb forces. The magnetic field \( \mathbf{B} \) is assumed perpendicular to the orbit plane.

From Eq. (31.9), we obtain for the kinetic energy

\[
T = \frac{1}{2} m r^2 \dot{\phi}^2 ; \quad \mathbf{v} = r \dot{\phi} \quad ; \quad \dot{\phi} = \frac{d\phi}{dt} \tag{31.10}
\]

where \( \phi \) is the polar angle in the motion plane. The force acting on the electron when \( B = 0 \) may be derived from Eqs. (31.3) and (31.9). In fact, if \( L \) is the Lagrangian function of the system, then

\[
||\mathbf{F}_1|| = \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{r}} \right) = \frac{\partial L}{\partial r} = mr \dot{\phi}^2 - \frac{Ze^2}{Dr} = \frac{m}{r} v^2 - \frac{Ze^2}{Dr} \tag{31.11}
\]

When \( B \neq 0 \), the Lorentz force \( \mathbf{F}_2 \) acting on the electron

\[
||\mathbf{F}_2|| = \frac{e}{c} ||\mathbf{B} \times \mathbf{v}|| \quad = \frac{eBv}{c} \tag{31.12}
\]

must be equal to \( ||\mathbf{F}_1|| \) in order to maintain a stable orbit, i.e.

\[
\frac{mv^2}{r} = \frac{Ze^2}{Dr} + \frac{eBv}{c} \tag{31.13}
\]

In order to get \( v \) and \( r \) as a function of \( \mathbf{B} \), we introduce the Bohr-
Sommerfeld quantization condition (Chapter II)

\[ \oint p d\lambda = nh \quad n >> 1 \quad (31.14) \]

where the integral extends over a complete orbit, and \( \bar{p} \) is the generalized impulse component within the orbit plane (Appendix H):

\[ m\bar{v} = \bar{p} + \frac{e}{c} \bar{A} \quad ; \quad \bar{A} = \frac{1}{2} \bar{B} x r \quad ; \quad \bar{B} = \text{curl} \bar{A} \quad . \quad (31.15) \]

The substitution (31.15) in (31.14) gives

\[ m \oint \bar{v}.d\lambda - \frac{e}{c} \oint \bar{A}.d\lambda = nh \quad , \quad (31.16a) \]

Since \( \bar{v} \) is a vector parallel to \( d\lambda \) with constant module \( v \), and noting that from the Stokes Theorem

\[ \oint \bar{A}.d\lambda = / \text{curl} \bar{A}.dS = \pi r^2 B \quad , \quad (31.16b) \]

thus Eq. (31.16a) furnishes the desired result:

\[ mvr - \frac{e}{2c} Br^2 = n\hbar \quad . \quad (31.17) \]

The elimination of \( v \) from Eqs. (31.13) and (31.17) gives an equation for \( r \):

\[ r \frac{Zm e^2}{\hbar^2} + \frac{e^2 B^2}{4c^2 \hbar^2} r^4 = n^2 \quad (31.19) \]

Defining the Bohr radius \( a_o \) and Landau radius \( R \) as
Eq. (31.18) is recast in its more usual expression as

\[ \frac{r}{a_0} + \frac{1}{4} \left( \frac{r}{R} \right)^4 = n^2 \]  \hspace{1cm} (31.20)

Eq. (31.20) yields the electron accessible radii; these radii define orbits whose structure are basically those corresponding to trajectories in classical minima (effective potential minimum). The radius \( r \) has the following asymptotic properties (cf. Eq. (31.20)):

\[ \lim_{B \to 0} r = n^2 a_0; \quad \lim_{Z \to 0} r = (2n)^{1/2} R. \]  \hspace{1cm} (31.21)

Replacing (31.17) and (31.18) into the classical Hamiltonian function (Eq. (31.8)), one gets the semiclassical eigenvalues \( E_n(Z,B) \):

\[ E_n(Z,B) = \frac{n}{2} \frac{\hbar}{mc} + \frac{e^2 B^2}{4mc^2} r^2 - \frac{Ze^2}{2D_x} \]  \hspace{1cm} (31.22)

This last equation enables one to analyse some interesting properties fulfilled by the exact eigenvalues associated with the quantum Hamiltonian. The introduction of a coordinate dilatation in (31.22) (see Appendix A) gives us:

\[ E_n(Z,B) = \frac{n}{2} \frac{\hbar}{mc} + \alpha^2 \frac{e^2 B^2}{4mc^2} x^2 - \alpha^{-1} \frac{Ze^2}{2D_x} \]  \hspace{1cm} (31.23)

the choice \( \alpha = B^{-1/2} \) leads to the following scaling relation:
\[ E_n(Z,B) = BE_n(Ze^{-1/2},1) \quad . \tag{31.24} \]

Eq. (31.24) is coincident with another one easily inferred from an equivalence relation of the quantum Hamiltonian /86/ (see Appendix H).

On the other hand, the choice \( \alpha = n^2 \) gives

\[ E_n(Z,B) = n^{-2}E_1(Z,B) \quad ; \quad b = n^3B \tag{31.25} \]

which is coincident with Eq. (30.6) (when \( n_r >> \lambda \)).

The asymptotic properties of \( E_n(Z,B) \) can be studied from (31.21). In the limit of small fields, it is immediate to find the hydrogen-like atom eigenenergies:

\[ \lim_{B \to 0} E_n(Z,B) = -\frac{1}{2n^2} \left( \frac{Z^2e^2m}{\hbar^2D^2} \right) \quad . \tag{31.26} \]

Moreover, when \( B \) is large enough, \( r \) can be expanded in power series of \( R \), and the first terms of this series are

\[ r^4 = 4n^2R^4 - 2^{1/2} \frac{4}{a_0} R^5 + O(R^6) \tag{31.27} \]

Upon inserting of (31.27) in Eq. (31.22), one gets:

\[ E_n(Z,B) - n\hbar \frac{eB}{mc} - \left( \frac{\hbar e^2Z^2}{2nmeD} \right)^{1/2} + O(\lambda) \quad . \tag{31.28} \]

The first term in the l.h.s. of (31.23) corresponds to the Landau spectrum (Appendix H), with \( w = eB/mc \) the 2D oscillator frequency. Furthermore, Eq. (31.28) assures the existence of a \( B^{-1/2} \) power series expansion in the semiclassical limit for large fields strengths. Ac-
According to the scaling relation (31.24), this last expansion implies that $E_n(Z,B)$ can be expanded as a $Z$ power series. For the exact eigenvalues such expansion is superimposed to the logarithmic terms commented before for the binding energy /63-65/.

Another topic worth discussing, regarding the Bohr semiclassical model, is the occurrence of equally spaced spectral lines when a hydrogen-like atom is placed in a magnetic field. Particularly important is the study of line spacings near the ionization threshold at zero field, i.e. when $E_n = 0$. This spacing may be compared with the Garton and Tomkins experimental result of about $3\hbar^2/2$. The Bohr model was applied previously /6,16/ to study such level spacing and there seems to exist some controversy on its applicability. In fact, as we show below, all previous treatments performed on this model /6,16/ are mistaken. We present here the correct treatment of this problem for the first time.

In order to study the spacing, let us consider a fixed $B$ value for the field strength and regard $n$ as a continuous variable. Accordingly, there is an $n$ value for which the eigenvalue is zero for every $B$ value. According to (31.25), $E_n$ depends on $n$ in an explicit manner through $E_1(Z,b)$. Then, the line spacings can be given in terms of

$$\frac{dE_n}{dn} = -\frac{2E_n}{n} + n^{-2} \left( \frac{dE_1}{dn} \right), \quad (31.29)$$

Now, from Eqs. (31.23) and (31.25),

$$E_1 = \frac{Me}{2mc} b + \frac{e^2}{4mc^2} b^2|x|^2 - \frac{Ze^2}{2D} \frac{1}{x} \quad (31.30)$$

with $x = r/n^2$ is given by Eq. (31.18), which in this case satisfies

$$\frac{Ze^2}{Dk^2} x + \frac{b^2e^2}{4c^2k^2} x^4 = 1 \quad , \quad (31.31)$$
As a consequence, the dependence of $E_1$ on $n$ is via $b$ and $x$:

$$\frac{dE_1}{dn} = \left( \frac{\partial E_1}{\partial b} \right)_x \frac{\partial b}{\partial n} + \left( \frac{\partial E_1}{\partial x} \right)_b \frac{\partial x}{\partial n}$$  \hspace{1cm} (31.32)

and in its turn, $x$ depends on $n$ through $b$ according to Eq. (31.31). Replacing in Eq. (31.29), we are led to

$$\frac{dE_n}{dn} = -\frac{2}{n} E_n + n^{-2} \left( \frac{\partial b}{\partial n} \left\{ \left( \frac{\partial E_1}{\partial x} \right)_b + \left( \frac{\partial E_1}{\partial x} \right)_b \frac{\partial x}{\partial b} \right\} \right),$$  \hspace{1cm} (31.33)

where, for $B$ fix, one has:

$$\frac{\partial b}{\partial n} = \frac{3}{n} b \hspace{1cm} (31.34)$$

From Eq. (31.30)

$$\left( \frac{\partial E_1}{\partial b} \right)_x = \frac{E_1}{b} + \frac{ze^2}{2Dbx} + \frac{e^2}{4mc^2} bx^2,$$  \hspace{1cm} (31.35)

moreover, Eqs. (31.30) and (31.31) give the result:

$$\left( \frac{\partial E_1}{\partial x} \right)_b \frac{\partial x}{\partial b} = -\frac{be^2}{4mc^2} x^2 \hspace{1cm} (31.36)$$

Finally, the substitution (31.34) - (31.36) into (31.33) gives the following formula for the line spacing

$$\frac{dE_n}{dn} = \frac{E_n}{n} + \frac{3zc^2}{2Dxn^3}$$  \hspace{1cm} (31.37)

Now, for a given $E_n$ value, the quantum number $n$, $b$ and $x$ remain fix. To compute $x$ and $n$ we proceed as follows. From (31.31)
and replacing in (31.30) one has an equation for \( x \) in terms of \( E_1 \)

\[
E_1 = \frac{\hbar^2}{m \kappa^2} \left( 1 + \left( 1 - \frac{Ze^2 m}{\kappa} \right)^{1/2} \right) - \frac{3}{2} \frac{Ze^2}{\kappa} \quad \text{for } 0 < x < a_0 .
\]

(31.39)

The rearrangement of Eq. (31.39) yields a cubic equation for \( x \):

\[
\frac{m^2 E_1^2}{\kappa^4} x^3 + \frac{3m^2 Ze^2 E_1}{\kappa^4} x^2 + \frac{9m^2 Ze^4}{2 \kappa^6} - \frac{2mE_1}{\kappa^2} x - \frac{2mZe^2}{\kappa^4} = 0 .
\]

(31.40)

Eq. (31.40) allows the calculation of \( x \), and Eq. (31.38b) gives \( n^3 \), completing the spacing computation (31.37). Eq. (31.39) provides an appropriate alternative expression for such level spacing:

\[
\frac{dE_n}{dn} = \frac{\hbar \omega}{2} + \frac{\hbar^2}{m} (n^3 x^2)^{-1} .
\]

(31.41)

In order to determine \( dE_n/dn \) at the ionization threshold for zero field, we must take \( E_1 = 0 \) in (31.40). The \( x \) value is found at once

\[
x_0 = \lim_{E_1 \to 0} x = \frac{8}{9} \frac{\kappa^2}{Ze^2 m} .
\]

(31.42)
and thereupon the n-value

\[ n_0^3 = \lim_{E_n \to 0} n^3 = \frac{27}{32} \frac{4\pi c}{\hbar} \left( \frac{2e^2}{D\hbar^2} \right)^2. \]  
(31.43)

The replacement of (31.42) and (31.43) into (31.41) gives the desired result:

\[ \lim_{E_n \to 0} \frac{dE_n}{dn} = 2\hbar \omega \]  
(31.44)

Eq. (31.44) is wholly rigorous and reveals that the Bohr model does not predict the experimental result \(3\hbar \omega/2\) (in contrast with the affirmation in refs. 6 and 16). Previous analysis \(6,16\) are incorrect because of the simplifications introduced. Then, the coincidence of such treatments with the experimental result for the lines spacing can be considered in any case merely fortuitous \(87\). Notwithstanding, the model predicts that \( (dE_n/dn) (E_n = 0) \neq \hbar \omega \) and besides the level spacing diminishes when the field intensity increases.

On the other hand, the relationship between \( n_0 \) and \( B \) is predicted in a nearly correct manner, and so Eq. (31.43) gives

\[ n_0 \approx 0.945 \lambda^{-1/3} \quad \lambda^{-1} = \frac{2e^2}{D\hbar^2} \]  
(31.45)

with \( \lambda \) the dimensionless field. The 1D J\textsuperscript{WKB} result is \(29\)

\[ n_0 \approx 1.16 \lambda^{-1/3} \]  
(31.46)

which makes up a reasonable agreement with (31.45). The Bohr model only gives the correct level spacing when

\[ E_1 = 2/3 \quad n_0 \lambda^{1/3} = 1.2114 \]  
(31.47)
but not for zero energy. Such a flaw in the model is not surprising at all when one takes into account its naivety in not having considered any energy contribution along the magnetic field direction.

In closing this section on nonperturbative approximation for eigenvalues of the Zeeman effect of hydrogen-like atoms, it is important to point out the significance of recent contributions on approximate symmetries of the eigenvalue spectrum /83/. Such findings have given rise to an intense theoretical search in relation with the possible existence of an approximate separability of the problem within the small field range /89-91/, although the Hamiltonian is not separable. Together with this separability, several authors have looked for integrals of motion and approximate adiabatic invariants for the Zeeman effect for hydrogen-like atoms /89-91/. Undoubtedly, these results throw a new perspective on the quantization semiclassical methods.

As a final comment, we deem appropriate to summarize some relevant previous work on this subject.

This will allow one to grasp properly the relevance of several later applications of the RSPT, taking the Zeeman effect of hydrogen-like atoms as illustrative examples.

In short, the outstanding facts are;

i) At present there exist a very good numerical description of all important physical properties for the Zeeman effect of hydrogen-like atoms, at small field regimes (Coulomb or Rydberg) or very high ones (Landau). The best results are provided by the Rayleigh-Ritz variational method, using basis sets of symmetry adapted functions.

ii) There are large difficulties to link both extreme regimes, and, consequently, it is troublesome to know the physical properties in the intermediate regime. This zone is the most important and presents the major interest in Solid State Physical Chemistry and Astrophysics.

iii) Some properties of the Zeeman effect of hydrogen-like atoms in the intermediate field region can be approximated by means of semiclassical methods. However, the improvements for such methods are very difficult to implement.

iv) There are no accurate analytic expressions for eigenvalues provided by the variational techniques. The published analytic formulas are not
accurate enough, and besides they do not describe the intermediate field range.

§.32. Application of perturbation methods

This paragraph is concerned with the application of RSPT to the Zeeman effect in hydrogen-like atoms. Although the progresses on this field are very recent, they have been remarkable. The PSPT has allowed obtaining excellent results for several properties.
puted for the ground state, with 27 significative figures.

Recently, Johnson et al. /102/ generalized the Bender and Wu method (§.9) to obtain the first RS coefficients for several hydrogen atom states in perpendicular electric and magnetic fields.

All these methods permit one to get a large number of RS coefficients, but they are so involved that their practical implementation beyond the ground state is rather difficult. Fernández and Castro /103/ have developed the perturbation theory without wave function for multi-dimensional systems, as an alternative method to obtain perturbation coefficients for several states (see §.9). These authors have computed the first and second-order coefficients for the 1S (ground state) and 2P_{\pm1} (first excite state) states, using the spectral notation corresponding at the zero-field limit. In the rest of this paragraph, these results will be extended for other states and superior perturbative orders. These results will be useful later on when dealing with the Zeeman effect in hydrogen-like atoms as an illustrative model. This procedure has been generalized to study the combined effect of crossed electric and magnetic fields /104/.

From the results derived in §.9 one obtains a recurrence relationship for the Zeeman effect, upon choosing in Eq. (9,17)

\[ S(\bar{r}) = r/n \]  

where \( n \) is the principal quantum number of the corresponding hydrogenic eigenvalue and selecting function \( f \) (Eq. (9,20)) as

\[ f = r^m \sin^n \theta \cos^t \phi \exp^{im \phi} ; \quad M, N = 0, 1, 2, \ldots; \quad m = 0, \pm 1, \pm 2, \ldots; \]

\[ t = 0, 1 \]  

Considering the Schrödinger equation (31.2) the potential terms can be expressed according with the convention introduced in §.9.

\[ V_o = -1/r \quad V_1 = \lambda^2 (x^2 + y^2) / 3 \]  

(32.3)
where, without any loss of generality, we have taken $Z = 1$. The substitution of Eqs. (32.2) and (32.3) in Eq. (9.21) gives the following recurrence relationship:

$$
\frac{M-n+1}{n} I_{M-1,n} = C_{M,N} I_{M-2,N} + \frac{1}{2} (N^2 - m^2) I_{M-2,N-2} + \\
+ \Delta E I_{M,N} - \frac{\lambda^2}{8} I_{M+2,N+2}
$$

(32.4)

with

$$
I_{M,N} = \langle \psi | r^M \sin^N \theta \cos^t \theta \ e^{i m \phi} | \phi \rangle
$$

(32.5a)

$$
\Delta E = E + 1/2 n^2
$$

(32.5b)

$$
C_{M,N} = \frac{1}{2} \{M(M+1) - (N+t)(N+t+1)\}
$$

(32.5c)

The application of the method for different states requires to assign the corresponding $n$, $m$ and $t$ values and to combine the recurrence relationship with the RSPT. In what follows, we present some illustrative examples.

**Example 1.** The most interesting states related to the various applications of the Zeeman effect in hydrogen-like atoms model are the tight-bound ones ($\S$.31), which are defined by the condition

$$
M = - l = -(n-1)
$$

(32.6)

These states are non-degenerate and their binding energies increase with the field strength $\lambda$ (see Appendix I).

The substitution of (32.6) into (32.4) yields a recurrence valid
for the tight-bound states:

\[
\frac{M-\ell}{1+\ell} I_{M-1,\ell+1} = C_{M,N} I_{M-2,N} + \frac{1}{2} (\ell^2 - \ell^2) I_{M-2,N-2} +
\]

\[
+ \Delta E I_{M,N} - \frac{\lambda^2}{8} I_{M+2,N+2}
\]

(32.7)

When \( M = N = \ell \), one has the starting condition to compute the eigenvalues:

\[
\Delta E = \frac{\lambda^2}{8} I_{\ell+2,\ell+2}
\]

(32.8)

together with the normalization condition for every state:

\[
I_{\ell,\ell} = 1
\]

(32.9)

Expanding \( \Delta E \) and the integrals \( I_{M,N} \) in power series of \( \lambda^2 \):

\[
\Delta E = \sum_{n=1}^{\infty} E^{(n)} \lambda^{2n}
\]

(32.10a)

\[
I_{M,N} = \sum_{n=0}^{\infty} I^{(n)}_{M,N} \lambda^{2n}
\]

(32.10b)

Eqs. (32.3) and (32.9) give us:

\[
E^{(n)} = \frac{1}{8} I^{(n-1)}_{\ell+2,\ell+2} \quad ; \quad n \geq 1
\]

(32.11a)

\[
I^{(n)}_{\ell,\ell} = \delta_{n0}
\]

(32.11b)
The computation scheme is completed when the coefficients $I_{n}^{(n)}$ are determined through the recurrence (32.7). For this purpose, Eqs. (32.10a), (32.10b) and (32.11a) are inserted in (32.7) to calculate the $\lambda^{2n}$-coefficient:

\[
\begin{align*}
M-1, N & \quad I_{n}^{(n)} \\
M-1, N & \quad I_{n}^{(n)} = C_{M,N} I_{M-2,N}^{(n)} + \frac{1}{2} \left( M^{2} - \lambda^{2} \right) I_{M-2,N-2}^{(n)} + \\
&+ \frac{1}{8} \sum_{s=0}^{n-1} I(s) M, N I_{M+2, N+2}^{(n-s)} - \frac{1}{8} I_{M+2, N+2}^{(n-1)}.
\end{align*}
\]

The precedent equation must be used in a recursive manner in order to obtain the coefficient $I_{n}^{(n)}$ (and through this the coefficient $E^{(n+1)}$). To conclude such calculation one must determine the coefficients $I_{i,j}^{(n-q)}$ fulfilling the conditions $0 \leq q \leq 0 \leq i < \lambda + q + (q + 3)$ and $0 \leq j < (\lambda + 2)(1+q)$.

The computation for the states $\lambda=0, 1, 2$ and 3 are shown in Table 9.1. These states are correlated with the $1s, 2p_{-1}, 3d_{-2}$ and $4f_{-3}$ hydrogen atom states. The computation was performed up to the perturbative order 20. The 20 coefficients for the $1s$ state agree with up to the last figure with the most accurate results published in the current literature /98/. One can guess a similar accuracy for the RS coefficients of the remaining states. Such coefficients will be used later on in connection with the construction of analytic expressions for eigenvalues from the information provided by the RSPT.

**Example 2.** In order to study non-tight-bounds, one must follow a similar method, although it becomes somewhat more involved. The first state considered correlates with the $2s$ hydrogen atom state. For the sake of brevity, we give just the recurrence relationship:

\[
\begin{align*}
I_{M-1,N}^{(n)} = & \frac{2}{M-1} \left( C_{M,N} I_{M-2,N}^{(n)} + \frac{N^{2}}{2} I_{M-2,N-2}^{(n)} - \frac{1}{8} \sum_{s=0}^{n-1} \left[ I_{3,2}^{(s)} - 21_{2,2}^{(s)} \right] \right) \\
I_{M,N}^{(n-1-s)} = & \frac{1}{3} I_{M+2,N+2}^{(n-1)}; \quad M = 2, 3, \ldots; N = 0, 2, 4, \ldots; n = 0, 1, \ldots
\end{align*}
\]

where
\[ E(n) = \frac{1}{3} \{ 2I_{2,2}(n-1) - I_{3,2}^{(n-1)} \} \]  \hspace{1cm} (32.14a)

\[ I_{0,0}^{(n)} = -\frac{1}{4} \delta_{n0} + \frac{1}{16} \sum_{s=0}^{n-1} \left[ I_{3,2}(s) - 2I_{2,2}(s) \right] I_{2,0}^{(n-1-s)} + I_{4,2}^{(n-1)} \]  \hspace{1cm} (32.14b)

\[ I_{1,0}^{(n)} = -\frac{3}{2} \delta_{n0} + \frac{1}{8} \sum_{s=0}^{n-1} \left[ I_{3,2}(s) - 2I_{2,2}(s) \right] I_{2,0}^{(n-1-s)} + I_{4,2}^{(n-1)} \]  \hspace{1cm} (32.14c)

Table 9.2 displays the results obtained for the first 20 RSPT coefficients computed via Eqs. (32.13) and (32.14a-c). A careful look at Tables 9.1 and 9.2 reveals that the RSPT gives rise an asymptotic divergent power series for the eigenvalues of the Zeeman effect for hydrogen-like atoms, and this divergence increases with \( \lambda \). This behavior has been studied by several authors \cite{96,105,106} by means of a generalization to many dimensions of the procedure presented in §1.11 for the harmonic oscillator. Up to now the asymptotic behavior for \( E(n) \) is known in closed form only for the ground state and is expressed by Eq. (11.90). The approximate result is

\[ |E(n)| \rightarrow \left( \frac{2n+1/2}{2!} \right) \]  \hspace{1cm} (32.15)

which is more strongly divergent than the behavior corresponding to the oscillators studied in §1.11 (compare with Eqs. (11.73) and (11.83)).

Naturally, the result (32.15) requires the employment of summation methods for divergent perturbative series, to get the eigenvalues \( E(\lambda) \).

A brief account of some relevant recent contributions on this subject follows. An elementary solution is the use of low-order Padé approximants for degenerate states \cite{107}, and higher order for the non-degenerate ground state \cite{93}. Results indicate that the method is not valid for \( \lambda > 1 \), and consequently one cannot get any information about the intermediate regime. Besides, there are theoretical reasons (see §1.13) to expect that the RS series for the Zeeman effect in hydrogen-
like atoms is not summable by the Padé method. Čižek and Vrscay /98/
have analysed an alternative technique which consists of the use of
Thiele extrapolants. Although results are quite reasonable for \( \lambda = 1 \),
the number of perturbational coefficients to be considered is extremely
large.

Another recent technique is the Euler method /108/ (see §.15) gen-
eralized by Silverman /109/, which gives sensible results for the
lowest eigenvalue for \( \lambda < 1 \), by using about 35 RS terms.

There have also been applied the Borel-Le Roy generalized method
/101,108,110,111/ (see §.14), and the quality of the results is quite
similar to that obtained via the Euler method just mentioned.

Other different procedure is to sum the divergent series by means
of a technique considering some known analytic property of the func-
tion \( E(\lambda) \). A specially important piece of information is the asymptotic
behavior of the energy for \( \lambda \gg 1 \) (Eq. (31.4) and Appendix H) /17,53,60-
68/. Galindo and Pascual made the first meaningful attempt in this
sense. They used \( |N+1/N| \) Padé approximants with a suitable coordinate,
chosen to reproduce the first term of Eq. (31.4) for the binding energy
/112/.

Recently, Cohen and Kais /113/ have applied the SVM (see §.21) to
continue analytically the perturbation expansion. The wave function
used by these authors allows one to take into account part of the
asymptotic behavior of the binding energy.

Patil /114/ has combined some dispersion relationships with some
RSPT orders to obtain approximate analytical formulas for the first
eigenvalues, and that also include the first asymptotic terms for the
binding energy. This analytical expressions give reasonable results
for the ground state and \( \lambda > 1 \), but the error increases rapidly for
higher states and field intensities.

Le Guillou and Zinn-Justin /101/ developed a very efficient method
to sum the RS series for the Zeeman effect in hydrogen-like atoms, by
introducing an order-dependent mapping (ODM) (§.18). Such ODM was ap-
plied to approximate binding energy as a function of the external
field. The procedure combines the RSPT up to 60-th order and the first
asymptotic terms of the binding energy (Appendix I).
The results derived for the ground state are remarkably accurate, and better than any other known result. However, the method based on this ODM does not constitute a general procedure to treat perturbational series, since the analytic information involved in building of the transformation makes the method exclusively valid for the Zeeman effect in hydrogen-like atoms. Moreover, it is not established in which systematic way one must choose the ODM to get the best approximation.

Arteca et al. /115-117/ have proposed a new point of view to treat the perturbation series using analytic properties of $E(\lambda)$, within the context of a general theory for the Zeeman effect in hydrogen-like atoms. The procedure is the so-called Variational Functional Method (VFM) (as well as some of its generalizations), that was presented in precedent chapters. A detailed discussion of the results is given in the next sections. The present treatment is not only a simple and accurate way to approach eigenvalues, but in addition it makes conceptually new contributions, regarding the analytic properties of the function under consideration.
NUMERICAL RESULTS

Table 9.1.

RS perturbation coefficients for the first strongly bound states of the Zeeman effect in Hydrogen atom (computed via the procedure described in §.32). a)

<table>
<thead>
<tr>
<th>n</th>
<th>$E^{(n)}(1s)$</th>
<th>$E^{(n)}(2p_1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.5</td>
<td>-1/8</td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>-0.2760416666666666</td>
<td>-116</td>
</tr>
<tr>
<td>3</td>
<td>0.121115451383887</td>
<td>16192</td>
</tr>
<tr>
<td>4</td>
<td>-0.9755405906396453</td>
<td>-57205264/15</td>
</tr>
<tr>
<td>5</td>
<td>0.1173630246122330</td>
<td>6242604544/5</td>
</tr>
<tr>
<td>6</td>
<td>-0.1959272760533517</td>
<td>-0.5246578495235231 (12)</td>
</tr>
<tr>
<td>7</td>
<td>0.4274361689521947</td>
<td>0.2719288070366074 (15)</td>
</tr>
<tr>
<td>8</td>
<td>-0.1136935282560349</td>
<td>-0.1699171093824181 (13)</td>
</tr>
<tr>
<td>9</td>
<td>0.409726018630245</td>
<td>0.1216305530753331 (21)</td>
</tr>
<tr>
<td>10</td>
<td>-0.1725156234947565</td>
<td>-0.110018392440783 (24)</td>
</tr>
<tr>
<td>11</td>
<td>0.8716665393270382</td>
<td>0.1117401621637270 (27)</td>
</tr>
<tr>
<td>12</td>
<td>-0.5210940934011392</td>
<td>-0.1310539020557425 (30)</td>
</tr>
<tr>
<td>13</td>
<td>0.3640532401232869</td>
<td>0.1761487030331318 (33)</td>
</tr>
<tr>
<td>14</td>
<td>-0.2940370939347646</td>
<td>-0.2693305161691009 (36)</td>
</tr>
<tr>
<td>15</td>
<td>0.2719572430769033</td>
<td>0.4652898043792428 (39)</td>
</tr>
<tr>
<td>16</td>
<td>-0.2056379426829352</td>
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</tr>
<tr>
<td>17</td>
<td>0.3301522613344236</td>
<td>0.1953914952529491 (46)</td>
</tr>
<tr>
<td>18</td>
<td>-0.4482314059482390</td>
<td>-0.4696543356732298 (49)</td>
</tr>
<tr>
<td>19</td>
<td>0.6612952596854647</td>
<td>0.1247151762591110 (53)</td>
</tr>
<tr>
<td>20</td>
<td>-0.1080080640806817</td>
<td>-0.3642185373074384 (56)</td>
</tr>
</tbody>
</table>

a) The power of ten that must be multiplied the coefficient is given between parenthesis.
Table 9.1. (Cont.)

RS perturbation coefficients for the first strongly bound states of the Zeeman effect in Hydrogen atom (computed via the procedure described in §.32).

<table>
<thead>
<tr>
<th>n</th>
<th>$E^{(n)}(3d_{-2})$</th>
<th>$E^{(n)}(4f_{-3})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-1/13</td>
<td>-1/32</td>
</tr>
<tr>
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a) The power of ten that must be multiplied the coefficient is given between parenthesis.
Table 9.2.

RS perturbation coefficients of the 2s state (first not tightly bound state of the Zeeman effect in Hydrogen atom) computed via the procedure outlined in §.32.\(^a\)

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<td>20</td>
<td>-0.6777732055534709 (56)</td>
</tr>
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</table>

\(^a\) The power of ten that must be multiplied the coefficient is given between parenthesis.
REFERENCES OF CHAPTER IX

/19/ S. Feneuille, Phys. Rev. A 26 (1932) 672.
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/53/ See Ref. /41/.
/92/ M. Bednár, Phys. Rev. A 15 (1977) 27. (see ref. /112/).