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53

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Large Order Perturbation Theory and Summation Methods in Quantum Mechanics

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La Plata, December 10, 1989

The authors

TABLE OF CONTENTS

LARGE ORDER PERTURBATION THEORY AND SUMMATION METHODS IN QUANTUM MECHANICS

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INTRODUCTION

The problems usually found in Theoretical Chemistry and Physical Chemistry involve the use of quantum mechanical models which, as a general rule, do not have exact solutions. Due to this very compelling reason a formidable effort has been devoted to develop approximate methods to solve the Schrödinger equation from the very birth of the Quantum Mechanics.

The main approximate procedures are three: a) the variational method, b) the perturbation theory (PT) and c) the semiclassical techniques. All of them are related to basic principles and have different optimum usefulness ranges.

The first two approximate procedures are general in the sense that they are not restricted to eigenvalue problems. On the other hand, the last two methods are basically self-contained because they allow one to approximate the system under consideration exclusively by means of specifications contained within its definition. Unlike these, the variational methods depend on the choice of a trial function which is not univocally determined when dealing with practical applications.

The general character of the PT and its closeness have made this method a favorite one since long time ago, although its application introduces two non-trivial problems. They are: i) to determine the perturbation coefficients up to a given order, and ii) to sum the perturbation series (PS) when it is divergent or slowly convergent.

The inefficient solution of these problems has been a severe drawback during a long while for an intensive use of PT. The calculation of a large number of coefficients for the Rayleigh-Schrödinger perturbation series (RSPT) is very difficult (if not impossible) for most problems in Chemistry and Physics. Besides, the appearance of divergent PS is the rule instead of the exception when dealing with quantum mecha nical models.

At the beginning of the 70's the state of affairs started to reverse due to several significant contributions regarding the nature and behavior of PS with zero convergence radii and the development of algebraic or recursive PT. Thus, we can say that nowadays PT has been "rediscovered" and the many problems that remain unsolved as well as the large number of potential applications of the method, have open new and unsuspected ways of research in this so exciting field of Mathematical Physics.

One must locate the main purpose of this work around this particular point. Our interest is the mathematical method embedded in the PT. Then, our point of view is concentrated on developing, optimizing and applying some aspects of the perturbative formalism as a recourse to make use of the significant information of a given system. In due course several models of physical chemistry interest will appear time and again along this book with the aim to illustrate and exemplify the central ideas developed around the method. These models and their intrinsic validity do not constitute an end on themselves. Even the compulsory resolution of the equations which arise from the models is not central in our approach to the problem. These equations can be solved via different possible methods, but our main interest and compromise is devoted to PT since sometimes this method is the only way to study some physical problems. However, in order to understand clearly the principles guiding the organization of this book it is necessary an additional comment.

Of late, there has been a remarkable interest in the development, through the application of approximate methods, of analytical expressions for different physical properties of quantum systems. Such nonnumerical formulas are more accurate the greater the analytical available information one can introduce in a systematic manner. Owing to this reason the joint study of approximate methods and their relationships with the essential analytical properties of the systems under

consideration has received a keen attention and considerable impulse. Among others, we can mention the dependence of energy, average values, etc. with mass of particles, external field intensities and other usual parameters.

In this work we will show various examples, combining semiclassical, variational and perturbative methods in a sole formalism.

Summing up, our work points out two main purposes:
i) To develop simple enough procedures to which one can incorporate the available analytical information coming from PT, the semiclassical methods and fundamental principles; and
ii) As soon as the main analytical properties are set up, to study which are the PS of physical chemistry interest that can be summed by means of such procedures.

The two main parts of this book are in correspondence with the viewpoints of analysing the above mentioned purposes.

The content of this book intends to be self-contained and due to it several standard and well-known results are found from time to time (but especially in Part A). However, we have deemed appropriate to present them here in an explicit way and particularly adapted to our specific needs, in order to offer a logic unity among several very different topics. We hope the reader will be benefited by this organizational aspect, since so specialized themes of current research are not discussed together in the current bibliography. Obviously, this is particularly suited for pedagogical purposes.

With regard to the applications of the formal results it is necessary to remark that though the physical models play an illustrative and exemplary role, we have chosen those ones which are under intensive study nowadays in the Mathematical Physics field. Among others, we can mention anharmonic oscillators, one-dimensional field theories, atoms within magnetic and electric fields, non-relativistic models for elementary particles, diatomic molecule vibrations, etc.

By no means our analysis can be considered exhaustive and complete with respect to these models, because their number and variety is very large, and furthermore this is not our purpose. But we present a summary perspective of all of them in such a way that we show which are

the phenomena that demand their introduction and which is the state of art of their knowledge.

Finally, let us introduce the structure of this book.

In Part A we discuss the semiclassical approximation for one-dimensional quantum systems and the building of the PS up to high orders. The semiclassical method is applied later on to study the asymptotic behavior of the PT coefficients for simple enough quantum systems. The discussion of the fundamentals of the modern PT is complemented by means of the analysis of different methods to sum up divergent series. Then, starting from first principles, we develop several methods of semiclassical nature, which allow us to employ in a systematic way the information provided by PT and some asymptotic series. These methods make it possible to deduce analytical expressions for eigenvalues and relevant average values for some simple quantum systems whose wave functions satisfy finite and infinite boundary conditions (BC).

Part B is entirely devoted to the systematic discussion of the summation of PS using high orders of the PT, by means of certain generalizations of the results presented in Part A. The sketched method allows one to renormalize the PS, that is to say, to enlarge its usefulness or to sum it up exactly, and attaining at the same time, the fulfilment of some basic analytical relationships related to the function under study. After making a deep and detailed study of the analytical and numerical properties of the method, it is applied to a large number of models of current interest in physical chemistry for which there is some associated power series expansion.

PART A

"Spectra are very touchy objects; they
are bound to react irrationally under
the slightest provocation"

K.O. Friedrichs, 1966

CHAPTER I

GENERAL PROPERTIES OF THE EIGENVALUE SPECTRUM

1. Some Fundamental Properties

In order to approximate the solutions of the stationary Schrödinger equation it is convenient to take into account from the very beginning some basic properties of the exact solutions. Although we consider unnecessary to discuss in a very general fashion the properties of the eigenvalue spectra, we believe it appropriate to make a presentation of certain mathematical properties which will be useful later on.

We are especially concerned with some rigorous results related to degeneracy, number of zeros, uncertainty relations, etc. satisfied by the eigen-functions of the Schrödinger equation.

Notwithstanding these relationships can be found in the current literature /1-3/, we present them here in a unified manner.

Let us consider the following eigenvalue differential equation, representing a stationary one-dimensional (1D) Schrödinger equation in appropriate units:

$$-\frac{1}{2}\psi_n''(x) + V(x)\psi_n(x) = E_n\psi_n(x) \qquad (1.1)$$

where n is the number of zeros of the wave function. For the sake of simplicity we will restrict our analysis to some general properties of the Schrödinger equation with Dirichlet boundary conditions (DBC), although they can be extended to other BC.

Theorem 1.1

Eq. (1.1) defined within the function space fulfilling the BC

$$\psi_n(a) = \psi_n(b) = 0 \quad ; \quad a,b \in R \quad ; \quad n = 0,1,2,... \tag{1.2}$$

has not degenerate solutions.

Proof:

We proceed by reductio ad absurdum. Let us assume that there exist at least two linearly independent functions ψ_i,ψ_j which have the same eigenvalue E. From (1.1) we get

$$-\frac{1}{2}\psi_i''\psi_j = (E - V(x))\psi_i\psi_j \tag{1.3a}$$

$$-\frac{1}{2}\psi_j''\psi_i = (E - V(x))\psi_i\psi_j \tag{1.3b}$$

and substracting (1.3b)-(1.3a) we have

$$\psi_i''\psi_j - \psi_i\psi_j'' = \frac{d}{dx}(\psi_i'\psi_j - \psi_i\psi_j') = 0 \quad . \tag{1.4}$$

Then, the wronskian is a constant $\forall x$

$$\psi_i'(x)\psi_j(x) - \psi_i(x)\psi_j'(x) = \text{constant} \quad . \tag{1.5}$$

Since the DBC are satisfied, the constant in (1.5) is null, as can be verified by choosing x=a or x=b.

Then,

$$\det \begin{vmatrix} \psi_i & \psi_j \\ \psi_i' & \psi_j' \end{vmatrix} = 0 \tag{1.6}$$

i.e., the functions ψ_i,ψ_j (and their derivatives) must be linearly dependent. This conclusion contradicts the original assumption, so that the theorem is proved.

Theorem 1.2

Let $\psi(x)$ be a solution of Eq. (1.1) with DBC. Then, if V(x) is an even function in the coordinate x, $\psi(x)$ has

a definite parity.

Proof:

From the hypothesis for $V(x)$, the change of x by -x in Eq. (1.1) gives

$$-\frac{1}{2}\psi''(-x) + V(x)\psi(-x) = E\psi(-x) \tag{1.7}$$

so that $\psi(x)$ and $\psi(-x)$ are eigenfunctions of the same Hamiltonian operator with identical eigenvalue. But from Theorem 1.1 both functions must be linearly dependent, i.e.

$$\psi(x) = k\psi(-x) \quad ; \quad k = \text{constant} \tag{1.8}$$

On reversing the sign once more in Eq. (1.8) we have

$$\psi(-x) = k\psi(x) = k^2\psi(-x) \quad , \quad \text{so that} \quad k^2 = 1.$$

Finally we deduce that $\psi(x)$ has definite parity:

$$\psi(x) = \pm\psi(-x) \tag{1.9}$$

Theorem 1.3 If $V(x) > E \quad \forall\, x \in (a,x_I)U(x_D,b)$, then $\psi(x)$ subjected to the conditions of Theorem 1.1 has not zeros within the interval $(a,x_I)U(x_D,b)$, usually called "forbidden classical region"

Proof:

Eq. (1.1) can be rewritten as

$$\psi''(x) = 2(V(x) - E)\psi(x) \tag{1.10}$$

where we have omitted the quantum number subscript. After multiplying Eq. (1.10) by $\psi(x)$ and integrating the resulting equation from a to $x < x_I$, we find

$$\int_a^x \psi(x')\psi''(x')dx' = \psi(x')\psi'(x')\Big|_a^x - \int_a^x \psi'(x')^2 dx' =$$

$$= 2\int_a^x (V(x') - E)\psi(x')^2 dx' \quad . \tag{1.11}$$

From the DBC we obtain

$$\psi(x)\psi'(x) = 2\int_a^x (V(x') - E)\psi(x')^2 dx' + \int_a^x \psi'(x')^2 dx' \qquad (1.12)$$

and by hypothesis both integrals in the r.h.s. of (1.12) are greater than zero, so that

$$\psi(x)\psi'(x) > 0 \quad . \qquad (1.13)$$

Since $\psi(x)$ has no singularities, $\psi'(x)$ remains finite and $\psi(x) \neq 0$. In the same way one can prove that $\psi(x) \neq 0$ if $x_0 < x < b$.

Theorem 1.4 Every eigenvalue E of Eq. (1.1) is larger than the minimum value of V(x) (say V_m)

Proof:

Because of the DBC Eq. (1.12) for x=b leads to

$$E = \frac{1}{2}\int_a^b \psi'(x)^2 dx + \int_a^b V(x)\psi(x)^2 dx \qquad (1.14)$$

where we have considered the normalization condition

$$\int_a^b \psi^*(x)\psi(x)dx \equiv ||\psi||^2 = 1 \quad . \qquad (1.15)$$

The application of the mean value theorem to the second integral in Eq. (1.14) gives the result

$$E > \int_a^b V(x)\psi(x)^2 dx > V_m \int_a^b \psi(x)^2 dx = V_m \quad . \qquad (1.16)$$

Theorem 1.5 If $E_i > E_j$ are two eigenvalues corresponding to Eq.(1.1), then $\psi_i(x)$ has at least one zero between two consecutive zeros of $\psi_j(x)$.

Proof:

The argument is similar to that used in Theorem 1.1. In fact, from Eq. (1.1) we obtain

$$\frac{d}{dx}(\psi_i'\psi_j - \psi_i\psi_j') = 2(E_j - E_i)\psi_i\psi_j \quad . \qquad (1.17)$$

If $x_{j1} < x_{j2}$ are two consecutive zeros of $\psi_j(x)$, we can integrate (1.17) within the interval (x_{j1}, x_{j2})

$$\psi_i(x_{j1})\psi_j'(x_{j1}) - \psi_i(x_{j2})\psi_j'(x_{j2}) = 2(E_j-E_i)\int_{x_{j1}}^{x_{j2}} \psi_i\psi_j dx \quad . \tag{1.18}$$

Let us now proceed via reductio ad absurdum, and suppose $\psi_i(x)$ has no zeros within the interval (x_{j1},x_{j2}). We can choose $\psi_j(x) > 0$ and $\psi_i(x) > 0 \quad \forall x \in (x_{j1},x_{j2})$ without loss of generality, then

$$\psi_j'(x_{j1}) > 0 \quad \text{and} \quad \psi_j'(x_{j2}) < 0 \tag{1.19}$$

and from Eq. (1.18) we have

$$(E_j-E_i)\int_{x_{j1}}^{x_{j2}} \psi_i(x)\psi_j(x)dx > 0 \quad . \tag{1.20}$$

Taking into consideration that $(E_j-E_i) < 0$, Eq. (1.20) assures us that the integral is negative in contradiction with the hypothesis. Therefore, $\psi_i(x)$ has at least one zero in (x_{j1},x_{j2}). This last theorem is embodied in a more general result known as the Oscillation Theorem, which establishes the relation between the number of eigenfunction nodes and the eigenvalue order.

It deserves to be pointed out that as a natural corollary of Theorem 1.5, the ground state has no nodes, farther than those imposed by the BC. This result is entirely valid for the precise conditions chosen in the formulation of the theorems. We deem that this last remark is necessary because there are multidimensional or/and many body particles Hamiltonians which do not necessarily satisfy the previous condition for the ground state /4-6/, and this fact is sometimes overlooked.

We complement this paragraph analysing some properties related to average values of operators defined over a Hilbert space $\overline{H}$.

Lemma 1.1 Let ψ and ϕ be two functions of the Hilbert space $\overline{H}$. Then the following inequality is satisfied (Schwartz inequality)

$$||\psi||^2||\phi||^2 \geq |\langle\psi|\phi\rangle|^2 \tag{1.21}$$

where $||...||$ and $\langle...|...\rangle$ denote the norm and scalar product respectively in $\overline{H}$.

Proof:

Let

$$\xi = \phi + k\psi \tag{1.22}$$

and choose k so that

$$\langle\xi|\psi\rangle = \langle\phi|\psi\rangle + k||\psi||^2 = 0 \tag{1.23}$$

therefore

$$\xi = \phi - \frac{\langle\phi|\psi\rangle}{||\psi||^2} \tag{1.24}$$

since

$$\langle\xi|\xi\rangle = ||\phi||^2 - \frac{|\langle\phi|\psi\rangle|^2}{||\psi||^2} \geq 0 \tag{1.25}$$

then, Eq. (1.21) follows at once.

Theorem 1.6 (Heisenberg inequality)
Let us consider $\psi\varepsilon\bar{H}$ and two Hermitean operators A,B (i.e. $A=A^+$, $B=B^+$) defined on $\bar{H}$. Then

$$\Delta A\Delta B \geq \frac{1}{2}|\langle|A,B|\rangle| \tag{1.26}$$

where $\Delta A(\Delta B)$ is the quadratic (or standard) deviation of A(B):

$$\Delta A = \langle(A-\langle A\rangle)^2\rangle^{\frac{1}{2}} \quad ; \quad \langle A\rangle \equiv \langle\psi|A\psi\rangle \tag{1.27}$$

Proof:

$$A' = A - \langle A\rangle \tag{1.28a}$$

$$B' = B - \langle B\rangle \tag{1.28b}$$

are easily proved to be Hermitean; i.e.

$$A'^+ = A' \quad ; \quad B'^+ = B' \quad . \tag{1.29}$$

A straightforward computation yields

$$||A'\psi||^2 = \langle A'\psi|A'\psi\rangle = \langle\psi A'^+A'|\psi\rangle = \langle\psi|A'^2\psi\rangle = \Delta A^2 \quad . \tag{1.30}$$

Since $[A,B] = [A',B']$, then

$$\langle\psi|[A,B]|\psi\rangle = \langle\psi|[A',B']|\psi\rangle = \langle A'\psi|B'\psi\rangle - \langle B'\psi|A'\psi\rangle$$

$$= \langle A'\psi|B'\psi\rangle - \langle A'\psi|B'\psi\rangle^* = 2\,i\,\mathrm{Im}\langle A'\psi|B'\psi\rangle \quad . \tag{1.31}$$

From the self-evident inequality

$$|\langle A'\psi|B'\psi\rangle| \geq |\mathrm{Im}\langle A'\psi|B'\psi\rangle| \tag{1.32}$$

and Eq. (1.31) the desired result follows:

$$|\langle[A,B]\rangle| \geq 2|\langle A'\psi|B'\psi\rangle| \quad . \tag{1.33}$$

Lemma 1.1 and Eq. (1.30) (and its analog for ΔB) complete the proof.

According to the proof given above the Heisenberg inequality holds provided that $B\psi$ belongs to the domain of A. This fact is usually overlooked in many text books which leads to absurd results. An example is the planar rigid rotator when A and B are the angular momentum and coordinate, respectively.

Theorem 1.6 allows us to derive a well-known formula which will be useful in forthcoming chapters.

Let H be a Hamiltonian for an N-dimensional system:

$$H(\bar{p},\bar{x}) = \frac{1}{2}\sum_{n=1}^{N} p_n^2 + V(\bar{x}) \tag{1.34a}$$

$$\bar{x} = (x_1, x_2, \ldots, x_N) \tag{1.34b}$$

$$\bar{p} = (p_1, p_2, \ldots, p_n) \tag{1.34c}$$

$$p_n = -i\frac{\partial}{\partial x_n} \tag{1.34d}$$

where without loss of generality $\hbar$ and the masses have been chosen to be equal to unity.

The particular choices

$$A = p_n \qquad \text{and} \qquad B = x_n \tag{1.35}$$

gives

$$[A,B] = -i \tag{1.36}$$

so that

$$\Delta p_n \Delta x_n \geq \frac{1}{2} \tag{1.37}$$

for every coordinate.

2. The Hellmann-Feynman Theorem

Usually the Hamiltonian depends on some parameter, such as masses, charges, coupling parameters, external field intensities, etc. The presence of these parameters raises naturally the inquiry about the dependence of the energy on them, so that it is important to determine the derivative of E with respect to such parameters. Furthermore, this derivative has a paramount theoretical relevance because of its relation to the knowledge of significant analytical properties of the energy function. (See also the discussion in Appendix A).

A well-known relationship involving the derivatives of the energy with respect to those parameters within the Hamiltonian is the Hellmann-Feynman theorem (HFT) /7,8/, which is the main theme in this paragraph. An excellent review on different applications of HFT can be found in Ref. /9/, although for the sake of our purposes it is appropriate here to make a short introduction of some basic equations.

Let $H(\lambda)$ be the Hamiltonian of the system under consideration, which depends on the parameter λ. This parameter appears in the H eigenfunctions and eigenvalues via the Schrödinger equation:

$$H(\lambda)\psi_n(\lambda) = E_n(\lambda)\psi_n(\lambda) \quad , \quad n=0,1,... \tag{2.1}$$

If it is assumed that

$$\langle \psi_n | \psi_m \rangle = \delta_{nm} \tag{2.2}$$

then

$$\langle \frac{\partial \psi_n}{\partial \lambda} | \psi_n \rangle + \langle \psi_n | \frac{\partial \psi_n}{\partial \lambda} \rangle = 0 \tag{2.3}$$

Defining the operator A by the relationship

$$\frac{\partial \psi_n}{\partial \lambda} = A\psi_n \quad \varepsilon \quad \bar{H} \tag{2.4}$$

Eq. (2.3) enables us to deduce that such operator is Anti-Hermitean, i.e.

$$A^+ = -A \quad . \tag{2.5}$$

This operator is very useful to deduce some general results in a very compact way. In fact, the derivation of Eq. (2.1) with respect to λ gives

$$\frac{\partial H}{\partial \lambda} \psi_n + HA\psi_n = \frac{\partial E_n}{\partial \lambda} \psi_n + E_n A\psi_n = \frac{\partial E_n}{\partial \lambda} \psi_n + AH\psi_n \tag{2.6}$$

which can be rewritten

$$H_1 \psi_n = \frac{\partial E_n}{\partial \lambda} \psi_n \tag{2.7a}$$

where

$$H_1 = \frac{\partial H}{\partial \lambda} + [H,A] \quad . \tag{2.7b}$$

Eq. (2.7a) has the appearance of an eigenvalue equation where $\partial E_n/\partial \lambda$ is an eigenvalue of the Hamiltonian H_1. Formula (2.7) is very adequate for an immediate generalization to get higher-order derivatives of E with respect to λ. For the second order we have

$$H_2 \psi_n = \frac{\partial^2 E_n}{\partial \lambda^2} \psi_n \tag{2.8a}$$

$$H_2 = \frac{\partial H_1}{\partial \lambda} + [H_1,A] = \frac{\partial^2 H}{\partial \lambda^2} + \frac{\partial}{\partial \lambda} [H,A] + [\frac{\partial H}{\partial \lambda},A] + [[H,A],A] \quad . \tag{2.8b}$$

The application of the functional $\langle \psi_m |$ to (2.7a) gives

$$\langle\psi_m|H_1\psi_n\rangle = \langle\psi_m|\frac{\partial H}{\partial\lambda}\psi_n\rangle + (E_m-E_n)\langle\psi_m|A\psi_n\rangle = \delta_{nm}\frac{\partial E_n}{\partial\lambda} \qquad (2.9)$$

which embodies the HFT as a particular case when n=m:

$$\langle\psi_n|\frac{\partial H}{\partial\lambda}|\psi_n\rangle \equiv \langle\frac{\partial H}{\partial\lambda}\rangle_n = \frac{\partial E_n}{\partial\lambda} \quad . \qquad (2.10)$$

3. Hypervirial Relations and General Boundary Conditions

There is a special class of mathematical relationships satisfied by the exact solutions of the Schrödinger equation which are known as Hypervirial Theorems /10/. These theorems are especially useful from the practical as well as from the theoretical point of view and they are particularly well suited to simplify the treatment and presentation of several aspects of our subject-matter. For this reason they deserve a brief but self-consistent display here.

In order to simplify the treatment, we will consider two different classes of hypervirial relations.

Definition. Let $\{\psi_n\}$ and $\{E_n\}$ be the sets of eigenfunctions and eigenvalues respectively of H, and let W be a linear operator whose range is contained within the domain of H. We call hypervirial relationships or theorems (HR) to those formulas relating the matrix elements of [H,W] and W. This last operator is termed the hypervirial operator (HO).

In order to deduce HR we consider the Schrödinger equation

$$H\psi_n = E\psi_n \qquad (3.1)$$

and a linear operator W such that $W\psi_n$ belongs to the domain of H, i.e.

$$W\psi_n \quad \varepsilon \quad D_H \quad . \qquad (3.2)$$

The computation of the matrix element of [H,W] gives the result

$$\langle\psi_n|[H,W]|\psi_m\rangle = \langle\psi_n|HW\psi_m\rangle - \langle\psi_n|WH\psi_n\rangle = (E_n-E_m)\langle\psi_n|W\psi_m\rangle \qquad (3.3)$$

which is the so-called HR.

Here, we restrict ourselves to a particular case of HR, and we consider the Hamiltonian

$$H = T + V(x) = -\frac{1}{2} D^2 + V(x) \quad ; \quad D = \frac{d}{dx} \tag{3.4}$$

where we have omitted all the physical constants without any loss of generality. The choice

$$W(x) = f(x)D \tag{3.5}$$

where $f(x)$ is a differentiable function of x, gives the result

$$[H,fD] = -\frac{1}{2}[D^2,f]D + f[V,D] = \frac{1}{2}[f,D]D +$$

$$+ \frac{1}{2} D[f,D] - fV' \quad ; \quad V' \equiv \frac{dV}{dx} \tag{3.6}$$

and

$$[H,fD] = -\frac{1}{2} f''D - f'D^2 - fV' \quad ; \; f' \equiv \frac{df}{dx} \; ; \; f'' \equiv \frac{d^2f}{dx^2} \; . \tag{3.7}$$

Now we want to write the commutator $[H,fD]$ exclusively in terms of H, V, f and their derivatives, so that we must get rid of D and D^2 in (3.7). This can be accomplished in the following way: first we compute the commutator

$$[H,f'] = -\frac{1}{2} [D^2,f'] = -\frac{1}{2} f''' - f''D \tag{3.8}$$

and so we get the first term in the r.h.s. of (3.7):

$$-\frac{1}{2} f''D = \frac{1}{4} f''' + \frac{1}{2} [H,f'] \; . \tag{3.9}$$

Besides, from (3.4) we know that

$$D^2 = 2(V-H). \tag{3.10}$$

Therefore, the substitution of (3.9) and (3.10) in (3.7) allows us to obtain

$$[H,fD] = \frac{1}{4} f''' + \frac{1}{2} [H,f'] - 2f'(V-H) - fV' \; . \tag{3.11}$$

Finally, we have to express fD in terms of H,f and related functions.

A straightforward computation gives

$$[H,F] = -\frac{1}{2}F'' - F'D \tag{3.12a}$$

which, upon choosing F'=f, leads to

$$fD = -\frac{1}{2}f' - [H,F] \ . \tag{3.12b}$$

The introduction of (3.11) and (3.12b) in (3.3) yields the result

$$\langle\psi_n|[H,fD]\psi_m\rangle = -\frac{1}{2}(E_n-E_m)\langle\psi_n|f'\psi_m\rangle + (E_n-E_m)\langle\psi_n|[H,F]\psi_m\rangle =$$

$$= \frac{1}{4}\langle\psi_n|f'''\psi_m\rangle + \frac{1}{2}\langle\psi_n|[H,f']\psi_m\rangle - \langle\psi_n|fV'\psi_m\rangle -$$

$$- 2\langle\psi_n|f'V\psi_m\rangle + 2E_m\langle\psi_n|f'\psi_m\rangle \ . \tag{3.13}$$

The particular choices $W_1=F$ and $W_2=f'$ in (3.3) gives

$$\langle\psi_n|[H,F]\psi_m\rangle = (E_n - E_m)\langle\psi_n|F\psi_m\rangle \tag{3.14a}$$

$$\langle\psi_n|[H,f']\psi_m\rangle = (E_n-E_m)\langle\psi_n|f'\psi_m\rangle \tag{3.14b}$$

and the insertion (3.14) in (3.13), after some simple rearrangements, yields

$$\frac{1}{4}\langle\psi_n|f'''\psi_m\rangle + (E_n+E_m)\langle\psi_n|f'\psi_m\rangle - 2\langle\psi_n|f'V\psi_m\rangle -$$

$$- \langle\psi_n|fV'\psi_m\rangle + (E_n-E_m)^2\langle\psi_n|F\psi_m\rangle = 0 \ . \tag{3.15}$$

This last equation is very useful for our purposes because it enables one to derive relations among matrix elements of properly chosen operators and the energy eigenvalues.

Relationships (3.15) under the condition (3.2) have been extensively used for a wide variety of 1D and separable ND systems. Some interesting examples are the anharmonic oscillators /11/ for which one chooses $f_N(x)=x^N$; central field potentials, such as radial Stark effect (linear confining potential) /12/; screened Coulomb potentials /13/, where the choice $f_N(r)=r^N$ ($r=|\vec{r}|$) is suitable, and spectroscopic rovibrational models /14-16/. The application of relations like (3.15) has allowed

the determination of matrix elements for powers of internuclear shifts /14-16/. Perturbed Morse oscillators have been studied via the set of functions $f_N(x) = (1 - e^{-x})^N$ /17/.

Periodic systems have also been treated in this way by choosing /18,19/ $f_N(\theta) = \exp(ik_N\theta)$ and $f_{NM}(\theta) = \cos^N\theta\sin^M\theta$.

An interesting enough example of separable N-dimensional model is the Stark effect in hydrogen /20,21/, which can be analysed with the help of parabolic coordinates. Recently, HR have been applied to study some separable problems in an approximate way, and in such case it deserves particular reference the combination of HR with the self-consistent field (SCF) approximation in order to uncouple two degrees of freedom /22,23/.

This short review does not intend to be complete but to present the reader an overview of the performance and ductility capabilities of HR to study different models of special interest in Physics and Chemistry. An exhaustive and complementary presentation of the subject can be found in Refs. /24,25/.

Up to this moment we have made the discussion starting from the condition (3.2). Now, our aim is to show how the HR can be generalized for those systems that fulfil some general BC.

If the system is confined to a volume V surrounded by a surface s we have (according to the Gauss theorem)

$$\int_V\{\psi_m\Delta w\psi_n - (\Delta\psi_m)(w\psi_n)\}dv = \int_s\{\psi_m\nabla(w\psi_n) - (\nabla\psi_m)(w\psi_n)\}\bar{n}\,ds \qquad (3.16)$$

The surface integral in the r.h.s. of (3.16) is not zero in general but in those cases where both ψ and $\nabla\psi$ vanishes on s. When the BC are finite it is necessary to add a surface contribution to the HR discussed above.

Since the HR with FBC have recently been discussed /26-29/, we will briefly summarize the final expressions for some 1D systems.

Let us consider the 1D problem defined via the Hamiltonian (3.4), such that

$$a \leq x \leq b \tag{3.17}$$

and the eigenfunctions $\psi_n(x)$ fulfilling the general BC

$$\psi(a) - A\psi'(a) = 0 \tag{3.18a}$$

$$\psi(b) - B\psi'(b) = 0 \tag{3.18b}$$

with A, B two real numbers.

BC (3.18) include, as particular cases, both DBC

$$\psi(a) = \psi(b) = 0 \quad ; \quad A \to 0 \quad ; \quad B \to 0 \tag{3.19}$$

and von Newmann boundary conditions (VNBC)

$$\psi'(a) = \psi'(b) = 0 \quad ; \; 1/A \to 0 \quad ; \quad 1/B \to 0 \tag{3.20}$$

As stated before, the most useful HR are those involving the commutators [H,f(x)] and [H,f(x)D]. In the first case the use of (3.16) enables us to obtain for 1D systems

$$\langle\psi_n|[H,f(x)]\psi_m\rangle = \frac{1}{2}\{\psi_n' f(x)\psi_m|_a^b - \psi_n(f(x)\psi_m)'|_a^b\} \tag{3.21}$$

which, in the diagonal situation reduces to

$$\langle\psi_n|[H,f(x)]\psi_n\rangle = -\frac{1}{2} f'(x)\psi_n(x)^2|_a^b \tag{3.22}$$

Equation (3.22) can be written in a more compact way from the following formulas /26,27/

$$\psi_n'(b)^2 = 2(2B^2(V(b) - E_n)-1)^{-1} \frac{\partial E_n}{\partial b} \tag{3.23a}$$

$$\psi_n'(a)^2 = 2(1-2A^2(V(a) - E_n))^{-1} \frac{\partial E_n}{\partial a} \tag{3.23b}$$

which are valid for the general BC (3.18) provided $||\psi_n|| = 1$.

It follows from (3.18), (3.22) and (3.23) that

$$\langle\psi_n|[H,f]\psi_n\rangle = A^2 f'(a)(1-2A^2(V(a)-E_n))^{-1}\partial E_n/\partial a -$$

$$- B^2 f'(b)(2B^2(V(b)-E_n)-1)^{-1}\partial E_n/\partial b \qquad (3.24)$$

When the HO is fD we get from (3.16) the HR /26,27/

$$\langle\psi_n|[H,fD]\psi_n\rangle = \frac{1}{2}\{\psi_n' f\psi_m' - \psi_n(f\psi_m')'\}\Big|_a^b \qquad (3.25)$$

and the diagonal case

$$\langle\psi_n|[H,fD]\psi_n\rangle = \frac{1}{2}\{f\psi_n'^2 - f\psi_n\psi_n'' - f'\psi_n\psi_n'\}\Big|_a^b \qquad (3.26)$$

On using (3.23) and the Schrödinger equation to express ψ_n'' as a function of $V(x)$ and E_n, we have /26,27/

$$\langle\psi_n|[H,fD]\psi_m\rangle = -\{f(b) + Bf'(b)(2B^2(V(b)-E_n)^{-1})^{-1}\}\frac{\partial E_n}{\partial b} -$$

$$- \{f(a) + Af'(a)(2A^2(V(a)-E_n)^{-1})^{-1}\}\frac{\partial E_n}{\partial a} \qquad (3.27)$$

The virial theorem (VT) with DBC and VNBC has a particular value for us. Its diagonal form has an identical expression for both BC:

$$\langle\psi_n|[H,xD]\psi_n\rangle = 2\langle\psi_n|T\psi_n\rangle - \langle\psi_n|xV'\psi_n\rangle =$$

$$= -b\frac{\partial E_n}{\partial b} - a\frac{\partial E_n}{\partial a} \qquad (3.28)$$

It is especially interesting to know some average values of operators for some simple 1D systems subjected to DBC /26-32/.

Such properties can be studied from Eq. (3.27) setting A=B=0 and considering the result (3.15) for the l.h.s. of (3.27). So we get the following diagonal HR:

$$\frac{1}{4}\langle\psi_n|f'''\psi_n\rangle + 2E_n\langle\psi_n|f'\psi_n\rangle - 2\langle\psi_n|f'V\psi_n\rangle -$$

$$- \langle\psi_n|fV'\psi_n\rangle = -f(b)\frac{\partial E_n}{\partial b} - f(a)\frac{\partial E_n}{\partial a} \qquad (3.29)$$

Eq. (3.29) is general enough for our purposes. For the VT, i.e. $f(x)=x$, Eq. (3.29) allows us to obtain the diagonal expression of (3.15) when

$$\lim_{l\to\infty} \; l \frac{\partial E_n}{\partial l} = 0 \quad ; \quad l = b-a \tag{3.30}$$

Although we will restrict ourselves to the employment of HR with DBC and VNBC, it has been demonstrated that HR with general BC (Eq. (3.18)) are extremely useful to study some 1D systems /32/. All the formulas deduced in this paragraph, as well as those previously shown, represent exact relationships satisfied by the true solutions of the Schrödinger equation. They are very useful and will be applied in the next chapters in connection with the methods to solve in approximate fashion the stationary Schrödinger equation.

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CHAPTER II

THE SEMICLASSICAL APPROXIMATION AND THE JWKB METHOD

4. Adiabatic Invariants

It is well-known that the Schrödinger equation cannot be solved in a closed manner but for a few simple problems. Then one must resort to approximate methods to obtain eigenfunctions, eigenvalues and expectation values of observables. The semiclassical methods make up a very valuable tool to get such information and their origin can be traced back to the birth of Quantum Mechanics. A renew interest has arisen during the last 20 years and today they have a remarkable relevance and currentness.

Here we will discuss some new aspects related to the Mathematical Physics methods which are useful to study some simple (but non-trivial) models. Two central approximate methods will be used: the semiclassical procedure and the PT. The first one is presented in this chapter.

The central purpose of this paragraph is to find an answer to the questions: How can one relate the Quantum Mechanics with the Classical Mechanics through a semiclassical approximation?

In order to go forward, let us introduce some elements belonging to the realm of Classical Mechanics.

Definition I

Let $\lambda(t)$ be a parameter describing the interation of the system with a variable external field. If $\Delta\lambda$ is the change in λ in a time interval Δt, the adiabatic regime is defined by the condition $\Delta\lambda/\lambda << \Delta t/\tau$, where τ is the period of the motion. In the limit $\Delta t \to 0$ we have

$$\tau \frac{d\lambda}{dt} << \lambda \tag{4.1}$$

Definition II

Let E be the energy of the system under an adiabatic regime. Then, when the system evolves the energy

$$E = E(\lambda) \tag{4.2}$$

does not remain constant due to the time dependence of λ. We call adiabatic invariant the relation between E and λ which holds constant, although E itself changes. In other words, an adiabatic invariant is any object that remains constant while the mechanical system evolves in an adiabatic trajectory. Within the adiabatic regime the energy changes with the time and its average value is

$$\overline{\frac{dE}{dt}} = \overline{\frac{dH}{dt}} = \frac{1}{\tau}\int_o^\tau \left(\frac{dE}{dt}\right)dt \tag{4.3}$$

where H is the Hamilton's function. If we consider /1/

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} \tag{4.4}$$

the average value (4.3) can be written in terms of the change of λ with t

$$\overline{\frac{dE}{dt}} = \overline{\frac{\partial H}{\partial \lambda}\frac{\partial \lambda}{\partial t}} \cong \frac{\partial \lambda}{\partial t}\overline{\frac{\partial H}{\partial \lambda}} \tag{4.5}$$

where we have considered a very small change of $\partial\lambda/\partial t$ with t in the adiabatic regime.

Our aim is to deduce a particularly useful adiabatic invariant from Eq. (4.5). To this end, it is convenient to rewrite the average value $\overline{\partial H/\partial\lambda}$ in terms of the coordinates and momenta.

For the sake of simplicity let us assume that the whole system can be described by only one generalized coordinate q and its conjugated momentum p. The Hamilton's canonical equations state that

$$dq = \frac{\partial H}{\partial p}\,dt \tag{4.6}$$

so that the average value of a mechanical variable H(t) can be written as

$$\bar{A} = \frac{1}{\tau}\int_o^\tau A(t)dt = \frac{1}{\tau}\oint \frac{A(q)}{\left(\frac{\partial H}{\partial p}\right)}\,dq = \oint A(q)\left(\frac{\partial H}{\partial p}\right)^{-1}dq/$$

$$/\{\oint \left(\frac{\partial H}{\partial p}\right)^{-1}dq\} \tag{4.7}$$

In Eq. (4.7) we have changed the time integral over the period τ into

a spatial integral over the closed forward-backward movement between the two classical turning points for a trajectory E = constant with a given λ-value.

Inserting (4.7) into (4.5) we have

$$\overline{\frac{dE}{dt}} = \frac{d\lambda}{dt} \oint \left(\frac{\partial H}{\partial \lambda}\right) \left(\frac{\partial H}{\partial p}\right)^{-1} dq \Big/ \oint \left(\frac{\partial H}{\partial p}\right)^{-1} dq \tag{4.8}$$

A further simplification in the numerator of (4.8) can be obtained by assuming that alongside an adiabatic trajectory, i.e. for a nearly constant λ-value, we have

$$H(q,p(\lambda)) = E \tag{4.9}$$

where $H(q,p(\lambda))$ is a function of p and q that depends parametrically on λ. Then, Eq. (4.9) assures us that $q = q(p,E(\lambda))$ so that there are only two independent variables in H. On the basis of this assumption and taking into account that E and λ remain nearly constant during an adiabatic trajectory, it follows that

$$\frac{dH}{d\lambda} = \frac{\partial H}{\partial p} \frac{\partial p}{\partial \lambda} + \frac{\partial H}{\partial \lambda} = 0 \tag{4.10}$$

that is to say

$$\left(\frac{\partial H}{\partial \lambda}\right) \left(\frac{\partial H}{\partial p}\right)^{-1} = -\left(\frac{\partial p}{\partial \lambda}\right) \tag{4.11}$$

Eqs. (4.8) and (4.11) allow us to prove the following theorem, which is the first main purpose of this paragraph.

Theorem 4.1

The integral $I = \oint p(q)dq$ is an adiabatic invariant.

Proof:

The substitution (4.11) in (4.8) gives

$$\overline{\frac{dE}{dt}} = -\frac{d\lambda}{dt} \oint \left(\frac{\partial p}{\partial \lambda}\right) dq \Big/ \oint \left(\frac{\partial H}{\partial p}\right)^{-1} dq \tag{4.12}$$

which enables us to obtain

$$\oint \left\{\frac{\partial p}{\partial E} \overline{\frac{dE}{dt}} + \frac{\partial p}{\partial \lambda} \frac{\partial \lambda}{\partial t}\right\} dq = 0 \tag{4.13}$$

where it has been taken into account that $(\partial H/\partial p)^{-1} = \partial p/\partial E$. Since p can be written in terms of only E and λ, Eq. (4.13) yields

$$\overline{\frac{d}{dt} \oint p(q,E(\lambda))dq} = \overline{\frac{dI}{dt}} = 0 \quad ; \quad I = \oint p(q,E(\lambda))dq \tag{4.14}$$

so that I remains constant during the period of motion, and consequently it is an adiabatic invariant.

Now the period of motion can be expressed in terms of E and I

$$\frac{\partial I}{\partial E} = \oint (\frac{\partial p}{\partial E})dq = \oint (\frac{\partial H}{\partial p})^{-1}dq = \int_o^\tau dt = \tau \quad ,$$

or, in other way,

$$\frac{\partial E}{\partial I} = \frac{1}{\tau} \tag{4.15}$$

This formulae will be useful later on. In particular the adiabatic invariant (4.14), known as phase area, is relevant to the semiclassical approximation. The adiabatic invariant I is a particular case of the so-called "action variables". It is possible to find a new set of variables related to q and p via the generating function $S_o(q,I)$ as follows:

$$p = \frac{\partial}{\partial q} S_o(q,I) \quad ; \quad w = \frac{\partial}{\partial I} S_o(q,I) \tag{4.16}$$

S_o is the so-called reduced action (i.e. the classical action in a conservative system) which depends on q and E, but we have chosen a dependence on q and I by way of (4.15) in order to relate E with I. The angular variable w and I are the so-called canonical variables /1/.

From the first equation in (4.16) we have

$$\Delta S_o = \oint pdq = I \tag{4.17}$$

where ΔS_o is the increase of the reduced action in each period.

Now we have the necessary tools to state the connection between classical and quantum theories. Such a relationship can be introduced in an axiomatic manner known as Ehrenfest's Adiabatic Hypothesis or Born's Mechanical Transformation /2/:

i) The Classical Mechanics laws can be applied to a quantum system

whenever it undergoes an adiabatic regime.

ii) A quantum system can be described in classical terms upon quantizing its adiabatic invariants (action variables) and describing its (semiclassical) trajectories with them.

However, there remains an open problem which is how to quantize an adiabatic invariant. This point is briefly discussed in the next paragraph.

5. Bohr-Sommerfeld Quantization Condition and JWKB Method

The so-called semiclassical approximation for separable systems was set up on a rigorous basis by Jeffreys, Wentzel, Kramers and Brillouin /3-7/. This formalism improves the first approach due to Bohr, Sommerfeld and Wilson /8/, and at the same time gives a solid foundation within the Quantum Mechanics context. Jeffreys, Wentzel, Kramers and Brillouin introduced the semiclassical method from different viewpoints. Here we will follow the argument proposed by Wentzel /4/ in order to obtain the quantization rule because it is simple and elegant. The demonstration by Wentzel was critized by Kramers /5/ and later on by Dunham /9/. However, more recently Fröman and Fröman /10/ have justified such a proof and gave rigorous and well-defined reasons for it. The present discussion partially incorporates Fröman and Fröman's ideas.

It is worth mentioning that the following procedure is not appropriate to describe all the applications of the semiclassical method. For this reason the discussion of the JWKB method will be completed in the next paragraph. Besides, Refs. /11/ and /12/ are adequate supplementary reviews.

Let us consider the 1D stationary Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi = 0 \qquad (5.1)$$

where $\psi(x)$ satisfies trivial BC

$$\lim_{x\to\pm\infty} x^N \psi(x) = 0 \quad ; \quad N>0 \qquad (5.2)$$

Let $V(x)$ be a simple potential well, so that $V > E$ if $x \in (-\infty, x_1) \cup (x_2, \infty)$, with x_1 and x_2 the classical turning points that obey

$$V(x_1) = V(x_2) = E.$$

Now, we change Eq. (5.1) into a new one, which is more appropriate for our present purposes, by means of the definition

$$\psi(x) = A \exp(i\phi(x)) = \exp(i\hbar^{-1} \int \chi(x) dx) \tag{5.3}$$

where $\chi(x)$ is a function to be determined. No approximation has been invoked to write $\psi(x)$ as in Eq. (5.3) (If, for instance, $\psi(x)$ is assumed to be a classical wave front /13/, then we obtain an approximate solution).

Since

$$\frac{d\psi}{dx} = \frac{i}{\hbar} \chi(x) \psi \tag{5.4}$$

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\hbar^2} \psi \chi^2(x) + \frac{i}{\hbar} \psi \frac{d\chi}{dx} \tag{5.5}$$

then Eq. (5.1) becomes

$$-\hbar^{-2} \chi^2 \psi + \frac{i}{\hbar} \psi \frac{d\chi}{dx} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \tag{5.6}$$

At those points where $\psi \neq 0$ (that is to say, excluding the zeros that ψ can have between the classical turning points, in accordance with Theorem 1.3), Eq. (5.6) can be written as a Ricatti equation

$$i\hbar \frac{d\chi}{dx} + (2m(E-V) - \chi^2) = 0 \tag{5.7}$$

The semiclassical approximation consists in the so-called eikonal expansion

$$\chi(x) = \sum_{n=0}^{\infty} \chi_n(x) \left(\frac{\hbar}{i}\right)^n \tag{5.8}$$

which is clearly a series in powers of $\hbar$. The expansion (5.8) enables one to think of classical Mechanics as the limit $\hbar \to 0$ of Quantum Mechanics. In other words, the series (5.8) can be viewed as a Taylor expansion around the classical limit.

The classical limit for $\chi(x)$ is obtained from Eq. (5.7) when $\hbar = 0$:

$$\chi_o(x) = (2m(E-V))^{\frac{1}{2}} = p(x) \tag{5.9}$$

where $p(x)$ is the classical momentum. The unnormalized semiclassical wavefunction ψ_{sc} /12,13/ then reads

$$\psi_{sc} = \exp(i\hbar^{-1}\int p(x)dx) \; ; \; x \neq x_o \text{ and } V(x_o) = E \tag{5.10}$$

Eqs. (5.7) and (5.8) lead to

$$i\hbar \sum_{n=0}^{\infty} (\hbar/i)^n \frac{d\chi_n}{dx} = 2m(V-E) + \sum_{j=0}^{\infty}\sum_{s=0}^{\infty} \chi_j\chi_s(\hbar/i)^{s+j} \tag{5.11}$$

from which the remaining functions χ_n can be obtained as:

$$-\frac{d}{dx}\chi_{j-1} = \sum_{s=0}^{j} \chi_s\chi_{j-s} \quad ; \quad j \geq 1 \tag{5.12}$$

The case j=0 is given by Eq. (5.9). In order to determine the coefficient of $\hbar^N$ it is necessary to solve recursively N first-order differential equations. This makes up the JWKB approximation of order N and the complexity of the problem increases markedly with N. Here we will restrict ourselves to the first-order case (N=1), which arises when j=1 in Eq. (5.12)

$$\chi_1 = -\frac{1}{2}\frac{\chi_o'}{\chi_o} \quad ; \; \chi_o' = \frac{d}{dx}\chi_o \tag{5.13}$$

Now we study the quantization condition for the first order approximation. For that purpose it is necessary to use an auxiliar relation derived from the residues theorem for analytical functions. If $f(z)$ is analytical in the region within the closed curve c except for n simple poles, then

$$\oint_c f(z)dz = 2\pi i \sum_{s=1} R_s \tag{5.14}$$

where R_s is the residue of the s-th pole.

The application of the result above to the function

$$f(z) = \frac{\psi_n'(z)}{\psi_n(z)} \tag{5.15}$$

gives

$$\oint_c \frac{\psi_n'(z)}{\psi_n(z)}\,dz = 2n\pi i \tag{5.16}$$

which is exact provided c encloses the n zeroes of ψ_n. We can consider $\psi_n(z)$ as an analytical extension into the complex plane of the n-th eigenfunction of (5.1) which has n real zeros.

The deformation of c so that the two classical turning points are included and the consideration of (5.4) enable us to obtain the result

$$\oint_c \frac{\psi_n'}{\psi_n}\,dz = i\hbar^{-1}\oint_c \chi(z)dz = i\hbar^{-1}\oint_c\{\chi_o + \frac{\hbar}{i}\chi_1 + \ldots\}dz = 2n\pi i \tag{5.17}$$

According to Eqs. (5.9) and (5.13) the contour integral of χ_1 is

$$\oint_c \chi_1(z)dz = -\frac{1}{4}\oint_c \frac{v'(z)}{v(z)}\,dz \quad ; \; v(z) = V(z) - E \tag{5.18}$$

The function $v'(z)/v(z)$ has two poles located in the classical turning points with residue 1. Since c encloses them we find

$$\oint_c \chi_1 dz = -\pi i \tag{5.19}$$

and Eq. (5.17) can be rewritten

$$\frac{i}{\hbar}\oint_c \chi_o dz - \pi i + \ldots = 2n\pi i \tag{5.20}$$

In order to deduce the first-order JWKB quantization rule two considerations are in order:

i) The eikonal series is truncated up to the first two terms in (5.17).

ii) The integral over the closed curve is transformed into an integral on the real interval between the turning points for a complete period of motion, which according to Theorem 1.3 contains all the zeros of $\psi_n(x)$.

Then, the use of (5.9) and (5.20) gives

$$\oint p(x)dx = (n + \frac{1}{2})h \tag{5.21}$$

which is the so-called first-order JWKB quantization condition. Eq. (5.21) enables us to compute the energy as a solution of the equation

$$\int_{x_2}^{x_1} (E_n - V(x))^{\frac{1}{2}} dx = \frac{h}{2} (2m)^{-\frac{1}{2}} (n + \frac{1}{2}) \quad ; \quad n \geq 0 \tag{5.22}$$

as an implicit function of n. Eq. (5.22) is expected to yield acceptable results when n>>1. Besides, it is clear from the argument above that the quantum number n labelling the states (Theorem 1.1), is the number of zeros of the wave function excluding those imposed by the boundary conditions.

Eq. (5.22) can be solved in an exact way just for a few potentials. Most frequently E_n is written as a series in powers of n, which can be iteratively obtained from Eq. (5.22).

Up to now just a few simple quantum mechanical models have been studied via the high-order JWKB theory and it is useful to verify the accuracy of the semiclassical energy eigenvalues. One of the most widely studied models is the quartic anharmonic oscillator

$$V(x) = x^2 + \lambda x^4 \tag{5.23}$$

for which Eq. (5.22) has been solved either in exact numerical or approximate analytical way.

The potential (5.23) has also been studied through a modified version of the JWKB method /14,15/ due to Miller and Good /16/, which is equivalent to the third-order JWKB method /17/, and by means of the fifth, sixth and even higher order approximation /18-20/. In this regard, the task has been formidable, but now we are certain that, in spite of its semiclassical nature, the JWKB method allows one to approach eigenvalues exactly.

The remainder of this section is devoted to presenting some results related to the first-order approximation (Eq. 5.21). The notation in Section 4 for the adiabatic invariants and the application of Eq. (5.21) gives us the way of quantizing the action variable

$$I = (n + \frac{1}{2})h \tag{5.24}$$

which contains the Bohr-Sommerfeld (or Wilson-Sommerfeld) quantization condition as a special case when n>>1:

$$I \cong nh \tag{5.25}$$

The combination of Eqs. (5.25) and (4.15) for the period τ of the motion supplies the relationship

$$\frac{\partial E_n}{\partial I} = \frac{\partial E_n}{\partial n}\frac{\partial n}{\partial I} = \frac{1}{\tau}$$

so that

$$\frac{\partial E_n}{\partial n} \cong \frac{h}{\tau} \tag{5.26}$$

Eq. (5.26) is the mathematical expression of the well-known Bohr correspondence principle which approximately states the change of the energy with the quantum number. This formula has a paramount relevance since it sets up an important analytical property for eigenvalues.

Let us consider the harmonic oscillator as a simple example. Since the classical energy function is

$$E = \frac{p^2}{2m} + \frac{k}{2} q^2$$

and the period τ

$$\tau = \frac{2\pi}{w} = 2\pi (k/m)^{-\frac{1}{2}}$$

then, Eq. (5.26) yields

$$E_n = n\hbar w + \text{constant.}$$

The exact computation of (5.21) provides the correct result (constant $= \hbar w/2$). In this case the integral can be solved in a closed way.

The form of the semiclassical wave function and its practical application is an open matter yet. This point is analysed in the next Section.

Let us bring to an end this section making some complementary comments about the semiclassical approximation. First of all, it is necessary to consider that the JWKB approximation is strictly valid within the set

of conditions given here, i.e. for 1D systems separable N-dimensional systems with trivial BC.

For other BC the semiclassical methods have to be modified accordingly. For example, in radial systems the centrifugal term must be changed by means of the Langer approximation /12/ to obtain a minimum in the effective potential function for the ground state. For finite boundary conditions the JWKB quantization condition is modified in such a way to introduce the boundary effect /21/.

The affair is much more troublesome for non-separable problems. These systems cannot be described in a semiclassical way as easily as the separable ones since their discrete spectrum (bound states) has regular as well as irregular regions, depending on the stability of the classic orbits. Basically, these systems must be studied from the quantization of every action variable by way of the rule due to Einstein /22/, Brillouin /23/ and Keller /24/ and improved by Maslov /12/:

$$I_k = (n_k + \frac{\alpha_k}{4})h \tag{5.27}$$

with n_k the k-th quantum number and α_k a positive integer number or zero (Maslov index) determined by the potential shape and the BC. In this case, I_k is given by

$$I_k = \oint_{c_k} p_k(q_k)dq_k \tag{5.28}$$

where c_k is a curve located on an invariant toroid /25/ which generally does not coincide with the classical trajectory. For further details, an excellent treatment of this subject can be found in Ref. /25/.

6. Applications of the JWKB Method

The construction of the semiclassical wave function poses a fundamental problem: the matching of asymptotic functions similar to those considered in Eq. (5.10) through the turning points. The discussion of this point is the subject matter of this section.

Let us consider the Schrödinger equation

$$\psi'' + q^2\psi = 0 \quad ; \quad q^2 = E-V \tag{6.1}$$

where for the sake of simplicity we have eliminated the numerical constants.

If x_o is a turning point for an arbitrary potential V as in Fig. 2.1 the general solution of Eq. (6.1) for x close to x_o can be written in terms of the Bessel functions $J_{\pm 1/3}$ as follows /26-28/

$$\psi(x) = [\frac{w(x)}{q(x)}]^{\frac{1}{2}}\{A_o J_{1/3}(w(x)) + B_o J_{-1/3}(w(x))\} \tag{6.2}$$

where

$$w(x) = \int_{x_o}^{x} q(x')dx' \tag{6.3}$$

and A_o, B_o are constants. The subscript in these constants denotes that ψ describes the neighborhood of x_o.

In order to obtain the asymptotic form of (6.2) for $x_o << x << x_1$ (obviously the approximation is valid when $x_o << x_1$) we consider that /26-28/

$$w^{\frac{1}{2}}J_{\pm 1/3}(w) \rightarrow (2/\pi)^{\frac{1}{2}}\cos(w - \frac{\pi}{4} \mp \frac{\pi}{6}) \tag{6.4}$$

which enables us to write the wave function as

$$\psi(x) \rightarrow (2/\pi q)^{\frac{1}{2}}\{A_o\cos(w - \frac{\pi}{4} - \frac{\pi}{6}) + B_o\cos(w - \frac{\pi}{4} + \frac{\pi}{6})\} \; ; \; q^2 > 0 \tag{6.5}$$

For the other asymptotic region ($x < x_o$; $q^2 < 0$) it is necessary to change the argument within the function (6.2) as follows:

$$q = i|q| = e^{i\pi/2}|q| \tag{6.6}$$

$$w = -i|w| = e^{3\pi i/2}|w| \tag{6.7}$$

Then, the asymptotic form of the Bessel functions become

$$w^{\frac{1}{2}}J_{\pm 1/3}(w) = (e^{3i\pi/2}|w|)^{\frac{1}{2}}J_{\pm 1/3}(e^{3i\pi/2}|w|) \rightarrow$$

$$\rightarrow (2\pi)^{-\frac{1}{2}}\{\mp e^{|w|} + e^{-|w|}\; e^{\pm\pi i/6}\} \tag{6.8}$$

and the wave function for $x<<x_o$ reduces to

$$\psi(x) \to (2\pi q)^{-\frac{1}{2}}\{(B_o-A_o)e^{|w|} + (A_o e^{i\pi/6} + B_o e^{-i\pi/6})e^{-|w|}\} \qquad (6.9)$$

The procedure can be repeated for the other turning point x_1 (see Fig. 2.1), and now the general solution is

$$\psi(x) = (\frac{w'}{q})^{\frac{1}{2}}\{A_1 J_{1/3}(w') + B_1 J_{-1/3}(w')\} \; ; \; w' = \int_x^{x_1} q(x')dx' \qquad (6.10)$$

It follows from Eq. (6.10) that the asymptotic form of the wavefunction on both sides of the turning point x_1 is:

$$\psi(x) \to (\frac{2}{\pi q})^{\frac{1}{2}}\{A_1\cos(w' - \frac{\pi}{4} - \frac{\pi}{6}) + B_1\cos(w' - \frac{\pi}{4} + \frac{\pi}{6})\} \; ; \; x<<x_1 \qquad (6.11)$$

$$\psi(x) \to (2\pi q)^{-\frac{1}{2}}\{(B_1-A_1)e^{|w'|} + (A_1 e^{i\pi/6} + B_1 e^{-i\pi/6})e^{-|w'|} \; ; \; x>>x_1 \qquad (6.12)$$

Eq. (6.12) describes the region III in Fig. 2.1.

Now our aim is to build the wave function for the bound state with energy E, as denoted in Fig. 2.1. Clearly, the wave function corresponding to the region I is given by (6.9).

Inasmuch as the state is bounded, we know that $E < \lim_{x\to\pm\infty} V(x)$, so that $\lim_{x\to\pm\infty} |w| = \infty$. This last condition implies that if the function (6.9) is to be finite for any x, then $A_o = B_o$, i.e.

$$\psi_I(x) = 2A_o(2\pi q)^{-\frac{1}{2}}(\cos\pi/6)e^{-|w|} = A_o(\frac{3}{2\pi q})^{\frac{1}{2}}e^{-|w|} \qquad (6.13)$$

It follows from (6.5) and the condition $A_o = B_o$ that the function in region II must be:

$$\psi_{II}(x) \to A_o(\frac{2}{\pi q})^{\frac{1}{2}}\{\cos(w - \frac{\pi}{4} - \frac{\pi}{6}) + \cos(w - \frac{\pi}{4} + \frac{\pi}{6})\} =$$

$$= (\frac{6}{\pi q})^{\frac{1}{2}}A_o\cos(w - \frac{\pi}{4}) \qquad (6.14)$$

The analysis of the turning point x_1 allows us to obtain the function $\psi_{III}(x)$ for $x>>x_1$. The employment of Eq. (6.12) with the condition $A_1 = B_1$ yields the solution

$$\psi_{III}(x) \to (\frac{3}{2\pi q})^{\frac{1}{2}} A_1 e^{-|w'|} \tag{6.15}$$

which is finite for every x.

In a similar way, Eq. (6.11) gives the function corresponding to zone II

$$\psi_{II}(x) \to (\frac{6}{\pi q})^{\frac{1}{2}} A_1 \cos(w' - \frac{\pi}{4}) \tag{6.16}$$

The functions $\psi_{II}(x)$ given by Eqs. (6.14) and (6.16) must be matched since they describe the motion in the same region. Therefore,

$$A_o \cos(w - \frac{\pi}{4}) = A_1 \cos(w' - \frac{\pi}{4}) \tag{6.17}$$

From the trigonometric identity

$$\cos\phi = (-1)^n \cos(n\pi - \phi) \tag{6.18}$$

it follows that

$$A_o = (-1)^n A_1 \quad ; \quad n\pi = (w - \frac{\pi}{4}) + (w' - \frac{\pi}{4}) = w + w' - \frac{\pi}{2} \tag{6.19}$$

in order to satisfy (6.17).

From the definitions of w and w', Eq. (6.19) yields a quantization condition

$$w + w' = \int_{x_o}^{x_1} q(x)dx = (n + \frac{1}{2})\pi \tag{6.20}$$

which is coincident with the first-order JWKB condition (Eq. (5.21)) after an appropriate change of variables.

The point of view followed here is quite different to that presented in Section 5. The present formulation does not allow one to obtain easily the high-order terms in the semiclassical approximation, but it does permit to deduce those properties requiring the use of the semiclassical wave function. The rest of this paragraph is devoted to study them.

We apply here the previous procedure to discuss the so-called tunneling effect, as sketched in Fig. 2.2.

The outgoing wave can be represented by the solution (6.5) for the turning point x_1 since in this case E > V:

$$\psi_{III}(x) \to (\frac{2}{\pi q})^{\frac{1}{2}}\{A_1\cos(w - \frac{\pi}{4} - \frac{\pi}{6}) + B_1\cos(w - \frac{\pi}{4} + \frac{\pi}{6})\},$$

$$w = \int_{x_1}^{x} q(x')dx' \tag{6.21}$$

The constants A_1, B_1 must be chosen in such a way that we have just one outgoing wave in the zone III (see Fig. 2.2), i.e.

$$B_1 = -A_1 e^{i\pi/3} \tag{6.22}$$

The insertion of this result into Eq. (6.21) plus the application of the Euler identity for the cosine function, yields

$$\psi_{III}(x) \to -i(\frac{3}{2\pi q})^{\frac{1}{2}}A_1 e^{i\pi/6}e^{i(w-\pi/4)} \tag{6.23}$$

which is the representation of the outgoing wave.

In zone II of Fig. 2.2, E < V and so we can employ Eq. (6.9) from the turning point x_1:

$$\psi_{II}(x) \to (2\pi q)^{-\frac{1}{2}}\{(B_1-A_1)e^{|w|} + (A_1 e^{i\pi/6} + B_1 e^{-i\pi/6})e^{|w|}\} \tag{6.24}$$

The substitution (6.22) in (6.24) leads us to

$$\psi_{II}(x) \to -A_1(2\pi q)^{-\frac{1}{2}}e^{|w|}(e^{i\pi/3} + 1) = -(\frac{3}{2\pi q})^{\frac{1}{2}}A_1 e^{i\pi/6}e^{|w|} \tag{6.25}$$

Upon considering that

$$|w| = \left|\int_{x_1}^{x} q dz\right| = \int_{x}^{x_1} |q|dx \quad ; \quad x_o \leq x \leq x_1 \tag{6.26}$$

and defining the auxiliar coefficient τ

$$|w| = \tau - |w'| \quad ; \quad \tau = \int_{x_o}^{x_1} |q|dz \quad ; \quad |w'| = \int_{x_o}^{x} |q|dx' \tag{6.27}$$

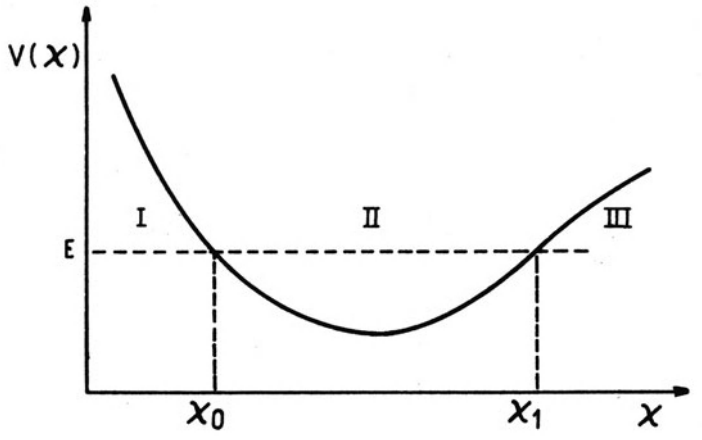

Fig. 2.1.: Potential well with two classical turning points.

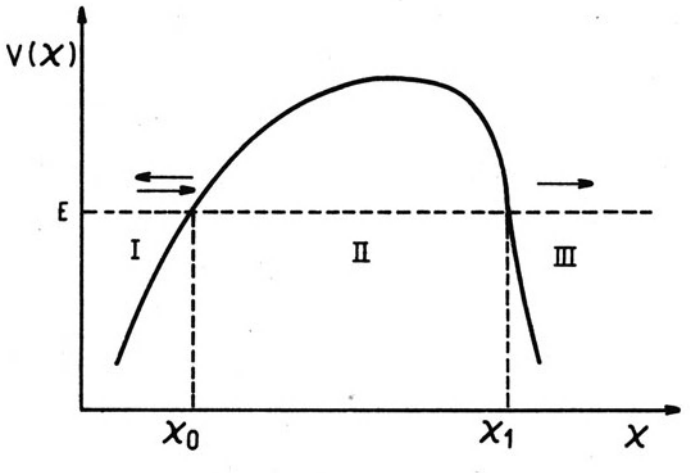

Fig. 2.2.: Potential barrier with two classical turning points.

the wave function (6.25) can be rewritten as

$$\psi_{II}(x) \to -(\frac{3}{2\pi q})^{\frac{1}{2}} A_1 e^{i\pi/6} e^{\tau} e^{-|w'|} \tag{6.28}$$

We have an alternative formula in zone II derived from the solution for the turning point x_o. Since E < V in zone II, we have to use the function (6.12):

$$\psi_{II}(x) \to (2\pi q)^{-\frac{1}{2}} \{ (B_o - A_o) e^{|w'|} + (A_o e^{i\pi/6} + B_o e^{-i\pi/6}) e^{-|w'|} \} \tag{6.29}$$

$$|w'| = \left| \int_x^{x_o} q dx' \right| = \int_{x_o}^{x} |q| dx' \tag{6.30}$$

The function (6.28) and (6.29) must be equal which implies the relationships

$$A_o = B_o \tag{6.31a}$$

$$A_o = -A_1 e^{(\tau + i\pi/6)} \tag{6.31b}$$

Finally, it remains to determine the shape of the wave in region I. It is easy to see that Eq. (6.11) must be used with w' given by (6.30):

$$\psi_I(x) \to (\frac{2}{\pi q})^{\frac{1}{2}} \{ A_o \cos(w' - \frac{\pi}{4} - \frac{\pi}{6}) + B_o \cos(w' - \frac{\pi}{4} + \frac{\pi}{6}) \} \tag{6.32}$$

The application of Eq. (6.31a) gives

$$\psi_I(x) \to (\frac{6}{\pi q})^{\frac{1}{2}} A_o \cos(w' - \frac{\pi}{4}) = (\frac{3}{2\pi q})^{\frac{1}{2}} A_o \{ e^{i(w' - \pi/4)} + e^{-i(w' - \pi/4)} \} \tag{6.33}$$

The transmission coefficient through the barrier can be computed as

$$T = \left| \frac{\bar{J}_I}{J_{III}} \right| \tag{6.34}$$

where $J = \mathrm{Im}(\psi \psi'^*)$ is the probability flux (or current) density. It must be remarked that our incoming and outgoing waves (Eqs. (6.33) and (6.23), respectively) possess the general form

$$\psi(x) = Nq^{-\frac{1}{2}}e^{\pm iw} \quad ; \quad w = \int_{\xi}^{x} q\,dx' \quad ; \quad \frac{dw}{dx} = q \tag{6.35}$$

so that it follows at once that

$$\psi' \equiv \frac{d\psi}{dx} = \{-\frac{N}{2}\, q^{-3/2}q' \pm iNq^{1/2}\}e^{\pm iw}$$

$$\psi\psi'^{*} = N^{*}N\{-\frac{1}{2}\, q^{-2} \mp i\}$$

and

$$\mathrm{Im}(\psi\psi'^{*}) = \pm|N|^{2} \tag{6.36}$$

From this last result and Eqs. (6.34), (6.23), (6.33) and (6.31b) we are led to

$$T = \frac{|-i\, e^{i\pi/6}A_1|^2}{|A_o|^2} = |ie^{-\tau}|^2 = e^{-2\tau} \tag{6.37}$$

where τ is given by Eq. (6.27).

The knowledge of the transmission coefficient T and the integral τ is very important in relation to the study of PT. We will see in a next chapter that it is possible to obtain meaningful information about the asymptotic form of the perturbation coefficients through the knowledge of the probability current density J(x) of a related problem with no bound states. For this reason JWKB method will be useful for our purposes, since it offers a way to determine J(x) from the asymptotic wave functions.

We complement the discussion of this Section with the model depicted in Fig. 2.3.

This system has not bound states but presents some features found previously when describing the models sketched in Figs. 2.1 and 2.2. The actual system has three classical turning points: x_o, x_1 and x_2. The asymptotic wave function around them can be determined following the procedure discussed before.

In the zone IV we have the outgoing wave, which is obtained from Eq. (6.23)

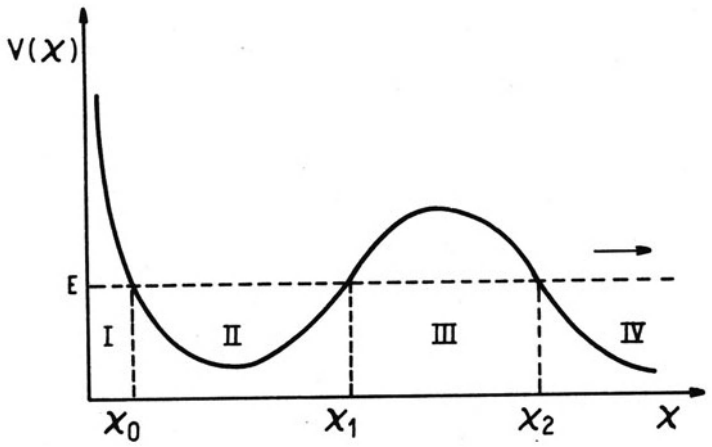

Fig. 2.3: Potential with well and barrier with three classical turning points.

$$\psi_{IV}(x) \rightarrow -iA_2\left(\frac{3}{2\pi q}\right)^{\frac{1}{2}} e^{i\pi/6} e^{i(w-\pi/4)} \quad ; \quad x>>x_2 \tag{6.38a}$$

$$w = \int_{x_2}^{x} q(x')dx' \tag{6.38b}$$

Similarly, the solution in zone III is provided by Eq. (6.28)

$$\psi_{III}(x) \rightarrow -\left(\frac{3}{2\pi q}\right)^{\frac{1}{2}} A_2 e^{i\pi/6} e^{\tau} e^{-|w'|}; \quad x_1<<x<<x_2 \tag{6.39a}$$

$$w' = \int_{x}^{x_1} q dz \; ; \quad |w'| = \int_{x_1}^{x} |q| dx \; ; \; \tau = \int_{x_1}^{x_2} |q| dx' \tag{6.39b}$$

The other solution for the area III is furnished by the propagation from x_1 which is obtained from Eq. (6.15) (used before for the description of the system shown in Fig. 2.1):

$$\psi_{III}(x) \rightarrow \left(\frac{3}{2\pi q}\right)^{\frac{1}{2}} A_1 e^{-|w'|} \; ; \; x_1<<x<<x_2 \tag{6.40}$$

where w' is given by Eq. (6.39b).

The solution for the area II from the turning point x_1 is obtained from Eq. (6.33) for the system shown in Fig. 2.2

$$\psi_{II}(x) \rightarrow \left(\frac{6}{\pi q}\right)^{\frac{1}{2}} A_1 \cos(w'-\pi/4) \quad ; \; x_o<<x<<x_1 \tag{6.41}$$

and the contribution to $\psi_{II}(x)$ from the turning point x_o is derived from Eq. (6.16) for the system depicted in Fig. 2.1:

$$\psi_{II}(x) \rightarrow \left(\frac{6}{\pi q}\right)^{\frac{1}{2}} A_o \cos(w''-\pi/4) \; ; \; x_o<<x<<x_1 \tag{6.42a}$$

$$w'' = \int_{x_o}^{x} q \, dx' \tag{6.42b}$$

Finally, it follows from Eq. (6.13) for the system shown in Fig. 2.1 that:

$$\psi_I(x) \rightarrow \left(\frac{3}{2\pi q}\right)^{\frac{1}{2}} A_o e^{-|w''|} \tag{6.43}$$

It is worth pointing out that on equating Eqs. (6.41) and (6.42) a kind of quantization condition (compare with Eq. (6.20)) is obtained

$$w' + w'' = \int_{x_o}^{x_1} q(x')dx' = (n + \tfrac{1}{2})\pi \tag{6.44}$$

which gives the resonance locations instead of the eigenvalues.

The computation of the current density for the motion towards zone IV of Fig. 2.3 can be made via Eqs. (6.23) and (6.36)

$$J(x) = \mathrm{Im}(\psi_{IV}(x)\psi'^{*}_{IV}(x)) = \frac{1}{2i}\{\psi_{IV}\psi'^{*}_{IV} - \psi'^{*}_{IV}\psi'_{IV}\} =$$

$$= -\frac{3}{2\pi}|A_2|^2 \tag{6.45}$$

It follows from equating Eqs. (6.39a) and (6.40) that

$$A_2 = -e^{-i\pi/6}e^{-\tau}A_1 \tag{6.46}$$

which gives J in terms of τ:

$$J = -\frac{3}{2\pi}|A_1|^2 e^{-2\tau} \tag{6.47}$$

We must note that

$$\lim_{x_2\to\infty} \tau = \lim_{x_2\to\infty} \int_{x_1}^{x_2} |(V-E)^{\frac{1}{2}}|dx = \infty$$

which tells us that the resonance states tend to the bound states in that limit because the condition

$$\lim_{x_2\to\infty} J = 0$$

corresponds obviously to an infinitely wide barrier.

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CHAPTER III

RAYLEIGH-SCHRODINGER PERTURBATION THEORY (RSPT)

"Now fills thy sleep with perturbations"

Richard III, W. Shakespeare, 1593

7. The Rayleigh-Schrödinger Perturbation Theory

We devote this Section to present RSPT in a way appropriate to our specific needs. There are several alternative manners to introduce this formalism which can be found in the standard literature /1-3/.

In what follows, we confine ourselves to bound states (i.e. discrete energy eigenvalues) since it is enough for our needs.

Let us consider the Schrödinger equation

$$H\psi_k(\lambda) = E_k(\lambda)\psi_k(\lambda) \tag{7.1}$$

$$H = H_o + \lambda V \tag{7.2}$$

where the eigenvalues and eigenfunctions assumed to be orthonormal of H_o are known

$$H_o|k\rangle = E_k^{(o)}|k\rangle \quad ; \langle i|j\rangle = \delta_{ij} \tag{7.3a}$$

H_o does not necessarily have any physical meaning and this issue is at this moment irrelevant. As usual, λ is the perturbation parameter. It is convenient to define the proper zeroth-order eigenfunction $|k\rangle$ as follows:

$$\lim_{\lambda\to 0} \psi_k(\lambda) = \psi_k(o) = |k\rangle \tag{7.3b}$$

They may be linear combinations of degenerate eigenfunctions of H_o /1-3/.

For the sake of concretness we focus our attention on a (g+1)-fold degenerate energy level. Let $\{|\bar{k}\rangle, \bar{k}=0,1,...\}$ be a set of orthonormal eigenfunctions of H_o so that $B = \{|\bar{s}\rangle, |\overline{s+1}\rangle, ... |\overline{s+g}\rangle\}$ corresponds to the above mentioned g-fold degenerate level. Then, we take $|k\rangle = |\bar{k}\rangle$ when $|\bar{k}\rangle \notin B$, and $|j\rangle \neq |\bar{j}\rangle$ when $|\bar{j}\rangle \in B$. The correct zero-order eigenfunctions $|j\rangle$ must be determined in a suitable way, as shown in what follows.

We can expand ψ_k in the complete basis set of eigenfunctions of H_o

$$\psi_k = \sum_i c_{ik}|i\rangle \tag{7.4}$$

where the sum is extended over all the states of the spectrum. On applying $\langle i|$ to (7.1) from the left and using (7.4) we have

$$E_i^{(o)}\langle i|\psi_k\rangle = -\lambda\langle i|V\psi_k\rangle + E_k\langle i|\psi_k\rangle = -\lambda\sum_j c_{jk}\langle i|V|j\rangle + E_k c_{ik} \tag{7.5}$$

which leads to

$$\{E_k - E_i^{(o)}\}c_{ik} = \lambda\sum_j V_{ij}c_{jk} \quad iV_{ij} \equiv \langle i|V|j\rangle \tag{7.6}$$

We arbitrarily impose the condition $c_{kk}=1$ to make the computation simpler. This choice gives rise to some restrictions on the set of functions $\{|k\rangle, k,0,1,...\}$, which will be analysed later on. The condition $c_{kk}=1$ plus the choice i=k in Eq. (7.6) leads us to

$$E_k = E_k^{(o)} + \lambda\sum_j V_{kj}c_{jk} \tag{7.7}$$

It deserves to be pointed out that there are other schemes to develop the perturbation expansion starting from different selections for c_{kk}. Although these alternatives are not the subject of this Section, it is meaningful to call attention to the fact that they can give rise to perturbation theories with quite different convergence properties. That is, such alternative approaches do not represent trivial changes with respect to the procedure discussed in this Chapter.

On introducing (7.7) into (7.6) we have

$$(E_k^{(o)} - E_i^{(o)})c_{ik} = -\lambda c_{ik}\sum_j V_{kj}c_{jk} + \lambda\sum_j V_{ij}c_{jk} \tag{7.8}$$

The RSPT consists of solving Eq. (7.8) by way of a λ-power series. In order to illustrate this procedure, we expand the coefficients c_{ij} (Eq. (7.4)) and E_k in Taylor series

$$c_{ij} = \sum_{r=0}^{\infty} c_{ij}^{(r)} \lambda^r \tag{7.9a}$$

$$E_k = \sum_{r=0}^{\infty} E_k^{(r)} \lambda^r \tag{7.9b}$$

which when substituted in (7.7) lead to

$$E_k^{(r)} = E_k^{(o)} \delta_{ro} + \sum_j V_{kj} c_{jk}^{(r-1)} \tag{7.10}$$

Eqs. (7.8) - (7.10) provide a recurrence relationship for the whole set of coefficients $c_{jk}^{(r)}$

$$(E_k^{(o)} - E_i^{(o)}) c_{ik}^{(r)} = -\sum_j \sum_{s=0}^{r-1} V_{kj} c_{jk}^{(s)} c_{ik}^{(r-1-s)} + \sum_j V_{ij} c_{jk}^{(r-1)} \tag{7.11}$$

This relation is given in terms of quantities which can be obtained from the spectrum of H_o.

Since $c_{kk}=1$ it follows that

$$c_{kk}^{(p)} = \delta_{po} \tag{7.12a}$$

Furthermore, the condition (7.3b) and the orthogonality condition yield

$$c_{ij}^{(o)} = \delta_{ij} \tag{7.12b}$$

which is not valid for the orthonormal set $\{|\bar{k}\rangle, k=0,1,...\}$ except when g=0. In the general case we can write

$$|k\rangle = \sum_{|\bar{j}\rangle \in B} A_{jk} |\bar{j}\rangle = \sum_{j=s}^{s+g} A_{jk} |\bar{j}\rangle \tag{7.13}$$

for those functions $|k\rangle$ belonging to the degenerate subspace of H_o under consideration. It must be taken note of the fact that, in general, $A_{jk} \neq \delta_{jk}$ because $\langle i|\bar{j}\rangle \neq \delta_{ij}$.

The use of the recurrence relationship (7.11) together with Eqs.

(7.12) allow us to obtain the perturbation corrections for the energy and wave function.

In order to exemplify the procedure, we compute the first perturbation terms.

a) First order: The selection r=1 in (7.11) gives

$$(E_k^{(o)} - E_i^{(o)})c_{ij}^{(1)} = - c_{ik}^{(o)} \sum_j V_{kj}c_{jk}^{(o)} + \sum_j V_{ij}c_{jk}^{(o)} \qquad (7.14)$$

and from the conditions (7.12) we have

$$(E_k^{(o)} - E_i^{(o)})c_{ik}^{(1)} = -\delta_{ik}V_{kk} + V_{ik} \qquad (7.15)$$

Then, we obtain the coefficients $c_{ik}^{(1)}$ corresponding to the correct zero-order wave functions

$$c_{ik}^{(1)} = V_{ik}/(E_k^{(o)} - E_i^{(o)}) \quad ; \quad i \neq k \qquad (7.16)$$

When $|i>$ and $|k>$ are degenerate we have

$$V_{ik} = 0 \quad ; \quad s \leq i,k \leq s+g \qquad (7.17)$$

instead of (7.16). For this reason, when $|i>$, $|k> \varepsilon \bar{B}$ the coefficients $c_{ik}^{(1)}$ must be computed via second order perturbation theory, as shown in what follows. Whenever there is degeneracy, the computation of the first order correction requires the knowledge of the coefficients A_{jk} (Eq. (7.13)), since usually one knows the set $\{|\bar{k}>, k=0,1,...\}$. The solution is simply obtained by changing $c_{ij}^{(o)}$ for A_{ij} and V_{ij} for $\bar{V}_{ij} \equiv <\bar{i}|V|\bar{j}>$ and considering that $E_k^{(o)} = E_i^{(o)}$, so that

$$0 = -A_{ik}E_k^{(1)} + \sum_{j=s}^{s+g} \bar{V}_{ij}A_{jk} \ , \ s \leq i,k \leq s+g \qquad (7.18)$$

where (7.10) is substituted for $E_k^{(1)}$. Eq. (7.18) can be rewritten in a more appropriate manner as

$$\sum_{j=s}^{s+g} \{\bar{V}_{jk} - E_k^{(1)}\delta_{ij}\}A_{jk} = 0 \ ; \ s \leq i,k \leq s+g \qquad (7.19)$$

This last equation tells us that the first-order energy perturbation corrections come from the roots of

$$\det(\underset{\sim}{\bar{V}} - E^{(1)}\underset{\sim}{I}) = 0 \; ; \; (\underset{\sim}{\bar{V}})_{ij} = \bar{V}_{ij} \; ; \; (\underset{\sim}{I})_{ij} = \delta_{ij}$$

$$\underset{\sim}{\bar{V}}, \underset{\sim}{I} \; \varepsilon \; R^{(g+1)x(g+1)} \tag{7.20}$$

The secular equation (7.19) yields the coefficients A_{jk} and consequently the functions $|k>$.

As a particular case, when g=0 Eq. (7.20) provides the first-order perturbation correction for a non-degenerate state:

$$E_s^{(1)} = \bar{V}_{ss} = V_{ss} \tag{7.21}$$

In what follows, we will continue our discussion with a basis set of correct zero-order functions since this particular set (via those properties like (7.17)) makes it simpler the analysis of higher-order perturbation corrections. However, it must be remembered that in case of degeneracy such a basis set have to be built as shown before.

b) Second order: The choice r=2 in Eq. (7.11) leads to

$$(E_k^{(o)} - E_i^{(o)})c_{ik}^{(2)} = -c_{ik}^{(o)} \sum_j V_{kj}c_{jk}^{(1)} - c_{ik}^{(1)} \sum_j V_{kj}c_{jk}^{(1)} +$$

$$+ \sum_j V_{ij}c_{jk}^{(1)} \tag{7.22}$$

On using Eq. (7.12) and (7.17), Eq. (7.22) becomes

$$(E_k^{(o)} - E_i^{(o)})c_{ik}^{(2)} = -\delta_{ik}V_{kk}c_{kk}^{(1)} - \delta_{ik} \sum_{|j>\notin\bar{B}} V_{kj}c_{jk}^{(1)} -$$

$$- V_{kk}c_{ik}^{(1)} + \sum_j V_{ij}c_{jk}^{(1)} \tag{7.23}$$

This last equation complements Eq. (7.16) and permits one to compute the coefficients $c_{ik}^{(1)}$ when $|i>$ and $|j>$ are non-degenerate states.

In such a case, Eq. (7.23) gives

$$0 = -V_{kk}c_{ik}^{(1)} + \sum_j V_{ij}c_{jk}^{(1)} = -V_{kk}c_{ik}^{(1)} + \sum_{|j>\notin\bar{B}} V_{ij}c_{jk}^{(1)} +$$

$$+ \sum_{|j>\varepsilon\bar{B}} V_{ij}c_{jk}^{(1)} = c_{ik}^{(1)}\{V_{ii} - V_{kk}\} + \sum_{|j>\notin\bar{B}} V_{ij}c_{jk}^{(1)} \tag{7.24}$$

Considering that $V_{ii} = E_i^{(1)}$ even when $|i>\varepsilon\bar{B}$ (see Eq. (7.21)), and using Eq. (7.16), we have from (7.24) the desired result

$$c_{ik}^{(1)} = \frac{1}{E_k^{(1)} - E_i^{(1)}} \sum_{|j>\notin\bar{B}} \frac{V_{ij}V_{jk}}{E_k^{(o)} - E_j^{(o)}}; \quad s \leq i,k \leq s+g \tag{7.25}$$

If degeneracy is not broken at first-order, i.e. if $E_k^{(1)} = E_i^{(1)}$, it is found that

$$\sum_{|j>\notin\bar{B}} \frac{V_{ij}V_{jk}}{E_k^{(o)} - E_j^{(o)}} = 0 \; ; \; |i>,|k> \; \epsilon \; \bar{B}, \; |i>\neq|k> \tag{7.26}$$

Eq. (7.26) instead of (7.25) may remove degeneracy at second-order.

Taking into consideration the cases $|i>\notin\bar{B}$ and $|k>\epsilon\bar{B}$ in Eq. (7.23), we can determine the coefficients $c_{ik}^{(2)}$. Since

$$(E_k^{(o)} - E_i^{(o)})c_{ik}^{(2)} = -c_{ik}^{(1)}V_{kk} + \sum_j V_{ij}c_{jk}^{(1)} \; ; \; s \leq k \leq s+g \; , \tag{7.27}$$

the insertion of Eqs. (7.16) and (7.25) into (7.27) gives:

$$c_{ik}^{(2)} = -\frac{V_{kk}V_{ik}}{(E_k^{(o)} - E_i^{(o)})} + \sum_{|j>\epsilon\bar{B}} \sum_{|l>\notin\bar{B}} \frac{V_{ij}V_{jl}V_{lk}}{(E_k^{(1)} - E_j^{(1)})(E_k^{(o)} - E_l^{(o)})(E_k^{(o)} - E_i^{(o)})} +$$

$$+ \sum_{|j>\notin\bar{B}} \frac{V_{ij}V_{jk}}{(E_k^{(o)} - E_i^{(o)})(E_k^{(o)} - E_j^{(o)})} \; ; \; |k>\epsilon\bar{B}; \; |i>\notin\bar{B} \tag{7.28}$$

when g=0 in Eq. (7.28), that is to say k=s, we are led to the second-order correction for the coefficients of the wave function

$$c_{is}^{(2)} = -\frac{E_s^{(1)}V_{is}}{(E_s^{(o)} - E_i^{(o)})^2} + \frac{1}{E_s^{(o)} - E_i^{(o)}} \sum_{l\neq s} \frac{V_{il}V_{ls}}{E_s^{(o)} - E_l^{(o)}} \; ; \; i\neq s \tag{7.29}$$

Let us consider again $|k>\epsilon\bar{B}$. For the purpose of calculating the second-order correction to the energy we have just to combine Eqs. (7.10), (7.12) and (7.17):

$$E_k^{(2)} = \sum_j V_{kj}c_{jk}^{(1)} = \sum_{|j>\epsilon\bar{B}} V_{kj}c_{jk}^{(1)} + \sum_{|j>\notin\bar{B}} V_{kj}c_{jk}^{(1)} =$$

$$= V_{kk}c_{kk}^{(1)} + \sum_{|j>\notin\bar{B}} V_{kj}c_{jk}^{(1)} = \sum_{|j>\notin\bar{B}} V_{kj}c_{jk}^{(1)} \tag{7.30}$$

The substitution of Eq. (7.16) in Eq. (7.30) allows us to get the desired result:

$$E_k^{(2)} = \sum_{|j>\notin\bar{B}} \frac{|V_{jk}|^2}{(E_k^{(o)}-E_j^{(o)})} \quad ; \quad s \leq k \leq s+g \tag{7.31}$$

The choice g=0 in the previous equation (k=s) yields the second-order correction to the energy for non-degenerate states:

$$E_s^{(2)} = \sum_{j\neq s} \frac{|V_{js}|^2}{E_s^{(o)}-E_j^{(o)}} \tag{7.32}$$

c) Third order: To simplify the discussion we confine ourselves to the correction for the energy. For that purpose, it is only necessary to replace (7.28) in (7.10) and for $|k>\varepsilon\bar{B}$ we get the result

$$E_k^{(3)} = \sum_j V_{kj}c_{jk}^{(2)} = \sum_{|j>\notin\bar{B}} V_{kj}c_{jk}^{(2)} = -E_k^{(1)} \sum_{|j>\notin\bar{B}} \frac{|V_{kj}|^2}{(E_k^{(o)}-E_j^{(o)})^2} +$$

$$+ \sum_{|j>\notin\bar{B}} \sum_{|m>\notin\bar{B}} \sum_{|n>\varepsilon\bar{B}} \frac{V_{jn}V_{nm}V_{mk}}{(E_k^{(1)}-E_n^{(1)})(E_k^{(o)}-E_m^{(o)})(E_k^{(o)}-E_j^{(o)})} +$$

$$+ \sum_{|j>\notin\bar{B}} \sum_{|n>\notin\bar{B}} \frac{V_{kj}V_{jn}V_{nk}}{(E_k^{(o)}-E_j^{(o)})(E_k^{(o)}-E_n^{(o)})} ; \quad s \leq k \leq s+g \tag{7.33}$$

When g=0 Eq. (7.33) (see Eq. (7.29)) gives the third-order correction to the energy for non-degenerate states:

$$E_s^{(3)} = -E_s^{(1)} \sum_{j\neq s} \frac{|V_{sj}|^2}{(E_s^{(o)}-E_j^{(o)})^2} + \sum_{j\neq s} \sum_{n\neq s} \frac{V_{sj}V_{jn}V_{ns}}{(E_s^{(o)}-E_j^{(o)})(E_s^{(o)}-E_n^{(o)})} \tag{7.34}$$

It is clear from Eqs. (7.21), (7.32) and (7.34) that the computation of the perturbation corrections to the energy becomes rapidly cumbersome as the order increases due to the presence of sums that are usually infinite.

Evidently, the procedure is not practical to determine even a moderately large number of perturbation coefficients. There are other alternative schemes to overcome these drawbacks and they will be discussed in the next sections.

Now we introduce an additional result which allows one to know beforehand whether there are null RS coefficients in some special cases.

Theorem 7.1

Let $H(\lambda)$ be a λ-dependent Hamiltonian (λ is the so-called perturbation parameter), such that a change of coordinates causes a change of sign on λ. Then, whenever there is no degeneration for each value of λ, all the odd perturbation corrections to the energy are null.

Proof:

Let U be a unitary transformation of the coordinates so that:

$$UH(\lambda)U^{-1} = H(-\lambda) \tag{7.35}$$

The Schrödinger equation for $H(\lambda)$ is:

$$H(\lambda)\psi_n(\lambda) = E_n(\lambda)\psi_n(\lambda) \tag{7.36}$$

where $E_n(\lambda)$ can be expanded in a power series of λ:

$$E_n(\lambda) = \sum_{m=0}^{\infty} E_n^{(m)}\lambda^m \tag{7.37}$$

Since U acts upon the coordinates and <u>not</u> upon λ, we can apply U on (7.36) and we get

$$UH(\lambda)\psi_n(\lambda) = UH(\lambda)U^{-1}U\psi_n(\lambda) = H(-\lambda)\{U\psi_n(\lambda)\} =$$

$$= E_n(\lambda)\{U\psi_n(\lambda)\} \tag{7.38}$$

Evidently $H(\lambda)$ and $H(-\lambda)$ have the same spectrum ordered in a different way since $U\psi_n \neq \psi_n$, i.e.

$$E_n(\lambda) = E_m(-\lambda) \tag{7.39}$$

If both sides of this last equation are expanded in a λ-power series we have:

$$E_n^{(i)} = (-1)^i E_m^{(i)} \quad ; \quad i \geq 0 \tag{7.40}$$

Since there is not degeneracy for every λ-value, and $E_n^{(o)}=E_m^{(o)}$ accord-

ing to (7.40), we conclude that m=n. Then, it follows from Eq. (7.40) that

$$\{1 - (-1)^i\}E_n^{(i)} = 0 \quad \text{and hence} \quad E_n^{(2i+1)} = 0;\ i=0,1,... \tag{7.41}$$

which proves the theorem.

Example: Let us consider the following perturbed bidimensional harmonic oscillator

$$H(\lambda) = -(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}) + x^2 + y^2 + \lambda xy \tag{7.42}$$

to exemplify the previous theorem.

The eigenvalues corresponding to the Hamiltonian (7.42) are easily shown to be given by

$$E_{nm}(\lambda) = (2n+1)(1+\lambda/2)^{\frac{1}{2}} + (2m+1)(1-\lambda/2)^{\frac{1}{2}};\ n,m=0,1,2,... \tag{7.43}$$

The spectrum is non-degenerate for $\lambda > 0$ but when $\lambda = 0$ we have

$$E_{nm}(0) = E_{nm}^{(o)} = 2(n+m+1) \tag{7.44}$$

The only non-degenerate state for all $\lambda > -2$ is the ground-state (E_{oo}).

The unitary operators U that yield a change of sign in $H(\lambda)$ can be easily found if one considers coordinate rotations

$$c_{2x}\begin{pmatrix}x\\y\end{pmatrix} = \begin{pmatrix}x\\-y\end{pmatrix}\ ;\quad c_{2y}\begin{pmatrix}x\\y\end{pmatrix} = \begin{pmatrix}-x\\y\end{pmatrix} \tag{7.45}$$

The effect of these transformations on $H(\lambda)$ is summarized by

$$E_{nm}(\lambda) = E_{mn}(-\lambda) \tag{7.46}$$

From the previous discussion, it is self-evident that the hypothesis of Theorem (7.1) are only fulfiled for the ground state, so that we may assert that

$$E_{oo}^{(2i+1)} = 0\ ;\ i = 0,1,2,... \tag{7.47}$$

The result (7.47) is verified by expanding the exact solution (7.43)

in a λ-power series.

8. Hypervirial Method to Generate the Perturbation Expansion.

In the preceding section we have seen that the usual formulation of the RSPT brings in some formulas which are extremely awkward to deal with, especially when one needs to compute a large number of perturbation coefficients.

Naturally, one has to resort to alternative formalisms to surmount this difficulty. Dalgarno et al /4-11/ developed a successful method to compute RS perturbation corrections without resorting to the explicit calculation of infinite sums. The procedure consists of determining the perturbation corrections by way of integrals involving an operator that it is a solution of a given differential equation.

The method is an improvement with regard to the Unsold approximation /12/ used previously to determine the sums that result from the computation of perturbation corrections. It has proved to be really effective to analyse those atomic /4,6,10,11/ and molecular properties /6-11/ which can be approximated in a reasonable manner through a small number of perturbation terms. Although the procedure allows one to solve a very troublesome problem like that of obtaining the second-order corrections for perturbed Coulomb systems (it must be remembered that the zero-order Hamiltonian has both discrete and continuous spectra), it is really hard to generalize the method beyond the third-order. Therefore, it is not an useful method to study high order PT.

Among the several methods proposed later on, the so-called Hypervirial-Perturbative Method (HPM) has shown to have a wide applicability for a large number of models. Originally the method was presented by Swenson and Danforth /13/ in order to study 1D anharmonic oscillators of particular interest within the realm of vibrational spectroscopy and field theories (see Appendices B and C). Killingbeck /14/ proposed an interesting generalization for radial problems.

Later on we have improved, generalized and extended the HPM with respect to its applicability (the pertinent references will be given afterwards in this section when dealing explicitly with some examples).

At present, the method can be applied to a very large class of systems fulfilling a basic condition: they must be one-dimensional or separable in 1D systems.

In the case of non-separable problems, one can resort to some special methods to be discussed later on.

The HPM is based on the combination of hypervirial theorems and recurrences, like those presented in section 3, the Hellmann-Feynman theorem (section 2) and the RSPT (section 7). The method permits the computation of the whole set of perturbation corrections to eigenvalues and to the matrix elements of functions belonging to a properly chosen set without being necessary to resort to the explicit calculation of the perturbation corrections to the wave function. Due to this characteristic the HPM is also called perturbation theory without wave function (PTWWF) /14/.

For the sake of simplicity and due to the fact that it is enough for our present aims, we develop here the HPM for 1D systems subjected to trivial BC:

$$H = -\frac{1}{2}D^2 + V_o(x) + \lambda V_1(x) = H_o + \lambda V_1(x); \quad D \equiv \frac{d}{dx}\ ;\ \lambda>0 \tag{8.1}$$

$$H_o\psi^{(o)} = E^{(o)}\psi^{(o)};\ H\psi(\lambda) = E(\lambda)\psi(\lambda) \tag{8.2}$$

where ψ obeys the condition

$$\lim_{|x|\to\infty} x^N\psi(\lambda) = 0;\ N > 0;\ \lambda \geq 0 \tag{8.3}$$

Now, we know that any 1D system defined through Eqs. (8.1)-(8.3) satisfies, according to Eqs. (3.15), (3.31) and (3.32), the following relation

$$\frac{1}{4}\langle f''' \rangle + 2E\langle f' \rangle - 2\langle f'V_o \rangle - 2\lambda\langle f'V_1 \rangle - \langle fV_o' \rangle - \lambda\langle fV_1' \rangle = 0 \tag{8.4}$$

where $f \equiv f(x)$ is a differentiable function and

$$\langle A \rangle \equiv \langle\psi|A\psi\rangle \tag{8.5}$$

If V_o and V_1 can be expanded in a power series of the variable x, the function f can be selected as

$$f(x) = x^N \tag{8.6}$$

Therefore (8.4) becomes

$$\frac{1}{4} N(N-1)(N-2)\langle x^{N-3}\rangle + 2NE\langle x^{N-1}\rangle - \{2N\langle x^{N-1}V_o\rangle + \\ + \langle x^N V_o'\rangle\} - \lambda\{2N\langle x^{N-1}V_1\rangle + \langle x^N V_1'\rangle\} = 0 \tag{8.7}$$

which makes up a recurrence relationship relating the eigenvalues with some matrix elements. On the other hand, the consideration of the HFT (Eq. (2.10)) gives the functional dependence of E on λ:

$$\partial E/\partial\lambda = \langle V_i\rangle \tag{8.8}$$

as well as an additional relation between the energy eigenvalues and some matrix elements.

The RSPT yields a λ-power series expansion for E:

$$E = \sum_{m=0}^{\infty} E^{(m)}\lambda^m \tag{8.9}$$

Besides, $\psi(\lambda)$ can also be expanded in a λ-power series so that the expectation value of a linear operator A can be written

$$\langle A\rangle = \sum_{m=0}^{\infty} A_m\lambda^m \tag{8.10}$$

where A_m is the m-th RS coefficient.

The HPM consists of introducing (8.9) and (8.10) into (8.7) and (8.8) in such a way that one can use the last couple of equations recursively to obtain the coefficients $\{E^{(m)}\}$ and $\{A_m\}$.

To this end it is first necessary to fulfill some conditions, which are discussed in what follows. First of all, we must have a starting point for the recurrence which must be related to the zero-order spectrum, since it is our reference system. An appropriate auxiliar condition is given by the normalization to unity for the exact wave function $\psi(\lambda)$ and the zero-order wave function $\psi^{(o)}$, that is

$$\langle\psi(\lambda)|\psi(\lambda)\rangle = \langle\psi^{(o)}|\psi^{(o)}\rangle = 1 \tag{8.11}$$

Upon expanding the expectation value

$$X^{(N)} \equiv \langle x^N \rangle \tag{8.12}$$

in a λ-power series as shown in (8.10) we have

$$X_m^{(o)} = \delta_{om} \tag{8.13}$$

because of (8.11). The recurrence relations are useful provided they allow the calculation of the $X_m^{(N)}$ terms related to the energy through the Hellman-Feynman theorem (8.8). This always happens in the case considered here when V_o and V_1 are polynomials. Upon introducing (8.9) and (8.10) into (8.8) and equating the coefficients of like powers on both sides of the resulting equation we have

$$E^{(m)} = \frac{1}{m}(V_1)_{m-1} \; ; \; m \geq 1 \tag{8.14}$$

where $(V_1)_{m-1}$ is the (m-1)th-order coefficient in the expansion of $\langle V_1 \rangle$ in power-series of λ.

Example: Let us consider the anharmonic oscillator models in order to show the use of the preceding equations. These models are very important and have a remarkable interest in several areas of Physics and Chemistry, since they describe quite accurately molecular vibrations, diffusion processes (see Appendix B) and some simple field theories (see Appendix C). Besides, such models have received considerable attention from the theoretical view point because they are among the simplest models without analytical solution that have some characteristic properties of more complicated systems. Here, they are selected in order to illustrate the employment of the HPM, and for the sake of concreteness we restrict ourselves to the quartic anharmonic oscillator defined by

$$V_o = x^2; \; V_1 = x^4; \; E^{(o)} = E_n^{(o)} = (n + \tfrac{1}{2})2^{\frac{1}{2}} \tag{8.15}$$

Upon introducing (8.15) into (8.7) one obtains the following reccurrence relationship:

$$\frac{1}{4} N(N-1)(N-2)X^{(N-3)} + 2NE_n X^{(N-1)} - 2(N+1)X^{(N+1)} -$$

$$- 2\lambda(N+2).X^{(N+3)} = 0 \tag{8.16}$$

where

$$X^{(N)} = \int_{-\infty}^{+\infty} |\psi|^2 x^N d_x \tag{8.17}$$

in accordance with (8.13).

Since the potential function is even, Theorem 1.2 gives

$$X^{(2s+1)} = 0; \; s \geq 0 \tag{8.18}$$

so that one has to consider only the odd-values of N in Eq. (8.16). It follows from (8.9), (8.10), and (8.16) that

$$\frac{1}{4} N(N-1)(N-2)X_s^{(N-3)} + 2N \sum_{j=0}^{s} E_n^{(j)} X_{s-j}^{(N-1)} - 2(N+1)X_s^{(N+1)} -$$

$$- 2(N+2)X_{s-1}^{(N+3)} = 0 \tag{8.19}$$

Eq. (8.14) leads to

$$E_n^{(s)} = \frac{1}{s} X_{s-1}^{(4)} \quad ; \quad s \geq 1 \tag{8.20}$$

which is complementary to the recurrence (8.19). Eqs. (8.19) and (8.20) are solved hierarchically for increasing values of N and s. This procedure has been used, for example, to compute 145 coefficients with 25 accurate figures for the ground state of the quartic anharmonic oscillator /15/.

The HPM is extremely useful to obtain the perturbation corrections in an analytical as well as a numerical way. The latter is due to the fact that the method is suitable for programming. However, a warning is necessary here, because such relations have to be handled with care due to the possible (and usual) increase of round-off errors which can spread with the growth of s.

The HPM has been applied to study many systems with trivial BC such as 1D oscillators of interest in field theories with scalar lagrangians /16/ central-field potentials /14,17/ and vibrational oscillators and other potentials with several parameters /18,19/. Moreover, some authors

have studied N-dimensional separable systems, such as the Stark effect in hydrogen /20,21/. Other simple but non-separable systems have been approximately treated via the combination of the HPM and the self-consistent approximation. Among them we mention the 1D atom models /22/ and the coupled oscillators /23/. The RS perturbation series for the perturbed Morse oscillator, which is frequently used to describe the vibrations of diatomic molecules, has also been calculated /24-27/. The method was applied either expanding the potential in power series /24/ or considering the complete potential together with some ad-hoc hypervirial operators /25/. The application of these procedures has allowed to compute the perturbation corrections to the energy as well as to several diagonal and off-diagonal matrix elements /26,27/.

Sometimes, the application of the HPM requires the choice of HO different to those of Eq. (8.6). The way to choose such operators will not be discussed here, but can be found in the literature /28/.

The HPM can be extended to systems with other BC, by means of a suitable change of the HR. Such modifications have already been analysed in section 3. The procedure to be followed afterwards is similar to that presented in this section, so it just remains to quote some systems which have been studied successfully by means of the HPM:

1) periodic systems, such as the plane rotor within an electric field (Mathieu equation) /29-31/;
symmetric-top molecules in external electric fields /32/ and the rotational Zeeman effect for H_2^+ /33/;

2) systems subjected to Dirichlet BC, such as symmetrically /34,35/ and non-symmetrically bounded harmonic oscillators /36/, the symmetrically bounded quartic oscillator /37/, N-dimensional radial oscillators /38, 39/, the hydrogen atom within spherical /39,40/ and parabollical impenetrable walls /41/, the Stark effect for the hydrogen atom within an impenetrable parabollic shell /42/ and the Stark effect for the 1D vacuum crystal model /43/;

3) systems subjected to VNBC, such as the harmonic oscillator /31/; and

4) model requiring general BC, such as the double well with DBC /44/ and some delta-function potentials /44/.

Finally, we deem necessary to point out that the HR have been really

useful in computing analytical matrix elements in a basis set of Bessel /45,46/ and Airy functions /47/.

9. Other Methods to Generate the Perturbation Expansion

There exist several procedures to compute the RS coefficients which avoid the sums involved in the theory. Such sums are usually infinite. In this regard we have commented that some methods like that due to Dalgarno /4-11/, and here we add another one based on the use of the Feynman rules /48,49/, allow one to calculate the lower corrections for a wide variety of problems. For higher-order corrections it is necessary to resort to other methods one of which was discussed in the preceding section 8. Here we discuss some other methods usually found in the current literature which are not as general as the HPM.

The most effective procedures to generate the RS series are based on the transformation of the RSPT equations /50/ into algebraic recurrences from which one can compute the perturbation coefficients. Here we will restrict ourselves to three methods, namely, the logarithmic PT, the generalized PTWWF, and the Bender-Wu method.

i) The logarithmic perturbation theory

This method has been studied by a large number of authors /51-71/. It consists of transforming the Schrödinger equation into the Ricatti equation (i.e. a non-linear differential equation for the logarithmic derivative of the wave function, which gives the method its name) and then applying PT.

Let us start with the one-particle Schrödinger equation (units are chosen so that $\hbar = 1$)

$$\{-\frac{1}{2}\Delta + V_o + \lambda V_1\}\psi = E\psi \tag{9.1}$$

where Δ denotes the Laplacian operator. Now we write the exact wave function $\psi(\bar{r})$ as

$$\psi(\bar{r}) = e^{-G(\bar{r})} \quad ; \quad \lim_{||\bar{r}|| \to \infty} \psi(\bar{r}) = 0 \tag{9.2}$$

with G a regular function. This condition restricts the following discussion to the ground state. From (9.2) we obtain

$$\Delta\psi = \nabla.\nabla\psi = -\{\nabla.\bar{g} - \bar{g}.\bar{g}\}e^{-G} = -\{\text{div}\ \bar{g} - g^2\}e^{-G} \tag{9.3}$$

with

$$\bar{g} \equiv \text{grad}\ G\ ;\ g \equiv ||\bar{g}|| \tag{9.4}$$

In this way (9.1) becomes the Ricatti equation

$$\text{div}\ \bar{g} - g^2 = 2(E - \lambda V_1 - V_o) \tag{9.5}$$

The RSPT now reads

$$E = \sum_{n=0}^{\infty} E^{(n)}\lambda^n \tag{9.6a}$$

$$G = \sum_{n=0}^{\infty} G_n\lambda^n\ ;\ \bar{g} = \sum_{n=0}^{\infty} \bar{g}_n\lambda^n;\quad \bar{g}_n \equiv \text{grad}\ G_n \tag{9.6b}$$

According to Eq. (9.5) the RS perturbation coefficients obey

$$\text{div}\ \bar{g}_n - \sum_{s=0}^{n} \bar{g}_s.\bar{g}_{n-s} = 2(E^{(n)} - V_1\delta_{n1} - V_o\delta_{no}) \tag{9.7}$$

For 1D systems

$$\text{div}\ \bar{g}_n = g_n' \tag{9.8}$$

The problem posed by Eq. (9.1) has thus been changed into a set of first-order differential equations. The integrating factor for those equations is $\psi_o^2 = e^{-2G_o}$, where ψ_o is a solution of (9.1) for $\lambda = 0$.

The first non-trivial case in (9.7) is n=1, which gives

$$\text{div}\ \bar{g}_1 - 2\bar{g}_o.\bar{g}_1 = 2(E^{(1)} - V_1) \tag{9.9}$$

Eq. (9.6b) can be rewritten

$$\{\text{div}\ \bar{g}_1 - 2\bar{g}_o.\bar{g}_1\}e^{-2G_o} = \text{div}\{\bar{g}_1 e^{-2G_o}\} \tag{9.10}$$

After multiplying (9.9) by the integrating factor, we have

$$\int_s \psi_o^2 \bar{g}_1 . \bar{n} ds = 2 \int_V \psi_o^2 (E^{(1)} - V_1) dV \tag{9.11}$$

s is the surface enclosing the volume V. Eq. (9.11) is the Gauss theorem. Since ψ_o vanishes on s we are led to the well-known result

$$E^{(1)} = \frac{1}{N} \int_V V_1 \psi_o^2 dV \; ; \; N = \int_V \psi_o^2 dV \tag{9.12}$$

For $n \geq 2$, Eq. (9.7) can be rewritten in a similar way as Eq. (9.9), i.e.

$$\text{div } \bar{g}_n - 2\bar{g}_o . \bar{g}_n = 2(E^{(n)} + \frac{1}{2} \sum_{s=0}^{n-1} \bar{g}_{n-s} . \bar{g}_s) \tag{9.13}$$

Upon multiplying Eq. (9.13) by the integrating factor and proceeding as in (9.10) and (9.11) one obtains

$$E^{(n)} = - \frac{1}{2} \sum_{s=0}^{n-1} \int_V (\bar{g}_{n-s} . \bar{g}_s) \frac{1}{N} \psi_o^2 dV \tag{9.14a}$$

$$g_n(\bar{r}) = \frac{2}{\psi_o^2(\bar{r})} \int^{(\bar{r})} (E^{(n)} + \frac{1}{2} \sum_{s=0}^{n-1} \bar{g}_s . \bar{g}_{n-s}) dV \tag{9.14b}$$

These two equations are treated recursively. The $E^{(1)}$ value is used to calculate g_1 from (9.14b) with n = 1 which is then used to obtain $E^{(2)}$ from (9.14a), etc. In some cases the method permits one to compute a very large number of perturbation corrections.

The logarithmic PT has been successfully applied to obtain a large number of RS coefficients for the ground state of many problems: the anharmonic oscillator /53-56/; the atomic Stark effect /57,58,64/; some confining particle models /66,67,69/, and the Zeeman effect in hydrogen /68,70/. A pedagogical review on this subject can be found in Ref. 71.

In order to apply the logarithmic PT to excited states it is necessary to take into account the zeroes of the wave function explicitly:

$$\psi_m(\bar{r}) = \sum_{i=1}^{m} (\bar{r} - \bar{r}_{oi}) e^{-G_m(\bar{r})} \tag{9.15}$$

However, the resulting equations are difficult to handle so that the procedure is not practical for large-order calculations.

ii) Generalized PTWWF. This method, developed by Fernández and Castro /72,73/, proves to be useful in treating some multidimensional systems such as hydrogen in electric and magnetic fields and the hydrogen-molecule ion.

Let us consider again the Hamiltonian (9.1), but now we write the correct zero-order wave function as

$$\psi_o = \lim_{\lambda \to 0} \psi(\bar{r}) = F(\bar{r})\phi(\bar{r}) \tag{9.16}$$

with

$$\phi(\bar{r}) = e^{-s(\bar{r})} \tag{9.17}$$

Taking into account that

$$\Delta\psi_o = \nabla.\nabla\psi_o = 2\nabla\phi.\nabla F + \phi\Delta F + F\Delta\phi \tag{9.18a}$$

$$\Delta\phi = \phi(\nabla s.\nabla s - \Delta s) \tag{9.18b}$$

we have

$$(V_o - E^{(o)})F = \frac{1}{2}\Delta F + FQ - \nabla s.\nabla F \tag{9.19a}$$

$$Q = \frac{1}{2}(\nabla s.\nabla s - \Delta s) \tag{9.19b}$$

Let us now consider a differentiable function $f(\bar{r})$, so that $f\phi$ belongs to the domain of the Hamiltonian operator. Then we know that

$$\langle\psi|Hf\phi\rangle = E\langle\psi|f\phi\rangle \tag{9.20}$$

and the use of Eq. (9.18) allows us to change Eq. (9.20) into

$$-\frac{1}{2}\langle\psi|\Delta f\phi\rangle + \langle\psi|\nabla s.\nabla s\phi\rangle - \langle\psi|(V_o - Q)\phi\rangle =$$

$$= E\langle\psi|f\phi\rangle - \lambda\langle\psi|V_1 f\phi\rangle \tag{9.21}$$

The main idea is to transform (9.21) into a recurrence relationship from which one can get all the RS coefficients. The energy E can be obtained by choosing $f \equiv F$ in (9.21) and resorting to Eq. (9.19):

$$\Delta E = E - E_o = \lambda \frac{\langle \psi | V_1 \psi_o \rangle}{\langle \psi | \psi_o \rangle} \tag{9.22}$$

In order to simplify the equations it is convenient to introduce the normalization /74/

$$\langle \psi | \psi_o \rangle = 1 \tag{9.23}$$

The substitution of the perturbation expansions

$$\psi = \sum_{n=0}^{\infty} \psi_n \lambda^n \; ; \; E = \sum_{n=0}^{\infty} E^{(n)} \lambda^n \tag{9.24}$$

into Eqs. (9.22) and (9.23) gives

$$\langle \psi_n | \psi_o \rangle = \delta_{no} \tag{9.25}$$

$$E^{(n)} = \langle \psi_{n-1} | V_1 \psi_o \rangle \tag{9.26}$$

provided the energy level is not degenerate.

If the zero-order level under consideration is g-fold degenerate, the function F in (9.16) must be chosen as

$$F = \sum_{n=1}^{g} c_n F_n \tag{9.27}$$

where the functions F_n are solutions of (9.19).

Upon introducing (9.27) into (9.16) and the resulting equation into (9.22) it is found that the first-order splitting of the energy level is given by

$$\sum_{n=1}^{g} \{V_1^{mn} - E_1 T^{mn}\} c_n = 0; \; m=1,2,\ldots,g \tag{9.28}$$

where

$$V_1^{mn} = \langle F_m \phi | V_1 F_n \phi \rangle \tag{9.29a}$$

$$T^{mn} = \langle F_n \phi | F_n \phi \rangle \tag{9.29b}$$

In order to use the procedure in an algebraic way avoiding the explicit calculation of the wave function, it is necessary to generate a recurrence relationship from Eqs. (9.21) and (9.22) and the RSPT (Eq. (9.24)). To this end we choose a set of functions

$$G = \{f_s; s=1,2,...\} \tag{9.30}$$

such that $\nabla s.\nabla f_s$, $f_s f_t$, Δf_s, $Q-V_o$ and V_1 can be written as a linear combination of functions belonging to G.

This set is obviously determined by the form of the functions V_o and V_1.

The procedure presented here will be applied later on (section 32) to compute large-order perturbation corrections for several states of the Zeeman effect in hydrogen.

iii) Bender-Wu Method

The algebraic method of Bender and Wu /48/ was devised to compute a large number of perturbation corrections for the quartic anharmonic oscillator model. In fact, the method applies to any anharmonic oscillator and, as the HPM, it allows one to obtain the perturbation corrections as analytical functions of the quantum number. For the sake of concreteness we consider the quartic anharmonic oscillator:

$$-\frac{1}{2}\psi_k'' + x^2\psi_k + \lambda x^4\psi_k = E_k\psi_k \; ; \; k=0,1,2,... \tag{9.31}$$

If ψ_k is written

$$\psi_k = u(x)v(x) \tag{9.32}$$

Eq. (9.31) becomes (the subscript k has been omitted to simplify the notation)

$$-\frac{1}{2}u'' + (x^2 + \lambda x^4 - E_k - \frac{1}{2}\frac{v''}{v})u - \frac{u'v'}{v} = 0 \tag{9.33}$$

when

$$v(x) = e^{-x^2/\sqrt{2}} \tag{9.34}$$

Eq. (9.33) reduces to

$$-\frac{1}{2}u'' + (\lambda x^4 - \varepsilon_k)u + 2^{\frac{1}{2}}u'x = 0 \tag{9.35}$$

where

$$\varepsilon_k = E_k - 2^{-\frac{1}{2}} \; ; \; \lim_{\lambda\to 0} \varepsilon_k = 2^{\frac{1}{2}}k \tag{9.36}$$

If u and ε_k in Eq. (9.35) are expanded as

$$u = \sum_{n=0}^{\infty} u_n(x)\lambda^n \; ; \; \varepsilon_k = \sum_{n=0}^{\infty} \varepsilon_k^{(n)}\lambda^n \tag{9.37}$$

then the coefficients are found to obey

$$-\frac{1}{2}u_n'' + x^4 u_{n-1} - \sum_{s=0}^{n} \varepsilon_k^{(s)} u_{n-s} + 2^{\frac{1}{2}}xu_n' = 0 \tag{9.38}$$

Next we expand the functions $u_n(x)$ in a Taylor series

$$u_n(x) = x^p \sum_{i=0}^{\infty} u_n^{(i)} x^{2i} \tag{9.39}$$

where the coefficients $u_n^{(i)}$ must be determined and p denotes the parity (p=0,1) of $\psi(x)$ (Cf. Theorem 1.2).

A straightforward calculation using Eqs. (9.38) and (9.39) leads to

$$-\frac{1}{2}(2r+p+2)(2r+p+1)u_n^{(r+1)} + u_{n-1}^{(r-2)} - \sum_{s=0}^{n} \varepsilon_k^{(s)} u_{n-s}^{(r)} + \\ + 2^{\frac{1}{2}}(2r+p)u_n^{(r)} = 0 \tag{9.40}$$

Since

$$\lim_{x\to 0} x^{-p}u(x) = a \neq 0 \tag{9.41}$$

it is concluded that

$$\sum_{n=0}^{\infty} u_n^{(o)}\lambda^n = a \quad \text{and} \quad u_n^{(o)} = a\delta_{no} \tag{9.42}$$

The two equations (9.40) and (9.42) provide a relation between the coefficients $u_n^{(m)}$ and the perturbation coefficients $\varepsilon_k^{(n)}$ (Cf Eq. (9.36)). It follows from (9.40) with r=0 and (9.42) that

$$a\varepsilon_k^{(n)} = \frac{-(p+1)(p+2)}{2} u_n^{(1)} + a2^{\frac{1}{2}p}\delta_{no} \tag{9.43}$$

Since a is an arbitrary constant we can choose it to be

$$a = \frac{1}{2}(p+1)(p+2) \tag{9.44}$$

so that Eq. (9.43) takes the simpler form

$$\varepsilon_k^{(n)} = -u_n^{(1)} + 2^{\frac{1}{2}p}\delta_{no} \tag{9.45}$$

In order to compute $\varepsilon_k^{(n)}$ we need to determine the coefficient $u_n^{(1)}$ by means of an appropriate recurrence. To this end, we introduce (9.45) into (9.40) and the resulting equation

$$-\frac{1}{2}(2r+p+2)(2r+p+1)u_n^{(r+1)} + 2^{\frac{1}{2}}(2r+p)u_n^{(r)} - u_{n-1}^{(r-2)} +$$

$$+ \sum_{s=0}^{n} u_s^{(1)} u_{n-s}^{(r)} - 2^{\frac{1}{2}p}u_n^{(r)} = 0 \tag{9.46}$$

can be written as

$$-\frac{1}{2}(2r+p+2)(2r+p+1)u_n^{(r+1)} + \{2^{\frac{1}{2}}(2r+p) - 2^{\frac{1}{2}p} + u_o^{(1)}\}u_n^{(r)} +$$

$$+ u_n^{(1)}u_o^{(r)} + \sum_{s=1}^{n-1} u_s^{(1)} u_{n-s}^{(r)} - u_{n-1}^{(r-2)} = 0 \tag{9.47}$$

We now introduce Eqs. (9.45) and (9.36) into (9.47) to obtain

$$-\frac{1}{2}(2r+p+2)(2r+p+1)u_n^{)r+1)} + 2^{\frac{1}{2}}(2r+p-k)u_n^{(r)} + u_n^{(1)}u_o^{(r)} +$$

$$+ \sum_{s=1}^{n-1} u_s^{(1)} u_{n-s}^{(r)} - u_{n-1}^{(r-2)} = 0 \tag{9.48}$$

A starting point is necessary to apply (9.48) in a recursive way. Such initial condition is obtained if one considers n=0 in Eq. (9.48) (from Eqs. (9.36) and (9.45) we get $u_o^{(1)} = 2^{\frac{1}{2}}(p-k)$) then

$$-\frac{1}{2}(2r+p+2)(2r+p+1)u_o^{(r+1)} + 2^{3/2}(r+p-k)u_o^{(r)} = 0 \tag{9.49}$$

which gives

$$u_o^{(r)} = 0 \quad \text{where } r > I_o = k-p \tag{9.50}$$

Let us suppose that a similar relation holds for other coefficients

$$u_{n-1}^{(r)} = 0 \quad \text{if} \quad r > I_{n-1} \geq I_o \tag{9.51}$$

where I_n is unknown at the moment. From Eq. (9.51) it is evident that

$$\text{if } r > I_{n-1} + 2 \quad \text{then} \quad u_{n-1}^{(r-2)} = u_o^{(r)} = \ldots = u_{n-1}^{(r)} = 0 \tag{9.52}$$

Besides, on substituting (9.52) in (9.48) we find that

$$-\frac{1}{2}(2r+p+2)(2r+p+1)u_n^{(r+1)} + 2^{\frac{1}{2}}(2r+p-k)u_n^{(r)} = 0 \tag{9.53}$$

which together with (9.51) gives

$$I_n = I_{n-1} + 2 \tag{9.54}$$

The condition (9.54) enables us to write the function u(x) as

$$u(x) = x^p \sum_{n=0}^{\infty} \sum_{r=0}^{k+2n-p} u_n^{(r)} x^{2i_\lambda n} \tag{9.55}$$

which yields the following starting point for the recurrence relation:

$$u_n^{(r)} = 0 \quad ; \quad r = k + 2n + 1 - p \tag{9.56}$$

The procedure is as follows: to calculate $\varepsilon_k^{(n)}$ we fix n,k,p and choose r = k+2n-p. Upon introducing (9.56) into (9.48), one has the coefficients $u_n^{(r)}$ in terms of the coefficients $u_m^{(s)}$, $s < r$, $m \leq n$. The next step is to set r=k+2n-p-1 in (9.48) and the procedure is repeated using the results of the precedent stage. The process finishes when r=1 and the RS coefficient is finally computed with Eq. (9.45).

Bender and Wu /48/ perfomed this calculation for the ground state (p = k=0; n-1,2,...) up to the order 75. However, this recursive method gives rise to considerable round off errors as pointed out by other authors /75/. When the perturbation order is less than 40 the RS coefficient is found to have 12 exact figures.

The method just outlined has also been applied to hydrogen in electric and magnetic fields /76,77/.

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CHAPTER IV

DIVERGENCE OF THE PERTURBATION SERIES

" Divergent series are the invention of the devil, and it is shameful to base on them any demonstration whatsoever".

N. H. Abel, 1828.

10. Divergence of the perturbation series

The RSPT (Chapter III) allows one to get an approximation to the eigenvalues (E_n) of a given Hamiltonian operator through a series in powers of a real parameter λ. However, the usefulness of the power series is conditioned by a fundamental question: its convergence.

As we know the computation of the RS coefficients is not a trivial task, but even in case of having them the use of the PT is not straightforward. The second problem to be solved is to sum the perturbation series, when it is divergent or has a finite convergence radius.

The determination of the convergence properties of the RS series makes up a whole chapter in Mathematical Physics and it has received a considerable attention from the beginning of 1970. Such convergence properties are basically determined by the properties of $E_n(\lambda)$ as an analytical function of λ. The singularities of $E_n(\lambda)$ in the λ plane determine the convergence radius of the Taylor series.

$$E_n(\lambda) = \sum_{m=0}^{\infty} E_n^{(m)} \lambda^m \quad . \tag{10.1}$$

Several years ago, Rellich |1,2| and Kato |3,4| gave a sufficient condition for a RS series to have a finite convergence radius. In what follows we show the main results and their applications because a rigorous proof is beyond the interest and level of this work.

The most important result we want to discuss is due to Rellich |1-4|

and is given in the theorem below:

Theorem 10.1

Let H_0 be a self-adjoint operator and V another linear operator such that $D_V \subseteq D_{H_0}$. If for every function $\phi \in D_{H_0}$ exist two real positive constants a and b <1 satisfying the condition

$$||V\phi|| \leq a\,||\phi|| + b\,||H_0\phi|| \tag{10.2}$$

then $H=H_0 + \lambda V$ is a self-adjoint operator $\forall\ \lambda \in R$ and its eigenvalues $E_n(\lambda)$ and eigenfunctions $\psi_n(\lambda)$ are analytical functions of λ in $\lambda=0$ and can be expanded in power series of λ with non-zero convergence radius.

We now present some examples of systems fulfilling theorem 10.1 for which the PT permits one to obtain convergent expansions for several observables of physical interest.

1) Periodic systems

For the sake of simplicity we consider a plane rigid rotator

$$H_0 = -\frac{d^2}{d\theta^2} \quad , \quad 0 \leq \theta \leq 2\pi \tag{10.3}$$

subjected to a nonsingular perturbation $V(\theta)$. However, the argument below applies to other rotational systems as well.

The eigenfunctions and eigenvalues of H_0 are

$$\phi_n = e^{in\phi} \tag{10.4a}$$

$$E_n = n^2 \qquad n = 0,1,\ldots \tag{10.4b}$$

since $|V(\theta)|$ is bounded in $(0,2\pi)$; i.e.

$$|V(\theta)| < V_0 \tag{10.5}$$

we have

$$||H_0\,\psi|| = \langle\psi|H_0^2|\psi\rangle^{\frac{1}{2}} \geq 0 \tag{10.6}$$

$$||V\psi|| = \langle\psi|V^2|\psi\rangle^{\frac{1}{2}} \leq V_0\,||\psi|| \tag{10.7}$$

from which it follows that the inequality (10.2) is satisfied for all $a>V_0$. It si therefore concluded that the perturbation series for the eigenfunctions and eigenvalues of H will have nonzero convergence radii.

As a particular case we consider

$$H = -\frac{d^2}{d\theta^2} + \lambda\cos\theta \tag{10.8}$$

whose eigenvalues $E_n(\lambda)$ have isolated double points on the complex λ plane. Every one of such singularities is a crossing point of a couple of eigenvalues /5/.

2) Systems with finite boundary conditions

Consider the Schrödinger equation

$$H\psi = E\psi \quad , \quad \psi(\pm x_0) = 0 \tag{10.9}$$

where

$$H = H_0 + \lambda V \quad , \quad H_0 = -\frac{d^2}{dx^2} \quad , \tag{10.10}$$

and V(x) is nonsingular in $[-x_0,x_0]$. The eigenvalues of H_0 are

$$E_n^{(0)} = (n+1)^2\,\pi^2 / (2x_0)^2 \quad , \; n = 0,1,\ldots \tag{10.11}$$

upon arguing as before we have

$$||H_0\psi|| \geq E_0^{(0)}\,||\psi|| \tag{10.12}$$

$$||V\psi|| \leq V_0\,||\psi|| \tag{10.13}$$

from which it follows that

$$a||\psi|| + b||H_0\psi|| \geq a||\psi|| + b\,E_0^{(0)}\,||\psi|| \tag{10.14}$$

will be larger than $||V\psi||$ provided that

$$a + bE_0^{(0)} \geq V_0$$

since a and b can be found that satisfies this last inequality we conclude that the RSPT series has a nonzero convergence radius.

3) Perturbed oscillators

We now consider perturbed oscillators of the form

$$H = H_0 + \lambda V(x) \quad , \quad H_0 = \frac{1}{2}\,(-\,d^2/dx^2 + x^2) \tag{10.15}$$

If

$$V(x) = x \tag{10.16}$$

then

$$||V\psi|| = <\psi|\,x^2|\psi>^{\frac{1}{2}} \leq <\psi\,|\,H_0|\psi>^{\frac{1}{2}} \leq <\psi\,|\,H_0^2|\psi>^{\frac{1}{4}} = ||H_0\psi||^{\frac{1}{2}} \tag{10.17}$$

from which it follows that a and b values can be found so that the inequality (10.2) is satisfied. This conclusion is in whole agreement with the fact that the eigenvalues of H are given by

$$H = (n + \tfrac{1}{2}) - \frac{\lambda^2}{2} \quad ; \tag{10.18}$$

i.e.the RSPT series reduces to two terms and has therefore infinite convergence radius.

In order to treat the perturbations

$$V_k(x) = x^{2k} \quad , \; k = 1,2,\ldots \tag{10.19}$$

it is convenient to consider the eigenfunctions and eigenvalues of H_0:

$$H_0\phi_n = (n + \tfrac{1}{2})\,\phi_n \tag{10.20}$$

when k=1 Eq. (8.7) leads us to

$$||V_1\phi_n|| = [\ \tfrac{3}{2}(n + 1/2)^2 + 3/8\ ]^{\frac{1}{2}} \tag{10.21}$$

since $||H_0\phi_n|| = (n + 1/2)^2$ and $||\phi_n|| = 1$ one cannot find two constants a and b satisfying (10.2). For this reason Theorem 10.1 does not give us any information in this case. However, a straightforward calculation shows that the eigenvalues of

$$H = H_0 + \lambda x^2 \tag{10.22}$$

are

$$E_n(\lambda) = (n + \tfrac{1}{2})\ (1 + \lambda 2\ )^{\frac{1}{2}}\ \ (1+2\lambda)^{1/2} \tag{10.23}$$

which exhibit a branch point at $\lambda=-1/2$. Therefore the RSPT converges for all $|\lambda| < \frac{1}{2}$.

When $k>1$ the potentials $V_k(x)$ are more singular at finity than $V_1(x)$ and Theorem 10.1 is not satisfied. Besides, the analytic properties of $E_n(\lambda)$ are not so simple as in the case k=1 and will therefore be discussed later on.

There exists a number of systems of great interest in Physical Chemistry which Theorem 10.1 predicts a convergent RS power series. These systems are embodied in the following theorem due to Kato |3,4|:

Theorem 10.2

> According to Theorem 10.1 the RSPT series will have nonzero convergence radius for a partition of the electrostatic Hamiltonian H
>
> $$H = H_0 + \lambda V \tag{10.24}$$
>
> of a molecule, atom or infinite crystal, provided that V has no stronger singularity than that corresponding to the pole of the Coulombic potential.

This Theorem has a paramount importance in Chemistry, so we deem it

appropriate to make some comments on it. Let us remark that the theorem assures us that considering the electron repulsions as a perturbation λV, the power series expansion in λ has nonzero convergence radius. This leads us to a known result: the power series in Z^{-1} for the electronic energy of atoms and molecules are convergent for $Z>Z_0$, with Z_0 finite /6/.

For diatomic molecules (we restrict ourselves to this case for the sake of simplicity) it is important to consider the perturbation potential V as depending on a parameter R (i.e. the internuclear distance). In order to make the discussion even simpler we choose Z=1 (i.e. unit nuclear charges) and the potential reads

$$V = \frac{1}{R} - \sum_{i=1}^{N} \left[|\bar{r}_i - \bar{R}| \right]^{-1} \qquad (10.25a)$$

where N is the number of electrons and $\bar{r}_i$ represents the coordinate of the i-th electron measured from a given coordinate origin, usually coincident with the position of one of the nuclei.

Let us now to re-write (10.25a)

$$V = \lambda \{ 1 - \sum_{i} \left[|1 - \bar{r}_i \lambda| \right]^{-1} \} \qquad (10.25b)$$

where $\lambda = R^{-1}$.

We see that λ appears within the potential itself, so that the hypothesis of Theorems 10.1 and 10.2 are not satisfied. In fact, it is well known that the series expansion in powers of R^{-1} possess zero convergence radius. We will discuss again this point later on.

There are a large number of systems with great physical importance that do not obey the Kato and Rellich theorems and they give rise to perturbation series with null convergence radius, that is to say, Taylor expansions that do not represent the function in any region of the complex plane λ. Finding out reasons of such divergences is one of the main problems in PT.

Ref./7/ is very valuable as a complete review on the subject and its applications before the discovery of the above mentioned reasons. The first exhaustive works on RS perturbations series with zero convergence

radius were made independently and from quite different viewpoints by Bender and Wu /8/ and Simon /9/ on the basis of the anharmonic oscillator model:

$$H = p^2 + x^2 + \lambda x^{2k} = -\frac{d^2}{dx^2} + x^2 + \lambda x^{2k} \qquad (10.26)$$

in particular for the quartic anharmonic oscillator (k=2).

As commented before, the model (10.26) has an utmost importance in Physics and Chemistry and especially interesting is the connection between this system and some field theories (see Appendix C). This particular problem originated the early study of the divergences in PT. The relevance of such study in PT is peculiarly noteworthy when one takes into account that usually some approximation method is the only way to obtain information in field theory, since it is impossible to make the calculation of matrix elements required by the VM or any other non-perturbative technique.

The fact that the RSPT gives rise to a power series with zero convergence radius implies two issues:

i) The eigenvalue E_n is not an analytical function in $\lambda=0$;
ii) The RS coefficients satisfy

$$\lim_{n\to\infty} |E_n^{(m+1)}/E_n^{(m)}| = \infty$$

We devote the remaining of this paragraph to discuss briefly the first point, while the second property will be analysed in the next paragraph.

Several authors have tried to give simple and intuitive explanations for the divergence of the RSP series for the eigenvalues of (10.26). Among them, we can mention the analysis made by Hioe et al /10-12/. The argument is as follows: the operator (10.26) in the momentum repesentation reads

$$\tilde{H} = p^2 - \frac{d^2}{dp^2} + \lambda \frac{d^{2k}}{dp^{2k}} \qquad (10.27)$$

In this case, the Schrödinger equation becomes the Navier-Stokes

equation for turbulent fluids. Then, the PT generates a power series expansion in λ, where the perturbation is that term with the derivative of highest order.

It is a well-known mathematical result that such expansion is divergent /10-12/. Obviously, this reasoning, although valid, does not explain the nature of the singularities responsible for such behavior.

Another argument used frequently to determine whether the RS expansion has a zero convergence radius is the so-called "change-of-sign-argument" This proposition was originally introduced by Dyson /13/ to explain the divergence of the power series for the electronic charge appearing in Quantum Electrodynamics. Later on, such explanation was critically reexamined by Killingbeck /14/, and then this subject stirred up a significant controversy about its interpretation and justification /15-19/.

In short, the basic idea is as follows: if the power series converges in a disc of radius $|\lambda_0|$ around the origin; then the series converges for positive and negative λ values provided $|\lambda| < |\lambda_0|$. However, when $\lambda<0$ the anharmonic oscillator does not hold any bound state. For this reason the convergence radius must be zero.

The conclusions derived from the change of sign argument should be taken with care /16,18,19/. The precedent argument assumes implicitly that the RSPT should approach something with a physical meaning, such as the energy of a bound state. But this is not necessarily so, and such an assuption has originated an apparent conceptual confusion /16, 13,19/, just recently cleared up. As a general rule, we can assert that the regular perturbations /4/ (i.e. those satisfying Theorems 10.1 and 10.2) converge to bound states, which is the sense usually asigned to the convergence towards physically meaningful quantities. In a similar way, those asymptotyc divergent perturbations (i.e. expansions with zero convergence radius) usually converge to the real part of the poles of the resolvent for the eigenvalue problems, although it is not through a simple term by term addition. Then, the perturbation series for those systems having singularities at $\lambda=0$ have some meaning for positive and negative values of λ. The main difference lies on the fact that in the first case the RSPT converges to a bound state by way of some appropriate method of sum, and in the second case to the real part of the system resonances.

So, we can assert a central conclusion which is of vital relevance in

what follows: the RSPT makes up an algorithm to derive a regular or asymptotyc power series, which when summed with a suitable method yields a quantity with a well defined physical meaning.

Let us recall here that the essential issue about the reason of non-analyticity of $E_n(\lambda)$ at $\lambda=0$ is not disclosed at all by the precedent discussion and the criteria presented before have just a certain predictive value with regard to obtaining or not power series with zero convergence radius.

The detailed explanation of the deep reasons of the divergence requires to know the analytic structure of $E_n(\lambda)$ in the plane. Naturally this is not a very simple matter, and it has been carried out thoroughly for a few eigenvalue problems.

The first system analysed was the quartic anharmonic oscillator /8,9/ and we sum up here the most relevant results:

i) The energy $E_n(\lambda)$ has a periodicity of 6π in $\arg(\lambda)$, i.e. when one turns over $\arg(\lambda)$ from 0 to 6π, the real eigenvalues are recovered for Re $\lambda>0$.

ii) For $\arg(\lambda) \simeq \frac{3\pi}{2}$ and $\frac{9\pi}{2}$ (asymptotic phase) there exist complex conjugated branch points linked by an arc-like branch line (see Fig. 4.1.)

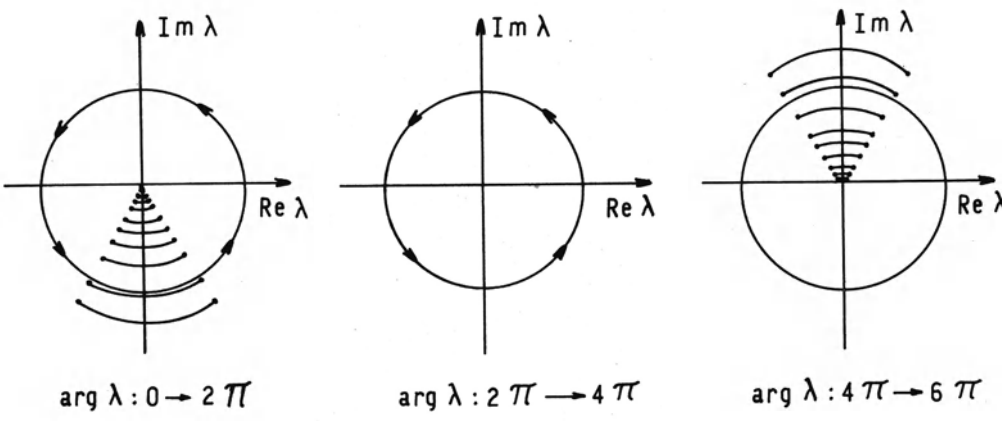

Fig.4.1: Simplified sketch of the $E(\lambda)$ structure (eigenvalue of the quartic anharmonic oscillator) for several sheets of the complex plane λ. Branch point singularities are denoted.

iii) Each pair of branch points (λ_b) corresponds to a crossing point between a pair of eigenvalues as

$$E_n(\lambda_b^{(n)}) = E_{n+1}(\lambda_b^{(n)}) \quad ; \quad n=0,1,2,... \tag{10.28}$$

The location of the singularities for the quartic anharmonic oscillator has been calculated by Shanley (P.E. Shanley Phys. Lett. A 117 (1986) 161). The results confirm rigorously some conjectures proposed by Bender and Wu /8/.

These branch points are unique, in the sense that every value only crosses the adjacent one.

iv) The sequence of branch points tends to an accumulation point at the origin $\lambda=0$ (see Fig. 4.1), so that $E_n(\lambda)$ has there a non-isolated singularity. Let us remark that this situation is more complicated than the isolated singularity which gives rise to a finite convergence radius for k=1. (Eq. (10.23)).

All these results remain qualitatively unchanged with respect to the anharmoniticity degree (k=2,3,...) /20/ and the number of terms in the perturbation potential /21/.

Katriel /22/ has proposed a differet alternative to analyse the analytic properties of $E_n(\lambda)$ regarding those viewpoints given by Bender and Wu/8/ and Simon /9/. The discussion presented in this paragraph has intended to give an overview of regular and asymptotyc RSP series and to analyse briefly the reasons of the divergence in a perturbation series.

It remains yet as an open question the way such a divergence reveals itself in the RS coefficients i.e. the rate of divergence of the power series. This poins is examined in detail in the next section.

11. Mathematical Methods to study the Asymptotic Behaviour of the RS coefficients

Let $E(\lambda)$ be an arbitrary function which can be expanded in a Taylor series

$$E(\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n \qquad (11.1)$$

At the moment we do not make any assuption about the convergence properties of (11.1). Our interest is to compute $E^{(n)}$, $n>> 1$, for the functions $E(\lambda)$ satisfying some specific properties.

The convergence radius R of (11.1) can be determined from the D'Alembert theorem:

$$\lim_{n\to\infty} |E^{(n+1)}| / |E^{(n)}| = R^{-1} \quad ; R \geq 0 \qquad (11.2a)$$

whenever this limit exists.

Another way to compute R is through the Cauchy-Hadamard theorem:

$$\sup \lim_{n\to\infty} |E^{(n)}|^{1/n} = R^{-1} \qquad (11.2b)$$

where Eq. (11.2b) denotes the superior limit of the sequence of positive numbers $|E^{(1)}|^{\frac{1}{2}}$, $|E^{(2)}|^{\frac{1}{2}}$,... . These theorems make evident the fundamental importance of the asymptotyc behaviour of $E^{(n)}$, $n>> 1$.

The aim of this section is to determine such behaviour for a wide class of functions, including those with R=0. According to our previous discussion in 10, these functions are of interest in Physics and Chemistry.

In the following we show a very useful relationship, which later on will allow us to compute $E^{(n)}$. Such relationship is the so-called "dispersion relation" and has been presented by several authors /9,23,24/ from quite different viewpoints. Here we introduce an alternative approximation which has some advantages:

Definition I: The power series (11.1) is asymptotic if for every integer m the condition

$$\lim_{|\lambda|\to 0} \{\lambda^{-m}(E(\lambda) - \sum_{i=0}^{m} E^{(i)} \lambda^i)\} = 0 \qquad (11.3)$$

is satisfied.

In agreement with (11.3), an asymptotic divergent (i.e. R=0) power series possess the following characteristic properties:

i) For a fixed number of terms m, the error diminishes monotonously as λ becomes smaller.

ii) For $|\lambda|<1$ the error diminishes at the beginning as m increases, then remains stationary and finally increases.

The asymptotic series can only give an acceptable approach to $E(\lambda)$ if both $|\lambda|$ and the number of terms in the sum are small enough.

Now let us consider a function $E(\lambda)$ fulfilling the following conditions:

i) $E(\lambda)$ is analytic for $\theta < \pi$, where $\lambda = |\lambda| e^{i\theta}$;

ii) $E(\lambda)$ is asymptotic (Eq. (11.3); and

$$\text{iii)} \lim_{|\lambda| \to \infty} E(\lambda) = 0 \qquad (11.4)$$

The discussion below also applies to functions that do not obey (11.4). For instance, if

$$\lim_{|\lambda| \to \infty} |\lambda|^{-\beta} E(\lambda) = e_0 \quad , \quad \beta > 0 \qquad (11.5)$$

we can define a new function

$$E'(\lambda) = \lambda^{-s} \{ E(\lambda) - \sum_{n=0}^{s} E^{(n)} \lambda^n \} \quad , \quad \beta < s < \beta + 1 \qquad (11.6)$$

which not only satisfies (11.4) but also gives rise to a power series expansion with the same asymptotic behaviour.

Let λ be a point in the complex plane where E is analytic. Taking the integration path C in the complex plane as shown in figure 4.2

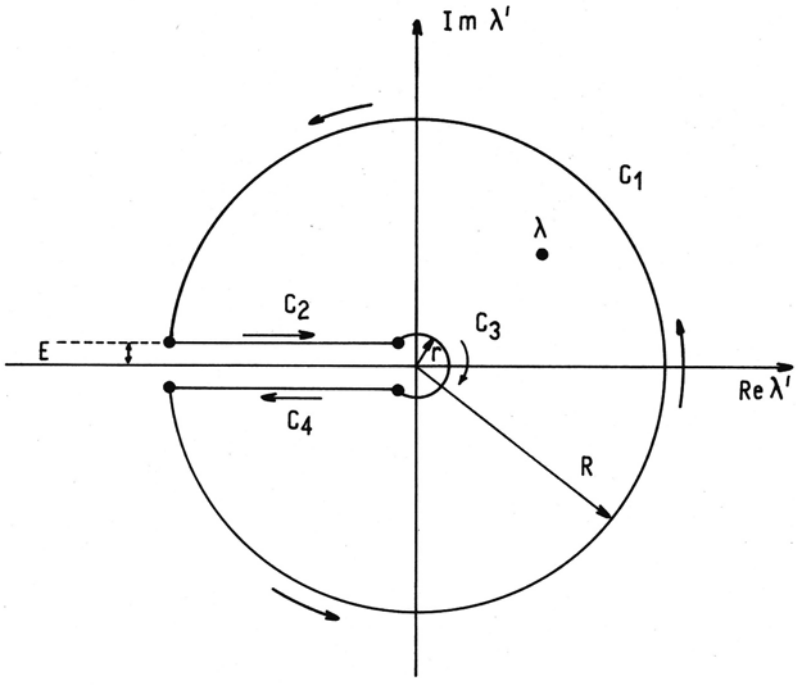

Fig. 4.2: Integration path for $E(\lambda)$ in the complex plane λ.

the Cauchy theorem assures that

$$E(\lambda) = \frac{1}{2\pi i} \oint_c \frac{E(\lambda')}{\lambda' - \lambda} d\lambda' \quad ; \quad c = \bigcup_{n=1}^{4} c_n \tag{11.7}$$

where c is a Jordan curve. Let us note that c does not cut the negative real axis, where the function is not analytic.

The condition (11.4) leads to

$$\lim_{R \to \infty} \int_{c_1} \frac{E(\lambda')}{\lambda' - \lambda} d\lambda' = 0 \tag{11.8}$$

Furthermore, since

$$\lim_{r\to 0} \int_{C_3} \frac{E(\lambda')}{\lambda' - \lambda}\, d\lambda' = 0 \tag{11.9}$$

we have finally that

$$\lim_{\substack{r\to 0\\ R\to\infty}} \oint_C \frac{E(\lambda')}{\lambda' - \lambda}\, d\lambda' = \lim_{\varepsilon\to 0} \int_{-\infty}^{0} \frac{D(\lambda')}{\lambda' - \lambda}\, d\lambda' \tag{11.10a}$$

where

$$D(\lambda') = \frac{1}{2\pi i}\{E(\lambda' + i\varepsilon) - E(\lambda' - i\varepsilon)\} = \frac{\mathrm{Im}E(\lambda' + i\varepsilon)}{\pi} \tag{11.10b}$$

If (11.10b) is introduced into (11.10a) we find the expression for $E(\lambda)$ as a generating function for a Stieltjes series /24/

$$E(\lambda) = \frac{1}{\pi}\int_{-\infty}^{0} \frac{\mathrm{Im}E(\lambda')}{\lambda' - \lambda}\, d\lambda' = \frac{1}{\pi}\int_{0}^{\infty} \frac{\{\mathrm{Im}E(-1/y)/y\}}{1 + \lambda y}\, dy \tag{11.11}$$

Upon expanding the integrand of (11.11) in a power series of λ

$$\int_{-\infty}^{0} \frac{\mathrm{Im}\,E(\lambda')}{\lambda' - \lambda}\, d\lambda' = \int_{-\infty}^{0} \frac{1}{\lambda'} \mathrm{Im}E(\lambda')\, (1 - \frac{\lambda}{\lambda'})^{-1}\, d\lambda' =$$

$$= \sum_{n=0}^{\infty} \lambda^n \{ \int_{-\infty}^{0} \lambda'^{-n-1}\, \mathrm{Im}E(\lambda')\, d\lambda' \} \tag{11.12}$$

and comparing this result with (11.1) we obtain the desired dispersion relation

$$E^{(n)} = \frac{1}{\pi} \int_{-\infty}^{0} \frac{\mathrm{Im}E(\lambda)}{\lambda^{n+1}}\, d\lambda \tag{11.13}$$

Eq.(11.13) tells us that the n-th coefficient in the Taylor expansion can be computed fron the knowledge of the imaginary part of E, analytically continued into the complex plane with $|\arg(\lambda) < \pi$. In other words, the coefficients $E^{(n)}$ are related to the discontinuity of $E(\lambda)$

through a cut in the Riemann surface.

There are several techniques to obtain the imaginary part of a function E with the above mentioned properties. These procedures have been developed recently and they have provided asymptotic form of the expansion coefficients $E^{(n)}$ (n>> 1) number of models of interest in Physics and Chemistry.

In this section we restrict ourselves to discuss two particular techniques and models of relevance for our present purposes, but they are really representative of the procedures applied to study other systems. In the following we present the results in a detailed manner fo the sake of clearness and to be useful from the pedagogical point of view.

Let us consider the integral (11.14) which is a function whose expansion as a power series in λ has a zero convergence radius:

$$E(\lambda) = \pi^{-\frac{1}{2}} \int_{-\infty}^{+\infty} e^{-(x^2 + \lambda x^4)}\, dx \qquad (11.14)$$

The integral (11.14) although apparently simple, has not an analytic expression as a function of λ and possess a marked interest in several Physics fields. For example, $E(\lambda)$ represents a zero-dimensional model in Field Theory for a Lagrangian with interaction ϕ^4 /25/, and it has been studied as an elementary test of different approximations /23,26-30/. Besides, (11.14) stands for the classic partition function of a quartic anharmonic oscillator, and so it has been used in Statistical Mechanics /31/. Here, we consider $E(\lambda)$ as an illustrative example, since its simplicity allows one to perform the necessary computation in a closed and rigorous way.

It is quite straightforward to verify that (11.4) is not analytic at the origin because the integral does not exist for $\lambda < 0$. Then, we know that the formal Taylor series for $E(\lambda)$ about $\lambda = 0$ has a null convergence radius.

In order to get some additional information about $E(\lambda)$ we must study its structure as a function depending on a complex variable. This function, the same as those to be studied later on, has two types of singularities:

i) Those due to the multivalued nature of the function which will be

termed "trivial" and can be determined through the dilatation relations. They are taken into account in the dispersion relation (11.13) to obtain the asymptotic behavior of the coefficients $E^{(n)}$.

ii) Those singularities called "essential" that determine the analyticity domain of $E(\lambda)$ and which are responsible for the divergence of the power series of λ around $\lambda = 0$.

The first kind of singularity is easily found. In fact, the change of variable $x = \lambda^{-\frac{1}{4}} y$ in Eq.(11.14) gives

$$E(\lambda) = \lambda^{-\frac{1}{4}} \pi^{-\frac{1}{2}} \int_{-\infty}^{+\infty} e^{-(y^4 + \lambda^{-\frac{1}{2}} y^2)} dy \qquad (11.15)$$

The dominant factor $\lambda^{-\frac{1}{4}}$ denotes that the Riemann surface consist of four sheets. That is to say, it is necessary to turn four times around the origin to get the initial value of the function. Consequently, the functions has cuts in the complex plane but it is analytic for $|\arg(\lambda)| < \pi$, as required by Eq.(11.13).

In order to study the analyticity of $E(\lambda)$ in the complex plane, we consider:

$$\lambda = |\lambda| e^{i\theta} \quad ; \quad |\lambda| > 0 \qquad (11.16a)$$

$$x = |x| e^{i\alpha} \quad ; \quad |x| > 0 \qquad (11.16b)$$

The substitutions (11.16a) and (11.16b) into $x^2 + \lambda x^4$ gives

$$x^2 + \lambda x^4 = |x|^2 e^{2i\alpha} + |\lambda| |x|^4 e^{4i\alpha + \theta i} \qquad (11.16c)$$

Then, if the integral (11.14) exists(i.e. its real part is finite) the following conditions must be fulfilled:

$$\mathrm{Re}\{e^{4i\alpha + \theta i}\} \geq 0 \qquad (11.17a)$$

$$\mathrm{Re}\{e^{2i\alpha}\} \geq 0 \qquad (11.17b)$$

From (11.17b) it follows that

$$\cos 2\alpha > 0 \text{ , then } -\pi < 4\alpha < \pi \text{ .} \qquad (11.18a)$$

In a similar way we get from (11.17b) that

$$\cos(4\alpha + \theta) > 0 \quad , \text{ then } \quad -\frac{\pi}{2} - 4\alpha < \theta < \frac{\pi}{2} - 4\alpha \tag{11.18b}$$

In order to obtain (11.18) we have restricted ourselves to the first sheet of the Riemann plane. Introducing (11.18a) in (11.18b) we deduce the domain of λ where $E(\lambda)$ is analytic:

$$-\frac{3\pi}{2} < \theta < \frac{3\pi}{2} \quad , \text{ then } \quad |\arg(\lambda)| < \frac{3\pi}{2} \tag{11.19}$$

The last result fixs the domain of λ where there exists a formal λ-power series expansion for $E(\lambda)$.

Nothing has yet been said about the singularities that make $E(\lambda)$ non-analytic in $\lambda=0$. It can be proved that the origin is an accumulative point of branch-point singularities (c.f. the discussion in §.10 for the anharmonic oscillator model).

Let us study some methods to obtain the RS coefficients for $E(\lambda)$. In the present case they can be simply obtained as follows

$$E(\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n \quad ; \quad E^{(n)} = 2\pi^{-\frac{1}{2}} \frac{(-1)^n}{n!} \int_0^{\infty} x^{4n} e^{-x^2} dx \tag{11.20}$$

Then

$$E^{(n)} = \pi^{-\frac{1}{2}} \frac{(-1)^n}{n!} \Gamma(2n + \tfrac{1}{2}) \tag{11.21a}$$

which according to the Stirling approximation behaves

$$E^{(n)} \cong \pi^{-1} \frac{(-4)^n}{2^{\frac{1}{2}}} (n-1)! \tag{11.21b}$$

when $n >> 1$.

We are interested in calculating $E^{(n)}$, $n>> 1$ approximately by general procedures. In this spirit, we show here two different approximations

Method I: A simple way to compute (11.20) in an approximate manner is by means of the saddle point, or steepest descent method, which is presented in a detailed form in the Appendix D.

Since the integral (11.20) can be written as

$$\int_0^\infty e^{-x^2} x^{4n} dx = \int_0^\infty e^{f(x)} dx \quad ; \quad f(x) = 4n \ln x - x^2 \tag{11.22}$$

it can be approximately computed by finding the largest contribution of the integrand.

We have

$$f'(x_0) = 0 \quad ; \quad x_0 = (2n)^{\frac{1}{2}} \tag{11.23}$$

which is a maximum because

$$f''(x_0) = -4 \tag{11.24}$$

From (11.23) and (11.24) we can expand $f(x)$ around x_0 in a Taylor series up to the second order

$$f(x) = f(x_0) - 2(x - x_0)^2 + \ldots \; ; \; f(x_0) = 2n \ln(2n) - 2n \tag{11.25}$$

and then substitute this result into (11.22) to obtain

$$\begin{aligned} &\int_0^\infty e^{f(x)} dx \simeq e^{f(x_0)} \int_0^\infty e^{-2(x-x_0)} dx = \\ &= e^{f(x_0)} \int_{-x_0}^\infty e^{-2y^2} dy \simeq 2e^{f(x_0)} \int_0^\infty e^{-2y^2} dy \end{aligned} \tag{11.26}$$

In (11.26), we have considered that $x_0 >> 1$. The substitution of (11.25) in (11.26) accomphishes the calculation

$$E^{(n)} \simeq 4\pi^{-\frac{1}{2}} \frac{(-1)^n}{n!} e^{f(x_0)} \int_0^\infty e^{-2y^2} dy - \frac{(-4)^n}{2^{\frac{1}{2}}\pi} (n-1)!$$

This procedure to determine $E^{(n)}$, $n >> 1$, is quite simple and obviously it can only be performed just in some particular cases.

Method II: We apply here the dispersion relation (11.13). Naturally, we must calculate $\mathrm{Im}\, E(\lambda)$.

The method to be followed is due to Zinn-Justin /23/ and is based on the fact that Eq.(11.13) contains the imaginary part of E along the axis

Re $\lambda<0$ where the function $E(\lambda)$ diverges. Then, we define the parameter

$$\lambda = -g = g\, e^{\pm i\pi} \quad ; \; g > 0 \tag{11.27}$$

and continue x into the complex plane according to (11.16b) so that

$$x^4 = g|x|^4\, e^{4i\alpha \pm i\pi} \tag{11.28}$$

In order to determine $\mathrm{Im}E(\lambda)$ it is necessary to compute $E(\lambda + i.0)$ and $E(\lambda - i.0)$ for $\lambda<0$. To this end we use the definition (11.14) with x-complex. Eq.(11.28) helps us to choose the appropriate paths of integration. In fact, first we set $4i\alpha \pm i\pi=0$ and

$$\alpha_{\pm} = \mp \frac{\pi}{4} \quad ; \; \alpha_- = \alpha_-(\lambda \to g\, e^{i\pi}); \; \alpha_+ = \alpha_+(\lambda \to g e^{-i\pi}) \tag{11.29}$$

Then, the integration paths are

$$C_+ : x = |x|\, e^{-i\pi/4} \tag{11.30a}$$

$$c_- : x = |x|\, e^{i\pi/4} \tag{11.30b}$$

as shown in Fig.4.3

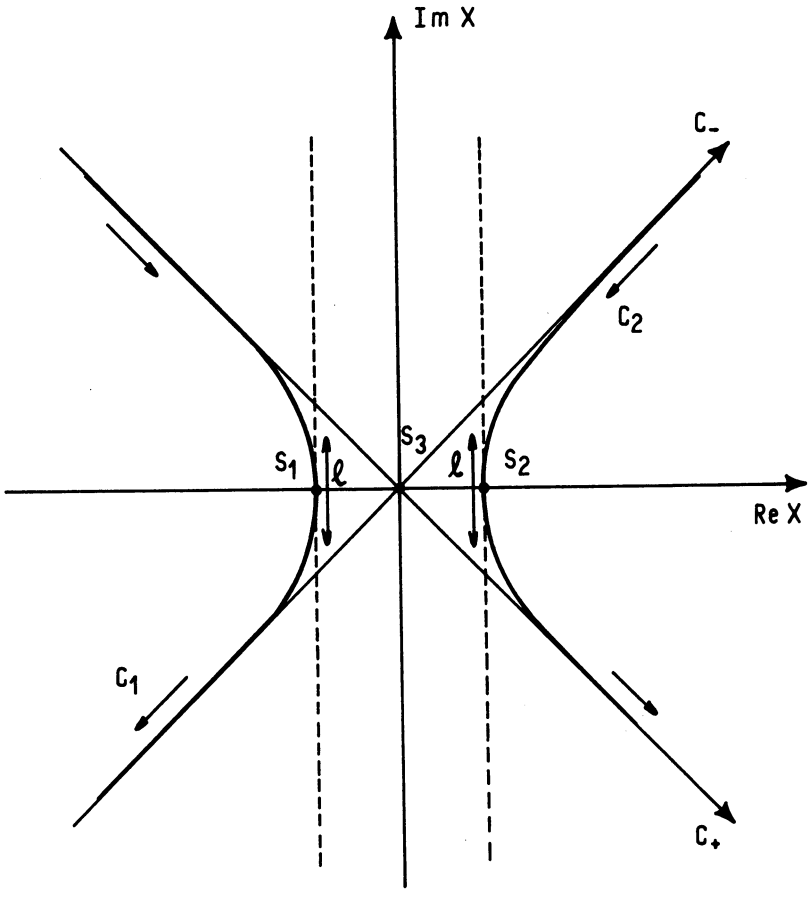

Fig. 4.3: Integration path in the x complex plane to compute ImE(λ) for the integral (11.14).

The notation $c_{\pm}$ denotes the location with respect to the cut in λ (see Fig. 4.2): c_+ and c_- correspond to the second and third quadrants, respectively. Hence,

$$E(\lambda + i.0) = \pi^{-\frac{1}{2}} \int_{c_+} e^{-(x^2 + \lambda x^4)} dx \qquad (11.31a)$$

$$E(\lambda - i.0) = \pi^{-\frac{1}{2}} \int_{c_-} e^{-(x^2 + \lambda x^4)} dx \qquad (11.31b)$$

Now, we apply the saddle point method to compute the integrals (11.31). The analysis of the function $f(x) = -(x^2 + \lambda x^4)$ allows us to find three stationary points

$$f'(x_0) = 0 \qquad (11.32a)$$

$$x_0: \begin{cases} s_1 = -(-2\lambda)^{-\frac{1}{2}} \\ s_3 = 0 \\ s_2 = (-2\lambda)^{-\frac{1}{2}} \end{cases} , \quad \lambda < 0 \qquad (11.32b)$$

with the following second derivatives

$$f''(s_1) = f''(s_2) = 4 \quad , \quad f''(s_3) = -2 \qquad (11.33)$$

Then, $f(x)$ has a maximun at the origin and two equidistant minima on the real x axis. On the basis of these results, $f(x)$ can be expanded in a Taylor series around the extrema:

$$f(x) = -x^2 \quad ; \quad x \simeq 0 = s_3 \qquad (11.34a)$$

$$f(x) = \frac{1}{4\lambda} + 2(x + (-2\lambda)^{-\frac{1}{2}})^2 \quad ; \quad x \simeq s_1 \qquad (11.34b)$$

$$f(x) = \frac{1}{4\lambda} + 2(x - (-2\lambda)^{-\frac{1}{2}})^2 \quad ; \quad x \simeq s_2 \qquad (11.34c)$$

Taking into account that from Eq.(11.31) ImE can be written

$$ImE = \frac{\pi^{-\frac{1}{2}}}{2i} \{ \int_{c_+} e^{-(x^2 + x^4)} dx - \int_{c_-} e^{-(x^2 + x^4)} dx \qquad (11.35)$$

then the contribution of s_3 in (11.35) is null when we apply the saddle point method. Therefore, there remains the contribution of s_1 and s_2 (which are different).

In order to compute them it is necessary to distort the integration so that they touch such poits as shown in Fig.4.3. (path C_1 and c_2). Hence, Eq. (11.35) can be rewritten as

$$\mathrm{ImE} = \frac{\pi^{-\frac{1}{2}}}{2i} \{ \int_{C_1} e^{-(x^2 + x^4)}\, dx + \int_{C_2} e^{-(x^2 + x^4)}\, dx \} \qquad (11.36)$$

The first integral is computed by means of (11.34b) and it is seen that there is only a significant contribution around s_1, so that (see Fig.4.3):

$$\int_{C_1} e^{f(x)} dx \simeq e^{\frac{1}{4}\lambda} \int_{C_1} e^{2(x + (-2\lambda)^{-\frac{1}{2}})^2}\, dx \simeq ie^{\frac{1}{4}\lambda} \int_{\ell/2}^{-\ell/2} e^{-2y^2}\, dy \simeq$$

$$\simeq -i\, e^{\frac{1}{4}\lambda} \int_{-\infty}^{+\infty} e^{-2y^2}\, dy = -i\, (\tfrac{\pi}{2})^{\frac{1}{2}} e^{\frac{1}{4}\lambda} \quad , \lambda \uparrow 0 \qquad (11.37)$$

In a similar way we have

$$\int_{C_2} e^{f(x)}\, dx \simeq -i\, (\tfrac{\pi}{2})^{\frac{1}{2}} e^{\frac{1}{4}\lambda} \qquad (11.38)$$

and finally we get the desired result (Eq.(11.36)):

$$\mathrm{ImE}(\lambda) = -2^{\frac{1}{2}} e^{\frac{1}{4}\lambda} \quad ; \qquad \lambda \uparrow 0 \qquad (11.39)$$

Since the largest contribution to the integral (11.13) comes from $\lambda \simeq 0$, we can obtain the desired result by introducing (11.39) into (11.13):

$$E^{(n)} = \frac{1}{\pi} \int_{-\infty}^{0} \frac{\mathrm{ImE}(\lambda)}{\lambda^{n+1}}\, d\lambda = -\frac{2^{-\frac{1}{2}}}{} \int_{-\infty}^{0} \frac{e^{\frac{1}{4}\lambda}}{\lambda^{n+1}}\, d\lambda =$$

$$= \frac{(-1)^n}{2^{\frac{1}{2}}\pi} \int_0^{\infty} y^{n-1}\, e^{-y/4}\, dy = \frac{(-4)^n}{2^{\frac{1}{2}}\pi} (n-1)! \qquad (11.40)$$

This result coincides with (11.21) and the computation is made with the help of Method I. The procedure described thus far is basically one of the most frequently employed up to now in order to study the asymptotic behavior of the perturbation coefficients when $n >> 1$. The method reveals the close connection between the asymptotic behavior and the

discontinuity of the function on the real negative axis of the λ plane. When applying the procedure to other problems, the main difficulty to overcome is to determine ImE. the Method II described above can be generalized to analyse other systems particularly interesting in field theory and quantum mechanics /32-35/. Brizin et al. applied it to different physical quantities within the context of the path integral /36/ and Zinn-Justin discussed the anharmonic oscillator model /23/.

The generalization made by these authors has been quite fruitful and exciting in several respects but it is not the only one. The first approximation to calculate the asymptotic behavior of $E^{(n)}$ has been due to Bender and Wu /8/ via semiclassical methods. From a different, more rigorous point of view, it was proved that Bender and Wu's results are totally correct /9/. The JWKB is certainly simpler than those procedures based on the path integral but it only applies to quantum-mechanical problems. We devote the remain of this paragraph to illustrate in detail the application of the JWKB to the study of the divergence of the RSPT for some anharmonic oscillators.

First of all, we need the following result:

Lemma 11.1 Let us consider the stationary 1D Schrödinger equation

$$-\psi'' + V(x)\psi = E\psi \tag{11.41}$$

Defining the quantum current density J(x) as /37/

$$J(x) = \frac{1}{2i}\{ \psi \psi'^* - \psi^*\psi' \} = Im\psi \psi'^* \tag{11.42}$$

we have

$$ImE = J(x) \Big/ \int_{-\infty}^{x} |\psi(x)|^2 dx' \tag{11.43}$$

Proof:

It is immediate from the consideration of Eq.(11.41) that

$$\psi^* \psi'' = (V - E) |\psi|^2 \tag{11.44a}$$

$$\psi \psi''^* = (V - E^*) |\psi|^2 \quad ; V = V^* \tag{11.44b}$$

and so

$$\Psi\,\Psi''^{*} - \Psi^{*}\,\Psi'' = \frac{d}{dx}\left(\Psi\,\Psi'^{*} - \Psi^{*}\,\Psi'\right) = |\Psi|^2 (E - E^{*}) =$$

$$= 2i\,\mathrm{Im}E\,|\Psi|^2 \qquad (11.45)$$

Finally, the integration of (11.45) gives us the desired result (11.43).

The Lemma 11.1 shifts the problem of determining ImE to the query of obtaining the current density J(x). The determination of J requires studying a problem of penetration through potential barriers, and for this reason we resort to the JWKB method presented in §.6.

Let us consider the anharmonic oscillator

$$H(Z,\lambda) = p^2 + Zx^2 + \lambda x^m \quad ; \; p^2 \; - \frac{d^2}{dx^2} \qquad (11.46)$$

and let $E(\lambda)$ be one of its eigenvalues. The dispersion relation (11.13) demands the computation of ImE for $\lambda \uparrow 0$, so that, taking into consideration Lemma 11.1, we must determine J for $\lambda \uparrow 0$. If $m > 2$ in (11.46), then for $\lambda > 0$ we have a problem without bound states, there is tunnelling through the barries, and $J \neq 0$. In what follows we consider some illustrative examples.

Example I: If m=3 in (11.43), there are no bound states since the potential is not bounded from below when $x \to -\infty$. Instead there are resonances ε which can be written as

$$\varepsilon = E + \frac{i}{2}\,\Gamma \qquad (11.47)$$

with E the resonance position and Γ the resonance width. It has been proved that (11.47) is an eigenvalue in some sheet of the complex plane of the Hamiltonian (11.46) analytically scaled /38/. The RSPT provides an asymptotic divergent power series for E (the real part of the resonance)/39/.

To compute $E^{(n)}$ we must have $J(\lambda \uparrow 0)$. The potential function for $\lambda > 0$ is shown in Fig. 4.4

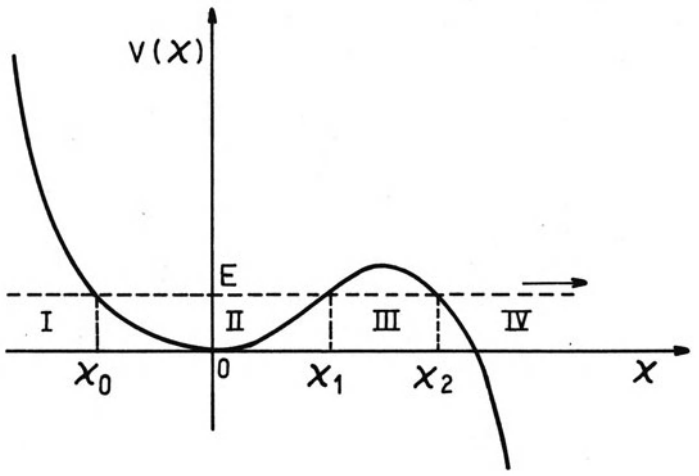

Fig. 4.4: Determination of the **RS** coefficients asymptotic behavior: resonances problem associated with the cubic anharmonic oscillator.

$$H = p^2 + V \quad ; \quad V = x^2 - gx^3 \quad ; \quad g = -\lambda > 0 \tag{11.48}$$

It is quite clear from Fig. 4.4 that J arises from tunneling towards zone IV. This state of affairs is the same as that discussed in §.6 and shown in Fig. 2.3. According to the results in §.6, J is given by (see Eq.(6.45)):

$$J = \mathrm{Im}\{\psi_{IV}(x)\ \psi'^{*}_{IV}\} = -\frac{3}{2\pi}\ |A_2|^2 \tag{11.49}$$

where A_2 is the coefficient for the asymptotic wave function in Zone III (Eq. (6.39)):

$$\psi_{III}(x) \to -e^{i\pi/6}\ (\frac{3}{2\pi q})^{\frac{1}{2}}\ A_2\ e^{\tau}\ e^{-|w'|} \tag{11.50}$$

$$\tau = \int_{x_1}^{x_2} (V(x) - E)^{\frac{1}{2}}\ dx \tag{11.51a}$$

$$|w'| = \int_{x_1}^{x} (V(x) - E)^{\frac{1}{2}}\ dx \quad ; \quad x_1 << x << x_2 \tag{11.51b}$$

The classical turning points x_1 and x_2 are shown in Fig. 4.4. To

obtain A_2 we proceed as follows: when $\lambda=0$ and $x\to\infty$ the function (11.50) must behave asymptotically as $\psi_n^{(0)}$, i.e. the zero -order eigenfunction

$$H(\lambda=0)\ \psi_n^{(0)} = E_n^{(0)}\ \psi_n^{(0)} \quad ; \quad E_n^{(0)} = 2n + 1 \quad ; \quad n=0,1,2,... \tag{11.52}$$

where n is the number of zeros of the wave function.

In order to obtain the asymptotic behavior of (11.50) as a function of x, we must know τ and w'. To this end we first compute the turning points:

$$x^2 - gx^3 - E = 0 \tag{11.53}$$

If $g \simeq 0$, then

$$x_0 \simeq -E^{\frac{1}{2}} \quad ; \quad x_1 \simeq E^{\frac{1}{2}} \tag{11.54a}$$

The third turning point is obtained by considering that $x_2 >> E^{\frac{1}{2}}$ when $g \to 0$:

$$x_2 \simeq 1/g \tag{11.54b}$$

The integral τ is computed by application of the method proposed in Ref. /38/ , i.e.

$$\tau \simeq \int_{E^{\frac{1}{2}}}^{1/g} (x^2 - gx^3 - E)^{\frac{1}{2}}\, dx = \tau_1 + \tau_2 \tag{11.55a}$$

$$\tau_1 = \int_{E^{\frac{1}{2}}}^{R} (x^2 - gx^3 - E)^{\frac{1}{2}}\, dx \tag{11.55b}$$

$$\tau_2 = \int_{R}^{1/g} (x^2 - gx^3 - E)^{\frac{1}{2}}\, dx \tag{11.55c}$$

where R satisfies the condition $E^{\frac{1}{2}} << R << 1/g$. When $g \to 0$ we have for the integral (11.55b):

$$\tau_1 \simeq \int_{E^{\frac{1}{2}}}^{R} (x^2 - E)^{\frac{1}{2}}\, dx = \frac{1}{2}\ \{\ x(x^2 - E)^{\frac{1}{2}} - E\ \ln(x + (x^2 - E)^{\frac{1}{2}})\}\ \Big|_{E^{\frac{1}{2}}}^{R} \simeq$$

$$\simeq \frac{1}{2}\ \{R^2 + E\ln\ [\frac{E^{\frac{1}{2}}}{2R}]\}\ - \frac{E}{4}\ + \ldots \quad ; \quad R >> E^{\frac{1}{2}} \tag{11.56}$$

To the purpose of computing (11.55c) it is suitable to re-write the integral as

$$\tau_2 = \int_R^{1/g} x\,(1 - gx)^{\frac{1}{2}}\,[1 - \frac{E}{(1 - gx)\,x^2}]^{\frac{1}{2}}\,dx \tag{11.57}$$

since $x >> E^{\frac{1}{2}}$, we know that

$$\frac{E}{(1 - gx)\,x^2} << 1 \tag{11.58}$$

On expanding the integrand of (11.57) up to the first order, we have

$$\tau_2 \simeq \int_R^{1/g} x(1 - gx)^{\frac{1}{2}}\,dx - \frac{E}{2}\int_R^{1/g} \frac{dx}{x\,(1 - gx)^{\frac{1}{2}}} \tag{11.59}$$

The first integral yields

$$\int_R^{1/g} x(1 - gx)^{\frac{1}{2}}\,dx = \frac{2}{15g^2}\,(2 + 3gR)\,(1 - gR)^{3/2} \simeq$$

$$\simeq \frac{4}{15g^2} - \frac{R^2}{2} + 0(g) \tag{11.60}$$

In a similar way we have /40/

$$\int_R^{1/g} \frac{dx}{x\,(1 - gx)^{\frac{1}{2}}} = -\ln\,[\frac{1 - (1 - gR)^{\frac{1}{2}}}{1 + (1 - gR)^{\frac{1}{2}}}] \simeq -\ln\,(\frac{gR}{4}) \tag{11.61}$$

The integral τ_2 follows from (11.59)-(11.61)

$$\tau_2 = \frac{4}{15g^2} - \frac{R^2}{2} + \frac{E}{2}\ln\,(gR/4) \tag{11.62}$$

so that

$$\tau \simeq \frac{4}{15g^2} + \frac{E}{2}\ln\,(\frac{gE^{\frac{1}{2}}}{8}) - \frac{E}{4} \tag{11.63}$$

It is worth noticing that the final result does not depend upon R. This fact is hardly surprising since such parameter is arbitrary.

When $g \to 0$ and $E << x << 1/g$, the computation of $|w'|$ yields in Eq. (11.56) up to the same number of terms as

$$|w'| \simeq \int_{E^{1/2}}^{x} (x^2 - E)^{1/2}\, dx = \frac{1}{2}\left\{ x^2 \left(1 - \frac{E}{x^2}\right)^{1/2} - \right.$$

$$\left. - E \ln \left(x + x \left(1 - \frac{E}{x^2}\right)^{1/2}\right) + E \ln E^{1/2} \right\} \simeq$$

$$\simeq \frac{1}{2}\left\{x^2 \left[1 - \frac{E}{2x^2}\right] - E \ln 2x + \frac{E}{2} \ln E \right\} =$$

$$= \frac{x^2}{2} - \frac{E}{2} \ln 2x + \frac{E}{4} (\ln E - 1) \qquad (11.64)$$

In order to determine the asymptotic behavior of (11.50) we must study $e^{-|w'|}$ for $x >> E^{1/2}$. Eqs. (11.64) and (11.52) allow us to obtain

$$e^{-|w'|} \simeq (2x)^{E/2}\, E^{-E/4}\, e^{E/4}\, e^{-x^2/2} =$$

$$= 2^{(n + 1/2)} \left\{\left[\frac{e}{2n + 1}\right]^{(n + 1/2)}\right\}^{1/2} x^{(n + 1/2)}\, e^{-x^2/2} \qquad (11.65)$$

which holds for all n values.

It seems to be necessary to point out that the result (11.65) does not depend on the anharmonic degree m of the Hamiltonian (11.46), because to obtain (11.65) we have started from (11.64) and the limit condition $g \to 0$. In this last equation there are just those terms corresponding to the harmonic oscillator since only the turning point at $x_I = E^{1/2}$ appears.

Considering that for $x >> x_1$, Eq. (11.51c) reduces to

$$q \simeq x \qquad (11.66)$$

we can easily express the asymptotic behavior ($g \to 0$, $x \to \infty$) of (11.50). In fact, the substitution of Eqs. (11.65) and (11.66) in Eq. (11.50) yields

$$\Psi_{III}(x) \to \{-e^{\tau} \; A_2 \; e^{i\pi/6} \; (\tfrac{3}{2\pi})^{\frac{1}{2}} \; [(\tfrac{2e}{n+\frac{1}{2}})^{(n+\frac{1}{2})^{\frac{1}{2}}}]\} x^n \; e^{-x^2/2} \qquad (11.67)$$

Then, it only remains to identify Eq.(11.67) with the asymptotic behavior of $\psi_n^{(0)}$ (Eq. (11.52)) in order to assure the correct behavior of the semiclassical wave function when $g \to 0$.

The asymptotic behavior of the normalized zero order wave function /37/:

$$\psi_n^{(0)} = (2^n \; n! \; \pi^{\frac{1}{2}})^{-\frac{1}{2}} \; H_n(x) \; e^{-x^2/2} \qquad (11.68a)$$

$$H_n(x) = (-1)^n \; e^{x^2} \; \frac{d^n}{dx^n} \; e^{-x^2} \qquad (11.68b)$$

is easily found to be

$$H_n(x) \to (-2)^n \; x^n \qquad (11.69a)$$

$$\psi_n^{(0)}(x) \to (-1)^n \; [\frac{2^n}{n! \; \pi^{\frac{1}{2}}}]^{\frac{1}{2}} \; x^n \; e^{-x^2/2} \qquad (11.69b)$$

Therefore, it follows from equating (11.69b) and (11.67) that A_2 is given by

$$A_2 = (-1)^{n+1} \; [\frac{2^n}{n!}]^{\frac{1}{2}} \; (\frac{4\pi}{9})^{\frac{1}{4}} \; [\frac{n+\frac{1}{2}}{2e}]^{(2n+1)/4} \; e^{-\tau} \; e^{-i\pi/6} \qquad (11.70)$$

and consequently

$$|A_2|^2 = \frac{(2\pi)^{\frac{1}{2}}}{3} \; \frac{1}{n!} \; [\frac{n+\frac{1}{2}}{e}]^{n+\frac{1}{2}} \; e^{-2\tau} \qquad (11.71)$$

$$J = -\frac{1}{(2\pi)^{\frac{1}{2}}} \frac{e^{-2\tau}}{n!} \left[\frac{n + \frac{1}{2}}{e}\right]^{(n + \frac{1}{2})} \tag{11.72}$$

It follows from the discussion above that (11.72) is a general tunnelling expression for any Hamiltonian of the form (11.46) when $\lambda \to 0$.

In order to determine ImE, it is just necessary to consider that

$$\int_{-\infty}^{x} |\psi|^2 \, dx' \simeq \int_{-\infty}^{+\infty} |\psi_n^{(0)}|^2 \, dx = 1 \quad , \qquad x >> 1 \tag{11.73}$$

from which we conclude that Eq.(11.72) represents ImE according with Lemma 11.1.

In particular, using (11.63) we have

$$e^{-2\tau} \simeq \left[\frac{g(2n + 1)^{\frac{1}{2}}}{8}\right]^{-(2n + 1)} e^{n + \frac{1}{2}} \, e^{-8/15g^2} \tag{11.74}$$

which when introduced into

$$\mathrm{Im}E(g) = -\frac{e^{-8/15g^2}}{(2\pi)^{\frac{1}{2}}} g^{-(2n + 1)} \frac{32^{n + \frac{1}{2}}}{n!} \; ; \quad g \to 0 \tag{11.75}$$

Making the appropriate change of variables, it is verified at once that Eq.(11.75) agrees with the result reported by Yaris et al. /38/. Now, we are able to calculate the asymptotic form of the k-th coefficient of the RS perturbation series by way of the dispersion relation (11.13). It is necessary to take into account that since ImE(g) has been computed for $g \to 0$ it is then convenient to re-write (11.13) in terms of $g=-\lambda$, i.e.:

$$E_n^{(k)} = \frac{(-1)^k}{} \int_0^{\infty} \frac{\mathrm{Im}E(g)}{g^{k + 1}} \, dg \tag{11.76}$$

If (11.75) is introduced into (11.77) we have

$$E_n^{(k)} \simeq -\frac{(-1)^k\, 32^{n+\frac{1}{2}}}{(2\pi^3)^{\frac{1}{2}}\, n!} \int_0^\infty e^{-8y^2/15}\, y^{k+2n}\, dy =$$

$$= \frac{(-1)^{k+1}\, 32^{n+\frac{1}{2}}}{(2\pi^3)^{\frac{1}{2}}\, 2(n!)} \left(\frac{15}{8}\right)^{(k+2n+1)/2} \Gamma\left(\frac{k+2n+1}{2}\right) \qquad (11.77)$$

The result for the lowest resonance n = 0 is

$$E_n^{(k)} \simeq (-1)^{k+1}\, \frac{2}{\pi^{3/2}} \left(\frac{15}{8}\right)^{(k+1)/2} \left[\frac{k}{2} - \frac{1}{2}\right]! \qquad (11.78)$$

where the following notation is used: $\Gamma(a+1) = a!$.

We deem it meaningful to point out that in order to calculate E(k), it is only necessary to calculate $\mathrm{Im}E(g)$ for $g \downarrow 0$. This contribution is dominant in the integral only if $k \gg 1$, so that our procedure gives us the asymptotic behavior of the coefficients $E_n^{(k)}$ for $k \gg 1$.

Example II: Now we consider the quartic anharmonic oscillator (i.e. m = 4 in Eq.(11.46)) which was the first system studied with regard to the asymptotic behavior of the RSPT. Krieger /41/ performed a primary simplified analysis, but the first complete results are due to Bender and Wu /8/ and Simon /9/. Here we apply the procedure followed in Example I, which is practically the same as that used in Ref. /42/. It is necessary to calculate the discontinuity of $E(\lambda)$ through the negative λ axis. In this region the potential function is

$$V(x) = x^2 - gx^4 \quad ; \quad g > 0 \qquad (11.79)$$

which is shown in Figure 4.5.

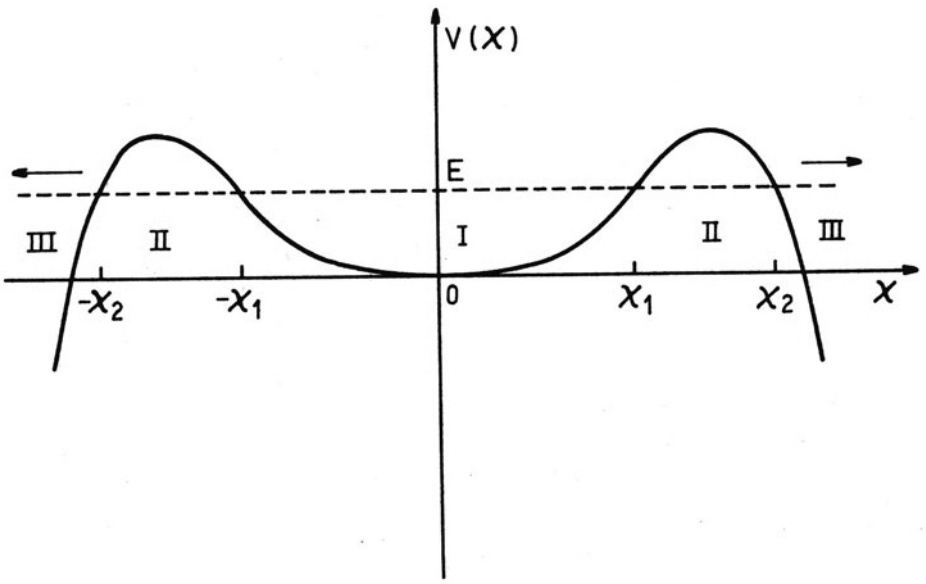

Fig. 4.5: Determination of the RS coefficients asymptotic behavior: resonances problem associated with the quartic anharmonic oscillator.

The potential is even and in this case there is tunneling towards zone IV. Obviously, the contribution to the probability current density in both zones is the same.

The procedure to be followed is the same as that described in Example I. If J denotes the flux through one of the barriers, then Lemma 11.1 and Eq.(11.73)allow us to write in this case

$$\mathrm{Im}\, E(\lambda) = 2\, J(\lambda) \tag{11.80}$$

where J is given by (11.72). Evidently, the main difference between both

problems rests upon the analytical form of τ.

The classical turning points for $g \to 0$ approximately are

$$x_1 \simeq E^{1/2} \quad ; \quad x_2 \simeq g^{-1/2} \tag{11.81}$$

as shown in Fig. 4.5. The computation of τ is straightforward and the results are

$$\tau = \tau_1 + \tau_2 \tag{11.82a}$$

$$\tau_1 = \int_{E^{1/2}}^{R} (x^2 - gx^4 - E)^{1/2}\, dx \tag{11.82b}$$

$$\tau_2 = \int_{R}^{g^{-1/2}} x(1-gx^2)^{1/2} \left|1 - \frac{E}{x^2(1-gx^2)}\right|^{1/2} dx$$

$$E^{1/2} << R << g^{-1/2} \tag{11.82c}$$

The result for (11.82b) when $g \to 0$ is given by Eq. (11.56). The second integral is

$$\tau_2 \simeq \int_{R}^{g^{-1/2}} x(1-gx^2)^{1/2}\, dx - \frac{E}{2} \int_{R}^{g^{-1/2}} \frac{dx}{x(1-gx^2)^{1/2}} \tag{11.83}$$

The two terms in (11.83) can be approximated by

$$\int_{R}^{g^{-1/2}} x(1-gx^2)^{1/2} dx = \frac{1}{3g} (1-gR^2)^{3/2} \simeq \frac{1}{3g} - \frac{R^2}{2} + O(g) \tag{11.84a}$$

$$\int_{R}^{g^{-1/2}} \frac{dx}{x(1-gx^2)^{1/2}} = \ln \left|\frac{1+(1-gR^2)^{1/2}}{Rg^{1/2}}\right| \simeq \ln \left|\frac{2}{Rg^{1/2}}\right| \tag{11.84b}$$

Introducing (11.84a) and (11.84b) into (11.83) and adding up (11.56) we have

$$\Gamma \simeq \frac{1}{3g} + \frac{E}{4} \ln\left(\frac{gE}{16}\right) - \frac{E}{4} + \ldots \tag{11.85}$$

The insertion of (11.85) into (11.72) gives for (11.80) the result

$$\mathrm{Im}E(g) = -\left(\frac{2}{\pi}\right)^{1/2} \frac{1}{n!} \left(\frac{8}{g}\right)^{n+1/2} e^{-2/3g} \tag{11.86}$$

The asymptotic form of the RSPT coefficients in obtained by introducing (11.86) into (11.76), which yields

$$E_n^{(k)} \simeq (-1)^{k+1} \left(\frac{2}{\pi}\right)^{1/2} \frac{8^{n+1/2}}{n!} \int_0^\infty y^{k+n-1/2} e^{-2y/3}\, dy \simeq$$

$$\simeq 2\,(-1)^{k+1} \left(\frac{6}{\pi}\right)^{1/2} \frac{8^n}{n!} \left(\frac{3}{2}\right)^{k+n} \Gamma(n+k+1/2) \tag{11.87}$$

Once again, after an appropriate change of units we are led to the result published in Refs. /8,42/. Particularly importat for the rest of the book is the analytical asymptotic form of the RS coefficients for the ground state of the quartic anharmonic oscillator (n = 0):

$$E_0^{(k)} \simeq -2 \left(\frac{6}{\pi}\right)^{1/2} \left(-\frac{3}{2}\right)^k (k-1/2)! \tag{11.88}$$

The analysis presented in this section is especially relevant to understand the properties of the perturbation expansions. Let us remark that in the examples I and II and the function (11.4) analysed previously we have found power series with a zero convergence radius and coefficients increasing approximately as the factorial of the perturbation order. This sort of situation is quite general and the majority of perturbation series arising in eigenvalue problems of interest in Physical Chemistry, field theory, statistical mechanics, etc. have this feature.

It is not our aim to find the asymptotic form of the RS coefficients for mere awkward problems, since the computation is truly complicated. The intention is to present some illustrative examples in order to introduce the large order PT summation methods.

We close this section with the result for the asymptotic coefficients of two problems to be treated later on:

i) Zeeman effect for the hydrogen atom: the perturbation corrections for the ground-state energy of

$$H = -\frac{\Delta}{2} - \frac{1}{r} + \frac{\lambda}{8}(x^2 + y^2) \tag{11.89}$$

behave asymptotically ($n >> 1$) as /43-45/:

$$E^{(n)} \to (-1)^{n+1} \left(\frac{4}{\pi}\right)^{5/2} \left(\frac{8}{\pi^2}\right)^n (2n + \tfrac{1}{2})\,! \tag{11.90}$$

ii) Analogously, for

$$H = -\frac{\Delta}{2} - \frac{1}{r} + \lambda r \tag{11.91}$$

we have /46/

$$E^{(n)} \quad -\frac{18}{\pi e^3}\, n\, n!\, \left(-\frac{3}{2}\right)^n \tag{11.92}$$

Eqs. (11.90) and (11.92) have been obtained by means of techniques which represent variations or generalizations of the two methods presented in this pharagraph: the contour integral and the JWKB method.

There are other interesting systems having similar behaviors as those discussed here, and they will be analysed afterwards in succeeding chapters of this book.

It is important to point out a feature shared by all the examples presented so far: the k-th coefficient posses the general expression

$$E^{(k)} \sim a\, k^b\, c^k\, (k!) \qquad (11.93)$$

where a, b and c are real numbers.

The knowlwdge of the general form of the RS coefficient for $k >> 1$ has a remarkable importance to tackle the remaining central problem: to extract useful information from the divergent power series, in such a way that one can calculate $E(\lambda)$ for all λ-values.

The study of this fundamental problem(more precisely, the pertùrbation series) is the aim of practically the rest of this book.

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CHAPTER V

PERTURBATION SERIES SUMMATION TECHNIQUES

"J'ai eté forcé d'admettre diverses propositions
qui paraîtront peut-etre un peu dures; par exemple,
qu'une série divergente n'a pas de somme".

A. L. Cauchy, Analyse Algébrique, 1821

§.12. Introduction to the summability of divergent or slowly convergent series.

In the preceding chapters, we have discussed two central problems in PT: the calculation of the coefficients of the perturbation series and the determination of their asymptotic behavior.

Since the majorities of perturbation series arising in quantum mechanics and field theory have zero convergence radius, we are faced with a third main problem: to sum the divergent series. An asymptotic divergent power series (see Eq. (11.3)) represents a Taylor expansion around the origin of a function that is not analytic at this particular point. Then, the original power series must be changed into an appropriate function in order to obtain useful results.

Such a function approximates what will be called "the sum of the divergent series", and must be built from the coefficients of the divergent series. In this manner, use is made of the information embodied within the original RSPT coefficients.

From a strict mathematical viewpoint, the divergent series have been studied in a rigourous way since the beginning of this century and Borel's papers /1/ make up a seminal reference.

The summation method initially used, is the subject matter of the Hardy's fundamental work /2/, but the greater number of applications studied in such a book correspond to series with finite convergence radius, so it automatically leaves out the great majority of problems belonging to the physical chemistry realm. Hence, the applications of tech-

niques to sum divergent series in RSPT is quite recent. The first application to quantum mechanics was the use of the Padé /3/ and Borel /4/ methods in studying the anharmonic oscillator model in 1970. From that moment on, a large amount of work has been done along this line of research, and a considerable proportion of it is related to the above-mentioned methods.

Since 1979 there have evolved some alternative summation techniques, which because of being more specific enable one to get better results than those derived from the Padé and Borel methods.

These procedures represent a compromise solution between the mathematical rigor and the accuracy of the numerical computation, because their convergence properties are not known quite well, but at the same time they have proved to be numerically useful. One of the aims of this work is to develop the theory and the applications of a new alternative method to sum up divergent series. The procedure is based on the appropriate employment of some analytical properties of the function whose (divergent) power series must be summed. In order to judge the value of this method and understand its generality, we devote this chapter to a brief analysis of the most important summation techniques that appear in the standard literature thus providing a reference and comparative framework.

§.13.Padé Approximants.

Padé approximants are widely used to analytically continue Taylor expansions beyond their convergence radii. In order to outline the method let us consider the function f (z) which can be expanded as

$$f(z) = \sum_{n=0}^{\infty} f_n z^n \qquad (13.1)$$

The Padé approximant /M/N/(or /N,M/) for f(z) is defined as the rational function

$$f^{/M/N/}(z) = P^{/M/}(z) \; /Q^{/N/}(z) \qquad (13.2)$$

which is unique whenever

$$f^{/M/N/}(z) - \sum_{n=0}^{M+N} f_n z^n = O(z^{N+M+1}) \qquad (13.3)$$

The functions P and Q are polynomials of degree M and N, respectively, and their coefficients can be determined as a function of the set $\{f_n\}$ (see Appendix E).

The bibliography on Padé approximants is really considerable and References /5-7/ are quite general. Although the properties of the Padé approximants are well known and can be seen in the standard literature, we need to consider here the following issues:
i) Construction of the approximants (already discussed in Appendix E);
ii) The conditions under which the approximants converge; and
iii) The problems of chemical and physical interest to which they have been applied.

Although a rigorous presentation of the analytical results on the convergence properties of the Padé approximants is beyond the scope of this work, in what follows we summarize the most important theorems about this aspect and they will be a reference point in the next chapters.

Theorem 13.1 (Stieltjes theorem):

Let us suppose that there is a function $\rho(x)$ which is positive for all $x \geq 0$ and exponentially decreasing as $x \to \infty$ (that is to say $\lim_{x\to\infty} x^n \rho(x) = 0$ for all $n \geq o$) so that it satisfies the equation

$$f_n = (-1)^n \int_0^\infty \rho(x) x^n dx \qquad (13.4)$$

Under these conditions we say that f(z) can be expanded in a Stieltjes series. Then, for every $j \geq o$ and $z \in R_0^+$, the limit

$$f^{(j)}(z) = \lim_{N\to\infty} f^{|N+j/N|}(z) \qquad (13.5)$$

exists and

$$f^{(j)}(z) = \int_0^\infty (1+xz)^{-1} \rho_j(x)dx \qquad (13.6)$$

where $\rho_j(x)$ is a function with the same properties as $\rho(x)$.

It is known that when j is even (odd) then $f^{|N+j/N|}$ $(z>0)$ decreases (increases) as N increases.

In order to determine if the sequence of Padé approximants converge, according to Theorem 13.1, it is necessary to know whether $\rho(x)$ exists and is unique.

Theorem 13.2:

If $|f_n| \leq C^{n+1}(2n)!, C>0$, then there exists at most one function $\rho(x)$ which allows one to express f(z) as a Stieljes series.

Theorem 13.3:

The function $\rho(x)$ is unique iff $f^{(1)}(z) = f^{(0)}(z)\ \forall z \in R_0^+$.

Let us analyse some significant consequences of these three theorems. The mathematical methods developed in §.11 enable us to determine the asymptotic behaviour of the coefficients f_n of the power series and consequently we can verify whether the hypotheses of Theorem 13.2 is fulfilled. If such Theorem is satisfied and the sequence of diagonal $|N/N|$ and non-diagonal $|N+1/N|$ Padé approximants converge towards the same value for $N \to \infty$, then f(z) gives rise to a Stieltjes series and all the Padé sequences $|N+j/N|$ converge rigorously to $f(z) \forall\ z \in R_0^+$. Moreover, the sequences with j even (odd) is a rigorous upper (lower) bound to f(z).

The Padé approximants have been very useful to obtain the first satisfactory results from perturbation series of interest in physics and physical chemistry.

One of the first examples considered was the anharmonic oscillator. For the general anharmonic oscillator (11.46)

$$H(g,\lambda) = p^2+gx^2+\lambda x^{2K} \tag{13.7}$$

the asymptotic behavior of the perturbation coefficient $(E_N^{(n)})_K$ for the (N+1)th state is |8|

$$(E_N^{(n)})_K \to (-1)^{n+1} a(K-1) \frac{b^N}{N!} c^n \left\{ \frac{\Gamma\left(\frac{2K}{K-1}\right)}{\left[\Gamma\left(\frac{N}{N-1}\right)\right]^2} \right\}^{\frac{(nK-n+1)}{2}} \cdot (nK-n+N-\tfrac{1}{2})!$$

$$\cdot (nK-n+N-\tfrac{1}{2})! \tag{13.8}$$

where a, b and c are positive constants. This result was obtained from the method presented in §.11. Evidently, all the states of the quartic anharmonic oscillator ($K = 2, N \geq 0$) satisfy the Theorem 13.2. In fact, they can be approximated via the Padé approximants /3,9/.

The Padé method for the sextic anharmonic oscillator (K=3) is on the verge of divergence and only the ground state (N=0) fulfils the Theorem 13.2. The oscillators with $K \geq 4$ do not satisfy such theorem. It has been found that the Padé approximants do not converge when the RSPT is applied to these models because the function $\rho(x)$ in Eq.(13.4) is not unique /10/.

It often happens that even though the Padé approximants prove to be convergent they approach the limit rather too slowly for practical purposes. Simon /9/ studied the convergence properties of the approximants for the quartic anharmonic oscillator with |N/N| and |N+1/N| (N = 1,2,.....20) approximants, i.e. with 40th- and 41st- order P T.

The sequence of Padé approximants shows an acceptable convergence rate towards the exact result (obtained from non-perturbative numerical techniques) for $\lambda \leq 1.0$. The convergence rate decreases as λ increases, and, when $\lambda \simeq 10.0$ the result is so poor that the method is not longer

applicable for larger λ-values.

As a general rule, we can assert that the Padé approximation does not enable one to get satisfactory results in the "infinite coupling regime" from the perturbation series associated with the "zero coupling regime" whenever it has a null convergence radius. However, the approximants yield very good results for intermediate couplings. For this reason, there have been several practical applications such as: 1) strong-interaction dynamics /11/; 2) poles and zeros of experimentally determined functions /12/; 3) Born series in scattering problems /13/; and 4) thermodynamic properties of the Ising model /14/ among others /15/.

Summarizing, it may be stated that the Padé approximants make up a systematic and general method to derive rational or continued fraction approximations for some physical quantities, from the corresponding power series expansions, with the additional advantage that its implementation is truly easy.

However, the method does not take into account available analytical information of the function under study (such as a symptotic behavior, limit conditions, etc). Besides, from the numerical viewpoint it is not very efficient for those models considered in this book.

Another disadvantage of the Padé method is its non-regular behavior, so that, if (13.1) converges for $|z|<|z_0|$ one cannot assure beforehand that $f^{|N/N|}$ converges within this interval.

§.14. Borel transform and Borel-Padé summation method.

The Borel transform method is another relevant general method to sum the RSPT series. The procedure has been widely studied lately and has remarkable advantages over the Padé method.

For the sake of simplicity, we start from the formula /1,2/

$$\int_0^\infty x^n e^{-x/z} dx = z^{n+1}\, n! \qquad (14.1)$$

in order to present the method. Now let us consider a given function f(z) which can be expanded in an asymptotic power series

$$f(z) = \sum_{n=o}^{\infty} f_n z^n \quad ; \quad |f_n| \leq C^{n+1} n! \; ; C>0 \tag{14.2}$$

Then, the Borel transform B(x) of the series (14.2) is defined as

$$B(x) = \sum_{n=o}^{\infty} B_n x^n \; , \; B_n = f_n/n! \; , \; \forall |x| < C^{-1} \tag{14.3}$$

Let us assume that the analytical continuation of $B(x) \forall x \geq 0$ exists and is bounded by

$$B(x) \leq e^{Dx} \quad ; \quad D \geq 0. \tag{14.4}$$

Then for every z such that $|\ | < D^{-1}$ the "Borel sum" of f(x) exists and is given by

$$f(z) = \frac{1}{Z} \int_0^{\infty} B(x) e^{-x/z} \, dx \tag{14.5}$$

Eq. (14.5) allows us to conclude that if f(z) gives rise to a convergent series in a given region, then one can substitute (14.3) in (14.5) and exchange the sum and integral operations. The application of (14.1) gives the series expansion (14.2). Therefore, both the series (14.3) and the inverse transform (14.5) converge. This property shows the regular character of the procedure and it represents a significant difference with regard to the Padé method.

Let us treat a quite simple illustrative problem in order to show how to handle the Borel transform. We consider a series with null convergence radius, whose coefficients are

$$f_n = (-1)^n \, n! \tag{14.6}$$

This series has been frequently discussed in the current literature /16/ in relation to other summation methods.

From (14.6) the Borel transform coefficients are

$$B_n = (-1)^n \tag{14.7}$$

and the series is summable (which is not the case with the original one, with coefficients (14.6))to:

$$B(x) = (1+x)^{-1} \leq 1 \forall x \geq o \tag{14.3}$$

The transform (14.3) is bounded, as required by Eq. (14.4) with D=0, and then it is an analytic function $\forall x \geq o$. The final result for f(z) is (see Eq.(14.5)):

$$f(z) = \int_0^\infty \frac{e^{-x}}{1+zx}\, dx \; ; \; |z| < \infty \tag{14.9}$$

Eq. (14.9) is an analytical representation for the function with Taylor coefficients (14.6).

It is worth pointing out that according to (14.9), the coefficients f_n correspond to a Stieltjes series because

$$f_n = (-1)^n \int_0^\infty x^n \rho(x) dx \; ; \; \rho(x) = e^{-x} \tag{14.10}$$

In fact, the Padé method applies to this series.

The application of the Borel transform requires the following information: i) The analytic region where the method allows one to sum the series, and ii) The analytic continuation, i.e. how to build the function B(x) from Eq. (14.3).

The determination of the analytical domain is quite simple whenever the original Taylor expansion has a finite convergence radius. Such domain is determined by the branch point singularities of f(z) (usually, square-root singularities for eigenvalue problems). Let us suppose that f(z) has n branch points, which we denote as belonging to the set $A = \{z_1, z_2, \ldots, z_n\}$. We must remember that if z_i is complex, then $z_i^* \in A$. In order to build the required region we proceed as follows: every branch point z_i is associated with a semiplane D_i of the complex plane, determined by

$$D_i = \{z/: \text{Im } z \lesseqgtr -\frac{\text{Re}z_i}{\text{Im}z_i} \text{Re}z + \frac{|z_i|^2}{\text{Im}z_i} \; ; \text{ when } \text{Im}z_i \lesseqgtr 0\} \qquad (14.11a)$$

and

$$D_i = \{z/: \text{Re } z \lesseqgtr \text{Re}z_i \; ; \text{ when } \text{Re}z_i \lesseqgtr 0, \; \text{Im}z_i = 0\} \qquad (14.11b)$$

The analyticity domain Ω is

$$\Omega = \bigcap_{i=1}^{n} D_i \qquad (14.12)$$

Let us note that the origin is included in every D_i and consequently in Ω. When Ω corresponds to a finite area of the complex plane, then Ω is the area enclosed within a polygon called "Borel polygon". Fig. 5.1. shows the shape of such polygon for a particular case where $A = \{z_1, z_1^*, z_2, z_2^*\}$.

For every $z \in \Omega$ the Borel transform exists and f(z) may be approximated through (14.5). Then, it is said that f(z) is summable by the Borel method. Let us remark that the convergence domain in the Borel method is always larger than the corresponding domain of the Taylor series, which is a disc around the origin and whose radius is the smallest $|z_i|$.

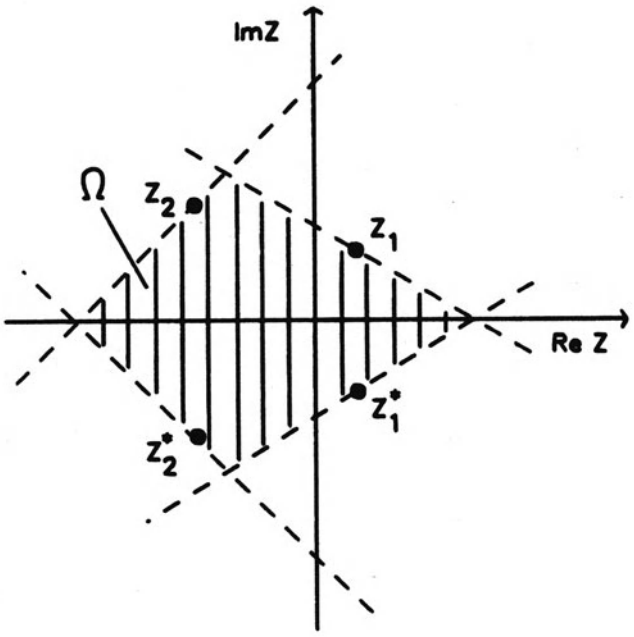

Fig. 5.1. Analyticity domain Ω of the Borel transform of a function f(z) with four branching points.

When f(z) is not analytical around the origin, that is to say, when f(z) gives rise to a divergent asymptotic series expansion, the analyticity domain must be determined in a different way, by means of the Watson-Nevanlinna theorem /17-19/. The explicit consideration of this extension lies beyond the scope of this book. The second basic problem is related to the construction of B(x) from Eq. (14.3). The first procedure used to construct the analytic continuation of the Borel transform was the Padé approximants approach /4,20/, and it is known as the Borel-Padé method:

$$f(z) \cong \frac{1}{z} \int_0^\infty B^{|N+j/N|}(x)\, e^{-x/z}\, dx \qquad (14.13a)$$

$$|B^{|N+j/N|}(x) - \sum_{s=1}^{2N+j} B_s x^s| = O(x^{2N+j+1}) \qquad (14.13b)$$

This method has been widely applied to several problems in Quantum Mechanics and Field Theory, such as anharmonic oscillators /4,20/; level crossing models /21/, and confining potentials /22-24/.

In the case of the anharmonic oscillators, for instance, the RSPT series may be summed disregarding the power of the anharmonic term. This is another advantage of the Borel method over the Padé one (see § .13).

There are other techniques for analytical continuation which have been recently used, and that make use of the available information about the asymptotic behavior of the RSPT coefficients (§ .11). In essence, the procedure consists in the following: from the analysis presented in § .11 and the D'Alembert criterion (Eq.(11.2)), one computes the convergence radius R_B of the Borel transform. Then one makes a conformal transformation in such a way to send the singularity nearest to the origin of the Borel transform towards infinity. Finally, one can apply the Borel-Padé method in the new region. For example, Eqs. (11.2), (11.33) and (14.3) permit us to obtain R_B for the ground state of the quartic anharmonic oscillator:

$$R_B^{-1} = \lim_{n\to\infty} \left| \frac{n!E_0^{(n+1)}}{(n+1)!E_0^{(n)}} \right| = \lim_{n\to\infty} \left| -\frac{3}{2} \frac{(n+1/2)!}{(n-1/2)!(n+1)} \right| = \frac{3}{2} \tag{14.14}$$

Several alternative methods have been discussed in the current literature to combine the Borel transform with a conformal transform /18,25-28/. Reference /18/ is an excellent review on the subject. Of late, a new analytical continuation procedure based on the first confluent form of the Wynn epsilon algorithm has been developed /29/. Such procedure has been applied to the anharmonic oscillators /30/ and the results compare favourably with those from the method based on the conformal transformation.

The Borel transform can be appropriately generalized in order to employ the knowledge about the asymptotic structure of the coefficients f_n. One can verify at once that the transform defined through the pair of equations (Borel - Le Roy transform):

$$B_b(x) = \sum_{n=0}^{\infty} \frac{f_n}{(an+b)!}\, x^n \qquad (14.15a)$$

$$f(z) = \frac{1}{z^{b+1}} \int_0^{\infty} x^b\, B_b(x^a z^{1-a})\, e^{-x/z}\, dx \qquad (14.15b)$$

is equivalent to that defined by way of Eqs. (14.3) and (14.5). However, Eqs. (14.15a) and (14.15b) provide an extra degree of freedom through the coefficients a and b, which can be chosen to set the convergence radius of (14.15a). This generalized transformation has been applied to simple field theories, such as ϕ^{2N} /25,28,31/ and also is eigenvalue problems such as the Zeeman effect for the hydrogen atom /32/. It is of importance to note that eventually the parameter b may be used in a variational way so as to improve the convergence rate. Some other problems have been studied by means of alternative representations of the Borel transform. Among them, one should quote, for example, the following contributions: A. Sidi, SIAM, J. Math. Anal. 17 (1936) 1222; V.S. Popov, V.M. Vaynberg and V.D. Mur, Sov. J. Nucl. Phys. 44 (1930) 714; C.M. Bender, L.R. Mead and N. Papanicolau, J. Math. Phys. 28 (1987) 1016. On summarizing the main conclusions about the Borel method we can remark the following aspects: i) The procedure allows one to sum a wide set of problems, including those which are summable through the Padé approximants (Stieltjes series);
ii) The method permits the introduction, in a systematic way, of the available analytical information about the function. In this regard, it is especially useful to take into account the asymptotic behavior of the RSPT coefficients (§ .11) in order to remove the singularities of the Borel transform.
iii) The method is regular and the convergence region is well-known.

From a practical point of view the utilization of the Borel method presents some serious drawbacks which will be taken into account in the next chapters: the analytical extension of a given function is not a simple problem, disregarding the procedure chosen to obtain it (Padé approximants or conformal transformation). Besides, in order to obtain f(z) it is necessary a numerical integration (Eqs.(14.5), (14.13a) and (14.15b)) which is always a nuisance when the number of coefficients f_n

is large enough. From the numerical perspective, results are quite acceptable for intermediate $|z| \lesssim 1$. However, this method the same as the Padé one, does not allow to obtain satisfactory results for the majority of problems in Quantum Mechanics when $|z| > 1$..

As a typical example we mention the lowest eigenvalue of the quartic anharmonic oscillator. The Borel transform built from the first 80 RSPT coefficients is accurate up to the fourth or fifth figure for a λ value as small as unity. Therefore, such a procedure is not suitable for obtaining the coefficients of the strong-coupling expansion from the RSPT.

It is worth mentioning here that other transforms have recently been introduced for studying divergent series of physical interest such as the Mellein transform (D. Birmingham and S.Sen, J. Phys. A 20 (1987) 4557), the Iwin transform (E.J. Weniger, communication presented at the Sanibel Symposia, Part B, Florida, USA, 1987) and the Euler-Knopp method (B. Gabutti, Numer. Math. 43 (1984) 439).

§.15. Euler Summation Method

Although the Euler method /2,33/ is one of the earliest procedures devised to accelerate the convergence rate of power series, its application to RSPT is very recent /34-36/.

The method applies to a formal Taylor expansion with sign alternating coefficients:

$$f(z) = \sum_{n=o}^{\infty} (-1)^n f_n z^n \quad ; \quad f_n > o \tag{15.1}$$

Euler method consists in the replacement of (15.1) by a power series in the z' variable, defined as

$$z' = \frac{z}{z+1} \tag{15.2}$$

Then, f(z) may be written in the following way

$$f(z) = \sum_{s=0}^{\infty} \bar{f}_s \, z'^{s} \qquad (15.3)$$

although there exist other alternative manner to write f(z) in terms of the variable z' /35/. Substituting (15.2) in (15.3) and identifying the coefficients of the z powers, we have the relation

$$\bar{f}_s = \sum_{i=0}^{s-1} \binom{s-1}{i} f_i \, (-1)^{i+1} \quad , \quad s \geq 1 \quad ; \quad \bar{f}_0 = f_0 \qquad (15.4)$$

when the original series is not sign alternating, the Euler transformation can be chosen

$$z' = \frac{z}{1-z} \qquad (15.5)$$

Euler method presents some important features: it is regular and always increases the convergence rate of the Taylor expansions within the convergence interval. Under certain conditions, the convergence domain of the z' power series agrees with the analyticity (and convergence) region of the Borel transform /2/.

In order to point out the relevent properties of this transform we present some simple examples. To begin with consider

$$f(z) = (1+z)^{1/2} \qquad (15.6)$$

which gives rise to a convergent Taylor expansion for $|z|<1$. The substitution (15.2) and the replacement into (15.6) gives

$$f(z) = (1-z')^{-1/2} \qquad (15.7)$$

which has a convergent Taylor expansion for all $|z'|<1$ and thereby for all $z\geq 0$.

This elementary example makes it clear one of the nicest properties of Euler method; i.e. that the variable z' is bounded while the original one (z) is not. Such characteristic should smooth the divergence rate of f(z') in case f(z) would have a zero convergence radius, or to increase it if such radius were different from zero.

Similar conslusions are drawn for the logarithmic series

$$\ln(1+z) = z(1-\frac{z}{2} + \frac{z^2}{3} - \frac{z^3}{4} + \ldots.) \qquad (15.3)$$

which appears in Solid State Physics, related to the Madelung constant /15,35/. The series (15.8) is absolutely convergent for $|z|<1$, conditionally convergent for z=1 divergent when z>1. The change of variable (15.2) gives

$$\ln(1+z) = z'(1+\frac{z'}{2} + \frac{z'^2}{3} + \frac{z'^3}{4} + \ldots.) \qquad (15.9)$$

that converges for $|z'|<1$ and consequently for z>0.

Bhattacharyya /35/ has studied this series in a very exhaustive way from a numerical viewpoint, by means of several variations of the Euler transform and other summation methods.

The procedure followed above to introduce the Euler transform is known as repeated application /35,36/ because all the z-powers turn into powers of z'. There exists an alternative consisting in the application of the transformation a finite number of times /35/. The idea is quite straightforward: first of all it is necessary to generalize the transformation through an auxiliar function /33/

$$g(z) = \sum_{n=0}^{\infty} g_n z^n \qquad (15.10)$$

which allows us to express the original function f(z) as

$$f(z) = \frac{1}{g(z)}\{f(z)g(z)\} = \frac{1}{g(z)}\sum_{s=0}^{\infty}\{\sum_{n=0}^{s} f_n g_{s-n}(-1)^n\} z^s \qquad (15.11)$$

The function (15.10) can be chosen so that the absolute value of the coefficients in (15.11) is smaller than the original ones. There are many choices of g(z) /33/ but it is enough for our purposes to select

$$g(z) = 1+z \quad ; \quad g_0 = g_1 = 1 \quad ; \quad g_s = 0 \quad \text{when} \quad s \geq 2 \qquad (15.12)$$

The substitution (15.12) in (15.11) gives

$$f(z) = \frac{f_0}{1+z} + z' \sum_{n=0}^{\infty} (-1)^n (f_n - f_{n-1}) z^n \quad ; \quad f_{-1} = 0 \qquad (15.13)$$

Eq. (15.13) is equivalent to just one application of the Euler transformation. The algorithm can be repeated several times, using the procedure (15.11) in the summation (15.13), in order to draw out every power of z'. Obviously, to apply (15.13) it is necessary to cut off the summation up to a given order and then to analyse the convergence properties for $N \to \infty$.

Although the transform (15.11) way be useful for some problems /33/, its application is not practical /35/ since it requires enough information about the analytical properties of f(z) in order to select an appropriate g(z).

Bhattacharyya /35/ introduced a generalization of the Euler transform based on the change of variables

$$z' = \frac{z}{(1+nz)^m} \qquad (15.14)$$

where n and m are adjustable parameters. This transformation has been studied within the context of the low order RSPT for the anharmonic oscillator (Appendices B and C); lineal confining model (Appendix G) and z^{-1} PT for atoms.

The numerical results obtained from this method for power series with zero convergence radius are satisfactory only when $|z|<1$. Besides, the method can yield minor improvements with regard to the Padé approximants, but up to now it is not known whether it is convergent.

The modification proposed by Silverman /36/ has been more successful. This author uses m = 1 in (15.14) and a transformation similar to (15.11). The procedure has been applied to the Zeeman effect for the ground state of the hydrogen atom. The results derived from the RSPT up to the order 35 are excellent for small and moderate field strengths and they compare favorably with those obtained via the Borel method.

§.16. Perturbation series renormalization techniques

During the last years several authors have developed new techniques to sum perturbation series for eigenvalue problems.

These methods, called renormalization techniques, are based upon mapping the original perturbation parameter into a more convenient one. Such procedures are specially important for us since they introduce new ideas regarding the methods presented in §§.13-15.

The method usually called of renormalization of the perturbation series consists on rearranging the Hamiltonian operator before applying the RSPT/37-39/. Such procedure is closely related to the Hamiltonian partition techniques /40-44/. In order to fix ideas, let us consider the operator

$$H(g,\lambda) = H_0 + \lambda W \tag{16.1a}$$

$$H_0 = T + gV \tag{16.1b}$$

where T and $\lambda W+gV$ are, respectively, the kinetic and potential energy

operators. If $E^{(0)}$ and $E(g,\lambda)$ are eigenvalues of H_0 and $H(g,\lambda)$, respectively, the RSPT yields

$$E(g,\lambda) - E^{(0)} = \sum_{n=1}^{\infty} E^{(n)} \lambda^n \tag{16.2}$$

where, the series expansion (16.2) is supposed to be divergent for any finite λ value.

The renormalization of the Hamiltonian consists in rewriting it as follows:

$$H(g,\lambda) = H_0' + \lambda W'(\lambda,\mu) \tag{16.3a}$$

$$H_0' = T + (g+\mu)V \; ; \; W'(\lambda,\mu) = W - \frac{\mu}{\lambda} V \; , \tag{16.3b}$$

where μ is a real parameter. If the eigenvalues $E'^{(0)}(\mu)$ and eigenfunctions of H_0 are known we can apply the RSPT, where W' is the perturbation, and obtain

$$E(g,\lambda) = \sum_{n=0}^{\infty} E'^{(n)}(\mu) \lambda^n \tag{16.4}$$

Clearly, the partial sums for the series (16.2) and (16.4) are different and one can somehow expect to enlarge the range of validity of the RSPT series.

This can be achieved by a suitable choice of the arbitrary parameter μ. Killingbeck /37/ and Austin and Killingbeck /38/ have resorted to a stability criterion of variational nature. The basic idea is simple: if the expansion (16.4) were convergent, the limit of the sequence of partial sums

$$SE_N'(\mu) = \sum_{n=0}^{N} E'^{(n)}(\mu) \lambda^n \quad , \quad N \geq 1 \tag{16.5}$$

would be μ independent because H does not depend on such parameter. Then, μ can be chosen so that /37,38/:

$$\left(\frac{\partial}{\partial \mu} SE'(\mu) \right)_{(\mu=\mu^*)} = 0 \qquad (16.6)$$

This procedure has been applied by Killingbeck /37/ to study anharmonic oscillators, models with lineal confining potentials, and helium-like atoms. Numerical results derived from the use of about 10 perturbation orders in Eq. (16.5) are good for $\lambda \leq 1.0$, but they are not satisfactory for larger λ-values.

For this reason, Austin and Killingbeck /38/ have proposed to express (16.5) as a Padé approximant, before applying the condition (16.6). Although this modification leads to improvement, results are not acceptable for $\lambda >> 1$. Recently, Austin /39/ has obtained better eigenvalues for the anharmonic oscillators and resonances for the Stark effect in hydrogen by combining the perturbation-series renormalization method with other renormalization procedure, based on dilation relationships previously developed /45-47/.

We devote the remainder of this section to briefly present the essence of the method.

Pascual /45/ and Dmitrieva and Plindov /46,47/ have developed a different procedure to renormalize the perturbation series, introducing the Hamiltonian rearrangement from a different standpoint. The importance of this new approximation, based on what is called re-scaled perturbation series, has simultaneously been pointed out by Banerjee /48/, through a different argument. The method is applied as follows: suppose that $V(\bar{r})$ and $W(\bar{r})$. $\bar{r} = (x_1, x_2, .., x_n)$. are homogeneous functions of degree m and n, respectively, i.e.

$$V(a\bar{r}) = a^m V(\bar{r}) \quad ; \quad W(a\bar{r}) = a^n W(\bar{r}) \qquad (16.7)$$

Since T is an homogeneous operator of degree -2, it follows that (see Appendix A):

$$H(g,\lambda) = a^{-2} \{T + a^{m+2} gV + a^{n+2} \lambda W\} \qquad (16.8)$$

If $a = \lambda^{-1/(n+2)}$, then

$$H(g,\lambda) = \lambda^{2/(n+2)} H(g\lambda^{-(m+2)/(n+2)},1) \qquad (16.9a)$$

On the other hand, choosing $a = g^{-1/(m+2)}$ we have

$$H(g,\lambda) = g^{2/(m+2)} H(1,\lambda g^{-(n+2)/(m+2)}) \qquad (16.9b)$$

The relations (16.9) are the starting point of the method. Consider the operator $\bar{H}$ defined as

$$\bar{H} = T + \mu V + V(W - \mu(1-\nu)V + \nu W = H(\mu(1-\nu),\nu) \qquad (16.10)$$

If we choose $g = \mu(1-\nu)$ we have precisely the partition discussed in Refs./37-39/. In order to have another equation, we apply the dilation relationship (16.9b) into the definition (16.10), and we are led to

$$\bar{H} = \{\mu(1-\nu)\}^{2/(m+2)} H(1,\nu\{\mu(1-\nu)\}^{-(n+2)/(m+2)}) \qquad (16.11)$$

The choice

$$\lambda = \nu\{\mu(1-\nu)\}^{-(n+2)/(m+2)} \qquad (16.12)$$

and Eq. (16.11) gives the result

$$H(1,\lambda) = \{\mu(1-\nu)\}^{-2/(m+2)} \bar{H} \tag{16.13}$$

The change of variables (16.12) provides us with a partition of the Hamiltonian (16.1) different to that employed in Eq. (16.3). On applying the RSPT to $\bar{H}$ we obtain a series in powers of ν:

$$\bar{E}(\mu) = \sum_{n=0}^{\infty} \bar{E}^{(n)}(\mu)\nu^n \tag{16.14}$$

The convergence properties of the resulting power series (16.14) are found to be different from those of the original expansion in powers of λ.

If $S\bar{E}_N$ is the sequence of partial sums for the series (16.14),

$$S\bar{E}_N(\mu) = \sum_{n=0}^{\infty} \bar{E}^{(n)}(\mu)\nu^n \quad , \tag{16.15}$$

the eigenvalues of H are then approximated by

$$E(1,\lambda) \simeq \{(1-\nu)\mu\}^{-2/(m+2)} S\bar{E}_N(\mu) \tag{16.16}$$

The new procedure also presents an adjustable arbitrary parameter μ. It can be determined from the stability condition (16.6) or by means of the so-called Scaling Variational Method (SVM), (see §.21).

The series (16.15) is hoped to have better convergence properties than (16.5) because the variable ν is bounded whereas λ is not. Besides, the partial sums $S\bar{E}_N(\mu)$ exhibit the actual large-λ behavior by virtue of the dilatation relation (16.13).

The procedure has been applied to the anharmonic oscillators (45-47) using a few perturbation coefficients, and it has been shown that results are quite satisfactory even for $\lambda >> 1$. However, the expansions

employed in Refs. /45-47/ are asymptotic and they do not converge for $1/\lambda \to 0$. This drawback was overcome by means of the construction of Padé approximants from the sequence (16.15) /45/.

Recently, other alternative renormalization techniques of perturbation series based on different partitions of the Hamiltonian have been presented /49-50/. The reason of the divergence of these renormalized series is a problem with great theoretical interest and will be studied later on.

In brief, we can state that the renormalization techniques of Hamiltonians provide for some eigenvalue problems, more accurate results than those obtained from the general procedures displayed in §§.13-15. The former are certainly less general than the latter and it must be remembered that the renormalization techniques take into account some analytical information about the function that gives rise to the divergent series.

Up to the moment, the renormalization techniques have been just studied from a numerical standpoint and their convergence properties are not in general known. In this regard, the properties and possibilities related to the method are an exciting open issue, and we will return to this topic later on.

§.17. Wick ordering and perturbation series summation

Caswell /51/ has presented a very interesting method to sum some power series arising in quantum mechanics and field theory. The method is based on building a convergent sequence from the perturbation expansion by means of a normal ordering (Wick-ordering) of the Hamiltonian for the problem under study. The procedure has a more restricted validity regarding those discussed in the precedent paragraphes. However, since it brings in several new ideas to sum perturbation series we deem it worthwhile to examine the method here.

Caswell's method /51/ is rigorously applicable only to the field theory described by the Hamiltonian

$$H(m^2,\lambda) = \frac{1}{2}\dot{\phi}^2 + \frac{m^2}{2}\phi^2 + \lambda\phi^4 \quad , \quad \lambda>0 \tag{17.1a}$$

$$[\phi,\dot{\phi}] = i \tag{17.1b}$$

where ϕ is a 1D field associated with the particle of mass m, and $\dot{\phi}$ its time-derivative. As shown in Appendix C, the model (17.1) is equivalent to the quantum problem

$$H(m^2,\lambda) = -\frac{1}{2}\frac{d}{dx^2} + \frac{m^2}{2}x^2 + \lambda x^4 \quad , \quad \lambda>0 \tag{17.2}$$

where the eigenfunctions of H vanish as $|x|\to\infty$.

It follows from the Symanzik theorem /9/, discussed in Appendix A that

$$H(m^2,\lambda) = mH(1,\lambda m^{-3}) \tag{17.3}$$

Eq. (17.3) and the fact that the eigenvalues $E(m^2,\lambda)$ of $H(m^2,\lambda)$ can be expanded in a power series of λ (RSPT) allow us to conclude that E can be expanded as

$$E(m^2,\lambda) = m\sum_{n=0}^{\infty} E^{(n)}\,(\lambda m^{-3})^n \tag{17.4}$$

This expansion is divergent as argued before.

The central idea of Caswell's procedure /51/ is to rearrange H in its normal form in order to find a connexion between the RSPT and another power series with a bounded variable. To begin with the Hamiltonian H is expressed in the second quantization representation and then it is ordered in normal form, i.e. with all the creation operators to the left of the annihilation ones. This transformation is

usually denoted as

$$:H: = \frac{1}{2} : \dot{\phi}^2 : + \frac{M^2}{2} : \phi^2 : + \lambda : \phi^4 : \qquad (17.5)$$

where M the effective or renormalized mass. In Appendix F it is shown the relation between H and :H:, which for quantum-mechanical Hamiltonians is:

$$H = :H: + \frac{M}{2} - \frac{3\lambda}{4M}2 \qquad (17.6)$$

where M and m are related by (see Appendix F):

$$(m/M)^2 + 6\lambda M^{-3} = 1 \qquad (17.7)$$

If $\bar{E}(M^2,\lambda)$ are the eigenvalues of :H:, Eq. (17.6) assures us that they are connected to $E(m^2,\lambda)$ through the equation

$$E(m^2,\lambda) = \bar{E}(M^2,\lambda) + \frac{M}{2} - \frac{3\lambda}{4M}2 \qquad (17.8)$$

The dilation transformation (17.3) for :H: allows to expand $\bar{E}(M^2,\lambda)$ as

$$\bar{E}(M^2,\lambda) = M \sum_{n=0}^{\infty} E_M^{(n)} \, (\lambda M^{-3})^n \qquad (17.9)$$

and the coefficients $E_M^{(n)}$ can be expressed in terms of $E^{(n)}$.

From Eq. (17.7) it follows that (λM^{-3}) is bounded while λm^{-3} is not (Eq.(17.4)). This implies that the convergence properties of (17.9) must be different from those of the original series, so that it should be possible to sum the divergent series by way of a transformation similar to that determined by Eq.(17.7). However, if one strictly uses

the variable λM^{-3} derived from the definition (17.7), the power series (17.9) makes up a new divergent series. In order to circumvent this drawback, Caswell /51/ proposed to modify the equation determining the mass M through a factor ℓ:

$$(m/M)^2 + \ell\lambda M^{-3} = 1, \quad \ell>0 \tag{17.10}$$

and to approximate the eigenvalues $\bar{E}(M^2,\lambda)$ by means of a sequence $S\bar{E}_N$ given by

$$S\bar{E}_N(\ell) = M \sum_{n=0}^{N} E_M^{(n)} (\ell)(\lambda M^{-3})^n \tag{17.11}$$

Since the function $\bar{E}(M^2,\lambda)$ does not depend upon the parameter ℓ, it seems reasonable to determine it in such a way that $S\bar{E}_N$ does not depend on it when N increases.

Consequently, Caswell proposed to find out the optimun $\ell(=\ell^*)$ via the condition

$$\left(\frac{\partial}{\partial\ell} \lim_{\lambda\to\infty} \{M^{-1} SE_N\}\right) (\ell=\ell^*) = 0 \tag{17.12}$$

so that from Eq. (17.8) the eigenvalues are approximated as

$$E(M^2,\lambda) \simeq S\bar{E}_N(\ell^*) + \frac{M}{2} - \frac{3\lambda}{4M}2 \tag{17.13}$$

The numerical study of Eq.(17.13) for $N\simeq 20$ (i.e. applying the RSPT up to the order 20) shows that the method appears to succeed in summing the perturbation series for any $\lambda>0$. Thus, the method has yielded results for the quartic anharmonic oscillator which are by far more exact than those computed via the Padé and Borel-Padé method up to the same perturbation order.

The procedure has also been applied to the two-well potential ob-

tained when $m^2<0$, but results are much less accurate than those for the quartic anharmonic oscillator. It will be shown later on, that the renormalized mass is unbounded in this case.

The method presented so far can only be applied to the quartic anharmonic oscillator (Eq.(17.1)), and, as an illustrative example, it is shown in Appendix F that the sextic anharmonic oscillator

$$H = \frac{1}{2}\dot{\phi}^2 + \frac{m^2}{2}\phi^2 + \lambda\phi^6 \tag{17.14}$$

cannot be normal ordered to obtain a new sextic anharmonic oscillator. Therefore, it is not longer possible to define the effective mass M in an equation like (17.7). In spite of this hindrance, Caswell /51/ suggested, on the basis of dimensionality arguments, the following equation for the renormalized mass M

$$(m/M)^2 + \frac{\ell\lambda}{M^4} = 1 \tag{17.15}$$

Results computed for the sextic potential and its associated two-well potential are not so accurate as those obtained for the quartic anharmonic oscillator. It deserves to be mentioned that other possible rearrangements of the perturbation series have recently been discussed starting from the second quantization representation of Hamiltonians /52-54/. Although their validity is restricted to specific eigenvalue problems, all these methods make up a significative undertaking to combine the method of perturbation series summation with some analytic properties of the function under study.

Along the same line, one should include some recent promising developments. Particularly interesting seems to be the approaches based on information theory (J.N. Silverman, D. Bonchev and O.E. Polansky, Phys. Rev.A 34 (1986) 1736), approximation theory (L.S.Luo and J. Nuttall, Phys. Rev. Lett. 57 (1986) 224) and the principle of maximum entropy (C. M. Bender, L. R. Mead and N. Papanicolau, J. Math. Phys. 23 (1987) 1016).

§.13. Summation of perturbation series through order-dependent mappings

In the last few years, there has been an interesting development of a new method to sum some perturbation series that occur in quantum mechanics and field theory. The procedure is based on a change of the perturbation parameter by means of the so-called order-dependent mapping /55-57/. Although it seems to be highly accurate, the method has only been applied to field theories like ϕ^4 in several dimensions, to the quartic anharmonic oscillator /55/, and the Zeeman effect for the hydrogen atom /57/.

The technique is based on an extension of those methods used to increase the range of validity of the Taylor expansion for a given function beyond its convergence radii (see §.15). In order to fix ideas, let us consider a function f(z) which can be formally expanded in an asymptotic-divergent power series

$$f(z) = \sum_{n=0}^{\infty} f_n z^n \tag{13.1}$$

Introducing the change of variable /55,56/.

$$z = h(\xi, g) \; ; \; \xi \varepsilon R \tag{13.2}$$

such that

$$h(\xi, g) \to O(g) \; ; \; g \to 0 \tag{13.3}$$

the original series can be rewritten

$$f(h(g)) = \sum_{n=0}^{\infty} P_n(\xi) \, g^n \tag{13.4}$$

A nice feature of this method is that the function h(g) can be

chosen according to some known analytic properties of f(z).

It deserves to be pointed out that up to the moment there is not a systematic procedure to build $h(\xi,g)$. For example, to study the anharmonic oscillator and field theories, the following transformation was proposed /55/:

$$z = \xi g(1-g)^{-s} \quad : \quad s>0 \tag{18.5}$$

where f(z) corresponds to the eigenvalues of the Hamiltonian and s is obtained from the asymptotic behavior of f(z) when $|z|\to\infty$. A transformation recently proposed to treat the PT for the Zeeman effect in the hydrogen atom is, on the contrary, more involved /57/. As shown by Eq.(18.5) the variable g remains finite for all z values which is certainly most convenient.

As argued by Zinn-Justin et al /55-57/ the parameter ξ can be chosen so that the sequence of partial sums

$$F_N(\xi) = \sum_{n=0}^{N} P_n(\xi) g^n \tag{18.6}$$

exhibits the greatest convergence rate

This last condition is attained by choosing $\xi(=\xi_N)$ to be a root of the last coefficient of the sum (18.6):

$$P_N(\xi_N) = 0 \tag{18.7}$$

The assumption (18.3) assures us that the coefficient $P_n(\xi)$ can be written in terms of the original ones $\{f_j \; ; \; j = 0,1,\ldots,n\}$. Then the parameter ξ_N obtained from Eq. (18.7) depends upon the member of terms in F_N (Eq.(18.6)), and consequently the transformation (18.2) is an order-dependent mapping.

No rigorous convergence proof for this method has been given except in some simple cases. However, there is enough numerical evidence to quess that whenever the coefficients f_N diverge as $(N!)^M$, the series can be summed by way of an order-dependent mapping of the form $\xi_N \to N^{-M}$ /55-56/.

Despite the lack of rigorous analytical proofs, the numerical study of this kind of transformations /55-57/ has shown that they allow one to sum series with an N! divergence for any $z \geq 0$. When the order-dependent mapping can be applied it seems preferable to other methos such as the Padé (§.13) and Borel-Padé (§.14) ones.

All the precedent discussion, plus the subjects analysed in §§.16 and 17 suggest that the most powerful, summation techniques of PS are those that allow taking into account analytic information about the function being approximated. We have seen that such information can be obtained from operator rearrangements in eigenvalue problems, or through asymptotic expansions.

Having arrived at this point, an interesting enough question is: in which systematic way can one relate the analytic properties of a given function f(z) with a summation technique of divergent power series? A possible manner to shed light on this point should consist in comparing the procedures presented in §§.16-18 in order to find out their most relevant features.

Starting from the next chapter on, we will study this subject matter, and the first point discussed will be: which are the basic analytic properties to consider in order to approximate a given function that can be expanded in a asymptotic divergent power series?

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CHAPTER VI

FOUNDATIONS OF THE VARIATIONAL FUNCTIONAL METHOD (VFM)

§. 19. Energy of parameter-dependent systems

It has been shown in precedent chapters that it is convenient to employ some analytic information about the function whose power series expansion one wants to sum. Hence, it is appropriate to discuss here the analytic properties that should be considered. An interesting way to carry out this task will be analysed from this chapter onwards.

Recently, Rosen /1/ proved that a certain kind of semiclassical functionals which are made an extremum in the configuration space, fulfil the VT and HFT for a system of anharmonic coupled oscillators. Similar conclusions had been derived previously by Orland /2/. This author studied which differential equation determined , following a different approach, the approximate parametric dependence of the eigenvalues of an anharmonic oscillator Hamiltonian.

Since this two contributions are a cornerstone within the context of this book, we deem it meaningful discussing some interesting, related features.

Our purpose is to study quite general functional representations for the eigenvalues associated with quantum mechanical systems of interest in chemical-physics. The intention is to try to define such functionals taking into consideration several analytic properties. These semiclassical functionals are the starting point to develop a systematic method to build approximate solutions of the stationary Schrodinger equation, which will allow us to take advantage of the information contained in those methods discussed in previous chapters.

Let us consider a 2K-anharmonic oscillator (whose relevance in Molecular Physics, Theoretical Chemistry and Field Theory is examined in Appendices B and C):

$$H(g,\lambda = p^2 + gx^2 + \lambda x^{2K} \quad ; \quad g,\lambda,K > 0 \qquad (19.1)$$

$E_n(g,\lambda)$ is the n-th eigenvalue associated with (19.1). No analytic expresion is known for $E_n(g,\lambda)$ for $K > 2$, with K integer.

From the discussion in Chapter I, we know that $E_n(g,\lambda)$ satisfies the HFT

$$\frac{\partial E_n}{\partial \lambda} = \langle x^{2K} \rangle \quad , \qquad (19.2)$$

and the VT

$$2\langle T \rangle = \langle xV' \rangle \quad , \qquad (19.3)$$

which in this case (Hamiltonian (19.1)) has the form

$$\langle p^2 \rangle = g\langle x^2 \rangle + K\lambda\langle x^{2K} \rangle \quad . \qquad (19.4)$$

The VT (19.4) gives for E_n

$$E_n = 2g \langle x^2 \rangle + (K+1)\lambda\langle x^{2K} \rangle = 2g\langle x^{2K} \rangle + (K+1)\lambda\frac{\partial E_n}{\partial \lambda} \qquad (19.5)$$

From Eq. (19.5), Orland /2/ derived a differential equation for the energy, within the framework of semiclassical-like approximation as:

$$\langle x^{2s} \rangle \simeq \langle x^2 \rangle^s \qquad (19.6)$$

This last equation is not valid, in general, and it should be re-written introducing an appropriate dependence with s, n and λ:

$$\langle x^{2s} \rangle = B_n^{(s)}(\lambda) \langle x^2 \rangle^s \qquad (19.7)$$

Orland /2/ and Rosen /1/ have set, quite arbitrarily, $B_n^{(s)}(\lambda) = 1$. Later on we will discuss this latter function in greater detail.

The replacement of (19.6) into (19.5), and the choice g = 1 (which does not introduce any lack of generality), gives

$$E_n = 2\left(\frac{\partial E_n}{\partial \lambda}\right)^{1/K} + (K+1)\,\lambda\,\frac{\partial E_n}{\partial \lambda} \quad . \qquad (19.8)$$

This equation, which hereforth will be called "Orland equation", determines the approximate dependence of E_n with the coupling parameter λ (self-coupling) appearing in the Hamiltonian (19.1). This procedure allows one to transform the original problem of a second-order linear eigenvalue differential equation into a first-order non-linear eigenvalue differential equation.

In order to solve Eq. (19.3), one can try a parametric solution through the power series method /2/, and so we make

$$\partial E_n/\partial \lambda = p^{-K} \qquad (19.9a)$$

which, subtituted into (19.8), leads to:

$$E_n = 2p^{-1} + (K+1)\lambda p^{-K} \qquad (19.9b)$$

Now we consider that E_n and λ can be expanded in power series of p:

$$E_n = \sum_m E_n^{(m)} p^m \qquad (19.10a)$$

$$\lambda = \sum_m \lambda_m p^m \qquad (19.10b)$$

The substitution of (19.10) into (19.9b) yields:

$$\sum_m E_n^{(m)} p^m = 2p^{-1} + (K+1) \sum_m \lambda_m p^{m-K} \quad . \qquad (19.11)$$

The coefficients $E_n^{(m)}$ and λ_m are related to each other via the Eq. (19.9a):

$$\partial E_n / \partial p = \frac{\partial \lambda}{\partial p} \; p^{-K} \quad , \qquad (19.12)$$

from which one gets:

$$m E_n^{(m)} = (m+K) \; \lambda_{m+K} \quad . \qquad (19.13)$$

The insertion of (19.13) into (19.11) gives rise to a recursion relationship for the coefficients λ_m:

$$\sum_m \{\frac{m+K}{m} - (K+1)\} \; \lambda_{m+K} \; p^m = 2p^{-1} \quad . \qquad (19.14)$$

When m = -1:

$$\lambda_{K-1} = -K^{-1} \quad , \qquad (19.15a)$$

while for $m \neq 1$

$$\lambda_s = 0 \ , \text{ for any } s = (K \pm 1) \tag{19.15b}$$

These results enable one to express the expansion (19.10b) as

$$\lambda = -K^{-1} \ p^{K-1} + a \ p^{K+1} \tag{19.16}$$

where $a = \lambda_{K+1}$ is an integration constant of the Orland equation, whose value must be appropriately chosen.

Replacing (19.6) in (19.9b) one gets a compact parametric formula for the energy:

$$E_n = \left(\frac{K-1}{K}\right) \ p^{-1} + (K+1) \ ap \tag{19.17}$$

A careful analysis of the meaning of Eqs. (19.16) and (19.17) reveals that the energy given by (19.17), with p determined from (19.16), fulfils the Orland equation for any λ-value, i.e., it satisfies the VT and HFT.

The very fact of the fulfillment of these two theorems assures one that the dependence of E_n on λ (deduced from Eqs. (19.16) and (19.17)) is, qualitatively, that corresponding to the exact eigenvalue. From the quantitative point of view, the approach is limited by the employment of the semiclassical formula (19.6), and by the choice of constant a in Eq. (19.16).

For the quartic anharmonic oscillator (K = 2), Orland /2/ chose constant a in such a way so as to fit a given eigenvalue, computed numerically up to a desired accuracy.

This author obtained quite satisfactory results for E_n within a wide range of n and λ values. We will not discuss here other possible parametrization methods, but we will focus our attention to the study

of general relationships akin to the solutions of Orland equation.

It is important here to analyse also Eq. (19.8) from a different viewpoint. Let us consider the following functional F(q), which is associated to the model described by the Hamiltonian (19.1) (with g=1):

$$F(q) = \frac{A}{q^2} + q^2 + \lambda q^{2K} \quad , \quad A = \text{constant} \tag{19.18}$$

This functional includes three terms, with the same homogeneity degree in q as that in x for the terms in the Hamiltonian (19.1).

From the extremum condition for f(q)

$$(\partial F/\partial q)\ (q = q^*) = 0 \quad , \quad \text{then } \frac{A}{Kq^{*2}} = \frac{q^{*2}}{K} + \lambda q^{*2K} \quad , \tag{19.19}$$

we get a minimum, since

$$\frac{\partial^2 F}{\partial q^2} = \frac{6A}{q^4} + 2 + 2K(2K-1)\ \lambda q^{2K-2} \quad ,$$

$$\left(\frac{\partial^2 F}{\partial q^2}\right)(q = q^*) = 8 + 4(K^2+K)\ \lambda q^{*2K-2} > 0 \ , \ \forall \ \lambda>0 \tag{19.20}$$

Finally, we have

$$F(q^*) = \left(\frac{K+1}{K}\right)\frac{A}{q^{*2}} + \left(\frac{K-1}{K}\right) q^{*2} \tag{19.21}$$

It is worth noting that Eqs. (19.19) and (19.21) are identical to (19.16) and (19.17), respectively, provided that

$$A = a\ K \quad \text{and} \quad p = q^{*2} \tag{19.22}$$

The conclusion derived from the precedent equation is highly significant: a functional like (19.18), constructed taking into account the structure of the Hamiltonian defining the model, satisfies the Orland equation when minimized, and consequently it fulfils the VT and the HFT, within the context of a semiclassical approximation. It is clearly seen that this procedure to solve Eq. (19.8) is easier than the previous one; moreover, the functional approximation seems more suitable for further generalization.

It is particularly illustrative to show the manner in which F obeys a relation ship similar to HFT. From the extremum condition, we know that q depends upon λ, and moreover A is a constant independent of λ. Then, when deriving (19.18) with respect to such parameter, one gets

$$\frac{\partial F}{\partial \lambda} = \left(\frac{\partial F}{\partial q}\right)_{\lambda} \frac{\partial q}{\partial \lambda} + \left(\frac{\partial F}{\partial \lambda}\right) q \quad , \tag{19.23}$$

and, from the property $\left(\frac{\partial F}{\partial q}\right)_{\lambda} (q = q^*) = 0$, it follows that

$$\left(\frac{\partial F}{\partial \lambda}\right) (q = q^*) = \left(\frac{\partial F}{\partial \lambda}\right)_{q} (q = q^*) \quad . \tag{19.24}$$

In the particular example of an anharmonic oscillator, one has:

$$\left(\frac{\partial F}{\partial \lambda}\right) (q = q^*) = q^{*2K} \quad . \tag{19.25}$$

Evidently, Eq. (19.25) is equivalent to the HFT iff $q^{*2K} = \langle x^{2K} \rangle$, with F the approximation to E.

Up to this moment, we have used a simple model (a 1D oscillator) to study the equation determining the dependence of the energy with those parameters contained within the Hamiltonian. However, Rosen /1/ obtained equivalent results for the more general Hamiltonian

$$H = \sum_{i=1}^{N} \left(-\frac{\partial^2}{\partial x_i^2} + \xi_i x_i^2 + \sum_{j=1}^{N} \gamma_{ij} x_i^2 x_j^2\right) \tag{19.26}$$

This Hamiltonian describes a set of anharmonically coupled oscillators. Rosen /1/ showed that the functional

$$F = 2A\left(\sum_{i=1}^{N} q_i^2\right)^{-1} + \sum_{i=1}^{N} \xi_i q_i^2 + \sum_{i=1}^{N}\sum_{j=1}^{N} \gamma_{ij} q_i^2 q_j^2 \qquad (19.27)$$

subjected to the extremum condition on $\bar{q} = (q_1, q_2, \ldots, q_N)$

$$F(q = q^*) = \min_{(\bar{q})} F(\bar{q}) \qquad (19.28)$$

obeys the equations

$$F = 2 \sum_{i=1}^{N} \xi_i \frac{\partial F}{\partial \xi} + 3 \sum_{i=1}^{N}\sum_{j=1}^{N} \gamma_{ij} \frac{\partial F}{\partial \gamma_{ij}} \qquad (19.29a)$$

$$\frac{\partial F}{\partial \xi_i} \quad \frac{\partial F}{\partial \xi_j} = \frac{\partial F}{\partial \gamma_{ij}} \qquad (19.29b)$$

Eq. (19.29a) is determined from VT and HFT, while Eq. (19.29b) follows from the semiclassical approximation $\langle x_i^2 x_j^2 \rangle \simeq \langle x_i^2 \rangle \langle x_j^2 \rangle$.

Instead of presenting the rather involved proof given by Rosen /1/, which is valid just for (19.26), we present a more general and simpler proof, /3/ that can be used for a wider set of models. The proof is given here in detail, since it is of relevance in what follows.

Let us consider a functional $F(\bar{q})$, corresponding to an N-dimensional system, with the following structure:

$$F(\bar{q}) = \hat{T}(\bar{q}) + \hat{V}(\alpha, \bar{q}) \qquad (19.30)$$

with α a set of parameters contained in the Hamiltonian (which, consequently, have been transferred to the functional). We will discuss here the meaning of the terms $\hat{T}$ and $\hat{V}$, but we will see that the extremum of

$F(\bar{q})$ satisfies, under certain conditions, relations identical to the VT and HFT.

Theorem 19.1:

Let $F(\bar{q})$, given by (19.30), be a functional depending on $\bar{q}$ and the set of parameters α. Let $\hat{T}$ be a homogeneous function of degree -2 in $\bar{q}$. Then, $F(\bar{q})$ satisfies the following pair of equations:

$$2T(q=q^*) = \{\bar{q}.\nabla\hat{V}\} \quad (\bar{q}=\bar{q}^*), \quad \bar{q}^* = (q_1^*, q_2^*, \ldots, q_N^*) \tag{19.31}$$

$$(\frac{\partial F}{\partial \alpha}) \quad (\bar{q} = \bar{q}^*) = (\frac{\partial F}{\partial \alpha})_{\bar{q}} \quad (\bar{q}=\bar{q}^*) \tag{19.32}$$

when

$$(\frac{\partial F}{\partial q_i})_\alpha \quad (q_i = q_i^*) = 0 \quad ; \quad i = 1,2,\ldots,N \tag{19.33}$$

Proof: The application of the virial operator v

$$v = \sum_{i=1}^{N} q_i \frac{\partial}{\partial q_i} = \bar{q}.\nabla \tag{19.34}$$

to the functional (19.30), gives

$$\bar{q}.\nabla F = \sum_{i=1}^{N} q_i (\frac{\partial F}{\partial q_i})_\alpha = \sum_{i=1}^{N} \{q_i (\frac{\partial \hat{T}}{\partial q_i})_\alpha + q_i (\frac{\partial \hat{V}}{\partial q_i})_\alpha\}$$

$$= -2\hat{T} + \sum_{i=1}^{N} q_i (\frac{\partial \hat{V}}{\partial q_i})_\alpha \tag{19.35}$$

The extreme condition (19.33) leads us to Eq. (19.31), which represents the equivalent to the T for the functional F. On the other hand, if we study the variation of F with α

$$\frac{\partial F}{\partial \alpha} = \left(\frac{\partial F}{\partial \alpha}\right)_{\bar{q}} + \sum_{i=1}^{N} \left(\frac{\partial F}{\partial q_i}\right)_{\alpha} \left(\frac{\partial q_i}{\partial \alpha}\right) \tag{19.36}$$

and apply (19.33), one is led to Eq. (19.32), which is analogous to the HFT, and generalizes Eq. (19.24).*

From above theorem, several points are open to discussion, which may be summed up as follows:

i) The analytical form of $\hat{T}$ is not completely specified. The condition of $\hat{T}$ being a function of degree -2 in q ($=||\bar{q}||$ can be fulfilled by a large class of functions /1/.

ii) The analytical form of $\hat{V}(\alpha,\bar{q})$ is not determined for a given Hamiltonian.

iii) Although the HFT fixes the dependence of F on α, we have not stated anything regarding the dependence of F upon the quantum numbers that define the state of the system. This last dependence must be determined appropriately in order to get a reasonable approximation to E_n by means of a functional F.

In principle, Theorem (19.1) would allow one to formulate a new method to obtaining approximate energies for parameter-dependent systems, if those points commented previously could be answered satisfactorily. This method, which from now on will be called Variational Functional Method (VFM), will be the central subject of the chapters to follow. The procedure will be developed from the functional (19.32) and, as will be seen, it combines characteristic features of the variational, semiclassical and perturbation methods.

§.20. Semiclassical functional expressions for the energy

This section is devoted to discussing some recent results /4,5/, which can be considered as antecedents to the VFM, whose general outlines were introduced in §.19.

Banerjee /4/ has analysed some properties of the solutions of the Schrodinger equation for the Hamiltonian

$$H = p^2 + gV(x) \tag{20.1}$$

by associating a functional with its eigenvalues. It is interesting to examine the way such a functional is built: let us suppose that s is the interval length of the variable x where the motion is constrained with x_1 and x_2 the classical turning points. From the semiclassical viewpoint, one can consider that within s there is an integral number of half wavelengths L/2 in order to avoid destructive interferences:

$$s = \frac{n}{2} L \quad ; \quad n = 1,2,... \quad . \tag{20.2a}$$

From the de Broglie equality /4/, it is possible to relate the impulse p with s, i.e.

$$p = \frac{h}{L} = \frac{\hbar n \pi}{s} \quad , \tag{20.2b}$$

and finally one gets a semiclassical functional expression for the energy

$$E(s) = \frac{\hbar^2 \pi^2 n^2}{s^2} + gV(s) \tag{20.3}$$

Eq.(20.3) shows in a natural way the functional dependence of degree -2 associated with the kinetic energy.

It is noteworthy to realize that the semiclassical condition (20.2a) leads to a dependence of A on n^2 in (19.20) when n>>1. We shall return to this point in the next section.

Theorem (19.1) assures us that the functional (20.3) satisfies the VT and HFT whenever

$$(\frac{\partial E}{\partial s})_g \ (s = s^*) = 0 \quad . \tag{20.4}$$

Banerjee /4/ has discussed the possibility of inserting an additional constant C within the functional so as to make E(s) fulfil the Bohr correspondence principle (Eq.(5.25)):

$$E = C \frac{\hbar^2 \pi^2 n^2}{s^2} + gV(s); \quad (\frac{\partial E}{\partial n}) \ (s = s^*) = \frac{h}{\tau_c} \tag{20.5}$$

with τ_c the classical period of motion:

$$\tau_c = \int_{x_1}^{x_2} p(x)^{-1} \ dx \ ; \ p(x_1) = p(x_2) = 0 \quad . \tag{20.6}$$

The combination of (20.5) and (20.6) allows one to get the constant C:

$$C = \frac{s^{*2}}{2n} \oint (E-gV(x))^{-1/2} \ dx \quad . \tag{20.7}$$

The occurrence of C into E(s) means an additional improvement for the functional because it introduces more information about the analytical properties of the eigenvalues. In this case, it is the correct dependence on the quantum numbers in the semiclassical limit. Our purpose when developing the VFM is precisely this: to introduce in the functional as much theoretical information available about the eigenvalues, in such a menner to obtain simple enough analytical expressions for them. In the next chapters we extend the VFM in a systematic manner; Banerjee's contribution /4/ can be considered a significant ante-

cedent of such generalizations.

A quite different approach has been presented recently /5/, in order to construct semiclassical functionals. In order to introduce the central ideas, we follow Gerck et al's arguments /5/, with some minor modifications according to our present needs. Let us consider the Schrodinger equation associated with the operator (20.1) (with $m=\hbar=1$):

$$- \Psi'' (x) + gV(x)\Psi(x) = E\Psi(x); \; 0 \leq x < \infty \qquad (20.8)$$

with the boundary condition:

$$\Psi(x \to \infty) = 0 \quad . \qquad (20.9)$$

To derive a functional one can discretize Eq. (20.3), i.e., to transform the second-order differential equation into a finite-difference recurrence. For that purpose, we consider the following auxiliary result. Let U be a set of functions satisfying the boundary condition (20.9):

$$U = \{u_1, u_2, u_3\} \equiv \{e^{-\alpha x}, xe^{-\alpha x}, x^2 e^{-\alpha x}\} \quad . \qquad (20.10)$$

Defining an approximation to Ψ via the set U

$$\Psi(x) = \sum_{n=1}^{3} c_n u_n \quad , \qquad (20.11)$$

it is possible to determine three real constants a, b, c, such that

$$\Psi''(x) = a\Psi(x-b) + c\Psi(x) \quad . \qquad (20.12)$$

The substitution of (20.11) into (20.12), and the identification of

the coefficients of the linearly independent functions u_i gives

$$a = 2\alpha^2/e \tag{20.13a}$$

$$b = 1/\alpha \tag{20.13b}$$

$$c = -\alpha^2 \tag{20.13c}$$

Now we introduce an N-point grid: $x_1, x_2, \ldots, x_k, \ldots, x_N$, and the auxiliary parameter:

$$x_k - x_{k-1} = \nabla x_k = \frac{1}{\alpha_k} \quad . \tag{20.14}$$

For every point of the mesh, Eq.(20.12) can be written as:

$$\Psi_k''(x) = a_k \Psi_k(x-b) + c_k \Psi_k(x) \quad ; \quad \Psi_k(x) = \Psi(x_k) \tag{20.15}$$

which together with Eqs.(20.13) can be transformed into

$$\Psi_k'' = a_k \Psi_{k-1} + c_k \Psi_k \tag{20.16}$$

The introduction of Eq.(20.16) into Eq.(20.8) yields the desired recurrence relationship:

$$-2\,\frac{\alpha_k^2}{e}\,\Psi_{k-1} + \alpha_k^2\,\Psi_k + gV_k\Psi_k = E\,\Psi_k \quad ; \quad V_k \equiv V(x_k) \tag{20.17}$$

Eq.(20.17) can be given a matricial form:

$$\underset{\sim}{H}\,\underset{\sim}{\Psi} = E\underset{\sim}{\Psi} \quad ; \quad \underset{\sim}{\Psi} \equiv \begin{bmatrix} \Psi_1 \\ \vdots \\ \Psi_N \end{bmatrix}$$

$$\underset{\sim}{H} = \begin{bmatrix} \alpha_0^2+V_0 & 0 & 0 & \cdots \\ -\alpha_1^2/e & \alpha_1^2+V_1 & 0 & \cdots \\ 0 & -2\alpha_2^2/e & \alpha_2^2+V_2 & \cdots \\ 0 & 0 & \cdot & \\ \cdot & & \cdot & \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \\ & \cdot & & \end{bmatrix} \tag{20.13}$$

where vector E contains the eigenvalues of a bidiagonal matrix

$$E_n = \alpha_n^2 + gV_n \tag{20.19}$$

In order to derive a functional form for E_n from (20.19) Gerck et al. /5/ have introduced a semiclassical approximation as follows:

$$x_n(x_n - x_{n-1})^{-1} = (1 - \frac{x_{n-1}}{x_n})^{-1} \simeq s_1 n + s_2 + O(n^{-1}) \tag{20.20}$$

Eqs.(20.14) and (20.20) allows one to express the grid points x_n as functions of n, for n>>1:

$$x_n = x_n \left(\frac{\alpha_n}{\nabla x_n}\right)^{-1} = x_n (x_n - x_{n-1})^{-1} \alpha_n^{-1} \simeq (s_1 n + s_2)\alpha_n^{-1} +$$

$$O((n\alpha_n)^{-1}) \quad . \tag{20.21}$$

Constants S_1 and s_2 must be determined in some appropriate manner. Eq.(20.21) leads at one to the desired functional, when replacing (20.21) into (20.19):

$$E_n = \frac{(ns_1+s_2)^2}{y_n^2} + gV(y_n) \quad ; \quad y_n = (s_1 n+s_2)/\alpha_n \qquad (20.22)$$

The arbitrary parameter α can be computed in a variational way. Eq.(20.22) transforms such variational condition in an extreme condition with respect to y_n:

$$\left(\frac{\partial E_n}{\partial y_n}\right)_g \; (y_n = y_n^*) = 0 \quad . \qquad (20.23)$$

From the precedent analysis, one can stress two important facts:
i) The term of degree -2 in the functional (20.22) has a constant proportional to n^2, the same result Banerjee /4/ got from the de Broglie condition.
ii) The term corresponding to the potential energy in the functional (20.22) possesses, in a natural way, terms with the same homogeneity degree as those in the Hamiltonian. We have seen previously (§.19) that the same happened for the solutions of Orland's equation (19.3).

Gerck et al. /5/ only applied the present formulation to some radial problems characterized by a potential V with just one term. In these cases, the constants s_i in (20.20) were numerically estimated to fit the results corresponding to some particular solvable problems.

The formultation given by Gerck et al. /5/ presents some drawbacks when considering its possible generalization: the inclusion of terms with $O(n^{-1})$ into Eq.(20.20) transforms the bi-diagonal H matrix into a tri-diagonal matrix, and consequently the simple functional structure for E_n is lost.

All in all, the procedures presented in §.19 and §.20 reveal a close relationship between the CFM and the semiclassical approaches. In what follows we will discuss other related approximations that contribute to a general formulation, suitable to be applied to a large set of problems.

§. 21. Scaling Variational Method

The so-called Scaling Variational Method (SVM) embodies the analysis of the quantum mechanical properties of a system, by using trial wavefunctions, with a scaling factor which can be variationally optimized /6-8/. The optimum choice of such a factor gives an upper bound to the energy of the lower state associated with every irreducible representation corresponding to the eigenfunctions of the Hamiltonian operator. This section is devoted to presenting a brief discussion on the method and its more relevant properties, in order to make transparent its relationship with the VFM.

Let us consider a wavefunction $\Psi(\bar{x})$ normalized in a N-dimensional space:

$$||\Psi(\bar{x})|| = 1 \quad ; \quad \bar{x} = (x_1,\ldots,x_N) \quad , \tag{21.1}$$

and introduce within it a scaling factor a>0 by means of the unitary operator U_a (see Appendix A):

$$U_a\Psi(\bar{x}) = a^{1/2}\,\Psi(a\bar{x}) \quad . \tag{21.2}$$

The functional E(a) for the Hamiltonian H = T+V, defined through the wave function (21.2), gives

$$E(a) = \langle\Psi(\bar{x})|U_a^{+}HU_a\Psi(\bar{x})\rangle = a\langle\Psi(a\bar{x})H\Psi(a\bar{x})\rangle = \langle H\rangle(a) \quad . \tag{21.3}$$

The SVM consists in determining a such that

$$\left(\frac{\partial E(a)}{\partial a}\right)\ (a = a^*) = 0 \quad , \tag{21.4}$$

which leads to the fulfillment of the VT /9/:

$$\langle U_a^*\Psi(\bar{x}) \,||\, H,\bar{x}.\nabla \,|\, U_a^*\Psi(\bar{x})\rangle = \langle |H,\bar{x}.\nabla| \rangle (a^*) = 0 \qquad (21.5a)$$

$$2\langle T\rangle(a^*) = \langle \bar{x}.\nabla V\rangle(a^*) \qquad (21.5b)$$

From the results given in Appendix A we have

$$\langle T\rangle\ (a^*) = (a^*)^{-2}\ \langle T\rangle\ (1) \quad , \qquad (21.6)$$

Then, if V is a homogeneous function of degree m

$$\langle \bar{x}.\nabla V\rangle(a^*) = (a^*)^m\ m\langle V\rangle(1) \quad . \qquad (21.7)$$

Finally, Eqs.(21.5b), (21.6) and (21.7) allow one to get an expression for the optimum scaling factor a*:

$$a^* = \{\frac{m\langle V\rangle(1)}{2\langle T\rangle(1)}\}^{1/(m+2)} \qquad (21.8)$$

The substitution of Eqs. (21.6), (21.7) and (21.8) into Eq.(21.5) gives the extreme value of the functional E(a):

$$E(a^*) = \{(\frac{m}{2})^{2/(m+2)} + (\frac{2}{m})^{m/(m+2)}\}\ \{\langle T\rangle(1)\}^{m/(m+2)} \ .$$

$$.\{\langle V\rangle(1)\}^{2/(m+2)} \qquad (21.9)$$

Furthermore, it is easily deduced from previous relations:

$$(\frac{\partial^2 E(a)}{\partial a^2})\ (a = a^*) = 2(m+2)\ \langle T\rangle(1) > 0 \text{ iff } m > -2 \quad . \qquad (21.10)$$

Eq.(21.10) determines the condition to be satisfied by the potential $V(\bar{x})$ in order to get a minimum in $E(a^*)$.Eq.(21.9) has been used to show that the SVM predicts the correct analytic dependence of the energy on the quantum numbers defining the system /10,11/, and on the parameters contained in the Hamiltonian /10-15/. It is worth mentioning that the dependence on the quantum numbers predicted by the SVM is coincident with that provided by the JWKB method (Chapter II), and besides, the result seems to be independent of the chosen basis set $\{\Psi_i(\bar{x})\}$ /10,11/.

The above results are valid even when the potential $V(\bar{x})$ consists of two terms with different homogeneity degrees:

$$V(\bar{x}) = \lambda_1 V_1(\bar{x}) + \lambda_2 V_2(\bar{x}) \quad , \tag{21.11a}$$

$$\bar{x}.\nabla V_1 = m_1 V_1 \quad ; \quad x.\nabla V_2 = m_2 V_2 \quad ; \quad m_1 \neq m_2 \quad . \tag{21.11b}$$

In this latter case, there is no simple equation for the scaling factor a^* when applying the SVM (cf. §.16). The choice of the trial functions from any one of the two possible zero-order problems, i.e.:

$$H_i^0 \psi = E_i \psi_i \; ; \; H_i^0 = T + \lambda_i V_i, \; i = 1 \text{ or } i = 2 \quad , \tag{21.12}$$

enables us to obtain the RSPT up to the first order when the extreme $E(a^*)$ is expanded in power series of $\lambda_2 = 0 (\lambda_1 = 0)$, if $H_1^0 (H_2^0)$ is employed. The SVM allows the fulfillment of the RSPT together with the VT, whenever the scaling factor is variationally adjusted. This result suggests that the RSPT is a possible source of additional analytical information on the eigenvalues. This information may be introduced within the functional representations for the energy. This idea has been used by several authors to design variational renormalized perturbation series (§. 16), combining PT with the SVM /16-19/. Recently, it has been proved that identical conclusions to those derived here for the analytical structure of $E(a^*)$ are also valid for other useful quantities, such as $\psi_n(0)$ /20/.

The SVM presents an alternative respect to those methods discussed in §.20, in order to study the more relevant analytic properties of the energy function. In a later chapter, we shall see that the VFM permits the unification of previous different approaches in a simple and elegant way.

§.22. VFM from Heisenberg inequalities

Let us consider an N-dimensional problem given by a Hamiltonian H (atomic units are used throughout, i.e. $\hbar$=m=1):

$$H = \sum_{n=1}^{N} p_n^2 + V(\bar{x}) \; ; \; \bar{x} = (x_1,\ldots,x_N) \; ; \; p_n = -i\frac{d}{dx_n} \quad , \tag{22.1}$$

and its corresponding Schrodinger equation:

$$H\psi(\bar{x}) = E\psi(\bar{x}) \; ; \; \lim_{|x_i|\to\infty} \psi(\bar{x}) = 0 \; ; \; i = 1,2,\ldots,N \quad . \tag{22.2}$$

Our purpose is to build a variational functional (VF) corresponding to the eigenvalues E, and satisfying the Theorem (19.1). To that purpose, we start from the Heisenberg inequalities to get a function of -2 degree which represents the kinetic energy term of the VF. Using the results in §.1, we have

$$(\Delta p_i)^2 \, (\Delta x_i)^2 = A_i \geq \frac{1}{4} \quad ; \quad i = 1,2,\ldots,N \quad , \tag{22.3}$$

with $(\Delta M)^2 = \langle M^2 \rangle - \langle M \rangle^2$ the quadratic deviation associated with the operator M. Taking into account the boundary condition (22.2), we get

$$\langle p \rangle = -i \, \langle \Psi | \Psi' \rangle = -\frac{i}{2} \lim_{R\to\infty} |\Psi|^2 \Big|_{-R}^{R} = 0 \quad , \tag{22.4}$$

so that Eq. (22.3) leads to:

$$\langle p_n^2 \rangle = \frac{An}{q_n^2} \quad , \quad q_n = \Delta x_n \quad . \tag{22.5}$$

The use of Eq. (22.5) permits us to find the representation of the functional $\hat{T}(\bar{q})$ (Eq.(19.32)) as a function of degree -2 in the set of coordinates $\{q_i\}$ (assuming that A_n does not depend on q_n):

$$\hat{T}(\bar{q}) = \sum_{n=1}^{N} p_n^2 = \sum_{n=1}^{N} \frac{A_n}{q_n^2} \quad ; \quad \bar{q} = (q_1, \ldots, q_N) \quad . \tag{22.6}$$

The functional $F(\bar{q})$ can now be written in a general form:

$$F = \sum_{n=1}^{N} \frac{A_n}{q_n^2} + \hat{V}(\bar{q} - \bar{q}_0) \tag{22.7}$$

where $\hat{V}(\bar{q} - \bar{q}_0)$ is the representation of the expectation value $\langle \psi | V(\bar{x}) \psi \rangle$ in terms of $\bar{q}$. Vector $\bar{q}_0 = (\bar{q}_{01}, \ldots, q_{0N})$ has to be introduced due to the fact that V cannot be totally determined in terms of $\bar{q}$, as will be seen later on.

According to theorem 19.1, the functional (22.7) satisfies relationships similar to VT and HFT, when it is minimized in the configuration space. In this case, it is a minimization with respect to the quadratic deviations represented by q_i, that is to say

$$E \simeq F(q^*) \tag{22.8a}$$

$$\left(\frac{\partial F}{\partial q_i}\right) (q_i = q_i^*) = 0 \quad ; \quad \bar{q}^* = (q_1^*, q_2^* \ldots\ldots q_N^*) \tag{22.8b}$$

In order to complete the construction of F, we must find $V(\bar{q} - \bar{q}_0)$. Rosen /1/ applied certain semiclassical relations, which make up an appropriate starting point for our analysis. The semiclassical equalities can be justified by way of the following argument /21/: if N is the space dimension, a wide class of operators fulfil the property

$$\langle AB \rangle = \langle A \rangle \langle B \rangle + O(1|N) \quad . \tag{22.9}$$

Since the limit $N \to \infty$ can be related to the semiclassical limit of large quantum numbers $n \to \infty$, one concludes that for some operators /21/:

$$\lim_{n\to\infty} \{\langle A^2 \rangle - \langle A \rangle^2\} = 0 \quad . \tag{22.10}$$

For those potentials that obey the property

$$V((x_1,\ldots,x_i,\ldots,x_N)) = V((x_1,\ldots,-x_i,\ldots,x_N)) \; ; \; i=1,2,\ldots N \tag{22.11}$$

and considering that, as follows, from Theorem 1.2, $\langle x_i \rangle = 0$ for every i, Eq.(22.10) suggests the equality

$$\langle x_i^{2s} \rangle = B_{si} \langle x_i^2 \rangle^s = B_{si}\, q_i^{2s} \quad , \tag{22.12}$$

which is a suitable starting point to express $\tilde{V}(\bar{q})$ in terms of $\{q_i\}$. The semiclassical approximation proposed by Rosen /1/ consists of making

$$B_{si} = 1 \; , \; \forall s,i \quad , \tag{22.13}$$

which, for those models considered by the author (as well as for other models), is never fulfilled, even in the semiclassical limit. Eq.(22.13) corresponds to

$$\tilde{V}(\bar{q}) = V(\bar{q}) \quad , \tag{22.14}$$

i.e., the functional representation of the potential, $\tilde{V}$, is obtained through the change of coordinates by the quadratic deviations in the potential V. However, since Eq.(22.13) is not exactly satisfied, Rosen's approach does not take into account the correct number of

integration constants for the differential equation (19.31). This drawback suggests that the functions $\{B_{si}\}$ can play a relevant role when introducing additional analytical information about E into the functional F. Such functions the same as $\{A_i\}$, are unknown, up to here, but they will be dependent upon the quantum numbers and upon the whole set of parameters contained within the Hamiltonian.

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CHAPTER VII

APPLICATION OF THE VFM TO ONE-DIMENSIONAL SYSTEMS WITH TRIVIAL BOUNDARY CONDITIONS.

§. 23. Anharmonic oscillators and variational functional: general properties.

Let us consider a 2K- anharmonic oscillator, defined by the Hamiltonian

$$H(g,\lambda) = p^2+gx^2 + \lambda x^{2K} \quad ; \quad K = 2,3,\ldots,\lambda>0 \tag{23.1}$$

which, due to the Symanzik Theorem /1/, satisfies the unitary equivalence relationship (Appendix A)

$$H(g,\lambda) = \lambda^{1/(K+1)} \; H(g\lambda^{-2/(K+1)},1) \tag{23.2}$$

The eigenvalue $E(g,\lambda)$ associated with $H(g,\lambda)$ possesses a formal power series expansion in λ (with zero convergence radius) and a power series expansion in $\lambda^{-2/(K+1)}$ (with nonzero convergence radius):

$$E(1,\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n \quad ; \quad \lambda<<1 \quad , \tag{23.3a}$$

$$E(1,\lambda) = \lambda^{1/(K+1)} \sum_{n=0}^{\infty} e^{(n)} \lambda^{-2n/(K+1)} \quad ; \; \lambda>>1 \quad . \tag{23.3b}$$

Considering the general equations given in §.22, the VF associated with $E(g,\lambda)$ can be built from the Heisenberg inequalities:

$$(\Delta x)^2 \; (\Delta p)^2 = \langle p^2\rangle\langle x^2\rangle = A_n>0 \quad , \tag{23.4}$$

where we have omitted any reference to the quantum number in the average values. Then, the functional is

$$F_n(q) = \frac{A_n}{q^2} + q^2 + \lambda B_n q^{2K} \qquad (23,5a)$$

where

$$q^2 = \langle x^2 \rangle \quad , \qquad (23.5b)$$

$$B_n = \langle x^{2K} \rangle \langle x^2 \rangle^{-K} \quad , \qquad (23.5c)$$

and g = 1 in (23.5a) (which does not imply any loss of generality). Functions A_n and B_n must depend on λ, in addition to their natural dependence upon n. Such dependence can be determined as follows: from Theorem (19.1) we know that

$$\left(\frac{\partial F_n}{\partial \lambda}\right) (q = q^*) = \left(\frac{\partial F_n}{\partial \lambda}\right)_q (q = q^*) \qquad (23.6)$$

with q* the solution of the extreme condition equation

$$\left(\frac{\partial F_n}{\partial q}\right) (q = q^*) = 0 \qquad (23.7)$$

Deriving Eq. (23.5a) with respect to λ we find the result

$$\left(\frac{\partial F_n}{\partial \lambda}\right)_q = \frac{1}{q^2} \frac{\partial A_n}{\partial \lambda} + q^{2K} B_n + \lambda q^{2K} \frac{\partial B_n}{\partial \lambda} \qquad (23.8)$$

Eq.(23.8) provides a connection between A_n and B_n when the functional obeys the HFT, i.e.

$$\left(\frac{\partial F_n}{\partial \lambda}\right)\ (q = q^*) = \left(\frac{\partial E_n}{\partial \lambda}\right) = \langle x^{2K} \rangle = B_n\, q^{*2K} \tag{23.9}$$

Finally, the use of Eqs.(23.6) and (23.8) allows one to conclude that the HFT (Eq.(23.9)) is fulfilled iff

$$\frac{\partial A_n}{\partial \lambda} = -\lambda\ q^{*(2K+2)}\ \frac{\partial B_n}{\partial \lambda} \tag{23.10}$$

Eq.(23.10) is highly significant: if one wants to build a suitable approximation to the eigenvalue $E(1,\lambda)$ by way of the VF, then Eq. (23.10) must be solved, together with Eqs. (23.7) and (23.9), instead of the Schrödinger equation.

Obviously, this task is a very difficult one, so that it must be done in an approximate fashion. It has been proved that an acceptable description of $E(1,\lambda)$ can be obtained by means of the trivial solution of Eq. (23.10), that is to say, choosing A_n and B_n as constants independent on λ /2/. This approach makes up the first generalization regarding the original procedure by Rosen /3/.

Eq.(23.10) represents an unnecessary hindrance when trying to find a sensible functional representation for $E(1,\lambda)$, because it introduces two functions depending on λ. The very reason of this drawback is Eq. (23.5b). We show in what follows a way to develop the VFM theory using just one function $B_n = B_n(\lambda)$. Let us define F_n in an alternative way

$$F_n = \frac{A'_n}{q'^2} + q'^2 + \lambda\ B'_n q'^{2K} \tag{23.11}$$

where now A'_n does not depend on λ; that is, A'_n and B'_n are not coincident with A_n and B_n, as in Eqs.(23.4) and (23.5c). Considering the extreme condition with regard to q' in (23.11) we have

$$\left(\frac{\partial F_n}{\partial q'_n}\right)\ (q' = q'^*) = 0 \tag{23.12a}$$

$$A'_n = q'^{*4} + \lambda K B'_n \, q'^{*(2K+2)} \tag{23.12b}$$

Then, the extreme of F_n can be written as

$$F_n(q^*) = \frac{A'_n}{q'^{*2}} + q'^{*2} + \lambda B'_n \, q'^{*2K} = 2q'^{*2} + \lambda(K+1)B'_n \, q'^{*2K} \tag{23.13}$$

It is straightforward to verify that this extreme is a minimum:

$$\frac{\partial F_n}{\partial q'^2} = 6\frac{A'_n}{q'^4} + 2K(2K-1)\,\lambda B'_n \, q'^{(2K-2)} \quad , \tag{23.14}$$

$$\left(\frac{\partial^2 F_n}{\partial q'^{*2}}\right)(q' - q'^*) = 4+4(K^2+K)\,\lambda B'_n \, q'^{*(2K-2)} > 0 \quad . \tag{23.15}$$

The approximation to $E(1,\lambda)$ is determined by $F_n(q'^*)$. In order to get the HFT, we compute the derivative of F_n with respect to λ:

$$\left(\frac{\partial F_n}{\partial \lambda}\right)_{q'} = q'^{2K} \frac{\partial(\lambda B'_n)}{\partial \lambda} \tag{23.16}$$

and it follows at once that such theorem is satisfied iff

$$\langle x^{2K} \rangle = q'^{*2K} \frac{\partial(\lambda B'_n)}{\partial \lambda} \tag{23.17}$$

Eq.(23.17) allows one to find an expression for $B'_n(\lambda)$:

$$B'_n(\lambda) = {}_0\int^{\lambda} \langle x^{2K} \rangle \, q'^{*-2K} \, d\lambda + \lim_{\lambda \to 0} \{\lambda B'_n(\lambda)\} \tag{23.18}$$

Now we intend to establish a relationship among the expectation values $\langle x^2 \rangle$ and q'^*, B'_n , A'_n. Let us remind that when introducing the functional (23.11), Eqs.(23.5b) and (23.5c) are not valid any longer. Then, we start from the VT satisfied by the eigenfunctions associated with $H(1,\lambda)$:

$$2\langle T \rangle = \langle xV' \rangle \quad ; \quad \langle p^2 \rangle = \langle x^2 \rangle + K\lambda \langle x^{2K} \rangle \quad , \tag{23.19}$$

which permits one to write the energy as

$$E(1,\lambda) = 2\langle x^2 \rangle + (K+1)\ \lambda \langle x^{2K} \rangle \quad . \tag{23.20}$$

Considering that $F_n(q'^*) = E(1,\lambda)$, and substituting into (23.20), one obtains the first desired equation:

$$\langle x^2 \rangle = q'^{*2} - \frac{\lambda^2}{2}\ (K+1)\left(\frac{\partial B'_n}{\partial \lambda}\right)\ q'^{*2K} \tag{23.21}$$

On the other hand, introducing (23.21) and (23.17) in (23.19), and using (23.12b), it is found that

$$\langle p^2 \rangle = \frac{A'_n}{q'^{*2}} + \frac{K-1}{2}\ \lambda^2\ q'^{*2K}\ \left(\frac{\partial B'_n}{\partial \lambda}\right) \tag{23.22}$$

Eqs.(23.21) and (23.22) plainly reveal that all important expectation values as well as the energy can be computed for any λ in terms of the function $B'_n(\lambda)$.

Up to now, the function $B'_n(\lambda)$ is unknown; nevertheless , some of its general features can be determined, as shown below. Making $\lambda=0$, one deduces from (24.11) that

$$q'^*(\lambda=0) = (A'_n)^{1/4} \tag{23.23}$$

Since $q'^*(\lambda=0)$ is solely related to A'_n, this constant may be determined from the knowledge of the eigenvalue spectrum for $\lambda=0$ (which is usually known). Eq.(23.23) permits one to obtain

$$\lim_{\lambda\to 0} F_n(q'^*) = 2\,(A'_n)^{1/2} = \lim_{\lambda\to 0} E_n(1,\lambda) = E_n(1,0) \quad , \tag{23.24}$$

from where:

$$A'_n = \frac{1}{4}\, E_n(1,0)^2 \quad . \tag{23.25}$$

From Eqs. (23.17) and (23.24) we find a first property for $B'_n(\lambda)$:

$$0 < \{\lim_{\lambda\to 0} B'_n(\lambda) = B'_n(0)\} < \infty \quad , \tag{23.26}$$

since $\langle x^{2K}\rangle > 0 \;\forall\; K$.

In order to study the behavior of $B'_n(\lambda)$ for large enough λ values, we start from Eq.(23.12b). It is easily seen that for $\lambda>>1$, the following limit condition holds:

$$q'^{*2K} \to \{\frac{A'_n}{\lambda K B'_n}\}^{K/(K+1)} \quad ; \quad \lambda>>1 \quad . \tag{23.27}$$

The use of Eqs.(23.27) and (23.13) allows one to derive the asymptotic structure of the functional:

$$F_n(q'^*) \to \left[\frac{A'_n}{K}\right]^{K/(K+1)} (K+1)\,(\lambda B'_n)^{1/(K+1)} +$$

$$O(\lambda^{-1/(K+1)}) \quad ; \quad \lambda>>1 \tag{23.28}$$

The comparison between Eq. (23.28) and the λ dominant term in Eq.

(23.3b) for the exact eigenvalues, gives the condition

$$0 < \{\lim_{\lambda\to\infty} B_n'(\lambda) = B_n'(\infty)\} < \infty \tag{23.29}$$

Inequalities (23.26) and (23.29) suggest that $B_n'(\lambda)$ is a bounded function, in the sense that it must remain finite for all $\lambda \geq 0$. This result is particularly important within the context of this book, since it implies that the VFM allows changing the former problem of describing a monotonously increasing function (i.e., $E(1,\lambda)$), for another simpler one of adjusting a bounded function (i.e. $B_n'(\lambda)$).

Let us study now in detail the limiting values of $B_n'(\lambda)$. It follows at once from Eqs.(23.26), (23.17) and (23.23) that

$$B_n'(0) = (A_n')^{-K/2} \lim_{\lambda\to 0} \langle x^{2K} \rangle \tag{23.30}$$

Besides, from Eqs.(23.21) and (23.26), one concludes that

$$\lim_{\lambda\to 0} \langle x^2 \rangle = \lim_{\lambda\to 0} q'^{*2} = (A_n')^{1/2} \tag{23.31}$$

The last equation reveals that q'^2 can be interpreted as $\langle x^2 \rangle$ (and, in this case, as the quadratic deviation $(\Delta x)^2$) only if $\lambda\to 0$. Then, the relationship between the expectation values $\langle x^{2K} \rangle$ and $\langle x^2 \rangle^K$ can be considered as B_n' only when $\lambda\to 0$. When combining Eqs.(23.30) and (23.31), one obtains

$$B_n'(0) = \lim_{\lambda\to 0} \{\langle x^{2K} \rangle \langle x^2 \rangle^{-K}\} \tag{23.32}$$

Since $B_n'(\lambda)$ is a bounded function, Eq.(23.18) allows one to express $B_n'(\lambda)$ for $\lambda\to 0$ as follows

$$B_n'(\lambda) = \frac{1}{\lambda} \int_0^{\lambda} \langle x^{2K} \rangle \, (q'^*)^{-2K} \, d\lambda' \tag{23.33}$$

It is appropriate to make here a comment on the construction of the VF. As remarked previously, the choice of A_n and B_n as constants is a trivial solution of Eq.(23.10). Then, a solution like this one could be given in terms of the functions; for example, a possible choice would be:

$$A_n = A'_n \quad ; \quad B_n = B'_n(0) \tag{23.34}$$

Let us analyse carefully the meaning of this last solution. The substitution of (23.25) and (23.30) in (23.11) gives

$$F_n(q'^*) = \frac{A'_n}{q'^{*2}} + q'^{*2} + \lambda\{\lim_{\lambda\to} \langle x^{2K}\rangle\} \, (A'_n)^{-\frac{K}{2}} \, q'^{*2K} \tag{23.35}$$

and the change of variables

$$a^{*2} = A'^{1/2}_n \, (q'^*)^{-2} \tag{23.36}$$

transforms (23.35) into

$$F_n(a^*) = (A'_n)^{1/2} \, a^{*2} + (A'_n)^{1/2} \, a^{*-2} + \lambda a^{*-2K} \lim_{\lambda\to 0}\langle x^{2K}\rangle \tag{23.37}$$

On the other hand, from the VT (Eq.(23.19)) and Eq.(23.25) it follows the equality

$$(A'_n)^{1/2} = \frac{1}{2} E_n(1,0) = \lim_{\lambda\to 0} \langle p^2\rangle = \lim_{\lambda\to 0} \langle x^2\rangle \tag{23.38}$$

The insertion of this equation into (23.37) yields an expression for the extreme value of the functional in terms of a*, i.e.:

$$F_n(a^*) = a^{*2} \lim_{\lambda\to 0} \langle p^2\rangle + a^{*-2} \lim_{\lambda\to 0} \langle x^2\rangle + \lambda a^{*-2K} \lim_{\lambda\to 0} \langle x^{2K}\rangle \tag{23.39}$$

Eq.(23.39) can be written by means of an unitary operator U_a^* that generates dilatations (see §.21):

$$F_n(a^*) = \langle \psi^{(0)} | U_a^{\dagger} H(1,\lambda) U_a^* \psi^{(0)} \rangle \qquad (23.40a)$$

where

$$U_a \psi^{(0)}(x) = a^{1/2} \psi^{(0)}(ax) \quad ; \quad U_a^+ = U_{1/a} \qquad (23.40b)$$

and considering that $\psi^{(0)}(x) = \lim_{\lambda \to 0} \psi(x)$ is an eigenfunction of the Hamiltonian operator H(1,0) (zero-order Hamiltonian). Eq.(23.40a) is the same result arising from the SVM (§.21) and given by Eqs.(21.3) and (21.4), because $F_n(q'^*)$ is equal to the expectation value of the Hamiltonian in a zero-order basis set with a scaling factor, and where such mean value is an extreme /4,5/.

The extreme condition of the functional (Theorem 19.1) corresponds in this case with the variational extreme condition that fixes the constant $\underline{a}$ (dilatation factor) in the SVM. Consequently, the present discussion shows clearly that the SVM is a particular case of the VFM, subjected to the choice defined by Eq.(23.34).

As noted previously /5/, the SVM gives a reasonable qualitative description for the anharmonic oscillators eigenvalues for not very large λ-values. The VFM explains plainly the reason, since there exists a functional associated with the SVM which satisfies the VT and HFT (Theorem 19.1), but it contains only specific information on the problem for $\lambda \to 0$.

It has been pointed out that the SVM assures a proper dependence of the eigenvalues on the quantum numbers similar to that obtained via the JWKB method. It can be proved at once that such dependence is wholly assured by the choice $A_n = A'_n$ (Eq.(23.25)), and that it does not depend on the choice of $B'_n(\lambda)$. For that purpose, consider the harmonic oscillator eigenvalues

$$E_n(1,0) = (2n+1) \qquad (23.41)$$

and substitute them into Eqs.(23.25) and (23.28); the dependence on the quantum number for the asymptotic behavior of the functional is obtained immediately

$$F_n(q'^*) \to \{(4K)^{-K/(K+1)}(K+1)\left[B_n'(\infty)\right]^{1/(K+1)}\}(2n+1)^{2K/(K+1)}\lambda^{1/(K+1)} + O(\lambda^{-1/(K+1)}) \qquad (23.42)$$

which is precisely the dependence of the eigenvalues as the quantum numbers in the semiclassical limit. It is evident that from a suitable choice of $B_n'(\infty)$, one can get the JWKB result (instead of the SVM) for the constant between curly brackets in Eq.(23.42). In the same fashion as Eq.(23.32) determines the specific form of $B_n'(0)$, Eq.(23.42) is adequate to yield the constant $B_n'(\infty)$. However, this task presents a serious drawback: usually the coefficients $\{e^{(n)}\}$ are not analytically known. Some of these coefficients have been computed numerically for certain oscillators /6-8/. Due to this lack, we can employ the semiclassical result as an approximate starting point, making $e^{(n)} = e^{(n)}(JWKB)$. In §.5 we have discussed the first orders in the JWKB approximation for 1D problems. In the present situation the approximation up to the second order gives /6-8/:

$$e^{(0)} = e_n^{(0)} = 2^{K/(K+1)}C1\{(n+1/2) + \delta_K(n+1/2)^{-1} + O(n+1/2)^{-2})\}^{2K/(K+1)} \qquad (23.43a)$$

$$C_1 = 2^{(K-2)/(K+1)}\{(K+1(\pi\Gamma(1/K)\Gamma(1/2K)^{-2}\}^{2K/(K+1)} \qquad (23.43b)$$

$$\delta_K = \frac{2K-1}{12\pi(K+1)}\,\mathrm{ctg}\,(\frac{\pi}{2K}) \qquad (23.43c)$$

The substitution of (23.43) in (23.3b) and the identification of the first term in the power series expansion with the asymptotic expression (23.42) yields the following expression for $B_n'(\infty)$ as a function of K and n:

$$B'_n(\infty) = \left(\frac{C1}{K+1}\right)^{K+1} (2K)^K \left\{1+\frac{\delta_K}{(n+1/2)}2\right\}^{2K} \qquad (23.44)$$

Note that unlike $B'_n(\infty)$ (Eq.(23.44)), $B'_n(0)$ (Eq.(23.32)) cannot be expressed in a simple way as a function of K. Notwithstanding, $B'_n(0)$ can be computed in a straightforward manner for K = 2,3,... by means of the hypervirial relationships given in §.3.

These results allow one to have a different trivial solution for Eq.(23.10) from that studied previously (Eq.(23.34)), i.e.,

$$A_n = A'_n \quad ; \quad B_n = B'_n(\infty) \qquad (23.45)$$

This solution is particularly important, since it shows that the VFM is general enough so as to unify the SVM with other approximations, such as those given by Rosen /3/ and Fernández and Castro /5/. Besides, it shows that the VFM makes up an alternative method for extending, the JWKB semiclassical series, so that one can get valid results within the whole range of the parameter λ.

The present discussion for the VFM makes clear the connection between the results predicted by the JWKB and SVM approximations. These relations have been discussed in the literature /5/, but the treatment given here on this point is somewhat more detailed.

The bounded character of function $B'_n(\lambda)$ is a very convenient feature, because this property makes the method specially appropriate to approxime eigenvalues of Hamiltonians with two well different regimes of values for those parameters contained within it. In the present case, the regimes correspond to $\lambda \to 0$ and $1/\lambda \to 0$, whose characteristic expansion series are (23.3a) and (23.3b), respectively. The choice of the constants as in Eq.(23.45), allows one to introduce information on the analytic behaviour of energy for $1/\lambda$ via A'_n, and that corresponding to the $1/\lambda \to 0$ regime by way of $B'_n(\infty)$.

There are other alternative choices for B'_n, keeping B'_n constant.

Naturally, it can be selected B_n' as an adjustable parameter, so as to fit an "exact" eigenvalue (numerically determined) for a given λ-value. This procedure was followed by Orland /9/, in a different context regarding that one presented here. This author considered just one free parameter. According to our previous discussion, it is convenient to use two parameters, A_n' and B_n'. The first one is particularly suitable for fixing the dependence of the eigenvalues with respect to the quantum numbers. The results derived from different choices of B_n' (as a constant) can be seen in a comparative fashion in Ref./2/, where the quartic (K=2) anharmonic oscillator is the reference model.

§.24. Translation of Coordinates and Variational Functional.

We have briefly discussed in §.22 the inclusion of a parameter $\bar{q}_0$ when constructiong the VF in those cases where the potential has no definite parity (see Eq.(22.7)). Such a modification must be introduced since the functional has not a single extreme with respect to the variations in $\bar{q}$ for that class of potential function.

This multiplicity of solutions may be set aside by way of $\bar{q}_0$. In other terms, the parameter $\bar{q}_0$ can be used in such a manner so as to obtain a single valued potential for all the roots $\bar{q}^*$. This property was applied by Gersch and Braden /10/ in order to study radial systems;

Since we will not study again with the present formalism problems without definite parity, let us consider a very simple model to illustrate the main ideas.

We consider a shifted oscillator whose Hamiltonian is

$$H(g,\lambda) = p^2 + gx^2 + \lambda x \quad . \tag{24.1}$$

The associated eigenvalues are well known, viz:

$$E_n(g,\lambda) = (2n+1)\, g^{1/2} - \frac{\lambda 2}{4g} \quad . \tag{24.2}$$

In order to simplify matters, the VF is defined as

$$F_n(q) = \frac{A}{q^2} + \hat{V}(q-q_0) = \frac{A}{q^2} + g(q-q_0)^2 + \lambda(q-q_0) \quad . \tag{24.3}$$

The variational extreme condition,

$$\left(\frac{\partial F_n}{\partial q}\right)\ (q=q^*) = 0 \tag{24.4}$$

gives for (24.3)

$$A = gq^{*3}\ (q^* - q_0 + \frac{\lambda}{2g}) \quad . \tag{24.5}$$

It can be seen that now q_0 may be chosen in order to have a single real root for q* and for that purpose we make

$$q_0 = \frac{\lambda}{2g} \quad , \tag{24.6}$$

i.e.,

$$q^* = \left(\frac{A}{g}\right)^{1/4} \quad . \tag{24.7}$$

Thus, substitution of Eqs.(24.5)-(24.7) into Eq.(24.3) yields the functional extreme value

$$F_n(q^*) = \frac{A}{q^{*2}} + g(q^{*2} - 2q_0q^* + q_0^2) + \lambda(q^*-q_0) =$$

$$2\left(\frac{A}{g}\right)^{1/2} - \frac{\lambda^2}{4g} \tag{24.8}$$

Evidently, the choice of A subjected to Eq.(23.25)

$$A = \frac{1}{4} E_n(1,0)^2 = (n+1/2)^2 \quad , \tag{24.9}$$

permits one to obtain the exact eigenvalues (Eq.(24.2)) from Eq.(24.8).

The meaning of the parameter q_0 appears at once from the following considerations: Eq.(24.3) allows one to get

$$(\frac{\partial F_n}{\partial \lambda})_q = -q_0 = -\frac{\lambda}{2g} \quad , \tag{24.10}$$

and besides the eigenvalues fulfil the HFT, so that

$$\frac{\partial E_n}{\partial \lambda} = -\frac{\lambda}{2g} = \langle x \rangle \quad . \tag{24.11}$$

Finally, the equality between Eqs.(24.10) and (24.11) gives

$$q_0 = - \langle x \rangle \quad . \tag{24.12}$$

We see that the q_0 factor is related to the translation of shifting the system undergoes respect to that of zero-order. In the case of even parity, i.e. $\langle x \rangle = 0$ (Theorem 1.3), then $q_0 = 0$. This last condition was used in previous paragraphs.

Now we can derive other meaningful results. From the HFT we know that

$$\frac{\partial E_n}{\partial g} = \langle x^2 \rangle \quad , \tag{24.13}$$

and a further application of Theorem 19.1 yields

$$\left(\frac{\partial F_n}{\partial g}\right)_q (q = q^*) = \left(\frac{A}{\sigma}\right)^{1/2} + \frac{\lambda^2}{4\sigma 2} = \langle x^2 \rangle \quad . \tag{24.14}$$

The introduction of Eqs.(24.6), (24.7) and (24.12) into Eq.(24.14) gives

$$q^{*2} = \langle x^2 \rangle - q_0^2 = (\Delta x)^2 \quad , \tag{24.15}$$

which confirms the fact that, when inserting the q_0-factor, the variable q* becomes again a quadratic deviation.

§.25. Central Field Systems

This section is devoted to discussing the application of the precedent method for comparting in an approximate fashion, the eigenvalues of central field systems.

Let H be the Hamiltonian describing a particle subjected to a central field:

$$H = p^2 + V(r) = \sum_{n=1}^{3} p_n^2 + V(r) \quad ; \quad r^2 = x_1^2 + x_2^2 + x_3^2 \quad ; \quad p_n = -i \frac{d}{dx_n} \, , \tag{25.1}$$

with p_n the linear momentum associated with the n-th cartesian coordinate. According to the results derived in §.22, the functional can be written as

$$F(\bar{q}) = \sum_{n=1}^{3} \frac{An}{q_n^2} + \hat{V}(q) \quad , \tag{25.2a}$$

where

$$q \equiv ||\bar{q}|| \quad ; \quad \bar{q} = (q_1, q_2, q_3) \quad . \tag{25.2b}$$

In order to adapt the functional (25.2a) to the specific symmetry character of the radial systems, we start from the extreme condition of F

$$\left(\frac{\partial F}{\partial q_n}\right)\ (q_n = q_n^*) = 0 \quad ; \quad n = 1,2,3 \quad , \tag{25.3}$$

which gives

$$\frac{A_n}{q_n^{*2}} = \frac{1}{2}\, q_n^*\ \left(\frac{\partial V}{\partial q_n}\right)\ (q_n = q_n^*) \quad . \tag{25.4}$$

Since $\hat{V}$ depends only on q, we have

$$\frac{\partial\, \hat{V}}{\partial q_n} = \left(\frac{\partial \hat{V}}{\partial q}\right)\ \left(\frac{\partial q}{\partial q_n}\right) = \frac{q_n}{q}\ \left(\frac{\partial \hat{V}}{\partial q}\right) \quad , \tag{25.5}$$

which, after introducing this result into Eq.(25.4), gives

$$\frac{A_n}{q^{*2}} = \frac{1}{2}\, q_n^{*2} q^{*-1}\ \left(\frac{\partial V}{\partial q}\right)\ (q_n = q_n^*) \quad . \tag{25.6}$$

From Theorem (19.1) we know that F(q) satisfies the HFT and the VT, through the condition (25.3). In order to change the functional's symmetry, we sum over the coordinate number on both sides of Eq.(25.6)

$$2 \sum_{n=1}^{3} \frac{A_n}{q_n^2} = q^*\ \left(\frac{\partial \hat{V}}{\partial q}\right)\ (q = q^*) \quad , \tag{25.7}$$

which makes up the VT for the functional F, as a function of q. Eq. (25.7) can be re-written in a more convenient way. From Eq.(25.6) one obtains

$$\left\{ \sum_{n=1}^{3} A_n^{1/2} \right\} = \frac{1}{2}\, q^{*3}\ \left(\frac{\partial \hat{V}}{\partial q}\right)\ (q = q^*) \quad , \tag{25.8}$$

which gives another expression for the VT in terms of V:

$$2\,\frac{A}{q^{*2}} = q^{*}\,\left(\frac{\partial V}{\partial q}\right)\,(q = q^{*}) \quad ; \quad A^{1/2} = \sum_{n=1}^{3} A_n^{1/2} \quad . \tag{25.9}$$

Eq.(25.9), unlike Eq.(25.7), depends solely of q, which is the natural variable for a spherical symmetry problem. This last result leads to a functional depending just on q:

$$F(q) = \frac{A}{q^2} + \hat{V}\,(q) \quad ; \quad \left(\frac{\partial F(q)}{\partial q}\right)\,(q = q^{*}) = 0 \tag{25.10}$$

The functional (25.10), in contrast with (25.2), has only a single A term for the kinetic energy $\hat{T}$, which must be fitted through the use of some known analytic property for the eigenvalues. Furthermore, this result allows one to derive the following conclusion: the VF obtained from the application of those equations derived in §.22 (i.e., by means of cartesian coordinates) may be adapted to the model's symmetry, by way of the extreme condition in the configuration space. The relevance of this point will be plainly seen in the next chapter, when dealing with problems subjected to non-radial symmetry.

§. 26. Application of the variational functional to systems with confining potential.

The aim of this section is to present some simple applications of the VFM formulated previously to radial systems with two-term potentials. The VF to be used is adapted to the radial symmetry via the arguments given in §.25.

Let us consider the set of problems defined by

$$H = p^2 + V(r) \quad , \tag{26.1}$$

with

$$V(r) = -\frac{g}{r} + \lambda r^K \quad ; \quad K>0. \tag{26.2}$$

The cases K = 1,2 correspond with the models known as linear and harmonic confining potentials, respectively. They provide appropriate phenomenological descriptions for high energy interaction spectra within the realm of quark theory /11-13/, (see Appendix G).

Furthermore, the model K = 1 has been studied in relation with the radial Stark effect /14,15/. Here we restrict ourselves to use potentials (26.2) as simple examples to apply the method with the purpose of analysing its properties.

From Eq.(25.10) we can construct the functional associated with eigenvalues of (26.2), which is defined through the equations

$$F(q) = \frac{A}{q^2} - \frac{g}{q} + \lambda B q^K \quad ; \quad \left(\frac{\partial F(q)}{\partial q}\right) (q = q^*) = 0 \quad , \tag{26.3}$$

where functions A and B have the meaning discussed previously in §.23 for anharmonic oscillators. Let us consider that, by definition, A does not depend on g and λ, and that such dependence could appear, eventually, in function B. A and B must depend on quantum numbers. The HFT is given by (Theorem 19.1)

$$\left(\frac{\partial F}{\partial \lambda}\right) (q = q^*) = q^{*K} \frac{\partial(\lambda B)}{\partial \lambda} = \langle r^K \rangle \tag{26.4}$$

In addition to the energy, there are other important expectation values related to the model (26.2), mainly $\langle p^2 \rangle$ and $\langle 1/r \rangle$. All of them can be expressed in terms of B, using a similar argument to that followed in §.23. We start from the VT:

$$\langle p^2 \rangle = \frac{1}{2} g \left\langle \frac{1}{r} \right\rangle + \frac{K\lambda}{2} \langle r^K \rangle \tag{26.5}$$

which allows one to write the eigenvalues as

$$E = -\frac{1}{2} g \left\langle \frac{1}{r} \right\rangle + \frac{K+2}{2} \lambda \langle rK \rangle \tag{26.6}$$

On the other hand, the F extreme value is obtained from (26.3)

$$F(q^*) = -\frac{g}{2q^*} + \frac{K+2}{2} \lambda B q^{*K} \quad . \tag{26.7}$$

The identification of (26.6) with (26.7), together with Eq.(26.4), leads one at once to the equality:

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{q^*} + \frac{K+2}{g} \lambda^2 q^{*K} \left(\partial B / \partial \lambda \right) \quad . \tag{26.8}$$

Finally, substituting Eqs.(26.4) and (26.8) in Eq.(26.5) gives the result

$$\langle p^2 \rangle = \frac{A}{q^{*2}} + (K+1) \lambda^2 q^{*K} \left(\partial B / \partial \lambda \right) \quad . \tag{26.9}$$

It is worth pointing out again that the choice B=constant yields semiclassical-like relationships:

$$\langle p^2 \rangle = \frac{A}{q^{*2}} \; ; \; \left\langle \frac{1}{r} \right\rangle = \frac{1}{q^*} \; ; \; \langle r^K \rangle = B q^{*K} \quad . \tag{26.10}$$

In order to illustrate the VFM's properties, we choose A and B as constants, determined in an appropriate fashion. A may be obtained by way of the condition $\lambda \to 0$, as in §.23. From the extreme condition (26.3), we have

$$\lim_{\lambda \to 0} q^* = \frac{2A}{g} \quad , \tag{26.11}$$

which substituted in (26.7) gives

$$\lim_{\lambda\to 0} F(q^*) = -\frac{1}{4A} q^2 \qquad (26.12)$$

Since for $\lambda\to 0$ the model turns out to be a Coulomb potential, we know that

$$\lim_{\lambda\to 0} E = -\frac{1}{4n^2} q^2; \quad n = n_r+\ell+1 \geq 1 \quad , \qquad (26.13)$$

where n_r and ℓ are the number of radial and angular zeros of the wavefunction associated with the eigenvalue E, respectively. The comparison between (26.12) and (26.13) yields:

$$A = n^2 \qquad (26.14)$$

In order to get a simple enough functional valid within the whole range of λ-values, it is convenient to introduce into B the analytic information about the problem when $g\to 0$ (or $\lambda\to\infty$), since the information for the opposite regime ($\lambda\to$) is contained into A.

The eigenvalues for K = 1,2 are known in the limit $g\to 0$; accordingly, such information could be used to adjust B. For an arbitrary K-value, the eigenvalues are not known, and so one must take recourse of approximate formulas to obtain general results. The JWKB method /12/ is an appropriate source to derive such approximate results. Then, let us consider the Hamiltonian

$$H' = p^2 + \lambda\, r^K \qquad (26.15)$$

whose classical eigenvalues are /12/ (see chapter II)

$$E = E_{n_r,\ell} \simeq \lambda^{2/(K+2)} \{D_K (n_r + \frac{\ell}{2} + \frac{3}{4})\}^{2K/(K+2)} \qquad (26.16a)$$

$$D_K = 2K\pi^{1/2}\Gamma(\frac{3}{2}+\frac{1}{K})\,\Gamma(\frac{1}{K})^{-1} \qquad (26.16b)$$

Eq'(26.16a) is exact just for K = 2 (isotropic harmonic oscillator) and turns to be correct for $K \neq 2$ only when $n_r >> \ell$.

From the extreme condition (26.3) for $g \to 0$, one gets

$$q^* \to (\frac{2A}{\lambda KB})^{1/(K+2)} \quad . \qquad (26.17)$$

Substituting (26.17) into (26.7) one gets the following dominant term for the functional extreme value when $g \to 0$

$$F(q^*) \to (K+2)\ 2^{-2/(K+2)}\ (\frac{A}{K})^{K/(K+2)}\ \{\lambda B\}^{2/(K+2)} \qquad (26.18)$$

The comparison between Eqs.(26.16a) and (26.18) reveals that, in accordance with Theorem 19.1, the VFM predicts the correct growth of the eigenvalues as functions of λ.

It was shown in §.23 that the determination of A from the spectrum corresponding to $\lambda \to 0$ allows one to describe properly the dependence of the eigenvalues with the quantum number at the semiclassical limit. Our present case is different because the spectrum at the regime $\lambda \to 0$ has an "accidental" degeneracy in ℓ, which is broken when $\lambda \to 0$.

Obviously, the equivalence between Eqs.(26.16a) and (26.18) may be gotten through the constant B in the $\lim_{\lambda \to \infty} B(\lambda)$. The comparison of both equations leads to the result

$$B = 2(D_K)^K\ \{\frac{K^K}{(K+2)^{K+2}}\}^{1/2}\{\frac{n_r+\ell/2+3/4}{n}\}^K \quad . \qquad (26.19)$$

The choice of constants A and B through Eqs.(26.14) and (26.19),

respectively, completes the construction of a simple functional (Eq. (26.3)) which permits a qualitative description of $E(g,\lambda)$ as a K-function within the whole range of g and λ values. It is important to recall that such functional gives the qualitative analytic structure of the eigenvalue spectrum via the extreme condition. Besides, the given choice for A and B allows the connection of the hydrogen atom eigenvalues with JWKB semiclassical ones as in Eq.(26.15).

Now we proceed to show the usefulness of previous equations by means of a simple, illustrative example.

Example: Let us consider K = 1, viz. the lineal confining model /11/. We start from Eq.(26.16b) to define the functional:

$$D_1 = \frac{3\pi}{2} \quad . \tag{26.20a}$$

One gets the constant B when replacing into Eq.(26.19):

$$B = 3^{-1/2}\ \pi\left[\frac{n_r+\ell/2+3/4}{n}\right] \quad . \tag{26.20b}$$

The eigenvalues are then approximated by the extreme value of the functional (Eqs.(26.3) and (26.7)):

$$F = \frac{3A}{q^{*2}} - \frac{2}{q^*} \quad ; \quad g = 1 \quad , \tag{26.21}$$

where q* is the root of Eq.(26.3):

$$2n^2 = q^* + \lambda 3^{-1/2}\ \pi\left[n_r+\frac{\ell}{2}+\frac{3}{4}\right]\ n^{-1}\ q^{*3} \quad . \tag{26.22}$$

In order to make a comparison with "exact" results (numerically obtained) /11/, we present some figures for the first states in a wide range of λ-values. The nomenclature is the same as in Ref.11, and the

approximated eigenvalues $E_{n_r,\ell}$ are: $E_{0,0}(1S)$, $E_{1,0}(2S)$, $E_{0,1}(1P)$, $E_{2,0}(3S)$, $E_{1,1}(2P)$, $E_{0,2}(1D)$ and $E_{1,2}(2D)$. Results for $F(q^*)$ are given in Table 7.1 for several λ-values, which have been chosen in such a way to enable a proper comparison with those presented in Ref. 11. The results are really excellent considering the naive character of the present approximation scheme, since it just involves Coulomb and lineal confining models eigenvalues (the latter at the semiclassical level).

An analysis of Table 7.1 permits one to derive the following conclusions:

i) The accuracy of the results increases with n_r for a given ℓ-value, as one might expect. However, it is remarkable that the semiclassical condition seems to be already accurate enough for the state 3S ($n_r = 2$, $\ell = 0$), and that the agreement for such state is up to the last given figure.

ii) The accuracy of the results decreases when ℓ increases, for a fix n_r-value. This fact is perfectly reasonable, since it involves a departure from the semiclassical condition $n_r >> \ell$.

iii) The results improve when λ diminishes, for a given state, since the functional has the correct behaviour for $\lambda \to 0$.

iv) The level ordering of the spectrum is important to understand the characteristic transitions in high-energy spectra, as those occuring in elementary particles theory /12,13/. Then, it is noteworthy that the VFM allows one to approach in a simple and quick way the eigenvalues with a correct level ordering. This prediction even acquires more relevance when considering that the use of a semiclassical approximation for the Hamiltonian (26.15) introduces ficticius degeneracies /16-18/.

Present conclusions are valid for any other potential $V(r)=r^K$, $K>1$. All the present approximate numerical results are lower bounds for the exact eigenvalues, which is probably due to the employment of JWKB information.

Furthermore, these results complement and generalize Banerjee's work /19/ on this field, where he got a simple expression for eigen-

values associated with this model and subjected to the correct ordering. This author applied the Rayleigh-Ritz method with a scaled basis set together with some concepts from perturbation regime theory to derive a functional dependent on the quantum numbers.

NUMERICAL RESULTS

Table 7.1. First eigenvalues of the Hamiltonian $H = p^2 + \lambda r - 1/r$ computed with the VFM with B = B(JWKB).

	States						
λ	1S [a]	1P	2S	1D	2P	3S	2D
500	139.1 [b]	201.3	252.5	254.0	300.7	344.0	344.9
	(140.6) [c]	(207.7)	(252.9)	(265.5)	(304.4)	(344.0)	(352.0)
125/2	33.0	49.3	61.9	62.7	74.3	35.1	35.5
	(33.4)	(50.9)	(62.0)	(65.4)	(75.3)	(85.1)	(87.3)
500/27	13.8	21.4	27.0	27.5	32.5	37.4	37.7
	(14.1)	(22.1)	(27.0)	(28.7)	(33.1)	(37.4)	(38.5)

a) Nomenclature for the states according to Ref./11/.

b) Results from the functional of §.26.

c) Exact results numerically determined. 1S state numerical results were obtained in our laboratory. The remaining results have been gotten from Ref./11/.

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CHAPTER VIII

APPLICATION OF THE VFM TO ONE-DIMENSIONAL SYSTEMS WITH BOUNDARY CONDITIONS FOR FINITE VALUES OF THE COORDINATES.

§. 27. Variational functional and finite boundary conditions

Quantum Systems subjected to finite BC are valuable in several fields of Chemistry and Physics. Thus, a large number of phenomena require the use of bounded quantum models in order to rationalize them in a natural manner.

The two most usually employed BC are Dirichlet BC (DBC) and von Neumann BC (VNBC). Some illustrative phenomena where finite BC are used are:

i) Properties of matter highly compressed: the state of atoms, molecules or ions within matter under large pressures may be described by mimicking the effect of neighbor electronic charges by way of an infinite potential surface. So the characteristic wavefunction of the system fulfils DBC, since it has a zero at that surface. These conditions enable one to define the pressure acting on the particle under consideration and to study the dependence of such property with several other physical properties, such as polarizability, magnetic shielding and hyperfine splitting /1-3/.

ii) Electronic properties of metals: within the context of Wigner and Seitz theory of solids, the wavefunction describing the electron movement obeys VNBC on the surface that limits a given atomic volume /9-12/. In addition, other solid state properties, such as thermal properties and second order phase transitions can be analysed via some simple models subjected to DBC /13-16/.

iii) Astronomical applications: there is a large assortment of astronomical phenomena which can be explained through particular models and equations of bounded systems.

Some well-known examples are the proton-deuteron transformation as an energy source in dense stars /17/; electronic properties in white-dwarf stars /18/; rate of escape of stars from galactic clusters /45/, etc.

Other illustrative examples can be seen in Refs./19,20/.

Several models have been studied to describe bounded systems. Among them, it is worth mentioning the hydrogen atom surrounded by a spherical impenetrable surface /1-7,21-36/; a penetrable one /7,37/, surfaces with different geometries /33,40/; enclosed hydrogen atom subjected to external fields /41-43/; bounded harmonic oscillator /13-15, 17, 18. 36, 44-56/; multidimensional isotropic oscillators /36,57/; enclosed quartic oscillators /58/ and 1D bounded linear potentials /16, 59-61/, as well as atoms and molecules enclosed within boxes with different BC/62-69/.

All these models were studied by means of several approximate methods, such as Rayleigh-Ritz variational procedure, the semiclassical JWKB approximation, numerical integration of Schrödinger equation and perturbation theory. A comprenhensive list of these methods may be found in Ref. 20 and references therein.

Our interest is to show the usefulness of the VFM to study bounded systems, and to derive simple analytic expressions for the eigenenergies. From the theoretical standpoint it is relevant to apply the VFM to bounded systems, in order to illustrate how the formalism is adapted to the finite BC /70-72/.

In §.19 it was shown the essential role played by the VT and HFT in determining the variational functional that approaches the eigenvalues of quantum systems. Within the realm of bounded systems the starting point is similar, but the VT has a different form. Such theorem possesses an identical expression for those systems subjected to DBC and VNBC under isotropical deformations (see §.3), i.e.

$$-2\langle T\rangle + \langle vV\rangle = 3\Omega \frac{\partial E}{\partial \Omega} \tag{27.1a}$$

$$v = \sum_{n=1}^{N} \bar{r}_n . \nabla_n \tag{27.1b}$$

with v the virial operator associated with the N-particle system, T, V and E having the usual meanings, and Ω the configuration space volume where particles are confined. For isotropic deformations, Ω depends

just on one parameter and the BC are verified on the surface limiting Ω.

The r.h.s of Eq.(27.1a) is zero for a so-called macroscopic condition, that corresponds to

$$\lim_{\Omega\to\infty} (\Omega\frac{\partial E}{\partial \Omega}) = 0 \qquad (27.2)$$

However, this term (virial of the"constraint forces" introduced by the finite BC) is in general nonzero, and this fact introduces a difference regarding the treatment presented in §.19. Therefore, the first step is to restate Theorem 19.1 for this new sort of systems, and to use it as a starting point to construct the variational functional. For the sake of simplicity we restrict the analysis to that situation where the limiting surface enclosing the volume Ω is a sphere with radius r_o. In such a case the VT states:

$$-2 \langle T\rangle + \langle vV\rangle = r_o\frac{\partial E}{\partial r_o} \quad ; \quad r_o = (3\Omega/4\pi)^{1/3} \quad . \qquad (27.3)$$

This result enables one to extend Theorem 19.1 as follows:

Theorem 27.1: Let $\hat{T}(\bar{q}, r_o)$ be a functional of degree -2 in $q\equiv||\bar{q}||$ and r_o, i.e.,

$$\hat{T}(a\bar{q},ar_o) = a^{-2}\hat{T}(\bar{q}, r_o) \qquad (27.4)$$

with $\bar{q}$ an N dimensional vector, and let $\hat{V}(\bar{q})$ be a functional depending just on $\bar{q}$. Then, the functional $F(\bar{q}, r_o)$ given as:

$$F(\bar{q},r_o) = \hat{T}(\bar{q},r_o) + \hat{V}(\bar{q}) \qquad (27.5)$$

satisfies relations like VT and HFT, when F takes an extreme value in

configuration space.

Proof: The proof follows a similar argument as that employed for Theorem 19.1. Starting from the relationship

$$\bar{q}.\nabla F + r_o \frac{\partial F}{\partial r_o} = \bar{q}.\nabla \hat{T} = \bar{q}.\nabla \hat{V} + r_o \frac{\partial \hat{T}}{\partial r_o} \quad , \tag{27.6}$$

and applying (27.4) and Euler Theorem for homogeneous functions, one gets:

$$\bar{q}.\nabla F + r_o \frac{\partial F}{\partial r_o} = -2\hat{T} + \bar{q}.\nabla \hat{V} \quad . \tag{27.7}$$

If q is chosen in such a way that F is an extreme in configuration space, viz.

$$\left(\frac{\partial F}{\partial q_i}\right) \; (q_i = q_i^*) = 0 \; ; \quad i = 1,2,\ldots,N \tag{27.8}$$

we obtain for Eq.(27.7) the result

$$r_o \left(\frac{\partial F}{\partial r_o}\right) \; (q=q^*) = -2 \; \hat{T}(q^*, r_o) + (\bar{q}.\nabla \hat{V}) \; (q=q^*) \tag{27.9}$$

where $q^* \equiv ||\bar{q}^*||$ and $\bar{q}^* \equiv (q_1^*, q_2^*, \ldots, q_N^*)$. The comparison of Eqs.(27.3) and (27.9) allows us to conclude that F fulfils a relationship like VT, playing the functional F the role of eigenvalue E.

Let us analyse the dependence of F with any parameter α explicitty contained within the functional:

$$\frac{\partial F}{\partial \alpha} = \left(\frac{\partial F}{\partial \alpha}\right)_q + \sum_{n=1}^{N} \left(\frac{\partial F}{\partial q_i}\right)_\alpha \frac{\partial q_i}{\partial \alpha} \tag{27.10}$$

By application of condition (27.8) we get

$$(\frac{\partial F}{\partial \alpha})\ (q = q^*) = |\frac{\partial F}{\partial \alpha}|_q\ (q = q^*) \qquad (27.11)$$

and this equation is similar to HFT (see chapter VI)*.

Notice that this Theorem does not allow one to construct an unique functional from the HFT and VT, rather it assures only under conditions such Theorems are satisfied for certain type of functionals.

The comparison between theorems 27.1 and 19.1 allows one to verify that finite BC introduce in the functional a substantial difference consisting in an explicit dependence on r_o. We have chosen in Theorem 27.1 that dependence in such a manner that T is an homogeneous function of degree -2 in q and r_o. However, there is a different alternative to formulate the functional satisfying the VT and it may be stated in the following

Corollary 27.1: Let $\tilde{T}(q,r_o)$ be a function of degree -2 in $q \equiv ||\bar{q}||$ and r_o, and $\hat{V}(\bar{q},r_o)$ a function of degree m in $\bar{q}$ and r_o. Then, the functional $F = \hat{T}\ (\bar{q},r_o)$ when made an extreme with regard to q, satisfies the VT and HFT in a similar fashion as the eigenvalues of H = T+V (subjected to DBC or VNBC) do, with V an homogeneous function of degree m in the coordinates.

Proof: The proof is similar to that followed in Theorem 27.1. Now it must be taken into account the equation

$$\bar{q}.\nabla F + r_o \frac{\partial E}{\partial r_o} = \bar{q}.\nabla\hat{V} + r_o\frac{\partial T}{\partial r_o} + \bar{q}.\nabla\hat{V} + r_o\frac{\partial\hat{V}}{\partial r_o} = -2\hat{T} + m\tilde{V}\ \ * \ . \qquad (27.12)$$

These two precedent Theorems permit one to derive the following practical consequence to construct the functional: when the Hamiltonian possesses terms with definite homogeneity, then the functional must have similar terms consisting of homogeneous functions with the same degree.

Theorem 27.1 allows one to define a number of functionals to des-

cribe bounded systems with the restriction imposed on the $\hat{T}$ structure. Under the hypotheses of the Theorem, a possible general expression for $\hat{T}$ should be

$$\hat{T} = \frac{A_1}{qr_o} + \frac{A_2}{r_o}2 + \frac{A_3}{q^2} + \frac{A_4}{q^2-r_o^2} + \frac{A_5}{(q-r_o)}2^{+\ldots,q<r_o} \qquad (27.13)$$

Obviously, in order to perform any computation and verify the usefulness of the extended VFM presented in this section, it is necessary to cut the expansion (27.13) off.

The following illustrative example may be helpful to fix ideas:

Example: Let us consider the bounded 1D harmonic oscillator /7,13-15, 17,18,36,44-56/, which has been used to test several approximate methods. Despite its simplicity, this model is not trivial in the sense that its associated stationary Schrödinger equation is not solvable in a close (analytic) way.

The Hamiltonian is

$$H = p^2 + \lambda x^2 \; ; \; \lambda \geq 0; \; -x_o/2 \leq x \leq x_o/2 \quad , \qquad (27.14a)$$

with the DBC for the eigenfunctions ψ_n, viz:

$$\psi_n(-x_o/2) = \psi_n(x_o/2) = 0 \qquad (27.14b)$$

The eigenvalues satisfy the asymptotic properties

$$\lim_{x_o \to \infty} E_n = (2n+1)\, \lambda^{1/2} \qquad (27.15a)$$

$$\lim_{\lambda \to 0} E_n = \frac{(n+1)^2 \pi^2}{x_o^2} \quad ; \quad n = 0,1,2,\ldots \qquad (27.15b)$$

corresponding to the nonbounded harmonic oscillator and the particle in a box models, respectively. The simplest functional fulfilling Theorem 27.1 must comprise three terms within the functional $\hat{T}$ for the kinetic energy. Accordingly, let us consider the functional

$$F(q,x_o) = \frac{A}{q^2} - \frac{B}{qx_o} + \frac{C}{x_o^2} + \lambda q^2 \quad ; \quad A,B,C > 0 \ , \tag{27.16}$$

with the simplest representation for $\hat{V}$ (cf.§.22). The meaning of the particular choice of constants, as well as the consideration of three terms for $\hat{T}$ will be evident in the ensuing analysis.For the sake of simplicity, we consider that A,B,C only depend on n (and not upon λ or/and x_o).

The extreme condition for F leads us to

$$\lambda q^{*4} + \frac{Bq^*}{2x_o} - A = 0 \quad . \tag{27.17}$$

This equation determines q^* as a function of A and B for a given value of λ. Since q^* is related with a quadratic deviation, then it happens to be bounded $q^* \in (0,x_o)$. Consequently, Eq.(27.17) for $\lambda=0$ assures that A and B must have the same sign, and it makes clear the particular choice of signs in Eq. (27.16). The substitution (27.17) in (27.16) gives the extreme value of $F(q,x_o)$, which can be shown at once is a minimum:

$$F(q^*,x_o) = -\frac{B}{2x_o q^*} + \frac{C}{x_o^2} + 2\lambda q^{*2} \quad . \tag{27.18}$$

Eq.(27.18) makes up a reasonable approximation to the eigenvalue E_n, due to Theorem 27.1. Therefore, constants A,B and C can be determined through the application of the asymptotic properties (27.15a) and (27.15b) to the minimum $F(q^*,x_o)$.

In order to use the condition (27.15b), we start from Eq.(27.17)

$$\lim_{\lambda \to 0} q^* = \frac{2A}{B} x_o \quad . \tag{27.19}$$

Substitution of (27.19) into Eq.(27.18) gives

$$\lim_{\lambda \to 0} F(q^*, x_o) = \frac{C - B^2/4A}{x_o^2} \tag{27.20}$$

Finally, from Eqs.(27.15b) and (27.20) one gets a relationship among the constants and the quantum numbers:

$$C - \frac{B^2}{4A} = (n+1)^2 \pi^2 \quad . \tag{27.21}$$

This last equation makes clear the need to introduce a third constant $C>0$. In order to determine the three constants, it is necessary to have two additional relations which are satisfied by the exact eigenvalues. One of them is given by Eq.(27.15a), and to apply it we start from Eq.(27.17):

$$\lim_{x_o \to \infty} q^* = (A/\lambda)^{1/4} \quad , \tag{27.22}$$

which substituted into (27.18) yields:

$$\lim_{x_o \to \infty} F(q^*, x_o) = 2(\lambda A)^{1/2} \quad . \tag{27.23}$$

From Eqs.(27.23) and (27.15a), one gets A:

$$A = (n+1/2)^2 \quad , \tag{27.24}$$

which presents a quadratic dependence with the quantum numbers, as discussed in Chapters VI and VII. It is important to point out that the presence of DBC is expressed in the functional by the very need to employ a larger number of constants than those discussed in other previous sections. Consequently, the two asymptotic properties are not enough to determine the whole set of constants within the functional.

A third particularly useful relation is that provided by the RSPT in λ, which up to the first order gives /56/:

$$E_n \simeq \frac{(n+1)^2\pi^2}{x_o^2} + \frac{x_o^2}{4}\left[\frac{1}{3} - \frac{2}{(n+1)^2\pi^2}\right]\lambda + O(\lambda^2) \qquad (27.25)$$

In order to use the previous relation it is necessary to expand $F(q^*,x_o)$ in power series of λ. To that purpose, we start from Eqs. (27.17) and (27.19), which lead one to:

$$q^* \simeq \frac{2A}{B} x_o - \frac{32A^4}{B^5}\lambda x_o^5 + O(\lambda^2) \qquad (27.26)$$

The substitution (27.26) into (27.18) and considering just first order terms in λ, we find that

$$F(q^*,x_o) \simeq \frac{1}{x_o^2}\{C - \frac{B^2}{4A}\} + \frac{4A^2}{B^2} x_o^2 \lambda + O(\lambda^2) \qquad (27.27)$$

The identification of terms between Eqs.(27.27) and (27.25) leads one to Eq.(27.21) for the zero-order, while one finds

$$\frac{4A^2}{B^2} = \frac{1}{12}\{1 - \frac{6}{(n+1)^2\pi^2}\} \qquad (27.28)$$

for the first-order terms.

Eqs.(27.24) and (27.28) gives B as a function of n; i.e.

$$B = 4(n+1)(n+1/2)^2\{3\pi^2/[(n+1)^2\pi^2 - 6]\}^{1/2} \qquad (27.29)$$

Finally, C is obtained upon substituting (27.24) and (27.29) into Eq.(27.21):

$$C = (n+1)^2\pi^2 \left\{1+\frac{12(n+1/2)^2}{(n+1)^2\pi^2-6}\right\} \quad . \tag{27.30}$$

The procedure displayed above allows one to derive a reasonable representation of the eigenvalues, because $F(q^*,x_o)$ fulfils HFT and VT for bounded systems, and besides it has a correct behavior for $\lambda<<1$ (PT up to the first order) as well as for $x_o \to \infty$.

This treatment must be considered merely as a practical implementation of Theorem 27.1, rather than an accurate approach to eigenvalues. In the next section we shall see a quite different and more appropriate formulation for bounded systems subject to DBC.

Although plenty of information was introduced within the precedent functional, there is nothing in it that assures us that other properties will be described properly, as for example the agreement between the sign of $(\partial F(q,x_o)/\partial x_o)$ $(q = q^*)$ and the sign of $\frac{\partial E}{\partial x_o} n \Psi E_n, x_o$.

A rigorous result for those systems obeying DBC states that /19,54/

$$\partial E/\partial x_o \propto - \psi_n'(x_o)^2 < 0 \quad . \tag{27.31}$$

which is a particular case of Eqs. (3.25). This important relationship is related with the pressure that keeps the system confined. For example, in a 3D system: /1/

$$p = - \partial En/\partial \Omega \quad . \tag{27.32}$$

It is straightforward to verify that the functional (27.16) does not reproduce the pressure in a correct fashion. From Theorem (27.1) and Eqs. (27.16), (27.17) and (27.21) we deduce at once that

$$\left|\frac{\partial F(q,x_o)}{\partial x_o}\right|_q (q = q^*) = B \left(\frac{1}{A}\right)^{1/4} x_o^{-2} > 0 \quad ; \quad x_o >> 1 \tag{27.33a}$$

$$\left[\frac{\partial F(q,x_o)}{\partial x_o}\right]_q \quad (q = q^*) = -2\pi^2 \ (n+1)^2 \ x_o^{-3} < 0 \quad , \quad x_o << 1 \qquad (27.33b)$$

which assures that at least the derivative presents one change of sign for finite x_o. Due to this drawback, we will not insist in the application of this procedure. However, it is noteworthy that a similar failure is akin to other standard methods used for enclosed systems /36/.

In closing this section, it must be pointed out that, from a theoretical standpoint, the precedent treatment presents a significant novelty regarding all the previous ones: the incorporation of the RSPT to the VF. This result makes up the first step in our proposed original program, i.e. to combine series expansions with approximate functions built on the basis of known analytic properties.

§. 28. Functionals for Systems with Dirichlet Boundary conditions.

This section is devoted to develop a rather different formalism regarding the one discussed in §.27 and it will allow us to apply the VFM to systems with DBC/73/. The method yields physically coherent results, while other related approximations for enclosed systems may not. /36/

We proceed in an inductive way to derive the new functional. For that purpose, let us consider the following 1D Hamiltonian

$$H(g,\lambda) = p^2 + gx^{2m} + \lambda x^{2K} \quad ; \quad \lambda, g \geq 0 \quad ; \quad m \neq K \ ; \ x \in R, \qquad (28.1)$$

and its associated Schrödinger equation

$$H(g,\lambda) \ \psi_n(x) = E_n(g,\lambda) \ \psi_n(x) \quad . \qquad (28.2)$$

Defining a new parameter x_o as

$$\lambda = x_o^{-2K} \quad , \tag{28.3}$$

the Hamiltonian (23.1) of the generalized oscillator turns to

$$H(g,\lambda) = \bar{H}(g,x_o) = p^2 + gx^{2m} + (x/x_o)^{2K} \tag{23.4}$$

which fulfils a scaling relationship

$$\bar{H}(g,x_o) = x_o^{-2K(K+1)}\, H(gx_o^{2(m+1)K/(K+1)},1) \quad . \tag{28.5}$$

When g = 0, (23.1) corresponds to a purely 2K-anharmonic oscillator, which can be transformed into a particle-in-a-box model (with box length $2x_o$), considering that

$$\lim_{K\to\infty} \left(\frac{x}{x_o}\right)^{2K} = \begin{cases} 0 \text{ for } |x|<x_o \\ \infty \text{ for } |x|>x_o \end{cases} \quad , \quad x_o > 0 \quad . \tag{28.6}$$

From Eqs.(23.5) and (23.6), Eq.(28.2) for g = 0 changes to

$$\{\lim_{K\to\infty} \bar{H}(0,x_o)\}\psi_n(x) = x_o^{-2}\, \{\lim_{K\to\infty} E_n(0,1)\}\psi_n(x) \quad , \tag{28.7a}$$

where the eigenfunction satisfies the condition

$$\psi_n(x) = 0 \quad ; \quad |x| \geq x_o \quad , \tag{28.7b}$$

and the eigenvalue es

$$\lim_{K\to\infty} E_n(0,1) = (n+1)^2 \frac{\pi^2}{4} \quad . \tag{28.7c}$$

These equations assure that, in the limit $K \to \infty$, the eigenvalues of $H(g,\lambda)$ with trivial BC are transformed into those of $H(g,0)$ for DBC at $x = \pm x_o$. This is an important property and makes up a suitable starting point to obtain by means of the VFM the eigenvalues of $H(g,0)$ with DBC.

Let $F_n^{(K)}$ be the VF associated with the generalized oscillator defined through the Hamiltonian (28.1) with trivial BC. According to preceding discussion in §.22 and §.23 such functional can be written as

$$F_n^{(K)} = \frac{A_n}{q^2} + gB_n q^{2m} + (q/x_o)^{2K} \tag{28.8}$$

where function B_n is introduced via semiclassical arguments, as discussed in §.22. For the sake of simplicity, we will consider B_n dependent only on n.

Application of Theorem (19.1) to the functional (28.8) assures that the VF will satisfy the VT and HFT, if q^* is chosen at the extreme value of $F_n^{(K)}$:

$$\left(\frac{\partial F_n^{(K)}}{\partial q}\right)(q = q^*) = 0 \quad , \quad mB_n g q^{*(2m+2)} + K x_o^{-2K} q^{*(2K+2)} - A_n = 0$$

$$0 < q^* < x_o \tag{28.9}$$

Under these conditions, $F_n^{(K)}(q^*)$ is an approximation to $E_n(g,\lambda)$, with λ given by Eq. (28.3). In order to obtain an appropriate expression approaching the eigenvalues $E_n(g,0)$ of the enclosed system with DBC, one must take the limit $K \to \infty$, as discussed before. Such an approximation may be written as F_n, and is given by

$$F_n = \lim_{K \to \infty} F_n^{(K)}(q^*) \tag{28.10}$$

Now it can be seen that F_n obeys the VT for systems under DBC (Eq. (27.3)). When applying Theorem (19.1) to functional (28.8), it is found that $F_n^{(K)}$ depends parametrically on x_o in the following way:

$$\left(\frac{\partial F_n^{(K)}}{\partial x_o}\right)\ (q = q^*) = \left(\frac{\partial F_n^{(K)}}{\partial x_o}\right)(q = q^*) = -2Kq^{*2K}/x_o^{2K+1} \quad . (28.11)$$

From the definitions

$$\hat{T} = \frac{A_n}{q^2} \quad ; \quad \hat{V}(q) = gB_n q^{2m} \quad ; \quad \hat{W}(q) = (q/x_o)^{2K} \quad , \qquad (28.12)$$

and considering that Theorem (19.1) assures that $F_n^{(K)}$ satisfies the VT for systems with trivial BC, we find that

$$-2\hat{T}(q^*) + q^* \left(\frac{\partial}{\partial q}\left[\hat{V}(q) + \hat{W}(q)\right]\right)\ (q = q^*) = 0 \quad . \qquad (28.13)$$

The substitution (23.11) into (28.13), transforms the VT as follows:

$$-2\hat{T}(q^*) + q^* \left(\frac{\partial V}{\partial q}\right)\ (q = q^*) = x_o \left(\frac{\partial F_n^{(K)}}{\partial x_o}\right)\ (q = q^*) \qquad (28.14)$$

which permits to obtain the VT for systems under DBC in the limit $K \to \infty$.

Eq. (28.11) makes evident the advantages of this formalism with respect to that discussed previously in §.27, since $\partial F_n^{(K)}/\partial x_o < 0$ is obtained for all K. Then, the pressure is positive for the non-confined system is derived

$$\lim_{x_o \to \infty} \left[\frac{\partial F_n^{(K)}}{\partial x_o}\right] = 0 \quad , \quad \forall\ K \quad . \qquad (28.15)$$

Eqs, (28.11) and (23.15) show that F_n possesses the proper dependence on X_o, and fulfils the VT and HFT for DBC. As noted before, such correct dependence on x_o is seldom attained in an approximate model.

The example presented so far is useful to limit the suitable way to

derive a variational functional adapted to DBC. The information gathered to this extent for many-particle enclosed systems lead us to a more general result.

Let us consider the N particle system confined within a sphere of radius r_o, whose Hamiltonian is

$$H = \sum_{i=1}^{N} p_i^2 + V(\bar{r}) \quad ; \quad \bar{r} = (\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N) \; ; p_j = -i\nabla_j \tag{28.16a}$$

$$H\psi_n = E_n\psi_n \; ; \; \psi_n(||\bar{r}_i|| > r_o) = 0 \quad ; \quad i = 1,2,\ldots,N \tag{28.16b}$$

In order to approximate the eigenvalues, our main result lies in the following

Theorem 23.1: Let us consider the functional $F(\bar{q}) = \hat{T}(\bar{q}) + \hat{V}(\bar{q}) + \hat{W}(\bar{q})$, such that $\hat{T}(\bar{q})$ is an homogeneous function of degree -2. If $\hat{W}(\bar{q})$ is given by

$$\hat{W}(\bar{q}) = \sum_{i=1}^{N} \left(\frac{q_i}{r_o}\right)^K \quad ; \quad \bar{q} = (\bar{q}_1, \bar{q}_2, \ldots, \bar{q}_N) \; ; \; \bar{q}_i \equiv (q_{i1}, q_{i2}, q_{i3})$$

$$q_i \equiv ||\bar{q}_i|| \; ; \; i = 1,2,\ldots N \quad ; \quad K > 0 \tag{23.16c}$$

then $F(\bar{q})$ satisfies the VT and HFT for bounded systems in the limit $K \to \infty$ whenever it is extreme with respect to variations in q_i:

$$\left(\frac{\partial F(\bar{q})}{\partial q_i}\right)(q_i = q_i^*) = 0 \quad ; \quad i = 1,2,\ldots,N \tag{28.17}$$

Proof: The demonstration is similar to that employed for Theorem 19.1. Considering a parameter λ contained into the functional, we know that

$$\frac{\partial F(q)}{\partial \lambda} = \left(\frac{\partial F(q)}{\partial \lambda}\right)_{q} + \nabla F(\bar{q}).\frac{\partial \bar{q}}{\partial \lambda} \; ; \; \nabla = (\bar{V}_1, \bar{V}_2, \ldots, \bar{V}_N) \qquad (28.18)$$

and from (28.17) it follows the relationship

$$\left(\frac{\partial F(\bar{q})}{\partial \lambda}\right) (q_i = q_i^*) = \left(\frac{\partial F(q)}{\partial \lambda}\right)_{q} (q_i = q_i^*) \qquad (28.19)$$

which is a HFT-like formula

In order to prove the fulfillment of VT for DBC, we resort to a particular case of Eq. (28.19), choosing $\lambda = r_o$. The functional depends explicitly on r_o through $\hat{W}(\bar{q})$, then:

$$\left(\frac{\partial F(\bar{q})}{\partial r_o}\right) (q_i = q_i^*) - \left(\frac{\partial \hat{W}(\bar{q})}{\partial r_o}\right)_{q} (q_i = q_i^*) = -\frac{K}{r_o} \hat{W}(\bar{q}^*) \; . \qquad (28.20)$$

Besides, at the extreme condition for $F(\bar{q})$ we have

$$\bar{q}^*.(\nabla \hat{T})(\bar{q} = \bar{q}^*) + \bar{q}^*.(\nabla \hat{V})(\bar{q} = \bar{q}^*) + \bar{q}^*.(\nabla \hat{W})(\bar{q} = \bar{q}^*) = 0 \qquad (28.21)$$

Taking into account that $\hat{T}$ and $\hat{W}$ are homogeneous functions of degree -2 and K, respectively, and using Eq. (28.20), Eq.(28.21) leads to

$$-r_o \left(\frac{\partial F(\bar{q})}{\partial r_o}\right) (\bar{q} = \bar{q}^*) = -2\hat{T}(\bar{q}^*) + \bar{q}^*.(\nabla \hat{V}) (\bar{q} = \bar{q}^*) \qquad (28.22)$$

Finally, at the limit $K \to \infty$ in Eq. (28.22), we introduce DBC

$$q_i^* < r_o \; \forall \; i$$

since $\hat{W}(\bar{q})$ converts into an infinite term for $q_i^* > r_o$. Then, Eq. (28.22) is identical to the VT for a system sybjected to DBC.*

It is interesting to point out that there are other possibilities for $\hat{W}(\bar{q})$ which verify Theorem 28.1 too. In fact, there are infinite functions that tend to zero if $q<r_o$ and to infinite if $q>r_o$.

We present an additional example for other possible choice for $\hat{W}(\bar{q})$ leading to a similar result.

Let us consider again the problem of approaching the eigenvalues of $H(g,0)$ with DBC at $\pm x_o$ (Eqs. (28.1) and (28.4)). Now we propose the functional

$$F_n^{(j)} = \frac{A_n}{q^2} + gB_n q^{2m} + j\ tg\theta \quad ; \quad \theta = \frac{q\pi}{2x_o} \tag{28.23}$$

The variable q may be related to a quadratic deviation (§.§. 22 and 23), so that $q \geq 0$. If $q < x_o$ at the limit $j \to 0$, then the third term in (28.23) is zero, which in addition is singular at $q = x_o$. These facts suggest that having $j\ tg\theta$ the required properties for $W(q)$, $F_n^{(j)}$ could describe a bounded system with DBC in the limit $j \to 0$. Such a guess can be verified at once if we note that when $j,g \to 0$, $F_n^{(j)}$ yields the eigenvalues associated with the particle-in-a-box model.

For that purpose, we start from the extreme condition of VF to determine the q-value when $g \to 0$:

$$\lim_{g\to 0} \left(\frac{\partial F_n^{(j)}}{\partial q}\right) (q = q^*) = -2A_n \lim_{g\to 0} (q^*)^{-3} + \frac{j\pi}{2x_o} \lim_{g\to 0} \cos^{-2}\theta = 0 \tag{28.24}$$

In order to have a finite result for q^* in the limit condition $j \to 0$, the following condition must be satisfied for the second term in the l.h.s of (28.24):

$$\lim_{j\to 0} \lim_{g\to 0} \cos\theta = 0 \quad = \quad \lim_{j\to 0} \lim_{g\to 0} q^* = x_o \tag{28.25}$$

This relation reveals the role of the term j tgθ, which confines the q* values within the interval $|0,x_o|$. The use of (28.24) and the expression of tgθ as a function of q* allow us to find the minimum value of the functional

$$\lim_{g\to 0} \min_{(q)} F_n^{(j)} = \frac{A_n}{q^{*2}} + j^{1/2} \{\frac{4A}{\pi q^{*3}} x_o - j\}^{1/2} \quad , \tag{28.26}$$

which through Eq.(28.25) is transformed into:

$$\lim_{j\to 0} \lim_{g\to 0} \min_{(q)} F_n^{(j)} = \frac{A_n}{x_o^2} \quad . \tag{28.27}$$

Eq. (28.27) yields the eigenvalues of a particle-in-a-box model when A_n is chosen as

$$A_n = (n+1)^2 \pi^2/4 \tag{28.28}$$

Summing up, the present approximation for the eigenfunctions of H(g,0) obeying DBC is represented by

$$F_n = \lim_{j\to 0} \min_{(q)} F_n^{(j)} \tag{28.29}$$

such that $q^* \varepsilon |0,x_o|$ when $g \geq 0$. Furthermore, it is easily shown that this new functional permits a correct definition for the pressure that holds the quantum system confined. For that purpose, we compute the following derivative

$$\frac{\partial F_n^{(j)}}{\partial x_o} = \{-2\frac{A_n}{q^3} + 2mg\, B_n q^{2m-1} + \frac{\pi j}{2x_o} \cos^{-2}\theta\}(\frac{\partial q}{\partial \theta}) - \frac{j\theta}{x_o} \cos^{-2}\theta \quad , \tag{28.30}$$

and then introduce the extreme condition of $F_n^{(j)}$:

$$\left(\frac{\partial F_n^{(j)}}{\partial x_o}\right)\ (q = q^*) = \frac{-j\theta}{x_o}\cos^{-2}\theta<0 \quad , \quad \forall\ j \geq 0 \quad . \qquad (23.31)$$

The conclusion coming from Eq. (23.31) is similar to that obtained previously from (23.11). The application of Eq. (23.31) allows one to get the VT for the system subjected to DBC, as expected:

$$x_o\left(\frac{\partial F_n^{(j)}}{\partial x_o}\right)\ (q = q^*) = -2\ \frac{A_n}{q^{*2}} + 2m\ gB_n q^{*2m} \quad . \qquad (28.32)$$

The limit $j \to 0$ of the above expression gives the VT.

§.29. Bounded harmonic oscillator: Approximation of its eigenvalues with the VFM.

This section is devoted to apply the formalism presented in §.23 to discuss the bounded harmonic oscillator under DBC/13-15,17,18,36,44-56/:

$$H = p^2 + x^2 \quad ; \quad x \in |-x_o, x_o| \quad , \qquad (29.1a)$$

$$H\psi_n(x) = E_n\psi_n(x) \quad ; \quad \psi_n(\pm x_o) = 0 \quad . \qquad (29.1b)$$

This model has not analytic solution, i.e. there is not an explicit or implicit formula for E_n as a function of x_o. A wide variety of approximate techniques have been employed to solve Eq. (29.1b), among which we can mention the following ones:

i) solution of the differential equation by expanding the wave function as a power series of the coordinate; this expansion is coincident with the confluent hypergeometric function/45,48-52/. This method yields good numerical results, but it does not provide approximate analytical expressions.

ii) The JWKB procedure /49/ which supplies analytic formulas.

iii) The application of PT to approach eigenvalues. This method was applied by resolution of the differential equations posed by PT /47/ and obtaining the perturbation corrections from the series expansion of the confluent hypergeometric equation /15,50/, and by means of the hypervirial perturbation method /36,54-56/. The application of PT has been complemented with the aid of some simple summation techniques, such as the Padé approximants method /53/, or the Vawter hyperbolic cotangent method /36/. The results derived from the hypervirial perturbation method are accurate enough within a wide range of x_o-values, so that they will be considered as the "exact" ones for our present needs.

For the purpose of applying the VFM we start from the functional (28.3), with m=g=1. Accordingly, we have the VF

$$F_n^{(K)} = \frac{A_n}{q^2} + B_n a^2 + (q/x_o)^{2K} \quad , \tag{29.2}$$

and the corresponding approximation to eigenvalues

$$F_n = \lim_{K\to\infty} F_n^{(K)} \ (q^*) \quad . \tag{29.3}$$

The q^* value at the minimum of $F_n^{(K)}$ is given by:

$$A_n = B_n q^{*4} + K x_o^{-2K} q^{*(2K+2)} \tag{29.4}$$

where the constants A_n, B_n must be determined for every specific calculation. As discussed in §.§. 27 and 28, it seems appropriate to determine A_n from the spectrum of the particle-in-a-box model (viz., when $x_o \to 0$) and B_n via the eigenvalue spectrum of the harmonic oscillator model (viz., when $x_o \to \infty$).

In order to obtain A_n, we consider the $\Gamma_n^{(K)}$ minimum value in terms of q^* via Eq. (29.4):

$$F_n^{(K)}(q^*) = 2B_n q^{*2} + (K+1)\,(q^*/x_o)^{2K} \quad . \tag{29.5}$$

The asymptotic behavior of q^* for $K>>1$ and $x_o<<1$ is (Eq. (29.4)):

$$q^* \to \left(\frac{A_n x_o^{2K}}{K}\right)^{1/(2K+2)} \quad , \tag{29.6}$$

which substituted in Eq. (29.5) yields the functional asymptotic behavior

$$\min_{(q)} F_n^{(K)} \to (K+1)x_o^{-2K}\,(A_n x_o^{2K}/K)^{K(K+1)} \quad . \tag{29.7}$$

Then, the limit value as in Eq. (29.3) allows one to find the following rigorous result

$$\lim_{x_o \to 0} x_o^2 F_n = A_n \quad . \tag{29.8}$$

If

$$A_n = (n+1)^2\pi^2/4 \tag{29.9}$$

the functional reproduces the eigenvalues of the particle-in-a-box model. The result is the same as that given by Eq. (28.28), obtained through a different procedure.

In order to determine B_n, we start again from (29.4), and obtain the following asymptotic behavior

$$q^* \to (A_n/B_n)^{1/4} \quad ; \quad K>>1 \quad ; \quad x_o>>1 \tag{29.10a}$$

which substituted into (29.5) and (29.3) gives:

$$\lim_{x_o \to \infty} F_n = 2\,(A_n B_n)^{1/2} \quad . \tag{29.10b}$$

The r.h.s of Eq. (29.10b) must be equal to (2n+1) to get the correct expression for the VF with the non-bounded harmonic oscillator eigenvalues, and therefore it yields the constant B_n:

$$B_n = \left|\frac{2n+1}{(n+1)\pi}\right|^2 \quad . \tag{29.11}$$

Eqs. (29.3) - (29.5), (29.9) and (29.11) permit one to compute numerically F_n for different n and x_o-values. Since the limit (29.3) must be taken numerically, we present the following test: since for $q^* < x_o$

$$\lim_{K \to \infty} (q^*/x_o)^{2K} = 0 \quad , \tag{29.12}$$

we have an alternative formula for F_n:

$$F_n \simeq \frac{A_n}{q^{*2}} + B_n q^{*2} \quad , \tag{29.13}$$

which is rigorous when $K \to \infty$. Eq. (29.13) provides a different way to compute F_n (cf. eqs. 29.1 and 29.5). Since both procedures must coincide for $K \to \infty$, it is interesting to know the minimum K-value to get coincidence within a given accuracy degree. Table 8.1 shows some results for n = 0 and $x_o = 1$, and we see that $K = 10^6$ is large enough so as to make the necessary computations.

In order to analyse the properties of F_n (Eq. (29.3)), we present the results for the first three states (n = 0,1,2) with increasing K, $K = 10^5$, 10^6 and 10^7, until convergence. Eigenvalues (numerically stable up to the last figure) are displayed in Table 8.2 for different

x_o-values, together with other results /54,56/ for the sake of comparison. Numerical values reveal that present results are a lower bound regarding the "exact" ones within the whole range of x_o-values, and besides they tend too quickly towards the harmonic oscillator limit. As expected beforehand, these results have a relative error higher for intermediate x_o-values, since we have not introduced within the VF any information regarding this range of values. However, it is interesting to point out that the functional dependence of E_n with x_o is nearly correct, which lay stress on the property that the VFM is capable to describe the most relevant features of the dependence of E_n on x_o. Due to the fact that the procedure described is quite simple, we think it makes up a direct and strightforward option regarding other methods like the JWKB, Padé approximants and hyporbolic cotangent approximations.

In spite of the fact that here we have chosen the harmonic oscillator model to exemplify the use of the VFM in its simplest version (A_n,B_n constants), the treatment is equally applicable to other, quite different problems.

NUMERICAL RESULTS

Table 8.1

Convergence analysis of the functional $F_n^{(K)}$ for the bounded harmonic oscillator (DBC) at lim K→∞ (n=0 and $x_0 = 1$)

K	$F_n/2$ a)	$F_n/2$ b)
10^2	1.3414	1.3291
10^3	1.2927	1.2915
10^4	1.23547	1.23535
10^5	1.28450	1.28449
10^6	1.28438	1.28438
10^7	1.23437	1.23437

a) Computed from Eq. (29.5)

b) Computed via Eq. (29.13)

Table 8.2

First three eigenvalues of the bounded harmonic oscillator with DBC

n	x_o	$F_n/2$ [a]	$E_n/2$ [b]
0	0.50	4.9475	4 95113
	0.75	2.2217	2 22990
	1.00	1.2344	1.29846
	1.25	0.8687	0.88947
	1.50	0.6623	0.68893
	1.75	0.5530	0.58749
	2.00	0.5111	0.53746
	2.25	0.5000	0.51415
	2.50	0 5000	0 50495
1	0 50	19 768	19.77453
	1.00	5.0433	5.07558
	1.50	2.4497	2.50490
	2.00	1.6396	1 76432
	2 50	1.5020	1 55131
	3.00	1.5000	1.50608
2	0.50	44.449	44 4521
	1.00	11.244	11 2588
	1.50	5.2514	5.28549
	2.00	3.3387	3.39979
	2.50	2.6561	2.73734
	3.00	2.5000	2 54113

a) Results obtained from the VFM (§.29).

b) Exact values /54,56/.

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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, occuring 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 $\bar{B}$. 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):

$$H\psi_{\{n\}} = E_{\{n\}}\psi_{\{n\}} \tag{30.1}$$

$$H = -\frac{\hbar^2}{2\mu}\Delta + \frac{e}{2\mu c}\bar{B}.\bar{L} + \frac{e^2}{8\mu c}2\ B^2r^2\ \mathrm{sen}^2\theta - \frac{Z}{Dr} \tag{30.2}$$

with μ the reduced mass for the two-body (nucleus and electron) system, and D the dielectric constant of the medium (considered as a continum) 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, sonce no implicit or explicit expression exists for $E_{\{n\}}$ as a function of $B \equiv ||\bar{B}||$. 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

$$H = -\frac{\hbar^2}{2\mu}\Delta + \frac{e}{2\mu c}\bar{B}.\bar{L} + \frac{e^2}{8\mu c}2\ B^2\rho^2 - \frac{Z}{D(z^2+\rho^2)1/2} \tag{30.3a}$$

$$\rho^2 = x^2+y^2 = r^2-z^2 \tag{30.3b}$$

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

Several characteristic phenomena with very strong associated mag-

netic 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 literature 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 $B \simeq 2 \times 10^9$G (Appendix H); as a comparison, typical intense magnetic field attainable in the laboratory has a strength of 10^4G (1T) /6,8/.

However, since long ago it is well known that (30.3) is an appropriate 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,

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

For electronic absorption problems of impurities involving excitons, the typical constant values are $D^* \simeq 10$, where $m_n^* >> m_e^*$, 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 x 10^4G makes up a local (real) field on an exciton of 3,6 x 10^{10}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 10^5T.

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

$$P \simeq 3{,}9 \times 10^5 B^2 \qquad (30.5)$$

For example, a field of 0.5T gives rise to a pressure of around 1 atm, but for B≈10^3 T the pressure is 10^6 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 $E_{\{n\}}$ fulfils (in an approximate fashion) a scaling relation with n_r (number of radial zeros in the wave function), such as /15-17/

$$E_{n_r}(Z,B) \simeq n_r^{-2} E_0(Z, Bn_r^3) \quad . \tag{30.6}$$

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 /6/. 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 $n_r \simeq 50$ "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 <r> 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 $n_r >> 1$ 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 /18,19/).

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

$$(6s^2)\ ^1S_0 \rightarrow (6s\ np)\ ^1P_1$$

in a magnetic field of about 10^4 G. They observed occurrence of the so-called "quasi-Landau resonances" for the levels $n \simeq 75$, 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 5.3×10^{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

$$H_e = H(Z,\lambda) + H_p, \tag{31.1}$$

$$H(Z,\lambda) = -\frac{\Delta}{2} - \frac{Z}{r} + \frac{\lambda^2}{8}(x^2+y^2) \quad ; \quad r^2 \equiv x^2+y^2+z^2, \tag{31.2}$$

$$H_p = \frac{\lambda}{2}(L_z + g_s S_z) \quad , \tag{31.3}$$

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 $\{|SM_S LM_L>\}$, 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 λ^2-term in the Hamiltonian with respect to the λ-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 polynomals for the angular part of the wave function), the quadratic Zeeman effect region ($\lambda \simeq 0.1$ in Eq. (31.2)) is described by an abundant mixture of different ℓ-functions.

This effect, called "inter-ℓ-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 polynomals as basis sets /43/;

eigenfunctions of the Hamiltonian at zero field (λ=0) /44-46/ and properly chosen functions adapted to the cylindrical symmetry. This approach has been found useful for field strengths around $\lambda \simeq 1$.

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 contimum 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 $\lambda^2 >> \lambda$. 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

$$\psi(\rho,z) = N \exp(-(a_1 z^2 + a_2 \rho^2)); \; a_1 > 0; \; a_2 > 0 \quad . \qquad (31.4)$$

Function (31.4) is suitable to represent the ground state associated with the Hamiltonian for large magnetic field strengths. A significative and particularly important result arising from a simple function as Eq. (31.4) is that the variational energy(an extremun 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:

$$\varepsilon_0 = \frac{\lambda}{2} - E_0 = \frac{1}{2} \ln^2(\frac{\lambda}{8}) + O(\ln\lambda + \ln\ln\lambda); \; m = 0, \; \lambda >> 1 \quad . \qquad (31.5)$$

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

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

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 deffects 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 superstrong 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 strictily 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 motion along the Z-direction may be obtained through a 1D Schrödinger equation with an effective potential. The first term of such potential ($\lambda \to \infty$) is a sort of 1D coulombic potential in each subspace of m. The expression for effective Hamiltonian in z is (Appendix I)

$$H(z) = \langle \psi_m(x,y) | H \psi_m(x,y) \rangle \simeq \frac{1}{2}\lambda \{ -\frac{1}{2} \frac{d^2}{dz^2} - \lambda^{-1/2} \frac{c_m}{|z|+g_m} \} \qquad (31.7)$$

where $\psi_m(x,y)$ is a function belonging to the fundamental band of Landau states, and c_m, g_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 eigenvalues 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 approximats analytical expressions for eigenvalues and other physical properties, except for some suitable fitting of the numerical results /76/. However, even these pseudo-analytic expressions 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

$$H = \frac{p^2}{2m} - \frac{Ze^2}{Dr} \; ; \quad p = m\bar{v} \quad , \tag{31.8}$$

where m, e and $\bar{v}$ are the electron mass, charge and velocity, respectively. D corresponds to the dielectric constant for the medium. We restric the analysis to circular orbits, so that

$$dr/dt = \dot{r} = 0 \tag{31.9}$$

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

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

$$T = \frac{1}{2} mr^2\dot{\phi}^2 \quad ; \quad v = r\dot{\phi} \quad ; \quad \dot{\phi} = \frac{d\phi}{dt} \tag{31.10}$$

where ϕ is the polar angle in the motion plane. The force acting on the electron when B = 0 may be derived from Eqs. (31.8) and (31.9). In fact, if L is the Lagrangian function of the system, then

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

When $B \neq 0$, the Lorentz force $\bar{F}_2$ acting on the electron

$$||\bar{F}_2|| = \frac{e}{c} ||\bar{B}x\bar{v}|| = \frac{eBv}{c} \quad , \tag{31.12}$$

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

$$\frac{mv^2}{r} = \frac{Ze^2}{Dr^2} + \frac{eBv}{c} \quad . \tag{31.13}$$

In order to get v and r as a function of $\bar{B}$, we introduce the Bohr-

Sommerfeld quantization condition (Chapter II)

$$\oint p\,d\bar{\ell} = nh \quad ; \quad n>>1 \tag{31.14}$$

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

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

The substitution (31.15) in (31.14) gives

$$m \oint \bar{v}.d\bar{\ell} - \frac{e}{c}\oint \bar{A}.d\bar{\ell} = nh \quad , \tag{31.16a}$$

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

$$\oint \bar{A}.d\ell = \int_S \text{curl } \bar{A}.d\bar{S} = \pi r^2 B \quad , \tag{31.16b}$$

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

$$mvr - \frac{e}{2c}Br^2 = n\hbar \quad . \tag{31.17}$$

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

$$r\,\frac{Zme^2}{D\hbar^2} + \frac{e^2B^2}{4c^2\hbar^2}\,r^4 = n^2 \tag{31.18}$$

Defining the Bohr radius a_o and Landau radius R as

$$a_o = D\hbar^2/me^2Z \tag{31.19a}$$

$$R = (c\hbar/eB)^{1/2} \tag{31.19b}$$

Eq. (31.18) is recast in its more usual expresion as

$$\frac{r}{a_o} + \frac{1}{4}\left(\frac{r}{R}\right)^4 = n^2 \quad . \tag{31.20}$$

Eq. (31.20) yields the electron accesible 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)):

$$\lim_{B\to 0} r = n^2 a_o \quad ; \quad \lim_{Z\to 0} r = (2n)^{1/2} R \quad . \tag{31.21}$$

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

$$E_n(Z,B) = \frac{n}{2}\hbar\frac{eB}{mc} + \frac{e^2B^2}{4mc^2}r^2 - \frac{Ze^2}{2Dr} \quad . \tag{31.22}$$

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

$$E_n(Z,B) = \frac{n\hbar}{2}\frac{eB}{mc} + \alpha^2\frac{e^2B^2}{4mc^2}x^2 - \alpha^{-1}\frac{Ze^2}{2Dx} \quad . \tag{31.23}$$

the choice $\alpha = B^{-1/2}$ leads to the following scaling relation:

$$E_n(Z,B) = BE_n(ZB^{-1/2},1) \quad . \tag{31.24}$$

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 $n_r >> \ell$).

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:

$$\lim_{B\to 0} E_n(Z,B) = -\frac{1}{2n^2}\left(\frac{Z^2e^4m}{\hbar^2D^2}\right) \quad . \tag{31.26}$$

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

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

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

$$E_n(Z,B) - n\hbar\left(\frac{eB}{mc}\right) \sim \left(\frac{\hbar Be^3Z}{2nmeD}\right)^{1/2} + O(\ell) \quad . \tag{31.28}$$

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-

cording 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 ocurrence 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 $3\hbar\omega/2$ /20/. 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

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

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

$$E_1 = \frac{\hbar e}{2mc} b + \frac{e^2}{4mc^2} b^2x^2 - \frac{Ze^2}{2D}\frac{1}{x} \tag{31.30}$$

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

$$\frac{Ze^2m}{D\hbar^2} x + \frac{b^2e^2}{4c^2\hbar^2} x^4 = 1 \quad . \tag{31.31}$$

As a consequence, the dependence of E_1 on n is via b and x:

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

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

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

where, for B fix, one has:

$$\frac{\partial b}{\partial n} = \frac{3}{n} b \quad . \qquad (31.34)$$

From Eq. (31.30)

$$\left(\frac{\partial E_1}{\partial b}\right)_x = \frac{E_1}{b} + \frac{Ze^2}{2Dbx} + \frac{e^2}{4mc^2} bx^2 \quad ; \qquad (31.35)$$

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

$$\left(\frac{\partial E_1}{\partial x}\right)_b \frac{\partial x}{\partial b} = - \frac{be^2}{4mc^2} x^2 \quad . \qquad (31.36)$$

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

$$\frac{dE_n}{dn} = \frac{E_n}{n} + \frac{3Zc^2}{2Dxn^3} \qquad (31.37)$$

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)

$$\frac{b^2e^2x^2}{4mc^2} = \frac{\hbar^2}{mx^2} - \frac{Ze^2}{Dx} \quad , \tag{31.38a}$$

$$\frac{\hbar eb}{2mc} = \frac{\hbar^2}{mx^2}\{1 - \frac{Ze^2mx}{D\hbar^2}\}^{1/2} \quad , \tag{31.38b}$$

and replacing in (31.30) one has an equation for x in terms of E_1

$$E_1 = \frac{\hbar^2}{mx^2}\{1+(1-\frac{Ze^2mx}{D\hbar^2})^{1/2}\} - \frac{3}{2}\frac{Ze^2}{Dx}\,;\ 0\leq x<a_o \quad . \tag{31.39}$$

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

$$\frac{m^2E_1^2}{\hbar^4}x^3 + \frac{3m^2Ze^2E_1}{D\hbar^4}x^2 + \frac{9m^2Z^2e^4}{4D^2\hbar^4} - \frac{2mE_1}{\hbar^2}x -$$

$$- \frac{2mZe^2}{D\hbar^2} = 0 \quad . \tag{31.40}$$

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:

$$\frac{dE_n}{dn} = \frac{\hbar w}{2} + \frac{\hbar^2}{m}(n^3x^2)^{-1} \quad . \tag{31.41}$$

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

$$x_o = \lim_{E_1\to 0} x = \frac{8}{9}\frac{D\hbar^2}{Ze^2m} \quad , \tag{31.42}$$

and thereupon the n-value

$$n_o^3 = \lim_{E_1 \to 0} n^3 = \frac{27}{32} \frac{\hbar c}{Be} \left(\frac{Ze^2 m}{D\hbar^2}\right)^2 \quad . \tag{31.43}$$

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

$$\lim_{E_n \to 0} \frac{dE_n}{dn} = 2\hbar w \tag{31.44}$$

Eq. (31.44) is wholly rigorous and reveals that the Bohr model does not predict the experimental result $3\hbar w/2$ (in constract 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 $(dE_n/dn)\ (E_n = 0) \neq \hbar w$ and besides the level spacing diminishes when the field intensity increases.

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

$$n_o \simeq 0.945\lambda^{-1/3} \ ; \ \lambda^{-1} = Z^2 e^3 cm^2 / D^2 \hbar^3 B \tag{31.45}$$

with λ the dimensionless field. The 1D JWKB result is /29/

$$n_o \simeq 1.16\ \lambda^{-1/3} \quad , \tag{31.46}$$

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

$$E_1 = 2/3 \ ; \ n_o\ \lambda^{1/3} = 1.2114 \tag{31.47}$$

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 RSPT 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 multidimensional 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 $2p_{+1}$ (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)

$$S(\bar{r}) = r/n \quad , \tag{32.1}$$

where n is the principal quantum number of the corresponding hydrogenic eigenvalue and selecting function f (Eq. (9.20)) as

$$f = r^M \mathrm{sen}^N\theta \cos^t\theta e^{im\phi} \quad ; \quad M,N = 0,1,2,\ldots; \; m=0,\pm1,\pm2,\ldots,$$

$$t = 0,1. \tag{32.2}$$

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

$$V_o = -1/r \qquad V_1 = \lambda^2(x^2+y^2)/8 \tag{32.3}$$

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:

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

$$+ \Delta E\, I_{M,N} - \frac{\lambda^2}{8} I_{M+2,N+2} \qquad (32.4)$$

with

$$I_{M,N} = \langle \psi | r^M \operatorname{sen}^N \theta \cos^t \theta\, e^{im\phi} | \phi \rangle \qquad (32.5a)$$

$$\Delta E = E + 1/2n^2 \qquad (32.5b)$$

$$C_{M,N} = \frac{1}{2}\{M(M+1) - (N+t)(N+t+1)\} \qquad (32.5c)$$

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 (§.31), which are defined by the condition

$$M = -\ell = -(n-1) \quad , \qquad (32.6)$$

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

The substitution of (32.6) into (32.4) yields a recurrence valid

for the tight-bound states:

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

$$+ \Delta E\, I_{M,N} - \frac{\lambda^2}{8} I_{M+2,N+2} \quad . \tag{32.7}$$

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

$$\Delta E = \frac{\lambda^2}{8} I_{\ell+2,\ell+2}, \tag{32.8}$$

together with the normalization condition for every state:

$$I_{\ell,\ell} = 1 \quad . \tag{32.9}$$

Expanding ΔE and the integrals $I_{M,N}$ in power series of λ^2:

$$\Delta E = \sum_{n=1}^{\infty} E^{(n)}\, \lambda^{2n} \tag{32.10a}$$

$$I_{M,N} = \sum_{n=0}^{\infty} I^{(n)}_{M,N}\, \lambda^{2n} \tag{32.10b}$$

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

$$E^{(n)} = \frac{1}{8}\, I^{(n-1)}_{\ell+2,\ell+2} \quad ; \quad n \geq 1 \tag{32.11a}$$

$$I^{(n)}_{\ell,\ell} = \delta_{n0} \quad . \tag{32.11b}$$

The computation scheme is completed when the coefficients $I^{(n)}_{\ell+2,\ell+2}$ 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 λ^{2n}-coefficient:

$$\frac{M-\ell}{1+\ell}\, I^{(n)}_{M-1,\ell+1} = C_{M,N}\, I^{(n)}_{M-2,N} + \frac{1}{2}\,(M^2-\ell^2)\, I^{(n)}_{M-2,N-2} +$$

$$+ \frac{1}{8} \sum_{s=0}^{n-1} I^{(s)}_{\ell+2,\ell+2}\, I^{(n-1-s)}_{M,N} - \frac{1}{8}\, I^{(n-1)}_{M+2,N+2} \quad . \tag{32.12}$$

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

The computation for the states $\ell=0,1,2$ 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:

$$I^{(n)}_{M-1,N} = \frac{2}{M-1}\,\{C_{M,N}\, I^{(n)}_{M-2,N} + \frac{N^2}{2}\, I^{(n)}_{M-2,N-2} - \frac{1}{8} \sum_{s=0}^{n-1} \left[I^{(s)}_{3,2} - 2I^{(s)}_{2,2}\right]$$

$$I^{(n-1-s)}_{M,N} - \frac{1}{3}\, I^{(n-1)}_{M+2,N+2}\}; \quad M = 2,3,\ldots; N = 0,2,4,\ldots \quad n = 0,1,\ldots \tag{32.13}$$

where

$$E^{(n)} = \frac{1}{3}\{2I_{2,2}^{(n-1)} - I_{3,2}^{(n-1)}\} \tag{32.14a}$$

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

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

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 ℓ. This behavior has been studied by several authors /96,105,106/ by means of a generalization to many dimensions of the procedure presented in §.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

$$|E^{(n)}| \to ((2n+1)/2)! \quad , \tag{32.15}$$

which is more strongly divergent than the behavior corresponding to the oscillators studied in §.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 /107/, and higher order for the non-degenerate ground state /98/. 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 §.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 $\lambda \simeq 1$, the number of perturbational coefficients to be considered is extremely large.

Another recent technique is the Euler method /103/ (see §.15) generalized by Silverman /109/, which gives sensible results for the lowest eigenvalue for $\lambda \gtrsim 1$, 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 function $E(\lambda)$. A specially important piece of information is the asymptotic behavior of the energy for $\lambda >> 1$ (Eq. (31.4) and Appendix H) /17,58,60-68/. 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 $\lambda \geq 1$, 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 applied 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)]

n	$E^{(n)}(1s)$	$E^{(n)}(2p_{\pm 1})$
0	-0.5	-1/8
1	0.25	3
2	-0.2760416666666664	-116
3	0.1211154513083887 (1)	16192
4	-0.9755405906394653 (1)	-57205264/15
5	0.1173630246122330 (3)	6242604544/5
6	-0.1959272760533517 (4)	-0.5246578495235231 (12)
7	0.4274361639521947 (5)	0.2719288070366074 (15)
8	-0.1136935282560349 (7)	-0.1699171093824181 (18)
9	0.4097260186330245 (8)	0.1216305530753331 (21)
10	-0.1725156234947565 (10)	-0.1100183924440783 (24)
11	0.8716665393270382 (11)	0.1117401621637270 (27)
12	-0.5210940934011392 (13)	-0.1310539020557425 (30)
13	0.3640532401232869 (15)	0.1761487030331318 (33)
14	-0.2940370393476464 (17)	-0.2693305161691009 (36)
15	0.2719572430769033 (19)	0.4652898043792423 (39)
16	-0.2856379426829352 (21)	-0.9024911281033203 (42)
17	0.3381522613344236 (23)	0.1953914952529491 (46)
18	-0.4482314059482390 (25)	-0.4696543856732298 (49)
19	0.6612952596854647 (27)	0.1247151762591110 (53)
20	-0.1080080640806817 (30)	-0.3642185373074384 (56)

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).

n	$E^{(n)}(3d_{-2})$	$E^{(n)}(4f_{-3})$
0	-1/18	-1/32
1	27/2	40
2	-147987/32	-200960/3
3	1396635997/256	3381002240/9
4	-0.1042082539730307 (11)	-0.3329328337047697 (13)
5	0.2661323134527461 (14)	0.3857554194892650 (17)
6	-0.8406506587846045 (17)	-0.5404625241696400 (21)
7	0.3156352771567792 (21)	0.8304669048497595 (25)
8	-0.1379591422332777 (25)	-0.1632010053654965 (30)
9	0.6927597243062660 (28)	0.3398404771134897 (34)
10	-0.3964943306124325 (32)	-0.7839222373097735 (38)
11	0.2571749937694331 (36)	0.2031952807164131 (43)
12	-0.1381694053348719 (40)	-0.5787849775253664 (47)
13	0.1546554030782052 (44)	0.1313313549394281 (52)
14	-0.1421934433296272 (48)	-0.6292028239343073 (56)
15	0.1456420259608559 (52)	0.2391038700455903 (61)
16	-0.1654930431342770 (56)	-0.9958178478772188 (65)
17	0.2077674003013358 (60)	0.4534253995185415 (70)
18	-0.2870457206118755 (64)	-0.2251364399563629 (75)
19	0.4347556440961387 (68)	0.1215771742966442 (80)
20	-0.7192654779041029 (72)	-0.7121524234783501 (84)

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)]

n	$E^{(n)}(2s)$
0	-1/3
1	7/2
2	-478/3
3	202576/9
4	-744745648/135
5	0.1831650923102710 (10)
6	-0.3204391786512023 (12)
7	0.4389596735728531 (15)
8	-0.2816897679290545 (18)
9	0.2137332357317471 (21)
10	-0.1897900716893362 (24)
11	0.1955823529627524 (27)
12	-0.2321429979067009 (30)
13	0.3151014434719351 (33)
14	-0.4857971635820124 (36)
15	0.8452044545889403 (39)
16	-0.1649430121661903 (43)
17	0.3590184717445867 (46)
18	-0.8670399595321733 (49)
19	0.2312096400478561 (53)
20	-0.6777773205534709 (56)

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

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CHAPTER X

APPLICATION OF THE VFM TO THE ZEEMAN EFFECT IN HYDROGEN

§.33. Derivation of the variational functional

Let us consider a hydrogen atom of nuclear charge Z, placed in an external uniform magnetic field along the $x_3 \equiv z$ direction. The Hamiltonian operator describing this system in the non-relativistic approximation, and with suitable units (Appendix H), is:

$$H_e = -\frac{1}{2}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\partial^2}{\partial x_3^2}\right) + \frac{m^2}{2\rho^2} + \frac{\lambda^2}{8}\rho^2 + \frac{\lambda}{2}\left(L_{x_3} + g_s S_{x_3}\right) - \frac{Z}{r} \qquad (33.1.)$$

where

$$r^2 = x_1^2 + x_2^2 + x_3^2 = \rho^2 + x_3^2 \qquad (33.2)$$

Let $E(Z,\lambda)$ denote the set of eigenvalues of that portion of H excluding the paramagnetic field terms (Eq. (31.1)), i.e.:

$$E(Z,\lambda) = \langle H(Z,\lambda)\rangle = \langle H_e\rangle - \frac{\lambda}{2}(m + g_s m_s);\ m=0,\pm1,\pm2,\ldots$$

$$m_s = \pm 1/2 \qquad (33.3)$$

The importance of this problem was already widely discussed in §.30. As pointed out, the eigenvalue problem has no analytic solution due to the coupling of the two coulombic degrees of freedom (ρ and x_3). Our purpose is to apply the VFM to derive valid approximate expressions for $E(Z,\lambda)$, $\forall\lambda \geq 0$ /1,2/.

From the Heisenberg inequalities (in cartesian coordinates), we found in §.22 an appropriate form of the VF, which here reduces to

$$F = \frac{A_1}{q_1^2} + \frac{A_2}{q_2^2} + \frac{A_3}{q_3^2} + \hat{V}\ (\bar{q}) \qquad (33.4)$$

$$\bar{q} = (q_1,\ q_2,\ q_3) \qquad (33.5)$$

with $\{A_i\}$ constants not depending on λ. The parameters $\{q_i\}$ are proportional to the uncertainties in each cartesian coordinate (see Chapter VI). In accordance with the BC defining the problem, such parameters satisfy the following proportionality relation:

$$q_i^2 \ \alpha\ \langle x_i^2 \rangle \quad . \qquad (33.6)$$

The functional $\hat{V}(q)$ is the expectation value of the potential $V = -\frac{Z}{r} + \lambda^2\rho^2/8$ in terms of $\{q_i\}$.

In order to construct this functional we follow the procedure depicted in Chapter VI. Thus, the simplest choice is suggested at once by the expression of the potential function:

$$\hat{V}(q) = -C\ Z/q + \frac{\lambda^2}{8}(q_1^2 + q_2^2)\ B \quad ;\ q = ||\bar{q}|| \qquad (33.7)$$

Keeping ourselves within the simplified scheme employed up to now, we will assume that B and C are constants depending just on the quantum numbers. It must be noted that the two constants introduced in V(q) are not redundant, unlike the models studied in Chapter VII. This is due to the fact that these last models were reducible to 1D systems, while the present one demands a multidimensional functional. Up to certain point, the present state of affairs is quite similar to that found in Chapter VIII, where the finite BC made it necessary to modify the VF, with the introduction of an additional constant. It is well known that the exact eigenvalue $E(Z,\lambda)$ fulfils two fundamental Theorems,

determining the dependence on the parameters contained within H: VT

$$\sum_{n=1}^{3} \langle p_n^2 \rangle = \langle \frac{Z}{r} + \frac{\lambda}{4} \rho^2 \rangle \quad , \tag{33.8}$$

and HFT

$$\frac{\partial E}{\partial Z} = - \langle \frac{1}{r} \rangle \quad , \tag{33.9a}$$

$$\frac{\partial E}{\partial \lambda} = \frac{\lambda}{4} \langle \rho^2 \rangle \quad . \tag{33.9b}$$

From Theorem 19.1 , the F extreme condition

$$(\frac{\partial F}{\partial q_i}) \ (q_i = q_i^*) = 0 \quad ; \quad i = 1,2,3 \tag{33.10}$$

allows the fulfilment of VT and HFT-like equations, viz.

$$2 \sum_{i=1}^{3} \frac{A_i}{q_i^{*2}} = \frac{CZ}{q^*} + \frac{\lambda}{4}^2 B \ (q_i^{*2} + q_i^{*2}) \quad , \tag{33.11a}$$

$$(\frac{\partial F}{\partial \lambda}) \ (q_i = q_i^*) = \frac{\lambda}{4} B \ (q_1^{*2} + q_2^{*2}) \quad , \tag{33.11b}$$

$$(\frac{\partial F}{\partial Z}) \ (q_i = q_i^*) = - \frac{C}{q^*} \quad . \tag{33.11c}$$

The extreme values of variables q and $\{q_i\}$ are determined from (33.10), which immediately allow one to obtain the couple of relationships

$$-2 \frac{A_i}{q_i^{*3}} + \frac{\lambda}{4}^2 B \ q_i^* + \frac{ZC}{q^{*3}} q_i^* = 0 \quad ; \quad i = 1,2 \quad , \tag{33.12a}$$

$$-2\frac{A_3}{q_3^{*3}}+\frac{ZC}{q^{*3}}q_3^* = 0 \quad . \tag{33.12b}$$

The Hamiltonian's cylindrical symmetry for $\lambda\neq 0$ does not permit the separate determination of q_1^* and q_2^*. Thus, it is natural to compute just $q_1^{*2} + q_2^{*2}$ and q_3^*, since they are enough to describe completely the system. We start from Eqs. (33.12) to determine such coordinates, and we are led to

$$q_1^{*2} + q_2^{*2} = \left[A_1^{1/2} + A_2^{1/2}\right] \left\{\frac{2q^{*3}}{\frac{\lambda^2}{4}Bq^{*3}+ZC}\right\}^{1/2} , \tag{33.13a}$$

$$q_3^* = \left[\frac{2A_3q^{*3}}{ZC}\right]^{1/2} , \tag{33.13b}$$

The calculation is completed with Eq.(33.5)

$$q^{*2} = q_1^{*2} + q_2^{*2} + q_3^{*2} \tag{33.13c}$$

Once the constants A_3, C, B and $(A_1^{1/2} + A_2^{1/2})$ are known, Eqs. (33.13) are solved iteratively.

As discussed in Chapter VI, the VFM allows one to approach the eigenvalue $E(Z,\lambda)$ through the functional extreme. Using Eqs. (33.11a) (VT for F) and (33.13a) in F, such extreme can be expressed at once in terms of q* and the aforesaid constants:

$$F(\bar{q}^*) = \frac{-ZC}{2q^*} + \frac{\lambda^2}{4}\left|A_1^{1/2}+A_2^{1/2}\right| \left\{\frac{2B^2q^{*3}}{ZC + \frac{\lambda^2Bq^{*3}}{4}}\right\}^{1/2} \tag{33.14}$$

Finally, to complete the F construction it remains to determine the involved constants. Before discussing this problem, it is convenient to analyse some relations that will be useful later on.

From the HFT for F (Eqs.(33.11b, c)) and HFT for E (Eqs.(33.9)), we obtain the expectation values

$$\langle \rho^2 \rangle = B(q_1^{*2} + q_2^{*2}) \tag{33.15a}$$

$$\langle \frac{1}{r} \rangle = \frac{C}{q^*} \tag{33.15b}$$

for the state under consideration.

Applying the same procedure as in Chapters VII and VIII, we gather the constants involved within the functional from the knowledge of the system properties at zero field (λ=0) and infinite field (which is equivalent to make Z=0). From Eq.(33.14) we get:

$$\lim_{\lambda \to 0} F(\bar{q}^*) = - \frac{ZC}{2} \lim_{\lambda \to 0} q^{*-1} \tag{33.16}$$

and, on the other hand, Eqs. (33.13) allow one to deduce

$$\lim_{\lambda \to 0} q^{*-1} = \frac{ZC}{2A} \quad ; \quad \sqrt{A} = \sum_{i=1}^{3} A_i^{1/2} \tag{33.17}$$

so that Eq.(33.16) takes the form:

$$\lim_{\lambda \to 0} F(\bar{q}^*) = - \frac{Z^2 C^2}{4A} \tag{33.18}$$

Imposing the correlation between the VF and the correct eigenvalue at zero field:

$$E(Z,0) = \lim_{\lambda \to 0} F(\bar{q}^*) \quad , \tag{33.19}$$

we derive a first relation to be satisfied by the constants

$$\frac{C^2}{A} = \frac{2}{n^2} \quad ; \quad n = n_r+\ell+1 \quad ; \quad n_r \ell \geq 0 \qquad (33.20)$$

where, as usual, n is the principal quantum number of the hydrogen-like atom. Since $\{q_i\}$ satisfy the proportionality relationship (33.6) it could be concluded that

$$\langle r^2 \rangle \alpha q^{*2} \quad . \qquad (33.21)$$

But this relation, unlike (33.15) is not an equality for all λ, because now we have not any theorem relating derivatives of the VF with $\langle r^2 \rangle$. However, we can determine, without any loss of generality, the constant C so that (33.21) is obeyed at zero-field

$$\langle r^2 \rangle \ (\lambda=0) = \lim_{\lambda \to 0} q^{*2} \quad . \qquad (33.22)$$

Substitution of (33.22) into (33.15b) permits the determination of the constant C:

$$C = \sqrt{\{\langle \frac{1}{r} \rangle^2 \langle r^2 \rangle\}(\lambda=0)} = \frac{1}{n\sqrt{2}} \{5n^2+1-3\ell(\ell+1)\}^{1/2}, \qquad (33.23)$$

since the involved expectation values are well-known in the hydrogen-like eigenfunctions basis set /3,4/. Notice that C-constant is Z independent.

Eqs. (33.20) and (33.23) allow us to fix the correct E and $\langle r^2 \rangle$ values when $\lambda \to 0$. There is an additional relation for the correct behavior of $\langle \rho^2 \rangle$ when $\lambda \to 0$.

The hydrogen atom fulfils /3/

$$\langle \rho^2 \rangle \ (\lambda=0) = \frac{2}{3} f \langle r^2 \rangle \ (\lambda=0) \qquad (33.24a)$$

where

$$f = f(m,\ell) = 1 + \frac{3m^2 - \ell(\ell+1)}{(2\ell+3)(2\ell-1)} \tag{33.24b}$$

Inserting Eqs. (33.15a) and (33.22) in (33.24a), we obtain

$$B \lim_{\lambda\to 0} (q_1^{*2} + q_2^{*2}) = \left[\frac{2}{ZC}\right]^{1/2} B(A_1^{1/2}+A_2^{1/2}) \lim_{\lambda\to 0} q^{*3/2} =$$

$$\frac{2f}{3} \lim_{\lambda\to 0} q^{*2} \quad , \tag{33.25}$$

and together with Eqs. (33.17) and (33.20) yields other relationship among the constants:

$$B\ (A_1^{1/2} + A_2^{1/2}) = \frac{2^{1/2} nfC}{3} \quad . \tag{33.26}$$

In order to complete the functional's construction, we have to determine the constant $A_1^{1/2} + A_2^{1/2}$. Since such a constant appears in the purely cylindrical symmetry term of F, it seems appropriate to determine it from the knowledge of the energy at infinite field strength, where the term containing the constant is dominant. For $\lambda\to\infty$ (equivalent to $Z\to 0$), the functional extreme (Eq. (33.14)) follows

$$\lim_{Z\to 0} F(\bar{q}^*) = (2B)^{1/2}\ (A_1^{1/2} + A_2^{1/2})\ \frac{\lambda}{2} \quad . \tag{33.27}$$

This behavior can be matched with the Landau spectrum by way of

$$E(0,\lambda) = (\frac{N+1}{2})\lambda = \lim_{Z\to 0} F\ (\bar{q}^*) \tag{33.23}$$

and finally the desired result follows:

$$A_1^{1/2} + A_2^{1/2} = \frac{N+1}{(2B)^{1/2}} \quad , \tag{33.29}$$

where N=0,1,... is the Landau quantum number (Appendix H), labelling the problem states with Z→0. In order to perform any computation, it is necessary to know the correlation among the quantum numbers (n,ℓ,m) and N /4-6/. It must be pointed out that only m is a good quantum number, since the angular momentum L in the axis x_3 is conserved. Notwithstanding, it is possible to correlate properly the Coulombic regime states with the Landau ones through the constants contained within F. The substitution of (33.29) in (33.26) and using (33.23), we get the B constant in closed form:

$$B = \frac{2}{9(N+1)^2} f^2 \left(5n^2 + 1 - 3\ell(\ell+1)\right) \quad . \tag{33.30}$$

Constant A_3 is computed with the aid of Eqs. (33.17) and (33.20)

$$A_3^{1/2} = \frac{1}{2} \left\{5n^2+1-3\ell(\ell+1)\right\}^{1/2} - \frac{N+1}{(2B)^{1/2}} \quad , \tag{33.31}$$

and it concludes the calculation procedure.

Summing up, the constructed functional allows one to obtain a function satisfying HFT and VT and, furthermore, having the same behavior as the exact eigenvalue for λ→0 and λ→∞. In addition, the insertion of an extra constant permits one to get the correct $\langle\rho^2\rangle$ (λ=0) and $\langle r^2\rangle$ (λ=0) values.

Since the functional obeys the first aforesaid expectation value, it is implied that the VFM yields the RSPT up to the first order. We will see that, on spite of its simplicity, the functional gives an excellent approximation to the exact eigenvalue E(Z,λ).

It is appropriate to analyse some scaling properties fulfilled by F, through the extreme condition (33.10), before performing any actual

calculation.

To this end, let us denote with $F(\bar{q}^*\ ;\ Z,\lambda)$ the minimum F value (Eq. (33.14)), representing the hydrogen-like atom energy with Z nuclear charge, in a field $|\lambda|$. Scaling the parameter q* (see Appendix A) through Eq. (33.14), and re-writing the formula in an unitary equivalence form, we obtain

$$F(\bar{q}^*;Z,\lambda) = \lambda\{-\frac{ZC_\alpha^{-1}}{2q^*\lambda} + \frac{1}{4}\,(A_1^{1/2}+A_2^{1/2})\left[\frac{2B^2q^{*3}}{\frac{ZC}{\alpha^3\lambda^2}+\frac{Bq^{*3}}{4}}\right]^{1/2}\} \quad . \tag{33.32}$$

The choice

$$\alpha = \lambda^{-1/2} \quad , \tag{33.33}$$

transforms Eq. (33.32) into

$$F(\bar{q}^*;Z,\lambda) = \lambda\{-\frac{C}{2q^*}\,(\frac{Z}{\lambda^{1/2}}) + \frac{1}{4}\,(A_1^{1/2}+A_2^{1/2})\left[\frac{2B^2q^{*3}}{\frac{ZC}{\lambda^{1/2}}+\frac{Bq^{*3}}{4}}\right]^{1/2}\} \tag{33.34}$$

and it yields the following equivalence relationship

$$F(\bar{q}^*;\ Z,\lambda) = \lambda F(q^*;\ Z\lambda^{-1/2},1) \quad . \tag{33.35}$$

Eq. (33.35) is the same as that satisfied by the exact eigenvalue $E(Z,\lambda)$. This property assures us that the VF will have an approximately correct dependence upon λ within the whole range of field intensities. Moreover, relationship (33.35) simplifies at a large extent the computation scheme, since they must only be done for Z=1.

§.34. Results for several functions of physical interest.

Equations deduced in §.33 allow one to compute the eigenvalue E $(1,\lambda)$ (Z=1 in our calculations), within a reasonable accuracy, whenever the correlation among quantum numbers (n,m,ℓ) and N is provided /4-6/. Besides, HFT makes up the way to obtain $\langle\rho^2\rangle$ and $\langle r^{-1}\rangle$ plausible approximate values.

The computational scheme is as follows: After selecting the state under study (i.e. fix (n,m,ℓ) and N values), the constants appearing in the functional are computed via Eqs. (33.23) and (33.29)-(33.31). Then q* is determined through an iterative solution of the coupled equations (33.13), and energy as well as expectation values are obtained from Eqs. (33.14) and (33.15), respectively.

We can add another calculation based on the fact that (33.21) turns into a equality when $\lambda\to 0$ (Eq. (33.22)). For $\lambda\neq 0$ one could rigorous guess that it might still be a reasonable approximation to $\langle r^2\rangle$. The goodness of this result is discussed in this paragraph. Let us remark that $E,\langle r^2\rangle$ and $\langle\rho^2\rangle$ are the most significant quantities from the physical viewpoint, because the first one stands for the atomic energy, and the two remaining ones describe the approximate atomic "shape".

Some results are shown in Figs. 10.1 and 10.2 for a large range of field intensities.

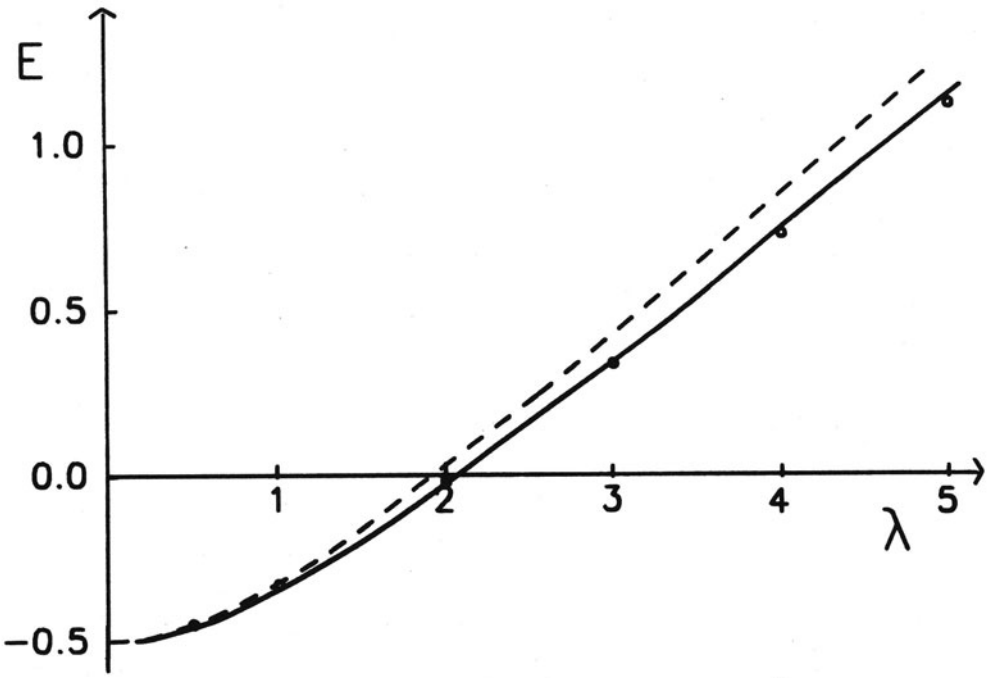

Fig. 10.1: Ground state energy of the Zeeman effect in the Hydrogen atom for low and middle field strengths.

------ Results obtained from the VFM ($n_r=\ell=m=0$)

——— Results obtained from the VFM ($n\to\infty, \ell=m=0$)

o "Exact" results /7/.

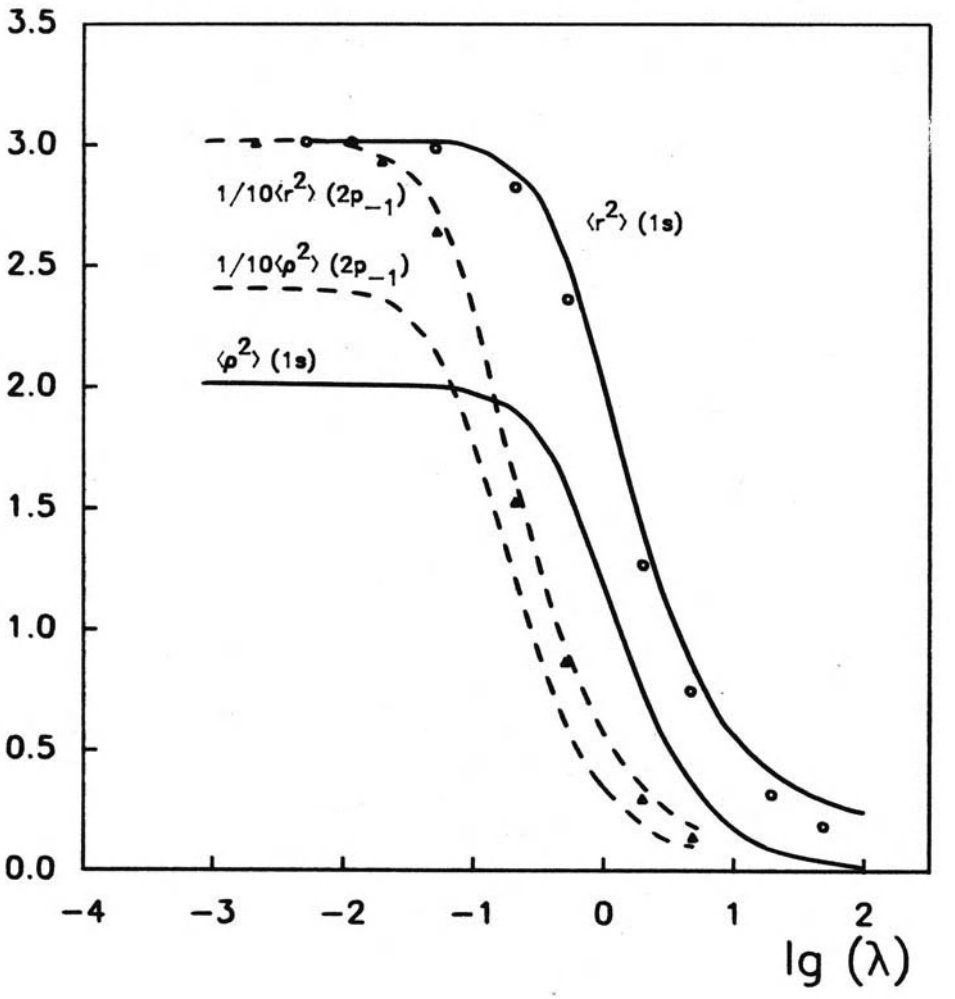

Fig. 10.2: Approximate average values of O^2 and r^2 for the Zeeman effect in Hydrogen atom states by way of the VFM.

——— 1s state

----- $2p_{-2}$ state

o "Exact" results for the 1s state /7/

Δ "Exact" results for the $2p_{-1}$ state /7/

For the sake of simplicity, we have chosen the first two Landau states (N+m=0), which the two most studied tight-bound states (see Chapter IX). For $\lambda \to 0$, these states correlate with the hydrogen atom states 1s and $2p_{-1}$. The quantum numbers assignments are

$$(n,m,\ell;N) = (1,0,0;1) \to \text{"1s" state} \tag{34.1a}$$

$$(n,m,\ell;N) = (2,-1,1;1) \to \text{"}2p_{-1}\text{" state} \tag{34.1b}$$

The broken line in Fig. 10.1 shows the ground state energy change (34.1a) for low and intermediate field intensities. The results reveal some noteworthy features:

i) For $\lambda \leq 1$ results agree satisfactorily with the exact ones obtained with the most accurate numerical, variational techniques available /7/. This is not surprising since the greatest information introduced within the functional corresponds to $\lambda \to 0$. Nevertheless, the agreement is remarkable, since we have only used the RSPT first-order information. It is well known that RSPT is asymptotically divergent, and this property hinders its practical application for $\lambda \geq 0$ /8/. Consequently, the extension performed through the VFM is quite meaningful.

ii) For larger field intensities ($\lambda \geq 1$) present results lack accuracy and yield an upper bound to the eigenvalue $E(1,\lambda)$ (Eq. (34.1a)). However, it is worth noting that the curve shape obtained from the VFM is quite similar to the exact one. This result shows that the main dependence of E on λ may be guaranteed through the VT and HFT obeyed by the VF. The remaining differences could be removed by including higher orders of RSPT within the VF. This point will be discussed later on.

Fig. 10.2 displays the results for $\langle \rho^2 \rangle$ and $\langle r^2 \rangle$ within the field range $1^{-03} \leq \lambda \leq 10^2$, for those states described by Eqs. (34.1). Results show that q^{*2} is an excellent approximation to $\langle r^2 \rangle$ /7/, in the whole field intensity range. A similar conclusion can be reached for the present approximation to $\langle \rho^2 \rangle$ (in principle more accurate than that obtained for $\langle r^2 \rangle$), although there are not exact data available to make the necessary comparisons.

In closing this paragraph, we can remark that VFM makes up a quite simple formalism to describe up to a satisfactory degree the more important physical properties of the Zeeman effect in the hydrogen-like atoms. Present conclusions about the atomic "shape" for the two considered states are correct /9/: the atom distorts turning to be a "needle" oriented along the field direction. That is to say, the electronic density tends to concentrate on the nucleus, and in less proportion across the directions normal to the field. Additional results on the application of the VFM to this system can be seen in Refs. /1,2/.

§. 35. Scaling laws and semiclassical behavior of the Variational functional.

Eq. (33.35) represents a scaling relationship in the magnetic field and it is fulfilled by the VF made an extreme in the configuration space.

As shown in Appendix H, this relationship can be expressed as a scaling law in the nuclear charge Z. There exists an additional relation satisfied by the exact eigenvalues at the semiclassical limit, i.e. for large n and N quantum numbers. This law is represented in an approximate fashion by Eq. (30.6) (it was discussed in Chapter IX regarding Rydberg atoms placed in magnetic fields). As analysed in §.31, and elementary semiclassical model allows one to account for such a law (cf.Eq. 31.25).

Let us discuss the VF behavior regarding the scaling in quantum numbers. Let us consider those states obeying the relation

$$n = N+1 \quad ; \tag{35.1}$$

redefining the functional constants and variables as follows

$$A_i' = A_i/n^2 \quad , \tag{35.2a}$$

$$\lambda' = n^3\lambda \quad , \tag{35.2b}$$

$$q'^* = q^*/n^2 \; ; \; \bar{q}'^* = (q_1'^*, q_2'^*; q_3'^*) \; ; \; q'^* = ||\bar{q}'^*||, \tag{35.2c}$$

$$F'^* = n^2 F^* = n^2 F(\bar{q}^*; Z, \lambda) \quad . \tag{35.2d}$$

From Eqs. (35.1) and (35.2a) together with Eqs. (33.29), (33.31) and (33.23), we have

$$A_1'^{1/2} + A_2'^{1/2} = \frac{1}{(2B)^{1/2}} \quad , \tag{35.3}$$

$$A_3'^{1/2} = 2^{-1/2} \, (C - B^{-1/2}) \quad ; \tag{35.4}$$

$q_i'^*$ values are derived from Eqs. (33.13), (35.1) and (35.2):

$$q_1'^{*2} + q_2'^{*2} = (A_1'^{1/2} + A_2'^{1/2}) \left\{ \frac{2q'^{*3}}{\frac{\lambda'^2 B q'^{*3}}{4}} + ZC \right\}^{1/2} \tag{35.5a}$$

$$q_3'^{*2} = \left\{ \frac{2A_3 q'^{*3}}{ZC} \right\}^{1/2} \tag{35.5b}$$

Finally, Eqs. (35.2a) and (33.14) yield the extreme functional expression F'*:

$$F'^* = n^2 F^* = -\frac{ZC}{2q'^*} + \frac{\lambda'^2}{4} B^{1/2} \left\{ \frac{q'^{*3}}{ZC + \frac{\lambda'^2 B q'^{*3}}{4}} \right\}^{1/2} \tag{35.6}$$

Eq. (35.6) is the desired result: F'* depends exclusively on $n^3\lambda$, such as it is required by the scaling law (30.6). Then, the VFM obeys the relation (30.6) as well as other semiclassical approximations like (31.25) do. F'* depends on λ' and its only explicit dependence on the quantum numbers is through C and B. This function F'* behaves similarly to the ground state (n = N+1 = 1), since it satisfies the same asymp-

totic relationships:

$$F'^{*}\ (\lambda' = 0) = -Z^2/2 \quad , \tag{35.7}$$

$$F'^{*}\ (Z = 0) = \lambda'/2 \quad . \tag{35.8}$$

Accordingly, there is an infinite family of curves F'* with the same asymptotic behavior as the ground state. We can obtain a sole function not depending on n taking the limit $n\to\infty$. This is possible due to the fact that C and B have finite limits:

$$\lim_{n\to\infty} C = \left(\frac{5}{2}\right)^{1/2} \quad , \tag{35.9}$$

$$\lim_{n\to\infty} B = \frac{10}{9} f^2 \quad . \tag{35.10}$$

Substitution of (35.9) and (35.10) into (35.6), after taking the limit $n\to\infty$, allow one to express F'* as a function depending on λ', m and ℓ.

This last result is especially interesting, since it leads to a similar result to that obtained through semiclassical approximations in 1/n power series expansions /10,11/. In such a approximation, the ground state is obtained with the limit $n\to\infty$; accordingly, it seems plausible to use the limit $n\to\infty$ in F'* with $m=\ell=0$ to approximate this particular state.

Fig.10.1 displays in broken line, the results for the lowest eigenvalue ($N=m=\ell=0$) obtained via Eq. (35.6) at the limit $n\to\infty$ ($n_r\to\infty$) (Eqs. (35.9) and (35.10) with f=1).

These results reveal the following characteristics:

i) For $\lambda<<1$ they are worse than those discussed in §.34. This behavior is quite understandable considering that $(\partial F'^{*}/\partial\lambda)(\lambda'=0)$ differs from the correct value $(\partial F^{*}/\partial\lambda)(\lambda=0) = (\partial E/\partial\lambda)(\lambda=0)$. That if, F' scaled

with $n_r \to \infty$ does not satisfy the perturbative expansion up to the first order.

ii) Within the interval $1 \leq \lambda \leq 5$ results are extremely accurate. We can assume that in this range the dilatation effects on quantum numbers have the largest importance.

In §.30 we made a thorough discussion on recent physical applications of the Zeeman effect in hydrogen-like atoms for magnetic fields of arbitrary intensity, and it was commented that quasi-Landau resonances at the ionization threshold at zero field for Rydberg atoms possessed a deep interest /4,12-14, and Refs. Chapter IX/. Recently, Feneuille /15/ has developed an empirical law to join the Landau and Coulomb regimes from the quasi-Landau spectrum experimental data. This law fulfils the dependence on the quantum numbers (30.6), and on this basis the author conjectured that there should be a theoretical justification for his successful empirical law. We have proved in §.31 that an elemental semiclassical model predicts such a law, and recently it has been proved that the quantization method JWKB (for a plane normal to the magnetic field direction) explains quite well such dependence on the quantum numbers /16/. These authors have presented another different explanation of the Feneuille law through the employment of the variational method discussed in §.20 /16/. Then, the VFM, as presented in this section, is an alternative formulation to rationalize empirical laws like that of Ref. /15/. Precisely, Fig. 10.1 (broken line) shows that VFM describes very well the ionization limit zone (E=0) to zero-field, which is that of greater interest for quasi-Landau resonances.

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CHAPTER XI

COMBINATION OF VFM WITH RSPT: APPLICATION TO ANHARMONIC OSCILLATORS

§.36. An elementary extension of the VFM for anharmonic oscillators.

In §.23 the VFM was applied to an 2K-anharmonic oscillator

$$H(g,\lambda) = p^2 + gx^2 + \lambda x^{2K} \tag{36.1}$$

whose eigenvalues (for g=1) are called $E(1,\lambda)$. We saw that energy and expectation values of greatest interest can be approached starting from the functional

$$F_n(q) = \frac{A_n}{q^2} + q^2 + \lambda B_n q^{2K} \quad , \tag{36.2a}$$

$$\left(\frac{\partial F_n}{\partial q}\right) \; (q = q^*) = 0 \quad . \tag{36.2b}$$

From now on, we will remove the prime symbol over the variables used in §.23 in order to simplify the writing. As stated before, A_n was chosen as a function depending solely on the quantum number n, independent of λ. In other words, the energy and expectation values are wholly determined from the knowledge of the function $B_n(\lambda)$.

Up to this moment, we have discussed a scheme based on considering all the constants inserted within the functional as independent of perturbation parameters, such as external fields or self-couplings. These constants happened to be two (A and B) for 1D systems (or systems reducible to 1D ones) with trivial BC, while they are three (A, B and C) for non-separable systems with two degrees of freedom or with BC for finite coordinate values.

In order to improve this approximation, it is necessary to build

$B_n(\lambda)$ in an appropriate manner. To obtain an analytic representation of $B_n(\lambda)$ two conditions must be assured:

i) The λ-dependence of $B_n(\lambda)$ must not modify the dependence of F_n with λ, guaranteed by the extreme condition (VT and HFT).

ii) The Taylor expansion of $B_n(\lambda)$ as a λ-power series must lead to the correct Taylor expansion of $E_n(\simeq F_n(q^*))$, i.e. it has to lead term by term to the RSPT.

Accordingly, we have combined VFM and RSPT through the function $B_n(\lambda)$. This is a key point within the logic structure of this book and one of our main proposals: to relate semiclassical and analytic properties of eigenvalue problem with PT, so as to induce by way of VFM a summation method of perturbation series. Within the proposed scheme, the analysis of the $B_n(\lambda)$ function makes up a further step regarding the generality and accuracy degree in the description of quantum systems by means of the VFM.

The functional $F_n(q)$ can be expanded in λ-power series, as well as the eigenvalue $E(1,\lambda)$. According to Eqs. (23.3a) and (23.3b), the possible expansions for F_n are:

$$F_n = \sum_{m=0}^{\infty} F_n^{(m)} \lambda^m \; ; \; \lambda << 1 \quad , \tag{36.3}$$

$$F_n = \lambda^{1/(K+1)} \sum_{m=0}^{\infty} F_n'^{(m)} \lambda^{-2m/(K+1)} \; ; \; \lambda >> 1 \quad . \tag{36.4}$$

Moreover, we know that the extreme condition (36.2b)

$$A_n = q^{*4} + \lambda K B_n q^{*(2K+2)} \quad , \tag{36.5}$$

leads to two possible expansions for q^* (see Eq. (23.27)):

$$q^* = \sum_{m=0}^{\infty} q_m^* \lambda^m \quad ; \quad \lambda << 1 \tag{36.6}$$

$$q^* = \lambda^{-1/2(K+1)} \sum_{m=0}^{\infty} q'^*_m \lambda^{-2m/(K+1)} \quad ; \quad \lambda >> 1 \quad . \qquad (36.7)$$

The expansions (36.3), (36.4), (36.6) and (36.7) exist iff B_n can be expanded as:

$$B_n(\lambda) = \sum_{m=0}^{\infty} B_n^{(m)} \lambda^m \quad ; \quad \lambda << 1 \qquad (36.8)$$

$$B_n(\lambda) = \sum_{m=0}^{\infty} B_n'^{(m)} \lambda^{-2m/(K+1)} \quad ; \quad \lambda >> 1 \qquad (36.9)$$

As stated in §.23, $B_n(\lambda)$ is a bounded function, $\forall\ \lambda \geq 0$. The procedure to build $B_n(\lambda)$ consists of using the theoretical information to determined some coefficients $\{B_n^{(m)}\}$, $\{B_n'^{(m)}\}$ and then to generate a function whose Taylor expansion has such coefficients.

Coefficients $\{B_n^{(m)}\}$ can be determined by way of the λ-power series (36.3) and (36.6). Keeping in mind that the constant A_n was fixed through the use of the limit $\lambda \to 0$ for $E(1,\lambda)$ (Eq. (23.26)), viz.

$$A_n = \frac{1}{4} E_n(1,0)^2 = \frac{1}{4} E_n^{(0)2} \quad , \qquad (36.10)$$

it is easily seen that in order to determine $B_n^{(M)}$ one must know up to $F_n^{(M+1)}$. Then, making the assignment

$$E_n^{(m)} = F_n^{(m)} \quad ; \quad m = 0,1,2,\ldots, M+1 \qquad (36.11)$$

we can obtain $B_n^{(0)},\ldots,B_n^{(M)}$ as a function of RS coefficients $E_n^{(m)}$. Some results are presented in what follows. The procedure consists of introducing (36.6) and (36.8) in (36.5) and identifying the λ-powers to obtain the q^* coefficients as $B_n^{(m)}$ functions. For the sake of brevity, we restrict ourselves up to the order $O(\lambda^2)$, using the auxiliar relationship

$$q^{*2K} = q_0^{*2K}\{1+ \frac{2Kq_1^*}{q_0^*}\lambda+\left[4K\frac{q_2^*}{q_0^*} + 2K(2K-1)(\frac{q_1^*}{q_0^*})^2\right]\lambda^2+...\} \qquad (36.12)$$

we can collect all the contributions up to the order $O(\lambda^2)$ for the different terms of Eq. (36.5). For the first term in the r.h.s. it is enough to take K=2 in Eq. (36.12), while for the second term we have

$$\lambda B_n q^{*2K+2} = q_0^{*2K+2}\{B_n^{(0)}\lambda + (B_n^{(1)} + \frac{2(K+1)}{q_0^*}q_1^* B_n^{(0)})\lambda^2+...\} \quad . \qquad (36.13)$$

The substitution of these equations into (36.5) and the identification of coefficients multiplying a given λ power, yields at once

$$A_n = q_0^{*4} \quad , \qquad (36.14a)$$

$$4\, q_1^*\, q_0^{*3} + K\, B_n^{(0)}\, q_0^{*2K+2} = 0 \quad , \qquad (36.14b)$$

$$8q_2^*\, q_0^{*3} + 12q_1^{*2}\, q_0^{*2} + Kq_0^{*2K+2}\left[B_n^{(1)} + \frac{2(K+1)}{q_0^*}\, q_1^*\, B_n^{(0)}\right] = 0 \qquad (36.14c)$$

so that we find,

$$q_0^* = A_n^{1/4} \quad , \qquad (36.15a)$$

$$q_1^* = -\frac{K}{4}\, B_n^{(0)}\, q_0^{*2K-1} \quad , \qquad (36.15b)$$

$$q_2^* = (\frac{2K-1}{32})\, K^2 B_n^{(0)2} q_0^{*4K-3} - \frac{K}{8}\, B_n^{(1)}\, q_0^{*2K-1} \quad . \qquad (36.15c)$$

To determine the coefficients $\{B_n^{(m)}\}$, firstly we combine properly Eqs. (36.2a) and (36.2b) to obtain

$$F_n(q^*) = 2q^{*2} + (K+1)\ \lambda B_n q^{*2K} \tag{36.16}$$

and then we substitute (36.3) in the l.h.s. and (36.12) and (36.8) into the r.h.s.. Up to second order in λ, we have

$$F_n^{(0)}+F_n^{(1)}\lambda+F_n^{(2)}\lambda^2+\ldots = 2q_0^{*2}+4q_1^*q_0^*\lambda+4(2q_2^*q_0^*+q_1^{*2})\lambda^2 +$$

$$+ (K+1)q_0^{*2K}\{B_n^{(0)}\lambda+\left[B_n^{(1)}+\frac{2Kq_1^*}{q_0^*}\ B_n^{(0)}\right]\lambda^2\} +\ldots \tag{36.17}$$

The computation scheme is completed after the identification of λ-powers and the use of Eqs. (36.11) and (36.15):

$$B_n^{(0)} = \left[\frac{2}{E_n^{(0)}}\right]^K E_n^{(1)} \quad , \tag{36.18}$$

$$B_n^{(1)} = \frac{1}{2}\left[\frac{2}{E_n^{(0)}}\right]^K \{2E_n^{(2)} + K^2\ \frac{E_n^{(1)2}}{E_n^{(0)}}\} \quad . \tag{36.19}$$

Coefficients $E_n^{(m)}$ can be determined for every oscillator (i.e. for each K-value) using the procedures studied in Chapter III /1,2/. The first perturbative coefficients (to be employed in this chapter later on) are listed below for the quartic (K = 2) and sextic (K = 3) oscillators:

$$E_n^{(0)} = (2n+1) \quad ; \quad K = 2,3 \tag{36.20a}$$

$$E_n^{(1)} = \frac{3}{8}\{1+(2n+1)^2\} \quad ; \quad K = 2 \tag{36.20b}$$

$$E_n^{(1)} = \frac{5}{16}(2n+1)\{5+(2n+1)^2\} \quad ; \quad K = 3 \tag{36.20c}$$

$$E_n^{(2)} = -\frac{1}{8}(2n+1)\left\{\frac{67}{8} + \frac{17}{9}(2n+1)^2\right\} \; ; \; K = 2 \qquad (36.20d)$$

$$E_n^{(2)} = -\frac{1}{512}(2n+1)\left\{\frac{19277}{2} + 4145(2n+1)^2 + \frac{393}{2}(2n+1)^4\right\} \; ;$$

$$K = 3 \qquad (36.20e)$$

Coefficients $\{B_n'^{(m)}\}$ (Eq.(36.9)) can be derived by means of a analogous procedure to that discussed before. In order to calculate the coefficient $B_n'^{(M)}$ we need to include the perturbation coefficients associated with the expansion (36.4) up to the order $F_n'^{(M)}$. These coefficients are determined:

$$F_n'^{(m)} = e_n^{(m)} \; ; \; m = 0,1,2,\ldots,M \qquad (36.21)$$

To the purpose to compute coefficients $\{B_n'^{(m)}\}$ we apply the following procedure: firstly we make the change of variable $q=y\lambda^{-1/2(K+1)}$ in the functional (36.2a), to obtain

$$\lambda^{-1/(K+1)} F_n(y) = \frac{A_n}{y^2} + \sigma y^2 + B_n y^{2K} \; ; \; \sigma=\lambda^{-2/(K+1)} \; . \qquad (36.22)$$

The extreme condition (36.2b) leads to

$$A_n = \sigma y^{*4} + KB_n y^{*2K+2} \qquad (36.23a)$$

$$\sigma^{1/2} F_n(y^*) = 2\sigma y^{*2} + (K+1) B_n y^{*2K} \; . \qquad (36.23b)$$

Both sides in Eqs. (36.23a) and (36.23b) can be expanded in σ-power series, according with Eqs. (36.4) and (36.7). The first equation

(36.23a) relates coefficients $\{q_m'^*\}$ and $\{B_n'^{(m)}\}$ and the results up to the second order are

$$A_n = B_n'^{(0)} \, q_0'^{*2K+2} \, K \quad , \tag{36.24a}$$

$$\frac{q_0'^{*4}}{K} + 2B_n'^{(0)}(K+1)q_1' \, q_0'^{*2K+1} + B_n'^{(1)} q_0'^{*2K+2} = 0 \quad , \tag{36.24b}$$

$$4q_1'^* \, q_0'^{*3} + KB_n'^{(2)} \, q_0'^{*2K+2} + 2K(K+1)B_n'^{(1)} \, q_1'^* \, q_0'^{*2K+1} +$$

$$+ K(K+1)B_n'^{(0)} \, q_0'^{*2K} \{(2K+1) \, q_1'^{*2} + 2q_2' \, q_0'^* \} = 0 \quad . \tag{36.24c}$$

Finally, the second equation (36.23b) yields the desired result by employing Eqs. (36.21) and (36.24):

$$B_n'^{(0)} = \left(\frac{K}{A_n}\right)^K \left(\frac{e_n^{(0)}}{K+1}\right)^{K+1} \quad , \tag{36.25}$$

$$B_n'^{(1)} = \left\{\frac{e_0^{(0)K}}{A_n(K+1)}\right\}^K \left[e_n^{(1)} - \frac{(K+1)A_n}{Ke_n^{(0)}}\right] \quad . \tag{36.26}$$

$$B_n'^{(2)} = \left[\frac{e_0^{(0)K}}{A_n(K+1)}\right]^K \left[e_n^{(2)} + \frac{K}{2e_n^{(0)}} \left\{e_n^{(1)} + \frac{1-K^2}{K^2} \frac{A_n}{e_n^{(0)}}\right\}\right] \quad . \tag{36.27}$$

Unlike what happens with λ-series expansion for $E(1,\lambda)$, the coefficients $e_n^{(m)}$ are not known in analytical form for anharmonic oscillators. It is easy to understand the reasons because $e_n^{(m)}$ are the RS coefficients of a quartic oscillator perturbed by an harmonic potential and the corresponding exact eigenfunctions and eigenvalues of the quartic oscillator are not known. The first coefficients $e_n^{(m)}$ have been numerically computed for the lowest states of K anharmonic-oscillators (K=2,3,4) /3,4/. For those states with large quantum numbers, the first coefficients can be computed by means of the first-order JWKB method, as developed in Chapter II /3-5/. Results are as follows:

$$e_n^{(0)} = 2^{K/(K+1)}\, C_1 \{(n+1/2) + \delta_k (n+1/2)^{-1}\}^{2K/(K+1)} \quad , \tag{36.28a}$$

$$e_n^{(1)} = 2^{(K+2)/(K+1)}\, C_2 (n+1/2)^{2/(K+1)} \quad , \tag{36.28b}$$

$$C_1 = 2^{(K-2)/(K+1)} \{(K+1)\pi\Gamma(\tfrac{1}{K})\Gamma(\tfrac{1}{2K})^{-2}\}^{2K/(K+1)} \tag{36.28c}$$

$$C_2 = 2^{(2-K)/(K+1)} \{(K+1)\pi\Gamma(\tfrac{1}{K})\Gamma(\tfrac{1}{2K})^{-2}\}^{2/(K+1)} \frac{\Gamma(\tfrac{1}{K})\Gamma(\tfrac{3}{2K})^2}{\Gamma(\tfrac{3}{K})\Gamma(\tfrac{1}{2K})^2} \quad , \tag{36.28d}$$

$$\delta_K = \frac{2K-1}{12\pi(K+1)} \operatorname{Ctg}(\tfrac{\pi}{2K}) \quad . \tag{36.28e}$$

Our problem is to build a bounded function $B_n(\lambda)$ such that it can reproduce one or both expansions with coefficients (36.18)-(36.19) and (36.25)-(36.27). To the purpose of choosing a suitable function representing $B_n(\lambda)$, it is convenient to study some of its numerical properties.

The "exact" function $B_n(\lambda)$ is that leading to $F_n(q^*) = E_n \; \forall \; \lambda$, n. Then, we can use the "exact" eigenvalues E_n to determine B_n for different oscillators. To this end, let us start from the equality:

$$F_n(q^*) = E_n(1,\lambda) \quad . \tag{36.29}$$

Eqs. (36.16) and (36.29) allow one to write the following equation for B_n:

$$B_n = \frac{E_n - 2q^{*2}}{(K+1)\lambda q^{*2K}} \quad . \tag{36.30}$$

Upon inserting Eq. (36.30) into (36.5), one gets a biquadratic

equation that yields the q*-value satisfying exactly (36.29):

$$\left[\frac{1-K}{1+K}\right]q^{*4} + \frac{KE_n q^{*2}}{K+1} - A_n = 0 \quad . \tag{36.31}$$

As discussed in §.23, the interval $0 \leq \lambda \leq \infty$ corresponds with the interval $A_n^{1/4} \geq q^* > 0$, what assures us that the only acceptable root of Eq. (36.31) is:

$$q^{*2} = \frac{K+1}{2(K-1)} \left\{ \frac{KE_n}{K+1} - \left[\frac{K^2 E_n^2}{(K+1)^2} - 4A_n \left(\frac{K-1}{K+1} \right) \right]^{1/2} \right\} \quad . \tag{36.32}$$

Eqs. (36.30) and (36.32) allow one to obtain numerically the function $B_n(\lambda)$ for any anharmonic oscillator from the knowledge of the eigenvalues. The results in the literature for K = 2,3,4, for several n, λ values /6/, were used to perform such computations.

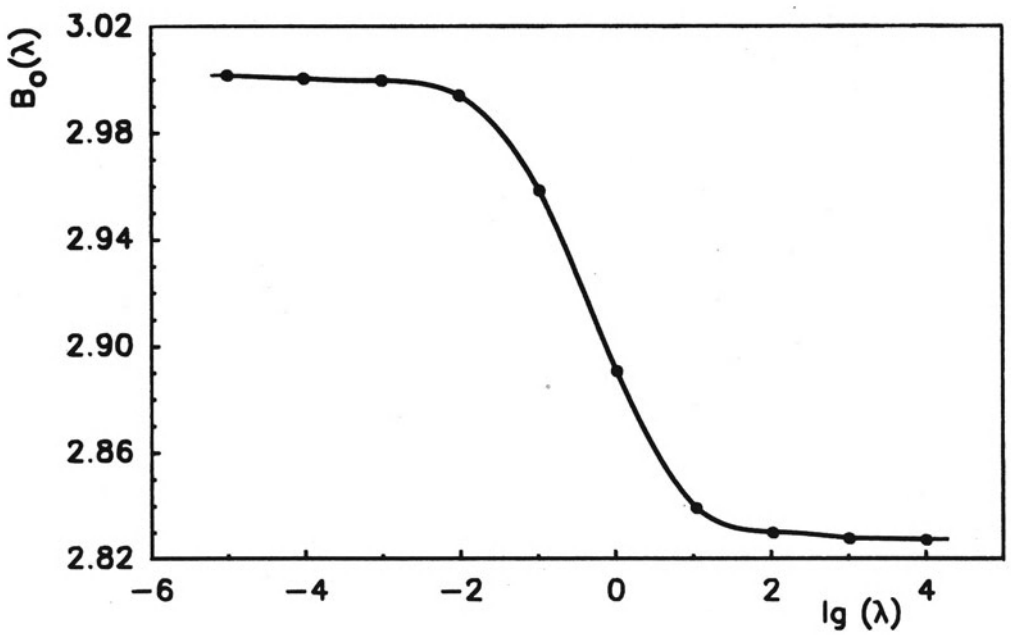

Fig. 11.1: $B_0(\lambda)$ function for the quartic anharmonic oscillator. Exact results are given by circles and the analytic expression for $B_n(\lambda)$ with full line.

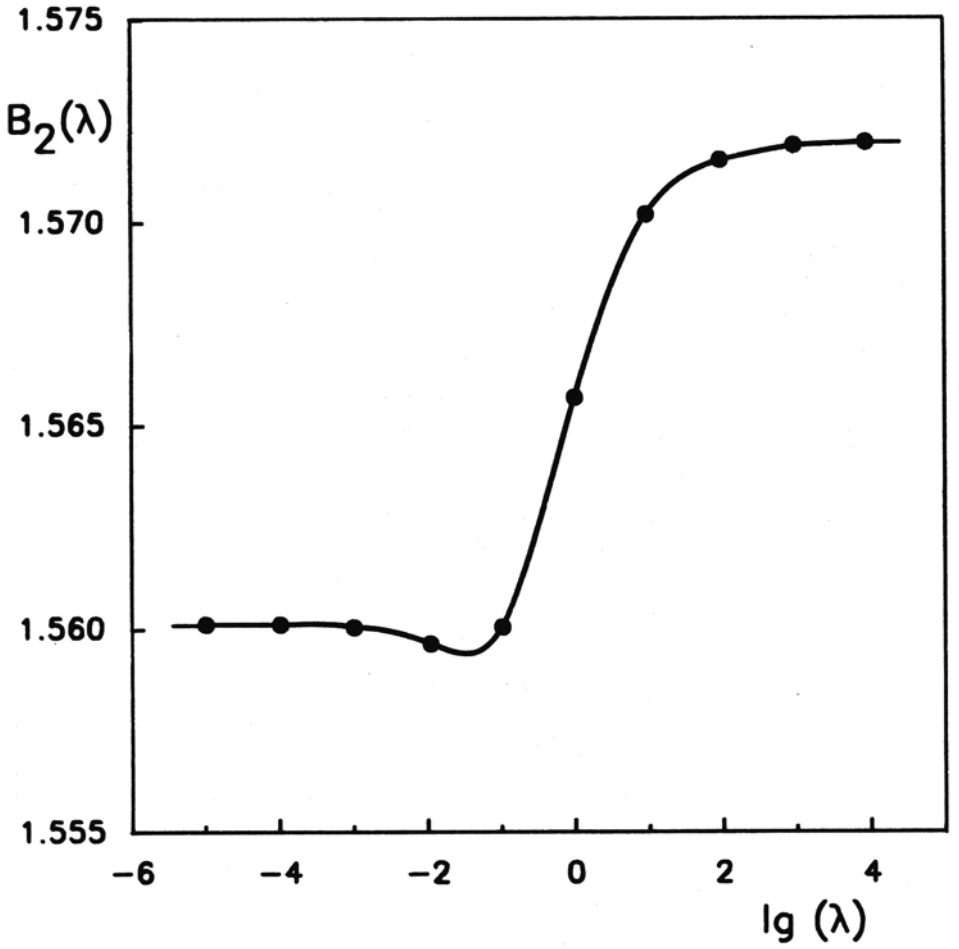

Fig. 11.2: $B_0(\lambda)$ function for $B_2(\lambda)$ of the quartic anharmonic oscillator. Exact results are given by circles and the analytic expression for $B_n(\lambda)$ with full line.

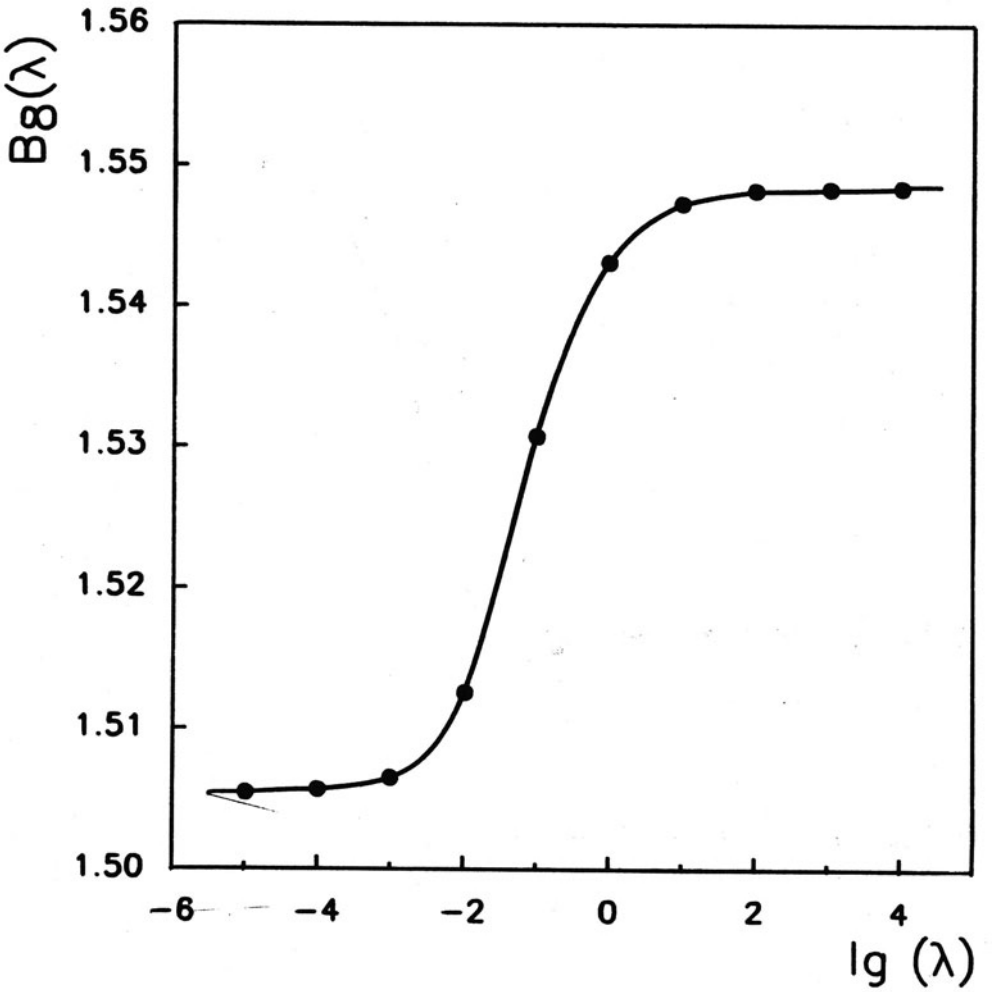

Fig. 11.3: $B_0(\lambda)$ function for $B_8(\lambda)$ of the quartic anharmonic oscillator. Exact results are given by circles and the analytic expression for $B_n(\lambda)$ with full line.

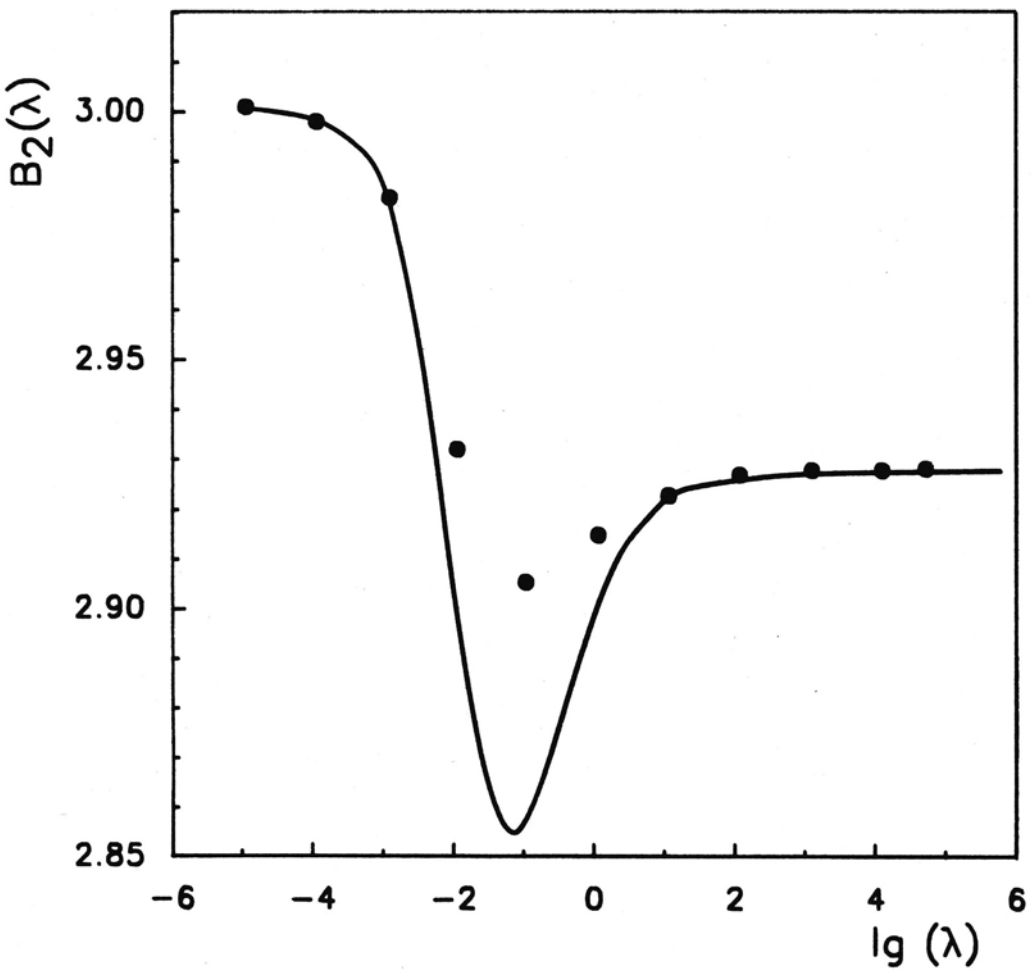

Fig. 11.4: $B_0(\lambda)$ function for $B_2(\lambda)$ corresponding to the sextic anharmonic oscillator. Exact results are given by circles and the analytic expression for $B_n(\lambda)$ with full line.

Figs. 11.1-4 display the results for $B_n(\lambda)$ (dots) as a function of lg λ for different n,K values. Fig.11.1 shows the result for $B_0(\lambda)$ when K = 2 and here $B(\lambda)$ is a monotonously decreasing function ($B_0^{(0)} > B_0'^{(0)}$) and besides it takes values only within a relatively reduced interval. Fig.11.2 displays the results for $B_2(\lambda)$, K = 2. Unlike the situation of $B_o(\lambda)$, now the function presents a minimum and $B_2^{(0)} < B_2'^{(0)}$. Fig.11.3 completes the discussion for the quartic anharmonic oscillator (K = 2) with the function $B_8(\lambda)$, which is representative of those states where $B_n(\lambda)$ is a monotonously increasing λ-function ($B_n^{(0)} < B_n'^{(0)}$). All states associated with the quartic anharmonic oscillator have a function $B_n(\lambda)$ that fits one of the three aforesaid behaviors. In order to describe the situations for all oscillators, we have to add a case of which $B_2(\lambda)$, K = 3, is an example (fig.11.4). In this case $B_2(\lambda)$ has a minimum but $B_2^{(0)} > B_2'^{(0)}$.

Summarizing, we have found that any state of any anharmonic oscillator can be classified among one of the 4 categories exemplified through figs.11.1-4. One can make the following state classification

i) Type I State: $B_n(\lambda)$ is a monotonously decreasing function.

ii) Type II a State: $B_n(\lambda)$ possesses a minimum and $B_n^{(0)} > B_n'^{(0)}$.

iii) Type II b State: $B_n(\lambda)$ has a minimum and $B_n^{(0)} < B_n'^{(0)}$.

iv) Type III State: $B_n(\lambda)$ is a monotonously increasing function.

Table 11.1: State classification for the anharmonic oscillators with K = 2,3,4 obtained with the method given in §.36.

K	Type I	Type IIA	Type IIB	Type III
2	$n \leq 1$	-	n=2	$n \geq 3$
3	$n \leq 1$	n=2	n=3	$n \geq 4$
4	$n \leq 1$	n=2	n=3, 4	$n \geq 5$

Table 11.1 shows the classification of the quantum states for every oscillator (K = 2,3,4) according to the previous criterion. We will see in the next paragraph that the study of other bounded functions associated with anharmonic oscillators leads, in a very natural way, to the same classification which could be considered an essential feature of the quantum system, and not a mere peculiarity of $B_n(\lambda)$.

Table 11.1 allows one to extract some conclusions:

1) The lowest states of even and odd parity (n=0,n=1) correspond to type I states;

2) Very large quantum number states belong to type III class;

3) Type II (a or b) states seems to be a transition between type I and III states, since the change $B_n^{(0)} > B_n'^{(0)}$ to $B_n^{(0)} < B_n'^{(0)}$ takes place in them. Such states are relatively few and in principle, they seem to be more awkward to describe because they have minima in B_n.

The previous numerical analysis permits us to draw some general conclusions about the universal function $B_n(\lambda)$ for anharmonic oscillators. A particularly interesting property (depicted in figs.11.1 and 11.3) is that $B_n(\lambda)$ is a bounded function having, except for type II states, an unique inflexion point, given by:

$$\frac{\partial^2 B_n(\lambda)}{\partial(\ln\lambda)^2}(\lambda = \lambda_i) = 0 = -\left(\frac{\partial^2 B_n(\lambda)}{\partial\lambda^2}\right)(\lambda=\lambda_i)\lambda_i = \left(\frac{\partial B_n(\lambda)}{\partial\lambda}\right)(\lambda=\lambda_i) \tag{36.33}$$

Figs. 11.1-4 reveal one of the VFM advantages: the problem of determining $E_n(1,\lambda)$ (an unbounded function) has been transformed into the study of $B_n(\lambda)$ (bounded function that takes values within a relatively small interval), which is an easier task.

There exists another property of the exact function $B_n(\lambda)$, which gives an additional clue about its analytic structure. Fig.11.5 displays the functions $B_n(\lambda)$ for n = 10, 100, 1000 and K = 2. These curves can practically be superimposed to each other by a translation. Noticing the localization of the inflexion points, one concludes that such translation is $\lambda \simeq 10^{-2}$ for n = 100 and $\lambda \simeq 10^{-3}$ for n = 1000. These results are verified also for the remaining oscillators (K = 3,4), and

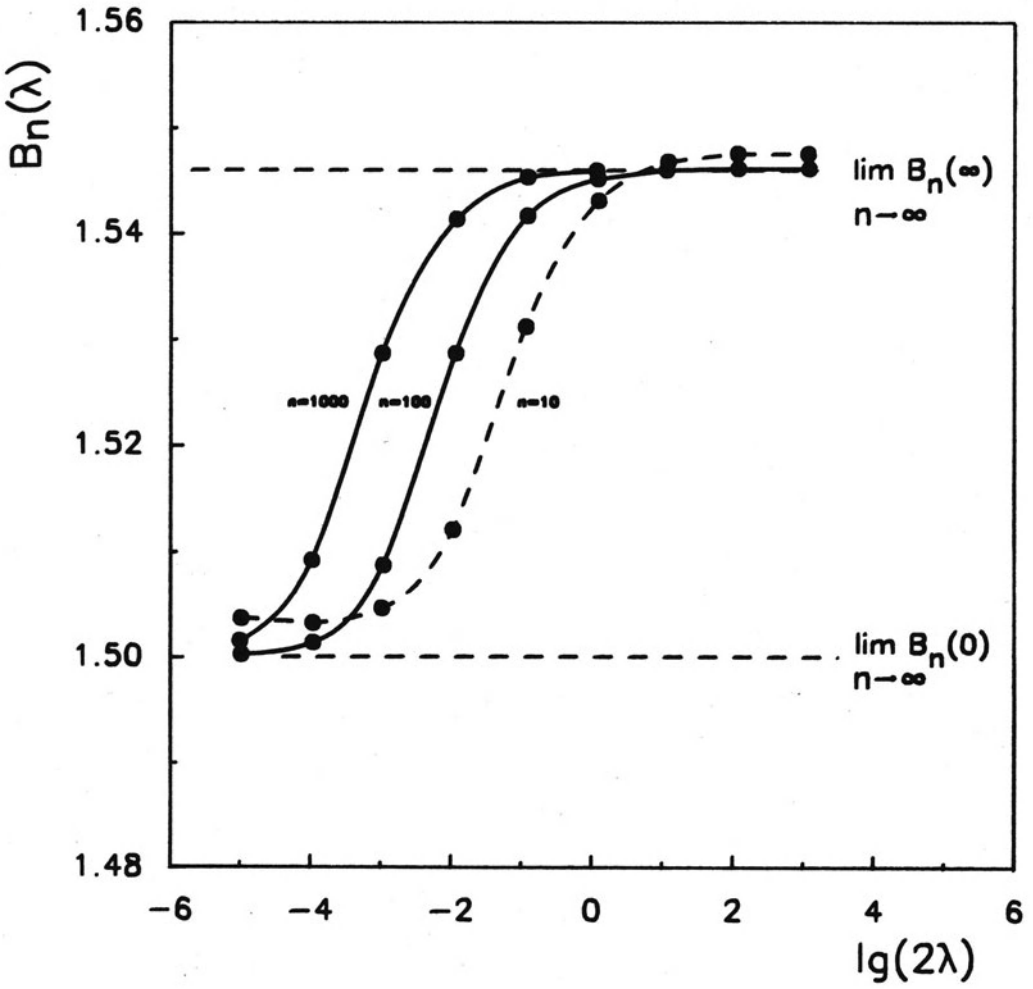

Fig. 11.5: $B_0(\lambda)$ function for $B_n(\lambda)$, n=10, 10^2, 10^3 of the quartic anharmonic oscillator. Exact results are given by circles and the analytic expression for $B_n(\lambda)$ with full line.

they suggest a "natural" variable to describe $B_n(\lambda)$:

$$\xi_n = \lambda\ (n+1/2)^{K=1} \quad . \tag{36.34}$$

It is worth pointing out that this variable coincides with that one employed by Hioe et al /3,4/ and Banerjee et al. /6,7/ to describe the eigenvalues of anharmonic oscillators. In the next paragraph we analize in depth the meaning of variable (36.34).

Now we are in position to present an analytic expression for $B_n(\lambda)$. An elementary solution consists of building an explicit relation of $B_n(\lambda)$ with ξ_n:

$$B_n(\lambda) = B_n(\xi_n) \quad . \tag{36.35}$$

From the numerical and analytical information discussed here we have designed a very simple formula for (36.35) for type I and III states /1/. The purpose is to construct an approximate B_n expression such that the function fulfils simultaneously Eqs. (36.18) and (36.19) (when $\lambda \to 0$) and (36.25)-(36.26) (when $1/\lambda \to 0$). For that purpose, $B_n(\lambda)$ is given the following structure:

$$B_n(\xi_n) = B_n'^{(0)} + \frac{B_n^{(0)} - B_n'^{(0)}}{\{1+\xi_n C_n(\xi\ )\}^{2/(K+1)}} \quad , \tag{36.36a}$$

$$C_n(\xi_n) = C_n^{(0)} + \{C_n'^{(0)} - C_n^{(0)}\}\{\xi_n/(\xi_n+1)\}^{2/(K+1)} \quad , \tag{36.36b}$$

$$C_n^{(0)} - \tfrac{1}{2}B_n^{(1)}(n+1/2)^{1-K}\left\{\frac{K+1}{B_n'^{(0)} - B_n^{(0)}}\right\} \quad , \tag{36.36c}$$

$$C_n'^{(0)} = (n+1/2)^{1-K}\left\{\frac{B_n^{(0)} - B_n'^{(0)}}{B_n'^{(1)}}\right\}^{(K+1)/2} \quad , \tag{36.36d}$$

in terms of known quantities. Function (36.36) is an explicit function depending on λ, n and K, but does not possess the correct analytic structure determined by (36.8) and (36.9) beyond the established order to fix the number of constants. The function is very simple and allows one to introduce the higher corrections into VFM. Let us remind that (36.36) describes type I and III states. Figs. 11.1,2 and 5 show for these states (full line) the result for $B_n(\lambda)$ using Eq. (36.36). The comparison with the exact (circles) results shows the goodness of the approximation within the whole λ range.

Type II states must be computed in a different way, if one desires to obtain an explicit dependence of $B_n(\lambda)$ on n and λ. Here we have chosen the method of considering these states as a transition between type I and III states and have derived a suitable formula /1/. We will not discuss such expression, since it does not add any new conceptual value; rather, we can discuss the obtained results in Figs. 11.3 and 11.4. Type II states cannot be approached satisfactorily around the minimum zone, but such departures from the exact values have a very small influence in the final calculation of $E_n(1,\lambda)$.

Eqs. (36.36) allow a straightforward calculation of the eigenvalues $E_n(1,\lambda)$: given λ, n and K, one can compute $B_n(\lambda)$ and A_n (Eq. (36.10)) and then solve Eq. (36.5) to obtain q*. Finally, Eq. (36.16) determines the approximate eigenvalues.

Results for quartic and sextic anharmonic oscillators are displayed for a wide range of λ, n-values in Ref. /1/. We can briefly discuss the quality of the results:

i) For K = 2, the largest percent relative error is 0.023% for n = 0 and $\lambda \simeq 1$. As we move away from this condition (for $n>0$ and $\lambda \lesssim 1$ or $\lambda \gtrsim 1$) the error steadily decreases. We must remind that within the functional $F_n(q)$ we have introduced via $V_n(\lambda)$ the correct $E_n(1,\lambda)$ behavior for $\lambda \to 0$ and $1/\lambda \to 0$.

ii) For the oscillator K = 3 the largest percent relative error is 0.1554 for $\lambda \simeq 1$ and n = 0 too. The agreement with the exact result /6/ is excellent, but no so good as for K = 2. This difference is easily understandable, taking into account that the RS perturbation series for K = 3 is more strongly divergent than that for K = 2 /8/.

The expression derived here for the anharmonic oscillator eigen-

values is better than other simple analytic formulas obtained from the employment of a comparable information. Some of these alternative expressions can be seen in Ref. /9/.

§.37. Application of the VFM to the theory of anharmonicity regimes.

Within the context of the quantum theory of anharmonic oscillations, it is important to know the so-called anharmonicity regimes. Essentially, the problem posed by such regimes is as follows: which is the range of (λ,n)-values where the oscillator is better described as a perturbed harmonic oscillator (harmonic regime), and which that one where the system is more satisfactorily described as a purely anharmonic oscillator perturbed by an harmonic term (anharmonic regime). The region comprised between both regimes is usually called "boundary layer" /3, 4/.

The knowledge of (λ,n) values defining the harmonic and anharmonic regimes is relevant to decide the most useful mathematical method to approximate the eigenvalues. This knowledge allows one to establish which is the most significative information, whether the perturbation expansion about $\lambda\to 0$ or that one corresponding to $1/\lambda\to 0$. Let us remind that, as seen in §.36, both sorts of information can be included within the function $B_n(\lambda)$.

Hioe et al /3,4/ have defined the regimes according to an energy $E_n(1,\lambda)$ criterion as follows: for a given n-value, the harmonic regime corresponds to a λ-interval where $E_n(1,\lambda)$ does not differ more than 10% from $E_n(1,0)$. Analogously, the anharmonic regime is defined as that λ-range where $E_n(1,\lambda)$ does not deviate no more than 10% from $\lambda^{1/(K+1)}e_n^{(0)}$. This definition is quite arbitrary, since $E_n(1,\lambda)$ is a monotonously increasing function without any evident peculiarity in its λ- dependence justifying such a choice.

On the other hand, Hioe et al. /3,4/ have found that these regimes can be described by means of the variable

$$\xi_n = \lambda(n+1/2)^{K-1} \tag{37.1}$$

in such a way that $\xi_n<<1$ corresponds to the harmonic regime, and $\xi_n>>1$ to the anharmonic region. Banerjee /6/ and Banerjee et al. /7/ have suggested a better method to define both regimes. They used the Rayleigh-Ritz variational method for a modified Biswas et al's function /10/, introducing a scaling parameter η to describe the n-th eigenvalue, by means of the wave function

$$\psi_n(x,\lambda) = e^{-\eta(n,\lambda)x^2} \sum_{i=1}^{n} a_i x^i \qquad (37.2)$$

They found that the suitable η dependence with λ and n is given by

$$\eta(n,\lambda) = \frac{1}{2} + s\xi^{1/(K+1)} \quad ; \quad s = \text{constant} \qquad (37.3)$$

and from this equation they concluded that both perturbational regimes can be associated with $\xi_n^{1/(K+1)} <<1/2$ (harmonic region) and $\xi_n^{1/(K+1)} >>1/2$ (anharmonic region).

Kesarwani and Varshni /11,12/ employed the variable

$$0 < \alpha \quad \frac{\lambda^{2/3}}{1+\lambda^{2/3}} < 1 \qquad (37.4)$$

to characterize the change of regime with λ. However, the well-known fact that the boundary layer moves towards smaller λ-value as n increases, forces one to disregard (37.4) for any state other than the ground state of the quartic anharmonic oscillator. Let us note that this shift is properly taken into account by ξ_n and $\xi_n^{1/(K+1)}$.

All the above criteria propose a suitable variable to set the change of regime forth, but they do not permit to relate both regions and the boundary layer with some essential properties of the physical system. Recently, we have shown /13/ that some expectation values are more apt than the energy to define this regimes. Some derived conclusions are in line with the aims of this book, so that they are sketchy discussed here.

An expectation value considered is

$$X_n(\lambda,K) = \langle x^2\rangle_n \, (n+1/2)^{-1} \quad ; \quad \langle x^2\rangle_n = \langle \psi_n(\lambda) | x^2 \psi_n(\lambda)\rangle \qquad (37.5)$$

and it is quite useful since it happens to be a monotonously decreasing bounded λ-function. In order to perform the analysis, E_n and $\langle x^{2K}\rangle_n$ are computed numerically for a large enough set of quantum states for $0.0001 \leq \lambda \leq 10{,}000$ and $K = 2,3,4$. The Rayleigh-Ritz variational procedure combined with a trigonometrical basis set was used. This particular set of functions provides very accurate results /14/. From these computations, the VT allows us to obtain $\langle x^2\rangle_n$ as follows:

$$\langle x^2\rangle_n = \frac{1}{2} \{E_n - (K+1)\lambda \langle x^{2K}\rangle_n\} \qquad (37.6)$$

The shape of function (37.5) is displayed in Fig. 11.6 (logarithmic graph)

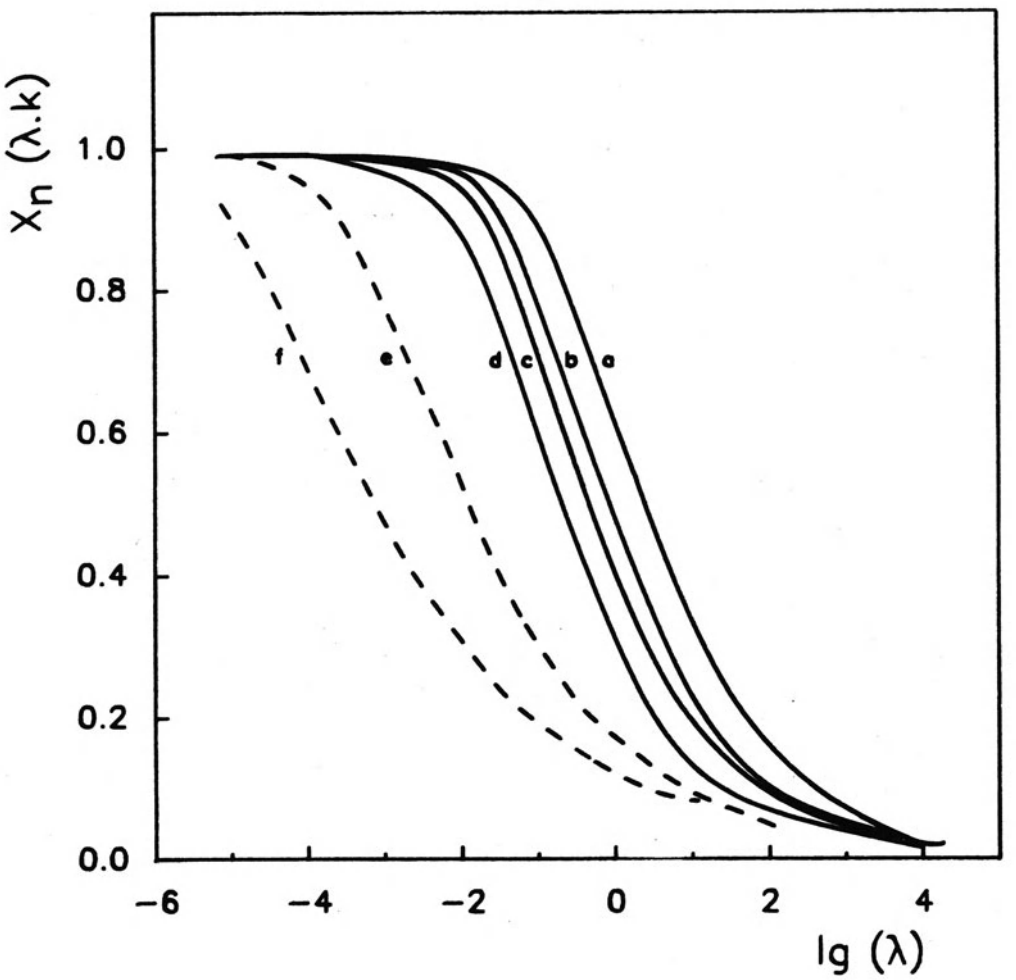

Fig.11.6: Function $X_n(\lambda,K)$ for several n and K values.

(a): K=2, n=0
(b): K=2, n=2
(c): K=2, n=4
(d): K=2, n=10
(e): K=3, n=10
(f): K=4, n=10

It is clearly seen that regions can be assigned at once: $X_n \simeq 1$ (harmonic regime), $X_n \simeq 0$ (anharmonic regime) and the boundary layer between them. As a special feature we note that the function X_n has a sole inflexion point, defining precisely the transition between both regimes:

$$\left[\frac{\partial^2 X_n}{\partial (\lg\lambda)^2}\right] (\lambda = \lambda_i^*) = 0 \qquad (37.7)$$

These inflexion points locate into the boundary layer established according to Hioe et al's criterion /3,4/, so that they define properly the change of regime.

Eq. (37.7) can be written in terms of the energy by way of HFT and Eq.(37.6) /13/:

$$-K\left(\frac{\partial E_n}{\partial \lambda}\right)(\lambda = \lambda_i^*) + K\lambda_i^*\left(\frac{\partial^2 E_n}{\partial \lambda^2}\right)(\lambda = \lambda_i^*) = -(K+1)\lambda_i^{*2}\left(\frac{\partial^3 E_n}{\partial \lambda^3}\right) \cdot$$

$$\cdot(\lambda = \lambda_i^*) \qquad (37.8)$$

The calculation of the variable ξ_n at the inflexion point

$$\xi_n^{(i)} = \lambda_i^* \, (n+1/2)^{K-1} \qquad (37.9)$$

Table 11.2: Inflexion points of the function X_n for the state n=10 of several anharmonic oscillators.

K	λ_i^*	$\xi_{10}^{(i)\,1/(K+1)}$
2	$5{,}02 \times 10^{-2}$	0,81
3	$3{,}16 \times 10^{-3}$	0,77
4	$1{,}78 \times 10^{-4}$	0,73

reveals that $(\xi_n^{(i)})^{1/(K+1)}$ (n=10) is practically independent on K. Besides, such quantity changes slightly with n. A numerical estimation shows that

$$0.5 < (\xi_n^{(i)})^{1/(K+1)} < 1.0, \ \forall\ n,\lambda,K \quad . \tag{37.10}$$

The result (37.10) shows that Banerjee's hypothesis /6,7/ defines the suitable variable, whenever it is calculated at the inflexion points of the function X_n. Thus, Eq. (37.10) determines a sort of universal constant for the anharmonic oscillators: when $\xi_n^{1/(K+1)} > 1$ the natural regime is the anharmonic one, while the harmonic region corresponds to $\xi_n^{1/(K+1)} < 1/2$.

The aforesaid conclusions sustain themselves for other average values, such as $\langle x^{2K} \rangle$, and other functions. The following functions are scaling-invariant and they are especially useful for our purposes:

$$\tilde{A} = \langle x^2 \rangle \langle p^2 \rangle \tag{37.11}$$

$$\tilde{B} = \langle x^{2K} \rangle \langle x^2 \rangle^{-K} \tag{37.12}$$

The first function represents the product of coordinate and momentum uncertainties, and both are closely related to the VFM foundation. $\tilde{A}$ and $\tilde{B}$ can be computed from E_n and $\langle x^{2K} \rangle$.

$$\tilde{A} = \frac{1}{4} \{E-(K+1)\lambda\langle x^{2K}\rangle\} \{E + (K-1)\lambda\langle x^{2K}\rangle\} \tag{37.13}$$

$$\tilde{B} = \frac{2^K \langle x^{2K} \rangle}{\{E-(K+1)\lambda\langle x^{2K}\rangle\}^K} \tag{37.14}$$

Substituting (37.6) and HFT into (37.11) and (37.12) we are led to the relationship between these two functions:

$$\frac{\partial \tilde{A}}{\partial \lambda} = -\lambda \, \langle x^2 \rangle^{K+1} \, \frac{\partial \tilde{B}}{\partial \lambda} \tag{37.15}$$

and their second derivatives

$$\frac{\partial^2 \tilde{A}}{\partial \lambda^2} = -\frac{\partial \tilde{B}}{\partial \lambda} \frac{\partial}{\partial \lambda} \{\lambda \langle x^2 \rangle^{K+1}\} - \lambda \langle x^2 \rangle^{K+1} \frac{\partial^2 \tilde{B}}{\partial \lambda^2} \tag{37.16}$$

Eq. (37.15) reveals that $\tilde{A}$ and $\tilde{B}$ slopes have opposite signs. Besides, it assures that when extremes exist, they appear at the same λ-value for both functions. Because of Eq. (37.16), whenever $\tilde{A}$ has a maximum (minimum) then $\tilde{B}$ has a minimum (maximum).

The inflexion points of functions $\tilde{A}$ and $\tilde{B}$ are suitable too for defining the boundary layer between the regimes, and in fact they are very close to those determined from X_n. Functions $\tilde{A}$ and $\tilde{B}$ lead to a classification of the states in an equivalent way as that shown in §.36 from the function $B_n(\lambda)$. Previous computations have shonw /13/ that type I, II, III states defined according to $\tilde{B}$(or $\tilde{A}$) are exactly the same as those classified as I, II, III states in §.36 for the oscillators. Eventually, there are very small differences regarding types IIa and IIb. Summing up, the function $\tilde{A}$ allows one to reach a classification on the basis of the following criteria:

i) Type I states: States whose product of coordinate-momentum uncertainties is monotonously increasing.

ii) Type II states: States whose product of coordinate-momentum uncertainties is maximum for $\lambda = \lambda_o$, $0 < \lambda_o < \infty$.

iii) Type III states: States whose product of coordinate-momentum uncertainties is monotonously decreasing.

The coincidences found in this paragraph and those extracted in the precedent one reveal that the states classification and the inflexion points (with $\ln\lambda$) of several bounded quantities seem to be intrinsic properties of the 2K anharmonic oscillator quantum models.

On the ground of these similarities, we have analized the $B_n(\lambda)$ inflexion points (Eq.(36.33)) since, unlike those discussed before, they can be determined in an analytic way. This is an interesting consequence of having an explicit formula (although approximate) for $B_n(\xi_n)$. Function $B_n(\lambda)$ is closely related with B; accordingly, it is not surprising the remarkable agreement among the properties of these functions. From Eqs. (37.12), (23.17) and (23.21) the following relationship between both functions can be deduced at once

$$\hat{B} = \frac{B_n + \lambda(\frac{\partial B_n}{\partial \lambda})}{\{1-\lambda\frac{2(K+1)}{2}q^{*2K-2}(\frac{\partial B_n}{\partial \lambda})\}^K} \qquad (37.17)$$

Obviously, this formula is only valid for the exact B, B_n, and q* quantities (see §.23).

Table 11.3: Inflexion points of the function $B_n(\lambda)$ for type I and III states of the quartic anharmonic oscillator.

n	$\xi_n^{(i)} = \lambda_i(n+1/2)$
0	1.740
1	1.717
3	1.641
4	1.716
5	1.726
6	1.730
7	1.729
8	1.730
9	1.729
10	1.730
100	1.728
1000	1.728

Table 11.3 shows the numerical results derived for the quartic anharmonic oscillator (K=2) expressed as $\xi_n^{(i)} (=\lambda_i (n+1/2)^{K-1})$. Let us note that in spite of the difficult computation procedure, results show that inflexion points satisfy the condition

$$\xi_n^{(i)} \simeq 1.73 \qquad (37.18)$$

This particular constant, associated with the anharmonic oscillator model as a whole, is in good agreement with the results found from the inflexion points of X_n.

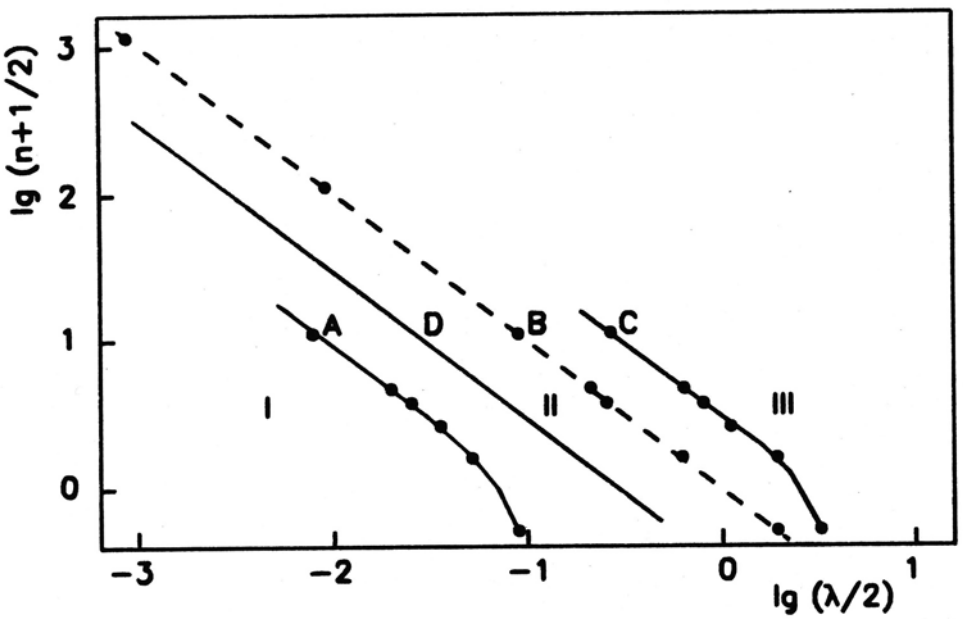

Fig. 11.7: Anharmonicity regimes of the quartic anharmonic oscillator.

Zone I: Harmonic regime
Zone II: Dividing zone
Zone III: Anharmonic regime
A, C: Regime limits according to Ref. /4/
B: Inflexion points of $B_n(\lambda)$
D: Inflexion points of X_n

Fig. 11.7 compares these results. Curves A and C denote the boundaries of the intermediate zone (II), computed according to the criteria given in Refs. /3,4/ for K=2. Zones I and III correspond with the harmonic and anharmonic regimes, respectively. The line B joins the $B_n(\lambda)$ inflexion points (Eq.(37.18)) and D joins those corresponding to X_n. As we can see, such inflexion points are located within the boundary layer, and they allow one to establish the anharmonicity regimes in a very natural fashion.

§.38. Another extension of the VFM for anharmonic oscillators.

The heuristic procedure suggested in §.36 to construct the function $B_n(\lambda)$ though useful, is not completely satisfactory from the theoretical standpoint. There are basically two reasons:
a) The analytic structure of $B_n(\lambda)$ is not totally correct, since it does not predict the expansion (36.9) about $1/\lambda=0$;
b) The VFM presented in this way cannot easily be generalized to other eigenvalue problems.

The purpose of this paragraph is to solve the aforesaid drawbacks ans so to propose the key idea allowing us to discuss different problems to the anharmonic oscillator models studied in this chapter /2/.

The central idea inspiring the proposed extension is to change the explicit representation of $B_n(\lambda)$ with n,λ into an implicit representation in terms of another variable. The natural variable to achieve this end is a function depending on q, say h(q). The necessary condition is that h(q) must simultaneously satisfy the expansions (36.8) and (36.9) for the 2K-anharmonic oscillators. The simplest functions fulfilling such conditions are

$$h(q) = u = \lambda q^{*2K+2} \quad , \tag{38.1a}$$

and

$$h(q) = v = q^{*4} \quad . \tag{38.1b}$$

The verification can be made from Eqs.(36.6) and (36.7):

$$u = \lambda\{\sum_m q_m^* \lambda^m\}^{2K+2} \equiv \{\sum_m q_m'^* \lambda^{-2m/(K+1)}\}^{2K+2} \quad , \tag{38.2}$$

$$v = \{\sum_m q_m^* \lambda^m\}^4 \equiv \lambda^{-2/(K+1)} \{\sum_m q_m'^* \lambda^{-2m/(K+1)}\}^4 \quad , \tag{38.3}$$

i.e., u and v are expanded as λ- and $\lambda^{-2/(K+1)}$-power series. Then an expansion in u or v-power series is an analytic representation for $B_n(\lambda)$ that guarantees the correct structure established in Eqs. (36.8) and (36.9):

$$B_n(\lambda) = \sum_{m=0}^{\infty} b_n^{(m)} u^m \quad , \tag{38.4}$$

$$B_n(\lambda) = \sum_{m=0}^{\infty} b_n'^{(m)} v^m \quad , \tag{38.5}$$

Of course, to make any explicit computation the series (38.4) and (38.5) have to be cut off so that q* is determined through (36.5). Up to now, coefficients $\{b_n^{(m)}\}$ and $\{b_n'^{(m)}\}$ are unknown, but they can easily be obtained from the disposable theoretical information: RSPT (Eqs.(36.3) and (36.11) and the power series expansion for the eigenvalue when $1/\lambda \to 0$ (Eqs.(36.4) and (36.20)).

The representations (38.4) and (38.5) for $B_n(\lambda)$ allow one to adjust expansions associated with the eigenvalue $E_n(1,\lambda)$. However, there exists an optimun condition to use Eqs. (38.4) and (38.5). Let us note that these variables are bounded $\forall\ \lambda \geq 0$, since the following relationships are fulfilled:

$$\lim_{\lambda\to 0} u = 0; \quad \lim_{\lambda\to\infty} u = \{\frac{(K+1)A_n}{K e_n^{(0)}}\}^{1/2} \quad , \tag{38.6}$$

$$\lim_{\lambda\to 0} v = (n+1/2)^2 \quad ; \quad \lim_{\lambda\to\infty} v = 0 \quad . \tag{38.7}$$

The fact that u and v are finite $\forall\ \lambda$ is a key property to understand the advantages of using (38.4) and (38.5). By means fo these variables it is possible to soften the divergent behavior of the original power series in λ.

On the other hand, Eq. (38.2) assures us that u^j gives rise to λ^i-terms, $i \geq j$. Likewise, u^j generates all the terms in $\lambda^{-2/(K+1)}$ powers. Then, the power series (38.4) seems to be more appropriate than (38.5) to introduce the RSPT information through coefficients $\{E_n^{(m)}\}$, since in this way the coefficients $\{b_n^{(m)}\}$ previously computed are invariant with respect the addition of PT higher orders.

In a similar fashion we can conclude that the power series expansion (38.5) is the suitable one to introduce coefficients $\{e_n^{(m)}\}$, corresponding to the asymptotic expansion for $\lambda >> 1$, because v^j adds terms proportional to $\lambda^{-2i/(K+1)}$, $i \geq j$.

We present a brief illustration to show how to handle the precedent equations, choosing an approximation level similar to that one employed in §.36.

Example I: Let us consider the insertion within the functional $F_n(q^*)$ of the first three coefficients $E_n^{(i)}$ and the dominant coefficient $e_n^{(0)}$ for $1/\lambda \to 0$. To this purpose, we truncate the $B_n(\lambda)$ expansion up to the second order:

$$B_n(\lambda) \simeq b_n^{(0)} + b_n^{(1)}\ u + b_n^{(2)}\ u^2 \quad . \tag{38.8}$$

The substitution of (38.3a) into (38.8) gives $B_n(\lambda)$ as a power series of λ

$$B_n(\lambda) \simeq b_n^{(0)} + (q_0^{*2K+2}\ b_n^{(1)})\lambda + O(\lambda^2) \tag{38.9}$$

Eqs.(36.18), (36.19) and (36.15a) allow one to obtain from the first coefficients of the expansion (38.9) the result

$$b_n^{(0)} = \left[\frac{2}{E_n^{(0)}}\right]^K E_n^{(1)} \tag{33.10a}$$

$$b_n^{(1)} = \frac{1}{2}\left[\frac{2}{E_n^{(0)}}\right]^{2K+1}\left\{2E_n^{(2)} + K^2\frac{E_n^{(1)^2}}{E_n^{(0)}}\right\} \tag{38.10b}$$

The coefficient $b_n^{(2)}$ can now be determined so as to fulfil the condition

$$\lim_{\lambda\to\infty} B_n(\lambda) = b_n^{(0)} + b_n^{(1)}\sqrt{\frac{K+1}{K}\frac{A_n}{e_n^{(0)}}} + b_n^{(2)}\left\{\frac{K+1}{K}\frac{A_n}{e_n^{(0)}}\right\} =$$

$$= B_n'^{(0)} \tag{33.11}$$

where Eq. (38.6) was used.

The insertion of (38.10) and (36.25) in (38.11) yields:

$$b_n^{(2)} = \left\{\frac{Ke_n^{(0)}}{A_n(K+1)}\right\}^{2(K+1)}\left\{\left[\frac{e_n^{(0)}}{K+1}\right]^{K+1}\left[\frac{K}{A_n}\right]^K - b_n^{(0)} - \right.$$

$$\left. - \left[\frac{(K+1)A_n}{Ke_n^{(0)}}\right]^{K+1} b_n^{(1)}\right\} \tag{38.12}$$

Eqs.(38.10a), (38.10b) and (38.12) complete the construction of function $B_n(\lambda)$. The u-value comes from Eqs. (36.5) and (38.1a). Finally, the functional is computed at its extreme value (Eq.(36.16)). The proposed procedure applied to the ground state of the quartic anharmonic oscillator gives

$$B_0(\lambda) \cong 3 - 6\lambda q^{*6} - 46.73413509\lambda^2 q^{*12} \quad . \tag{38.13}$$

This and other states are extremely well described by (33.3) and $B_n(\lambda)$-values are practically exact. For example, the obtained results cannot be distinguished from the exact ones in Figs. 11.1-5. Several eigenvalues results are presented in Ref./2/. However, it is interesting to point out that the largest percent error corresponds to n=0 and intermediate λ-values, which is the zone where we have not introduced any information at all. For λ=1 and n=0 the maximum error for E_n is 0.042% (K=2) and 0.32% (K=3). The agreement is excellent and comparable with that one discussed in §.36.

Example II: Let us consider the introduction into the functional $F_n(q^*)$ of the coefficients $E_n^{(0)}$, $E_n^{(1)}$, $e_n^{(0)}$ and $e_n^{(1)}$. For this purpose, it is convenient to truncate $B_n(\lambda)$ as follows:

$$B_n(\lambda) \simeq b_n'^{(0)} + b_n'^{(1)}\, v + b_n'^{(2)}\, v^2 \quad . \tag{33.14}$$

The insertion of (33.3) in (38.14) gives the formula for $1/\lambda \to 0$:

$$B_n(\lambda) \simeq b_n'^{(0)} + [b_n'^{(1)} q_0'^{*4}]\lambda^{-2/(K+1)} + O(\lambda^{-4/(K+1)}) \quad , \tag{33.15}$$

and together with Eqs. (36.24a), (36.25) and (36.26), one is led to

$$b_n'^{(0)} = \left[\frac{e_n^{(0)}}{K+1}\right]^{K+1} \left[\frac{K}{A_n}\right] \quad , \tag{33,16a}$$

$$b_n'^{(1)} = \left[\frac{Ke_n^{(0)}}{(K+1)A_n}\right]^{K+2} \left\{e_n^{(1)} - \frac{(K+1)A_n}{Ke_n^{(0)}}\right\} \quad . \tag{33.16b}$$

Coefficient $b_n'^{(2)}$ is determined when the condition $\lambda \to 0$ is introduced in Eq. (33.14), so as to employ the associated information with both perturbative regimes:

$$\lim_{\lambda \to 0} B_n(\lambda) \simeq b_n'^{(0)} + (n+1/2)^2\, b_n'^{(1)} + (n+1/2)^4\, b_n'^{(2)} = B_n^{(0)} . \tag{33.17}$$

Substituting Eqs. (36.18) and (33.16) into Eq. (38.17), one gets

$$b_n'^{(2)} = \left[\frac{2}{E_n^{(0)}}\right]^4 \{\left[\frac{2}{E_n^{(0)}}\right]^K E_n^{(1)} - \left[\frac{K}{A_n}\right]^K \left[\frac{e_n^{(0)}}{K+1}\right]^{K+1} -$$

$$- \left[\frac{E_n^{(0)}}{2}\right]^2 \left[\frac{Ke_n^{(0)}}{A_n(K+1)}\right]^2 (e_n^{(1)} - \frac{(K+1)A_n}{Ke_n^{(0)}})\} \quad . \qquad (38.18)$$

Eqs. (33.14), (38.16a), (33.16b), (38.18) determine function $B_n(\lambda)$ approximately. Numerical results /2/ are alike those discussed in Example I. In order to make a comparison with Eq. (33.13), we present the figures for n=0 and K=2:

$$B_0(\lambda) \simeq 11.53417411 + 7.33516213\, q^{*4} + 23.1125657 q^{*3} \qquad (38.19)$$

Eq. (38.14) as well as (38.8), describes satisfactorily the shape of the function $B_n(\lambda)$ for any type state.

As in Example I, the results for $F_n(q^*)$ possess a maximum relative error for n=0 and $\lambda \simeq 1$. Thus, for $\lambda=1$ in the ground state the errors are 0.011% (K=2) and 0.05% (K=3). Results improve when n>0 and $\lambda \leq 1$, $\lambda \geq 1$, so that the agreement is quite good. It may be seen that eigenvalues are obtained with a larger accuracy from (38.14) than by use of (38.8). This difference is probably due to the fact that the λ-power series is asymptotically divergent, while that corresponding to $\lambda^{-2/(K+1)}$ powers has a finite convergence radius /15/.

If one supresses the information concerning the limit $1/\lambda \to 0$ when applying (38.8), the VFM extension presented in this paragraph is closely related to some summation techniques discussed in Chapter V. This point was analysed in Ref./2/ and is the central subject in a next chapter within the frame of the generalized VFM.

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CHAPTER XII

GEOMETRICAL CONNECTION BETWEEN THE VFM AND THE JWKB METHOD

§.39. VFM and JWKB integrals for 1D systems with even potentials.

Previous paragraphs were devoted to discussing several functional energy representations of physical systems, through the generalization of semiclassical relationships, and the Heisenberg inequalities or the de Broglie hypothesis. It has been shown that all these approximations lead to eigenvalues depending on quantum numbers and parameters contained within the Hamiltonian, similarly to those obtained via the JWKB method and the variational theorem /1-13/ (see Chapter VI).

The aim of this section is to study the link between the JWKB method and the VFM from a different standpoint. The new formalism to be presented leads one to algebraic equations whose roots are the eigenvalues, and where one can introduce the information steming from RSPT.

The inspiring idea of this connection comes from the remarkable similarity between semiclassical and variational results. This suggests the existence of some kind of relation by which the semiclassical JWKB equations could be written in terms of some extreme functional.

In order to establish such a connection between the JWKB method and the VFM, let us consider a 1D problem with an even bounded from below potential, monotonously increasing for $x>0$:

$$H = p^2 + V(x) \quad ; \quad p \equiv -i\frac{d}{dx} \tag{39.1a}$$

$$V(x) = V(-x) \quad ; \quad \frac{dV}{dx} > 0 \ , \ x>0 \ ; \ V(0) = 0 \tag{39.1b}$$

where, without any loss of generality, we have chosen the potential minimum at the origin.

Within the first order JWKB approximation the energy associated with

the n-th bound state satisfies Eq. (5.21) ($\hbar$=m=1, as in the choice of units for Eq. (39.1a)):

$$S_1 = \oint p(x)dx = (2n+1)\pi;\ p = (E-V(x))^{1/2};\ n=0,1,2,... \qquad (39.2)$$

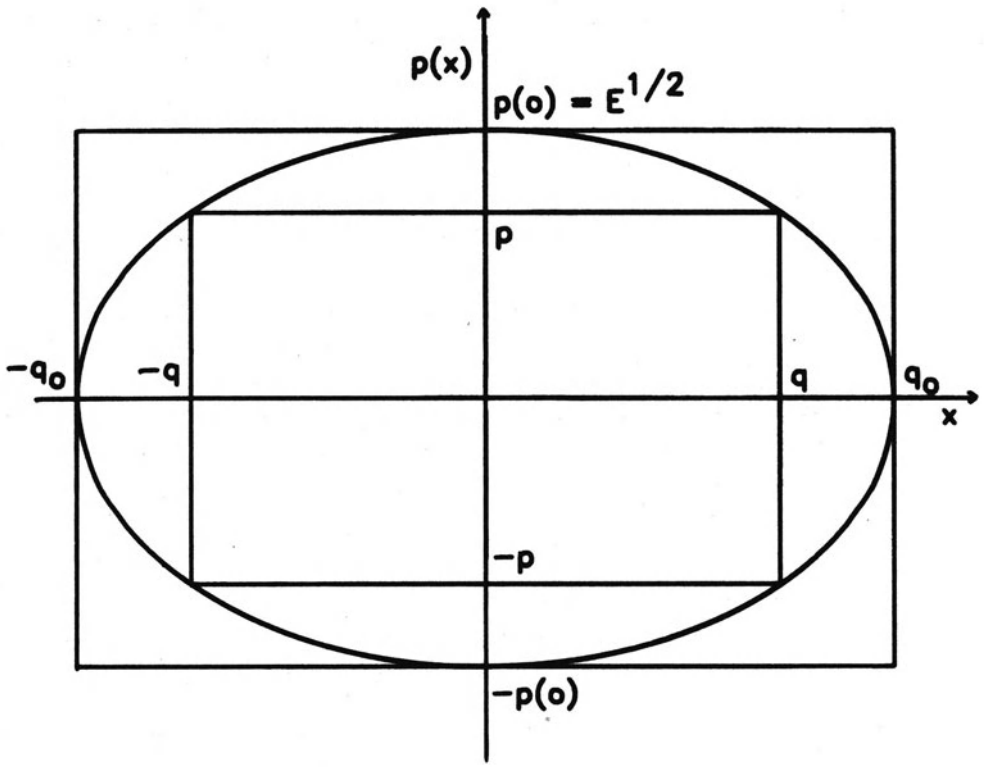

Fig. 12.1: Classical path $p(x) = (E-V(x))^{1/2}$ vs x for an arbitrary 1D system with an even, bounded from below and monotonously increasing potential function V(x).

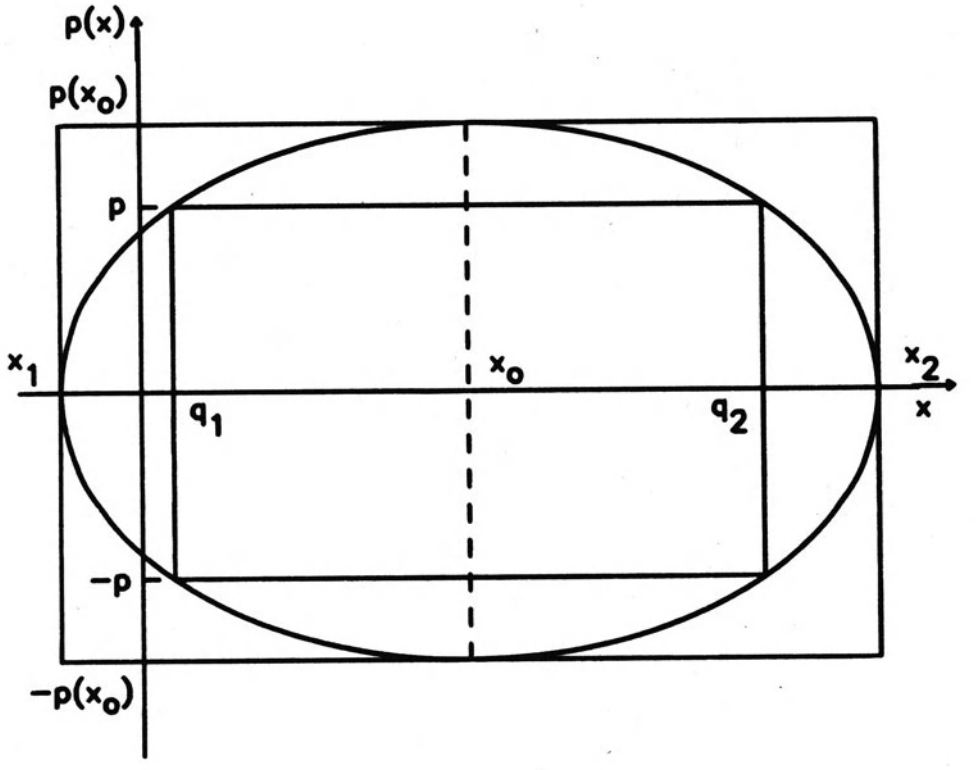

Fig. 12.2: Idem Fig. 12.1 for an odd V(x).

Fig. 12.1 shows a typical phase space trajectory p(x) vs x, for a quantum state with energy E. Obviously, the curve shape in Fig. 12.1 is ruled by the potential V(x) structure, which for the time being is irrelevant. Eq. (39.2) is a formula for the area enclosed within the phase space trajectory.

Our objective is to find out the semiclassical energy expression without solving explicitly the JWKB integral. For that purpose, let S(E) be the area of an rectangle inscribed in the trajectory (fig.12.1):

$$S(E) = 4pq, \tag{39.3}$$

where p is arbitrary and $\pm$ q are the roots of the algebraic equation $V(q) = E-p^2$. Then,

$$S(E) = 4q\ (E-V(q))^{1/2}\ , \tag{39.4}$$

and

$$E = \frac{S^2}{16q^2} + V(q)\quad . \tag{39.5}$$

Up to this moment S and q are indetermined. However, let us notice that Eq. (39.5) reveals the salient features of a variational functional. To make clearer this similarity, we choose the inscribed rectangle with maximum area:

$$\left(\frac{\partial S}{\partial q}\right)_E = 0\quad . \tag{39.6}$$

From Eqs. (39.5) and (39.6), and considering that E is constant, we derive the following relationship when S is maximum:

$$\frac{\partial E}{\partial q} = \left(\frac{\partial E}{\partial S}\right)_q \left(\frac{\partial S}{\partial q}\right) + \left(\frac{\partial E}{\partial q}\right)_S = \left(\frac{\partial E}{\partial q}\right)_S = 0 \tag{39.7}$$

Then, the final result makes clear that the semiclassical energy (E) may arise from the pair of Equations (39.5) and (39.7), instead of the integral (39.2). These two equations represent a functional and its extreme condition, and they make up the basic conditions existing in other variational methods previously studied /1-5,13/. This equivalence shows plainly why one gets the same (qualitative) results when using the JWKB method and the SVM /11,12,14,15/: both procedures carry to the same system of equations and they only differ about the S choice.

The geometrical condition represented by Eq. (39.6) totally determines S. For a potential like $V(x) = x^{2K}$, the following lemma is used to obtain the area:

Lemma 39.1: For $V = x^{2K}$, then

$$S = 2K^{3/2}(K+1)^{-(K+1)/2K}\Gamma\left(\frac{3K+1}{2K}\right) \frac{S_1}{\Gamma\left(\frac{3}{2}\right)\Gamma\left(\frac{1}{2K}\right)} \quad . \tag{39.8}$$

Proof. The calculation of S_1 for the proposed potential gives

$$S_1 = \oint (E-q^{2K})^{1/2} dq = 2\int_{-q_o}^{q_o} (E-q^{2K})^{1/2} dq = 4\int_{0}^{q_o} (E-q^{2K})^{1/2}\, dq \tag{39.9}$$

where $p(q_o) = 0$ defines the classical turning points changing the variable as in $z = q^{2K/E}$, (39.9) turns into a first class Euler integral:

$$S_1 = \frac{2}{K} E^{(K+1)/2K} \int_0^1 z^{(1-2K)/2K} (1-z)^{1/2}\, dz = \frac{2}{K} E^{(K+1)/2K} \beta\left(\frac{1}{2K};\frac{3}{2}\right) =$$

$$= \frac{2}{K} E^{(K+1)/2K} \frac{\Gamma\left(\frac{1}{2K}\right)\ \Gamma\left(\frac{3}{2}\right)}{\Gamma\left(\frac{3K+1}{2K}\right)} \quad . \tag{39.10}$$

On the other hand, the area of the inscribed rectangle is

$$S(q^*) = 4q^* \ (E-q^{*2K})^{1/2} \quad , \tag{39.11}$$

where

$$(\frac{\partial S}{\partial q}) \ (q=q^*) = 4(E-q^{*2K})^{1/2} - 4Kq^{*2K}(E-q^{*2K})^{-1/2} = 0 \quad , \tag{39.12}$$

and

$$q^* = (\frac{E}{K+1})^{1/2K} \quad . \tag{39.13}$$

Then, Eq. (39.12) allows one to show that $S(q^*)$ is a maximum area:

$$(\frac{\partial^2 S}{\partial q^2}) \ (q=q^*) = -8K^{1/2} \ (\frac{E}{K+1})^{(1-K)/2K} < 0 \ \forall K>0 \tag{39.14}$$

Finally, the substitution (39.13) in (39.11) yields

$$S = 4K^{1/2} \ (\frac{E}{K+1})^{(K+1)/2K} \tag{39.15}$$

The combination of Eqs. (39.10) and (39.15) completes the proof*.

Lemma 39.1 gives the constant S in the functional (39.5); applying Eq. (39.2), we get the result:

$$S = C_K \ (2n+1) \ ; \ C_K = \frac{2\pi K^{3/2}\Gamma((3K+1)/2K)}{(K+1)^{K+1/2K}\Gamma(\frac{3}{2})\Gamma(\frac{1}{2K})} \quad , \tag{39.16}$$

which whows that S is proportional to n, as discussed in Chapter VI.

It must be noted that the quotient between the phasic area and the inscribed rectangle area, S_1/S, is independent from n for a potential V(x) having just one term. For those potentials with two or more terms a relationship dependent on n should be expected. Notwithstanding, it must be remembered that the most important part of the E_n dependence with n is guaranteed by Eqs. (39.5) and (39.7).

For a potential having more than one term, a different alternative may be followed. One can maintain the S form given by lemma 39.1, and modify the functional (39.5):

$$E = \frac{S^2}{16q^2} + \hat{V}(q) \quad , \tag{39.17}$$

where $\hat{V}(q)$ is a function that can be chosen according to the VFM theory (Chapters VI and VII).

There exists another interesting energy expression, arising from geometric-like relationships. In order to discuss it, we start with:

Lemma 39.2: Let S_2 be the area of the smallest rectangle completely containing S_1 (as shown in Fig. 12.1), for $V = x^{2K}$. Then

$$S_2 = C'_K S_1 \; ; \; C'_K = 2K \frac{\Gamma(\frac{3K+1}{2K})}{\Gamma(\frac{3}{2})\Gamma(\frac{1}{2K})} \tag{39.18}$$

Proof: From Fig. 12.1 it follows at once that for S_2:

$$S_2 = 4p(0)q_0 = 4E^{1/2}E^{1/2K} = 4E^{(K+1)/2K} \tag{39.19}$$

The use of Eqs. (39.10) and (39.19) leads to (39.18)*.

Lemma 39.2 and Eq. (39.19) give the q_0 value at the classical turning point:

$$q_0 = \frac{\pi C'_K}{4} \frac{2n+1}{E^{1/2}} \quad . \tag{39.20}$$

Considering that $E = V(q_0)$, then we have the desired equation:

$$E = V\left(\{\frac{\pi C'_K}{4} \frac{2n+1}{E^{1/2}}\}\right) \quad . \tag{39.21}$$

Eq. (39.21) is a compact and elegant result for the approximate semiclassical eigenvalues, expressed as an algebraic equation. This formula adopts a peculiarly simple expression when the phase space curve is elliptical (from now on we will use the denomination elliptical approximation for such a case). In this case we get from lemma 39.2:

$$C'_1 = 4/\pi \quad . \tag{39.22}$$

Let us consider a simple example of application of Eq. (39.21), using again the anharmonic oscillator (see Appendices A and B):

$$H(g,\lambda) = p^2 + gx^2 + \lambda x^{2K} \quad . \tag{39.23}$$

Restricting ourselves to the elliptical approximation, Eqs. (39.23) and (39.21) give the following formula for the eigenvalues associated with $H(1,\lambda)$:

$$E = \frac{(2n+1)^2}{E} + \frac{(2n+1)^{2K}}{E^K} \lambda \quad . \tag{39.24}$$

Due to the elliptic approximation, the correct result is found when $\lambda \to 0$, although only a qualitative correct behavior with n and λ for $1/\lambda \to 0$:

$$E \simeq \lambda^{1/(K+1)} \, (2n+1)^{2K/(K+1)} \tag{39.25}$$

The iterative solution of Eq. (39.24) around $\lambda=0$ yields a power series in λ, whose first terms are:

$$E \simeq (2n+1) + \frac{1}{2} (2n+1)^{K} \lambda - \frac{1}{8} (2K-1)(2n+1)^{2K-1}\lambda^{2}+... \tag{39.26}$$

A comparison between Eq. (39.26) and Eqs. (36.20) (obtained by means of algorithms studied in §§.8 and 9) shows that, naturally, the power series deduced from (39.24) does not coincide with the RSPT. The result is by no means surprising since we have used the elliptical approximation corresponding to the harmonic potential, which is a very gross approximation. However, Eq. (39.26) possesses an interesting property: the dominant behavior for $n>>1$ in every perturbational correction is properly predicted.

If one wants to go beyond the elliptical approximation, then

$$E = \tau_{V} \left(\frac{2n+1}{E^{1/2}}\right) \tag{39.27}$$

where τ_{V} is some transform of the potential $V(x)$. A simple manner to make this extension consists of keeping up as far as possible the structure of Eq. (39.24).

Let us consider the generalization of Eq. (39.24) expressed in terms of the following equation

$$E^{K+1} = (2n+1)^{2} \, E^{K-1} + \lambda (2n+1)^{2K} \, D(E) \tag{39.28}$$

where $D(E)$ is an unknown function to be determined.

Eq. (39.28) makes up an alternative starting point to combine the RSPT with equations representing the qualitatively correct behavior of the energy eigenvalue. The geometrical considerations previously invoked allow one to obtain an algebraic equation whose roots are the eigenvalues.

To build D(E) one can follow a procedure as in §.38. According to the Symanzik theorem /16/ (Appendix A) the harmonic oscillator eigenvalue satisfies the following scaling law (Eq.(23.3)):

$$E(1,\lambda) = \lambda^{1/(K+1)}\, E(\lambda^{-2/(K+1)},1) = \lambda^{1/(K+1)} e \ , \qquad (39.29)$$

where E can be expanded in λ-series and e in $\lambda^{-2/(K+1)}$-series. Then, D(E) can be expanded in $\lambda(\lambda\to 0)$ power series as well as $\lambda^{-2/(K+1)}$ $(1/\lambda\to 0)$-power series in order to maintain the correct analytic structure in Eq. (39.28).

The following variables

$$u' = \lambda E^{-(K+1)} = e^{-(K+1)} \ , \qquad (39.30a)$$

$$v' = E^{-2} = \lambda^{-2/(K+1)}\, e^{-2} \ , \qquad (39.30b)$$

are a suitable pair to give an analytic representation of D(E), since any u' and v' power gives rise to λ and $\lambda^{-2/(K+1)}$ powers.

It is natural to represent D(E) as a power series expansion, viz.

$$D(E) = \sum_{i=0}^{\infty} D^{(i)}\, u'^{\,i} \qquad (39.31a)$$

$$D(E) = \sum_{i=0}^{\infty} D'^{(i)}\, v'^{\,i} \qquad (39.31b)$$

A simple analysis, similar to the one made in §.33, assures us that

the expansion (39.31a) is adequate to introduce the λ-expansion, while the v'-power series (39.31b) is suitable to employ the information regarding the anharmonic regime ($1/\lambda \to 0$).

Eq.(39.21) leads to alternative expressions with respect to those proposed by (39.28). Another possibility would be the following one

$$E^{K+1} = (2n+1)^2 E^{K-1} L(E) + \lambda \overset{\alpha}{C}_n (2n+1)^{2K} \qquad (39.32)$$

where $\overset{\alpha}{C}n$ is a constant introduced to achieve the correct result when $1/\lambda \to 0$ (Eq.(39.25)). Function L(E) can be written in terms of the variables u' and v' (Eqs.(39.30)):

$$L(E) = \sum_{n=0}^{\infty} L^{(n)} u'^n \quad , \qquad (39.33a)$$

$$L(E) = \sum_{n=0}^{\infty} L'^{(n)} v'^n \quad , \qquad (39.33b)$$

whose use is similar to that previously discussed for D(E).

A particularly simple and useful way to apply Eqs. (39.28) and (39.32) is the following: to introduce the $\lambda^{-2/(K+1)}$ power series expansion by means of (39.28) and (39.31b), and Eqs. (39.32) and (39.33a) to introduce the RSPT. The example below is an illustrative application.

Example. Let us to determine the first $\{D^{(i)}\}$ and $\{L^{(i)}\}$ coefficients so as to fit the $\{E^{(i)}\}$ and $\{e^{(i)}\}$ coefficients (Eq.(23.2)). Eq. (39.28) for $\lambda \to 0$ gives $E_n^{(0)}$ at once. Now, we incorporate the first two coefficients $e^{(0)}$ and $e^{(1)}$ by way of $D'^{(0)}$ and $D'^{(1)}$:

$$E^{K+1} \simeq (2n+1)^2 E^{K-1} + \lambda (2n+1)^{2K} \{D'^{(0)} + \frac{D'^{(1)}}{E^2}\} \quad . \qquad (39.34)$$

Substituting (39.30b) into (39.34), we get the result

$$e^{K+1} \simeq (2n+1)^{2K} \{D'^{(0)} + D'^{(1)} e^{-2} \lambda^{-2/(K+1)}\} + (2n+1)^{2} \lambda^{-2/(K+1)} e^{K-1} \quad . \tag{39.35}$$

Finally, taking into account that

$$e \simeq e_n^{(0)} + \lambda^{-2/(K+1)} e_n^{(1)} + \ldots \quad ,$$

we have the first two coefficients of the D(E) expansion

$$D'^{(0)} = e_n^{(0)K+1} (2n+1)^{-2K} \quad , \tag{39.36a}$$

$$D'^{(1)} = D'^{(0)} \{(K+1) e_n^{(1)} - (2n+1)^2 (e_n^{(0)})^{-1}\} \quad . \tag{39.36b}$$

Following the same steps for the other case, we rewrite Eq.(39.32) as

$$E^{K+1} = (2n+1)^2 E^{K-1} \{L^{(0)} + L^{(1)} E^{-(K+1)}\} + \lambda \tilde{C}_n (2n+1)^{2K} \tag{39.37}$$

It is possible to introduce the coefficients $E_n^{(0)}$ and $E_n^{(1)}$ through $L^{(0)}$ and $L^{(1)}$ and $e_n^{(0)}$ by way of $\tilde{C}_n$, in order to have an equation with the same number of adjustable constants as in (39.34). Thus, making

$$E \simeq E_n^{(0)} + \lambda E_n^{(1)} + \ldots$$

we find at once from (39.37) the following results:

$$L^{(0)} = 1 \tag{39.38a}$$

$$L^{(1)} = \{(K+1)\, E_n^{(1)} E_n^{(0)} K + (1-K) E_n^{(1)} E_n^{(0)} (K-2) - \tilde{C}_n\}\, E^{(0)2} \qquad (39.38b)$$

$$\tilde{C}_n = D'^{(0)} \qquad (39.38c)$$

As an example, we consider the ground state of the quartic anharmonic oscillator (K=2, n=0) and compare the numerical results obtained from Eqs. (39.34) and (39.37). Coefficients $E_n^{(0)}$ and $E_n^{(1)}$ are well known (Eqs.(36.20)) and coefficients $e_n^{(0)}$ and $e_n^{(1)}$ were determined from the published data in Ref./17/:

$$e_o^{(0)} = 1.060362090 \quad ; \quad e_o^{(1)} = 0.362022684 \qquad (39.39)$$

Table 12.1

Quartic anharmonic oscillator ground state as a function of the parameter λ.

λ	$E^{a)}$	$E^{b)}$	$E^{c)}$
10^{-5}	1.00000750	1.00000681	1.00000750
10^{-4}	1.00007499	1.00006813	1.00007499
10^{-3}	1.00074893	1.00068055	1.00074869
10^{-2}	1.00739525	1.00673406	1.00737367
10^{-1}	1.06638663	1.06140633	1.06528550
1	2.46022754	2.44711146	2.44917407
10	2.46022754	2.44711146	2.44917407
10^2	5.00609714	4.99872897	4.99941754
10^3	10.64308128	10.63950624	10.63978871
10^4	22.86315714	22.86148152	22.86160887

a) Eq. (39.37)

b) Eq. (39.34)

c) Exact results /18/

Computed results are compared with "exact" ones /13/ in Table 12.1. The agreement is quite acceptable in the whole range of λ, in spite of the simplicity of the employed expressions.

§. 40. VFM and JWKB integrals for 1D systems with potentials without defined parity and central field systems.

In this section the geometrial relations studied in §.39 are extended to potentials without defined parity and central field potentials.

Let $H = p^2+V(x)$ the Hamiltonian corresponding to a 1D system and $V(x)$ a potential bounded from below:

$$V(x_o) \leq (V(x) \; ; \; \frac{dV}{dx} \gtrless 0 \text{ whenever } (x-x_o) \gtrless 0 \quad . \tag{40.1}$$

The classical momentum take values $0 \leq p(x)^2 \leq E-V(x_o)$, for a given state with total energy E. For such a state, it is possible to build a rectangle of sides 2p and $q_2 - q_1$, where

$$V(q_1) = V(q_2) = E-p^2 \tag{40.2}$$

under the condition of being inscribed within the phase space trajectory (Fig.12.2). The rectangular area is

$$S = 2p(q_2 - q_1) \tag{40.3}$$

and has its maximum value when $\partial S/\partial p = 0$. Since E remains fixed, q_1 and q_2 are interdependent through p; then, it is possible to replace the difference $q_2 - q_1$ by $q - q_0$, where q describes the p-variation and q_0 is a constant(to be used in order to have a unique eigenvalue for each quantum number). On the basis of these considerations, we find the following functional

$$E = \frac{S^2}{4(q-q_0)^2} + \hat{V}(q), \tag{40.4a}$$

with the extreme condition

$$\left(\frac{\partial E}{\partial q}\right)_S = 0 \quad ; \quad \frac{\partial S}{\partial q} = \frac{\partial S}{\partial p} = 0 \quad . \tag{40.4b}$$

Function $\hat{V}(q)$ is, in general, a transform of the potential.

A similar functional form for the energy can be derived from quite different considerations /2,4,5/. Again, the approach presented here brings to light the relationship among variational and semiclassical methods.

Let us recall the attention to the way the condition (40.4b) was introduced within the functional. It has not been required the extreme condition for the functional, but a maximum area of the rectangle within the phase space trajectory. This choice is not arbitrary, because only under this condition the relation (lemma 39.1)

$$\frac{S}{S_1} = C(K) \tag{40.5}$$

is satisfied, independently of E, whenever $V(x) = (x-x_o)^{2K}$.

Let us consider now an equation analogous to (39.21) for potentials without definite parity. If x_1 and x_2 are the classical turning points ($p(x_1) = p(x_2) = 0$) and S_2 the area of inscribed the phase space trajectory (Fig.12.2):

$$S_2 = 2p(x_o)\ (x_2 - x_1) \quad ; \quad x_1 < x_2 \quad . \tag{40.6}$$

By extension of lemma 39.2, this latter area is proportional to the

phase space

$$\frac{S_2}{S_1} = C'(K) \tag{40.7}$$

with $C'(K)$ independent of E when $V(x) = (x-x_o)^{2K}$. Eqs.(40.6) and (40.7) lead us to

$$2x_2 = \frac{C'(K)S_1}{p(x_o)} + x_1 + x_2 \quad , \tag{40.8}$$

so that the energy E satisfies:

$$E = V(x_2) = V(\{\frac{C'(K)S_1}{2(E-V(x_o))^{1/2}} + \frac{x_1+x_2}{2}\}) \quad . \tag{40.9}$$

Eq.(40.9) turns, in general, into a trascendental equation for the energy, after x_o, x_1 and x_2 are determined. For an even potential (i.e., $x_1 = -x_2$), and choosing $V(x_o) = 0$, we meet again Eq. (39.21). Within the elliptical approximation for the trajectory, we have the result

$$\frac{C'(1)S_1}{2} = 2n+1 \quad . \tag{40.10}$$

Eqs. (40.4) and (40.9) are valid not only for 1D problems but they can be extended to 3D systems with central field potentials. In these latter cases our problem is to approach the eigenvalues associated with the Hamiltonian

$$H = p_x^2 + \frac{g^2}{x^2} + V(x) \quad ; \quad p_x \equiv -i\frac{d}{dx}, \; x \geq 0. \tag{40.11}$$

with $g^2 = \ell(\ell+1)$. In order to apply the geometric procedure developed before, it is necessary to consider as potential V(x) the effective

potential function U(x)

$$U(x) = g^2 x^{-2} + V(x) \quad . \tag{40.12}$$

When V(x) is supersingular and not bounded from below, i.e.

$$V(x) = -\lambda r^{-\nu} \quad ; \quad \lambda > 0 \quad , \nu > 2 \tag{40.13}$$

the effective potential (40.12) is not bounded from below either, for $\ell = 0$. In order to surmount this problem, it is necessary to introduce the Langer transformation /19/:

$$g = \ell + 1/2 \quad , \tag{40.14}$$

which is characteristic of the semiclassical approximation for radial potential problems. The JWKB quantization condition is

$$\oint p(x)dx = (2n_r+1)\pi \tag{40.15a}$$

$$p(x) = \{E - g^2 x^{-2} - V(x)\}^{1/2} \tag{40.15b}$$

where n_r is the number of radial zeros in the wave function.

In the following we present some simple examples illustrating the application of the equations derived in this paragraph.

Example I: Let us consider the 1D problem without defined parity

$$V(x) = \alpha x^2 + \beta x \quad . \tag{40.16}$$

The minimum potential value is at:

$$V'(x_o) = 0 \quad ; \quad x_o = -\beta/2\alpha \quad , \tag{40.17}$$

which gives the maximum impulse

$$V(x_o) = -\beta^2/4\alpha \quad , \tag{40.18a}$$

$$p(x_o) = \{E + \frac{\beta^2}{4\alpha}\}^{1/2} \quad . \tag{40.18b}$$

The classical turning points are

$$E - V(x) = E - \alpha x^2 - \beta x = 0 \quad , \tag{40.19a}$$

$$x_{1,2} = \frac{\beta \pm (\beta^2+4\alpha E)^{1/2}}{-2\alpha} \quad , \tag{40.19b}$$

where x_1 (x_2) corresponds to the sign choice +(-) in (40.19b).

Above equations give

$$\frac{x_1 + x_2}{2} = -\frac{\beta}{2\alpha} \quad . \tag{40.19c}$$

The replacement (40.13b) and (40.19c) in (40.9), and the application of the elliptical approximation (Eq.(40.10))yield the result

$$E = V(\frac{2n+1}{p(x_o)} - \frac{\beta}{2\alpha}) = \alpha\,[\frac{2n+1}{p(x_o)} - \frac{\beta}{2\alpha}]^2 + \beta[\frac{2n+1}{p(x_o)} - \frac{\beta}{2\alpha}] =$$

$$= \alpha[\frac{2n+1}{p(x_o)}]^2 - \frac{\beta^2}{4\alpha} = \alpha\frac{(2n+1)^2}{E+\frac{\beta^2}{4\alpha}} - \frac{\beta^2}{4\alpha} \quad . \tag{40.19d}$$

Finally, Eq. (40.19d) leads us to:

$$E = (2n+1)\ \alpha^{1/2} - \frac{\beta^2}{4\alpha} \quad , \tag{40.20}$$

which is the correct result. The procedure offers an alternative approach regarding that discussed in §.24 with respect the role played by the scaling in the VF theory.

Example II. Let us consider now the radial effective potential in a hydrogen-like atom:

$$V(x) = g^2x^{-2} - Zx^{-1} \quad , \tag{40.21}$$

whose minimum value is at

$$V'(x_o) = 0 \quad ; \quad x_o = 2g2Z^{-1} \quad . \tag{40.22}$$

The maximum impulse is

$$V(x_o) = -Z^2/4g^2 \tag{40.23a}$$

$$p(x_o) = \frac{1}{2g}\ (Z^2+4g^2E)^{1/2} \tag{40.23b}$$

From Eq. (40.23b) we find the appropriate condition to obtain bound states:

$$\frac{-Z^2}{4g^2} \leq E \leq 0 \tag{40.24}$$

This particular problem makes easier to use Eqs. (40.6) and (40.7)

instead of Eq. (40.9). The classical turning points are

$$x^2E + Zx - g^2 = 0 \tag{40.25a}$$

$$x_{\pm} = \frac{1}{4E}\{-Z^{\pm}(Z^2 + 4g^2E)^{1/2}\} \tag{40.25b}$$

and from (40.24) $x_- > 0$, $x_+ < 0$, so that

$$x_- - x_+ = x_2 - x_1 = -\frac{1}{E}(Z^2+4g^2E)^{1/2} \tag{40.25c}$$

The area of the rectangle inscribing the phase space trajectory (Eq.(40.6)) is

$$S_2 = 2p(x_o)\ (x_2 - x_1) = -\frac{Z^2+4g^2E}{gE} = C'S_1 \tag{40.26}$$

which determines the energy

$$E = -\frac{Z^2}{4g^2+C'gS_1} \tag{40.27}$$

The result makes clear the difficulties of the method to study radial potentials, since Eq. (40.7) presents an involved dependence on n_r and ℓ. In this regard, the geometrical approximation presented here has similar drawbacks as those shown by the JWKB method for radical problems. Such difficulties, closely related to the practical implementation of the formalism, do not occur when the geometric method is combined with the RSPT, as done in §.39 (Eqs. (39.28) and (39.32)).

§. 41. Generalization of geometrical relations and RSPT.

Classical trajectories for systems having an arbitrary number of degrees of freedom are quite complicated. The extension to these systems of the geometrical ideas developed in this chapter becomes thus cumbersome.

In order to apply the method to a greater number of systems it seems more appropriate to follow an alternative path. The generalization we propose below is the first attempt to introduce in a systematic manner the PT into a semiclassical functional, a subject to which is devoted the remaining of the book. Some results on this topic have been recently published /20/.

Let $E(1,\lambda)$ (using the notation as in §§. 23 and 24) be an eigenvalue of some Hamiltonian system, which can be expanded as follows:

$$E(1,\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n \tag{41.1a}$$

$$E(1,\lambda) = \lambda^{\beta} e(\lambda) = \lambda^{\beta} \sum_{n=0}^{\infty} e^{(n)} \lambda^{\alpha n} , \quad \alpha<0 \tag{41.1b}$$

about $\lambda=0$ and $1/\lambda=0$, respectively.

We define now a couple of bounded variables and whose powers can be expanded both in λ-and λ^{α}-power series (by extension of (39.30)). The simplest choice is

$$u' = \lambda E^{-1/\beta} = e^{-1/\beta} \tag{41.2}$$

$$v' = E^{\alpha/\beta} = \lambda^{\alpha} e^{\alpha/\beta} \tag{41.3}$$

Eqs. (41.1) assure us that u'^m gives rise to λ^j ($j \geq m$) terms and all the λ^{α} powers. Analogously, we conclude that v'^m originates all the λ-powers and $\lambda^{\alpha j}$ ($j \geq m$) terms.

Using variables (41.2) and (41.3), Eqs. (39.23) and (39.32) can be generalized through the following relationship /20/:

$$E^{1/\beta} = E^{(\alpha+1)/\beta} L(E) + \lambda D(E) \quad . \tag{41.4}$$

This last equation includes as a particular case that in §.39 for anharmonic oscillators ($\alpha = -2/(K+1)$, $\beta = 1/(K+1)$).

Due to (41.2) and (41.3), the functions L(E) and D(E) may be constructed as follows:

$$L(E) = \sum_{n=0}^{\infty} L^{(n)} u'^{n} \quad , \tag{41.5a}$$

$$L(E) = \sum_{n=0}^{\infty} L'^{(n)} v'^{n} \quad , \tag{41.5b}$$

$$D(E) = \sum_{n=0}^{\infty} D^{(n)} u'^{n} \quad , \tag{41.5c}$$

$$D(E) = \sum_{n=0}^{\infty} D'^{(n)} v'^{n} \quad . \tag{41.5d}$$

The set of coefficients $\{D^{(n)}, D'^{(n)}\}$ and $\{L^{(n)}, L'^{(n)}\}$ can be determined using an arbitrary number of coefficients $\{E^{(n)}\}$ and $\{e^{(n)}\}$. Both power series expansions (41.1a) and (41.1b) may be added into Eq. (41.4) since, by construction, the solutions of these equations have expansions in λ-and λ^{α}-power series. Notwithstanding, from a practical standpoint it is convenient to use (41.5a) and (41.5c) into (41.4) if coefficients $\{E^{(n)}\}$ are introduced. In a similar manner, in order to introduce coefficients $\{e^{(n)}\}$ it is more suitable to employ Eqs. (41.5b) and (41.5d).

Let us stress on the meaning of the extension discussed in this paragraph: the original problem (Schrödinger formulation via a second-order differential equation) has been transformed into another quest of searching for the roots of an algebraic equation constructed from the power series expansions (41.1). Several open points in our ap-

proach can be mentioned:

i) Conditions for the existence of real roots in Eq. (41.4),

ii) Convergence of the solutions towards the eigenvalues, when the involved perturbation coefficients increase,

iii) Influence upon the results of Eq. (41.1) of possible spurious terms not considered within the expansion (41.1b) (see Appendix I).

These questions remain open to research. Our preliminary studies have shown that Eq. (41.1) may present in certain cases a multiplicity of real roots.

Although in the next sections we will present a more efficient formalism to sum RSPT, the basic principle is the same as the one discussed here: to develop non-numerical E-expressions, considering essential analytical properties of the function. In our present case, such properties correspond to the asymptotic expansions (41.1a) and (41.1b). The basic structure of such expansions of the energy of quantum systems is fixed by the VT and HFT.

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PART B

A GENERAL METHOD FOR SUMMATION OF PERTURBATION SERIES.

CHAPTER XIII

GENERALIZATION OF THE FUNCTIONAL METHOD AS A SUMMATION TECHNIQUE OF PERTURBATION SERIES.

§.42. Generalization of the FM: Connection between semiclassical relations and renormalized series.

As seen previously the application of the RSPT is frequently linked to the problem of summing divergent power series expansions. Precedent chapters were devoted to show the use of the VFM as a systematic way to construct expressions for eigenvalues associated with some quantum mechanical systems. Such formulas provide a working scheme, suitable to introduce the information brought forth by PT. The remaining of this book will consider the generalization of the VFM as a summation technique of divergent power series.

Our approach to the summation of perturbation series is somewhat wider and with more physical content than the majority of the usual techniques (see Chapter V). The formalism to be extended in this chapter and to be applied in the next ones, has some note-worthy advantages:

i) A wider applicability range, no restricted to eigenvalue problems.

ii) A systematic technique to combine analytic properties (for example, asymptotic expansions) with PT.

iii) A unification of several well-established summation techniques of perturbation series, and

iv) Better numerical results for a large set of models.

The content of this paragraph is based on two recent publications /1,2/. Our present problem can be set up in a very general manner as follows: Let $E(\lambda)$ be a function to be approximated, and about which one knows it can be expanded in power series as

$$E(\lambda) = \sum_{i=0}^{\infty} E^{(i)} \lambda^i \quad , \quad \lambda << 1 \quad , \tag{42.1}$$

$$E(\lambda) = \lambda^{\beta} e(\lambda) = \lambda^{\beta} \sum_{i=0}^{\infty} e^{(i)} \lambda^{\alpha} \; ; \quad \alpha < 0 \; , \; \lambda >> 1 \quad . \tag{42.2}$$

Now we generalize the VFM starting from the properties (42.1) and (42.2). The essential constituent parts of the VFM are a variational functional and its extreme condition. They determine the nearly correct growth with λ of the eigenvalues of quantum mechanical systems through VT and HFT. Thence, it seems natural to associate with (42.1) and (42.2) two (and only two) equations playing the role of a functional and its extreme condition:

Following above conception, let $F(q)$ be a functional associated with $E(\lambda)$:

$$F(q) = \frac{A}{q^2} + q^s + \lambda q^t B(\lambda, q), \tag{42.3}$$

whose structure represents a straightforward extension of functional like (36.2a). For the time being, s and t are two unknown exponents. The usual extreme condition on q for $F(q)$ (i.e., $(\partial F/\partial q)\lambda = 0$) gives:

$$2A = sq^{s+2} + \lambda t q^{t+2} B + \lambda \, q^{t+3} (\partial B/\partial q)\lambda. \tag{42.4}$$

guarantees that q and $F(q)$ can be expanded in λ-power series. Our first task consists on determining s and t from the properties (42.1) and (42.2).

Here a brief comment is in order. According to the approach discussed in precedent chapters, (42.3) can be associated with a Hamiltonian having a potential $V(x) = |x|^s + \lambda |x|^t$, whose expectation value is represented by the last two terms of F. On the other hand, the term Aq^{-2} should stand for the kinetic energy expectation value.

Such an analogy is purely formal, since the posed problem is defined, in a very general way, only by the expansions (42.1) and (42.2). Therefore, the function $E(\lambda)$ does not have to be a quantum eigenvalue function.

Nevertheless, above association makes up a truly suitable argument to understand, from a mathematical standpoint, the very essence of our generalization. The reasoning is as follows. We know that a quantum system defined by a potential function having two terms, so that one of them possesses the perturbation parameter λ, has an associated functional like (42.3). Accordingly, due to the extreme condition (42.4), the functional admits unique expansions in the regimes corresponding to $\lambda \to 0$ and $1/\lambda \to 0$. To make the proposed generalization, we reason in the opposite way: given the characteristic asymptotic expansions of a function, we associate with them a unique functional with two terms as a potential contribution.

In accordance with the above argument, one should seek for a unique F, whose structure is wholly determined by the coefficients α and β.

Before analysing the relation between (s,t) and (α,β) it is convenient to turn back to Eq. (42.4). The F extreme condition plays the fundamental role of relating the variables q and λ, and assuring us that F possesses the correct asymptotic dependence on λ. Therefore, we can abstract the mathematically essential information in Eq. (42.4), and transform it into the simplest equation relating λ with q. Such equation is

$$q^{s+2} + \lambda\rho\, q^{t+2} = 1 \tag{42.5}$$

where ρ is a real parameter, that can be used to improve the convergence properties of the renormalized series to be derived from the functional (42.3).

Now we are in position to determine the $F(q)$ functional structure. The following theorem gives the general answer:

Theorem 42.1: Let $F(q)$ be the functional (42.3), where q is a root of Eq. (42.5). Thus, if $B(\lambda,q)$ can be expanded in λ and λ^{α} power series,

then F(q) satisfies the power series expansions (42.1) and (42.2) iff

$$S = -\frac{2}{\beta}(\alpha+\beta) \quad ; \quad t = \frac{2}{\beta}(1-\beta) \tag{42.6}$$

Proof: The change of variable $q = q' \lambda^{-1(t+2)}$ in Eq. (42.3) gives

$$F(q) = \lambda^{2/(t+2)} \{Aq'^{-2} + \lambda^{-(s+2)/(t+2)} q'^{s} + q'^{t} B(\lambda,q)\} =$$

$$= \lambda^{2/(t+2)} F' \quad . \tag{42.7}$$

Eq. (42.5) assures that F and q have the same power series expansions. On the other hand, we have assumed $B(\lambda,q)$ can be expanded in λ- and λ^{α}-power series. Accordingly, in order to fulfil Eqs. (42.1) and (42.2), it is necessary to prove that $F = \lambda^{\beta}F'$, with F' a function with a λ^{α}-power serie expansion. Eq. (42.7) makes certain the fulfilment of this property whenever

$$\beta = 2/(t+2) \quad ; \quad \alpha = -(s+2)/(t+2) \quad , \tag{42.8}$$

which leads at once to (42.6).*

Eq. (42.5) provides the q-value for every functional (that is to say, for every couple of exponents (α,β)) and $\lambda\rho$ value. This equation is algebraic whenever α and β are rational numbers, and has some interesting properties that are studied below.

Lemma 42.1: Eq. (42.5) has one and only one (real) root q, obeying $q^{2/\beta} \varepsilon |0,1|$, if $\lambda\rho>0$.

Proof: For the sake of convenience, Eq. (42.5) is rewritten as

$$v + \lambda\rho v^{(t+2)/(s+2)} = 1 \quad , \quad v = q^{s+2} \quad , \qquad (42.9a)$$

and due to (42.6)

$$f(v) = v + \lambda\rho v^{-1/\alpha} - 1 = 0 \quad . \qquad (42.9b)$$

Eqs. (42.5) allows us to deduce the q asymptotic properties

$$\lim_{\lambda\to 0} q = 1 \quad , \quad \text{then} \lim_{\lambda\to 0} v = 1 \quad , \qquad (42.9c)$$

$$\lim_{\lambda\to 0} q^{t+2} = \lim_{\lambda\to\infty} q^{2/\beta} = 0 \quad , \quad \text{then} \lim_{\lambda\to\infty} v^{-1/\alpha} = 0 \quad , \qquad (42.9d)$$

so that q results a bounded variable. The substitution (42.9c) and (42.9d) in (42.9b) yields the result

$$f(0) = -1 \quad , \quad f(1) = \lambda\rho > 0 \quad , \qquad (42.9e)$$

and so f(v) has at least one root when $v^{-1/\alpha} \in |0,1|$, i.e. when $q^{2/\beta} \in |0,1|$. In order to have more than one root, f(v) should possess at least one extreme within the interval. A straightforward calculation gives

$$f'(v) = 1 - \frac{\lambda\rho}{\alpha} v^{-(\alpha+1)/\alpha} > 0 \quad \forall v > 0 \quad , \qquad (42.9f)$$

then it is evident that the root is unique.*

Corollary: If q is a root of (42.5), then $q^{2/\beta}$ is a bounded and monotonously increasing function of $\lambda \; \forall \; \lambda\rho > 0$.

Lemma 42.2: $\forall\ \lambda\rho<0$ and $\alpha\varepsilon(-1,0)$, Eq.(42.9a) has two real roots such that $q^{2/\beta}\ \varepsilon[1,\infty)$.

Proof: Eq. (42.9) can appropriately be written as

$$\lambda\rho = v^{1/\alpha}\ (1-v) \quad . \tag{42.10a}$$

In order to study the number of roots we have to examine the number of v-values assigned to each $\lambda\rho$-value. The analysis of the extreme values of $\lambda\rho$ as a v-function shows

$$\left[\frac{\partial}{\partial v}(\lambda\rho)\right|\ (v=v_c) = 0 \Rightarrow v_c = (\alpha+1)^{-1} \tag{42.10b}$$

so that only one extreme v_c appears, and accordingly the number of roots is two at most. On the other hand, the functional (42.3) is real if $q>0$ $(v>0)$. Consequently, according to (42.10b), v_c exists iff $|\alpha|<1$ so that $v_c > 1$ and so $q_c^{2/\beta}\geq 1$. Under these conditions, two v roots will appear in some range of $\lambda\rho$ values such that $|\lambda\rho|<|\lambda\rho_c|$. It remains to be proved that in this case $\lambda\rho_c<0$.

From (42.10b) and (42.9a) it follows that

$$q_c = (\alpha+1)^{\beta/2\alpha} \quad , \tag{42.10c}$$

and its substitution in (42.5) yields

$$\lambda\rho_c = \alpha(\alpha+1)^{-(\alpha+1)/\alpha} < 0 \quad \forall\ \alpha\varepsilon(-1,0) \quad . \tag{42.10d}$$

On the other hand, Eq. (42.10a) makes sure that

$$\lim_{v\to\infty} \lambda\rho = 0 \quad , \quad \alpha\varepsilon(-1,0) \quad , \tag{42.10e}$$

This last equation assures us that $\lambda\rho=0$ is an asymptotic value for v and, therefore, since v_c is unique, there exists only one root for $\lambda\rho>0$ (lemma 42.1) and two roots for $\lambda\rho<0$ (Eq. (42.20d)). The situation is clearly depicted in Fig. 13.1*

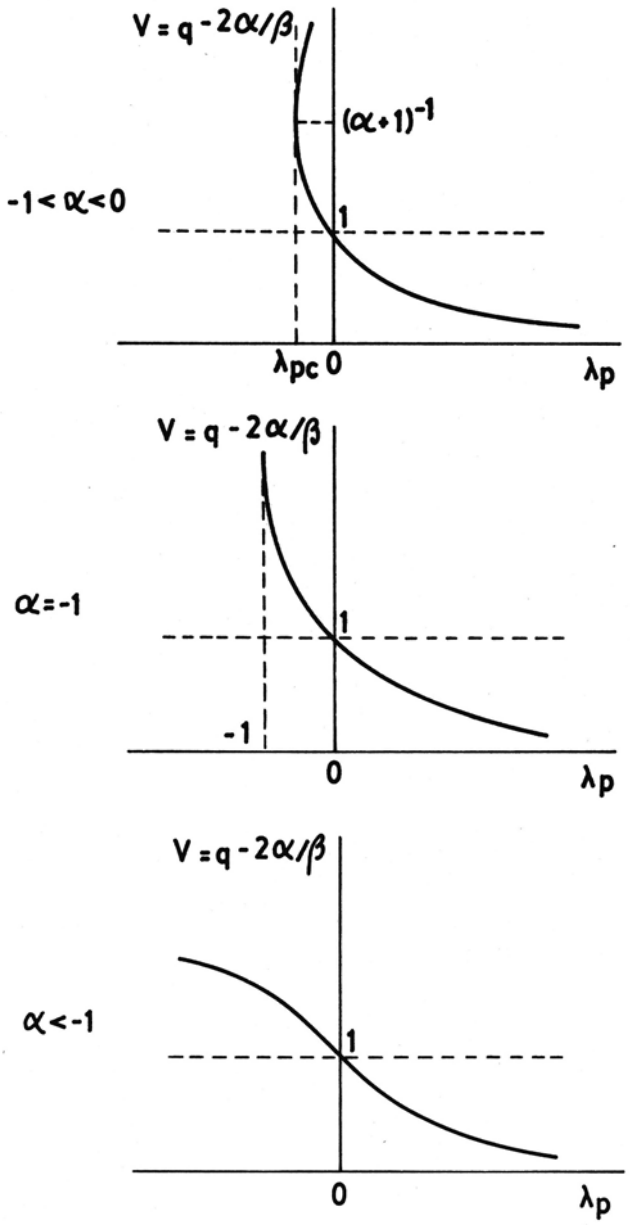

Fig. 13.1: Qualitative dependence of the roots of Eq. (42.9) upon $\lambda\rho$ for different α-values.

For other α values ($\alpha \leq -1$) the analysis is simpler than that corresponding to Lemma 42.2. The case is also displayed in Fig. 13.1. It is evident that whenever $\alpha \leq -1$, there is only one q-value for $\lambda\rho<0$. If $\alpha=-1$ there are no roots when $\lambda\rho<-1$, as well as there are no roots for $\rho<\rho_c$ (Eq. (42.10d)) if $\alpha \varepsilon (-1,0)$.

Lemmas 42.1 and 42.2 set up the essential properties in order to select the q-value for the functional. Let us note that the optimum working zone is $0<\lambda\infty(\rho>0)$, which is the usual range in the perturbative parameter.

Our next step is to build the function $B(\lambda,q)$. To this purpose, we apply the same argument introduced in §.33, searching for variables that may be expanded in λ- and λ^{α} power series, as demanded by theorem 42.1.

From Eq. (42.5) it follows that q^{s+2} and λq^{t+2} can be expanded in λ-series, the same as q. Besides, the use of the change of variable introduced in theorem 42.1, transforms Eq. (42.5) into

$$\lambda^{-(s+2)/(t+2)}\, q',^{s+2} + \rho q',^{t+2} = \lambda^{\alpha} q',^{s+2} + \rho q',^{t+2} = 1, \quad (42.11)$$

which shows that such variables can also be expanded in λ^{α}-power series. Hence, the definition of the variables

$$u = \lambda q^{t+2} \quad , \quad (42.12)$$

$$v = q^{s+2} \quad , \quad (42.13)$$

allows us to have two alternative analytic representations for $B(\lambda,q)$:

$$B = \sum_{n=0}^{\infty} b^{(n)}\, u^{n} \quad , \quad (42.14)$$

$$B = \sum_{n=0}^{\infty} b'^{(n)} v^n \quad , \tag{42.15}$$

where coefficients $\{b^{(n)}\}$ and $\{b'^{(n)}\}$ must be determined from the available analytical information (for example, RSPT). Variables u and v are bounded when $\lambda\rho>0$, according with Lemmas 42.1 and 42.2:

$$\lim_{\lambda\to 0} u = 0 \quad ; \quad \lim_{\lambda\to\infty} u = 1/\rho \quad , \tag{42.16a}$$

$$\lim_{\lambda\to 0} v = 1 \quad , \quad \lim_{\lambda\to\infty} v = 0 \quad . \tag{42.16b}$$

The procedure consists of solving Eq. (42.5) to obtain u(or v), and then to compute B by way of Eq. (42.14) (or Eq. (42.15)). Finally, the functional F is derived from Eq. (42.3). The expansions (42.14) and (42.15) generalize Eqs. (38.4) and (38.5) for anharmonic oscillators. By an immediate extension of the argument discussed in §.33, we know that it is convenient to use (42.14) to introduce the coefficients in (42.1), while (42.15) is the appropriate equation to insert the coefficients of the power series (42.2).

However, it is worth mentioning again that, due to the construction itself, both expansions (42.1) and (42.2) can be introduced into any B expressions.

Let us now discuss how to write constants A and $\{b^{(n)}\}$ as $\{E^{(n)}\}$-functions. The procedure is as follows: the replacement of (42.12) in (42.5) gives

$$\lambda = u(1-\rho u)^{1/\alpha} \quad . \tag{42.17}$$

Multiplying (42.3) by q^2 and using (42.12) together with Theorem 42.1, one gets

$$(\frac{u}{\lambda})^{\beta} \bar{F} = A + (\frac{u}{\lambda})^{-\alpha} + u\, B(u) \quad ,$$

which by way of (42.17) can be rewritten as

$$(1-u)^{-\beta/\alpha} F = A + 1 - \rho u + u\, B(u) \quad . \tag{42.18}$$

F and $(1-u)^{-\beta/\alpha}$ power series expansions are written as

$$F = \sum_{n=0}^{\infty} \tilde{F}_n\, u^n \tag{42.19}$$

$$(1-u)^{-\beta/\alpha} = \sum_{n=0}^{\infty} \binom{-\beta/\alpha}{n} (-\rho u)^n \quad , \tag{42.20}$$

where

$$\binom{c}{m} = \frac{c(c-1)(c-2)\ldots(c-m+1)}{m!} \quad . \tag{42.21}$$

The replacement of (42.19) (42.14) and (42.20) into Eq. (42.18) leads us to

$$\sum_{n,m=0}^{\infty} \binom{-\beta/\alpha}{n} (-\rho)^n \tilde{F}_m\, u^{n+m} = A+1 - \rho u + \sum_{j=0}^{\infty} b^{(j)} u^j \tag{42.22a}$$

which allows us to deduce the result

$$\sum_{n=0}^{r} \binom{-\beta/\alpha}{n} (-\rho)^n \tilde{F}_{r-n} = (A+1)\, \delta_{r0} - \rho\delta_{r1} + b^{(r-1)}(1-\delta_{r0}) \quad . \tag{42.22b}$$

In order to express the coefficients $\tilde{F}_r$ in terms of $E^{(i)}$, we impose

to F the condition of reproducing the first RSPT coefficients, that is to say

$$F = \sum_{i=0}^{M} E^{(i)} \lambda^i + R_M(\lambda) \qquad (42.23)$$

where R_M is some remainder. The replacement of (42.17) into (42.23) permits one to obtain the u-coefficient (i.e. $\hat{F}_j$) in (42.19):

$$\hat{F}_j = \sum_{m=0}^{j} E^{(m)} \binom{m/\alpha}{j-m} (-\rho)^{j-m} \quad ; \; j \leq M \quad . \qquad (42.24)$$

The insertion of (42.24) into (42.22b) yields a recursive relationship for the coefficients $b^{(m)}$:

$$\sum_{j=0}^{r} \sum_{m=0}^{j} E^{(m)} \binom{m/\alpha}{j-m} \binom{-\beta/\alpha}{r-j} (-\rho)^{r-m} = (A+1)\delta_{r0} - \rho\delta_{r1} +$$

$$+ b^{(r-1)} (1-\delta_{r0}) \quad . \qquad (42.25)$$

This last formula can be simplified considering that

$$\sum_{j=0}^{r} \sum_{m=0}^{j} E^{(m)} \binom{m/\alpha}{j-m} \binom{-\beta/\alpha}{r-j} (-\rho)^{r-m} = \sum_{m=0}^{r} E^{(m)} \left\{ \sum_{j=m}^{r} \binom{m/\alpha}{j-m} \binom{-\beta/\alpha}{r-j} \right\}$$

$$(-\rho)^{r-m} = \sum_{m=0}^{r} E^{(m)} \left\{ \sum_{n=0}^{r-m} \binom{m/\alpha}{n} \binom{-\beta/\alpha}{r-m-n} \right\} (-\rho)^{r-m} =$$

$$= \sum_{m=0}^{r} E^{(m)} \binom{(m-\beta)/\alpha}{r-m} (-\rho)^{r-m} \quad ,$$

so that we have the final expression

$$\sum_{m=0}^{r} \binom{(m-\beta)/\alpha}{r-m} E^{(m)} (-\rho)^{r-m} = (A+1)\delta_{r0} - \rho\delta_{r1} + b^{(r-1)} (1-\rho_{r0}), \; 0 \leq r \leq M. \qquad (42.26)$$

Eq. (42.26) provides an analytical formula to obtain the coefficients $b^{(r)}$ in terms of ρ. The choice r=0 in this equation ($b^{(-1)} = 0$) gives the A-value:

$$A = E^{(0)}-1 \quad . \tag{42.27}$$

Owing to Eq. (42.26), coefficients $b^{(r)}$ come of ρ-polynomials:

$$b^{(r)} = \sum_{j=0}^{r+1} E^{(r+1-j)} b_j^{(r)} \rho^j \quad . \tag{42.23}$$

where $b_j^{(r)}$ are rational numbers which can be easily computed from (42.26).

Coefficients $b'^{(n)}$ can be deduced analogously. Eq.(42.10a) yields a λ-expression as a function of v. In order to have F as a function of v, it is necessary to multiply (42.3) by q^2, and to use Theorem (42.1) and Eq. (42.13):

$$v^{-\beta/\alpha} \lambda^{\beta} F' = A+v + v^{-1/\alpha} B(v) \quad . \tag{42.29}$$

When considering Eq.(42.10a), we are led to

$$(1-v)^{\beta} \rho^{-\beta} F' = A+v+\frac{1-v}{\rho} B(v) \quad . \tag{42.30}$$

According to Theorem 42.1, F' is a function that can be expanded in a λ^{α}-power series, therefore

$$\tilde{F}' = \sum_{n=0}^{\infty} F'_n v^n \quad . \tag{42.31}$$

The substitution of (42.31) into (42.30), and the identification of

v powers give

$$\rho^{-\beta}\sum_{j=0}^{r}\binom{\beta}{r-j}(-1)^{r-j}\overset{\gamma}{F}'_j = A\delta_{r0}+\delta_{r1}+\frac{1}{\rho}\{b'^{(r)}-b'^{(r-1)}\},r\geq 0. \qquad (42.32)$$

Taking into account Theorem 42.1, F' happens to satisfy the expansion (42.2) up to the M-th order:

$$F' = \sum_{i=0}^{M} e^{(i)}\,\lambda^{\alpha i} + R_{M} \quad . \qquad (42.33)$$

The replacement of (42.10a) into (42.33) gives us $\overset{\gamma}{F}'_j$:

$$\overset{\gamma}{F}'_j = \sum_{i=0}^{j} e^{(i)}\,(-1)^{j-1}\,\rho^{-i\alpha}\binom{i\alpha}{j-i} \quad , \qquad (42.34)$$

from where results a recurrence relationship for the coefficients $b'^{(s)}$:

$$\rho^{-\beta}\sum_{j=0}^{r}\sum_{i=0}^{j}\binom{i\alpha}{j-i}\binom{\beta}{r-j}\,(-1)^{r-i}\,e^{(i)}\,\rho^{-i\alpha} = A\delta_{r0}+\delta_{r1}+\frac{1}{\rho}\{b'^{(r)} -$$

$$- b'^{(r-1)}\} \quad . \qquad (42.35)$$

The formula can be simplified through a procedure similar to that discussed before for Eq. (42.26), giving

$$\sum_{i=0}^{r}(-1)^{r-i}\,\rho^{-(\beta+i\alpha)}e^{(i)}\binom{\beta+i\alpha}{r-i} = A\delta_{r0}+\delta_{r1}+\frac{1}{\rho}\{b'^{(r)}-b'^{(r-1)}\} \ ,$$

$$0\leq r\leq M \quad . \qquad (42.36)$$

For r=0, we have an equation that relates A, $e^{(0)}$ and $b'^{(0)}$:

$$b'^{(0)} = \rho^{1-\beta}\, e^{(0)} \sim A\rho \quad , \tag{42.37}$$

where A is given by (42.27). Eq. (42.36) tells us that the $b'^{(r)}$ coefficients can be expresed as

$$b'^{(r)} = \{\rho^{1-\beta} \sum_{j=0}^{r} b'^{(r)}_j\, e^{(j)} \rho^{-j\alpha}\} - (A+1)\rho \quad , \tag{42.33}$$

where $b'^{(r)}_j$ are rational numbers, which can be easily determined for any pair of α,β values.

Eqs. (42.26) and (42.36) complete the construction of B. Since we have introduced the coefficients up to $E^{(M)}$ (or $e^{(M)}$), it is convenient to make a slight modification in the writing to account for the number of coefficients involved from the series (42.1) and (42.2). We use the following notation for the approximation to $E(\lambda)$:

$$F^{(M)} = Aq^{-2} + q^s + \lambda q^t\, B_M \quad , \tag{42.39a}$$

$$B_M = \sum_{n=0}^{M-1} b^{(n)}\, u^n \quad , \tag{42.39b}$$

$$B_M = \sum_{n=0}^{M} b'^{(n)}\, v^n \quad . \tag{42.39c}$$

Now the point at issue is to analyse the conditions under which $F^{(M)}$ converges toward E when M increases. The factor ρ plays a fundamental role in this problem. As will be shown later on, ρ is our key to be able to sum several power series beyond their convergence domain by means of the formalism developed along this paragraph.

In precedent chapters we have analysed some models of physical interest where the available analytic information consisted of a set of coefficients $\{E^{(0)}, E^{(1)}, \ldots, E^{(M)}; e^{(0)}\}$. Nontrivial examples of

RSPT were anharmonic oscillators, confining potentials and Zeeman effect. As done in all these cases, it would be advantageous to use the functional defined by Eqs. (42.39a), (42.39b), (42.17) and (42.26) to introduce also the correct behavior for $\lambda >> 1$. This can be accomplished by means of $e^{(0)}$:

$$\lim_{\lambda \to \infty} \lambda^{-\beta} F^{(N)} = e^{(0)} \quad , \tag{42.40}$$

for a given N. To reach such a condition, one can choose N=M+1 and fix $b^{(M)}$ in such a manner to satisfy the limit (42.40). Theorem 42.1 and Eq. (42.16a) lead us to

$$\lambda^{-\beta} F^{(M+1)} \simeq A\rho^{\beta} + \rho^{\beta-1} \sum_{n=0}^{M} b^{(n)} \rho^{-n} + O(\lambda^{\alpha}) \quad , \tag{42.41}$$

which gives for the coefficient $b^{(M)}$ the result:

$$b^{(M)} = \rho^{M} \{\rho^{1-\beta} (e^{(0)} - A\rho^{\beta}) - \sum_{n=0}^{M-1} b^{(n)} \rho^{-n}\} \quad . \tag{42.42}$$

One can expect that $F^{(M+1)}$ (with $b^{(M)}$ given by (42.42)) should be a better approximation to E than that made up by Eqs. (42.39a) and (42.39b), every time that ρ is suitably determined. From now on, we will call Functional Method (FM) to the above technique of approaching functions $E(\lambda)$ by way of functionals such as $F^{(M+1)}$. Such a denomination is due to its close relationship with the VFM studied in Part A of this book.

§.43. Connection between the FM and other summation techniques.

In the previous paragraph we have formulated from a general viewpoint a method to sum perturbation series by extension of the VFM, which has a semiclassical nature. Such a procedure is closely related to other power series summation methods and this paragraph deals with such connections. This analysis not only has a conceptual interest but also it will allow us to address some issues left open in §.42.

Chapter V was devoted to discussing several methods to sum perturbation series. General procedures such as Padé or Borel methods (§§. 13 and 14) cannot be directly compared with the FM because both use quite different information. Let us remark that FM has been formulated taking into account the expansion (42.2) for $1/\lambda \to 0$ with $\beta \varepsilon R$, while Padé and Borel-Padé methods could only render a similar behavior for $1/\lambda \to 0$ if β is an integral number. Due to this, we will discuss instead other methods where the available information on asymptotic expansions is employed.

To begin with, it is convenient to start the analysis with the so-called geometrical approximation (GA) /3,4/, which is devised to improve the convergence rate of the RSPT for eigenvalue problems. Let us consider the Hamiltonian H and its associated Schrödinger equation:

$$H\psi = E(\lambda)\psi \quad , \quad H = H_o + \lambda V \quad , \tag{43.1a}$$

$$H_o \psi^{(0)} = E^{(0)} \psi^{(0)} \quad . \tag{43.1b}$$

The GA consists of writing H as

$$H = H_o' + V', \; H_o' = \mu H_o, V' = \lambda V + (1-\mu) H_o, \; \mu \varepsilon \; R_o^+ \; . \tag{43.2}$$

The basic idea is quite simple: apply RSPT to (43.2) and then set the μ value (free parameter) in accordance with some appropriate criterion. The application of equations deduced in §.7 allows us to find without any further difficulty the first three perturbative correc-

tions due to V':

$$E'^{(0)} = \mu\, E^{(0)} \quad , \tag{43.3a}$$

$$E'^{(1)} = (E^{(1)} + \frac{1-\mu}{\lambda} E^{(0)})\lambda \quad , \tag{43.3b}$$

$$E'^{(2)} = \frac{\lambda^2}{\mu} E^{(2)} \quad , \tag{43.3c}$$

$$E'^{(3)} = \lambda^3 \mu^{-2}\{E^{(3)} + \frac{\mu-1}{\lambda} E^{(2)}\} \quad . \tag{43.3d}$$

The usual μ choice is in agreement with the so-called Wigner rule and it consists of setting the third order correction equal to zero:

$$E'^{(3)}(\mu = \mu^*) = 0 \Rightarrow \mu^* = 1 - \frac{\lambda E^{(3)}}{E^{(2)}} \quad . \tag{43.4}$$

The calculation of E at the third-order approximation

$$E \simeq E'^{(0)} + E'^{(1)} + E'^{(2)} \tag{43.5}$$

and the replacement of (43.3) and (43.4) in (43.5) gives the result

$$E \simeq E^{(0)} + \lambda E^{(1)} + \frac{\lambda E^{(2)}}{1 - \frac{\lambda E^{(3)}}{E^{(2)}}} \quad . \tag{43.6}$$

Eq. (43.6) is coincident with a /2/1/ Padé approximant (see Appendix E). Then, the GA (closely related with the Feenberg dilatation method /5,6/) can be reduced to some types of Padé approximants by means of a suitable choice of μ. In order to compare the GA and FM, it is appropriate to see the preceding equations from a different standpoint. The GA is essentially a partitioning tecnique, that is to say, a method where some parameters are introduced within the

Hamiltonian, and through it, into the perturbation corrections. However, there exists another alternative manner to introduce an adjustable parameter in the Rayleigh-Schrödinger expansion, and it is via the integral $\langle\psi^{(0)}|\psi^{(i)}\rangle$. For the sake of simplicity we chose in §.7 $\langle\psi^{(0)}|\psi^{(i)}\rangle = \delta_{i0}$, but in general it could be given an arbitrary value:

$$\Gamma_i = \langle\psi^{(0)}|\psi^{(i)}\rangle \quad . \tag{43.7}$$

In order to introduce Γ_i within the RS expansion, we proceed as follows. Firstly the energy and wave function are expanded in λ-power series. Defining

$$\psi^{(i)} = \bar{\psi}^{(i)} + \Gamma_i \psi^{(0)}, \quad \langle\bar{\psi}^{(i)}|\psi^{(0)}\rangle = \delta_{i0}, \tag{43.8}$$

substituting into (43.1), and applying $\langle\psi^{(0)}|$ on both sides of the resulting equations give

$$\langle\psi^{(0)}|V\bar{\psi}^{(i-1)}\rangle = \sum_{s=2}^{i} E^{(s)} \Gamma_{i-s} \; ; \; \Gamma_{0=1} \quad , \tag{43.9a}$$

$$\langle\psi^{(0)}|V\psi^{(0)}\rangle = E^{(1)} \quad . \tag{43.9b}$$

Manifestly, the condition $\Gamma_s = \delta_{s0}$ leads us to the equations studied in §.7. The use of Eq. (43.7) gives a new perturbative coefficients

$$E'^{(i)} = \langle\psi^{(0)}|V\bar{\psi}^{(i-1)}\rangle \quad . \tag{43.10}$$

The application of this modified perturbation theory up to the second order yields

$$E = \frac{\langle\psi^{(0)}|H\psi\rangle}{\langle\psi^{(0)}|\psi\rangle}$$

$$\simeq \frac{\langle\psi^{(0)}|H\psi^{(0)}\rangle + \lambda\Gamma,\langle\psi^{(0)}|H\psi^{(0)}\rangle + \lambda^2\langle\psi^{(0)}|V\bar{\psi}^{(1)}\rangle + \ldots}{1 + \Gamma_1\lambda}$$

$$\simeq E^{(0)} + E^{(1)}\lambda + \frac{E^{(2)}\lambda^2}{1+\Gamma_1\lambda} \quad . \tag{43.11}$$

Parameter Γ_1, offers a degree of freedom; such a parameter can be fixed in order to fulfil the Wigner rule on the basis of Eqs. (43.9) and (43.10):

$$E'^{(3)} = E^{(3)} + \Gamma_1 E^{(2)} = 0 = \Gamma_1 = - E^{(3)}/E^{(2)} \quad . \tag{43.12}$$

It is quite evident the connection between the parameters μ^* (Hamiltonian partitioning) and Γ, (PT):

$$\Gamma_1 = \frac{\mu^*-1}{\lambda} \quad . \tag{43.13}$$

Above discussion makes clear the equivalence between a partitioning technique and the employment of integrals of the perturbative corrections as adjustable parameters. Other choices for Γ_i lead us to other partitioning techniques or alternative approximations to sum the perturbation expansion /4/.

Let us consider now another important equivalence. The PT partial sum in the GA can be written as:

$$S_N E' = \sum_{s=0}^{N} E'^{(s)} \quad , \tag{43.14}$$

which, considering (43.3), gives

$$E \simeq S_3 E' = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} \{\frac{2}{\mu} - \frac{1}{\mu^2}\} + \frac{\lambda^3 E^{(3)}}{\mu^2} \quad . \tag{43.15}$$

Parameter μ can be determined as follows. Since μ is a fictitious parameter in the PT expansion, the eigenvalues will not depend on it. Therefore, μ can be fixed by means of a sensitivity or convergence criterion. We know that since E does not depend upon μ, then all the derivatives $d^jE/d\mu^j$ must be zero, so that a suitable sensitivity criterion could be

$$\left(\frac{dE}{d\mu}\right)(\mu = \mu^*) = 0 \quad . \tag{43.16a}$$

Now, considering that the sequence $S_N E'$ (Eq.(43.14)) makes up an approximation to E, we have

$$\left(\frac{\partial S_N E'}{\partial \mu}\right)(\mu = \mu^*) = 0 \quad . \tag{43.16b}$$

The choice N = 3 in Eq. (43.16b) and the use of (43.15) gives the result (43.4) for μ^*. This finding is quite significative: the sensitivity of convergence condition regarding a fictitious parameters introduced into the RSPT or PT like series, happens to be equivalent to the application of a Hamiltonian partitioning technique (such as the GA), plus a condition such as the Wigner rule.

The previous result allows us to study the connection with the FM. First of all, let us note that the application of the FM to the eigenvalue problem (43.1) introduces a change of variables (42.17) which according to in §.42, can be written as

$$u - \frac{\lambda}{q^{s-t}+\lambda\rho} \quad . \tag{43.17}$$

Let as now study under which condition this transformation is similar to that one introduced through the GA. Eq. (43.11) suggests a change of variables $\lambda \to \lambda/(1+\lambda\Gamma_1)$. This change of variables appears in (43.17) iff s=t, which according Theorem 42.1 corresponds with $\alpha = -1$. This is a first relevant result, since it shows that the FM contains the Euler method (§.15) as a particular case (α=-1) /7/.

Let us apply the FM to a function $E(\lambda)$ satisfying (42.2), with $\alpha=-\beta=-1$. The use of Theorem (42.1) and Eqs. (42.39a) and (42.39b) with M=3 gives

$$F^{(3)} = Aq^{-2}+1+\lambda b^{(0)}+\lambda^2 b^{(1)} q^2+\lambda^3 b(2) q^4 \qquad (43.18a)$$

where

$$q^2 = 1/(1+\lambda\rho) \qquad (43.18b)$$

On the other hand, the application of Eqs. (42.26) - (42.28) yields

$$A = E^{(0)}-1 \; ; \; b^{(0)} = E^{(1)}-A\rho \; ; \; b^{(1)} = E^{(2)}, b^{(2)} = E^{(3)}+E^{(2)} \; \rho \quad . \qquad (43.19)$$

Introducing (43.19) into (43.18a), and rearranging appropriately the resulting expression, the functional $F^{(3)}$ built with PT information up to third-order happens to be

$$F^{(3)} = A+1+\lambda E^{(1)} + \frac{\lambda^2 E^{(2)}+2\rho\lambda^3 E^{(2)}+\lambda^3 E^{(3)}}{(1+\lambda\rho)^2} \quad . \qquad (43.20)$$

The functional provides us a ρ-dependent expression and we know that eigenvalue cannot depend upon it. Then, using a similar argument as before, we have an optimum ρ-value from the sensitivity condition

$$\left(\frac{\partial F^{(3)}}{\partial \rho}\right) (\rho = \rho^*) = 0 \quad , \qquad (43.21)$$

which, according to (43.20), gives

$$\rho^* = - E^{(3)}/E^{(2)} \quad . \qquad (43.22)$$

The result (43.22) is coincident with (43.12), derived from a quite different point of view. Precedent discussion allows us to extract several conclusions:

i) FM contains the GA for eigenvalue problems as a particular case ($\alpha=-\beta=-1$).

ii) Since the FM assures us the correct asymptotic expansions for the function $E(\lambda)$ under study, we conclude that the GA will only give the $E(\lambda)$ correct dependence with λ for $\lambda>>1$ if $\alpha=-\beta=-1$.

iii) The FM induces on the RSPT power series a rearrangement which, in principle, can be connected with a Hamiltonian partitioning.

iv) The FM can be related with other perturbative techniques through a suitable handling of the parameter ρ.

v) The constant ρ plays the role of adjustable parameter in the FM, in such a way that it can improve the F convergence toward the function E. The ρ optimization may be made through an appropriate sensitivity (stability) or plateau criterion.

The remaining of the section is devoted to establish the connections of the FM with other summation methods. However, it is convenient to present here the criterion to be used in order to determine ρ. As seen before, ρ is a parameter on which $E(\lambda)$ cannot depend. Consequently, as M increases one expects that $F^{(M)}$ transforms itself into a ρ-independent function. Thence, the relation $F^{(M)}$ vs ρ must exhibit a plateau, whose extension will have to increase when $M\to\infty$. The criterion to be followed is obviously to choose ρ^* such that it belongs to that plateau. The suitable ρ-value is determined according to the following rules (to be called in what follows Sensitivity Rules or Sensitivity Criteria):

1) Stationary Point (SP): ρ^* is chosen in such a way that $F^{(M)}$ is an extreme $((\partial F^{(M)}(\partial\rho)_\lambda)(\rho=\rho^*)=0$. When there are more than one extreme point, the one with the lowest absolute value for the second derivative $(\partial^2 F^{(M)}/\partial\rho^2)(\rho=\rho^*)$ is chosen.

2) Inflexion Point (IP): When there are no SP's, ρ^* is chosen as the inflexion point$((\partial^2 F^{(M)}/\partial\rho^2)\ (\rho=\rho^*)=0)$ with lowest absolute value of

its first derivative $|(\partial F^{(M)}/\partial\rho)|(\rho=\rho^*)$. We will study the convergence properties of the functional $F^{(M)}$ through its IP's even in those cases where there exist SP's, so as to establish the influence of both sorts of points on the numerical results.

3) Inexistence of SP and IP: When $F^{(M)}$ has neither SP nor IP for $\rho\varepsilon R$, it will be necessary to take recourse of an alternative criterion. Computations allowing ρ^* will be chosen as $\rho^* = \mathrm{Re}(\bar{\rho}), (\partial F^{(M)}/\partial\rho)(\rho=\rho)= =0$, with the lowest value of the second derivative.

The FM has a very interesting property: the $F^{(M)}$ extremes are independent of λ, i.e.

$$\left(\frac{\partial F^{(M)}}{\partial\rho}\right)_\lambda (\rho=\rho^*) = 0, \ \forall\ \lambda\varepsilon R_o^+ \quad . \tag{43.23}$$

A rigorous proof of (43.23) is somewhat troublesome, although direct, and it will be given in the next paragraph (§.44) in the framework of a slightly different formalism. Notwithstanding, it is possible to extract some conclusions from (43.23). As a first practical consequence, this result allows us to make the ρ^* calculation just once, say, for $\lambda=1$.

According to the discussion presented in §.42, the $F^{(M)}$ λ-power series expansion may be written as

$$F^{(M)} = \sum_{n=0}^{M} E^{(n)}\lambda^n + \sum_{n=M+1}^{\infty} F_n(\rho^*)\lambda^n \quad , \tag{43.24}$$

and applying (43.23) to (43.24) we find that

$$\left(\frac{\partial F_n}{\partial\rho}\right)_\lambda (\rho=\rho^*) = 0, \ \forall n>M \quad . \tag{43.25}$$

Eq. (43.25) is equivalent to Eq. (43.23), but it is simpler form the computational point of view. Let us now make use of this result for a problem with $\alpha=-\beta=-1$ (Eq. (43.13)). The result for the fourth order coefficient is

$$F_4 = - (E^{(2)}\rho^2 + 2E^{(3)}\rho) \quad . \tag{43.26}$$

The employment of (43.25) leads us again to (43.22) for ρ (which is independent of λ).

Regarding the Sensitivity Rule 2, it is worth mentioning that IP's depend on λ, although their variation takes place within a finite interval, $\rho^* \varepsilon (\rho_1^*, \rho_2^*)$, with $\rho_1^* = \rho^*$ $(\lambda=0)$ and $\rho_2^* = \rho^*(1/\lambda=0)$. This property will be also demonstrated rigorously in §.44.

Let us compare now the SVM (§.21) with the FM. Although the SVM is not a summation method of perturbation series, it happens to be particularly important regarding our present interest. Let us assume that the Hamiltonian (43.1a) possesses the following specific structure

$$H_o = p^2 + |x|^s \ , \ p \equiv -id/dx \quad , \tag{43.27a}$$

$$V = |x|^t \quad , \tag{43.27b}$$

and we are interested in the approach of the ground state energy. As discussed previously (§.21) /8-10/, the SVM provides an energy upper bound:

$$E(\lambda;a) = \langle \psi_a^{(0)} | H \psi_a^{(0)} \rangle \geq E(\lambda); \psi_a^{(0)} = a^{1/2} \psi^{(0)}(ax) . \tag{43.28}$$

and the extreme condition $\partial E(\lambda;a)/\partial a = 0$ allows that $E(\lambda;a)$ fulfils the VT, which leads us to the following result:

$$\min_{(a)} E(\lambda;a) = \frac{2}{s+2} a^2 E^{(0)} + \frac{s}{s+2} a^{-2} E^{(0)} + \lambda a^{-t} E^{(1)} \quad , \tag{43.29a}$$

where a is a root of the algebraic equation

$$a^{-(s+2)} + \frac{\lambda(s+2)t}{2sE^{(0)}} E^{(1)} a^{-(t+2)} = 1 \quad . \tag{43.29b}$$

Now the FM is applied starting from (43.27). The use of Eqs. (42.39a) and (42.39b) with M=1 yields

$$F^{(1)} = \frac{E^{(0)}-1}{q^2} + q^s + \lambda b^{(0)} q^t \quad , \tag{43.30}$$

where q is given by Eq. (42.5). The application of Eq. (42.26) allows us to find the coefficient $b^{(0)}$, which assures us the correct result of the first order RSPT, viz.

$$b^{(0)} = E^{(1)} + \frac{s+2-2E^{(0)}}{s+2} \rho \quad . \tag{43.31}$$

The optimum parameter ρ^* is determined via the Sensitivity Rule 1 (Eq. (43.25)). In order to apply this condition, Eq. (43.30) is expanded in λ-power series

$$F^{(1)} = E^{(0)} + E^{(1)} \lambda + F_2\lambda^2 + \ldots \quad , \tag{43.32a}$$

where a straightforward computation gives the coefficient F_2

$$F_2 = \frac{sE^{(0)}}{(s+2)^2} \rho^2 - \frac{tE^{(1)}}{(s+2)} \rho \quad . \tag{43.32b}$$

Finally Eq. (43.25) with n=2 yields the optimum parameter ρ^*

$$\rho^* = \frac{t(s+2)}{2sE^{(0)}} E^{(1)} \quad . \tag{43.33}$$

The result (43.33) makes sure that ρ^* is unique $\forall\ \lambda\epsilon R_o^+$. Inserting this factor into (42.5) gives us:

$$q^{s+2} + \frac{t(s+2)E^{(1)}\lambda q^{t+2}}{2sE^{(0)}} = 1 \quad . \tag{43.34}$$

It is obvious that making q=1/a brings (43.29b). This fact proves that the SVM is a particular case of the FM where $F^{(1)}$ is chosen for the μ-power series ($\lambda \to 0$) and rule 1 is applied to determine ρ^*.

It can be easily proved that there exists a close relationship among the FM and several rearrangement techniques of perturbation series based on Hamiltonian partitionings (§.16) /11-15/. The choice s=2, t=2K in (43.27) allows us to find once more the anharmonic oscillator results. In this case Eq. (42.17) leads us to the following change of variables for the functional (which is built through the use of the power series expansion associated with the small coupling regime ($\lambda \to 0$):

$$\lambda = u(1-\rho u)^{-(K+1)/2} \quad , \tag{43.35}$$

with $\alpha = -2/(K+1)$ and $\beta = 1/(K+1)$. This transformation is coincident with that one employed by Dmitrieva and Plindov /12,13/ (§.16), who determined ρ such that the VT is satisfied. The introduction of the change of variables $x \to (1-\rho u)^{1/4}x$ in H by means of a dilatation (the procedure is given in Appendix A) gives

$$\bar{H} = (1-\rho u)^{1/2}\, H = p^2+x^2+u(x^{2K}-\rho x^2) \quad , \tag{43.36}$$

which is the sort of rearrangement used in Refs. /11-13/. If E is an H eigenvalue, and $\bar{E}$ is an $\bar{H}$ eigenvalue, then both are related via the equation

$$E = (1-\rho u)^{-1/2}\, \bar{E}(u) = (1-\rho u)^{-1/2} \sum_{n=0}^{\infty} \bar{E}^{(n)}(\rho)\, u^n \quad . \tag{43.37}$$

It is important to make clear the difference between the methods in Refs. /11-15/ and their connection with the FM. The FM introduces into the Hamiltonian H the change of variables (43.35), and gives an approximation to the eigenvalues by means of a functional as follows

$$F = (1-\rho u)^{-1/2}\{A+1-\rho u+uB(u)\} \quad . \tag{43.38}$$

Since the term between curly brackets is a function of u, it is evident that when comparing with (43.37) this term is the functional approximation to the $\bar{H}$ eigenvalues. The relationship can even be more explicit writing

$$\bar{E}^{(0)} = A+1, \; \bar{E}^{(1)} = b^{(0)} - \rho \quad , \quad \bar{E}^{(n)} = b^{(n-1)}$$

$$\text{when } n \geq 2 \tag{43.39}$$

This equivalence found among the FM and the techniques applied in Refs. /11-13/ is quite revealing: the FM introduces in the PT a transformation that can be associated with a partition or rearrangement of the Hamiltonian. Such rearrangement is determined by a coordinate and momentum scaling relationship (Appendix A), so that is different with respect to other partitioning techniques such as Feenberg's /16-20/ or Löwdin's /21/. According to the discussion at the beginning, we can assert that the FM is equivalent to the Feenberg method (GA) when $\alpha = -\beta=-1$.

The conclusions derived here may be extended without any further inconvenience to all the quantum mechanical problems with a Hamiltonian like $H = T+V_1+V_2$, with V_1 and V_2 homogeneous functions in the coordinates, whenever the solutions of $T+V_1$ are known.

This property follows at once from the discussion presented in §.16. However, there exist significative implementation differences among the FM and the procedures in Refs. /11-13/. These last techniques construct the series (43.37) from the RSPT and determine ρ via the VT, which is equivalent to obtain it according with the SVM (first-order PT). Within the context of this method, the ρ-value is

constant for each quantum state and independent of the perturbational order. Notice that the Hamiltonian in Eq. (43.36) remains as $H = H_o + uV'(\rho)$, $V'(\rho) = x^{2K} - \rho x^2$, where u plays the role of a bounded perturbational parameter (§.42). However, when $x \to \pm\infty$, $V'(\rho)$ is more singular than x^2 if ρ = constant, and in consequence the hypothesis of Theorem 10.1 are not fulfilled. It is not difficult to see that the procedure presented in Refs. /11-13/ transforms a series with zero convergence radius (λ-series) into another asymptotic series, in powers of $u (0<u<1/\rho)$. The u-power series (43.37), studied by Pascual /11/ and Dmitrieva and Plindov /12,13/ for several oscillators is a more slowly divergent series than the original λ-series, but it requires the employment of other summation method (such as Padé approximants) to be able to work up to higher perturbation orders.

The FM determines ρ^* by means of the sensitivity rules, that make up an elaborate criterion taking into account the convergence $F^{(M)} \to E$, when $M \to \infty$. Obviously, ρ^* depends on M through the functional, so that the previous arguments on the singularity character of $V'(\rho)$ are not applicable here.

The renormalized series technique by Killingbeck and Austin /11,15/ is based upon a Hamiltonian rearrangement similar to (43.36) (§.16):

$$H = p^2 + x^2 + \lambda x^{2K} = p^2 + m'^2 x^2 + \lambda (x^{2K} - \rho x^2) \quad , \tag{43.40}$$

with m' a fictitious "mass", given by:

$$m'^2 = 1 + \lambda \rho \quad . \tag{43.41}$$

As shown in §.16, the method consists of generating the perturbative expansion in λ-power series with ρ determined by application of sensitivity criteria, and m. by Eq. (43.41). As shown before, the FM makes a similar rearrangement not in H but in $\bar{H}$, and besides it gives rise to a u-expansion and not a λ-expansion. The relationship between u and λ is determined by a scaling relation of the Hamiltonian for every ρ, which does not happen in Eq. (43.41). Due to this difference, there is no manner to assure that the asymptotic dependence ($\lambda >> 1$)

predicted for $E(\lambda)$ is the correct one when the perturbative procedure of Refs. /14,15/ is applied. In fact, Austin has presented an extension for the renormalized series procedure /22/ with the purpose of obtaining good results for $\lambda>1$. This author has pointed out /23/ that it is necessary to employ a FM-like formalism to get acceptable results in the large coupling regime ($1/\lambda\to 0$).

Let us now study the connection between the FM and the method discussed in §.17, that is to say, a normal rearrangement of operators /24/. As shown in §.17, the normal ordering (Wick-ordering) can be performed correctly for the quartic anharmonic oscillator, with the sole resort of defining a renormalized mass. The application of Eqs. in §.17 and Appendix F to the oscillator defined by Eq. (43.40), with K=2, allow us to know the relation between the Hamiltonian H and its normal rearrangement, :H:,

$$H = :H: - \frac{3\lambda}{4M^2} + M \tag{43.42}$$

where M is the renormalized mass. This mass was determined by Caswell /24/ in terms of the real mass m, by means of a generalization of the Wick ordering, upon introducing a parameter ℓ such that

$$m^2 = M^2 - \frac{1\lambda}{M} \quad , \ell \varepsilon R \quad . \tag{43.43}$$

The Wick ordering happens to be the particular case $\ell=3$. The parameter ℓ is obtained via a sensitivity criterion of the renormalized series (§.17):

$$E = M \sum_{n=0}^{\infty} E_M^{(n)} \, (\lambda/M^3)^n, \quad M = M(\lambda) \tag{43.44}$$

where coefficients $E_M^{(n)}$ are computed in such a manner that (43.44) gives rise to the RSPT series:

$$E = m \sum_{n=0}^{\infty} E^{(n)} (\lambda m^{-3})^n \tag{43.45}$$

In order to show that the FM contains as a particular case the Caswell method /24/, we resort to the general equations presented in §.42. From Eq. (42.18) we have

$$F = (1-\rho u)^{\beta/\alpha}\{A+1-\rho u+uB(u)\} = (1-\rho u)^{\beta/\alpha} \sum_{n=0}^{\infty} \bar{E}^{(n)} u^n \quad , \qquad (43.46a)$$

which can be transformed into the following equation

$$F = v^{\beta/\alpha} \sum_{n=0}^{\infty} \bar{E}^{(n)} (\lambda v^{-1/\alpha})^n \quad , \qquad (43.46b)$$

when one takes into account Eqs. (42.5), (42.12) and (42.13). Coefficients $\bar{E}^{(n)}$ are given by (43.39). Eq. (43.46b) reveals that the FM can be associated not only with Hamiltonian partitionings but also with a renormalized PT. For the anharmonic oscillator models $\beta/\alpha = -1/2$, so that Eq. (43.36b) yields

$$F = v^{-1/2} \sum_{n=0}^{\infty} \bar{E}^{(n)} \{\lambda v^{(K+1)/2}\}^n \quad . \qquad (43.47)$$

When K = 2, Eqs. (43.47) and (43.44) are equivalent to each other whenever the renormalized mass is taken as follows

$$v = m^2 M^{-2} \quad . \qquad (43.48)$$

The substitution of (43.48) into (43.47) gives

$$F = M \sum_{n=0}^{\infty} \{\bar{E}^{(n)} M^{3n-1}\} (\lambda M^{-3})^n \quad , \qquad (43.49)$$

hence,

$$E_m^{(n)} = \bar{E}^{(n)} m^{3n-1} \quad . \qquad (43.50)$$

The replacement of (43.48) into (42.9) completes the equivalence ($\alpha = -2/3$):

$$v + \lambda\rho v^{-1/\alpha} = m^2 M^{-2} + \lambda\rho m^3 M^{-3} = 1 \quad , \tag{43.51a}$$

$$\ell = \rho m^3 \quad . \tag{43.51b}$$

Naturally, if ρ and ℓ are determined by way of the same criterion the FM and Caswell method give the same result for the anharmonic oscillator models. Notice, nevertheless, that Caswell resorts to renormalized mass and normal ordering concepts to sum the PT, but these arguments are exclusively valid for the quartic anharmonic oscillator modes. For $F \geq 3$ there is no longer any justification to keep the same equations from the normal ordering standpoint. On the contrary, the FM is based on eigenvalue asymptotic expansions and they allow us to construct equations of general validity, such as (43.46b). The analysis performed here makes clear that the FM permits one to generalize methods based on the renormalization of the PS of quantum mechanical system eigenvalues, and the expression of such generalization is Eq. (43.46b).

Eq. (42.5) was proposed in §.42 to determine q preserving the fundamental structure of the VF extreme condition within the VFM formalism. Here, the connection established with the method based upon the normal ordering allows us to have a different point of view: this equation can be seen as a generalization of the one determining a renormalized perturbative parameter. This relationship shows once more that the fundamental common contents of all these summation methods are originated from scaling relationships arising from the Hamiltonian.

In order to complete the present discussion we turn to study the relation among the FM and the summation methods presented in §.18. The order-dependent transformations (ODT) /25,26/ have been used to sum with a great accuracy perturbative expansions of anharmonic oscillators and simple field theories /25/, as well as the ground state of the hydrogen atom in a magnetic field /26/.

The method consists of a change of variables, from the original λ

to a new g, in terms of the following transformation (§.18):

$$\lambda = \xi g(1-g)^{-s} \quad , \tag{43.52}$$

where ξ is an adjustable parameter introduced to minimize the error of the truncated series. The transformation (43.52) was employed by Seznec and Zinn-Justin /25/ to study the anharmonic oscillator models but it is quite different regarding that one chosen by Le Guillou and Zinn-Justin /26/ for the Zeeman effect. Different s values were employed in Ref. /25/ to compare the convergence behavior of the g power series expansion and the authors found that s = 3/2 is a suitable choice, as it should be from a Hamiltonian partition (similar to (43.37)).

Eq. (43.53) can be immediately related with the transformation $\lambda \to u$ or $\lambda \to v$ in the FM. The identification

$$\xi = 1/\rho, \quad g = \rho u, \quad s = -1/\alpha \tag{43.53}$$

transforms (43.52) into (42.17). Then, it is evident that if $\alpha = -2/3$ for the quartic anharmonic oscillator (K=2) then we are led to s = 3/2 (used in Ref. /25/). Consequently, it follows at once that whenever s and ξ are chosen as in (43.53), the FM will yield the same results as the ODT method. Likewise, the FM provides a systematic method to build such transformations according to the asymptotic properties of the function $E(\lambda)$.

Recently, it has been discussed another definition of the perturbation parameter to sum the RSPT, in relation with the Padé (§.13) and Borel-Padé (§.14) methods. The procedure was applied to screened Coulombic potential models (whose importance is analysed in Appendix G). For the sake of simplicity, we comment on the method for the following radial Hamiltonian:

$$H(Z,\lambda) = \frac{1}{2}p^2 - \frac{Z}{r} + \lambda r \quad , \tag{43.54}$$

studied in Refs. /27-30/. The Symanzik Theorem (Appendix A) assures us the fulfilment of the unitary equivalence:

$$H(Z,\lambda) = \lambda^{2/3}\, H(Z\lambda^{-1/3},1) \quad . \tag{43.55a}$$

Moreover, $E(\lambda)$ can be expanded as

$$E(\lambda) = \lambda^{2/3} \sum_{n=0}^{\infty} e^{(n)}\, \lambda^{-n/3} \quad . \tag{43.55b}$$

In agreement with the transformation (43.55a), the change of variables

$$\lambda' = \lambda(1+\gamma\lambda)^{-1/3} \tag{43.56}$$

was applied in Refs. /27-31/ to build a λ' power series expansion. When using (43.56) consistently with the property (43.55), it is necessary to resort to Padé $|N+1/N|$ or Borel-Padé approximants in the variable λ'. But such transformation does not lead to a $\lambda^{-1/3}$-power series expansion of $E(\lambda)$ when $\lambda>>1$. This can be plainly seen since:

$$\lambda' = \lambda^{2/3}\, \gamma^{-1/3}\, (1+\frac{1}{\gamma\lambda})^{-1/3} \simeq \lambda^{2/3}\gamma^{-1/3}\, \{1-\frac{1}{3\gamma\lambda}+O(\lambda^{-2})\}, \tag{43.57}$$

is not coincident with (43.55b).

The application of the FM permits us to find out the correct transformation (Eqs. (42.17) and (43.55b)):

$$\lambda = u(1-\rho u)^{-3} \quad . \tag{43.58}$$

Eq. (43.58) will be used in a next chapter to show the advantages of applying the FM.

Summing up, we have seen how a variety of methods designed to sum perturbation series can be described in an unified manner as limit cases of the FM. Likewise, this method permits one to understand clearly the existing common element in all these methods.

We have discussed in this section how the FM formulated in §.42 from the $E(\lambda)$ asymptotic expansions leads to scaling relations. These relations can be deduced from the Hamiltonian of which $E(\lambda)$ is an eigenvalue. This fact suggests us that the FM can be also formulated starting from dilatation relationships, instead of asymptotic expansions. This is the subject of the next paragraph.

§.44. Formulation of the FM from scaling laws (dilatation relationships).

The FM is presented here following a different viewpoint. This formalism is the most appropriate to make the numerical applications in the next chapters, so that we give a detailed account of it. Some results to be discussed in this section can be found in Refs. /32,33/.

Let $E(Z,\lambda)$ be an unknown real function depending on two real variables $0 \leq Z, \lambda < \infty$. The approach is wholly general, so that $E(Z,\lambda)$ does not need to be the eigenvalue of any Hamiltonian.

Our starting point is the expansion in λ-power series (Taylor expansion)

$$E(1,\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n \qquad (44.1)$$

that we want to transform into a convergent sequence. In order to achieve this, let us consider that there exists the following relationship

$$E(Z,\lambda) = \lambda^{\beta} E(Z\lambda^{\alpha},1) \quad , \qquad (44.2)$$

where α,β are real constants. We will call (44.2) "dilatation relation-

ship" or "rescaling relationship", since it represents a property allowing a change of scale (or units) in the E expression.

As we are considering a quite general problem, Eq. (44.2) does not necessarily imply the existence of a λ^{α} power series expansion about $1/\lambda = 0$. In order to exist such an expansion, it is required that $E(Z,\lambda)$ can be expanded in Z power series about $Z = 0$. From Eq. (44.2) we know that whenever $E(Z,1)$ can be expanded in Z-power, with coefficients $\{e^{(n)}\}$, then $E(1,\lambda)\lambda^{-\beta}$ can be expanded in λ^{α}-power series with the same set of coefficients.

A brief comment on the nature of the FM approximation is in order. The FM is suitable to approach $E(1,\lambda)$ functions that can be expanded in λ-power series about $\lambda=0$, and in λ^{α}-power series about $1/\lambda=0$. This is the case for anharmonic oscillator systems and confining potential models (Appendices B and G, respectively). If the problem under consideration fulfuls a dilatation relationship like (44.2), but does not admit a Z-power series expansion, in principle, results will not be completely satisfactory. This is due to the fact that, by construction, the functional will be forced to have a λ^{α}-power series expansion. This situation occurs, for example, in the Zeeman effect of the hydrogen atom (Appendix I).

Eq. (44.2) may be rewritten in an alternative way. We start from

$$\lambda = bc \qquad (44.3a)$$

with b,c two arbitrary constants. The replacement of (44.3a) into (44.2) gives

$$E(Z,\lambda) = E(\lambda,bc) = b^{\beta}c^{\beta}E(Zb^{\alpha}c^{\alpha},1) = b^{\beta}E((Zb^{\alpha}),c) \quad . \qquad (44.3b)$$

The choice

$$Zb^{\alpha} = 1 \quad ,$$

in (44.3b) yields

$$E(Z,\lambda) = Z^{-\beta/\alpha}\, E(1,Z^{1/\alpha}) \quad . \tag{44.4}$$

Eqs. (44.2) and (44.4) are equivalent to each other, and are obtained as particular cases of (44.3b).

For the sake of convenience, we define the following function

$$\bar{E}(k,w) = E(k(1-w),w) \quad , \tag{44.5}$$

where k and w are two real variables. The application of the scaling law (44.3) to (44.5) allows one to get

$$\bar{E}\,(k,w) = \{k(1-w)\}^{-\beta/\alpha}\, E(1,w(k(1-w))^{1/\alpha}) \quad . \tag{44.6}$$

In order to construct a convergent sequence toward $E(1,\lambda)$ we proceed as follows: defining

$$\lambda = wk^{1/\alpha}(1-w)^{1/\alpha} \quad , \tag{44.7}$$

from (44.6) we have

$$E(1,\lambda) = k^{\beta/\alpha}(1-w)^{\beta/\alpha}\, \bar{E}(k,w) \tag{44.8a}$$

$$= \lambda^{\beta} w^{-\beta}\, \bar{E}(k,w) \quad . \tag{44.8b}$$

Eq. (44.7) determines the w value as a function of k and λ. It is straighforward to prove that the substitution

$$w = \rho u \tag{44.9a}$$

$$k = \rho^{-\alpha} \tag{44.9b}$$

in (44.7) leads us to Eq. (42.17) for the variable u:

$$\lambda = u\{1-\rho u\}^{1/\alpha}$$

This equivalence is very illustrative and makes sure that the change of variables suggested in §.42 (see Eq. (42.5)) retains all the relevant information contained within the functional extreme condition. In view of this equivalence, the same results found in §.42 for (42.5) are valid for the w roots of (44.7). For the sake of completeness we write the results in terms of w, although it is not necessary to prove them.

Lemma 44.1: There exists only one root w such that $(wk^{1/\alpha}\lambda^{-1}) \varepsilon |0,1|$ if $\lambda k^{-1/\alpha} > 0^*$.

Lemma 44.2: Variable w is bounded: $\lim_{\lambda\to 0} w = 0$, $\lim_{\lambda\to\infty} w = 1$, if $\rho>0^*$.

Notice that, from Eqs. (42.5), (42.12), (42.13) and (44.9a),

$$w = 1-v \quad . \tag{44.10}$$

The application of Lemma 44.2 (and the results summarized in Fig. 13.1) allows us to conclude that $w<0$ whenever $\lambda k^{-1/\alpha}<0$. This condition goes beyond those established by the Lemmas 44.1 and 44.2, so that we can add the following result on the basis of Lemma 42.2, Eqs. (44.9) and Fig. 13.1:

Lemma 44.3: i) when $-1 < \alpha < 0$ there are two roots $w \breve{\varepsilon}(-\infty,0|$ iff: $\alpha(\alpha+1)^{-(\alpha+1)/\alpha} \leq \lambda k^{-1/\alpha} \leq 0$. One of these roots varies between $-\infty$

and $\alpha/(\alpha+1)$ if $0 \geq \lambda k^{-1/\alpha} \geq \alpha(\alpha+1)^{-(\alpha+1)/\alpha}$, while the other one changes between $\alpha/(\alpha+1)$ and 0 if $\alpha(\alpha+1)^{-(\alpha+1)/\alpha} \leq \lambda k^{-1/\alpha} \leq 0$.

ii) There exists just one root $w \in (-\infty, 1]$ if $\lambda k^{-1/\alpha} \geq -1$ and $\alpha = -1$*.

In order to fulfil the condition i) of Lemma 44.3 we should have $\lambda<0$ and $k>0$, because only in particular cases $k^{-1/\alpha}<0$.

In order to build the sequence that approximates $E(1,\lambda)$, it is necessary to find out an appropriate expression for $\bar{E}(k,w)$. Assuming the validity of the $\bar{E}$ expresion

$$\bar{E}(k,w) = \sum_{n=0}^{\infty} \bar{E}^{(n)} w^n \quad , \quad \bar{E}^{(n)} \equiv \bar{E}^{(n)}(k) \qquad (44.11)$$

we are led towards a w-power series expression for $E(1,\lambda)$. Then, coefficients $\bar{E}^{(n)}$ can be obtained in terms of $E^{(n)}$ in the expansion (44.1).

In order to achieve this, (44.1) is substituted into (44.8a)

$$\sum_{n=0}^{\infty} \bar{E}^{(n)} w^n = k^{-\beta/\alpha}(1-w)^{-\beta/\alpha} \sum_{n=0}^{\infty} E^{(n)} \lambda^n \quad , \qquad (44.12)$$

and the use of (44.7) leads to

$$\sum_{n=0}^{\infty} \bar{E}^{(n)} w^n = k^{-\beta/\alpha} \sum_{n=0}^{\infty} E^{(n)} k^{n/\alpha} w^n (1-w)^{(n-\beta)/\alpha} =$$

$$= \sum_{n=0}^{\infty} \sum_{j=0}^{\infty} k^{(n-\beta)/\alpha} (-1)^j E^{(n)} \binom{(n-\beta)/\alpha}{j} w^{j+n} \quad . \qquad (44.13)$$

The identification of coefficients at both sides of (44.13) yields the desired formula for the coefficient $\bar{E}^{(m)}$:

$$\bar{E}^{(m)} = \sum_{j=0}^{M} (-1)^{m-j} \binom{(j-\beta)/\alpha}{m-j} E^{(j)} k^{(j-\beta)/\alpha} \qquad (44.14)$$

The comparison between Eqs. (44.14) and (42.26) makes evident that coefficients $\bar{E}^{(n)}$ can be related with $b^{(n)}$ of the FM. To find such a relation, Eq. (44.9b) must be employed in (44.14):

$$k^{(\beta/\alpha-m/\alpha)} \bar{E}^{(m)} = \sum_{j=0}^{M} (-1)^{m-j} \rho^{m-j} \binom{(j-\beta)/\alpha}{m-j} E^{(j)} , \qquad (44.15)$$

and from (42.26) we find the result

$$\bar{E}^{(m)} = k^{(m-\beta)/\alpha} \{ (A+1)\delta_{m0} - k^{-1/\alpha}\delta_{m1} + b^{(m-1)}(1-\delta_{m0}) \} . \qquad (44.16)$$

This last relationship shows that $\bar{E}^{(m)}$ can be computed similarly to what was done before, involving rational numbers $b_j^{(n)}$ (Eq. (42.28)).

The properties of the combinatorial numbers (Eq. (42.21) allow us to deduce from Eq. (44.14) another useful relation

$$\bar{E}^{(m)} = \sum_{j=0}^{m} \frac{(a+bj+m-j-1)!}{(m-j)!(a+bj-1)!} E^{(j)} k^{-a-bj}, a=\beta/\alpha, b=-1/\alpha . \qquad (44.17)$$

The equivalence found so far between the formalisms developed in §.42 and §.44 reveals the close relationship between the use of asymptotic expansions to approach the function $E(1,\lambda)$ (Eqs. (42.1) and (42.2)), and the scaling laws (Eqs. (44.2) and (44.4)).

The sequence that approximates $E(1,\lambda)$ can be obtained via the truncation of the expansion (44.11). Including up to the N-th order PT, we have:

$$SE_N = k^{\beta/\alpha}(1-w)^{\beta/\alpha} S_N(k,w) ; S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)}(k) w^n , \qquad (44.18)$$

where N = 1,2,... is the number of RS coefficients incorporated into the sequence SE_N (cf.Eq. (44.14)). The following condition holds regarding the convergence properties of the sequence SE_N:

$$\lim_{N\to\infty} SE_N = E(1,\lambda), \text{ iff } \lim_{N\to\infty} S_N(k,w) = \bar{E}(k,w) \quad . \tag{44.19}$$

The parameter k plays an essential role in the FM (as it arises from the discussion made for ρ in (§.43) for accelerating the convergence rate of SE_N toward $E(1,\lambda)$. In order to establish a convergence criterion that allows us to choose k, we proceed as follows. By taking the limit in (44.3b), and using the Lemma (44.2), we have

$$\lim_{\lambda\to\infty} \{\lambda^{-\beta} E(1,\lambda)\} = \bar{E}(k,1) \quad . \tag{44.20}$$

On the other hand, the scaling law gives

$$\lim_{\lambda\to\infty} \{\lambda^{-\beta} E(1,\lambda)\} = E(0,1) \tag{44.21}$$

which leads us to the following result

$$\bar{E}(k,1) = E(0,1) \tag{44.22}$$

Eq. (44.22) shows that $\bar{E}(k,1)$ must be independent of k. This equation and Eq. (44.19) indicate that the graph $S_N(k,1)$ vs k must have a plateau whose extension should increase with N. Thence, an appropriate criterion will be to choose $k = k^*$, such that k^* belongs to this plateau. The k^* value determined in this way is, in general, dependent upon N. The criterion to be applied is simply that one represented by the Sensitivity Rules (§.43):

1) SP: $k^* = k^S_{N_2}$ such that $(\partial S_N/\partial k)\ (k = k^S_N,\ w = 1) = 0$ and minimum value of $(\partial^2 S_N/\partial k^2)\ (k = k^S_N,\ w = 1)$.

2) IP: $k^* = k_N^I$ such that $(\partial^2 S_N/\partial k^2)\ (k = k_N^I,\ w = 1) = 0$ with minimum value of $(\partial S_N/\partial k)\ (k = k_N^I,\ w = 1)$.

3) Inexistence of SP and IP: $k^* = \mathrm{Re}(k_N^S)$ with the lowest absolute value of the second derivative, or $k^* = \mathrm{Re}(k_N^I)$ with the lowest absolute value of the first derivative.

Now we can prove some relevant properties representing the sequence of SE_N extremes, and so to extract some conclusions about the k_N^S and k_N^I values. Likewise, since SE_N is our approximation to $E(1,\lambda)$, the conclusions to be derived are extended at once to $F^{(N)}$ (§.42), due to the conexions (44.9) and (44.16).

It is necessary here an auxiliar result regarding the dependence of the variable w with respect the parameter k. The derivation of (44.7), keeping λ constant, yields

$$0 = w^\alpha(1-w) + \{k\alpha w^{\alpha-1}(1-w) - kw^\alpha\}\left(\frac{\partial w}{\partial k}\right)_\lambda \quad , \tag{44.23}$$

and its rearrangement leads us to the desired equation:

$$\left(\frac{\partial w}{\partial k}\right)_k = w(1-w)/\{k\lfloor(\alpha+1)w-\alpha\rfloor\} \quad . \tag{44.24}$$

Theorem 44.1: The extremes k_N^S of the sequence $SE_N(k)$ are independent of λ.

Proof: We start from (44.13), rewritten as

$$SE_N = (1-w)^{\beta/\alpha} \sum_{n=0}^{N} \bar{\varepsilon}(n)\ w^n \quad ; \quad \bar{\varepsilon}(n) = k^{\beta/\alpha}\ \bar{E}(n) \quad ; \tag{44.25a}$$

considering (44.14) we have

$$\bar{\varepsilon}(n) = \sum_{j=0}^{n} (-1)^{n-j} \binom{(j-\beta)/\alpha}{n-j} E(j) k^{j/\alpha} \quad . \tag{44.25b}$$

The differentiation of (44.25a) with respect to k (λ constant) gives

$$\left(\frac{\partial SE_N}{\partial k}\right)_\lambda = -\frac{\beta}{\alpha}(1-w)^{\beta/\alpha-1}\left(\frac{\partial w}{\partial k}\right)_\lambda \sum_{n=0}^{N} \bar{\varepsilon}(n)\, w^n +$$

$$+(1-w)^{\beta/\alpha} \sum_{n=0}^{N} n w^{n-1}\, \bar{\varepsilon}(n) \left(\frac{\partial w}{\partial k}\right)_\lambda + (1-w)^{\beta/\alpha} \sum_{n=0}^{N} w^n \frac{\partial \varepsilon(n)}{\partial k} \quad . \qquad (44.26a)$$

A straightforward rearrangement, together with the use of Eq.(44.24), lead us to the result

$$P_N(w) = (1-w)^{-\beta/\alpha}\, k\{(\alpha+1)w-\alpha\} \left(\frac{\partial SE_N}{\partial k}\right)_\lambda = -\frac{\beta}{\alpha} w \sum_{n=0}^{N} \bar{\varepsilon}(n)\, w^n +$$

$$+(1-w) \sum_{n=0}^{N} n w^n\, \bar{\varepsilon}(n) + k\{(\alpha+1)w-\alpha\} \sum_{n=0}^{N} w^n \frac{\partial \bar{\varepsilon}(n)}{\partial k} \quad . \qquad (44.26b)$$

This last equation may be rewritten as follows:

$$P_N(w) = \sum_{n=0}^{N} \{(-\beta/\alpha+n)\, \bar{\varepsilon}(n)\, w^{n+1} + n\bar{\varepsilon}(n)\, w^n +$$

$$+ k(\alpha+1)\, w^{n+1} \frac{\partial \bar{\varepsilon}(n)}{\partial k} - \alpha k\, w^n \frac{\partial \bar{\varepsilon}(n)}{\partial k} \} \quad , \qquad (44.26c)$$

i.e.,

$$P_N(w) = \sum_{n=0}^{N+1} P_N(n)\, w^n \quad , \qquad (44.27a)$$

where

$$P_N^{(n)} = \{(-\beta/\alpha+1-n)\ \bar{\varepsilon}^{(n-1)} + (\alpha+1)k\ \frac{\partial\bar{\varepsilon}^{(n-1)}}{\partial k} + n\bar{\varepsilon}^{(n)} -$$

$$- \alpha k\ \frac{\partial\bar{\varepsilon}^{(n)}}{\partial k}\}\ ,\ n \leq N \qquad , \qquad (44.27b)$$

$$P_N^{(N=1)} = -(N+\beta/\alpha)\ \bar{\varepsilon}^{(N)} + k(\alpha+1)\ \frac{\partial\bar{\varepsilon}^{(N)}}{\partial k} \qquad . \qquad (44.27c)$$

Let us analyse carefully the coefficients (44.27b). To this end, we replace the coefficients $\bar{\varepsilon}^{(n)}$ by the expressions given in Eq. (44.25b). From the application of the auxiliary formulas

$$\bar{\varepsilon}^{(n)} = k^{n/\alpha}E^{(n)} + \sum_{j=0}^{n-1}(-1)^{n-j}\binom{(j-\beta)/\alpha}{n-j}E^{(j)}k^{j/\alpha}\ , \qquad (44.28a)$$

$$k\ \frac{\partial\bar{\varepsilon}^{(n)}}{\partial k} = \frac{n}{\alpha}k^{n/\alpha}E^{(n)} + \sum_{j=0}^{n-1}\frac{1}{\alpha}(-1)^{n-j}\binom{(j-\beta)/\alpha}{n-j}E^{(j)}k^{j/\alpha}\ , \qquad (44.28b)$$

it is easy to verify that the contribution to $E^{(n)}$ cancels out, so that

$$P_N^{(n)} = \sum_{j=0}^{n-1}(-1)^{n-j}E^{(j)}k^{j/\alpha}\{\binom{(j-\beta)/\alpha}{n-j-1}\ |n-1+\beta/\alpha-j-\partial/\alpha| +$$

$$+ \binom{(j-\beta)/\alpha}{n-j}\ (n-j)\} \qquad . \qquad (44.29a)$$

Taking into consideration that:

$$\binom{(j-\beta)/\alpha}{n-j} = \frac{((j-\beta)/\alpha)((j-\beta)/\alpha-1....((j-\beta)/\alpha - n+j+1)}{(n-j)!} =$$

$$= \binom{(j-\beta)/\alpha}{n-1-j} \frac{(j-\beta)/\alpha - n+j+1}{n-j} \quad , \tag{44.29b}$$

we obtain from (44.29a)

$$P_N^{(n)} = 0 \quad ; \quad 0 \leq n \leq N \tag{44.30}$$

Then, the only contribution to $P_N(w)$ comes from (44.27c), that is:

$$\left(\frac{\partial SE_N}{\partial k}\right)_\lambda = \frac{(1-w)^{\beta/\alpha} w^{N+1}}{k\{(\alpha+1)w-\alpha\}} P_N^{(N+1)}(k) \quad . \tag{44.31}$$

Using Lemmas 44.1 and 44.2, it is easy to see that

$$\left(\frac{\partial SE_N}{\partial k}\right)_\lambda (k = k_N^S) = 0 \quad \text{iff} \quad P_N^{(N+1)}(k_N^S) = 0, \ \forall \lambda, w, \tag{44.32}$$

therefore the stationary points of the sequence SE_N are determined by the N polynomial roots (Eqs.(44.27c), (44.28a) and (44.28b)):

$$\sum_{j=0}^{N} (-1)^{N-j} E^{(j)} (k_N^S)^{j/\alpha} \{j+j/\alpha-(N+\beta/\alpha)\} = 0 \tag{44.33}$$

independently of the λ-value.*

This Theorem possesses a fundamental importance since it assures us that the SE_N extremes do not change even when $\lambda \to \infty$. Consequently, taking into account that, from Eqs. (44.13), (44.8b) and Lemma 44.2,

$$\lim_{\lambda \to \infty} \lambda^{\beta} SE_N = S_{N(k,1)} \quad , \tag{44.34}$$

then by Theorem 44.1 one can commute the limit with the derivative respect of k (λ constant), and get:

$$\lim_{\lambda\to\infty} \{\lambda^{-\beta}(\frac{\partial SE_N}{\partial k})_\lambda\} = (\frac{\partial S_N(k,1)}{\partial k}) \quad . \tag{44.35}$$

This equation assures that the SE_N extremes (Eq. (44.33)) are the same as those of the sequence $S_N(k,1)$:

$$(\frac{\partial S_N(k,1)}{\partial k})(k = k_N^S) = (\frac{\partial SE_N}{\partial k})(k = k_N^S) = 0, \ \lambda < \infty \quad . \tag{44.36}$$

Above result allows us to affirm that if $S_N(k_N^S,1)$ converges to $E(0,1)$ (Eq.(44.22)), then SE_N will tend toward $E(1,\lambda), \forall\lambda$, since $w<1$ whenever $\lambda<\infty$. Notice that the sequence $S_N(k,1)$ represents the most unfavourable case to sum the series (44.1) around $\lambda<\infty$, since it corresponds to the study at the limit $1/\lambda\to 0$. This new formulation of the FM is particularly suitable to analyse the convergence rate of the sequence SE_N within the whole range of λ-values. It will be employed in the forthcoming chapters to perform different applications.

In addition, Theorem (44.1) proves the relation (43.23) for the sequence $F^{(N)}$ (see §.43).

There are also some general properties for the IP's of the sequence SE_N.

Theorem 44.2: IP's k_N^I of the sequence SE_N change within a finite interval, when λ increases from 0 to ∞.

Proof: Let us start deriving Eq. (44.31) with respect to k:

$$(\frac{\partial^2 SE_N}{\partial k^2})_\lambda = \{\frac{(N+1)w^N(1-w)^{\beta/\alpha}}{k|(\alpha+1)w-\alpha|} P_N(N+1) = \frac{\beta w^{N+1}(1-w)^{\beta/\alpha-1}}{\alpha k|(\alpha+1)w-\alpha|} P_N(N+1) -$$

$$-\frac{(\alpha+1)w^{N+1}(1-w)^{\beta/\alpha}}{k|(\alpha+1)w-\alpha|^2} P_N^{(N+1)}\}\left(\frac{\partial w}{\partial k}\right)_\lambda - \frac{w^{N+1}(1-w)^{\beta/\alpha}}{k^2|(\alpha+1)w-\alpha|} P_N^{(N+1)} +$$

$$+ \frac{w^{N+1}(1-w)^{\beta/\alpha}}{k|(\alpha+1)w-\alpha|} \frac{\partial P_N^{(N+1)}}{\partial k} \quad . \qquad (44.37)$$

Taking into account Eqs. (44.24) and (44.31), we can write Eq.(44.37) in a more compact manner by introducing $\left(\frac{\partial SE_N}{\partial k}\right)_\lambda$:

$$\left(\frac{\partial^2 SE_N}{\partial k^2}\right)_\lambda = \{\left|\frac{N+1}{w} - \frac{\beta}{\alpha(1-w)} - \frac{\alpha+1}{(\alpha+1)w-\alpha}\right| \frac{w(1-w)}{k|(\alpha+1)w-\alpha|} +$$

$$+ \frac{1}{P_N^{(N+1)}} \frac{\partial P_N^{(N+1)}}{\partial k} - \frac{1}{k}\} \left(\frac{\partial SE_N}{\partial k}\right)_\lambda \quad . \qquad (44.33)$$

On the basis of Eq. (44.38), we see that SP and IP cannot be coincident in general terms, since Theorem 44.1 establishes that SP are the roots of $P_N^{(N+1)}$. Therefore, IP's are determined by the zeros of the term between curly brackets, which can be rewritten as:

$$\{N\alpha(\alpha+1)(w-w^2) - (N+1)\alpha^2(1-w) - \frac{\beta w^2}{\alpha}(\alpha+1) + \beta w\} P_N^{(N+1)} +$$

$$+ k\alpha\{(\alpha+1)w-\alpha\}^2 \frac{\partial P_N^{(N+1)}}{\partial k} - P_N^{(N+1)} \alpha\{(\alpha+1)w-\alpha\}^2 = 0 \quad . \qquad (44.39)$$

Eq. (44.39) represents an N-degree polynomial whose roots are k_N^I. Notice that the polynomial coefficients depend upon w but not on λ. Accordingly (Lemma 44.2) they are bounded for $0 \leq \lambda < \infty$, so that the same happens with the polynomial roots.*

Precedent result assures us that k_N^I depends on λ; then the IP's of $S_N(k,1)$ (Rule 2) are the IP's of $\lambda^{-\beta} SE_N$ only when $\lambda \to \infty$. These k values will be employed to study the convergence of the sequence SE_N for $N \to \infty$.

At this point, some comments on the actual application of the method may be useful and convenient. The approximation to the function $E(1,\lambda)$ is obtained analysing the SE_N ($=SE_N(k,w)$) convergence when the number of terms (N) increases. Since the function SE_N depends on the bounded variable w, one hopes that it makes up a better approximation to the original series. We will call SE_N a "renormalized sequence" or "renormalized series", by extension of the RSPT renormalized series (§.43). On the other hand, the application of the sensitivity Rules reduces the convergence research to the study of the critical points (IP and SP) of $S_N(k,1)$, which will be termed a renormalized sequence too, because it is related to the infinite coupling limit of the sequence SE_N.

It is possible to examine from another point of view why $SE_N(k,w)$ and $S_N(k,w)$ are renormalized sequences. Let us consider a Hamiltonian:

$$H(Z,\lambda) = p^2 + ZV_1 + V_2 \quad , \tag{44.40}$$

with associated eigenvalues $E(Z,\lambda)$. If $H(Z,\lambda)$ satisfies a dilatation relationship (unitary equivalence):

$$H(Z,\lambda) \simeq \lambda^{\beta} H(Z\,\lambda^{\alpha},1) \quad , \quad \alpha<0 \tag{44.41}$$

the eigenvalues satisfy the equality (44.2). Therefore, $\bar{E}(k,w)$ (Eq. (44.5)) is an eigenvalue of the following operator:

$$H(k(1-w),w) = p^2 + kV_1 + w(V_2 - kV_1) \tag{44.42}$$

which is a partitioned and renormalized Hamiltonian, due to the existing relationship between the λ and w variables. Then, we can see that $S_N(k,w)$ is a renormalized sequence that approximates the eigenvalues associated with (44.42), while $SE_N(k,w)$ approaches those related to (44.40).

Moreover, notice that $H(Z,\lambda)$ fulfils a scaling law like (44.41)

whenever V_1 and V_2 are homogeneous functions of the coordinates of degree $S = -2(\alpha+\beta)/\beta$ and $t = 2(1-\beta)/\beta$, respectively (Theorem 42.1).

In addition, let us remark that the FM involves an ODT, since k* is order-dependent (Eqs.(44.33) (44.39)) and $E(1,\lambda)$ is approximated by $SE_N(k_N^*,w)$. Although the Sensitivity Rules fix totally the k-value, the analytical dependence of k upon the order N is an important, open issue, which will be discussed in the next chapters.

Up to here, the problem that remains is to determine under which condition $S_N(k,1)$ converges toward $E(0,1)$ when $N\to\infty$. This is a very cumbersome mathematical problem and so far we cannot offer a complete and rigorous proof. However, we will study a number of examples, some of which can be analysed in a thorough way, to obtain general conclusions on the convergence properties of the renormalized sequence SE_N.

This section is completed with a brief discussion about a possible extension of the FM. Let us suppose that (44.1) fulfils a more general relationship than (44.2), for example

$$E(Z,\lambda) = f(\lambda^{\beta})E(Z\lambda^{\alpha},1) \quad . \tag{44.43}$$

Proceeding similarly as done at the beginning of this section, we start from the relation

$$E(Z,bc) = f(c^{\beta}b^{\beta})\ E(Zc^{\alpha}b^{\alpha},1)\ ,\ \lambda = bc \quad . \tag{44.44a}$$

The multiplication by $f(c^{\beta})$ and the use of (44.43) gives

$$f(c^{\beta})\ E(Z,\lambda) = f(c^{\beta}\lambda^{\beta})\ E(Zb^{\alpha},c) \quad . \tag{44.44b}$$

The choice $Zb^{\alpha} = 1$ and Eq. (44.44a) lead us to

$$E(Z,\lambda) = f(\lambda^{\beta})\ \{f(\lambda^{\beta}Z^{\beta/\alpha})\}^{-1}\ E(1,\lambda Z^{1/\alpha}) \quad . \tag{44.45}$$

A renormalized series can be constructed on the basis of Eq.(44.45)

$$\bar{E}(k,w) = E(k(1-w),w) = f(w^{\beta})\{f(w^{\beta}k^{\beta/\alpha}(1-w)^{\beta/\alpha})\}^{-1}E(1,wk^{1/\alpha}(1-w)^{1/\alpha}) \quad . \tag{44.46a}$$

and defining the parameter λ as

$$\lambda = wk^{1/\alpha}(1-w)^{1/\alpha} \tag{44.46b}$$

we find

$$E(1,\lambda) = \{f(w^{\beta})\}^{-1}f(w^{\beta}k^{\beta/\alpha}(1-w)^{\beta/\alpha})\bar{E}(k,w) \quad . \tag{44.46c}$$

The FM may be applied from Eqs. (44.46b) and (44.46c) whenever two conditions are fulfilled:

i) $E(Z,\lambda)$ may be expanded in Taylor series about $\lambda = 0$,

ii) $1/f(w^{\beta})$ and $f(w^{\beta}k^{\beta/\alpha}(1-w)^{\beta/\alpha})$ can be expanded in w power series.

The scaling laws (44.43) are not the most usual ones, so that we have this subject here. However, an eigenvalue problem of physico-chemical interest to be discussed in §.61 fulfils the dilatation law

$$E(1,\lambda) = e^{-\lambda}E(\lambda^{-1},1) \quad , \tag{44.47a}$$

$$\alpha = -1, \ \beta = 1, \ f(\lambda) = e^{-\lambda} \quad . \tag{44.47b}$$

In case a scaling law like (44.2) or (44.43) is not known one can directly resort to the asymptotic expansion of the function for $\lambda<<1$ and $\lambda>>1$ (Eqs.(42.1) and (42.2)). As seen in this paragraph, the FM

equations are equivalent to those deduced in §.42, so that exponents α and β may be obtained from these asymptotic expansions, and then employing the formalism developed here. Some illustrative examples of this procedure will be given in next chapters.

Finally, we can summarize the working scheme for the forthcoming chapters: the different applications to be studied will be analysed with the formalism displayed in this section since it is the most compact and best adapted for systematic studies of convergence. We will only make reference to the FM presented in §.42 in order to introduce simultaneously the information pertaining to both λ regimes (cf. Eq.(42.42)).

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CHAPTER XIV

PROPERTIES OF THE FM: SERIES WITH NON-ZERO CONVERGENCE RADII.

§.45. Simple eigenvalue problems with branch-point singularities.

The aim of this chapter is to analyse the possibilities of the FM to increase the convergence radii of the power series expansions of some simple functions. For this purpose, we will consider here functions that have square-root type branch-points. Such functions lead to power series expansions with nonzero finite convergence radius.

Firstly, we consider a simple two-level model which has been studied by several authors due to its interest in atomic and molecular physics /1-3/. This model is useful since its eigenvalues depend upon a parameter λ and presents a levels crossing in the complex plane λ. This problem appears frequently in the study of electronic levels of diatomic molecules within the context of the Born-Oppenheimer approximation /4/. Consequently, the model may be applied to mimic the interaction between two electronic states, laying aside the effect due to the remaining ones.

The model is defined by the following matrix representation of the Hamiltonian

$$H(Z,\lambda) = \begin{bmatrix} 3\lambda/2 & 2\lambda \\ 2\lambda & 4Z-3\lambda/2 \end{bmatrix} \quad . \tag{45.1}$$

Matrix elements have been chosen in such a way to have a strong coupling between both eigenvalues /2,3/, viz. the two levels cross for nonreal λ values. Recently, model (45.1) was analysed within the framework of the formalism developed in §.42 /5/. Here we use the formalism presented in §.44 to introduce the FM.

In order to start with the method, it is necessary a dilatation relationship, which is obtained at once from the matrix (45.1):

$$H(Z,\lambda) = \lambda \begin{vmatrix} 3/2 & 2 \\ 2 & 4Z\lambda^{-1-3/2} \end{vmatrix} = \lambda H(Z\lambda^{-1},1) \quad . \qquad (45.2)$$

This yields the following relation for the eigenvalues associated with H:

$$E_n(1,\lambda) = \lambda E_n(\lambda^{-1},1), \; n = 1,2 \qquad (45.3)$$

and the corresponding exponents $\beta = -\alpha = 1$, as shown in §.44.

According to the discussion in §.43, Eq. (45.3) assures us that for this problem the FM is an extension of the Euler's method /6,7/ and the GA /8,9/.

The two eigenvalues are given by the roots of the characteristic equation

$$\det(H-EI) = 0 \quad , \qquad (45.4)$$

which immediately leads to

$$E_{1,2}(1,\lambda) = 2 \pm \frac{1}{2} (25\lambda^2 - 24\lambda + 16)^{1/2}. \qquad (45.5)$$

Subindex 1 corresponds to the ground state (-sign) and 2 to the excited state (+ sign).

Function $E_{1,2}(1,\lambda)$ are analytical functions of λ within a finite domain determined by the branch-point singularities. Such singularities λ_b are defined by the level crossing

$$E_1(1,\lambda_b) = E_2(1,\lambda_b) \quad , \qquad (45.6)$$

i.e.

$$\lambda_b = \frac{12}{25} \pm \frac{16}{25} \quad . \tag{45.7}$$

As seen in §.14, the Taylor expansion of (45.5) converges within a disc of radius R, where

$$R = |\lambda_b| = \frac{4}{5} \quad . \tag{45.8}$$

Our proposal is to study the changes the FM produces on the convergence domain given by (45.3). To this end, we begin with the change of variables introduced by the FM. The substitution (45.3) in (44.7) yields

$$\lambda = wk^{-1} \ (1-w)^{-1} \Rightarrow w = \frac{\lambda k}{1+\lambda k} \quad . \tag{45.9}$$

From Eq. (44.3) we get the following expression for $E(1,\lambda)$

$$E(1,\lambda) = \frac{1}{k(1-w)} \ \bar{E}(k,w) \quad , \tag{45.10a}$$

which may be written as a power series in w:

$$E(1,\lambda) = \frac{1}{k(1-w)} \ \sum_{n=0}^{\infty} \bar{E}^{(n)} \ w^n \quad . \tag{45.10b}$$

Eq. (45.10b) assures us that $E(1,\lambda)$ can be written as a function depending on variable w. Accordingly, we will write $E(1,\lambda)$ in terms of w and study the convergence domain of the Taylor expansion in w powers.

First of all, the branch-point singularities have to be considered. Such singularities are given by the zeros of the square-root in (45.5).

The use of (45.9) gives the singularities w_b associated with λ_b (Eq. (45.7)):

$$w_b = \frac{k\lambda_b}{1+k\lambda_b} = \frac{k\lambda_b+k^2|\lambda_b|^2}{1+2k\mathrm{Re}\lambda_b+k^2|\lambda_b|^2} \quad , \tag{45.11a}$$

so that

$$|w_b| = \frac{|k||\lambda_b|}{(1+2k\mathrm{Re}\lambda_b+k^2|\lambda_b|^2)^{1/2}} \quad . \tag{45.11b}$$

The branch-points (45.7) imply that singularities w_b are located on a disc of radius R'

$$R' = |w_b| = |k| \frac{(400+384+256k^2)^{1/2}}{16k^2+24k+25} \quad . \tag{45.12}$$

The power series in w has, in addition, another singularity which is the pole

$$w_p = 1 \quad , \tag{45.13}$$

corresponding to $1/\lambda=0$.

In order to obtain the convergence region associated with the FM it is necessary to consider the two following cases:

i) If $R' < |w_p| = 1$ then (45.10b) converges in a disc of radius R', i.e.

$$-R' < w < R' \tag{45.14a}$$

The substitution of (45.9) into (45.14a), and a straightforward rearrangement of the resulting equation, allow us to find

$$-\frac{R'}{1+R'} < \lambda k < \frac{R'}{1+R'} + \frac{2\lambda kR'}{1+R'} \quad . \tag{45.14b}$$

The analysis of the r.h.s. inequality leads us to the following convergence region

$$-\frac{R'}{1+R'} < \lambda k < \frac{R'}{1-R'} \quad , \tag{45.14c}$$

that is to say

$$-\frac{R'}{k(1+R')} < \lambda < \frac{R'}{k(1-R')} \quad , k>0$$

$$-\frac{R'}{(1-R')|k|} < \lambda < \frac{R'}{(1+R')|k|} \quad , \quad k<0 \qquad . \qquad (45.14d)$$

ii) If $R'>|w_p| = 1$ then $E(1,\lambda(w))$ converges as a w-power series within a disc of radius $|w_p|$:

$$-1<w<1 \qquad . \qquad (45.15a)$$

To find out the convergence domain in terms of λ, it is necessary to compute the limit $R'\to 1$ in Eqs. (45.14d), and thus we have

$$-\frac{1}{2k} < \lambda < \infty \text{ if } k>0; \quad -\infty < \lambda < \frac{1}{2|k|} \text{ if } k<0 \qquad (45.15b)$$

To sum up, the application of the FM yields a w power series that converges within a disc, such that the w finite real interval is in correspondence with a λ finite real interval when the pair of branch points w_b determines the convergence domain, and semi-infinite when such a domain is determined by the pole w_p.

The transition between both regimes is defined by the k-value corresponding to the condition $R' = 1 = |w_p|$.

On the basis of Eq.(45.12), this last condition leads us to

$$384k^3 + 976k^2 + 1200k + 625 = 0 \qquad , \qquad (45.16)$$

whose only real root is:

$$k = -25/24. \qquad (45.17)$$

Result (45.17) shows the FM gives the exact seem the Taylor expansion for all λ in the range $-\infty<\lambda<\frac{1}{2}|k|$, when $k<-25/24$.

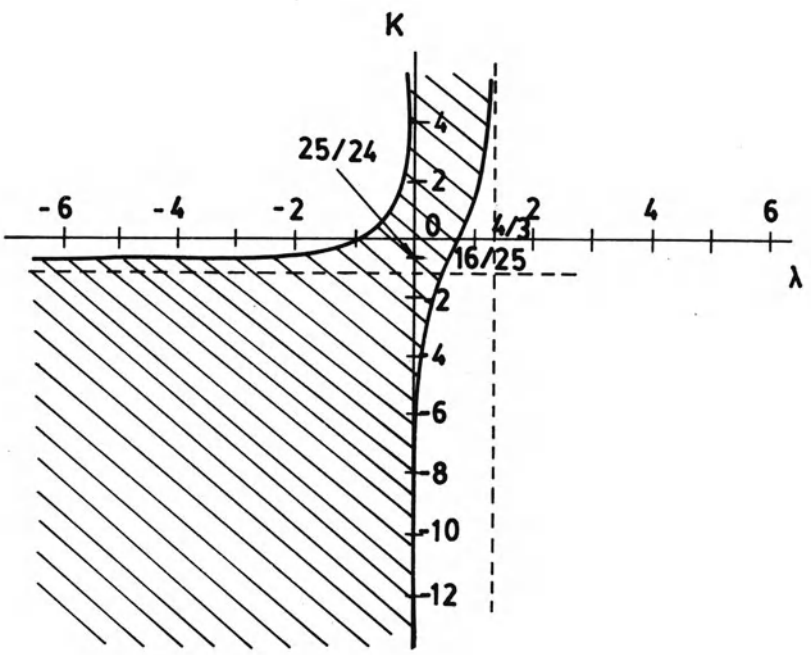

Fig. 14.1: Real plane k-λ for the ground state of the two-level system.
(The shadowed zone denotes the region where there is convergence when applying the FM).

Fig. 14.1 depicts the k-λ(real) plane, where the shaded area denotes the convergence intervals obtained from Eqs. (45.14d), (45.15b) and (45.12). The Figure makes clear that the FM extends appreciably the convergence regarding the eigenvalues original expansion in λ-power series; this expansion converges only for λ within the interval (-4/5, 4/5). As well, notice from Figure 14.1 that the MF allows one to sum the power series in a more efficiently way when $\lambda<0$.

Let us analyse some limit conditions of the convergence intervals. Considering that $\lim_{k\to 0} R'/k = 4/5$, then Eq. (45.14d) leads us to

$$-4/5 < \lambda < 4/5, \text{ when } k\to 0 \quad , \tag{45.18}$$

i.e. the λ-power series expansion corresponds to the limit $k\to 0$.

On the other hand, from (45.15b) it is found that

$$-\infty < \lambda < 0, \text{ when } k\to -\infty \quad . \tag{45.19}$$

Taking into account that (45.12) implies

$$R' \simeq 1 - \frac{3}{4k} + O(k^{-2}) \text{ when } |k| >> 1 \tag{45.20}$$

we find out at once another important asymptotic property for the convergence interval

$$0 < \lambda < \frac{4}{3} \text{ when } k\to\infty \quad . \tag{45.21}$$

The three limit conditions (45.18), (45.19) and (45.21) are clearly seen in Fig. 14.1.

Let us discuss briefly the relation with other summation methods. From Eqs. (14.11), (14.12), and inequalities (45.7), we deduce that

the Taylor expansion of function (45.5) is Borel summable (§.14) within the interval

$$-\infty<\lambda<\frac{|\lambda_b|^2}{Re(\lambda_b)}=\frac{4}{3} \quad . \tag{45.22}$$

The comparison of (45.22) with Eqs. (45.19) and (45.21) tells us that the FM sums the Taylor expansion (45.5) in the same region where the Borel transform is analytical. This result possesses general validity. In order to make explicit this point, let us consider an arbitrary function having as unique singularities the pair of branch-points (λ_b, λ_b^*), where

$$\lambda_b = \lambda_1+i\lambda_2 \; ; \; \lambda_1\neq 0, \; \lambda_2\neq 0 \tag{45.23}$$

From the discussion in §.14, we know the Borel transform of such a function is analytic in a region Ω given by Eqs. (14.11) and (14.12), so that the Borel method permits to sum the Taylor expansion in λ-power series within the following intervals:

$$-\infty<\lambda<\frac{|\lambda_b|^2}{Re(\lambda_b)} \quad \text{when } Re(\lambda_b)>0 \quad , \tag{45.24a}$$

$$-\frac{|\lambda_b|^2}{Re(\lambda_b)}<\lambda<\infty \text{ when } Re(\lambda_b)<0 \quad . \tag{45.24b}$$

Now we examine the result of combining the Borel method and FM, that is, applying such a transformation to the expansion (45.10b) in w-power series.

Let us analyse what happens when performing the change of variables (45.9). The singularities in the w variable are located in

$$w_b=\frac{\lambda_b k}{1+\lambda_b k} \; , \; w_b^*=\frac{\lambda_b^* k}{1+\lambda_b^* k} \; , \; w_p=1 \quad . \tag{45.25}$$

Since, from Eq. (45.9), one has:

$$\lim_{w\to-\infty} \lambda = -\frac{1}{k} \quad , \tag{45.26}$$

the following connections are found:

$$\text{If } k>0\text{: } w\varepsilon(-\infty,1| \text{ and } \lambda\ \varepsilon|-\frac{1}{|k|},\infty\ ) \quad , \tag{45.27a}$$

$$\text{If } k<0\text{: } w\varepsilon(-\infty,1| \text{ and } \lambda\ \varepsilon(-\infty,\frac{1}{k}| \quad . \tag{45.27b}$$

According to the singularities (45.25), the Borel method would allow us to sum the representation in a w power series within the interval $(-\infty,1|$. Then, the combination of the Borel transform and FM yields convergence in λ within the intervals (45.27). Now, in order to make (45.27) coincident with (45.24), it is necessary to choose k carefully. It is straightforward to prove that the suitable k value ($k=\bar{k}$) is that one locating w_b and w_b^* as singularities on the imaginary axis of the w plane: we make $w_b = i\gamma$ and then replace into (45.25):

$$\lambda_1\bar{k} + \bar{k}i\lambda_2 = -\frac{\gamma^2}{1+\gamma^2} + i\frac{\gamma}{1+\gamma^2} \quad . \tag{45.28}$$

The equality between the real and imaginary parts yields the desired result

$$\gamma = -\lambda_1/\lambda_2 = -\,\mathrm{Re}(\lambda_b)/\mathrm{Im}(\lambda_b) \quad , \tag{45.29a}$$

$$\bar{k} = -\,\lambda_1/(\lambda_1^2+\lambda_2^2) = -\mathrm{Re}(\lambda_b)/|\lambda_b|^2 \tag{45.29b}$$

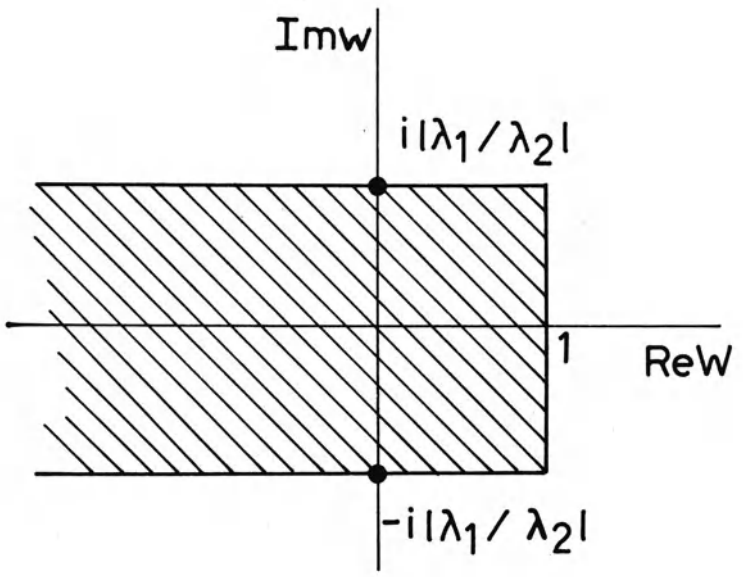

Fig. 14.2: Complex plane w for the function $E(1,\lambda)$ with a couple of the branch point conjugated singularities: $\lambda = \lambda_1 \pm i\lambda_2$. (k-value chosen according to Eq. (45.29). The shadowed area denotes Borel transform analyticity domain).

Fig. 14.2 depicts the complex plane w and the singularities location.

The optimum $\bar{k}$ value possesses the interesting property of maximizing the modulus of $|w_b|^2/k^2 = u_b^2$ (Eqs. (44.9a) and (44.9b)). It can be verified at once considering that

$$\frac{\partial}{\partial k}\left|\frac{|w_b|^2}{k^2}\right| = -\frac{1}{k}\,|w_b|^2\,(w_b + w_b^*) \quad , \qquad (45.30a)$$

and thus

$$\frac{\partial}{\partial k}\left|\frac{|w_b|^2}{k^2}\right|(k=\bar{k}) = 0 \text{ iff } (w_b+w_b^*)(k=\bar{k})=2\mathrm{Re}(w_b(k=\bar{k}))=0 \quad , \qquad (45.30b)$$

because $|w_b|>0$.

The precedent analysis enables us to extract the following conclusions:

i) FM allows one to sum a Taylor expansion within the convergence region of the Borel method, for a problem with a couple of singularities (λ_b,λ_b^*). This result is important, since the FM is easier to apply than the Borel method.

ii) If $\alpha = -1$, the FM transforms (by means of a suitable choice of k) the analyticity domain of the Borel transform, determined by (λ_b,λ_b^*), into another one specified by the purely imaginary singularities (w_b,w_b^*). This last point reveals, in a very simple case, the sort of conformal transformation introduced by the application of the FM.

The application of Eq. (45.29b) to the model (45.5) gives the k-value for which the singularities (other than w_p) are purely imaginary:

$$\bar{k} = -\frac{3}{4} \qquad (45.31)$$

Fig. 14.1 shows that when k is given by (45.31), FM sequences converge in a finite interval of λ, although larger than the one corresponding to the Taylor expansion.

The discussion presented before does not say anything regarding the convergence rate of the different methods (FM, Borel, Padé, etc.). The next paragraph is devoted to study numerically this issue, considering the simple model function (45.5) as an example.

§.46. Numerical Results for Simple Examples.

The simple model (45.1), whose eigenvalues are given by (45.5), is employed again to test numerically the approach discussed in preceding sections. In §.45 it was seen that the FM sums the Taylor expansion associated with (45.5) within the same region where it is Borel summable. We verify in this section that the convergence rate is greater when the FM is applied.

Let us consider the ground state E_1.

$$E_1(1,\lambda) = 2 - 2(1-\frac{3}{2}\lambda+\frac{25}{16}\lambda^2)^{1/2} \quad , \tag{46.1}$$

though the conclusions are the same for E_2. Taking into consideration that:

$$(1+a\lambda+b\lambda^2)^{1/2} = (1+a\lambda\{1+\frac{b\lambda}{a}\}^{1/2} = \sum_{n=0}^{\infty} \binom{1/2}{n} a^n\lambda^n(1+\frac{b\lambda}{a})^n =$$

$$= \sum_{n=0}^{\infty} \sum_{m=0}^{n} \binom{1/2}{n} \binom{n}{m} a^{n-m} b^m \lambda^{n+m} \tag{46.2}$$

where combinatorial coefficients are given by (42.21), we are led at once to the λ power series expansion of (46.1) (which serve a RSPT):

$$E_1^{(0)} = 0 \tag{46.3a}$$

$$E_1^{(n)} = -2(-\frac{24}{25})^n \sum_{s=0}^{n} \binom{1/2}{s} \binom{s}{n-s} (\frac{36}{25})^s \quad , \quad n\geq 1 \ . \tag{46.3b}$$

We present an illustrative application of the FM including a small number of terms. From (46.3) it is found that the first five terms are

$$E_1(1,\lambda) = \frac{3}{2}\lambda - \lambda^2 - \frac{3}{4}\lambda^3 - \frac{5}{16}\lambda^4 + \frac{9}{64}\lambda^5 + \ldots \tag{46.4}$$

To the purpose of determining the renormalized sequence $SE_N(k,w)$ we resort to the equations discussed in §.44: Eq. (45.2) establishes that $\beta = -\alpha = 1$ in this case, which leads us to the following set of equations to apply the FM (Eqs. (44.7), (44.8), (44.11) and (44.14)):

$$E_1(1,\lambda) = k^{-1}(1-w)^{-1}\,\bar{E}(k,w) \tag{46.5a}$$

$$w = \frac{\lambda k}{1+\lambda k} \tag{46.5b}$$

$$\bar{E}(k,w) = \sum_{n=0}^{\infty} \bar{E}^{(n)}\, w^n \tag{46.5c}$$

$$\bar{E}^{(n)} = \sum_{j=0}^{n} (-1)^{n-j} \binom{1-j}{n-j} E_1{}^{(j)} k^{1-j} \tag{46.5d}$$

The N-th order truncated sequences are then (Eq.(44.18)):

$$SE_N = k^{-1}\,(1-w)^{-1}\,S_N(k,w) \tag{46.6a}$$

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)}\, w^n \tag{46.6b}$$

The choice of the first three terms in Eq. (46.4) allows us to obtain the first coefficients $\bar{E}^{(n)}$ by way of Eq.(46.5d):

$$\bar{E}^{(0)} = 0$$

$$\bar{E}^{(1)} = \frac{3}{2}$$

$$\bar{E}^{(2)} = -\frac{1}{k}$$

$$\bar{E}^{(3)} = -\left(\frac{1}{k} + \frac{3}{4k^2}\right)$$

$$\bar{E}^{(4)} = -\left(\frac{1}{k} + \frac{3}{2k^2} + \frac{5}{16k^3}\right)$$

$$\bar{E}^{(5)} = -\frac{1}{k} - \frac{9}{4k^2} - \frac{15}{6k^3} + \frac{9}{64k^4} \qquad (46.7)$$

The renormalized series truncated up to the third-order is

$$SE_3 = \frac{\lambda^3(3k^2/2-2k-3/4)+\lambda^2(3k-1)+3\lambda/2}{1+2k\lambda+\lambda^2k^2} \qquad (46.8)$$

A straightforward computation shows that SE_3 possesses only one SP as a function of k:

$$\left(\frac{\partial SE_3}{\partial k}\right)_{\lambda} (k=k^*=k_3^s) = 0 \; ; \; k_3^s = -3/4 \qquad (46.9)$$

where k_3^s is the k-optimum value according to the Sensitivity Rules of §.44. Now, replacing (46.9) in (46.8) we have

$$E_1(1,\lambda) \simeq SE_3(k_3^s) = \frac{3\lambda}{2}\left|\frac{1-17\lambda/21}{1-3\lambda/4}\right| \qquad (46.10)$$

which is precisely the Padé approximant $|2/1|$ corresponding to the λ-power series expansion (see Appendix D). This result verifies the conclusions established in §.43 when discussing the connection between the FM and GA. Eq. (43.22) gives in our case

$$k^* = -E^{(3)}/E^{(2)} = -3/4 \qquad (46.11)$$

which coincides with (46.9). Notice that the k-value is negative, which assures an enlarged convergence interval with respect to the

Taylor expansion (see Fig. 14.1). Moreover, $k = \bar{k}^*$ (Eq. (45.31)), what locates the branch-point singularities in the imaginary axis of the variable w.

From the knowledge of coefficients (46.7) it is easy to compute higher orders of the renormalized series.

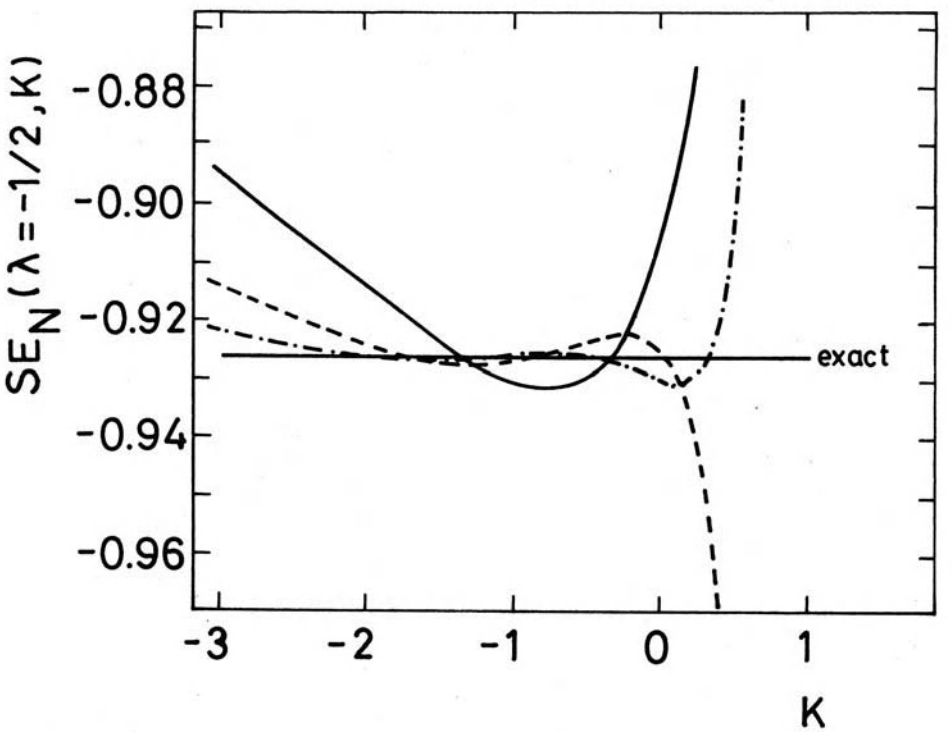

Fig. 14.3: Approximation to the two level system lowest eigenvalue (for $\lambda = -1/2$) by way of several renormalized sequences $SE_N(k,w)$.

———— N = 3
--------- N = 4
-.-.-.-.- N = 5

Fig. 14.3 compares SE_3, SE_4 and SE_5 as functions of k. The exact result is displayed too for the sake of completeness.

A careful perusal at Fig. 14.3 allows us to confirm our predictions:

i) Sequences $SE_N(k,w(\lambda))$, as functions of k, present a plateau that tends to increase with N;

ii) The plateau corresponds to an oscillation about the exact result;

iii) The oscillation amplitude of the plateau decreases when N increases;

iv) The oscillations mainly locate in the zone $k<0$, where the convergence interval of the renormalized series is greater if $\lambda<0$ ($\lambda= -1/2$ in our example).

Sequences SE_4 and SE_5 have the following SP's:

$$k_4^s = -\ 5/4 \qquad (46.12a)$$

$$k_5^s = -3/4 \quad ; \quad k_5^s = -1.61602540378 \qquad (46.12b)$$

According to the Sensitivity Rules (§.44), the second value in (46.12b) must be chosen.

Previous results permit us to compute $SE_N(k_N^s,w)$ as a function of λ. Table 14.1 compares the results, with those arising from the series (46.4), as well as the exact ones.

Table 14.1:

Lowest eigenvalue of the two level model (45.1) studied by means of the sequences SE_N for several λ-values.[a)]

$-\lambda$	$-SE_3$	$-SE_4$	$-SE_5$	$-E^{b)}$	$-E_1(1,\lambda)^{c)}$
0.5	0.9318	0.9275	0.9267	0.9302	0,9262
1.0	2.0714	2.0432	2.0367	2.2031	2.0311
1.5	3.3088	3.2368	3.2195	4.6186	3.2022
2.0	4.6000	4.4694	4.4375	10.5000	4.4031
2.5	5.9239	5.7243	5.6753	24.2212	5.6199

a) Results correspond to the stationary points $SE_N(k_N^S, w)$.

b) Series (46.4) up to the fifth order.

c) Exact result (Eq.(46.1)).

We can see that the renormalized series converges faster than the Taylor expansion. Beyond the convergence interval the FM gives quite acceptable results, in spite of the small number of terms considered.

Table 14.2:

Lowest eigenvalue of the two level model (45.1) computes with different methods.

$-\lambda$	$SE_5^{a)}$	$-E^{\|3/2\|b)}$	$-E'^{\|3/2\|c)}$	$-SE_6'^{d)}$	$-E_1(1,\lambda)^{e)}$
0.5	0.9258 0.9267	0.9260	0.9257	0.9263	0.9262
1.0	2.0248 2.0367	2.0283	2.0216	2.0326	2.0311
1.5	3.1769 3.2195	3.1915	3.1604	3.2059	3.2022
2.0	4.3440 4.4375	4.3793	4.2978	4.4097	4.4031
2.5	5.5130 5.6753	5.5783	5 4174	5.6293	5.6199

a) Results obtained by way of the FM. The first value corresponds to $k_5^S=-3/4$ and the second to $k_5^S= -1.61602540378$.

b) Calculated by means of Eq. (46.13) (Padé method).

c) Calculated by means of Eq. (46.14) (Borel-Padé method).

d) Results obtained by way of the FM using Eqs. (46.19) and (46.20).

e) Exact result (Eq.(46.1)).

In table 14.2 we compare the results obtained from different methods, using the same number of coefficients $E^{(n)}$. For the sake of completeness, the $|3/2|$ Padé approximant (see Appendix E).

$$E_1^{|3/2|} = \frac{3\lambda}{2}\left\{\frac{1-13\lambda/6+21\lambda^2/16}{1-3\lambda/2+13\lambda^2/16}\right\} \qquad (46.13)$$

and the |3/2| Borel-Padé approximant (built as shown in §.14):

$$E_1'^{|3/2|} = \frac{3\lambda}{2}\int_0^\infty \left|\frac{1-121x\lambda/210+31x^2\lambda^2/960}{1-17x\lambda/70+233x^2\lambda^2/6720}\right| xe^{-x}dx \qquad (46.14)$$

are included. The Romberg integration method was applied to compute (46.14).

It is worth remarking that the choice in (46.13) and (46.14) of approximants |N+1/N| keeps the correct behavior for $1/\lambda \to 0$, according to Eq. (45.3). Thus, expressions (46.13) and (46.14) are comparable with SE_5, since they satisfy the same scaling law and have an identical number of coefficients $E^{(n)}$. For a more complete comparison, both k-values are incorporated in (46.12b) to compute SE_5. Results show that not only the FM is easier to apply but it yields better results than the Borel-Padé method. Moreover, SE_5 and $E^{|3/2|}$ have nearly the same accuracy.

In order to complete this analysis on the numerical properties of the FM, we show how the results are improved by adding of the dominant coefficient in the $1/\lambda$-power series expansion. Here we employ the following equation

$$e^{(0)} = \lim_{|\lambda|\to\infty} |\lambda|^{-1} E_1(1,\lambda) = \lim_{|\lambda|\to\infty} |\lambda|^{-1} SE_N(k_N^S, w(\lambda)) \qquad (46.15)$$

which is equivalent to write

$$e^{(0)} = S_N(k,1) \qquad (46.16)$$

To fulfil the previous equation we follow the procedure depicted at the end of §.42. Thus, we add the coefficient $\bar{E}^{(6)}$ in the sequence $S_N(k,w)$. Due to (46.16), for N = 6

$$\bar{E}^{(6)} = e^{(0)} - \sum_{n=0}^{5} \bar{E}^{(n)} \quad . \tag{46.17}$$

We could have obtained the same result via the application of Eqs. (42.42) and (44.16).

In this example, Eq. (46.1) leads us to

$$e^{(0)} = -\frac{5}{2}\frac{\lambda}{|\lambda|} \tag{46.18}$$

and on the basis of (46.7), Eq. (46.17) happens to be

$$\bar{E}^{(6)} = -\{\frac{5}{2}\frac{\lambda}{|\lambda|} + \sum_{n=0}^{5} \bar{E}^{(n)}\} = -\frac{5}{2}\frac{\lambda}{|\lambda|}\ -\frac{3}{2}+\frac{4}{k}+\frac{9}{2k^2}+\frac{45}{16k^3}+\frac{9}{64k^4} \tag{46.19}$$

Function $E(1,\lambda)$ may be approximated through the sequence $SE'_6(k,w)$, where the prime symbol has been added to denote that $\bar{E}^{(6)}$ is given by (46.19), but not by (44.14).

Since the FM is more suitable to sum $E_1(1,\lambda)$ with $\lambda<0$, we have chosen $e^{(0)} = 5/2$. The computation of the SE'_6 SP's gives the appropriate k-value (i.e. k=k*):

$$k^* = k_N^S \simeq -1.201 \quad . \tag{46.20}$$

The introduced modification yields

$$S_6(k,1) = 5/2, \ \forall\ k \in R \quad , \tag{46.21}$$

so that now the SE_6' extremes do not coincide with those for $S_6(k,1)$ (which, in fact, does not possess anyone).

In the same manner, it may be numerically verified that (46.20) is a SP of SE_6' $\forall$ λ. This is hardly surprising due to Theorem 44.1, which assures the invariant character of SP's independently of the coefficients $E^{(n)}$. Then, this result must hold even when $\bar{E}^{(N)}$ is fitted with $e^{(0)}$.

Results displayed at the fifth column in Table 14.2 were obtained from (46.20) for SE_6'. These are the most accurate results presented in this section. This strongly suggests the convergence can be improved if the coefficient $e^{(0)}$ associated with the limit (46.15) is taken into consideration.

§.47. Geometrical Series and FM.

This section is concerned with the application of FM to a very simple power series: the geometrical series. The problem is elementary, and it is chosen as a first test for all the methods for summation of power series /6/.

Let us consider the function

$$E(Z,\lambda) = \frac{1}{Z+\lambda} \quad , \tag{47.1}$$

which fulfils the following scaling law

$$E(Z,\lambda) = \lambda^{-1} E(Z\lambda^{-1},1) \quad , \tag{47.2}$$

and gives us the exponents $\alpha = \beta = -1$ (Eq.(44.2)).

Function $E(1,\lambda)$ may be expanded as a power series in λ (geometrical series):

$$E(1,\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n \; ; \; E^{(n)} = (-1)^n \quad , \qquad (47.3)$$

which converges $\forall\ |\lambda|<1$. This function possesses a singularity at $\lambda = -1$, so that our task is constrained to look for within the region $\lambda \geq 0$.

Our aim is to employ the formalism developed in §.44 to reconstruct function (47.1) from (47.3).

The exponents previously found enable us to have the following sequence approaching $E(1,\lambda)$

$$SE_N = k(1-w)\ S_N(k,w) = w\lambda^{-1}\ S_N(k,w), \qquad (47.4a)$$

$$\lambda = w/(k(1-w)) \quad , \qquad (47.4b)$$

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)} w^n \quad , \qquad (47.4c)$$

Coefficients $\bar{E}^{(n)}$ may be computed in a closed form from application of (44.17):

$$\bar{E}^{(n)} = \sum_{j=0}^{n} \frac{(1+j+n-j-1)!}{(n-j)!(1+j-1)!} (-1)^j k^{-1-j} = \frac{1}{k} \sum_{j=0}^{n} \binom{n}{j} \left(-\frac{1}{k}\right)^j =$$

$$= \frac{1}{k}\, y^n \quad , \qquad (47.5)$$

with

$$y = 1 - k^{-1} \quad . \qquad (47.6)$$

In order to apply the FM, it is necessary to study the convergence properties of the sequence (47.4c) for $N,\lambda\to\infty$, as shown in §.44. In agreement with the Sensitivity Rules, the critical points of the sequence $S_N(k,1)$ must be analysed:

$$S_N(k,1) = \sum_{n=0}^{N} \bar{E}(n) = k^{-1} \sum_{n=0}^{N} y^n \quad . \tag{47.7}$$

To make all the calculations analytically, we have to find out a closed formula for (47.7), considering that:

$$\frac{1}{1-y} = \sum_{n=0}^{N} y^n + y^{N+1} \frac{1}{1-y} \quad , \tag{47.8}$$

we get:

$$S_N(k,1) = k^{-1} \left|\frac{1-y^{N+1}}{1-y}\right| = 1-y^{N+1} \quad . \tag{47.9}$$

Eqs.(47.9) represents the limit of the sequence $S_N(k,w)$ when $\lambda\to\infty$, as an explicit function of the order N and the parameter k. The analysis of SP's associated with (47.9) yields

$$\frac{\partial}{\partial k} S_N(k,1) = - \frac{N+1}{k^2} y^N = 0 \tag{47.10}$$

so that

$$y = 1-k^{-S} = 0 \;\forall\; N \geq 1 = k^S = 1 \tag{47.11}$$

Notice that k^S does not depend upon the order N. The substitution of (47.11) into (47.9) gives

$$S_N\ (k^S,1) = \forall\ N \geq 1 \tag{47.12}$$

which is the correct result, as follows from (47.1):

$$\lim_{\lambda\to\infty} \lambda E(1,\lambda) = 1 \qquad (47.13)$$

Result (47.12) tells us that the geometrical series is summable for $\lambda\to\infty$ (w=1) throughout the sequence $S_N(k^S,1)$. This fact, together with Theorem 44.1, assure the series is summable too via the FM, $\forall\ \lambda>0$ $(0\leq w\leq 1)$.

On the other hand, the study of the convergence radius of (47.4c) by means of the D'Alembert theorem (Eq. 11.2a) yields

$$\lim_{N\to\infty} \left|\frac{\bar{E}(N+1)}{\bar{E}(N)}\right| = y = \frac{k-1}{k} = \frac{1}{R}\ ,\ k = \text{constant} \qquad (47.14)$$

so the convergence radius is maximum (infinite) when k→1. Taking into account that due to (47.4b) the singularity associated with $E(1,\lambda)$ at $\lambda = -1$ is sent toward infinity in $E(1,\lambda(w))$:

$$\lim_{w\to\infty} \lambda = -1 \quad , \quad k = 1 \qquad (47.15)$$

and, on the basis of Eq.(47.14) for k = 1, the expansion (47.4c) converges for $w<\infty$, then it is possible to sum the original series $\forall\ \lambda>-1$ and not only for $\lambda>0$.

The computation of IP's associated with (47.9) gives

$$\frac{\partial^2 S_N(k,1)}{\partial k^2} = \frac{N+1}{k^4}\, y^{N-1}\,\{2yk-N\} = 0 \quad , \qquad (47.16)$$

so that we have two possible results:

$$y = 0 \quad \forall\ N \geq 2 \qquad (47.17a)$$

$$2yk - N = 0 \quad \forall\, N \geq 1 \quad . \tag{47.17b}$$

Condition (47.17a) leads us again to the conclusion that FM sums the geometrical series $\forall\ \lambda > -1$:

$$S_N(k^I,1) = 1, \quad \forall N \geq 2 \ , \ k^I = 1 \quad . \tag{47.18}$$

Eq. (47.17b) introduces an important novelty since it leads to

$$k^I = k_N^I = \frac{N}{2} + 1 \quad . \tag{47.19}$$

This equation shows that k^I depends upon N, so that FM changes the variable λ by w, by means of an order-dependent transformation.

Let us analyse the $S_N(k_N^I,1)$ convergence when one chooses the IP's sequence given by (47.19). The replacement of (47.19) into (47.9) yields.

$$S_N(k_N^I,1) = 1- \left(1-\frac{2}{N+2}\right)^{N+1} \tag{47.20}$$

and the limit for $N \to \infty$ is

$$\lim_{N\to\infty} S_N(k_N^I,1) = 1-\lim_{N\to\infty} \left(1-\frac{2}{N+2}\right)^{N+1} = 1 - \exp\left\{ \lim_{N\to\infty} (N+1) \ln\left(1 - \right.\right.$$

$$\left.\left. - \frac{2}{N+2}\right)\right\} = 1- \exp\left\{\lim_{N\to\infty} \left(-2\frac{N+1}{N+2}\right)\right\} = 1-e^{-2} \quad . \tag{47.21}$$

So that the series converges toward

$$\lim_{\lambda\to\infty}\lim_{N\to\infty} S_N(k_N^I,w) = 0.8646647...<1 \qquad (47.22)$$

which is a lower bound to the exact result.

Summing up, Eqs. (47.10) and (47.18) imply that $S_N(k,1)$ has coincident SP and IP at $k^S = k^I = 1$. The sequence built from these critical points converges to the exact sum value. On the other hand, there exists another sequence constructed from k_N^I (Eq.(47.19))which does not converge toward the exact value. In order to settle upon which IP sequence must be chosen, we resort to the Sensitivity Rules. The first derivative in IP (47.19) gives

$$\left|\frac{\partial}{\partial k} S_N(k_N^I,1)\right| = 4\,\frac{N+1}{(N+2)}2\left(1-\frac{2}{N+2}\right)^N \qquad (47.23)$$

which is larger than the corresponding one at $k^I = 1$. Thus, the proposed rules for the optimum k* remove the sequence converging to the incorrect result.

Preceding conclusion introduces a note of attention: FM gives rise to order-dependent sequences for some functions $E(1,\lambda)$; these sequences have the following general form

$$k_N = \delta_N + \delta' \qquad (47.24)$$

and they converge toward an incorrect value. Obviously, such sequences must be removed by way of the Sensitivity Rules in order to apply properly the FM. We will return on this point in forth coming sections to discuss the importance of the sequences SE_N with k depending on the order.

Let us remark that when we discuss the incorrect convergence through a sequence with k given by (47.19), we are considering the convergence

for $1/\lambda \to 0$ in an expansion about $\lambda=0$ (which is the most unfavourable case). Thus, for intermediate λ-values (beyond the convergence radius when it is nonzero finite) results can be quite close to $E(1,\lambda)$.

The results obtained for the geometrical series with $k^S=k^I=1$ lead us to the change of variables (Eq.(47.4b)):

$$w = \frac{\lambda}{1+\lambda} \tag{47.25}$$

which is the Euler transformation /6/. This is a hardly surprising result since we know that Taylor expansion of $E(1,\lambda)$ converges $\forall |\lambda|<1$ and the Laurent expansion for $|\lambda|>1$. The Euler method provides a continuous transition from the Taylor to the Laurent expansions, so that the series converges $\forall \lambda \geq 0$.

Besides, it may be noted the criterion to make null the last coefficient of the renormalized series

$$\bar{E}^{(N)} = k^{-1} y^N = 0 \tag{47.26}$$

leads us again to k = 1, and consequently to the exact sum for $1/\lambda \to 0$. This criterion has been used by several authors when applying order-dependent transformations to sum divergent series /10,11/. Such criterion leads here to the correct result, as our Sensitivity Rules do.

Finally, we can note that the different k_N^S values obtained in §.46 for the model (45.1) do not make up an order-dependence like (47.21), but they simply correspond to situations with different convergence rates within the region where the series originated by the FM is convergent.

§.43. Further comments on series with non-zero convergence radii.

The results obtained in §.45 are valid too for other power series expansions with convergence radii determined by branch-points. For example, the Pöschl-Teller potential /12/ is an eigenvalue problem with similar characteristics to those discussed in §.45. The Hamiltonian operator corresponding to this model is

$$H(Z,\lambda) = p^2 + Z\{\sin(\frac{x}{\sqrt{2}})\}^{-2} + \lambda\{\cos(\frac{x}{\sqrt{2}})\}^{-2} \quad . \qquad (48.1)$$

If $E(Z,\lambda)$ denotes the associated eigenvalues, the ground state is /12/:

$$E(1,\lambda) = \frac{1}{8}\{26+8\lambda+10(1+8\lambda)^{1/2}\} \qquad (48.2)$$

which clearly shows a square-root type singularity.

This model is interesting because it includes as particular cases the harmonic oscillator and the particle-in-a-box model. Notwithstanding, Hamiltonian (48.1) is interesting for us due to other reasons. Unlike other models previously discussed, operator (48.1) is not dilatable through an unitary transformation. In other words, we cannot deduce from it the exponents α and β. Naturally, this impossibility is due to the presence of trigonometric functions within the Hamiltonian.

This sort of Hamiltonians must be treated in a different manner in order to apply the FM to sum the perturbative series.

There exists a wide sort of models in Physical Chemistry that have the above features. Among them, we can mention the case of rotational systems in external fields, which have deserved much attention within the PT field /13-19 and references therein/. Such models include molecular (top or linear) dipolar rotors in electric fields /13-15/, and the rotational Zeeman effect /16/, i.e. the shift of molecular rotational levels in the presence of an external magnetic field.

All the rotor-like models introduce certain drawbacks in relation to the periodic BC. In this case one must resort to asymptotic expansions of the operator itself in order to generate the energy asymptotic expansions. We will consider an illustrative example to fix ideas.

Eigenvalues $E_{J,m}$ for the rotational Stark effect of a dipolar diatomic molecule, under the Born-Oppenheimer and rigid-rotor approximations, are determined from the following Schrödinger equation /13/:

$$\{-\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}+\frac{m^2}{\text{sen}^2\theta}-g\cos\theta\}\psi(\theta)=E_{J,m}\psi(\theta) \quad , \quad (48.3a)$$

where

$$g=2\mu IF\hbar^{-2} \quad , \quad E_{J,m}=2IW_{J,m}\hbar^{-2} \quad , \quad (48.3b)$$

with μ the molecular permanent dipole moment, I its moment of inertia and F the electric field strength. The angle θ is the one formed between the electric field direction and the molecular axis. Rotational energies are represented by $W_{J,m}$, where $J = 0,1,2,...$ and $m = 0, \pm 1, \pm 2,..., \pm J$ are the two quantum numbers defining a state of the system. $E_{J,m}$ are the dimensionless eigenvalues, where the dimensionless field strength is represented by g.

Notice that the change of variables $\theta\rightarrow\theta+\pi$ introduces a change of sign in the perturbation parameter g. On the other hand, all the states are non-degenerate /19/. Thus, from Theorem 7.1, we conclude that the odd order perturbative corrections in g are null for the energy series expansion. Consequently, eigenvalues may be written as follows:

$$E_{J,m}=\sum_{n=0}^{\infty}E_{J,m}^{(n)}\lambda^n \quad , \quad \lambda=g^2 \quad (48.4)$$

In order to get the eigenvalues asymptotic expansion for $g>>1$ we must look for the Hamiltonian asymptotic expansion.

Basically, the procedure takes into account that when the field is

infinitely strong ($g\to\infty$), the molecule tends to line up along it, i.e. $\theta\to 0$. At this limit, oscillation amplitudes decrease and the energy absolute value increases, so that the system behaves like a perturbed 2D isotropic oscillator, whose force constant increases with the external field /20/.

The computation of the Hamiltonian expansion at the limit $\theta\to 0$ gives /20/:

$$\{z\frac{d^2}{dz^2}+\frac{1}{2}\frac{d}{dz}-\frac{a_m}{z}-\frac{z}{4}+\frac{\sigma}{16}-a_m\sum_{s=0}^{\infty}A_s\sigma^{s+1}z^s+$$

$$+\frac{1}{2}\sum_{s=0}^{\infty}L_s\sigma^{s+1}z^{s+2}\}\chi(z)=\xi_{J,m}\chi(z) \quad , \qquad (48.5a)$$

where

$$a_m=\frac{4m^2-1}{16} \quad , \quad L_s=(-1)^s\frac{1}{(2s+4)!} \quad , \qquad (48.5b)$$

$$A_s=2c_s-\sum_{i=0}^{s-1}c_ic_{s-i-1} \quad , \quad s\geq 1;\ A_0=2c_0,\ c_s=2|B_{2s+2}|\frac{2^{2s+1}-1}{(2s+2)!} \quad , \qquad (43.5c)$$

with B_{2s+2} the Bernoulli numbers. The variable z in (48.5a) is given by

$$\theta=(\sigma z)^{1/2} \quad ; \quad \sigma=(2/g)^{1/2} \quad , \qquad (48.5d)$$

in terms of the new parameter σ, which tends to zero when $1/g\to 0$. Eigenvalues $\xi_{J,m}$ are related to the original one as follows,

$$\xi_{J,m}=-\frac{\sigma}{4}(E_{J,m}+g) \qquad (48.5e)$$

The Hamiltonian in Eq. (48.5a) has a polynomial in σ, so that it assures us the existence of the following formal power series expansion for the energy:

$$\xi_{J,m}=\sum_{n=0}^{\infty}\xi_{J,m}^{(n)}\sigma^n=\sum_{n=0}^{\infty}\{2^{n/2}\xi_{J,m}^{(n)}\}g^{-n/2} \qquad (48.6)$$

The combination of Eqs.(48.5e) and (48.6) yields the desired asymptotic expansion for the function $E_{J,m}$, which written in terms of λ happens to be

$$E_{J,m} = \lambda^{1/2} \sum_{n=0}^{\infty} e_{J,m}^{(n)} \lambda^{-1/4} \quad , \tag{48.7a}$$

where

$$e_{J,m}^{(0)} = -1, \; e_{J,m}^{(n)} = -2^{(n+1)/2} \xi_{J,m}^{(n-1)} \quad , \; n \geq 1 \quad . \tag{48.7b}$$

Eqs. (48.4) and (48.7a) makes up the starting point to apply the FM to this rotational system, since it gives the exponents $\beta = 1/2$ and $\alpha = -1/4$.

It is noteworthy that recently a large number of coefficients $\{E_{J,m}^{(n)}\}$ and $\{e_{J,m}^{(n)}\}$ have been computed for several rotational systems /13-19/. Thus, there exists the necessary information to perform the pertinent research on the convergence of perturbation series. Work has been done recently /16-19/ through the formalism displayed in §.42 /16/, as well as with the one presented in §.44 /17/. We will not expose these results here since we are more interested in the power series with zero convergence radius. However, it is appropriate to comment that FM appears to be an excellent tool to study rotational systems within the RSPT framework /19/.

The model (48.3a) was chosen as an example to illustrate how exponents α and β are determined for the eigenvalues of non-dilatable Hamiltonians. Another examples appear in eigenvalue problems leads to Taylor expansions like (48.4), with non-zero convergence radii. They are determined by conjugated pairs of branch-points which, in the case of Mathieu equation for functions with period π, are purely imaginary. If g_s denotes the perturbational parameter at the singularity, then it has the following form:

$$g_s = \pm i|g_s| \quad . \tag{48.8}$$

When one knows the $|g_s|$ value, then it is possible to employ the transformation introduced by the FM in such a manner to remove suitably the singularity. The generalized Euler transformation happens to be appropriate ($\alpha = -1$ in Eq. (44.7)). Here, the FM changes the variable λ in the expansion (48.4) by the following one

$$w = \frac{k\lambda}{1+\lambda k} \quad , \quad k \geq 0 \tag{48.9}$$

The singularity (48.8) gives us w_s:

$$w_s = \frac{g_s^2 k}{g_s^2 k - 1} \quad , \tag{48.10}$$

and the parameter k can be selected in such a way that $|w_s| = 1$ ($w_s = -1$):

$$k^* = 1/2g_s^2 \quad . \tag{48.11}$$

The choice $k = k^*$ allows one to apply the FM which gives a Taylor expansion in w-powers converging for $|w|<1$. According to Eq. (48.9), the interval $-1<w<1$ corresponds with $-1/g_s^2 <\lambda<\infty$. Thence, the FM would permit to sum the expansion (48.4) for $-\infty<g<\infty$ by removing the singularity g_s.

Recent results /19/ have shown that this procedure possesses a similar quality degree as those derived from the application of the formalism described in §.44, determining k from the Sensitivity Rules.

Other rotational models are described by the Mathieu equation for functions with period 2π. In this case the treatment to be followed must be different, due to the presence of singularities like

$$g_s = g_1 \pm i\, g_2 \quad , \quad g_1 \neq 0 \tag{48.12}$$

which cannot be treated through the Euler transformation. Some recent results /21/ have shown that existing the difficulties may be solved by means of appropriate conformal transformations.

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CHAPTER XV

PROPERTIES OF THE FM: SERIES WITH ZERO CONVERGENCE RADII.

§.49. FM and asymptotic properties of Taylor coefficients of a series with zero convergence radius.

This section starts the analysis of models with power series expansions with zero convergence radius. Our first aim is to apply the formalism developed in §.44 to a simple model with the above features and to determine the conditions under which the FM leads to a convergent sequence.

Let us consider the zero-dimensional field theory model introduced by Eq. (11.14):

$$E(g,\lambda) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-gx^2-\lambda x^4}\, dx \qquad (49.1)$$

The coefficients of the λ-power series expansion associated with (49.1) behave asymptotically as shown in Eq. (11.21).

In order to apply the FM, it is first necessary to obtain the dilatation transformation, which in this case happens to be

$$E(g,\lambda) = \frac{1}{\sqrt{\pi}} \lambda^{-1/4} \int_{-\infty}^{+\infty} e^{-g\lambda^{-1/2}x^2-x^4} dx = \lambda^{-1/4}\, E(g\lambda^{-1/2},1) \quad , \qquad (49.2)$$

therefore $\beta = -1/4$ and $\alpha = -1/2$. The application of Eqs. (44.7) and (44.8) makes up the starting point to construct the sequence converging towards $E(1,\lambda)$:

$$E(1,\lambda) = k^{1/2}\ (1-w)^{1/2}\ \bar{E}(k,w); \bar{E}(k,w) = E(k(1-w),w) \tag{49.3a}$$

$$\lambda = wk^{-2}\ (1-w)^{-2} \quad . \tag{49.3b}$$

Seznec and Zinn-Justin studied the change of variables (49.3b) to introduce an ODT /1/. Arteca et al /2/ have analysed the connection between both procedures.

According to the function structure (49.1), we obtain from (49.3a) the following result for $\bar{E}(k,w)$

$$\bar{E}(k,w) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} e^{-kx^2+w(kx^2-x^4)}\ dx \quad , \tag{49.4}$$

that can be expressed as a w-power series

$$\bar{E}(k,w) = \sum_{n=0}^{\infty} \bar{E}^{(n)}\ w^n \quad , \tag{49.5a}$$

with coefficients $\bar{E}^{(n)}$ given by

$$\bar{E}^{(n)} = \frac{1}{\sqrt{\pi}n!} \int_{-\infty}^{+\infty} (kx^2-x^4)^n\ e^{-kx^2}\ dx \quad . \tag{49.5b}$$

As shown in §.43, k must be order-dependent because $E(1,\lambda)$ has zero convergence radius. In order to study such dependence upon the order, we resort to the argument introduced in Ref. /1/. Seznec and Zinn-Justin /1/ determined the parameter k making null the last term in the renormalized series.

Let us apply the saddle-point method (Appendix C) to compute $\bar{E}^{(n)}$. For this purpose, Eq. (49.5b) is rewritten as follows:

$$\bar{E}^{(N)} = \frac{1}{\sqrt{\pi}N!} \int_{-\infty}^{\infty} e^{F(x)}\, dx \; ; \; F(x) = -kx^2 + N\ln(kx^2 - x^4) . \qquad (49.6)$$

The equation determining the F(x) extreme points x* is

$$2kx^{*4} - x^{*2}(2k^2 + 4N) + 2Nk = 0 \quad , \qquad (49.7)$$

which can be rewritten as

$$t^2 - (\delta+2)t + \delta = 0 \quad , \qquad (49.8)$$

where

$$x^{*2} = \alpha t \; ; \; \delta = k/\alpha = k^2/N > 0 \quad . \qquad (49.9)$$

The two roots of Eq. (49.3) are

$$t_{\pm} = \frac{\delta+2}{2} \pm \frac{1}{2}(\delta^2+4)^{1/2} \qquad (49.10)$$

with $0 \leq t_+ < \delta$ and $\delta < t_- < \infty$.

The replacement of (49.9) in (49.6) yields the F(x) extreme value

$$F(x^*) = F(t) = -Nt + N\ln N + N\ln(t - t^2/\delta) \quad . \qquad (49.11)$$

Taking into account (49.8), the precedent relationship may be written as

$$e^{F(t)} = e^{-Nt}\, N^N\, (1-\frac{2t}{\delta})^N \quad . \qquad (49.12)$$

The root t_- in (49.10) gives

$$1-\frac{2t_-}{\delta} = t_- - \frac{t_-^2}{\delta} > 0 \text{ since } \delta > t_- \quad , \qquad (49.13a)$$

whereupon

$$e^{F(t_-)} = e^{-Nt_-}\, N^N\, (1-\frac{2t_-}{\delta})^N > 0 \quad . \qquad (49.13b)$$

On the other hand, the second root leads us to

$$1-\frac{2t_+}{\delta} = -\{\frac{2}{\delta} + (1+\frac{4}{\delta^2})^{1/2}\} < 0 \quad , \qquad (49.14a)$$

after which it follows that $e^{F(t_+)}$ alternates in sign:

$$e^{F(t_+)} = (-1)^N\, e^{-Nt_+}\, N^N\, (\frac{2t_+}{\delta} - 1)^N \qquad (49.14b)$$

According to the criterion presented in Ref. /1/, k has to be chosen so that $\bar{E}^{(N)} = 0$. Then, the contributions to the integral coming from the extremes t_+ and t_- must cancel out, i.e.

$$e^{F(t-)} = \gamma e^{F(t_+)} \; ; \; \gamma = e^{im\pi} \quad , \; m = 0, \pm 1 \quad , \qquad (49.15)$$

with m = 0 when N is odd and $m = \pm 1$ when N is even. The substitution of (49.13b) and (49.14b) into (49.15) yields

$$e^{-Nt_-}\left|1-\frac{2t_-}{\delta}\right|^N = \gamma e^{-Nt_+}\left|\frac{2t_+}{\delta}-1\right|^N \quad . \tag{49.16}$$

We can select the N-th root of (49.16), considering that

$$\lim_{N\to\infty}\gamma^{1/N} = \lim_{N\to\infty}\{\cos(\tfrac{m\pi}{N}) + i\sin(\tfrac{m\pi}{N})\} = 1 \tag{49.17}$$

which leads us to the following equation for large N-values

$$e^{-(t_- - t_+)} = \frac{2t_+ - \delta}{\delta - 2t_-} \tag{49.18}$$

The insertion of Eq. (49.10) into (49.18) determines a trascendental equation in δ:

$$e^{(4+\delta^2)^{1/2}} = \frac{2+(\delta^2+4)^{1/2}}{-2+(\delta^2+4)^{1/2}} \tag{49.19}$$

which has a unique positive real root

$$\delta = 1.3254363337 \quad . \tag{49.20}$$

This allows us to complete the search for the dependence of k upon the order N when N>>1:

$$k^2 \simeq \delta N \quad , \quad \delta \neq \delta(N) \quad . \tag{49.21}$$

Eq. (49.21) is valid for N>1 because it has been determined according to the saddle-point approximation for $\bar{E}(k,w)$.

Next we can compute the asymptotic form of the coefficient $\bar{E}^{(N)}$ by way of Eq. (D.7)

$$\bar{E}^{(N)} \to \frac{1}{N!\sqrt{\pi}}\, e^{\bar{F}(t_-)} \left|\frac{2\pi}{-\bar{F}''(t_-)}\right|^{1/2} , \tag{49.22}$$

where for the sake of simplicity we have used $t = t_-$.

Eq. (49.6) gives for the second derivative

$$F''(x) = -2k + 2N\,\frac{k-6x^2}{kx^2-x^4} - 2Nx^2 \left|\frac{k-2x^2}{kx^2-x^4}\right|^2 , \tag{49.23a}$$

and (49.7) yields

$$F''(x) = -2k + 2N \left|\frac{k-6x^2}{x^2k-x^4}\right| - \frac{4}{N}\, k^2x^2 . \tag{49.23b}$$

The replacement of (49.9) into (49.23b) gives the desired result

$$F''(t) = N^{1/2}\{-2\delta^{1/2} - 4t - \delta^{1/2} + 2\delta^{1/2} \left|\frac{1-6t_-/\delta}{t_- - t_-^2/\delta}\right|\} . \tag{49.24}$$

Eqs. (49.20) and (49.10) allow us to obtain numerically

$$F''(t_-) = -AN^{1/2} , \quad A = 11.870553667 \tag{49.25}$$

The substitution of (49.25) and (49.13b) into (49.22) leads us to the following result:

$$\bar{E}^{(N)} \to 2^{1/2}\, A^{-1/2}\, N^{-1/4}\, \frac{N^N}{N!}\, e^{(1-t_-)N} \left(1 - \frac{2t_-}{\delta}\right)^N \tag{49.26}$$

Taking into account the Stirling approximation (Eq. (D.21)), the last equation may be rewritten in a more suitable manner as

$$\bar{E}^{(N)} \to (\pi A)^{-1/2} N^{-3/4} B^N , \quad B = 0.5154353373 \qquad (49.27)$$

The result (49.27) is very important and gives us

$$\lim_{N\to\infty} |\bar{E}^{(N)}| = 0 \qquad (49.28a)$$

$$\lim_{N\to\infty} |\bar{E}^{(N)}/\bar{E}^{(N-1)}| = B \qquad (49.28b)$$

Although in this case the property (49.28b) does not permit us to compute the convergence radius in w (since we are not dealing with a series but an order-dependent sequence), the analysis performed before shows that (49.5a) converges for $w = 1$. Moreover, Lemma 44.1 assures us that if the sequence converges for $w = 1$, then the same happens for $1/\lambda \to 0$. In other words, the FM sums the λ-power series associated with (49.1) $\forall\ \lambda \geq 0$. Remember that the employed series is asymptotically divergent: $\bar{E}^{(n)} \propto (n-1)!$.

From Eq. (49.27) we can estimate the error arising from the truncation up to the order N. This error is of the order of the last term kept, viz

$$\varepsilon_N = \bar{E}^{(N)} w^N \qquad . \qquad (49.29)$$

The contribution w^N can be determined from the transformation (49.3b). Noticing that $k \to \infty$ when $N \to \infty$ (Eq. (49.21)), then Eq. (49.3b) yields

$$w \simeq 1 - \frac{1}{k\lambda^{1/2}} + \ldots , \quad k >> 1 \qquad (49.30)$$

and thus

$$w^N = e^{N\ \ln w} \simeq \exp\{N\ \ln|1-\frac{1}{k\lambda^{1/2}}+....|\} \simeq$$

$$\simeq e^{-N/k\lambda^{1/2}} = e^{-(N/\delta\lambda)^{1/2}} \qquad (49.31)$$

Then, the complete formula for the error is

$$\varepsilon_N = (\pi A)^{-1/2}\ N^{-3/4}\ B^N\ e^{-(N/\delta\lambda)^{1/2}} \quad . \qquad (49.32)$$

In line with the discussion presented in §.44, the largest error corresponds to $1/\lambda \to 0$, that is precisely the condition under which we have tested the convergence.

Up to here we have followed Seznec and Zinn-Justin's criterion and the Saddle-point approximation /1/. Considering the discussion of §.44, the k (=k*) value for the FM must be chosen according to the Sensitivity Rules. Thus, it is important to verify whether the conclusions derived here are also obtained from the Sensitivity Rules for IP and SP sequences. The answer is affirmative, as will be shown in the next paragraph. Some consequences are discussed in Ref. /3/.

It is worth noting that the chosen k value used to prove the convergence of (49.5a) presents a non linear dependence upon the order N (Eq. (47.21)).

Our analysis reveals that such dependence, $k^2 = \delta N$, is essential to get $\varepsilon_N \to 0$ when $N \to \infty$.

Let us now generalize the procedure depicted at the beginning of this section to obtain the expected k-dependence upon the order. We consider a function with a formal divergent asymptotic expansion in λ-power series like (Eq. (11.93)):

$$E(1,\lambda) = \sum_{n=0}^{\infty} E^{(n)}\lambda^n \ , \ E^{(n)} \to a\ n^b c^n\ (pn+q)! \quad . \qquad (49.33)$$

Assuming a usual scaling law for (49.33), we have

$$E(1,\lambda) = \lambda^{\beta}\, E(\lambda^{\alpha},1) \tag{49.34}$$

The FM associates a sequence $S_N(k,w)$ with $E(1,\lambda)$

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)}\, w^n \tag{49.35a}$$

where (c.f. Eq. (44.14)):

$$\bar{E}^{(N)} = \sum_{s=0}^{N} (-1)^{N-s} \binom{(s-\beta)/\alpha}{N-s} E^{(s)} k^{(s-\beta)/\alpha} \quad . \tag{49.35b}$$

Next, we set the last coefficient of (49.35a) equal to zero, and, by using (49.35b), get an approximate behavior for k:

$$k^{N/\alpha} E^{(N)} \simeq \text{constant}\; k^{(N-1)/\alpha}\, E^{(N-1)} \tag{49.36}$$

The substitution of (49.33) into (49.36) allows us to deduce the k dependence upon the order:

$$\rho = k^{-1/\alpha} \simeq \delta N \tag{49.37}$$

If $\alpha = -1/2$, then it follows Eq. (49.21). Eq. (49.37) shows the sort of k dependence on N to be expected in order to have a convergent sequence $S_N(k,1)$ (and from it SE_N). As stated before such k vs N dependence is determined through a dilatation relationship and the knowledge of the approximate asymptotic behavior of the coefficients $E^{(n)}$.

It seems that the convergence rate of power series by these order-dependent transformations depends on the α and β exponents. In Appendix J we provide an analysis of the conformal mappings between λ and

w complex planes, as functions of α and β. As it is shown there, these transformations remove a growing number of singularities in λ from inside the convergence domain when N increases. The way and rate with which these λ-singularities are removed depends on α and β, and fixes the efficiency of the FM as a summation method. We propose in Appendix J an approximate quantitative measure for such an efficiency, as a function of the exponents characterizing the Symanzik scaling law.

§.50. Application of the FM to integrals of interest in field theory and statistical mechanics.

Let us consider again the field theory elementary model (49.1) to study numerically the λ-power series convergence by the FM.

The model defined by

$$E(1,\lambda) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} e^{-(x^2+x^4)} dx = \lambda^{-1/4} E(\lambda^{-1/2},1) \quad , \qquad (50.1)$$

has two associated power series expansions

$$E(1,\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n \; ; \; E^{(n)} = (-1)^n \frac{(4n)!}{n!(2n)!2^{4n}} , \lambda \to 0 \quad , \qquad (50.2a)$$

$$E(1,\lambda) = \lambda^{-1/4} \sum_{n=0}^{\infty} e^{(n)} \lambda^{-n/2} \; ; \; e^{(n)} = (-1)^n (2n-\tfrac{3}{4})!/$$

$$2\pi^{1/2} n!) \; ; \; \frac{1}{\lambda} \to 0 \quad . \qquad (50.2b)$$

We choose the expansion (50.2a) and analyse the convergence behavior of the renormalized series when $1/\lambda \to 0$. In line with equations presented in §.44, the FM approches to $E(1,\lambda)$ through the sequence

$$E(1,\lambda) \simeq SE_N = k^{1/2} (1-w)^{1/2} S_N(k,w) \quad , \qquad (50.3a)$$

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)} w^n \quad , \tag{50.3b}$$

where w is a root of Eq. (44.7), i.e.

$$\lambda k^2 w^2 - w(1+2\lambda k^2) + \lambda k^2 = 0 \quad . \tag{50.3c}$$

According to the Lemma (44.2) the chosen root is

$$w = \frac{1}{2\lambda k^2} \{1 + 2\lambda k^2 - (1 + 4\lambda k^2)^{1/2}\} \quad . \tag{50.3d}$$

Coefficients $\bar{E}^{(n)}$ arise from Eq. (44.14), and for the model (50.1) they are

$$\bar{E}^{(n)} = \sum_{s=0}^{n} (-1)^{n-s} \binom{-(4s+1)/2}{n-s} E^{(s)} k^{-(4s+1)/2} \quad . \tag{50.3e}$$

The k-value must be determined according to the Sensitivity Rules by studying the critical points of the sequence $S_N(k,1)$

$$S_N(k,1) = \sum_{n=0}^{N} \bar{E}^{(n)} \quad . \tag{50.4}$$

When analysing the convergence of SE_N toward $E(1,\lambda)$, the most unfavourable condition corresponds to the case $1/\lambda \to 0$. Thus, one can expect that $S_N(k,1)$ converges to $\lambda^{1/4} E(1,\lambda)$, i.e.

$$S_N(k,1) \to e^{(0)} = \Gamma(1/4)/2\pi^{1/2} = 1.022765672... \tag{50.5}$$

The computational procedure is quite simple. The first and second derivatives of (50.4) are obtained at once from (50.3e):

$$\frac{d}{dk} S_N(k,1) = -\frac{1}{2} \sum_{n=0}^{N} \sum_{s=0}^{n} (-1)^{n-s} (4s+1) \binom{-(4s+1)/2}{n-s} E^{(s)} k^{-(4s+3)/2} , \tag{50.6a}$$

$$\frac{d^2}{dk^2} S_N(k,1) = \frac{1}{4} \sum_{n=0}^{N} \sum_{s=0}^{n} (-1)^{n-s} (4s+1)(4s+3) \binom{-(4s+1)/2}{n-s} E^{(s)} k^{-(4s+5)/2} . \tag{50.6b}$$

After determining the zeros of (50.6a) and (50.6b) for N = 1,2,... the Sensitivity Rules yield the optimum parameters k_N^S and k_N^I which allow us to study the convergence (50.5). Finally, Eqs. (50.3a), (50.3b) and (50.3d) give the approximation to the function $E(1,\lambda)$.

Before discussing the numerical results, it is suitable to make some general comments on the computational procedure:

i) A very simple computer program is needed to determine the roots of Eqs. (50.6a) and (50.6b) for N = 1,2,...

ii) Intrinsic errors in the computational scheme can be further reduced by determining k_N up to 15 significant figures and using double precision.

iii) A binary bisection algorithm is employed to compute the zeros of (50.6a) and (50.6b), since although it is slower than other approximation procedures, it does not present major convergence problems.

iv) The greatest limitation regarding the accuracy of the results for $S_N(k,1)$ lies in the accuracy of the coefficients $E^{(n)}$. Our computational experience comfirms up to a good degree a rule pointed out by Le Guillou and Zin-Justin /4/ when studying the Zeeman effect in hydrogen. This rule may be stated as follows: to approach in an efficient way the function under consideration by means of a sum method and 2N

terms of the RSPT, then the RS coefficients must be known up to N significant figures.

For the model (50.1), coefficients $E^{(n)}$ are known with the desired accuracy for any n, so that round off and truncation errors of the particular computer machine must be considered. It is more convenient to compute them in a recursive manner:

$$E^{(n)} = - \frac{(4n-1)(4n-3)}{4n} E^{(n-1)} \quad , \; n > 1 \quad . \qquad (50.7)$$

Eq. (50.7) allows us to compute up to $E^{(24)} \simeq 1{,}6 \times 10^{37}$ without making any further modification. The maximum figure N = 24 is large enough for our convergence analysis

Table 15.1: Convergent renormalized sequences obtained by means of the FM for the integral (50.1).

N	k_N^S a)	$S_N(k_N^S,1)$ a)	k_N^S b)	$S_N(k_N^S,1)$ b)
1	1.5811383301	0.954325		
2			2.2750692367	0.988061
3	2.2686203055	1.01093		
4			2.7262835278	1.01714
5	2.7921625419	1.02036		
6			3.1595269728	1.02163
7	3.2320935106	1.02224		
8			3.5477633258	1.02252
9	3.6189740554	1.02265		
10			3.9000505775	1.02271
11	3.9683323435	1.02274		
12			4.2241693568	1.02275

13	4.2893393194	1.02275898		
14			4.5257119252	1.02276249
15	4.5879464926	1.02276405		
16			4.8087160792	1.02276490
17	4.868275699	1.02276528		
18			5.0761745862	1.02276548
19	5.1333196163	1.02276557		
20			5.3303680520	1.02276563
21	5.3853608114	1.02276565		
22			5.5729670487	1.022765661
23	5.6259528357	1.022765666		
24			5.8062772752	1.022765669

a) Sequence A.

b) Sequence B.

Table 15.1 (cont.)

N	k_N^I c)	$S_N(k_N^I, 1)$ c)
1	2.41522945772	0.882458
2	3.34026841135	0.911606
3	4.45010636123	0.915744
4	5.57824977631	0.917569
5	6.71611510403	0.918499
6	7.85917109226	0.919037
7	9.00532549791	0.919377
8	10.1534807862	0.919605
9	11.3030048228	0.919766
10	12.4535072544	0.919384
11	13.6047337191	0.919972
12	14.7565112320	0.920041
13	15.9087179817	0.920095
14	17.0612656726	0.920138
15	18.2140887189	0.920173
16	19.3671373726	0.929292
17	20.5203732075	0.920227
18	21.6737660678	0.920247
19	22.8272919532	0.920265
20	23.9809315232	0.920280
21	25.1346690179	0.920293
22	26.2884914640	0.920304
23	27.4423880853	0.920314
24	28.5963498558	0.920323

c) Sequence C.

Table (15.1) shows results for k_N^* and $S_N(k_N^*,1)$, $1 \leq N \leq 24$. It is to be noted that whenever N is even, $S_N(k,1)$ only presents two IP, while for the case N odd there are one IP and one SP. Thus, we have two convergent sequences through IP and one from the SP, which can be arranged according to their dependence upon the order N.

The dependence of k_N^* on N for the several sequences is numerically fitted by means of a regression analysis /5/. In the following we call A,B,C to the sequence through the SP and the two sequences from the IP, respectively,

From the last six values for the A sequence, we find the dependence (N odd):

$$(k_N^S)^2 = (1.169 \pm 0.001) + (1.3253 \pm 0.0003)\ N \qquad (50.8a)$$

$$r = 0.9999999952 \quad , \qquad (50.8b)$$

where r is the correlation coefficient /5/. It must be pointed out that in order to obtain the accidental errors (50.8a), we have employed a 99% confidence interval.

The result obtained from the last six values of the sequence B (even) is

$$(k_N^I)^2 = (1.958 \pm 0.008) + (1.323 \pm 0.002)\ N \qquad (50.9a)$$

$$r = 0.99999971 \quad . \qquad (50.9b)$$

Finally, the sequence C (for any N) gives for the last 12 values a different dependence.

$$k_N^I = (0.912 \pm 0.003) + (1.1534 \pm 0.0007)\ N \qquad (50.10a)$$

$$r = 0.999999934 \quad . \tag{50.10b}$$

Results (50.8) - (50.10) are very suggestive and they permit us to extract important conclusions, which are displayed in what follows:

i) The method permits one to obtain, from a Taylor expansion with zero convergence radius, order-dependent convergent sequences depending on the order. The structure of such dependence upon the order is determined in a natural way by the Sensitivity Rules for the $S_N(k,1)$ critical points.

ii) Among the three sequences, two of them predict a perfect linear correlation between k^2 and N, which is in agreement with the expected behavior for this model according to Eq. (49.37). As well, as discussed in §.47, there appears a sequence with linear correlation between k and N.

iii) The numerical fitting made for the linear correlations $k^2 = \delta N$ in the A and B sequences allows us to obtain as the most accurate result

$$\delta = 1.3253 \pm 0.0003 \tag{50.11}$$

which is in excellent agreement with Eq.(49.20). Let us recall this last equation was derived from a completely different procedure: to make null the last coefficient of the renormalized series /1/.

iv) A and B sequences converge uniformly from below toward the exact result (50.5). Table 15.1 gives the following results

$$S_{23}(k_{23}^S,1) = 1.022765666 \text{ , sequence A} \tag{50.12a}$$

$$S_{24}(k_{24}^I,1) = 1.022765669 \text{ , sequence B} \tag{50.12b}$$

For N = 24 we find an error of about 3×10^{-9} with respect to the exact result. For the sake of comparison, Eq. (49.32) yields the following error when $1/\lambda \to 0$ (predicted from the saddle point argument):

$$\varepsilon_{24} = 1{,}9 \times 10^{-9} \quad . \tag{50.13}$$

The agreement is noteworthy, revealing that the FM allows one to obtain the expected convergence rate through its critical point sequences. Likewise, we may note that our predictions about the Sensitivity condition (plateau) for $S_N(k,1)$ as a k-function is fulfiled quite well: the second derivatives decrease permanently following a sequence of SP's, and the same happens for the first derivative via a sequence of IP's.

v) Sequence C (which has a k vs N linear dependence) converges to an incorrect result from below the exact one. We can estimate in an approximate fashion that

$$S_N(k_N^I,1) \simeq 0.9203 \pm 0.0001, \quad N>>1 \tag{50.14}$$

Though the model (50.1) has been studied by several authors with order-dependent transformations, the three sequences (50.12a), (50.12b) and (50.14) are completely original (see Ref. /3/).

vi) Results (50.12) assures us that for $\lambda<\infty$ we have an approximation to the exact result $E(1,\lambda)$ with 9 decimal places at least. In order to perform this calculation, we show in Table 15.2 the coefficients $\bar{E}^{(n)}$ obtained by means of k_{24}^S of the sequence B.

Table 15.2: Coefficients $\bar{E}^{(n)}$ of the renormalized series for the model (50.1) up to the 24th-order.

n	$\bar{E}^{(n)}$ a)		n	$\bar{E}^{(n)}$	
0	0.415002883507	(0)	13	0.40476199735	(-3)
1	0.198268994508	(0)	14	0.18336771682	(-3)
2	0.133743080530	(0)	15	0.7953303026	(-4)
3	0.943947765661	(-1)	16	0.3312447890	(-4)
4	0.659163380150	(-1)	17	0.132364863	(-4)
5	0.446492425652	(-1)	18	0.59834208	(-5)
6	0.290791541167	(-1)	19	0.18782714	(-5)
7	0.181312788840	(-1)	20	0.6683934	(-6)
8	0.108006956255	(-1)	21	0.229294	(-6)
9	0.61416078404	(-2)	22	0.7595	(-7)
10	0.33332446288	(-2)	23	0.2416	(-7)
11	0.17272408240	(-2)	24	0.784	(-8)
12	0.85509054517	(-3)			

a) Figures must be multiplied by a power of ten given between parenthesis. Results were rounded off according to the significant figures given for k_{24}^{I}.

The FM permits a straightforward calculation of $E(1,\lambda)$, since coefficients $\bar{E}^{(n)}$ are determined just once. Table (15.3) displays the results for SE_{24} as an approximation to $E(1,\lambda)$ in a wide range of λ-values. This computation was accomplished via Eqs.(50.3a), (50.3b) and (50.3d), and the approximate results are compared with the exact ones (determined with the Romberg integration method).

Table 15.3 : Results obtained for the function (50.1) in a wide range of λ-values.

λ	$E(1,\lambda)$ exact [a]	SE_{24} [b]
10^{-4}	0.9999250328	0.9999250328
10^{-3}	0.9992532545	0.9992532545
10^{-2}	0.9928039079	0.9928039080
10^{-1}	0.9445918017	0.9445918016
1	0.7720521778	0.7720521778
10	0.5201607637	0.5201607634
10^{2}	0.3128864550	0.3128864541
10^{3}	0.1799548854	0.1799548843

a) Numerically computed by the Romberg integration method.

b) Calculated with the coefficients from Table 15.2.

A careful look at Table 15.3 allows one to verify that all previous predictions are fulfiled. Results obtained through the FM are better, regarding accuracy and convergence rate, than those derived from the use of the Padé and Borel-Padé methods /6/. Taking into account that (50.1) describes a classical partition function for an anharmonic quartic oscillator /7/, we can conclude the FM permits one to have up to a considerable accuracy degree such a function for any temperature (proportional to λ).

A closely related problem with (50.1) is that one determined by the anharmonic mean quadratic displacement function

$$\langle x^2 \rangle = \int_0^\infty x^2 \, e^{-\beta' V(x)} dx \Big/ \int_0^\infty e^{-\beta' V(x)} dx \quad , \qquad (50.15)$$

where V(x) is quartic anharmonic potential

$$V(x) = v_2 x^2 + v_4 x^4 \quad , \tag{50.16a}$$

and

$$\beta' = (k'T)^{-1} \quad , \tag{50.16b}$$

with k' the Boltzmann constant and T the absolute temperature. Function (50.15) has been thoroughly studied because it is useful to interpret several experimental data such as the dynamical answer of ferroelectric materials, of order-disorder and displaceable type /8/, as well as the dependence upon the temperature of the isocoric dielectric polarizability of some liquids /9,10/. The relationship between the function (50.15) and the polarizability of any material medium is discussed in Appendix K.

Owing to the deep interest about expression (50.15) there have been several alternative proposals to derive simple and accurate formulas to compute it as a function of the temperature /10,11/. The FM is particularly suitable to obtain analytical expressions for this specific function, due to its similitude with (50.1).

Function (50.15) has been recently studied /12,13/ by means of the formalism developed in §.42.

In order to apply the FM it is convenient to rewrite (50.15) as follows (see Appendix K):

$$E(1,\lambda) = 2\beta' v_2 \langle x^2 \rangle = \int_0^\infty x^2 e^{-(x^2+\lambda x^4)} dx \; / \; \int_0^\infty e^{-(x^2+\lambda x^4)} dx \quad , \tag{50.17a}$$

$$\lambda = v_4/(\beta' v_2^2) \quad . \tag{50.17b}$$

Notice that the study of the behavior $1/\lambda \to 0$ in $E(1,\lambda)$ corresponds to the function (50.15) at the limit $T \to \infty$.

Function (50.17) obeys a scaling law

$$E(1,\lambda) = \lambda^{-1/2} E(\lambda^{-1/2},1) \qquad (50.18)$$

which follows at once from the change of variables $y^4 = \lambda x^4$. Eq.(50.13) provides the exponents $\alpha = \beta = -1/2$ (see Appendix J). In order to use the FM, we have at our disposal the expansions (50.17) in λ and $\lambda^{-1/2}$ power series. Keeping only up the first coefficients /11-14/ we are led to

$$E(1,\lambda) = 1-3\lambda + 24\lambda^2 - 297\lambda^3 + 4896\lambda^4 - 100273\lambda^5 + \ldots =$$

$$= \sum_{n=0}^{\infty} E^{(n)} \lambda^n \quad , \qquad (50.19a)$$

$$\lambda^{1/2} E(1,\lambda) = 0.6759782399 - 0.2715267096\ \lambda^{-1/2} + 0.07722148863\ \lambda^{-1} -$$

$$- 0.0155666445\ \lambda^{-3/2} + 0.00173008354\ \lambda^{-2} - \ldots = \sum_{n=0}^{\infty} e^{(n)} \lambda^{-n/2}.$$

(50.19b)

The expansion (50.19a) has a zero convergence radius, although appropriately rewritten as a continuum fraction it is convergent /10/ (see also Appendix K). However, the employment of the continuum fraction is not convenient since it converges very slowly for $\lambda \geq 1$. For example, to obtain a reasonable result for $\lambda = 10$, it is necessary to use around 200 terms in the continuum fraction /10/.

We have only introduced the first terms of the expansions (50.19) so as to make a direct comparison with the results reported by Booth

/11/, which up to now are the most accurate analytical expressions in the current literature. Booth resorted to the following expression to approximate (50.17):

$$E(1,\lambda) \simeq \sum_{i=0}^{n} a_i (\lambda + c_i^2)^{-1/2} \quad . \qquad (50.20)$$

The 2n parameters a_i and c_i are adjusted in such a way that (50.20) fulfils the following relationships:

$$\frac{1}{i!} \left(\frac{d^i E}{d\lambda^i}\right) (\lambda = 0) = E^{(i)} \quad , \quad i = 0,1,2,\ldots,2n-1 \quad , \qquad (50.21a)$$

$$\lim_{\lambda \to \infty} \lambda^{1/2} E = e^{(0)} \quad . \qquad (50.21b)$$

It must be pointed out that (50.20) allows one to use the combined information arising from both λ-series expansions (Eqs. (50.19)). However, (50.20) has a serious drawback leading to a $\lambda^{-1/2}$ power series expansion when $\lambda \to \infty$, as required by the function $E(1,\lambda)$. We know that the FM permits one in a natural and direct way to include both expansions.

The use of Eqs. (44.8) and (44.18), together with the coefficients α and β, lead to the approximation given by the FM for the function (50.17):

$$SE_N = k(1-w)\ S_N(k,w) \qquad (50.22a)$$

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)}\ w^n \qquad (50.22b)$$

The variable w is given by (50.3d) since the models (50.1) and (50.17) are characterized by $\alpha = -1/2$, Eq.(44.17) furnishes the coefficients $\bar{E}^{(n)}$:

$$\bar{E}^{(n)} = \sum_{j=0}^{n} \binom{j+n}{2j} E^{(j)} k^{-(2j+1)} \qquad (50.22c)$$

In order to perform a full comparison with formula (50.20) we incorporate $e^{(0)}$ in our computations before determining k* in agreement with the Sensitivity Rules. The introduction of the coefficient $e^{(0)}$ may be made in an analogous fashion as done in Eq. (46.17), resorting to the procedure developed at the end of section §.42. The necessary steps to be followed are:

i) From the five coefficients in (50.19a) we determine $\bar{E}^{(0)}$, $\bar{E}^{(1)}$,..., $\bar{E}^{(5)}$.

ii) $e^{(0)}$ is added by way of $\bar{E}^{(6)}$, using Eq. (46.16), which in this present case is

$$\bar{E}^{(6)} = e^{(0)} - \sum_{n=0}^{5} \bar{E}^{(n)} \quad . \qquad (50.23)$$

The approach to (50.17) will be denoted as SE_6', where the prime symbol is affixed to denote that $\bar{E}^{(6)}$ in (50.22b) is given by (50.23). The k-optimum value (k*) is chosen as an IP or SP of the sequence SE_6' This particular example presents a stationary point at k* = 3.2628, independently of λ. These values are used to compute SE_6' (k*,w) and the results are compared in Table 15.4 with respect the exact ones (determined with the Romberg's integration method) and those reported by Booth /11/ (obtained with the same number of coefficients). Evidently, our results are far superior in quality, within the whole range of λ-values.

Table 15.4: Compared results for the classic statistical average value of the quadratic shift in the quartic anharmonic oscillator, Eq. (50.17), for a wide range of λ-values.

λ	$E(1,\lambda)$ exact [a]	$E(1,\lambda)$ [b]	SE'_6 [c]
10^{-4}	0.9997002	0.99970	0.9997002
10^{-3}	0.997024	0.99702	0.997024
10^{-2}	0.972144	0.97214	0.972144
10^{-1}	0.817561	0.81858	0.817558
1	0.467919	0.48921	0.467901
10	0.188902	0.20276	0.188896
10^{2}	0.064958	0.06721	0.064957
10^{3}	0.0211072	0.02136	0.0211071

a) Results determined by way of a numerical integration via the Romberg method.

b) Eq. (50.20) with n = 3 (Ref./11/).

c) Results determined with the FM (Eq.(50.24)), k*=3.2628.

Summing up, we have shown that the FM provides an accurate approximation to the classical statistical average value of the means square displacement in a quartic anharmonic oscillator for arbitrary temperatures. Results were obtained from a T-power series expansion which has a zero convergence radius.

Since sometimes it is necessary to have accurate analytical expressions for $E(1,\lambda)$, we write here the formula provided by the FM (used to make the computations presented in Table 15.4):

$$E(1,\lambda) \simeq SE'_6 = 3.2628\ (1-w)\ \{0.3064852274 + 0.2201178179w +$$

$$+ 0.01122851323\ w^2 + 0.0373476866\ w^3 + 0.0050596001\ w^4 -$$

$$- 0.0032274428\ w^5 - 0.0020897815\ w^6\ \}\quad , \qquad (50.24)$$

where w is given by (50.3d) with $k = k^* = 3.2628$. The comparison of (50.24) with the original series (50.19a) plainly reveals the advantages in the use of the FM because the function is represented as a power series of a parameter $|w|<1$ with coefficients decreasing in absolute value when the order increases.

§.51. Convergence conditions for the FM: Discussion of integrals with factorial divergence.

We have discussed in preceding sections some functions of interest in Physical Chemistry, which have associated power series expansions with zero convergence radius. These problems can be studied in an approximate fashion up to a good accuracy degree via the FM from the knowledge of a scaling law. Furthermore, the functions analysed in §.§. 49 and 50 fulfil an additional condition, viz. they present power series expansions for both regimes of the λ parameter.

The purpose of this section is to study the convergence properties when one employes the FM to sum the power series about $\lambda = 0$, for those functions that cannot be expanded in power series about $1/\lambda = 0$.

Once again, simple functions are chosen so as all the computations can be performed in an analytical manner. Nevertheless, the conclusions to be derived are also valid when more involved problems are considered.

Let us consider a function $E(Z,\lambda)$, for $|\arg(\lambda)|<\pi$ and having an

associated asymptotic divergent expansion in λ-power series

$$E(Z,\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n, \quad E^{(n)} = E^{(n)}(Z) \quad , \tag{51.1}$$

with the property

$$\lim_{|\lambda| \to \infty} E(Z,\lambda) = 0 \quad . \tag{51.2}$$

For the time being, we shall not discuss the role of the Z parameter which is chosen equal to one.

Function $E(1,\lambda)$ may be represented as a Cauchy integral using the integration path as shown in Fig. 4.2.:

$$E(1,\lambda) = \frac{1}{2\pi i} \int_C \frac{E(1,x)}{x-\lambda} \, dx \quad , \tag{51.3}$$

where C avoids the singularity at $|\arg(k)| = \pi$. Using the same notation as in Fig. 4.2., and the property (51.2), Eq. (51.3) changes into

$$E(1,\lambda) = \frac{1}{2\pi i} \lim_{\substack{r \to 0 \\ R \to \infty}} \oint_C \frac{E(1,x)}{x-\lambda} \, dx = \int_{-\infty}^{0} \frac{D(x)}{x-\lambda} \, dx \quad , \tag{51.4a}$$

where

$$D(x) = \frac{1}{2\pi i} \lim_{\varepsilon \to 0} \{E(1,x+i\varepsilon) - E(1,x-i\varepsilon)\} = \frac{\mathrm{Im}E(1,x)}{\pi} \quad . \tag{51.4b}$$

Eq. (51.4b) can be rewritten in a more suitable way so as to obtain an integral representation for $E(1,\lambda)$:

$$E(1,\lambda) = -\int_0^{\infty} \frac{D(-x)}{x+\lambda} \, dx = \int_0^{\infty} \frac{G(t)}{1+\lambda t} \, dt \quad , \tag{51.5a}$$

with

$$t = x^{-1} \ , \ G(t) = - D(-t^{-1}) t^{-1} \quad . \tag{51.5b}$$

Eq. (51.5a) is an integral representation of $E(1,\lambda)$, and may be employed to generate the λ-power series expansion. The expansion of the denominator of (51.5a) as a λ-power series and the identification term by term with Eq. (51.1) yields:

$$E^{(n)} = (-1)^n \int_0^\infty t^n \, G(t) \, dt \quad . \tag{51.6}$$

Functions $E(1,\lambda)$, whose expansions (51.1) diverge as

$$E^{(n)} = (-1)^n \, \Gamma \, (An+B) = (-1)^n \, (An+B-1)! =$$

$$= (-1)^n \int_0^\infty t^{An+B-1} \, e^{-t} \, dt \quad , \tag{51.7}$$

are especially interesting and will be considered in what follows.

The equality between (51.7) and (51.6) gives the $E(1,\lambda)$ representation, whose power series expansion has the property (51.7):

$$E(1,\lambda) = \int_0^\infty \frac{t^{(A-1)n+B-1}}{1+\lambda t} \, e^{-t} \, dt \quad . \tag{51.8}$$

Let us consider a series whose coefficients are

$$E^{(n)} = (-1)^n \, n! \quad , \quad A = B = 1 \quad . \tag{51.9}$$

This function can be generated as follows:

$$E(Z,\lambda) = \int_0^\infty \frac{e^{-t}}{Z+\lambda t}\, dt \quad . \tag{51.10}$$

The function $E(Z,\lambda)$ evidently satisfies the dilatation relationship

$$E(Z,\lambda) = \lambda^{-1} E(Z\lambda^{-1},1) = Z^{-1} E(1,\lambda Z-1) \quad . \tag{51.11}$$

The integral (51.10) is not expandable in λ^{-1}-power series. Besides, $\lambda E(1,\lambda)$ does not remain finite when $1/\lambda = 0$, so that such behavior cannot be described by the FM of §.44. Let us analyse the way (51.10) diverges when $1/\lambda \to 0$. The change of variables $y = (1+\lambda t)/\lambda$ in (51.10) yields:

$$E(1,\lambda) = \frac{e^{1/\lambda}}{\lambda} \int_{1/\lambda}^\infty \frac{e^{-y}}{y}\, dy \quad . \tag{51.12}$$

It is convenient to rewrite Eq. (51.12). We start from the following relationship

$$\int_{1/\lambda}^\infty \frac{e^{-y}}{y}\, dy = \int_1^\infty \frac{e^{-y}}{y}\, dy + \int_1^{1/\lambda} \frac{1-e^{-y}}{y}\, dx - \int_1^{1/\lambda} \frac{dy}{y} \quad ; \tag{51.13a}$$

The subsequent power series expansion leads to

$$\int_{1/\lambda}^\infty \frac{e^{-y}}{y}\, dy = -\ln\left(\frac{1}{y}\right) - C_1 - C_2 + \sum_{n=0}^{\infty} (-1)^n \frac{(1/\lambda)^{n+1}}{(n+1)(n+1)!} \tag{51.13b}$$

where C_1 and C_2 are constants given by

$$C_1 = \int_1^{\infty} e^{-y}\, y^{-1}\, dy \;;\; C_2 = \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)(n+1)!} \qquad (51.13c)$$

Replacing (51.13b) into (51.12a), we get the $E(1,\lambda)$ asymptotic behavior

$$E(1,\lambda) \to e^{1/\lambda}\, \frac{\ln\lambda}{\lambda} + \frac{e^{1/\lambda}}{\lambda} \left\{ -(C_1+C_2) + \sum_{n=0}^{\infty} (-1)^n \frac{\lambda^{-(n+1)}}{(n+1)(n+1)} \right\} . \qquad (51.14)$$

Due to the presence of the factor $\frac{\ln\lambda}{\lambda}$ in (51.14), the FM cannot be applied to study the convergence behavior of the sequence SE_N when $1/\lambda \to 0$.

In order to apply the FM it is necessary that $E(1,\lambda)$ remains finite for $1/\lambda = 0$. For that purpose we consider an expansion with coefficients

$$E^{(n)} = (-1)^n\, (n+1)! \quad , \quad A = 1,\ B = 2 \qquad (51.15)$$

arising from the function (Z=1)

$$E(Z,\lambda) = \int_0^{\infty} \frac{te^{-t}}{Z+\lambda t}\, dt \qquad . \qquad (51.16)$$

Function (51.16) fulfils the same scaling law (51.11) as (51.10), but here

$$\lim_{\lambda\to\infty} \lambda E(1,\lambda) = 1 \qquad (51.17)$$

Let us analyse how the FM allows one to approximate the limit (51.17) using the λ-power series. We start analysing the renormalized series, so we write the following expression from Eq. (51.16)

$$\bar{E}(k,w) = E(k(1-w),w) = \int_0^\infty \frac{xe^{-x}}{k-kw+wx}\,dx = \frac{1}{k}\int_0^\infty \frac{xe^{-x}}{1+\frac{w}{k}(x-k)}\,dx \quad , \tag{51.18a}$$

and its associated power series expansion

$$\bar{E}(k,w) = \sum_{n=0}^{\infty} \bar{E}^{(n)}\, w^n \; ; \; \bar{E}^{(n)} = \frac{1}{k}\int_0^\infty x(1-\frac{x}{k})^n\, e^{-x}\,dx \quad , \tag{51.18b}$$

with

$$w = \lambda k/(1+\lambda k) \quad . \tag{51.18c}$$

Let us determine the conditions under which $\lim_{N\to\infty} \bar{E}^{(N)} = 0$. To this end, we write the N-th coefficient as follows:

$$\bar{E}^{(N)} = I_1 + I_2 \tag{51.19a}$$

$$I_1 = \frac{1}{k}\int_0^k x(1-\frac{x}{k})^N\, e^{-x}\,dx \; ; \; I_2 = \frac{1}{k}\int_k^\infty x(1-\frac{x}{k})^N\, e^{-x}\,dx \quad . \tag{51.19b}$$

Considering that $(1-\gamma)^N < e^{-N\gamma}$ $\forall$ $\gamma < 1$, we can find a bound for the integral $I_1(x<)$:

$$0<I_1<\frac{1}{k}\int_0^k xe^{-(1+N/k)x}\,dx < \frac{1}{k}\int_0^\infty xe^{-(1+N/k)x}\,dx = \frac{k}{(N+k)^2} \tag{51.20a}$$

Regarding the integral I_2 it is convenient to change the integration interval to $(0,\infty)$ making $y = x - k$:

$$I_2 = \frac{e^{-k}}{k} \int_0^{\infty} (-1)^N \left(\frac{y}{k}\right)^N (y+k)\, e^{-y}\, dy =$$

$$= \frac{e^{-k}}{k} \left\{ \left(-\frac{1}{k}\right)^N \int_0^{\infty} y^{N+1}\, e^{-y}\, dy - \left(-\frac{1}{k}\right)^{N-1} \int_0^{\infty} y^N e^{-y}\, dy \right\} =$$

$$= (-1)^N\, k^{-(N+1)}\, (N+1)!\, e^{-k} \left\{1 + \frac{k}{N+1}\right\} \qquad (51.20b)$$

so that it follows the bound

$$|I_2| < \frac{(N+1)!}{k^{N+1}} \left\{1 + \frac{k}{N+1}\right\} \quad . \qquad (51.20c)$$

Finally we have

$$0 < |\bar{E}^{(N)}| = |I_1 + I_2| < |I_1| + |I_2| < \frac{(N+1)!}{k^{N+1}} \left(1 + \frac{k}{N+1}\right) +$$

$$+ \frac{k}{(N+k)^2} \quad . \qquad (51.21)$$

Evidently, Eq. (51,21) shows that $\bar{E}^{(N)}$ remains finite when $N \to \infty$ if k depends properly upon the order N. Let us introduce a dependence on the order like

$$k = \delta N^r \ , \ r > 0 \qquad (51.22)$$

and look for the r-values that make $\bar{E}^{(N)}$ zero when $N \to \infty$. The substitution of (51.22) in (51.20b), and the application of the Stirling approximation (Appendix D) yields

$$|I_2| \to N^{N(1-r)}\ \delta^{-(N+1)}\ \{1+\delta N^{r-1}\} e^{-(N+1+\delta N^r)};\ N>>1\ . \quad (51.23)$$

which immediately gives

$$\lim_{N\to\infty} |I_2| = 0 \text{ when } r \geq 1 \quad , \quad (51.24a)$$

$$\lim_{N\to\infty} |I_2| = \infty \text{ when } 0<r<1 \quad . \quad (51.24b)$$

On the other hand, the replacement of (51.22) into (51.20a) yields

$$|I_1| < \frac{\delta N^r}{(N+\delta N^r)^2} \quad , \quad (51.25)$$

and thus

$$\lim_{N\to\infty} |I_1| = 0 \ ;\ r>0 \quad . \quad (51.26)$$

The use of (51.24), and (51.26) in (51.21), allows us to find out the desired relation

$$\lim_{N\to\infty} |\bar{E}^{(N)}| = 0 \text{ when } r\geq 1 \quad (51.27a)$$

$$\lim_{N\to\infty} |\bar{E}^{(N)}| = \infty \text{ when } 0<r<1 \quad . \quad (51.27b)$$

Eq. (51.27b) assures us that (51.18b) does not converge for $1/\lambda \to 0$ ($w\to 1$) if $r<1$.

In order to study the convergence when $r \geq 1$, we resort to the re-

normalized sequence $S_N(k,w)$ truncating (51.13b), i.e.

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)} w^n = \frac{1}{k} \int_0^\infty x e^{-x} \sum_{n=0}^{N} w^n (1-\frac{x}{k})^n \, dx \qquad (51.28)$$

Making use of the partial sum of the geometrical series (Eq.(47.3)), Eq. (51.28) may be transformed into

$$S_N(k,w) = \frac{1}{k} \int_0^\infty x \frac{1-(1-x/k)^{N+1} w^{N+1}}{1-(1-x/k)w} e^{-x} \, dx \quad . \qquad (51.29)$$

The renormalized sequence (51.29) should converge to $\bar{E}(k,w)$ if $N \to \infty$. In order to see this behavior, we write the precedent equation as follows

$$S_N(k,w) = \int_0^\infty \frac{xe^{-x}}{k(1-w)+wx} dx - \frac{w^{N+1}}{k} \int_0^\infty xe^{-x} \frac{(1-x/k)^{N+1}}{1-w(1-x/k)} dx =$$

$$= \bar{E}(k,w) - R_N(k,w) \qquad (51.30)$$

where R_N is the remainder to be examined:

$$R_N(k,w) = \frac{w^{N+1}}{k} \int_0^\infty xe^{-x} \frac{(1-x/k)^{N+1}}{1-w(1-x/k)} dx =$$

$$= w^{N+1} \int_0^\infty xe^{-x} \frac{(1-x/k)^{N+1}}{k+w(x-k)} dx \quad . \qquad (51.31)$$

Due to Eq. (51.30), the convergence analysis of $S_N(k,w)$ when $\lambda, N \to \infty$ turns into the study of $R_N(k,1)$ at the limit $N \to \infty$. The discussion is made in a similar fashion as done for $\bar{E}^{(N)}$. Thus, we have

$$R_N(k,1) = A_1 + A_2 \qquad (51.32a)$$

$$A_1 = \int_0^k e^{-x} (1-\frac{x}{k})^{N+1} dx \; ; \; A_2 = \int_k^\infty e^{-x} (1-\frac{x}{k})^{N+1} dx \quad . \qquad (51.32b)$$

It is found at once the following bound for A_1:

$$A_1 \leq \int_0^k e^{-x} e^{-x(N+1)/k}\, dx \leq \int_0^\infty e^{-x}\left(\frac{N+1}{k} + 1\right) dx = \frac{k}{N+1+k} \qquad (51.33a)$$

where the equality is valid when $N,k \to \infty$. Similarly, it is found for A_2

$$A_2 = e^{-k} \int_0^\infty e^{-y} \left(-\frac{y}{k}\right)^{N+1} dy = \left(-\frac{1}{k}\right)^{N+1} e^{-k} (N+1)! \quad , \qquad (51.33b)$$

and the application of (51.22) permits one to write the remainder as

$$R_N(k,1) \leq \left(-\frac{1}{N^r}\right)^{N+1} \delta^{-(N+1)} e^{-\delta N^r} (N+1)! + \frac{\delta N^r}{N+1+\delta N^r} \quad . \qquad (51.34)$$

When $N \to \infty$, the first term at the r.h.s. in (51.34) is infinite if $r<1$, and null when $r \geq 1$. This result find for the remainder that

$$\lim_{N\to\infty} R_N(k,1) = \frac{\delta}{1+\delta} \text{ if } r = 1 \quad , \qquad (51.35a)$$

$$\lim_{N\to\infty} R_N(k,1) = 1 \quad \text{if} \quad r>1 \quad . \qquad (51.35b)$$

Eq. (51.35) is important since it shows that R_N is not zero when $w = 1$ $(1/\lambda \to 0)$ and therefore $S_N(k,w)$ does not converge to $\bar{E}(k,w)$ when $N \to \infty$. Notice that, since $\delta>0$, the smallest remainder occurs when $r = 1$, that is to say, when the order dependence is setted by the scaling law ($\alpha=-1$ in Eq. (49.37)). The situation found here is similar to that one discussed in §.47 for the geometrical series, in the sense that order-dependent sequences with a linear correlation k vs N do not converge to the exact result. However, we have found a new fact: considering a function with $\alpha=-1$, and an asymptotically divergent power series expansion about $\alpha=0$, the sequences like $k=\delta N$ are those converging nearest the exact result.

According to the FM, the δ parameter must be found first determining

the $S_N(k,1)$ sequences of IP and SP and then to fit them linearly with N. The result (51.35a) makes certain that the introduced error will be less when the slope δ decreases.

Now, we have all the necessary elements to find the $S_N(k,w)$ value when $N\to\infty$. In order to take the limit $N\to\infty$ in (51.31), we notice that from Eq. (51.18c) it follows that

$$\ln w = -\ln\left(1+\frac{1}{\lambda k}\right) \simeq -\frac{1}{\lambda k} \quad \text{when } k>>1 \text{ and } \lambda>1 \tag{51.36}$$

which enables us to obtain the following result with the help of (51.22) (r = 1):

$$\lim_{N\to\infty} w^{N+1} = e^{-1/\delta\lambda} \tag{51.37}$$

In addition to this, we know that

$$\lim_{N\to\infty} \{k+w(x-k)\} = \lim_{N\to\infty} \left\{ \frac{\delta N(1+\lambda x)}{1+\lambda\delta N} \right\} = \frac{1}{\lambda} + x \tag{51.38a}$$

and

$$\lim_{N\to\infty} \left(1-\frac{x}{k}\right)^{N+1} = \lim_{N\to\infty} \left(1-\frac{x}{\delta N}\right)^{N+1} = e^{-x/\delta} \tag{51.38b}$$

The substitution of (51.37) and (51.38) into (51.30) yields

$$\lim_{N\to\infty} S_N(k,w) = \bar{E}(k,w) - e^{-1/\delta\lambda} \int_0^\infty \frac{x e^{-x(1+1/\delta)}}{x+1/\lambda}\, dx \tag{51.39}$$

and the change of variables $y = (\delta+1)x/\delta$ turns (51.39a) into

$$\lim_{N\to\infty} S_N(k,w) = \bar{E}(k,w) - \lambda e^{-1/\delta\lambda} \left(\frac{\delta}{\delta+1}\right)^2 \int_0^\infty \frac{y e^{-y}}{1+\frac{\lambda\delta}{1+\delta} y}\, dy =$$

$$- \bar{E}(k,w) - \lambda e^{-1/\delta\lambda} \left(\frac{\delta}{1+\delta}\right)^2 E(1,\lambda\delta/(1+\delta)) \qquad (51.40)$$

Finally, Eq. (44.8b) with $\beta=-1$ (See Eq. (51.11)) allows us to find the FM estimate for $E(1,\lambda)$:

$$\lim_{N\to\infty} SE_N = E(1,\lambda) - e^{-1/\delta\lambda} \left(\frac{\delta}{1+\delta}\right)^2 E(1,\delta\lambda/(1+\delta)) \qquad (51.41)$$

The remainder in Eq. (51.41) is not null for $\lambda>0$ and for this reason the FM permits one to construct a sequence converging to a lower bound for $E(1,\lambda)$. This sequence is determined by an order dependent mapping where k is proportional to N. The direct application of the FM and the Sensitivity Rules lead to the same result.

Before proceeding to verify numerically our predictions, we show that it is possible to draw identical conclusions regarding the remainder $R_N(k,1)$ by means of a totally algebraic treatment of the FM equations

The application of Eq. (44.8a) to (51.16) leads us to

$$E(1,\lambda) = k^{-1}(1-w)^{-1}\,\bar{E}(k,w) = k^{-1}(1-w)^{-1} \sum_{n=0}^{\infty} \bar{E}^{(n)}\, w^n \qquad (51.42)$$

where according to Eq. (44.18)

$$\bar{E}^{(n)} = \sum_{j=0}^{n} \frac{n!}{(n-j)!\,j!}\, E^{(j)} k^{-(1+j)} \qquad (51.43)$$

On introducing the coefficients (51.15) into (51.43) and setting $k=\delta N$, we have

$$\bar{E}^{(n)} = \frac{1}{k} \sum_{j=0}^{n} \frac{n!\,(j+1)}{(n-j)!} \left(-\frac{1}{\delta N}\right)^j = \frac{1}{k}\left\{1 - \frac{2n}{\delta N} + \frac{3n(n-1)}{\delta^2 N^2} - \ldots\right\} \qquad (51.44a)$$

The partial sum for N>>1 is

$$\sum_{n=0}^{N} \bar{E}^{(n)} = \frac{1}{k} \{N - \frac{2}{\delta N} (\frac{N2}{2}) + \frac{3}{\delta^2 N^2} (\frac{N^3}{3}) - \ldots\} =$$

$$= \{ \frac{1}{\delta} - \frac{1}{\delta}2 + \frac{1}{\delta}3 - \ldots\} \quad . \qquad (51.44b)$$

Finally

$$\lim_{N\to\infty} \sum_{n=0}^{N} \bar{E}^{(n)} = - \sum_{n=1}^{\infty} (- \frac{1}{\delta})^n = -(-1 + \frac{1}{1+1/\delta}) = \frac{1}{1+\delta} \qquad (51.45)$$

which leads to (51.40) when $1/\lambda \to 0$.

In order to complete this section, let us verify that the Sensitivity Rules allow to derive the convergent sequence previously obtained. Results corresponding to k_N^S and $S_N(k_N^S,1)$ are shown in Table 15.5 for $N \leq 31$.

Table 15.5: Convergent renormalized sequence for the function (51.16).

N	k_N^S	$S_N(k_N^S,1)$	N	k_N^S	$S_N(k_N^S,1)$
1	2.0000	0.4959	17	6.7794	0.7264
3	2.6258	0.6037	19	7.3594	0.7310
5	3.2371	0.6496	21	7.9377	0.7349
7	3.8392	0.6757	23	8.5145	0.7381
9	4.4349	0.6928	25	9.0901	0.7409
11	5.0238	0.7048	27	9.6646	0.7434
13	5.6131	0.7138	29	10.2381	0.7456
15	6.1975	0.7208	31	10.8107	0.7475

A standard linear regression for the 6 last SP yields

$$k_N^S = (1.91 \pm 0.03) + (0.287 \pm 0.001)N \; ; \; r = 0.99999911 \qquad (51.46)$$

According to the precedent equations, $S_N(k_N^S,1)$ should converge to $1/(1+\delta) \simeq 0.78$ when $N \to \infty$ in agreement with the last approximation in Table 15.5 $S_{31}(k_{31}^S,1) \simeq 0.75$.

It is to be noted that several problems of Physical and Physical Chemistry interest present a situation similar to that discussed in this section, that is, there are functions fulfilling scaling laws which cannot be expanded around $1/\lambda = 0$. Such cases will be discussed in forthcoming chapters.

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CHAPTER XVI

APPLICATION OF THE FM TO THE ANHARMONIC OSCILLATOR.

> "I had stated,... solutions of physical problems must always be in finite terms or convergent series, otherwise nonsense is made...Then came a partial renoval of ignorant blindness. In some physical problems divergent series are actually used"
>
> O. Heaviside, Electromagnetic Theory, 1889.

§.52. Renormalization of the RS perturbation series with the FM: convergence to the ground state of the purely quartic oscillator.

This paragraph is devoted to the application of the FM developed in §.44 to a widely studied power series with zero convergence radius: the RSPT for anharmonic oscillators. As discussed before, the anharmonic oscillator models are closely related with a $\lambda\phi^{2M}$ field theory (Appendix B). The model is also found when describing molecular vibrations, diffusion processes, laser theories, etc. (Appendix A). We have resorted to this model time and again in preceding chapters but right now we are able to obtain highly accurate results.

Physically meaningful properties are frequently associated with the limit $1/\lambda \to 0$ when one considers power series expansions in the parameter λ. This is just the case when the PT is applied to field theories. The FM is suitable for such sort of research because it allows one to construct convergent sequences approaching the limit $1/\lambda \to 0$ of the function under consideration while keeping the correct asymptotic analytic behavior with respect to λ. Thus, this section is dedicated to analyse the convergence properties of the FM series when $1/\lambda \to 0$ for the quartic anharmonic oscillator ground state.

The starting point is the Symanzik theorem for the anharmonic oscillators /1/ (Eqs.(23.3)):

$$H(g,\lambda) = p^2+gx^2+\lambda x^{2K} \tag{52.1a}$$

$$H(g,\lambda) = \lambda^{1/(K+1)}\ H(g\lambda^{-2/(K+1)},1) \tag{52.1b}$$

which yields the following scaling law for the eigenvalues $E(g,\lambda)$ of $H(g,\lambda)$:

$$E(g,\lambda) = \lambda^{1/(K+1)}\ E(g,\lambda^{-2/(K+1)},1) \tag{52.2}$$

It must be remembered that $E(1,\lambda)$ may be expanded as power series of λ and $\lambda^{-2/(K+1)}$ around $\lambda=0$ and $1/\lambda=0$, respectively. The latter possesses a finite convergence radius /1/. The existence of both Taylor expansions makes the FM particularly suitable for this model (c.f. §.51).

According to (52.2) the exponents α, β for the quartic anharmonic oscillator K = 2 are

$$\alpha = -2/3 \quad , \quad \beta = 1/3 \tag{52.3}$$

Therefore Eq. (44.7) yields the following change of variables to build the renormalized sequence:

$$k^3\lambda^2(1-w)^3 - w^2 = 0 \tag{52.4}$$

The third-order algebraic equation (52.4) has a real root fulfilling Lemmas 44.1-44.3 given by /2/:

$$\left(\frac{w}{\lambda k^{3/2}}\right)^{1/3} = \frac{1}{3\lambda k^{3/2}}\left(2\cos\left(\frac{\pi-\phi}{3}\right)-1\right);\ \lambda k^{3/2} < 2/3^{3/2} \tag{52.5a}$$

$$\phi = \arccos\left(1-\frac{27}{2}\lambda^2 k^3\right) \tag{52.5b}$$

and

$$\left(\frac{w}{\lambda k^{3/2}}\right)^{1/3} = -\frac{1}{3\lambda k^{3/2}}\left(1+\frac{2}{\operatorname{sen}(2x)}\right);\ \lambda k^{3/2} > 2/3^{3/2} \tag{52.6a}$$

$$\chi = \operatorname{arc\,tg}\left(\operatorname{tg}^{1/3}(\psi/2)\right)\ ;\ \psi = \operatorname{arc\,sen}\ (1/\cos\phi) \tag{52.6b}$$

Eq. (44.18) provides the sequence SE_N approaching $E(1,\lambda)$ for $\lambda>0$:

$$E(1,\lambda) = (\lambda/w)^{1/3}\bar{E}(k,w) = (\lambda/w)^{1/3}E(k(1-w),w) \simeq SE_N \tag{52.7a}$$

$$SE_N = (\lambda/w)^{1/3}S_N(k,w) \tag{52.7b}$$

$$\bar{E}(k,w) \simeq S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)} w^n \tag{52.7c}$$

It is worth noticing that $\bar{E}(k,w)$ is an eigenvalue of the Hamiltonian $H(k(1-w),w) = p^2+kx^2+w(x^4-kx^2)$, as discussed in §.43, provided k does not depend on the perturbation order.

Eq.(44.14) gives us the coefficients $\bar{E}^{(n)}$ in terms of the original RSPT coefficients $\{E^{(n)}\}$:

$$\bar{E}^{(n)} = \sum_{j=0}^{n} (-1)^{n-j} \binom{(1-3j)/2}{n-j} k^{(1-3j)/2} E^{(j)} \tag{52.8}$$

The k-value is obtained from the Sensitivity Rules (§.44). The calculation procedure was presented in §.50, and consists of determining the sequences $S_N(k_N^I,1)$ and $S_N(k_N^S,1)$ for increasing N values. As pointed out before, these sequences must converge towards the infinite coupling regime eigenvalue, which for the ground state is found to be /3/:

$$S_N(k^*,1) \to \lim_{\lambda\to\infty} \lambda^{-1/3}\, E(1,\lambda)=E(0,1)=1.06036209048418... \quad (52.9)$$

Before verifying this result, we deem it suitable to recall the discussion in §.43, where it was shown that the transformation (52.4) coincides with those found by Caswell /4/ and Seznec and Zinn-Justin /5/ provided the adjustable parameter is determined in every case in accordance with the same criterion. The FM introduces a convergence criterion to find out k* which is different from those used by other authors.

In order to make the numerical computations with (52.7), it is necessary to have the coefficients $E^{(n)}$ as input data. Here we resort to the RSPT coefficients calculated by Bender and Wu /6/ with twelve significant figures. These results are not the most accurate ones and other authors claim to have obtained better values /7,8/; however only Bender and Wu /6/ coefficients have been published with a large enough number of significant figures. According to the rule suggested by Le Guillou and Zinn-Justin (see §.49), if the coefficients $E^{(n)}$ have 12 significant figures one may not be able to use more than about 24 RS coefficients in a stable numerical way. Consequently, the first 24 coefficients of Ref./6/ were chosen to perform the computations. Numerical results present an interesting new feature with respect to the analysis made in preceding chapters: the number of IP and SP grows quickly with N, which leads to a larger number of convergent sequences.

The use of the RSPT up to the 24-th order yields 4 IP sequences and 3 SP sequences. Numerical results for $S_N(k^*,1)$ applying both sequences are displayed in Tables 16.1 and 16.2, respectively. In addition to this Fig. 16.1 shows the plane $k^{3/2}$ vs N with the four IP sequences (a similar graf is valid for the SP sequences, so that it is not worthwile to present them).

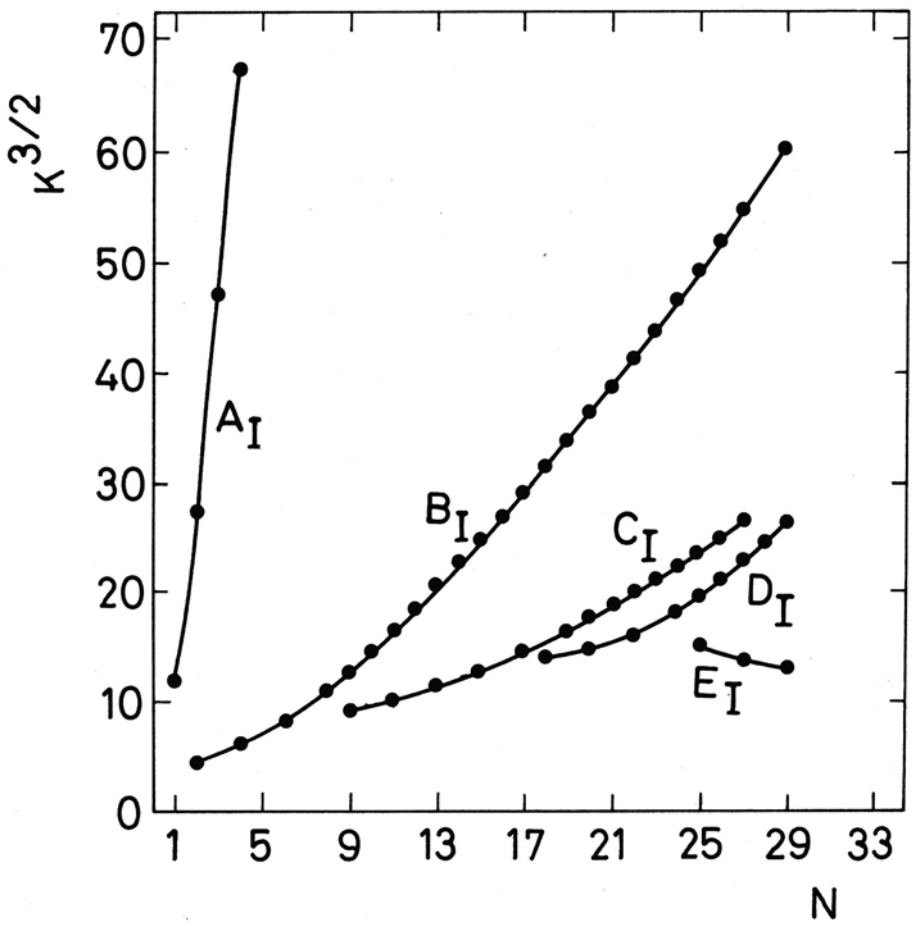

Fig. 16.1: Plane $(k_N^I)^{3/2}$-N for the inflexion points of the renormalized sequence $S_N(k,1)$ for the ground state of the quartic anharmonic oscillator.
(Full lines stand for those sequences where k_N^I grows linearly with N).

Table 16.1

Convergent sequences $S_N(k_N^I,1)$ for the ground state of the quartic anharmonic oscillator, computed with the FM.

N	$S_N(k_N^I,1)$ a)	$S_N(k_N^I,1)$ b)	$S_N(k_N^I,1)$ c)	$S_N(k_N^I,1)$ d)
1	1.28780			
2	1.29135	1.062210554		
3	1.29507			
4	1.29705	1.060313985		
5	1.29836			
6	1.29929	1.060324170		
7	1.29998			
8		1.060333114		
9		1.060334450	1.060360734	
10		1.060335690		
11		1.060336848	1.060362090	
12		1.060337896		
13		1.060338836	1.060362197	
14		1.060339676		
15		1.060340426	1.060362165	
16		1.060341098		
17		1.060341700	1.060362143	
18		1.060342243	1.060362108	
19		1.060342734	1.060362136	
20		1.060343179	1.060362134	1.060362095
21		1.060343584	1.060362132	
22		1.060343955	1.060362130	1.060362090
23		1.060344294	1.060362129	
24		1.060344606	1.060362127	1.060362089

a) Lineal sequence k_N^I-N, A_I.

b) Lineal sequence k_N^I-N, B_I.

c) Lineal sequence k_N^I-N, C_I.

d) Lineal sequence k_N^I-N, D_I.

Table 16.2

Convergent sequences $S_N(k_N^S,1)$ for the ground state of the quartic anharmonic oscillator.

N	$S_N(k_N^S,1)$ a)	$S_N(k_N^S,1)$ b)	$S_N(k_N^S,1)$ c)
1	1.081687177		
3	1.060811607		
5	1.060321330		
6	1.060313826	1.060333510	
7	1.060314156		
8	1.060315655	1.060356803	
9	1.060317570		
10	1.060319528	1.060361337	
11	1.060321379		
12	1.060323073	1.060362084	
13	1.060324600		
14	1.060325971	1.060362171	
15	1.060327198	1.060362173	1.060362158
16	1.060328299	1.060362169	
17	1.060329288	1.060362166	1.060362118
18	1.060330180	1.060362163	
19	1.060330987	1.060362160	1.060362100
20	1.060331788	1.060362158	
21	1.060332385	1.060362155	1.060362091
22	1.060332994	1.060362153	
23	1.060333552	1.060362150	1.060362083

a) Lineal sequence k_N^S-N, A_S.

b) Lineal sequence k_N^S-N, B_S.

c) Lineal sequence k_N^S-N, C_S.

The 4 IP sequences (called A_I, B_I, C_I and D_I in Fig. 16.1) and the 3 SP sequences A_S, B_S and C_S) show a linear dependence k* vs N. According to our previous discussions , the renormalized sequence $S_N(k^*_N,1)$ is not expected to converge to the exact result when k* is proportional to N. In spite of the fact that the number of coefficients is not large enough, results displayed in Tables 16.1 and 16.2 permit us to estimate the limit of each sequence to be:

i) Sequence A_I, $S_N(k^*,1) = 1.30 \pm 10^{-2}$

ii) Sequences B_I and A_S, $S_N(k^*,1) = 1.06035 \pm 10^{-5}$

iii) Sequences C_I and B_S, $S_N(k^*,1) = 1.0603622 \pm 10^{-7}$

iv) Sequences D_I and C_S, $S_N(k^*,1) = 1.06036209 \pm 10^{-8}$ (52.10)

It is clearly seen that the sequence of limits (52.10) approaches the "exact" result (52.9).

This last fact is easily understood when applying the Sensitivity Rules to the IP and SP given in Tables 16.1 and 16.2. It is found that every new IP sequence that arises when including an increasing number of perturbation corrections (where k^I increases linearlly with N) has IP with smaller absolute values of the first derivative than those corresponding to the previous sequences . Analogously, every new SP sequence that arises when N increases, corresponds to SP with smaller absolute values of the second derivative than the previous sequences.

Then, in order to apply the Sensitivity Rules to the SP and IP sequences, we must pass from one sequence to another as N increases in order to build a new sequence that converges towards the exact result. In other words, we expect to achieve convergence through a new sequence that envelops those with a linear dependence k vs N. The IP and SP sequences constructed via the Sensitivity Rules are shown in Table 16.3 as a function of the number of terms N. We can estimate the limit of such sequences to be

$$S_N(k^*_N,1) = 1.060362090 \pm 10^{-9} \quad ; \quad N>>1 \qquad (52.11)$$

Table 16.3

Convergent sequences for the ground state of the anharmonic oscillator obtained from the stability rules*.

N	$S_N(k_N^I,1)$ a)	N	$S_N(k_N^S,1)$ b)
1	1.28780	1	1.081687177
2	1.062210554	3	1.060811607
4	1.060313985	5	1.060321330
6	1.060324170	6	1.060333510
8	1.060333114	8	1.060356803
9	1.060360734	10	1.060361337
11	1.060362090	12	1.060362084
13	1.060362197	14	1.060362171
15	1.060362165	15	1.060362158
17	1.060362143	17	1.060362118
18	1.060362108	19	1.060362100
19	1.060362136	21	1.060362091
20	1.060362095	23	1.060362083
22	1.060362090		
24	1.060362089		

* Sequences have a nearly lineal dependence $k_N^{3/2}$-N.

a) The sequence goes successively by the sequences termed A_I, B_I, C_I and D_I, wherein k grows linearly with N.

b) The sequence goes successively by the sequences A_S, B_S and C_S, wherein k grows linearly with N.

The agreement obtained with respect to the exact result is one part in 10^9 for the IP sequence and one part in 10^3 for the SP sequence, with N = 24 and N = 23, respectively. These results are highly accurate and make up, together with those published in Refs. /4,5/ the best values obtained from the RSPT. Likewise, it is to be noted that FM results compare favorably, because of their simplicity, with those derived from variational methods, which in order to give the same accuracy require quite large basis set expansions /9-12/.

Furthermore, Table 16.3 makes clear an interesting feature: the convergence towards E(0.1) is not smooth, since some "jumps" happen when the sequence is changed. This characteristic has been pointed out by Caswell /4/ and Seznec and Zinn-Justin /5/, although these authors did not analyse the reasons of such convergence property.

On the other hand, Fig. 16.1 shows that the slope of the k vs N lines decreases as N increases and new sequences appear. Besides, we notice that the first k-values in the IP and SP sequences correspond approximately to straight lines $k^{3/2} = N\delta$. Since for this model $\alpha=-2/3$, it can be expected that the convergence of $S_N(k_N^*,1)$ to E(0,1) occurs through an order dependent transformation of this sort (see §.49). Once again, numerical results confirm that sequences arising from the FM converge towards the correct result following a dependence on the order imposed by the dilatation relationship. A linear regression using the smallest IP for N = 15, 18 and 20 yields

$$(k_N^I)^{3/2} = (6.5 \pm 0.9) + (0.42 \pm 0.05)\ N\ ;\ r=0.99999957 \qquad (52.12)$$

This result agrees with the value $\delta \simeq 0.377$ obtained numerically by Seznec and Zinn-Justin /5/ from the zeros of the last coefficient of the renormalized series. Clearly, the agreement is not as good as that obtained in §.50 (Eq.(50.8)) presumably because the linear correlation $k^{3/2}$ vs N is not directly settled down but constructed superimposing sequences with linear correlations k vs N.

Table 16.4

Coefficients $\bar{E}^{(n)}$ of the renormalized series for the ground state of the quartic anharmonic oscillator.*

n	$\bar{E}^{(n)}$ a)		$\bar{E}^{(n)}$ b)	
0	0.26299075623	(1)	0.24834781510	(1)
1	-0.12065160816	(1)	-0.11201271151	(1)
2	-0.23073344992	(0)	-0.20272585839	(0)
3	-0.7973954570	(-1)	-0.6475236479	(-1)
4	-0.3156530069	(-1)	-0.2316902959	(-1)
5	-0.1289030748	(-1)	-0.8346935524	(-2)
6	-0.5188328005	(-2)	-0.2871727967	(-2)
7	-0.1993422009	(-2)	-0.896253152	(-3)
8	-0.704179802	(-3)	-0.229739068	(-3)
9	-0.212621616	(-3)	-0.315338694	(-4)
10	-0.426727923	(-4)	0.131430977	(-4)
11	0.59491932	(-5)	0.150942966	(-4)
12	0.136778476	(-4)	0.925515192	(-5)
13	0.104972047	(-4)	0.448324468	(-5)
14	0.618161805	(-5)	0.132771227	(-5)
15	0.312235206	(-5)	0.61449906	(-6)
16	0.138426736	(-5)	0.14617238	(-6)
17	0.52764284	(-6)	0.71101	(-9)
18	0.1566400	(-6)	-0.274356	(-7)
19	0.1951216	(-7)	-0.219329	(-7)
20	-0.1861024	(-7)	-0.133016	(-7)
21	-0.2140450	(-7)	-0.57500	(-8)
22	-0.1524550	(-7)	-0.6354	(-8)
23	-0.9363708	(-8)	-0.2776	(-8)
24	-0.65154	(-8)		

*

i) Figures must be multiplied by a power of ten given between parenthesis. Results were rounded off according to the significant figures given for k_{24}^{I}.

a) Computed via $k_{24}^{I}=6.9164137863$.

b) Computed via $k_{23}^{S}=6.1676637263$.

Table 16.4 shows the coefficients $\bar{E}^{(n)}$ of the sequence $S_N(k,w)$ obtained via k_{24}^I and k_{23}^S according to the Sensitivity Rules. These coefficients allow us to get an excellent approximation to the lowest eigenvalue of the anharmonic oscillator for all $\lambda>0$, and besides they yield an implicit expression for $E(1,\lambda)$. After determining the w-value from Eqs. (52.5) and (52.6), we compute $SE_N(k_{24}^I,w)$ and $SE_N(k_{23}^S,w)$. Results are presented in Table 16.5 and compared with the exact ones /13/.

Table 16.5

Ground state energy of the quartic anharmonic oscillator $H(1,\lambda) = p^2+x^2+\lambda x^4$ for several λ-values.

λ	$E(1,\lambda)$ a)	$SE_{24}(k_{24}^I,w)$ b)	$SE_{23}(k_{23}^S,w)$ c)
10^{-4}	1.0000749369	1.0000749857	1.0000749912
10^{-3}	1.0007436927	1.0007436931	1.0007436922
10^{-2}	1.0073736721	1.0073736721	1.0073736721
10^{-1}	1.0652855095	1.0652855093	1.0652855095
1	1.3923516415	1.3923516426	1.3923516412
10	2.4491740721	2.4491740728	2.4491740633
10^2	4.9994175451	4.9994175437	4.9994175130
10^3	10.6397387113	10.6397387073	10.6397386342
10^4	22.861603870	22.861608862	22.361603681

a) Variational "exact" values /13/.

b) Computed via the renormalized series up to the 24-th order and resorting to the PI sequences with the coefficients given in Table 16.4.

c) Computed via the renormalized series up to the 23-th order and resorting to the PE sequences with the coefficients given in Table 16.4.

The remarkable agreement (up to 9 significant figures for the whole range $\lambda>0$) is not surprising, since on the basis of the former discussion, we had convergence up to 9 significant figures for E(0,1) and this is precisely the most unfavourable case since it formally corresponds to the limit $\lambda\to\infty$. In conclusion, we have shown that the eigenvalues for the quartic anharmonic oscillator model can be accurately approximated for all $\lambda>0$ by summation of the RSPT through the FM.

In closing this section, we deem it appropriate to make a brief discussion about the problem with $g<0$. This case corresponds to a Hamiltonian (52.1a) describing a double-well potential. This model has been widely applied to study molecular vibrations, rotational barriers, phase transitions, etc. (see Ref. /14/ and references therein). It is convenient to rewrite the Hamiltonian (52.1a) (K = 2) in terms of $Z = -g>0$:

$$H(-Z,\lambda) = p^2 - Zx^2+\lambda x^4 \tag{52.13}$$

Once again we apply the procedure given in Appendix A to obtain the scaling law fulfiled by $H(-Z,\lambda)$:

$$H(-Z,\lambda) = Z^{-1/2}\, H(-1,\lambda Z^{-3/2}) \tag{52.14}$$

In order to build the renormalized series one resorts to (52.14):

$$H(k(1-w),w) = k^{1/2}(w-1)^{1/2}\, H(-1,wk^{-3/2}(w-1)^{-3/2}) \tag{52.15}$$

Evidently, the condition $w\geq 1$ must be satisfied in order to apply the FM since

$$\lambda = wk^{-3/2}\,(w-1)^{-3/2} \tag{52.16}$$

has to be positive. Besides, it follows from (52.16) that

$$E(-1,\lambda) \sim k^{-1/2}(w-1)^{-1/2}\bar{E}(k,w) \qquad (52.17)$$

The function $\bar{E}(k,w)$ is an eigenvalue of $H(k(1,w),w)$. The change of perturbation parameters (52.16) reveals the key difficulty in the application of the FM to the present model: the interval $0\leq\lambda<\infty$ is mapped onto $\infty>w\geq 1$. Then, it will be extremely difficult to approach the eigenvalues of a double-minimum potential problem when $\lambda<<1$ because it follows that $w>>1$. It is not difficult to understand why this case is not so easily treated if one takes into account that the potential function has two infinitely deep and separated minima, when $\lambda\to 0$.

§. 53. Further results for the eigenvalues of quartic anharmonic oscillators.

In this paragraph we direct our attention to some other aspects of the eigenvalues of the quartic anharmonic oscillator regarding the FM.

Firstly, we deem it relevant to show the effect of taking into account the leading coefficient of the large-λ series given by

$$E(0,1) = e^{(0)} \qquad (53.1)$$

In the previous section it was accuratly obtained by means of the RSPT and the FM.

In order to introduce this coefficient into the FM we may resort to the procedure described in §.42 and applied in §.50.

For that purpose, $E(1,\lambda)$ is approximated by means of the following sequence

$$SE'_N = (\lambda/w)^{1/3}\, S'_N(k,w) \qquad (53.2a)$$

where

$$S'_N(k,w) = \sum_{n=0}^{N-1} \bar{E}^{(n)} w^n + \bar{E}^{(N)} w^N \qquad (53.2b)$$

We have split the sequence $S'_N(k,w)$ into two parts, so that the first (N-1) coefficients $\bar{E}^{(n)}$ are computed from the RSPT up to the (N-1)-th order (Eq. (52.8)) and the N-th coefficient is set so as to introduce (53.1). This last purpose may be attained as in Eq. (50.23):

$$\bar{E}',(N) = e^{(0)} - \sum_{n=0}^{N-1} \bar{E}^{(n)} \qquad (53.3)$$

According to (53.2) and (53.3) one may approach $E(1,\lambda)$ through

$$SE'_N = (\lambda/w)^{1/3}\{e^{(0)} w^N + \sum_{n=0}^{N-1} \bar{E}^{(n)} (w^n - w^N)\} \qquad (53.4)$$

where w us given by (52.5) and (52.6).

Our aim is to use (53.4) to obtain a simple analytical approximate expression for the lowest eigenvalue as a function of λ. Therefore, we consider only two perturbation corrections (Eq.(36.20)):

$$E^{(0)} = 1, \; E^{(1)} = 3/4, \; E^{(2)} = -21/16 \qquad (53.5)$$

in addition to $e^{(0)}$. Eq.(52.8) enables us to get at once

$$\bar{E}^{(0)} = k^{1/2} E^{(0)} \qquad (53.6a)$$

$$\bar{E}^{(1)} = k^{-1}\{E^{(1)} - \frac{k^{3/2}}{2} E^{(0)}\} \qquad (53.6b)$$

$$\bar{E}^{(2)} = k^{-5/2}\{E^{(2)} + E^{(1)} k^{3/2} - \frac{1}{8} k^3 E^{(0)}\} \qquad (53.6c)$$

which yields SE'_N as a function of k. The suitable k-value is next determined according to the Sensitivity Rules, i.e.

$$\left(\frac{\partial SE'_N}{\partial k}\right)\ (k = k^*) = 0 \tag{53.7}$$

The proper root of (53.7) is found to be

$$k^* \simeq 2.9096 \tag{53.8}$$

disregarding the λ value. On using this k value Eq. (53.4) becomes

$$SE'_3 = (\lambda/w)^{1/3}\{1.7057549648 - 0.595110017\ w - 0.04634197750\ w^2 - 0.003940805138\ w^3\} \tag{53.9}$$

In spite of its extreme simplicity, Eq. (53.9) is very accurate, as follows from the comparison with the (numerical) exact results in Table 16.6.

Table 16.6

Ground state energy of the quartic anharmonic oscillator obtained by way of Eq. (53.9)

λ	$SE'_3\ (k^*,w)$ [a]	$E(1,\lambda)$ [b]
10^{-4}	1.0000750	1.0000750
10^{-3}	1.0007487	1.0007487
10^{-2}	1.0073736	1.0073737
10^{-1}	1.0652807	1.0652855
1	1.3923160	1.3923516
10	2.4491391	2.4491741
10^2	4.9993984	4.9994176
10^3	10.639779	10.639789
10^4	22.861605	22.861609

a) Computed with Eq. (53.9).

b) Ref. /13/, results rounded off to eight meaningful figures.

The largest error of about $\pm$ 3 x 10^{-5} occurs in the intermediate-λ regime. Eq.(53.9) is a most accurate and simple formula for the ground state energy of the quartic anharmonic oscillator. Some previous results on the usefulness of taking into account $e^{(0)}$ within the FM context are found in Ref./10/.

As a further test of the accuracy of (53.9) we calculate the coefficient $e^{(1)}$ of the $\lambda^{-2/3}$-power series expansion (Eq.(23.36)). When $1/\lambda \to 0$, Eq. (52.4) yields immediately

$$w \simeq 1 - \frac{1}{k} \lambda^{-2/3} + O(\lambda^{-4/3}) \tag{53.10}$$

which, when introduced into (53.9) gives

$$SE_3' \simeq \lambda^{1/3}\{ \sum_{n=0}^{3} \bar{E}^{(n)} + \lambda^{-2/3} \frac{1}{3k} \sum_{n=0}^{3} E^{-(n)} \ (1-3n) + \ldots\} =$$

$$= \lambda^{1/3}\{e^{(0)} + \tilde{e}^{(1)} \ \lambda^{-2/3} + \ldots.\} \tag{53.11}$$

where

$$\tilde{e}^{(1)} = \frac{1}{3k} \sum_{n=0}^{3} \bar{E}^{(n)} \ (1-3n) \tag{53.12}$$

is our approximation to $e^{(1)}$. Eqs. (53.8) and (53.9) yield the following numerical result

$$\tilde{e}^{(1)} = 0.361930 \tag{53.13}$$

which is an noteworthy approximation to the "exact" value obtained numerically by Hioe et al /15/: $e^{(1)} = 0.362022$. This agreement is further evidence of the convenience of using a transformation that assures the correct large-coupling behavior of the function whose pertur-

bative expansion is considered.

Up to now we have not explicitly considered the higher eigenvalues of the quartic anharmonic oscillator model. These states have not been widely studied from the RSPT standpoint, so that a large enough number of accurate perturbation coefficients is not available. The HPM (§.8) has allowed the calculation of 11 accurate RS coefficients. This number is not large enough to make a reasonable convergence study via the FM. However, some useful and important information about the excited states may be attained through the application of the renormalized secuences. The remainder of this section is devoted to discussing this issue.

It is well-known that when m is large enough the eigenvalues E_m can be approached via the JWKB method (Chapter II). Then one may assume that the use of the FM to sum the perturbative expansion for the quartic anharmonic oscillator for large enough quantum numbers will allow one to approximate the eigenvalues at the semiclassical limit. In order to verify this conjecture, we proceed to perform an analytical preliminary study.

For the sake of simplicity, let us consider the following sequence

$$S_3(k,1) = \sum_{n=0}^{3} \bar{E}_m^{(n)} \tag{53.14}$$

that approaches $\bar{E}_m(k,1) = E_m(0,1)$ where $E_m(0,1)$ is the m-th eigenvalue of the quartic oscillator. We must add the coefficient $\bar{E}_m^{(3)}$ to those listed in (53.6), which is easily derived from Eq. (52.8):

$$\bar{E}_m^{(3)} = k^{-4} \{E_m^{(3)} + \frac{5}{2} k^{3/2} E_m^{(2)} + k^3 E_m^{(1)} - \frac{1}{16} k^{9/2} E_m^{(0)}\} \tag{53.15}$$

The perturbational coefficient $E_m^{(3)}$ is found in the current literature /4/ and complements the list in §.36:

$$E_m^{(3)} = \frac{375}{1024} (2m+1)^4 + \frac{1707}{512} (2m+1)^2 + \frac{4617}{3072} \tag{53.16}$$

On introducing (53.6) and (53.15) into (53.14) we have

$$S_3(k,1) = \frac{5}{16}\, k^{1/2}\, E_m^{(0)} + 3k^{-1} E_m^{(1)} + \frac{7}{2}\, k^{-5/2} E_m^{(2)} + k^{-4} E_m^{(3)} \qquad (53.17)$$

In order to obtain a simple analytical expression, k is chosen as proposed by Pascual /16/ and Dmitrieva and Plindov /17,18/. The procedure is closely related with the SVM (see §§.16 and 21), viz.

$$\{ \frac{\partial}{\partial k}\, S_1(k,1) \}\ (k = k^*) = 0 \qquad (53.18a)$$

where

$$S_1(k,1) = \frac{1}{2}\, k^{1/2}\, E_m^{(0)} + k^{-1}\, E_m^{(1)} \qquad (53.18b)$$

The root is found to be:

$$k_m^* = \{\frac{3}{2}\ (2m+1 + \frac{1}{2m+1})\}^{2/3} \qquad (53.19)$$

which is not suitable for the ground state (m=0) (see §.43), but allows one to obtain a renormalized asymptotic series for excited states. Such series is slowly divergent and its range of utility increases with m.

Finally Eqs. (39.20), (53.16), (53.17) and (53.19) yield

$$S_3(k^*,1) = \frac{5}{16}\ (\frac{3}{2})^{1/3}\ u^{4/3}(1+u^{-2})^{1/3} +$$

$$\frac{9}{8}(\frac{2}{3})^{2/3}(1+u^2)\ (u+u^{-1})^{-2/3} - \frac{7}{16}\ (\frac{2}{3})^{5/3}\ u\{\frac{67}{8} + \frac{17}{8}\ u^2\}\ \{u+u^{-1}\}^{-5/3} +$$

$$+ \left(\frac{2}{3}\right)^{8/3}\left(\frac{4617}{3072} + \frac{1707}{512}\,u^2 + \frac{375}{1024}\,u^4\right)\,(u+u^{-1})^{-8/3} \qquad (53.20)$$

where u=2m+1. Retaining only the two most important terms when m>>1, the preceding equation may be rewritten in an appropriate fashion to compare with Eq.(36.28):

$$S_3(k^*,1) \cong \frac{291}{64}(9^{-1/3})\left\{\frac{u}{2}+\frac{65}{1164u}+O(m^{-2})\right\}^{4/3} \qquad (53.21)$$

Eq. (53.21) is a noteworthy approximation to the eigenvalues of the quartic oscillator ($H(0,1) = p^2+x^4$) in the semiclassical limit (Eq. (36.28)):

$$E_m(0,1) = e_m^{(0)} = (3/\sqrt{2})^{4/3}(\Gamma(\tfrac{1}{4}))^{-8/3}\pi^2\left(\frac{u}{2}+\frac{1}{24\pi u}+O(m^{-2})\right\}^{4/3} \qquad (53.22)$$

Eqs. (53.21) and (53.22) show that the error of the third-order FM expression is only 0.038% and 5.3% for the first and second WKBJ coefficients, respectively.

In order to obtain more accurate results the abovementioned 11 RS coefficients have been used and k* has been computed via Eq. (53.19). The $S_{11}(k_m^*,1)$ values for m = 10, 20, 30,..., 100 are compared with exact numerical values of $e_m^{(0)}$ /3/ in Table 16.7

Table 16.7

Excited eigenvalues of the purely quartic oscillator, obtained by means of the method given in §.53.

m[a)]	$S_{11}(k_m^*,1)$ [b)]	m	$S_{11}(k_m^*,1)$
10	50.2562	60	513.971
20	122.6046	70	636.386
30	208.2323	80	759.502
40	303.912	90	887.834
50	407.874	100	1020.990

a) Quantum number.

b) Renormalized seguence with k_m^* determined from Eq. (53.19). Results were cut off up to have the number of significant figures as to get coincidence with the "exact" results (Ref./13/).

Approximate JWKB coefficients can be obtained from the equation

$$\frac{S_{11}(k_m^*,1)}{(\frac{u}{2})^{4/3}} \simeq C + \frac{4}{3} DC \, (\frac{u}{2})^{-2} \tag{53.23}$$

where C and D are determined from a least square fitting for m = 10, 20, 30,..., 100. Linear regression yields:

$$C = 2.185069 \pm 10^{-6} \; ; \; D = 0.0264 \pm 10^{-4} \quad r = 0.99979. \tag{53.24}$$

The C value exhibits an error of 1.4×10^{-5}% with respect to the first JWKB coefficient

$$(3\sqrt{2})^{4/3}\pi^2 \, |\Gamma(\tfrac{1}{4})|^{-8/3} = 2.1850693013... \tag{53.25a}$$

while D has an error of 0.47% regarding the second JWKB coefficient

$$\frac{1}{12\pi} = 0.0265258238... \qquad (53.25b)$$

Summing up: the eigenvalues of the quartic anharmonic oscillator may be approached in a very good fashion via the FM for large or small λ and m values.

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CHAPTER XVII

APPLICATION OF THE FM TO MODELS WITH CONFINING POTENTIALS

§.54. Convergence of renormalized series in the strong coupling limit.

Quantum mechanical models with confining potentials have deserved remarkable attention in recent years, because they provide convenient phenomenological potentials to explain the hadronic spectroscopy within the context of quark theory. The aim of this chapter is to employ the FM to calculate the eigenvalues of these models by purely numerical approaches and also to derive accurate analytical expressions. We do not discuss here the applicability of the model, since this question is beyond the scope of this book. However, the interested reader may resort to Appendix F for additional details about the importance and usefulness of the confining models in elementary particle physics.

For the sake of concreteness we restrict ourselves to the linear confining potential. The eigenvalues of

$$H(Z,\lambda) = \frac{1}{2} p^2 - \frac{z}{r} + \lambda r \ , \ p = -i \nabla \qquad (54.1)$$

may be associated with the mass resonances corresponding to the bound-state annihilation of quark-antiquark pairs. This model has been discussed in relation with the "charmonium" (quark-antiquark system with charm quantum number) by Eichten et al /1/.

The operator $H(Z,\lambda)$ satisfies a scaling law which can be easily obtained from a unitary transformation (Symanzik Theorem /2/) shown in Appendix A. The result is the following unitary equivalence between operators

$$H(Z,\lambda) = \lambda^{2/3} H(Z\lambda^{-1/3},1) = Z^2 H(1,\lambda Z^{-3}) \qquad (54.2)$$

which yields the corresponding relationship for their eigenvalues:

$$E(Z,\lambda) = \lambda^{2/3} E(Z\lambda^{-1/3},1) = Z^2 E(1,\lambda Z^{-3}) \qquad (54.3)$$

clearly, the FM exponents are $\alpha = -1/3$ and $\beta=2/3$.

$E(1,\lambda)$ can be expanded in a Taylor series around $\lambda=0$:

$$E(1,\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n \qquad (54.4)$$

which is asymptotically divergent. The asymptotic behavior of the RS coefficients $E^{(n)}$ has been studied /3/ and it reveals that (54.4) diverges more strongly than the RSPT series for the anharmonic oscillator (§.11) because

$$E^{(n)} \to - (-\frac{3}{2})^n (18/\pi e^3) n(n!) \qquad (54.5)$$

This fact suggests that the summation of the RSPT series will be more difficult for this model than for the quartic anharmonic oscillator.

From the analytical point of view the eigenvalues of (54.1) and those studied in Chapter XVI are similar, since in every case there is a λ^{α}-power series expansions around $1/\lambda = 0$, in addition to the RS expansion around $\lambda = 0$ /4/. According to the discussion presented in Chapter XV such feature makes both models suitable for the FM.

Physical applications require to know the eigenvalues of (54.1) for $\lambda>1$ and usually for λ values as large as $\lambda = 500$. For this range of λ values it is difficult to obtain Rayleigh-Ritz variational results since on the one hand the eigenfunctions of $H(0,1)$ are very difficult to handle, and on the other the set of eigenfunctions for the discrete spectrum of $H(0,1)$ is not complete. This state of affairs leads us to consider the RSPT as a significative practical tool for obtaining eigenvalues.

Since the ground state of (54.1) has received the greatest attention in the current literature we will restrict ourselves to examine such particular case. In order to apply the RSPT it is necessary to have the coefficients $E^{(n)}$. Privman /5/ has computed the first 20 coefficients accurately applying the logarithmic derivative method (see §.9) and they are used in this chapter. There are several prior applications of summation techniques to the present perturbative series which are summarized below.

i) The Padé approximants for this model converge /4/ and they have been intensively studied /6-8/. However, numerical results show that even when resorting to about 20 RS coefficients it is not possible to obtain a reliable approximation when $\lambda>1$. Actually, for $\lambda = 1$ the accuracy is not better than just three significant figures.

ii) The renormalized series obtained by splitting the Hamiltonian are expected to yield accurate results even for $\lambda>1$ /9,10/. The main disadvantage of this method, which must in principle be similar to the FM, is that a separate calculation is required for every λ value.

iii) Other successful contributions are based on the Borel-Padé method (§.14), combined with a transformation that removes the singularity nearest to the origin in the Borel transform /11-13/. Popov and Weinberg /11-13/ have combined the Borel method and the RSPT up to the 40th-order, using the coefficients of Ref. /14/. The convergence of the resulting sequences for $1/\lambda\to 0$ was firstly studied in Refs. /11-13/. The value of E(0,1) obtained using 40 perturbative coefficients and the change of variables (43.57) in the Borel transform presents an error of 5% with respect the exact numerical value. In spite of the huge task (it is required to integrate the Padé approximants in the variable (43.57) numerically), the procedure fails to provide the correct large-λ behavior.

It is shown in what follows that the FM allows one to obtain highly accurate results resorting to a relatively small number of perturbative coefficients. Some of the following results obtained from the formalism of §.42 and that one developed in §.44 have been published /15-17/.

The application of the equations developed in §.44 to the model (54.1), leads to an approximation SE_N to $E(1,\lambda)$ given by:

$$E(1,\lambda) = (\lambda/w)^{2/3}\ \bar{E}(k,w) \simeq SE_N \tag{54.6}$$

where

$$SE_N = (\lambda/w)^{2/3}\ S_N(k,w) \tag{54.7}$$

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)}\ w^n \tag{54.8}$$

The coefficients $\bar{E}^{(n)}$ are obtained from Eq. (44.14) in terms of the RS coefficients:

$$\bar{E}^{(n)} = \sum_{j=0}^{n} (-1)^{n-j}\ \binom{2-3j}{n-j} E^{(j)} k^{2-3j} \tag{54.9}$$

Eq. (44.7) tells us that w is a root of the algebraic equation

$$\lambda k^3 (1-w)^3 - w = 0 \tag{54.10}$$

The root fulfilling the Lemmas 44.1 - 44.3 is

$$(w/\lambda k^3)^{1/3} = -\ 2(3\lambda k^3)^{-1/2}/\mathrm{tg}(2\chi) \tag{54.11a}$$

$$\chi = \mathrm{arc\ tg}(\mathrm{tg}^{1/3}(\phi/2)) \tag{54.11b}$$

$$\phi = \mathrm{arc\ tg}\ (-2/(27\lambda k^3)^{1/2}) \tag{54.11c}$$

Eq. (54.11) gives w as a function of λ where, as usual, k is determined according to the Sensitivity Rules.

Now we can study the convergence behavior of the renormalized series when $1/\lambda \to 0$. According to what was found before $S_N(k,1)$ should converge to $\bar{E}(k,1) = E(0,1)$ when $N \to \infty$. $E(0,1)$ is an eigenvalue of $H(0,1) = p^2/2 + r$. When the eigenvalue of the angular momentum operator L^2 is zero, i.e. $l = 0$, the Hamiltonian can be chosen to be $H(0,1) = -\frac{1}{2}\frac{d^2}{dr^2} + r$ and its eigenvalues are related to the zeros of the Airy Function $A_i(\xi)$. This function satisfies the differential equation

$$-A_i''(\xi) + \xi A_i(\xi) = 0 \tag{54.12}$$

and its zeros $A_i(\xi_o) = 0$ are proportional to the eigenvalues $E(0,1)$:

$$E(0,1) = \xi_o/2^{1/3} \tag{54.13}$$

For the ground state we have /18/:

$$E(0,1) = 1.855757081... \tag{54.14}$$

In order to determine the convergence of the sequence $S_N(k,1)$ to (54.14) we consider the IP sequence $S_N(k_N^I,1)$ and the SP sequence $S_N(k_N^S,1)$, in accordance with the Sensitivity Rules.

The FM presents a noteworthy property: the distribution of the SP and IP of $S_N(k,1)$ as a function of N seems to be the same for different models with divergent RS series. This feature is evident when comparing Figs. 16.1 and 17.1.

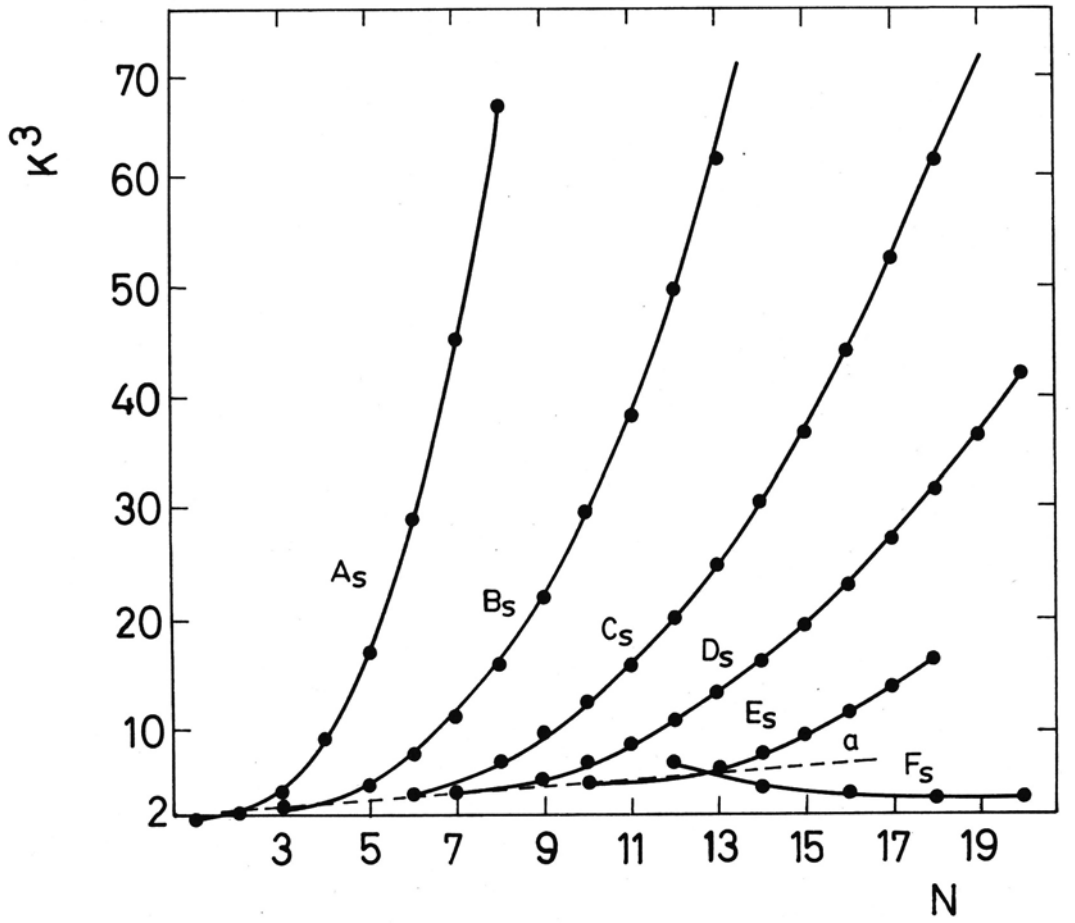

Figure 17.1: Plane $(k_N^S)^3$-N for the $S_N(k,1)$ renormalized sequence stationary points of the ground state of the linear confining potential model.

(Full lines denote sequences where k_N^S grows linearly with N).

The latter shows the $(k_N^S)^3$ - N plane corresponding to the model (54.1). The structure of the plane $(k_N^I)^3$ - N is similar, for which reason it is not discussed here.

The full lines A_S, B_S, C_S, D_S and E_S are nearly straight lines. As argued in former chapters, we know that such k_N values give rise to sequences S_N converging to wrong limits. The convergence rate for this model is slower than the one for the quartic anharmonic oscillator, so that we cannot estimate the limits of these sequences as accurately as done before. A plain difference arises when comparing Figs. 16.1 and 17.1: there are more linear sequences for every N value in the case of the linear confining model. This fact seems to be related to a stronger divergence of the RSPT and as a general rule the perturbation series is more difficult to sum via the FM.

In addition to this, Fig. 17.1 shows a curve (F) with negative slope. This dependence is hard to understand and is probably due to the lack of enough accuracy of the input coefficients. In order to avoid possible numerical error, we have truncated the series so that the points on the anomalous curve do not appear. For Fig. 17.1 it corresponds to N = 13.

The examination of the $(k_N^S)^3$ - N plane reveals that the slopes of the straight lines $k_N^S \simeq \delta N$ decrease as we proceed upwards. This fact suggests that the sequences tend to arrange themselves along a straight line $(k_N^S)^3 \simeq \delta N$, which according to Eq. (49.37) is the expected behavior for the convergent FM sequences.

Table 17.1

Convergent sequences $S_N(k_N^S,1)$ and $S_N(k_N^I,1)$ computed via the FM corresponding to the ground state of the linear confining potential model.

N	$S_N(k_N^S,1)$ a)	N	$S_N(k_N^I,1)$ a)	N b)	$S_N(k_N^S,1)$ c)	N b)	$S_N(k_N^I,1)$ c)
1	1.9656	3	1.9086	1(A)	1.9656	3(B)	1.9086
2	1.7858	4	1.8499	2(A)	1.7858	4(C)	1.8499
3	1.9008	6	1.8324	3(B)	1.9008	7(D)	1.8762
5	1.8210	7	1.8762	7(D)	1.8722	11(F)	1.8793
6	1.8621	9	1.8735	10(E)	1.8571		
7	1.8722	10	1.8397	13(E)	1.8582		
9	1.8329	11	1.8793				
10	1.8571	13	1.8820				
12	1.8926						
13	1.8582						

a) Sequence obtained from the SR.

b) The sort of sequence with k-N linear dependence to which belongs the critical point is denoted between parenthesis.

c) Sequence built looking for straight lines in the $(k_N^*)^3$-N plane.

Table 17.1 shows the sequences $S_N(k_N^S,1)$ and $S_N(k_N^I,1)$ obtained from the application of the Sensitivity Rules to the set of SP and IP of $S_N(k,1)$. In accordance with the argument above, the Sensitivity Rules allow us to construct a sequence crossing all the linear ones. Results in Table 17.1 reveal plainly that convergence for this model is slower than for the ones discussed previously so that more perturbation coefficients are required to attain similar accuracy. On spite of this slowness, we can perform the following estimate resorting to the RSPT up to the 13-th order with both sequences:

$$S_N(k_N^*,1) \simeq 1.86 \pm 0.03 \qquad (54.15)$$

with an error of 16.4% this is perhaps the best estimate of the large-coupling limit obtained from RSPT.

Table 17.1 shows two additional sequences $S_N(k_N^S,1)$ and $S_N(k_N^I,1)$, built from linear correlations $(k_N^*)^3 \simeq \delta N$. The SP straight line is labelled a in Fig. 17.1 and is of the following form:

$$(k_N^S)^3 = (0.4 \pm 0.1)\ N + (1.3 \pm 0.9),\ r=0.998 \qquad (54.16)$$

According to the discussion above $E(1,\lambda)$ can be approximated by $S_{13}(k_{13}^S,1)$, where

$$k_N^S = 1.8307185377 \qquad (54.17)$$

is obtained from Table 17.1. The renormalized coefficients $\bar{E}^{(n)}$ are shown in Table 17.2. Since they have roughly the same value it is not difficult to understand why the convergence rate is so slow for this model.

Table 17.2

Renormalized series $\bar{E}^{(n)}$ coefficients for the ground state of the linear confining potential model.

n	$E^{-(n)}$ a)	n	$\bar{E}^{(n)}$
0	-1.675765182	8	0.0262887052
1	4.170880783	9	-0.0464438718
2	-0.989952787	10	-0.0216663149
3	0.383136662	11	0.0425081413
4	0.052040299	12	0.0178521079
5	-0.0939791961	13	-0.0264276612
6	-0.033934645		
7	0.0586310572		

a) Computed with $k_{13}^S = 1.8307185377$. Results have been cut off up to retain the last figure remaining stable for a variation of 10^{-10} in k_{13}^S.

Estimates of $E(1,\lambda)$ for several λ values obtained from SE_{13} are compared with accurate nonperturbative calculations /1/ in Table 17.3.

Table 17.3

Ground state energy of the linear confining potential model for several λ-values.

λ	$SE_{13}(k_{13}^{S},w)$ a)	$E^{\|16/15\|}$ b)	$E(1,\lambda)$ c)	SE_7' d)
500.000000000	108.46643	106.9	108.36530	108.35487
62.500000000	24.87047	24.792	24.85630	24.85263
18.518518510	10.009187		10.005967	10.004464
7.812500000	5.014643		5.013781	5.013090
4.000000000	2.796003	2.79573	2.795754	2.795423
2.314814815	1.640123		1.640050	1.639885
1.457725948	0.972105		0.972086	0.972003
0.976562500	0.556771	0.556764	0.556767	0.556724
0.685871056	0.284113		0.284115	0.284093

a) Renormalized sequence obtained from coefficients given in Table 17.2 (see §.54).

b) Borel-Padé method with the RSPT up to the 31th order plus a suitable transformation to remove the closest singularity to the origin /12/.

c) "Exact" result from the numerical integration of the Schrödinger equation /1/.

d) Renormalized sequence obtained from the RSPT up to the 6th order plus the addition of the coefficient $e^{(0)}$ (see §.55) with $k_7^* = 1.5465$.

The unusual λ-values appearing in Table 17.3 correspond to values of $(4/\lambda)^{1/3}$ ranging from 0.2 to 1.8 and steps of 0.2. For the sake of completeness we have also added the results obtained from the Borel-Padé method (via the transformation (43.57)) using 31-th order RSPT /12/. Despite its simplicity, the FM is as accurate as the Borel-Padé procedure in the small and intermediate range of λ-values, and better than this method for large enough λ-values. The results given in Table 17.2 are the most accurate ones obtained to this moment by means of the RSPT for the same order.

§.55. Further results for eigenvalues of confining potential models.

This paragraph is devoted to some miscellaneous applications of the FM to confining potential models.

To begin with we consider, as in precedent sections, the effect of adding the coefficient $e^{(0)} = E(0,1)$ to the FM renormalized series. The procedure to be followed in order to incorporate such coefficient was explained yet in §.50 and we will not give further details here.

The eigenvalue $E(1,\lambda)$ may be approximated by means of the sequence

$$E(1,\lambda) \simeq SE'_N = (\lambda/w)^{2/3} S'_N(k,w) \tag{55.1a}$$

where

$$S'_N(k,w) = \sum_{n=0}^{N-1} \bar{E}^{(n)} w^n + \bar{E}'^{(N)} w^N \tag{55.1b}$$

$$\bar{E}'^{(N)} = e^{(0)} - \sum_{n=0}^{N-1} \bar{E}^{(n)} \tag{55.1c}$$

The renormalized coefficients $\bar{E}^{(n)}$, $n \leq N-1$, and w are given by Eqs. (54.9) and (54.11), respectively. The optimum k-value is given by

$$\left(\frac{\partial SE'_N}{\partial k}\right)_\lambda \quad (k = k_N^*) = 0 \tag{55.2}$$

In order to demonstrate the advantageous effect of introducing $e^{(0)}$ into the renormalized sequence SE'_N, we have employed half the number of perturbative coefficients $E^{(n)}$ previously used. Numerical results yield (Eq. (55.2)):

$$k_7^* = 1.5465 \quad . \tag{55.3}$$

k_7^* and Eqs. (55.1) lead to the results given in the last column of Table 17.3. The agreement is excellent though a much smaller number of perturbation terms have been used.

Although all the numerical applications in this chapter, refer to the linear confining potential model, it is just a particular example of

$$H = \frac{1}{2} p^2 + \frac{Z}{r} f(r) \tag{55.4}$$

The linear confining model corresponds to

$$f(r) = 1 - \frac{\lambda}{Z} r^2 \ , \ \lambda>0 \tag{55.5}$$

Another confining model studied recently is defined by

$$f(r) = 1 - \frac{\lambda}{Z} r^3 \ , \ \lambda>0 \tag{55.6}$$

and it is called "Coulombic-harmonic". The greatest interest on this model arises from the fact it resembles part of the Hamiltonian operator for the Zeeman effect in hydrogen, but it makes up a simpler problem /18/. A large number of RS perturbation coefficients for the ground state of this model have been calculated, and their asymptotic behavior has been shown to be /19/:

$$E^{(n)} \to - \frac{1}{512\pi^3} \left(- \frac{64}{\pi^2}\right)^n (2n+1)! \ , \ Z = 1 \tag{55.7}$$

The Hamiltonian corresponding to (55.6) fulfils a dilatation relationship /19/ and every eigenvalue can be expanded in a $\lambda^{-1/4}$-power series with nonzero convergence radius /19/. Therefore the FM can be applied as discussed in §.54.

The model defined by

$$f(r) = 1-(\frac{\lambda}{2} r^2 + \frac{g}{2} r^3),\ \lambda,g>0 \qquad (55.8)$$

has also received considerable attention /20,21/. The perturbation series for (55.6) and (55.8) have only been treated by means of Borel-Padé methods /13/ and convergence proves to be rather slow. The screened coulomb potentials are also given by the general expression (55.4) although they are not considered to be confining potentials.

Among such models the most widely known one is probably the Yukawa or Debye-Hückel potential given by

$$f(r) = e^{-\lambda r} \qquad (55.9)$$

It has many applications in nuclear and atomic physics, solid state theory and plasma physical-chemistry. This model has been treated by means of perturbation theory. A large number of perturbative coefficients have been determined for the ground /5,22/ and several excited states /23/. The RS perturbation series in powers of λ for the eigenvalues is divergent, and the asymptotic behavior of the coefficients proves to be /3/

$$E^{(n)} \to - (-2 \ln n)^{-n}\, n! \qquad (55.10)$$

It is certanly different from those discussed before and shows that the perturbation series is not as strongly divergent as the one for the linear confining potential (cf Eq. (54.5)). Due to the available information, the FM is very easy to apply in this case. The starting point

is the unitary equivalence

$$H(Z,\lambda) = p^2 - \frac{Z}{r} e^{-\lambda r} = \lambda^2 H(Z\lambda^{-1},1) \qquad (55.11)$$

which is easily obtained by means of the scaling transformation discussed in Appendix A.

The eigenvalues of this model are not as important as the critical parameters λne, $n = 1, 2, \ldots$, $e = 0, 1, \ldots n-1$ for which $E_{ne}(\lambda ne)=0$ /24,25/.

Another useful screening Coulomb potential, which can also be treated by the FM, is given by

$$f(r) = e^{-\lambda r} \cos\lambda r \qquad (55.12)$$

It has been applied to the investigation of the electronic properties of metals and semiconductors with ionic impurities /26/, and to the Thomas-Fermi potential /27/:

$$f(x)^{3/2} = x^{1/2} \frac{d^2 f(x)}{dx^2} \; ; \; x = 2(\frac{4}{3\pi})^{2/3} Z^{1/3} r \qquad (55.13)$$

which makes up the simplest Density Functional Theory.

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CHAPTER XVIII

APPLICATION OF THE FM TO THE ZEEMAN EFFECT IN HYDROGEN

§.56. Convergence of renormalized series for the Landau regime.

The Zeeman effect in the hydrogen-like atoms (ZEHA) is a problem of remarkable interest in several physic and chemistry fields, and was discussed in Chapter IX. Likewise, the VFM (developed in Chapter V) was applied to the ZEHA in Chapter X. Quite accurate results were obtained by taking into account the asymptotic properties of eigenvalues of the model Hamiltonian.

The aim of this Chapter is to apply the FM to the ZEHA making use of the RSPT series and all the available information about the eigenenergies. The RSPT coefficients for the first states have been computed by several authors /1-3/. Tables 9.1 and 9.2 show our results for the first five states which will be used in this Chapter. Calculations using the FM described in §§.44 and 42 have recently been published /3,4/.

The part of the Zeeman Hamiltonian that is relevant to our discussion is (c.f. Eq. (31.1)):

$$H(Z,\lambda) = -\frac{1}{2}\Delta - \frac{Z}{r} + \frac{1}{8}\lambda^2(x^2+y^2), r^2 = x^2+y^2+z^2 \qquad (56.1)$$

where suitable units are chosen (Appendix G).

In order to apply the FM we introduce a scaling law for the eigenvalues $E(Z,\lambda)$ of (56.1). It may be derived from the dilatation relationship satisfied by the Hamiltonian operator as discussed in Appendix G:

$$H(Z,\lambda) = \lambda H(Z\lambda^{-1/2},1) \qquad (56.2)$$

According to what was shown in §.44, the scaling law for the function under study must be written in terms of the parameter which explicitly appears in the power series. In this case, the parameter is λ^2 because (cf. Eq. (32.10)):

$$E(Z,\gamma) = \sum_{n=0}^{\infty} E^{(n)} \gamma^n \; ; \quad \gamma = \lambda^2 \tag{56.3}$$

Thus, the equivalence relation (56.2) leads to the following scaling law for $E(Z,\gamma)$

$$E(Z,\gamma) = \gamma^{1/2} E(Z\gamma^{1/4},1) \tag{56.4}$$

which provides the exponents $\alpha = -1/4$ and $\beta = 1/2$.

A very important difference between the ZEHA and the problems studied before is that $E(Z,\gamma)$ cannot be expanded in power series about $Z = 0$. This means that though $E(Z,\gamma)$ satisfies (56.4) it does not yield a $\gamma^{-1/4}$-power series because of the logarithmic terms which are characteristic of the binding energy (Appendix H). This fact alone allows us to predict that FM results for this model will not be as accurate as those obtained previously for the anharmonic oscillators or the linear confining potential models. Up to certain point, we can assert that the conclusions drawn in §.51 are qualitatively valid for ZEHA.

However, it is not unreasonable to think that the FM must be a better approach for highly excited states because, as shown in §.31, the eigenvalues in the semiclassical limit, have a $\gamma^{-1/4}$ expansion.

It follows from the general equations derived in §.44 that the eigenvalues $E(Z,\gamma)$ may be approximated through the following sequences SE_N:

$$E(1,\gamma) = (\gamma/w)^{1/2} \bar{E}(k,w) \simeq SE_N \tag{56.5}$$

$$SE_N = (\gamma/w)^{1/2} S_N(k,w) \tag{56.6}$$

$$\bar{E}(k,w) \simeq S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)} w^n \qquad (56.7)$$

where the new variable w is a root of the algebraic equation

$$k^4 \gamma (1-w)^4 - w = 0 \qquad (56.8)$$

The coefficients $\bar{E}^{(n)}$ of the renormalized series are connected with the original RSPT coefficients $E^{(n)}$ through Eq. (44.14) which for the present case reads:

$$\bar{E}^{(n)} = \sum_{j=0}^{n} (-1)^{n-j} \binom{2-4j}{n-j} E^{(j)} k^{2-4j} \qquad (56.9)$$

It is worth noticing that the transformation (56.8) differs from those used previously in summing the RS series for the ZEHA /5,6/. Among them we mention the order-depending mapping (ODM) /5/ based on the asymptotic properties of the binding energy /7,8/, the Borel transform /5/ and the generalized Euler transformation /6/. According to Eq. (56.8) the FM gives rise to an ODM since k depends upon N when applying the Sensitivity Rules (§.44) to the sequence $S_N(k,1)$. However, present ODM requires less analytical information about $E(Z,\gamma)$ than the transformation used by Le Guillou and Zinn-Justin /5/, since we have only resorted to the property (56.4).

All the computations for this model may be performed in an analytic way because the real root of (56.8) fulfilling the Lemmas 44.1 - 44.3 is determined in closed form. The result is /9/:

$$(w/\gamma k^4)^{1/4} = \frac{1}{2} \{ | 4 (\tfrac{1}{4}\psi^2 - \frac{1}{\gamma k^4})^{1/2} - \psi |^{1/2} - \psi^{1/2} \} \qquad (56.10a)$$

$$\psi = -4 (3\gamma k^4)^{-1/2} \{ tg(2x) \}^{-1} \qquad (56.10b)$$

$$\chi = \text{arc tg}\{\text{tg}^{1/3}(\phi/2)\} \tag{56.10c}$$

$$\phi = \text{arc tg}\{-\frac{16}{3}(\frac{\gamma k^4}{3})^{1/3}\} \tag{56.10d}$$

In order to approach an eigenvalue $E(Z,\gamma)$ by way of the sequence SE_N, it is necessary to determine the optimum k value (say k*) which is a critical point of the renormalized sequence $S_N(k,1)$. According to Eq.(56.7), $S_N(k,1)$ should approximate $\bar{E}(k,1) = E(0,1)$ when $N\to\infty$, where (see Appendix G):

$$\lim_{\gamma\to\infty} \gamma^{-1/2} E(1,\gamma) = E(0,1) = \frac{M+1}{2} \tag{56.11}$$

and $M = 0,1,2,\ldots$ is the quantum number labelling the states of the 2D isotropic oscillator obtained when $\gamma\to\infty$ (or $Z\to 0$). In such a case the electron oscillates in a plane perpendicular to the applied field. Then, Eq. (56.11) describes the Landau spectrum but for the continuum states and the paramagnetic terms which have been removed (Appendix G).

Since the correlation between the states in the Coulomb ($\gamma\to 0$) and Landau ($1/\gamma\to 0$) regimes is known /10,11/, we can verify whether, given any quantum state, the FM allows one to sum the RSPT in the limit $1/\gamma\to 0$.

The application of summation methods to the RSPT for ZEHA has been mainly restricted to the ground state, which becomes the 1s Coulomb state when $\gamma = 0$ /2,4-6/. Here, we restrict ourselves to examine the $1s\,2p^{+}_{-1}$ and 2s states. When $Z = 0$ the 1s and $2p_{-1}$ states merge into the Landau ground state (Appendix G) and exhibit an increasing binding energy as γ increases (Appendix H). Such states are usually called tight-bound and are associated with the following M-values.

$$M(1s) = 0 \quad , \quad M(2p_{-1}) = 1 \tag{56.12}$$

The 2s and $2p_{+1}$ states correlate with the third and fourth Landau states respectively. The corresponding M-values are

$$M(2p_{+1}) = 1, \quad M(2s) = 0 \tag{56.13}$$

The 2s state shows different features from the 1s and $2p_{+1}$ ones, since its binding energy exhibits a maximum at a finite γ-value /12/. This property yields an additional difficulty when one tries to sum the corresponding perturbation series. The critical points of $S_N(k,1)$ for the states 1s, 2s, and $2p_{+1}$ have been calculated for N = 0 up to 20, 15, and 13, respectively. To determine the convergent sequence we have analysed the $(k_N)^4$-N plane for every case according to Eq.(49.37) with $\alpha = -1/4$. Results are discussed in what follows.

i) Case I (1s):

The structure of the $(k_N^*)^4$-N plane for the ZEHA is similar to that found for other $k_N^{-1/\alpha}$-N planes. Fig. 18.1 presents

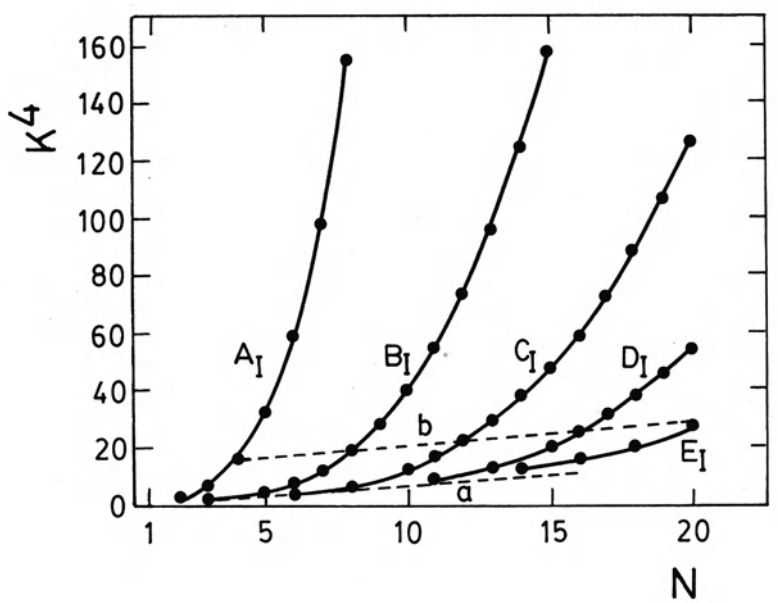

Fig. 18.1: $(k_N^I)^4$-N plane for the inflexion points of the renormalized sequences $S_N(k,1)$ of the 1s state of ZEHA.
(Full lines are for those sequences where k_N^I grows linearly with N).

some points for $(k_N^I)^4$-N with $N \leq 20$. The RS coefficients used are those in Table 9.1.

Table 18.1

$S_N(k_N^I,1)$ convergent sequences for the 1s state of the ZEHA obtained from the straight lines of Fig. 18.1.

N a)	$S_N(k_N^I,1)$ b)	N a)	$S_N(k_N^I,1)$ c)
3 (B_I)	0.4750	4 (A_I)	0.5156
6 (C_I)	0.4806	8 (B_I)	0.5332
		12 (C_I)	0.5467
		16 (D_I)	0.4687

a) The sort of sequence with k-N linear dependence to which belongs the critical point is denoted between parenthesis.

b) Inflexion points in the straight line "a" (Figure 18.1).

c) Inflexion points in the straight line "b" (Figure 18.1).

The outcome is nearly the same for the case $(k_N^S)^4$-N. As expected, there appears a large number of IP which originate sequences with a linear dependence $k_N^I \simeq \delta N$, marked in the Figure as A_I, B_I, C_I, D_I and E_I. These sequences do not converge towards the exact result, as previously discussed, and, besides, they converge so slowly that it has not been possible to determine their limits. The SP sequences converge even more slowly.

According to the scaling law (56.4) and the argument leading to Eq. (49.37), the correct limit should follow from sequences $(k_N^I)^4 \simeq \delta N$. Fig. 18.1 makes it clear that such a sequence can be built from IP's belonging to different sequences $k_N \simeq \delta N$. For the models examined in Chapters XVI and XVII, the application of the Sensitivity Rules led

naturally to sequences with the required features. This does not seem to be the case of the ZEHA, at least for the considered member of RS coefficients. In other words, the choice (for every N) of IP's with lowest first derivative value does not lead to a straight line in the $(k_N^I)^4$-N plane.

In order to overcome the abovementioned difficulty, we have proceeded in a different way by looking for a stright-line in the $(k_N^I)^4$-N plane and starting from it we have generated the sequence $S_N(k_N^I,1)$. To find out the appropriate straight line, we have worked as follows:

a) We split the $(k_N^I)^4$-N plane in two parts by means of a straight line, so that in one of them there are no IP's. This straight line passes through the first IP's of the sequences B_I and C_I, and is denoted as "a" in Fig. 18.1. It is nearly the envelope of the first members of the sequences A_I- E_I.

b) We look for a second straight line, approximately parallel to the first one, which contains the largest number of IP's belonging to different sequences. This line is marked with "b" in Fig. 18.1 and passes through just one IP of every sequence $k_N \simeq \delta N$, for N = 4,8,12 and 16.

The linear dependence may be estimated via a regression analysis and the result is:

$$(k_N^N)^4 = (0.8 \pm 0.3)\ N + (13 \pm 4)\ ,\ r = 0.9991 \qquad (56.14)$$

The sequences $S_N(k_N^I,1)$ obtained following the lines "a" and "b" (Eq. (56.14)) are displayed in Table 18.1. The accuracy of the results supports the choice of the straight lines $(k_N)^{-1/\alpha}$-N, since in spite of the slow convergence of the sequence $S_N(k,1)$, we can estimate

$$S_N(k_N^I,1) \simeq 0.50 \pm 0.05,\ N>>1 \qquad (56.15)$$

which is in good agreement with M = 0 in Eq.(56.11). The oscillation is too large to obtain highly accurate results in the high-field regime.

However, it must be taken into account that only 16 RSPT coefficients (zero-field limit) are employed to estimate the Landau eigenvalue (infinite-field limit).

In order to show the accuracy of the present approach for the lowest eigenvalue and for the whole range of λ values, we have used the k^I-value corresponding to the last point on "b" (Fig. 18.1):

$$k_{16}^I = 2.24699417369 \qquad (56.16)$$

The renormalized coefficients $\bar{E}^{(n)}$, $n \leq 16$, are shown in Table 18.2

Table 18.2

Renormalized sequence $\bar{E}^{(n)}$ coefficients for the 1s state of the ZEHA.

n	$\bar{E}^{(n)}$ a)	n	$\bar{E}^{(n)}$
0	-0.2524491420 (1)	9	-0.1370177476 (0)
1	0.5098437763 (1)	10	-0.1200679616 (0)
2	-0.2427606254 (1)	11	-9.1735519413 (-1)
3	0.1360453082 (0)	12	0.1255858375 (0)
4	0.1565960417 (0)	13	0.2137936444 (0)
5	0.1461970244 (0)	14	0.1554263910 (0)
6	0.9678088241 (-1)	15	-0.5918477234 (-1)
7	0.1344913598 (-1)	16	-0.3093538524 (0)
8	-0.7364419124 (-1)		

a) $k_{16}^I = 2.24699417869$ (straight line "b") was used in the computation. Power of ten that must multiply each coefficient is denoted between parenthesis.

They can be used, together with Eqs.(56.6), (56.7), (56.10) and (56.16) to build SE_{16} for the 1S state.

Results are compared in Table 18.3 with those determined by

Table 18.3

Lowest eigenvalue of Hamiltonian (56.1) (1s state) for several field strengths λ.

λ	SE_{16} a)	SE'_{20} b)	$E(1,\lambda^2)$ c)
0.01	-0.499975005	-0.499975001	-0.499975005
0.1	-0.497526480	-0.497526430	-0.497526480
0.2	-0.490381565	-0.490381565	-0.490331565
0.6	-0.4274595	-0.4274556	-0.42746229
1.0	-0.331114	-0.331041	-0.3311689
2.0	-0.021305	-0.019968	-0.0222139
3.0	0.338399	0.343336	0.335467
6.0	1.54362	1.57283	1.531755
10.0	3.27316	3.35652	3.252204
20.0	7.79409	8.06697	7.78462
60.0	26.427	27.690	26.795
100.0	45.211	47.572	46.211
200.0	92.249	97.483	95.273
300.0	139.293	147.473	144.645
2000.0	937.97	997.94	990.696

a) Computed with the renormalized series up to the 16th order with $k^I_{16} = 2.2469941786$.

b) Computed with the renormalized series up to the 20th order plus the addition of the dominant behavior at infinite field with $k^*_{20} = 2.756838835$ (Eq.(57.1)).

c) Variational results /12,13/.

Wunner et al /12,13/, which can be considered to be "exact" for the present purposes. The latter values have been obtained via the varia-

tional method using Coulombic as well as Landau orbitals (see §.31 for further details). Our approximation to the ground state of ZEHA is comparable with Silverman's results /6/ obtained by means of the repeated application of Euler transform to the 35th-order RSPT /2/. In fact, within the interval $10 \leq \lambda \leq 100$ our results are even more accurate. This fact illustrates some of the advanteges of the FM over the Euler transform. The former procedure is simpler and permits one to incorporate a greater amount of analytical information about $E(1,\gamma)$.

Since the FM mapping cannot give rise to logarithmic terms, present approach does not yield accurate binding energies for $\lambda \geq 100$. Thus, they cannot be compared with those derived by Le Guillou and Zinn-Justin /5/ through their rather involved order-dependent mapping.

ii) Case II ($2p_{\pm 1}$)

Fig. 18.2 shows the $(k_N^I)^4$-N plane for the IP's of the sequence $S_N(k,1)$ corresponding to the $2p_{\pm 1}$ states. Since Figs. 18.1 and 18.2 are similar, we will restrict to point out only the main differences. The RS series associated with the $2p_{\pm 1}$ states are more strongly divergent than the 1S one (see Table 9.1) a fact which is revealed by the larger member of IP sequences with linear dependence k_N^I-N that occur in the former case. Such sequences are shown in Fig. 18.2 with full lines called A_I, B_I, C_I, D_I and E_I. For N = 15 it seems to arise a new sequence F_I. In order to construct a sequence approaching E(0,1) one must proceed as in Case I, i.e. looking for straight lines in the $(k_N^I)^4$-N plane. Three of them are found which are named "a", "b" and "c" in Fig. 18.2. They contain an IP belonging to each branch $k_N \simeq \delta N$. The sequence arising from "c" involves 5 IP for N = 3,6,9,12 and 15 which can be fit by the following linear regression

$$(k_N^I)^4 = (10 \pm 4)\ N + (222 \pm 42) \qquad (56.17)$$

The results coming from the sequences associated with "a", "b" and "c" are presented in Table 18.4. The estimated Landau limit is in this case less accurate than the one for the 1s state (Eq. (56.15)). In spite of the oscillation it is clearly found that

$$S_N(k_N^I,1) \simeq 1,0 \pm 0,2\ ,\ N>>1 \qquad (56.18)$$

Table 18.4

Convergent sequences $S_N(k_N^I,1)$ for the $2p_{\pm 1}$ state of the ZEHA obtained from the straight lines of Fig. 18.2.

N a)	$S_N(k_N^I,1)$ b)	N a)	$S_N(k_N^I,1)$ c)	N a)	$S_N(k_N^I,1)$ d)
3 (B_I)	1.1588	5 (B_I)	1.1098	3 (A_I)	0.9497
6 (C_I)	0.9297	8 (C_I)	1.0039	6 (B_I)	1.0689
		11 (D_I)	1.0507	9 (C_I)	1.0483
		14 (E_I)	0.9733	12 (D_I)	0.9731
				15 (E_I)	1.1883

a) The sort of sequence with k-N linear dependence to which belongs the inflexion point is given between parenthesis.

b) Inflexion points in the straight line "a"

c) Inflexion points in the straight line "b"

d) Inflexion points in the straight line "c"

which is in acceptable agreement with the actual value if one takes into account that just 15 RS coefficients have been used.

The approximation to $E(1,\gamma)$ is built by means of the last point on "c" that corresponds to

$$k_{15}^I = 4.39082096726 \qquad (56.19)$$

The renormalized coefficients are shown in Table 18.5 and the eigenvalues are compared in Table 18.6 with the "exact" data /12,13/.

Table 18.5

$\bar{E}^{(n)}$ coefficients of the renormalized sequence for the $2p_{\pm 1}$ state of ZEHA.

n	$\bar{E}^{(n)}$ a)	n	$\bar{E}^{(n)}$
0	-0.24099135953 (1)	8	-0.2039991113 (0)
1	0.49754344302 (1)	9	0.1690336956 (0)
2	-0.21148867613 (1)	10	0.4859040227 (0)
3	0.37577501385 (0)	11	0.285806640 (0)
4	0.33942784157 (0)	12	-0.4629740576 (0)
5	0.1553443561 (0)	13	-0.9993819445 (0)
6	-0.11582599788 (0)	14	-0.3380552073 (0)
7	-0.29950362586 (0)	15	0.1346150366 (1)

a) k_{15}^{I} = 4.39082096726 (Straight line "c") was used. Power of ten that must multiply each coefficient is given between parenthesis.

Table 18.6

Energy associated to the $2p_{\pm 1}$ state of Hamiltonian (56.1) for several λ field strength values.

λ	SE_{15} a)	SE'_{15} b)	$E(1,\lambda^2)$ c)
0.01	-0.124701	-0.124701	-0.124701
0.1	-0.100846	-0.100846	-0.100846
0.2	-0.050559	-0.050566	-0.050539
0.6	0.223978	0.222923	0.225376
1.0	0.539055	0.533680	0.543403
2.0	1.39128	1.35944	1.400387
3.0	2.29220	2.21587	2.29645
6.0	5.14423	4.86594	5.07671
10.0	9.13330	7.89582	8.87458
20.0	19.5350	17.7721	18.53453
60.0	63.1870	55.8798	57.8031
100.0	107.991	94.547	97.3653
200.0	221.766	192.076	196.653
2000.0	2323.08	1973.66	1993.048

a) Computed with the renormalized series up to the 15th order and $k_{15}^{I} = 4.39082096726$.

b) Computed with renormalized series up to the 15th order plus the dominant behavior at the infinite field limit and $k_{15}^{I}=4.41293433$ (Eq.(57.1)).

c) "Exact" results /12,13/.

Present results are the first large-order perturbation calculation for the states $2p_{\pm 1}$ since previous applications of the RSPT do not take into account more than third order /1,4,14/. Besides, the range

of λ values in those papers is tipically $\lambda \leq 0.01$.

Results shown in Table 18.6 for $\lambda \leq 20.0$ are accurate enough for most of the practical applications and are certainly much better than those reported by Patil /14/ who resorted to information corresponding to the asymptotic behavior for the binding energy.

iii) Case III (2s):

This state is not as interesting as the tight bound ones discussed before. For this reason it has not been so widely studied. However, since we have found remarkable difficulties in applying the FM to it, we deem it suitable to discuss briefly the outcome of our numerical investigation.

The structure of the $(k_N^*)^4$-N plane is similar to that found above except that the oscillation is even larger, so that it is not possible to make any reasonable estimation of the Landau limit using the available 13 perturbation corrections. This result is hardly surprising since the asymptotic properties of the 2s state are wholly different from those corresponding to the 1s and $2p_{\pm 1}$ states. As said before the binding energy exhibits a maximum at a finite value of the field strength.

In order to obtain useful results for this state, one has to proceed in a different way discussed in the next paragraph.

§.57. Further results for the Zeeman eigenvalues.

It will be shown in what follows how to improve the renormalized series by introducing information about the large-field regime.

The main coefficient E(0,1) of the large-λ series can be taken into account in many different ways. One of them,which is specially simple and appropriate for our purposes, consists in the determination of the parameter k such that

$$S_N'(k^*,1) = \sum_{n=0}^{N} E^{(n)} = E(0,1) \qquad (57.1)$$

This equation has solutions for each quantum state considered in §.56. We have used N = 20, 15 and 13 terms for the 1s, $2p_{\pm 1}$ and 2s states, respectively.

For the 1s state it is found that

$$k^*_{20} = 2.756833835 \tag{57.2}$$

The eigenvalues are thus aproximated by

$$E(1,\gamma) \simeq SE'_N = (\gamma/w)^{1/2} S'_N (k^*,w) \tag{57.3}$$

where w is given by (56.10).

Results obtained with the help of (57.3) (n=20) are presented in the third column of Table 18.3. They approach the exact eigenvalues /12,13/ more closely than the results obtained in §.56 only when $\lambda > 200.0$. The conclusion is that whenever the FM leads to a strongly oscillatory sequence, inclusion of E(0,1) does not noticeably improve the results for intermediate λ-values.

For the $2p_{\pm 1}$ states, the root is

$$k^*_{15} = 4.41293433 \tag{57.4}$$

Results are shown in the third column of Table 13.6. It is found that SE'_{15} is more accurate than SE_{15} (see §.56) when $\lambda \geq 20$. Clearly, introduction of the coefficient E(0,1) represents a larger improvement for the $2p_{\pm 1}$ states than for the 1s state.

The effect of taking into account E(0,1) is even more important for the 2s state. It is to be remembered that in §.56 we did not present any result for such state due to the strong oscillation of the $S_N(k_N,1)$ sequence.

Now, Eq. (57.1) yields

$$k^*_{13} = 8.0498714 \tag{57.5}$$

and results obtained from SE'_{13} are displayed in Table 18.7 together with the "exact" ones /12,13/. The function $SE'_N(\bar{\lambda})$ tends to the exact Landau limit from above as λ increases and provides a coarse upper bound in the intermediate field regime. It can be proved that for the 2s state

$$E(1,\gamma) \leq \lambda/2 \tag{57.6}$$

Table 18.7

Energy of the 2s state of Hamiltonian (56.1) as a function of the λ field strength.

λ	SE'_{13} a)	$E(1,\lambda^2)$ b)
0.001	-0.12499650	0.12499650
0.01	-0.12465157	-0.12465157
0.1	-0.097734	-0.0980892
0.2	-0.04375	-0.04899
0.6	0.2233	0.14723
1.0	0.5010	0.33956

a) Computed with the renormalized series up to the 13th order and the addition of the dominant behavior at the infinite field limit with $k^*_{13} = 8.0498714$.

b) "Exact" results /12,13/.

for all $\lambda \geq 0$. Table 19.7 only shows results for $\lambda \leq 1$, because the inequality (57.6) is not satisfied otherwise. However, SE'_{13} is a reasonable approximation to the eigenvalue when $\lambda \leq 0.1$. It is worth noticing that the 13th-order RSP series yields approximately 10^6 when $\lambda = 0.1$ while on the other hand SE'_{13} exhibits an error of only 0.4%.

Another way of including the correct large-γ behavior was described in §§.53 and 55, and firstly introduced in §.42. The procedure consists of adding a coefficient $\bar{E}^{(N+1)}$ to the renormalized series so that

$$\bar{E}^{(N+1)} = E(0,1) - \sum_{n=0}^{N} \bar{E}^{(n)} \qquad (57.7)$$

and then determining k* by means of the Sensitivity Rules. This method was applied in Ref./4/ and provides results that are similar to those presented above. Results for the 1s state obtained through criterion (57.7) with N = 5 and 6 are compared in Fig. 18.3 with the exact ones and those coming from several Padé approximants /2/ using a much larger number of perturbative corrections. Clearly, no further comment is required.

§.53. FM approximation to the binding energy.

In the preceding sections we have presented quite acceptable results for several eigenvalues of the ZEHA basing the construction of the renormalized series upon a scaling law. Among the published results derived from the RSPT, only Le Guillou and Zinn-Justin's ones /5/ are better than ours. However, as pointed out in §.56, both order-dependent mappings are different since we have not taken into account the large-field behavior of the binding energy /7,8,15/ (Appendix H).

To achieve a better approximation to the binding energy, it is necessary to incorporate the appropriate analytical information into the FM. The purpose of this paragraph is to show how to adapt the FM in order to describe the behavior of the hydrogen atom in very strong magnetic fields. The procedure is briefly outlined in what follows.

The binding energy ε_m for a state with magnetic quantum number m is defined by

$$\varepsilon_m = \frac{M+1}{2}\lambda - E_m(1,\gamma) \ , \ \gamma = \lambda^2 \qquad (58.1)$$

The tight-bound quantum states are those with $m = -\ell$, where ℓ is the angular momentum quantum number for the Coulombic state obtained at zero field strength. For these particular states ε_m possess a well-known asymptotic form at very large field strengths /7,8,15/, which can be written as follows (see Appendix H):

$$\varepsilon_m = \frac{1}{2}\ln^2(\tfrac{\lambda}{8}) - 2\ln(\tfrac{\lambda}{8})\ln\ln(\tfrac{\lambda}{8}) + 2(C_\ell+\ln 2)\ln(\tfrac{\lambda}{8}) +$$

$$+ 2(\ln\ln(\tfrac{\lambda}{8}))^2 - 4(C_\ell - 1+\ln 2)\ln\ln(\tfrac{\lambda}{8}) + O(1), m = -\ell \qquad (58.2a)$$

where

$$C_\ell = -\frac{1}{2}(C_E+q_\ell) \ , \ q_\ell = \frac{1}{\ell} + q_{\ell-1} \ , \ \ell \neq 0; \ q_o = 0 \qquad (58.2b)$$

and $C_E = 0.5772156649...$ is the Euler-Mascheroni constant /9/.

Our aim is to obtain an expression for the magnetic field intensity λ in terms of the binding energy ε_m. This transformation will furnish the starting point to apply the FM.

Eq. (58.2a) can be rewritten in a more convenient form as follows: the definition of the variable u_m

$$u_m^2 = 2\,\varepsilon_m \qquad (58.3)$$

leads to the more compact expression

$$u_m^2 = \{\ln(\tfrac{\lambda}{8}) - 2\ln\ln(\tfrac{\lambda}{8}) + 2G_\ell\}^2 + 8\ln\ln(\tfrac{\lambda}{8}) \_ O(1) \qquad (58.4)$$

where

$$G_\ell = C_\ell + \ln 2 \qquad (58.5)$$

It is not difficult to verify that Eqs. (58.2a) and (58.4) agree up to the last term. Without loss of accuracy one can also write

$$u_m = \{\ln(\tfrac{1}{8}) - 2\ln\ln(\tfrac{\lambda}{8}) + 2\,G_\ell\}\,\{1 + \frac{8\ln\ln(\lambda/3)}{(\ln(\frac{\lambda}{8}) - 2\ln\ln(\frac{\lambda}{8}) + 2G_\ell)^2}\}^{1/2} +$$

$$+ O(1) \qquad (58.6)$$

which when expanded in Taylor series yields

$$u_m \simeq \ln(\tfrac{\lambda}{8}) - 2\ln\ln(\tfrac{\lambda}{8}) + 2G_\ell + 4\ln\ln(\tfrac{\lambda}{8})/\ln(\tfrac{\lambda}{8}) + O(\{\frac{\ln\ln\lambda}{\ln\lambda}\}^2) \qquad (58.7)$$

It is therefore clear that the iterative solution of

$$u_m = \ln(\lambda/8) + 2\,G_\ell - 2\,\ln u_m \qquad (58.8)$$

where $\lambda >> 1$ gives rise to all the terms appearing in Eq. (58.7). Eq. (58.8) is particularly interesting because it allows one to get a very simple expression for λ as a function of u_m:

$$\frac{\lambda}{2} = u_m^2\, e^{u_m + C_E + q_\ell} \qquad (58.9)$$

Eq. (58.9) may be viewed as a mapping relating two expansion variables, namely, λ and u_m.

Table 18.8

Comparison of results for the binding energy asymptotic behavior of the 1s state of ZEHA.

λ	u_m a)	$(2\varepsilon_m)^{1/2}$ b)	λ	u_m a)	$(2\varepsilon_m)^{1/2}$ b)
10^2	1.97434	2.99219	10^7	10.2025	10.5807
10^3	3.26864	4.25834	10^8	12.1549	12.4658
10^4	4.80194	5.58120	10^9	14.1530	14.4139
10^5	6.49920	7.09989	10^{10}	16.1871	16.4097
10^6	8.31019	8.78113	10^{20}	37.5310	37.6100

a) Computed with Eq. (58.9).

b) Computed with Eq. (58.2a).

Eqs. (58.2a) and (58.9) are compared in Table 18.8. Clearly, the latter is a good description of the binding energies for intense magnetic fields.

In order to attain a reasonable approximation for any field strength, it is necessary to build-in the correct behavior when $\lambda \to 0$. Although Eq. (58.9) is not accurate when $\lambda < 10$, it makes up an appropriate starting point, since u_m remains finite for any finite λ value and $u_m(\lambda=0)=0$. On the other hand Eq. (58.2a) is not valid if $\lambda < 8$, which plainly shows the advantage of using implicit expressions to take into account the large-λ regime. The small-λ behavior can be introduced in many different ways.

Here we restrict ourselves to suggest a simple formulation which

allows one to examine the possibilities of the method. The RSPT power series expansion

$$E_m(1,\gamma) = \sum_{n=0}^{\infty} E_m^{(n)} \lambda^{2n} \tag{58.10}$$

and Eq. (58.1) lead to

$$u_m = \{-2E_m^{(0)} + (M+1)\lambda - 2 \sum_{n=1}^{\infty} E_m^{(n)} \lambda^{2n}\}^{1/2} \tag{58.11}$$

If it is then introduced into the r.h.s. of Eq. (58.9) one finally gets a λ-power series for

$$F(1,\lambda) = u_m^2 \, e^{u_m + C_E + q_\ell} \tag{58.12}$$

which will be a suitable representation for the binding energy u_m whenever

$$F(1,\lambda) = \sum_{n=0}^{\infty} F^{(n)} \lambda^n \tag{58.13a}$$

$$\lim_{\lambda \to \infty} \lambda^{-1} F(1,\lambda) = 1/2 \tag{58.13b}$$

are satisfied. Eqs. (58.13) allow us to apply the FM in order to find an analytical expression for $F(1,\lambda)$ instead of $E(1,\lambda)$. Eqs. (58.12) and (58.13b) assure the correct asymptotic behavior of u_m when $\lambda >> 1$.

In order to apply the FM, it is necessary to determine the exponents α and β, as discussed before. Clearly, Eq. (58.13b) suggests $\beta = 1$.

In order to find α it must be remembered that powers of $\lambda^{-1/2}$ also appear in the large-λ expansion /7,8,15/. They have certainly been taken into account before in §§. 56 and 57.

In the present case they will occur if the expansion gives rise to powers of u_m^2. To this end it is sufficient that $F(1,\lambda)$ behaves as

$$F(1,\lambda) = \lambda \sum_{n=0}^{\infty} f^{(n)} \lambda^{-n/2} \simeq \frac{\lambda}{2} + f^{(1)} \lambda^{1/2}, \quad \lambda >> 1 \tag{58.14}$$

because if

$$\ln F(1,\lambda) \overset{\sim}{=} \ln\left(\frac{\lambda}{2}\right) + 2f^{(1)} \lambda^{-1/2} \tag{58.15}$$

is substituted into (58.12), we obtain the above mentioned binding energy terms. Then the expansion (58.14) suggests that $\alpha = -1/2$ when considering the results of §§. 42 and 44.

It therefore follows from the results above and Eqs. (44.7), (44.8), (44.14) and (44.18) that the FM sequences must be

$$F(1,\lambda) \simeq SF_N = (\lambda/w) S_N(k,w), \tag{58.16a}$$

$$S_N(k,w) = \sum_{n=0}^{N} \bar{F}^{(n)} w^n, \tag{58.16b}$$

where

$$\bar{F}^{(n)} = \sum_{j=0}^{n} (-1)^{n-j} \binom{2-2j}{n-j} F^{(j)} k^{2-2j} \tag{58.16c}$$

and w is the new expansion parameter, related to λ by

$$\lambda = w k^{-2} (1-w)^{-2} \tag{58.16d}$$

The root of Eq. (58.16d) fulfilling Lemmas 44.1-44.3 is

$$w = \frac{1}{2\lambda k^2}\{1+2\lambda k^2-(1+4\lambda k^2)^{1/2}\} \tag{58.16e}$$

Since our aim is merely to illustrate the way of applying the FM, only a few RSPT corrections are considered in what follows in addition to the first term in (58.14) (i.e. $f^{(0)} = 1/2$).

In order to make the procedure as simple as possible, k is chosen as described in §.57 to be a root of

$$S_N(k_N^*,1) = f^{(0)} = 1/2 \tag{58.17}$$

Finally, considering Eqs. (58.12), (58.16a) and (58.17) it is possible to determine u_m from the implicit equation

$$u_m^2\, e^{u_m+C_E+q_\ell} = (\lambda/w)\; S_N(k_N^*,w) \tag{58.18}$$

and then to obtain the eigenvalue $E_m(1,\lambda^2)$ from Eqs. (58.3) and (58.1).

In order to apply the method one only needs the coefficients $\{F^{(n)}\}$. Since the computation is straightforward but somewhat involved, we present results only for $F^{(n)}$ with $n\leq 4$. The starting point is Eq.(58.11), which gives

$$u_m^2 = -2E_m^{(0)} + (M+1)\lambda - 2E_m^{(1)}\lambda^2 - 2E_m^{(2)}\lambda^4 + O(\lambda^6) \tag{58.19}$$

Upon taking the square root on both sides of (58.19) and expanding in a λ-power series up to λ^4 terms, we have

$$u_m = \{-2E_m^{(0)}\}^{1/2}\{1-\frac{M+1}{4E_m^{(0)}}\lambda + \lambda^2\left[\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}}\right] +$$

$$+ \lambda^3 \left|-\frac{(M+1)^3}{128E_m^{(0)3}} + \frac{(M+1)E_m^{(1)}}{8E_m^{(0)2}}\right| + \lambda^4 \left|\frac{E_m^{(2)}}{2E_m^{(0)}} - \frac{E_m^{(1)2}}{8E_m^{(0)2}} - \frac{5}{2048}\frac{(M+1)^4}{E_m^{(0)4}}\right| \} +$$

$$+ O(\lambda^5) \tag{58.20}$$

from which it follows that

$$e^{u_m} = e^{(-2E_m^{(0)})^{1/2}} \{1 + \frac{M+1}{2(-2E_m^{(0)})^{1/2}}\lambda - \frac{(M+1)^2}{16E_m^{(0)}}\lambda^2$$

$$+ \frac{(M+1)^3}{48(-2E_m^{(0)})^{3/2}}\lambda^3 + \frac{(M+1)^4}{1536E_m^{(0)4}}\lambda^4\}$$

$$x\{1 + (-2E_m^{(0)})^{1/2}\left(\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}}\right)\lambda^2$$

$$- E_m^{(0)}\left(\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}}\right)\lambda^4\}$$

$$x\{1 + (-2E_m^{(0)})^{1/2}\left(\frac{(M+1)E_m^{(1)}}{8E_m^{(0)2}} - \frac{(M+1)^3}{128E_m^{(0)3}}\right)\lambda^3\}$$

$$x\{1 + (-2E_m^{(0)})^{1/2}\left(\frac{E_m^{(2)}}{2E_m^{(0)}}\right) - \frac{E_m^{(1)2}}{8E_m^{(0)2}} - \frac{5}{2048}\frac{(M+1)^4}{E_m^{(0)4}}\right)\lambda^4\}$$

$$+ O(\lambda^5) \quad . \tag{58.21}$$

and

$$e^{u_m} = e^{(-2E_m^{(0)})^{1/2}} \{1 + \frac{M+1}{2(-2E_m^{(0)})^{1/2}}\lambda + ((-2E_m^{(0)})^{1/2}\left(\frac{E_m^{(1)}}{2E_m^{(0)}}\right. -$$

$$- \frac{(M+1)^2}{32E_m^{(0)2}}) - \frac{(M+1)^2}{16E_m^{(0)}}) \lambda^2 + (\frac{(M+1)^3}{43(-2E_m^{(0)})^{3/2}} + \frac{M+1}{2} (\frac{E_m^{(1)}}{2E_m^{(0)}}$$

$$- \frac{(M+1)^2}{32E_m^{(0)2}}) + (-2E_m^{(0)})^{1/2} (\frac{(M+1)E_m^{(1)}}{8E_m^{(0)2}} - \frac{(M+1)^3}{128E_m^{(0)3}})) \lambda^3$$

$$+ (\frac{(M+1)^4}{1536E_m^{(0)4}} + \frac{(M+1)^2}{8(-2E_m^{(0)})^{1/2}} (\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}}) - E_m^{(0)} (\frac{E_m^{(1)}}{2E_m^{(0)}}$$

$$- \frac{(M+1)^2}{32E_m^{(0)2}}) + \frac{M+1}{2} (\frac{(M+1)E_m^{(1)}}{8E_m^{(0)2}} - \frac{(M+1)^3}{128E_m^{(0)3}} + (-2E_m^{(0)})^{1/2} (\frac{E_m^{(2)}}{2E_m^{(0)}}$$

$$- \frac{E_m^{(1)2}}{8E_m^{(0)2}} - \frac{5(M+1)^4}{2048E_m^{(0)4}})) \lambda^4 + O(\lambda^5) \quad . \tag{58.22}$$

On introducing (58.19) and (58.22) into (58.12), the following formulas for the coefficients $F^{(n)}$ are obtained

$$F^{(0)} = -2E_m^{(0)} \Omega\ell \tag{58.23a}$$

$$F^{(1)} = \{2 + (-2E_m^{(0)})^{1/2}\} \frac{M+1}{2} \Omega\ell \tag{58.23b}$$

$$F^{(2)} = \{\frac{(M+1)^2}{8} + (-2E_m^{(0)})^{3/2} (\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}}) + \frac{(M+1)^2}{2(-2E_m^{(0)})^{1/2}}$$

$$- 2E_m^{(1)}\} \Omega\ell \tag{58.23c}$$

$$F^{(3)} = \{\frac{(M+1)^3}{48(-2E_m^{(0)})^{1/2}} - (M+1)E_m^{(0)} (\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}})$$

$$+ (-2E_m^{(0)})^{3/2}\left(\frac{(M+1)E_m^{(1)}}{3E_m^{(0)2}} - \frac{(M+1)^3}{128E_m^{(0)3}}\right) - \frac{(M+1)E_m^{(1)}}{(-2E_m^{(0)})^{1/2}}$$

$$+ (M+1)(-2E_m^{(0)})^{1/2}\left(\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}}\right) - \frac{(M+1)^3}{16E_m^{(0)}}\}\Omega_\ell, \qquad (58.23d)$$

$$F^{(4)} = \{-2E_m^{(2)} - 2E_m^{(1)}(-2E_m^{(0)})^{1/2}\left(\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}}\right)$$

$$+ \frac{(M+1)^2E^{(1)}}{8E_m^{(0)}} + \frac{(M+1)^4}{43(-2E_m^{(0)})^{3/2}} + \frac{(M+1)^2}{2}\left(\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}}\right)$$

$$+ (M+1)(-2E_m^{(0)})^{1/2}\left(\frac{(M+1)E_m^{(1)}}{8E_m^{(0)2}} - \frac{(M+1)^3}{128E_m^{(0)3}}\right) - \frac{(M+1)^4}{763E_m^{(0)}}$$

$$+ \frac{(M+1)^2}{8}(-2E_m^{(0)})^{1/2}\left(\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}}\right)$$

$$+ 2E_m^{(0)2}\left(\frac{E_m^{(1)}}{2E_m^{(0)}} - \frac{(M+1)^2}{32E_m^{(0)2}}\right)$$

$$- (M+1)E_m^{(0)}\left(\frac{(M+1)E_m^{(1)}}{8E_m^{(0)2}} - \frac{(M+1)^3}{128E_m^{(0)3}}\right)$$

$$+ (-2E_m^{(0)})^{1/2}\left(\frac{E_m^{(2)}}{2E_m^{(0)}} - \frac{E_m^{(1)2}}{3E_m^{(0)2}} - \frac{5}{2043}\frac{(M+1)^4}{E_m^{(0)4}}\right)\}\Omega_\ell, \qquad (58.23e)$$

where

$$\Omega_\ell = \exp\{(-2E_m^{(0)})^{1/2} + C_E + c_\ell\} \tag{58.24}$$

Preceding results allow us to obtain the coefficients $\{\bar{F}^{(n)}\}$ of the renormalized sequence SF_N. The first terms are

$$\bar{F}^{(0)} = k^2 F^{(0)} \tag{58.25a}$$

$$\bar{F}^{(1)} = -2k^2 F^{(0)} + F^{(1)} \tag{58.25b}$$

$$\bar{F}^{(2)} = k^2 F^{(0)} + k^{-2} F^{(2)} \tag{58.25c}$$

$$\bar{F}^{(3)} = 2k^{-2} F^{(2)} + k^{-4} F^{(3)} \tag{58.25d}$$

$$\bar{F}^{(4)} = 3k^{-2} F^{(2)} + 4k^{-4} F^{(3)} + k^{-6} F^{(4)} \tag{58.25e}$$

Eq.(58.17) for N = 2 and N = 4 is used to determine k in order to examine the effect of adding perturbational corrections to Eq.(58.13). The first case (N = 2) gives

$$F^{(1)} + (k_2^*)^{-2} F^{(2)} = 1/2 \tag{58.26}$$

and the second one (N = 4)

$$F^{(1)} + 6(k_4^*)^{-2} F^{(2)} + 5(k_4^*)^{-4} F^{(3)} + (k_4^*)^{-6} F^{(4)} = 1/2 \tag{58.27}$$

The procedure just developed is applied to the first four tight-bound states and results are discussed in what follows.

Example 1: The first state is 1s. Resorting to the data in Table 9.1 and considering m = M = 0 in Eqs. (58.23), we obtain

$$F^{(0)} = \Omega_o;\ F^{(1)} = \frac{3}{2}\,\Omega_o;\ F^{(2)} = -\frac{1}{4}\,\Omega_o;\ F^{(3)} = -\frac{23}{48}\,\Omega_o;$$

$$F^{(4)} = \frac{49}{64}\,\Omega_o \qquad (58.23a)$$

where

$$\Omega_o = e^{1+C_E} = 4.341456789 \qquad (58.28b)$$

The roots of Eqs. (58.26) and (58.27) are found to be

$$k^*_2 = 0.4230722162 \qquad (58.29)$$

and

$$k^*_4 = 1.357649309 \qquad (58.30)$$

from which one builds two approximations to $F(1,\lambda)$ named SF_2 and SF_4 respectively. Numerical results obtained from (58.18) are shown in Table 18.9 for a wide range of λ-values. Careful examination of Table 18.9 makes it clear that SF_2 gives somewhat better results than SF_4

Table 18.9

Energy of the 1s state of Hamiltonian (56.1) as a function of the λ field strength from procedure discussed in §.58.

λ	$E^{a)}$	$E^{b)}$	$E^{c)}$
2000.0	991.7598	992.0069	990.696
1000.0	493.1416	493.4034	492.370
200.0	95.55188	95.80990	95.273
100.0	46.32549	46.56458	46.21091
10.0	3.154161	3.277650	3.252203
3.0	0.271992	0.328427	0.335467
2.0	-0.068129	-0.029651	-0.022214
1.0	-0.352008	-0.335441	-0.331169
0.2	-0.491286	-0.490494	-0.490332
0.1	-0.497674	-0.497535	-0.497526
0.001	-0.4999752	-0.49997500	-0.49997500

a) Computed with Eq. (58.18) using SF_2.

b) Computes with Eq. (58.18) using SF_4.

c) "Exact" results /13/.

for $\lambda > 1000$ whereas for $\lambda < 100$ the accuracy of SF_4 is much larger. Upon comparing present results with those obtained in §§. 56 and 57 (Table 18.3) it is concluded that Eq. (58.18) yields better eigenvalues for $1 \leq \lambda \leq 100$. This result is remarkable since only the first two RSPT corrections were introduced into SF_4. As far as we know no algorithm has been presented which is at the same time as simple and as accurate as the present one. For the sake of completeness we add the coefficients computed with k_4^*:

$$\bar{F}^{(0)} = 8.923829538 \; ; \; \bar{F}^{(1)} = -10.58547389 ; \bar{F}^{(2)} = 8.267169084$$

$$\bar{F}^{(3)} = -1.996150364; \; \bar{F}^{(4)} = -4.109374367 \qquad (58.31)$$

In order to show the convenience of using the transformation (58.9), we have chosen an extremely strong field: $\lambda^2/3 = 10^{60}$. Le Guillou and Zinn-Justin's method (with 60 RS coefficients, extrapolating to infinity and adjusting the first three terms in (58.2a)) yields $60 \leq u_o \leq 61$ for the 1s state. The FM with only 4RS coefficients (second order RSPT in γ) yields $u_o = 60.64$, the exact result being $u_o = 60.69$ /5/.

Example 2

On using the coefficients given in Table 9.1 and the choice m = M = 1 in Eqs. (58.23) we have the following coefficients for the state $2p_{-1}$:

$$F^{(0)} = \frac{\Omega_1}{4} \; ; F^{(1)} = \frac{5}{2}\,\Omega_1; \; F^{(2)} = -4\Omega_1; \; F^{(3)} = -\frac{68}{3}\,\Omega_1; \; F^{(4)} = \frac{10877}{24}\,\Omega_1 \qquad (58.32a)$$

where

$$\Omega_1 = e^{C_E+3/2} = 7.982212739 \qquad (58.32b)$$

The optimum k values are chosen to be the largest real roots of Eqs.(58.26) and (58.27) which in this case are

$$k_2^* = 1.281061829 \qquad (58.33)$$

$$k_4^* = 3.519732541 \qquad (58.34)$$

respectively. They allow one to build the approximations SF_2 and SF_4 which are then introduced into (58.18) to compute the eigenvalues $E(1,\lambda^2)$. Present results are compared with the exact ones in Table 18.10.

Table 18.10

Energy of the $2p_{-1}$ state of Hamiltonian (56.1) as a function of the λ field strength from procedure discussed in §.58.

λ	$E^{a)}$	$E^{b)}$	$E^{c)}$
2000.0	1994.2222	1994.330	1993.018
1000.0	995.30007	995.41296	994.3616
200.0	197.10504	197.21566	196.653
100.0	97.65472	97.75842	97.3653
10.0	8.86663	8.93293	8.87458
3.0	2.25345	2.29746	2.29645
2.0	1.357060	1.393808	1.400387
1.0	0.507371	0.532495	0.543403
0.2	-0.060173	-0.054310	-0.050539
0.1	-0.104226	-0.102068	-0.100846
0.01	-0.124714	-0.1247-2	-0.124701

a) Computed with Eq. (58.18) using SF_2.

b) Computed with Eq. (58.18) using SF_4.

c) "Exact" results /13/.

Conclusions are similar to those drawn in Example 1. Present treatment makes up the first successful application of the binding energy asymptotic properties for this particular state.

For the sake of completeness, we give the $\bar{F}^{(n)}$ coefficients obtained from k_4^*:

$$\bar{F}^{(0)} = 24.72194503;\ \bar{F}^{(1)} = -29.43835303;\ \bar{F}^{(2)} = 22.1446101$$

$$\bar{F}^{(3)} = -6.333475378;\ \bar{F}^{(4)} = -10.54476258 \qquad (58.35)$$

Example 3.

$3d_{-2}$ is the third tight-bound state. The RS coefficients in Table 9.1 and Eqs. (58.23) (with m = M = 2) lead us to the following results:

$$F^{(0)} = \Omega_2/9\ ;\ F^{(1)} = \frac{7}{2}\,\Omega_2;\ F^{(2)} = -\frac{81}{4}\,\Omega_2;\ F^{(3)} = -\frac{3699}{24}\,\Omega_2;$$

$$F^{(4)} = \frac{1135455}{64}\,\Omega_2 \qquad (58.36a)$$

where

$$\Omega_2 = e^{C_E+11/6} = 11.14007535 \qquad (58.36b)$$

The optimum k values are:

$$k_2^* = 2.420923881 \qquad (58.37a)$$

$$k_4^* = 6.348622330 \qquad (58.37b)$$

Approximate eigenvalues obtained from SF_2 and SF_4 are displayed in Table 18.11, together with the "exact" ones computed by Wunner et al /13/.

Table 18.11

Energy of the $3d_{-2}$ state of Hamiltonian (56.1) as a function of the λ field strength from procedure discussed in §.58.

λ	$E^{a)}$	$E^{b)}$	$E^{c)}$
2000.0	2995.188	2995.262	2994.031
1000.0	1496.1255	1496.2023	1495.1949
200.0	297.66756	297.74096	297.19800
100.0	148.12751	148.19600	147.81883
10.0	14.11604	14.16028	14.09179
3.0	3.919972	3.951259	3.942848
2.0	2.500318	2.527506	2.528828
1.0	1.116675	1.137278	1.146952
0.2	0.103140	0.111173	0.118679
0.1	0.003771	0.008073	0.012161
0.01	-0.054376	-0.054279	-0.054247

a) Computed with Eq. (58.18) using SF_2.

b) Computed with Eq. (58.18) using SF_4.

c) "Exact" results /13/.

Conclusions are similar to those for the previous examples. Present results for the $3d_{-2}$ state are the first ones obtained from RSPT. For the sake of completeness, we show the $\bar{F}^{(n)}$ coefficients computed through k_4^*:

$$F^{-(0)} = 49.88897756;\ \bar{F}^{(1)} = -60.73769141;\ \bar{F}^{(2)} = 44.2919922$$

$$\bar{F}^{(3)} = -12.77935486;\ \bar{F}^{(4)} = -20.11392349 \qquad (58.38)$$

Example 4

The next tight-bound state is $4f_{-3}$. The RS coefficients in Table 9.1 and Eqs.(58.23) (with m = M = 3) give the results

$$F^{(0)} = \Omega_3/16;\ F^{(1)} = \frac{9}{2}\,\Omega_3;\ F^{(2)} = -64\Omega_3;\ F^{(3)} = -\frac{3680}{3}\,\Omega_3;$$

$$F^{(4)} = \frac{957559}{4}\,\Omega_3 \tag{58.39a}$$

where

$$\Omega_3 = e^{C_E+25/12} = 14.30413989 \tag{58.39b}$$

The optimum k values are found to be

$$k_2^* = 3.78596908 \tag{58.40a}$$

$$k_4^* = 9.722789555 \tag{58.40b}$$

Present and accurate numerical eigenvalues /13/ are compared in Table 18.12.

Table 18.12

Energy of the $4f_{-3}$ state of Hamiltonian (56.1) as a function of the λ field strength from procedure discussed in §.58.

λ	$E^{a)}$	$E^{b)}$	$E^{c)}$
2000.0	3995.745	3995.305	3994.622
1000.0	1996.5937	1996.6548	1995.6916
200.0	397.9759	398.0334	397.5163
100.0	198.3838	198.4369	198.0700
10.0	19.24845	19.28247	19.21223
3.0	5.508988	5.533403	5.521409
2.0	3.577199	3.598664	3.596760
1.0	1.675479	1.692282	1.700031
0.2	0.232983	0.240900	0.249912
0.1	0.077062	0.082064	0.088140
0.01	-0.028221	-0.027921	-0.027708

a) Computed with Eq. (58.18) using SF_2.

b) Computed with Eq. (58.18) using SF_4.

c) "Exact" results /13/.

Conclusions are the same as before. This state has not been treated before by means of RSPT. The coefficients $\bar{F}^{(n)}$ for k_4^* are:

$$\bar{F}^{(0)} = 84.51300375;\ \bar{F}^{(1)} = -104.6573730;\ \bar{F}^{(2)} = 74.82383846$$

$$\bar{F}^{(3)} = -21.33170284;\ \bar{F}^{(4)} = -32.85264205 \qquad (58.41)$$

Although just a few RS coefficients have been taken into account in the approach above its advantages have been made clear enough:

i) The amount of analytical information about the large-λ regime introduced by Eq. (58.9) is larger than in other methods /1,5,14/.

ii) The algorithm is easier than others so that a reasonable accuracy can be obtained by means of a pocket programmable calculator.

In order to close this section, we deem it appropriate to show an alternative procedure to calculate the binding energy, which could be more convenient to introduce higher perturbation orders.

Eq. (58.1) allows one to write ε_m as a λ-power series:

$$\varepsilon_m = - E_m^{(0)} + \frac{M+1}{2} \lambda - \sum_{n=1}^{\infty} E_m^{(n)} \lambda^{2n} \tag{58.42}$$

which, through Eq. (58.9) may be transformed into a u-power series

$$\varepsilon_m = \sum_{n=0}^{\infty} A_m^{(n)} u_m^n \tag{58.43}$$

The new coefficients $\{A_m^{(n)}\}$ can be written in terms of the coefficients $\{E^{(n)}\}$ provided by the RSPT.

Now, Eq. (58.43) suggest that the FM may also be applied if ε_m is considered to be a function of u_m instead of a function of λ. Proceeding in accordance with this alternative standpoint, we have to introduce the asymptotic expansion when $u_m >> 1$. Obviously, this behavior is furnished by Eq. (58.3), which assures us that

$$\varepsilon_m \to \frac{1}{2} u_m^2 \text{ if } 1/\lambda \to 0 \tag{58.44}$$

Thus, we can write the following formal asymptotic expansion for ε_m:

$$\varepsilon_m = u^{\beta} \sum_{n=0}^{\infty} a_m^{(n)} u_m^{n\alpha} \tag{58.45}$$

where $\beta = 2$; $a_m^{(0)} = 1/2$ and $\alpha<0$ is an auxiliar exponent, which can be set to get the largest convergence rate.

Summarizing, the procedure to be followed should be:

i) given a λ value, the FM is applied to the series (58.43), where the u_m value is determined for each λ, according to Eq. (58.9).

ii) α is chosen, so that the convergent rate is large enough. Since the coefficient $a_m^{(0)}$ is known, it may be convenient to resort to the FM formulation developed in §.50, since it allows one to use at the same time the coefficients $\{A_m^{(n)}\}$ and the asymptotic coefficient for $1/u_m \to 0$ $(a_m^{(0)})$.

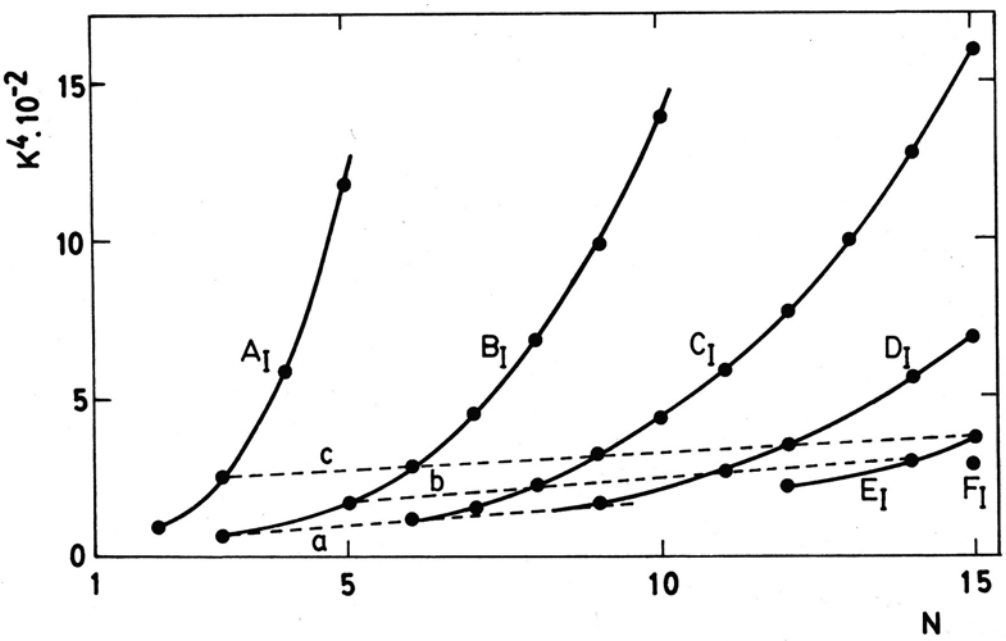

Fig. 18.2: $(k_N^I)^4$-N plane for the inflexion points of the renormalized sequences $S_N(k,1)$ for the $2p_{\pm 1}$ state of ZEHA.
(Full lines are for those sequences where k_N^I grows linearly with N).

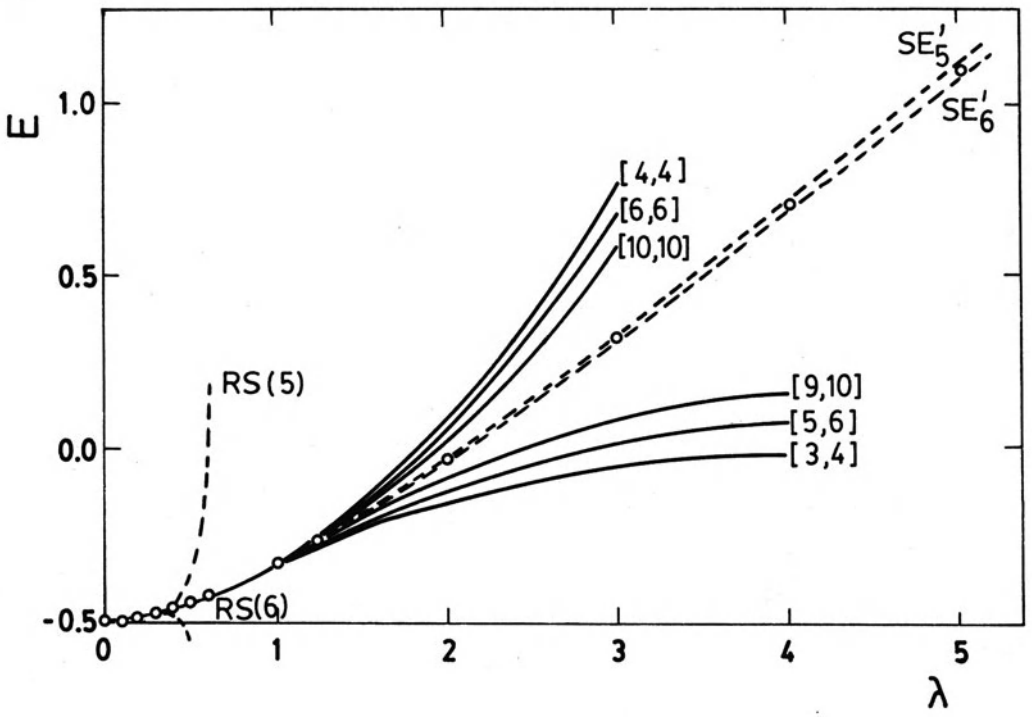

Fig. 18.3: Different approximations for the energy associated to the ground state of the hydrogen atom placed within a magnetic field in the intermediate strengths range.

——— Padé approximants

------- FM with SE'_5 and SE'_6

..... "Exact" results /13/

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CHAPTER XIX

APPLICATION OF THE FM TO THE STARK EFFECT IN HYDROGEN.

§.59. Approximation to Stark resonances.

The Stark effect in hydrogen has deserved a remarkable attention since the birth of Quantum Mechanics /1-9/.

The system consists of hydrogen (or a hydrogen-like atom with nuclear charge Z) placed into an homogeneous electric field of strength F. The model Hamiltonian is

$$H_S = -\frac{\hbar^2}{2m}\Delta - \frac{Ze^2}{r} + eFz \qquad (59.1a)$$

where we have considered an infinite nuclear mass so that m is the electron mass and the applied electric field is chosen to be along the z-axis.

It is convenient to change the operator (59.1a) into a dimensionless one by way of a scaling procedure (see Appendix A). Thus, we have

$$H_S = \frac{me^4}{\hbar^2} H(Z,\lambda) \quad , \quad H(Z,\lambda) = -\frac{\Delta}{2} - \frac{Z}{r} + \lambda z \qquad (59.1b)$$

$$\lambda = F/F_0 \; ; \; F_0 = m^2e^5/\hbar^4 \qquad (59.1c)$$

where $me^4/\hbar^2$ is the atomic unit of energy (Hartree) and F_0 the atomic unit of field strength which equals 5.14 x 10 V/m. The λ parameter represents the dimensionless field.

Although this model is usually presented in elementary textbooks as a very simple problem it is far from being so. The essential difficulty is that the electric field F (no matter how weak it may be) transforms the Coulomb spectrum which is discrete for negative energies

and continuous for positive ones, into another one wholly continuous for all energy values. However, there exist quasi-bound states or resonances, embedded in the continuum, whose life time τ decreases when F increases. Such resonant states may be described as complex eigenvalues of a complex scaled Hamiltonian (59.1) /10/:

$$\varepsilon = E - i\Gamma/2 \tag{59.2}$$

where the real numbers $E = E(Z,\lambda)$ and $\Gamma = \Gamma(Z,\lambda)$ are the resonance location and width, respectively. Then, the Stark effect looks totally different from the models discussed in preceding chapters. It is worth noticing that anharmonic oscillators (Chapter XVI) and confining potentials (Chapter XVII) have similar features to those mentioned above only when the perturbation parameter is negative. Up to 15 years ago, theoretical and experimental advances in this field were very modest because the field strengths used were rather small. In such cases, the electron-nuclei interaction is very much stronger than the electron-electric field one and the quasi-bound states have a large lifetime (that is, a small resonance width).

As commented in §.30 regarding the Zeeman effect, the Stark effect has received a remarkable renewed interest in the last years due to the experimental study of atomic properties in very strong electric fields /11-15/. A comprehensive review on this subject has been published by Kleppner /16/. It must be noted that atomic properties in intense static electric fields may be related with phenomena taking place in laser radiation fields, such as photodissociation and multiphotonic ionization /16/. Since the study of static fields is simpler, it is easy to understand why so much interest has been focused on them.

For the ground state of the hydrogen atom the electron-field and electron-nuclei interactions are similar when $\lambda \simeq 1$, which corresponds to the application of a field of about 10^{11} V/m (Eq. 59.1c). This field intensity is much larger than those usually obtained in laboratory. From now on, F' will denote the field strength at which both interactions are similar for a given quantum state (i.e. $F' \simeq F_0$ for the ground state). F' decreases quickly with the principal quantum number so that high-field research is mainly concentrated on the Rydberg states for alkaline atoms.

A simple argument allows us to examine the dependence of the Stark shift on the principal quantum number for Rydberg states. In fact, the energy level of a valence electron in an alkaline atom can be approximately written /16/:

$$E_n(\ell) = -\frac{1}{2}(n-\sigma_\ell)^{-2} \; ; \; \ell = 0,1,2,\ldots n-1 \qquad (59.3)$$

where σ_ℓ is the quantum deffect which accounts for the breakdown of the ℓ-degeneracy characteristic of the Coulomb potential. When n is large enough, the energy difference $E_n(\ell) - E_n(\ell')$ can be approximately written

$$\Delta E_{\ell\ell'} \equiv E_n(\ell) - E_n(\ell') \simeq \frac{\sigma}{n^3}; \; \sigma = \sigma_{\ell'} - \sigma_\ell \qquad (59.4)$$

If a small electric field ($F>>F^2$) is applied, the ns-state undergoes a second-order Stark-effect /17,18/. On using RSPT the energy shift $\delta E_n(F)$ is easily found to be

$$\delta E_n(F) \simeq e^2F^2 \sum_{m\neq n} \frac{(z_{mn})^2}{Em-E_n} \qquad (59.5)$$

where z_{mn} is a matrix element of the z coordinate. In order to have just a rough estimation of the n-dependence, one may keep only the main terms in the summation:

$$\delta E_n(F) \simeq e^2F^2 \frac{|\langle r\rangle_n|^2}{\Delta E_{01}} \qquad (59.6)$$

where $\langle r\rangle_n$ is the expectation value of r in the state under consideration. A large field regime is that for which the Stark shift is of the order of the difference between adjacent Coulomb energy levels; in other words $\Delta E_{01} \simeq \delta E_n(F')$ for the ns state. According to Eq. (59.6) we have

$$F'^2 \simeq e^{-2}(\Delta E_{01})^2 \, |\langle r\rangle_n|^{-2} \qquad (59.7)$$

Since the atomic radius is approximately given by $|\langle r \rangle_n|$ which is nearly proportional to n^2, Eqs. (59.4) and (59.7) yield

$$F' \sim \text{constant } n^{-5} \tag{59.8}$$

Eq. (59.8) shows the decreasing rate of the field intensity as the electron jumps to higher excited states. For example, when $\sigma = 0.1$ and $n = 30$, the electron-nuclei and electron-field interactions /16/ are equal when $F \simeq 20$ V/cm.

Several methods have been applied to approximate both the real part of a given resonance $E(Z,\lambda)$ and its width $\Gamma(\lambda)$. Among the non-perturbative procedures we can mention the following ones:

i) Variational procedures based on various trial functions /19-21/, including stabilization techniques /22-24/. These methods provide some of the most accurate results for either small ($\lambda \leq 0.02$) or large ($0.02 \leq \lambda \leq 0.12$) fields. However, they fail to give a sole wavefunction for the whole range of field strengths /19-24/. It has also been pointed out that in order to study resonances it is convenient to resort to the complex scaling or complex coordinate methods /25-27/.

ii) Semiclassical methods /7-9, 28-30/ based on approximations to the JWKB integrals. These procedures allow one to obtain acceptable results for all the resonances, but require the numerical computation of elliptical integrals.

Preceding bibliography on non-perturbative methods is not complete and additional references may be obtained therein.

The application of RSPT to (59.1) is based on the consideration of the electric field as the perturbation, λ being the perturbation parameter. The procedure yields a formal λ-power series expansion for $E(Z,\lambda)$. In the case of the lowest resonance E_o, corresponding to the 1s state of the hydrogen-like atom, the RS coefficients of the odd powers of λ are null, so that

$$E_o(Z,\lambda) = \sum_{n=0}^{\infty} E_o^{(n)} \gamma^n \; ; \; \gamma = \lambda^2 \tag{59.9}$$

It is well-known that the expansion (59.9) is asymptotically divergent /31/, but summable through the Borel method /10/. In general, the RSPT converges to the real part of the resonances (resolvent poles) for Hamiltonians without point spectrum.

Significant efforts have been made during the last years to determine the RS coefficients as a function of the quantum numbers of the unperturbed system. The fourth-order correction was obtained in analytical form in 1974 /32/ and the fifth-order one was determined employing the formalism discussed in §.8 based on hypervirial relations and parabolic coordinates /33,34/. Numerical results for the RS coefficients for several states were recursively calculated up to very high orders /35-41/, through hypervirial relationships (§.8) and the logarithmic derivative method (§.9). The most remarkable results for E_o are due to Privman /40/ who has determined 30 coefficients. Because of the divergence of (59.9), the large-order behavior of the $E_o^{(n)}$ coefficients has deserved great attention. It can be obtained by means of a dispersion relation similar to that examined in §.11 (Eqs. (11.13) and (11.76)) /25,42/:

$$E_o^{(n)} = -\frac{1}{\pi}\int_0^\infty \lambda^{-(2n+1)}\,\Gamma_o(\lambda)\,d\lambda \qquad (59.10)$$

The method has been generalized so that it applies to any state /43/. In order to determine $E^{(n)}$ via Eq. (59.10) it is necessary to know the resonance width for $\lambda \downarrow 0$, which requires the analytical prolongation of the eigenvalues into the complex plane. The structure of $\Gamma_o(\lambda \downarrow 0)$ was studied long time ago /6,18/, although it has been rigorously obtained just recently /44/. Approximately one has

$$\Gamma_o(\lambda) \to -\frac{4}{\lambda}\, e^{-2/3\lambda} \qquad (59.11)$$

The form of $\Gamma(\lambda)$ is known for all the states as a function of the quantum numbers /43, 45-48/. On introducing (59.11) into (59.10) the following asymptotic behavior is obtained:

$$E_0^{(n)} \to -\frac{4}{\pi}\left(\frac{3}{2}\right)^{2n+1}(2n)! \qquad (59.12)$$

which corresponds to a very strong divergence. Furthermore, it is worth noticing that all the RS coefficients for $E_o(\lambda)$ are negative unlike the models previously studied.

Silverstone /35/ made an exhaustive examination of the range of validity of the RSPT in a wide interval of λ-values and truncated (59.9) so that the absolute value of the last term retained is the smallest of the whole set. This can be achieved because the power series expansion (59.9) is asymptotic. Beyond the interval determined by Silverstone /35/, it is a must to introduce summation methods to obtain accurate results for $E(Z,\lambda)$ via the RSPT. The application of the summation methods for the Stark resonances is not as successful as in other systems, mainly due to the non-alternation of the perturbation coefficient signs. The proof of the convergence of the Borel transform of (59.9) is based on the fact that the series for purely imaginary λ-values is alternating. Padé approximants have been used to extend the range of validity of the RSPT /50/, though their application must be suitably modified to obtain reasonable results for E and Γ at intermediate field intensities /49/.

Recently, the renormalized series method /50/ has been applied to the Stark effect, combined with the Padé approximants and a stabilization method. In this way, Austin /50/ obtained good enough approximations to the real part of the resonances, by means of the 16-th order PT. Furthermore, it was shown that the change in the approximate E value due to the addition of the last renormalized coefficient amounts approximately to Γ /50/, which agrees with the comment formerly made by Reinhardt /49/.

The aim of this paragraph is the application of the FM to the Stark effect using the first orders of the RSPT. For the sake of simplicity, we will restrict ourselves to the first resonance. As before we make use of the formalism developed in §.44. However, it is worth mentioning that the formalism developed in §.42 has also been applied to the Stark effect in hydrogen /51/.

In order to apply the FM we need a scaling law for $E(Z,\gamma)$. It may be derived without further difficulty from the Hamiltonian properties. Upon scaling the cartesian coordinates in (59.1) and using the Symanzik theorem one has the following unitary transformation (see Appendix A):

$$H(Z,\lambda) = \lambda^{2/3} H(Z\lambda^{-1/3}, 1) \tag{59.13}$$

which yields the desired dilatation relationship

$$E(Z,\gamma) = \gamma^{1/3} E(Z\gamma^{-1/6}, 1) \tag{59.14}$$

and the corresponding FM exponents $\beta = 1/3, \alpha = -1/6$. It is interesting to note that $E_o(Z,\gamma)$ presents an asymptotic behavior for $\gamma >> 1$ which has nothing to do with a $\gamma^{-1/6}$ power series /44/:

$$|E| \to \gamma^{1/3} \left(\frac{1}{2} \ln\gamma\right)^{2/3} + O(\gamma^{1/3} \{\ln\ln|\sqrt{\gamma}|\}^{-1/3}) \tag{59.15}$$

This behavior is even more anomalous than that for the Zeeman effect since $\gamma^{-1/3} |E_o|$ does not remain finite when $1/\gamma \to 0$. For this reason we cannot study the convergence when $\gamma \to \infty$ and consider only the range $\gamma \leq 0.1$.

The FM exponents obtained above and Eq. (44.18), allow one to approximate $E(1,\gamma)$ by

$$E(1,\gamma) \simeq SE_N = \left(\frac{\gamma}{w}\right)^{1/3} S_N(k,w) \tag{59.16a}$$

where

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)} w^n \tag{59.16b}$$

and

$$\bar{E}^{(n)} = \sum_{j=0}^{n} (-1)^{n-j} \binom{2-6j}{n-j} E^{(j)} k^{2-6j} \tag{59.17}$$

Eq. (44.7) becomes

$$\gamma = wk^{-6} (1-w)^{-6} \tag{59.18}$$

which must be numerically solved for every γ-value.

The calculation is carried out as before, except for minor modifications to apply the Sensitivity Rules to SE_N instead of to $S_N(k,1)$. However, the properties of the FM for this problem are different from those discussed up to now, and we can guess that they are characteristic of systems without bound-states. Firstly, we note that since all the coefficients $E^{(n)}$ are negative, the sequence of partial sums

$$S_N(\gamma) = \sum_{n=0}^{N} E^{(n)} \gamma^n \tag{59.19}$$

is monotonously decreasing, i.e. $S_N(\gamma) > S_{N+1}(\gamma)$, and unbounded. For this reason, SE_N is found to be a monotonously increasing function of k, $k>0$, for every pair of γ and N values. Within this interval, SE_N does not possess neither SP nor IP.

The calculations show that SE_N only has IP and SP (in the latter case it is an isolated minimum) if N is smaller than (say) N', and $\rho = k^6 < 0$ (Eq. 44.9b). According to Lemma 44.3 the root of Eq.(59.18) fulfilling the condition above obeys $-1/5 \leq w \leq 0$ for $-(5/6)^5/(6\gamma) = \rho c \leq \rho \leq 0$. Within this w interval, one may apply the Sensitivity Rules 1 and 2. The IP and SP obtained in this way satisfy Theorems 44.1 and 44.2.

When N>N', a different criterion must be used because there is neither IP nor SP. We have found it suitable to determine $\rho = \rho^*_N$ according to the following criterion for each γ-value:

$$\left(\frac{\partial SE_N}{\partial \rho}\right)(\rho = \rho^*_N) = \left(\frac{\partial SE_{N-1}}{\partial \rho}\right)(\rho = \rho^*_N) \tag{59.20}$$

This condition is worth a brief comment. If for a given pair of γ and ρ-values, one draws a smooth curve joining the points (N, SE_N) (Fig.19.1), one obtains the inflexion points $\partial^2 SE_N / \partial N^2 = 0$ located

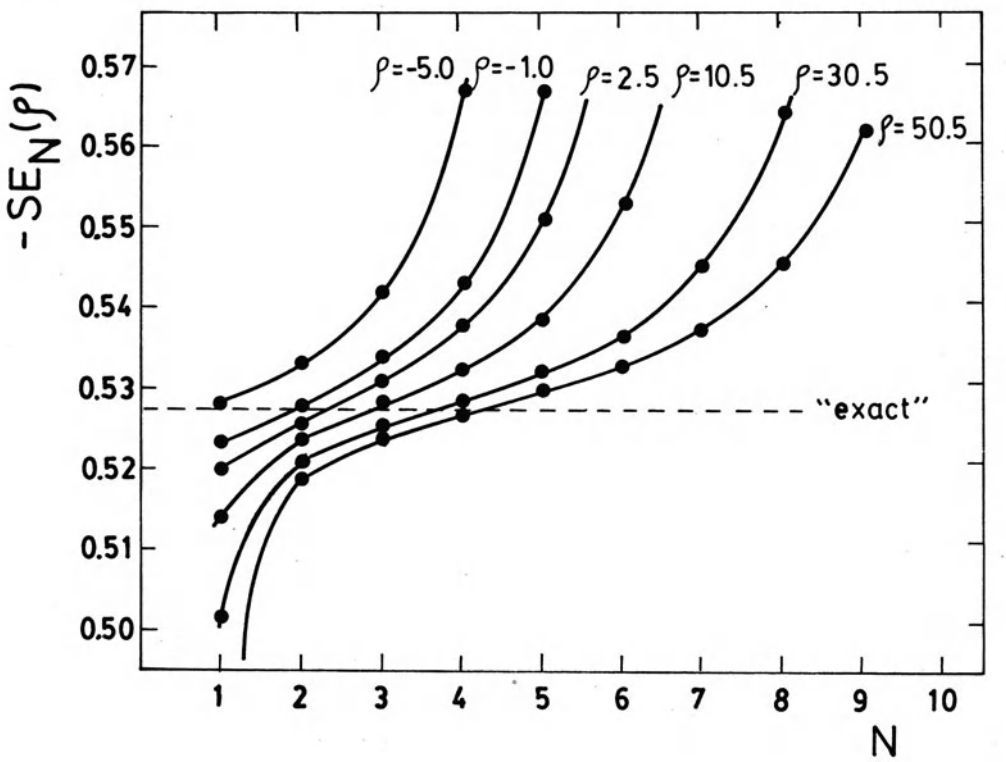

Fig. 19.1: Dependence of the SE_N sequence with N for several ρ values of the lowest resonance real part of the stark effect in the hydrogen atom. Results are for the field strength $\lambda = 0.1$.

between two consecutive N values. In particular, Fig. 19.1 shows the results obtained for $\sqrt{\gamma} = 0.1$ and different ρ-values. We can extract two main conclusions from such inflexion points:

i) They seem to be reasonable approximations to the real part of the resonance.

ii) The fact that the inflexion points arise, for a given ρ-value, with the addition of perturbational terms resembles what takes place when applying the Rayleigh-Ritz method to problems without bound states /22-24/. In order to perform such calculation it is usual to employ different basis sets of parametrized functions and the resonances are approximated by the inflexion points arising from the results for an increasing number of variational basis functions /22-24/. It is really revealing that the FM leads to a similar conclusion for the RSPT where the number of perturbative corrections plays the role of the size of the basis set in the variational method .

Since N is a discontinuous variable the inflexion points are approximately determined by means of Eq. (59.20).

In order to apply the criterion (59.20) to the sequence SE_N, it is necessary to obtain N' for each γ-value. This problem is solved by computing N' as the smallest positive integer satisfying

$$0 < \lim_{\rho \downarrow \rho_c} \left(\frac{\partial SE_{N'}}{\partial \rho}\right) \leq \lim_{\rho \downarrow \rho_c} \left(\frac{\partial SE_N}{\partial \rho}\right), \quad N \geq N' \tag{59.21}$$

which assures us that $(\partial SE_N/\partial\rho) > 0$ for all $\rho > \rho_c$ and $N \geq N'$. The calculation of N' is the starting point to build the optimum sequence

$$SE_N = \left(\frac{\gamma}{w}\right)^{1/3} S_N(\rho_N^*, w) \tag{59.22}$$

for every γ-value. For the largest γ-values considered, i.e. $\sqrt{\gamma} = 0.1$, it is found that N = 1 according to (59.21), so that the sequence $S_N(\rho_N^*, w)$ for such γ-value is completely determined by criterion (59.20). Fig. 19.2 shows the convergence rate of SE_N as a function of N for

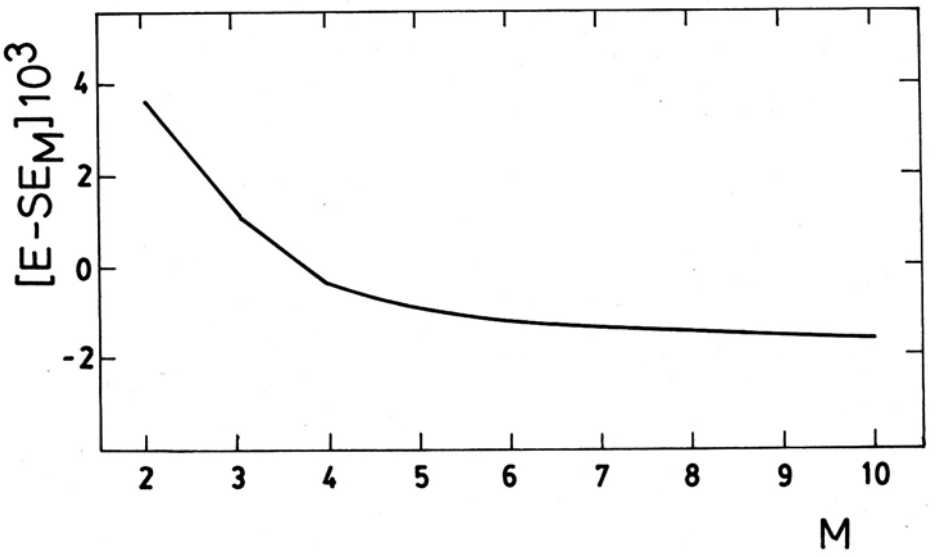

Fig. 19.2: Convergence of the $SE_N(\rho = \rho_N^*)$ sequence at $\lambda = 0.1$ for the lowest resonance of the Stark effect in the hydrogen atom.

$N \leq 10$. The perturbational coefficients used in the calculation were taken from Ref. /40/.

It seems that SE_N converges towards a limit slightly larger than the actual resonance /19,49/ and that the error decreases as γ decreases and the convergence rate increases.

Table 19.1

First resonance for the Stark effect in the hydrogen atom as a function of the applied field λ.

λ	$(k^*_{10})^6$	$-SE_{10}$ [a]	$-\|5/5\|$ [b]	$-E$ [c]	$-E$ [d]
0.03	11.30	0.502742749	0.50274261		0.502742726
0.04	50.42	0.503771750	0.50378279	0.503772	0.5037715
0.05	124.43	0.50610205	0.5061030	0.506076	0.5061054
0.06	236.94	0.5091572	0.509903	0.509205	0.5092036
0.08	693.25	0.517053	0.517262	0.517121	0.517559
0.10	1634.45	0.52588	0.539636	0.526333	0.527425 [e]

a) Computed through Eqs. (59.20) and (59.22).

b) Padé approximant $|5/5|$.

c) Average value of Padé approximants $|N/N|$, $6 \leq N \leq 16$, built from the renormalized series /50/.

d) Variational "exact" results /19/.

e) "Exact" result /49/.

Results obtained from SE_{10} are compared in Table 19.1 with both the "exact" ones /19,49/ and those derived by Austin /50/ through renormalized series. Besides, we have added the diagonal Padé approximant $|5/5|$ (Appendix D) which involves the same number of perturbational corrections as SE_{10}. For the sake of completeness we have included the

roots of Eq. (59.20). Results displayed in Table 19.1 enables us to draw the following conclusions:

i) The FM leads to better results than the Padé approximants of the same order, though in this case the difference is not as remarkable as those for the problems encountered before.

ii) Present results are comparable with Austin's /50/. It must be taken into account that the latter correspond to a stabilization of $|N/N|$ determinants, built from renormalized series and $6 \leq N \leq 16$. Evidently, the FM allows one to obtain similar results with much less effort and employing a smallest number of RS coefficients.

iii) In the whole range of γ values studied the following inequality is fulfilled

$$|SE_{10} - E(1,\gamma)| < \Gamma \tag{59.23}$$

which is an additional indicator of the attained accuracy /50/.

As shown in Appendix the mapping between the λ and w complex planes is, in the case of the Stark effect, many-valued unlike the other models discussed here. Therefore, it is not surprising that so many difficulties have been found when applying the FM to such system.

§.60. Upper and lower bound to the real part of the Stark resonances.

The application of the FM to the Stark effect in the hydrogen atom presents a very interesting feature: it is found to yield upper and lower bounds to the real part of the resonances. Although the argument to be presented is far from rigorous, it will allow us to derive qualitatively correct results.

The real part of the resonance, $E(1,\gamma)$, becomes increasingly negative when the applied electric field intensity, $\lambda = \gamma^{1/2}$, increases. On the basis of the notation introduced in §.59, it means that

$$s_o > E(1,\gamma) \tag{60.1}$$

for all $\gamma>0$. Besides s_N is known to possess the following properties (§.59):

$$s_N > s_{N+1}\ ,\ \lim_{N\to\infty} s_N(\gamma) = -\infty,\quad \gamma>0 \tag{60.2}$$

It follows from (60.1) and (60.2) that there exists a positive integer M such that

$$s_N(\gamma)>E \text{ if } N\leq M \text{ and } s_N(\gamma)<E \text{ if } N>M \tag{60.3}$$

Evidently, the determination of M will provide upper and lower bounds to $E(1,\gamma)$. It should be noted that the study of the properties of the sequences $s_N(\gamma)$ made here is completely different from Silverstone's /35/ who did not get bounds to $E(1,\gamma)$.

In order to obtain M we resort to the FM. The sequence chosen to approach $E(1,\gamma)$ satisfies an inequality like (60.2):

$$SE_N(\rho_N^*)>SE_{N+1}(\rho_{N+1}^*);\ \rho_N^* = (k_N^*)^6 \tag{60.4}$$

where ρ_N^* is computed in agreement with criterion (59.20) and fulfuls

$$\left(\frac{\partial \rho^*_N}{\partial N}\right)_\gamma >0 \tag{60.5}$$

On the other hand, Eq. (59.21) enables us to know the change of SE_N with ρ:

$$\left(\frac{\partial SE_N}{\partial \rho}\right)_\gamma > 0, \quad \rho_c < \rho < 0, \quad N \geq N', \quad \rho_c = -\frac{1}{6\gamma}\left(\frac{5}{6}\right)^5 \tag{60.6a}$$

$$\left(\frac{\partial SE_N}{\partial \rho}\right)_\gamma > 0 \quad \forall N \text{ when } \rho > 0 \tag{60.6b}$$

Since ρ may be negative, in what follows we use this variable instead of k.

Under certain conditions, the sequences SE_N and s_N may be related. For that purpose, we take into account that if $k<<1$, then $\gamma \to wk^{-6}$ (Eq.(59.18)). Furthermore, Eq. (59.17) leads to $\bar{E}^{(n)} \to E^{(n)}\ k^{-6n+2}$, so that $S_N(k,w) \to s_N(\gamma)k^2$. Finally, Eq. (59.16) yields

$$\lim_{\rho \to 0} SE_N = s_N(\gamma) \tag{60.7}$$

From Eqs. (60.6b) and (60.7) we have

$$SE_N > s_N(\gamma) \text{ if } \rho_N^* > 0 \tag{60.8}$$

Now, the open question is to determine the N-value for which $\rho_N^* > 0$.

Here, we introduce the working hypothesis that the FM always gives better results than the original divergent series, i.e.

$$|SE_N - E| < |s_N - E| \quad \forall N, \ \rho_c < \rho \tag{60.9}$$

Inequalities (60.8) and (60.9) yield

$$E(1,\gamma) > s_N(\gamma) \text{ if } \rho_N^* > 0 \tag{60.10}$$

On defining a positive integer N* such that

$$0 < \lim_{\rho \to 0} \left(\frac{\partial SE_{N^*}}{\partial \rho}\right)_\gamma \leq \lim_{\rho \to 0} \left(\frac{\partial SE_N}{\partial \rho}\right)_\gamma, \quad N \geq N^* \tag{60.11}$$

Eq. (60.6a) assures us that

$$N' < N^* \tag{60.12}$$

because $\rho_c < 0$. Since ρ_N^* increases with N (Eq. (60.5)) when the criterion (59.20) is used and SE_N fulfils (60.4), it is clear that N* gives rise, because of the definition (60.11) to a sequence that obeys the property

$$\rho_N^* > 0 \; \forall \; N > N^* \tag{60.13}$$

Inequalities (60.8), (60.10) and (60.13) give

$$E(1,\gamma) > s_N(\gamma), \quad N > N^* \tag{60.14}$$

which together with (60.3) leads to

$$M < N^* + 1 \tag{60.15}$$

Considering that the sequence of positive values of ρ_N^* starts with the condition (60.13), inequality (60.12) yields

$$\rho_c < p_{N'}^* < 0 \tag{60.16}$$

according to the criterion (59.20). Resorting to (60.6a) and (60.7) we obtain

$$SE_{N'} < s_{N'}(\gamma) \tag{60.17}$$

The introduction of the hypothesis (60.9) leads to

$$E(1,\gamma) < s_{N'}(\gamma) \tag{60.18}$$

which completes our analysis giving

$$N' < M \tag{60.19}$$

Summing up: the FM allows one to obtain bounds to $E(1,\gamma)$ by means of the perturbative sequences s_N as follows:

$$s_{N'}(\gamma) < E(1,\gamma) < s_{N^*+1}(\gamma) \tag{60.20}$$

where N' and N* are determined for each γ according to Eqs. (59.21) and (60.11), respectively.

Table 19.2

Upper and lower bounds to the first resonance of the Stark effect in the hydrogen atom (see §.60).

λ	N' [a]	N^* [b]	$-s_{N'}$	$-s_{N^*+1}$	$-e$ [c]
0.03	9	10	0.502074269	0.502074276	0.5020742726
0.04	6	7	0.503770659	0.503772207	0.5037715
0.05	3	5	0.50604885	0.50611505	0.5061054
0.06	3	4	0.50904386	0.50929989	0.50920360
0.08	2	3	0.5166752	0.51929425	0.5175595
0.10	1	2	0.5225	0.53296246	0.5274248 [d]

a) Computed with Eq. (59.21).

b) Computed with Eq. (60.11).

c) "Exact" results /19/.

d) "Exact" result /49/.

Values of $s_{N'}$ and s_{N^*+1} for $\lambda \leq 0.1$ are compared in Table 19.2 with the actual resonance position /19,49/. Obviously, Eq. (60.20) is satisfied for all the strength considered of the field.

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CHAPTER XX

FM AND VIBRATIONAL POTENTIALS OF DIATOMIC MOLECULES

§.61. Vibrational potentials for diatomic molecules.

The electronic energy of diatomic molecules as a function of the distance between the atoms is usually expanded around any of the following points: the united atom, the separated atoms or equilibrium. This last possibility is only valid for bound molecular states.

The first approximation has been examined from different standpoints /1-4/. In the united atom limit, the electronic energy E(R) can be written

$$E(R) = E_0 + E_2R^2 + E_3R^3 + E_4R^4 + E_5R^5(1-ClnR)+... \qquad (61.1)$$

where R is the internuclear distance and E_0 the united-atom energy. E(R) is the eigenvalue of the electronic Hamiltonian in the Born-Oppenheimer approximation. The logarithmic terms in (61.1) are characteristic of one-electron systems /3,4/, and they also appear in higher order terms of the expansion. Eq.(61.1) is only valid for very small R-values and, besides, the coefficients E_n for $n > 2$ are known for just a few systems. These facts make it difficult to calculate E(R) for all R values from the united atom expansion. Additional information on this issue may be found in Ref. /5/.

Recently, the second expansion has deserved a remarkable attention. At present, nearly all the knowledge on this problem is restricted to the ground state of H_2^+ . The electronic Hamiltonian for this molecule is

$$H(R) = \frac{1}{2}\,p^2 - \frac{1}{r} - \frac{1}{||\bar{R}-\bar{r}||} \qquad (61.2)$$

The separated-atoms limit for the ground state $\sigma_g 1s$ corresponds to a dissociation as $H(1s) + H^+$. Here, the electronic energy has a awkward

asymptotic dependence upon R given by /6-8/:

$$E(R) = \sum_{n=0}^{\infty} E^{(n)} R^{-n} - 4Re^{-(R+1)}(1+O(R^{-1})), R>>1 \qquad (61.3)$$

where all the coefficients $E^{(n)}$ are negative /8/:

$$E^{(0)} = -1/2;\ E^{(1)} = -1,\ E^{(2)} = -9/4, \text{ etc.} \qquad (61.4)$$

In principle one may obtain the electronic energy for an arbitrary R-value by summing the expansion (61.4). However, it is known to be strongly divergent /8-10/ since it has been found that

$$|E^{(n)}| \to e^{-2}\ (n+1)!\ 2^{-n} \qquad (61.5)$$

which leads to an expansion with zero convergence radius. Furthermore, it is supposed that the expansion is not summable even via the Borel method.

Lately, in order to take advantage of the large amount of information contained in Eq. (61.3) /11/, a number of summation methods have been tried although no successful results have been publised. It is to be noted that (61.3) has some features that, as shown in preceding chapters, make it troublesome the approach through the FM: the asymptotic behavior of E(R) is not an alternating series in powers of 1/R. The exponential term appearing in Eq. (61.3) is closely related with the splitting, at finite R-values, of the electronic energies of the molecular states $\sigma_g 1s$ and $\sigma_u 2p$, which are degenerate at the separated-atoms limit /8-11/. This behavior cannot be described via the RSPT, since it only approaches, through the R^{-1} power series expansion, the average energy of these states. We may assume that the renormalized series developed in §.44 will not probably converge to the correct limit when $R \to 0$.

On the other hand, the expansion about equilibrium seems to be promising and it has already given a good deal of information for a large number of molecules. Due to the interest on this problem, we devote the remaining of this paragraph to examine the third approximation, keeping

in mind the possible application of the FM.

The study of the electronic energy of diatomic molecules about the equilibrium position makes it possible to build the so-called vibrational potential U(R) given by the sum of the electronic energy and the repulsive internuclear potential. Later on, we will show that this potential may be approximated in terms of a power series expansion which has an empirical character, unlike all those previously studied in this book. It means that one has to resort to experimental data to construct the potential.

The natural source of information is vibrational-rotational spectroscopy and there exist some comprehensive works on the use of available experimental data /5,12-14/. For repulsive interactions, one can resort to scattering experiments in order to gather information about the electronic potential.

The more relevant information necessary to generate a bound state potential curve is given by the vibrational energy levels (corresponding to the experimental vibrational frequencies) and the rotational constants. In what follows, we will show briefly the way such constants are employed.

Let us consider the nuclear motion of a diatomic molecule. The problem will be discussed within the context of the Born-Oppenheimer approximation and the Schrodinger equation is known to be

$$\{-\frac{\hbar^2}{2\mu}\frac{1}{R^2}\frac{\partial}{\partial R} + \frac{K}{R^2} + U(R)\}\,\chi_{nJ}(R) = E_{nJ}\chi_{nJ}(R) \qquad (61.6)$$

where R is the internuclear distance, μ the reduced mass of the system, $J = 0,1,\ldots$ the angular momentum quantum number and $k = J(J+1)\hbar^2/2\mu$. Eq.(61.6) can be rewritten in a more suitable form by defining a new function $P_{nJ}(\lambda)$ as

$$\chi_{nJ}(R) = R^{-1}P_{nJ}(\lambda) \qquad (61.7)$$

where

$$\lambda = \frac{R-R_e}{R_e} \tag{61.8}$$

and R_e is the equilibrium internuclear distance:

$$U(R_e) = \min_{(R)} U(R) \tag{61.9}$$

On introducing (61.7) into (61.6) and taking into account that

$$\frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} \chi_{nJ}(R) = \frac{R}{R_e^2} \frac{\partial^2}{\partial \lambda^2} P_{nJ}(\lambda) \tag{61.10}$$

the following equation is obtained:

$$\{-\frac{\hbar^2}{2\mu R_e^2} \frac{\partial^2}{\partial \lambda^2} + \frac{K}{R^2} + U(R)\} P_{nJ}(\lambda) = E_{nJ} P_{nJ}(\lambda) \tag{61.11}$$

As said before we are interested in the expansion of U(R) around equilibrium:

$$U(R) = \sum_{m=0}^{\infty} \frac{1}{m!} U^{(m)}(R_e)(R-R_e)^m = U(R_e) +$$

$$+ \sum_{m=2}^{\infty} \{\frac{1}{m!} R_e^m U^{(m)}(R_e)\} \lambda^m \tag{61.12}$$

which enables us to define the so-called Dunham potential /15/:

$$V(\lambda) = U(R)-U(R_e) = a_0\lambda^2(1+a_1\lambda+a_2\lambda^2+\ldots) \tag{61.13}$$

The Dunham coefficients a_n can be determined from experiment. For

this purpose, we expand the R^{-2} term in Eq.(61.11) in λ-power series:

$$\frac{1}{R^2} = \frac{1}{R_e^2}(1+\lambda)^{-2} = R_e^{-2} \sum_{n=0}^{\infty} (n+1)\ (-\lambda)^n. \qquad (61.14)$$

Therefore, the expansion of the effective potential for the nuclear motion is found to be

$$\frac{K}{R^2} + V(\lambda) = B_e J(J+1) - 2J(J+1)\ B_e\lambda + \lambda^2\ (a_0+3B_eJ(J+1)) +$$

$$+ \sum_{n=3}^{\infty} \lambda^n\{a_0a_{n-2}+(-1)^n(n+1)B_eJ(J+1)\} \qquad (61.15a)$$

where B_e is the rotational constant at equilibrium:

$$B_e = \hbar^2/(2\mu R_e^2) \qquad (61.15b)$$

If we keep up to the second-order terms,

$$\frac{K}{R^2} + V(\lambda) \simeq B_eJ(J+1) - 2J(J+1)B_e\lambda + \{a_0+3J(J+1)B_e\}\lambda^2 =$$

$$+ B_eJ(J+1) + (a_0+3J(J+1)B_e)\{\lambda - \frac{B_eJ(J+1)}{a_0+3J(J+1)B_e}\}^2 -$$

$$- \frac{B_e^2J^2(J+1)^2}{a_0+3J(J+1)B_e} \qquad (61.16)$$

the nuclear Hamiltonian can be approximately written as an harmonic oscillator:

$$H \simeq \frac{\hbar^2}{2\mu R_e^2}\frac{\partial^2}{\partial\lambda^2} + U(R_e) + J(J+1)B_e - \frac{B_e^2J^2(J+1)^2}{a_0+3J(J+1)B_e} +$$

$$+ (a_0+3J(J+1)B_e)\{\lambda - \frac{B_eJ(J+1)}{a_0+3J(J+1)B_e}\}^2 + O(\lambda^3) \qquad (61.17)$$

whose eigenvalues are approximations to the rotational-vibrational energy levels. They can be written

$$E_{nJ} \simeq U(R_e) + J(J+1)B_e+(n+1/2)\hbar w_e(J) - \frac{B_e^2J^2(J+1)^2}{a_0+3J(J+1)B_e} +... \qquad (61.18)$$

where the frequency $w_e(J)$ is given by

$$w_e(J) = \{\frac{2}{\mu R_e^2}|a_0+3J(J+1)B_e|\}^{1/2} \qquad (61.19)$$

Eq.(61.18) suggests that the eigenvalues E_{nJ} may be written in terms of n and J as follows:

$$E_{nJ} = \sum_{r=0}^{\infty}\sum_{s=0}^{\infty} Y_{rs}(n+1/2)^rJ^s(J+1)^s \qquad (61.20)$$

where the first coefficients Y_{rs} are

$$Y_{00} = U(R_e),\ Y_{01} = B_e,\ Y_{10} = \hbar w_e(0) = \hbar(\frac{2a_0}{\mu R_e^2})^{1/2}$$

$$Y_{02} = -B_e^2/a_0,\ \text{etc.} \qquad (61.21)$$

In order to calculate the Dunham coefficients the rotational-vibrational spectrum is fitted by (61.20) which yields a set of Y_{rs} values. Then the Schrödinger equation is solved in order to express the a_n is in terms of the Y_{rs}'s. Clearly, in order to calculate the coefficients of the powers $(n+1/2)^r$ with $r \geq 2$ it is necessary to add anharmonic terms to the effective potential. For this reason the Schrödinger equa-

tion cannot be exactly solved and one is forced to resort to approximate methods. The first calculation was carried out by Dunham /15/ who made use of the JWKB method up to the first-order together with the Langer transformation /16/ consisting of substituting $(J+1/2)^2$ for $J(J+1)$. Later on, the procedure was extended to higher orders of the semiclassical approximation /17,18/. This approach enables one to know analytically around 5 or 6 coefficients a_n in terms of some of the constants Y_{rs} (see Ref./14/).

Preceding equations show that there are more parameters Y_{rs} than Dunham coefficients when the series is truncated up to a given power of λ. Then, in order to determine the latter it is necessary to make the algorithm self-consistent. It is worth mentioning that lack of self-consistent in the results may reveal some important phenomena, such as the non-validity of the Born-Oppenheimer approximation /15, 17,19,20/.

Owing to the approximate nature of the calculation just outlined the coefficients a_n exhibit errors that increase with the order n. This fact makes the Dunham series rather inaccurate even for moderately large λ values.

Another drawback of the Dunham series is that it has a finite convergence radius due to the Coulomb repulsion which is proportional to $1/R$. Therefore $V(\lambda)$ is singular at $\lambda=-1$ and the Dunham series diverges when:

$$|\lambda| > 1 \text{ or } R>2R_e \qquad (61.22)$$

Here, we are interested in the convergence properties of the Dunham series. Since the Dunham series does not converge for all R values it is not possible to obtain any information about the large-R behavior of the potential from such expansion. It is therefore evident the relevance of applying some summation technique to prolong analytically the expansion (61.13), since otherwise one cannot make use of all the information contained in the Dunham coefficients.

There are several options to surmount these difficulties. A particularly accurate method to determine the vibrational potential is the so-

called RKR procedure (developed by Rydberg, Klein and Rees)/5,13,21-23/. The RKR procedure resorts to the same information as Dunham method /15/ does, and is also of a semiclassical nature. However, it allows one to obtain the classical turning points, instead of the coefficients of a power series expansion. Although the RKR procedure provides excellent potential energy curves for several diatomic molecules (see, for example, Refs./24-28/), its application presents some complications which are discussed below in order to provide a framework for further comparison and discussion. The basic idea of the RKR method is very simple: if R_+ and R_- denote the right and left classical turning points, the first order JWKB approximation (Chapter II) allows us to determine the semiclassical eigenvalues by way of the following integral:

$$\int_{R_-}^{R_+} (E_{nJ}-W_J(R))^{1/2}\, dR = h(n+1/2)/(8\mu)^{1/2} \qquad (61.23a)$$

where (see Eq.(61.9))

$$W_J(R) = KR^{-2}+U(R) \qquad (61.23b)$$

Rotational-vibrational spectroscopy furnishes energies E_{nJ} and rotational constants $B_e(n)$. E_{nJ} and Eq.(61.23a) are not enough to obtain R_+ and R_- for each n, so that it is necessary to resort to a second condition involving the rotational constants $B_e(n)$, i.e. /5/:

$$B_e(n) = (E_{n+1,J}-E_{nJ})(8\mu)^{-1/2}\hbar \int_{R_-}^{R_+} (E_{nJ}-W_J(R))^{-1/2} \cdot R^{-2}dR \qquad (61.24)$$

Eqs.(61.23) and (61.24) completely determine the turning points R_+ and R_-, after proposing an approximate form for W(R). Since those equations are not practical it is convenient to use two other equivalent relations, which are derived by way of the procedure presented in Appendix J (see also Refs./22,29,30/). They are

$$R_+ - R_- = \hbar \left(\frac{2}{\mu}\right)^{1/2} \hbar^{-1} \int_{n_0}^{n} (E_{nJ}-E_{n'J})^{-1/2} dn' \qquad (61.25a)$$

$$\frac{1}{R_-} - \frac{1}{R_+} = (8\mu)^{1/2} \hbar^{-1} \int_{n_0}^{n} B_e(n') (E_{nJ}-E_{n'J})^{-1/2} \, dn' \qquad (61.25b)$$

where the real number n_0 is obtained from the equation /30/:

$$E_{n_0 J} = \min_{(R)} W_J(R) \qquad (61.26)$$

The integrals in (61.25) are computed numerically, by means of series expansions /25,29/ and the effect of higher-order JWKB approximations /31/ can also be taken into account.

In whichever of the preceding conditions, it is really difficult to attain good results for R_+ and R_- for large enough n-values. Thus, although the RKR method is not limited by convergence problems, from the practical point of view it does not allow to obtain a representation of the vibrational potential for distances two or three times larger than R_e.

To obtain an explicit analytical representation of $V(\lambda)$ in terms of λ (i.e. of R), the simplest way is to sum the Dunham expansion by means of some suitable method. Several procedures have been proposed to this end /32-38/ such as the Padé approximants /32/ and new power series expansions /33-38/ with better convergence properties. The latter are specially interesting and may be summarized in the following expression

$$V(\lambda) = v_0 f(\lambda)^2 \{1+v_1 f(\lambda)+v_2 f(\lambda)^2+....\} \qquad (61.27)$$

where the function $f(\lambda)$ must be chosen in such a manner to attain the largest radius /39,40/ and rate of convergence. The original Dunham series corresponds to $f(\lambda) = \lambda$ and $v_n = a_n \; \forall \; n \geq 0$. Simmons et al/33/,

Ogilvie /38/, and Thakkar /34/ proposed the following functions $f(\lambda) = \lambda/(1+\lambda)$, $f(\lambda) = \lambda/(2+\lambda)$, and $f(\lambda) = sgn(p)\{1-(1+\lambda)^{-p}\}$, respectively, where p is an adjustable real parameter. It is easy to see that Simons' et al /33/ proposal is the Euler transformation /41/, which has a solid quantum mechanical foundation on the basis of an appropriate partition of the Hamiltonian /33/. Some of the above mentioned methods have been discussed and compared /35-37/.

Although all of the preceding methods /32-38/ yield quite acceptable vibrational potentials they exhibit some drawbacks. For example, only low-order Padé approximants and series expansions can be constructed since just the first Dunham coefficients are known, and, furthermore, results are found to be strongly dependent on the accuracy of such coefficients. For this reason the convergence radius of the series cannot be easily computed and the singularity at $\lambda = -1$ only provides an upper bound to them /32-40/. Due to the lack of reliable information about convergence radii, it seems more suitable to refer to the ranges of utility of the power series /36/. An additional disadvantage of the methods used to extend the range of utility of the Dunham series consists in the fact that usually they cannot describe ionic and covalent diatomic molecules with similar accuracy. For example, Padé approximants /32/ are suitable for describing ionic and non-covalent molecules, while just the opposite happens with Thakkar's method /34/. This difference is due to the different asymptotic behavior of the vibrational potentials in the dissociation limit.

To make matters worse some of the series lead to potentials with non-physical maxima and even negative dissociation energies! /33/. Diagonal $|N/N|$ Padé approximants with $N>2$ /32/, present poles which are zeros of the denominator polynomial.

On the basis of the preceding discussion we may now apply the FM to sum the Dunham series employing the experimental coefficients and the asymptotic behavior of the vibrational potential.

Our aim is to obtain the spectroscopic dissociation energy D_e:

$$\lim_{R\to\infty} V(\lambda) = \{ \lim_{R\to\infty} U(R) \} - U(R_e) = D_e \qquad (61.28)$$

by means of the FM series built from the Dunham coefficients. This is a quite difficult task because we are using a Taylor expansion around $\lambda = 0$ to obtain the value of $V(\lambda)$ when $\lambda \to \infty$. In this regard, present problem is similar to those examined in previous chapters. An abridged version of the results in the next sections has been published in Ref. /42/.

§.62. Kratzer-Fues potential and FM

Unfortunately, when applying the summation methods to extend the range of utility of the Dunham series, it is not possible to make a thorough convergence analysis since no more than 7 or 8 coefficients of the Dunham expansion for diatomic molecules are available, and even this happen in a few cases.

In order to examine rigorously the convergence behavior of the FM series we have to resort to a simplified model for the vibrational potential such that all Dunham coefficients are analytically known. Here, we consider the Kratzer-Fues potential /43-46/. This model, has been discussed by means of high-order JWKB method. It is convenient to write the potential as follows

$$V_{KF}(R) = D_e\{(R_e/R)^2 + 1 - 2\frac{R_e}{R}\} \tag{62.1}$$

so that

$$\min_{(R)} V_{KF}(R) = V_{KF}(R_e) = 0, \quad \lim_{R\to\infty} V_{KF}(R) = D_e \tag{62.2}$$

In terms of $\lambda = (R-R_e)/R$ this potential reads

$$V_{KF}(\lambda) = D_e\lambda^2(1+\lambda)^{-2} \tag{62.3}$$

whose λ-power series expansion is considered here. The function (62.1) has a pole of order two at $R = 0$ ($\lambda = -1$).

In order to apply the FM to (62.1) it is preferable to study the function

$$E(\lambda) = D_e^{-1}\lambda^{-2}V_{KF}(\lambda) = (1+\lambda)^{-2} \qquad (62.4)$$

which can be expanded in Taylor series around $\lambda = 0$ and $1/\lambda = 0$, respectively, as follows:

$$E(\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n \ , \ E^{(n)} = (-1)^n(n+1), \ |\lambda|<1 \qquad (62.5a)$$

$$E(\lambda) = \lambda^{-2} \sum_{n=0}^{\infty} e^{(n)}\lambda^{-n}; \ e^{(n)} = E^{(n)}, \ |\lambda|>1 \qquad (62.5b)$$

The expansion (62.5a) is the Dunham series for the Kratzer-Fues potential where $a_0 = D_e$ and $a_n = E^{(n)}$ for $n \geq 1$. It follows from these expansions that $\alpha = -1$ and $\beta = -2$ (see §§ 42 and 44) which are the parameters that determine the form of the FM series.

It is worth noticing that $E(\lambda)$ is closely related to the generating function for the geometric series studied before in §.47. Therefore, results are expected to be similar.

Resorting to (44.18), we write the sequence SE_N that approaches $E(\lambda)$ as follows:

$$SE_N = (\lambda/w)^{-2}S_N(k,w) \qquad (62.6)$$

where

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)} w^n \qquad (62.7a)$$

and

$$\bar{E}^{(n)} = k^{-2}\, y^{n(n+1)};\ y = 1 - k^{-1} \tag{62.7b}$$

The variable w is given by a generalized Euler transformation

$$w = \lambda k/(1+\lambda k) \tag{62.7c}$$

The form of the coefficients $\bar{E}^{(n)}$ is simple enough to allow the exact calculation of $S_N(k,w)$.

In order to obtain k we apply the Sensitivity Rules (§.44) to the partial sum $S_N(k,1)$ which is easily found to be

$$S_N(k,1) = (N+1)y^{N+2} - (N+2)y^{N+1} + 1 \tag{62.8}$$

This function has only one stationary point (SP)

$$k_N^S = 1 \tag{62.9}$$

for all $N \geq 1$ and it is found that

$$S_N(k_N^S,1) = 1 \tag{62.10}$$

In addition to this there are two inflection points (IP). One of them is

$$k_N^I = 1 \quad \forall\ N \geq 2 \tag{62.11}$$

which leads us again to (62.10). This IP fulfils the Sensitivity Rules since it leads to the lowest first derivative of $S_N(k,1)$. The second IP is linearly dependent on N

$$(k_N^I)' = \frac{N}{3} + 1 \tag{62.12}$$

and, as shown in precedent paragraphs, it gives rise to a sequence with a wrong limit. In fact, it is not difficult to prove that:

$$\lim_{N\to\infty} S_N((k_N^I)',1) = 1-4/e^3 < 1 \tag{62.13}$$

The discussion above suggests that the FM allows one to sum the Dunham expansion in the most unfavorable case $1/\lambda = 0$. According to this the spectroscopic dissociation energy may be calculated from a power series expansion about the equilibrium position. This proposal will be verified in the forthcoming sections.

Since SE_N converges property (provided k_n is given by Eqs.(62.9) and (62.11) for $w = 1$, then the same happens for $0 \leq w \leq 1$, i.e. for all $\lambda > 0$. Then the FM provided an exact analytical representation for the Kratzer-Fues potential when $R \geq R_e$.

The branch $R < R_e$ must be carefully studied, since $\lambda < 0$ and $w > 1$. In order to examine this situation, k is considered to be an arbitrary parameter. The convergence radius of (62.7a) is easily found to be

$$\lim_{n\to\infty} |\bar{E}^{(n+1)}/\bar{E}^{(n)}| = \frac{k-1}{k} \tag{62.14}$$

which shows that the convergence radius of the series is infinite only when $k = 1$. Since $w \to \infty$ when $\lambda \to -1/k$, then the Sensitivity Rules and the FM allow us to sum the Dunham expansion of the Kratzer-Fues potential for any R. Obviously, the ocurrence of the IP's and SP's exactly at $k = 1$ cannot be assured in a general case so that the FM sequences will have a spurious singularity in $0 < R < R_e$. This drawback is not really

important because usually the greatest interest is placed upon the branch $R < R_e$. Furthermore, there exist several suitable representations for $V(\lambda)$ for $R < R_e$ but not for $R > R_e$.

§.63. Dunham series for ionic molecules.

The FM may be applied to the vibrational potential of any diatomic molecule, if two power series expansions are available. We know that the potential U(R) (Eq.(61.13)) can be approximated by means of the Dunham series. On the other hand, the following asymptotic expansion

$$V(R) = D_e - \frac{C}{R} + O(R^{-2}) = D_e - \frac{C}{\lambda R_e} + O(R^{-2}), C>0 \qquad (63.1)$$

is valid for ionic molecules in the larger regime /5/. $-C/R$ is the Coulombic interaction between the nuclei. The molecules considered here have a bound ground state $^1\Sigma^+$. This state is mainly ionic for internuclear distances about the equilibrium separation and for larger distances it crosses (strictly speaking it is an avoided crossing) a covalent state /5/. For the sake of simplicity, we will assume the ground state to be totally ionic, that is to say, we do not consider the crossing and suppose dissociation into ions. This fact accounts for the second term in (63.1).

It is convenient to apply the FM to the function

$$E(\lambda) = \lambda^{-2} a_0^{-1} V(R) \qquad (63.2)$$

for which the FM exponents are found to be $\alpha = -1$ and $\beta = -2$ on the basis of the Dunham expansion and (63.1). The coefficients $E^{(n)}$ of the expansion of $E(\lambda)$ in λ-power series are connected with the Dunham coefficients by

$$E^{(0)} = 1; \; E^{(n)} = a_n, \; n \geq 1 \qquad (63.3)$$

Our aim is to treat 20 alkaline halides, as illustrative examples of ionic molecules, in order to obtain some general conclusions on the usefulness of the FM. We will employ the Dunham coefficients given in Ref. /32/ since they make up a very complete data set. No more than three Dunham coefficients are available for such molecules with an acceptable degree of accuracy. For this reason four-term renormalized series will at most be considered here.

The use of the formalism developed in §.44 gives the sequence SE_N approaching (63.2) as

$$SE_N = (w/\lambda)^2 S_N(k,w) \tag{63.4}$$

where

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)} w^n \tag{63.5}$$

and

$$w = \lambda k/(1+\lambda k) \tag{63.6}$$

The first terms of the sequence (63.5) are

$$\bar{E}^{(0)} = k^{-2};\ \bar{E}^{(1)} = a_1 k^{-3} + 2k^{-2};\ \bar{E}^{(2)} = a_2 k^{-4} + 3a_1 k^{-3} + 3k^{-2};$$

$$\bar{E}^{(3)} = a_3 k^{-5} + 4a_2 k^{-4} + 6a_1 k^{-3} + 4k^{-2} \tag{63.7}$$

As usual, the parameter k is determined by the Sensitivity Rules for $S_N(k,1)$. This sequence yields an approach D_N to the dissociation energy (Eqs.(63.2) and (63.4)) as follows

$$D_N = a_0 S_N(k,1) \tag{63.8}$$

In case of convergence for all $R > R_e$, one concludes that $D_N \to D_e$ when $N \to \infty$.

The FM is completely different from the approaches previously developed to study ionic molecules /32,33/. It is worth noticing that when $k = 1$, Eq. (63.6) becomes the Euler transformation formerly employed by Simons et al /33/. This connection between both procedures makes clear the importance of k, since the SPF method /33/ leads to spurious maxima without physical sense in the approximate vibrational potential, or even to negative dissociation energies. As shown below when k is obtained according to the Sensitivity Rules these anomalies do not take place.

The calculation of the SP's and IP's has been performed as usual. We have resorted to the IP with largest k-value (k_2^I and k_3^I for N = 2,3, respectively) in agreement with the Sensitivity Rules. In Table 20.1 we present percent absolute deviations for the estimated dissociation energy with respect to the experimental data /32/. It may be seen that d_N(NaF) is much larger than the corresponding values for the other molecules, which is probably due to errors in the Dunham coefficients. For this reason, we have this molecule out of the forthcoming discussion.

The average percent absolute deviation $\overline{d_2}$ for the remaining molecules is 2.1%, which is noteworthy less than $\overline{d_3}$ (6.0%). Surely, this is due to the fact that the error in a_3 is larger than the one for a_2. Our best approximation to the dissociation energy, i.e. D_2, is by far better to that obtained by means of the |2/2| Padé approximants /32/, which for the same molecular set and resorting to the same number of Dunham coefficients, yields an average deviation of 5.9%. Our results are even slightly better than those obtained via the Rittner empirical potential /5/, usually used to fit RKR curves, for which the average error is 2.9%.

Then, we conclude that D_2 is an excellent approximation to D_e, still more when one considers that the experimental results used in the comparison above possess an error of about 1%.

Regarding other procedures it is seen that, though Thakkar method /34/ yields very good results for covalent molecules, it gives an average error of 25% when applied to ionic molecules. It is possible to

Table 20.1

Absolute value of the percent relative deviation of dissociation energies predicted by the FM for 20 alkaline halides.

Molecule	k_3^I	d_3 [a)]	k_2^I	d_2 [a)]
LiF	3.0300	6.3	2.4388	1.9
LiCl	3.1778	0.9	2.5271	5.2
LiBr	3.3993	7.6	2.6740	0.5
LiI	3.3773	4.9	2.6613	2.2
NaF	3.7161	17.3	2.9776	12.3
NaCl	3.5566	5.1	2.8320	0.6
NaBr	3.4643	0.7	2.7523	5.4
NaI	3.6375	2.9	2.8822	3.7
KF	3.7591	12.9	2.9650	4.0
KCl	3.8509	7.0	3.0329	0.2
KBr	3.8791	7.0	3.0720	0.0
KI	3.9268	6.1	3.0912	1.3
RbF	3.6345	2.0	2.9006	3.7
RbCl	4.0069	8.7	3.1449	1.5
RbBr	3.9853	7.0	3.1339	0.0
RbI	4.0916	8.5	3.2199	1.6
CsF	3.8713	4.1	2.9924	5.5
CsCl	4.1548	8.4	3.2378	0.4
CsBr	4.0606	7.0	3.1718	0.7
CsI	4.2036	7.1	3.2857	0.6

a) $d_N = 100|1-D_N/D_e|$.

obtain an acceptable estimation of D_e by means of the $|2/3|$ approximants built from the Simons et al series (5.8%). This last procedure (which introduces the correct dominant behavior for $1/R \to 0$) seems to have been considered worthless by several authors /34/.

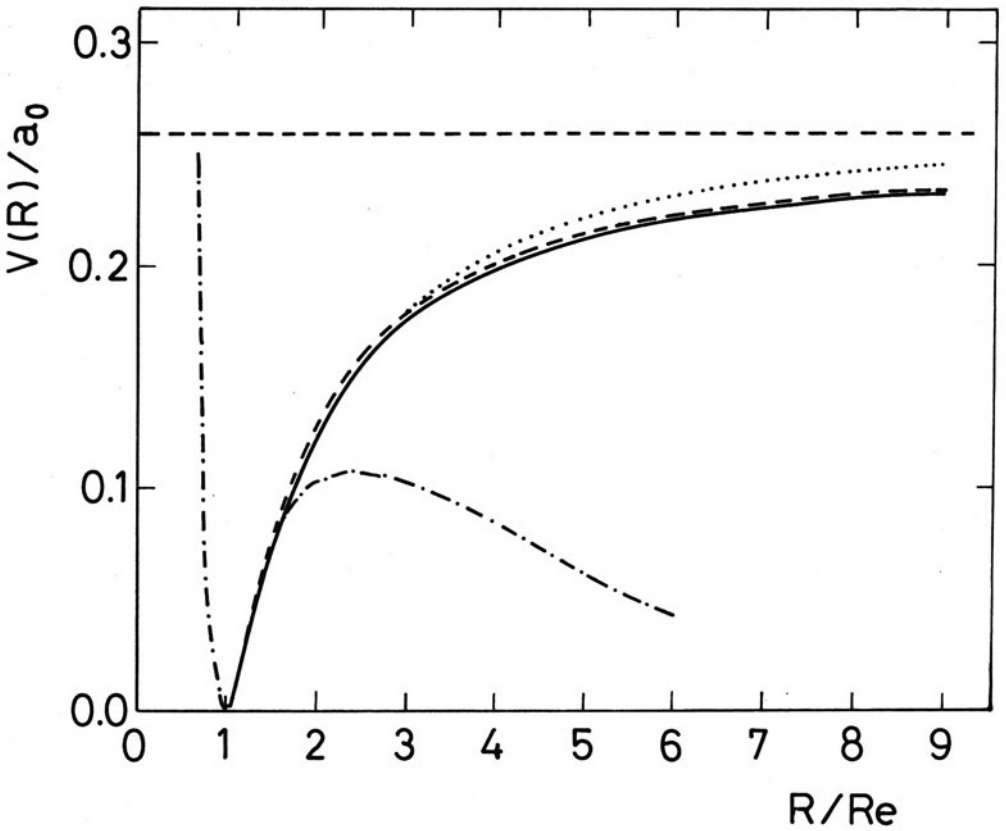

Fig. 20.1: Vibrational potential energy of KI built from the use of the first three coefficients of the Dunham series.

——— FM: λ^2 SE_2, k = k_2^I.

------- FM: SE_4' + D_e /a_0, k = k_4^I.

..... Padé approximant |2/2|.

-.-.-.- Simons et al series: $\lambda^2 SE_2$, k = 1 /33/.

Fig. 20.1 shows the vibrational potential (in units of a_0) of KI, obtained from the three first Dunham coefficients and several approximate methods. Our approach (i.e. $\lambda^2 SE_N$) and the |2/2| Padé approximants /32/ yield quite acceptable potential curves for $R > R_e$ which agree with Simons' et al /33/ (k = 1 in the FM) for $R_e \leq R \leq 1.5\ R_e$. It is well known that in this range the SPF function is a good approximation to the RKR potential /33/. As shown in Fig. 20.1, the SPF curve /33/ does not have any physical sense for $R \leq R_e$ because it presents a local maximum at $R \simeq 2.5\ R_e$. On the other hand, the FM curve ($k = k_2^I \simeq 3.1$) does not possess any anomalous feature.

One of the most relevant advantages of the FM regarding other proposed methods, is the possibility of systematically using all the available experimental information. For example, if D_e is known, it can be introduced into the renormalized series to obtain a better approximation to the vibrational potential. To this end, the following function is defined

$$E'(\lambda) - a_0^{-1} \{V(\lambda) - D_e\} \tag{63.9}$$

which has the asymptotic behaviors

$$E'(\lambda) = - a_0^{-1} D_e + \lambda^2 + a_1 \lambda^3 + a_2 \lambda^4 + .. \lambda << 1 \tag{63.10a}$$

$$E'(\lambda) = \lambda^{-1} \{ -C a_0^{-1} R_e^{-1} + O(\lambda^{-1}) \};\ \lambda >> 1 \tag{63.10b}$$

Now, we can apply the FM with the exponents $\alpha = \beta = -1$. The coefficients of the λ-power series expansion of $E'(\lambda)$ are $E'^{(0)} = -D_e/a_0$, $E'^{(1)} = 0$, $E'^{(2)} = 1$ and $E'^{(n)} = a_{n-2}$ for $n > 2$. The inclusion of the Dunham coefficient a_2 allows us to construct the function

$$SE_4' = \left(\frac{w}{\lambda}\right) \sum_{n=0}^{4} \bar{E}'^{(n)}\ w^n;\ w = \lambda k/(1+\lambda k) \tag{63.11}$$

Once again, the k-value may be obtained according to the Sensitivity

Rules when w = 1. Finally, $(SE'_4 + D_e/a_0)$ represents our approximation to the potential $V(\lambda)/a_0$. For the KI molecule we have obtained k_4^I = 4.890 and results are also plotted in Fig. 20.1. We see that this new approximation is nearly the same as that provided by the |2/2| approximant when $R_e \leq R \leq 3R_e$ and it does not differ appreciably from SE_2.

Summarizing it can be concluded that the FM is really useful to treat empirical series, such as the Dunham expansion, and obtain a very good approximation to the dissociation energies and vibrational potentials. It must be remembered that RKR curves are not usually available for ionic molecules due to the lack of enough experimental information, and this fact emphasizes the usefulness of the FM.

§.64. Dunham series for covalent molecules.

The asymptotic properties of the vibrational potentials for ionic and covalent diatomic molecules for large R values are very different each other. This difference makes it necessary the use of different methods to sum efficiently the Dunham series for both classes of molecules. Engelke /36/ suggested the necessity of introducing the correct behavior of the potential about 1/R = 0 into the methods of analytical prolongation in order to obtain reasonable results for the dissociation energy. Precisely, one of the main advantages of the FM is that it allows one to approximate the vibrational potential by way of a sequence SE_N that embodies such analytical information.

Covalent molecules are considered here that have a bound ground state which is covalent for distances around the equilibrium position. This state may cross an ionic state for larger internuclear distances. However, in §.63 we will not take into account such crossings and consider just the covalent dissociation in neutral atoms. Under these conditions, the vibrational potential has the following typical expansion

$$V(R) = D_e + C'R^{-6} + \ldots; \quad R>>1 \qquad (64.1)$$

where the term $C'R^{-6}$ corresponds to a Van der Waals' interaction. To apply the FM we proceed as in the preceding section defining the func-

tion $E(\lambda)$:

$$E(\lambda) = \lambda^{-2} V(R) a_0^{-1} \tag{64.2}$$

which has the following series expansions

$$E(\lambda) = \sum_{n=0}^{\infty} E^{(n)} \lambda^n;\ E^{(0)} = 1;\ E^{(n)} = a_n, n \geq 1, \lambda < 1 \tag{64.3a}$$

$$E(\lambda) = \lambda^{-2} \{ a_0^{-1} D_e + C' R_e^{-6} \lambda^{-6} + \ldots \};\ \lambda >> 1 \tag{64.3b}$$

Though higher-order terms in (64.3b) do not correspond to a λ^{-6} power series we apply the FM with $\alpha = -6, \beta = -2$ for the sake of simplicity. These coefficients and Eq.(44.7) leads us to the following change of variables

$$\lambda^{-6} = k w^{-6} (1-w) \tag{64.4}$$

The FM approaches $E(\lambda)$ by means of the following sequence (Eqs. (44.18)):

$$SE_N = \left(\frac{w}{\lambda}\right)^2 S_N(k,w) \tag{64.5a}$$

where

$$S_N(k,w) = \sum_{n=0}^{N} \bar{E}^{(n)} w^n \tag{64.5b}$$

and the coefficients $\bar{E}^{(n)}$ are computed from Eq.(44.14):

$$\bar{E}^{(n)} = \sum_{i=0}^{n} (-1)^{n-i} \binom{-(i+2)/6}{n-i} E^{(i)} k^{-(i+2)/6} \qquad (64.5c)$$

In order to check the convergence of the sequence towards the dissociation energy we carry out the calculations for w = 1. Due to the large, negative α value (α = -6), the IP's and SP's are found to be complex for some N values. In such cases we have chosen the real part (R_e) of k_N^S as the optimum k-value, although $R_e(k_N^I)$ is another reasonable choice leading to similar conclusions.

We have made use of the Dunham coefficients given in Refs. /5,14,32/ for the covalent molecules CO, HF and HCl and results are compared in Table 20.2 with those coming from other methods. Results are expressed in absolute percent deviation from experimental data. A careful look at Table 20.2 shows that FM and Thakkar's procedures /34/ seem to be the only ones giving reasonable results. However, Thakkar power series does not appear to be reliable because all the coefficients are of comparable magnitude so that the error in the approximation to the dissociation energy increases as more Dunham coefficients are added /36/. This fact is clearly seen when one compares results for HCl with those for CO and HF in Table 20.2. On the other hand, the FM seems to converge slowly and smoothly from above so that it appears to converge towards the right limit. Notwithstanding, it should be desirable to include a greater number of Dunham coefficients to verify numerically whether the FM sequence is actually convergent.

In order to verify the importance of taking into account the correct asymptotic behavior of the vibrational potential into renormalized series (as pointed out be Engelke /36/), we have compared the dissociation energy for HCl obtained from the FM with covalent (α = -6, β = -2) and ionic (α = -1, β = -2) exponents. Results are displayed in Table 20.3. It is seen that the sequence with covalent parameters approaches more quickly the experimental values than the sequence constructed with the ionic parameters. This difference is even more noteworthy if we consider that the pole in the potential energy at R = 0 (λ = -1) corresponds to w < 1 in the covalent case and w > 1 in the ionic one. This feature suggests that the largest error should arise for the renormalized series in the covalent case, since such singularity would have a disastrous effect on the convergence when $w \to 1$.

Table 20.2

Relative percent deviation of the dissociation energies of CO, HF and HCl obtained from the FM. ($\delta_N = 100(1-D_N/D_e)$).

Molecule	N	k	δ_N a)	δ_N b)	δ_N c)	δ_N d)
CO	1	781.9	67.4		-133.0	-103.0
	2	689.0*	46.4	-143.0	-82.0	290.0
	3	116.8	40.9		-36.0	342.0
	4	85.8*	23.0	182.0	-3.6	229.0
HF	1	265.6	71.4		-164.0	-210.0
	2	433.9*	56.9	-161.0	-126.0	-96.0
	3	51.5	47.3		-104.0	-68.0
	4	29.9*	26.4	-182.0	-46.0	117.0
	5	33.6	25.9		7.1	264.0
HCl	1	353.3	64.3		-205.2	-261.1
	2	435.9*	43.8	-194.7	-141.9	-17.5
	3	71.1	36.9		-75.9	145.4
	4	56.0*	16.3	-1931.0	-5.5	327.6
	5	21.5	16.9		63.2	434.0
	6	7.2	8.9		143.4	796.1

* $\{Re(k_N^S)^{-1/6}\}^{-6}$

a) Obtained via the FM

b) Padé approximants |(1+N/2/(1+N/2)| /32,34/.

c) Thakkar method /34/.

d) Eq.(22) in /33/.

Table 20.3

Dissociation energy of HCl from the FM considering different asymptotic behaviors for the vibrational potential.

N	D_N/a_0 [a)]	D_N/a_0 [b)]
1	0.062371	0.604240
2	0.099036	0.493981
3	0.111204	0.454131
4	0.147554	0.423698
5	0.146513	0.412272
6	0.162115	0.400771

D_e/a_0 (experimental): 0.17629

a) Covalent asymptotic behavior: $\beta = -2$; $\alpha = -6$.

b) Ionic asymptotic behavior: $\beta = -2$; $\alpha = -1$.

However, the fact that the covalent description is the most appropriate (Table 20.3) leads us to conclude that it is very important to take into account the analytical behavior of the vibrational potential to predict the dissociation energy with a reasonable accuracy.

Summing up, the FM provides an especially useful way to attain information from the vibrational spectra by means of the employment of empirical power series. Furthermore, the FM allows one to incorporate systematically all the available experimental information to derive acceptable potential energy curves. This method may be applied to approximate some other functions with similar characteristics, such as dipole moments of diatomic molecules /47-49/.

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APPENDIX A

SCALING LAWS OF SCHRÖDINGER OPERATORS.

Some of the basic features of the analytic structure of eigenvalues of Schrödinger operators follow from the so-called scaling laws satisfied by them. These scaling laws express the dilatation properties of operators, when scaling the parameters on which such operators depend. The aim of this appendix is to discuss briefly the derivation of these scaling laws as unitary transformations. These relations will allow one to perform changes of units in Schrödinger equations, as well as studying the structure of asymptotic expansions for the eigenvalues, as functions dependent on several physical parameters.

Let us consider a multidimensional Schrödinger operator, dependent on two real parameters λ and Z, as follows:

$$H(Z,\lambda) = p^2 + ZV_1(\bar{r}) + \lambda V_2(\bar{r}), \quad Z,\lambda \in R \tag{A.1}$$

$$\bar{r} = (x_1, x_2, \ldots, x_N) \in R^N , \tag{A.2}$$

where $p^2 = \bar{p}.\bar{p}$, with $\bar{p}$ the conjugated N-dimensional momentum operator. We shall assume $V_1(\bar{r})$ and $V_2(\bar{r})$ to be homogeneous functions with degrees n_1 and n_2, respectively. Let us consider now a normalized wavefunction $\chi(\bar{r})$:

$$||\chi(\bar{r})|| = 1 \tag{A.3}$$

and a scaling factor a, $a \geq 0$, introduced in $\chi(\bar{r})$ as follows:

$$U_a \chi(\bar{r}) = a^{N/2} \chi(a\bar{r}) \tag{A.4}$$

It is immediate to prove that U_a is unitary, since:

$$||U_a\chi(\bar{r})|| = 1 \tag{A.5a}$$

$$U_a^{+} = U_a^{-1} = U_{1/a} \tag{A.5b}$$

The operator U_a defines an infinite, uniparametric dilatation group (scaling group). The following similarity transformations on coordinates and momenta are easily proved:

$$U_a x_j^m U_a^{+} = a^m x_j^m,$$

$$U_a p_j^m U_a^{+} = a^{-m} p_j^m; \; p_j = -i\partial/\partial x_j, \; j = 1,2,\ldots,N. \tag{A.6}$$

From Eqs.(A.6), one deduces the similarity transformation on the Hamiltonian operator $H(Z,\lambda)$:

$$U_a H(Z,\lambda) U_a^{+} = a^{-2}p^2 + Za^{n_1}V_1 + \lambda a^{n_2}V_2$$

$$= a^{-2}\{p^2 + Za^{n_1+2}V_1 + \lambda a^{n_2+2}V_2\}$$

$$= a^{-2}H(Za^{n_1+2}, \lambda a^{n_2+2}) \tag{A.7}$$

Eq.(A.7) represents a unitary equivalence of operators (Symanzik theorem), often written simply as (see §.16):

$$H(Z,\lambda) \simeq a^{-2}H(Za^{n_1+2}, \lambda a^{n_2+2}), \; a > 0 \tag{A.8}$$

From the above equivalence, it follows a strict equality of eigen-

values

$$E(Z,\lambda) = a^{-2}H(Za^{n_1+2},\ \lambda a^{n_2+2}),\ a > 0$$

which displays the basic dilatation property of the energy function. Eq. (A.8) is a general scaling law (Symanzik scaling) of the Hamiltonian operator. It can be given a more familiar form by choosing $a = Z^{-1/(n_1+2)}$:

$$H(Z,\lambda) \simeq Z^{2/(n_1+2)}\ H(1,\lambda Z^{-(n_2+2)/(n_1+2)}),\ n_1 \neq -2, \qquad (A.9a)$$

or, by choosing $a = \lambda^{-1/(n_2+2)}$,

$$H(Z,\lambda) \simeq \lambda^{2/(n_2+2)} H(Z\lambda^{-(n_1+2)/(n_2+2)},1),\ n_2 \neq -2. \qquad (A.9b)$$

Relations (A.9a) and (A.9b) are totally equivalent to each other. The corresponding eigenvalue equalities allows one to relate different energies in the (Z,λ)-parameter space. This type of relationships will be used many times throughout this work. Notice that a similar procedure can be followed to relate $E(Z,\lambda)$ with the eigenvalues of a slightly modified family of operators, such as: $Hg(Z,\lambda) = gp^2+ZV_1+\lambda V_2, g>0$. The reader is left to prove that the following two equivalences hold:

$$Hg(Z,\lambda) \simeq g^{n_1/(n_1+2)} H(Z,\lambda g^{-n_2/(n_1+2)}),\ n_1 \neq -2, \qquad (A.10a)$$

$$Hg(Z,\lambda) \simeq g^{n_2/(n_1+2)} H(Zg^{-n_1/(n_2+2)},\lambda),\ n_2 \neq -2. \qquad (A.10b)$$

APPENDIX B

APPLICATIONS OF THE ANHARMONIC OSCILLATOR MODEL.

The anharmonic oscillator model defined by the following Hamiltonian

$$H(Z,\lambda) = p^2 + Zx^2 + \lambda x^{2N},\ 0 \leq Z,\lambda < \infty,\ N=2,3,\ldots,\ p=-id/dx \qquad (B.1)$$

has played a relevant role in several fields of the Physics and Chemistry, and yet today deserves a noticeable attention. The interest in the properties of the $H(Z,\lambda)$ eigenvalue spectrum is justified by the different applications of the model in connection with several phenomena. The model has also theoretical interest, since it is a simple system exhibiting characteristic properties of other more complex models.

We do not intend here to present a review on the vast bibliography of the anharmonic oscillator model. Rather, we want to present an overview of the main phenomena and theories that demand the introduction of the operator (B.1) since throughout this book anharmonic oscillator models are used for several analyses, the discussion of this Appendix will serve as a reference, in order to justify the employment of this model.

Anharmonic oscillations are especially important in three well defined fields: 1) molecular vibrations, 2) diffusion processes and laser theories, and 3) simple field theories. Here we discuss the first two themes, and the third one is examined in Appendix C.

Evidently, the greatest physico-chemical interest on anharmonic oscillations lies in their occurrence in some molecular vibrations, where the quartic contribution (N=2 in (B.1)) is the most important one.

Bell /1/ was the first author who pointed out that out-of-plane "bending", vibrations in four-number rings should be basically of fourth degree (i.e. Z=0 and N=2 in Eq. (B.1)). From that proposal on, abundant experimental evidence confirmed the importance of vibrational oscillations with quartic anharmonicity. Among the earliest contributions we can mention the following results: i) study and interpretation of the

microwave spectrum of trimethylene oxide ($(CH_2)_3O$) /2,3/; ii) examination of the far infrared spectrum of trimethylene oxide /4/, by means of out-of-plane ring oscillations; iii) out-of-the-molecular-plane $-CH_2$ group oscillations in diazomethane /5/, where the quartic anharmonicity term to be introduced is smaller than in case ii).

Later experiments showed that the effects associated with quartic anharmonicity appear in a large set of ring compounds /6/, such as cyclobutane /7/ and cyclobutanone /8/. Some vibrations, like those appearing in cyclopentane, require the consideration of 2D quartic anharmonic oscillations /9/.

Although one may expect a small quartic contribution in the vibrational potential for low frequency (large amplitude) oscillations, the quartic anharmonicity in ring compounds arises owing to more fundamental reasons. Since there is no detailed discussion in the current literature, we briefly show here the reasons supporting the appearance of quartic anharmonic vibrations.

Let us consider an ABA bond belonging to a ring compound, initially located in the plane 1 (A_1BA_1) (see Fig. B.1)

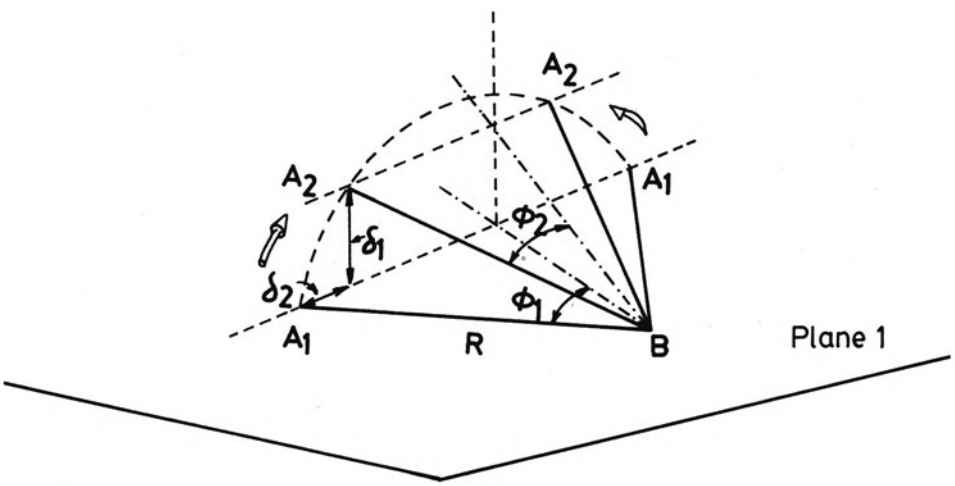

Fig. B.1: Bond vibration in a ring-like molecule (The molecular remaining is omitted).

The bond angle corresponding to this initial state is $2\phi_1$. Let us assure negligible the forces among atoms not linked by classical chemical bonds. Accordingly, bond lengths (R) do not change when a vibration takes place, that is to say, atoms move along circles. This situation is depicted in Fig. B.1, where the ring deformation vibrations are such that atoms move from A_1 to A_2. Along such a motion, the bond angle changes $2\Delta\phi = 2(\phi_1-\phi_2)$.

Now, the potential energy for the ring deformation is due to the interactions among bonds, under the conditions previously described, i.e. the potential is associated with the deformation $\Delta\phi$ of the bond angle. Since it is necessary to set forth the molecular potential in terms of atomic coordinates, we need to relate such coordinates with $\Delta\phi$.

Fig. B.1 shows that during the vibrational motion, atoms A move on a distance ℓ given by

$$\ell^2 = \delta_1^2 + \delta_2^2 \tag{B.2}$$

The following trigonometric relationships hold, among angles appearing in Fig. B.1:

$$\delta_1^2 = R^2(\sin^2\phi_2 - \sin^2\phi_1), \tag{B.3a}$$

$$\delta_2^2 = R^2(\sin\phi_2 - \sin\phi_1)^2 \tag{B.3b}$$

from where:

$$\ell^2/R^2 = 2(\sin^2\phi_2 - \sin\phi_1\sin\phi_2) \tag{B.4}$$

Eq. (B.4) may be easily rewritten in terms of the change in the bond angle

$$\ell^2/R^2 = 2(\cos^2 \Delta\phi - \cos\Delta\phi)\ \sin^2\phi_1 + (\sin 2\phi_1 - \sin\phi_1)\sin(2\Delta\phi) +$$

$$+ 2\sin^2\Delta\phi\ \cos^2\phi_1 \qquad \text{(B.5)}$$

In the approximation of small oscillations ($\Delta\phi >> \Delta\phi^2$), Eq. (B.5) may be simplified as follows

$$y^2 = \ell^2/R^2 \simeq A\Delta\phi + B\Delta\phi^2 \qquad \text{(B.6a)}$$

$$A = \frac{1}{2}\ (\sin 2\phi_1 - \sin\phi_1);\ B = (3\cos^2\phi_1 - 1) \qquad \text{(B.6b)}$$

and then

$$\Delta\phi \simeq \frac{y^2}{A} - \frac{B}{A^3}\ y^4 \qquad \text{(B.7)}$$

In case the interaction among bonds and atoms is weak, not only atoms move along a circular pathway, but the rotation around the bonds may be considered as free. In such a case, the restoring force for oscillations arises from the bond angle distortions, and it could be considered harmonic. Accordingly, the potential is:

$$V = k\Delta\phi^2 \simeq \frac{k}{A^2}\ y^4 \qquad \text{(B.8)}$$

The above situation takes place mainly in small strain-free cycles, i.e. nonplanar cycles. Eq.(B.8) assures us that for such cycles atoms move (in small vibrations) in quartic oscillations, and not harmonic ones, about their equilibrium positions.

When there are strains in the cycles, atoms do not move along circu-

lar pathways. In this case, rotation is hindered and the contribution to the molecular potential may depend upon the sign of $\Delta\phi$. Thus, we can write

$$V = k_1\Delta\phi + k_2\Delta\phi^2 \simeq \frac{k_1}{A}\, y^2 + \left(\frac{k_2}{A^2} - \frac{Bk_1}{A^3}\right) y^4, \qquad (B.9)$$

which yields a quartic anharmonic vibrational potential. Eq.(B.9) shows that force constants and bond angles determine the sign of Z. When $Z<0$, the vibrational potential is a double well, which is characteristic of molecular inversion and hydrogen bond problems.

The quartic anharmonic oscillation is a distinctive feature of quasiplanar cycles, such as cyclobutane and cyclopentane. However, other planar cycles with weaker bonds (such as $(AlCl_3)_2$) vibrate like a quartic anharmonic oscillator.

Above discussion reveals the importance of knowing the eigenvalues associated with (B.1) in a function of $\lambda>0$, that is to say, for quartic anharmonic and purely quartic oscillators.

The need to know the eigenvalue spectrum of anharmonic oscillators also arises in a natural way within a different context, such as diffusion processes /10-12/. We give here a brief account of this subject to show the way in which anharmonic oscillations are involved.

For a 1D diffusion process, such as the movement of ions through a membrane /10/, the probability density P(x,t) is determined by the Fokker-Planck equation

$$\frac{\partial}{\partial t} P(x,t) = \frac{\partial}{\partial x}\left\{\left(\frac{dU(x)}{dx}\right) P(x,t)\right\} + D\,\frac{\partial^2}{\partial x^2} P(x,t) \qquad (B.10)$$

where D is the diffusion coefficient and U(x) is an external potential acting on the system. The case D = 0 corresponds to the Liouville continuity equation /10/.

The model potential for diffusional processes

$$U(x) = \frac{Z}{2} x^2 + \frac{1}{4} x^4 \ , \tag{B.11}$$

has deserved a considerable interest in the current literature, due to its non-trivial character and intrinsic simplicity. The replacement of (B.11) in (B.10) yields

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \{(Zx + x^3)P\} + D \frac{\partial^2 P}{\partial x^2} \tag{B.12}$$

which has also been examined in relation to laser theory /13-15/. Likewise, Eq. (B.12) represents the zero-order description of more general Markov processes at the thermodynamic limit /12/.

Let us prove in the following the solution of Eq. (B.12) may be related to the Schrödinger equation associated with an anharmonic oscillator. Without any loss of generality, we choose D = 1. Defining thus $P_0=P(x,0)$ as the stationary solution of Eq.(B.10), i.e.

$$U''P_0 + U'P_0' + P_0'' = 0 \tag{B.13}$$

where primes mean derivation with respect to coordinates. The integration of (B.13) subjected to the boundary conditions for P

$$\lim_{|x|\to\infty} x^N P_0 = 0 \ , \ N>0 \tag{B.14}$$

gives

$$U' = -P_0'/P_0 \tag{B.15}$$

Defining:

$$P(x,t) = \{P_0(x)\}^{1/2} S(x) e^{-\mu t} \qquad (B.16)$$

and substituting it into (B.10) one gets:

$$-\mu P_0 S = (U'' P_0 + P_0' U' + P_0'') S - \frac{S}{2}(P_0' U' + P_0'' + \frac{1}{2P_0} P_0'^2) + (U' P_0 + P_0') S'$$

$$+ P_0 S'' \quad . \qquad (B.17)$$

The replacement of Eqs. (B.13) and (B.15) into (B.17) yields

$$-S'' + \{ \frac{U'^2}{4} - \frac{U''}{2} \} S = \mu S. \qquad (B.18)$$

Eq. (B,13) is a Schrödinger-like equation corresponding to the Hamiltonian operator

$$H = p^2 + V \ , \ V(x) = \frac{1}{2} (U'^2 - 2U'') \qquad (B.19)$$

where S is the eigenfunction and μ its associated eigenvalue. Resorting to the potential (B.11), Eq. (B.19) gives the following potential

$$V(x) = (\frac{1}{4} Z^2 - \frac{3}{2}) x^2 + \frac{Z}{2} x^4 + \frac{1}{4} x^6 - \frac{Z}{2} \qquad (B.20)$$

Thus, in order to obtain the temporal phase μ of the probability density, it is necessary to know the eigenvalue spectrum corresponding to the anharmonic oscillator (B.20). The analysis of other diffusional potentials leads to other anharmonic vibrational potentials in (B.19) /16/.

APPENDIX C

EQUIVALENCE AMONG QUANTUM MECHANICAL ANHARMONIC OSCILLATORS AND FIELD THEORIES ϕ^N.

The relevance of anharmonic oscillators within the context of molecular vibrations and diffusional processes ruled by the Fokker-Planck equation was discussed in Appendix B. Such oscillators are also of interest regarding some simple field theories. The aim of this Appendix is to describe this latter connection. The approach to be followed is basically due to Bender and Wu /17/, although it will be discussed here in more detail.

The field theory under consideration is defined by the Hamiltonian

$$H = \frac{1}{2}\dot{\phi}^2 + \frac{1}{2}\phi^2 + \lambda\phi^4 \quad , \tag{C.1}$$

where ϕ is a 1D space-time scalar field and $\dot{\phi}$ its time-derivative. They satisfy the commutation rule:

$$[\phi,\dot{\phi}] = i \quad . \tag{C.2}$$

In order to deduce rigorously the coordinate and momentum representation of (C.1), we write ϕ in terms of creation and annihilation operators in the Fock space /18-20/:

$$\phi = (1/2)^{1/2}\ (ae^{-it} + a^+ e^{it}) \tag{C.3a}$$

$$\dot{\phi} = (1/2)^{1/2}\ (-iae^{-it} + ia^+e^{it}) \tag{C.3b}$$

where operators a and a^+ fulfil the commutation rule

$$[a,a^+] = 1. \tag{C.4}$$

The substitution of (C.3) into (C.1) yields for t = 0

$$H = (a^{+}a + 1/2) + \frac{\lambda}{4}\,(a+a^{+})^{4} \tag{C.5}$$

Let us consider an H-eigenstate $|E\rangle$ with eigenvalue E

$$H\,|E\rangle = E|E\rangle \tag{C.6}$$

function $|E\rangle$ may be written as a lineal combination of the complete set of eigenstates in the Fock space

$$|E\rangle = \sum_{n=0}^{\infty} A_n (n!)^{1/2}\,|n\rangle \tag{C.7}$$

where $|n\rangle$ is a state of the Fock space, given by

$$|n\rangle = (n!)^{-1/2}(a^{+})^{n}\,|0\rangle \quad , \tag{C.8a}$$

with

$$\langle n|m\rangle = \delta_{nm},\ a^{+}a|n\rangle = n|n\rangle \quad . \tag{C.3b}$$

The replacement of (C.7) into (C.6), together with the use of Eqs. (C.8), leads us to a recurrence for the coefficients A_n:

$$EA_n = (n+1/2)A_n + \frac{\lambda}{4}\{A_{n-4} + 4(n-2)\,A_{n-2} + 6n(n-1)A_n +$$

$$+ 4n(n+1)(n+2)A_{n+2} + (n+1)(n+2)(n+3)(n+4)A_{n+4}\} \quad . \tag{C.9}$$

On the other hand, coefficients A_n must fulfil the condition

$$\sum_{n=0}^{\infty} |A_n|^2 \, n! < \infty \quad , \tag{C.10}$$

so as to make $|E\rangle$ square integrable. In order to turn to the Schrödinger representation, we first determine a differential equation leading to the recurrence (C.9). Upon introducing of the generating function

$$f(z) = \sum_{n=0}^{\infty} A_n z^n, \tag{C.11}$$

it is easy to show that (C.9) is equivalent to the following equation

$$Ef(z) = \frac{1}{2} f(z) + z \frac{d}{dz} f(z) + \frac{\lambda}{4} \left(z+\frac{d}{dz}\right)^4 f(z) \ . \tag{C.12}$$

Making

$$f(z) = h(z) e^{-z^2/2} \tag{C.13}$$

and taking into account that

$$\left(z+\frac{d}{dz}\right) f(z) = h'(z) e^{-z^2/2} \tag{C.14}$$

Eq. (C.12) is transformed into:

$$Eh(z) = \frac{1}{2} h(z) + (zh'(z) - z^2 h(z)) + \frac{\lambda}{4} h''''(z) \tag{C.15}$$

Let us now introduce a Fourier transformation, so as to change the derivatives in (C.15) by coordinate powers. To define the Fourier transform it is necessary that $h(z) \to 0$ along the imaginary axis in the

complex plane. Thus, we resort to (C.11) and the Cauchy formula

$$A_n = \frac{1}{2\pi i} \oint_c \frac{h(z)}{z^{n+1}} e^{-z^2/2} dz \qquad (C.16)$$

Let us suppose h(z) does not tend to zero; without any loss of generality one can consider h(z) a constant. Then, the greatest contribution to (C.16) comes out of the imaginary axis

$$|A_n| \simeq \frac{1}{2\pi} \int_c \exp(z^2/2-(n+1)\ln z)dz \qquad (C.17)$$

Resorting to the saddle point method (Appendix D), one can get the dominant behavior of (C.17) when n>>1, i.e.

$$|A_n| \to \text{constant}.(n!)^{-1/2} n^{1/4} \qquad (C.18)$$

which does not satisfy the condition (C.10). Then, h(z) must be zero for z imaginary and $|z|>>1$. Accordingly, one can define without further difficulty the Fourier transform along the imaginary axis

$$h(z) = \int_{-\infty}^{+\infty} g(x)e^{xz}dx \quad , \qquad (C.19a)$$

so that

$$g(x) = \int_{-\infty}^{+\infty} h(z)e^{-xz}dz \; . \qquad (C.19b)$$

Eqs. (C.19) permit one to have

$$xg(x) = \int_{-\infty}^{+\infty} h'(z)e^{-xz}dz \quad , \qquad (C.20a)$$

which gives the following auxiliary result

$$-(g(x) + xg'(x)) = \int_{-\infty}^{+\infty} zh'(z)e^{-xz}dz \quad . \qquad (C.20b)$$

Likewise, (C.19) leads us to

$$x^4 g(x) = \int_{-\infty}^{+\infty} h''''(z)e^{-xz}dz \qquad (C.20c)$$

The calculation of transform (C.19b) in (C.15) and the use of relationships (C.20) give the equation

$$g''(x) + xg'(x) + (E+1/2)\, g(x) - \frac{\lambda}{4} x^4\, g(x) = 0 \qquad (C.21)$$

The definition

$$g(x) = e^{-x^2/4}\, \Psi(x) \quad , \qquad (C.22)$$

transforms Eq. (C.21) into the sought equation:

$$H\Psi(x) = E\Psi(x);\ H = p^2 + \frac{1}{4} x^2 + \frac{\lambda}{4} x^4;\ p = -i\frac{d}{dx} \quad . \qquad (C.23)$$

Eq. (C.23) suggests an asymptotic behavior like $\Psi(x) \to \exp(\pm|x|^3)$ when $|x| >> 1$. Eqs. (C.19a) and (C.22) require the choice of a behavior such that

$$\lim_{|x|\to\infty} \Psi(x) = 0 \quad , \qquad (C.24)$$

in order to be able to determine $h(z)$, and thereon the coefficients $\{A_n\}$ corresponding to the $|E>$ expansion in the Fock space. Eq.(C.23)

is the Schrödinger equation of a quartic anharmonic oscillator, whose eigenvalues E are the same as those associated with the field Hamiltonian (C.1). It is noteworthy that the eigenfunctions of both Hamiltonians (C.1) and (C.23) are related each other, and that the normalization condition of $|E\rangle$ leads in a natural way to the boundary conditions (C.24) for $\Psi(x)$.

The argument followed in this Appendix has the appeal to avoid the definition of an explicit formulation of the field ϕ and operators a_1 a^+ in terms of coordinates or/and momenta. The connection presented here plainly justifies the examination of the analytical and numerical properties of the Schrödinger equation for anharmonic oscillations. Some basic features of this simple, 1-D field theory model are supposed to be present also in more realistic theories.

APPENDIX D

CALCULATION OF INTEGRALS BY THE SADDLE-POINT METHOD

In several sections of this book it is necessary to compute integrals in an approximate way, determining the largest contribution to them. The suitable procedure to achieve this purpose is the so-called saddle-point method or steepest-descent method or Darwin-Fowler method. Due to our present needs, we restrict ourselves to discuss only functions depending upon one variable /21/.

Let $J(z)$ be a function of a complex variable z, expressed by the following path integral

$$J(z) = \int_C e^{zf(t)}\, dt, \qquad (D.1)$$

where $f(t)$ is a function of the complex variable t. If one wants to compute $J(z)$ when $|z| >> 1$, the result will not be very accurate (unless C is chosen in a very peculiar manner), since the integrand becomes oscillatory. In order to compute approximately the integral, it is necessary to find a region where $Re(zf(t))$ is maximum and, consequently, it provides the largest contribution to the integrand.

The largest contribution is related to the critical point

$$f'(t = t_o) = 0 \qquad (D.2)$$

which is a saddle point in the complex variable t/21/ when choosing the integration path C, we must note that: i) it must contain t_o, and ii) since t_o is a saddle-point, the integral divergence is avoided when taking the steepest-descent from t_o, i.e. the direction where t_o is a maximum.

By expanding $f(t)$ up to the second-order about t_o

$$f(t) \simeq f(t_o) + \frac{1}{2} f''(t_o) (t-t_o)^2 , \qquad (D.3)$$

J(z) is approximated as

$$J(z) \simeq e^{zf(t_o)} \int_C e^{zf''(t_o) (t-t_o)^2/2} dt. \qquad (D.4)$$

The approximation (D.4) is better when $|z|$ is the largest. In order to introduce the steepest descent approximation, we introduce first the following change of variables:

$$Zz''(t_o) (t-t_o)^2 = -|z|s^2, \; z = |z|e^{i\phi} , \qquad (D.5a)$$

so that

$$s = \{e^{i(\pi+\phi)} f''(t_o)\}^{1/2} (t-t_o) . \qquad (D.5b)$$

$$J(z) \simeq \{e^{i(\pi+\phi)} f''(t_o)\}^{-1/2} e^{zf(t_o)} \int_C e^{-|z|s^2/2} ds. \qquad (D.6)$$

when $|x| \to \infty$, the greatest contribution to the integral comes from $s \to 0$ ($t \to t_o$). Thus, we can consider s as a real variable, to distort the path C and integrate between $-\infty < s < \infty$, without any modification of the result. Therefore, Eq. (D.6) turns into

$$J(z) \simeq \{e^{i(\pi+\phi)} f''(t_o)\}^{-1/2} e^{zf(t_o)} \int_{-\infty}^{+\infty} e^{-|z|s^2/2} ds =$$

$$= \{ze^{i\pi} f''(t_o)\}^{-1/2} e^{zf(t_o)} (2\pi)^{1/2} . \qquad (D.7)$$

Expression (D.7) represents the dominant term of an asymptotic series to obtain the other terms we must take into account the fluctuations of f(t) around the saddle-point t_o. In order to get such fluctuations f(t) may be written as

$$f(t) = f(t_o) - w(t)^2 \tag{D.8}$$

to have an integral in the variable w. In order to obtain this change, we make

$$dt = \left(\frac{\partial t}{\partial w}\right) dw; \quad \left(\frac{\partial t}{\partial w}\right) = \sum_{i=0}^{\infty} a_i w^i \tag{D.9}$$

and replace (D.8) and (D.9) into Eq. (D.7)

$$J(z) \simeq e^{zf(t_o)} \sum_{i=0}^{\infty} a_i \int_{-\infty}^{+\infty} w^i e^{-zw^2} dw =$$

$$= (a_0^2/z)^{1/2} e^{zf(t_o)} \sum_{i=0}^{\infty} (a_{2i}/a_0)\Gamma(i+1/2) z^{-i}, \tag{D.10}$$

where $\Gamma(x)$ is the gamma function.

If only remains to determine the set of coefficients $\{a_i\}$, which must done for each function f(t). In what follows, we present a simple illustrative example /21/.

Example: Let us consider the gamma function defined as

$$\Gamma(z+1) = \int_0^{\infty} e^{-x} x^z dx = z^{z+1} \int_0^{\infty} e^{-tz} t^z \, dt \quad . \tag{D.11}$$

To determine the asymptotic behavior of $\Gamma(z+1)$ when $|z| \to \infty$, we apply the procedure given before. Thus,

$$\Gamma(z+1) = z^{z+1} \, J(z) \quad , \tag{D.12a}$$

where

$$J(z) = \int_0^\infty e^{z(\ln t - t)} dt = \int_C e^{zf(t)}\, dt. \tag{D.12b}$$

The extreme of f(t)

$$f'(t) = \frac{1}{t} - 1, \quad t_o = 1 \tag{D.13}$$

allows us to obtain the most important contribution to the integrand

$$f(t_o) = -1 \tag{D.14}$$

In order to get the coefficients $\{a_i\}$, we resort to Eq. (D.3)

$$w = (t - 1 - \ln t)^{1/2} \tag{D.15}$$

One can write w as a Taylor series about $t_o = 1$, and the necessary auxiliary results up to the third order are

$$w(1) = 0 \tag{D.16a}$$

$$w'(t) = \frac{1}{2t}\{(t-1-\ln t)/(t-1)^2\}^{-1/2}, \quad \lim_{t\to 1} w'(t) = 2^{-1/2} \tag{D.16b}$$

$$w''(t) = -\frac{1}{2t^2}\{(t-1-\ln t)/(t-1)^2\}^{-1/2} -$$

$$- \frac{1}{4t}\{(t-1-\ln t)/(t-1)^2\}^{-3/2} \left|\frac{(t-1)^2/t - 2(t-1-\ln t)}{(t-1)^3}\right|$$

$$\lim_{t\to 1} w''(t) = -\frac{2^{1/2}}{3} \qquad \text{(D.16c)}$$

$$w'''(t) = \frac{1}{t^3}\{(t-1)-\ln t)/(t-1)^2\}^{-1/2}$$

$$+ \frac{1}{2t^2}\{(t-1-\ln t)/(t-1)^2\}^{-3/2}\{\frac{(t-1)^2/t-2(t-1-\ln t)}{(t-1)^2}\}$$

$$+ \frac{3}{8t}\{(t-1-\ln t)/(t-1)^2\}^{-5/2}\{\frac{(t-1)^2/t-2(t-1-\ln t)}{(t-1)^3}\}^2$$

$$- \frac{1}{4t}\{(t-1-\ln t)/(t-1)^2\}^{-3/2}$$

$$x\{\frac{-(t-1)^3/t^2 - 3\{(t-1)^2/t-2(t-1-\ln t)\}}{(t-1)^4}\}$$

$$\lim_{t\to 1} w'''(t) = 7\sqrt{2}/12 \qquad \text{(D.16d)}$$

The final result is

$$w(t) \simeq 2^{-1/2}(t-1) - \frac{2^{1/2}}{6}(t-1)^2 + \frac{7\left(2^{1/2}\right)}{72}(t-1)^3 \quad . \qquad \text{(D.17)}$$

The inversion of Eq. (D.17) through succesive iterations permits us to express (t-1) in w-power series

$$(t-1) \simeq 2^{1/2} w + \frac{2}{3} w^2 + \frac{2^{1/2}}{18} w^3 \quad . \qquad \text{(D.18)}$$

Eq.(D.9) gives the first two coefficients which are necessary to ob-

tain the term proportional to 1/z in the sum of Eq. (D.10), i.e.

$$a_o = 2^{1/2};\ a_2 = 2^{1/2}/6 \tag{D.19}$$

The substitution of Eqs.(D.19) and (D.14) in Eq.(D.10) and resorting to Eq. (D.12a), gives us the desired result

$$\Gamma(z+1) = z! \simeq (2\pi z)^{1/2}\left(\frac{z}{e}\right)^{z}\left\{1+\frac{1}{12z} + O(z^{-2})\right\} \tag{D.20}$$

The dominant term when $|z|\to\infty$ in Eq.(D.20) is the so-called Stirling approximation.

APPENDIX E

CONSTRUCTION OF PADÉ APPROXIMANTS

The aim of this Appendix is to display a simple algorithm to construct rational functions or Padé approximants. These approximants have been widely used to extend analytically the Taylor expansions beyond their convergence radii. Therefore, they have been employed to obtain satisfactory results for several physical properties from the knowledge of divergent or slowly convergent perturbative expansions.

Here we restrict ourselves to a brief presentation of the results akin to our purposes. The interested reader may refer to the bibliography given in Refs./22-25/.

Let us consider an N+M degree polynomial F(x), which may correspond, for example, to a truncated Taylor expansion

$$F(x) = \sum_{n=0}^{N+M} F_n x^n \quad . \tag{E.1}$$

The Padé Approximant |M/N| is defined via the rational function $P^{(M)}/Q^{(N)}$, such that

$$F(x) - \frac{P^{(M)}(x)}{Q^{(N)}(x)} = O(x^{M+N+1}) \quad , \tag{E.2}$$

where $P^{(M)}(x)$ and $Q^{(N)}(x)$ are two polynomials of degree M and N, respectively:

$$P^{(M)}(x) = \sum_{n=0}^{M} P_n x^n \quad , \tag{E.3a}$$

$$Q^{(N)}(x) = \sum_{n=0}^{N} Q_n x^n \quad . \tag{E.3b}$$

The meaning of the formal identity (E.2) lies in the fact the approximant $|M/N|$ gives rise to an x-power series expansion whose coefficients are coincident with the F_n ones up to the (N+M)-order.

Coefficients $\{P_n\}$ and $\{Q_n\}$ may be obtained from $\{F_n\}$ in a very simple way. Multiplying (E.2) by $Q^{(N)}(x)$ we have the result

$$C(x) = Q^{(N)}(x)F(x) = \sum_{s=0}^{\infty} C_s x^s = P^{(M)}(x)+O(x^{N+M+1}), \quad (E.4a)$$

where

$$C_s = \sum_{n=0}^{s} Q_n F_{s-n}; \; Q_n = 0 \text{ when } n \geq M+1 \quad . \quad (E.4b)$$

The identification of coefficients in (E.4a) yields

$$\sum_{n=0}^{s} Q_n F_{s-n} = P_s \; , \; 0 \leq s \leq N \quad , \quad (E.5a)$$

$$\sum_{n=0}^{s} Q_n F_{s-n} = 0 \; , \quad N+1 \leq s \leq N+M \quad (E.5b)$$

Eqs.(E.5) show that it is necessary to know the N+M coefficients F_n to accomplish the calculation of polynomials $p^{(M)}$ and $Q^{(N)}$. The procedure starts from solving the system of algebraic equations (E.5b), by choosing, for example, $Q_o = 1$. Then, the obtained coefficients are employed to solve (E.5a).

The computation of $|M/N|$ approximants can also be made in a recursive manner, by means of the Wynn identity /23/. Moreover, the construction and study of rational functions can be performed through a different standpoint, within the context of the Theory of continued fractions /26/.

A brief account on the convergence properties of Padé approximants and their applications is presented in §.13.

APPENDIX F

NORMAL ORDERING OF OPERATORS

This Appendix is devoted to study the normal ordering of operators and its ulterior application to the Hamiltonian rearrangements known as "Wick-ordering". The results to be shown will allow us to discuss the connection between such Hamiltonian rearrangement and the methods of summation of perturbation series /27/.

Let us consider the field theory model defined through the following Hamiltonian H

$$H(m^2,\lambda) = \frac{1}{2}\dot{\phi}^2 + \frac{1}{2} m^2 \phi^2 + \lambda\phi^{2N} \quad , m^2 > 0 \tag{F.1}$$

and the commutation relationship

$$[\phi,\dot{\phi}] = i \tag{F.2}$$

where ϕ is the time-space field and $\dot{\phi}$ its temporal derivative.

In Appendix C, we proved that (F.1) and (F.2) are equivalent to a 2N-anharmonic oscillator quantum-mechanical Hamiltonian, defined upon wavefunctions fulfilling trivial BC.

Let us consider an effective (or renormalized) mass M, whose role will be evident in the following, and write the field in terms of creation and annihilation operators /18/ like (Eqs.(C.3)):

$$\phi = (2M)^{-1/2} \{a e^{-iMt} + a^+ e^{iMt}\} \quad , \tag{F.3a}$$

$$\dot{\phi} = -i(M/2)^{1/2} \{a e^{-iMt} - a^+ e^{iMt}\} \quad , \tag{F.3b}$$

where

$$[a,a^{+}] = 1 \quad . \tag{F.4}$$

Let: ϕ^{N}: denote the field ϕ^{N} ordered in a normal way, i.e. with all the creation operators (a^{+}) placed at the left of the annihilation ones (a). From now on, we consider the case t = 0. Thus, $:\phi^{N}:$ is expressed by the so-called Newton binomial operator /28/:

$$:\phi^{N}: = (2M)^{-N/2} \sum_{n=0}^{N} \binom{N}{n} a^{+n} a^{N-n} \quad . \tag{F.5}$$

Analogously, the field operator ϕ^{N} normally ordered is given by

$$:\dot{\phi}: = (-i)^{N}(M/2)^{N/2} \sum_{n=0}^{N} \binom{N}{n} (-a^{+})^{n} a^{N-n} \quad . \tag{F.6}$$

Therefore, we can define the Hamiltonian in its normal ordering :H: like that operator with all its components normally ordered, viz

$$:H(M^{2},\lambda): = \frac{1}{2}:\dot{\phi}^{2}: + \frac{1}{2} M^{2}:\phi^{2}: + \lambda:\phi^{2N}: \tag{F.7}$$

where M plays the role of the original mass m (Eq.(F.1)). In order to have the connection between M and m it is necessary to find the relation between H and :H:. Then, we resort to Eqs. (F.5) and (F.4) to arrive at

$$\dot{\phi}^{2} = -\frac{M}{2}(a^{2}-a^{+}a-aa^{+}+a^{+2}) = -\frac{M}{2}(a^{2}-2a^{+}a+a^{+2}) + \frac{M}{2} =$$

$$= :\dot{\phi}^{2}: + \frac{M}{2} \quad . \tag{F.3}$$

In a similar manner, we obtain

$$\phi^2 = :\phi^2: + \frac{1}{2M} \quad . \tag{F.9}$$

Eqs. (F.8) and (F.9) permit us to relate H and :H: when $\lambda=0$:

$$:H(M^2,0): = \frac{1}{2} :\phi^2: + \frac{1}{2} M^2 :\phi^2: = \frac{1}{2} \phi^2 + \frac{1}{2} M^2 \phi^2 - \frac{M}{2} \quad , \tag{F.10}$$

that is,

$$H\ (m^2,0) = :H(M^2,0): + \frac{M}{2} \quad , \tag{F.11}$$

iff

$$\lim_{\lambda \to 0} M = m \quad . \tag{F.12}$$

The consideration of the normal ordering for the complete Hamiltonian ($\lambda \neq 0$) is more complex. Let us consider the field theory $\lambda\phi^4$ (N=2) Eq.(F.3a) leads us to the result

$$\begin{aligned} \phi^4 = (4M^2)^{-1} \{ & a^4 + 2a^2a^+a + 2a^+a^3 + 4a^+aa^+a + a^{+4} + a^2a^{+2} \\ & + 2a^+aa^{+2} + a^{+2}a^2 + 2a^{+3}a \} + (2M^2)^{-1} \{a^2 + 2a^+a + a^{+2}\} \\ & + (4M^2)^{-1} \quad , \end{aligned} \tag{F.13}$$

which must be rearranged to attain the field $:\phi^4:$. Eq. (F.4) allows us to obtain at once the following results:

$$a^2a^{+2} = a^{+2}a^2 + 4a^+a + 2 \quad , \tag{F.14a}$$

$$a^2a^+a = a^+a^3 + 2a^2 \quad , \tag{F.14b}$$

$$a^+aa^+a = a^{+2}a^2 + a^+a \quad , \tag{F.14c}$$

$$a^+aa^{+2} = a^{+3}a + 2a^{+2} \quad . \tag{F.14d}$$

The substitution (F.14) in (F.13) and the employment of Eq.(F.5) yields the desired result

$$:\phi^4: = \phi^4 - \frac{3}{M}\phi^2 + \frac{3}{4M^2} \quad . \tag{F.15}$$

Eqs. (F.7), (F.10) and (F.15) permits us to find the operator :H:,

$$:H(M^2,\lambda): = \frac{1}{2}\phi^2 + \frac{1}{2}M^2\phi^2 + \lambda\phi^4 - \frac{3\lambda}{M}\phi^2 + \frac{3\lambda}{4M^2} - \frac{M}{2} \; . \tag{F.16}$$

Notice that $:\phi^4:$ (Eq.(E.15)) contains contributions of ϕ^4 and ϕ^2, and that these last terms were already present in the original Hamiltonian H. This fact allows us to define the effective mass M such that H and :H: only differ in a constant. Thus, we can write from Eq. (F.16):

$$:H(M^2,\lambda): = H(m^2,\lambda) + \frac{3\lambda}{4M^2} - \frac{M}{2} \quad , \tag{F.17}$$

where

$$\frac{m^2}{2} = \frac{M^2}{2} - \frac{3\lambda}{M} \quad . \tag{F.18}$$

Eq.(F.18) determines the M-value for every pair of m and λ values. Eq.(F.17) gives a direct relation between eigenvalues E and $\bar{E}$ corresponding to the quantum Hamiltonian H and :H: associated with the field Hamiltonians H and :H:, respectively (Appendix C):

$$E(m^2,\lambda) = \bar{E}(M^2,\lambda) + \frac{M}{2} - \frac{3\lambda}{4M^2} \quad . \tag{F.19}$$

The simple relationship (F.19) provides a basis to the construction of a renormalized perturbation series. The method consists of approximating the better-behaved function $\bar{E}(M^2,\lambda)$, and then to retrieve the original function $E(m^2,\lambda)$. /27/

On the other hand, one cannot define an effective mass M as done in Eq.(F.18) if the field theory has other interaction than ϕ^4, unless several, quite restrictive conditions are satisfied. For example, the interaction $\lambda\phi^6$ (N=3 in Eq.(F.1)) requires the computation of $:\phi^6:$ to construct :H:. The preceding procedure yields /29/.

$$:\phi^6: = \phi^6 - \frac{15}{2M}\phi^4 + \frac{45}{4M^2}\phi^2 - \frac{15}{8M^3} \tag{F.20}$$

and it introduces a term ϕ^4 which is not present in the original Hamiltonian. Then H and :H: do not differ in a constant, so that it is no longer possible to renormalize the RSPT from the normal ordering theory. In this case it is necessary to resort to a different procedure (see §.17).

APPENDIX G

APPLICATIONS OF MODELS WITH CONFINING POTENTIALS.

The purpose of this Appendix is to give a brief overview on models with confining potentials. Such potentials are used as examples of application several times in this book, to illustrate different computational methods.

Confining potentials possess an special relevance in elementary particle Physics. In 1974 some very intense bosonic transitions (J/Ψ) produced by matter-antimatter annihilation in large accelerators were discovered. These transitions were interpreted by means of the so-called charmonium model /30-33/, which basically is a bounded system between the charm quark-antiquark pair ($c\bar{c}$). The bound states of this system are similar to those in positronium, and are related with the bosonic resonances found experimentally.

The interaction among quarks is not completely known yet from first principles (field theory). However, the basic components must be an attractive, singular term at very small distances (gluonic exchange term), and another, confining term for large enough distances. This last term takes into account the experimental fact that quarks have not been observed as free components. Although some simple relativistic models have been applied to obtain the charmonium bound states /34/, the most used, phenomenological potentials are those like /30-33,35-39/

$$V = -\frac{Z}{r} + \lambda r^K, \quad K>0 \ , \ Z,\lambda>0 \quad . \tag{G.1}$$

The potential (G.1) can be seen as a non-relativistic limit of the quark-antiquark interaction, and reduces the high-energy spectrum problem to the following eigenvalue equation

$$H(Z,\lambda)\,\Psi_{n\ell} = E_{n\ell}(Z,\lambda)\,\Psi_{n\ell}, \quad \Psi_{n\ell}(r\to\infty) = 0 \quad , \tag{G.2a}$$

where

$$H(Z,\lambda) = -\frac{1}{2\mu}\Delta - \frac{Z}{r} + \lambda r^K, \quad \Delta = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\ell(\ell+1)}{r^2}, \qquad (G.2b)$$

which μ the charmonium reduced mass. It is necessary to point out that the preceding potential is not a realistic representation of the physical interaction but a qualitative phenomenological description of the standing out experimental features. Among these properties one can mention the level ordering, the relative gap among them, the dependence of the energy (and the square of the wavefunction at the origin) upon the particle mass, etc. Several thorough studies /40-45/ have allowed one to construct a successful charmonium model with the potential (G.1), giving strength to the non-relativistic phenomenological approach. The model is even better for the b quark (bottom) pair, much havier. As a model for generic quark-antiquark pairs, potential (G.1) is known as a quark potential.

Even though potentials like (G.1) are the most employed, they are not the only ones capable of reproducing some experimental features, such as the ordering /35,41,42/:

$$E_{n\ell}(Z,\lambda) < E_{n\ell'}(Z,\lambda), \text{ when } \ell > \ell' \quad . \qquad (G.3)$$

Another potential used in this field is the so-called logarithmic confining potential /36,38/:

$$V = -\frac{Z}{r} + g \ln(1 + \lambda r), \quad g > 0 \; . \qquad (G.4)$$

The confining potential most widely cited in the current literature is the linear confining potential, defined by K = 1 in Eq. (G.1) /33, 35/:

$$H(Z,\lambda) = \frac{1}{2\mu} p^2 - \frac{Z}{r} + \lambda r \quad . \qquad (G.5)$$

The eigenvalues $E_{n\ell}(Z,\lambda)$ associated with $H(Z,\lambda)$ have been obtained by numerical integration of the Schrödinger equation for some λ-values ($\lambda>1$). The good agreement obtained via the model (G.5) for other properties related to the energy and wave function /35/ has made it the best and simplest approximation to the quarkonium.

The model has been the subject of several examinations within the context of approximate variational and perturbational methods. Throughout this work the model is presented several times as an illustrative example in perturbation theory and semiclassical methods.

Other confining models have been proposed with $K \simeq 0.1$ /38/, $K = 2$ /36,44/, $K \simeq 0.5$ /39,46/. The reader interested in this topic is refered to Ref. /47/, where other important properties contained in the quark theories and their phenomenological potentials are discussed at length.

Model (G.5) has also been employed in relation to the radial Stark effect /48-50/, with $\lambda<0$. In this case, the spectrum consists of resonances embedded in the continum, the same as in the normal Stark effect. Since the potential function in (G.5) depends only upon one variable, it possess a computationally simpler problem than the normal Stark effect. This latter property has made the model (G.5), with $\lambda<0$, a suitable tool for simulation studies of resonances.

APPENDIX H

HAMILTONIAN OF AN HYDROGEN ATOM IN A MAGNETIC FIELD.

The eigenvalues associated with the Hamiltonian of an hydrogen atom in a magnetic field (Zeeman effect) are considered in several chapters of this book. The aim of this Appendix is to construct the Hamiltonian describing the Zeeman effect and discuss some of its elementary properties.

According to the classical electrodynamics, the Hamilton function corresponding to a particle with electric charge $q = -e$ and mass m, subjected to a magnetic field, is /51/

$$H = \frac{1}{2m} \left(\bar{p} + \frac{e}{c} \bar{A}\right)^2 + e\phi \qquad (H.1)$$

where $\bar{A}$ and ϕ are the vector and scalar potentials, respectively. $\bar{A}$ is related with the magnetic induction vector $\bar{B}$ as

$$\bar{B} = \text{cur}\ell\ \bar{A} \quad , \qquad (H.2a)$$

i.e.,

$$\bar{A} = \frac{1}{2} (\bar{B} \times \bar{r}) \quad . \qquad (H.2b)$$

In order to obtain the Hamiltonian operator from (H.1), we make the change $\bar{p} \rightarrow -i\hbar\nabla$, so that

$$H_c = -\frac{\hbar^2}{2m} \Delta - \frac{ie\hbar}{mc} \bar{A}.\nabla - \frac{ie\hbar}{2mc} \nabla.\bar{A} + \frac{e^2}{2mc^2} A^2 + e\phi \ , \qquad (H.3)$$

with Δ the Laplacian and $A = ||\bar{A}||$. For the sake of simplicity, we

choose the field such that $\text{div}\bar{A} = \phi = 0$. To attain a simpler expression for (H.3), we resort to the following auxiliary relation (which results from (H.2b)):

$$- \frac{ie\hbar}{mc} \bar{A}.\nabla + \frac{e^2}{2mc^2} A^2 = \frac{e}{2mc} (\bar{B} \times \bar{r}).\bar{p} + \frac{e^2}{8mc^2} (\bar{B}x\bar{r}).(\bar{B}x\bar{r}) =$$

$$= \frac{e}{2mc} \bar{B}.\bar{L} + \frac{e^2}{8mc^2} B^2 r^2 \sin^2\theta \qquad (H.4)$$

where $\bar{L} = \bar{r}x\bar{p}$, $B = ||\bar{B}||$ and θ is the angle between vectors $\bar{r}$ and $\bar{B}$. The replacement of (H.4) into (H.3), and the condition $\text{div}\,\bar{A} = \phi = 0$, yields

$$H_c = - \frac{\hbar^2}{2m} \Delta + \frac{e^2}{2mc} \bar{B}.\bar{L} + \frac{e^2}{8mc^2} B^2 r^2 \sin^2\theta \quad . \qquad (H.5)$$

In case the particle has in addition an intrinsic spin angular momentum, there also exists a magnetic momentum μ_s aligned with the spin vector $\bar{S}$. This magnetic momentum is /52,53/:

$$\mu_s = - \frac{e}{2mc} g_s \bar{S} \qquad (H.6)$$

where $g_s \simeq 2$ is the so-called spin "g" fector /52,53/. The magnetic momentum (H.6) introduces an additional contribution to the energy given by $- \mu_s.\bar{B}$. Then, (H.5) changes into:

$$H_c = - \frac{\hbar^2}{2m} \Delta + \frac{e}{2mc} (\bar{B}.\bar{L} + g_s \bar{B}.\bar{S}) + \frac{e^2}{8mc^2} B^2 r^2 \sin^2\theta . \qquad (H.7)$$

The choice of $\bar{B}$ as a homogeneous field along the z-axis direction

$$\bar{B} = (0,0,B) \quad , \qquad (H.8)$$

gives for (H.7)

$$H_c = -\frac{\hbar^2}{2m}\Delta + \frac{eB}{2mc}(L_z+g_s S_z) + \frac{e^2}{8mc^2}B^2(x^2+y^2), \qquad (H.9)$$

where L_z and S_z are the z-components of the angular momenta $\bar{L}$ and $\bar{S}$, respectively /54/.

Since

$$|H_c, L_z| = |H_c, S_z| = 0 \qquad (H.10)$$

the operators L_z and S_z are associated with constants of motion and their eigenvalues provide good quantum numbers to label the states of the system. Then, L_z and S_z furnish and additive contribution to the eigenvalues of the operator

$$H_c' = -\frac{\hbar^2}{2m}\Delta + \frac{e^2}{8mc^2}B^2(x^2+y^2), \qquad (H.11a)$$

where

$$H_c = H_c' + \frac{eB}{2mc}(L_z+g_s S_z) \quad . \qquad (H.11b)$$

Introducing a dilatation in the Cartesian coordinates by means of a factor α (see Appendix A)):

$$H_c' = \frac{\hbar^2\alpha^{-2}}{m}\left\{-\frac{\Delta}{2} + \frac{B^2e^2\alpha^4}{8c^2\hbar^2}(x^2+y^2)\right\}, \qquad (H.12a)$$

and choosing $\alpha = (e/c\hbar)^{-1/2}$, we get the following unitary equivalence:

$$H_c' = \frac{e\hbar}{mc}\left\{-\frac{\Delta}{2} + \frac{B^2}{8}(x^2+y^2)\right\} = \left(\frac{e\hbar}{mc}\right)h_c' \quad . \qquad (H.12b)$$

The dimensionless operator h_c' describes a particle moving freely along the z-axis under the influence of a harmonic potential in the x-y plane. The corresponding Schrödinger equation is

$$(h_c' + \frac{1}{2}\frac{\partial^2}{\partial z^2})\ \Psi_{n_x,n_y}(x,y) = (n_x+n_y+1)(\frac{B}{2})\Psi_{n_x,n_y}(x,y), \quad (H.13)$$

where the Landau quantum number

$$N = n_x + n_y \quad , \quad (H.14)$$

labels the eigenvalues associated with the 2D oscillator. Eqs.(H.12)-(H.14) lead us to the desired eigenvalues of the original Hamiltonian H_c

$$E = (N+m+g_s m_s+1)\ (\frac{e\hbar}{mc})\ \frac{B}{2} + \frac{1}{2m}\ p_z^2 \quad , \quad (H.15)$$

where $m = 0, \pm 1, \pm 2, \ldots$ and $m_s = \pm 1/2$ (for an electron) are the magnetic and spin quantum numbers, respectively, and $p_z = \hbar K (-\infty < K < \infty)$.

Our interest is to examine the spectrum of the hydrogen like atom in a magnetic field. To this end, it is only necessary to add the interaction between the electron with the nucleus of charge Ze in the Hamiltonian H_c. Obviously, the two body problem requires the change of mass m by the reduced mass μ, although for the sake of simplicity we take $\mu \simeq m$. Therefore, the Hamiltonian may be written as

$$H_c = H_D + H_p \quad , \quad (H.16a)$$

$$H_D = -\frac{\hbar^2}{2m}\Delta - \frac{Ze^2}{r} + \frac{e^2B^2}{8mc^2}(x^2+y^2) \quad , \quad (H.16b)$$

$$H_p = \frac{eB}{2mc}(L_z + g_s S_z) \quad , \quad (H.16c)$$

where H_D and H_p describe the diamagnetic and paramagnetic parts of H_c, respectively. H_D is the most significant part of the operator, since the eigenvalues and eigenfunctions of H_p are known and besides $|H_p, H_D| = 0$.

Upon scaling the diamagnetic term H_D:

$$H_D = \frac{\hbar^2\alpha^{-2}}{m}\{-\frac{\Delta}{2} - \frac{e^2m\alpha}{\hbar^2}\frac{Z}{r} + \frac{\alpha^4e^2B^2}{\hbar^2c^2 8}(x^2+y^2)\}, \qquad (H.17)$$

and choosing the factor α appropriately:

$$H_D = (me^4\hbar^{-2})\, H(Z,\lambda) \quad , \qquad (H.18a)$$

$$H(Z,\lambda) = -\frac{\Delta}{2} - \frac{Z}{r} + \frac{\lambda^2}{8}(x^2+y^2) \quad , \qquad (H.18b)$$

$$\lambda = B/B_o \ , \ B_o = m^2e^3c\hbar^{-3} = 2.35 \times 10^9 \text{ gauss} = 2.35\times10^5 \text{ tesla}$$

$$1 \text{ T(tesla)} = 100 \text{ weber/m}^2 \quad . \qquad (H.18c)$$

The dimensionless Hamiltonian $H(Z,\lambda)$ will be the subject of study in this work. The atomic units of energy and field are $me^4\hbar^{-2}$ (hartree) and B_o, respectively.

In closing this Appendix, we show the scaling laws satisfied by $H(Z,\lambda)$. Following Appendix A we get:

$$H(Z,\lambda) = a^{-2}(-\frac{\Delta}{2} - \frac{Za}{r} + \frac{\lambda^2}{8}a^4(x^2+y^2)). \qquad (H.19)$$

The choice $a = Z^{-1}$ gives the following unitary equivalence:

$$H(Z,\lambda) \simeq Z^2H(1,\lambda Z^{-2}) \qquad (H.20)$$

and, on the other hand, the selection $a = \lambda^{-1/2}$ yields

$$H(Z,\lambda) \simeq \lambda H(Z\lambda^{-1/2},1) \qquad (H.21)$$

Relationships (H.20) and (H.21) are equivalent to each other, and are employed often in this book.

APPENDIX I

ASYMPTOTIC BEHAVIOR OF THE BINDING ENERGY FOR THE ZEEMAN EFFECT IN THE HYDROGEN ATOM.

In the preceding Appendix we have obtained the Hamiltonian operator associated with the Zeeman effect in hydrogen, in the non-relativistic approximation. We want to discuss here the behavior of the energy when $\lambda >> 1$, since it is used in several paragraphs of this book.

The asymptotic behavior of eigenvalues for the Zeeman effect in strong fields has deserved a great deal of attention /55-67/. In this Appendix we restrict ourselves to expose a summary of those aspects akin to our interest and adapted to our needs.

Let $H(Z,\lambda)$ be the Hamiltonian describing the Zeeman effect in hydrogen-like atoms, leaving the magnetic and spin parts out (notation as in Appendix H):

$$H(Z,\lambda) = -\frac{\Delta}{2} + \frac{\lambda^2}{8}\rho^2 = \frac{Z}{r} \; ; \; \rho^2 = r^2 - z^2 \qquad (I.1a)$$

$$\Delta = \Delta_\rho + \Delta_z, \; \Delta_z = \partial^2/\partial z^2 \; , \Delta = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{L^2}{r^2} \qquad (I.1b)$$

where Z is the nuclear charge and L the angular momentum operator in units of $\hbar$. If $\Psi(\rho,z)$ is an eigenfunction of $H(Z,\lambda)$, the adiabatic approximation /55/ allows us the approximate separation

$$\Psi(\rho,z) = \Psi_N(\rho)\; f(z) \qquad (I.2)$$

such that $\Psi_N(\rho)$ is a Landau orbital, viz.

$$\langle \Psi_N | -\frac{1}{2}\Delta + \frac{1}{2}\rho^2 | \; \Psi_N \rangle = (N+1) \qquad (I.3)$$

The number $N - n_x + n_y$ is the Landau quantum number, and it depends on the magnetic quantum number m. The adiabatic approximation is asymptotically correct for $\lambda >> 1$.

In order to write a differential equation for f(z), it is convenient to rearrange the Hamiltonian. By resorting to the scaling law introduced in Appendix H, we get

$$H(1,\lambda) = \frac{\lambda h}{4} \tag{I.4a}$$

$$h = - \Delta + \rho^2 - (\frac{8}{\lambda})^{1/2} r^{-1} \quad , \tag{I.4b}$$

where, without any loss of generality, we have chosen Z=1. Next, (I.2) -(I.4) allow us to obtain the desired equation

$$\langle \Psi_N | H(1,\lambda) | \Psi_N \rangle \, f = E_m(1,\lambda) \, f, \tag{I.5a}$$

where

$$\langle \Psi_N | H(1,\lambda) | \Psi_N \rangle = \frac{\lambda}{4} \langle \Psi_N | h \Psi_N \rangle = \frac{\lambda}{4} \{ h_z^{(N)} + 2(N+1) \} \tag{I.5b}$$

and the operator $h_z^{(N)}$ depends only on z

$$h_z^{(N)} = - \Delta_z - (\frac{8}{\lambda})^{1/2} \langle \Psi_N | r^{-1} | \Psi_N \rangle \quad . \tag{I.5c}$$

The substitution of (I.5c) and (I.5b) into (I.5a) yields the differential equation for f:

$$\frac{\lambda}{4} h_z^{(N)} \, f = - \varepsilon_m \, f \quad , \tag{I.6}$$

where $\varepsilon_m > 0$ is the so-called binding energy of the state under consideration:

$$\varepsilon_m = \frac{N+1}{2}\,\lambda - E_m(1,\lambda) \quad . \tag{I.7}$$

The most interesting states are the tight-bound ones, for which ε_m is a monotonously increasing function of λ. These states are given by /67/:

$$-m = \ell = N \tag{I.8}$$

where ℓ is the azimuthal quantum number. This is the suitable number to describe all the properties of the tight-bound states, i.e.,

$$\frac{\lambda}{4}\, h_z^{(\ell)}\, f(z) = -\,\varepsilon_\ell\, f(z) \quad . \tag{I.9}$$

To obtain the asymptotic form of ε_ℓ as a function of λ, we have to know the explicit dependence of $h_z^{(\ell)}$ with z. Avron et al./66,67/ have proved the following result, which makes up our starting point:

$$\langle \Psi_\ell | \frac{1}{r} | \Psi_\ell \rangle = V_\ell(z) = \frac{1}{\ell!} \int_0^\infty (t^2+z^2)^{-1/2}\, e^{-t}\, t^\ell dt \tag{I.10}$$

Eq. (I.10) leads us, as a limit case to the potential in the Schiff and Snyder Hamiltonian /55/:

$$V_\ell(z) \to \frac{1}{|z|} \quad \text{if} \quad z^2 >> 1 \quad . \tag{I.11}$$

Finally, Eqs. (I.10), (I.5c) and (I.9) permit us to write the following eigenvalue equation for ε_ℓ:

$$\frac{\lambda}{4}\{-\Delta_z-(\frac{8}{\lambda})^{1/2}V_\ell(z)\}\,f(z) = -\varepsilon_\ell\, f(z) \quad . \qquad (I.12)$$

In order to have a general idea on the structure of ε_ℓ as a function of λ, we must take into account the following theorem /67/, which is stated for the sake of completeness:

Theorem I.1: The eigenvalues of Eq.(I.12) are bounded from above by $\tilde{\varepsilon}_o$, which is the lowest eigenvalue of

$$\frac{\lambda}{4}\{-\Delta_z-(\frac{8}{\lambda})^{1/2}\frac{1}{(|z|+\sqrt{\ell+1})}\}f_n(z) = \tilde{\varepsilon}_n\, f_n(z)$$

$$\tilde{\varepsilon}_o > -\varepsilon_\ell \; . \; * \qquad (I.13)$$

Eigenvalues $\tilde{\varepsilon}_n$ were studied by Loudon /56/, van Haeringen /62/ and Gesztesy /63/. Our present interest is restricted to examine the asymptotic behavior of eigenvalues when $\lambda\to\infty$. From Ref./63/ it follows that for

$$\{-\Delta_z-\frac{c}{|z|+\alpha}\}\,f_n(z) = \tilde{\varepsilon}'_n\, f_n(z) \quad , \qquad (I.14a)$$

then

$$\tilde{\varepsilon}'_o \to -c^2\ln^2(2c\alpha) \text{ if } |\alpha c| \ll 1 \quad . \qquad (I.14b)$$

The change of variables $c = (8/\lambda)^{1/2}$, $\alpha = (\ell+1)^{1/2}$, gives for (I.14b),

$$\tilde{\varepsilon}'_o \to -\frac{2}{\lambda}\ln^2(\lambda/8) \quad , \tag{I.15}$$

and due to Theorem I.1, we have the desired result:

$$\varepsilon_\ell > \frac{1}{2}\ln^2(\lambda/8) \ , \ \ell \geq 0 \ , \ \lambda >> 1 \quad . \tag{I.16}$$

Eq.(I.16) yields a rigorous expression showing the tight-bound character of the considered states. Above discussion makes clear the asymptotic behavior of the binding energy is closely related to the adiabatic separability of the wavefunction for very strong fields.

Avron et al /64-67/ found an asymptotic relationship for ε_ℓ from Eq.(I.12), whose first term coincides with (I.16). Since it is useful within the context of this book, we present such relationship in what follows. To this end, we have to make some minor changes to be in accordance with the original Hamiltonian (I.1). The Hamiltonian used by Avron et al /67/ is

$$H_A = p^2 + \frac{B^2}{4}\rho^2 - \frac{1}{r} \tag{I.17}$$

The scaling law depicted in Appendix H (see also Appendix A) proves at once that H_A is unitarily equivalent to $H(1,\lambda)$:

$$H_A = \frac{1}{2}H(1,\lambda), \ \lambda = 4B \quad . \tag{I.18}$$

Eq.(I.18) and results of Ref./67/ yield the following expansion for the binding energy:

$$\varepsilon_\ell = \frac{1}{2}\ln^2(\tfrac{\lambda}{8}) - 2\ln(\tfrac{\lambda}{8})\ln\ln(\tfrac{\lambda}{8}) + 2\{(C_\ell+\ln 2)\ln(\tfrac{\lambda}{8})\} +$$

$$+ 2\{\ln\ln(\tfrac{\lambda}{8})\}^2 - 4\{C_\ell - 1 + \ln 2\}\ln\ln(\tfrac{\lambda}{8}) + O(1) \qquad \text{(I.19a)}$$

where

$$C_\ell = -\tfrac{1}{2}(q_\ell + C_E)\ , \quad q_\ell = \tfrac{1}{\ell} + q_{\ell-1},\ \ell \neq 0,\ q_o = 0\ , \qquad \text{(I.19b)}$$

and $C_E = 0.577215664901...$ is the Euler-Mascheroni constant. Formula (I.19a) arises from the expansion of the following implicit expression /67/:

$$\mu = \tfrac{1}{2}\ln(\frac{\lambda}{8\mu^2}) - \tfrac{1}{2}(C_E + q_\ell + \ln 2) + \frac{\pi^2}{12\mu} - (\tfrac{8}{\lambda})^{1/2}\ln(\tfrac{\lambda}{8\mu}) +$$

$$+ 2(\tfrac{8}{\lambda})^{1/2}\,\mu\frac{(\ell+1/2)!}{\ell!} + (\tfrac{8}{\lambda})^{1/2}\frac{(\ell+1/2)!}{\ell!}\,D_\ell + \delta\ , \qquad \text{(I.20a)}$$

where

$$\mu = (\varepsilon_\ell/2)^{1/2}\ , \qquad \text{(I.20b)}$$

$$D_\ell = q_{\ell+1/2} + 2\ln 2 - 2 + C_E - 2C_\ell \qquad \text{(I.20c)}$$

$$C_\ell = \int_0^\infty \{y(y^2+1)^{-1/2} - 1\}\ln y\, dy = 0.30685 \qquad \text{(I.20d)}$$

and δ is the truncation error:

$$\delta \simeq \tfrac{5}{4}(\ln\lambda)^{-2} + O(\lambda^{-1/2}) \qquad \text{(I.20e)}$$

Notice in (I.19a) the occurrence of terms corresponding to a $\lambda^{-1/2}$-power series, besides the logarithmic terms. The appearence of such terms may be understood taking into consideration the scaling law (H.21) obeyed by the Hamiltonian operator.

APPENDIX J

PERTURBATION PARAMETER MAPPING

As shown before, the summation method is based on a mapping that changes the original unbounded perturbation parameter into a bounded one. The purpose of this appendix is to discuss such a transformation in more detail.

To this end consider the following mapping

$$\lambda = w/\{k(1-w)\}^a \quad , \quad a>0 \tag{J.1}$$

from the complex w plane, $w = u+iv$, to the complex λ plane, $\lambda = x+iy$, where k is a real number. Clearly, upon substituting $-1/\alpha$ for a one is led to the transformation discussed in §.44 and §.49.

Since $\lambda(w)$ has a singular point at $w = 1$ the region of the w plane which is useful for summing the λ series is given by the condition $|w|<1$. This unit disk is mapped onto a region in the λ plane with boundary $\Lambda(x_b,y_b)=0$, which is obviously determined by $\lambda(w_b)=x_b+iy_b$, where $w_b=u_b+iv_b$ and $u_b^2+v_b^2=1$.

In order to find Λ, it is convenient to define

$$\theta = \arg\,(1-w), \quad r = |1-w|. \tag{J.2}$$

A straightforward calculation shows that $r = |2(1-u_b)|^{1/2}$ and $\cos\theta\geq 0$ which, together with Eq. (J.1), leads to the following parametric expression for

$$x_b = -\cos(a-2)\theta/(2k\cos\theta)^a \quad ,$$

$$y_b = -\sin(2-a)\theta/(2k\cos\theta)^a \quad , \quad |\theta|\leq\pi/2. \tag{J.3}$$

These equations allow one to draw the following conclusions about Λ

1) It is symmetric around the real axis because $x_b(-\theta) = x_b(\theta)$ and $y_b(-\theta) = -y_b(\theta)$.

2) $x_b = -1/(2k)^a$ and $\partial x_b/\partial y_b = 0$ for $y_b = 0$.

3) When $|\theta| \to \pi/2$ it follows that

a) $x_b \to +\infty$ if $0<a<1$ or $4j+3<a \leq 4j+5$, $j = 0,1,\ldots$

b) $x_b \to -\infty$ if $4j+1<a<4j+3$

c) $x_b = -1/(2k)$ if $a = 1$

It is clear from 2) and 3) that $y_b = 0$ is a maximum of $x_b(y_b)$ when $4j+1<a\leq 4j+3$ and a minimum when either $0<a<1$ or $4j+3<a\leq 4j+5$.

4) When $a>4$ then $y_b|\theta|<\pi/2$ and the mapping is found to be multivalued.

5) $y_b = \pm 1/|2k \cos\pi/(2a-4)|^a$ for $x_b = 0$ when either $0<a<1$ or $4j+3<a<4J+5$.

6) When $|x_b| \to \infty$ (i.e. $|\theta| \to \pi/2$) the absolute value of the slope $\partial y_b/\partial x_b$ tends towards $|\tan(a-2)\frac{\pi}{2}|$.

It has been found in Chapter XV that the k value increases boundless by as the number of terms in the renormalized series increases. Therefore, according to what was argued above, it is clear that the intercept between $\curvearrowleft$ and the x axis (i.e. $x_b = -1/(2k)^a$ and $y_b = 0$) approaches the origin as k increases. As a result, less and less singular points remain within the region enclosed by $\curvearrowleft$.

It is also worth mentioning that numerical results suggest that the smaller the absolute value of $\tan(a-2)\frac{\pi}{2}$, the larger the convergence rate of the renormalized series. Among all the examples studied in this book the one with the largest convergence rate is precisely the integral discussed in § .50, for which $a = 2$.

APPENDIX K

APPLICATIONS OF THE FUNCTION $\langle x^2 \rangle$

The purpose of this Appendix is to present a brief account on the applications of the function $\langle x^2 \rangle$, which represents a classical statistical mean value in a quartic anharmonic oscillator. The function to be analysed is closely related to the polarizability in material media. For example, in order to study the polarizability of some non-polar liquids in the range of low frequencies (1 to 10 MHz), it was found that the isocoric dielectric polarizability depends on the temperatura. Vij and Scaife /68/ studied the benzene polarizability as a function of the temperature and the interpretation of experimental results required the introduction of anharmonicities into the Clausius-Mosotti equation to describe the interaction with the solvent /69/. Other problem involving the function $\langle x^2 \rangle$ is the study of the dynamical answer of order-disorder and displacive type ferro-electric materials, at higher temperatures than the Curie temperature /70,71/. In this case it is also mandatory to introduce anharmonicities in the oscillations to describe properly the dependence with the temperature of the dielectric susceptitibility of the ferro-electric material.

To establish the relation between $\langle x^2 \rangle$ and the polarization of a medium with anharmonic oscillations, let us consider a classical Hamiltonian function H describing the 1D oscillation of a charge q in a dielectric environment

$$H = \frac{1}{2} p^2 + V \ , \qquad \text{(K.1a)}$$

$$V = v_2 x^2 + v_4 x^4 \quad . \qquad \text{(K.1b)}$$

The potential (K.1b) is appropriate to describe the anharmonicities in a first approximation /69,71). The application of a constant electric field, with local intensity F at the charge q, transforms the Hamiltonian (K.1a) into

$$H = \frac{1}{2} p^2 + W(F), \quad W(F) = V + qFx \qquad \text{(K.2)}$$

The application of the field F gives rise to a polarization of the medium where the charge q is placed. If the system is described (in a first approximation) by a constant density n_o of identical charges q, then the polarizability P can be written as

$$P = n_o \langle \partial H/\partial F \rangle = n_o q \langle x \rangle (F) \ , \qquad (K.3)$$

where $\langle A \rangle (F)$ denotes the classical statistical mean value of the mechanical variable A:

$$\langle A \rangle (F) = \int_{-\infty}^{+\infty} A e^{-\beta' H} dpdx / \int_{-\infty}^{+\infty} e^{-\beta' H} dpdx; \ \beta' = (kT)^{-1}, \qquad (K.4)$$

which is a function depending on F through the Hamiltonian (K.2).

If the applied field is very low (as it happens with the phenomena discussed at the begining of this Appendix), $\langle x \rangle (F)$ can be expanded as an F-power series. Thus, taking into account that

$$e^{-\beta' w} \simeq e^{-\beta V} \{1 - \beta' q F x + O(F^2)\}, \qquad (K.5)$$

and that V is an even function of the coordinates, we have the following results:

$$\int_{-\infty}^{+\infty} x e^{-\beta' w} dx \simeq \beta' q F \int_{-\infty}^{+\infty} x^2 e^{-\beta' V} dx + O(F^2) \qquad (K.6a)$$

$$\int_{-\infty}^{+\infty} e^{-\beta' w} dx \simeq \int_{-\infty}^{+\infty} e^{-\beta' V} + O(F) \qquad (K.6b)$$

Replacing (K.6) into (K.3), and considering the definition (K.4), we obtain

$$P \simeq -n_o \beta' q^2 F \langle x^2 \rangle (0) + O(F^2) \ , \qquad (K.7)$$

which reveals that function $\langle x^2 \rangle$ is directly proportional to the polarizability, for small enough fields.

In order to study the dependence of P on the temperature, it is convenient to make the change of variables $(\beta' v_2)^{1/2} x \to x$ in the expression for $\langle x^2 \rangle$. Thus, we have

$$\langle x^2 \rangle(0) = \frac{1}{\beta' v_2} E(1,\lambda) \quad , \quad \lambda = v_4 kT/v_2^2 \tag{K.8a}$$

where

$$E(g,\lambda) = \xi_1(g,\lambda)/\xi_o(g,\lambda) \quad , \tag{K.8b}$$

$$\xi_n(g,\lambda) = \int_0^\infty x^{2n} e^{-gx^2-\lambda x^4} \quad , \tag{K.8c}$$

Formula (K.8b) allows one to write $E(1,\lambda)$ as a continued fraction /69/. This possibility is quite useful, because Eq. (K.8a) does not provide an analytic formula for $\langle x^2 \rangle$ (0) as a function of the temperature. On the other hand, functions $\xi_n(1,\lambda)$ are formally expandable in λ-power series but they yield divergent series. Then, one must resort to a different method to attain an analytic expression for $\langle x^2 \rangle$ (0) as a function of λ; the continued fraction is a sensible alternative since it is convergent /69/. We start by integrating (K.8c) by parts:

$$\xi_{n-1}(1,\lambda) = \frac{2}{2n-1} \xi_n(1,\lambda) + \frac{4\lambda}{2n-1} \xi_{n+1}(1,\lambda) \quad , \tag{K.9}$$

and, upon by rewriting the above equation as,

$$\frac{\xi_n(1,\lambda)}{\xi_{n-1}(1,\lambda)} = \frac{1}{2} \cfrac{2n-1}{1+2\lambda \cfrac{\xi_{n+1}(1,\lambda)}{\xi_n(1,\lambda)}} \tag{K.10}$$

the continued fraction may be constructed in a recursive way. The final result is

$$\frac{\xi_n(1,\lambda)}{\xi_{n-1}(1,\lambda)} = \frac{1}{2\lambda}\,\frac{(2n-1)\lambda}{1+\dfrac{(2n+1)\lambda}{1+\dfrac{(2n+3)\lambda}{1+\dfrac{(2n+5)\lambda}{1+\ldots.}}}} = \frac{1}{2\lambda}\sum_{i=0}^{\infty} \dagger(2n-1+2i)\lambda \ . \qquad \text{(K.11)}$$

The substitution of (K.11) into (K.3b) allows us to obtain the polarizability P like the following function of T:

$$P \simeq -n_o q^2 \frac{F}{v_2} \sum_{i=0}^{\infty} \dagger\,(2i+1)\,(v_4 lT/v_2^2) \qquad \text{(K.12)}$$

The continued fraction converges slowly, so that Eq. (K.12) is not very useful. Thence, it is more convenient to resort to summation methods of divergent series in order to have an analytical expression for $\langle x^2 \rangle$ (0) valid for any temperature.

APPENDIX L

RKR METHOD TO OBTAIN VIBRATIONAL POTENTIALS OF DIATOMIC MOLECULES.

The aim of this Appendix is to describe the determination of the classical turning points of the vibrational potential in a diatomic molecule with the RKR method (Rydberg-Klein-Rees). The present description essentially follows that given in Refs. /72,73/ and completes the discussion exposed in § .61.

Let us consider a molecular state with rovibrational energy E_{nJ}. The effective potential W(R) associated with the nuclear motion is

$$W(R) = U(R) + KR^{-2}, \quad K = J(J+1)\hbar^2/2\mu \tag{L.1}$$

where R is the internuclear distance and μ the reduced mass. The vibrational potential is represented by U(R). Our purpose is to determine the turning points R_+ and R_-:

$$W(R_+) = W(R_-) = E_{nJ}. \tag{L.2}$$

For this purpose, we resort to the auxiliary function

$$A(E_{nJ},K) = \int_{R_-}^{R_+} (E_{nJ} - W(R))dR \quad , \tag{L.3}$$

which fulfils the following properties

$$\left(\frac{\partial A}{\partial E_{nJ}}\right)_K = R_+ - R_- \quad , \tag{L.4a}$$

$$\left(\frac{\partial A}{\partial K}\right)_{E_{nJ}} = \frac{1}{R_+} - \frac{1}{R_-} \quad . \tag{L.4b}$$

The function (L.3) may be suitably rewritten as a double integral. The argument is as follows: starting from the integral /74/:

$$\int \left(\frac{E-x}{x-W}\right)^{1/2} dx = \{(x-W)(E-x)\}^{1/2} - \frac{W-E}{2} \int \{(x-W)(E-x)\}^{-1/2} dx + cte$$

$$= \{(x-W)(E-x)\}^{1/2} - (W-E)\,\mathrm{arctg}\left(\left\{\frac{W-x}{x-E}\right\}^{1/2}\right) + cte \qquad (L.5)$$

we can obtain

$$\int_{W}^{E_{nJ}} \{(E_{nJ}-x)/(x-W)\}^{1/2}\, dx = \frac{\pi}{2}\,(E_{nJ}-W) \quad . \qquad (L.6)$$

Eq. (L.6) allows us to rewrite $A(E_{nJ},K)$ as

$$A = \frac{2}{\pi} \int_{R_-}^{R_+} dR \int_{W}^{E_{nJ}} \{(E_{nJ}-x)/(x-W)\}^{1/2}\, dx \qquad (L.7)$$

When R changes from R_- to R_+, the potential W reaches a minimum value, given by

$$A = \frac{1}{\pi} \int_{\min W}^{E_{nJ}} (E_{nJ}-x)^{1/2}\, dx \oint (x-W)^{-1/2}\, dR \qquad (L.8)$$

Eq. (L.8) is appropriate to introduce the first-order JWKB quantization condition (Chapter II)

$$\oint (x-W)^{1/2}\, dR = h(n+1/2)/(2\mu)^{1/2} \qquad (L.9)$$

From Eq. (L.9) we obtain:

$$\phi\ (x-W)^{-1/2}\ dR = h\ (2\mu)^{-1/2}\ \left(\frac{\partial x}{\partial n}\right)_K^{-1} \quad . \tag{L.10}$$

and this term may be inserted in Eq. (1.8) to yield

$$A = \hbar\ (2/\mu)^{1/2} \int_{\min W}^{E_{nJ}} (E_{nJ}-x)^{1/2}\ \left(\frac{\partial n'}{\partial x}\right)_K dx \tag{L.11}$$

By changing the integration variable to the quantum numbers, one gets from Eq. (L.11):

$$A = \hbar\ (2/\mu)^{1/2} \int_{n_o}^{n} (E_{nJ}-E_{n'J})^{1/2}\ dn' \quad , \tag{L.12}$$

where the integral's lowest limit is a real number satisfying the condition:

$$\min W = E_{n_o J} \quad . \tag{L.13}$$

By resorting to the higher orders in the JWKE approximation, such a limit may be computed as /75/:

$$n_o = -\frac{1}{2} - Y_{00} w_e^{-1} = -\frac{1}{2} - \min U\ (\mu R_e^2/2a_0)^{1/2} \quad , \tag{L.14}$$

where a_o is the first Dunham coefficient ($a_o - R_e^2(\frac{d^2U}{dR^2})(R_e)/2$).

Eqs. (L.4a) and (L.12) allow us to obtain a first relation explicitly involving the classical turning points

$$R_+ - R_- = \hbar\ (2/\mu)^{1/2} \int_{n_o}^{n} (E_{nJ}-E_{n'J})^{-1/2}\ dn' \tag{L.15}$$

On the other hand, the combination of Eqs. (L.4b) and (L.12) gives

$$\frac{1}{R_-} - \frac{1}{R_+} = \hbar\,(2/\mu)^{1/2} \int_{n_o}^{n} (E_{nJ}-E_{n'J})^{-1/2} \left(\frac{\partial E_{n'J}}{\partial K}\right) dn' . \quad \text{(L.16)}$$

The dependence of $E_{n'J}$ on K can be calculated from the first terms of the eigenvalue expansion in power series of the quantum numbers n' and J /76/:

$$E_{n'J} \simeq \text{cte.} + \frac{2\mu}{\hbar^2} B_{n'} K + \ldots \quad \text{(L.17)}$$

where $B_{n'}$ is the rotational constant corresponding to the vibrational state with quantum number n'. Eq. (L.17) permits us to obtain the second desired formula

$$\frac{1}{R_-} - \frac{1}{R_+} = (8\mu)^{1/2} \hbar^{-1} \int_{n_o}^{n} (E_{nJ}-E_{n'J})^{-1/2} B_{n'} dn' . \quad \text{(L.18)}$$

Thus, Eqs. (L.16) and (L.18) provide the way to calculate the turning points R_+ and R_- in terms of the experimental quantities E_{nJ}, B_n and n_o. The integrals involved can be computed numerically, although in practice is cumbersome due to the singularities associated with the extremes of the integration interval. These problems can be overcome by means of a polynomial representation of E_{nJ} and B_n, which allows one to remove the singularities /75/.

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SUBJECT INDEX

A

B

C

D

M

N

O

P

Q

R

S

T

V

W

Y

Z