THE UNIVERSITY OF HULL

# NUMERICAL AND PERTURBATION THEORETIC METHODS FOR THE SOLUTION OF THE SCHRÖDINGER EQUATION

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> The great book of Nature lies ever open before our eyes and the true philosophy is written in it ... But we cannot read it unless we have first learned the language and the characters in which it is written ... It is written in mathematical language and the characters are triangles, circles and other geometrical figures ...
>
> Galileo Galilei

## ABSTRACT

In the present work we present a numerical and perturbation theoretic approach to the solution of the one-particle Schrödinger equation. The numerical methods developed can be used to find energy eigenvalues for one-dimensional problems as well as for radial ones. Expectation values are determined by an approach based on eigenvalue calculations, without the explicit use of wave functions.

Hypervirial and Hellmann-Feynman theorems are used to obtain perturbation series to high order for polynomial type radial perturbations of the hydrogen atom. One such perturbation leads to an apparently new phenomenon in Rayleigh-Schrödinger perturbation theory.

Wynn's algorithm is used to get Padé approximants for the perturbation series. The series for the energy and for the quantities $\langle r^N \rangle$ are treated, and both types of series can be found using the hypervirial method.

Several applications of the numerical techniques are given; it is emphasized that theoretical manipulations are needed to transform the problem to an appropriate numerical form. It is demonstrated that a slight modification in the numerical techniques developed permits treatment of quasi-bound states as well as bound states. It is also shown how to calculate a local quantity, $\psi(0)$, using energy calculations, and how to reduce the problem of treating angular terms in the quadratic Zeeman effect problem to a radial integration problem.

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# CHAPTER I

## INTRODUCTION

As can be seen from the title of this work, our aim is to develop mathematical techniques to solve the one-particle Schrödinger equation; that is, we are interested in how to calculate eigenvalues and eigenfunctions for a certain Hamiltonian. We may ask "what role do the eigenvalues and eigenfunctions play in the context of quantum mechanics, and why is the Schrödinger equation so relevant in quantum mechanics?" To answer these questions, and to be familiar with the ideas about quantum mechanics at the time the Schrödinger equation began to gain importance, we would like to summarize some of Erwin Schrödinger's own ideas about "wave mechanics" in the year 1926 [1].

### 1.1. The Wave Function $\psi$

Schrödinger derived a differential equation for the eigenfunction $\psi$. One of his concerns was to find the value of $|\psi|^2$, which was initially thought to be a smeared out charge density. Max Born changed the concept of $|\psi|^2$ by regarding quantum mechanics as describing the motion of definite point particles. Within this context he considered $|\psi|^2$ to be a probability density, so that expectation values such as $\langle r\rangle$ are averages of the type used in traditional probability theory.

Schrödinger used perturbation theory to solve the problem of the Stark effect for the hydrogen atom, where the potential function is equal to $\lambda z$. Although this is an unbound state problem, it is possible to use perturbation theory for small values of $\lambda$ up to low order, and still get reasonable results. The Rayleigh-

Schrödinger approach to perturbation theory involves the calculation of perturbed wavefunctions $\psi_n$ of various orders n.

The usual view is to use perturbation theory to work out the change in the energy $\Delta E$, after adding the perturbation to the Hamiltonian, if the unperturbed eigenfunction $\phi_0$ and the potential function are known. However, in the present work we reverse this argument; we calculate $\Delta E$ numerically for arbitrary potential V so as to find $\langle V \rangle$ without explicitly recording the wavefunction. This reduces the importance of $\psi$ in the calculation, and in our work on hypervirial methods $\psi$ is completely eliminated. This means that series for $\Delta E$, $\langle r \rangle$ etc. result without any calculation of the perturbed wavefunctions $\psi_n$.

## 1.2. Summary of Selected Previous Works

Kato [2,1949] gives an improved and much simpler treatment of the theory of regular perturbations, based on the use of resolvents and contour integrals. His method allows the derivation of explicit formulae representing eigenvalues and eigenvectors up to any order in the perturbation parameter $\lambda$. Dalgarno and Lewis [3,1956] describe a general sum rule which has many variants; it permits, for example,, the exact calculation of the long range forces between a proton and a hydrogen atom using conventional perturbation theory. Their method finds the second order energy $E_2$ by solving a differential equation, whereas the traditional method (which has many similarities with matrix methods) represents $E_2$ as a summation over terms involving excited states. This sum-over-states involves continuum states, which are difficult to handle; the differential equation approach indirectly allows an estimate of these continuum contributions to be made. The limitation of the Dalgarno-Lewis method is the difficulty which may arise in solving the differential equation. The sum rule technique appears to have applications to many fields; it will work well for perturbed oscillator and hydrogen atom problems, which are popular test problems for perturbation and numerical methods.

Perturbation theory can also be applied to modify numerical integration methods for finding $\psi$. Riehl, Diestler and Wagner [4,1974] re-formulate the method of "reference-functions" to treat the problem of finding $\psi$ for the radial Schrödinger equation in piecewise analytic form. Ordinary Rayleigh-Schrödinger-perturbation theory is used to obtain the solution in a succession of intervals of the independent (radial) variable. The perturbation technique (carried to first order, taking the zero-order potential to be constant) is tested against the highly efficient Numerov direct-integration method on the Lennard-Jones potential. It is found that, under the restrictions imposed on the perturbation methods, the Numerov procedure is almost always more effective, except for partial waves of low angular momentum.

Adam, Ixaru and Corciovei [5,1974] develop a very simple perturbative numerical algorithm for the solution of the radial Schrödinger equation. This algorithm uses the same basic approximation (a step function approximation for the potential well) as that previously reported by Riehl et.al. (op.cit.). It shows, however, an $O(h^5)$ rate of convergence in the step size h, as compared to the $O(h^4)$ rate of convergence of the algorithm given in the work of Riehl et.al. A comparison with the Numerov method for eigenvalue problems proves the high efficiency of this algorithm.

Killingbeck [6,1977] presents a work which reviews some of the modern articles in perturbation theory in the context of traditional results from the theory of real and complex variables. He compares the two major versions of time-independent perturbation theory, the Rayleigh-Schrödinger (RS) and Brillouin-Wigner (BW) theories and reviews the alternative techniques for evaluating the terms in the energy series. The sum-over-states method, the differential equation method, and the variational principle method are treated with emphasis on their inter-relations. Some specific variational principles are studied, including those for upper and lower bounds to the second order energy, with comments on the extra problem arising if the unperturbed function is not known exactly.

Don Secrest, Cashion and Hirschfelder [7,1962] present a numerical method for accurate calculation of the energy eigenvalue of one-dimensional Schrödinger equations. It is applicable to systems for which the potential is either analytic or has no pole of order greater than two. The method is based on a power series expansion of the wave function $\psi$ at large distances. The method uses two trial energies, E and $E+\delta E$, and varies them until the calculated wave functions at some large distance L are of opposite sign. Secrest et.al. (op.cit.) estimate an energy eigenvalue so as to make $\psi(L) = 0$; when this requirement is achieved they increase L in order to see if the value of E varies. This idea is used in our present work, with the difference that we use three trial energies to estimate E. Our method (section 2.1.4.) does not require a series of fixed L values, since the programme takes the limit $L \rightarrow \infty$ during the calculation (as explained in section 2.1.4.). However, the energy eigenvalue obtained in our work refers to a particular strip width h, and an h-extrapolation is needed (section 2.1.4.).

With the use of high-speed computing machines, the large number of terms required in the power series in the method presented by Secrest et.al. (op.cit.) can be computed easily; nevertheless, it has been tested on the C.B.M. Pet Minicomputer and it was not possible to make it work, because the wavefunction increased considerably, so as to overflow the capacity $(10^{38})$ of the Pet. However it works satisfactorily on a programmable calculator which can handle numbers as large as $10^{99}$.

Killingbeck [8,1977] treats the radial Schrödinger equation, converting it to a recursive one which can be treated satisfactorily by a programmable pocket calculator. His calculations show that the eigenvalue error varies very smoothly with the integration strip width h. The method is applied to a problem for which the traditional energy perturbation series is divergent asymptotic. This method, which we call the R-method, is used in this work (section 2.1.4.) to find the energy eigenvalue of a system with potential function equal to $\lambda r - r^{-1}$. We investigate the dependence of the error on h using perturbation theory and test problems, and show that the R-method can be improved in several respects. If the potential V is finite we show that a perturbation approach is possible which is much simpler than any previously used.

Killingbeck [9,1977] gives some more applications of programmable calculators. He finds the energy eigenvalue for one-dimensional problems (with $-\infty < x < +\infty$) directly by purely numerical methods. This can be done if the relevant Schrödinger equation is transformed into a difference equation. This one-dimensional-R-method is also used in this work for $V = x^2$ and $x^4$(in section 2.1.2. of this thesis.)

Killingbeck [10,1978] uses several techniques to study the ground state properties of a hydrogen atom with the polynomial perturbation $2\lambda r + 2\lambda^2 r^2$. He uses a numerical method to calculate the energy eigenvalue, and using in addition the Hellmann-Feynman theorem he finds $\langle r^2 \rangle$ values without explicit calculation of the wavefunction. We develop these ideas further (section 3.1.4.) and we check that the Rayleigh-Schrödinger energy series agrees (for $\lambda>0$) with the exact eigenvalue $-\frac{1}{2}+3\lambda$. For $\lambda<0$ the shape of the potential curve shows that bound states still exist but their energy differs from $-\frac{1}{2}+3\lambda$; this is discussed in section 4.1.

Biswas et.al. [11,1973] calculate non-perturbatively the ground state and the excited levels of the generalized anharmonic oscillator defined by the Hamiltonian $H = -d^2/dx^2+x^2+\lambda x^{2m}$, m = 2, 3, ..., using Hill determinants. For the $\lambda x^4$ perturbation they compared their ground state eigenvalues, for various values of $\lambda$, with the Borel-Padé sum of the asymptotic perturbation series for the energy.

The numerical solution of the Schrödinger equation is often achieved by means of step-by-step integration procedures, of which the best known one is the Numerov method. Killingbeck [12,1979] shows that a much more simple "global" application of perturbation theory leads to useful ways of improving the accuracy of various step-by-step methods. He demonstrates that expectation values can be determined by an approach based only on eigenvalue computations, without the use of wavefunctions. He improves the so-called R-method (section 2.1.2.) by changing to a new variable F(x) defined by $R(x) = 1+h^2F(x)$, leading to a method which we call the F-method. We use these ideas and apply this method to the same test potentials as used for the R-method (that is $V = x^2$ and $x^4$) to show the improvement of changing from one method to another.

Bolton and Scoins [13,1956] treat the Schrödinger differential equation to calculate eigenvalues, using finite difference techniques.

They compare this way of solving these equations with the Rayleigh-Ritz variational method.

Numerical procedures for solving the Hartree-Fock equations have been described by many authors. Froese [14,1963] develops a procedure for solving these equations on a computer (IBM 7090). She uses the Numerov method as well as "the tail procedure" and finds out that these two methods complement each other. She uses the hydrogen atom radial equation as a test problem to compare different methods.

The numerical solution of the one-dimensional Schrödinger equation is also treated by Blatt [15,1967]. He discusses the various problems encountered e.g. choosing a step size; in this connection, he develops a midpoint formula to be used with the Numerov method. He discusses how to find the eigenvalue iteratively when already close to it, and comments on other problems arising during the process of numerical integration.

Hajj, Kobeisse and Nassif [16,1974] use higher-order difference schemes in order to find a numerical solution of Schrödinger's radial equation. These schemes are a family of difference equations which are extensions of the well-known Numerov difference equations, and give highly convergent approximate solutions. Hajj et.al. (op. cit.) uses a "shooting method" to solve the Schrödinger equation, rather than using matrix methods, because shooting methods are simpler, requiring smaller storage and a shorter programme. A correction formula is used to estimate E for each trial solution, and this corrected energy is then used as input to the next integration.

Raptis and Allison [17,1978] develop an exponential-fitting method to be applied to the numerical solution of the radial

Schrödinger equation. Their method is based on a two-step numerical integration formula, with all the advantages of the Numerov method, but with the ability to integrate solutions of oscillatory and exponential form more efficiently. Their work belongs to a class of methods which allow the strip width h to vary with position during the numerical integration, whereas for our problems we find that a fixed-h approach is adequate.

Mitra [18,1978] calculates the ground state and the first two excited state energy levels for an oscillator with perturbing potential of type $\lambda x^2/(1+gx^2)$. He uses the Ritz variational method in combination with the Givens-Householder algorithm for numerical computations. Galicia and Killingbeck [19,1979] give a simple numerical method for calculating the eigenvalues of the Schrödinger equation for the perturbed oscillator considered by him. The direct numerical integration method is more accurate than the matrix approach for this kind of Hamiltonian . The method used is an $h^4$ process for bound potentials and it is shown to be more simple than the Numerov method. In section 2.2.2. we give an explanation of this method and the results for the energy eigenvalues of the three lowest even parity states obtained by our modified R-method and by Mitra's matrix approach. Direct methods also permit the calculation of expectation values such as $\langle x^2\rangle$. Results for this expectation value are also given in section 2.2.2.

Tipping [20,1976] presents a method whereby matrix elements are derived directly in terms of the energy eigenvalues, and of the potential parameters, without explicit use of the eigenfunctions. This method consists of determining "initial" matrix elements via quantum mechanical sum rules, and then generating all additional elements through an exact hypervirial recursion relationship.

The method is illustrated by sample calculations for the $x^4$ oscillator, and it is shown how to obtain results more accurate than those computed by direct integration employing numerical eigenfunctions.

Swenson and Danforth [21,1972] apply a set of hypervirial theorems plus the Hellmann-Feynman theorem to a general anharmonic oscillator. The exact energy and expectation values of powers of the position coordinate are expanded in a power series of the anharmonic coupling constant. It is shown that the use of the above theorems enables one to express each term in these expansions solely in terms of the unperturbed energy and known constants. This procedure eliminates the usual tedious calculations of sums over intermediate states of products of matrix elements, which arises in nth order Rayleigh-Schrödinger perturbation theory.

The Padé approximants are a particular type of rational fraction approximation to the value of a function (Baker [22,1970]). Wynn [23,1956] has designed an algorithm to evaluate Padé approximants; the novelty of this algorithm is that it directly produces the numerical value of the approximants for a given $\lambda$ without explicitly constructing the approximants as rational fractions at an intermediate stage.

Killingbeck [24,1978] shows that hypervirial relations yield the series for the energy and expectation values for a hydrogen atom with perturbation $\lambda r$, up to fifth order in $\lambda$, without calculation of perturbed wave functions. He makes a Padé approximant analysis of the energy series. In a subsequent paper Killingbeck and Galicia [25,in the press] use hypervirial relations together with the Hellmann-Feynman theorem to get the energy coefficients of a power series for the hydrogen atom with potential function

$\lambda r - r^{-1}$ and $\lambda r^2 - r^{-1}$. In the present work (section 3.1.1.) we develop a programme which calculates the perturbation series up to high order, for any hydrogen atom state and for a perturbing potential $\lambda r^P$ (P a positive integer). The programme also enables us to get the series for expectation values of type $\langle r^N \rangle$.

We have developed a programme which uses Wynn's algorithm to calculate Padé approximants. It is used by Killingbeck and Galicia (op.cit.) to obtain the energy value for the potentials mentioned above. Their results indicate that the exact energy lies between the $[L+1, L]$ and $[L, L]$ Padé approximants. In this work we apply it to several perturbing potentials and expectation values (section 3.2.3.).

The problem of calculating the eigenfunction $\psi$ at the origin for radial Hamiltonians, such as that for the Charmonium system, is shown by our approach to be reducible to a sequence of energy calculations. Killingbeck and Galicia (op.cit.) consider this problem, performing the calculations by the use of a pseudo-angular momentum term in a numerical integration approach. They show how a first principles approach to s state hypervirial relations produces terms not given by the usual commutator approach. The problem of $\psi(0)$ is also discussed in the present work, which gives typical results (section 4.3).

Hazi and Taylor [26,1970] apply the stabilization method of calculating resonance energies to the elastic scattering from a one-dimensional model potential containing a barrier. For sufficiently large basis sets, the stabilization method yields good approximations to the inner part of the exact scattering wave functions at energies equal to the eigenvalues of the truncated matrix of the Hamiltonian in both the resonant and non-resonant energy regions.

Quasi-bound-state energy calculations are made for a perturbed oscillator and a perturbed hydrogen atom by Killingbeck [27,1978]. He describes a simple numerical variant of the well-known stabilization method; the results are compared with those from the least-square and perturbation-series methods. These ideas are further discussed in this work in section 4.1.

Austin [28,1980] uses the hypervirial and Hellmann-Feynman theorems to obtain perturbation series for the perturbed hydrogen atom to high order. He shows that although the series diverges, the diagonal Padé approximants converge to an accurate eigenvalue. This aspect of the Padé approximants is also demonstrated in this thesis (section 3.2.2.)

Austin (op.cit.) treats the problem of the Stark effect (i.e. perturbation $\lambda z$), where there are no bound states, by using Padé approximants and parabolic coordinates. For the radial perturbation $\lambda r$, Killingbeck [10] and Austin (op.cit.) demonstrated that even for $\lambda < 0$ there is still convergence of the diagonal Padé approximants, over a smaller range of $\lambda$. This is also considered in the present work (section 4.1.1.) where typical results are given.

As we mentioned at the beginning of the introduction, Schrödinger treated the problem of the Stark effect (i.e. perturbation $\lambda z$) and obtained the energy perturbation series up to second order. Things have changed since then; with the development of modern computational methods it is possible to handle the series to very high order and interpret the results in terms of the theory of quasi-bound states.

Killingbeck [29,1979] treats the problem of the hydrogen-atom quadratic Zeeman effect using perturbation theory. The important step for solving this problem is the right choice of the unperturbed Hamiltonian. We develop these ideas further in this thesis (section 4.3), using the F-method of section 2.1.4. to perform the numerical integrations.

## 1.3. Summary of Present Work

In chapter two we give a perturbation theoretic treatment of numerical integration methods to solve the Schrödinger equation. It is shown that after converting the equation to a recursive one it becomes so simple that it could be handled by a programmable pocket calculator.

We choose the test potentials $V = x^2$ and $x^4$ to show the improvements which can be made by introducing several modifications of the original simple method. The numerical methods developed can be used to find the energy eigenvalue for one-dimensional problems (with $-\infty < x < \infty$) as well as for radial problems (with $0 \leqslant x < \infty$).

It is shown how the accuracy in the calculated energy depends on the choice of the strip width h. It is shown how to get a projected energy eigenvalue by means of an extrapolation process in the quantity $h^2$.

It is demonstrated that expectation values can be determined by an approach based on eigenvalue calculations, without the explicit use of wave functions.

In chapter three, the hypervirial theorem, together with the Hellmann-Feynman theorem, is used in order to obtain power series for the energy and expectation values of the type $\langle r^N \rangle$ for the hydrogen atom with perturbing potential $\lambda r$ (with positive integer P). This approach is used for the ground state as well as for some excited states. The Charmonium type potential $(-1/r+2\lambda r+2\lambda^2r^2)$ is also treated by hypervirial methods and is shown to have some interesting properties.

Wynn's algorithm is used in section 3.2 to obtain Padé approximants to power series. The basic point about this algorithm is that it directly produces the numerical value of the approximants for a given $\lambda$ without explicitly constructing the approximants as rational fractions at an intermediate stage. It is demonstrated for several of the perturbation problems of interest that, although the perturbation series diverge, the $[L+1,L]$ approximants converge from above to the correct quantity required and the diagonal Padé approximants (i.e. $[L,L]$) converge from below.

Another application of Wynn's algorithm is given in section 3.2.3 for the calculation of expectation values such as $\langle r\rangle$ and $\langle r^2\rangle$.

In chapter four further applications of the numerical techniques are given, with some emphasis on the theoretical manipulations needed to transform the problem to an appropriate numerical form.

The problem of quasi-bound states is considered in section 4.1, with the aid of the R-method of section 2.1.4 and of the Padé approximants of section 3.2. It is shown that for the hydrogen atom with perturbing potential $2\lambda r+2\lambda^2r^2$ there are bound states even for $\lambda< 0$. This problem shows that interesting feature of a Rayleigh-Schrödinger energy series which is convergent (finite) but which does not give the energy correctly.

In section 4.2 it is shown how to deal with the $\psi(0)$ problem (i.e. the calculation of the wavefunction at $r = 0$). The basic principle involved is that of reducing the calculation of the required quantity ($\psi(0)$ in this case) to the calculation of an expectation value, and thence (by the methods of section 2.2.5) to eigenvalue calculations, which can be performed accurately by the method of section 2.1.4.

In the last part of this work, the hydrogen-atom quadratic Zeeman effect is analyzed. The relevant idea is to make a suitable choice of the unperturbed Hamiltonian. The 1s, 2s, 2p, $2p_{\pm 1}$, $3d_{\pm 2}$ and $3d_{\pm 1}$ states are studied in section 4.3.3. Some selected BASIC programmes and their associated flow-charts are given in the appendices, together with comments on their use and on modifications which can be made in order to perform several different calculations.

# CHAPTER 2

## A PERTURBATION-THEORETIC APPROACH TO NUMERICAL INTEGRATION METHODS

### 2.1. Numerical Integration Methods

### 2.1.1. Introduction

The numerical solution of the one-particle Schrödinger equation has attracted continuous interest over many years. The Numerov method, which is a step-by-step integration procedure, has been used and improved recently by many authors.

Our interest is to create simple numerical methods which could be used to solve the one-particle Schrödinger equation, even with a programmable calculator, avoiding the use of large matrices. Using the Rayleigh-Ritz method to solve the Schrödinger equation it is necessary to choose suitable basis functions. It is not always easy to find a suitable basis for a particular physical problem, and then there are also the problems of constructing and diagonalizing the Hamiltonian matrix. This makes fairly large demands on computing power and storage capacity, and so is not suitable for small machines. The direct finite-difference methods described in this work are designed so that it is possible to find information about the solutions of the differential equation for a given potential without such problems arising.

### 2.1.2. R-Method

We choose the Schrödinger equation to be of the form

$$-\frac{1}{2}D^2\psi + V\psi = E\psi \tag{2.1}$$

where V is the potential function and E the unknown energy, which will assume some definite trial values during the course of the numerical integration procedure. We can represent the second derivative $D^2\psi$ in the finite difference form [9]

$$D^2\psi = \frac{1}{h^2}\left[\psi(x+h) + \psi(x-h) - 2\,\psi(x)\right] \tag{2.2}$$

yielding the result

$$\psi(x+h) + \psi(x-h) - 2\psi(x) = 2\,h^2(V-E)\,\psi(x) \tag{2.3}$$

Since storing all the $\psi(x)$ values requires a lot of storage capacity, we want to avoid retaining the full wave function while solving the equation.

To this end we introduce the variable R(x) defined as

$$R(x) = \frac{\psi(x+h)}{\psi(x)} \tag{2.4}$$

That is, we have defined the new function R(x) as the ratio of the wave functions at neighbouring points. In this way we can "see" the behaviour of the wave functions as x increases.

Putting equation (2.4) into equation (2.3) we obtain

$$R(x) + \frac{1}{R(x-h)} = 2\left[1 + h^2(V-E)\right] \tag{2.5}$$

The advantage of dealing with R(x) instead of $\psi(x)$ is that initially we only need to store the value of R(0), if we start at $x = 0$; this value can easily be found to be $R(0) = 1 + h^2[V(0)-E]$ if we suppose that $\psi(h)=\psi(-h)$, which yields the result. $R(0) = 1/R(-h)$. This condition is valid for even parity solutions when the potential V is of even parity.

We have chosen the potentials $V = x^2$ and $x^4$ to test the efficiency of our method. The first potential can be treated exactly by analytical methods, while the second cannot. Because of the symmetry in the potential function we integrate along the positive x axis only. As noted previously, if we have $\psi(h)=\psi(-h)$ we can get an <u>even</u> parity solution. To get an <u>odd</u> parity solution, for which $\psi(0) = 0$, we start again at $x = 0$ but with $R(0) = \infty$.

With these ideas in mind we can start our programme using, for example, a Casio fx-201P programmable calculator. The usual boundary conditions for a quantum-mechanical eigenvalue problem require the wave function to vanish at both ends of some range of x. In this case we start at x = 0 and require that $\psi(\infty)=0$. The second derivative, $D^2\psi$, can only be zero at one value of x, for a fixed E, if the potential is monotonic in x, as it is for our problem. This condition is valid only if the wave function is positive everywhere. As we know, from elementary quantum mechanics, a great variety of potentials have a wave function which is nodeless for the ground state. The nodes start appearing as E increases, each excited state having one more node than the one below it. Therefore if we start our programme using a trial energy E we have to observe the behaviour of the function R(x). If R(x) is negative at some x, that means that we have reached a node. This indicates that our trial E was too high, if we are interested in the ground state energy eigenvalue. On the other hand, if R(x) passes through unity from below this occurrence shows that $\psi(x)$ is increasing with x, which suggests that E was too low. Trying various E values it is possible to "sandwich" the required E, up to as many decimal places as we want.

The stopping condition ($R<0$ or $R>1$) can be written as $R(1-R)<0$, giving only <u>one</u> stopping instruction to the calculator. As we can see from equation (2.5) the E value depends on h; we can also see this dependence in table 1. If we write the energy as E(h), to show its h- dependence, then the eigenvalue of equation (2.1) is E(0). The quantity E(h)-E(0) is a function of $h^2$, as we shall discuss in more detail later.

A linear extrapolation (in $h^2$) gives the result $E = 0.7071068$ for $V = x^2$, which fits to the analytical result $E = \frac{1}{2}\sqrt{2}$ . For $V = x^4$ we find $E = 0.6679875$.

Table 1

Energy Eigenvalues Using R-Method

| $V$<br>$h^2$ | $x^2$ | $x^4$ |
|---|---|---|
| 0.0004 | 0.7070818140 | 0.6679494995 |
| 0.0008 | 0.7070567848 | 0.6679115115 |
| 0.0012 | 0.7070319225 | 0.6678739205 |

### 2.1.3. F-Method

As we have seen in the previous section, to get the energy value to high accuracy we need to use small h values, in which case it will be necessary to perform hundreds of step-by-step calculations. Consequently the resulting E value may be affected by rounding errors. If h is very small we know that $R(x)$ is of the order $1-h^2E$; this means that we can remove the integer 1, since it is giving redundant information. In this way we can gain two or more significant figures at each step. In order to do so we define the F function as follows

$$R(x) = 1 + h^2 F(x) \tag{2.6}$$

Substituting this definition into equation (2.5) and using the equality $1/(1 + x) = 1 - x/(1 + x)$, we obtain

$$F(x) = \frac{F(x-h)}{1 + h^2 F(x-h)} + 2(V-E) \tag{2.7}$$

We use the same potential as the one used for the R-method to show the effect of using equation (2.6), using again a Casio fx-201P calculator. The starting value takes the form $F(0) = V(0)-E$. Because of the fact that both the equation (2.7) and our potentials depend on $h^2$ we can shorten the programme by storing $h^2$

instead of h. The stopping condition is that $R(1-R) = (h^2F)[1+h^2F(x-h)]$ shall be positive. Some typical results are shown in table 2.

Table 2

Energy Eigenvalues Using F-Method

| $h^2$ \ V | $x^2$ | $x^4$ |
|---|---|---|
| 0.0004 | 0.7070817835 | 0.6679487405 |
| 0.0008 | 0.7070567805 | 0.6679112155 |
| 0.0012 | 0.7070317726 | 0.6678736915 |

To find the energy very accurately we fit the results in Tables 1 and 2 to the expansion $E(h) = E(0) + Ah^2 + Bh^4$, and find the E(0) value. We shall reserve this analysis until section 2.2.3., where results for several methods are grouped together and analysed. However, it is already clear from Tables 1 and 2 that the change from the R-method to the F-method begins to affect the results at the sixth or seventh decimal place for our simple test potentials.

### 2.1.4. Radial Problem

Considering equation (2.1) we assume $\psi$ to take the form $\mathcal{Y}_\ell \phi(r)$ where $\mathcal{Y}_\ell$ is a solid harmonic of degree $\ell$. Making the substitution in (2.1), and multiplying throughout by r, leads to an equation for the function $\phi$, (Killingbeck [8]):

$$2r(V-E)\phi = rD^2\phi + (2\ell+2)D\phi \tag{2.8}$$

where D is the derivative. To make equation (2.8) much simpler we introduce the finite difference approximations

$$h^2D^2\phi \rightarrow \phi(r+h) + \phi(r-h) - 2\phi(r) \tag{2.9}$$

$$2hD\phi \rightarrow \phi(r+h) - \phi(r-h) \tag{2.10}$$

The resulting difference equation will only simulate (2.1) in the limit h→0, but it will be shown that very good results can be obtained without approaching the limit too closely.

The next step is the introduction of a ratio variable $R(r)$, defined by the equation

$$\phi(r+h) = R(r)\,\phi(r) \qquad (2.11)$$

With the substitutions (2.9), (2.10) and (2.11), the differential equation (2.1) is converted to a recursive equation to calculate the values of $R(r)$:

$$R(r)\Big[r + h(\ell + 1)\Big] + R(r-h)^{-1}\Big[r-h(\ell + 1)\Big] = 2r\Big[1 + h^2(V-E)\Big] \qquad (2.12)$$

This equation can be worked out using a programmable calculator. We can start at $r = h(\ell + 1)$, since in this case $R(h\ell)$ can be assigned <u>any</u> finite value. If we deal with $\ell = 0$ (s states) equation (2.12) takes the simple form

$$(r+h)R(r) + (r-h)R(r-h)^{-1} = 2r\Big[1 + h^2(V-E)\Big] \qquad (2.13)$$

We have applied this equation to the problem of finding the energy eigenvalue for the potential $V = \lambda r - r^{-1}$ using a Casio fx-201P programmable calculator. The starting co-ordinate is $r = h$. It is possible to change to the variable $Y = R^{-1}$, so that the stopping condition becomes simply $Y < 1$. Results for this problem are shown in table 3, which refers to the lowest eigenvalue.

Table 3

Energy Eigenvalues for $V = \lambda r - r^{-1}$ Using R-Method

| $h$<br>$\lambda$ | 0.04 | 0.02 | Using $h^2$ law |
|---|---|---|---|
| 0.01 | -0.484940100 | -0.485092750 | -0.485143(633) |
| 0.02 | -0.470345403 | -0.470501254 | -0.470553(205) |
| 0.03 | -0.455988774 | -0.456146081 | -0.456198(516) |
| 0.04 | -0.441847514 | -0.442007440 | -0.442060(749) |
| 0.05 | -0.427903578 | -0.428065541 | -0.428119(529) |
| 0.10 | -0.360671692 | -0.360842678 | -0.360899(673) |
| 0.15 | -0.296751531 | -0.296929501 | -0.296988(824) |

A study of the error E(h) - E(0) shows that it is proportional to $h^2$ up to fairly large h values. We have applied an extrapolation law which holds in the $h^2$ region:

$$E = \frac{1}{3}\left[4E(h) - E(2h)\right] \qquad (2.14)$$

The first two columns of table 3 show results for the energy eigenvalue using two different h values. From these results we can say that, although the calculator displays nine decimal figures, after using equation (2.14), we can only consider the results to be accurate up to the sixth one. Even so, we show the results up to 9 figures enclosing the last three in brackets since those figures are not reliable.

We can easily pick out an excited state by allowing an appropriate number of nodes to appear, that is, instead of stopping the calculation when $R^{-1} < 1$ we allow the programme to continue until $R^{-1}$ fulfils the stopping condition for the second or third time, depending on the particular excited state which we are interested in. Results for the first excited state for $V = \lambda r - r^{-1}$ are shown in table 4; this time we did the calculations using a C.B.M. Pet mini computer; we have applied again an $h^2$ law.

Table 4

2s State Energy Eigenvalues

| $\lambda$ \ h | 0.1 | 0.05 | $h^2$ law |
|---|---|---|---|
| 0.01 | -0.0695784343 | -0.0696481205 | -0.0696713(492) |
| 0.02 | -0.0200291862 | -0.0201021321 | -0.0201264(474) |
| 0.03 | +0.0259161898 | +0.0259400819 | +0.0260117(581) |

It is convenient to get an equation for the radial problem using the F-method to show the advantage of this method over the R-method. In order to do so we apply the same criterion as to get equation (2.12), i.e. we put equation (2.6) into equation (2.12) use again the equality $1/(1+x) = 1-x/(1+x)$, and obtain

$$(r+h)F(r)-(r-h)F(r-h)\left[1+h^2F(r-h)\right]^{-1}$$

$$=2r(V-E) \tag{2.15}$$

The function $\left[1+h^2F(r-h)\right]^{-1}$ can be replaced by its equivalent $R(r-h)^{-1}$ which yields the equation

$$(r+h)F(r)+(r-h)F(r-h)R(r-h)^{-1}=2r(V-E) \tag{2.16}$$

We have written a programme based on this equation for the PET. It gives many advantages over the R-method. It uses <u>three</u> trial E values (E, E±δE) at the same time, evaluating the appropriate functions, $W = V-E$, $W+\delta E$, and $W-\delta E$, whereas in the previous programmes only $W = V-E$ for one E was used. The idea behind this theory can easily by understood by looking at the next diagram.

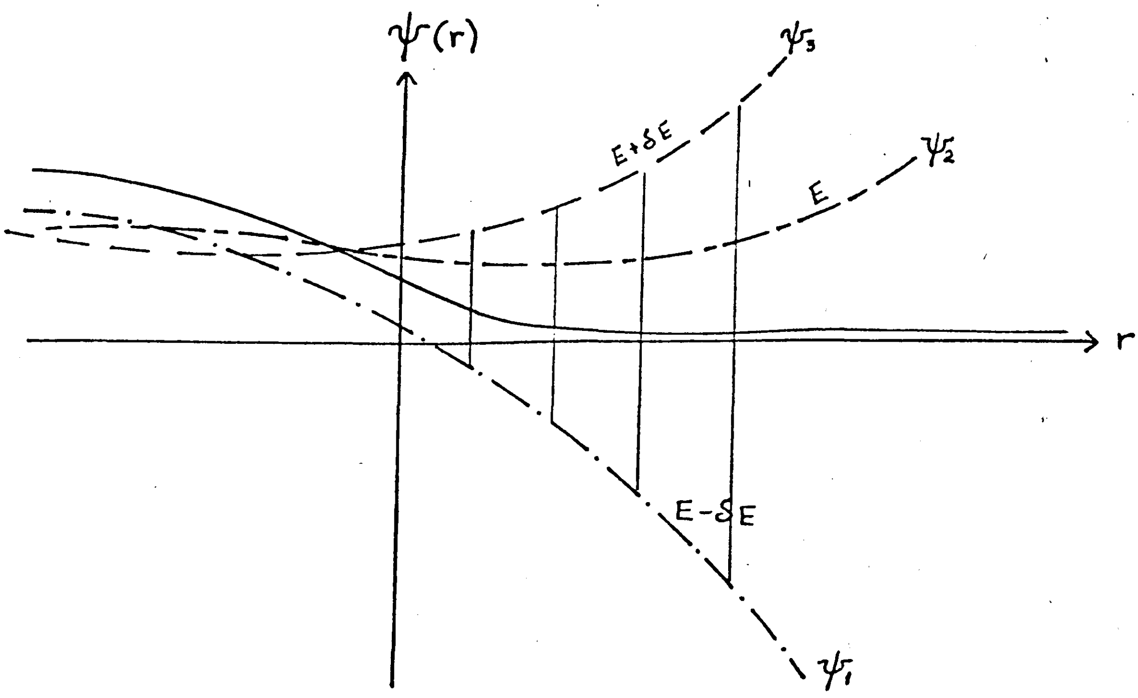


Figure 1

The BASIC-programme is given in Appendix A1 with a more detailed explanation of its use.

The programme is written in such a way that it is possible to know whether each of the three trial E's is too high or too low, as it shows the number of nodes that each function, $\psi_1$, $\psi_2$, or $\psi_3$, has passed through. It also calculates the corresponding wave functions, using equation (2.4) as a recursive equation, starting at $\psi(h) = 1$ for each of the three trial E values.

When the true E(h) value falls between two of the trial E values, the programme interpolates to get a "predicted" value for E, first using $\psi_1$ and $\psi_2$ by means of the relation $\mathcal{E}_1 = E - \delta E/(1 - \psi_2/\psi_1)$ to get an initial predicted E value. It then calculates $\mathcal{E}_2 = E - 2\delta E/(1 - \psi_3/\psi_1)$ to get a second predicted value. Finally a third interpolated $\mathcal{E}_3$ value is calculated as a result of dealing with $\mathcal{E}_1$ and $\mathcal{E}_2$ to get a predicted E(h) to a higher order of accuracy. The interpolations are designed to find that E(h) value which would make $\psi$ tend to <u>zero</u> at large r values.

A remarkable result was found while running the programme. As the wave functions are calculated for increasing r values, passing through several nodes, the ratios $\psi_2/\psi_1$, $\psi_3/\psi_1$, etc. reach constant limiting values, giving as a result a stable predicted E(h) value, even though the individual functions $\psi_1$, $\psi_2$ and $\psi_3$ deviate markedly from zero at large r.

Table 5 shows the results of dealing with the potential $V = \lambda r - r^{-1}$; these can be compared with the results of table 3.

Table 5

Energy Eigenvalues for $V = \lambda r - r^{-1}$ Using F-Method

| $\lambda$ \ h | 0.04 | 0.02 | $h^2$ law |
|---|---|---|---|
| 0.01 | -0.484940031 | -0.485092755 | -0.485143(663) |
| 0.02 | -0.470345488 | -0.470500864 | -0.470552(656) |
| 0.03 | -0.455987767 | -0.456146606 | -0.456199(552) |
| 0.04 | -0.441847575 | -0.442007719 | -0.442061(100) |
| 0.05 | -0.427903551 | -0.428065849 | -0.428119(948) |
| 0.10 | -0.360671584 | -0.360842928 | -0.360900(043) |
| 0.15 | -0.296751664 | -0.296929955 | -0.296989(385) |

## 2.2. Perturbation Theory in $h^2$

### 2.2.1. Introduction

Up to this point we have noted that $E(0) - E(h\ )$ is a function of $h^2$; we now formalize this notion by regarding $h^2$ as a perturbation parameter, using some standard results of perturbation theory to improve the accuracy of the eigenvalue computations [12]. The basic quantity which we study is the second order finite difference operator $\delta^2$, with the defining equation

$$\delta^2\psi = \psi(x+h) + \psi(x-h) - 2\psi(x) \tag{2.17}$$

In the methods of section 2.2.3. we used $h^{-2}\delta^2$ to replace $D^2$ in the Schrödinger equation. Using a Taylor series expansion, however, it is clear that $h^{-2}\delta^2$ actually represents a formal series;

$$h^{-2}\delta^2\psi = D^2\psi + \frac{1}{12}h^2D^4\psi + \frac{1}{360}h^4D^6\psi - - - \tag{2.18}$$

We can use the Schrödinger equation in the form

$$D^2\psi = 2(V-E)\psi = \phi\psi \tag{2.19}$$

to simplify equation (2.18), yielding the result

$$h^{-2}\delta^2\psi = \phi\psi + \frac{1}{12}h^2 D^2(\phi\psi) + O(h^4) \qquad (2.20)$$

The Numerov method involves replacing the second derivative $D^2(\phi\psi)$ by the difference operator $h^{-2}\delta^2(\phi\psi)$ and dropping the higher order terms.

This yields the Numerov equation

$$h^{-2}\delta^2\psi = \phi\psi + \frac{1}{12}\delta^2(\phi\psi) \qquad (2.21)$$

Our (alternative) approach is to note that the term $\frac{1}{12}h^2 D^4\psi$ plays the role of a perturbation term, showing that (to order $h^2$) the effect of using $h^{-2}\delta^2$ to replace $D^2$ is equivalent to adding the perturbing operator $\frac{1}{12}h^2 D^4$ to the Hamiltonian operator.

### 2.2.2. Modified R-Method

Our aim is to find an equivalent relation to equation (2.16) without requiring the storage of the functions $\phi(x)$, $\phi(x+h)$, and $\phi(x-h)$ which the Numerov method requires. (It also needs certain instructions to make the transfers $\phi(x+h) \rightarrow \phi(x) \rightarrow \phi(x+h)$ as one passes from one step to the next).

Using a perturbation analysis we know that the first order effect of a perturbing operator $\lambda V$ is to give an energy shift of the form $\lambda\langle V\rangle$ where $\langle V\rangle$ is the expectation value of the operator V with respect to the unperturbed wave function. For our particular problem we need an expression for the expectation value of the operator $D^4$, taken with respect to the $\psi$ which obeys equation (2.19). We find

$$\langle D^4\rangle = \int \psi D^4\psi\, dx = \int (D^2\psi)(D^2\psi)\, dx + \text{b.t.}$$
$$= \int \psi\phi^2\psi\, dx + \text{b.t.} = \langle\phi^2\rangle + \text{b.t.} \qquad (2.22)$$

The boundary terms, b.t., which arise by integration by parts, are given by

$$\text{b.t.} = \Big[\psi D^3\psi - D\psi\,\psi\phi\Big]_A^B \qquad (2.23)$$

For bound state problems, like the one we are dealing with, the boundary terms vanish, with $A = -\infty$ and $B = \infty$, provided that the potential function V is <u>bounded</u>. Therefore it follows that the expectation value of $D^4$ is equal to $\langle\phi^2\rangle$, where $\phi^2$ is a multiplying function instead of a differential operator.

If two perturbing operators give the same expectation value, then they will give the same first order perturbed energy, giving an energy difference only at the $\lambda^2$ term. Therefore, if we replace the term $\frac{1}{12}h^4D^4\psi$ by its equivalent, i.e. $\frac{1}{12}h^4\phi^2$ in equation (2.20) we will get the value of the energy with an error proportional to the square of the perturbing parameter, i.e. $h^4$, because as we have pointed out the perturbation parameter is $h^2$. This leads to an equation for the R-method of the form

$$R(x) + R(x-h)^{-1} = 2 + h^2(V-E) + \frac{1}{12}h^4(V-E)^2 \qquad (2.24)$$

Equation (2.24) gives an $h^4$ process (for bounded potentials). The right hand side is a function of (V-E) at the <u>single</u> co-ordinate x, so the method is more simple than the Numerov method, which requires the retention of the (V-E) values at three neighbouring points.

As an example to show the advantages of this improved R-method, we deal with the potential $V = x^2 + \lambda x^2/(1+gx^2)$. Mitra [18] has used a matrix approach to solve this problem. He deals with the perturbed oscillator Schrödinger equation

$$-D^2\psi + \left[x^2 + \lambda x^2/(1+gx^2)\right]\psi = E\psi \qquad (2.25)$$

To solve equation (2.25) using the traditional Rayleigh-Ritz method it is necessary to choose the basis functions and then evaluate the matrix elements of the Hamiltonian. For this particular potential there is an extra difficulty. At large g values, e.g. g = 100, the perturbing potential is concentrated in a small bump near the origin. As a consequence, the numerical integration process which yields the matrix elements becomes difficult to perform accurately, and any error at this stage necessarily affects the eigenvalues resulting from the final matrix diagonalization.

We present a better way of solving this problem using equation (2.24)(Galicia and Killingbeck [19]). Table 6 shows a comparison between Mitra's method and our direct numerical integration method; we can see that even at large g values our method still works, giving a very accurate result.

We use equation (2.24) in a similar manner to equation(2.5), with starting condition $R(0) = R(-h)^{-1}$ at $x = 0$. However, the value of R(0) is given by

$$2R(0) = 2 + h^2\phi'(1 + \frac{1}{12}h^2\phi')$$

where $\phi' = (V-E)$, since in this case our Schrödinger equation is of the form $-D^2\psi + (V-E)\psi$ instead of equation (2.1). To incorporate the starting condition in the programme we can use a dividing factor K. R(0) is evaluated with $R(-h)^{-1} = 0$ and the result is divided by K, which is initially set equal to 2. At the end of the first cycle the instruction K = 1 is used to go back to the correct equation for all later x values. The stopping condition is as for equation (2.5).

## Table 6

## Eigenvalues of the Three Lowest Even-Parity States

| h | $\lambda = 0.1$<br>$\varepsilon = 0.1$ | 100<br>0.1 | 0.1<br>100 | 100<br>100 |
|---|---|---|---|---|
| 0.05 | 1.043173894<br>5.181095365<br>9.272820 | 9.976128009<br>49.29306035<br>87.447805 | 1.000841232<br>5.000928080<br>9.000952 | 1.836334485<br>5.928328447<br>9.949162 |
| $0.05/2^{1/4}$ | 1.043173987<br>5.181095215<br>9.272819 | 9.976154200<br>49.29287438<br>87.446244 | 1.000841333<br>5.000927960<br>9.000950 | 1.836335907<br>5.928328893<br>9.949162 |
| 0 | 1.04317408<br>5.18109506<br>9.272818 | 9.976180<br>49.29269<br>87.4447 | 1.00084143<br>5.0009278<br>9.000948 | 1.8363373<br>5.9283293<br>9.949162 |
| Mitra | 1.04317<br>5.18109<br>- | 9.97618<br>49.29269<br>- | 1.00084<br>5.00093<br>- | 1.8364<br>5.928<br>- |

Table 6 also shows results for the 2s and 3s excited states; they were calculated using the procedure explained in section 2.1.4.

Direct methods also permit the calculation of expectation values such as $\langle x^2 \rangle$, and allow us to "pick out" an excited state simply by increasing the number of nodes.

Table 7 shows results for the expectation value $\langle x^2 \rangle$ for the ground state. The way in which they are calculated is as follows. We do two calculations to get two E values, using $(1+\epsilon)x^2$ and $(1-\epsilon)x^2$ instead of $x^2$ in the potential function of equation (2.25). $\epsilon$ is a very small number, e.g. 0.001.

The value of $\langle x^2 \rangle$ is then given by

$$\langle x^2 \rangle = \frac{1}{2\varepsilon}\left[E_+ - E_-\right] \tag{2.26}$$

where $E_+$ and $E_-$ are the two energies.

Table 7

Ground State $\langle x^2 \rangle$ Values, $h = (0.05)/(2)^{1/4}$

| $g$ \ $\lambda$ | 0.1 | 100 |
|---|---|---|
| 0.1 | 0.48147 | 0.49997 |
| 100 | 0.05041 | 0.46524 |

In terms of first order perturbation theory, we are using the idea that the perturbations $\pm\varepsilon x^2$ change the energy by an amount $\pm\varepsilon\langle x^2\rangle$ if $\varepsilon$ is small; the use of the difference $(E_+ - E_-)$ removes any $\varepsilon^2$ error terms. In order to get a very good estimate of $\langle x^2 \rangle$ it is best to use two different h values to calculate $E_+$ and $E_-$, and then use an $h^2$-law to get a projective $E_+$ and $E_-$ value. The results shown in Table 7 were calculated using only one h value since looking at Table 6 we can see that the value of the energy is accurate up to 5 or 6 decimal places. This assures an accuracy for $\langle x^2 \rangle$ up to 5 decimal places. For $g = 100$ and $\lambda = 0.1$ there is an error in the value of $\langle x^2 \rangle$ because in this case the energy eigenvalue is not very accurate at this h value. For this particular case it will be necessary to use another h value to get $E_+$ and $E_-$ before calculating $\langle x^2 \rangle$.

If we use the Schrödinger equation in the form of equation (2.1) the corresponding R-equation takes the form

$$R(x) + R(x-h)^{-1} = 2 + 2h^2(V-E) + \frac{1}{6}h^4(V-E)$$

which in terms of the function $\phi = 2(V-E)$ takes the form

$$R(x)+R(x-h)^{-1}=2+h^2\phi+\frac{1}{12}h^4\phi^2 \qquad (2.27)$$

We have applied this equation to the potential $V=x^2$, using the same computing programme as for Mitra's problem, adding a multiplying factor of 2 for the function $\phi$. Results are shown in table 8 using different h values in order to extrapolate. The extrapolation will be done in section 2.2.4.

Table 8

Energy Eigenvalues for $V = x^2$

| h<br>Method | 0.01 | 0.02 | 0.03 |
|---|---|---|---|
| R-Method without correction | 0.7071010936 | 0.7070819496 | 0.7070506032 |
| F-Method without correction | 0.7071005320 | 0.7070817835 | 0.7070505262 |
| R-Method with correction | 0.7071038460 | 0.7070942890 | 0.7070786658 |
| F-Method with correction | 0.7071067800 | 0.7071067790 | 0.7071067712 |

## 2.2.3. Modified F-Method

An $h^4$ process based on the F-Method can also be developed. The one dimensional recursive relation takes the form

$$F(x)=F(x-h)\left[1+h^2F(x-h)\right]^{-1}+2(V-E)+\frac{1}{3}h^2(V-E)^2 \qquad (2.28)$$

In terms of the function $\phi$ it takes the form

$$F(x)=F(x-h)\left[1+h^2F(x-h)\right]^{-1}+\phi+\frac{1}{12}h^2\phi^2 \qquad (2.29)$$

We have applied this equation to the potential $V = x^2$ to compare the results with the previous methods. The starting condition is $F(0)=\frac{1}{6}h^2E^2-E$, and the stopping one is the same as for the R-Method;

the results are in table 8 together with those for the improved R-method.

### 2.2.4. $h^2$ - Extrapolation Process

In order to get an improved value of the energy we can use an $h^2$ process of extrapolation. We have calculated E for the potential $V = x^2$ using different strip widths and using our four one-dimensional numerical methods. To be able to use the same extrapolation formula for all our previous results we need first to calculate the energy using the R and F-Methods of sections 2.1.2. and 2.1.3. using two more values for h, e.g. h = 0.01 and 0.03.

The extrapolation formulae are

$$E = \frac{1}{3}\left[4E_1 - E_2\right] \tag{2.30}$$

and

$$E = \frac{1}{10}\left[15E_1 - 6E_2 + E_3\right] \tag{2.31}$$

Table 8 shows results for the eigenvalue E(h) using the R and F-Methods with and without the correction term. Table 9 shows results for the extrapolated eigenvalue using equations (2.30) and (2.31). The exact value, as we have pointed out is $E = 1/\sqrt{2} \approx 0.707106781$

Table 9

Energy Eigenvalues Using an $h^2$ - Extrapolation Process for $V = x^2$

| | R-Method without correction | F-Method without correction | R-Method with correction | F-Method with correction |
|---|---|---|---|---|
| $E_{(1,2)}$ | 0.707107474 | 0.707106781 | 0.707107032 | 0.707106780 |
| $E_{(1,3)}$ | 0.707092398 | 0.707092203 | 0.707099497 | 0.707106783 |
| $E_{(1,2,3)}$ | 0.707107529 | 0.707106780 | 0.707107062 | 0.707106780 |

At this stage we are now able to say that the modified F-Method is the one which gives the very best result, as we had predicted on the basis of perturbation-theoretic reasoning.

From table 8 we can see that even without the extrapolation formula it gives a very good estimate for the energy at $h = 0.01$. On the other hand even the "poor" R-Method gives a good estimate up to 6 figures using $E_{(1,2)}$.

We can use this $h^2$- extrapolation process for the potential of section 2.2.2., that is, $V = x^2 + \lambda x^2/(1+g x^2)$ with $h = 0.1$ and 0.05. Results are in table 10.

Table 10

Projected Energy Eigenvalue for $V = x^2 + \lambda x^2/(1+g x^2)$

| | $\lambda = 0.1$<br>$g = 0.1$ | 100<br>0.1 | 0.1<br>100 | 100<br>100 |
|---|---|---|---|---|
| $E_{(1,2)}$ | 1.04317426 | 9.97638864 | 1.00084178 | 1.83657797 |

### 2.2.5. Expectation Values

In section 2.2.2. we showed that expectation values can be calculated by means of (2.26). In order to get a very good value of $\langle x^N \rangle$ for a potential $V = x^N$ it is necessary to get the energy values, i.e. $E_+$ and $E_-$, up to a very high accuracy. We have proved, throughout the last sections, that the modified F-Method gives a very good estimate of the energy. Therefore we can rely on our previous results to obtain a good estimate of $\langle x^2 \rangle$ for $V = x^2$ and $\langle x^4 \rangle$ for $V = x^4$.

We have used h = 0.01 and h = 0.02 to calculate $E_+(0.01)$ and $E_+(0.02)$ and then we have applied an $h^2$- law to get $E_{+(1,2)}$ using (2.30). The same was done for $E_-$. We have used two different values for the perturbing parameter $\varepsilon$ (these are $\varepsilon = 0.01$ and $\varepsilon = 0.02$) in order to get two $\langle x^2 \rangle$ and $\langle x^4 \rangle$ values. We use them to get a projected value. Results for the energy and expectation values are shown in table 11 and table 12.

Table 11

Energy and Expectation Values for $V = x^2$

| | $\varepsilon = 0.01$ | $\varepsilon = 0.02$ |
|---|---|---|
| $E_+$ | 0.71063352 | 0.71414284 |
| $E_-$ | 0.70356236 | 0.70000000 |
| $\langle x^2 \rangle$ | 0.35355779 | 0.35357104 |

### Table 12

### Energy and Expectation Values for $V = x^4$

| | $\epsilon = 0.01$ | $\epsilon = 0.02$ |
|---|---|---|
| $E_+$ | 0.67020550 | 0.67241014 |
| $E_-$ | 0.66575218 | 0.66350300 |
| $\langle x^4 \rangle$ | 0.22266627 | 0.22267858 |

Therefore, using an $h^2$- law for the expectation values, we have

$$\langle x^2 \rangle = 0.353553(37)$$

and

$$\langle x^4 \rangle = 0.222662(16)$$

We note that the use of too small an $\epsilon$ value (e.g. $10^{-3}$, $10^{-4}$) can lead to rounding errors. The use of $\epsilon = 0.01$ and 0.02 avoids the rounding errors and gives results which can be reliably treated by an extrapolation process.

For example, we can see, from the results below, that although the values of $\epsilon$ are very small, i.e. 0.001 and 0.002, after applying an $h^2$- law the results should get worse for $\langle x^2 \rangle$ because of a loss of significant figures. Unreliable digits are bracketed.

| | $\epsilon = 0.001$ | $\epsilon = 0.002$ | $h^2$- law |
|---|---|---|---|
| $\langle x^2 \rangle$ | 0.35355(386) | 0.35355(397) | 0.35355(382) |
| $\langle x^4 \rangle$ | 0.22266(214) | 0.22266(208) | 0.22266(216) |

The virial theorem for the harmonic oscillator stands that $2E = (M+2)\langle X^M \rangle$, therefore for our particular case $\langle x^2 \rangle = \frac{1}{2}E$ and $\langle x^4 \rangle = \frac{1}{3}E$. We can use this result to show the accuracy of our results. First we need the value of the energy for $V = x^4$

for $h = 0.01$ and $0.02$. These energy values can be found using the F-method, equation (2.28). We have

$$E(0.01) = 0.6679862592$$

$$E(0.02) = 0.6679862516$$

hence

$$E_{(1,2)} = 0.667986261$$

Then, using $E_{(1,2)} = 0.707106781$ for $V = x^2$ we have

$$\langle x^2 \rangle = \tfrac{1}{2}E = 0.35355339$$

and

$$\langle x^4 \rangle = \tfrac{1}{3}E = 0.22266209$$

If we compare these results with the previous ones we can say that this method of calculating expectation values is much more accurate than that using a matrix approach. In general a matrix calculation will give $\langle x^N \rangle$ values in error by order $\eta$ when the eigenvalues are in error by order $\eta^2$, and the results for excited states (using a given basis size) are poorer than those for the ground state. The integration methods described in the present work do not suffer from these defects, as many trial calculations have shown. The ultimate limit appears to be set by the precision of the calculating apparatus, rather than by choice of basis functions, since basis functions are not used. Even <u>that</u> limit can be "postponed" by changing from the R function to the F function, as the results of the preceding sections show.

## 2.2.6. Direct Integration to Get $\langle x^N \rangle$

Numerical integration methods to calculate $\langle x^N \rangle$ have been developed by Killingbeck and Galicia [25]. Using a similar approach we have improved our F-Method to get expectation values *after* calculating the energy eigenvalue. The idea is simply as follows: the programme calculates the eigenfunction $\psi(x)$ as x increases, so that we can easily calculate the integrals $\int \psi x^2 \psi \, dx$ and $\int \psi^2 dx$ while the energy integration proceeds. We input the value of E that was given previously by the same programme (for that h value) and stop it when $\psi$ has reached a suitably small value. This requires a little care, since at very large x the calculated $\psi$ will depart from the true one, and these contaminating contributions to the integrals must be excluded. Experience shows that the estimates for $\langle x^N \rangle$ obtained differ from the true $\langle x^N \rangle$ by a term of order $h^2$ when h is small. Table 13 shows some results for the trial potential $V = x^2$.

Table 13

Expectation values for $V = x^2$

| | $h = 0.01$ | $h = 0.02$ | $h^2$ - law |
|---|---|---|---|
| $\langle x^2 \rangle$ | 0.35354508 | 0.35351999 | 0.35355344 |

# CHAPTER 3

# PERTURBATION METHODS IN $\lambda$

## 3.1. Hypervirial Theorem

### 3.1.1. Introduction

It has been shown by Killingbeck [24] that hypervirial relations yield the perturbation series for the energy E and for the expectation values $\langle r^N \rangle$ for a hydrogen atom with perturbation $\lambda r$, without the calculation of perturbed wave functions.

The classical mechanical equation of motion in terms of Poisson brackets and the corresponding Heisenberg quantum mechanical equation of motion provide a means for determining certain generalization of the virial theorem. The quantum mechanical treatment provides a set of integral conditions which might be used to determine the constants in an approximate wave function, as has been shown by Hirschfelder [30].

If W is a function of the co-ordinates and momenta, then for periodic motion (bound) the time average of the Poisson bracket (H,W) is zero. The commutator expectation value $\langle [W,H] \rangle$ in quantum mechanics is zero for any wave function corresponding to a stationary energy state of the system. It seems reasonable that with an appropriate selection of W there should be a dynamical relationship, in a time-average or space-average sense, which the system must obey.

Let W be an arbitrary function of the generalized co-ordinates and of the differential operators for their conjugate momenta. Let $\psi_m$ and $\psi_n$ be eigenfunctions with eigenvalues $E_m$ and $E_n$ respectively. Then, using the time-dependent Schrödinger equation we find

$$\frac{d}{dt}\int \psi_m^* W \psi_n \, d\tau = -(i/\hbar)\int \psi_m^* [W, H] \psi_n \, d\tau$$
$$= (i/\hbar)(E_m - E_n)\int \psi_m^* W \psi_n \, d\tau \qquad (3.1)$$

if $\psi_m$ and $\psi_n$ are eigenfunctions of the Hamiltonian operator H.

If the expectation value of W for a stationary energy state n is not infinite, equation (3.1) gives

$$0 = (i/\hbar)\int \psi_n^* [W, H] \psi_n \, d\tau \qquad (3.2)$$

This is what Hirschfelder calls the hypervirial theorem [HVT], as this relation corresponds to a generalization of the usual virial theorem, which follows from the particular choice $W = \bar{r}.\text{grad}$.

We define the operator

$$Q_W = (i/\hbar)[W, H] \qquad (3.3)$$

then equation (3.2) states that if $\psi$ is any solution to the Schrödinger equation, the expectation value of Q is equal to zero, i.e.

$$\int \psi^* Q_W \psi \, d\tau = 0 \qquad (3.4)$$

The Hellmann-Feynman theorem, (HFT) states that if $H = H(\lambda)$, where $\lambda$ is a parameter, then

$$\frac{\partial E_n}{\partial \lambda} = \langle \partial H/\partial \lambda \rangle_n \qquad (3.5)$$

We have already used this result to calculate expectation values in section 2.2.2.

As an application of the HVT and the HFT we treat the case of the potential $V = \lambda r - r^{-1}$. The Hamiltonian is taken to be

$$H = -\tfrac{1}{2}D^2 - r^{-1}D + V(r) \qquad (3.6)$$

where D is the operation of differentiation.

Choosing the function $W = r^N D$, and using the basic relations for commutators

$$[D, H] = DV + r^{-2}D \tag{3.7}$$

$$[r^N, H] = \frac{1}{2}N(N+1)r^{N-2} + Nr^{N-1}D \tag{3.8}$$

and the Jacobi identity $[AB, C] = A[B, C] + [A, C]B$, we arrive at the result

$$2NE\langle r^{N-1}\rangle = 2N\langle r^{N-1}V\rangle + \langle r^N(DV)\rangle - \frac{1}{4}N(N-1)(N-2)\langle r^{N-3}\rangle \tag{3.9}$$

Here we have used the diagonal hypervirial requirement that $\langle [r^N D, H]\rangle$ shall vanish for the eigenstates of equation (3.6). To make (3.6) and (3.9) refer to the radial eigenvalue problem for states of angular momentum $\ell$, we simply add the term $\frac{1}{2}\ell(\ell+1)r^{-2}$ into the potential $V(r)$.

The last term on the right of (3.9) simplifies a little if we use $W = r^{N+1}D$ instead of $r^N D$ in the hypervirial derivation, or simply set $N \rightarrow N+1$ in (3.9). We obtain the equation

$$(2N+2)E\langle r^N\rangle = (2N+3)\lambda\langle r^{N+1}\rangle - (2N+1)\langle r^{N-1}\rangle - \frac{1}{4}N(N^2-1)\langle r^{N-2}\rangle \tag{3.10}$$

if we take the case $V = -r^{-1} + \lambda r$.

In order to use this recursive relation we need a relationship between the energy E and the expectation values $\langle r\rangle$ and $\langle r^{-1}\rangle$. $\langle r\rangle$ is given by $\partial E/\partial\lambda$, according to the Hellmann-Feynmann theorem. Setting $N = 0$ in (3.10) yields the traditional virial theorem, $2E = 3\lambda\langle r\rangle - \langle r^{-1}\rangle$, so that $\langle r^{-1}\rangle$ can be calculated from E and $\langle r\rangle$. Postulating a power series for the energy, then, we can express the series for $\langle r \rangle$ and $\langle r^{-1} \rangle$ in terms of the energy coefficients, as follows,

$$E = \sum E_n \lambda^n \qquad n = 0, 1, 2, \dots \tag{3.11a}$$

$$\langle r \rangle = \sum (n+1) E_{n+1} \lambda^n = \partial E / \partial \lambda \tag{3.11b}$$

$$\langle r^{-1} \rangle = \sum (3n-2) E_n \lambda^n = 3\lambda \langle r \rangle - 2E \tag{3.11c}$$

We also express other $\langle r^N \rangle$ values as power series,

$$\langle r^N \rangle = X_{N,0} + X_{N,1} \lambda + X_{N,2} \lambda^2 + \cdots + X_{N,N} \lambda^N \tag{3.11d}$$

The idea in mind is to get as many $E_n$ values as possible and also to obtain the numerical values of the $X_{N,M}$. As we can see, the $X_{N,0}$'s do not depend on the perturbing term, so they can be calculated independently of $\lambda$. For the 1s state we can establish that $X_{N+1,0} = \frac{1}{2}(N+3)X_{N,0}$ holds, by using the explicit unperturbed function, but this procedure is cumbersome. In a subsequent section we will give a general equation which uses only the quantity $E_0$ to get the energy coefficients for excited states as well as for the ground state.

In order to describe the rest of the claculation we use the label $\{N,M\}$ for the equation arising by taking the $\lambda^M$ terms in (3.10) for some N.

We have found out that to get Q of the E-coefficients we need Q of the $X_{N,1}$, (Q-1) of the $X_{N,2}$, Q-2 of the $X_{N,3}$, etc., and 1 coefficient of the form $X_{N,Q-1}$.

Another important feature is that to get the value of the $X_{N,j}$ for some j we only need to know the set $X_{N,i}$ where i<j; this makes the calculation even easier. Killingbeck [24] has calculated up to $E_5$ by hand and Austin [28] calculated many $E_n$ using a computer.

We have developed a programme for the C.B.M. Pet mini-computer which calculates the perturbation series up to high order, for any state and for a perturbing potential $\lambda r^P$, where P is any positive integer.

The programme enables us to get the series for other expectation values. In particular the series for $\langle r \rangle$, $\langle r^2 \rangle$ and the higher $\langle r^N \rangle$ can be calculated up to high order also.

Since we have the obvious requirement $\langle r^0 \rangle = \langle 1 \rangle = 1$, it follows that we require all the $X_{0,M}$ with $M \neq 0$ to be equal to zero, with $X_{0,0} = 1$. The values of $E_0$ and $X_{0,0}$ must be given initially to start off the calculation for s states. For states with $\ell > 0$ the value of $X_{-1,0}$ is also required, but it follows from the virial relation $\langle r^{-1} \rangle = -2E_0$ for the unperturbed hydrogen atom problem. The details of the required initial input data will be discussed further in section 3.1.5.

### 3.1.2. Hyper Programme

As we pointed out previously it is possible to devise a general programme which calculates all the coefficients $X_{N,M}$ and the series for the energy up to high order, requiring only the input of the unperturbed energy $E_0$ and the angular momentum $\ell$.

The general equation for the coefficients $X_{N,0}$ takes the following form (with starting value $X_{0,0} = 1$),

$$(2N+2)E_0 X_{N,0} = -(2N+1)X_{N-1,0} - \frac{1}{4}N(N^2-1)X_{N-2,0} \quad (3.12)$$

If the perturbing potential is $\lambda r^P$ (instead of $\lambda r$) we obtain the following generalization of (3.10)

$$(2N+2)E_0\langle r^N\rangle = (2N+2+P)\lambda\langle r^{N+P}\rangle - (2N+1)\langle r^{N-1}\rangle - \frac{1}{4}N(N^2-1)\langle r^{N-2}\rangle - (2N+2)E'\langle r^N\rangle \qquad (3.13)$$

where $E' = \sum E_j \lambda^j \ (j>0)$

As the value of P increases, the size of the coefficients $X_{N,M}$ increases considerably, which yields two difficulties. When the numbers concerned are large, loss of significant figures occurs when the computer performs a long sequence of operations on the numbers. The minicomputer cannot calculate the $X_{N,M}$ beyond the point at which they reach its overflow level ($\sim 10^{38}$). If n(P) is the number of terms in the energy series obtainable for the 1s state with perturbation $\lambda r^P$, we find (for the C.B.M. Pet), n(1) = 26, n(4) = 8, and n(8) = 3.

Table 14 shows the energy coefficients for $V = \lambda r - r^P$ for P = 1,2,3,4 for the 1s state. We can see from these results that up to $E_{10}$ and for P = 1 and 2 the results are very accurate and reliable, whereas for P≥3 the size of the energy coefficients increases rapidly.

Table 14

1s State Energy Perturbation Coefficients

| P<br>En | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $E_0$ | -0.5 | -0.5 | -0.5 | -0.5 |
| $E_1$ | 1.5 | 3 | 7.5 | 22.5 |
| $E_2$ | -1.5 | -32.25 | -668.4375 | -17355.9375 |
| $E_3$ | 6.75 | 1362.75 | 264894.141 | 78606633.5 |
| $E_4$ | -49.6875 | -103280.8593 | -231369814 | -1.06540776E+12 |
| $E_5$ | 480.375 | 11477957.9 | 3.6606458E+11 | 3.4377598E+16 |
| $E_6$ | -5583 | -1.71918761E+09 | -9.54820392E+14 | -2.29200098E+21 |

| En \ P | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $E_7$ | 74557.3359 | 3.31953619E+11 | 3.85440636E+18 | 2.84124228E+26 |
| $E_8$ | -1114319.34 | -8.0350229E+13 | -2.29091021E+22 | -6.03880379E+31 |
| $E_9$ | 18329171.5 | 2.38890928E+16 | 1.92398529E+26 | - |
| $E_{10}$ | -328051588 | -8.5807826E+18 | -2.20644282E+30 | - |

To calculate the coefficients for the expectation values, for the potential $V = \lambda r - r^{-1}$, without using eigenfunctions we use equations (3.11b) and (3.11d).

The Hellmann-Feynman theorem provides an equation for $\langle r^2 \rangle$ for the potential $V = \lambda r^2 - r^{-1}$, which has the form

$$\langle r^2 \rangle = \sum (n+1) E_{n+1} \lambda^n$$

or in general, for $V = \lambda r^P - r^{-1}$ it yields the result

$$\langle r^P \rangle = \sum (n+1) E_{n+1} \lambda^n \tag{3.14}$$

We show results for $\langle r \rangle$ and $\langle r^2 \rangle$ for P = 1,2 for the 1s state. Although the programme can be used for different values of P and for other s states we do not give the details here because the results are not very accurate, since the size of the coefficients increases even more rapidly for these excited states. Results are shown in tables 15 and 16 respectively.

Table 15

1s State Expectation Value Coefficients, P = 1

|  | $\langle r \rangle$ | $\langle r^2 \rangle$ |
|---|---|---|
| $C_0$ | 1.5 | 3 |
| $C_1$ | -3 | -13.5 |
| $C_2$ | 20.25 | 115.5 |

| | $\langle r \rangle$ | $\langle r^2 \rangle$ |
|---|---|---|
| $C_3$ | -198.75 | -1299.375 |
| $C_4$ | 2401.875 | 17325 |
| $C_5$ | -33498 | -261571.078 |
| $C_6$ | 521901.351 | 4363821.61 |
| $C_7$ | -8914554.72 | -79268073.3 |
| $C_8$ | 164962543.5 | 1.55269662E+09 |
| $C_9$ | -3280515880 | -3.25761178E+10 |
| $C_{10}$ | 6.970375E+10 | 7.28399280E+11 |

Table 16

1s State Expectation Value Coefficients, P = 2

| | $\langle r \rangle$ | $\langle r^2 \rangle$ |
|---|---|---|
| $C_0$ | 1.5 | 3 |
| $C_1$ | -13.5 | -64.5 |
| $C_2$ | 677.25 | 4088.25 |
| $C_3$ | -59110.312 | -413123.43 |
| $C_4$ | 7309433.67 | 57389789.5 |
| $C_5$ | -1.18599208E+09 | -1.03151257E+10 |
| $C_6$ | 2.43142777E+11 | 2.32367533E+12 |
| $C_7$ | -6.15703651E+13 | -6.42801832E+14 |
| $C_8$ | 1.89459177E+16 | 2.15001835E+17 |
| $C_9$ | -6.98901374E+18 | -8.5807826E+19 |
| $C_{10}$ | 3.05369428E+21 | 4.03801904E+22 |

At first sight equation (3.13) might look rather difficult to solve, since we are replacing the energy and the expectation values by their corresponding series. When we first started looking at this way of calculating the energy coefficients we used a programmable pocket calculator [24]. Using the label $\{N,M\}$ we used the equations $\{2,M\}$ $(M\leq 4)$, $\{3,M\}$ $(M\leq 3)$, $\{4,1\}$, $\{4,2\}$ and $\{5,1\}$ to calculate the energy series to fifth order. We did not follow any special order to solve (3.13). In a second attempt to calculate two more energy coefficients we discovered that the coefficients $X_{N,M}$ can easily be calculated, as follows. We first calculate as many $X_{N,0}$ coefficients as we want, as they do not depend on anything but $E_0$. To get the energy to Qth order (for perturbation $\lambda r^P$) it suffices to calculate PQ of the $X_{N,0}$ coefficents. With these known coefficients we can now calculate the $X_{N,1}$ coefficients, that is, the coefficients for the energy and expectation value series at first order in $\lambda$. Although we can obtain PQ of these coefficients, we have found out that, to find the rest of the coefficients, we only require PQ-P of these $X_{N,1}$ coefficients. Then we calculate the $X_{N,2}$ requiring PQ-2P coefficients, and so on, until we finally calculate only one of the form $X_{N,Q-1}$. Therefore, what is relevant in solving this set of recursive equations is the fact that we do not need the coefficients of higher order in $\lambda$ to calculate the lower ones. And finally, to calculate $E_j$, for a given value of j, we only need the value of $X_{P,j-1}$. The BASIC programme and flow-chart are given in Appendix A2.

### 3.1.3. Hypervirial Results for Excited s States

We have already mentioned that the programme is written in such a way that only the value of $E_0$ needs to be stored to start off the programme. In this way we can obtain the energy coefficients for any s state. For other excited states, such as 2p, 3p, 3d, ..., an extra line must be added in order to include the dependence on the angular momentum; this will be discussed in a subsequent section. For the 2s state $E_0 = -0.125$ and for the 3s state $E_0 = -1/18$; giving these values, one at a time, we obtain the energy coefficients which are presented in table 17 and 18, for P = 1,2. As we can see from the results of tables (14-18) the energy and expectation values series are all alternating: this typical property of the series provides a clue to check whether the programme is working properly or not.

Table 17

2s and 3s States Energy Perturbation Coefficients, P = 1

| | 2s | 3s |
|---|---|---|
| $E_0$ | -0.125 | $-0.0555\bar{5}$ |
| $E_1$ | 6 | 13.5 |
| $E_2$ | -66 | -688.500001 |
| $E_3$ | 3312 | 152543.251 |
| $E_4$ | -271680 | -54048288.2 |
| $E_5$ | 28848384 | 2.45922332E+10 |

Table 18

2s and 3s States Energy Perturbation Coefficients, P = 2

| | 2s | 3s |
|---|---|---|
| $E_0$ | -0.125 | -0.05555 |
| $E_1$ | 42 | 207 |
| $E_2$ | -14784 | -670497.753 |
| $E_3$ | 19923456 | 7.73691005E+09 |
| $E_4$ | -4.53150566E+10 | -1.45951474E+14 |
| $E_5$ | 1.41421867E+14 | 3.66612987E+18 |

### 3.1.4. Charmonium Type Potentials

The problem of finding the energy eigenvalue for the charmonium system, in other terms, the bound quark-antiquark pair has attracted attention over the past years. Killingbeck [10] has dealt with this problem for the potential $V = -1/r + 2\lambda r + 2\lambda^2 r^2$ He has found out that the energy series for the ground state is finite and agrees with the exact eigenvalue for $\lambda > 0$. The series takes the form $E = E_0 + E_1\lambda = -\frac{1}{2} + 3\lambda$. He has proved that the next two energy coefficients $E_2$ and $E_3$ are equal to zero, by explicitly calculating the first order perturbed wave function.

If we set $W = f(r)D$ in the hypervirial argument of section 3.1.1 , and study a Hamiltonian with kinetic energy operator $T = -\alpha D^2$, then the following more general version of the hypervirial theorem is obtained,

$$2\langle f'T\rangle = \langle fV'\rangle - \frac{1}{2}\alpha\langle f'''\rangle \tag{3.15}$$

With $\alpha = \frac{1}{2}$, we obtain, using $V = -1/r + 2\lambda r + 2\lambda^2 r^2$,

$$2\langle f'(E + r^{-1} - 2\lambda r - 2\lambda^2 r^2)\rangle = \langle f(r^{-2} + 2\lambda r + 4\lambda^2 r)\rangle - \frac{1}{4}\langle f'''\rangle$$

Choosing the function f of the form $f = r^{N+1}$ , we obtain the recursive relation

$$(2N+2)E\langle r^N\rangle + (2N+1)\langle r^{N-1}\rangle + \frac{1}{4}N(N^2-1)\langle r^{N-2}\rangle = (4N+6)\lambda\langle r^{N+1}\rangle + (4N+8)\lambda^2\langle r^{N+2}\rangle \tag{3.16}$$

We have developed a programme to solve (3.16) to get energy coefficients, using the C.B.M. minicomputer. By means of this programme it is possible to check that the energy coefficients $E_n$ are all equal to zero, for $2 \leq n \leq 8$. We have calculated the coefficient $X_{1,8}$ of the $\langle r\rangle$ series at 8th order in $\lambda$ and $X_{2,7}$, which is the coefficient of $\langle r^2 \rangle$ series at 7th order in $\lambda$, by hand because they are the coefficients needed to calculate $E_9$. We found an error in the 9th significant figure for $X_{1,8}$ as given by the minicomputer. Using the "new" value for $X_{1,8}$ we found that $E_9 = 0$. The reason is that when the PET starts writing the numbers in exponential form there is a loss of accuracy in the 9th figure, that is, rounding errors affect the accuracy of the calculations. After this discovery we decided to run the programme in a big computer using Fortran. This time we found that indeed $E_9$, and also $E_{10}$, are equal to zero. Finally we ran the programme using Fortran double precision to avoid rounding errors. The results show that up to $E_{16}$ all the energy coefficients, except $E_0$ and $E_1$, are equal to zero.

We can infer that the rest of the coefficients are all equal to zero, having as a result a finite series for the energy. The programme, either in Basic or Fortran, is written so as to enable us to obtain the energy coefficients for excited states also. The BASIC programme is given in Appendix A3.

Since the programme is written in such a way as to allow us to get the energy coefficients for any state, we have used it to obtain the energy series for the 2s state; the results are shown in table 19.

Table 19

2s State Energy Perturbation Coefficients for $V = -1/r+2\lambda r+2\lambda^2 r^2$

$E_0 = -0.125$

$E_1 = 12$

$E_2 = -180$

$E_3 = 18720$

$E_4 = -2972160$

$E_5 = 600099840$

### 3.1.5. High Order Excited States

In section 3.1.3. it was mentioned that it is possible to include the dependence on the angular momentum $\ell$ in equation (3.13) or (3.16) for the calculation of the energy coefficients. The extra term to put on the r.h.s. of equation (3.13) or (3.16) is $N\ell(\ell+1)\langle r^{N-2}\rangle$, so that the total term involving $\langle r^{N-2}\rangle$ becomes $\frac{1}{4}N\left[(N^2-1)+4\ell(\ell+1)\right]\langle r^{N-2}\rangle$. If $\ell>0$ this term is not zero at N = 1. Thus, for the calculation of the energy coefficients for an excited state with $\ell\neq 0$ it is required to know the coefficients for the $\langle r^{-1}\rangle$ series at first order in $\lambda$, in order to start off the recursive calculation.

We need the value of $X_{-1,0}$ and $X_{-1,1}$. For the potential $-1/r+2\lambda r+2\lambda^2 r^2$, we can use the hypervirial theorem to show that $X_{-1,0} = -2E_0$ and $X_{-1,1} = E_1 = 2X_{1,0}$. Adding these values to the Hyper-Programme we find the energy series for the 2p state for the charmonium type potential; the coefficients are shown in table 20.

Table 20

2p State Energy Perturbation Coefficients for $V = 1/r+2\lambda r+2\lambda^2 r^2$

$E_0 = -0.125$

$E_1 = 10$

$E_2 = -139.5$

$E_3 = 16480$

$E_4 = -2700439$

$E_5 = 553828656$

### 3.1.6. Expectation Values for $V = -1/r+2\lambda r+2\lambda^2 r^2$

By means of equation (3.16) we can get all the coefficients $X_{N,M}$ for the 1s state. We put them into equation (3.11d) to obtain, without eigenfunctions, the series for $\langle r\rangle$ and $\langle r^2\rangle$ These coefficients are shown in table 21. The Rayleigh-Schrödinger series for $\langle r\rangle$ and $\langle r^2\rangle$ obey the following relationship based on the Hellmann-Feynman theorem

$$\frac{dE}{d\lambda} = 2\langle r\rangle_\lambda + 4\lambda\langle r^2\rangle_\lambda = 3 \tag{3.17}$$

For $\lambda > 0$, $dE/d\lambda = 3$. This result has been checked by Killingbeck [10].

We have also checked relation (3.17) for $\lambda = 0.1$ and $\lambda < 0$. For $\lambda$ negative the result is not exactly 3 but very close to it. We have used the partial sums to show that the value lies in the neighbourhood of 3. For $\lambda < 0$ the energy $E(\lambda)$ contains a component which is not given by the Rayleigh-Schrödinger series, as has been shown by Killingbeck [10]. The problem of a potential with $\lambda < 0$ will be discussed in more detail in the next chapter.

Table 21

1s State Expectation Value Coefficients for $V = -1/r+2\lambda r+2\lambda^2 r^2$

| | $\langle r\rangle$ | $\langle r^2\rangle$ |
|---|---|---|
| $C_0$ | 1.5 | 3 |
| $C_1$ | -6 | -27 |
| $C_2$ | 54 | 333 |
| $C_3$ | -666 | -4977 |
| $C_4$ | 9954 | 85563 |
| $C_5$ | -171126 | -1645947 |
| $C_6$ | 3291894 | 34845093 |
| $C_7$ | -69690186 | -802990017 |
| $C_8$ | 1.60598004E+09 | 1.99875992E+10 |
| $C_9$ | -3.99751984E+10 | -5.34279859E+11 |
| $C_{10}$ | 1.068559972E+12 | 1.52663509E+13 |

Within the theory of Padé approximants it is known that the [N,N] Padé approximant to a power series, (particularly if that series is a member of the class of Stieltjes series), converges fairly quickly as N increases. Having this in mind it is then possible to use the Padé approximants to get a good estimate of the energy eigenvalue or any of the expectation values. The use of Padé approximants in perturbation theory is often numerical; it is often the case that a formal proof that Padé approximants should work for a perturbation series lags behind the empirical demonstration that they do work.

## 3.2. Padé Approximants

### 3.2.1. Introduction

The Padé approximants are a particular type of rational fraction approximation to the value of a function, (Baker [22]).

Definition 3.1. - Let the [L, M] Padé approximant to the series $A(x)$ be denoted by

$$[L,M] = P_L(x)/Q_M(x) \qquad (3.18)$$

where $P_L(x)$ is a polynomial of degree at most L and $Q_M$ a polynomial of degree at most M. We require that the formal power series for P/Q agrees with the $A(x)$ series up to the (L+M)th power.

The following theorem is due to Frobenius, G., and Padé, H.:

Theorem 3.1. - (Theorem of Uniqueness). The [L,M] Padé approximant to any formal power series $A(x)$, when it exists, is unique. (For the proof see ref. [22] page 8).

This theorem holds whether the defining equations are nonsingular or not. If they are nonsingular, then they can be solved directly to yield

$$[L,M] = \frac{\begin{vmatrix} a_{L-M+1} & a_{L-M+2} & \cdots & a_{L+1} \\ \vdots & & \ddots & \\ a_L & a_{L+1} & \cdots & a_{L+M} \\ \sum_{j=M}^{L} a_{j-M}\lambda^j & \sum_{j=M-1}^{L} a_{j-M+1}\lambda^j & \cdots & \sum_{j=0}^{L} a_j \lambda^j \end{vmatrix}}{\begin{vmatrix} a_{L-M+1} & a_{L-M+2} & \cdots & a_{L+1} \\ \vdots & \vdots & \ddots & \vdots \\ a_L & a_{L+M} & \cdots & a_{L+M} \\ \lambda^M & \lambda^{M-1} & \cdots & 1 \end{vmatrix}} \tag{3.19}$$

where we define $a_n \equiv 0$ if $n<0$; $q_j \equiv 0$ if $j>M$; and, if the lower index on a sum exceeds the upper, the sum is replaced by zero.

Using the coefficients given in table 14 for the energy series for the potentials $V = \lambda r - r^{-1}$ and $\lambda r^2 - r^{-1}$, we have applied the determinant (3.19) for certain values of $\lambda$ to get the Padé approximants to these series. Killingbeck [24] gives some results for the potential $V = \lambda r - r^{-1}$ for $\lambda = 0.05$, 0.10, and 0.15. He shows that the $[L+1,L]$ approximants converge from above to the correct eigenvalue (as found by the method of section 2.1.2.), while the $[L,L]$ approximants converge from below.

This way of calculating the Padé approximants to a series is quite cumbersome since the determinants in (3.19) become bigger and bigger as the number of coefficients increases.

Since we are interested in the numerical value of the Padé approximants, rather than in the appearance of the polynomials, we shift to another way of calculating them.

### 3.2.2. Wynn's Algorithm

Wynn [23] has designed an algorithm to evaluate Padé approximants without the use of big determinants. The idea is based on the relation

$$S^{i+2}_{n-1} = S^{i}_{n} + \left(S^{i+1}_{n} - S^{i+1}_{n-1}\right)^{-1} \qquad \begin{array}{l} n = 1,2,3,\ldots \\ i = 0,1,2,\ldots \end{array} \qquad (3.20)$$

where $S^{m}_{\ell}$ is the $\ell$ element of column $m$ in an "S array". We start by considering all $S^{0}_{n}$ equal to zero and setting the $S^{1}_{n}$ equal to the partial sums of the series (for a given $\lambda$). Using relation (3.20) recurrently we form successive columns of the S array, and the $S^{m}_{\ell}$, with $m$ even, are exactly the $[L,M]$ Padé approximants to the series (for our chosen $\lambda$ value).

We have written a programme based on Wynn's algorithm for the C.B.M. Minicomputer which evaluates Padé approximants to the perturbation series, for the potential $V = \lambda r^{P} - r^{-1}$, for some $\lambda$ value. It is given in Appendix A4. The basic point about the programme is that it directly produces the numerical <u>value</u> of the approximants for a given $\lambda$ without explicitly constructing the approximants as rational fractions at an intermediate stage.

### 3.2.3. Applications of Wynn's Algorithm to Perturbation Series

We have applied Wynn's algorithm to the perturbation energy series for the potential $V = \lambda r^{P} - r^{-1}$ with P = 1,2. Results are shown in table 22 for the 1s and 2s states for selected values of $\lambda$. Although the Padé approximants method increases the range of $\lambda$ over which the series can give a good estimate of the energy, in practice there will still be an upper limit to the $\lambda$ value for which even the Padé approximants can give reliable results. The results indicate that the exact energy lies between $[L+1,L]$ and

$[L,L]$; the accurate energy was found using the F-method of section 2.1.3. Killingbeck and Galicia [25] have applied Wynn's algorithm to these series; whose results are those of table 22 in connection with the $\psi(0)$ problem (section 4.2).

Table 22

Padé Approximants for $V = \lambda r^P - r^{-1}$

| P | State | $\lambda$ | $[5,4]$ | $[5,5]$ | Exact |
|---|---|---|---|---|---|
| 1 | 1s | 0.10 | -0.360899563 | -0.360900277 | -0.3609000(43) |
| 1 | 2s | 0.01 | -0.069671275 | -0.069671614 | -0.0696715(21) |
| 2 | 1s | 0.01 | -0.472392041 | -0.472393160 | -0.4723927(36) |
| 2 | 2s | 0.0003 | -0.113392947 | -0.113393085 | -0.1133930(38) |

Another application of Wynn's algorithm is the calculation of expectation values, such as $\langle r\rangle$ and $\langle r^2\rangle$, using perturbation series. We have considered the potential $V = \lambda r - r^{-1}$ at a given $\lambda$ value.

a) By means of Wynn's algorithm it is possible to get a value for $\langle r\rangle$ and $\langle r^2\rangle$ starting from the perturbation series for them. For $\lambda = 0.05$ the results are as follows:

| | $[6,5]$ | $[6,6]$ |
|---|---|---|
| $\langle r\rangle$ | 1.38480039 | 1.38480040 |
| $\langle r^2\rangle$ | 2.51422862 | 2.51422869 |

b) Using the hypervirial relation

$$5\lambda\langle r^2\rangle = 3+4E\langle r\rangle \tag{3.21}$$

we can either calculate the value of $\langle r\rangle$ or $\langle r^2\rangle$ by obtaining E and $\langle r^2\rangle$ or $\langle r\rangle$, respectively, from Padé approximants for their series.

For $\lambda = 0.05$ we obtain:

$\langle r \rangle = 1.38480040$

$\langle r^2 \rangle = 2.51422865$

From these results we can check once more that the exact value lies between $\left[L+1, L\right]$ and $\left[L, L\right]$ Padé approximants.

Wynn's algorithm has also been used to get Padé approximants to the energy series for the charmonium type potential for the 2s state. Results are as follows, for $\lambda = 0.001$:

$\left[2,2\right] = -0.113163838$

$\left[2,1\right] = -0.113163044$

where we have used the energy coefficients given in table 19.

# CHAPTER 4

## FURTHER APPLICATIONS OF THE NUMERICAL TECHNIQUES

### 4.1. Quasi-Bound States

### 4.1.1. R-Method for $\lambda < 0$

In section 2.1.4. we applied the R-Method for a hydrogen-like potential, $\lambda r - r^{-1}$. In this section we present an approach to solve the Schrödinger equation with a perturbing operator which is unbounded from below.

Killingbeck [27] has looked at the problem of calculating the quasi-bound-state energy values for a perturbed oscillator and a perturbed hydrogen atom.

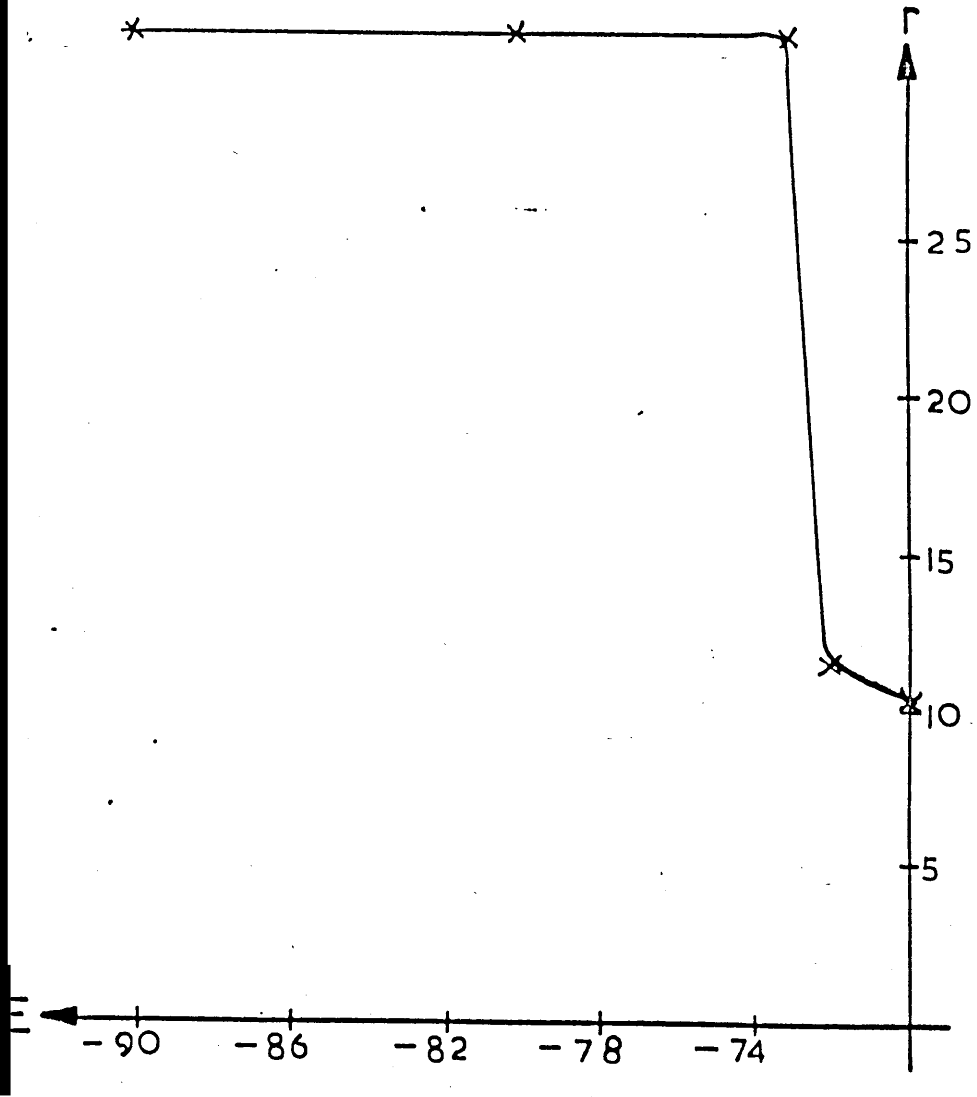
We use a different criterion to find the energy "eigenvalues" from the one used in previous sections. For a given $\lambda < 0$ and a value of the strip width h, we use our R-Method starting at $\psi(h) = 1$. The initial trial E is obtained using Padé approximants, e.g. the [5,5] gives a good estimate for different negative values of $\lambda$. The R-Method programme is modified so that it prints out the r values at which the wavefunction has a node. For example, if $\psi(r)$ is positive and $\psi(r+h)$ is negative, then the programme prints out the quantity $hR(r)\left[R(r)-1\right]^{-1}+r$. This is the interpolated estimate of the r value at which the wavefunction has a node. As E varies, the quantity $\left|\partial r/\partial E\right|$ for a given node will show a sharp maximum.

The most accurate energy value will be considered to be the one that lies between the maximum and minimum on the graph of r(E) against E. (Specimen graphs are shown here).

$E = -0.530663$

$\lambda = -0.02$

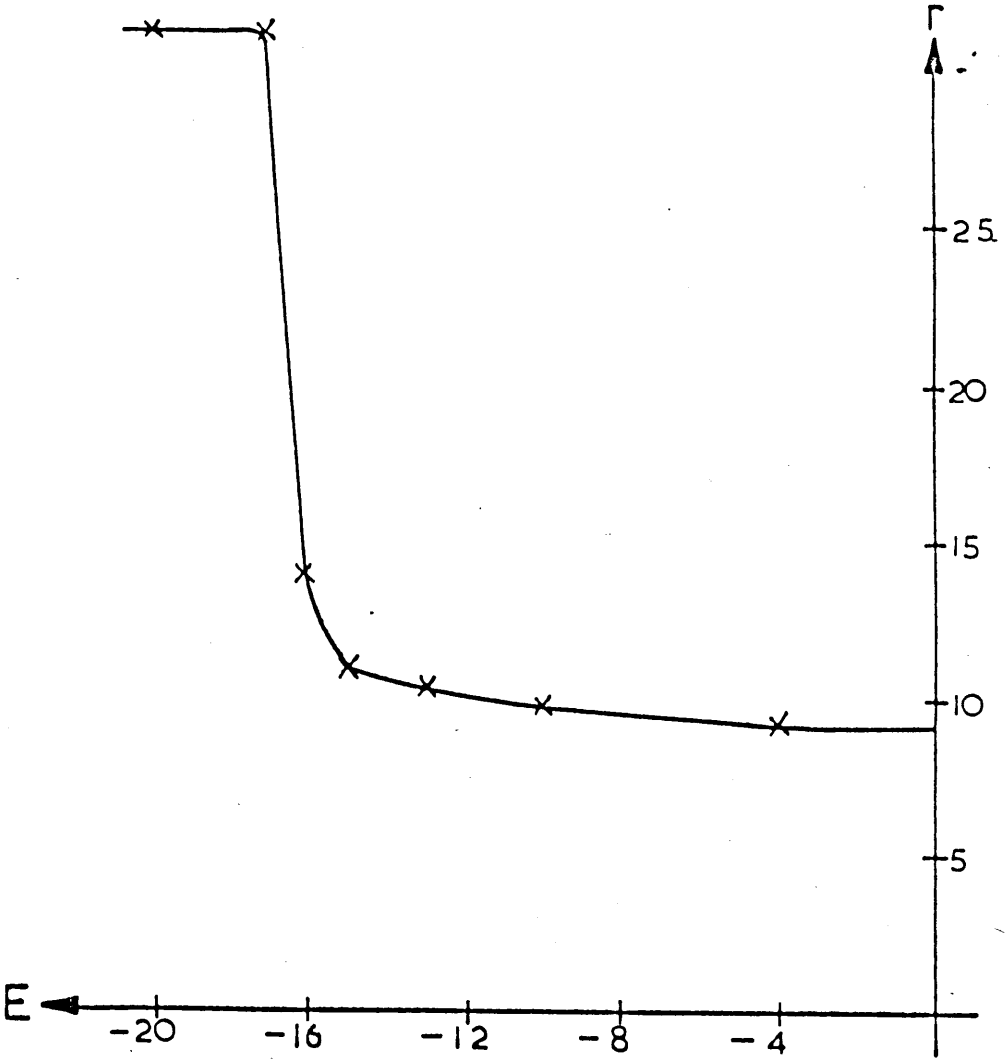
$h = 0.04$



SCALE $E = -0.5304 + E \times 10^{-6}$

$\lambda = -0.02$

$h = 0.02$

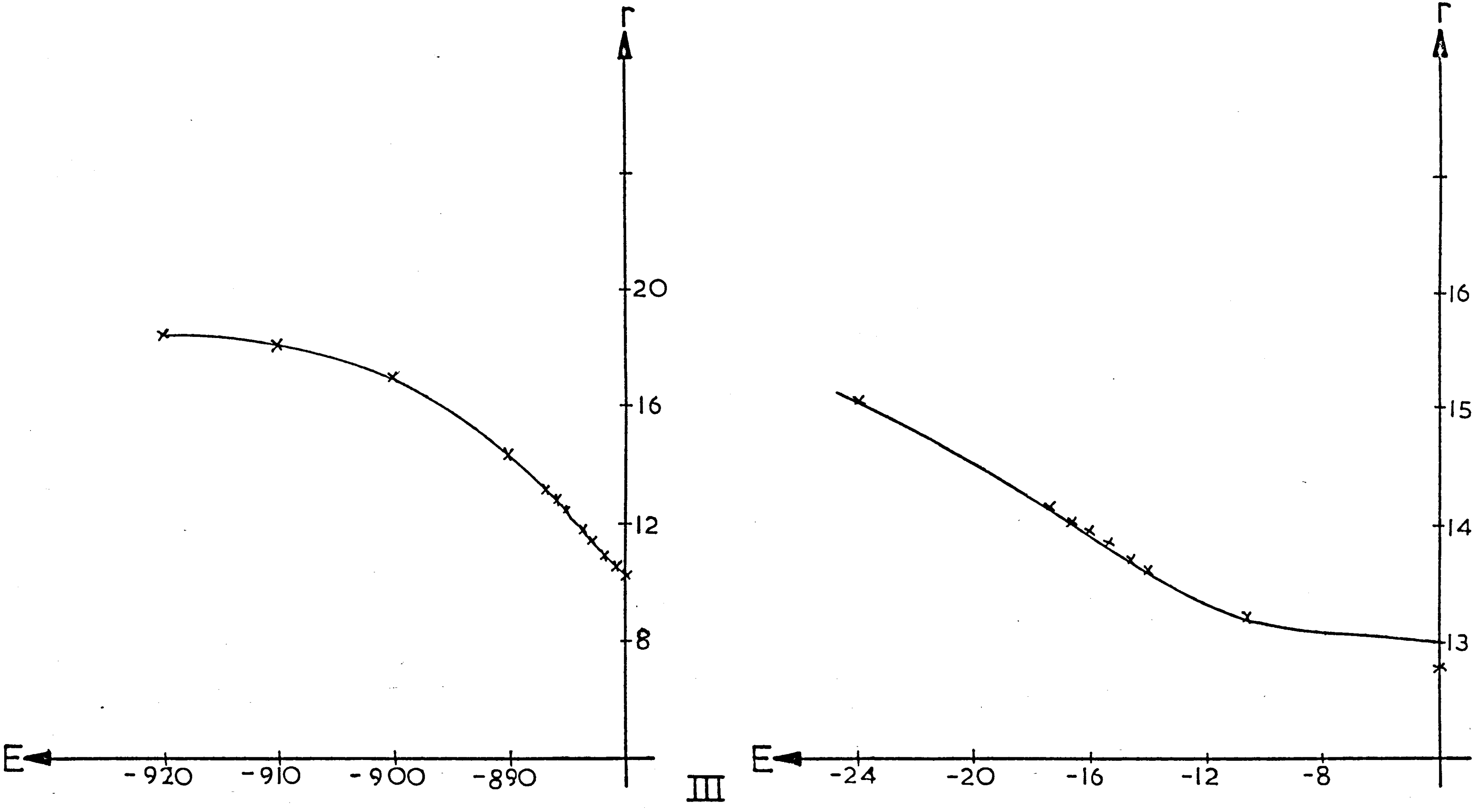


SCALE $E = -0.5306 + E \times 10^{-6}$

II

$\lambda = -0.04$ $E = -0.563059$ $\lambda = -0.04$

$h = 0.04$ $h = 0.02$



III

SCALE $E = -.562 + E \times 10^{-6}$ SCALE $E = -.5630 + E \times 10^{-6}$

It is easy to see from the graphs that as $\lambda$ gets more negative it renders it more difficult to decide which value of E is the most accurate. Using an $h^2$-law it is possible to get a good extrapolated result for the E value which corresponds to the limit of zero h. Some typical energy values are presented in table 23 together with the projected energy.

Table 23

Energy Values for $V = \lambda r - r^{-1}$, $\lambda < 0$ (First node)

| E(h) \ $\lambda$ | -0.01 | -0.02 | -0.03 | -0.04 | -0.05 |
|---|---|---|---|---|---|
| E(0.02) | -0.5151085 | -0.5306155 | -0.5465445 | -0.5630205 | -0.5802005 |
| E(0.04) | -0.5149615 | -0.5304725 | -0.5464055 | -0.5628875 | -0.5801105 |
| E | -0.515157 | -0.5306632 | -0.546590 | -0.56300 | -0.580230 |

We must bear in mind that this value for the energy is taken at the first node. We can see from the results of Table 24 that this value varies as we pass from node to node. Killingbeck [31] calculates the energy for a potential $V = 7.5r^2 e^r$ by a numerical integration procedure similar to the one described here and shows that the energy value, although changing slightly from node to node, stabilizes at higher node numbers.

We apply the method to the present problem for $\lambda = -0.02$ and -0.04. The results are grouped together in tables (24-27)

## Table 24

## R(E) Values for Selected Nodes, $\lambda = -0.02$, h = 0.04

| Node / Energy | 1 | 2 | 3 | 9 |
|---|---|---|---|---|
| -0.530470 | 10.36 | 31.48 | 36.68 | 57.20 |
| -0.530471 | 10.68 | 31.48 | 36.68 | 57.20 |
| -0.530472 | 11.20 | 31.48 | 36.68 | 57.20 |
| -0.530473 | 31.48 | 36.68 | 40.96 | 59.9 |
| -0.530474 | 31.48 | 36.68 | 40.96 | 59.9 |

## Table 25

## R(E) Values for Selected Nodes, $\lambda = -0.02$, h = 0.02

| Nodes / Energy | 1 | 2 | 3 | 9 |
|---|---|---|---|---|
| -0.530614 | 10.64 | 31.48 | 36.70 | 57.20 |
| -0.530615 | 11.18 | 31.48 | 36.70 | 57.20 |
| -0.530616 | 31.48 | 36.70 | 40.96 | 59.94 |
| -0.530617 | 31.48 | 36.70 | 40.96 | 59.94 |

## Table 26

## R(E) Values for Selected Nodes, $\lambda = -0.04$, h = 0.04

| Nodes / Energy | 1 | 2 | 3 | 9 |
|---|---|---|---|---|
| -0.562887 | 14.64 | 19.80 | 23.52 | 39.28 |
| -0.562888 | 14.88 | 19.92 | 23.64 | 39.36 |
| -0.562889 | 15.08 | 20.08 | 23.76 | 39.44 |
| -0.562890 | 15.28 | 20.20 | 23.88 | 39.48 |
| -0.562891 | 15.48 | 20.32 | 23.96 | 39.56 |

Table 27

R(E) Values for Selected Nodes, $\lambda = -0.04$, $h = 0.02$

| Nodes / Energy | 1 | 2 | 3 | 9 |
|---|---|---|---|---|
| -0.563019 | 14.14 | 19.50 | 23.30 | 39.14 |
| -0.563020 | 14.36 | 19.62 | 23.40 | 39.20 |
| -0.563021 | 14.60 | 19.76 | 23.52 | 39.28 |
| -0.563022 | 14.82 | 19.90 | 23.62 | 39.34 |
| -0.563023 | 15.04 | 20.04 | 23.74 | 39.42 |

Looking at the increments in the node position in tables (24-27), while varying the energy values, we can see that for $\lambda = -0.02$ the largest increment appears at the same energy value for different nodes, that is for $h = 0.04$ the value of E is -0.5304725, and for $h = 0.02$ the value of E is -0.5306155, as in table 23. However for $\lambda = -0.04$ the predicted E value changes from one node to another. From the results of table 26 we have for the first node E = -0.5628875; for n = 2, E = -0.5628885; for n = 3, E = -0.5628895. The predicted E value stabilizes at -0.562889 to six places of decimals for the higher nodes. From the results of table 27 we have for the first node E = -0.5630205, for the second E = -0.5630215, and then it stabilizes at E = -0.563021, also to six decimal places, for the higher nodes as before. Therefore a projected E value can be calculated using an $h^2$-law yielding the result E = -0.563065. This has changed slightly from the corresponding E value in table 23, which refers to the first node.

The resonance energies found from the preceding calculation are not the energies of true bound states, since there are none for $\lambda < 0$.

Within the context of operator theory a bound state function $\psi$ obeys the eigenvalue equation $H\psi = E\psi$. Another way to describe this is to say that the resolvent operator $R(E) = (H-E)^{-1}$ becomes an unbounded operator in Hilbert space if E is equal to an eigenvalue. This second way of describing things is unwieldy for bound state problems, but it is appropriate for our $\lambda<0$ case, since there will still be <u>complex</u> E values for which R(E) is unbounded. In other words, the spectrum of H (as defined by von Neumann) is the set of E values for which R(E) is unbounded, and the spectrum can contain more than just the usual eigenvalues corresponding to bound states. What the preceding calculation gives (Killingbeck [27]) is the real part of the complex E value at which R(E) has a singularity. It is in principle possible to estimate the imaginary part of E by manipulations based on the results of this kind of calculation (Killingbeck [31]) but we do not pursue this point further in the present work.

Many authors present different ways of solving the problem of quasi-bound states. There are various unbounded perturbing operators which, when added to the Hamiltonian, destroy in principle the bound states of the system (just as $-\lambda r$ does for our problem). Hazi and Taylor [26] use the stabilization method to calculate resonance energies. (They also describe how the imaginary part of the complex pole position can be estimated). For a given potential V(x), they compute the matrix of the exact Hamiltonian H(x) in a finite basis set consisting of the first N functions of the form $\psi_n(x) = (2^n n! \pi^{1/2})^{-1/2} H_n(x) \exp(-\tfrac{1}{2}x^2)$, n = 0, 1, ... For a given N, they obtain the matrix elements of the Hamiltonian as follows: $H^N_{nm} = \langle \psi_n(x), H(x)\psi_m(x) \rangle$, with

$\delta_{nm} = \langle \psi_n(x), \psi_m(x) \rangle$, n,m = 1, ..., . They use fifty functions and diagonalize the matrix $H^N$ to yield a set of N eigenenergies $\Theta_i^N$ and the corresponding eigenfunctions $\Phi_i^N(x)$ given by $\Theta_i^N \delta_{ij} = \langle \Phi_i^N(x), H(x)\Phi_j^N(x) \rangle$. These eigenfunctions are linear combinations of the first N functions $\psi_n(x)$ given above, i.e., $\Phi_i^N(x) = \sum_{n=1}^{N} C_{in} \cdot \psi_n(x)$, for each $i$ ; they are also square integrable, like the basis functions, and can be normalized such that $\delta_{ij} = \langle \Phi_i^N(x), \Phi_j^N(x) \rangle$.

They repeat this procedure for increasing values of N, observing the behaviour of $\Theta_i^N$ and $\Phi_i^N(x)$ as a function of N. For a Hamiltonian containing a potential with a barrier, like the one they deal with, certain of the eigenenergies change very little compared to other eigenvalues as N changes over a relatively large range, that is, they stabilize, and this "stable" energy is very close to the exact resonance energy $E_r$. This fact suggests that the "stable" eigenenergy and the corresponding eigenfunction are associated in some way with the resonant energy.

Our approach is much better than the matrix one because it avoids explicit construction and diagonalization of matrices of large dimension.

We should mention that, even for the true bound state problem, the Hazi and Taylor (op.cit.) approach may give problems. For example, Detwiler and Klunder [32] have discussed "super-singular perturbations" (such as $\lambda x^{-4}$, $\lambda |x|^{-3}$ ) for which any attempt to set up the Hamiltonian matrix in a basis of unperturbed states fails, since all the matrix elements are infinite ! Nevertheless, well defined perturbed eigenvalues can be found. Detwiler and Klauder (op.cit.) get the eigenvalues by a modification of a method due to Milne, but a preliminary calculation using the F method of section 2.1.4., while internally self-consistent, does not quite agree with their results. We suspect that there is an error either in their algebraic theory or in the operation of their programme.

### 4.1.2. Padé Approximants for $\lambda<0$

Using Wynn's algorithm for the potentials $V = \lambda r - r^{-1}$ and $\lambda r^2 - r^{-1}$ for $\lambda<0$ we have checked that the Padé approximants to the energy converge numerically to the quasi-bound energy. That this should happen theoretically was established by Graffi [33]. Results for the potential $V = \lambda r - r^{-1}$ are shown in table 28. We can see that as the value of $\lambda$ becomes more negative the Padé approximants to the energy become less accurate, although the exact value still lies between the $[L+1,L]$ and $[L,L]$ Padé approximants. Table 29 contains results for $V = \lambda r^2 - r^{-1}$; even in this case the Padé approximants apparently converge to a definite value. We have used only eight energy coefficients for the potential $V = \lambda r^2 - r^{-1}$ since the presence

Table 28

Padé Approximants for $V = \lambda r - r^{-1}$, for $\lambda<0$

| $\lambda$ | -0.01 | -0.02 | -0.03 | -0.04 | -0.05 |
|---|---|---|---|---|---|
| [5,5] | -0.51515729 | -0.53066398 | -0.54659147 | -0.56309361 | -0.58024036 |
| [5,4] | -0.51515730 | -0.53066398 | -0.54659144 | -0.56307433 | -0.57991074 |

Table 29

Padé Approximants for $V = \lambda r^2 - r^{-1}$ for $\lambda < 0$

| $\lambda$ | -0.001 | -0.002 | -0.003 | -0.004 | -0.005 |
|---|---|---|---|---|---|
| [4,4] | -0.50303373 | -0.50614213 | -0.50930827 | -0.51264553 | -0.51612015 |
| [4,3] | -0.50303373 | -0.50614211 | -0.50934220 | -0.51247232 | -0.51603676 |

of the higher ones spoils the results, that is, the [5,5] Padé approximant is less accurate than the [4,4]; this is due to the large size of the high order coefficients, which causes numerical errors which outweigh the theoretical gain of knowing more terms in the series.

Wynn's algorithm can also be used to get Padé approximants to $\langle r \rangle$ and $\langle r^2 \rangle$ for the Charmonium type potential of section 3.1.4. for $\lambda$ negative. The results show that also for this problem the exact value can be found between [L+1,L] and [L,L] Padé approximants. The results are presented in table 30.

Table 30

Padé Approximants to $\langle r \rangle$ and $\langle r^2 \rangle$ for $\lambda < 0$

$$V = -1/r + 2\lambda r + 2\lambda^2 r^2$$

| | $\lambda = -0.01$ | | $\lambda = -0.02$ | |
|---|---|---|---|---|
| | $\langle r \rangle$ | $\langle r^2 \rangle$ | $\langle r \rangle$ | $\langle r^2 \rangle$ |
| [4,4] | 1.56618686 | 3.30934285 | 1.64945466 | 3.73642426 |
| [4,3] | 1.56618686 | 3.30934281 | 1.64944941 | 3.73634769 |

### 4.1.3. Bound States for $\lambda < 0$

We have shown in the last section that when an unbounded negative potential is added to the Hamiltonian the bound states are all destroyed in principle. In this section we consider the case of the potential $V = -r^{-1} + 2\lambda r + 2\lambda^2 r^2$ for $\lambda < 0$. We apply the R-Method to this potential and find that the bound states still exist for $\lambda$ negative because the potential goes to $+\infty$ in all directions, whereas for a problem such as those of the last section the potential goes to $-\infty$, (Killingbeck [10]).

We use several extrapolation formulae, of increasing accuracy, to find a projected energy value. The formulae are as follows:

$$E_{(1,2)} = \tfrac{1}{3}\left[4E_1 - E_2\right] \tag{2.30}$$

$$E_{(1,2,4)} = \tfrac{1}{45}\left[64E_1 - 20E_2 + E_4\right] \tag{2.31}$$

$$E_{(1,2,3)} = \tfrac{1}{10}\left[15E_1 - 6E_2 + E_3\right] \tag{4.1}$$

$$E_{(1,2,3,4)} = \tfrac{1}{35}\left[56E_1 - 28E_2 + 8E_3 + E_4\right] \tag{4.2}$$

where $E_k$ is the energy value obtained using kh as the strip width. Results are given in table 31, including those for one positive value to show the advantage of using these new formulae to obtain a projected energy value. The quantity $-\frac{1}{2}+3\lambda$ is also shown in the table. We use the following h values: $h_1 = 0.05$, $h_2 = 0.10$, $h_3 = 0.15$, and $h_4 = 0.20$.

Table 31

Projected Energy Values for $V = -r^{-1} + 2\lambda r + 2\lambda^2 r^2$

| $E$ \ $\lambda$ | -0.025 | -0.050 | -0.100 | 0.100 |
|---|---|---|---|---|
| $E_{(1,2)}$ | -0.574998(146) | -0.649105(272) | -0.765825(303) | -0.199998(969) |
| $E_{(1,2,4)}$ | -0.574999(720) | -0.649106(925) | -0.765826(819) | -0.199999(904) |
| $E_{(1,2,3)}$ | -0.574999(736) | -0.649106(951) | -0.765826(837) | -0.199999(909) |
| $E_{(1,2,3,4)}$ | -0.574999(756) | -0.649106(985) | -0.765826(861) | -0.199999(914) |
| $3\lambda-\frac{1}{2}$ | -0.575000 | -0.649110 | -0.765830 | -0.200000 |

In section 3.1.4. we have shown that the energy series for this kind of potential, when $\lambda$ is positive, is finite. That is, the energy deviation $E(\lambda)+\frac{1}{2}-3\lambda$ is zero because the eigenfunction $\phi = \exp\left[-(r+\lambda r^2)\right]$ which is a solution of the equation $H\phi = E\phi$ is normalizable. For $\lambda<0$ this is not so, and $-\frac{1}{2}+3\lambda$ is only an upper bound, as shown below, where we use the data from Table 31.

| $\lambda$ | $E+\frac{1}{2}-3\lambda$ |
|---|---|
| -0.025 | 0.000000 |
| -0.050 | 0.000897 |
| -0.100 | 0.034173 |
| +0.100 | 0.000000 |

## 4.2. Calculation of $\psi^2(0)$ for the Charmonium Problem

In section 2.2.5. it was mentioned that, while performing a matrix calculation to get the value of $\langle x^N\rangle$, an error of order $\eta^2$ appears in the results if the eigenvalues are in error to order $\eta$. The integration methods considered in the present work do not have this weak point (Killingbeck and Galicia [25]). In some branches of traditional theory e.g. the theory of hyperfine interaction (Young and Uhlenbeck [35]) and the theory of excitons (Cabib, et.al.[36]), it is necessary to know the value of the square of the wavefunction at the origin. If one attempts to calculate the value of this local quantity by means of a matrix-variational method which optimizes the energy then a poor value of the local quantity will be obtained. Such a quantity is also required in recent non-relativistic models of the charmonium system, (which was mentioned previously in section 3.1.4.), when estimating the various decay rates of the system

(Kaushal and Muller-Kirsten [37]).

Eichten et.al. [38] and McCarter [39] have considered the Schrödinger equation in the form

$$-\alpha\nabla^2\psi - \frac{\beta}{r}\psi + \mu r^P\psi = E\psi \tag{4.3}$$

to solve the charmonium problem (with $P \geq 1$). The $r^P$ term represents a confining potential which prevents direct break up of the system, while the $\beta$ coefficient gives the size of the "gluon" force. $\beta$ is usually taken to be small; the coefficient $\alpha$ is inversely proportional to the quark mass (since the kinetic energy operator is conventionally written as $-\hbar^2/2m\nabla^2$).

To convert equation (4.3) into a one-parameter perturbed hydrogen atom equation it is necessary to introduce the change $\bar{r} \to k\bar{r}$ of length scale. By doing so we find the scaling relationship which indicates how the eigenvalues depend on the parameters $\alpha$, $\beta$ and $\mu$:

$$k^2E(\alpha,\beta,\mu) = E(\tfrac{1}{2},1,\lambda) \tag{4.4}$$

where $k = (2\alpha\beta^{-1})$ and $\lambda = \mu k^{P+2}$. Writing the radial factor in $\psi$ in the form $r^{-1}R$, equation (4.3) takes the form

$$-\frac{1}{2}D^2R + VR = ER \tag{4.5}$$

with

$$V = -r^{-1} + \lambda r^P + \frac{1}{2}\frac{l(l+1)}{r^2}$$

and the normalization condition

$$\int_0^\infty R^2 dr = 1$$

The s states are the ones of interest in connection with the $\psi(0)$ problem; for them the term involving the angular momentum $\ell$ does not appear. Since we have

$$DR = D(r\psi) = rD\psi + \psi$$

with the requirement $R(0) = 0$, then it follows that the wavefunction at the origin $\psi(0)$ will be given by the slope $DR(0)$ at the origin.

Kausal et.al. (op.cit.) present a way of calculating $\psi(0)$. They state that $\psi(0)$ can only be found if the wavefunction is explicitly normalized. They use W.K.B. approximations to calculate the value of $\psi$ at various points in space. Nevertheless, their value for $\psi(0)$ appears to be of low accuracy.

We decided to approach this problem by a numerical treatment involving expectation values and avoiding the use of wavefunctions. Multiplying equation (4.5) by a function $F(r)$ and integrating between 0 and $\infty$, we obtain the result

$$\int_0^\infty \left[D^2F+2F(E-V)\right] R\,dr = F(0)DR(0) \qquad (4.6)$$

if $D(FR) = 0$ at $\infty$ and $RDF = 0$ at 0.

For the special case $F = 1$ equation (4.6) is converted into an equation equivalent to that of Trivedi [40]. He suggests that if an <u>approximate</u> normalized R is used in the integral, and if E is replaced by the variational energy associated with R, then a reasonable estimate of $DR(0)$ for the exact eigenfunction can be obtained. For example, considering the groundstate of the hydrogen atom and using as a trial function an optimized Gaussian type function in (4.6) we find $DR(0) = 1.796$, as opposed to the exact value 2 and the poor value 0.980 obtained by simply substituting $r = 0$ in the approximate function. If the exact R is used in equation (4.6) the <u>same</u> DR(0) should result for different choices of F, provided that F(0) is non-zero. We do not discuss in detail Trivedi's work because we want to approach the problem using expectation values. In order to do so we simply multiply equation (4.5) by DR and integrate between 0 and $\infty$. Integration by parts on the r.h.s. leads to the result

$$2\int_0^\infty R^2(DV)dr = \left[DR(0)\right]^2 \qquad (4.7)$$

This relation involves the expectation value of DV. Therefore using (4.7) it is possible to reduce the $\psi(0)$ problem to the problem of finding an expectation value. Froman [41] uses equation (4.7) and estimates the value of $\langle(DV)\rangle$ by means of a W.K.B. approach. Since we are now familiar with the calculation of expectation values involving energies from the theory of section 2.2.5., we can reduce the problem of finding $\psi(0)$ to the $\langle(DV)\rangle$ problem, and then reduce the expectation value problem to a set of eigenvalue problems which can be solved using a numerical integration method.

For the particular case of the unperturbed hydrogen atom, with potential function $V = -r^{-1}$ for s states, we have $\langle(DV)\rangle = \langle r^{-2}\rangle = 2n^{-3}$, where n is the principal quantum number of the state concerned. The energy eigenvalue E is $\frac{1}{2}n^{-2}$, so that it yields the relation

$$\psi^2(0) = 2\langle(DV)\rangle = 4\frac{dE}{dn} \qquad (4.8)$$

This relation is called the Fermi-Segré formula (Froman and Froman [42]) and can be used also for the case of a <u>perturbed</u> Coulomb potential. This relation is relevant to us because it relates $\psi^2(0)$ to entities arising from energy calculations. However, it has two drawbacks; it involves the estimation of the derivative of a (hypothetical) smooth function E(n), whereas the actual eigenvalues form a discrete sequence; and, further, it is not exact if the perturbation is strong. These two causes of uncertainty render equation (4.8) unsuitable for accurate work in theoretical calculations, although it allows rough estimates of $\psi^2(0)$ to be obtained from empirically selected energies.

In section 2.2.5. we explained how to calculate expectation values using energies; equation (2.26) can be slightly modified to take the form

$$\langle r^N \rangle = \underset{\varepsilon \to 0}{\mathrm{Lt}} \frac{E(H+\varepsilon r^N)-E(H-\varepsilon r^N)}{2\varepsilon} \qquad (4.9)$$

Provided that the eigenvalues for the perturbed Hamiltonians $H \pm \varepsilon r^N$ can be evaluated accurately, equation (4.9) will allow us to estimate $\langle r^N \rangle$. We have tested this approach for different potentials in previous sections and it gives good results. The eigenvalue calculation can easily be performed by using the previously tested F-method of section 2.1.4. Starting from equation (2.12) we can obtain an equation for the F-method in the case where the states of angular momentum $\ell$ are required,

$$\left[r+h(\ell+1)\right]F(r)+\left[r-h(\ell+1)\right]F(r-h)\left[1+h^2F(r-h)\right]^{-1} = 2r(V-E) \qquad (4.10)$$

The terms on the left take care of $\ell$ completely, i.e. no centrifugal term needs to be included in the potential V. This feature is particularly useful for the $\psi^2(0)$ calculations, since for the charmonium problem we have

$$\mathcal{E}(DV) = \mathcal{E}(r^{-2}+\lambda Pr^{P-1}) \qquad (4.11)$$

The derivative of the Coulomb potential (DV) resembles a centrifugal term for which $\mathcal{E} = \frac{1}{2}\ell(\ell+1)$, so that $\ell \to 2\mathcal{E}$ as $\mathcal{E} \to 0$. To find $\langle (DV) \rangle$ using equation (4.9), for an s state, we use a "pseudo-angular momentum" $\ell = 2\varepsilon$. This takes care of the $r^{-2}$ term in (4.11). The second term in (4.11) can be added explicitly to V, or else we can use an "advanced potential" term, so that the potential becomes

$$V = -r^{-1} + \lambda(r+\varepsilon)^{P} \tag{4.12}$$

By using the pseudo-angular momentum and the advanced potential artifices together, it is possible to perform the calculations rather simply on a computer, since the programme can be written to make the adjustments automatically when $\varepsilon$ is given as part of the input data. Using two values $\pm\varepsilon$ we can estimate $\langle (DV) \rangle$ by means of equation (4.9).

The E value obtained using (4.10) is not the required Schrödinger equation eigenvalue, since it is arrived at by using a difference equation involving a finite strip width h. In section 2.2.4. it is explained how to get a projected energy value with the use of different values of h. We use the extrapolation formula (4.2) of the last section with h = 0.025 .

Further, to make sure that $\langle (DV) \rangle$ has been determined accurately, we perform the calculation twice, once for $\pm\varepsilon$ and once for $\pm 2\varepsilon$, and then perform an $\varepsilon^2$ type extrapolation to arrive at a good estimate of the limiting value which is formally specified in equation (4.9).

Equation (4.9) can be used also for excited states since the energy value can be found as explained in section 2.1.4. Thus $\psi^2(0)$ for excited s states can be found, and Table 32 shows some results for excited states.

Considering a potential of the form $V = \lambda r^{P}$ in (4.3), we are taking the "zero gluon" limit in the charmonium problem; this will make the results more likely to be useful, since it is usual in charmonium models to take the "gluon" coefficient to be small. With this restriction we can do the calculations for $\lambda = 1$ and obtain results for any other $\lambda$ by scaling. By calculating $\langle r^{P-1} \rangle$ we can find $\psi^{2}(0)$ from (4.7); the $\langle r^{-1} \rangle$ value provides a means of estimating the first order effect of introducing a weak gluon term.

The virial theorem relates the values of E and $\langle r^{N} \rangle$ in the form $E = \frac{1}{2}(P+2)\langle r^{P} \rangle$, so that the $\langle r^{P} \rangle$ found from this relation can be checked against the $\langle r^{P} \rangle$ found by a direct numerical calculation using the energy differencing approach based on equation (4.9).

We can also apply the ideas given in this section to the charmonium type potential of section 3.1.4, i.e., $V = r^{-1}+2\lambda r+2\lambda^{2}r^{2}$. This particular potential provides a clear-cut test case, since the <u>exact</u> ground state eigenfunction is known to be $r\exp\left[-(r+\lambda r^{2})\right]$. This means that $\langle r^{N} \rangle$ values which are of very high accuracy (i.e. virtually exact) can be computed by simple numerical integration using the known exact wavefunction.

Table 32 gives the results for the lowest three s states for the potential $V = r^{P}$ for P = 1,2, and 3. We used H = 0.025 for the calculation of the energies and $\varepsilon = 0.02$ and 0.04 for the calculation of $\langle r^{N} \rangle$ values. The results for $\psi^{2}(0)$ can be obtained from the results for $\langle r^{P} \rangle$ values using equation (4.7). Table 33 gives the results for the potential $V = -r^{-1}+2r+2r^{2}$. For the calculation of $\langle r \rangle$ and $\langle r^{2} \rangle$ we used $\varepsilon = 0.002$ and 0.004, and for the calculation of $\langle 2(DV) \rangle$ we used $\varepsilon = 0.04$ and 0.08. We also include results using the integration procedure explained in section 2.2.6. It is clear that this latter procedure, while satisfactory for finding $\langle r^N \rangle$ for $N>0$, is not as good as the $\varepsilon$ method for finding $\langle r^N \rangle$ with $N<0$.

Table 32

Results for the Lowest Three s States for $V = r^P$

| M = 1 | 1s | 2s | 3s |
|---|---|---|---|
| E | 1.85575709 | 3.24460763 | 5.38661378 |
| $\langle r \rangle$ | 1.237171 | 2.163072 | 3.591076 |
| $\langle r^2 \rangle$ | 1.836712 | 5.614655 | 15.47499 |
| $\langle r^{-1} \rangle$ | 1.051866 | 0.733486 | 0.512970 |
| M = 2 | | | |
| E | 2.12132034 | 4.94974747 | 7.77817459 |
| $\langle r \rangle$ | 0.948850 | 1.423275 | 1.779094 |
| $\langle r^2 \rangle$ | 1.060660 | 2.474874 | 3.889087 |
| $\langle r^{-1} \rangle$ | 1.341877 | 1.118230 | 0.995225 |
| M = 3 | | | |
| E | 2.27652238 | 6.28222760 | 10.7997582 |
| $\langle r \rangle$ | 0.842919 | 1.143043 | 1.363334 |
| $\langle r^2 \rangle$ | 0.827677 | 1.617848 | 2.322209 |
| $\langle r^{-1} \rangle$ | 1.491243 | 1.392730 | 1.309490 |

Table 33

Results for $V = -r^{-1}+2r+2r^2$

| Method | E | $\langle r \rangle$ | $\langle r^2 \rangle$ | $\langle 2(DV) \rangle$ |
|---|---|---|---|---|
| Exact | 5/2 | 0.60586289 | 0.44706856 | 25.693806 |
| Integration | 2.5 exact to 8 places | 0.605867 | 0.447072 | 24.96017 |
| $\varepsilon$-Method | | 0.605863 | 0.447069 | 25.69380 |

## 4.3. Quadratic Zeeman Effect

### 4.3.1. The E(s) Problem

The problem of the quadratic Zeeman effect for the hydrogen atom has relevance for astrophysics and also for the theory of simple excitons in solid state physics. Killingbeck [29] treats the problem by several techniques. In this section we present a perturbation approach which involves a numerical solution of the radial Schrödinger equation based on the s part of the potential.

Cabib et.al. (op.cit.) use a method involving fairly large matrices and numerical integration of the Schrödinger differential equation; their results for the ground state are very accurate.

We study the case of the hydrogen atom situated in a uniform magnetic field. The $z$ axis of a Cartesian system of axes is chosen to be along the direction of the field, with the nucleus at the origin. The magnetic quantum number of the energy eigenfunctions will be well defined because of the rotational symmetry about the $z$ axis; it will not change in the presence of the magnetic field. The Hamiltonian contains a linear and a quadratic term in the magnetic field strength.

Since the 1s ground state of the hydrogen atom has m = 0, then for such a state the linear term vanishes, giving a Hamiltonian of the form

$$H=-\frac{1}{2}\nabla^2-r^{-1}+\frac{1}{8}\gamma^2(x^2+y^2) \qquad (4.13)$$

We use atomic units, in which the ground state has energy $-\frac{1}{2}$. The quantity $\gamma^2$ is equal to $(e^2B^2/\mu c^2)$ in S.I. units; B represents the magnetic field strength and $e$ and $\mu$ the electronic charge and mass respectively. The numerical scale is such that a value of $\gamma = 1$ in (4.13) corresponds to a magnetic field strength of $2.35 \times 10^9$ G.

The perturbing potential due to the magnetic field is a sum of two tensor operators, of rank 0 and 2, which we refer to as the s and d parts of the perturbation. The Hamiltonian can be written as follows, to show this decomposition of the perturbation,

$$H=-\frac{1}{2}\nabla^2-r^{-1}+\frac{1}{8}\gamma^2\left[\frac{2}{3}r^2-\frac{1}{3}(3z^2-r^2)\right] \qquad (4.14)$$

where the s part is given by $\frac{1}{12}\gamma^2r^2$ and the d part by $-\frac{1}{24}\gamma^2(3z^2-r^2)$.

It has been shown by various authors that for $\gamma \leqslant 5$ the main problem in a matrix approach is to get the basis states to represent correctly the $\ell = 0$ component of the perturbed 1s wavefunction. The main idea to solve the present problem is to consider only the s part of the potential and to drop the corresponding d part. By doing so we are obtaining an eigenvalue which we denote by the symbol E(s); this is the energy due to only the s part of the potential; it is not the full perturbed energy E of the system. However, E(s) gives a very good upper bound to E. This arises because the d part in the perturbing term gives no first order energy shift when it is added to the Hamiltonian; it has zero expectation value for <u>any</u> s type function. To obtain the full perturbed energy E it will then be necessary to include the second order energy shift which is produced by adding the d part of the potential function to the Hamiltonian. By calculating E(s) very accurately we are essentially partitioning the Hamiltonian so that the s terms are treated exactly, with only the d term of the potential remaining to be treated as a perturbation. This potential problem can be treated using the F-method of section 2.1.4.

Finding E(s) by a matrix approach would involve using a <u>complete</u> s-state basis, with discrete and continuum basis functions (when described in terms of the unperturbed hydrogenic eigenfunctions). A comparison of our E(s) with the E(s) estimate from a matrix calculation will thus provide a good calibratory test for the adequacy of the matrix basis functions; indeed, there has been some dispute in the literature about how (and whether) it is possible to allow for continuum-type basis states in a matrix approach. The numerical integration approach avoids such problems by being implicitly equivalent to a "complete set" calculation without making any explicit mention of basis states.

## 4.3.2. Inclusion of the $\ell = 2$ term

As we pointed out in the previous section, the addition of the d potential term to the Hamiltonian does not alter the energy eigenvalue in first order. It does not change <u>any</u> expectation value of the type $\langle f(r) \rangle$ in first order, because the first-order function $\psi_1$ is of d type, and the matrix elements of $\langle s|f(r)|d\rangle$ type are equal to zero by the usual angular momentum selection rules.

The first-order function $\psi_1$ can be calculated explicitly when the d part of the potential $(3z^2-r^2)$ acts on an unperturbed hydrogenic 1s orbital $\phi_0$; $\psi_1$ is found to be a function of type $a(b+r)(3z^2-r^2)\phi_0$. Therefore we use this form for our trial $\psi_1$, with $\phi_0$ being the s eigenfunction associated with E(s), and with a and b variable. We use this trial $\psi_1$ in the Hylleraas functional, which gives a lower bound on the modulus of the second-order energy (Killingbeck [29]). Writing the potential as $V=\frac{1}{24}\gamma^2(3z^2-r^2)$ this functional takes the following form

$$F(\psi) = 2\langle\phi_0|V|\psi\rangle + \langle\psi|(H_0-E_0)|\psi\rangle \tag{4.15}$$

In order to convert all the terms in (4.15) into expectation values for the s function, we need a very simple but powerful identity. Consider the Hamiltonian $-\frac{1}{2}\nabla^2+U(r)$ for any local radial potential $U(r)$. If $\phi$ is <u>any</u> s-type eigenfunction with energy E, and $\mathcal{Y}_\ell$ is a <u>solid</u> harmonic of degree $\ell$, we can proceed in a manner similar to that used to derive hypervirial relations in section 3.1. and obtain the result

$$\langle\phi|r^P\mathcal{Y}_\ell[H,r^N\mathcal{Y}_\ell]|\phi\rangle = \langle\phi|r^{P+N-2}\mathcal{Y}_\ell^2|\phi\rangle\left[\tfrac{1}{2}\ell(P+N+2\ell+1)\right] \tag{4.16}$$

The inequality $|E_2|>F(\psi)$ becomes

$$|E_2|>\frac{8}{5}\langle br^4+r^5\rangle^2\langle 10b^2r^2+24br^3+15r^4\rangle^{-1}\left(\frac{1}{24}\gamma^2\right)^2 \tag{4.17}$$

A closure approximation also gives us the simple upper bound

$$|E_2|<\frac{4}{5}\langle r^4\rangle\left(E(2)-E(0)\right)^{-1}\left(\frac{1}{24}\gamma^2\right)^2 \tag{4.18}$$

E(2), the energy of the lowest d state in the radial problem, is obtained just as easily as E(0) (i.e. E(s)) by the F method of section 2.1.4. The upper bound is equal to -0.497527 and the lower bound equals -0.497528.

The main feature of the preceding calculation is the following: although the Hylleraas principle involves $\phi_0$, the use of the identity (4.16) allows us to express the required quantities in terms of expectation values $\langle r^N \rangle$ taken with respect to $\phi_0$. As pointed out previously, such expectation values can be calculated by using eigenvalue differencing methods and hypervirial relations, even though the explicit $\phi_0$ is not extracted during the eigenvalue calculations. Thus the whole of the proceding theory has been translated into a formalism which requires only the calculation which can be done accurately by various techniques (in particular, by the R and F methods discussed in this thesis).

### 4.3.3. Excited State Calculations

At first sight it seems that the p and d states should be considered as excited states, since the energy associated with them is higher than the energy for the 1s state, which is the ground state. However, if we take into consideration the magnetic quantum number m and the parity for these states, we can see that some of them can be considered as ground states, since they will have the lowest energy of their symmetry type. We can examine the following table, which shows the hydrogenic states and their quantum numbers.

| State | m | Parity |
|---|---|---|
| $1s_0$ | 0 | +1 |
| $2s_0$ | 0 | +1 |
| $2p_0$ | 0 | -1 |
| $2p_{-1}$ | -1 | -1 |
| $2p_{+1}$ | +1 | -1 |
| $3d_{-2}$ | -2 | +1 |
| $3d_{-1}$ | -1 | +1 |
| $3d_0$ | 0 | +1 |
| $3d_{+1}$ | +1 | +1 |
| $3d_{+2}$ | +2 | +1 |

The quantum numbers given remain unchanged when the magnetic field is turned on, and from the table we can see that all of the states, with the exception of the $2s_0$ state and the $3d_0$, can be considered as ground states since they all have different quantum numbers. Even so, as we will show below, the energy corresponding to the $2s_0$ excited state can be calculated using the same ideas as for the ground states. The main idea for calculating the energy in first order is to treat the potential for each particular state in such a manner that when adding the residual part of the potential no change will appear in the energy eigenvalue to first order. For the 1s state the residual part of the potential is of pure $\ell = 2$ type, as discussed in section 4.3.1., but we shall see that for p and d states the appropriate residual potential is not of definite $\ell$ type.

The Hamiltonian for the different states is as follows, with $H_0 = -\frac{1}{2}\nabla^2 - r^{-1}$

$$1s_0, \quad H = H_0 + \frac{1}{12}\gamma^2 r^2 - \frac{1}{24}\gamma^2(3z^2 - r^2) \tag{4.19}$$

$$2p_0, \quad H = H_0 + \frac{1}{20}\gamma^2 r^2 - \frac{1}{24}\gamma^2(3z^2 - \frac{9}{5}r^2) \tag{4.20}$$

$$2p_{-1}, \quad H = H_0 + \frac{1}{10}\gamma^2 r^2 + \frac{1}{2}\gamma m - \frac{1}{24}\gamma^2(3z^2 - \frac{3}{5}r^2) \tag{4.21}$$

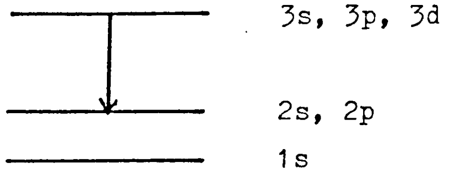
$$3d_{-1}, \quad H = H_0 + \frac{1}{14}\gamma^2 r^2 + \frac{1}{2}\gamma m - \frac{1}{24}\gamma^2(3z^2 - \frac{9}{7}r^2) \tag{4.22}$$

$$3d_{-2}, \quad H = H_0 + \frac{3}{28}\gamma^2 r^2 + \frac{1}{2}\gamma m - \frac{1}{24}\gamma^2(3z^2 - \frac{3}{7}r^2) \tag{4.23}$$

The last term in equations (4.19-4.23) represents the residual potential. Treating the potentials in this way we can be sure that when adding the residual part of the potential to the Hamiltonian there will not be a change in the energy eigenvalue in first order. For example, the residual operator $(3z^2 - \frac{9}{5}r^2)$ has zero expectation value for <u>any</u> state of $p_0$ type, as can be verified by explicit calculation. The $2p_0$ energy for the Hamiltonian $H_0 + \frac{1}{20}\gamma^2 r^2$ can be found by the F-method (section 2.1.4.).

The energy eigenvalue associated with the $2p_{+1}$ state can easily be calculated from the results for the $2p_{-1}$ state. The term $\frac{1}{2}\gamma m$ gives the linear Zeeman term in equations (4.21-4.23); for the $2p_{-1}$ state we have $m = -1$ and for the $2p_{+1}$ state we have $m = 1$; therefore they differ in energy by an amount $\gamma$, which means that to get the energy eigenvalue for the $2p_{+1}$ state it will only be necessary to add this amount to the resulting energy for the $2p_{-1}$ state. In a similar way we can calculate the energy eigenvalue for the $3d_{+1}$ state and for the $3d_{+2}$ state, with the difference that the $3d_{+2}$ and $3d_{-2}$ states differ in energy by an amount $2\gamma$.

The $2s_0$ state can be treated by means of equation 4.19 and the ideas about excited states of section 2.1.4. This is so because the contribution of $E_2$ to the exact energy is small for this state, since the 3d state, which is the one which couples with the 2s state, is far above the 2s state. We can understand this idea by looking at the energy level diagram;



Therefore, for the 2s state we can get a good estimate by calculating the energy up to first order, whereas for the 3s state the influence of the 3d state is much stronger, and presumably gives a value for $E_2$ which is larger than the $E_2$ for the 1s and 2s states.

The energy eigenvalue results for the ground states and for 2s are given in table 34. They were obtained using the F-method (for $\gamma = 0.1$). It was found to be sufficient to use strip widths equal to 0.1, 0.2, and 0.3 to get projected energy eigenvalues after using equation (2.31). Table 34 includes also the results of Praddaude [43]

Table 34

Energy Eigenvalue (at $\gamma = 0.1$)

| State | Energy | Praddaude results |
|---|---|---|
| $1s_0$ | -0.497520 | -0.497525 |
| $2s_0$ | -0.095923 | -0.098085 |
| $2p_{-1}$ | -0.150522 | -0.150845 |
| $2p_0$ | -0.111752 | -0.112410 |
| $3d_{-2}$ | -0.086575 | -0.087835 |
| $3d_{-1}$ | -0.054255 | -0.057810 |

Praddaude used a large matrix basis of Laguerre functions (essentially scaled hydrogenic functions) to calculate the energy eigenvalues. We can see from table 34 that our energies are very close to (but slightly higher than) his. This is in accord with theory, since for the ground states concerned our calculation is equivalent to a variational calculation which uses as trial function the exact eigenfunction of the Hamiltonian with the residual potential subtracted. The resulting energy estimate must thus be an upper bound to the exact energy. The results show that our estimate is already a good one. For the case of, for example, the $2p_o$ state, our calculation would be equivalent to the use of a complete p type basis, which is in practice impossible in a matrix calculation. The small extra lowering of the energy must be due (for $2p_o$) to the f type functions in Praddaude's basis set, and could be computed in our approach by a Hylleraas variational calculation of $E_2$, as outlined for the 1s state in section 4.3.2. Since our results correspond to those which would arise from complete basis sets of particular $\ell$ types, they should be of value to workers who employ matrix diagonalization methods, since they provide standard test values. Thus, if the p basis states used by any worker are inadequate, this will show up as an eigenvalue estimate which is higher than our 2p eigenvalues. Adding the f basis states cannot remove any error due to the use of a poor set of p basis states.

# CONCLUSION

With the development of pocket calculators, mini-computers and big computers, it seems reasonable to attempt to solve mathematical and physical problems with their aid.

The task of finding simple numerical methods which can be treated by a programmable pocket calculator is an interesting challenge: it calls for a clear theoretical understanding of the problems treated and if a satisfactory method is obtained this allows other research workers to treat the problem by themselves without large scale computing facilities. Further, a method compact enough to work on a small machine will probably be a time-saving method for a big machine.

The numerical methods presented in this work have been tested for Schrödinger equations involving several perturbed and unperturbed potentials. These methods have been shown to be very effective and to be more simple and accurate than the widely used matrix calculations.

The use of a ratio variable R(r), (section 2.1.2), makes this numerical method rather simple to apply and yet it gives accurate results even when treating perturbation problems for potentials such as $V = \lambda r^{p} - r^{-1}$ . It has been demonstrated that the change from the R-method to the F-method, (section 2.1.3), improves the accuracy of the results.

The results of section 2.2 show that the error in the energy eigenvalue varies as $h^2$ over an extended range of h values. An $h^2$ extrapolation process works accurately without the requirement of using complicated integration formulae in the integration process. In general the eigenvalue error seems to be well represented by a power series in $h^2$.

It has been demonstrated (section 2.2) that perturbation theory, used in a "global" sense, gives a correction term in the integration formula which is more simple than any previously derived using step-by-step perturbation theory.

The F-method of section 2.1.4. allows us to get an interpolated energy eigenvalue using three trial energies (i.e. E, $E \pm \delta E$); in this way we need to perform only an outward integration. This makes our method more easy to use, in comparison with previous methods, which usually employ an outward and an inward integration and get an improved energy estimate by using a formula involving the slope "mis-match" at some intermediate r. Some position r = L must be used to start the inward integration, and may have to be revised to simulate adequately the boundary condition $\psi(\infty) = 0$. However, this difficulty also is avoided in our programmes, which take the limit $L \to \infty$ during the calculation, as explained in the quoted sections.

It has been shown, (section 2.2.5), that expectation values such as $\langle r^N \rangle$ can be calculated without storing the explicit value of $\psi$. This is done by using energy calculations, which can be performed by the method of section 2.1.4 (or, indeed, by any accurate method).

Hypervirial methods (section 3.1) make it possible to calculate some perturbation series up to high order without any calculation of the perturbed wave functions of various orders. Further, the series for various $\langle r^N \rangle$ also result from the calculation. The various perturbation series can then be treated (even when divergent) by means of Padé approximants. We have shown several examples in which the diagonal Padé approximants (i.e. $[L,L]$) converge from below to the correct quantity required, and the $[L+1,L]$ converge from above.

In section 3.1.4 an apparently new perturbation phenomenon has been treated; this arises in the case of a hydrogen atom with perturbing potential $2\lambda r + 2\lambda^2 r^2$. The Rayleigh-Schrödinger energy series for the ground state converges to an exact value; we have demonstrated that this value is not the true energy for negative values of $\lambda$, although there still exists bound states.

The R and F methods presented in chapter 2 are particularly suited to handle the various problems described in chapter 4. These methods avoid many of the lengthy calculations and inaccuracies involved in the matrix diagonalization methods, both for bound and quasi-bound states. The concomitant penalty which arises from this gain in calculational simplicity is, of course, the need to study the relevant theory carefully in order to re-write it in a form which permits application of the numerical methods.

# APPENDIX A1

## F-METHOD

### A1.1 BASIC Programme

```
  5  PRINT "-A(D2)+V = H"
 10  PRINT "ALPHA, LAMDA, H, E, DE"
 15  INPUT A, L, H, E, DE
 20  PRINT "NODES" : INPUT Q
 25  PRINT "AM" : INPUT AM
 30  E = E+DE
 35  N = AM
 40  W = 1: WW = 1 : W2 = 1
 45  R = 1 : RR = 1 : R2 = 1
 50  N = N+1  : X = N*H
 55  N1 = N+AM+1  : N2 = N-AM-1
 60  T = (-1/X)+L*X-E
 65  TT = T+DE  : T2 = T+2*DE
 70  T = T*N/A  : TT = TT*N/A  : T2 = T2*N/A
 75  F = (F/R)*N2+T  : F = F/N1
 80  FF = (FF/RR)*N2+TT  : FF = FF/N1
 85  F2 = (F2/R2)*N2+T2  : F2 = F2/N1
 90  R = 1+H*H*F
 95  RR = 1+H*H*FF  : R2 = 1+H*H*F2
100  W = W*R  : WW = WW*RR  : W2 = W2*R2
105  IFR<0 THEN Z = Z+1
110  IFRR<0 THEN ZZ = ZZ+1
115  IFR2<0 THEN Z2 = Z2+1
120  IFZ<Q THEN GOTO 50
125  P = E-DE/(1-WW/W)
130  PP = E-(2 DE)/(1-W2/W)
135  P2 = P+(PP-P)/(1-W2/WW)
140  PRINT "1ST" P
145  PRINT "2ND" P2
150  PRINT Z, ZZ, Z2
155  GOTO 50
```

### A1.2 Comments on the F-Method Programme

The input variables are as follows. Alpha (A) is either 1 or $\frac{1}{2}$ depending whether the Schrödinger equation is used in the form $-D^2\psi+(V-E)\psi = 0$, or $-\frac{1}{2}D^2\psi+(V-E)\psi = 0$ respectively (i.e. $-\alpha$ is the coefficient of $D^2$ in the kinetic energy operator). Lamda (L) represents the value of the perturbing parameter in the potential function. H represents the strip width to be used in the numerical integration.

E is the trial energy and DE is the increment of the energy (so that the trial energies used are actually E and E$\pm$DE). Nodes (Q), the number of nodes, i.e. 1 for the ground state, 2 for the first excited state, and so on. AM represents the value of the angular momentum, i.e. it is 0 for an s state, 1 for a p state, and so on. (In the method of section 3.1.3 A.M. can usefully be given a non-integer value). The variable W represents the wavefunction.

The potential function is given in line 60; this is the <u>only</u> line that has to change in order to use the programme for a different potential function. We use the potential $-1/r+\lambda r$ in the preceding specimen programme.

There is not a stopping condition for this problem. The reason for this is that the person who runs the programme will have to stop it manually when the two energies shown on the screen reach a stable value; otherwise the PET will stop it by itself when reaching its overflow capacity. The two displayed energies (lines 140 and 145) are the first and second order interpolated energies calculated in the manner discussed in section 2.1.4.

The discussion of section 2.2.2. shows that the accuracy of our numerical integration methods can be improved (when the potential V is bounded at r = 0) by the simple procedure of using the quantity $(V-E)+\frac{1}{12}h^2(V-E)^2$ instead of $(V-E)$ in the numerical integration. This is accomplished in the programme by including three extra lines (between lines 65 and 70) which carry out this replacement. For example the instruction

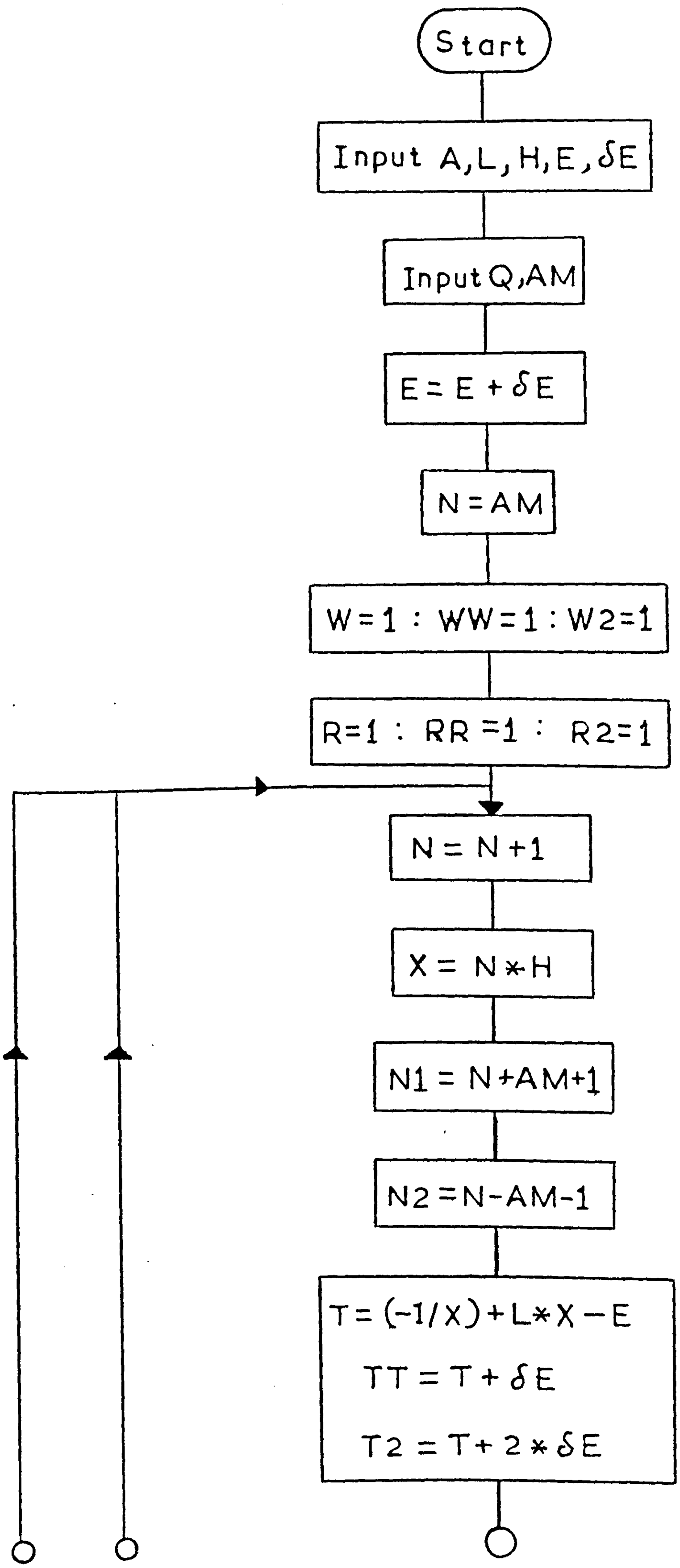
```
T = T+T*T*H*H/12
```

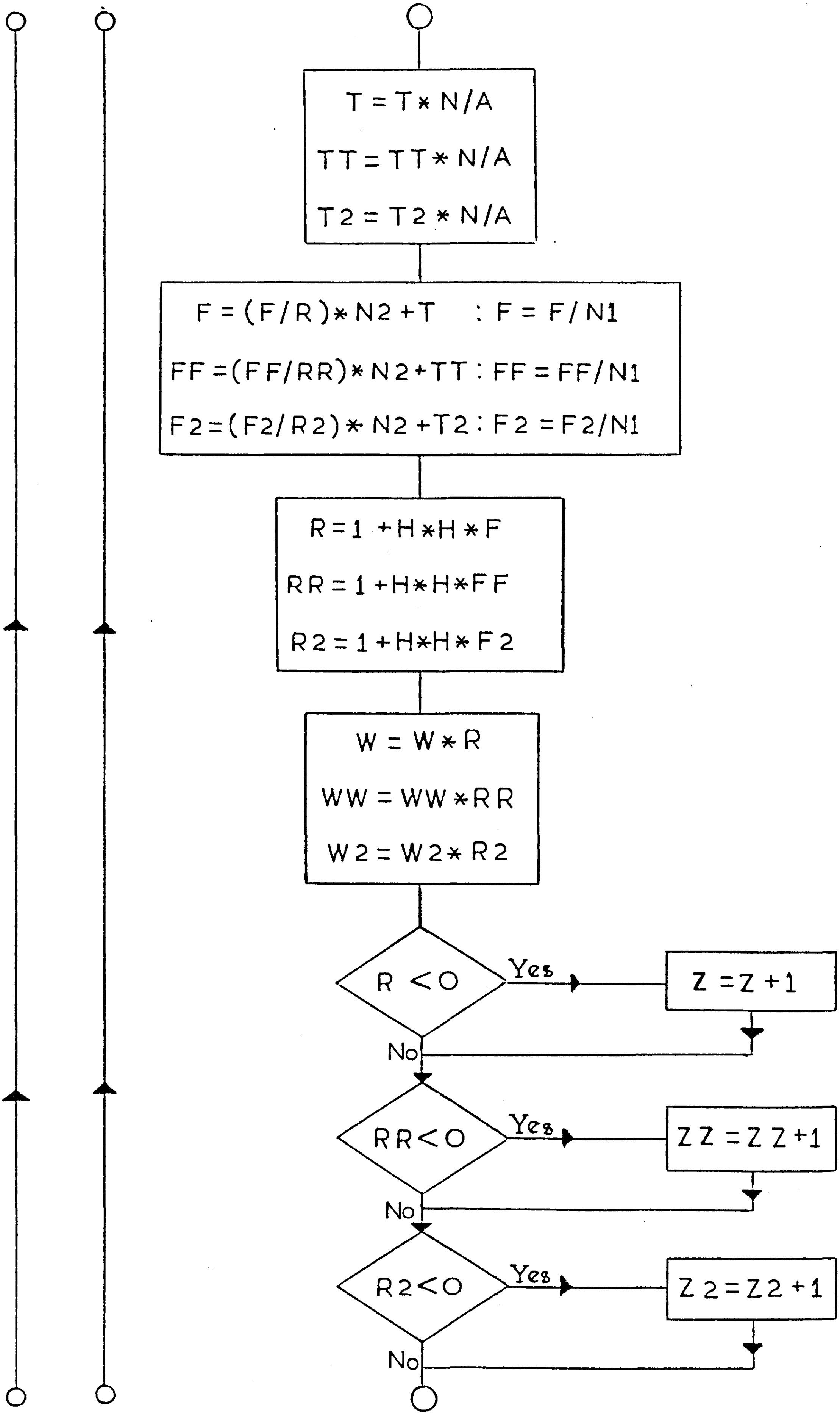
(with similar lines for TT and T2) would serve this purpose

## A1.3 <u>Flow-chart</u>

The flow-chart is shown in figure A1.

# F-METHOD


Start
Input A,L,H,E,δE
Input Q,AM
E=E+δE
N=AM
W=1 : WW=1 : W2=1
R=1 : RR=1 : R2=1
N=N+1
X= N*H
N1 = N+AM+1
N2=N-AM-1
T=(-1/X)+L*X-E
TT=T+δE
T2=T+2*δE


T = T * N/A
TT = TT * N/A
T2 = T2 * N/A
F = (F/R) * N2 + T : F = F/N1
FF = (FF/RR) * N2 + TT : FF = FF/N1
F2 = (F2/R2) * N2 + T2 : F2 = F2/N1
R = 1 + H * H * F
RR = 1 + H * H * FF
R2 = 1 + H * H * F2
W = W * R
WW = WW * RR
W2 = W2 * R2
R < O
Yes
Z = Z + 1
No
RR < O
Yes
ZZ = ZZ + 1
No
R2 < O
Yes
Z2 = Z2 + 1
No

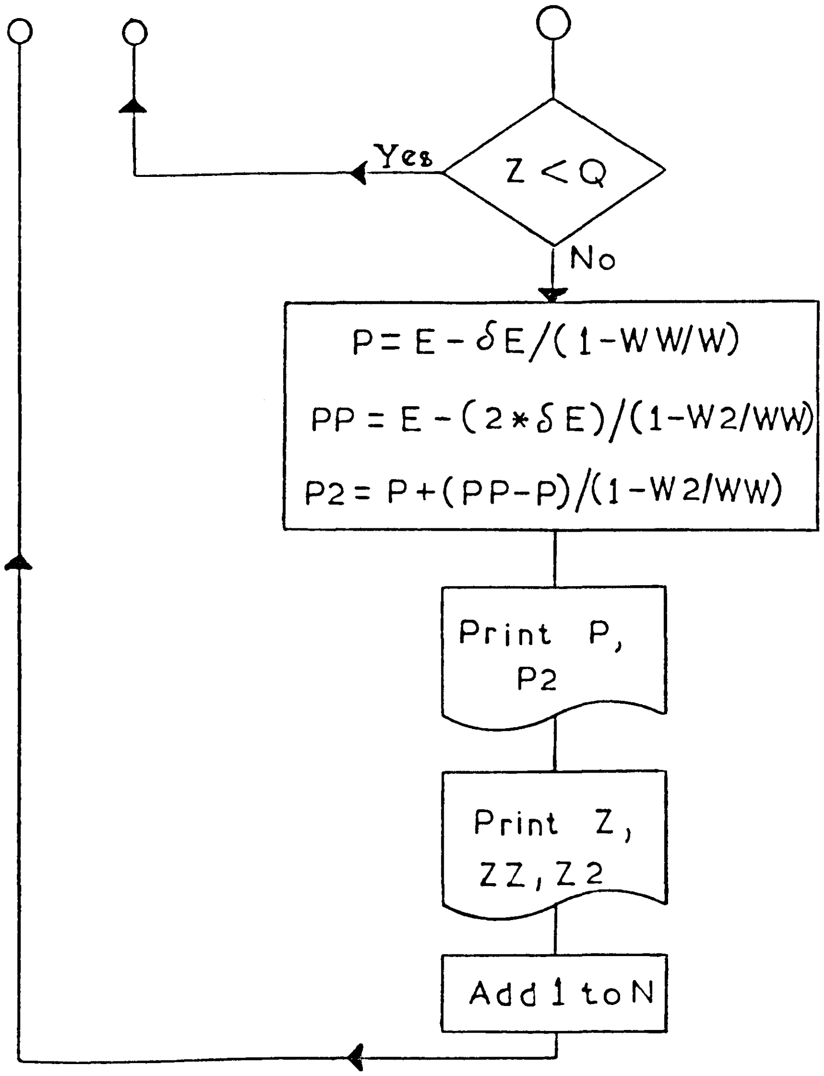

Yes
Z < Q
No
P = E - δE/(1-WW/W)
PP = E - (2*δE)/(1-W2/WW)
P2 = P+(PP-P)/(1-W2/WW)
Print P, P2
Print Z, ZZ, Z2
Add 1 to N

Figure A1

# APPENDIX A2

## HYPER

### A2.1 BASIC Programme

```
  5  PRINT "ENERGY COEFFICIENTS FOR V =-1/R+λR↑P"
 10  INPUT "P VALUE"; P
 15  INPUT "Q VALUE"; Q
 20  DIM X(8*Q,Q)
 25  DIM E(Q+1)
 30  INPUT "E VALUE"; E(0)
 35  V = Q*P
 40  X(0,0) = 1
 45  X(1,0) = -3/(4*E(0))
 50  FOR I = 2 TO V
 55  X(I,0) = (-(2*I+1)*X(I-1,0)-I*(I*I-1)*X(I-2,0)/4)/((2*I+2)*E(Q))
 60  PRINT "A"; I; X(I,0)
 65  NEXT I
 70  E(1) = X(P,0)
 75  R = V-P
 80  FOR M = 1 TO Q
 85  FOR I = 1 TO R
 90  T = 0
 95  FOR N = 1 TO M
100  S = E(N)*X(I,M-N)
105  T = T+S
110  NEXT N
115  IF I = 1 THEN 125
120  IF I<>1 THEN
125  X(I,M) = (2*I+P+2)*X(I+P,M-1)-(2*I+1)*X(I-1,M)
130  X(I,M) = (X(I,M) — (X(I,M)-(2*I+2)*T)/((2*I+2)*E(0))
135  GOTO 150
140  X(I,M) = (2*I+P+2)*X(I+P,M-1)-(2*I+1)*X(I-1,M)-I*(I*I-1)*X(I-2,M)/4
145  X(I,M) = (X(I,M)-(2*I+2)*T/((2*I+2)*E(0))
150  PRINT I; M; X(I,M)
155  E(M+1) = X(P,M)/(M+1)
160  NEXT I
165  IF I>R THEN R = R-P
170  NEXT M
175  FOR J = 0 TO Q
180  PRINT J; E(J)
185  NEXT J
```

### A2.2 Comments on the Hyper Programme

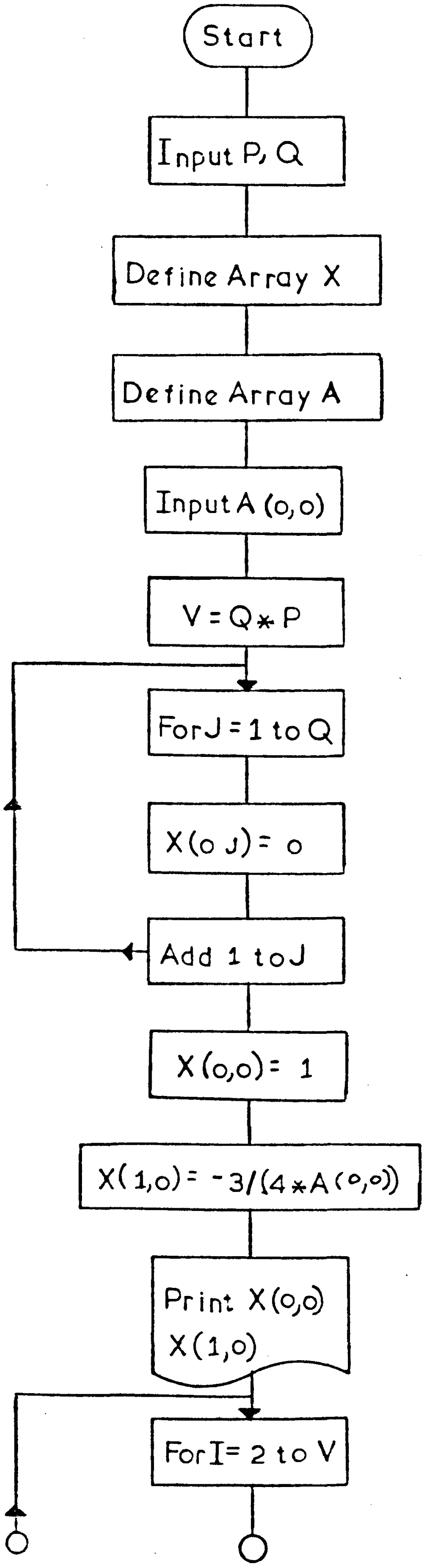
The input variables are as follows. P is the power of r in the potential function $V = \lambda r^{P} - r^{-1}$ (P is a positive integer). Q is the number of energy coefficients wanted. E(0) is the value of the unperturbed energy for the hydrogen s state considered. (Modification to allow treatment of states with $\ell > 0$ is possible).

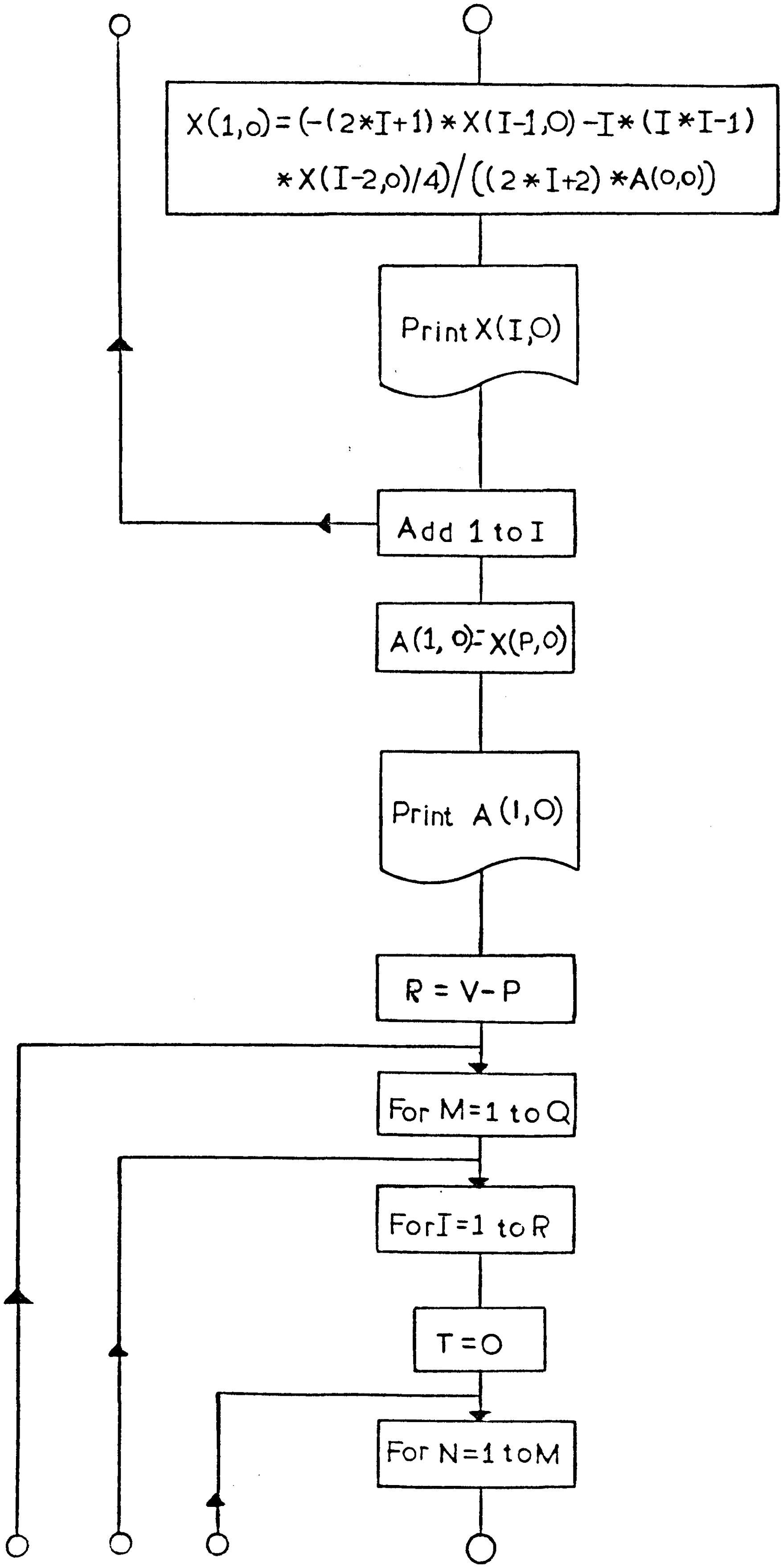
The element X(0,0) of the array X(I,M) is equivalent to $X_{0,0}$ in the text (section 3.1.1.), and is equal to 1, i.e., the value of the zero order coefficient in the series for $\langle r^0 \rangle \equiv 1$

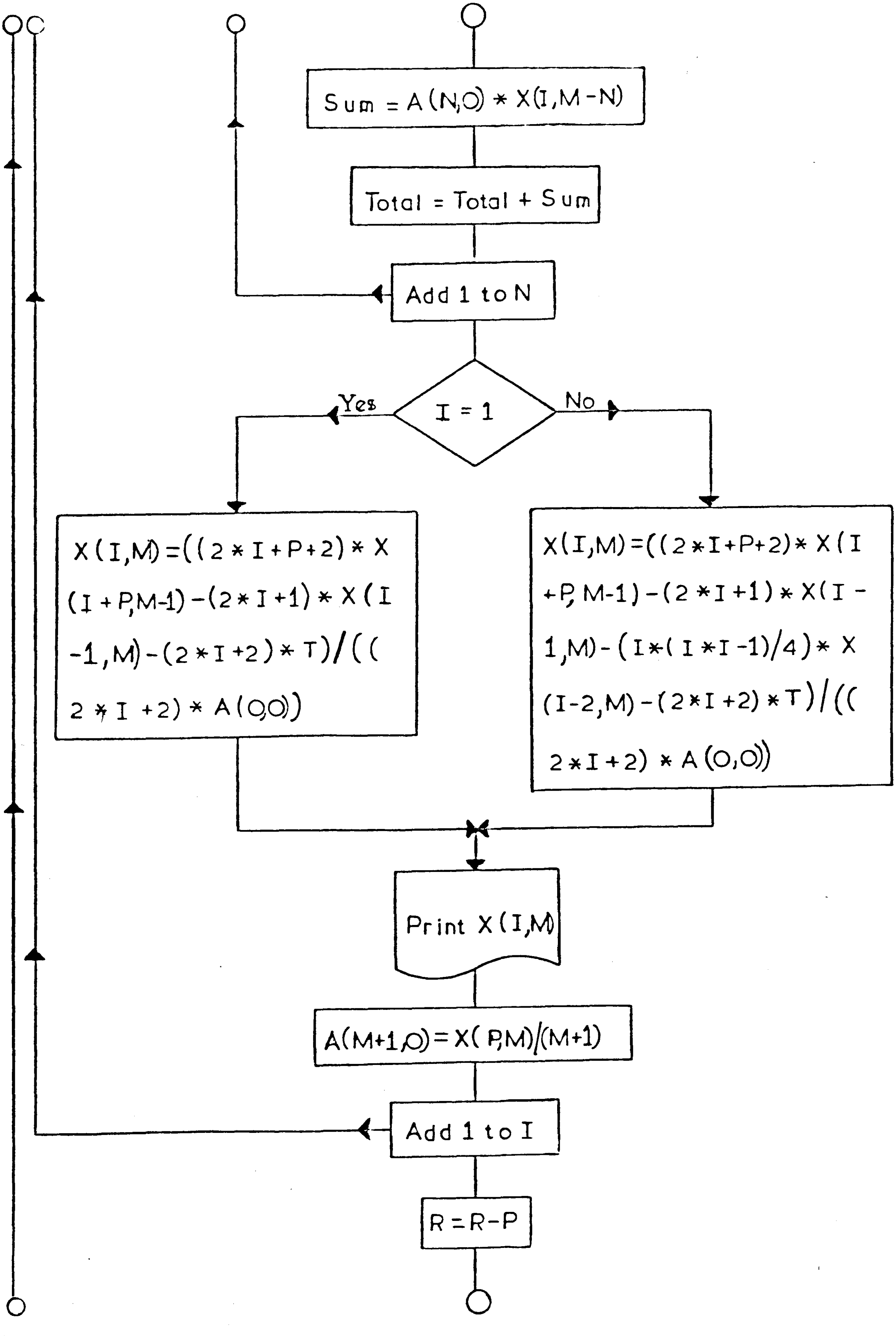
### A2.3 Flow-chart

The flow-chart is shown in figure A2.

HYPER


Start
Input P, Q
Define Array X
Define Array A
Input A (o,o)
V = Q * P
For J = 1 to Q
X(o J) = o
Add 1 to J
X(o,o) = 1
X(1,o) = -3/(4*A(o,o))
Print X(o,o)
X(1,o)
For I = 2 to V


X(1,o)=(-(2*I+1)*X(I-1,O)-I*(I*I-1)
*X(I-2,o)/4)/((2*I+2)*A(0,0))
Print X(I,O)
Add 1 to I
A(1,0)=X(P,0)
Print A(1,0)
R = V-P
For M=1 to Q
For I=1 to R
T=O
For N=1 to M


Sum = A (N,O) * X(I,M-N)
Total = Total + Sum
Add 1 to N
I = 1
Yes
No
X(I,M)=((2*I+P+2)*X(I+P,M-1)-(2*I+1)*X(I-1,M)-(2*I+2)*T)/((2*I+2)*A(O,O))
X(I,M)=((2*I+P+2)*X(I+P,M-1)-(2*I+1)*X(I-1,M)-(I*(I*I-1)/4)*X(I-2,M)-(2*I+2)*T)/((2*I+2)*A(O,O))
Print X(I,M)
A(M+1,O)=X(P,M)/(M+1)
Add 1 to I
R=R-P

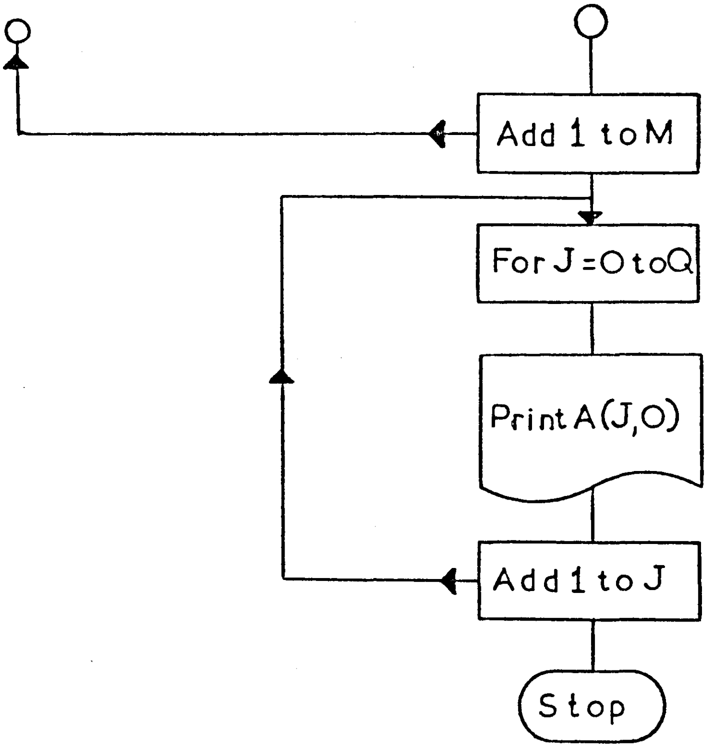


Figure A2

# APPENDIX A3

## 2-HYPER

### A3.1 BASIC Programme

```
  5  PRINT "ENERGY COEFFICIENTS FOR V = -1/R+2λR+2λ↑2R↑2"
 10  INPUT "Q VALUE"; Q
 15  DIM E(Q+1), B(8*Q,Q)
 20  INPUT "L VALUE"; L
 25  INPUT "E VALUE"; E(0)
 30  B(0,2) = -2*E(0)
 35  B(1,2) = 1
 40  FOR M = 0 TO Q-2
 45  FOR N = 1 TO Q-1
 50  S = 0
 55  FOR P = 0 TO M
 60  S = S+E(P)*B(N+1,M+2-P)
 65  NEXT P
 70  R = (4*N+6)*B(N+2,M+1)+(4*N+8)*B(N+3,M)
 75  R = R-(2*N+1)*B(N,M+2)-N*(NXN-1)*B(N-1,M+2)/4
 80  R = R+N*L*(L+1)*B(N-1,M+2)
 85  B(N+1,M+2) = (R/(2*N+2)-S)/E(0)
 90  PRINT N-1; M-1; "  "; B(N+1,M+2)
 95  E(M+1) = (2*B(2,M+2)+4*B(3,M+1))/(M+1)
100  B(0,3) = E(1)
105  NEXT N
110  NEXT M
115  FOR J = 0 TO Q
120  PRINT "E"; "J"; E(J)
125  NEXT J
```

### A3.2 Comments on 2-Hyper Programme

This programme, which is meant to be used to find the energy coefficients for the potential $V = -r^{-1} + 2\lambda r + 2\lambda^2 r^2$, can be used for the potential $V = \lambda r - r^{-1}$ by replacing line 70 by R = (2*N+3)*B(N+2, M+1) and line 95 by E(M+1) = B(2,M+2)/(M+1).

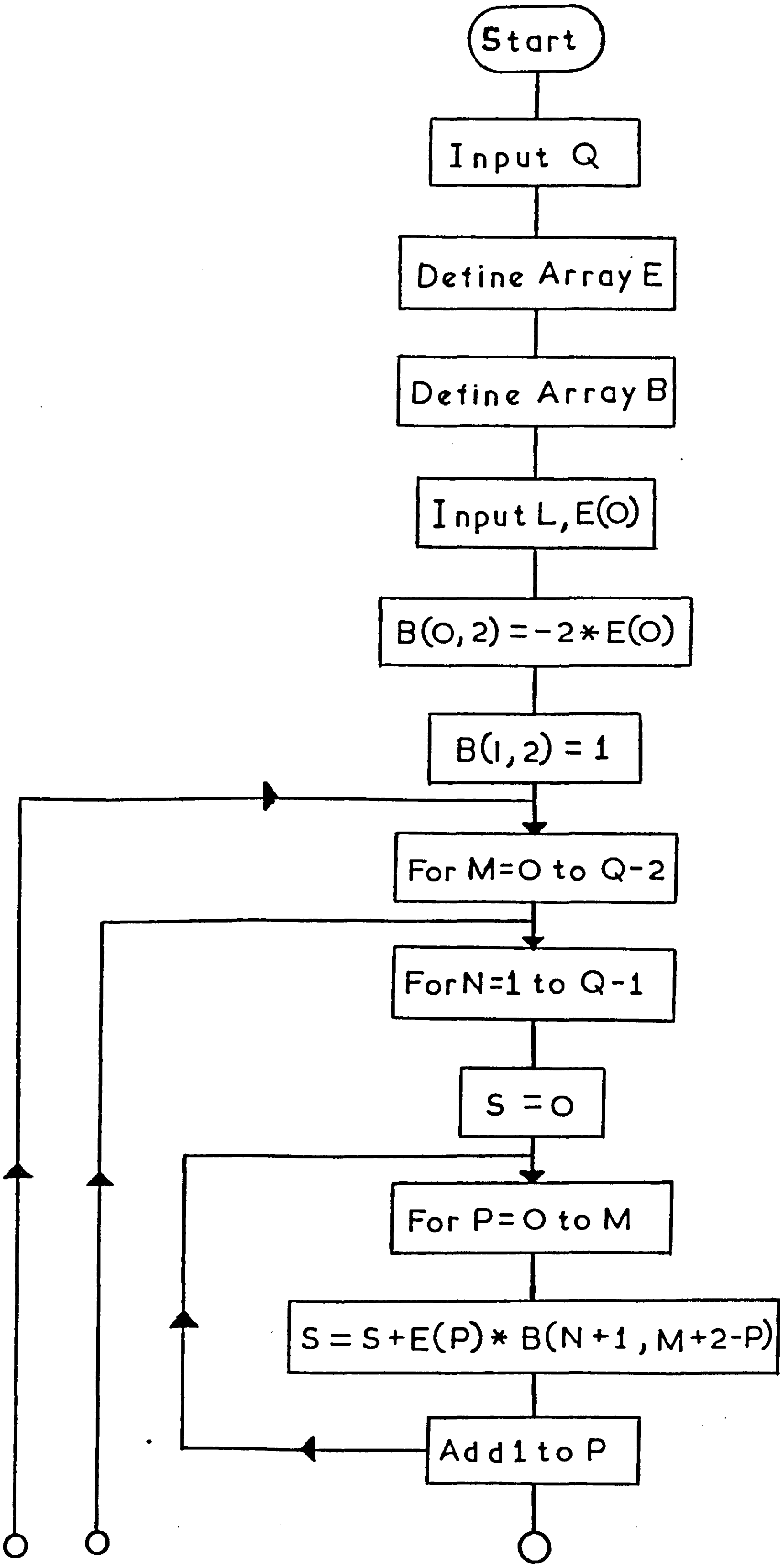
The input variables represent the same as for the Hyper programme, with the addition of L, the angular momentum. The programme works for p and d states as well as s ones. The relevant modification is explained theoretically in section 3.1.5. and is executed in the programme by inclusion of line 80, which appropriately modifies the coefficient of

B(N-1,M+2).

## A3.3 Flow-chart

The flow-chart is shown in figure A3.

## 2-HYPER


Start
Input Q
Define Array E
Define Array B
Input L, E(O)
B(O, 2) = -2 * E(O)
B(1, 2) = 1
For M=O to Q-2
For N=1 to Q-1
S = O
For P=O to M
S = S+E(P) * B(N+1, M+2-P)
Add 1 to P

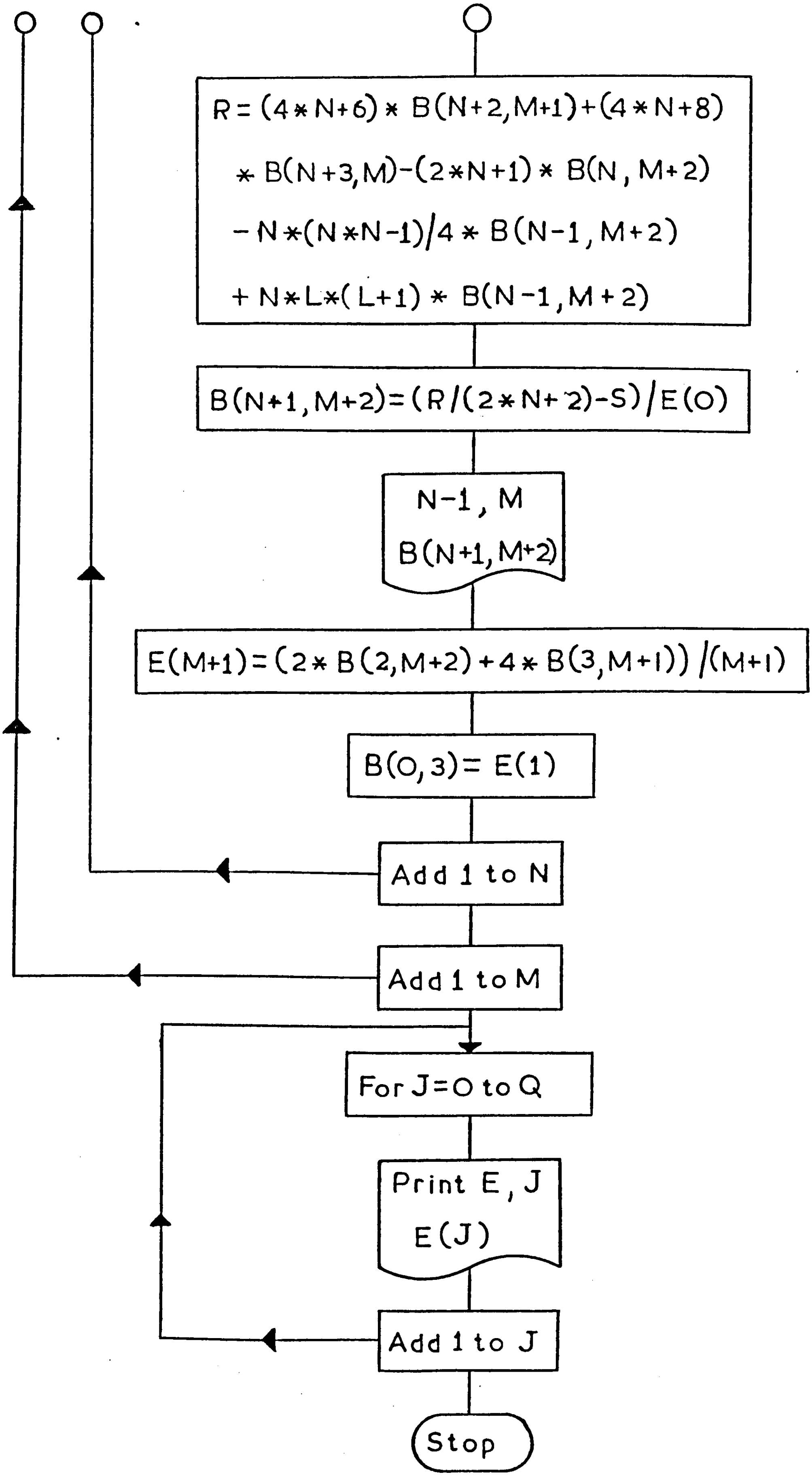

R = (4*N+6) * B(N+2,M+1)+(4*N+8) * B(N+3,M)-(2*N+1) * B(N, M+2) - N*(N*N-1)/4 * B(N-1, M+2) + N*L*(L+1) * B(N-1,M+2)
B(N+1,M+2)=(R/(2*N+2)-S)/E(0)
N-1, M
B(N+1,M+2)
E(M+1)=(2*B(2,M+2)+4*B(3,M+1))/(M+1)
B(0,3)= E(1)
Add 1 to N
Add 1 to M
For J=0 to Q
Print E, J
E(J)
Add 1 to J
Stop

Figure A3

# APPENDIX A 4

## WYNN

### A4.1 BASIC Programme

```
  5  PRINT "PADE APPROXIMANTS"
 10  INPUT "Q VALUE"; Q
 15  DIM C(Q+20)
 20  DIM T(Q+5,Q+5)
 25  INPUT "C(0) VALUE"; C(0)
  .
  .
  .
 30  INPUT "C(Q) VALUE"; C(Q)
 35  INPUT " λVALUE"; L
 40  T(1,3) = C(0)↑2/(C(0)-C(1)*L)
 45  T(0,1) = C(0)-(C(1)*L*(T(1,3)-C(0)))/(T(1,3)-C(0)-C(1)*L)
 50  FOR I = 0 TO Q
 55  T(I,0) = 0
 60  NEXT I
 65  T(1,1) = C(0)
 70  FOR I = 2 TO Q+1
 75  T(I,1) = T(I-1,1)+C(I-1)*(L↑(I-1))
 80  PRINT T(I,1)
 85  NEXT I
 90  J = 1
 95  FOR M = 1 TO Q+1
100  FOR N = J TO Q+1
105  T(N,M+1) = T(N-1,M-1)+(T(N,M)-T(N-1,M)↑(-1)
110  PRINT N-1-M/2; M/2; T(N,M+1)
115  NEXT N
120  IF N>Q+1 THEN J = J+1
125  IF J>Q+1 THEN 35
130  NEXT M
```

### A4.2 Comments on the Wynn Programme

The input variables are as follows. Q is the number of coefficients of the power series which is to be used. C(0), C(1), ... C(Q) are the numerical values of the coefficients. λ (L) is the value of the perturbation parameter in the potential function, for our problems, but in general is the λ value for which the sum of the power is required.

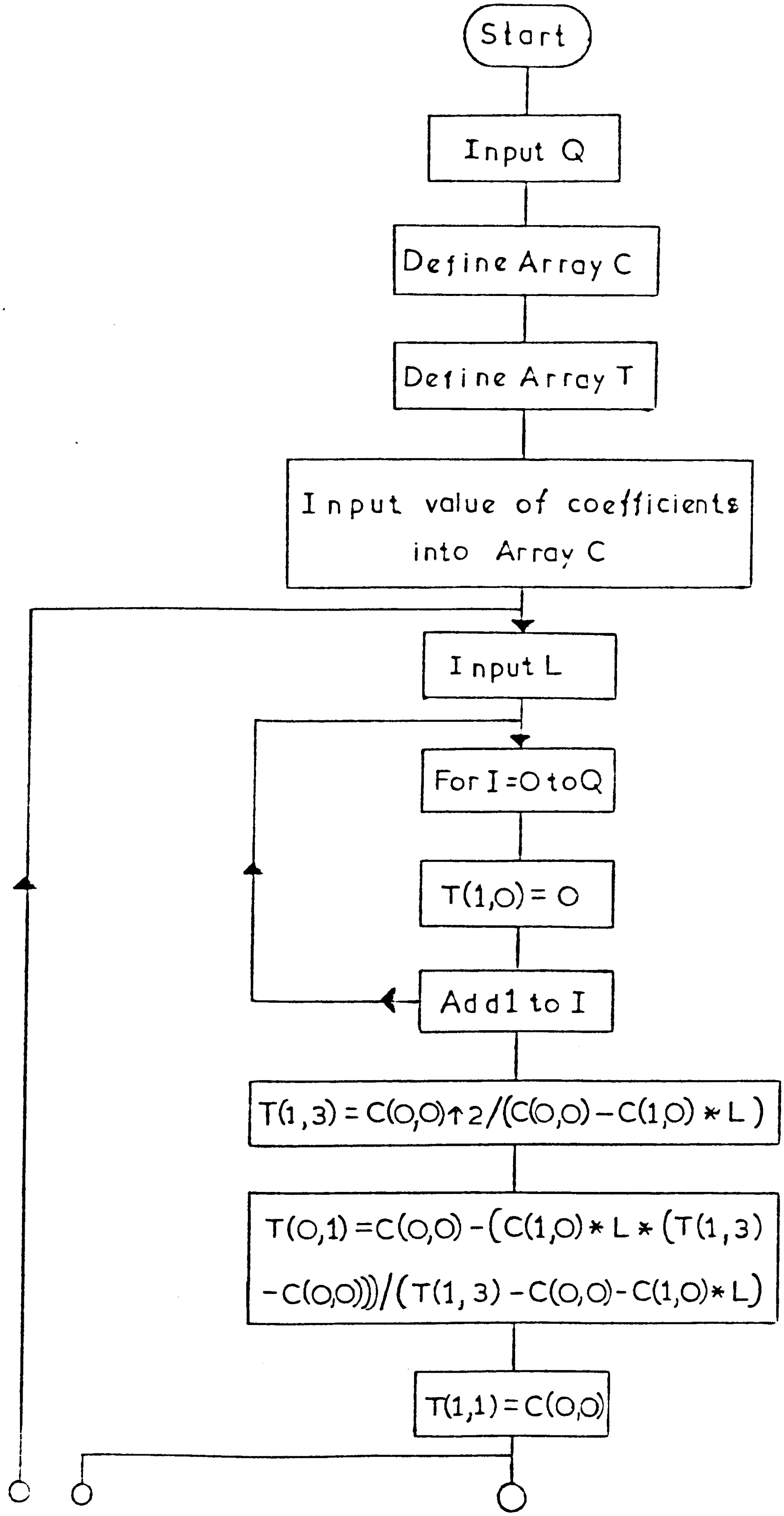
Wynn's algorithm allows us to calculate Padé approximants of the form $[J,J]$, $[J,J-1]$, ..., $[J,1]$ only, but the programme is written so as to calculate also the approximants $[0,1]$, $[1,2]$, etc. which are not mentioned in Wynn's original algorithm.

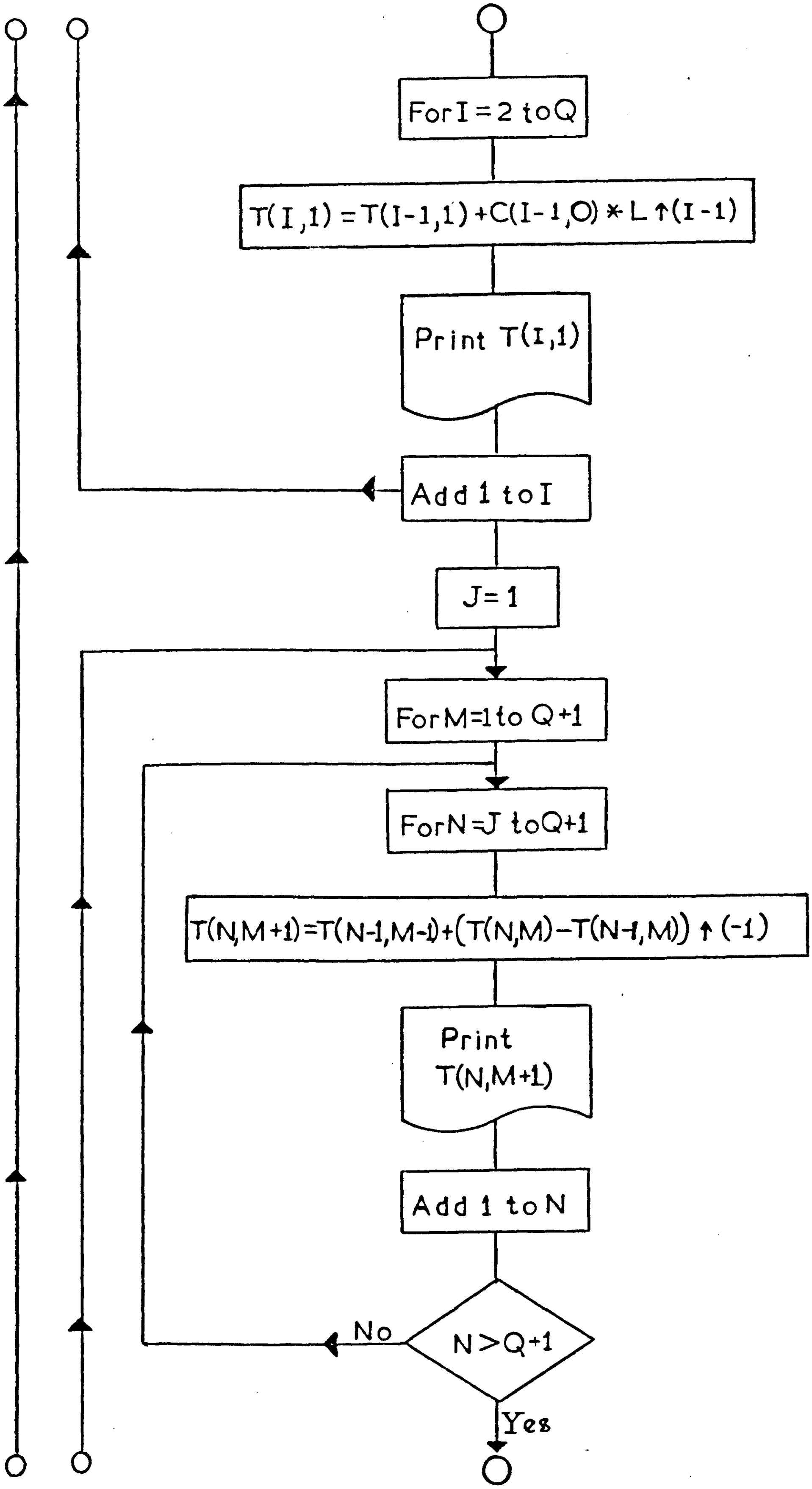
For numerical purposes it is often sufficient to know the values of $[J,J]$ and $[J,J-1]$ because, as has been discussed in section 3.2.3., the exact value often lies between these approximants. The line 110 of the programme displays first the $[N,1]$ coefficients, then the $[N,2]$ coefficients, and so on, together with their labels.

### A4.3 Flow-chart

The flow-chart is shown in figure A4.

# WYNN


Start
Input Q
Define Array C
Define Array T
Input value of coefficients into Array C
Input L
For I = 0 to Q
T(1,0) = 0
Add 1 to I
T(1,3) = C(0,0)↑2/(C(0,0) − C(1,0) * L)
T(0,1) = C(0,0) − (C(1,0) * L * (T(1,3) − C(0,0)))/(T(1,3) − C(0,0) − C(1,0) * L)
T(1,1) = C(0,0)


For I = 2 to Q
T(I,1) = T(I-1,1) + C(I-1,O) * L ↑ (I-1)
Print T(I,1)
Add 1 to I
J = 1
For M=1 to Q+1
For N=J to Q+1
T(N,M+1)=T(N-1,M-1)+(T(N,M)−T(N-1,M)) ↑ (-1)
Print T(N,M+1)
Add 1 to N
No
N > Q+1
Yes

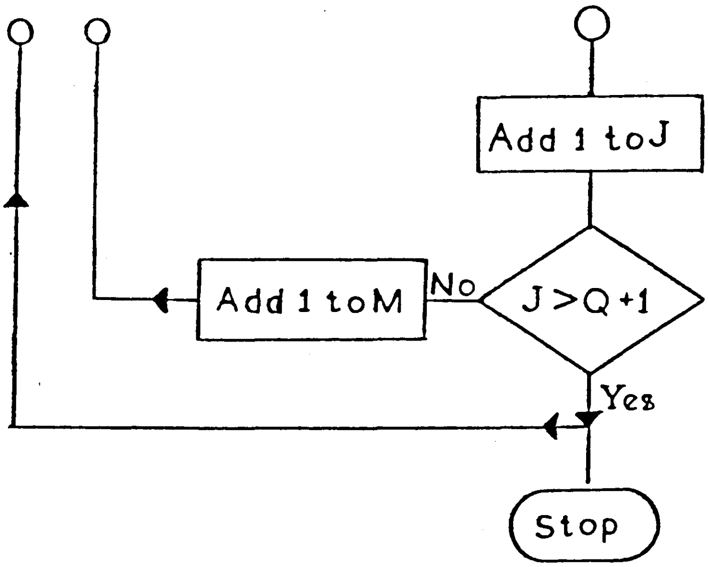


Figure A4

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# PUBLICATIONS

The following papers, concerned with the present work, have been accepted for publication.

1. Galicia, S. and Killingbeck, J., Accurate Calculations of Perturbed Oscillator Energies. Phys. Lett. A71 (1979) 17.
2. Killingbeck, J. and Galicia, S. The $\Psi$ (o) Problem for Charmonium Hamiltonians. (In the Press).