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SOME PROBLEMS IN THE THEORY OF LARGE AMPLITUDE VIBRATIONS IN TRIATOMIC MOLECULES

BY

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ABSTRACT

In a first part, the hamiltonian for nuclear motion of arbitrary amplitude is formulated in terms of orthogonal internal coordinates. A family of such coordinates is discussed and a particular system is derived (symmetric representation). Plots of the molecular potential in such coordinates serve to determine coordinates in which the potential approaches separability[1]. A linear molecule (CO_2) illustrates the discussion.

In a second part, the set of 1-dimensional Schroedinger equations involved in the previous hamiltonian are solved numerically. A technique (the Renormalized Numerov method) is adapted to various situations concerning both the shape of the Schroedinger equation and the boundary conditions. A new algorithm is proposed as a generalization to unusual situations in order to cover most of the situations arising in the study of either vibrational or scattering problems in molecular quantum theory.

PREFACE.

The purpose of this work is to point out some problems arising in the quantum-mechanical study of large amplitude vibrations in triatomic molecules. One of the problems encountered in such a study concerns the choice of a suitable coordinate system in terms of which the kinetic energy operator is diagonal while the potential remains the most separable possible. Such a search of coordinates systems has been a fundamental preoccupation in molecular quantum theory during the past decades[18-23,72-75]; the spectrum of various alternatives has been initiated from the basic work of Wilson, Decius and Cross[12] for small amplitude vibrations. So far, no "ideal" system has been proposed and it is reasonable to think that such a system does not exist. Therefore, our preoccupation remains in the search of a system approaching this ideal for large amplitude vibrations.

On the other hand, the recent development of computer techniques allows us to consider numerical solutions of some problems as a valuable alternative to situations where no solutions (or at least where long and tedious treatments were required) were possible a few years ago. Without pretending to solve all the problems, such a development opens the way

to a new fashion of considering the theoretical approach in our field of investigation.

These considerations induce us to be preoccupied in this work firstly with coordinate systems considerations and in parallel with numerical solutions of the problems arising from the formulation of the equations describing a 3-body system in this context.

Essentially, this work is a modest addition to the fundamental work undertaken by R.Wallace in molecular quantum chemistry in order to constitute a footing to further search especially in the study of the N-body problem.

The reader may be discouraged by the length of this dissertation, but the nature of the subjects treated and the will to present a complete survey over of the areas oblige us to elaborate on certain points.

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CHAPTER 1.

INTRODUCTION.

The present thesis is divided into two parts.

(1): the derivation of the hamiltonian for the relative motion of a three atomic linear molecule (CO_2) leading to the consideration of three 1-dimensional Schroedinger equations describing the zeroth-order approximation of the problem.

(2): the numerical solutions of these equations.

The logical procedure to be followed in simplifying the quantum-mechanical description of the 3-body problem (as well as the N-body) in field free space is to take advantage of the invariance of the potential with respect to translation and rotation. By doing so the rotation-vibration hamiltonian may be expressed in terms of the 3 relative coordinates together with rotational (and translational) quantum numbers. It is unfortunate that almost all coordinates describing the relative motion are neither orthogonal to each other nor to the Euler angles describing rotation. In consequence, the quantum-mechanical vibrational kinetic energy operator couples vibrational coordinates and vibrational states corresponding to different angular momemtum quantum numbers. A choice of coordinates which minimizes such couplings is a desirable ideal.

The separation of the center of mass motion from the

remaining 3 coordinates in the center of mass/lab parallel frame is obvious; the separation of the rotational coordinates was treated by Hirschfelder and Wigner[5] and by Curtis et al [6]. These authors showed also how the hamiltonian for the relative motion could be obtained by integrating over the Euler angles. Unfortunately, the choice of the coordinates referred to was non-orthogonal and the resulting hamiltonian was of complicated form. In a series of later paper, Hirschfelder and Dahler[7], Jepsen and Hirschfelder[8] and Hirschfelder[9] showed how a "family" of orthogonal relative coordinates could be defined but they did not incorporate these into the previous hamiltonian. In a series of recent papers, Wallace[1-4,10] derived the expression for the three-body hamiltonian in incorporating the "family" of orthogonal relative coordinates into the original framework of Hirschfelder for the N-body problem. The resultant hamiltonian being re-expressed in polar coordinates, the "radial" coordinates are found to be orthogonal to each other and to all "angular" coordinates, being themselves orthogonal to each other but not to the Euler angles. Searching among the members of the "family" of coordinates, it is usually possible to find a "member" in which the molecular potential approaches separability. Maximal orthogonality of coordinates and near potential separability allow a partitioning of the hamiltonian into "large" and "small" components where the "large" component is of sufficiently simple form to permit solution of its

eigenproblem; the resulting eigenfunctions constitute a suitable basis for a matrix representation of the entire hamiltonian.

In the second chapter, after a brief discussion of the Hirschfelder coordinates family for the N-body, we restrict our attention to the 3-body problem. So far only three members of the "family" of orthogonal coordinates were used in the derivation of the hamiltonian, these representations are designated in what follows by the "discrete" representations since they correspond to three "physically" representable coordinates. We propose here a general scheme permitting the transformation from one member to the others. Furthermore, we extend the " discrete family" to a "continuous family" containing an infinity of members which may be obtained one from each other in using the previous scheme. In particular a " member" appears to be particularly interesting considering the separability of the potential. We called it the "symmetric" representation since it is related to the principal axes of inertia in a symmetric manner.

The discussion of the hamiltonian of the 3-body constitutes the aim of the third chapter. The remainder of this chapter is devoted to some features of how the theory may be applied in the case of the CO_2 molecule.

The second part of the thesis concerns the solutions of the various Schroedinger equations resulting from the treatement of the hamiltonian of the 3-body. Two different forms of these equations arise in such a treatement and

various boundary conditions have to be considered. The "radial" equations which do not involve explicitly the first derivative of the eigensolution and the "angle" equations (similar to the Legendre equation) which involves the first derivative. Furthermore the shape of the effective potential function in the second kind of equations leads to finite non-zero values of the eigensolution at the bounds, which represents non usual boundary conditions. So far finite difference techniques such as that due to Sturm[11] or, more recently, the log-derivative (L-D)[13] and Renormalized Numerov method[14,15] (R-N-M) can be applied to solve some of these equations under some specific boundary conditions (i.e., for situations where the first derivative term is absent and where the eigensolution is zero at the bounds). In a recent paper, Leroy and Wallace[16] extend the R-N-M so that it may be applied to equations which possess a first derivative term and/or which are characterized by boundary conditions other than $\Psi(x)=0$ at the bounds. Such boundary conditions arise in bound state problems for which the potential is finite at the bounds and its gradient is different from zero in addition to which the eigensolution must satisfy the usual requirements of continuity and be square integrable. A complete and formal developement of the theory accompanied by a new algorithm permitting the extention of the R-N-M to most of the situations encountered in the present context is presently achieved and will be submitted soon.

The second part is then presented as follows. In chapter 4, we resume most of the principal features of the numerical treatment of second-order ordinary differential equations. We emphasize particularly shooting and finite difference methods. In chapter 5, the L-D and R-N-M methods are briefly discussed and simple problems illustrate the process. The extention of the methods to problems where $\Psi(x)$ is different from zero at the bounds but where it is known that the first derivative of the solution is zero at the bounds is illustrated in the case of well-known problems and the numerical solutions are compared to their analytic counterparts. Chapter 6 consists of the elaboration of the scheme able to be applied to the very general problem involving both the first derivative term in the equation and where minimal information about the solution is available at the bounds. The scheme is tested over a problem where an analytic solution exists (the Legendre equation) and over a problem where no analytic solution is available but which may be solved by another way ("complete set" expansion in terms of associated Legendre polynomials). Results are compared.

P A R T O N E

COORDINATE SYSTEMS

AND

SCHROEDINGER EQUATIONS FOR THE 3-BODY SYSTEM.

CHAPTER 2. COORDINATES SYSTEMS.

1. INTRODUCTION-FORMALISM.

The instantaneous configuration of a system of N particles in space is fixed by 3N scalars which may be regarded as the components of a vector $\vec{X}$ belonging to a 3N-dimensional vector space E_{3N} where a basis B has been defined (figure 1-1). Let B be the canonical basis which elements are $\vec{e}_{\alpha i} = (0,\ldots,1,0,..0)$, 1 at the $(3\alpha+i)^{th}$ slot. Then if $x^{\alpha i}$ is the i^{th} cartesian coordinate of the α^{th} atom, the vector $\vec{X}$ is expressed in the only manner:

$$\vec{X} = \Sigma_{\alpha,i} x^{\alpha i} \vec{e}_{\alpha i} \qquad (\alpha=1,\ldots,N;\ i=1,2,3) \tag{1-1}$$

and since B is an orthonormal basis:

$$\langle \vec{e}_{\alpha i}, \vec{e}_{\beta j} \rangle = \delta_{\alpha\beta}\delta_{ij} \tag{1-2}$$

The position vector $\vec{R}^{\alpha}$ of atom α belongs to a 3-dimensional sub-space E^{α} (which is the ordinary 3-D cartesian space) and is expressed by:

$$\vec{R}^{\alpha} = \Sigma_i x^{\alpha i} \vec{e}_{\alpha i} \qquad (i=1,2,3) \tag{1-3}$$

FIGURE (1-1): COORDINATES OF THE N-BODY

$\vec{R}^{\alpha}$ is the vector position of particle α defined in a three-dimensional orthonormal frame by the components $x^{\alpha i}$, $x^{\alpha j}$ and $x^{\alpha k}$.

$\vec{R}^{\alpha\beta}$ is the bond distance vector defined by $\vec{R}^{\beta} - \vec{R}^{\alpha}$.

$\vec{q}^{i}$ is the vector joining the centers of mass of two groups of particles.

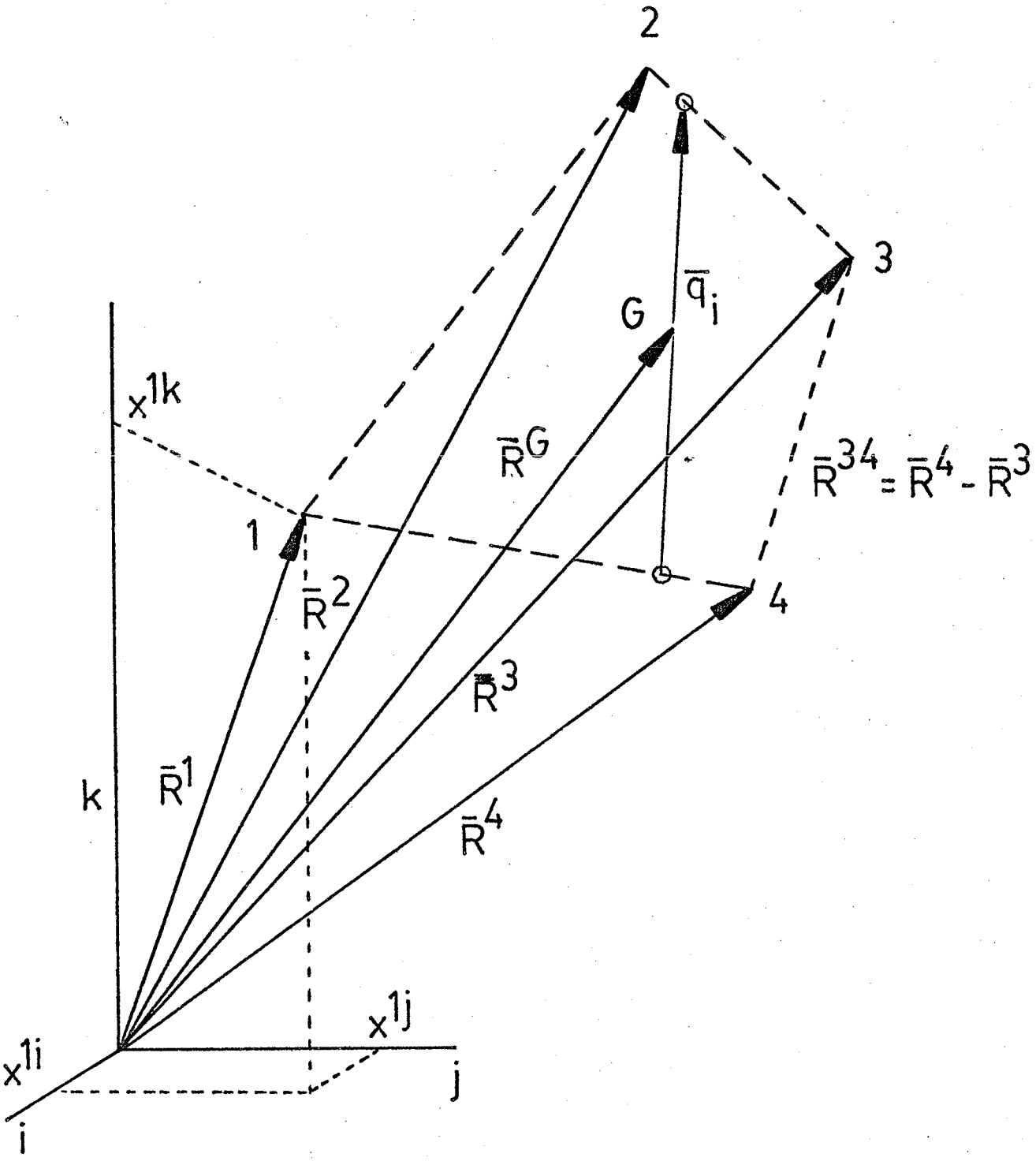

2
3
G
$\bar{q}_i$
x^{1k}
$\bar{R}^G$
$\bar{R}^{34} = \bar{R}^4 - \bar{R}^3$
1
$\bar{R}^2$
4
$\bar{R}^3$
k
$\bar{R}^1$
$\bar{R}^4$
x^{1j}
x^{1i}
j
i

FIG. (1.1)

We may also define the vectors $\vec{X}^i$ belonging to the N-dimensional subspace E^{*i} such that:

$$(1\text{-}4) \qquad \vec{X}^i = \Sigma_\alpha x^{\alpha i} \vec{e}_{\alpha i} \qquad (\alpha=1,\ldots,N)$$

The N dimensional space E_{3N} may then be regarded either as the tensor product (see appendix 1) of the spaces $E^1,\ldots,E^N$ or of the subspaces E^{*1}, E^{*2} and E^{*3}:

$$(1\text{-}5) \qquad E_{3N} = E^1 * \ldots * E^N = E^{*1} * E^{*2} * E^{*3}$$

Obviously the subspaces E^α are mutually orthogonal and so are the subspaces E^{*i}. Therefore we have the following relations:

$$(1\text{-}6) \qquad \langle \vec{R}^\alpha, \vec{R}^\beta \rangle = \Sigma_i x^{\alpha i} x^{\beta i} \delta_{\alpha\beta}$$

$$(1\text{-}7) \qquad \langle \vec{X}^i, \vec{X}^j \rangle = \Sigma_\alpha x^{\alpha i} x^{\alpha j} \delta_{ij}$$

$$(1\text{-}8) \qquad \langle \vec{X}^i, \vec{R}^\alpha \rangle = (x^{\alpha i})^2$$

The bond distance vectors $\vec{R}^{\alpha\beta} = \vec{R}^\beta - \vec{R}^\alpha$ are vectors of the 6-dimensional space $E_{\alpha\beta}$, direct sum of the spaces E_α and E_β ($E_{\alpha\beta} = E_\alpha \oplus E_\beta$), while the position vector of the center of mass of the system $\vec{R}^G$ belongs to E_{3N}. The vectors $\vec{q}_i$ defined by:

$$(1\text{-}9) \qquad \vec{q}_i = \vec{r}_c(A) - \vec{r}_c(B)$$

where $\vec{r}_c(A)$ and $\vec{r}_c(B)$ are respectively the centers of mass of the two groups of particles A and B will then belong to the 3a-dimensional space defined as the direct sum of the subspaces E_α, α belonging either to group A or B and a being the number of atoms involved in A and B.

Our (ideal) aim is to find an appropriate coordinate system such that the space E_{3N} could be expressed in the form of a tensor product of three subspaces E_T, E_R and E_V related respectively to the translations, the rotations and the vibrations of the system and mutually orthogonal. In other words we wish to express $\vec{X}$ in some coordinate system such that:

$$(1\text{-}10) \qquad \vec{X} = (q^1, q^2, \ldots, q^{3N-6}, s^1, s^2, s^3, x^{G1}, x^{G2}, x^{G3})$$

where q^i are internal coordinates, s^i, coordinates related to rotations (Euler's angles for example) and x^{Gi} related to the translations. The new coordinates are related to the old ones by single-valued continuous functions and we wish ideally that the metric tensor g_{ij} (see appendix 2) be diagonal or at least block-diagonal.

In order to simplify the writing, we shall temporarily consider the vectors $\vec{R}^\alpha$ as components of a N-dimensional vector space defined on the field of the 3x3 invertible matrices [17] such that the orthonormal basis is the set of $\vec{E}_\alpha = ((0,0,0), \ldots, (1,1,1), (0,0,0), \ldots, (0,0,0))$, (1,1,1) at the α^{th} slot.

In terms of this basis, $\vec{X}$ is expressed by:

$$(1\text{-}11) \qquad \vec{X} = (\vec{R}^1, \vec{R}^2, \ldots, \vec{R}^N)$$

Let A be the NxN matrix representing the operator transforming $\vec{X}$ into $\vec{Y}$ such that its components are the (N-1) bond distance vectors $\vec{R}^{\alpha\beta}$ and the vector position of the center of mass $\vec{R}^G$:

$$(1\text{-}12) \qquad \vec{Y} = A\vec{X}$$
$$= (\vec{R}^{12}, \vec{R}^{23}, \ldots, \vec{R}^{N-1,N}, \vec{R}^G)$$

The matrix A is then:

$$(1\text{-}13) \qquad A = \begin{bmatrix} -I & I & 0 & 0 & \ldots \\ 0 & -I & I & 0 & \ldots \\ 0 & 0 & -I & I & \ldots \\ \ldots & & & & \\ m_1 & m_2 & m_3 & & \ldots \end{bmatrix}$$

Our aim is then to find some matrix T such that applied to $\vec{Y}$ will provide a vector $\vec{Q}$ wich components are orthogonal projections on the three subspaces E_T, E_R and E_V, that is what we propose to explore in this chapter. A more formal and detailed discussion of the material presented in this introduction is certainely out of the purpose of this dissertation and is reserved for a further work.

2. HIRSCHFELDER COORDINATES FOR THE N-BODY PROBLEM.

Note: Most of the material presented in this section is issued from the references (5) to (9).

For a system constituted by N particles, the kinetic energy is given by:

$$2T = \Sigma_i m_i \dot{R}^2_i \qquad (2\text{-}1)$$

where the $\vec{R}_i$ are the position vectors of the particle relative to a fixed reference frame. As described in the first chapter, we want to define, for arbitrary amplitudes of motion, a set of coordinates $(\vec{Q}_i)$ such that the kinetic energy be of the form:

$$2T = \Sigma_i \dot{Q}^2_i \qquad (2\text{-}2)$$

We define the total mass of the system by $M = \Sigma_i m_i$ and the masses of groups of particles are:

$$M_A = \Sigma_\alpha m_\alpha \qquad (\alpha \in A) \qquad (2\text{-}3)$$

If we take $(1/2)\dot{Q}_N^2$ as the kinetic energy of the center of mass of the system the vector joining the origin of the fixed axes to the center of mass is obviously given by:

(2-4) $$\vec{Q}_N = M^{-1/2}\vec{R}_{CM} = M^{-1/2}\Sigma_i m_i \vec{R}_i$$

Let us define the following transformation of the normalized position vectors:

(2-5) $$(m_i)^{1/2}\vec{R}_i = \Sigma_k S_{ki}\vec{Q}_k(t)$$

where the S_{ki} form a unitary transformation and the $\vec{Q}_k(t)$ are the coordinates obtained by this transformation (the superscript (t) will appear clear later in the discussion). Therefore:

(2-6) $$\Sigma_i S_{ki} S_{ji} = \delta_{jk}$$

Since S is a unitary transformation, the new coordinates are given relative to the cartesians by:

(2-7) $$\vec{Q}_k(t) = \Sigma_i S_{ki}(m_i)^{1/2}\vec{R}_i$$

We may define the following vectors in the N-dimensional space:

(2-8) $$\vec{S}_i = (S_{i1},\ldots,S_{iN})$$

From (2-6) it is clear that the vectors $\vec{S}_i$ form an orthonormal set in the N-dimensional space.

From (2-4) and (2-7) we can choose:

(2-9) $$\vec{S}_N = (S_{N1},\ldots,S_{NN})$$

where for j=1,...,N:

(2-10) $$S_{Nj} = (m_j/M)^{1/2}$$

The remainder of the S_{kj} can be determined by the Schmidt orthogonalization process. The coefficients of $\vec{S}_1$ are determined in requiring that $\vec{Q}_i$ be a linear combination of $\vec{R}_1$ and $\vec{R}_2$ such that $\vec{S}_1$ be orthogonal to $\vec{S}_N$ and so on. In this manner we obtain for j=1,...,N-1:

(2-11) $$S_{kj} = -[m_k m_j/M_k M_{k-1}]^{1/2} \qquad (j<k+1)$$

(2-12) $$S_{kk} = [M_{k-1}/M_k]^{1/2} \qquad (j=k+1)$$

(2-13) $$S_{kj} = 0 \qquad (j>k+1)$$

Using this result, the vectors $\vec{Q}_k(t)$ are expressed by:

(2-14) $$\vec{Q}_k(t) = [m_{k+1}/M_k M_{k+1}]^{1/2}[\Sigma_j m_j(\vec{R}_{k+1}-\vec{R}_j)]$$
$$(j=1,\ldots,k;\ k=1,\ldots,N-1)$$

and

(2-15) $$\vec{Q}_N(t) = M^{-1/2}\Sigma_j m_j \vec{R}_j \qquad (j=1,\ldots,N)$$

Clearly $\vec{Q}_N(t)$ is equal to the square root of the total mass of the system times the vector position of the center of mass. The

other coordinates are proportional to a vector connecting the center of mass of the previously considered particles to a new particle. It is preferable to express the relation (2-14) as a function of the vector position of the center of mass of the previously considered particles (group A) in defining it by:

$$\vec{r}_C(A) = \Sigma_\alpha m_\alpha \vec{r}_\alpha / M_A \qquad (\alpha \in A) \tag{2-16}$$

Then the vectorial coordinate joining the group A to the group B is given by:

$$\vec{\varrho}_i(t) = [M_A M_B/(M_A+M_B)]^{1/2}[\vec{r}_C(A)-\vec{r}_C(B)] \tag{2-17}$$

Obviously if a group consists of a single particle, M_A is the mass and $\vec{r}_C(A)$ is the position vector of the single particle. It appears therefore that different sets of coordinates may be constructed depending on how the N particles have been divided; the kinetic energy of the total system is the sum of the kinetic energies for the individual subsystems.

Figure (2-1) illustrates some different ways to partition a system of 6 particles: each ball represents a particle, each rod a coordinate vector and each small loop a connection at the center of mass of the two ends of the rod. This form of coordinates suggests a "mobile" representation introduced by Hirschfelder and al.

As this figure illustrates, there are many different sets satisfying (2-2) and the nature of the problem will permit to

FIGURE (2-1):HIRSCHFELDER COORDINATES:6-BODY

Three different ways to represent the 6-body system in Hirschfelder coordinates: ● represent atoms and O represent the centers of mass of groups of atoms. ⊗ is the center of mass of the whole system.

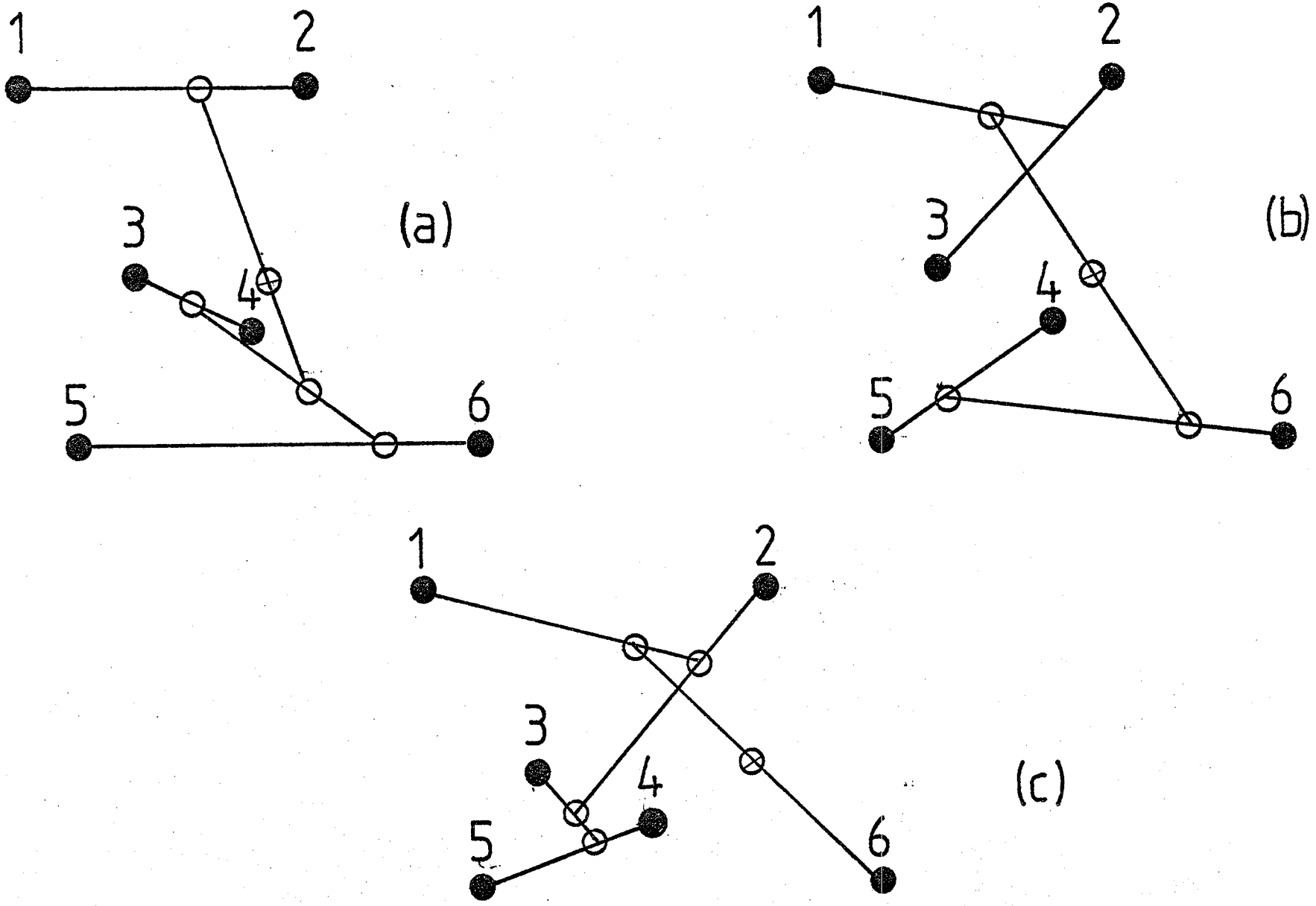


fig.(2-1)

decide which set is the most appropriate. We note that the first coordinate $\vec{Q}_N$ is common to all sets; in the rest of the discussion, we shall drop the superscript (t) for this coordinate. The previous introduction of this superscript is now legitimated since different systems of relative coordinates may be constructed for a system. As we shall see later, a three-particle system may be represented by three different "mobiles" and therefore there exist at least three sets of relative coordinates by which we can express the configuration of the system.

Each coordinate $\vec{Q}_i^{(t)}$ is then proportional to some vector expressing the difference between the position vectors of the centers of mass of two groups of particles A and B:

$$\vec{q}_i^{(t)} = \vec{r}_c(A) - \vec{r}_c(B) \tag{2-18}$$

We have now to show that the kinetic energy operator has the following form:

$$2T = \Sigma_i A_i \dot{q}_i^2 = \Sigma_i \dot{Q}_i^2 \tag{2-19}$$

where:

$$A_i = M_{Ai} M_{Bi} / (M_{Ai} + M_{Bi}) \tag{2-20}$$

and $\vec{Q}_i = (A_i)^{1/2} \vec{q}_i$

The momenta conjugate to these coordinates are:

(2-21) $$\vec{\pi}_i = \Lambda_i \vec{q}_i \quad ; \quad \vec{P}_i = \vec{Q}_i$$

and therefore:

(2-22) $$2T = \Sigma_i \pi_i^2 / \Lambda_i = \Sigma_i P_i^2$$

We note that for a particular "mobile", each coordinate $\vec{q}_k^{(t)}$ is related to any of the other coordinates $\vec{q}_l^{(t)}$ in one of three ways: if $\vec{q}_k^{(t)}$ joins the centers of mass of groups A and B while $\vec{q}_l^{(t)}$ joins the centers of mass of groups C and D then the three possibilities are:

(1) A and B are completely independent of C and D

(2) C and D are contained in either A only or B only

(3) A and B are contained in either C only or D only

These relations guarantee that the kinetic energy operator contains no cross-terms.

In fixed coordinates, the hamiltonian is given by:

(2-23) $$H = \Sigma_i \pi_i^2 / 2m_i + V$$

The new set of coordinates is obtained by the transformation:

(2-24) $$\vec{q}_j = \Sigma_i A_{ij} \vec{r}_i$$

Therefore

(2-25) $$\vec{\pi}_i = \Sigma_k A_{ik} \vec{\pi}'_k$$

We may therefore transform the hamiltonian to the new coordinates:

(2-26) $$H = (1/2)\Sigma_i (1/m_i)\Sigma_k \Sigma_l A_{ik} A_{il} \vec{\pi}'_k \vec{\pi}'_l + V$$

or

(2-27) $$H = (1/2)\Sigma_k \Sigma_l [\Sigma_i (1/m_i) A_{ik} A_{il}] \vec{\pi}'_k \vec{\pi}'_l + V$$

The quantity between the brackets should therefore be:

(2-28) $$\Sigma_i (1/m_i) A_{ik} A_{il} = \lambda_k \delta_{kl}$$

Therefore, if A and B are two groups of particles and $\vec{q}_k^{(t)}$ is the vector coordinate between them:

(2-29) $$\vec{q}_k^{(t)} = \Sigma_\alpha m_\alpha \vec{r}_\alpha / M_A - \Sigma_\beta m_\beta \vec{r}_\beta / M_\beta \quad (\alpha \in A \text{ and } \beta \in B)$$

Then the A_{ik} are defined as follows:

(2-30) $A_{ik} = m_i / M_A$ if m_i is in A

(2-31) $A_{ik} = - m_i / M_A$ if m_i is in B

(2-32) $A_{ik} = 0$ if m_i is neither in A or B

If $\vec{q}_l^{(t)}$ is another coordinate we can prove [9] in considering the three possible cases that:

$$\Sigma_i A_{ik}A_{il}/m_i = 0 \tag{2-33}$$

Finally, any set of coordinates $(\vec{Q}_i^{(t)}, \vec{Q}_N)$ can generate another suitable set $(\vec{Q}_j^{(r)}, \vec{Q}_N)$, where i and j = 1,...,N-1 which satisfies (2-2) by a unitary transformation R in the (N-1) dimensional space:

$$\vec{Q}_i^{(r)} = \Sigma_j R_{ij}\vec{Q}_j^{(t)} \qquad (i,j=1,\ldots,N-1) \tag{2-34}$$

Squaring and adding over i leads to:

$$\Sigma_i Q'^2_i = \Sigma_i \Sigma_j \Sigma_k R_{ij}R_{ik}\vec{Q}_j\vec{Q}_k \qquad (i,j,k=,\ldots,N-1) \tag{2-35}$$

If R is unitary, then:

$$\Sigma_i R_{ij}R_{ik} = \delta_{jk} \qquad (i=1,\ldots,N) \tag{2-36}$$

and

$$\Sigma_i Q'^2_i = \Sigma_j Q_j^2 \qquad (i,j=,\ldots,N-1) \tag{2-37}$$

Thus any unitary transformation applied to an arbitrary acceptable set of coordinates $(\vec{Q}_i)$ produces another acceptable set of coordinates $(\vec{Q}'_k)$.

Note that some of the sets could be represented by a "mobile" as shown in the figure (2-1) while the others are purely "abstract" models to be thought as a set of vectorial coordinates in the (N-1) space and describing in a unique fashion the instantaneous configuration of the molecule.

We can suppose at that time that there exists some particular set(s) which will be representative of the symmetry of the molecule.

The system is completely defined by a set of N vectorial coordinates, i.e. by a set of 3N scalar coordinates. Three coordinates locate the center of mass of the system relative to the fixed axes and we had seen that the motion of the center of mass could easily be separated from the rotations and the vibrations. Furthermore three angular coordinates (usually the three Euler's angles) are needed to situate the spatial configuration of the system relative to the fixed axes; the 3N-6 remainder coordinates are the internal coordinates of the system.

Since the present study is principally oriented to three-body systems (therefore lying in a plane) once this plane is referred with respect to the fixed axes (operation which needs two angular coordinates) , we only need an angular extern coordinate which locates the plane relatively to some fixe axis of the molecule (i.e. one of the principal axes of inertia other than the axis perpendicular to the plane of the molecule).

3.NORMALIZED RELATIVE COORDINATE SYSTEMS FOR THE THREE-BODY SYSTEM.

a) Introduction.

The expressions derived in the previous section are quite more simple in the case of a system of three particles since the system lies in a plan and the number of representations as "mobiles" is reduced to three possibilities (figure 2-2).

We define (figure 2-3) the internal vector coordinate $\vec{r}_{ij}$ between atoms i and j by:

$$\vec{r}_{ij} = \vec{R}_j - \vec{R}_i \tag{2-38}$$

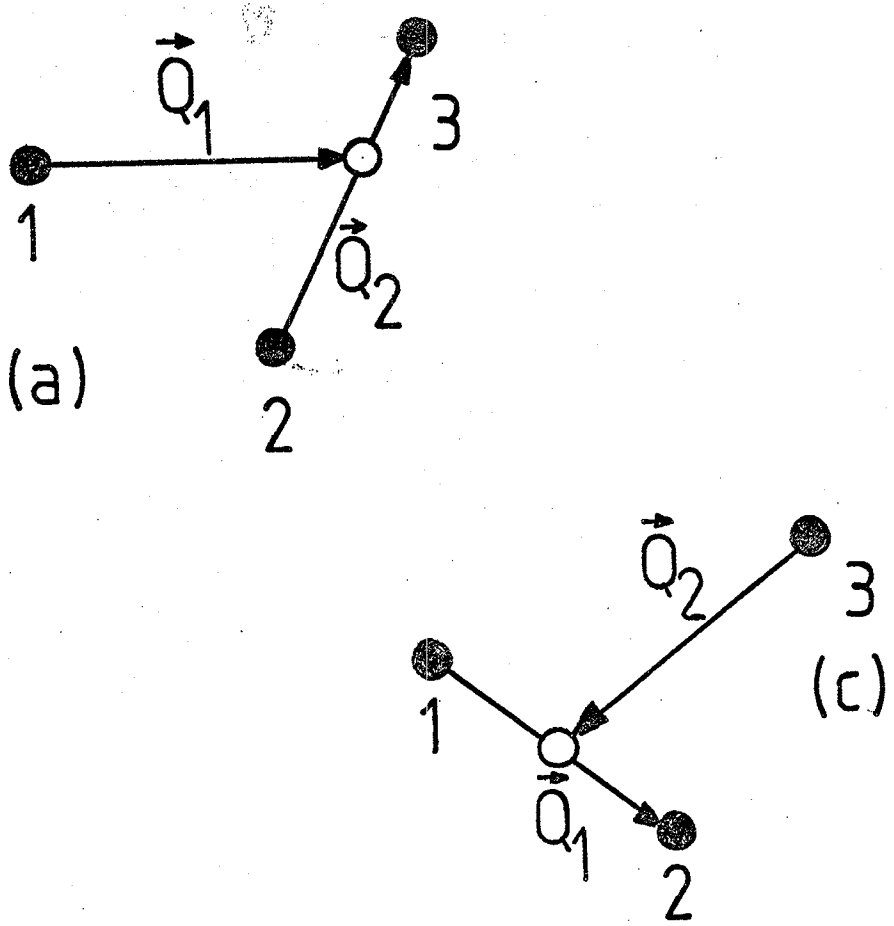
where the vector $\vec{R}_i$ is the position vector of the particle i relative to the fixed axes. The total mass is $M=m_1+m_2+m_3$ while the partial masses of the various groups of particles are defined by:

$$M_A = \Sigma_\alpha m_\alpha \quad (\alpha \in A) \tag{2-39}$$

In what follows the three representations of the figure (2-2) correspond to values of t respectively of 1, 2 and 3. The value of the indice t for other representations will be defined from the context (in particular for a representation obtained from t=i by a rotation through an angle θ, t will take the value

FIGURE (2-2):HIRSCHFELDER COORDINATES:3-BODY

The three "mobile" representations of the three body system. (a), (b) and (c) correspond respectively to the systems (1), (2) and (3) in the text.



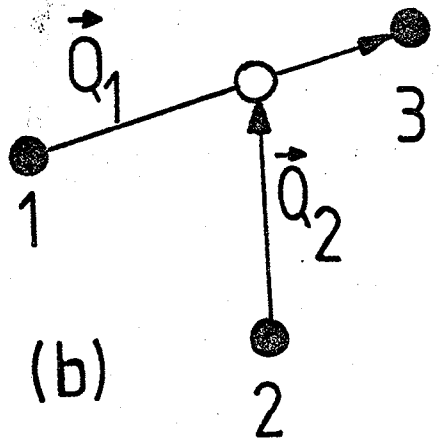


Fig.(2.2)

FIGURE (2-3):VECTOR AND SCALAR PARAMETERS FOR THE 3-BODY

The system of three different masses i,j,k lies in a plane. The couples $(\vec{\rho}_1^{(k)},\vec{\rho}_2^{(k)})$ are the Hirschfelder vector coordinates corresponding to t=k (see text). xGy is the reference frame attached to the system and corresponding to the principal axes of inertia (G is the center of mass). $\vec{z}_k$ is the vector joining G to particle k.

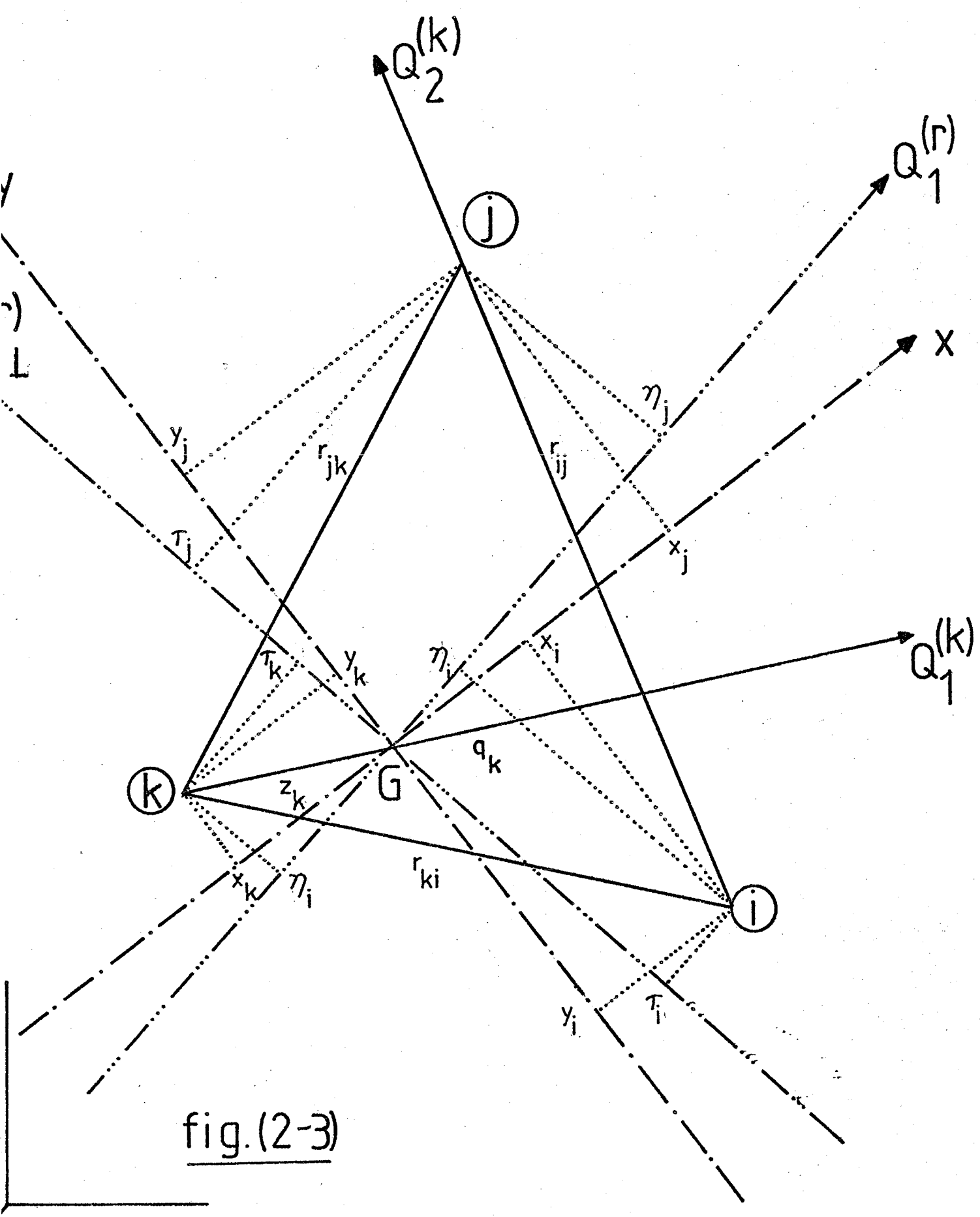

$Q_2^{(k)}$
$Q_1^{(r)}$
J
X
η_j
y_j
r_{jk}
r_{ij}
τ_j
x_j
$Q_1^{(k)}$
τ_k
y_k
η_i
x_i
q_k
k
G
z_k
r_{ki}
x_k
η_i
i
y_i
τ_i

fig.(2-3)

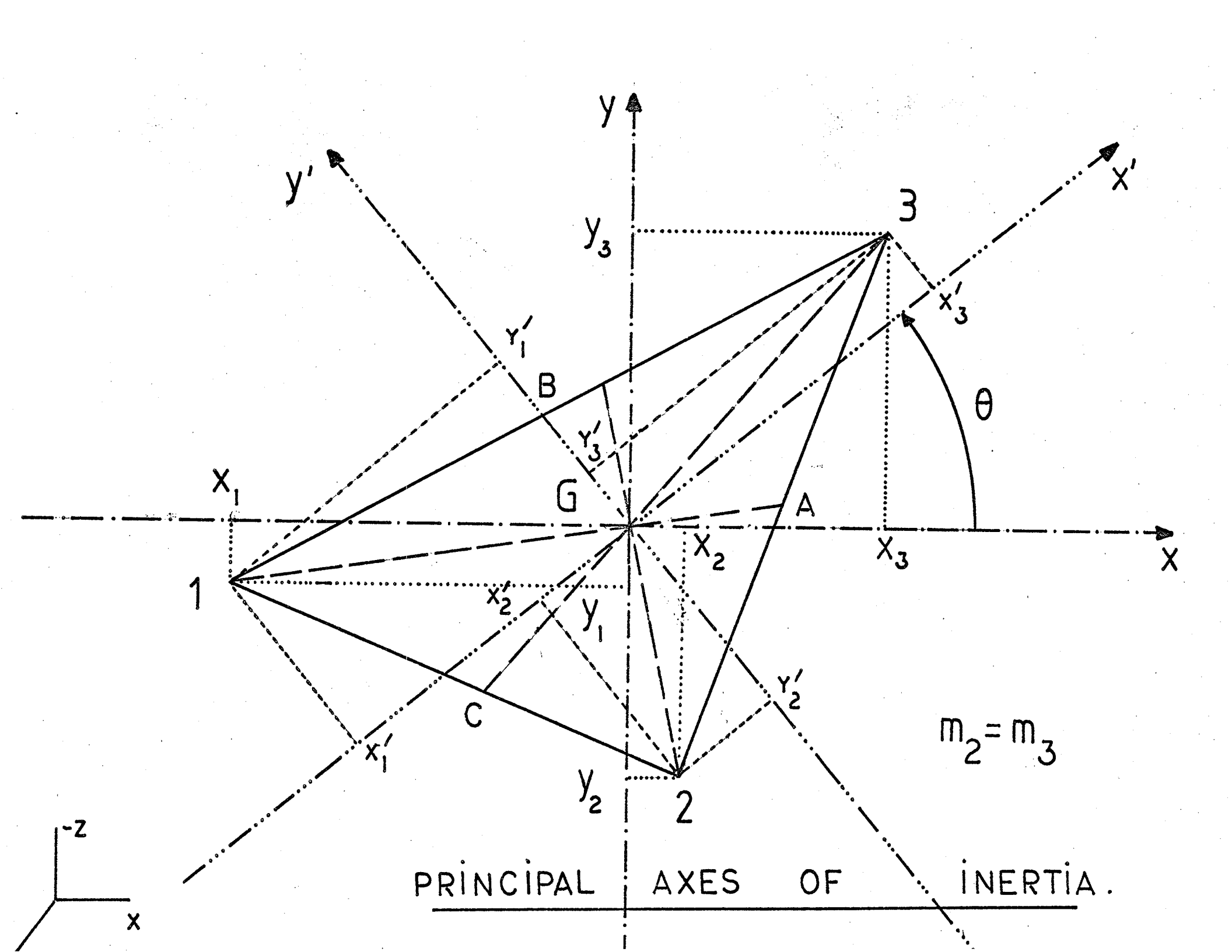
"θ_1"). According to the previous section, any set can generate another acceptable set by a unitary transformation (here a "kinematic" rotation[18-20]). In particular, we can conclude that any of the representations 1, 2 or 3 should be obtained from anyone of the others. If we choose the representation 1 as reference; therefore t=2 will be obtained by some angle $\theta_1^{(2)}$ and t=3 by $\theta_1^{(3)}$.

The goal of this section is to derive from an arbitrary discrete value of t a general method to obtain the other discrete representations t+1 and t+2 and in general any other representations. In particular a "symmetric" representation which has been introduced at the end of the previous section will reveal to be of considerable importance. Furthermore, we plan also to derive some relation between the orientation of this symmetric representation and the principal axes of inertia of the system.

The three vector coordinates $\vec{\mathrm{Q}}_i^{(t)}$ are equivalent to 9 scalar coordinates. Three of them concern the position of the center of mass and we have seen in section 2 that the translational KE operator is separable. Therefore 2 of the remaining coordinates will situate the plane of the molecule relative to the fixed axes while a third one will define the plane relatively to some fixed axis within the plane (i.e. a principal axis of inertia). The three remaining scalar coordinates are obviously some internal coordinates which will be derived in the next section.

FIGURE (2-4):PRINCIPAL AXES OF INERTIA:3-BODY

Gx' and Gy' are the instantaneous principal axes of inertia in the plane of the molecule. The third axis is perpendicular to the plane in G. xGy is an arbritrary cartesian frame. The angle θ is determined from the relations of appendix 5.


y
y'
x'
3
y_3
x'_3
y'_1
B
y'_3
θ
x_1
G
A
x_2
x_3
x
1
x'_2
y_1
y'_2
C
x'_1
y_2
2
$m_2 = m_3$
-z
x
PRINCIPAL AXES OF INERTIA.

b) Definitions.

The value of $\vec{q}_k^{(t)}$ in (2-18) is given here by:

$$\vec{q}_k = (m_i\vec{R}_i+m_j\vec{R}_j)/(m_i+m_j) - \vec{R}_k \tag{2-40}$$

The indice t is not necessary since no confusion is possible about the definition; physically, $\vec{q}_k$ is the vector joining particle k to the center of mass of the couple (i,j).

Let us define also for further utilisation the vector $\vec{z}_k$ (see figure 2-3) from the center of mass of the total system to the particle k by:

$$\vec{z}_k = (1-m_k/M)\vec{q}_k \tag{2-41}$$

Obviously the following relations hold:

$$r_{12}^{\,i} + r_{23}^{\,i} + r_{31}^{\,i} = 0 \tag{2-42}$$

$$\Sigma_k m_k z_k^{\,i} = 0 \tag{2-43}$$

where i indicates the ith cartesian coordinate of the vector.

The following quantities related to the various reduced masses will be of great help in the present discussion:

$$\Lambda = [m_1m_2m_3/M]^{1/2} \tag{2-44}$$

$$\Lambda_{ij} = \Lambda_{ji} = m_im_j/(m_i+m_j) \tag{2-45}$$

$$\alpha_k = [m_k(m_i+m_j)/M]^{1/2} \tag{2-46}$$

It is useful to define the angles ϕ_k such that:

(2-47) $$\sin\phi_k = [m_k M/(m_i+m_k)(m_j+m_k)]^{1/2}$$

(2-48) $$\cos\phi_k = [m_i m_j/(m_i+m_k)(m_j+m_k)]^{1/2}$$

and the normalizing constants d_k .

(2-49) $$d_k = [(m_k/\Lambda)(1-m_k/M)]^{1/2} = [\Lambda/\Lambda_{ij}]^{1/2} = \alpha_k \Lambda^{-1/2}$$

The following identities are easily derived from the above definitions:

(2-49-a) $$\Lambda^2 = \Lambda_{ij}\alpha_k^2$$

(2-49-b) $$\alpha_t \cos\phi_{t+1} + \alpha_{t+1}\cos\phi_t = \alpha_{t+2}$$

(2-49-c) $$\alpha_t - \alpha_{t+2}\cos\phi_{t+1} = \alpha_t \Lambda_{t+1,t+2}/m_{t+2}$$

(2-49-d) $$\sin(\phi_1+\phi_2+\phi) = 0$$

(2-49-e) $$\cos(\phi_1+\phi_2+\phi_3) = -1$$

(2-49-f) $$\phi_1 + \phi_2 + \phi_3 = \pi$$

(2-50) $$\sin\phi_k = (d_i d_j)^{-1}$$

(2-51) $$\cos\phi_k = \Lambda/(d_i d_j m_k)$$

(2-52) $$\mathrm{tg}\phi_k = m_k/\Lambda$$

(2-53) $$\Sigma_k[1-(m_k/M)]\sin^2\phi_k = \Sigma_k[1-(m_k/M)]\cos^2\phi_k = 1$$

(2-54) $$\Sigma_k[1-(m_k/M)]\sin 2\phi_k = \Sigma_k[1-(m_k/M)]\cos 2\phi_k = 0$$

(2-55) $$\alpha_k \sin\phi_k = m_k[(m_i+m_j)/(m_i+m_k)(m_j+m_k)]^{1/2}$$

(2-56) $$\alpha_i \sin\phi_k = \alpha_k \sin\phi_i = (\Lambda_{ik})^{1/2}$$

(2-57) $$\alpha_k \cos\phi_k = \Lambda[(m_i+m_j)/(m_i+m_k)(m_j+m_k)]^{1/2}$$

(2-58) $\alpha_i \cos\phi_k = m_i [m_j/M(m_i+m_k)]^{1/2}$

(2-59) $\sin(\phi_k \pm \phi_i) = \sin\phi_j [(m_k \pm m_i)/(m_k+m_i)]$

(2-60) $\cos(\phi_k \pm \phi_i) = \cos\phi_j [(m_j -/+ M/(m_i+m_k)]$

We are now able to define the normalized relative coordinates $\vec{Q}_i(t)$ from the relations (2-15) and (2-17)

We shall work out the representation of the "mobile"1 as an illustration and derive from this result a general relation for the other "mobiles" (reference or discrete representations) and for the sets which cannot be represented by a "mobile".

c) Reference representations ("mobiles").

As an example let us work out the representation of the "mobile" 1 in figure (2-2). Using the relation (2-17) we obtain:

GROUP A = (2,3); $M_A = m_2+m_3$; $\vec{r}_c(A) = (m_2\vec{R}_2+m_3\vec{R}_3)/(m_2+m_3)$

GROUP B = (1) ; $M_B = m_1$; $\vec{r}_c(B) = \vec{R}_1$

Therefore:

(2-61) $\vec{Q}_1^{(1)} = [m_1(m_2+m_3)/M]^{1/2}[(m_2\vec{R}_2+m_3\vec{R}_3)/(m_2+m_3) - \vec{R}_1]$

while

(2-62) $\vec{Q}_2^{(1)} = [m_2m_3/(m_2+m_3)]^{1/2}[\vec{R}_3 - \vec{R}_2]$

Using the identities of paragraph (b), we can write:

(2-63) $\vec{q}_1^{(1)} = \alpha_2 \cos\phi_3 \vec{r}_{12} + \alpha_3 \cos\phi_2 \vec{r}_{13}$

(2-64) $\vec{q}_2^{(1)} = \alpha_2 \sin\phi_3 \vec{r}_{23}$

In general, let a "mobile" representation defined by the indice t (by the way, t is the indice of the single atom in the representation), t being an element of the cyclic group $Z_3,+$, we can write either:

(2-65) $\vec{q}_1^{(t)} = \alpha_{t+1} \cos\phi_{t+2} \vec{r}_{t,t+1} + \alpha_{t+2} \cos\phi_{t+1} \vec{r}_{t,t+2}$

(2-66) $\vec{q}_2^{(t)} = \alpha_{t+1} \sin\phi_{t+2} \vec{r}_{t+1,t+2}$

or

(2-65-a) $\vec{q}_1^{(t)} = [m_t(m_{t+1}+m_{t+2})/M]^{1/2}[(m_{t+1}\vec{R}_{t+1} + m_{t+2}\vec{R}_{t+2})/(m_{t+1}+m_{t+2}) - \vec{R}_t] = -\alpha_t \vec{q}_t$

(2-65-b) $\vec{q}_2^{(t)} = [m_{t+1}m_{t+2}/(m_{t+1}+m_{t+2})](\vec{R}_{t+2} - \vec{R}_{t+1}) = \Lambda_{t+1,t+2}\vec{r}_{t+1,t+2}$

It will be convenient later to express the $(\vec{q}_i)$ only in terms of two of the bond distance vectors r_{ij}. Since we can write $\vec{r}_{ik} = \vec{r}_{ij} + \vec{r}_{jk}$, we can transform (2-65) and (2-66) in replacing $\vec{r}_{t,t+2}$ by $\vec{r}_{t,t+1} + \vec{r}_{t+1,t+2}$:
from (2-58), we have:

(2-67) $\alpha_{t+1} \cos\phi_{t+2} + \alpha_{t+2} \cos\phi_{t+1} = \alpha_t$

and from (2-56),

$$(2\text{-}68) \qquad \alpha_{t+1}\sin\phi\alpha_{t+2} = \alpha_{t+2}\sin\phi_{t+1}$$

therefore:

$$(2\text{-}69) \qquad \vec{Q}_1^{(t)} = \alpha_t\vec{r}_{t,t+1} + \alpha_{t+2}\cos\phi_{t+1}\vec{r}_{t+1,t+2}$$

$$(2\text{-}70) \qquad \vec{Q}_2^{(t)} = \alpha_{t+2}\sin\phi_{t+1}\vec{r}_{t+1,t+2}$$

The inverse transform is given by:

$$(2\text{-}71) \qquad \vec{r}_{t,t+1} = (\alpha_t)^{(-1)}[\vec{Q}_1^{(t)} - \text{cotg}\phi_{t+1}\vec{Q}_2^{(t)}]$$

$$(2\text{-}72) \qquad \vec{r}_{t+1,t+2} = [\alpha_{t+2}\sin\phi_{t+1}]^{(-1)}\vec{Q}_2^{(t)}$$

while expressed in terms of their cartesian components:

$$(2\text{-}73) \qquad Q_1^{(t),l} = \alpha_t r^l{}_{t,t+1} + \alpha_{t+2}\cos\phi_{t+1}r^l{}_{t+1,t+2}$$

$$(2\text{-}74) \qquad Q_2^{(t),l} = \alpha_{t+2}\sin\phi_{t+1}r^l{}_{t+1,t+2}$$

where l=1,2,3.

Figure (2-5-a) illustrates the relationships between the "mass-scaled" bond distance vectors $\alpha_t\vec{r}_{t,t+1}$, $\alpha_{t+2}\vec{r}_{t+1,t+2}$ and the set of $(\vec{Q}_i^{(t)})$ for t=1. The potential energy surfaces are usually constructed with respect to the bond distance (and/or bond angle) coordinates, the coordinates appear to be "skewed". We shall note that since the coordinates are vectors, this

FIGURE (2-5): RELATIONSHIPS BETWEEN Q AND THE BOND DISTANCE COORDINATES

a) i^{th} projection of the couple $(\vec{Q}_1{}^1, \vec{Q}_2{}^1)$ and the i^{th} projection of the mass scaled vector bond distance coordinates $\alpha_1\vec{r}_{23}$, $\alpha_3\vec{r}_{12}$. This represents also the transformation from a non-orthogonal cartesian system to an orthogonal system (see appendix 2).

b) The same system after a "kinematic" rotation of angle θ.

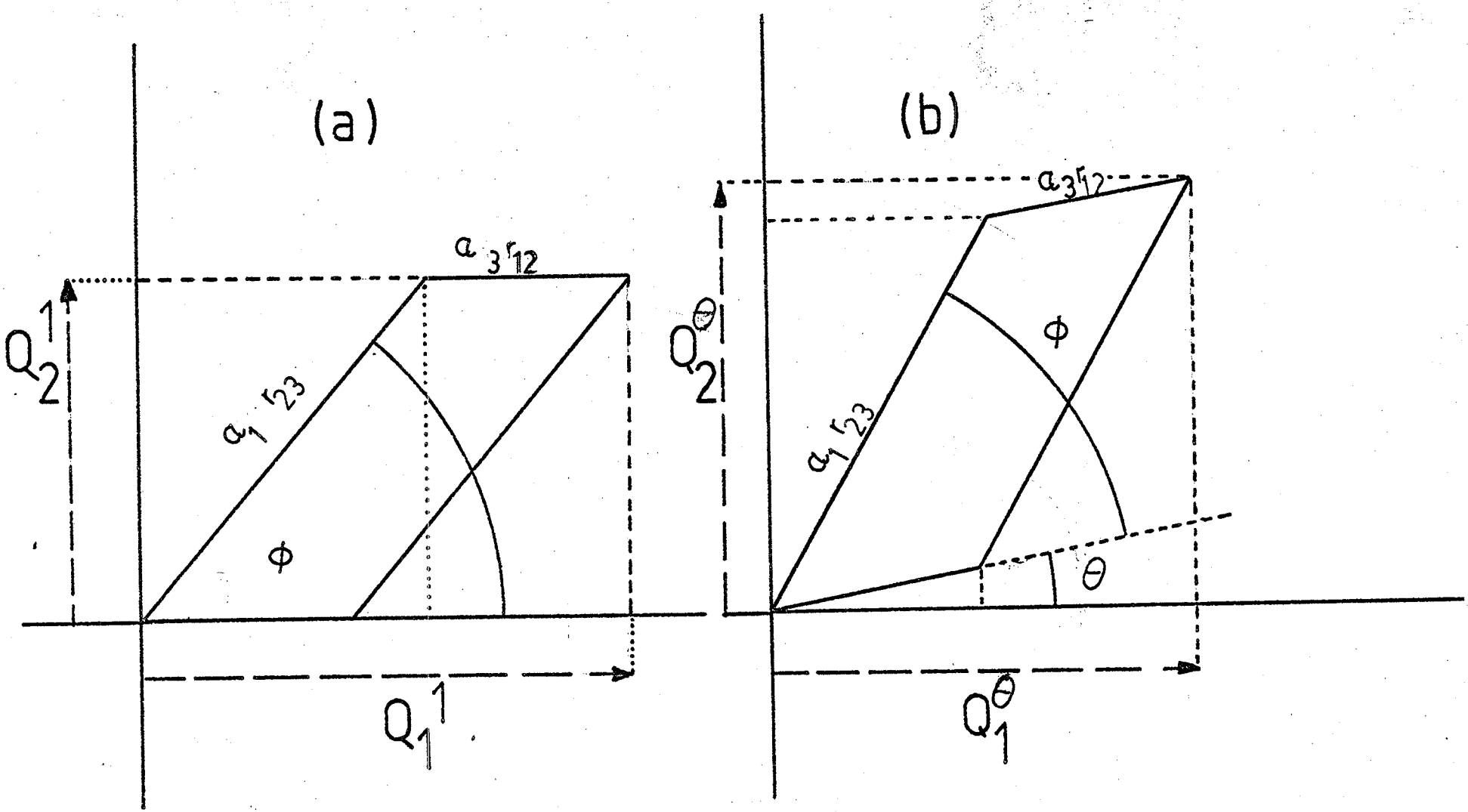


Fig.(2.5)

FIGURE (2-6): SYMMETRIC REPRESENTATION

The same system as in figure 2-5 after a "kinematic" rotation of angle $\theta=\phi_2/2-\pi/4$ corresponding to the symmetric representation (see section 5).

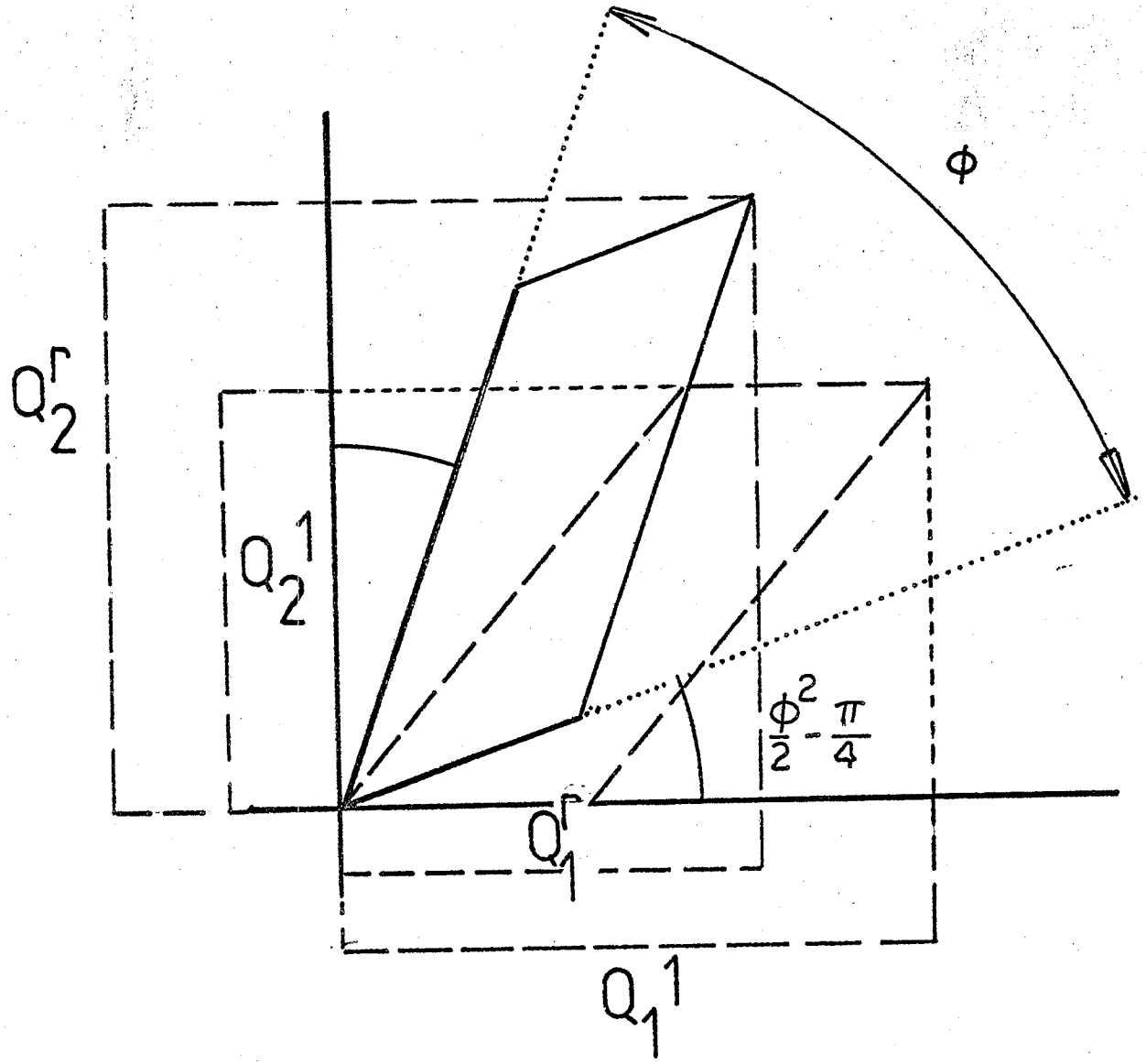


Fig.(2.6)

"vector" figure correspond to three figures in terms of scalar projections.

The $\vec{Q}_i^{(t)}$ appear therefore as some linear combinations of the "mass-scaled" bond distance vector coordinates. Since the system lies necessarily in a plane, any kinematic rotation through an angle θ is a unitary transformation as defined in (2-34) and will provide another acceptable set of coordinates $\vec{Q}_i^{(r)}$ given by:

$$\vec{Q}_1^{(r)} = \vec{Q}_1^{(t)}\cos\theta + \vec{Q}_2^{(t)}\sin\theta \tag{2-75}$$

$$\vec{Q}_2^{(r)} = -\vec{Q}_1^{(t)}\sin\theta + \vec{Q}_2^{(t)}\cos\theta \tag{2-76}$$

Using (2-69) and (2-70), we obtain:

$$\vec{Q}_i^{(r)} = \alpha_t\cos\theta\vec{r}_{t,t+1} + \alpha_{t+2}\cos(\phi_{t+1}-\theta)\vec{r}_{t+1,t+2} \tag{2-77}$$

$$\vec{Q}_j^{(r)} = -\alpha_t\sin\theta\vec{r}_{t,t+1} + \alpha_{t+2}\sin(\phi_{t+1}-\theta)\vec{r}_{t+1,t+2} \tag{2-78}$$

We may therefore expect to find the representations corresponding to the "mobiles" 2 and 3 by a suitable choice of the angle θ.

We note that the rotation of angle θ is <u>not</u> a rotation in the ordinary space but is an operator acting in the 2-dimensional space which elements are the vectors $\vec{Q}_t = (\vec{Q}_1^{(t)}, \vec{Q}_2^{(t)})$.

This distinction has been introduced in section 1 (page 10).

TABLE (2-1): PARAMETERS FOR THE 3-BODY.

m_1	m_2	m_3	α_1	α_2	α_3	ϕ_1	ϕ_2	ϕ_3
1.000	1.000	1.000	.817	.817	.817	60.00	60.00	60.00
1.000	1.000	2.000	.866	.866	1.000	54.74	54.74	70.53
1.000	1.000	3.000	.894	.894	1.095	52.24	52.24	75.52
1.000	2.000	2.000	.894	1.095	1.095	48.19	65.91	65.91
1.000	2.000	3.000	.913	1.155	1.225	45.00	63.43	71.57
1.000	3.000	3.000	.926	1.309	1.309	41.41	69.30	69.30
12.000	16.000	16.000	2.954	3.191	3.191	55.15	62.42	62.42
1.000	1.000	16.000	.972	.972	1.333	46.69	46.69	86.63
2.000	2.000	16.000	1.342	1.342	1.789	48.19	48.19	83.62
3.000	3.000	16.000	1.610	1.610	2.089	49.54	49.54	80.92

d) Transformation to the other discrete representations.

For t =1, 2, 3 in the relations (2-65) and (2-66) we obtain the various coordinates listed below:

$$(2\text{-}79)\quad \vec{\varrho}_1{}^1 = \alpha_2\cos\phi_3\vec{r}_{12} - \alpha_3\cos\phi_2\vec{r}_{31}$$

$$(2\text{-}80)\quad \vec{\varrho}_2{}^1 = \alpha_2\sin\phi_3\vec{r}_{23}$$

$$(2\text{-}81)\quad \vec{\varrho}_1{}^2 = -\alpha_1\cos\phi_3\vec{r}_{12} + \alpha_3\cos\phi_1\vec{r}_{23}$$

$$(2\text{-}82)\quad \vec{\varrho}_2{}^2 = \alpha_3\sin\phi_1\vec{r}_{31}$$

$$(2\text{-}84)\quad \vec{\varrho}_1{}^3 = -\alpha_2\cos\phi_1\vec{r}_{23} + \alpha_1\cos\phi_2\vec{r}_{31}$$

$$(2\text{-}84\text{-}a)\quad \vec{\varrho}_2{}^3 = \alpha_1\sin\phi_2\vec{r}_{12}$$

All the models can be expressed in terms of the same two values of $\vec{r}_{ij}$. Let us take for example the model "1" as reference and express the other models in terms of $\vec{r}_{12}$ and $\vec{r}_{23}$. When these expressions are tabulated, an interesting result occurs. The following table demonstrates this.

TABLE 2-2.

$\vec{R}_2$	$\vec{r}_{12}$	$\vec{r}_{23}$
$\vec{\varrho}_t$		
$\vec{\varrho}_1{}^1$ $\vec{\varrho}_2{}^1$	α_1 0	$\alpha_3\cos\phi_2$ $\phi_3\sin\phi_2$
$\vec{\varrho}_1{}^2$ $\vec{\varrho}_2{}^2$	$-\alpha_1\cos\phi_3$ $\alpha_3\sin\phi_1$	$\alpha_3\cos\phi_1$ $-\alpha_3\sin\phi_1$
$\vec{\varrho}_1{}^3$ $\vec{\varrho}_2{}^3$	$-\alpha_1\cos\phi_2$ $\alpha_2\sin\phi_1$	$-\alpha_3$ 0

We may now consider the 2 dimensional vector space E_{R2} which elements are the vectors $\vec{R}_2 = (\vec{r}_{12},\vec{r}_{23})$ and the 2 dimensional space E_{Q1} which elements are the vectors $\vec{Q}_t = (\vec{Q}_1(t),\vec{Q}_2(t))$. We may define on these spaces the operators:

(2-85) $$T_t : E_{R2} \longrightarrow E_{Q1} \; ; \quad T_t\vec{R}_2 = \vec{Q}_t$$

and

(2-86) $$R_\theta : E_{Q1} \longrightarrow E_{Q1} \; ; \quad R_\theta\vec{Q}_t = \vec{Q}_t$$

where t takes the values 1, 2 and 3. Obviously the operators T_1, T_2, T_3 and R_θ are 2x2 matrices. In taking t=1 as reference, we may now determine by which angle θ we must rotate the system "1" to obtain the two other ones. We have:

(2-87) $$R_\theta\vec{Q}_1 = R_\theta T_1\vec{R}_2 = \vec{Q}_r \qquad (r = 2 \text{ or } 3)$$

since:

(2-88) $$\vec{Q}_r = T_r\vec{R}_2$$

θ may be determined by solving the equation:

(2-89) $$R_\theta = T_r(T_1)^{-1}$$

where T_1^{-1} is given from the equations (2-71), (2-72):

$$(2\text{-}90)\quad T_1^{-1} = \begin{vmatrix} \alpha_1^{-1} & -\alpha_1^{-1}\cot g\phi_2 \\ 0 & (\alpha_3 \sin\phi_2)^{-1} \end{vmatrix}$$

As an example we will work out the model "2". Here r=2 and we have to solve:

$$R_\theta = T_2 T_1^{-1}$$

We obtain:

$$\cos\theta = -\cos\phi_3 \text{ and } \sin\theta = \sin\phi_3, \text{ i.e.: } \theta = \pi - \phi_3.$$

The results obtained for the other representations are presented in the table (2-3).

The transformation which permits to transform $\vec{Q}_t$ into $\vec{Q}_{t+1}$ is a rotation through an anle $\theta = \phi - \theta_{t+2}$ while the transformation from $\vec{Q}_t$ into $\vec{Q}_{t-1}$ is a rotation through an angle $\theta = \phi + \theta_{t+1}$. The figure (2-8-a) summarizes the process for three different molecules. The values of the "rotation" angles vary from 45 to 60 degrees. Figure (2-8-b) illustrates the case of CO_2. In the figure (2-7), we illustrate an interesting feature of the scalar projections of vectors $\vec{Q}_i$. The construction is as follows: we take the instantaneous scalar projections (on axis i) of the two mass-scaled bond distance

TABLE 2-3.

$\tilde{Q}_i(t)$	$\vec{r}_{12}$	$\vec{r}_{23}$	$\vec{r}_{31}$
	R_1 REPRESENTATION.		
$\tilde{Q}_1^1$	$\alpha_2\cos\phi_3$	0	$-\alpha_3\cos\phi_2$
$\tilde{Q}_2^1$	$-\alpha_2\sin\phi_3$	0	$-\alpha_2\sin\phi_3$
$\tilde{Q}_1^2$	$-\alpha_2$	0	$-\alpha_3\cos\phi_1$
$\tilde{Q}_2^2$	0	0	$\alpha_3\sin\phi_1$
$\tilde{Q}_1^3$	$\alpha_2\cos\phi_1$	0	α_3
$\tilde{Q}_2^3$	$\alpha_1\sin\phi_2$	0	0
	R_2 REPRESENTATION.		
$\tilde{Q}_1^1$	α_1	$\alpha_3\cos\phi_2$	0
$\tilde{Q}_2^1$	0	$\alpha_2\sin\phi_3$	0
$\tilde{Q}_2^1$	$-\alpha_1\cos\phi_3$	$\alpha_3\cos\phi_1$	0
$\tilde{Q}_2^2$	$-\alpha_3\sin\phi_1$	$-\alpha_3\sin\phi_1$	0
$\tilde{Q}_1^3$	$-\alpha_1\cos\phi_2$	$-\alpha_3$	0
$\tilde{Q}_2^3$	$\alpha_1\sin\phi_2$	0	0
	R_3 REPRESENTATION.		
$\tilde{Q}_1^1$	0	$-\alpha_2\cos\phi_3$	$-\alpha_1$
$\tilde{Q}_2^1$	0	$\alpha_2\sin\phi_3$	0
$\tilde{Q}_1^2$	0	α_2	$\alpha_1\cos\phi_3$
$\tilde{Q}_2^2$	0	0	$\alpha_3\sin\phi_1$
$\tilde{Q}_1^3$	0	$-\alpha_2\cos\phi_1$	$\alpha_1\cos\phi 2$
$\tilde{Q}_2^3$	0	$-\alpha_1\sin\phi_2$	$-\alpha_1\sin\phi_2$

vector coordinates $\vec{\tau}_1$ and $\vec{\tau}_2$ as sides of a triangle $O_iA_iB_i$; the angle between $\vec{\tau}_1$ and $\vec{\tau}_2$ is ϕ_2. Taking G_i, midpoint of the side A_iB_i, as center, we draw the circle of radius G_iO_i. For any member t of the family of vector coordinates $\vec{Q}$, we have the relation:

$$[(Q_1{}^t)_i]^2 + [(Q_2{}^t)_i]^2 = (O_iP_i)^2 = (X^i)^2.$$

From these considerations, we expect to establish the relationships between the "symmetric" representation and the instantaneous orientation of the principal axes of inertia.

FIGURE (2-7): "CONTINUOUS FAMILY" OF ORTHOGONAL HIRSCHFELDER COORDINATES

$(OAB)_i$ is the projection of the triangle formed by the mass scaled bond distance coordinates with angle ϕ_2. Once projected on some axis, the vectors Q_1 and Q_2 fall on the circle of radius $(OG)_i$ and center G_i.

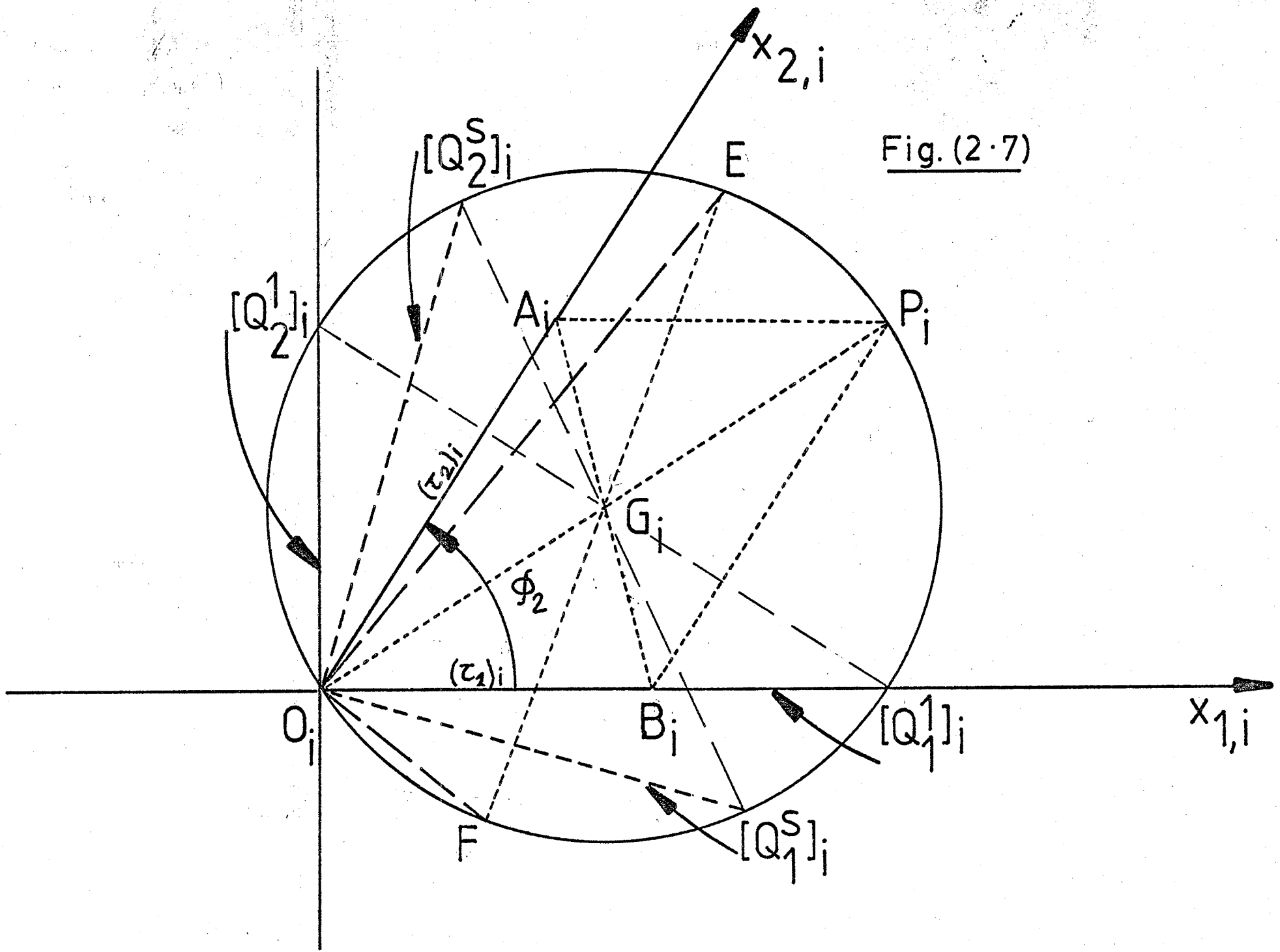


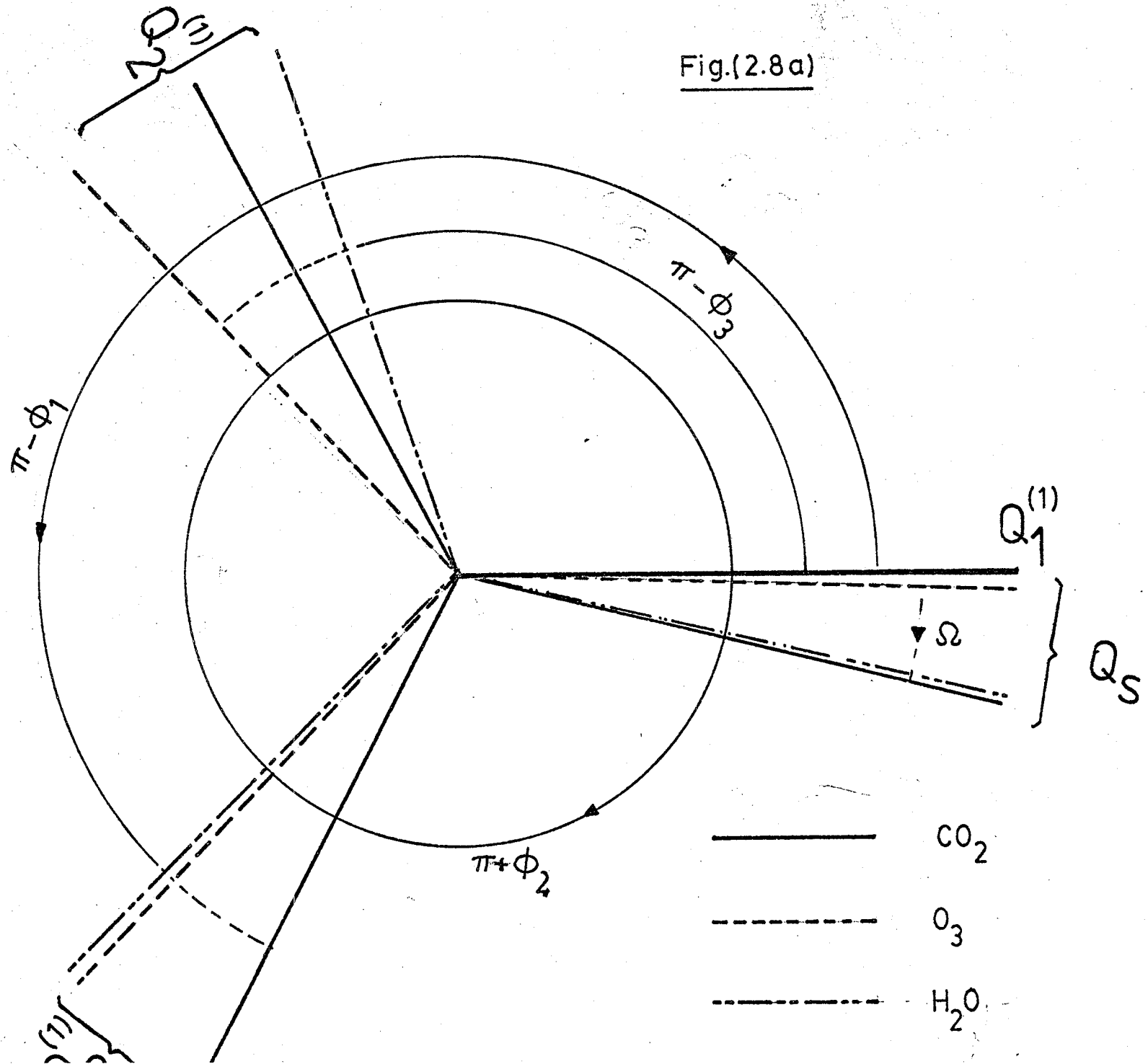
Fig. (2·7)

FIGURE (2-8): SCHEMATIC REPRESENTATION OF THE TRANSFORMATION OF THE DISCRETE VECTORS Q

a) For various ratios m_1/m_2. Note that for three equal masses, the angles equal 120 degrees and for an infinite mass attached to two negligeable masses, the angles are 135 and 90 degrees (He atom).

b) Illustration for the CO_2 molecule.

Fig.(2.8a)



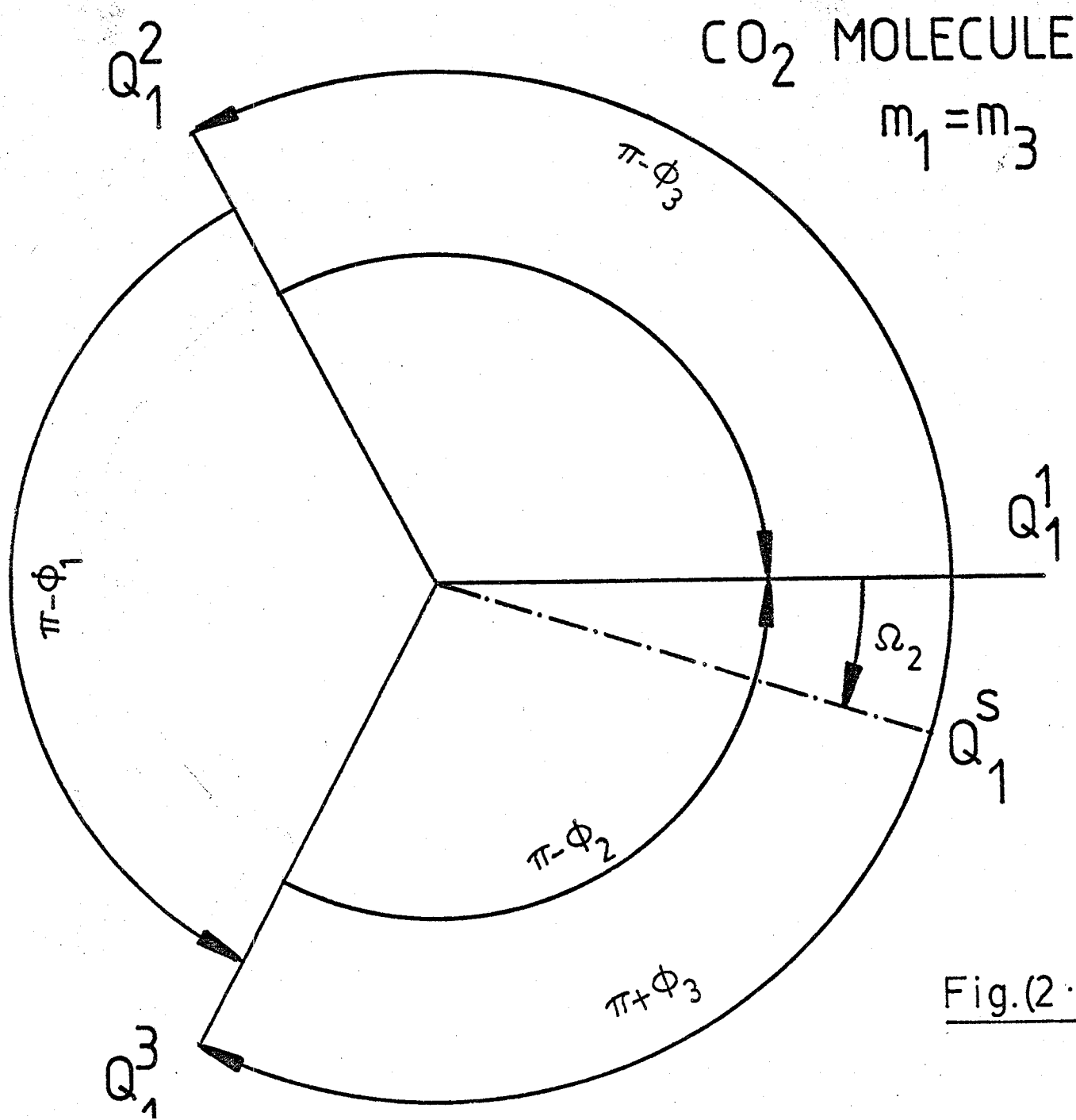

CO_2 MOLECULE
$m_1 = m_3$
Q_1^2
Q_1^1
Q_1^S
Q_1^3
$\pi - \phi_3$
$\pi - \phi_1$
$\pi - \phi_2$
$\pi + \phi_3$
Ω_2

Fig.(2·8.b)

4. SUMMARY.

The material discussed in the previous sections may introduce some confusion about the different ways of defining the configuration of a three-body system. Before continuing our investigations, let us summarize the previous results.

From table (2-2), we note that the configuration may be expressed in terms of the bond distance vector coordinates $\vec{R}_1$, $\vec{R}_2$ and $\vec{R}_3$. A simpler way of defining the system would be to express the configuration in terms of the "mass-scaled" vector bond distance coordinates. We then re-define these vectors by:

(2-91-a) $\vec{R}_1 = (\alpha_2\vec{r}_{12}, \alpha_3\vec{r}_{31})$

(2-91-b) $\vec{R}_2 = (\alpha_1\vec{r}_{12}, \alpha_3\vec{r}_{23})$

(2-91-c) $\vec{R}_3 = (\alpha_2\vec{r}_{23}, \alpha_1\vec{r}_{31})$

These representations are equivalent in the sense that they describe physically the same configuration of a system; in the present report, we shall concern ourselves with one representation, say $\vec{R}_2$, taking in mind that we can pass from one to the other ones.

In order to simplify the notations, we shall drop the index 2.

Each of the representations (2-91) may be transformed into the vector coordinates Q_t by the 2x2 matrices T_{ij} (i is the index of the representation, j the index of the vector Q)

defined by:

$$T_{11}=\begin{vmatrix}\cos\phi_3 & -\cos\phi_2\\ -\sin\phi_3 & -\sin\phi_2\end{vmatrix}\quad T_{12}=\begin{vmatrix}-1 & -\cos\phi_1\\ 0 & \sin\phi_1\end{vmatrix}\quad T_{13}=\begin{vmatrix}\cos\phi_1 & 1\\ \sin\phi_1 & 0\end{vmatrix}$$

$$T_{21}=\begin{vmatrix}1 & \cos\phi_2\\ 0 & \sin\phi_2\end{vmatrix}\quad T_{22}=\begin{vmatrix}-\cos\phi_3 & \cos\phi_1\\ -\sin\phi_3 & -\sin\phi_1\end{vmatrix}\quad T_{23}=\begin{vmatrix}-\cos\phi_2 & -1\\ \sin\phi_2 & 0\end{vmatrix}$$

$$T_{31}=\begin{vmatrix}-\cos\phi_3 & -1\\ \sin\phi_3 & 0\end{vmatrix}\quad T_{32}=\begin{vmatrix}1 & \cos\phi_3\\ 0 & \sin\phi_3\end{vmatrix}\quad T_{33}=\begin{vmatrix}-\cos\phi_1 & \cos\phi_2\\ -\sin\phi_1 & -\sin\phi_2\end{vmatrix}$$

The three discrete representations $\vec{Q}_j(i)$ are expressed by the general relation:

$$\vec{Q}_j(i) = T_{ij}\vec{R}_i \qquad (2\text{-}92)$$

where the index i expresses the fact that the coordinates are defined in terms of the representation $\vec{R}_i$. The three equivalent representations of the same vector $\vec{Q}_i$ are given by:

$$\begin{array}{ccc} T_{1i}\vec{R}_1 & T_{2i}\vec{R}_2 & T_{3i}\vec{R}_3 \\ = & = & = \\ \vec{Q}_i(1) & \vec{Q}_i(2) & \vec{Q}_i(3) \end{array} \qquad (2\text{-}92)$$

We note that the matrices T_{ij} have same determinant for a given representation:

$$\det(T_{ij}) = \sin\phi_i \quad \text{(for all j)} \qquad (2\text{-}93)$$

We defined at the end of the last section the matrices representing the rotations of angle $\pi-\phi_i$ and $\pi+\phi_i$ transforming respectively the $\vec{Q}_i$ into the $\vec{Q}_j$ and the $\vec{Q}_j$ into the $\vec{Q}_i$ within the same representation.

For the discrete representations, those matrices are given explicitely by:

(2-94)

$$S_{ij} = \begin{vmatrix} -\cos\phi_k & \sin\phi_k \\ -\sin\phi_k & -\cos\phi_k \end{vmatrix} \qquad S_{ji} = \begin{vmatrix} -\cos\phi_k & \sin\phi_k \\ \sin\phi_k & -\cos\phi_k \end{vmatrix}$$

where:

$$(2\text{-}95) \quad S_{ij}\vec{Q}_i(t) = \vec{Q}_j(t)$$

and

$$(2\text{-}96) \quad S_{ji}\vec{Q}_j(t) = \vec{Q}_i(t)$$

The following relations are easily derived:

$$(2\text{-}97) \quad S_{ji}S_{ij} = S_{ij}S_{ji} = I$$

$$(2\text{-}98) \quad S_{jk}S_{ij} = S_{ik}$$

$$(2\text{-}99) \quad S_{ki}S_{jk}S_{ij} = I$$

where I is the 2x2 unit matrix.

The figures (2-8) illustrate the rotations of $\vec{\Omega}_1(2)$ by the angles $\pi-\phi_3$ giving $\vec{\Omega}_2(2)$ and by $\pi+\phi_2$ (equivalent to $\pi-\phi_3 + \pi-\phi_1$) giving $\vec{\Omega}_3(2)$.

For an arbitrary rotation through an angle θ starting from the discrete vector $\vec{\Omega}_j(i)$ expressed in the representation $\vec{R}_i$ we obtain the vector $\vec{\Omega}_{\theta j}(i)$ given by:

$$S_{j\theta}\vec{\Omega}_j(i) = \vec{\Omega}_{\theta j}(i) \qquad (2\text{-}100)$$

As suggested by the figure (2-5), a value of the angle θ equal to $\phi_2/2 - \pi/4$ would provide a rotation such that the system represented by $\vec{R}_2$ will be symmetric relatively to the axes where the components of $\vec{\Omega}_{\theta 1}(2)$ are defined. The material related to this rotation constitutes the subject of the next section.

5. THE "SYMMETRIC REPRESENTATIONS.

a) General case.

Since from any representation sets of coordinates expressible by a "mobile" we could perform a rotation through an angle θ which gives another acceptable set of coordinates, for values of θ different of those obtained in the previous sections, we may expect to obtain representations which cannot be expressible as "mobiles". In particular, the following question arises: is it a particular value of θ which would generate a set such that the potential energy surfaces will be symmetric relatively to some fixed axes of the molecule?

For the sake of simplicity, let us start from the system described originaly by the vector $\vec{\Omega}_1(2)$ and let us rotate the axes through an angle $\Omega_2 = \phi_2/2-\pi/4$ as shown in figure (2-6). The matrix representing the rotation is given using the same notation as in the last section by:

(2-101)

$$S_{\Omega(2),1} = 2^{-1/2} \begin{bmatrix} \lambda_2^+ & \lambda_2^- \\ \lambda_2^- & \lambda_2^+ \end{bmatrix}$$

where:

(2-102) $\lambda_2^{\pm} = \cos\phi_2/2 \pm \sin\phi_2/2$

The following relations are easily derived:

(2-103) $(\lambda_i^{\pm})^2 = 1 \pm \sin\phi_i$

(2-104) $\lambda_i^{+}\lambda_i^{-} = \lambda_i^{-}\lambda_i^{+} = \cos\phi_i$

Applying the matrix to $\vec{Q}_1(2)$, we obtain:

(2-105) $S_{\Omega(2),1}\vec{Q}_1(2) = \vec{Q}_{s1}$

$= S_{\Omega(2),1}T_{21}\vec{R}_2$

Let us denote the matrix $S_{\Omega 2,1}T_{21}$ by the symbol Γ_2. Physically, this matrix represents the rotation needed to transform the vector $\vec{R}_2$ into the symmetric representation $\vec{Q}_{s2}$ (s_2 meaning the symmetric representation in $\vec{R}_2$) .

The explicit form of the matrix is given by:

(2-106) $$\Gamma_2 = 2^{-1/2}\begin{bmatrix} \lambda_2^{+} & \lambda_2^{-} \\ \lambda_2^{-} & \lambda_2^{+} \end{bmatrix}$$

This matrix is symmetric, normal but not orthogonal and is therefore not a rotation matrix. We have $\det(\Gamma_i) = \sin\phi_1$ and the eigenvalues of Γ_1 are $2^{1/2}\cos\phi_i/2$ and $2^{1/2}\sin\phi_i/2$.

We can define in the same fashion the symmetric

representations corresponding to the bases $\vec{R}_1$ and $\vec{R}_3$: Γ_1 and Γ_3. To each representation $\vec{R}_t$, it corresponds a symmetric representation Γ_t. We note that the symmetric representation is derived from the basic representation as well as from the others. We note also that the symmetric representation obtained from the vector representation $\vec{Q}_1(2)$ as starting point could be obtained in starting from the two other representations by performing rotations respectively of $(2\phi_3+\phi_2)/2-5\pi/4$ and $(3\pi/4-\phi_2/4)$. These results are obtained directly from the figure(2-8) or can be derived analyticaly by the procedure discussed in the section 3 [equation (2-89)].

As shown in the figure (2-6), the original potential energy surface remains intact as if the system is rotated as a whole through the angle $\phi_2/2-\pi/4$.

We can therefore conclude that for a given representation $\vec{R}_t$, say $\vec{R}_2$, the system being described by the components of $\vec{R}_2$,i.e., the mass-scaled bond distance vector coordinates which define without ambiguity an angle ϕ_2. This angle defines at its turn a rotation angle $\phi_2/2-\pi/4$ leading to a vectorial coordinate $\vec{Q}_{s2}$ that we called the symmetric representation of the system when the system is originally described by two arbitrary bond distance vector coordinates. There exists therefore a one-to-one correspondance between the way of choosing the representation of the system in terms of the internal coordinates and the definition of the symmetric representations. In other words, a unique symmetric representation corresponds to every fashion to define the system.

b) Particular case of three equal masses.

Let m be the mass of the three atoms, therefore, $\alpha = \alpha_1 = \alpha_2 = \alpha_3 = [2m/3]^{1/2}$ and the angles ϕ_i are equal to 60 degrees. The three representations $\vec{R}_i$ are identical and the Ω_i are equal to -15 degrees. Therefore the three matrices Γ_i are equal to:

$$(2\text{-}107) \qquad \Gamma_i = 6^{1/2}/4 \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} + 2^{1/2}/4 \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$$

If we define $a_{\pm} = \alpha(6^{1/2} \pm 2^{1/2})/4$, then:

$$(2\text{-}108\text{-a}) \qquad \vec{Q}^{s2}{}_1 = a_+\vec{r}_{12} + a_-\vec{r}_{23}$$

$$(2\text{-}108\text{-b}) \qquad \vec{Q}^{s2}{}_2 = a_-\vec{r}_{12} + a_+\vec{r}_{23}$$

c) Case of two identical atoms.

Since the choice of the representation is arbitrary, let us take $\vec{R}_2$ and label by 1 and 3 the atoms of same mass. Therefore, $\alpha_1 = \alpha_3$ and $\phi_1 = \phi_3$. The rotation of $\vec{Q}_2$ through the angle $\Omega_2 = \phi_2/2 - \pi/4$ will give the symmetric representation $\vec{Q}_{s2}$:

$$(2\text{-}109) \qquad \vec{Q}_{s2} = \Gamma_2\vec{R}_2$$

or in terms of the components:

$$(2\text{-}110\text{-a}) \qquad \vec{Q}^{s2}{}_1 = \alpha 2^{-1/2}[\lambda_2{}^+\vec{r}_{12} + \lambda_2{}^-\vec{r}_{23}]$$

$$(2\text{-}110\text{-b}) \qquad \vec{Q}^{s2}{}_2 = \alpha 2^{-1/2}[\lambda_2{}^-\vec{r}_{12} + \lambda_2{}^+\vec{r}_{23}]$$

It is intereresting to note (see table 2-1) that the symmetric representation approaches the basic representation Ω_{k-1} of the $R_k{}^{th}$ way to express the system as the ratio m/m_2 decreases since the angle Ω_k tends to zero as m/m_2 tends to zero. At the limit, a system constituted by 2 light particles attached to an heavy one would have its symmetric representation identical to the basic representation.

6.SCALAR COORDINATES.

From section 1, any vector coordinate $\vec{Q}_t$ could be considered either as an element of a 6-D vector space which components are the projections of $\vec{Q}_1{}^t$ and $\vec{Q}_2{}^t$ on the three axes of a cartesian frame attached on the system or as an element of a 2-D vector space which elements are the two vectors $\vec{Q}_1{}^t$ and $\vec{Q}_2{}^t$. Therefore the six ordered scalars constitute a way of defining completely the instantaneous configuration of the system. There exists an infinity of ways of defining these scalars coordinates. The subject of this section is to determine some particular set of coordinates in such a way that the three internal coordinates will be defined independently of the cartesian frame while a fourth coordinate will refer the plane of the system to the instantaneous principal axes of the molecule. The two remaining external coordinates are angles fixing the plane relatively to the fixed axes.

In this section, we shall discuss the internal scalar coordinates: q_1, q_2 and q_3 which are respectively the norms of the vectors $\vec{Q}_1(t)$, $\vec{Q}_2(t)$ and their angle. Obviously, these three scalars are independent of the refernce frame.

In a cartesian frame, the components of the discrete vector coordinate $\vec{Q}_t$ are:

$$\vec{Q}_t = (Q_{11}{}^t, Q_{12}{}^t, 0, Q_{21}{}^t, Q_{22}{}^t, 0) \qquad (2\text{-}111)$$

where we defined the plane with the coordinates 1 and 2.

In order to express the instantaneous configuration of the system without any consideration about its position relatively to the fixes axes in terms of the coordinate $\vec{Q}_t$ all we have to do is to calculate the norms of $\vec{Q}_1(t)$ and $\vec{Q}_2(t)$ and the from their scalar product, we could deduce their angle.

Starting from any representation $\vec{Q}_\theta$ obtained in the usual way from $\vec{Q}_1$:

$$\vec{Q}_\theta = R_\theta T_1 \vec{R}_2 = R_\theta \vec{Q}_1 \tag{2-112}$$

we find the components of $\vec{Q}_\theta$:

$$\vec{Q}_1{}^\theta = \alpha_1 \cos\theta \vec{r}_{12} + \alpha_3 \cos(\phi_2 - \theta)\vec{r}_{23} \tag{2-113}$$

$$\vec{Q}_2{}^\theta = -\alpha_1 \sin\theta \vec{r}_{12} + \alpha_3 \sin(\phi_2 - \theta)\vec{r}_{23} \tag{2-114}$$

We obtain therefore for the norms:

$$(q_1{}^\theta)^2 = \alpha_1{}^2 \cos^2\theta d_{12}{}^2 + \alpha_3{}^2 \cos^2(\phi_2 - \theta) d_{23}{}^2 + 2\alpha_1\alpha_3 \cos\theta \cos(\phi_2 - \theta) \cos\Omega_2 d_{12} d_{23} \tag{2-115}$$

$$(q_2{}^\theta)^2 = \alpha_1{}^2 \sin^2\theta d_{12} + \alpha_3{}^2 \sin^2(\phi_2 - \theta) - 2\alpha_1\alpha_3 \sin\theta \sin(\phi_2 - \theta) \cos\Omega_2 d_{12} d_{23} \tag{2-116}$$

where d_{12} and d_{23} are the bond distances and Ω_2 the bond angle of atom #2.

In order to define the third internal coordinate α_{12}^{θ}, the scalar product is given by:

(2-117) $$\vec{\Omega}_1^{\theta}.\vec{\Omega}_2^{\theta} = -\alpha_1^2\sin\theta\cos\theta d_{12}^2 + \alpha_3^2\sin(\phi_2-\theta)\cos(\phi_2-\theta)d_{23}^2 + \alpha_1\alpha_3 d_{12}d_{23}\cos\Omega_2\sin(\phi_2-2\theta)$$

and therefore:

(2-118) $$\cos\alpha_{12}^{\theta} = [\vec{\Omega}_1^{\theta}.\vec{\Omega}_2^{\theta}]/[q_1^{\theta}q_2^{\theta}]$$

In particular for the symmetric representation where $\theta = \phi_2-\pi/4$:

(2-119) $$q_1(2)^r = [1/2[(\alpha_1)^2d_{12}^2(1+(-)\sin\phi_2) + (\alpha_3)^2d_{23}^2(1-(+)\sin\phi_2) + \alpha_1\alpha_3\cos\phi_2\cos\Omega_2 d_{12}d_{23}]]^{1/2}$$

while the angular coordinate is given by:

(2-120) $$\cos\delta_{12}^r = [(\cos(\phi_2/2)(\alpha_1^2d_{12}^2 + \alpha_3^2d_{23}^2) + \alpha_1\alpha_3\cos\Omega_2 d_{12}d_{23}]/q_1^r q_2^r$$

Finally, it should be interesting to calculate the angle

between one of the symmetric representation coordinate, $\vec{Q}_1{}^r$ and one of the reference representation coordinate $\vec{Q}_1{}^{(1)}$:

Let the scalar product:

$$(2\text{-}121) \quad P_{1,1}{}^{1,r} = \vec{Q}_1{}^{(1)} \cdot \vec{Q}_1{}^{(r)} =$$
$$(1/2)^{1/2}[\alpha_1{}^2 d_{12}{}^2(\cos\phi_2/2 + \sin\phi_2/2)$$
$$+ \alpha_3{}^2 d_{23}{}^2 \cos\phi_2(\cos\phi_2/2 - \sin\phi_2/2) +$$
$$2\alpha_1\alpha_3 d_{12} d_{23} \cos\Omega_2 \cos\phi_2/2]$$

Therefore the angle between $\vec{Q}_1{}^{(r)}$ and $\vec{Q}_1{}^{(1)}$ is given by:

$$(2\text{-}122) \quad \cos\theta(1,1;r,1) = P_{1,1}{}^{1,r}/q_1{}^1 q_1{}^r.$$

In general, the angle between $\vec{Q}_i{}^t$ and $\vec{Q}_j{}^\theta$ is given by:

$$(2\text{-}123) \quad \cos\theta(i,t;j\theta) = P_{i,t}{}^{j,\theta}/q_i{}^t q_j{}^\theta$$

where:

$$(2\text{-}124) \quad P_{i,t}{}^{j,\theta} = \vec{Q}_i{}^{(t)} \cdot \vec{Q}_j{}^{(\theta)}$$

This formula will be useful in the determination of the orientation of the symmetric coordinates relative to the principal axes of inertia (appendix 5).

CHAPTER 3.

THE HAMILTONIAN FOR THE THREE-BODY: CO_2 MOLECULE.

1. INTRODUCTION.

This chapter is devoted to the derivation of the Schroedinger equations expressed in terms of the three scalar coordinates defined in the previous chapter. In a first section, we recall the general form of the hamiltonian for the N-body as defined by Curtis and Hirschfelder in reference (6) and re-expressed by Wallace in reference (10). The application of this form for the 3-body constitutes the aim of the second section where we summarize the results of Wallace. We introduce in the third section the results obtained in chapter 2. In particular we intend to show that for any "member" of the family of coordinates Q (and in particular for the "symmetric" representation) the useful properties of separability of the hamiltonian remain unchanged. Finally, the last section consists in the application of the various results in the case of the CO_2 molecule for which we give the potential energy surfaces obtained in the three "discrete" representations and in the "symmetric" representation. The solution of the equations constitutes the object of the second part.

2.THE HAMILTONIAN FOR A SYSTEM OF N PARTICLES.

In terms of the euclidean coordinates $x^{\alpha i}$ the KE operator of a system of N particles of total mass $M=\Sigma_\alpha m_\alpha$ may be written:

$$(3\text{-}1) \quad T = -(\hbar^2/2)\Sigma_{\alpha,i}(m_\alpha)^{-1}[\partial^2/\partial(x^{\alpha i})^2]$$

and the Schrodinger equation by:

$$(3\text{-}2) \quad (T + V)\Psi = E_t\Psi$$

where V is the potential energy operator and E_t the total energy of the system.
If the potential is independent of the position of the center of mass, then the state space may be expressed as the product of the spaces E_T and E_{RV} and Ψ as the product:

$$(3\text{-}3) \quad \Psi = \phi(R^G)\Phi(y_{\alpha i})$$

where ϕ is a function of the cartesian coordinates of the center of mass and Φ a function of the 3N-3 coordinates $y_{\alpha i}$ specifying the configuration relative to the center of mass. It is easy to see that the Schroedinger equation separates into an equation in ϕ which is the usual equation for a free particle of mass M and an equation in Φ which energy is

associated with the rotations and the vibrations of the system:

$$(3\text{-}4) \qquad (-(\hbar^2/2)\Sigma_{\alpha i}[\partial^2/\partial(y^{\alpha i})^2] + V)\Phi = E_{RV}\Phi$$

where the coordinates $y^{\alpha i}$ have been mass-scaled in some way. Under a transformation of the set of coordinates $(y^{\alpha i})$ into a new set $(q^{\alpha I})$ the KE operator takes the usual form (10):

$$(3\text{-}5) \qquad T = -(\hbar^2/2)[g^{-1/2}\Sigma_{i,j}(\partial/\partial q^i)g^{ij}g^{1/2}(\partial/\partial q^j)]$$

where the coordinates $q^{\alpha i}$ have been re-indexed in the following way: $3\alpha+i=j$, g^{ij} are the elements of the metric tensor (see appendix 2) and g the determinant of this tensor. If the new set is orthogonal such as the old, then the metric tensor is diagonal.

The first problem is now to separate the set (q^i) into two subsets, one constituted by the three external coordinates (s^1, s^2, s^3) specifying the orientation of the system and the other constituted by the subset of internal coordinates $(Q^1,\ldots,Q^{3N-6})$ invariant under rotations. In other words to express the function Φ in a sum of products of functions in s^i and of functions in Q^i. Obviously there exists a great variety of choice for the internal coordinates. Our second preoccupation will be then to determine the best choice, for a particular value of N and for any particular problem.

The potential energy operator is usually expressed in

terms of a Taylors series about the equilibrium configuration $(Q^i{}_{(0)})$:

$$(3\text{-}6) \qquad V(a_i) = \Sigma_{i,j} k_{ij} a_i a_j + \Sigma_{i,j,l} k_{ijl} a_i a_j a_l + \cdots$$

where $a_i = Q^i - Q^i{}_{(0)}$

If we could reduce the vibrational hamiltonian to a sum of terms describing independent one-dimensional oscillators $H_V(Q^i) = \Sigma_i h(Q^i)$ then the eigenstates would be simple products of the 1-dimensional eigenstates and the overall vibrational solutions would reduce to superpositions of 3N-6 uncoupled motions. Obviously such a separation is impossible and we are forced to make approximations. Two historical ways may be used[23]. The normal mode consists in neglecting all cubic and higher terms in the hamiltonian while the local mode consists in dropping all the cross terms (even the quadratic ones).

The method proposed here is to divide the potential into two terms V_o and V_c defined as follows:

$$(3\text{-}7) \qquad V_o(Q^i) = V(Q^1,Q^2,Q^3,\ldots,Q^{3N-6}) + V(Q^1,Q^2,Q^3,\ldots,Q^{(3N-6)}) + \ldots + V(Q^1,Q^2,Q^3,\ldots,Q^{(3N-6)})$$

the bars over the variables denoting equilibrium values. V_c is the remaining potential. In what follows, $V_o(Q^i)$ will be called the "separable" part of the potential, V_c the "non-separable" part and the "complete" potential $V=V_o+V_c$.

Obviously the contribution of the non-separable part of the potential will depend upon the system of coordinates in which it is expressed.

Therefore, the scheme may be expressed as follows:

a) to determine the coordinate system which minimizes the contribution of the non-separable part of the potential; this operation is performed by plotting the potential energy surfaces (2 coordinates vary while the remainder are at their equilibrium) for the various coordinate systems and determine among them the system for which the contribution of V_c is minimal.

b) to solve the separable part of the hamiltonian as a zero-order approximation of the solution.

c) to compute effects of the non-separable part in the basis of the separable states.

Since the potential function is invariant under rotations (V is usually a function of the internal coordinates), the eigensolutions of (3-4) will form bases of representation of the three dimensional rotation group. Let Ψ_s^L be an eigenfunction specified by the total angular momentum L and the quantum number referring to the z component of the angular momentum m. Then if R is the matrix representing the rotation of the coordinate system, $P_R\Psi_s^L$ will be a linear combination of the Ψ_m^L belonging to the same L (a rotation will mix the set of 2L+1 degenerate quantum states). In particular[24]:

$$P_R\Psi_s^L = \Sigma_m D^L(R)_{ms}\Psi_m^L \qquad (3\text{-}8)$$

where $D^{L}(R)_{ms}$ is the set of representation coefficients for the L^{th} irreducible representation of the rotation group. We define a "standard configuration" in such a way that all configurations which differ only by a pure rotation correspond to the same standard configuration. In practice this standard configuration is defined in terms of the position with respect to the center of mass of two "particles" in such a way that particle "1" is placed on the positive z-axis while particle "2" is placed on the positive half of the xOz plane. Therefore, if R is the a rotation matrix which brings the system into the standard configuration then:

$$P_R \Psi_s^L = \chi_s^L \qquad (3\text{-}9)$$

depends only upon the relative configuration and χ_s^L is a function of 3N-6 internal coordinates.

It is easy to see in applying the orthogonality of the representation coefficients:

$$\Sigma_s D^L(R)_{m's}{}^* D^L(R)_{ms} = \delta_{m'm} \qquad (3\text{-}10)$$

the definition (3-9) of χ_s^L and relation (3-8) that:

$$\Psi_m^L = \Sigma_s D^L(R)_{ms}{}^* \chi_s^L \qquad (3\text{-}11)$$

This expression means that the eigenfunction may be expressed

in terms of a linear combination of products of eigenfunctions depending upon rotation coordinates and eigenfunctions depending upon internal coordinates. In other words by this operation we express the space E_{RV} into a tensor product of E_R and E_V. The summation in (3-11) instead of a single term as in (3-3) could be explained from the degeneracy of the group representations leading to a mixing of the states. Therefore, in theory, if we substitute (3-11) in (3-4), we are able to separate the variables and obtain equations for the different functions. But since the $D_L(R)$ are well-known[25], we can integrate over the the rotational coordinates and obtain equations for the functions χ_s^L.

Let now Q_{nj} the j^{th} scalar coordinate of the n^{th} particle (see previous chapter for the definition of Q_{nj}: we recall here that the Q_{nj} are mutually orthogonal as cartesian projections of the vector coordinate Q_j but these vectors are <u>not</u> orthogonal in the ordinary 3-dimensional cartesian space) before a rotation and z_{nk} the coordinate after rotation represented by $R = (R_{jk})$:

$$z_{nk} = \Sigma_j R_{jk} Q_{nj} \qquad (3\text{-}12)$$

We have therefore the 3N-6 internal coordinates:

$$\begin{matrix} z_{13}, & z_{23}, & z_{33}, & \cdots, & z_{N-1,3} \\ \emptyset, & \emptyset, & z_{32}, & \cdots, & z_{N-1,2} \\ \emptyset, & z_{21}, & z_{31}, & \cdots, & z_{N-1,1} \end{matrix} \qquad (3\text{-}13)$$

These cartesian coordinates will be used later to derive the kinetic energy operator. Nevertheless, since these coordinates are not orthogonal to the Euler's angles describing the rotations and furthermore since the molecular potential is, in general, highly non-separable in such coordinates, it is preferable to re-express the cartesian scalar coordinates in terms of some kind of polar coordinates (mutually orthogonal). Figure (3-1-b) illustrates the choice of such a system $(r_1,\ldots,r_{N-1}, \theta_2,\ldots,\theta_{N-1}, \phi_3,\ldots, \phi_{N-1})$. From the evaluation of the metric tensor, it can be shown that the radial coordinates r_i are mutually orthogonal and orthogonal to the angular coordinates, including the Euler coordinates and that the internal angular coordinates are mutually orthogonal but not to the Euler coordinates in the actual way of defining the two first vector coordinates. Some other way of determining the orientation of these vectors are actually considered in connection with the particular orientation of the "symmetric " representation relatively to the principal axes of inertia of the molecule.

Since z_{12}, z_{22} and z_{11} are zero (by definition of the standard configuration), the equations defining the coordinates of orientation of the system in terms of the Q_{ij} are:

$$\Sigma_j R_{j1} Q_{1j} = 0$$

(3-14)
$$\Sigma_j R_{j2} Q_{1j} = 0$$

FIGURE (3-1-b): POLAR COORDINATES FOR THE N-BODY.

N-Body: polar coordinates.

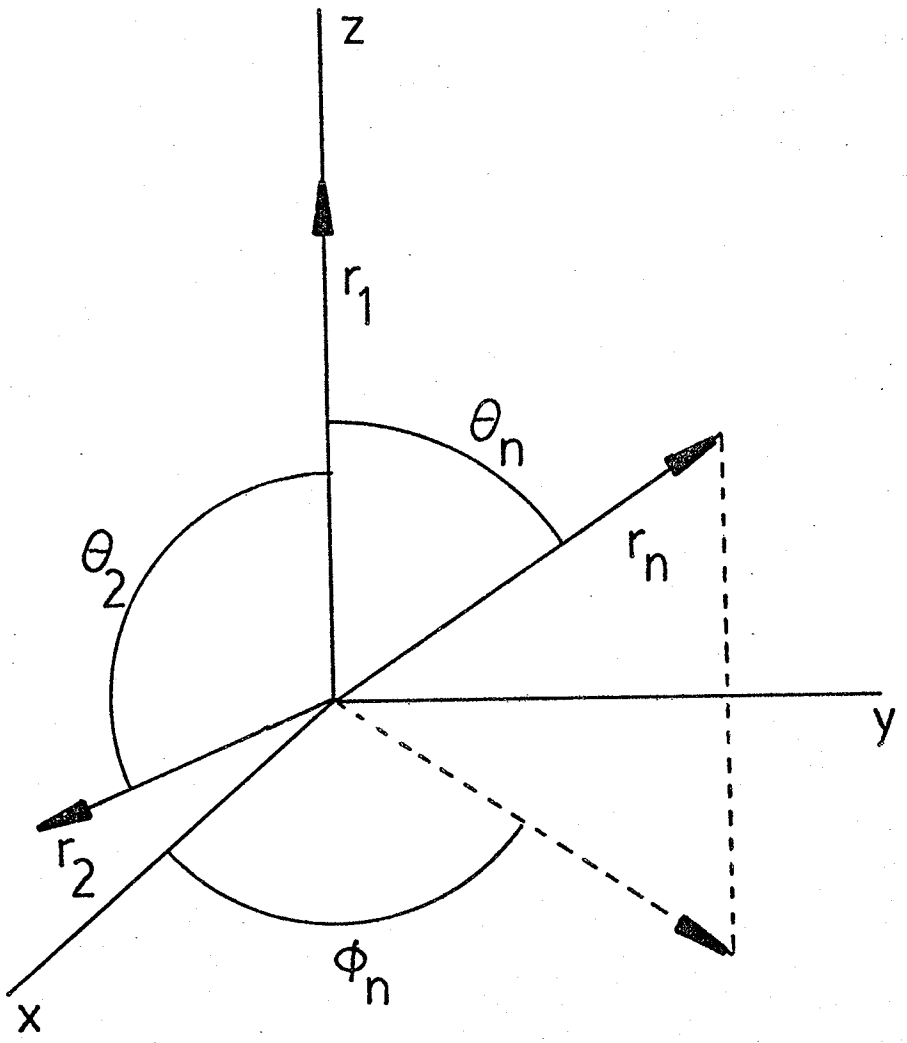


FIG. (3.1.b)

$$\Sigma_j R_{j2} Q_{2j} = 0$$

Using the properties of infinitesimal rotations we can obtain from (3-12) the derivatives of the coordinates z_{nk} with respect to the Q_{nj} and using the fact that χ_s^L depends only upon the internal coordinates, we can find by a straightforward but tedious calculation the expression of the Schroedinger equation.

As a result, Wallace found[10] the following equations:

$$\begin{aligned}(3\text{-}15)\quad & \Sigma_k \partial^2 \Psi_s^L / \partial Q_{jk}^2 \\ &= \Sigma_k \delta_{jj'} \partial^2 \Psi_s^L / \partial Q_{j'k} \partial Q_{jk} \\ &= \delta_{jj'} [(1/z_{21})[\delta_{2j'} - (z_{23}/z_{13})\delta_{1j'}]A_s + (2\delta_{1j'}/z_{13})B_s + C_{s,n}\end{aligned}$$

where:

$$A_s = \Sigma_s D^L{}_{ms}(R)^* \Lambda_{j1} \chi_s^L$$
$$B_s = \Sigma_s D^L{}_{ms}(R)^* \Lambda_{j3} \chi_s^L$$
$$C_{s,n} = \Sigma_{s,n} D^L{}_{ms}(R)^* \Lambda_{j'n} \Lambda_{jn} \chi_s^L$$

In terms of the polar coordinates defined earlier, the kinetic energy operator can be written in the form:

$$(3\text{-}16)\quad T = T_0 + T_1 + T_2$$

where:

(3-17) $2T_{\emptyset} = -\hbar^2[\partial^2/\partial r_n^2 + (2/r_n)\partial/\partial r_n]$

$-(1/r_1^2)[(\hbar s+\Sigma_n L_{nz})^2 + \Sigma_n L_{nz}^2 - [L(L+1)-s^2]\hbar^2]$

$-\hbar^2(r_1^{-2}+r_2^{-2})[\partial^2/\partial\theta_2^2 + \cot\theta_2\partial/\partial\theta_2 -$

$\csc^2\theta_2(s+\hbar^{-1}\Sigma_n L_{nz})^2]$

$+ \Sigma_n(r_1^{-2}+r_n^{-2})[1/2(L_{n+}L_{n-} + L_{n-}L_{n+}) + L_{nz}^2]$

where the summation over n is from 3 to N-1.

(3-18) $2T_1 = r_1^{-2}[-\hbar\partial/\partial\theta_2\Sigma_n(L_{n+}-L_{n-}) +$

$\cot\theta_2\Sigma_n(L_{n+}+L_{n-})(\hbar s+L_{nz}) + \Sigma_n\Sigma_k[L_{n+}L_{k-} + \cot\theta_2(L_{n+}+L_{n-})L_{kz}]]$

where the summation are from n,k=3 to N-1 and n different of k.

(3-19) $2T_2 = -\hbar\lambda_+/r_1^2[\hbar\partial/\partial\theta_2 + \Sigma_n L_{n+} +$

$\cot\theta_2(\hbar(s+1)+\Sigma_n L_{nz})]S_+ + \hbar\lambda_-/r_1^2[\hbar\partial/\partial\theta_2 + \Sigma_n L_{n-} -$

$\cot\theta_2(\hbar(s-1)+\Sigma_n L_{nz})]S_-$

where the summation is again over n=3 to N-1.

The terms λ_+ and λ_- are defined by:

(3-20) $\lambda_+ = [L(L+1)-s(s+1)]^{1/2}$

(3-21) $\lambda_- = [L(L+1)-s(s-1)]^{1/2}$

and the operators S are defined by:

(3-22) $S_{\pm}\chi_s^L = \chi^L{}_{s\pm1}$

3.THE HAMILTONIAN FOR THE THREE-BODY SYSTEM.

The general hamiltonian defined in the previous section for the N-body reduces to a simplier form in the case of a 3-particles system. For any vector coordinate system constituted by $\vec{Q}_1$ and $\vec{Q}_2$, we obtained in chapter 2 the expressions of the scalar coordinates q_1, q_2 and q_3 which are designed here with the notation of the previous section respectivelly by r_1, r_2 and θ_2. In other words, r_1 and r_2 are the norms of the vectors $\vec{Q}_1$ and $\vec{Q}_2$ while θ_2 is the angle between them taking in mind that the vector $\vec{Q}_1$ is oriented in the positive direction of the z-axis and $\vec{Q}_2$ is oriented in the positive direction of the xOz plane.

Let us take the "discrete" representation of "mobile" 1. Then, as discussed previously, the potential is expressed in the form:

$$(3\text{-}23) \qquad V(r_1,r_2,\theta_2) = V_{\emptyset}(r_1,r_2,\theta_2) + V_c(r_1,r_2,\theta_2)$$

where:

$$(3\text{-}24) \qquad V_{\emptyset}(r_1,r_2,\theta_2) = V(r_1,r_2,\theta_2) + V(r_1,r_2,\theta_2) + V(r_1,r_2,\theta_2)$$

the bars denote the equilibrium values.

As mentioned in reference (10), an alternate definition

for (3-24) is preferable:

$$(3\text{-}25)\qquad V_{\emptyset}(r_1,r_2,\theta_2) = V(r_1,r_2,\theta_2) + V(r_1,r_2,\theta_2) + (h^2/2)(r_1^{-2}+r_2^{-2})V(r_1,r_2,\theta_2)$$

With such a definition of the potential function, the hamiltonian takes the form:

$$(3\text{-}26)\qquad H = H_{\emptyset} + V_c(r_1,r_2,\theta_2) + T_1 + T_2$$

where:

$$(3\text{-}27)\qquad H_{\emptyset} = -(\hbar^2/2)[\partial^2/\partial r_1^2 + (2/r_1)\partial/\partial r_1 - r_1^{-2}[L(L+1)-2s^2]] + V(r_1,r_2,\theta_2)$$
$$-(\hbar^2/2)[\partial^2/\partial r_2^2 + (2/r_2)\partial/\partial r_2] + V(r_1,r_2,\theta_2)$$
$$-(\hbar^2/2)(r_1^{-2}+r_2^{-2})[\partial^2/\partial\theta^2 + \cot\theta_2(\partial/\partial\theta_2) - s^2\csc^2\theta_2 - V(r_1,r_2,\theta_2)]$$

$$(3\text{-}28)\qquad T_2 = -\hbar^2\lambda_+(L,s)/2r_1^2[\partial/\partial\theta_2 + (s+1)\cot\theta_2]S_+ + \hbar^2\lambda_-(L,s)/2r_1^2[\partial/\partial\theta_2 - (s-1)\cot\theta_2]S_-$$

$$(3\text{-}29)\qquad T_1 = \emptyset$$

Clearly $H_{\emptyset}$ is separable and its solution reduces to the solution of three 1-dimensional equations.
The angular equation is firstly considered; if $-\Lambda^s{}_j$ are the eigenvalues, we are then able to solve the angular equation at

first and to solve successively the two radial equations. The sequence of the operations are as follows:

$$(3\text{-}30) \qquad H_0(\theta_2)[A^s{}_j(\theta_2)\rangle = -\Lambda^s{}_j[A^s{}_j(\theta_2)\rangle$$

$$(3\text{-}31) \qquad H_0(r_1)[R^s{}_{L,j,\alpha}(r_1)\rangle = E^s{}_{L,j,\alpha}[R^s{}_{L,j,\alpha}(r_1)\rangle$$

$$(3\text{-}32) \qquad H_0(r_2)[R'^s{}_{j,\beta}(r_2)\rangle = E^s{}_{j,\beta}[R'^s{}_{j,\beta}(r_2)\rangle$$

where the hamiltonians are defined by:

$$(3\text{-}33) \qquad H_0(\theta_2) = \partial^2/\partial\theta_2{}^2 + \cot\theta_2\partial/\partial\theta - s^2\csc^2\theta_2 - V(r_1,r_2,\theta_2)$$

$$(3\text{-}34) \qquad H_0(r_1) = -(\hbar^2/2)[\partial^2/\partial r_1{}^2 + (2/r_1)\partial/\partial r_1 - r_1{}^{-2}[L(L+1)-2s^2+\Lambda^s{}_j]] + V(r_1,r_2,\theta_2)$$

$$(3\text{-}35) \qquad H_0(r_2) = -(\hbar^2/2)[\partial^2/\partial r_2{}^2 + (2/r_2)\partial/\partial r_2 - \Lambda^s{}_j/r^2{}_2] + V(r_1,r_2,\theta_2)$$

The zeroth-order eigenfunctions are then expressed by the product:

$$(3\text{-}36) \qquad [X^s{}_{L,j,\alpha,\beta}(r_1,r_2,\theta_2)\rangle = [R^s{}_{L,j,\alpha}(r_1)\rangle[R'^s{}_{j,\beta}(r_2)\rangle[A^s{}_j(\theta_2)\rangle$$

and will constitute a basis for the complete eigenproblem.

For a particular problem the choice of an appropriate coordinate system constitutes the capital step in the sense that the separability of the potential function will depend upon this choice.

The above discussion remains true for any of the "members"

of the family of orthogonal coordinates of chapter 2. The only requirement is to fix the first vector coordinate Q_1 in the positive direction of the z-axis and the second Q_2 in the positive half of the xOz plane. The scalar coordinates obtained in section 6 of chapter 2 are the polar coordinates introduced in the previous section. So far the three "discrete" representations have been tested on some triatomic molecules[1-4] with success. It remains then to introduce other members (i.e. non-discrete) and particularly the "symmetric" system. Preliminary tests on molecules already studied have given satisfactory results and we expect in a very near future to complete the calculations for these molecules.

We propose to discuss in the next section the case of the carbon dioxide molecule which constitutes an interesting illustration whereas the molecule is linear. Furthermore, the discrete representations present some difficulties: the equilibrium configuration of a radial coordinate is zero which leads to an infinite term in equation (3-34). For the symmetric representation, such situation does not arise.

4. COORDINATES SYSTEMS AND POTENTIAL ENERGY SURFACES: CO_2

a) Potential function.

We consider in this illustration the potential energy as a Taylor series through fourth-order terms in generalized internal coordinates:

$$(3\text{-}37) \quad V = \Sigma_{i<j} K_{ij} R^i R^j + \Sigma_{i<j<k} R^i R^j R^k + \Sigma_{i<j<k<l} R^i R^j R^k R^l$$

If R^1 and R^3 are the bond stretching coordinates and R^2 the bending coordinate, the force constants obtained by least-squares adjustment obtained by Parizeau[26] are:

$K_{11} = 8.014$	$K_{13} = 1.268$	$K_{22} = 0.393$
$K_{111} = -19.116$	$K_{113} = -1.516$	$K_{122} = -0.615$
$K_{1111} = 25.862$	$K_{1113} = -2.383$	$K_{1122} = 3.551$
$K_{1133} = -5.924$	$K_{1223} = 8.000$	$K_{2222} = -0.065$

The units of force constants are determined from equation (3-37) by requiring the potential energy to be in mdA when the coordinates R^1 and R^3 are expressed in A and R^2 in radians.

We can therefore plot the values of the potential in keeping the three coordinates alternatively at their equilibrium and varying the two other coordinates. Such plots are presented in the figures (3-2) were x_1, x_2 and x_3 are

respectively the coordinates r_1, r_2 and θ_2.

This potential expression is used here in order to illustrate the process; some more accurate refinement of the potential is needed in view to obtain a complete solution of the Schroedinger equations discussed in the previous section.

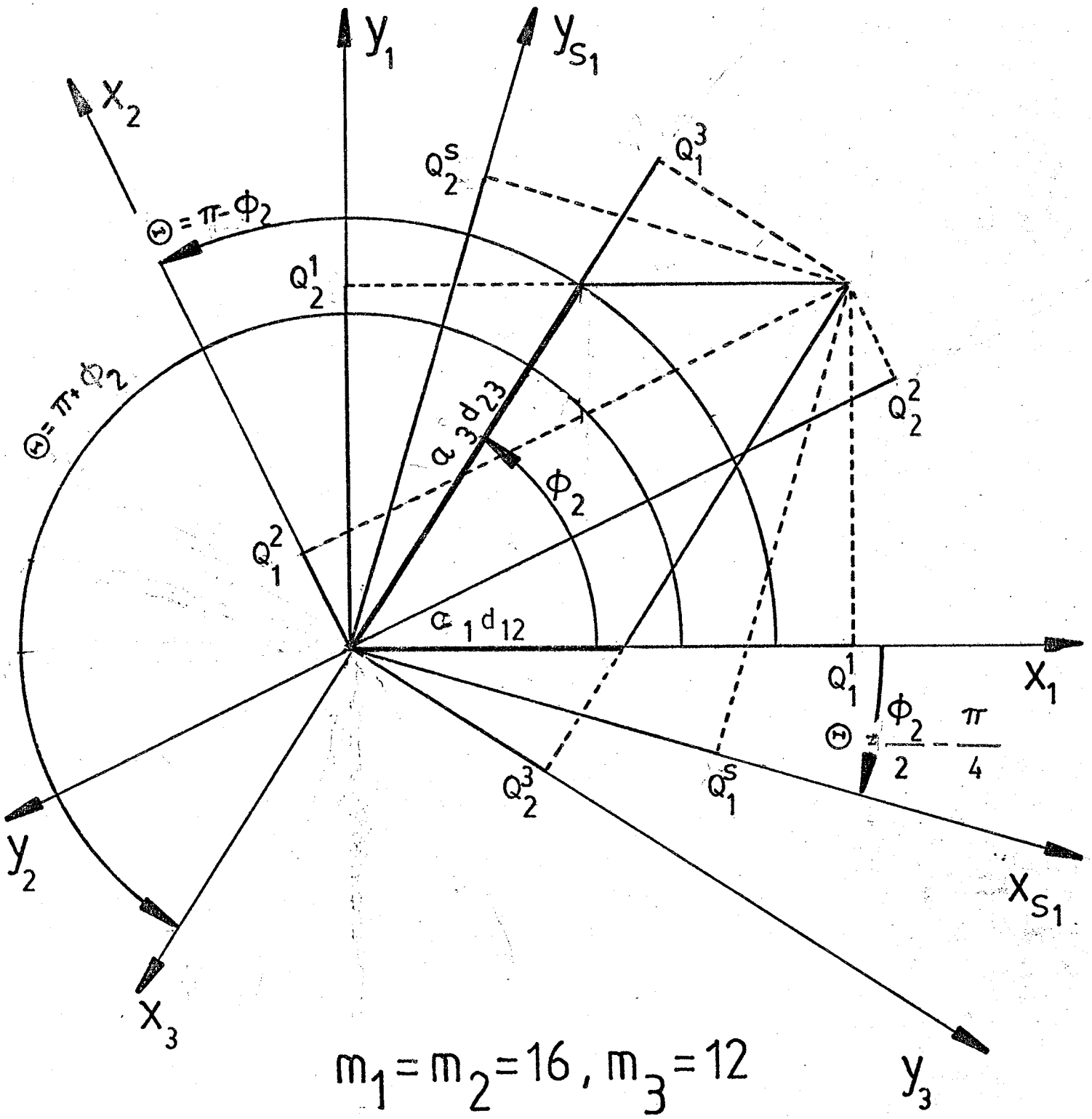
b)Coordinates systems.

Figures (3-2) resume the results obtained with the three discrete representation and the symmetric coordinates. Figure (3-1-a) shows schematically the transformation from mobile 1 representation to the mobiles 2 and 3 and to the symmetric coordinates when the carbon atom is labelled by "3". Again, this figure involves the cartesian projections of the various coordinate vectors $\vec{Q}_1$, $\vec{Q}_2$, $\vec{R}_{12}$ and $\vec{R}_{23}$. At equilibrium, the coordinate $\vec{Q}_2$ for "mobile" 3 is zero and we are not able to solve the radial equation. Furthermore, the potential expressed in terms of the other representations (which are "identical" as shown in the potential energy surfaces plots) is far from an acceptable separability. The symmetric representation in that case appears to be the best choice since the problem encountered with "mobile" 3 is avoided and the potential should be more separable than in the other coordinates.

FIGURE (3-i): COORDINATES OF CO_2 MOLECULE.

Projections of the vector coordinates on axis i. Atom 3 represents the oxygen.

CO_2 MOLECULE: COORDINATES.



$m_1 = m_2 = 16, m_3 = 12$

Fig. (3.1)

FIGURE (3-2):POTENTIAL ENERGY SURFACES FOR CO_2

In every cases, two scalar coordinates vary while the third coordinate is at its equilibrium configuration.

(a): "mobile 1"

(b): "mobile 2"

(c): "mobile 3"

(d): "symmetric representation"

x_1 and x_2 are the radial scalar coordinates and x_3 is the angle-bending coordinate.

Clearly, (a) and (b) are equivalent representations.

Fig.(3.2.a-1)

Molecule: OCO
Transf: UNIV3 Th=0

Pot: Total
X3=-1.00

V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1

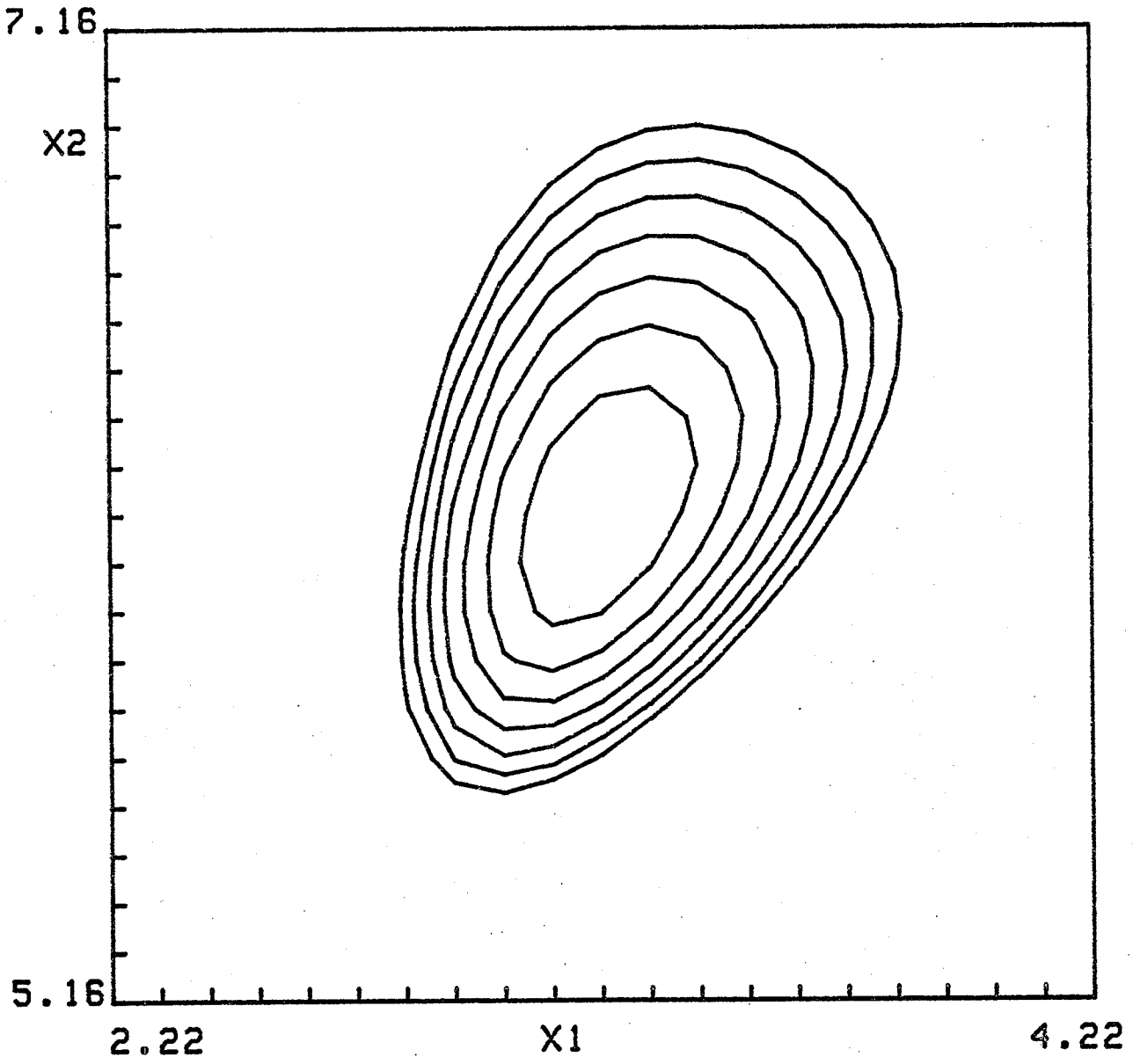


Fig.(3.2.a-2)

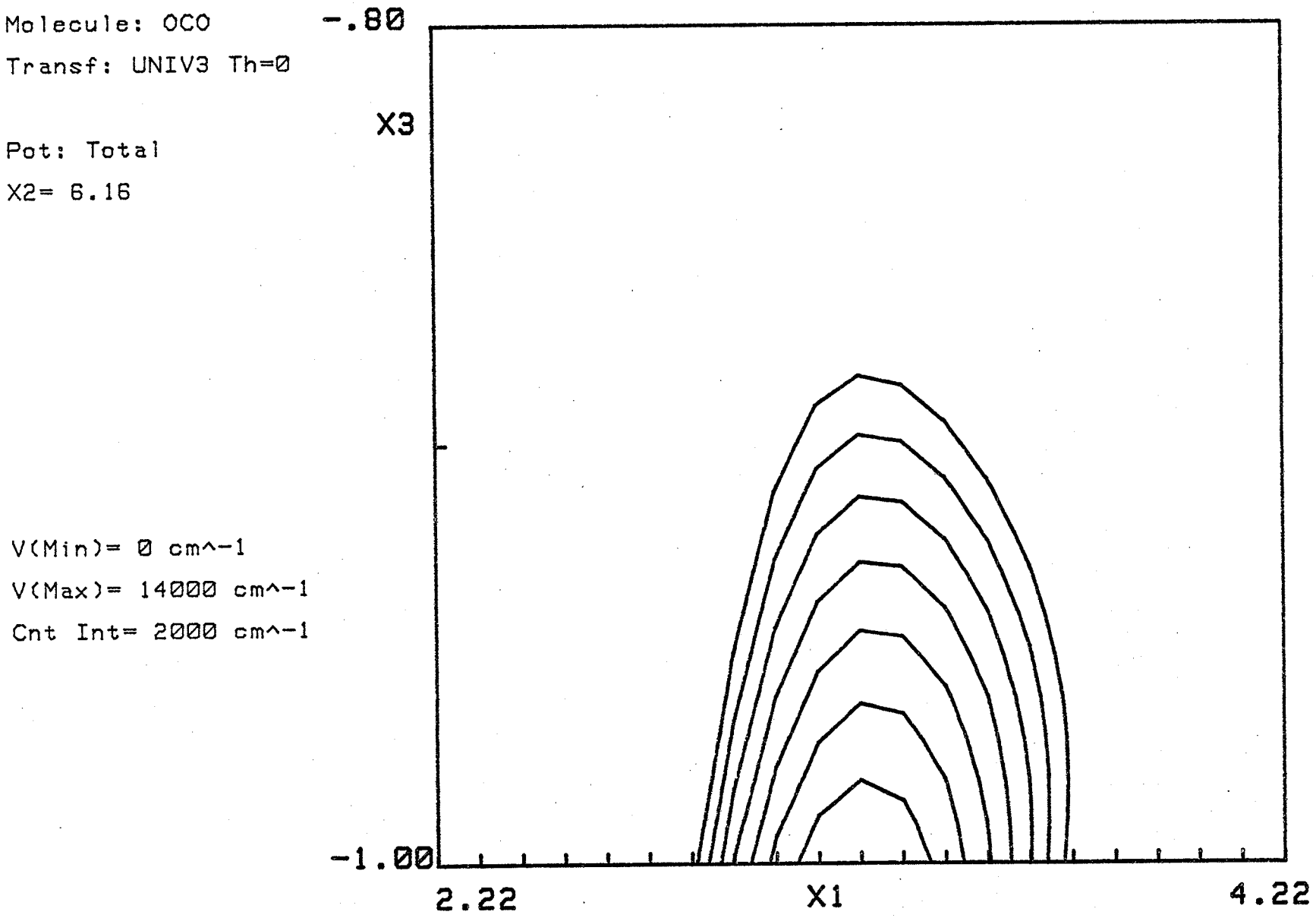

Molecule: OCO
Transf: UNIV3 Th=0
Pot: Total
X2= 6.16
V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1
-.80
X3
-1.00
2.22
X1
4.22

Fig.(3.2.a-3)

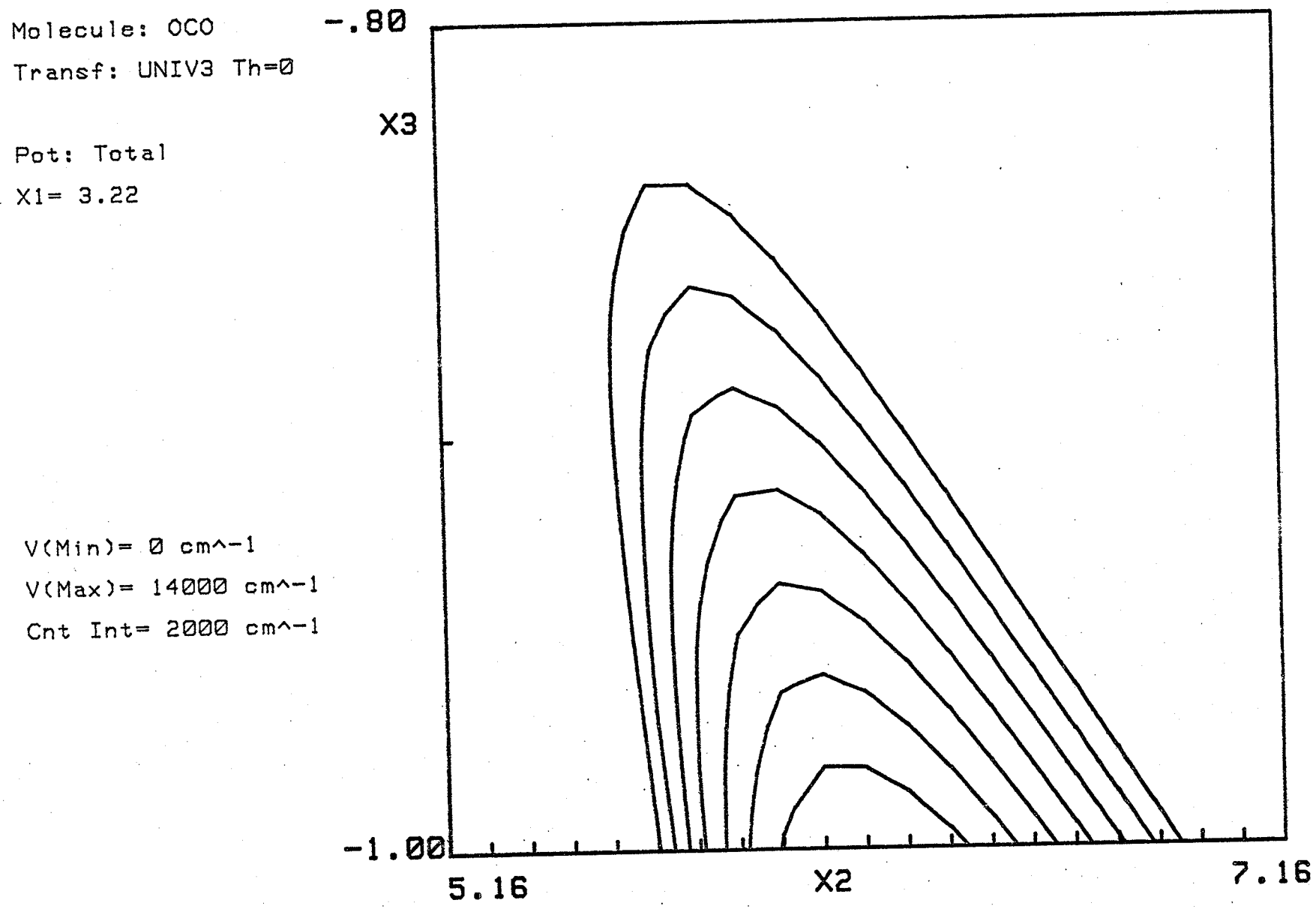

Molecule: OCO
Transf: UNIV3 Th=0
Pot: Total
X1= 3.22
V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1
-.80
X3
-1.00
5.16
X2
7.16

Fig.(3·2·b-1)

Molecule: OCO

Transf: UNIV3 Th=0

Pot: Total

X3= 1.00

V(Min)= 0 cm^-1

V(Max)= 14000 cm^-1

Cnt Int= 2000 cm^-1

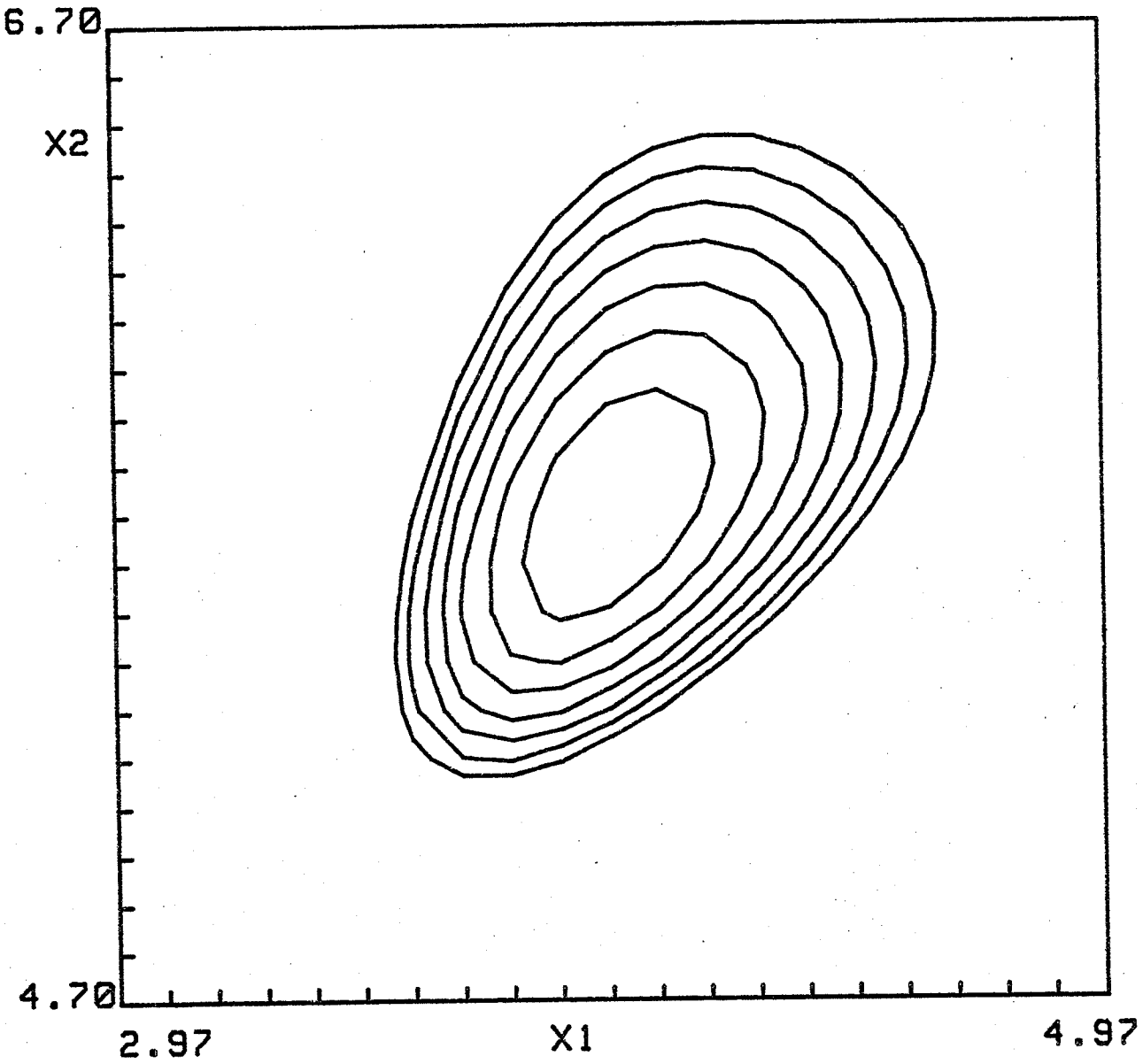


Fig.(3.2.b-2)

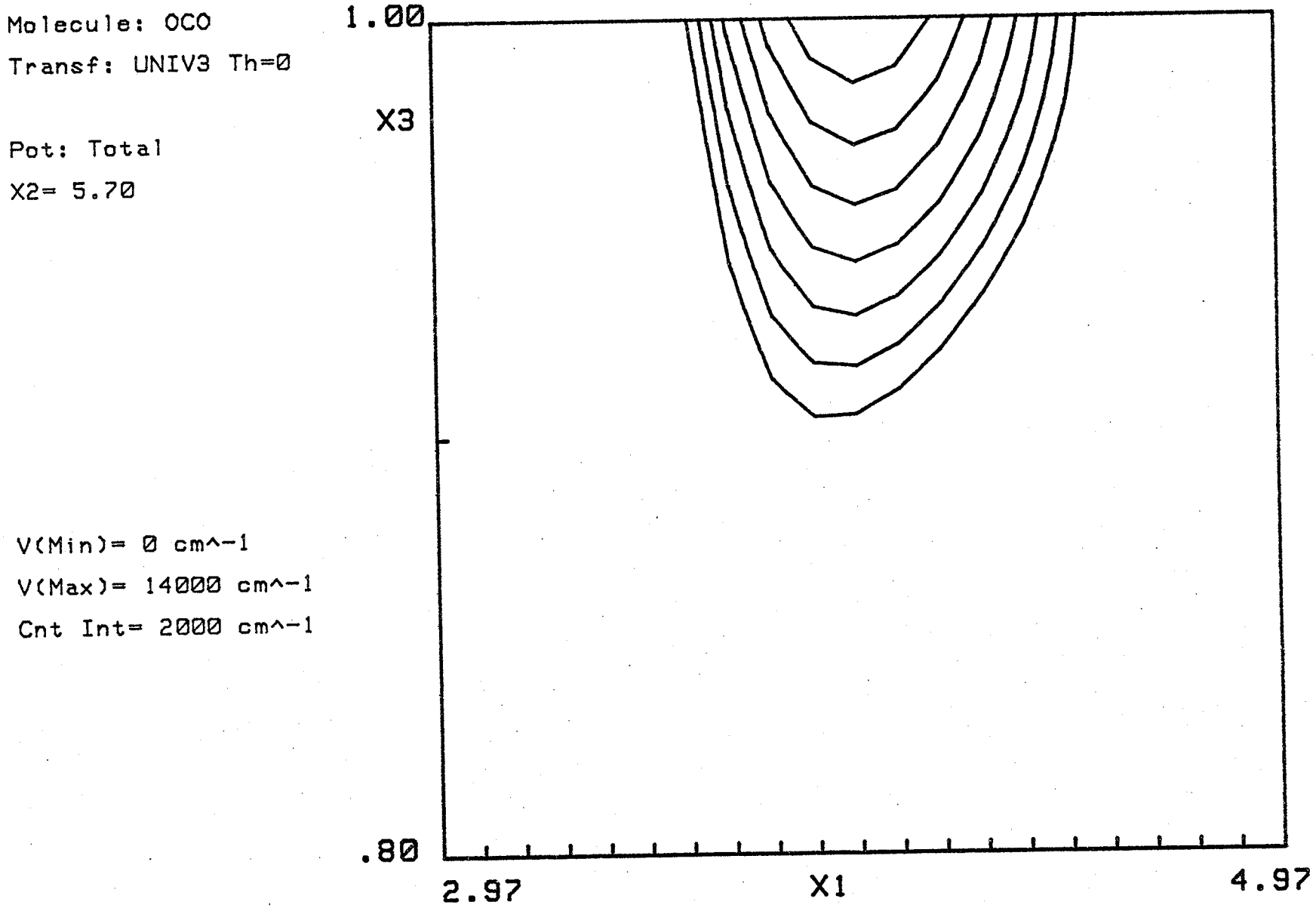

Molecule: OCO
Transf: UNIV3 Th=0
Pot: Total
X2= 5.70
V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1
1.00
X3
.80
2.97
X1
4.97

Fig.(3.2.b.-3)

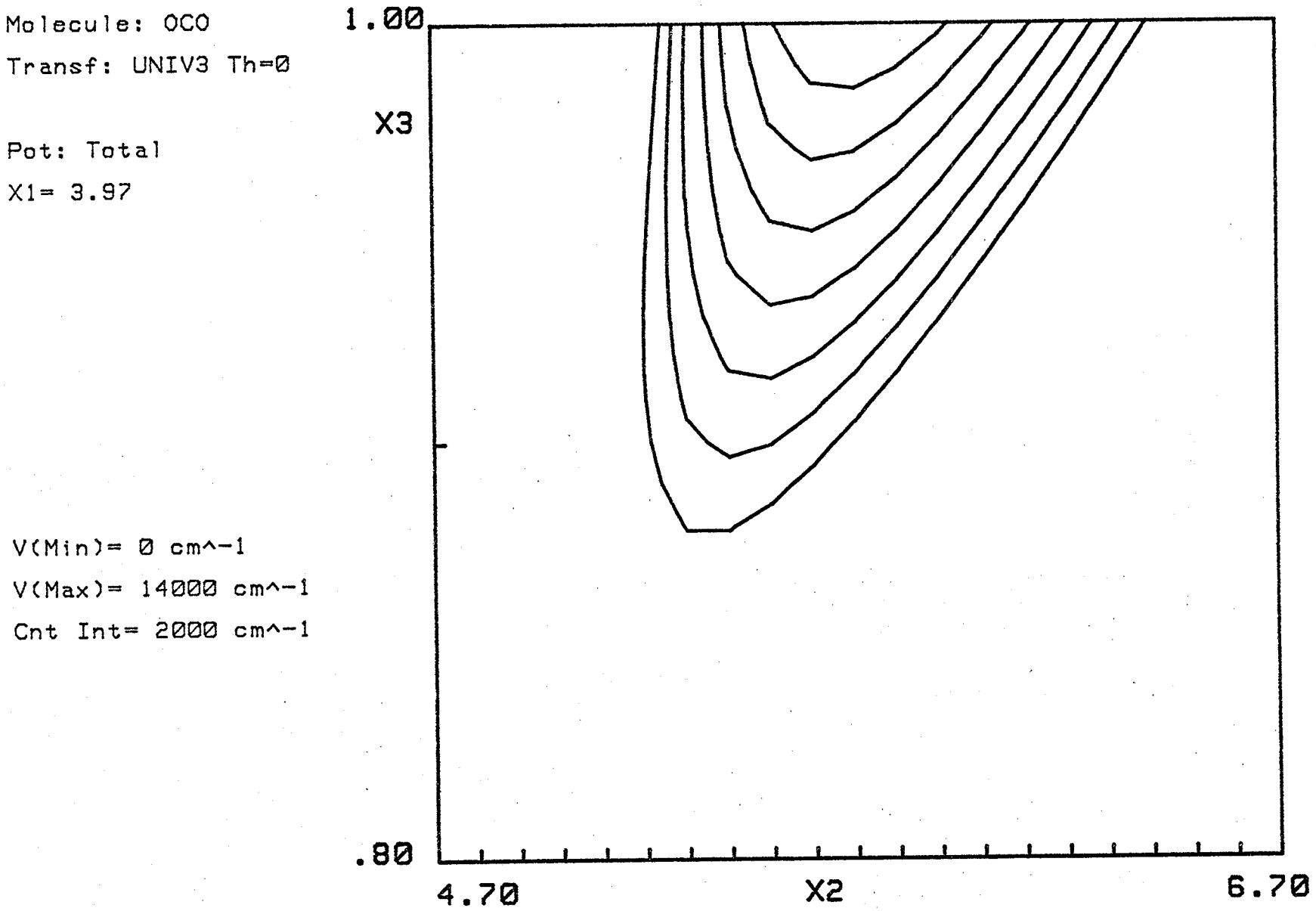
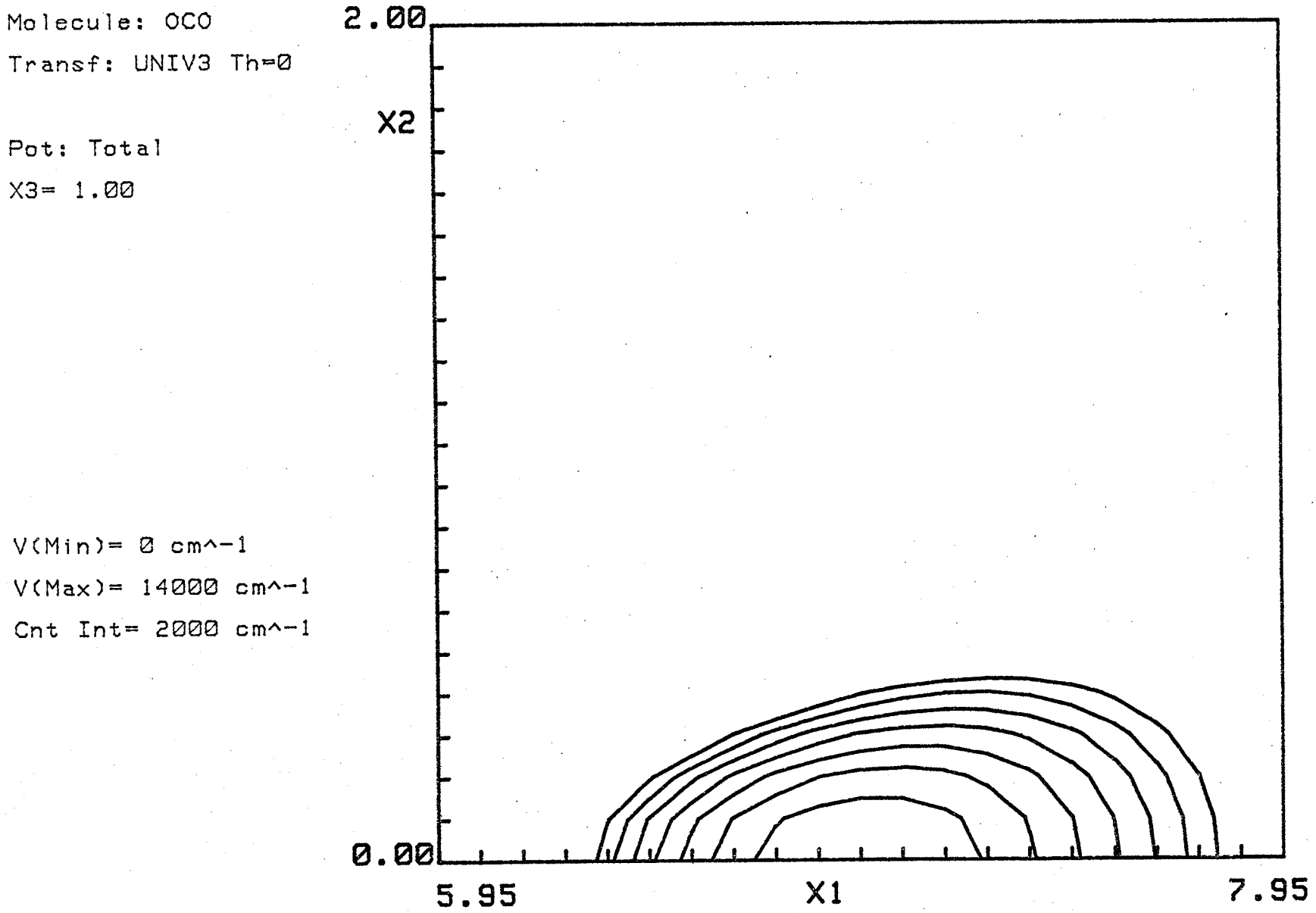

Molecule: OCO
Transf: UNIV3 Th=0
Pot: Total
X1= 3.97
V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1
1.00
X3
.80
4.70
X2
6.70

Fig.(3.2.c-1)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Transf: UNIV3 Th=0
Pot: Total
X3= 1.00
V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1
2.00
X2
0.00
5.95
X1
7.95

Fig.(3.2.c-2)

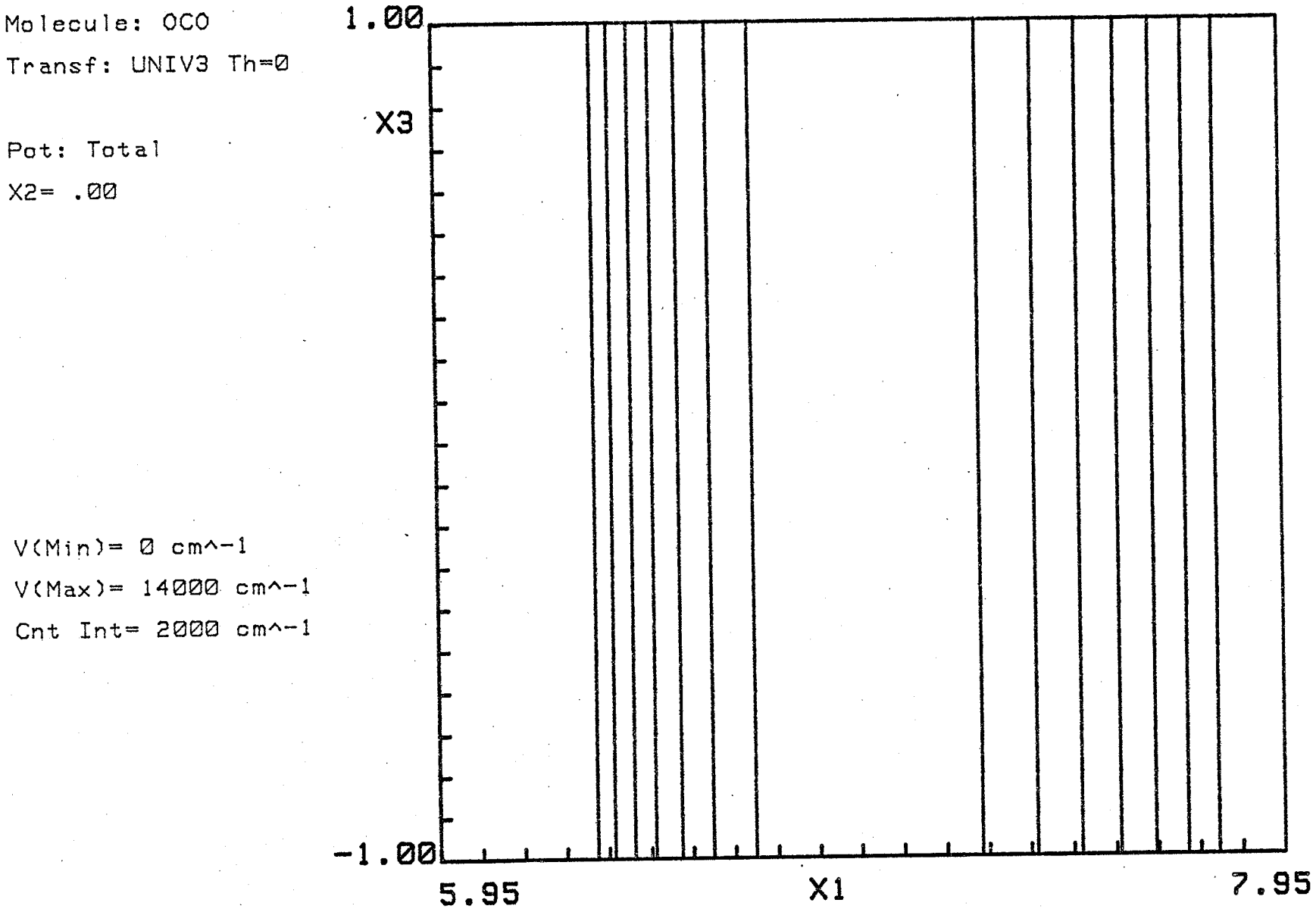
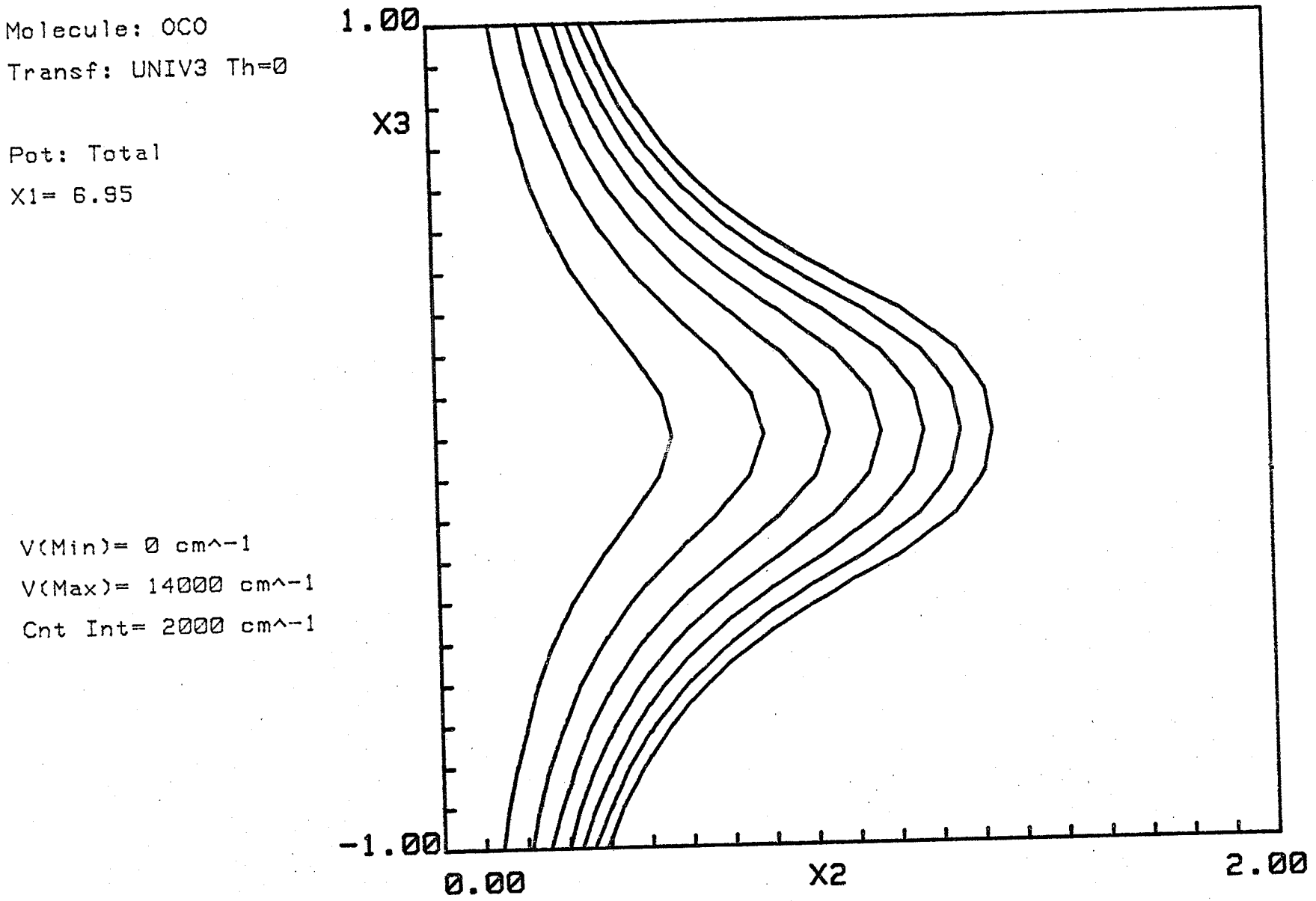

Molecule: OCO
Transf: UNIV3 Th=0
Pot: Total
X2= .00
V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1
1.00
X3
-1.00
5.95
X1
7.95

Fig.(3.2.c-3)


Molecule: OCO
Transf: UNIV3 Th=0
Pot: Total
X1= 6.95
V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1
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X3
-1.00
0.00
X2
2.00

Fig.(3.2.d-1)

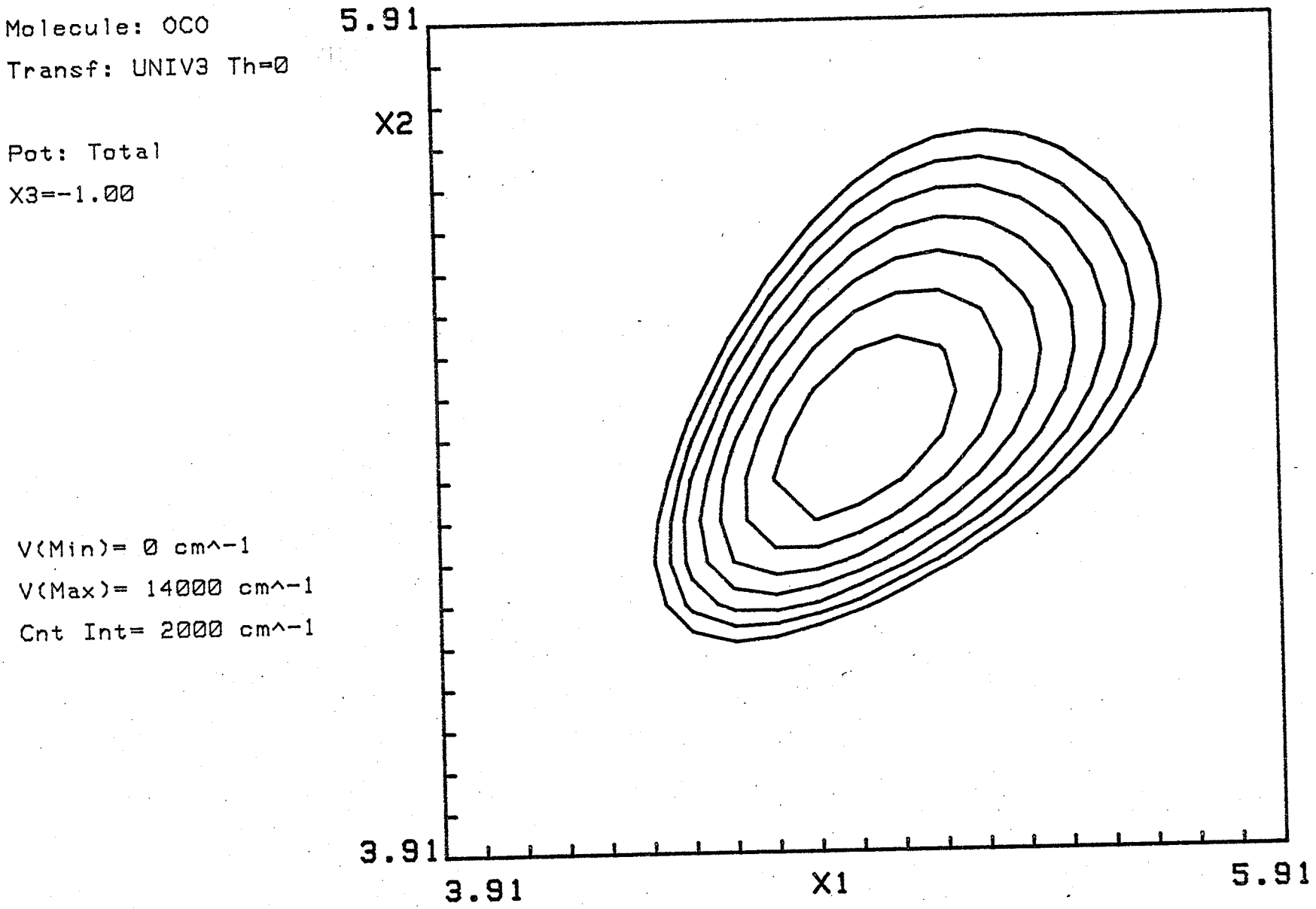

Molecule: OCO
Transf: UNIV3 Th=0
Pot: Total
X3=-1.00
V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1
5.91
X2
3.91
3.91
X1
5.91

Fig.(3.2.d-2)

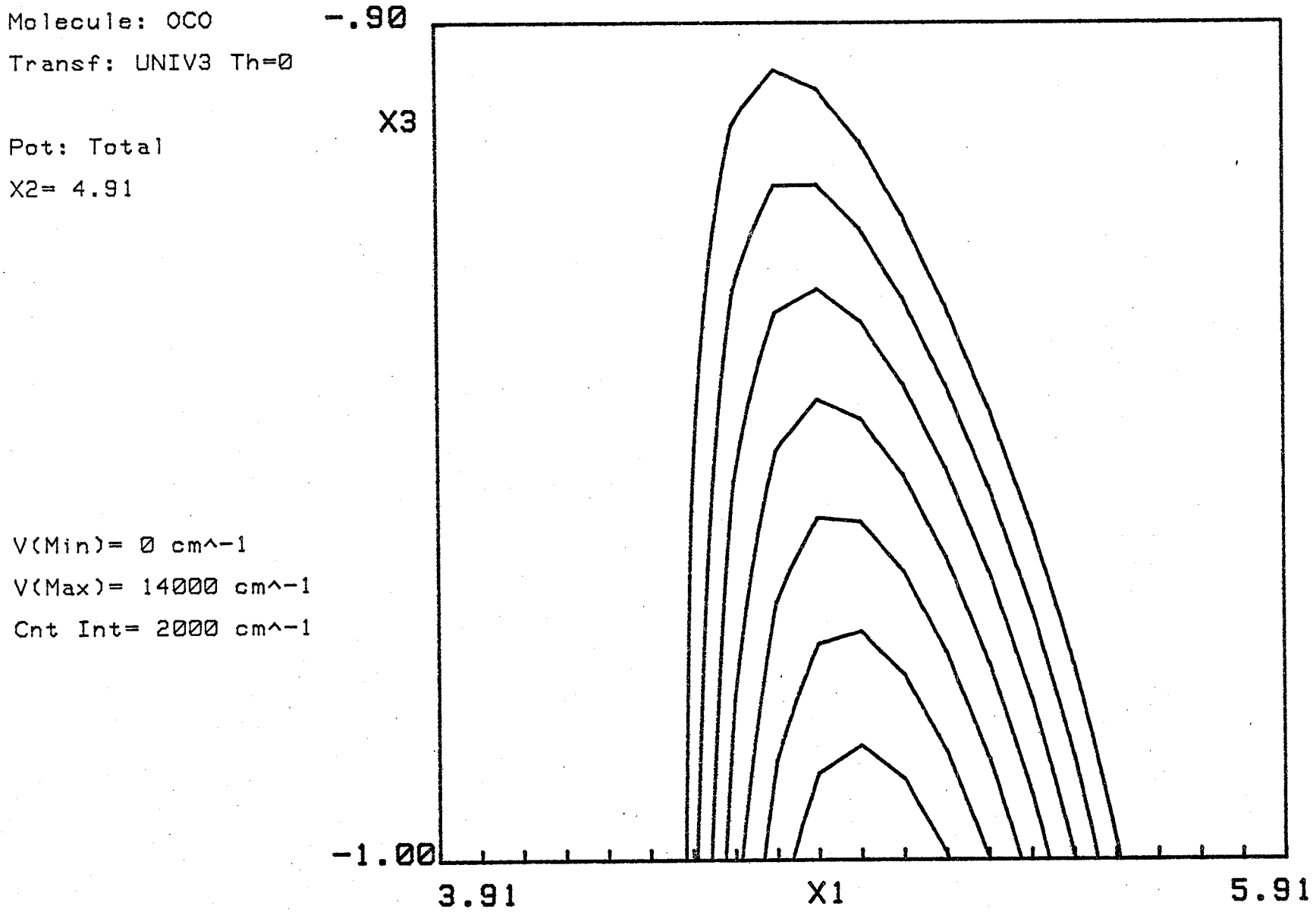
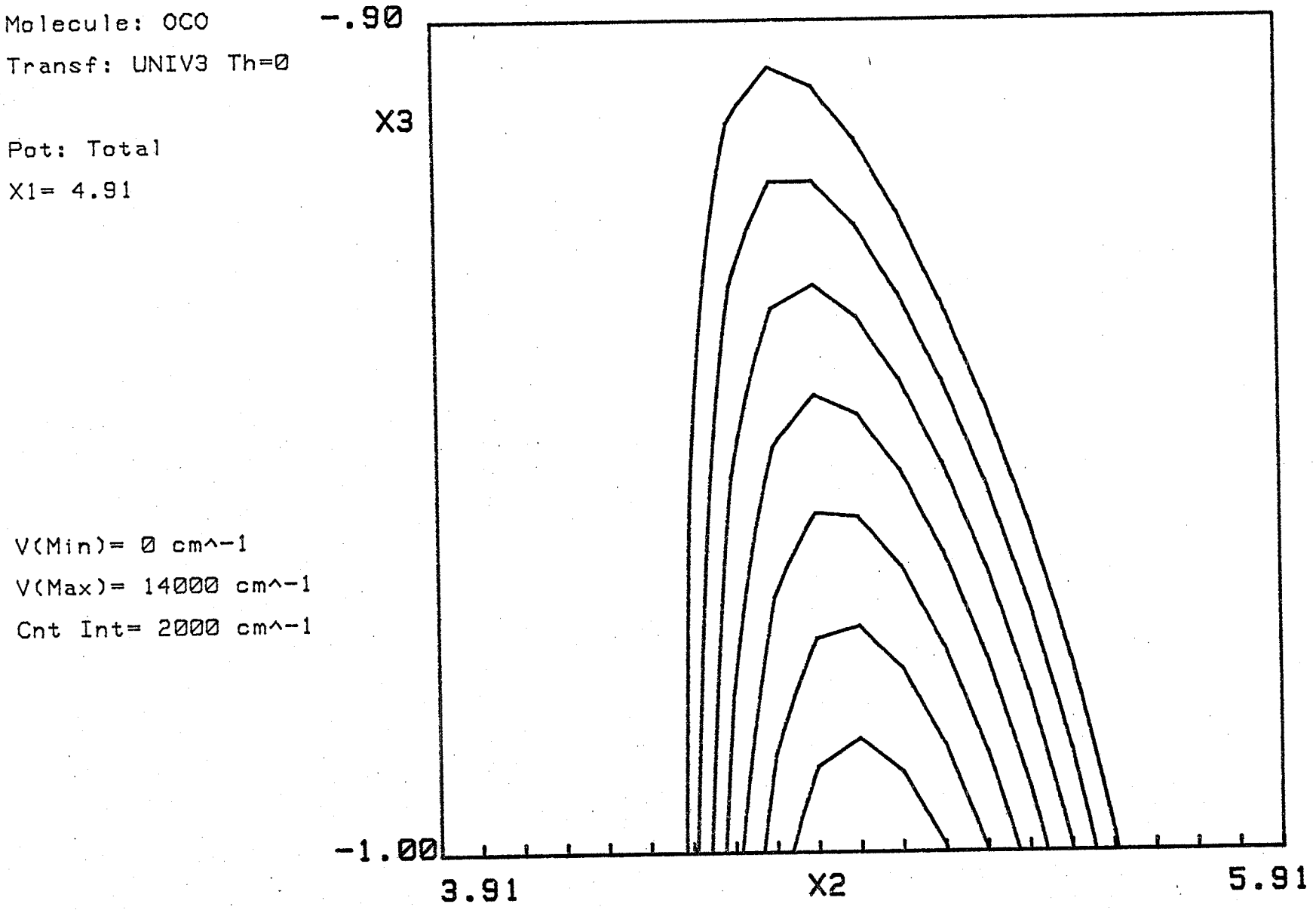

Molecule: OCO
Transf: UNIV3 Th=0
Pot: Total
X2= 4.91
V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1
-.90
X3
-1.00
3.91
X1
5.91

Fig.(3.2.d-3)


Molecule: OCO
Transf: UNIV3 Th=0
Pot: Total
X1= 4.91
V(Min)= 0 cm^-1
V(Max)= 14000 cm^-1
Cnt Int= 2000 cm^-1
-.90
X3
-1.00
3.91
X2
5.91

5.CONCLUSIONS.

Our actual investigations in the three-body problem could be resumed as follows.

- We have the necessary tools to proceed to the best choice in the various coordinates systems. An actual program permits the transformation of the bond distance and bond angle internal coordinates into any coordinate system member of the family of orthogonal coordinates. From the refinement of the potential, we can plot the potential energy surfaces in any of the coordinates and deduce the contribution of the non-separable part of the potential.

- The zeroth-order approximation of the molecular vibrational equation has been separated into three 1-dimensional equation, two of them are of "radial" type, the other is of "angular" type. These equations are obviously not analytically soluble. Therefore, we must use numerical methods, that is the subject of the second part of this work.

P A R T T W O

NUMERICAL SOLUTIONS OF THE ANGLE BENDING EQUATION

The numerical solution of the two kinds of 1-dimensional Schroedinger equations (radial and angular) derived in Part 1 constitutes the aim of this second part. We propose here a general scheme able to solve ordinary second order differential eigenvalue equations with various boundary conditions and containing explicitely or not a first derivative term.

Among the multitude of numerical methods permitting such a solution, we have adapted and extended the so-called renormalized Numerov method to problems which, at our knowledge, were never solved in such a way.

The present part of the dissertation is divided as follows:

- a general review of numerical methods having some interest in our field.
- a review of the renormalized Numerov method illustrated by simple examples
- the derivation of new algorithms which may be applied to problems where the Numerov algorithm cannot be used.
- the application of these algorithms to a problem having an analytic solution and to a problem without analytic solution.

CHAPTER 4: GENERAL REVIEW OF NUMERICAL SOLUTIONS OF SECOND ORDER DIFFERENTIAL EIGENVALUE EQUATIONS.

1. INTRODUCTION.

The subject of this chapter is to present a very general review of the methods currently used in order to solve equations discussed in the previous chapter. The subject is so large that our aim is to present in the most simple way some basic elements of the numerical techniques currently used in this kind of problems. In the present context, the solution of equations is carried out by a very large variety of methods having their own properties of accuracy, simplicity and adaptability.

We have to solve numerically second-order ordinary differential eigenvalue equations of the type:

$$y''(x) = p(x)y'(x) + q_E(x)y(x)$$

presenting a large variety of boundary conditions involving $y(a)$, $y(b)$, $y'(a)$ and/or $y'(b)$. Furthermore, the equations may present some singularities at the bounds.

As the new methods we plan to develop here involve both shooting and finite difference methods we shall emphasize particularly these two groups of techniques.

We refer the reader to general textbooks and publications listed in the bibliography for more details:references 27, 30, 31, 33 and 34 are more formal textbooks, reference 29 constitutes a survey of some problems arising in Boundary values problems and references 32, 35, 36, 41, 42, 43 and 45 are textbooks which emphasize more the applications of numerical analysis.

2. INITIAL AND BOUNDARY-VALUE PROBLEMS.

The numerical solution of ordinary differential equations can be carried out by two categories of techniques depending upon the specification of the conditions governing the problem.

When all the conditions are specified for one value of the independent variable (usually the initial point of the interval of integration), the problem is said to be of initial value type. For example, the following system:

$$y'(x) = f(x,y) \qquad a<=x<=b \tag{4-1}$$

$$y(a) = \alpha \quad (\alpha \text{ being an arbitrary constant})$$

The numerical methods solving this type of problem yield a sequence of approximations $y_n = y(x_n)$ on the set of points $x_{n+1} = x_n + h_n$ $(n=0,1,2,\ldots,N)$, $x_0 = a$ and $x_N = b$ where h_n is the stepsize, usually constant. The basic assumption concerning (4-1) is that $f(x,y)$ satisfies a Lipschitz condition [60] with respect to the maximum norm:

$$[f(x,y_1)-f(x,y_2)] <= L[y_1-y_2], \quad \text{for all } x \in [a,b] \tag{4-2}$$

If such a condition is met, it can be shown that there exists a unique solution to (4-1).

Well-known classical methods are available to solve initial-value problems, among them, the Runge-Kutta methods,

the multistep method and Taylor series method[28,32,40,42,43].

In initial-value problems, the initial conditions at x=a contain sufficient information for the solution be computed at x = a+h and so on.

We shall concern ourselves with the second category, the so-called boundary value problems where the conditions are specified at two different values of the independent variable (usually the boundary points). We define a two point boundary value problem by the following characteristics:

(i) an ordinary differential equation of degree n, or equivalently (footnote 1) n first-order differential equations to solve over the closed interval J=[a,b].

(ii) r boundary conditions at x=a.

(iii) (n-r) boundary conditions specified at x=b.

Note that more than n boundary conditions lead to insolubility of the system and less than n boundary conditions to multiple solutions.

For example, we may have the following system for a second order differential equation:

$$(4\text{-}3) \quad y''(x) = f(x,y,y') \qquad a<=x<=b$$

$$y(a) = \alpha \qquad y'(b) = \beta$$

In the most general case a two point boundary value

problem will be stated by the following system:

$$(4\text{-}4) \quad L[y(x)] = y'(x) - A(x)y(x) = f(x) \qquad a<=x<=b$$
$$B^{(\gamma)}[y(x)] = B_a{}^{(\gamma)}y(a) + B_b{}^{(\gamma)}y(b) = \beta \qquad \gamma=0,1$$

where $A(x)$, B_a and B_b are nxn matrices while $y(x)$, $f(x)$ and β are n-vectors. Usually, in the problems we shall concern with, the boundary conditions are partially separated[27,30] and represent then n independent linear constraints on $y(a)$ and $y(b)$.

Since the problems encountered in molecular chemistry are mostly second order ordinary differential equations problems and furthermore eigenvalue-eigenvectors problems, hence homogeneous, we shall define them by the general following system[34]:

$$(4\text{-}5) \quad L(E)[y(x)] = y''(x) - p(x)y'(x - q_E(x)y = 0; \quad a<=x<=b$$
$$\alpha_0 y'(a) + \alpha_1 y(a) = 0; \quad \beta_0 y'(b) + \beta_1 y(b) = 0$$

since $L[y(x)]$ is homogeneous, so are the boundary conditions.

In two point boundary value problems, there is not sufficient information at the initial point to start a step-by-step solution, hence a way must be found to determine the missing initial conditions and an approach other than step-by-step integration must be used. The problems have been attacked by a variety of techniques[34,35] among them: Picard's methods, interpolation methods, variational methods,

collocation methods, shooting methods and discrete methods, the two last methods will retain more specifically our attention since a complete survey [46] covering all two point boundary methods shows that they are the most used.

Footnote 1

Any given nth-order ordinary differential equation:
$y^{(n)}(t) = g(y,y^{(1)},\ldots,y^{(n-1)},t)$
can be replaced by a system of n first-order ordinary differential equations:

$$y_n = g(y_1,y_2,\ldots,y_n,t)$$
$$y_{n-1} = y_n$$
$$y_{n-2} = y_{n-1}$$
$$\ldots$$
$$y_1 = y_2$$

where:

$$y_1 = y$$
$$y_2 = y_1' = y^{(1)}$$
$$y_3 = y_2' = y_1 = y^{(2)}$$
$$\ldots$$
$$y_n = y_{n-1} = \ldots = y^{(n-1)}$$

and $y_k = dy_k/dt$

3.SHOOTING METHODS.

Let the two-point boundary value problem in its standard first-order form be given by:

$$(4\text{-}6) \qquad y' = f(x,y) \quad \text{or} \quad y'_i = f_i(x,y_1,y_2,\ldots,y_s) \qquad (i=1,2,\ldots,s)$$

with boundary conditions:

$$(4\text{-}7) \qquad y_i(a) = \alpha_i \qquad (i=1,2,\ldots,k)$$
$$y_i(b) = \beta_i \qquad (i=i_{k+1},\ldots,i_s)$$

so that we have k boundary conditions at x=a and s-k at x=b, where $0<k<s$. The system [(4-6),(4-7)] may be solved by initial value methods if we can find enough boundary values at x=a or x=b, i.e. if we can obtain values for all the s variables $y_i(x)$ at a or b. Suppose we estimate the values of $y_i(x)$ which are not already specified by (4-7), then we have enough information to integrate the system forwards from x=a and backwards from x=b. If our estimates are correct, the forwards and backwards solutions will be equal at intermediate points of the range. The problem is then to improve the initial estimates of the unknown boundary conditions until the solutions match: this is the basis of the shooting method. Since s boundary values are specified initially, so s unknown values have to be estimate in order

to start the process: let us call them $p_1, p_2, \ldots, p_s$ and take:

$$(4\text{-}8) \qquad y_j(a) = p_j \qquad (j=k+1,\ldots,s)$$

$$(4\text{-}9) \qquad y_j(b) = p_j \qquad (j=1,2,\ldots,k)$$

The forwards integration starts with the set $[\alpha_1,\alpha_2,\ldots,\alpha_k,p_{k+1},\ldots,p_s]$ and produces a solution $y_a(x,p)$ function of the parameters $p_{k+1},\ldots,p_s$. The backwards integration starts with the set $[p_1,p_2,\ldots,p_k,\beta_{k+1},\ldots,\beta_s]$ and produces the solution $y_b(x,p)$. The two solutions are computed as far as some matching point x=m in the interval [a,b]. At this point they should be equal if the values of the parameter p are correct. So we get the following equation for determining p:

$$(4\text{-}10) \qquad F(p) = y_a(x,p) - y_b(x,p) = 0$$

If the differential equations are linear so is $F(p)$ [34] and we write (4-10) in the form:

$$(4\text{-}11) \qquad F(p) = Ap - c = 0$$

where the matrix A and the vector c are not known initially. The solution of (4-11) can be carried out by choosing s+1 vectors $p^{(t)}$, t=0,1,2...,s such that the differences $p^{(0)} - p^{(j)}$, j=1,2,...,s are linearly independent. We then calculate

the corresponding values $F^{(t)}$ of F(p) by integrating (4-6). The results may be written:

$$(4\text{-}12) \qquad F^{(0)} = Ap^{(0)} - c$$

$$(4\text{-}13) \qquad F^{(j)} - F^{(0)} = A[p^{(j)} - p^{(0)}] \qquad (j=1,2,\ldots,s)$$

from which we can determine A and c and hence solve the equations (4-11) for p.

For example let us consider the Mathieu equation with periodic boundary conditions:

$$(4\text{-}14) \qquad y'' + (a-2q\cos 2x)y = 0$$

$$y(0) = y(2\pi) \quad ; \quad y'(0) = y'(2\pi)$$

It is known that a periodic solution exists for certain values of $a^{(47)}$. We take the values of y(0) and y'(0) as parameters and compute a forwards solution $y_a(x,p)$, obtain the matching condition at 2π directly from the periodic property which gives an equation to solve for p. Note that the value of y(0) is undetermined because the parameters can be reduced to a single quantity, the ratio y'(0)/y(0).

The best-known method for solving the system (4-10) is the Newton iteration$^{(35)}$ which takes the form:

$$(4\text{-}15) \qquad p^{(t+1)} = p^{(t)} - [J(p^{(t)})]^{-1}F(p^{(t)})$$

where J(p) is the jacobian matrix $[\partial F_i/\partial p_j]$ evaluated for

parameters p. Starting with a suitable approximation $p^{(0)}$, we calculate successive corrections by using (4-15) in the form:

$$[J(p^{(t)}](p^{(t+1)} - p^{(t)}) = -F(p^{(t)}) \qquad (4\text{-}16)$$

This represents a set of linear equations for the corrections to p(t) which can be solved provided the jacobian is non-singular. To apply this method we have to calculate the s elements of the vector $F(p^{(t)})$ and the s^2 elements of the jacobian matrix $J(p^{(t)})$. The computation of these derivatives is the lengthiest part of the process. In general, they may be obtained either by solving the variational equations for the system (4-6) or by approximating the derivatives using simple difference quotients[28]. Hopefully in the problems we are concerned with, some easier ways can be found as we shall discuss in the next sections.

Before discussing the discrete methods, let us mention a particular case, the so-called "parallel shooting methods". These methods are usefull in problems where the integration across [a,b] is difficult or impossible because of instability[29]. Basically the methods consist in choosing the mesh points unequally spaced according to the difficulty of interating (4-6) over different parts of the range: i.e., the points x_i are close together where (4-6) is particularly difficult to integrate[30]. The basic idea is to compute the solution over each subinterval (more or less) independently of the results in the other subintervals. Then simultaneously

with attempting to satisfy the boundary conditions the relevant continuity conditions are imposed at each interval interface.

4.FINITE DIFFERENCE METHODS.

The application of finite difference methods to two points boundary value problems is basically straightforward. Any derivative occuring in the differential equations are replaced by their finite difference approximations (appendix 3).

The method consists in converting the set of ordinary differential equations into a finite set of algebraic equations the solution of which yields approximations at discrete points. Ultimately, most applications of the method reduce to the solution of large systems of linear algebraic equations with band matrices (appendix 4). The differential equation can be approximate by many finite difference formulas, the choice of which is a compromise between simplicity, size of the truncation error, stability and consistency[27]. The relative merits of various formulas are discussed in any textbook of numerical analysis[27-31]. Finally, the set of linear algebraic equations may be solved by a variety of techniques among them, Gaussian elimination, direct matrix inversion, relaxation techniques, indirect iterative methods.

The choice of the finite difference formulas is of course very important and attention must be paid not only to accuracy but also to stability. The two more common problems encountered are:

(i) to solve the set of linear algebraic finite difference equations

(ii) to show that the solution of the finite difference equations y_k approaches the solution of the differential equations $y(x_k)$ at the point x_k.

On the other hand, the choice of the step size will constitute a compromise between accuracy and speed of computation. One practical way to ascertain the adequacy of the step size is to solve the problem for a step size h and for a step size h/2 and compare the solutions (some extrapolation techniques are described later). Finally, since the finite difference formulas involve three or more points, we may find that we have more variables than equations. Therefore additional equations must be introduced by forwards or backwards difference formulas. These extra equations should be so choosen that their truncation errors is approximatively the same as that for the main body of equations. Some common ways to do this are the use of Taylor's series approximations and to differentiate the differential equation and approximate it with a finite difference expression (an example is given at the end of this section). We illustrate these concepts by discussing the simple second-order problem:

$$y'' = f(x,y,y') \qquad a \leqslant x \leqslant b \tag{4-17}$$

$$y(a) = \alpha \; ; \; y(b) = \beta$$

If we take a uniform mesh $x_n = a + nh$ $(0<n<N)$ and $h = (b-a)/N$, then a simple difference approximation[27] gives rise to:

$$(4\text{-}18) \quad L_h(y_n) = h^{-2}[y_{n+1}-2y_n+y_{n-1}] - f[x_n, y_n, 2h^{-1}(y_{n+1}-y_{n-1})] = 0$$

$$y_0 = \alpha \quad ; \quad y_N = \beta \qquad 0<n<N$$

If f in (4-17) does not depend on y', a more accurate approximation is given by Numerov's algorithm[27,29,48]:

$$(4\text{-}19) \quad L_h(y_n) = h^{-2}[y_{n+}-2y_n+y_{n-1}] - (1/12)[f(x_{n+1}, y_{n+1}) + 10f(x_n, y_n) + f(x_{n-1}, y_{n-1}] = 0$$

$$y_0 = \alpha \quad ; \quad y_N = \beta \qquad 0<n<N$$

The approximate solution is then obtained by solving either the system (4-18) or (4-19) of N+1 equations in the N+1 unknowns.

The linearized form of (4-17) with discretization (4-18) is for a homogeneous equation:

$$(4\text{-}20) \quad L(y) = -y''(x) + p(x)y'(x) + q(x)y(x) = 0$$

$$y(a) = \alpha \quad ; \quad y(b) = \beta$$

where:

$$p(x) = (\partial/\partial y')f(x,y,y') \quad \text{and} \quad q(x) = (\partial/\partial y)f(x,y,y')$$

Let the interval be partitioned into an integral number N of subintervals having the uniform lenght $h = 1/N$, the partition points are denoted by $x_i = ih$ and the corresponding functional values in (4-20) by $p_i = p(x_i)$, $q_i = q(x_i)$ and $y_i = y(x_i)$. At each of the partition points, the derivatives are approximated by finite difference formulas, substituted into (4-20) and the resulting discretization of (4-20) are assembled into a system of N-1 linear equations in the N-1 unknown values y_i $(1<i<N-1)$. Because the finite difference formulas give only an approximation to the true derivatives, there is an error (local truncation error) associated with each equation which we shall denote by τ_i $(1<i<N-1)$. Since the set y_i is also a solution, we can write:

$$(4\text{-}21) \qquad L_h(y) = [S + P + Q]y + Bc = Ay + Bc = \tau$$

where:

L_h is the discrete operator corresponding to L

S, P, and Q are $(N-1)\times(N-1)$ matrices of coefficients associated respectively with the negative of the second derivative, the second and third terms in (4-20)

B is an $(N-1)\times 2$ matrix of boundary points coefficients

c is the vector of boundary values: $c_t = (\alpha, \beta)$

y is the column vector of elements y_i $(1<i<N-1)$

τ is the column vector of elements τ_i $(1<i<N-1)$

The equation which is solved to obtain a numerical solution is:

$$(4\text{-}22) \qquad A\underset{\sim}{y} = -Bc$$

where now $\underset{\sim}{y}$ is an approximation to y. The error commited by solving (4-22) in place of (4-21) provided that A is non-singular, is:

$$(4\text{-}23) \qquad y - \underset{\sim}{y} = A^{-1}\tau$$

If the matrix is monotone (i.e., for any $Ay>0$, $y>0$), then A is non-singular and it is frequently possible to bound the maximum row sum of A^{-1} by a constant independent of N:

$$(4\text{-}24) \qquad [y - \underset{\sim}{y}]_i < \Sigma_j A^{-1}{}_{ij}[\tau_j] < K_1[\tau] \qquad (i=1,\ldots,N)$$

For example, a second order solution is obtained from the approximations:

$$(4\text{-}25) \qquad y''_i = (1/h^2)\delta^2 y_i + O(h^2)$$

$$(4\text{-}26) \qquad y'_i = (1/h)m\delta y_i + O(h^2)$$

which, when substituted into (4-20) for i=1,...,N-1 produce a system of equations (with y=u)

(4-27) $L_h(u_j) = -(1/h^2)[u_{j-1}-2u_j+u_{j+1}] +$

$(1/2h)p_j[u_{j+1}-u_{j-1}] + q_j u_j = 0$

$u_0 = \alpha \quad ; \quad u_N = \beta \qquad (j=1,\ldots,N-1)$

multiplying by $h^2/2$:

(4-28) $(h^2/2)L_h(u_j) = -b_j u_{j-1} + a_j u_j - c_j u_{j+1} = 0$

$(j=1,\ldots,N-1)$

where:

(4-29) $a_j = 1+(h^2/2)q_j$

(4-30) $b_j = (1/2)[1+(h/2)p_j]$

(4-31) $c_j = (1/2)[1-(h/2)p_j]$

and the matrix A of equation (4-22) becomes:

$$A = \begin{bmatrix} a_1 & -c_1 & & & \\ -b_2 & a_2 & -c_2 & & \\ \cdots & \cdots & \cdots & & \\ & & -b_{N-2} & a_{N-2} & -c_{N-2} \\ & & & -b_{N-1} & a_{N-1} \end{bmatrix}$$

If we impose:

(4-32) $q(x) >= Q_* > 0 \quad ; \quad h < 2/P^*$

where

(4-33) $P^* = \max[p(x)] \quad (a<x<b)$

it follows that:

(4-34) $[b_j] + [c_j] = b_j + c_j = 1$

(4-35) $[a_i] > [c_1]$

(4-36) $[a_j] > [b_j] + [c_j] \quad ; \quad 2<j<N-2$

(4-37) $[a_{N-1}] > [b_{N-1}]$

The matrix A is then non-singular and the solution of (4-31-a) can be computed by a simple direct factorization of A described elsewhere.

The local truncation error in (4-24) can be stated as:

(4-38) $[u_j-y_j] < h^2[(M_4+2P^*M_3/120_*] \quad (j=1,\ldots,N)$

where:

(4-39) $M_3 = \max[y^{(3)}], \quad M_4 = \max[y^{(4)}] \quad (\text{over } [a,b])$

The difference solution converges to the exact solution as h tends to infinity and in fact, the error is at most $O(h^2)$. For equations in which $p(x)=0$, the error bounds are of $O(h^4)$. The errors of roundoff in computing can be estimated in the same way. Let U_j the computed quantities satisfying:

(4-40) $(h^2/2)L_h(U_j) = \lambda_j;\ U_\emptyset = \alpha + \lambda_\emptyset;\ U_N = \beta + \lambda_N$

The quantities λ_j represent the local roundoff errors committed in each computation. We define:

(4-41) $E_j = U_j - Y_j \quad ; \quad j=1,\ldots,N$

and we can find:

(4-42) $[1+(h^2/2)Q_*][E_j] < E + (h^2/2)\tau + \lambda \quad (j=2,\ldots,N-1)$

where:

(4-43) $\lambda = \max[\lambda_j] \quad (1<j<N)$

(4-44) $[E_\emptyset] = [\lambda_\emptyset]$

(4-45) $[E_N] = [\lambda_N]$

(4-46) $E = \max[E_j] \quad (1<j<N)$

where if we require that $h^2Q_*/2<1$,

(4-47) $E < (1/Q_*)[\tau + 2\lambda/h^2]$

Regrouping (4-38), (4-42) and (4-47), we obtain for sufficiently small h:

(4-48) $[U_j - Y_j] < h^2[(M_4+2P^*M_3)/12Q_*] + h^{-2}[2\lambda/Q_*]$

Remark

The matrix S in (4-21) has the form:

(4-49) $$S = h^{-2}J$$

where J is the band matrix:

$$\begin{bmatrix} 2 & -1 & & & & \\ -1 & 2 & 1 & & & \\ 0 & -1 & 2 & -1 & & \\ \cdots & & & & & \\ & & & & -1 & 2 \end{bmatrix}$$

5.EXTRAPOLATION TECHNIQUES.

As mentioned earlier some extrapolation techniques are available to improve the adequacy of the method chosen in order to solve a particular problem. The two best-known techniques for increasing the order of a finite difference method and thus improving the accuracy obtained from the different choices of the step size, formulas,... are discussed below.

The first extrapolation technique is based upon the following result:

(4-50) $$y_n = y(x_n) + h^2 e(x_n) + O(h^2) \qquad (1<=n<=N)$$

where:

(4-51) $$e''(x) - p(x)e'(x) - q(x)e(x) = -(h^2/12)[-y^{(4)}(x) + p(x)y^{(3)}(x)]$$

$$e(a) = 0 \quad ; \quad e(b) = 0$$

On evaluating the approximate solution at steplength h=k and h=k/2, we find (in an obvious notation) an improved solution with error $O(h^4)$:

(4-52) $$y_n = (4/3)y_{2n,k/2} - (1/3)y_{n,k} \qquad (1<=n<=N)$$

As a second technique let us mention the deffered

correction (Richardson's extrapolation) which has been put on a theoretical basis by Pereyra[28]. If an approximation is calculated with a simple truncated finite difference formula, it is reasonable to suppose that the error at each pivotal point is a function of the size of the interval h. Expanding this function as a Taylor series, we can write:

$$y - y(h) = Bh + Ch^2 + \ldots \tag{4-53}$$

It is also reasonable to suppose than the terms on the right decrease in size and, if the finite difference equation has meaning that $y(h) \to y$ as $h \to 0$.

If we calculate several approximate solutions using the same simple equations but with different intervals h_1, h_2,..., we can eliminate the terms B, C,.... If we write $y^{(r)}$ for $y(h_r)$, the solution y can be writen as a function of $y(h_r)$. For example, if we take $h_2=h_1/2$:

$$y = y^{(2)} + (1/2)[y^{(2)} - y^{(1)}] + O(h^4) \tag{4-54}$$

For $h_2 = h_1/2$ and $h_3 = h_2/2$, we have:

$$y = y^{(3)} + (20/45)[y^{(3)} - y^{(2)}] - (1/45)[y^{(3)} - y^{(1)}] + O(h^6) \tag{4-55}$$

If we consider for example the second-order differential equation (4-20), we can replace it by the finite difference

equation:

(4-56) $(1+hp_r/2)y_{r+1}(h) + (1-hp_r/2)y_{r-1}(h) - (2-h^2q_r)y_r(h) = 0$

Substituting the y_n from the Taylor series expansion, we find that the coefficient B in (4-53) is given by:

(4-57) $(\partial^2/\partial x^2)y_r + p_r(\partial/\partial x)y_r + q_r y_r = 0$

The successive later coefficients are calculated in the same way[32].

6.SINGULARITIES.

In the numerical solution of differential equations we can treat accurately only well-behaved functions with no singularities in the range of integration. Nevertheless it is usually possible to recognize from the differential equations the existence, position and type of singularity and to remove it by transformations involving the dependent and/or independent variables.

The theory of singular points is fully developed and results are available in standard textbooks[37].
If a point x=c is a regular singular point[38] of a linear differential equation:

$$p(x)y''(x) + q(x)y'(x) + r(x)y(x) = 0 \qquad (4\text{-}58)$$

then a series solution (of Frobenius type) exists near x=c in the form:

$$y = (x-c)^{r}\Sigma_i a_i (x-c)^{i} \qquad (i=0,\ldots,\text{infinity}) \qquad (4\text{-}59)$$

where r is not necessarily an integer. The values of r and the a_i are determined in the usual way, i.e. in replacing (4-59) and its derivatives in (4-58) and equating the coefficients of the different powers of x to zero. This method gives at least one solution at a regular singularity.

Another interesting method was introduced by J.C.Taylor[49]. The method consists in considering the solution y(x) as the section of a surface S:y=y(x,t) by a vertical plan, say t=0 and considering the analytic continuation of y(x), y(z) (z=x+it), which satisfies the differential equation:

$$y''(z,t) + p(z)y'(z,t) + q(z)y(z,t) = 0 \qquad (4\text{-}60)$$

over the t-plane and whose solutions reduce to those of the original equation when t=0. The equation (4-60) holds throughout the t-plane away from the singularities of p(x) and/or q(x). We can therefore attempt to use it to integrate as before but now we are free to choose a path which avoids the singularities. This technique is applicable without difficulty when the singularity does not occur at the boundary points whereas it introduces extrapoints in the difference equations when the singularity is present at a bound and additional difference equations must be introduced.

7.HIGH-ORDER FINITE DIFFERENCE METHODS.

The previous discussion deals with approaches where simple difference equations were used to approximate the solutions of differential equations. The present section will concern with some examples where the utilisation of higher order difference equations are used to improve the accuracy of the approximations.

As a first example, we shall resume a sixth-order method proposed by R.A.Usmani [50]. The boundary value problem can be stated as follows:

$$y''(x) = f(x)y(x) + g(x) \qquad a<x<b \tag{4-61}$$

$$y(a) = \alpha \qquad y(b) = \beta$$

where

i) $a<=x<=b$

ii) α and β are arbitrary finite constants

iii) $f(x)>0$ for $a<x<b$

iv) f and g are continuous functions on the range as their derivatives up to the sixth order.

In these conditions the system has a unique solution and using higher order difference equations, the solution ($y(x_n)$) satisfies:

(4-62) $(-1+A_{n+1})y_n + (2+B_{n+1})y_{n+1} + (-1+C_{n+1})y_{n+2} = D_{n+1}$

$(n=0,1,\ldots,N-1)$

where the A, B, C and D are defined in terms of the f_n and g_n and their first derivatives. The system (4-62) can be written in matrix notation as follows:

(4-63) $$MY = (J + Q)Y = B$$

where M is an nxn tridiagonal matrix which may be written as the sum of two nxn tridiagonal matrices J+Q where the non zero elements are:

(4-64) $j_{ii} = 2;\ j_{i,i+1} = j_{i+1,i} = -1$

$q_{ii} = B_i;\ q_{i,i+1} = C_i;\ q_{i+1,i} = A_i$

and $B = (b_i)$ is a N-dimensional column vector such that:

(4-65) $b_1=D_1-A_1;\ b_i=D_i\ (i=2,3,\ldots,N-1);\ b_N=D_N-C_N$

The system (4-63) can be solved by any method presented previously. It can be shown that the discretization error $e_n = y(x_n)-y_n$ is bounded by a factor of order in h^6:

(4-66) $\max[e_i] = E = O(h^6) = (1/8)M_8(b-a)^2h^6\ (1<=i<=N)$

where

(4-67) $$M_8 = \sup (29/302400)(d^8/dx^8)y(x) \quad \text{over } [a,b]$$

The second example proposed by J.N.Shoosmith[29] consists in using high-order central-difference[32] approximations to the derivatives at mesh points sufficiently far from the boundaries and using linear combinations of non symmetric finite difference discretizations near the bounds so as to force the total contribution of the highest derivative to the resulting linear system to take the form of a tridiagonal matrix of the form (4-49).

As a specific attempt to obtain high order accurate solutions, the sixth order central approximations are:

(4-68) $$y''_i = h^{-2}[\delta^2-(1/12)\delta^4+(1/90)\delta^6]y_i + O(h^6)$$

(4-69) $$y'_i = /h[\delta-(1/4)\delta^3+(1/30)\delta^5]y_i + O(h^6)$$

$(i=3,4,\ldots,N-3)$

but we are not able to use these equations at i=1,2,N-1,N-2 because to do so would requires the use of solution points outside the interval [a,b]. By substituting into (4-21) we are able to obtain N-5 equations in the unknowns y_i (i = 1,2,...,N-1). We shall consider an approach for obtaining the additional four equations required. The most obvious approach is to use sixth order non symmetric finite difference formulas for y''_i and y'_i at i=1,2,N-1,N-2.

For example,

(4-70) $$y''_i = (1/12h^2)[10y_0 - 15y_1 - 4y_2 + 14y_3 - 6y_4 + y_5] + O(h^4)$$

(4-71) $$y'_i = (1/12h)[-3y_0 -10y_1 \ 8y_2 - 6y_3 + y_4] + O(h^4)$$

The resulting algebraic equations are adjoigned to the N-5 equations already obtained but it is found that the matrix A is not monotone. Therefore, using combinations of such discretizations near the bounds in order to form various patterns of coefficients in the matrix A, we can force for example a row by row symmetric pattern in S such that the band of non zero elements in S tapers down in width towards the bounds.

CHAPTER 5: RENORMALIZED NUMEROV METHOD AND DERIVED METHODS.

1.INTRODUCTION.

The aim of this chapter is to provide some numerical ways to solve the equations derived in chapter 3. We recall that the n-dimensional Schroedinger equation describing the state of a n-body system was split into n 1-dimensional equations either of radial type or of "angle-bending" type. The radial equations can be stated as follows:

$$\Psi''(x) = q_{\lambda s}(x)\Psi(x) \qquad a<=x<=b \tag{5-0-1}$$

whereas the "angle-bending" equations are stated as follows:

$$\Psi''(x) = p(x)\Psi'(x) + q_{\lambda s}(x)\Psi(x) = 0 \qquad a<=x<=b \tag{5-0-2}$$

and in both cases, the boundary conditions are:

$$\Psi(x) + \alpha_x\Psi'(x) = 0 \qquad x=a,b \tag{5-0-3}$$

Clearly (5-0-1) is a particular case of (5-0-2) where $p(x)\Psi'(x)=0$.

Our preoccupation is to find among the methods described in the preceding chapter a method capable to be used in both

cases (5-0-1) and (5-0-2), easily solved even with boundary conditions different from $\Psi(x)=0$ at the bounds (usual boundary conditions), extendable to a system of coupled equations and with the higher possible accuracy. This is the subject of this chapter.

2. THE COOLEY-NUMEROV METHOD.

Let us consider the non-homogeneous eigenvalue problem:

$$\Psi''(x) = q_{\lambda s}(x)\Psi(x) + g(x) \qquad a<=x<=b \tag{5-1}$$

$$\Psi(a) = \alpha \quad ; \quad \Psi(b) = \beta$$

where the function $q_{\lambda s}$ is defined by:

$$q_{\lambda s} = k(x)[V_s(x) - \lambda] \tag{5-2}$$

$V_s(x)$ is a potential function depending upon a parameter s, λ are the eigenvalues of the problem.
Let us expand the solution $\Psi(x)$ in the following power series:

$$\Psi_{n+1} + \Psi_{n-1} = \Sigma_k[2h^{(2k)}/(2k)!]\Psi_n^{(k)} \tag{5-3}$$

$$\Psi_{n+1} - \Psi_{n-1} = \Sigma_k[2h^{(2k+1)}/(2k+1)!]\Psi_n^{(k+1)} \tag{5-4}$$

where k=0,1,2,...
Differentiating twice, multiplying the results respectively by $h^2/12$ and $h^2/6$ and substracting (5-3) and (5-4) from the respective results, we obtain:

$$(1/2)[\Psi_{n+1}+\Psi_{n-1}] - (h^2/24)[\Psi''_{n+1}+\Psi''_{n-1}] = \Psi_n + (5h^2/12)\Psi_n^{(2)} - (h^6/480)\Psi_n^{(6)} + \ldots \tag{5-5}$$

(5-6) $(1/2)[\Psi_{n+1}-\Psi_{n-1}] - (h^2/24)[\Psi''_{n+1}-\Psi''_{n-1}] = h\Psi'_n - (h^5/180)\Psi_n^{(5)} + \ldots$

Replacing the second derivative terms by the discretization of (5-1) and dropping the terms of the fourth order and higher, we obtain after regrouping:

(5-7) $\Psi_{n+1}[1-T_{\lambda,n+1}] - \Psi_n[2+10T_{\lambda,n}] + \Psi_{n-1}[1-T_{\lambda,n-1}] = (h^2/12)[g_{n+1} + 10g_n + g_{n-1}]$

(5-8) $\Psi_{n+1}[.5-T_{\lambda,n+1}] - \Psi_{n-1}[.5-T_{\lambda,n-1}] = (h^2/12)[g_{n+1} - g_{n-1} + (12/h)\Psi'_n]$

where we put:

(5-9) $T_{\lambda,n} = (h^2/12)q_{\lambda n}$

The equation (5-7) is known as the Numerov's algorithm whereas equation (5-8) is an algorithm which will be useful later in order to determine the first derivative of the solution. The local truncation errors are respectivelly of the orders of $(-h^6/240)\Psi_n^{(6)}$ and $(-h^5/90)\Psi_n^{(5)}$.

In the range $\lambda>V_s(x)$, corresponding to unbounded states of two particles, solutions of (5-1) exist for all λ and can be approximated using (5-7) to integrate outward starting with boundary values $\Psi_0=\alpha$ and $\Psi_1=\alpha+$ a small arbitrary number. For $\lambda<V_s(x)$, the solutions of (5-1) exist for a set of discrete values of λ; the purpose of this section is to

determine the method used to find these discrete values.

Some further transformations are currently used in order to simplify the formalism and to decrease the number of steps in the computations.

Let us define:

$$(5\text{-}10) \qquad (1-T_{\lambda,n})\Psi_n - (h^2/12)g_n = F_n$$

$$(5\text{-}11) \qquad (2+10T_{\lambda,n})(1-T_{\lambda,n})^{-1} = U_{\lambda,n}$$

$$(5\text{-}12) \qquad (.5-T_{\lambda,n})(1-T_{\lambda,n})^{-1} = A_{\lambda,n}$$

The equations (5-7) and (5-8) become:

$$(5\text{-}13) \qquad F_{n+1} - U_{\lambda,n}F_n + F_{n+1} = (h^2/12)g_n[10 + U_{\lambda,n}]$$

$$(5\text{-}14) \qquad A_{\lambda,n+1}F_{n+1} - A_{\lambda,n-1}F_{n-1} = h\Psi'_n +$$
$$(h^2/24)[g_{n+1}(1-T_{\lambda,n+1})^{-1} - g_{n-1}(1-T_{\lambda,n-1})^{-1}]$$

The boundary conditions expressed in terms of the F_n are some more complicated and care must be taken as we shall see later.

The usual numerical procedure for solving either (5-7) or (5-13) is to provide a first estimate of λ and integrate forward from x=a to some point x_m using the appropriate initial value Ψ_0 or F_0. Let us consider the case of the homogeneous equation (g(x) = 0). In such a case, the algorithms take the simple forms:

$$(5\text{-}15) \qquad \Psi_{n+1}(1-T_{\lambda,n+1}) - \Psi_n(2+10T_{\lambda,n}) + \Psi_{n-1}(1-T_{\lambda,n-1}) = 0$$

(5-16) $\Psi_{n+1}(.5-T_{\lambda,n+1}) - \Psi_{n-1}(.5-T_{\lambda,n+1}) = h\Psi'_n$

(5-17) $F_{n+1} - U_{\lambda,n}F_n + F_{n-1} = \emptyset$

(5-18) $A_{n+1}F_{n+1} - A_{n-1}F_{n-1} = h\Psi'_n$

Since (5-1) is homogeneous in $\Psi(x)$ the resulting Ψ_n values may be replaced by $\Psi_n^{(f)} = \Psi_n/\Psi_m$, n=1,...,m. The same procedure is used to integrate backwards from x_{N+1} to x_m and yields values $\Psi_n^{(b)}$, n=N+1,...,m such that $\Psi_m^{(b)}=\Psi_m^{(f)}=1$. Then a correction to λ is determined by the difference between the slopes of the two curves at the matching point x_m and the process is repeated until the two curves meet with the same derivative. The correction $D(\lambda)$ is usually calculated[36] by using:

$$(5\text{-}19) \qquad D(\lambda) = (\Psi'_{(f)}-\Psi'_{(b)}) \Big/ \int_a^b [\Psi(x)]^2 dx$$

where $\Psi'_{(f)}$ and $\Psi'_{(b)}$ are the derivatives at x_m of the curves resulting from the forward and backward integrations.
It can be shown[51] that the eigenvalues of the difference equations (5-15) or (5-17) are the zeroes of some appropriate functions $\Gamma(\lambda)$ of the trial eigenvalue λ. These zeroes can be calculated by the Newton-Raphson method (see appendix 3). The first-order correction is:

(5-20) $D(\lambda) = - \Gamma(\lambda)/\Gamma'(\lambda)$

and for λ near the real eigenvalue $\lambda_\emptyset$ by the second order correction:

$$D(\lambda) = \Delta\lambda + (\Delta\lambda)^2 Q \tag{5-21}$$

where:

$$\Delta\lambda = \lambda - \lambda_\emptyset$$

and:

$$Q = \Gamma''(\lambda_\emptyset)/2\Gamma'(\lambda_\emptyset)$$

The determination of the explicit form of the function $\Gamma(\lambda)$ can be avoided in using one of the two methods discussed in the two next sections.

3. THE LOG-DERIVATIVE METHOD.

This method and the following one have been developped by B.R.Johnson[13-15], they both share the following desirable properties: they are simple and easy to implement, the step size can be easily changed and no linear dependence or overflow difficulties arise when propagating the solution through classically forbiden regions. Unfortunately, these methods are applicable only in equations where the first derivative term is absent and where $g(x)=0$. Furthermore, the only boundary conditions used up to now are $\Psi(x)=0$ at both bounds.

The log-derivative of $\Psi(x)$ is defined to be:

$$\delta(x) = \Psi'(x)/\Psi(x) \qquad (5\text{-}22)$$

Differentiating equation (5-22) and using Eq.(5-1), we obtain the Ricatti equation:

$$\delta'(x) + q_\lambda(x) + \delta^2(x) = 0 \qquad (5\text{-}23)$$

This equation cannot be integrated by the usual numerical techniques because $\delta(x)$ diverges for certain values of x. The log-derivative algorithm has no difficulty propagating the solution across the whole interval.

The algorithm is as follows:

(5-24) $$\delta_n = (1+h\delta_{n-1})^{-1}\delta_{n-1} - h^{-1}U_n$$

where:

(5-25) $$U_n = \begin{cases} (h^2/3)q_{\lambda,n} & n=0,N \\ 2(h^2/3)q_{\lambda,n} & n=2,4,\ldots,N-2 \\ 8+8(1-(h^2/6)q_{\lambda,n})^{-1} & n=1,3,\ldots,N-1 \end{cases}$$

(5-24) is a two term recurrence relation that can be iterativly solved forward once δ_0 is specified:

(5-26) $$\delta_0 = \delta(x_0) - U_0/h$$

In actual practice it is somewhat more convenient and efficient to solve for the quantity:

(5-27) $$z_n = 1 + h\delta_n$$

It is easy to show:

(5-28) $$z_n = (2 - U_n) - z_{n-1}^{-1}$$

The initial term is calculated from the relation:

(5-29) $$z_0 = (1 - U_0) + h\delta(x_0)$$

Clearly once the initial value $\delta(x_{\emptyset})$ is known to be infinity, $z_{\emptyset}$ is also infinity provided that $q_{\lambda,\emptyset}<$infinity.

The backward integration recursion formula can be obtained by changing the sign of h and also changing n-1 by n+1 in (5-28) and the initial term for this integration is:

(5-30) $$z_N = (1 - U_N) - h\delta(x_N)$$

The result of doing the forward and the backward integrations is a right value $z_r(x_m)$ and a left value $z_l(x_m)$ at the matching point x_m from which we calculate the difference function $D(\lambda)$:

(5-31) $$D(\lambda) = z_r(x_m) - z_l(x_m)$$

Clearly this function is zero if λ is an eigenvalue.

4. THE RENORMALIZED NUMEROV METHOD.

a) Description of the method.

Let us start from the algorithm (5-17) which is a three term recursion relation. Let us divide the two members of this relation by F_n and define:

(5-32) $\quad R_n = F_{n+1}/F_n$

(5-33) $\quad S_n = F_{n-1}/F_n$

Substitute this into (5-17) to obtain the two term recurrence relations:

(5-34) $\quad R_n = U_n - 1/R_{n-1}$

(5-35) $\quad S_n = U_n - 1/S_{n+1}$

These equations can be iterated once the initial values R_1 and S_{N+1} are specified[14,15]. The value corresponding to the conditions $\Psi(x)=0$ at the two bounds are obviously $R_1=S_{N+1}=$infinity; this constitutes the usual boundary conditions. The discussion of other boundary conditions is reported in a later section. If the iteration is stopped at any point x_n, the quantities R_n, R_{n-1} are immediately available with no additional calculations in the forward iteration while the quantities S_n and S_{n+1} are available in

the backward iteration. From these quantities, we can calculate the solution at the points x_n, x_{n+1} and x_{n-1} to within a normalization factor:

$$(5\text{-}36) \qquad \Psi_{n+1} = F_n[1-T_{\lambda,n+1}^{-1}]R_n = F_n[1-T_{\lambda,n-1}]^{-1}S_{n+1}^{-1}$$

$$(5\text{-}37) \qquad \Psi_n = F_n[1-T_n]^{-1}$$

$$(5\text{-}38) \qquad \Psi_{n-1} = F_n[1-T_{\lambda,n-1}]^{-1}R_{n-1}^{-1} = F_n[1-T_{\lambda,n-1}]^{-1}S_n$$

In this sense, we are calculating a renormalized solution at each step.

As in the log-derivative method forwards and backwards iterations are performed which determine at some matching point x_m the values of R_m and S_m defining the correction function $D(\lambda)$.

In practice, we perform the backward iteration using (5-35), S_{N+1} being infinity. As this iteration proceeds the value of S_n is monitored and when the condition $S_n<1$ first occurs, the iteration is stopped and this point is by definition the matching point x_m. This is approximatively the position where the first derivative of the solution is zero. The forward iteration is then carried out. During the calculations, the nodes are counted (a node is located between x_n and x_{n+1} when $R_n<0$). The function $D(E)$ is computed from[14]:

$$(5\text{-}39) \qquad D(E) = [A_{m+1}(S_{m+1}^{-1}-R_m) - A_{m-1}(S_m-R_{m-1}^{-1})](1-T_{\lambda,m})$$

Two alternate definitions of D(E) can be used noting that the equality $R_m=S_{m+1}^{-1}$ is true only if λ is an eigenvalue. It follows that the following functions are zero at the eigenvalues:

$$(5\text{-}40) \qquad D_1(\lambda) = S_{m+1}^{-1} - R_m$$

$$(5\text{-}41) \qquad D_2(\lambda) = S_m - R_{m-1}^{-1}$$

These two functions are very similar in shape to (5-39) and it is easy to see that they differ only by a term of order h^2.

Once the eigenvalue has been calculated, the relations (5-34) and (5-35) are solved for this value giving the values of $R_2, R_3,\ldots,R_m, S_N,\ldots,S_m$. Since the normalization is arbitrary, we let $F_m=1$ and we are able to compute the values of F_n using (5-32) and (5-33) respectively for $n<m$ and $n>m$. Finally, using (5-10) we can compute the values of Ψ_n.

We mention also an interesting interpolation formula which can be used in order to calculate the value of the solution at points other than the grid points.
Suppose we want to compute the solution at x_α between x_i and x_{i-1}:

$$(5\text{-}42) \qquad x_i = x_\alpha + (1-\alpha h) \quad ; \quad x_{i-1} = x_\alpha - \alpha h \quad (0<\alpha<1)$$

For convenience we define $\beta=(1-\alpha)$. Using the same procedure as in the section 1 and in putting $\gamma_n=(h^2/6)q_{\lambda,n}$, we find:

$$(5\text{-}43) \qquad \Psi_{\alpha} = [(\alpha\beta)^{-1}+\gamma_{\alpha}]^{-1}[(\beta^{-1}-\gamma_i)\Psi_i + (\alpha^{-1}-\gamma_{i-1})\Psi_{i-1}]$$

The truncation error for this formula is of order h^4 which is the same as the cumulative error at a fixed value of x of the Numerov algorithm.

Remark

A variable mesh-point may be used between points where the integration is particularly difficult (at singular points for example). If we divide the interval h into (p+1) subintervals of length h/p between x_i and x_{i+1} and if R^*_{ip} are the iterated values of the function R on this interval, then it can be shown that the value R_{i+1} to be used in the further iteration is equal to $R^*_{i1}.R^*_{i2}.\ldots.R^*_{i,p+i}$.

b.Application to the Morse potential and the unsymmetrical double minimum potentials.

The functional form of both potentials are given by[14,51]:

$$(5\text{-}44) \qquad V(x) = D[1-\exp[-B(x-x_a)]]^2 + A\exp[-C(x-x_b)^2]$$

where the parameter A is zero for the Morse potential. The parameters (taken from table 1 in ref (51)) are as follows:

$D = 31250cm^{-1}$

$B = .29659463\mathring{A}^{-1}$

$C = 200\mathring{A}^{-2}$

$A = 10000cm^{-1}$

$x_a = 1.5\mathring{A}$

$x_b = 1.6\mathring{A}$

The analytic eigenvalues for the Morse potential are calculated from(52):

(5-45) $$E_n = 1000(n+1/2)-8(n+1/2)^2$$

Comparison between the analytic results and the numerical results obtained with 261 integration points are given in table (5-1). The interval is [1,2.5] and the required accuracy imposed on the zeroes of $D(\lambda)$ is only .1. The results were improved with 521 gridpoints and convergence occurs.

Results for the unsymmetric double minimum potential are given in table (5-2) and compared with those obtained in reference (51). The difference is small but significant and is probably due to differences in the calculated values of the Morse parameter B.

Table 5-1:Morse potential (261 points)

n	E_n^{anal}	E_n^{calc}
0	498	498.00897
1	1482	1482.00124
2	2450	2449.99610
3	3402	3401.98730
4	4338	4337.98265
5	5258	5257.97677
6	6162	6161.96413
7	7050	7049.89749
8	7922	7922.06288
9	8778	8777.90463
10	9618	9617.89714
11	10442	10441.83904
12	11250	11249.80544

Table 5-2: Unsymmetric double minimum potential (261 points)

n	E_n(1)	E_n^{calc}
0	1302.507	1302.504
1	3205.317	3205.309
2	4227.327	4227.342
3	5144.264	5144.326
4	6064.227	6064.317
5	7092.694	7092.984
6	7614.609	7614.828
7	8911.545	8911.853
8	9095.700	9095.972

(1):result from reference (51)

4. THE RENORMALIZED NUMEROV METHOD WITH $\Psi'(x)=0$ AT THE BOUNDS.

The purpose of this section is to discuss the method of the previous section with boundary conditions different of the ususal case $\Psi(x)=0$ at the bounds. We saw in section 3 that when the eigenfunction is zero at the bounds and non zero in the vicinity of the bounds the iterations may be performed from $R_1=S_{N+1}=$infinity. We propose here to determine the values of R_1 and S_{N+1} for the first derivative of the eigenfunction equal to zero at one or both bounds[16].

a) Determination of R_1 and S_{N+1}:

From (5-18), using (5-36), (5-37) and (5-38) we obtain the following expressions for $\Psi'(x)$:

$$\Psi'_n = (F_n/h)[A_{n+1}R_n - A_{n-1}R_{n-1}^{-1}] \qquad (5\text{-}46)$$
$$= (F_n/h)[A_{n+1}S_{n+1}^{-1} - A_{n-1}S_n]$$

If x_E is a grid point where $\Psi'(x_E)=0$ then the following equality holds:

$$R_E R_{E-1} = [S_E S_{E+1}]^{-1} = A_{E-1}/A_{E+1} \qquad (5\text{-}47)$$

In particular at the bound x=a:

(5-48) $$R_1 = A_\emptyset[R_\emptyset A_2]^{-1}$$

and at the bound x=b:

(5-49) $$S_{N+1} = A_{N+2}[S_{N+2}A_N]^{-1}$$

This introduces the external points $x_\emptyset$ and x_{N+2} therefore $A_\emptyset$, A_{N+2}, $R_\emptyset$ and S_{N+2} must be evaluated to apply the equalities. Using (5-34) and (5-35) respectively for R_1 and S_{N+1}, we obtain:

(5-50) $$R_1 = A_\emptyset U_1/(A_\emptyset+A_2)$$

(5-51) $$S_{N+1} = A_{N+2}U_{N+1}/(A_N+A_{N+2})$$

The evaluation of R_1 and/or S_{N+1} needs an estimate of the value of A_n at external points $x_\emptyset$ and/or x_{N+2}. Since the first derivative of the eigenfunction is zero at the bound, this inevitably accompanying the zero of the potential gradient at the bound, we can make the approximation $V_\emptyset=V_1$ (and/or $V_{N+2}=V_{N+1}$). The corresponding initial values of R and/or S are therefore:

(5-52) $$R_1 = A_1U_1/(A_1+A_2)$$

(5-53) $$S_{N+1} = A_{N+1}U_{N+1}/(A_N+A_{N+1})$$

Furthermore since the potential is slowly varying near its extremum and considering the fact that V appears in the

definition of A multiplied by a factor $h^2/12$ we could set $A_1=A_2$ (and/or $A_{N+1}=A_N$) and employ:

(5-54) $R_1 = U_1/2$

(5-55) $S_{N+1} = U_{N+1}/2$

This approximation has already been employed in the literature[14] in connection with the double minimum potential.

The remaining case where minimal information is available regarding $\Psi(x)$ or $\Psi'(x)$ at the bounds will be treated in the next section.

As illustrations of this original procedure we shall work out two standard equations having analytic solutions: the radial harmonic oscillator and the Mathieu equation.

In the first example our attention has been restricted to states having quantum number greater than zero. All such cases have $\Psi(x=0) = 0$ and $\Psi'(x=0) = 0$ and we have compared the results starting the iterations from R_1=infinity and $R_1=U_1/2$. In the second example, exept for s=0, all the levels are doubly degenerate sine and cosine series. Our method is then appropriate since the odd solutions correspond to one boundary condition and even solutions to another.

The degree of accuracy required determines the values of the input parameters, these being the integration bounds, the number of grid points and a tolerance factor regarding the desired accuracy of the results. This one depends upon the

usual sources and types of error. "Truncation error" can be reduced by diminishing the interval between adjacent grid points and, in limiting cases, by using extrapolation techniques.

For the specific case of the unbounded intervals in which $\Psi(x)$ tends to zero as x tends to infinity a point x_f is determined at which the eigenfunction is sufficiently close to zero and x_f is taken as upper bound. The accuracy error is reduced by choosing the eigenvalue tolerance factor sufficiently small to match desired accuracy. Finally "roundoff errors" can be treated as shown in section 3 of the chapter 4.

b) Radial harmonic oscillator.

The system to be considered is that of reduced mass m in a potential of the form[53]:

$$V(r) = (1/2)mw^2r^2 \qquad (5\text{-}56)$$

With a well-defined value of the angular momentum L, the radial Schroedinger equation is given by:

$$[-(\hbar^2/2m)d^2/dr^2 + mw^2r^2/2 + \hbar^2L(L+1)/2mr^2 - E_{nL}]R_{nL}(r) = 0 \qquad (5\text{-}57)$$

The eigenvalues of the equation are:

(5-58) $$E_{nL} = \hbar w(2n + L + 3/2)$$

By introducing the dimensionless variable $\gamma=r/a$, where $a = \hbar/mw$, the corresponding eigenfunctions are given by:

(5-59) $$R_{nL}(\gamma) = N_{nL}\exp(-\gamma^2/2)\gamma^{L+1}F(-n,L+3/2;\gamma)$$

where the $F(-n,L+3/2;\gamma)$ are the confluent hypergeometric functions and N_{nL} is a normalization factor. Defining the principal quantum number $\Lambda=2n+L$, each value of Λ greater than one can be realized by several combinations of n and L, the energy levels being degenerate. In what follows, the customary notation in terms of s,p,d,f,... states corresponding to L=0,1,2,3,... will be employed (e.g.,the state 1-p corresponds to $\Lambda=1$; n=0, L=1). With that notation and with relations (5-58) and (5-59) the values of the analytic eigenvalues and eigenfunctions may be determined.

The numerical solution of equation (5-57) proceeds as follows. This equation is expressible as:

(5-60) $$(d^2/d\gamma^2)R_\Lambda(\gamma) = [\gamma^2 + L(L+1)/\gamma^2 - 2E_{nL}]R_\Lambda(\gamma)$$

the interval of integration being from 0 to infinity. We have to evaluate for which finite value of γ (γ_f), the eigenfunction is sufficiently close to zero (the analytic

value at the upper bound). For fixed h, this is done by selecting successive values for $\aleph$ until the calculated eigenvalue remains constant (e.g., for the 5-s state, $\aleph_f$=7 is sufficient). Since an error of 4×10^{-6} remains constant for $\aleph_f$>7, we conclude that the remaining error is due to truncation and the accuracy depends only on the number of points of integration and the tolerance set for the eigenvalue calculation. For our purposes h was set at .03, the tolerance factor being 10^{-5}(the number of grid points being a function of $\aleph_f$). A second interval h=.015 was employed to verify the convergence rate of the solutions. The type of boundary conditions must also be specified. From its definition, the solutions are zero at x=0 and at infinity. Refering to equation (5-59), we observe that the first derivative of the eigenfunction is zero at x=0 for L>0 whereas it is non zero for L=0. For L>0, therefore, the initial value of R could be chosen either as infinity (since the solution is zero at r=0) or as $U_1/2$ (since the first derivative is zero at r=0). In the case of L=0, the initial value of R must be infinity. In both cases, the initial value of S is infinity or $U_{N+1}/2$ since the eigenfunction and its first derivative are zero at infinity. Tables (5-3) and (5-4) illustrate respectivelly the results obtained for L=0 and L=1. In both cases the analytic eigenvalue calculated from (5-58) is expressed in terms of hw. All the results are computed in taking $\aleph_f$ =7 exept in table (5-4) where (*) indicates $\aleph_f$=9.

TABLE 5-3: Eigenvalues: Radial harmonic oscillator (L=0)

n	E^{anal}	E^{num}	
		235 points	471 points
0	1.5	1.50000	1.50000
1	3.5	3.50000	3.50000
2	5.5	5.49999	5.50000
3	7.5	7.49999	7.50000
4	9.5	9.49999	9.50000
5	11.5	11.49999	11.50000
6	13.5	13.49998	13.50000
7	15.5	15.49997	15.50000

TABLE 5-4: Eigenvalues: Radial harmonic oscillator (L=1)

n	E^{anal}	E^{num}			
		235 points A	235 points B	471 points A	471 points B
0	2.5	2.49999	2.50000	2.50000	2.50000
1	4.5	4.49999	4.50000	4.50000	4.50000
2	6.5	6.49998	6.50000	6.50000	6.50000
3	8.5	8.49998	8.50000	8.50000	8.50000
4	10.5	10.49997	10.49999	10.49999	10.50000
5	12.5	12.49996	12.49999	12.49999	12.50000
6	14.5	14.49997	14.50002	14.50002	14.50002
7	16.5	16.60085	16.50041	16.50041	16.50041
7(*)	16.5	16.49993	16.49997	16.49997	16.50000

FIGURE (5-1):EIGENFUNCTIONS OF THE RADIAL HARMONIC OSCILLATOR, L=0

(a): n=0

(b): n=1

(c): n=2

(d): n=3

FIG. 5·1. Radial harmonic oscillator. L = 0

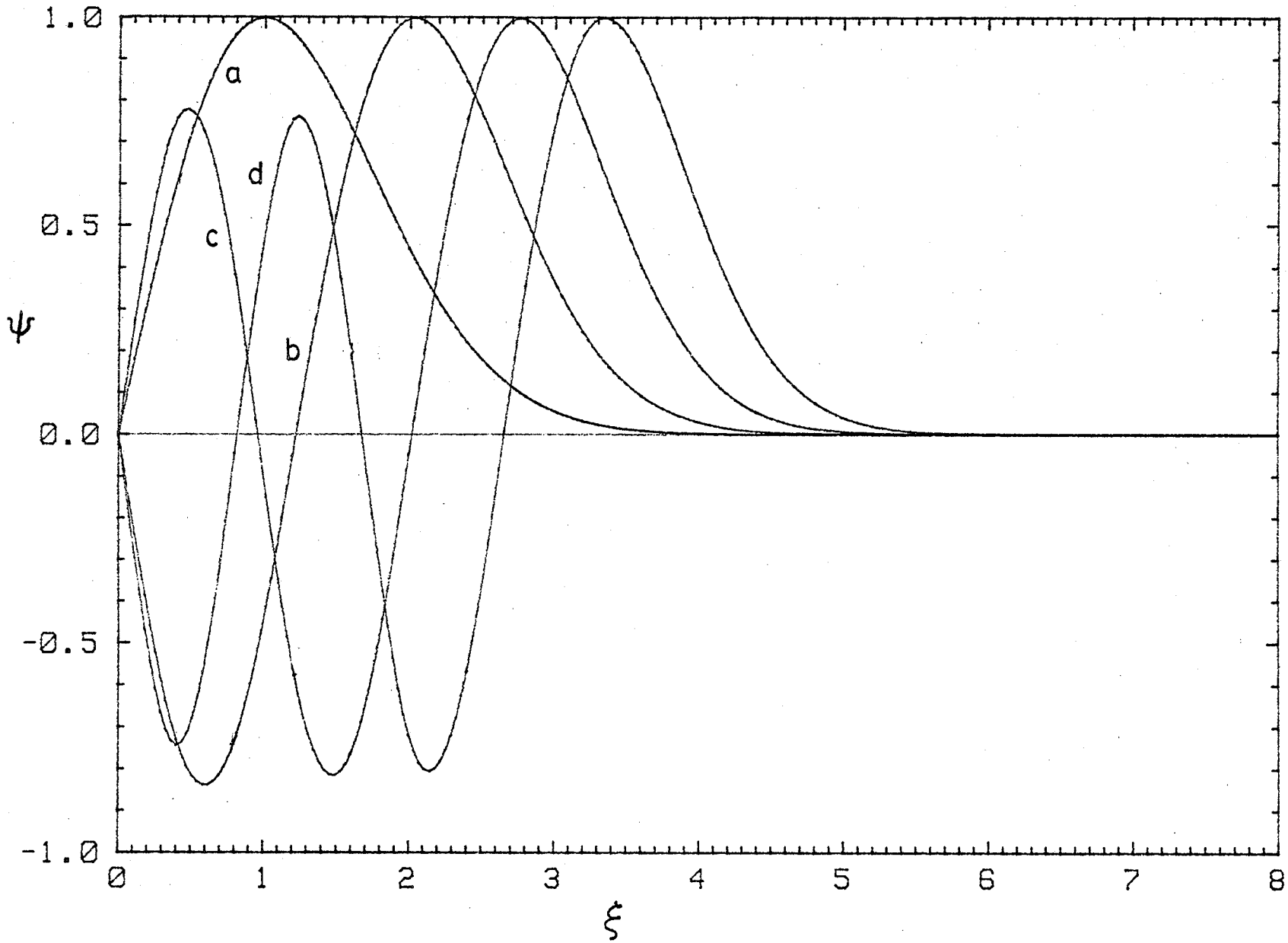


FIGURE (5-2): EIGENFUNCTIONS OF THE RADIAL HARMONIC OSCILLATOR, L=2

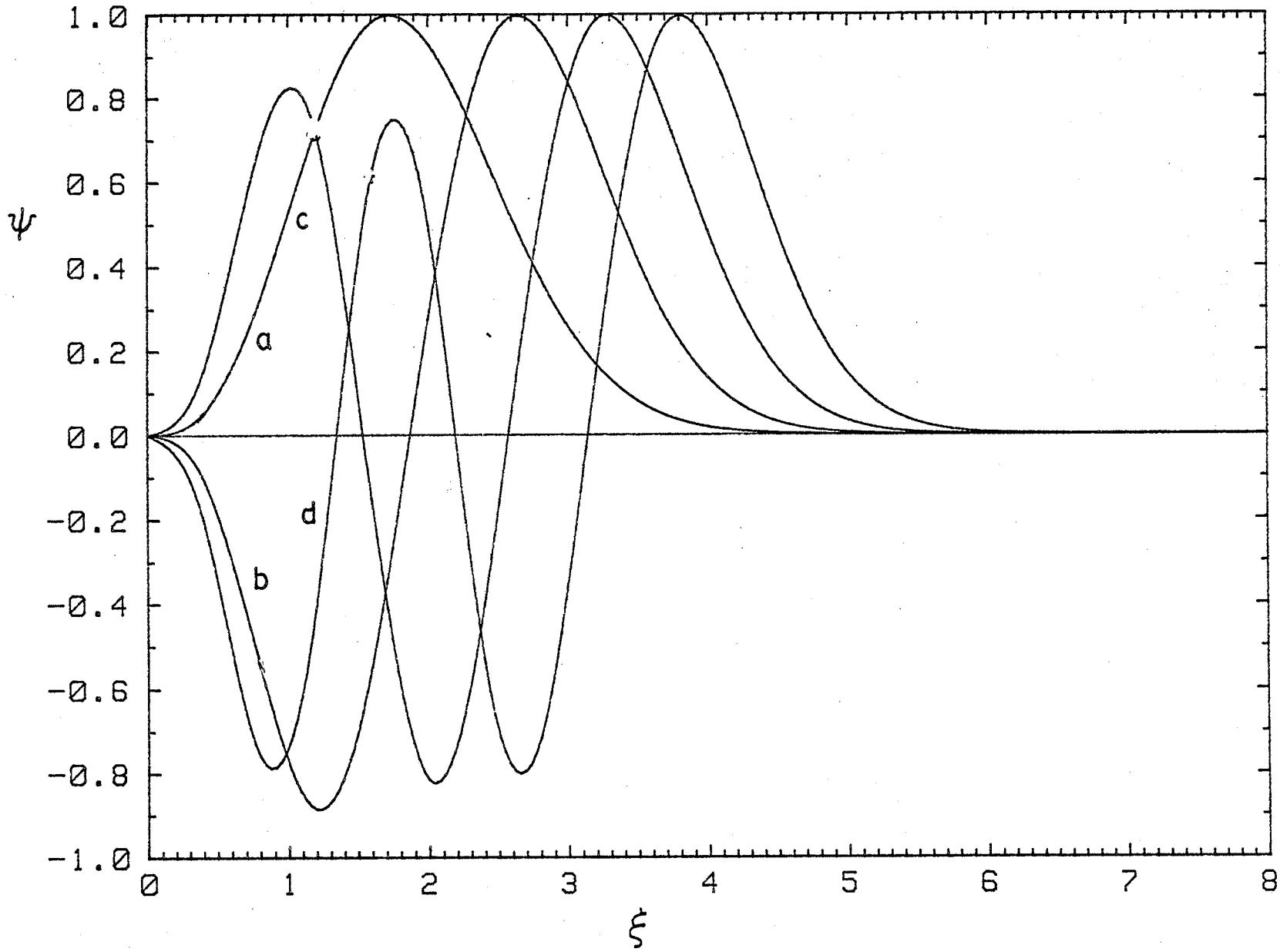
(a): n=0

(b): n=1

(c): n=2

(d): n=3

Radial Harmonic Oscillator (L=2) FIG. 5.2.



From these results we conclude that the calculation of the eigenvalues can be carried out with equivalent accuracy (to the fifth decimal place) using either set of initial conditions for L=1. Similar accuracy was obtained for L=2 and L=3.

Comparison of the computed numerical eigenfunctions with their analytic counterparts showed very close agreement over the entire range of integration (figures 5-2).

c) Torsional vibration.

Here we concern ourselves with the Mathieu equation. The Hamiltonian is given by(54):

(5-61) $$H_T = F^2_p + (V_3/2)(1-\cos 3\alpha)$$

The Schroedinger equation may be written in the form:

(5-62) $$\Psi''(\alpha) + (a - 2s\cos 2\alpha) = 0$$

Solutions are periodic (period π or 2π) and it can be shown than there exists a set of eigenvalues $a_n(s)$ corresponding to even solutions and a set $b_n(s)$ corresponding to odd solutions. The eigenfunctions are expressed as series:

(a) $$ce_n(\alpha,s) = \Sigma_m A^n_{2m+p} \cos(2m+p)\alpha$$

(5-63) (b) $se_n(\alpha,s) = \Sigma_m B^n_{2m+p} \sin(2m+p)\alpha$

(c) $B^n_{\emptyset} = \emptyset$

where p=Ø indicates a period of π and p=1 a period of 2π. m varies from Ø to infinity, (a) indicates the even solutions and (b) the odd.

There exists a three-term recurrence relation among the coefficients A and B. Since the concept of three term recursion is closely related to the concept of continuous fractions[55,56], the recursion relation may be interpreted as the fundamental recurrence formula for some continuous fraction, the roots of which are the eigenvalues a_n associated with the even periodic solutions and b_n with the odd periodic solutions. Usually the eigenvalues and the eigenfunctions are evaluated from power series[47] or may be found in textbooks of mathematical special functions.

In the numerical solution, we write the Mathieu equation as:

(5-64) $(d^2/d\alpha^2)U_{ns}(\alpha) = [2s\cos\alpha - (a/b)_n(s)]U_{ns}(\alpha)$

where $(a/b)_n$ denote eigenvalues corresponding to the parameter s and the quantum number n, the $U_{ns}(\alpha)$ being the eigenfunctions corresponding to $a_n(s)$ or $b_n(s)$. If s=Ø, the eigenfunctions are not degenerate. Otherwise, they are doubly degenerate, one even and one odd (figures 5-3). In terms of

FIGURE (5-3): THE MATHIEU FUNCTIONS

(a): odd periodic solutions (s=1)

(b): odd periodic solutions (s=10)

(c): even periodic solutions (s=1)

(d): even periodic solutions (s=10)

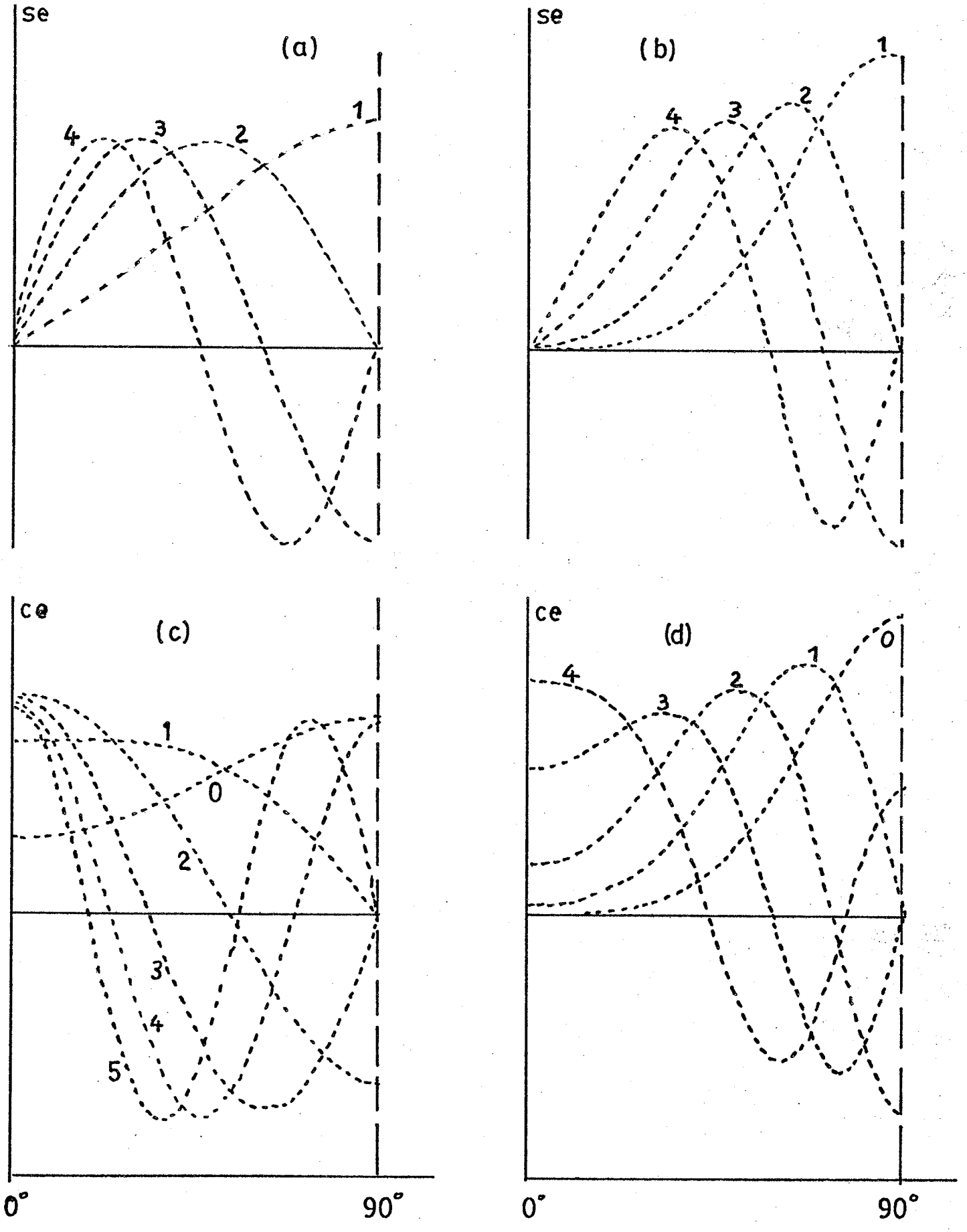
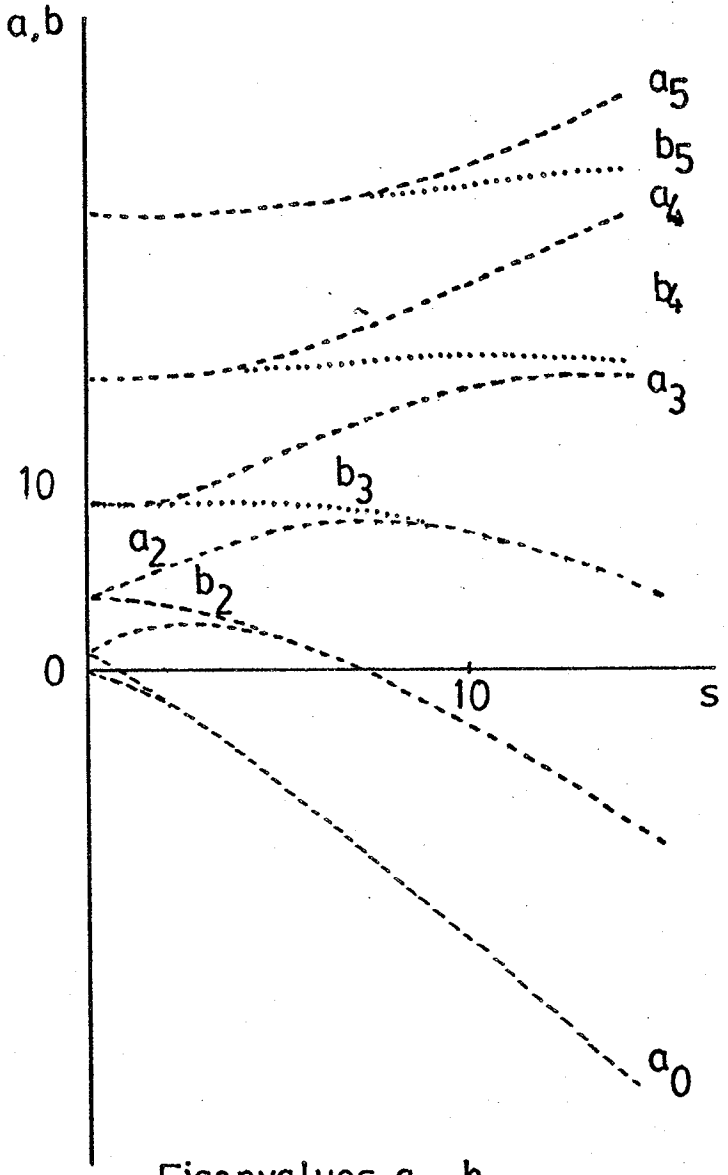


FIG. 5·3. Mathieu functions.

FIGURE (5-4): THE MATHIEU FUNCTIONS

Eigenvalues for different values of the parameter s.

FIG. 5·4. Mathieu functions.



Eigenvalues a_n, b_n.

standard notations, we shall designate by "a" the eigenvalues of the even solutions $ce_n(s)$ and by "b" the eigenvalues of the odd solutions $se_n(s)$.

Since the interval of integration is either $[0,\pi]$ or $[0,2\pi]$, problems involving "termination" errors do not exist here. The odd solutions were computed using infinity as initial values of R and S since all of those solutions are zero at the two bounds. As the even solutions have their first derivative equal to zero at both bounds, the initial values of R and S are respectivelly $U_1/2$ and $U_{N+1}/2$. In both cases computations were carried out with 101 and 201 grid points and a tolerance factor of 10^{-6}. The values of a_n and b_n were computed for s=0,1,10,20,30 and 50 and compared with those evaluated from the series expansions[47]. Tables (5-5) and (5-6) respectively compare analytic and numerically obtained eigenvalues corresponding to the even and odd solutions. In both cases the interval is $[0,\pi]$; (1) is the analytic result obtained from reference (47), (2) are the numerical results computed with 101 grid points and (3) with 201 grid points. For low values of the parameter s agreement is to the sixth decimal place, the error increasing for higher values of s and n. Such error was observed to diminish rapidly either by employing more integration points or by using the Richardson extrapolation (appendix 3).

As an illustration figures (5-4) show how the eigenvalues vary with the parameter s for the odd and even solutions. The concordance with the functions of reference (47) is exact up

TABLE 5-5: Eigenvalues:Mathieu equation(even solutions)

	n	0	1	2	5
	s				
(1)	0	.000000	1.000000	4.000000	25.000000
(2)	0	.000000	1.000000	4.000000	24.999937
(3)	0	.000000	1.000000	4.000000	25.000000
(1)	10	-5.800046	1.858187	7.449109	25.549972
(2)	10	-5.800047	1.858183	7.449083	25.549855
(3)	10	-5.800046	1.858186	7.449108	25.549963
(1)	20	-13.936979	-2.399142	7.717369	27.703769
(2)	20	-13.936982	-2.399152	7.717342	27.703565
(3)	20	-13.936980	-2.399143	7.717368	27.703750
(1)	30	-22.513038	-8.101105	5.077983	31.957821
(2)	30	-22.513041	-8.101124	5.077292	31.957538
(3)	30	-22.513038	-8.101106	5.077983	31.957793
(1)	50	-40.256779	-21.314899	-3.522165	40.050191
(2)	50	-40.256786	-21.314943	-3.522298	40.049590
(3)	50	-40.256780	-21.314902	-3.522173	40.050149

TABLE 5-6: Eigenvalues:Mathieu equation(odd solutions)

	n	1	2	5
	s			
(1)	0	1.000000	4.000000	25.000000
(2)	0	1.000000	4.000000	25.000000
(3)	0	1.000000	4.000000	25.000000
(1)	10	-5.790080	2.099460	25.510816
(2)	10	-5.790081	2.099458	25.510740
(3)	10	-5.790081	2.099460	25.510811
(1)	20	-13.936552	-2.382158	26.766426
(2)	20	-13.936554	-2.382168	26.766311
(3)	20	-13.936553	-2.383159	26.766419
(1)	30	-22.518004	-8.099347	27.967881
(2)	30	-22.513007	-8.099365	27.967688
(3)	30	-22.513004	-8.099348	27.967869
(1)	50	-40.256779	-21.314861	28.062766
(2)	50	-40.256786	-21.314904	28.062283
(3)	50	-40.256779	-21.314863	28.062736

to the 6th decimal place. In all examples considered to this points, prior knowledge of the boundary conditions relating to $\Psi(x)$ and/or $\Psi'(x)$ at $x=a$ and $x=b$ has been assumed.

We shall treat in the following section a simple way to determine R_1 and S_{N+1} when mimimal information is available concerning the behaviour of the eigenfunction at the bounds.

6. GRAPHICAL DETERMINATION OF THE INITIAL VALUES OF R AND S.

We discuss here the remaining case, that for which minimal information is available regarding $\Psi(x)$ or $\Psi'(x)$ at the bounds. The problem is treated here in a graphical approach using a double iterative process and will be attacked in another way in the next chapter.

Let us evaluate the equations pertinent to behaviour at the lower bound, the corresponding equations describing the upper bound being exact analogues. We can develop the following relation from the equations (5-34) to (5-38):

$$(5\text{-}65) \qquad R_1 = h(\Psi'_1/\Psi_1)[(A_1+A_2)/(1-T_1)] + A_1U_1/(A_1+A_2)$$
$$= h\delta(x_1)\gamma_1 + \beta_1$$

where $\delta(x_1)$ is the value of the log-derivative at the lower bound and γ_1 and β_1 are factors depending upon the potential. The potential at the bound must be finite in this case and, for the sole purpose of initiating the iteration, we shall again assume that the value of the potential at the external point is the same as at the bound. The iteration is started assuming $R_1^{\emptyset}=U_1/2$ (a superscript has been added to denote a new iterative process). The values of R at neighbouring points follow from the usual process will be $R_2^{\emptyset}$, $R_3^{\emptyset}$,.... The following observation can now be made. If $R_1^{\emptyset}$ happens to be the correct value (which we might denote by R_1^{r})

reflecting the choice of the correct boundary condition, then the graph of R versus gridpoint will be monotonic in the vicinity of the bound. Note here that if a node is present close to the bound, R is extremely rapidly decreasing and we must locally divide the interval around the bound (see remark in section 4) in order to have enough significant points to proceed at an extrapolation. If on the other hand, R_1^0 is a poor approximation, then the graph will not be monotonic but will show a "fracture" in the region of the first few points but will be monotonic for subsequent points. Extrapolating the "normal" part of the graph back to the bound will yield a new approximation to R, say R_1^1. This can serve as the starting point for a new calculation, i.e. an "outer" iteration. Our hypothesis is that the successive values R_1^0, R_1^1, R_1^2,... converge to the correct value of R, R_1^r. For the two problems described in the previous section and for the problems discussed in chapter 6, the hypothesis certainly is valid.

In practice the following procedure is employed. Starting with $R_1^0=U_1/2$, three situations arise corresponding to the behaviour of the potential V(x) at the bound.

(a) Infinite potential at the bound.

In this case as T_1 is infinite, the initial value R should be infinity, since an infinite potential at a bound leads to a zero value of the eigenfunction at the bound. This is perhaps the situation the most commonly encountered (harmonic

oscillator, Morse,...).

(b) Finite potential at the bound.

There are two possibilities.

(i) The potential has an extremum.

In this case, $A_1=A_2$, $\Psi'_1=0$ and theerefore $R_1=U_1/2$.

(ii) The first derivative of the potential is nonzero. This is the most general case in which no accurate information is available from the potential function: R_1^r is completely undetermined since the ratio $\delta(x_1)$ is unknown. Correspondingly, starting with $R_1^0=U_1/2$ as arbitrary value we face the three situations:

(a) $R_2^0>R_1^0$: the eigenfunction is either increasing and positive or decreasing and negative at an extremum. The requirements are satisfied only if the eigenfunction is zero at the bound. Iteration is (as seen previously) started from R_1^r=infinity, for example figure 5-5.

(b) $R_2^0<=R_1^0$ and the discrete curve shows a constant decreasing behaviour. Here the choice $R_1^0=U_1/2=R_1^r$ is correct and the eigenfunction is extremal at the bound (for example figure 5-6)

(c) $R_2^0<=R_1^0$ and the discrete curve shows a fracture between the second and the third point. The next approximation is

FIGURE (5-5): THE RADIAL HARMONIC OSCILLATOR (L=0,N=4)

Discrete function R and eigenfunction Ψ versus the first grid points n. $R^{\emptyset}_{1}$ is infinity and the function R is monotonic decreasing.

FIG. 5·5: Radial harmonic oscillator: L=0, n=4.

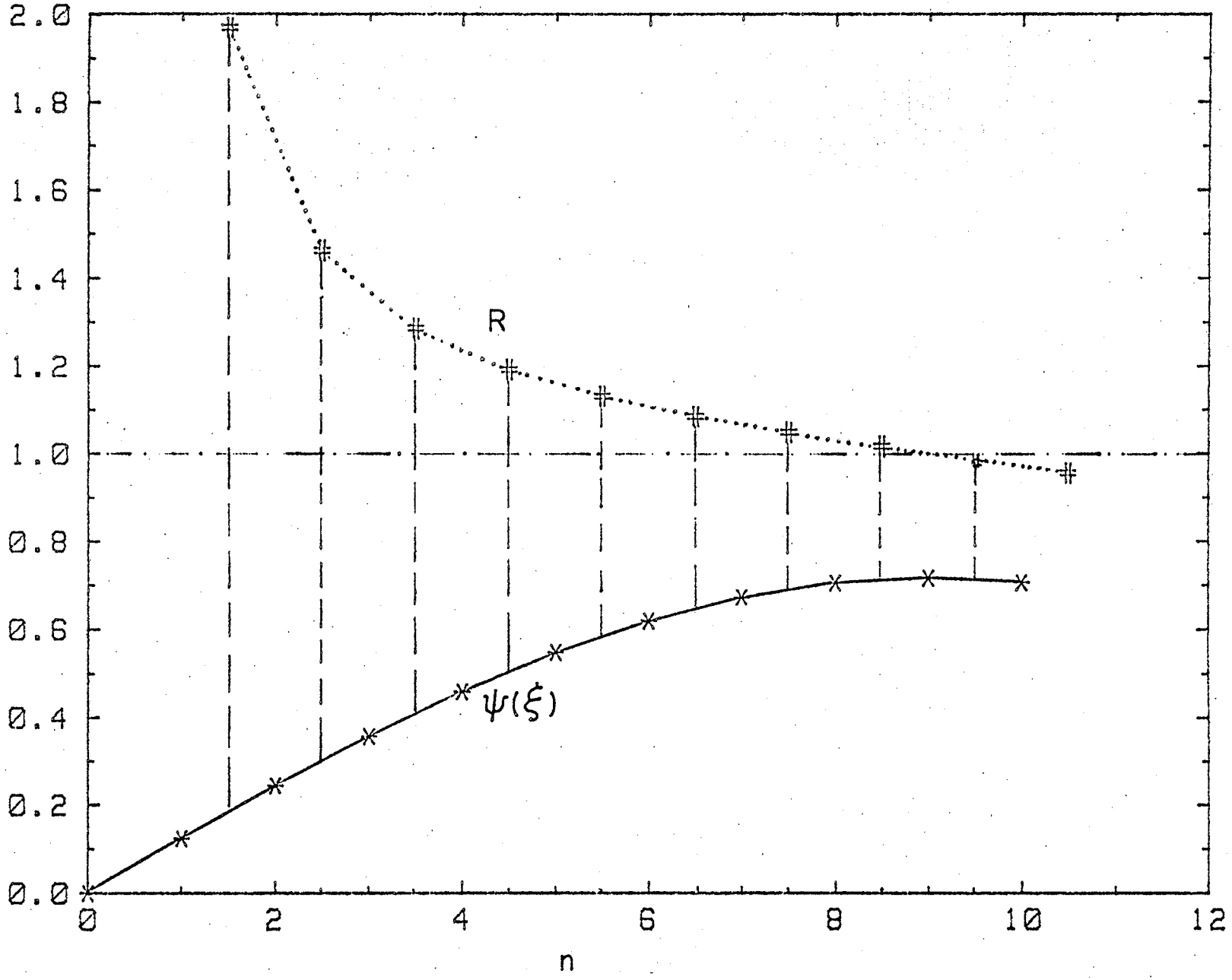


FIGURE (5-6): THE MATHIEU EQUATION ce(0,2)

Discrete function R and eigenfunction Ψ versus the first grid points n. $R^{0}_{1} = U_1/2 = 1$ and the function R is monotonic decreasing showing that R^{0}_{1} is the correct value.

FIG. 5·6: Mathieu equation: ce(0,2)

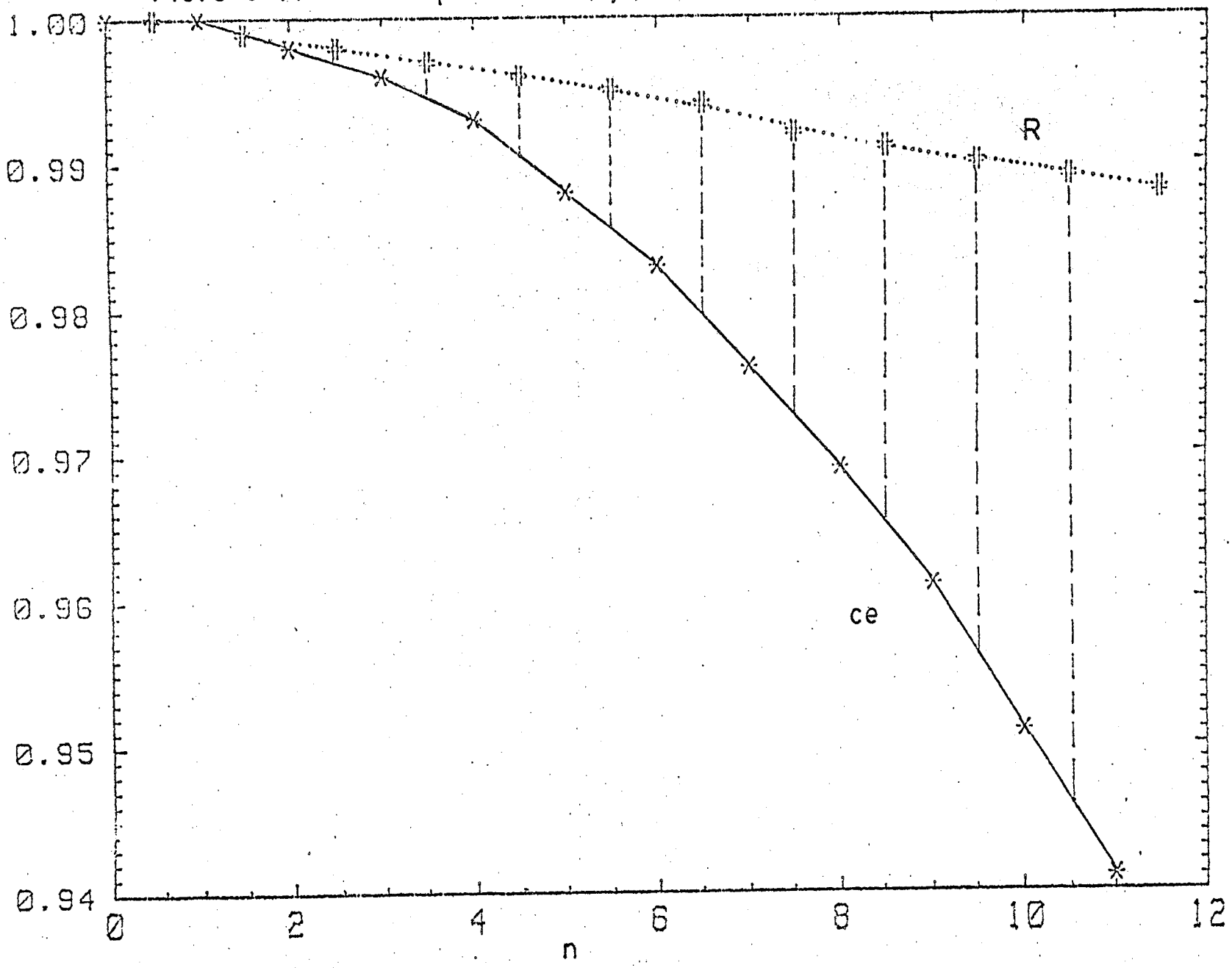


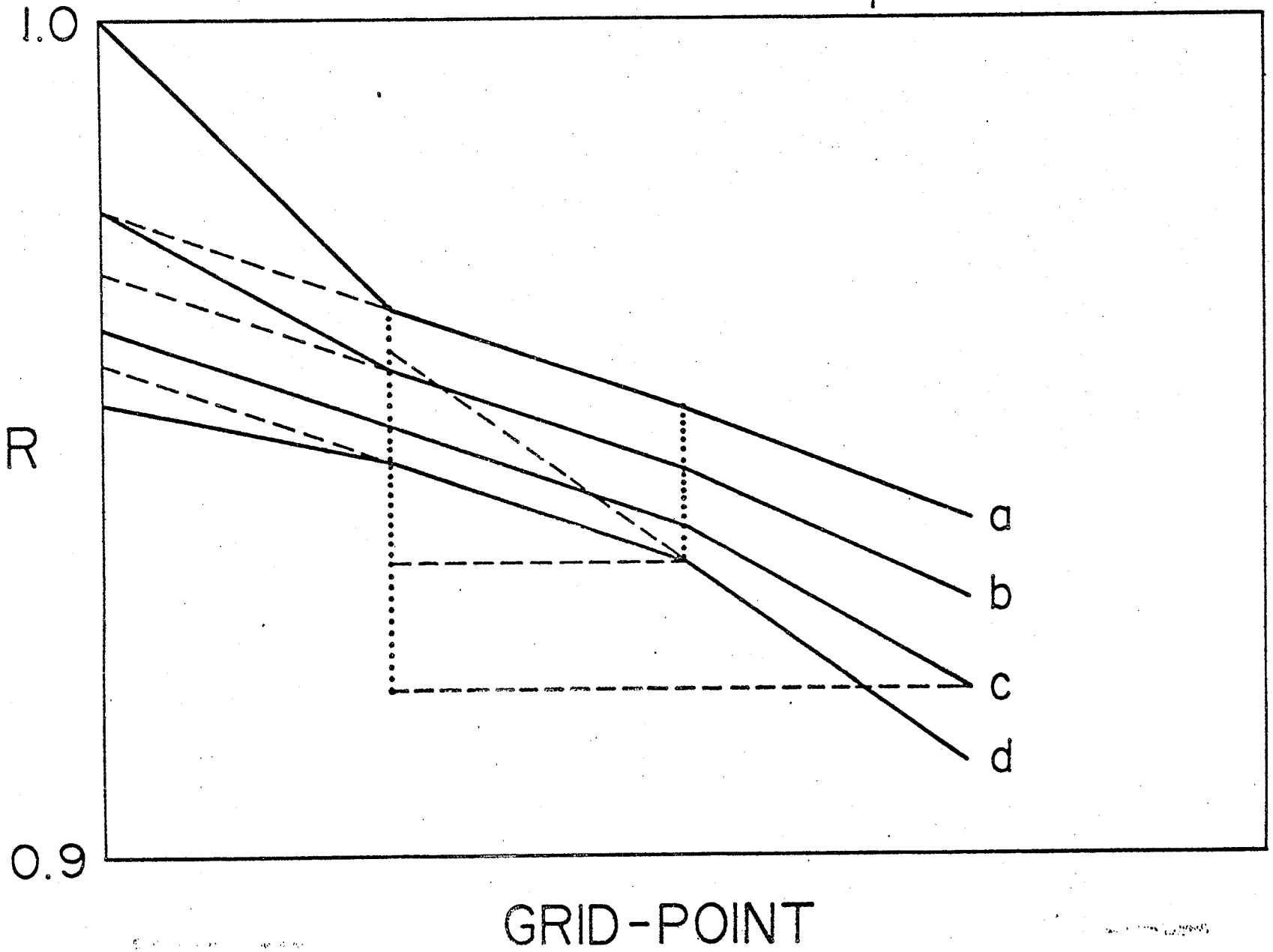
FIGURE (5-7): GRAPHICAL DETERMINATION OF $R^{\emptyset}_{1}$

(a) is the initial value $R^{\emptyset}_{1}$

(b), (c) are intermediate values

(d) is the final value of R^{r}_{n}

FIG. 5-7: EXTRAPOLATION R_1^r



then obtained by the following relation:

(5-66) $$R_1^k = 2R_1^{k-1} - R_1^{k-1} \qquad (k=1,2,....f)$$

The value R_1^k serves to initiate the next iteration and so on. The process is stopped at some value f of k where the absolute value of the difference $R_{1k} - R_1^{k-1}$ is lesser than some accuracy parameter. At that point and in order to ensure a monotonic variation of the discrete curve at the bound, we can use a second extrapolation:

(5-67) $$R_1^r = R_1^k + R_2^k - 2R_3^k + R_4^k$$

where R_1^r is the real value to be used in the iteration. Figure (5-7) illustrates the convergence of the process. The Mathieu equation (s=0, n=2) is illustrated in figure (5-6) where it appears that $U_1/2=R_1^0$ is the correct starting value. The radial harmonic oscillator (L=1, n=2) is illustrated in figures (5-8) and (5-9) with respectivelly R_1^0=infinity and $R_1^0=U_1/2$. We can see, as expected, that the eigenfunction is exactly the same in the two cases.

FIGURE (5-8): MATHIEU EQUATION: EVEN SOLUTIONS

$R^{\emptyset}_{1}$ is the proper value: $U_1/2 = 1$

FIGURE (5-9): RADIAL HARMONIC OSCILLATOR: L=, N=2

The iterations are started from two different initial values (infinity and $U_1/2$). The computed eigenfunctions are indentical since $\Psi(\emptyset)=\Psi'(\emptyset)=\emptyset$.

FIG.5.8

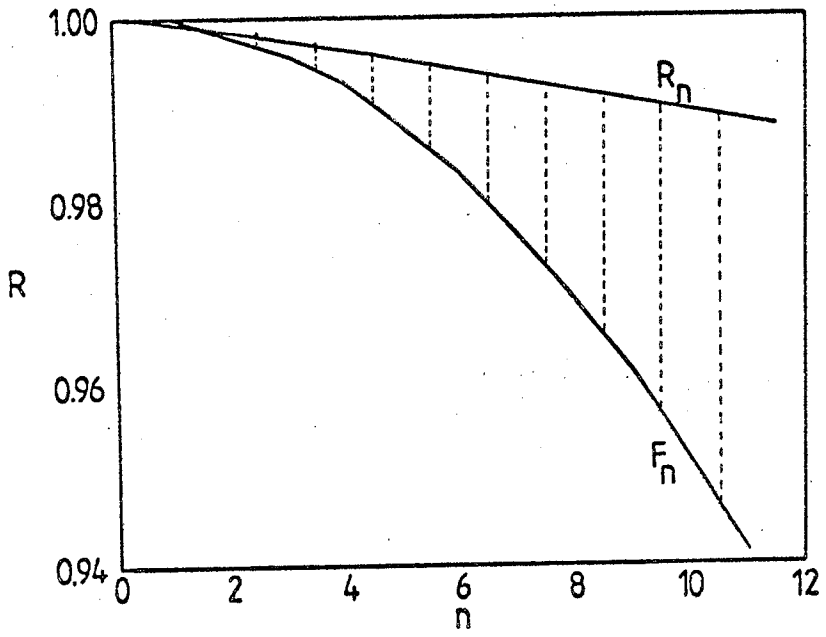
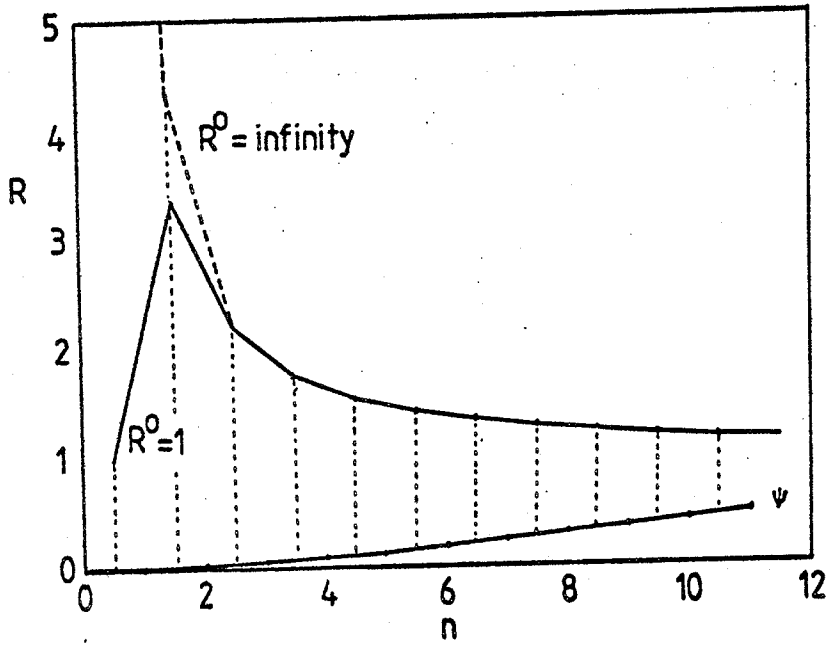

1.00
0.98
0.96
0.94
R
0
2
4
6
8
10
12
n
R_n
F_n

FIG.5.9


5
4
3
2
1
0
R
0
2
4
6
8
10
12
n
R^o = infinity
R^o=1
ψ

CHAPTER 6: SOLUTION OF THE "ANGLE-BENDING" EQUATION.

1.Two-term recurrence relations.

Our aim is to provide a numerical solution for the ordinary second-order differential eigenvalue equation:

$$(6\text{-}1) \qquad \Psi''(x) = p(x)\Psi'(x) + q_{\lambda,s}(x)\Psi(x) = 0 \qquad a<=x<=b$$

with boundary conditions:

$$(6\text{-}2) \qquad \Psi(a) = \alpha \;\; ; \;\; \Psi(b) = \beta$$

where:

$$(6\text{-}3) \qquad q_{\lambda,s} = k(x)[V_s(x) - \lambda]$$

and where α and β are arbitrary (known or not) constants, $p(x)$ and $q_{\lambda,s}$ are continuous on the interval $[a,b]$ except eventually at $x=a$ and/or $x=b$, $V_s(x)$ is analytic or at least may be expressed in the form of some polynomial expansion around the equilibrium configuration.

We want also to preserve the characteristics of the renormalized Numerov method in order to have a general scheme able to be adapted to equations where $p(x)\Psi'(x)=0$ and to

various boundary conditions.

In order to reach our goal we have to solve the four following difficulties:

(i) The explicit presence of the first derivative term does not enable us to apply directly the previous method since the Numerov algorithm applies only to equations where the first derivative term is absent.

(ii) The presence of singularities at x=a and/or x=b leads to the use of some alternate methods around the bounds.

(iii)The constants α and β are not necessarily known explicitly. In certain cases, only minimal informations are available from the potential function and some procedure as the graphical extrapolation or an alternate method must be used.

(iv) The function $q_{\lambda,s}$ is not necessarily positive on all the interval [a,b]. Therefore the operator L of equation (4-21) is not of "monotone" kind[30,31] (see appendix 4 and the discussion of section 3, chapter 4), in particular condition (4-32) is not always fulfilled.

The plan of this chapter is as follows: first, the theoretical development of techniques able to solve the considered problem. Secondly, the application of these techniques to a problem for which analytical solutions exists (Legendre equation). Finally the extention of the methods to a problem for which no analytical solution exists but which

can be solved in another fashion (Legendre equation with a potential) and which is the "angle-bending" equation encountered in the third chapter.

Difficulty (i) will be treated in four ways:

(a) using the algorithm (4-28) for two different values of the interval h and h/2, the cumulative error being of order h^2. The use of the Richardson extrapolation will yield a result in h^4.

(b) using a high-order algorithm with cumulative error of order h^4 .

(c) In removing the term $p(x)\Psi'(x)$ by a change of the dependent variable and applying directly the method of chapter 5. (d) in considering in equation (5-1) the term $g(x)$ as $p(x)\Psi'(x)$ and developing a new algorithm in h^4.

Difficulty (ii) has been treated in the previous chapter by a graphical fashion: we shall present in the following section an alternate way which has the advantage to remove the singularities at the bound and also prevent the operator L to be non monotone at the bounds. Therefore this method solves the difficulties (iii) and (iv).

The general procedure is as follows.
In the problem as stated in (6-1), we replace any derivatives by some finite difference approximations. The linearized difference equations may be written in a very general way in the form:

$$(6\text{-}4) \qquad A\Psi_{n-1} + B\Psi_n + C\Psi_{n+1} = \emptyset \qquad (\emptyset<n<N)$$

$$\Psi(a) = \alpha \quad ; \quad \Psi(b) = \beta$$

where A, B and C are some expressions depending upon the values of $p(x)$ and $q_{\lambda,s}(x)$ at various grid points. This three term recurrence relation may be expressed into a two term relation provided certain convervenge criteria are met[55,56]:

$$(6\text{-}5) \qquad R_n = -(B/C) - (A/C)R_{n-1}^{-1}$$

$$(6\text{-}6) \qquad S_n = -(B/A) - (C/A)S_{n+1}^{-1}$$

where

$$(6\text{-}7) \qquad R_n = \Psi_{n+1}/\Psi_n$$

$$(6\text{-}8) \qquad S_n = \Psi_{n-1}/\Psi_n$$

As usual the iterations may be performed once the initial values R_1 and S_{N+1} are defined.

a) Algorithm in $O(h^2)$: ALG(1).

Using (4-29), (4-30) and (4-31), we have:

$$(6\text{-}9) \qquad A = 1+hp_n/2 \quad ; \quad B = -(2+12T_n) \quad ; \quad C = (1-hp_n/2)$$

and

$$(6\text{-}10)\quad R_n = U_n/(1-hp_n/2) - [(1+hp_n/2)/(1-hp_n/2)]R_{n+1}^{-1}$$

$$(6\text{-}11)\quad S_n = U_n/(1+hp_n/2) - [(1-hp_n/2)/(1+hp_n/2)]S_{n+1}^{-1}$$

R_n and S_n can be iterated once R_1 and S_{n+1} (i.e. the ratios Ψ_2/Ψ_1 and Ψ_N/Ψ_{N+1}) are specified.

In order to obtain an accuracy similar to that of the Numerov algorithm, the computations must be carried out for two values of h (h and h/2) and the results introduced in the Richardson extrapolation formula (4-54) will yield results in $O(h^4)$. Then at each step of the computation R_n and S_n are evaluated for h and h/2 and extrapolated.

This procedure is somewhat lengthy since we use two iterations at every step.

b) <u>An high-order algorithm in $O(h^4)$: ALG(2).</u>

As an example how an high-order difference formula may be used, we choose an algorithm developed by Albassiny and Hoskins[57] from cubic splines. Any other high-order algorithm may be used in the same way.

In this case:

$$(6\text{-}12)\quad A = (1+hp_{n-1}/2-h^2q_{\lambda,n-1}/6)\alpha_{n+1}$$

$$(6\text{-}13)\quad B = (1-hp_{n+1})\alpha_n + (1+hp_{n-1})\alpha_{n+1} + h^3q_{\lambda,n}\gamma_n$$

$$(6\text{-}14)\quad C = (1-hp_{n+1}/2-h^2q_{\lambda,n+1}/6)\alpha_n$$

where

(6-15) $\alpha_n = (1+hp_{n-1}/3)(1-hp_n/3) + h^2p_{n-1}p_n/36$

(6-16) $\gamma_n = 1 - 7h(p_{n+1}-p_{n-1})/24 - h^2p_{n-1}p_{n+1}/12$

The cumulative error is here in $O(h^4)$.

c. A new algorithm in $O(h^4)$: ALG(3).

An alternate algorithm in $O(h^4)$ which can be reducible into the Numerov's algorithm when the first derivative term is absent has been derived in the following way.

We start from the relations (5-7) and (5-8). For convenience we let:

(6-17) $y_n = \Psi_n(1-T_{\lambda,n})$

and

(6-18) $A_n = (.5-T_{\lambda,n})/(1-T_{\lambda,n})$

We may consider the function $p(x)\Psi'(x)$ as the function $g(x)$ in (5-1). We obtain therefore respectively:

(6-19) $y_{n+1} - [(2+10T_{\lambda,n})/(1-T_{\lambda,n}]y_n + y_{n+1} = (h^2/12)[p_{n+1}\Psi'_{n+1} + 10p_n\Psi_n + p_{n-1}\Psi'_{n-1}]$

(6-20) $A_{n+1}y_{n+1} - A_{n-1}y_{n-1} = (h^2/12)[p_{n+1}\Psi'_{n+1} + (12/h)\Psi'_n - p_{n-1}\Psi'_{n-1}]$

Applying the expansions (5-3) and (5-4) to $[p(x)\Psi'(x)]$ and dropping the terms of the fourth order and higher as in section 1 of chapter 5, we obtain:

$$(6\text{-}21) \quad [p_n\Psi'_n]' = \Psi'_n(p'_n+p_n^2) + p_nq_{\lambda,n}\Psi_n$$

$$(6\text{-}22) \quad [p_n\Psi'_n]'' = \Psi'_n(3p_np'_n + p_n^3 + p''_n + q_{\lambda,n}) + \Psi_n(2q_{\lambda,n}p'_n + p_n^2q_{\lambda,n} + p_nq_{\lambda,n})$$

Replacing in (6-19) and (6-20) gives respectivelly the two algorithms in $O(h^4)$:

$$(6\text{-}23) \quad y_{n+1} - y_n[2+10T_{\lambda,n} + h^2(2T_{\lambda,n}p'_n+p_n^2T_{\lambda,n}+p_nT_{\lambda,n})]/(1-T_{\lambda,n}) + y_{n-1} = (h^2/12)[12p_n+h^2\alpha_n)\Psi'_n$$

and

$$(6\text{-}24) \quad A_{n+1}y_{n+1} - [2hp_nT_{\lambda,n}/(1-T_{\lambda,n})]y_n - A_{n-1}y_{n-1} = h\Psi'_n[1 + (h^2/6)(p'_n+p_n^2)]$$

where

$$(6\text{-}25) \quad \alpha_n = 3p_np'_n + p_n^3 + p''_n + q_{\lambda,n}p_n$$

We eliminate now Ψ'_n between (6-23) and (6-24) and we obtain after rearranging the terms:

$$(6\text{-}26) \qquad a_n y_{n-1} + b_n y_n + c_n y_{n+1} = 0$$

where:

$$(6\text{-}27) \qquad a_n = 6+6hp_nA_{n-1}+h^2(p'_n+p_n^2)$$

$$(6\text{-}28) \qquad b_n = -(1-T_{\lambda,n})^{-1}[12 + 60T_{\lambda,n}+ 2h^2(p'_n+p_2^2+5p'_nT_{\lambda,n}-p_n^2T_{\lambda,n})]$$

$$(6\text{-}29) \qquad c_n = 6-6hp_nA_{n+1}+h^2(p'_n+p_n^2)$$

Finally the two-term recurrence relations can be written as follows:

$$(6\text{-}30) \qquad R_n = (U_n/Y_n) - (Z_n/Y_n)R_{n-1}^{-1}$$

$$(6\text{-}31) \qquad S_n = (U_n/Z_n) - (Y_n/Z_n)S_{n+1}^{-1}$$

where:

$$(6\text{-}32) \qquad Y_n = [\alpha_n - hp_nA_{n+1}][1-T_{\lambda,n+1}]$$

$$(6\text{-}33) \qquad Z_n = [\alpha_n + hp_nA_{n-1}][1-T_{\lambda,n-1}]$$

$$(6\text{-}34) \qquad U_n = [(2+10T_{\lambda,n}\alpha_n - 2h^2p_n^2T_{\lambda,n}]$$

and

$$(6\text{-}35) \qquad \alpha_n = 1 + (h^2/6)(p'_n+p_n^2)$$

We note that R_n and S_n are defined here by:

$$R_n = \Psi_{n+1}/\Psi_n \quad \text{and} \quad S_n = \Psi_{n-1}/\Psi_n$$

in opposite of their definition in (5-32) and (5-33). The use of F_n as defined in (5-10) in this case presents some difficulties and the question remains open.

Clearly this algorithm reduces to the Numerov algorithm when $p(x)=0$ and furthermore to ALG(1) if we drop the terms of degree higher than h^2.

This algorithm presents therefore the advantages to have local truncation errors similar to those of the Numerov algorithm, to preserve the scheme used in the previous sections and to be able to solve both radial and "angle-bending" equations.

2.Solution by a change of the function.

The first derivative term $p(x)\Psi'(x)$ in (6-1) can be removed mathematically by a change of the function $\Psi(x)$:

(6-36) $$\Psi(x) = X(x)A(x)$$

This leads to an equation for which Numerov's algorithm may be used. However, the transformation may be difficult and considered mathematically, the transformed function may be badly behave especially at the bounds. This kind of transformation is successively used in the hydrogen atom and our assumption is that in case of Legendre type equations, a suitable change of function will give results similar to those obtained in the hydrogen atom.

Let us substitute (6-36) into (6-1):

(6-37) $$X''(x) + [(p(x)A(x)-2A'(x))/A(x)]X'(x) + [(q_{\lambda,s}(x)A(x) + p(x)A'(x) - A''(x))/A(x)]X(x) = 0$$

It is easy to see that in choosing:

(6-38) $$A(x) = \exp[\int (1/2)p(x)dx]$$

the system (6-1) becomes:

(6-39) $$X''(x) = [q_{\lambda,s}(x) + (1/4)p^2(x) - (1/2)p'(x)]X(x)$$

while the boundary conditions are:

(6-40) $$X(a) = \alpha/A(a) \quad ; \quad X(b) = \beta/A(b)$$

We introduce:

(6-41) $$Q_{\lambda,s}(x) = q_{\lambda,s}(x) + (1/4)p^2(x) - (1/2)p'(x)$$

(6-42) $$\tau_{\lambda,n} = (h^2/12)Q_{\lambda,s,n} = T_n + (h^2/24)(p_n{}^2/2 - p'_n)$$

The Numerov algorithm can be written in the form:

(6-43) $$X_{n-1}(1-\tau_{n-1}) - (2+10\tau_n)X_n + X_{n+1}(1-\tau_{n+1}) = 0$$

Finally, in performing the usual substitution:

(6-44) $$X_n(1-\tau_n) = F_n$$

we obtain the relations of the renormalized Numerov method (5-34) and (5-35) where now:

(6-45) $$U_n = (2+10\tau_n)/(1-\tau_n)$$

This algorithm will be referred as ALG(4) in what follows.

The use of this method for the evaluation of the eigenfunctions implies a supplementary step consisting in multiplying the function X(x) by A(x) and care must be taken especially at the bounds where some undetermination may result. For example in the Legendre-type equations, $A(x) = (1-x^2)^{-1/2}$ and A(-1)=A(1) are infinity and care must be taken in the evaluation of the boundary conditions in (6-40). Furthermore the change of function may present some problems concerning the volume element which must be verified for the transformation and it is necessary to make sure by examining the behaviour of X(x) at the bounds that $\Psi(x)$ is actually an acceptable solution of the equation in all the space including the bounds and that this solution is normalizable.[58]

Nevertheless in the applications we are concern with these remarks do not present any major difficulties. We carry out a study of the behavior of the solutions of equation (6-39) in (16) for a Legendre-type equation.

In table (6-1) we resume the various expressions of the discrete functions U_n, Y_n and Z_n involved in the general algorithms:

$$R_n = [U_n/Y_n] - [Z_n/Y_n]R_{n-1}^{-1} \qquad (6\text{-}46)$$

$$S_n = [U_n/Z_n] - [Y_n/Z_n]S_{n+1}^{-1} \qquad (6\text{-}47)$$

We note that for ALG(4) we may perform the iterations in terms of either Ψ_n or F_n. In working out the applications, we

remarked that ALG(4) works faster in terms of F_n.

Before presenting the results obtained from each of the algorithms we have to discuss how the boundary conditions will be translated in terms of the starting values R_1 and S_{N+1}.

TABLE 6-1: FUNCTIONS INVOLVED IN THE VARIOUS ALGORITHMS.

	U_n	Y_n	Z_n
ALG(1)(Ψ)	$2+12T_n$	$1-.5hp_n$	$1+.5hp_n$
ALG(3)(Ψ)	$(2+10T_n)\alpha_n-2h^2p_n^2T_n$	$\alpha_n^-(1-T_n)$	$\alpha_n^+(1-T_{n-1})$
ALG(4)(Ψ)	$2+10T_n$	$1-T_{n+1}$	$1-T_{n-1}$
ALG(4)(F)	$(2+10T_n)(1-T_n)^{-1}$	1	1

where:

$$\alpha^+ = \alpha_n + hp_nA_{n-1} \quad ; \quad \alpha^- = \alpha_n - hp_nA_{n+1}$$

3. Initial values of R and S by series expansions.

We present here an alternate way to determine the starting values R_1 and S_{N+1} of the iterations whereas the boundary conditions $\Psi(a)$ and $\Psi(b)$ are not explicitly defined. This way of doing has the advantage relative to the graphical extrapolation discussed earlier to release the problem of singularities at the bounds. Basically the method consists of expanding in a Frobenius series the solution around the bounds for the grid points a and a+h and to calculate the ratio R_1 using these values. In some cases, as we shall see in the applications, a better result is obtained in starting the iterations with $R_2=\Psi_3/\Psi_2$.

a) Frobenius series expansion.

We recall here the well-known technique of expanding the solution of a differential equation around a singular point[38].

Let the equation:

(6-48) $$p(x)y''(x) + q(x)y'(x) + r(x)y(x) = 0$$

x=a is a regular singular point if p(a)=0 and if the two following conditions are fulfilled:

(6-49) $\lim(x-a)q(x)/p(x)$ and $\lim(x-a)^2 r(x)/p(x)$

both exists whereas x tends to a.

In such conditions the equation (6-48) has a Frobenius-type solution of the form:

(6-50) $y = (x-a)^c(\Sigma_j a_j(x-a)^j) \qquad (j=0,1,2,\ldots)$

where the series $\Sigma_j a_j(x-a)^j$ converges for all x such that $[x-a]<R$, R being the distance from x=a to the nearest singularity.
The determination of the coefficients c and a_j is performed in taking the derivatives of y(x) in (6-50) and replacing in (6-48) and finally in equating the terms of same degree in x.

b.Legendre-type equations without change of function.

We consider here the Legendre equation where a potential function V(x) has been added:

(6-51) $\Psi''(x) = [(2x/(1-x^2)]\Psi'(x) + [1/(1-x^2)][s^2/(1-x^2) + V(x) - \lambda]\Psi(x) = 0 \qquad (-1<x<1)$

with the boundary conditions:

(6-52) $\Psi(-1) = \alpha \quad ; \quad \Psi(1) = \beta$

The case where $V(x)=\emptyset$ corresponds to the "pure" Legendre equation while the case for which $V(x)$ is non zero corresponds to the "angle-bending" equation. The upper bound in this case is determined by the equilibrium of the potential (see section 5).

Clearly $x=-1$ is a regular singular point. If $V(x)$ is expressed in terms of the following expansion:

$$(6\text{-}53) \qquad V(x) = \Sigma_i A_i (x-x_{eq})^i \quad (i=1,2,\ldots)$$

where x_{eq} is the equilibrium of the potential then in using the procedure described in the previous paragraph, we find:

$$(6\text{-}54) \qquad c = s/2$$

$$(6\text{-}55) \qquad a_\emptyset = 1$$

$$(6\text{-}56) \qquad a_1 = (s^2-s-2\lambda)/4(s+1)$$

$$(6\text{-}57) \qquad a_2 = [s^4+5s^3-4s^2(\lambda-2)-4s(2\lambda-2A_1-1) + 4(\lambda^2-2\lambda+2A_1)]/[32(s+1)(s+2)]$$

Near $x=-1$, the solution may then be expressed in the form:

$$(6\text{-}58) \qquad \Psi(x) = (x+1)^{s/2} + a_1(x+1)^{s/2+1} + a_2(x+1)^{s/2+2}$$

Replacing x by -1 and by $-1+h$, we may evaluate the ratio $R_1=\Psi(-1+h)/\Psi(-1)$.

The same procedure can be used at the upper bound $x=1$

since it constitutes also a regular singular point for the pure Legendre equation.

c.Solution of Legendre-type equations with change of function.

In this case, using equation (6-39), the coefficients of the expansion are given by:

(6-59) $c = (s+1)/2$

(6-60) $a_0 = 1$

(6-61) $a_1 = (s^2-2\lambda-1)/4(s+1)$

(6-62) $a_2 = [2c^2(2c^2-c-\lambda-1)+2c(2A_1+\lambda)+\lambda^2]/[16c(2c+1)]$

The same procedure as previously can be carried out in order to calculate R_1

We obtain:

(6-63) $X(x) = (1+x)^{(s+1)/2}[1 + a_1(1+x) + a_2(1+x)^2]$

and we can use $R_1=X_2/X_1$ as starting value.

The evaluation of R_1 expressed in terms of the function $F_n=(1-T_n)X_n$ is obtained in the following way:
starting from the general equation at the grid point x_n, we write:

(6-64) $X''_n = Q_n X_n$

multiplying both sides by $h^2/12$ and replacing in the expression of F_n we obtain:

(6-65) $$F_n = X_n - (h^2/12)X''_n$$

The second derivative of X(x) at grid point x_n is determined from (6-63):

(6-66) $$X''(x) = A(1+x)^{(s-3)/2} + B(1+x)^{(s-1)/2} + C(1+x)^{(s+1)/2}$$

where:

(6-67) $$A = (s^2-1)/4$$

(6-68) $$B = a_1(s+3)(s+1)/4$$

(6-69) $$C = a_2(s+3)(s+5)/4$$

Replacing in (6-65) we can obtain the values of F_n at x=-1 and x=-1+h and therefore the value of R_1.

We note here that boundary conditions such that X(-1)=0 does not imply necessarily F(-1)=0; this situation occurs only if X''(-1)=0. Therefore the starting values R_1 will differ if ALG(4) is used in terms of Ψ_n or in terms of F_n. Such a situation occurs in the hydrogen atom for the cases $l<2$[15].

Both procedures are tested in the next section with the

"pure" Legendre equation and compared with the results obtained from the graphical extrapolation technique.

4.Discussion of the Legendre Equation.

a) General observations.

We consider here the case $V(x)=0$ in the equation (6-51). The interval of integration is $[-1,1]$ and we know the analytic solutions of this problem so that our methods could be tested.

In order to obtain a numerical solution, let us write the equation in the form:

$$(6\text{-}74) \quad (d^2/dx^2)\ \Psi^s_L(x) = p(x)(d/dx)\Psi^s_L(x) + q_{L,s}\Psi^s_L = 0$$

where:

$$(6\text{-}75) \quad p(x) = 2x/(1-x^2)$$

$$(6\text{-}76) \quad q_{L,s} = (1-x^2)^{-1}[s^2(1-x^2)^{-1} - \lambda_L]$$

and the boundary conditions are:

$$(6\text{-}77) \quad \Psi^s_L(-1) = \alpha \ ; \ \Psi^s_L(1) = \beta$$

α and β being unknown. Nevertheless the "effective" potential may be considered as the function $s^2/(1-x^2)$. For s different from zero, this potential is infinite at both bounds and the minimum of the potential is s^2 at $x=0$ [see figure (6-1)].

With an infinite potential at the bounds we may expect (for s>0) that the eigenvectors are zero at the bounds. For s=0, the potential is zero everywhere (note the indeterminacy 0/0 at the bounds[58,59]).

In this form we may consider (6-74) as an eigenvalue second-order differential equation with eigenvalues $\lambda_L = L(L+1)$ and the corresponding eigenfunctions are the Legendre polynomials (s=0) and associated Legendre functions (s>0) $P^s_L(x)$.

We recall here some of the Legendre functions[59] and the figures (6-2) illustrate their behaviour.

P^s_L	$L(L+1)$
$P^0_0 = 1$	0
$P^0_1 = x$	2
$P^0_2 = (1/2)(3x^2-1)$	6
$P^0_3 = (1/2)(5x^3-3x)$	12
$P^0_4 = (1/8)(35x^4-30x^2+3)$	20
$P^0_5 = (1/8)(63x^5-70x^3+15x)$	30
$P^1_1 = -(1-x^2)^{1/2}$	2
$P^1_2 = -3x(1-x^2)^{1/2}$	6
$P^1_3 = -(3/2)(5x^2-1)(1-x^2)^{1/2}$	12
$P^2_2 = 3(1-x^2)$	6
$P^2_3 = 15x(1-x^2)$	12
$P^3_3 = -15(1-x^2)^{3/2}$	12

We note (see figures) that for s=0 the values of the polynomials at the bounds are:

$$P^0_L(-1) = (-1)^L \quad ; \quad P^0_L(1) = 1$$

while for s>0:

$$P^{s}_{L}(-1)=P^{s}_{L}(1)=0$$

Furthermore, for s<3, the first derivative of the polynomials at the bounds is different from zero while it is zero for s>=3.Finally the second derivative is different from zero for s<5 and equal to zero at the bounds for s>=5.

The numerical solutions are carried out with ALG(1), ALG(3) and ALG(4) where the iterations are started from R_1 and S_{N+1} obtained both from graphical extrapolation and the series expansion methods. Figure (6-4) is an illustration of the behavior of the function D(λ) for s=3. The nodes correspond to the zeroes of the function and are the "eigenvalues of the equation (6-74).

b)Numerical solution without change of function.

ALG(1) AND ALG(3)

Case s=0

Using ALG(1) with 201 and 401 points.

The initial values R_1 and S_{N+1} are determined either by the graphical extrapolation or the expansion technique; the results are similar. In the first case, figure (6-3-A) illustrates the discrete curves of R versus grid points for $R_1=U_1/2$ as starting value while figure (6-4-B) shows for the same polynomials the curves obtained starting from R_1^r after the extrapolations.

In the second case, we used (6-58) for x=-1, x=-1+h for R_1 and x=1, x=1-h for S_{N+1}. Table (6-2) resumes the results obtained from the two algorithms. As we can see in comparing columns (1) and (3), we obtained an equivalent accuracy with both algorithms and in comparing columns (2) and (5) both methods used in the evaluation of the initial conditions give similar results.

Case s>0

In this case both graphical extrapolation and expansion methods show that the initial values of R and S are infinity. Figures (6-5-A1,A2) illustrate the process of graphical extrapolation for P^1_3 and the results are given in table (6-3). The use of infinity as starting values of the iterations leads to inaccurate results especially for s=1 [see tables (6-3) to (6-5)]. A better approximation was obtained in starting the iterations from $R_2=\Psi_3/\Psi_2$ and $S_{N+1} = \Psi_{N-2}/\Psi_{N-1}$ where the values of Ψ were determined from the series expansion. This method is nevertheless limited for very high values of L since the first node of the solution appears closer to the bound as L increases.

c.Numerical solution using a change of the function.

ALG(4)

Case s=0

In that case X(x)=0 at the bounds and F_n is given by:

(6-78) $$F_n = (h^2/12)\chi''(x)$$
$$=(h^2/12)[-.25(1+x)^{-3/2} -(3\lambda/8)(1+x)^{-1/2}$$
$$+[15(\lambda^2-1)/64](1+x)^{1/2}$$

ALG(4) in terms of the F_n is initiated by $R_1=S_{N+1}=0$ while in terms of the χ_n, the iterations are started with the values $R_1=S_{N+1}$=infinity. The results are given in table (6-2), column (4). Obviously, this method does not give accurate results and it can be shown that the convergence in using more grid points is very slow (convergence rate is of order of h, see below). As in section b, iterations started from values R_2 and S_N(and higher values) give better results [table (6-6),columns (1) to (4)].

Case s>0

Again $\chi(x)=0$ at the bounds and since $\chi''(x)$ is infinity for s<3 we must take the same starting values for R and S than in the case s=0. For s=3, $\chi''(x)$ is finite at the bounds and equal to 2 and the iterations start from values determined by (6-78). For s>3, $\chi''(x)=0$, $R_1=S_{N+1}$=infinity. As shown in table (6-6) we obtained accurate results with this method.

d.Rate of convergence.

The previous results deal with the eigenvalues of the

Legendre equation and compare between the different methods the accuracy obtained with a same interval length h. Customarly the tests of numerical methods where analytic solutions are available consist of comparing the solutions (here the eigenfunctions) obtained with an interval h and with another interval h'. From this the real rate of convergence of the solution may be determined. Theoretically ALG(1) has a truncation error of order h^2 while ALG(3) and ALG(4) have truncation errors of order h^4. We know (see section 3 of chapter 4) that the absolute value of the discretization error is bounded by a factor of order h^2 [ALG(1)] and h^4 [ALG(3),ALG(4)]. Let E_h and $E_{h/2}$ be these bounds for the values obtained with intervals h and h/2. (i.e., E_h is the absolute value of the maximum error max[$\Psi_n-\Psi(x_n)$] on the whole interval [-1,1] using h). Therefore, for ALG(1) we should obtain $E_h/E_{h/2}=1/4$ and for ALG(3), ALG(4), the ratio should be 1/16. Excluding Ψ_1 and Ψ_{N+1} which are determined by the series expansion and therefore not iterated , tests performed with 21 and 41 grid points give a good concordance (exept in the case of ALG(4), for s=0).

Obviously a more detailed discussion of this subjet is out of the purpose of the present dissertation and we shall restrict ourselves to propose a scheme which appeared to work with great satisfaction in the "pure" Legendre case and also in the "angle-bending" case.

e.Conclusions : general scheme.

As shown in the table (6-6), the best results are obtained by the following procedure:

s=0: ALG(3) or ALG(1) with either the graphical extrapolation or the series expansion method in order to determine R_1 and S_{N+1}.

0<s<4:ALG(4) using R_2, S_N (s=1,3); R_3, S_{N-1} (s=2) as starting values of the iterations whereas the values of the solution X non-iterated are calculated from the series expansions. The further transformation X into Ψ being carried out taking in mind the observations discussed earlier.

s>=4:ALG(4) or ALG(3) with R_1, S_{N+1} both infinity.

Table 6-2:

Numerical calculated eigenvalues of Legendre equation (s=0).
(1):ALG(1), 201 points. R_1 and S_{N+1} are calculated from the expansion method.
(2):ALG(1), 401 points with the same initial values R_1 and S_{N+1}.
(3):ALG(3), 201 points and initial values calculated from the expansion method.
(4):ALG(4), 201 points. R_1 and S_{N+1} are infinity.
(5):ALG(1), 201 points. R_1 and S_{N+1} determined from the graphical extrapolation.

Table 6-3:

Numerical calculated eigenvalues of Legendre equation (s=1).
(1):ALG(1), 201 points, R_1 and S_{N+1} are infinity.
(2):ALG(1), 201 points, R_2, S_N calculated from expansion as starting values.
(3):ALG(4), 201 points, R_1 and S_{N+1} are infinity.
(4):ALG(4), R_2 and S_N calculated from expansion as starting values.

Table 6-4:

Same legend as table 6-3 for s=2.

Table 6-5:

Numerical calculated eigenvalues of Legendre equation (s=3).
(1):ALG(1), 201 points, R_1 and S_{N+1} are infinity.
(2):ALG(4), 201 points, R_1 and S_{N+1} are calculated from expansion.

TABLE 6-2: LEGENDRE EQUATION:s=0

L	E^{an}	(1)	(2)	(3)	(4)	(5)
0	0	0.000000	0.000000	0.000000	-0.006991	0.000000
1	2	2.000009	2.000000	1.999997	1.978771	2.000000
2	6	5.999964	6.000000	5.999950	5.964851	6.000000
3	12	11.999564	11.999999	11.999320	11.952598	12.000000
4	20	19.998112	19.999991	19.995262	19.945494	19.999816
5	30	29.994304	29.999972	29.991624	29.951973	29.999264

TABLE 6-3: LEGENDRE-EQUATION:s=1

L	E^{an}	(1)	(2)	(3)	(4)
1	2	2.007534	2.000073	2.002971	2.000000
2	6	6.036730	6.000312	6.009427	6.000000
3	12	12.099484	12.000624	12.018897	12.000007
4	20	20.204949	20.000462	20.039835	20.000017
5	30	30.359335	29.998268	31.099742	30.000776
6	42	42.565944	41.990477	44.203275	42.003780

TABLE 6-4: LEGENDRE EQUATION:s=2

L	E^{an}	(1)	(2)	(3)	(4)
2	6	6.000000	6.000000	6.000836	6.000008
3	12	11.999650	11.999641	12.005715	12.000053
4	20	19.997901	19.997785	20.021340	20.000203
5	30	29.992855	29.992072	30.058443	30.000577
6	42	41.981500	41.977808	42.131624	42.001397
7	56	55.959466	55.945762	56.258570	56.003118

TABLE 6-5: LEGENDRE EQUATION:s=3

L	E^{an}	(1)	(2)
3	12	11.999967	12.000000
4	20	19.999446	20.000000
5	30	29.997369	30.000000
6	42	41.992073	42.000000
7	56	55.981088	56.000000
8	72	71.927641	71.999997

Table 6-6:

Comparison of ALG(1) and ALG(4) for Legendre equation using 201 points. The results are the relative maximum deviation between the calculated value of the eigenfunction and the corresponding value of the Legendre function: $[\max[y(x_i)-y_i]/y(x_i)$, $i=1,\ldots,N$.
(1): ALG(4) with R_1, S_{N+1} calculated from expansion as starting values.
(2): the same but R_2, S_N are the starting values.
(3): the same with R_3 and S_{N-1}
(4): the same with R_4 and S_{N-2}
(5): ALG(1) with R_1 and S_{N+1} calculated from expansion as starting values.

Table 6-7:

Parameters of the series expansion for the Legendre type equations. a_1, a_2 and c are the parameters (see text), R_1 the initial value for the iterations. The "angle-bending" equation is defined here with a potential as described in the text.

TABLE 6-6: LEGENDRE EQUATION:COMPARISON BETWEEN ALG(1) AND ALG(4)

s	L	(1)	(2)	(3)	(4)	(5)
0	0	-	6.9915	.8343	.2126	.0000
0	1	48.3619	1.0506	.1257	.0325	.0000
0	2	33.7630	.5858	.0687	.0116	.0000
0	3	26.0350	.3950	.0235	.0066	.0000
1	1	.0006	.0000	.0000	.0000	.3767
1	2	.0123	.0000	.0000	.0000	.6122
1	3	.0340	.0001	.0005	.0019	.8290
1	4	.0713	.0005	.0042	.0162	1.0247
2	2	.0039	.0001	.0000	.0000	.0000
2	3	.0134	.0004	.0001	.0001	.0029
2	4	.0305	.0010	.0004	.0005	.0105
2	5	.0571	.0019	.0011	.0030	.0238
3	3	.0000	.0000	.0000	.0000	.0003
3	4	.0002	.0000	.0000	.0000	.0028
3	5	.0007	.0000	.0000	.0000	.0088
3	6	.0019	.0000	.0001	.0004	.0189
4	4	.0000	.0000	.0000	.0000	.0004
4	5	.0000	.0000	.0000	.0000	.0028
4	6	.0000	.0000	.0000	.0000	.0079
4	7	.0000	.0000	.0000	.0000	.0171

TABLE 6-7:PARAMETERS OF THE SERIES EXPANSION:s=0

			Legendre		Angle-bending	
L	c	a_1	a_2	R_1	a_2	R_1
0	0	0	0	1.00000	432.5	1.03874
1	0	-1	-.0625	.99003	432.4	1.02976
2	0	-3	5.8125	.97015	438.3	1.01318
3	0	-6	29.625	.94075	462.1	.99861
4	0	-10	89.375	.90223	521.9	.95362

Table 6-8:

The "angle-bending" equation (J=0,K=0): determination by graphical extrapolationof the value of R_1 using 201 points on the interval [-1,-.1]. The extrapolated values R_1^k (first column) are obtained from the values of R_i^{k-1} (see text). The last column indicates the eigenvalues E obtained using R_1^k as initial value in the iteration.

Table 6-9:

Same legend for (J=0,K=1)

Table 6-10:

The "angle-bending" equation:
(1) eigenvalues obtained from ALG(1) with 2001 points and R_1 calculated from graphical extrapolation, S_{N+1} is infinity.
(2) same with 401 points.
(3) same but using Richardson extrapolation with 201 and 401 points
(4) results obtained from the series expansion with 201 points
(5) values obtained from the method of "complete set" (see text)

TABLE 6-8:ANGLE-BENDING EQUATION:J=0,K=0

k	(1)	(2)	(3)	(4)	(5)	E
0	1.00000	.93667	.92483	.91970	.91243	46.00961
1	.94851	.92146	.91600	.91350	.91197	44.05676
2	.92692	.91464	.91197	.91065	.90977	43.13029
3	.91731	.91152	.91011	.90933	.90874	42.69457
4	.91293	.91008	.90925	.90871	.90827	42.49091
5	.91091	.90941	.90885	.90843	.90805	42.39590
6	.90997	.90910	.90866	.90829	.90794	42.35144
7	.90954	.90895	.90858	.90823	.90790	42.33105
8	.90932	.90888	.90853	.90820	.90787	42.32061
9	.90923	.90885	.90852	.90819	.90786	42.31634
r	.90824	.90852	.90832	.90805	.90775	42.26922

TABLE 6-9:ANGLE-BENDING EQUATION (J=0,K=1)

k	(1)	(2)	(3)	(4)	(5)	E
0	1.00000	.79337	.72266	.64141	.50087	141.259
1	.86408	.74711	.67954	.58127	.37726	137.046
2	.81468	.72652	.65844	.54875	.29874	135.140
3	.79460	.71742	.64870	.53297	.25711	134.296
4	.78614	.71344	.64436	.52578	.23729	133.928
5	.78252	.71172	.64246	.52260	.22834	133.769
6	.78098	.71098	.64165	.52123	.22444	133.700
7	.78031	.71065	.64129	.52062	.22272	133.760
8	.78001	.71051	.64113	.52035	.22195	133.657
r	.72861	.68395	.61047	.46585	.04789	131.213

TABLE 6-10: ANGLE-BENDING EQUATION:EIGENVALUES (J=0)

K	(1)	(2)	(3)	(4)	(5)
0	xx.xxxx	xx.xxxx	xx.xxxx	xx.xxxx	xx.xxxx
1	yyy.yyyy	yyy.yyyy	yyy.yyyy	yyy.yyyy	yyy.yyyy
2	xxx.xxxx	xxx.xxxx	xxx.xxxx	xxx.xxxx	xxx.xxxx
3	xxx.xxxx	xxx.xxxx	xxx.xxxx	xxx.xxxx	xxx.xxxx

Figure (6-1): "Potential" function for the Legendre equation (s=0,1,2,3)

Legendre equation: potential. Fig.(6-1)

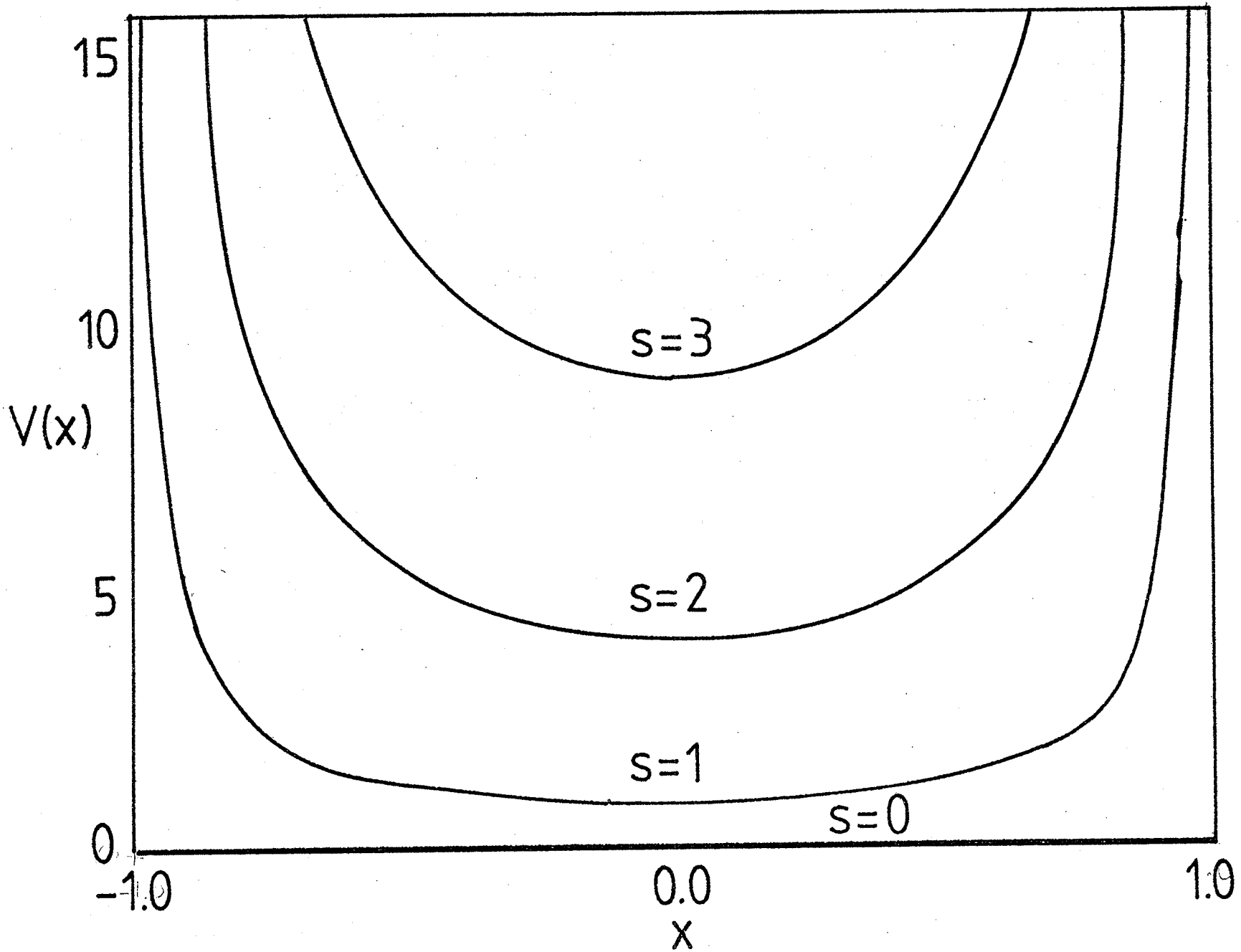


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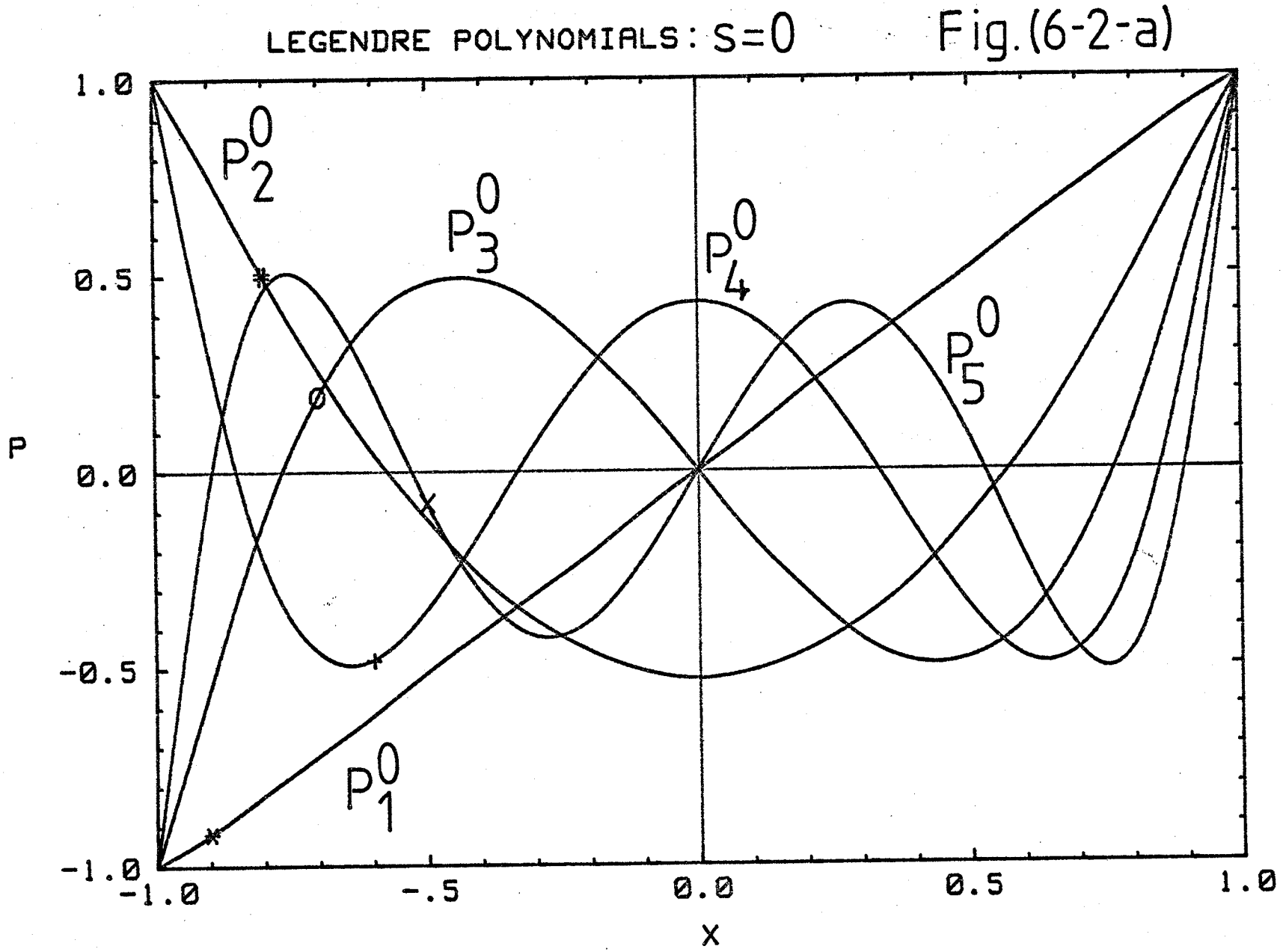
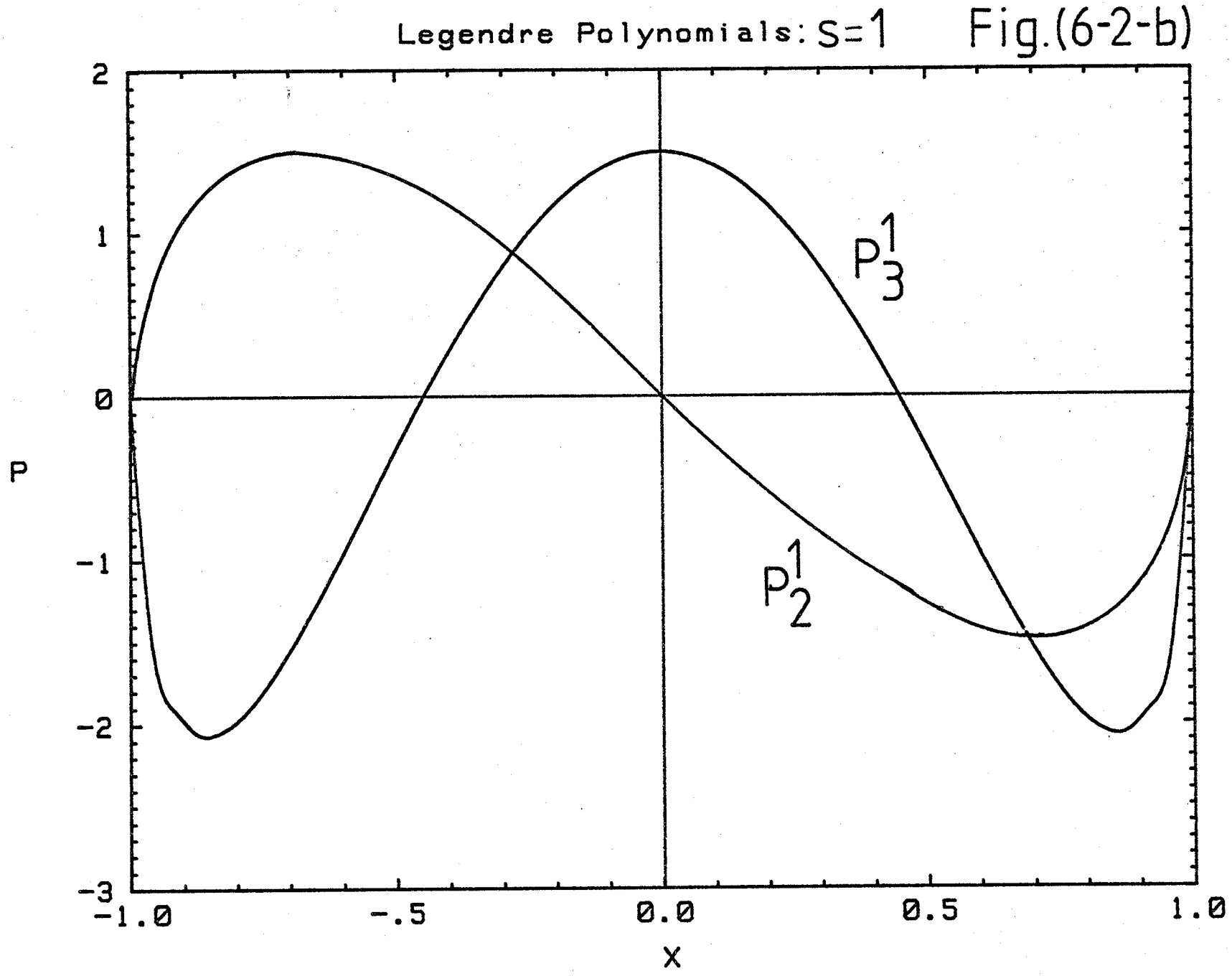
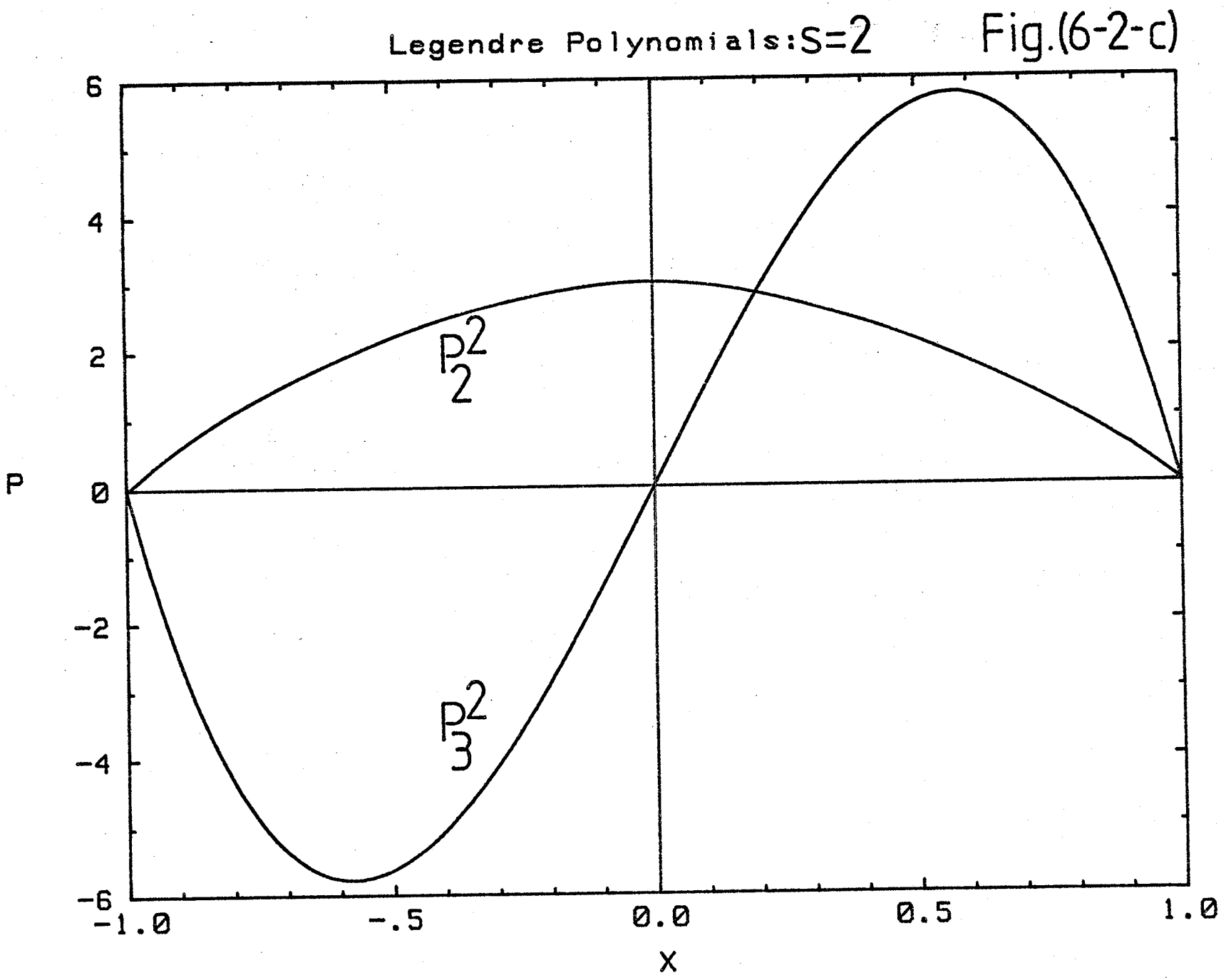
Figure (6-2): Legendre polynomials (a) and Legendre assotiated functions (b,c,d).


LEGENDRE POLYNOMIALS: S=0
Fig.(6-2-a)
1.0
0.5
0.0
-0.5
-1.0
P
-1.0
-.5
0.0
0.5
1.0
X
P_2^0
P_3^0
P_4^0
P_5^0
P_1^0


Legendre Polynomials: S=1
Fig.(6-2-b)
2
1
0
-1
-2
-3
P
-1.0
-.5
0.0
0.5
1.0
X
P_3^1
P_2^1


Legendre Polynomials:S=2
Fig.(6-2-c)
6
4
2
0
-2
-4
-6
P
P_2^2
P_3^2
-1.0
-.5
0.0
0.5
1.0
X

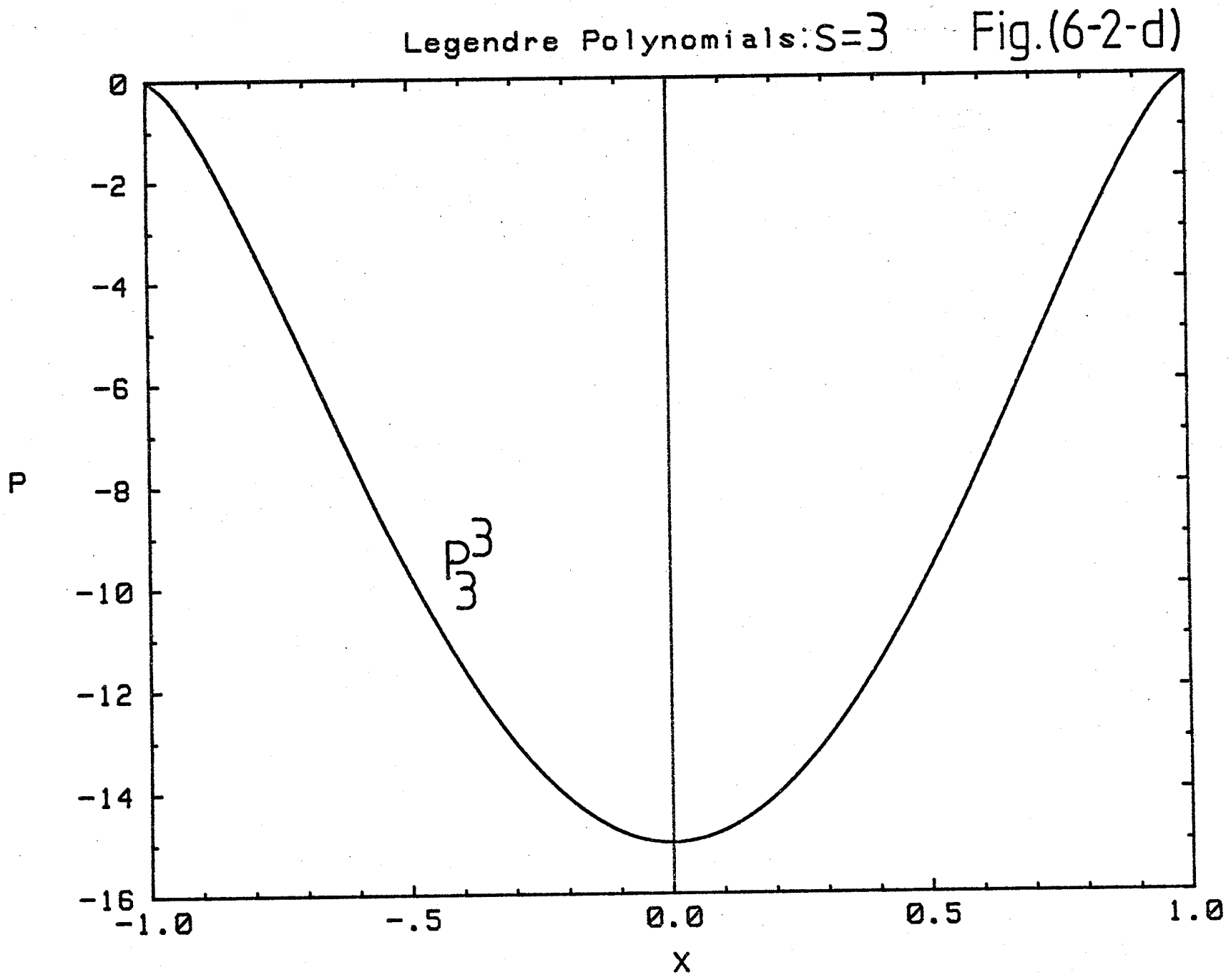

Legendre Polynomials:S=3
Fig.(6-2-d)
0
-2
-4
-6
-8
-10
-12
-14
-16
P
P_3^3
-1.0
-.5
0.0
0.5
1.0
X

Figure (6-3): R_n as a function of the grid points n for the Legendre equation (A and B) and the bending equation (C and D).

A. Legendre polynomials P_L (a.L=5; b.L=4; c.L=3; d.L=2; e.L=1). $R_1^{\emptyset}=U_1/2$ and the fractures have to be corrected (see text)

B. Same examples with the extrapolated values R_1^r.

C. Bending equation (J=0): $R_1^{\emptyset}=U_1/2$. a.K=2; b.K=1; c.K=0.

D. Bending equation (J=1); $R^{\emptyset}$ and $S_{N+1}^{\emptyset}$ are infinity.

FIG:6.3

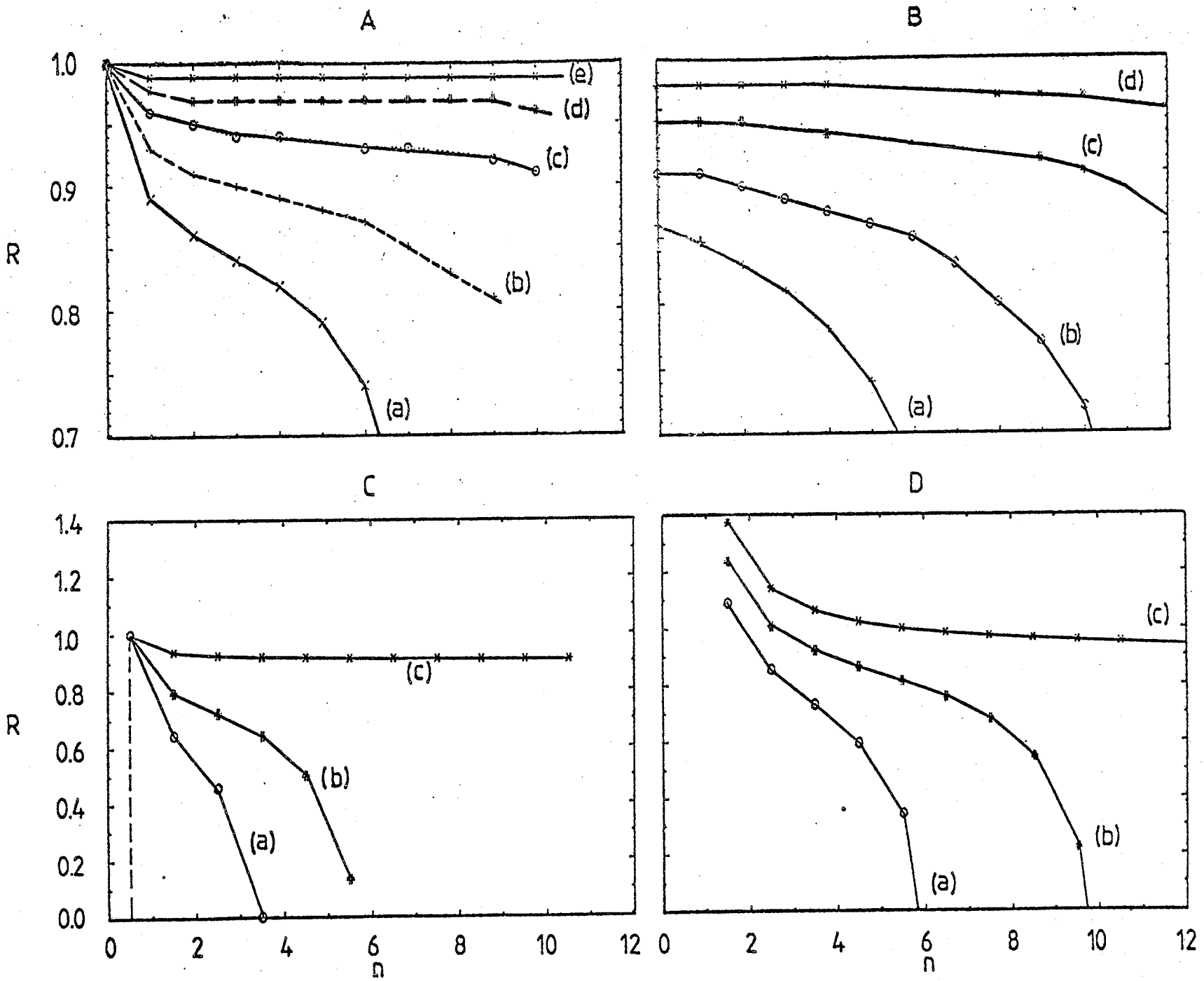


Figure (6-4): An illustration of the "correction" function $D(\lambda)$ for the Legendre equation (s=3). The dot lines indicate the eigenvalues 20, 30, 42,...

Fig.(6-4) Legendre equation:s=3.

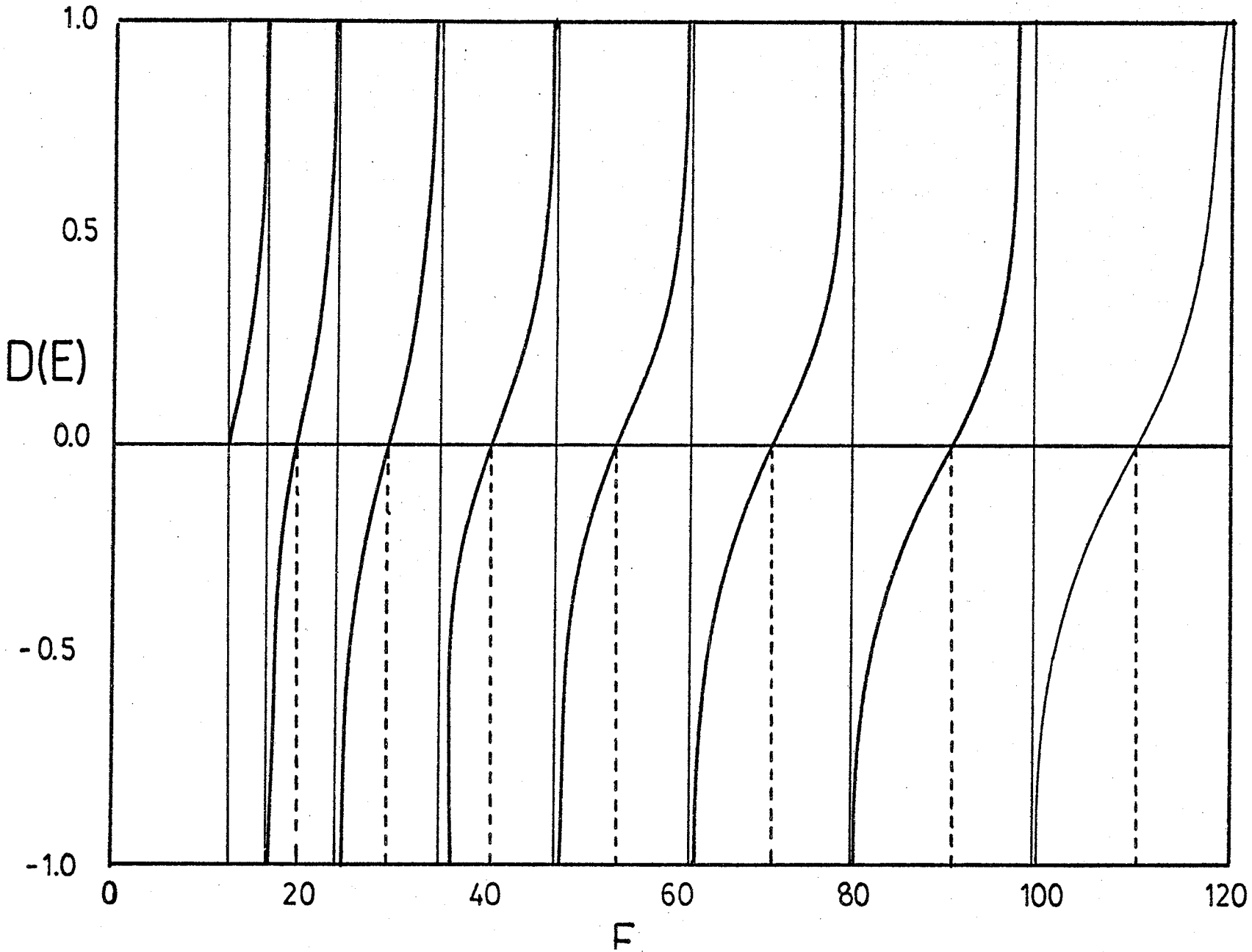


Figure (6-5): Different examples of the discrete function R_n for the first grid points n and the corresponding eigensolutions.

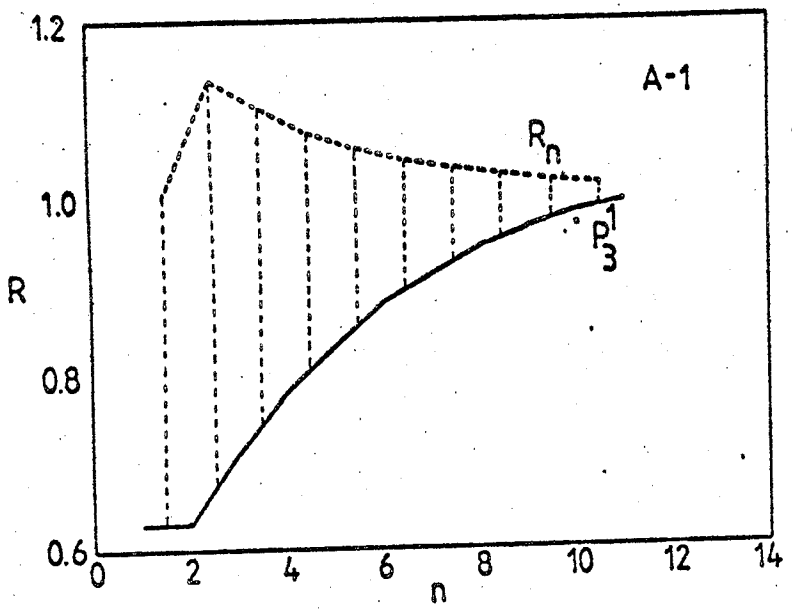
A-1: Legendre polynomial P_3^1. R_n is iterated using $R_1^{\emptyset}=U_1/2$ and $S_{N+1}^{\emptyset}=U_{N+1}/2$. The shape of the curve is not continuous and indicates that the real value should be R_1^r=infinity.

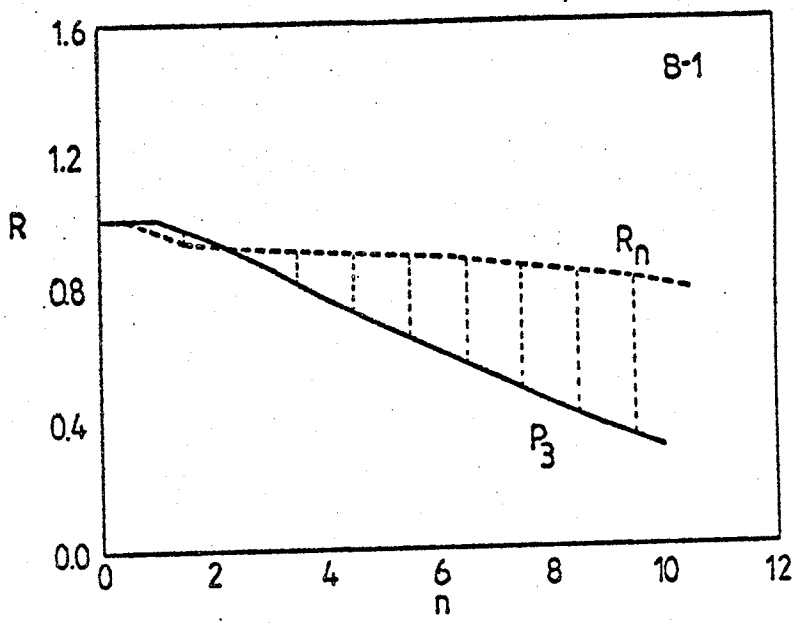
A-2: The same example with the proper value R_1^r=infinity.

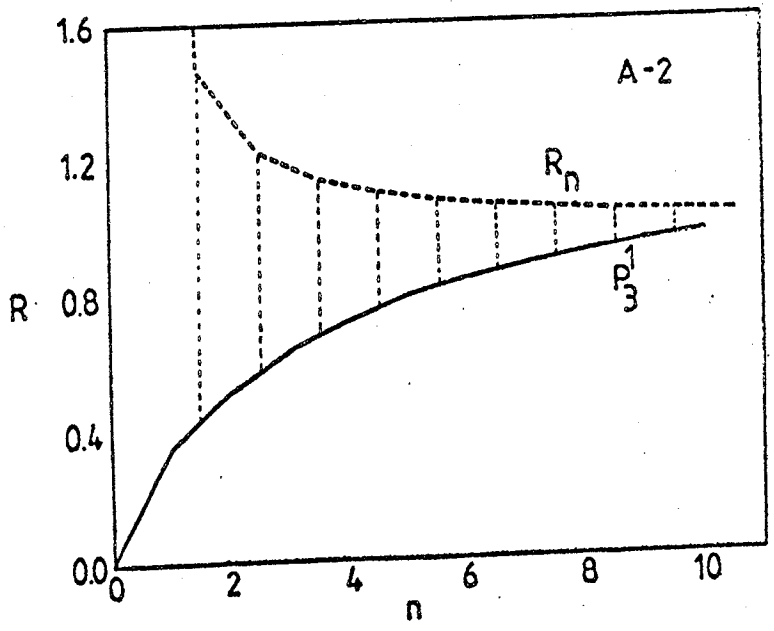
B-1: Legendre polynomial $P_3^{\emptyset}$. $R_n^{\emptyset}$ is iterated using $R_1^{\emptyset}=U_1/2$. The fracture in the curve indicates here that the proper value should be lesser than $U_1/2$.

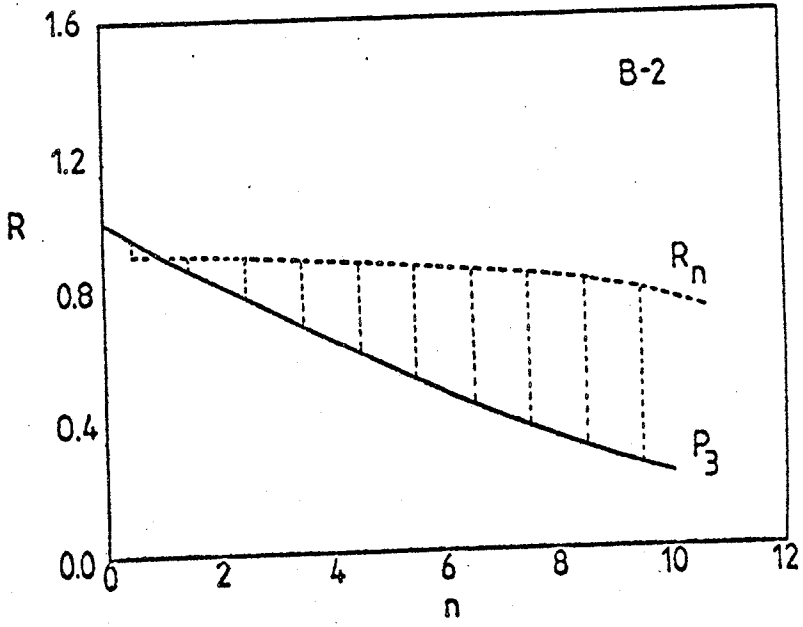
B-2: Same example with the extrapolated value R_1^r=0.9407. The fracture is corrected; the eigensolution shows monotonic decreasing behavior.

FIG. 6.5.


A-1
R_n
P_3^1
R
n
1.2
1.0
0.8
0.6
0
2
4
6
8
10
12
14


B-1
R_n
P_3
R
n
1.6
1.2
0.8
0.4
0.0
0
2
4
6
8
10
12


A-2
R_n
P_3^1
R
n
1.6
1.2
0.8
0.4
0.0
0
2
4
6
8
10


B-2
R_n
P_3
R
n
1.6
1.2
0.8
0.4
0.0
0
2
4
6
8
10
12

5. The Legendre equation with a potential.

The success attained for the "pure" Legendre equation leads us to use a similar scheme to solve the analogous equation including an arbitrary potential function V(x). This equation is the "angle-bending" equation which occurs in chapter 3 and whose numerical solution constitutes the goal of this part of the dissertation.

In order to test the methods of the previous section, we used a potential corresponding to an angle-bending of the acetylene since results obtained by an other method were available.

The potential is zero at -1 and tends to infinity as x tends to 1 and is expressible by the following expansion:

$$(6\text{-}79) \qquad V(x) = \Sigma_i A_i (x+1)^i \qquad (i=1,2,\ldots)$$

where the A_i are constants defined from a refinement process (least-square...).
For the purpose of the present test we choose these parameters as:

A_1=865.596, A_2=1065.19, A_3=118.02, A_4=138.8, A_5=-41, A_6=53.447

With these parameters, V(x) has the form illustrated in

figure (6-6). The effective potential is the sum of the "potential" occuring in the "pure" Legendre equation $s^2/(1-x^2)$ and V(x). This is illustrated in figures (6-7) for J=1,2,3. The case s=0 reduces obviously to V(x). The interval is [-1,-.1] and the various methods were tested for different values of h.

Equation (6-74) becomes here:

$$\Psi''(x) = p(x)\Psi'(x) + q_{K,J}(x)\Psi(x) \qquad (6\text{-}80)$$

where:

$$q_{K,J}(x) = (1-x^2)^{-1}[J^2/(1-x^2) + V(x) - E_{K,J}] \qquad (6\text{-}81)$$

The J=0 case corresponds once more to boundary conditions such that the eigenfunction is not zero at the lower bound but is zero at the upper bound. The first derivative is non zero at the lower bound and is zero at the upper bound. The J>0 case corresponds to boundary conditions such that the eigenfunction is zero at both bounds, its first derivative being non zero at the lower bound but zero at the upper one. Therefore the initial value R_1 has to be extrapolated either graphically or from the series expansion in the case J=0. In both cases S_{N+1} is infinity (since $\Psi(x)$ tends to zero very quickly) or as $U_{N+1}/2$ (since the first derivative of $\Psi(x)$ is zero at the upper bound).

The results of the graphical extrapolation of R_1 are

Figure (6-6): Potential function V(x) for the angle-bending equation (acetylene).

FIG.6·6.

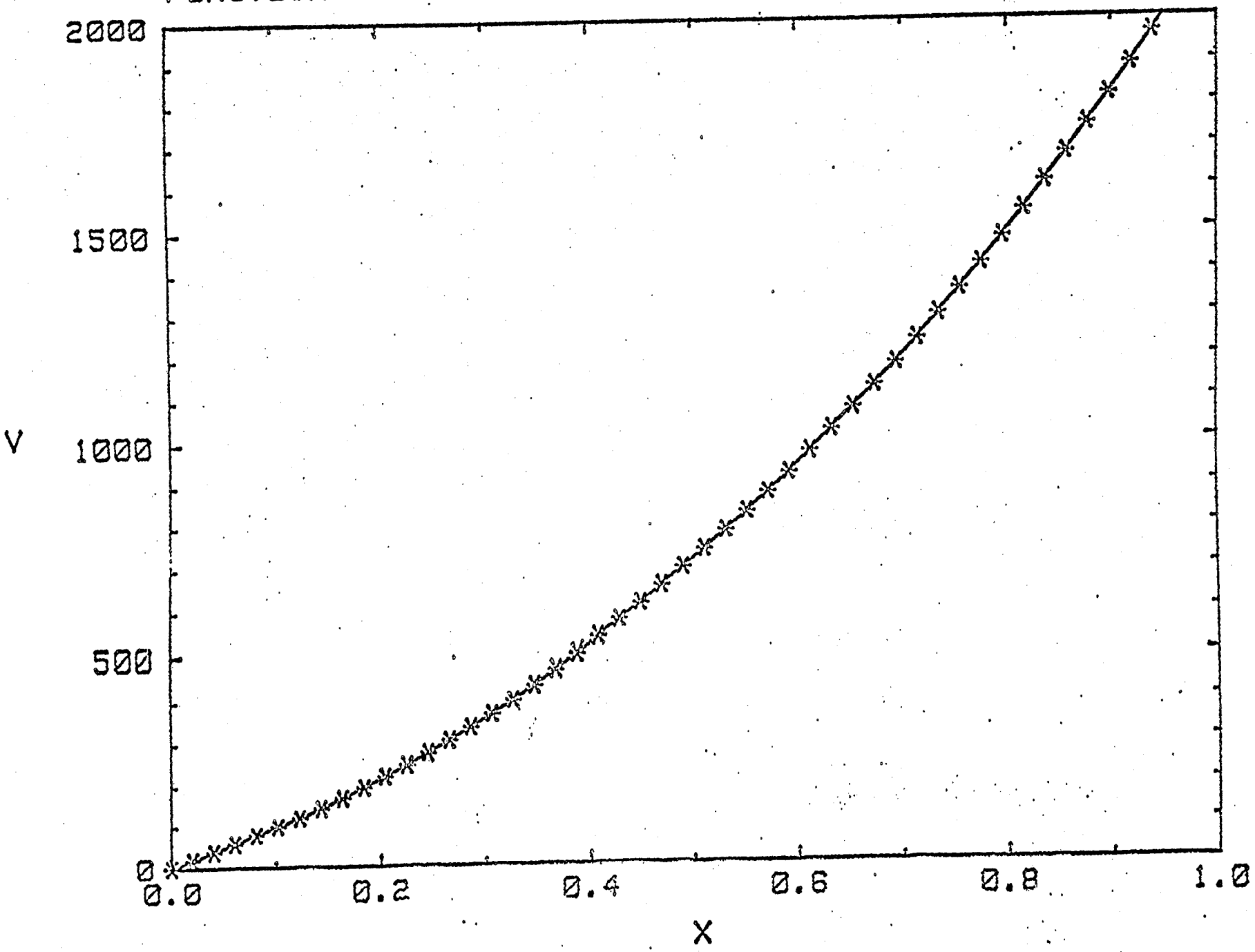

FUNCTION V(X)=POTENTIAL BENDING HCCH FROM POLYNOMIAL
2000
1500
1000
500
0
V
0.0
0.2
0.4
0.6
0.8
1.0
X

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Figure (6-7): Effective potential for the angle-bending equation (acetylene) as the result of the sum of the "Legendre potential" function and the potential V(x). The potential is infinity at the bound and becomes minimum closer to the bound as J decreases. For J=0, the potential is zero at the bound.

FIG. 6.7.A

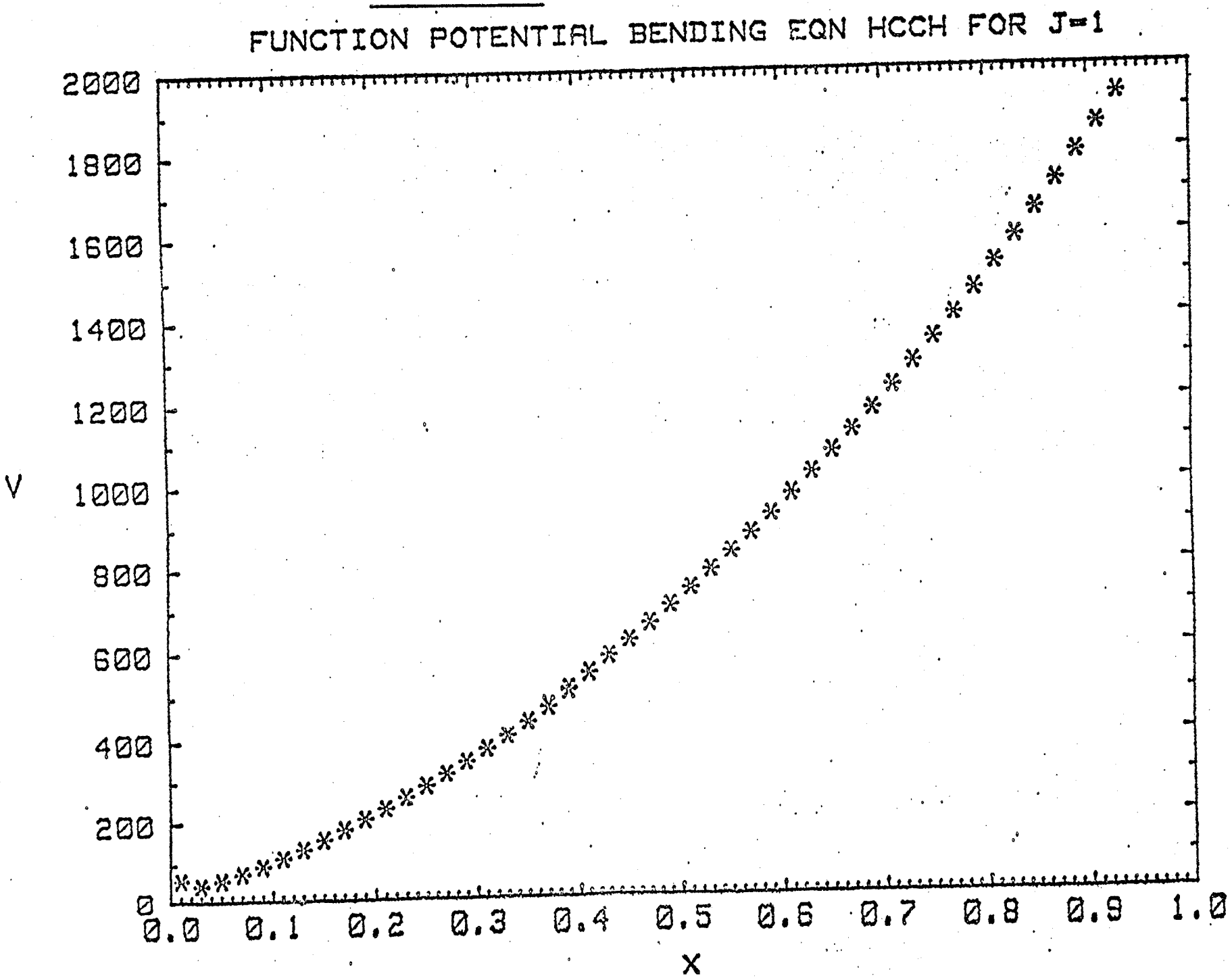

FUNCTION POTENTIAL BENDING EQN HCCH FOR J=1
2000
1800
1600
1400
1200
1000
800
600
400
200
0
V
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
X

FIG.6,7.B.

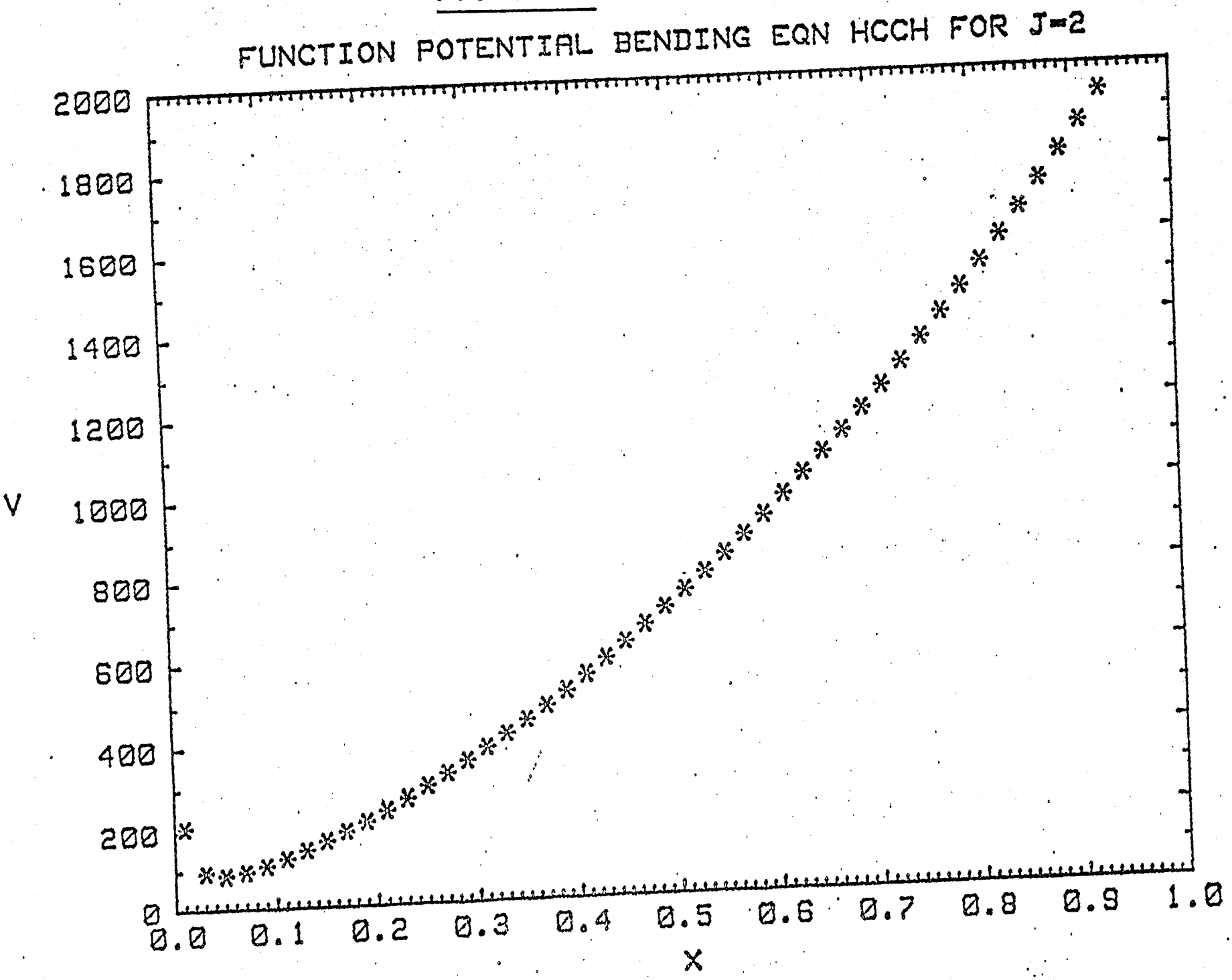
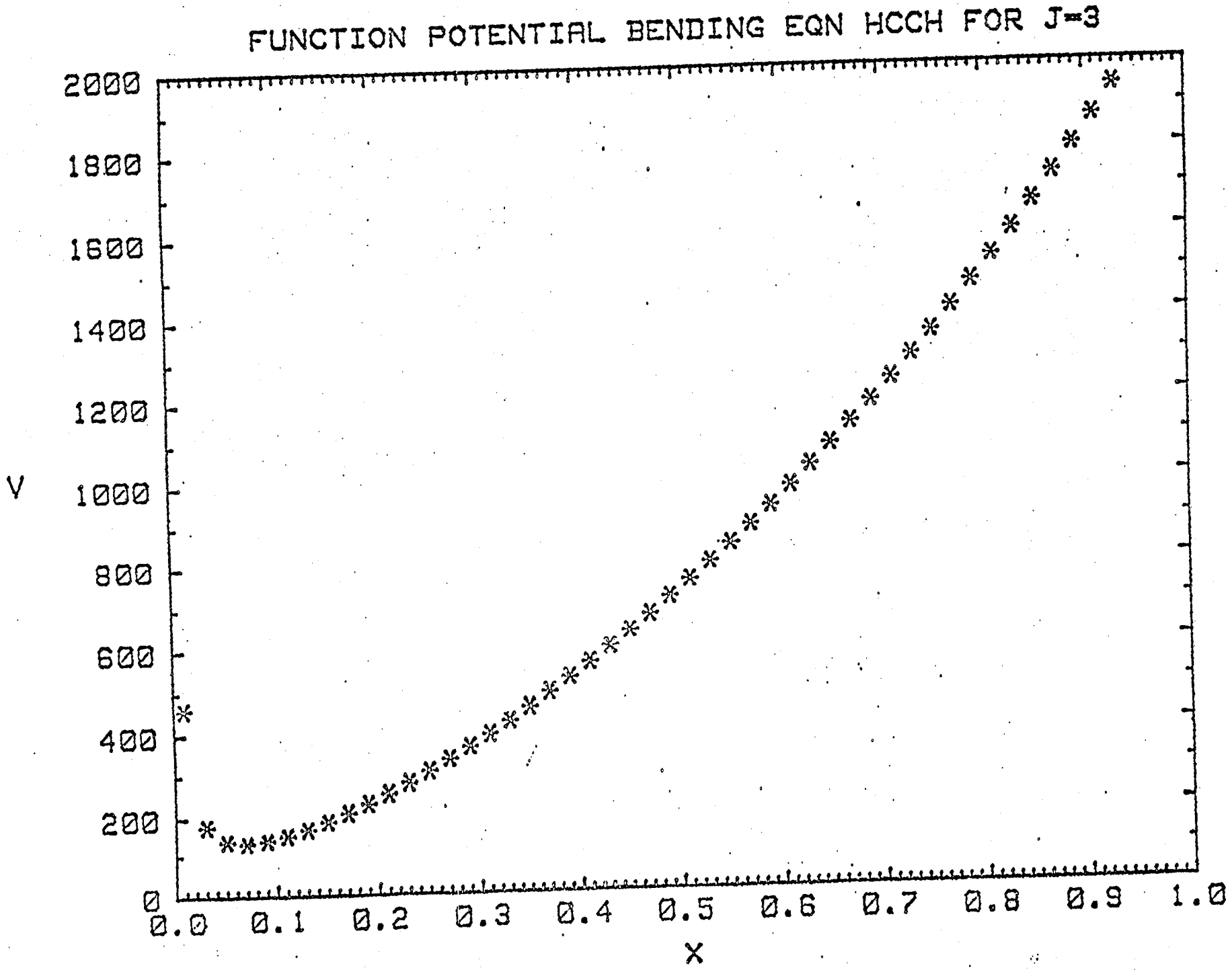

FUNCTION POTENTIAL BENDING EQN HCCH FOR J=2
2000
1800
1600
1400
1200
1000
800
600
400
200
0
V
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
X

FIG.6.7.C.

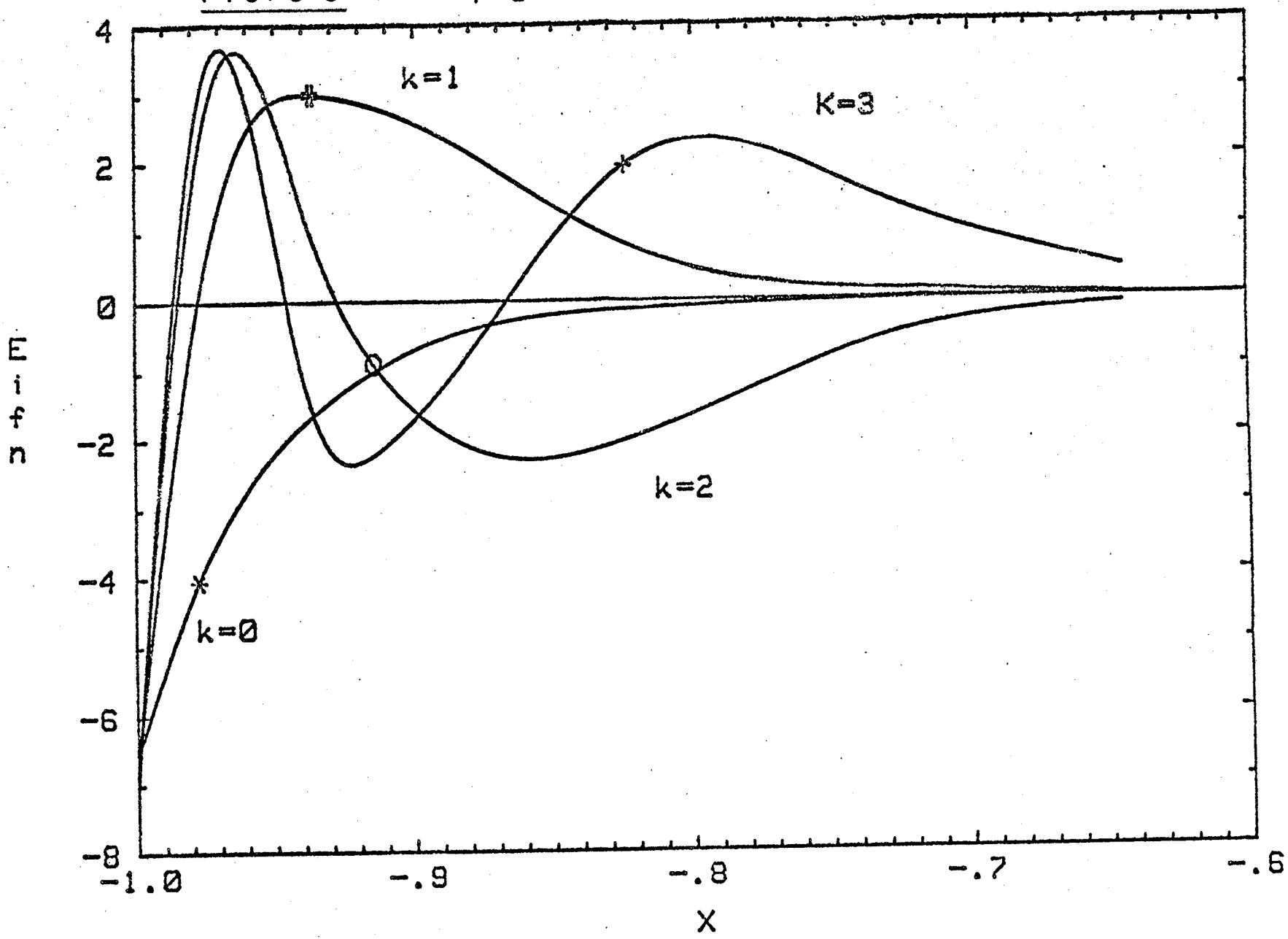

FUNCTION POTENTIAL BENDING EQN HCCH FOR J=3
2000
1800
1600
1400
1200
1000
800
600
400
200
0
V
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
X

given in tables (6-8) and (6-9) respectivelly for K=0 and K=1 (J=0) and illustrated in figures (6-3,C and D). Comparison with the expansion method is given in table (6-7). In both cases, the results obtained with ALG(1) and ALG(4) with different values of h are compared with the results obtained by the more customary expansion of the eigenfunction in terms of a "complete" set of associated Legendre functions. Agreement between the two is extremely close for both eigenvalues [see table (6-10)] and eigenfunctions [to the fifth decimal place, some eigenfunctions are illustrated in figure (6-8) for J=0].

The numerical methods presented here does have the great advantage of speed of computation together with the fact that the functional form of the eigenfunctions is immediately obtained rather than the usual series of eigenvector coefficients.

Figure (6-8): Some illustrations of the eigenfunctions of the angle-bending equation (acetylene) for k=0,1,2,3 (J=0).

FIG. 6.8. Eigenfunctions for J=0



CONCLUSIONS

A general program has been written in order to solve any equation occuring in the study of n-atomic systems since the solution of the zero order problem is reduced to n 1-dimensional equations belonging either to the radial or the "angle-bending" type. The only parameters needed as input are the bounds of the interval of integration , the value of the potential at the grid points, the values of the functions $p(x)$, $k(x)$ and $q_s(x)$ of the general equation and obviously the values of the different quantum numbers for which the equation is solved and the desired accuracy of the eigenvectors.

The determination of the boundary conditions (i.e. the starting values for the iterations) is carried out automatically from the form of the potential function while the choice of the algorithm is decided from the knowledge of the functions $p(x)$ and $k(x)$.

So far the program has been tested successfully on various problems such those encountered in this dissertation but also on the hydrogen atom, Airy functions (potential is kx) etc.

Nothing being perfect, some ameliorations are envisaged in a very near future, and the focus will be put on the

extention of the methods on coupled differential equations. An hybrid method between the log-derivative and the VIVAS method(46) has been developed very recently and seems to be at least equivalent in time of computation to the renormalized Numerov's method. Its extention to problems involving non traditional boundary conditions might be an interesting field of exploration in a continuity point of vue with the present work in connection with the numerical solution of the Schroedinger equation of a n-body problem.

APPENDIX 1: VECTOR SPACES.

1. Definitions.

Note: for more details about the material of this appendix, see references (60) and (66).

A vector space over the field K is a nonempty set X of elements (x,y,...) called vectors together with a vetor addition and a multiplication by scalars with their well-known properties. If K = R (reals), the vector space is a real vector space; if K = C (complex numbers), X is a complex vector space.

X' is a proper subspace of X if for any scalars α and β and for any vectors x_1 and x_2, then $\alpha x_1+\beta x_2$ belongs to X'.

A linear combination of the vectors $x_1,\ldots,x_n$ is an expression of the form:

(1) $$V = \Sigma_i \alpha_i x_i .$$

The set of all the linear combinations of the vectors of a subset M of X is the span (span(M)) of M and is a subspace of X. A subset M of X whose elements are $x_1,\ldots,x_r$ is said to be linearly dependent if the expression (1) holds for some

r-tuple of scalars not all zero. If the relation holds for $\alpha_i=0$ (all i), then the subset is linearly independent. If M is linearly dependent, at least one vector of M can be written as a linear combination of the others. For example, if (1) holds for α_r non zero, then

$$x_r = \Sigma_j \beta_j x_j \quad (j=1,\ldots,r-1) \tag{2}$$

where:

$$\beta_j = -\alpha_j/\alpha_r$$

2. Normed Spaces, Riemann spaces and euclidean spaces.

A metric space is a space on which a metric has been defined (that is a distance function). A normed space is a vector space with a metric defined by a norm N(x) with the usual properties of a norm.

The dimension of X is n (the maximum linearly independent vectors). Any subset of n+1 vectors is therefore linearly dependent.

Any set of n linearly independent vectors constitutes a basis for X. For an euclidean vector space, the usual notation is E_n.

If B is a basis for E_n, any vector of E_n has a unique representation as a linear combination of elements of B.

A real n-dimensional vector space could be represented by the set of all the ordered n-tuples of real numbers:

$$E_n = [x=(\alpha^1,\ldots,\alpha^n)] \tag{3}$$

the α^i being the components of x relative to the basis B_n. By convention, the elements of the basis are labeled with subscripts while the components of a vector are labeled with superscripts indices (61).

The canonical basis for E is $[e_i]$ here e_i = $(0,..,1,...,0)$, 1 at the i^{th} slot.

In a n-dimensional space R_n covered by a basis B_n, let us consider a 1-dimensional subspace C_1 determined by $x_i(t)$ where t is a real parameter varying continuously in some interval and i=1,...,n: C_i is called the arc of curve. Let now $f(x_1,...,x_n,x_1,...,x_n)$ be a prescibed function continuous in the interval $[t_1,t_2]$ and viewed as a function of t. The integral:

$$s = \int_{t_2}^{t_1} f(x,x)dt \tag{4}$$

is called the length of C and the space R_n is said to be metrized by the above formula.

A metric can be defined(62) in prescribing that the square of the arc ds is a positive quadratic form in the differentials dx^i:

(5) $$ds^2 = g_{ij}dx^i dx^j$$

where the $g_{ij}(x)$ are continuous functions in R_n. Such a metric vector space is called a Riemannian n-dimensional vector space.

If we can now operate a change of basis in such a way that $ds^2 = dx^i dx^i$, the space R_n is reduced to an euclidean n-dimensional vector space E_n.
The signification of the functions $g_{ij}(x)$ will appear clearly in the appendix 2.

3. Inner product spaces.

E_n is a real inner product space if we define a mapping $E_n X E_n \longrightarrow R$:

(6) $$\langle x,y\rangle = a \in R$$

such that:

(7)
$$\langle x+y,z\rangle = \langle x,y\rangle + \langle y,z\rangle$$
$$\langle \alpha x,y\rangle = \alpha\langle x,y\rangle$$
$$\langle x,y\rangle = \langle y,x\rangle$$
$$\langle x,x\rangle \geqslant 0$$
$$\langle x,x\rangle = 0 \text{ iff } x = 0$$

The norm is defined by:

(8) $$N(x) = [\langle x,x\rangle]^{1/2}$$

x and y are orthogonal iff $\langle x,y\rangle = 0$

x is orthogonal to the subset A if $\langle x,a\rangle = 0$ for all $a \in A$: we write: $x \perp A$

The subsets A and B are orthogonal ($A \perp B$) if $\langle a,b\rangle = 0$ for all $a \in A$ and $b \in B$.

In E_n the inner product is defined by:

(9) $$\langle x,y\rangle = \Sigma_j \xi_j^1 \xi_j^2$$

where $x = (\xi_j^1)$ and $y = (\xi_j^2)$

while the norm is:

(10) $$N(x) = [\Sigma_j (\xi_j)^2]^{1/2} \quad (j=1,\ldots,n)$$

Properties.

(11) $\langle x,y\rangle = 0$ implies that the set $[x,y]$ is linearly independent.

(12) $$N(\alpha x)^2 = \alpha^2 N(x)^2$$

(13) $$\text{abs}(\langle x,y\rangle) \leqslant N(x)N(y)$$ (Schwartz inequality)

(14) $$N(x+y) \leqslant N(x) + N(y)$$ (Triangle inequality)

(15) On any subspace E'_n of E_n the inner product is conserved.

Minimizing vector

Let M a subset of E_n. For any $x \in E_n$ there exists a unique $y \in M$ such that $N(x-y) = \delta$ ($\delta = \inf(N(x-y'))$, for all $y' \in M$). If M is a subspace of E_n then $z = x-y$ is orthogonal to M.

Direct Sum

E_n is the direct sum of two subspaces E' and E" ($E_n = E' + E"$) if each $x \in E_n$ has a unique representation $x = y+z$ ($y \in E'$; $z \in E"$)

The set of all vectors orthogonal to a subspace M of E_n (perp(M)) is the orthogonal complement of M:

(16) $$\text{perp}(M) = [z \in E_n;\ z \text{ orth to } M]$$

Tensor product.

The product $X_1 \otimes X_2 = X$ of two vectors spaces over the same field becomes a vector space if we define the two algebraic operations by:

(17) $$(x_1,x_2) + (y_1,y_2) = (x_1+y_1, x_2+y_2)$$

(18) $$\alpha(x_1,x_2) = (\alpha x_1, \alpha x_2)$$

Quotient space.

Let Y be a subspace of X. The coset of x X with respect to Y is denoted by x+Y and is equal to (v=x+y; $\forall y \in Y$). Under the algebraic operations:

(19) $(w+Y)+(x+Y)=(w+x)+Y$

(20) $\alpha(x+Y)=\alpha x+Y$

these cosets constitute the elements of a vector space called quotient space of X by Y and denoted by X/Y. Its dimension is called codimension of Y and:

(21) $\text{codim}Y = \dim(X/Y)$

Hyperplane

If Y is a subspace of X and codimY = 1, then every element of X/Y is called a hyperplane parallel to Y.

Projection theorem

If M is a subspace of E_n, then $E_n = M + \text{perp}(M)$

The operator P: $E_n \rightarrow M$ such that x $E_n \rightarrow$ y = Px is the projection of E_n onto M

Orthogonal and orthonormal sets

An orthogonal set is a subset of E_n whose elements are pairwise orthogonal.

An orthonormal set M is an orthogonal set whose elements have

norm 1.

Any orthonormal set is linearly independent.

There exists a basis (e_i) of orthonormal vectors for every vector space E_n.

Bessel inequality

(22) $$\Sigma_k \langle x, e_k \rangle^2 < N(x)^2$$

Gram-Schmidt process

An orthonormal set $B = (e_1, \ldots, e_r)$ can be constructed from an arbitrary linearly independent subset $M = (x_1, \ldots, x_r)$ and we have span(M) = span(B).

The construction is as follows:

(23) $$e_1 = x_1/N(x_1)$$

...

(24) $$v_n = [x_n - \Sigma_k \langle x_n, e_k \rangle e_k] \quad (k=1, \ldots, n-1)$$

(25) $$e_n = v_n/N(v_n)$$

The sum substracted on the right-hand side is the projection of x_n on span$(e_1, \ldots, e_{n-1})$.

An orthonormal set M is total in E_n if span(M) = E_n; its dimension is n.

Parseval equality

An orthonormal set M is total iff:

(26) $$\Sigma_k \langle x, e_k \rangle^2 = N(x)^2$$

Parseval relation

(27) $$\langle x, y \rangle = \Sigma_k \langle x, e_k \rangle \langle y, e_k \rangle$$

OPERATORS ON E_n

If x and y are column vectors:

(28) $$\langle x, y \rangle = x^t y$$

Let T a linear operator $E_n \longrightarrow E_n$ and a given basis (e_i):

(29) $$\langle Tx, y \rangle = x^t T^t y$$

If $T^t = T^{-1}$: T is unitary

If $T^t = T$: T is symmetric

If $T^t T = T T^t$: T is normal.

PROPERTIES OF PROJECTIONS.

1) $P^2 = P$

2) $\langle Px, y \rangle = \langle x, Py \rangle$

3) $\langle Px, x \rangle = N(Px)^2$

4) $P_1P_2 = P$ is a projection onto $P_1(E_n) \cap P_2(E_n)$. This is equivalent to $P_1P_2 = P_2P_1$

5) M_1 orthogonal to M_2 is equivalent to $P_1P_2 = \emptyset$

6) $P_1+P_2 = P$ is a projection of E_n onto $P_1(E_n) + P_2(E_n)$ is equivalent to $P_1(E_n)$ orthogonal to $P_2(E_n)$.

7) $P_1P_2 = P_2P_1$ implies $P_1 + P_2 - P_1P_2$ is a projection of E_n onto $M_1 + M_2$.

Invariant subspace.

Let $T: E_n \rightarrow E_n$ be a linear and bounded operator. A subspace M is invariant under T if $T(M) \subset M$ and $T(\text{perp}(M))$ perp(M)

Reduction of an operator

A subspace M of E_n reduces the operator T if M and perp(M) are invariant under T.
If P_1 is the projection of E_n onto M and $P_1T = TP_1$ then M reduces T. We have also $TP_2 = P_2T$ where P_2 is the projection of E_n onto perp(M).

APPENDIX 2: METRIC TENSOR.

We intend here to present some mathematical relations currently used in the study of transformations dealing with non cartesian coordinatess. In such spaces the hamiltonian operator is considerably more complicated to handle and the tensor analysis will give the necessary tools needed in order to perform the calculations. Furthermore working with non orthogonal coordinates systems such those encountered in this report needs necessarily some fundamental results of the study of tensors.

Most of the material of this section comes from the references (61-64)

1.Preliminary definitions.

A point in a n-dimensional space is an ordered n-tuple of scalars: $(x^1,\ldots,x^n)$.

A coordinate transformation is defined by the n independent relations:

$$(\emptyset\text{-}1) \qquad y^i = y^i(x^1,\ldots,x^n) \qquad (i=1,\ldots,n)$$

where the x^j are the coordinates of the point in the original reference frame while the y^i are those of the final frame

If the relations (Ø-1) are single-valued and continuous,

then to each coordinate set (y^j) will correspond a unique set (x^i). These relations define a transformation of coordinates from one frame to another.

We shall use the summation convention which consists of dropping the summation symbol Σ for repeated indices in an expression (dummy index-free index).

Co- and contravariant vectors.

If n quantities $A^1,\ldots,A^n$ in a coordinate system (x^i) are related to n quantities $B^1,\ldots,B^n$ in another coordinate system (y^j) by the relations:

$$(0\text{-}2) \qquad B^p = [\partial y^p/\partial x^q]A^q$$

(where p is the free index and q the dummy index running both from 1 to n) they are called components of a contravariant vector.

Conversely if the quantities A_q are related to the B_p by:

$$(0\text{-}3) \qquad B_p = [\partial x^q/\partial y^p]A_q$$

they are called components of a covariant vector.

These vectors are also called tensors of first rank.

Co- and contravariant tensors.

In a similar manner if n^2 quantities A^{qs} in a coordinate system (x^i) are related to n^2 quantities B^{pr} in another

coordinate system (y^j) by:

$$(0\text{-}4) \qquad B^{pr} = [\partial y^p/\partial x^q][\partial y^r/\partial x^s]A^{qs}$$

they are called contravariant components of a tensor of rank two.

Conversely, if A_{qs} are related to B_{pr} by:

$$(0\text{-}5) \qquad B_{pr} = [\partial x^q/\partial y^p][\partial x^s/\partial y^r]A_{qs}$$

they are the components of a covariant tensor of rank two.

We may also define mixed tensors such the Kronecker delta $\delta^j{}_k$ which is a mixed tensor of rank two.

Tensors of the same rank and type can be added and subtracted component by component.

From the similarity of tensors and matrices, we can define an inner product $A^{mp}{}_q B^r{}_{st}$ and an outer product $C^{prm}{}_{qs} = A^{pr}{}_q B^m{}_s$ of tensors. These operations are commutative and associative.

Matrices and tensors are two different concepts. While they can be compared in some ways, they differ in their fundamental definition and their application. Let u and v be two vectors of the same space S_n and A be a matrix which transforms u into v by v = Au. This relation may be interpreted in a different way. Suppose (u_i) are the components of u in the space S_n where a base (e_i) has been defined and (v_i) are the components of the same vector in S_n but where the base has been changed. Obviously A may be

regarded under the two aspects. In the first case the matrix looks like a tensor of the second rank whereas in the second case the matrix becomes rectangular and cannot therefore be regarded as a tensor. Thus a tensor is always a matrix but a matrix is not necessarily a tensor.

A line element ds is given by the quadratic form (also called metric of the space):

$$(0\text{-}6) \qquad (ds)^2 = g_{pq}dx^p dx^q$$

where g_{pq} is called the metric tensor and constitutes the object of this appendix. If the expression (0-6) can be reduced by some coordinate transformation to a form $dy^k dy^k$, then the space is called n-dimensional euclidean. In the general case, the space is called Riemannian.

Christoffel'symbols.

We define:

$$(0\text{-}7) \qquad [pq,r] = (1/2)(\partial g_{pr}/\partial x^q + \partial g_{qr}/\partial x^p - \partial g_{pq}/\partial x^r)$$

and

$$(0\text{-}8) \qquad \Gamma^s_{pq} = g^{sr}[pq,r]$$

respectivelly called Christoffel symbols of first and second kind.

Covariant derivative.

The covariant derivative of a tensor A_p with respect to x^q is denoted by $A_{p,q}$ and defined by:

(0-9) $$A_{p,q} = \partial A_p/\partial x^q - \Gamma^s_{pq} A_s$$

while the covariant derivative of the tensor A^p with respect to x^q is denoted by $A^p{}_{,q}$ and defined by:

(0-10) $$A^p{}_{,q} = \partial A^p/\partial x^q + \Gamma^p_{qs} A^s$$

For rectangular systems the Christoffel symbols are zero and the covariant derivatives are the usual partial derivatives. The distinction between the two kinds of derivatives is used in non orthogonal coordinates especially in the definition of the Laplacian operator.

2.n-Dimensional euclidean spaces.

Let us consider at first the euclidean n-dimensional space where an orthonormal basis has been defined by: (e_i). The square of the length between two infinitesimally neighbouring points is given by:

(1) $$(ds)^2 = \Sigma_i (dx^i)^2$$

Let us define a new base (E_i) such that:

$$(2) \qquad E_m = \alpha^i{}_m e_i \quad ; \quad e_i = \beta^m{}_i E_m$$

We used here the summation convention in omitting the symbol Σ for repeated indices.
Relative to the new base the components of a vector are given by some single-valued and continuous function:

$$(3) \qquad y^i = y^i(x^1,\ldots,x^n)$$

therefore the old components are given by:

$$(4) \qquad x^i = x^i(y^1,\ldots,y^n)$$

We note here that the vectors which transform under a change of base as the elements of the base are covariant whereas the vectors which transform as the inverse transform are contravariant.

Consider in the vicinity of a point P the infinitesimal distances along the axis:

$$(5) \qquad (dx^i) = \alpha^i{}_m (dy^m) \quad ; \quad (dy^m) = \beta^m{}_i (dx^i)$$

and recall the total derivative relations:

$$(6) \qquad dx^i = \frac{\partial x^i}{\partial y^m} dy^m \; ; \; dy^m = \frac{\partial y^m}{\partial x^i} dx^i$$

The homogeneous quadratic form (1) becomes successively:

$$(7) \qquad (ds)^2 = \alpha^i{}_l \alpha^i{}_m dy^l dy^m$$

$$= \frac{\partial x^i}{\partial y^m} \frac{\partial x^i}{\partial y^l} dy^l dy^m$$

$$= g'_{lm} dy^l dy^m$$

where

$$(8) \qquad g'_{lm} = g'_{ml} = \alpha^i{}_l \alpha^i{}_m$$

$$= \frac{\partial x^i}{\partial y^m} \frac{\partial x^i}{\partial y^l}$$

We have therefore the following correspondence:

$$\alpha^i{}_m = \partial x^i / \partial y^m \quad ; \quad \beta^m{}_k = \partial y^m / \partial x^k$$

There exists obviously $n(n+1)/2$ independent components g'_{lm}.

For example, in a 3-d space we have:

$$(9) \qquad (ds)^2 = g_{11}(dx^1)^2 + g_{22}(dx^2)^2 + g_{33}(dx^3)^2 + 2g_{12}dx^1dx^2$$
$$+ 2g_{23}dx^2dx^3 + 2g_{13}dx^1dx^3$$

3. Riemannian spaces and the metric tensor (g_{ij}).

Let dx^i be the components of an infinitesimal vector at the point $P(x^1,\ldots,x^n)$; we have seen that the infinitesimal length of arc is given by:

$$(10) \qquad (ds)^2 = g_{ik}dx^i dx^k \qquad (g_{ik} = g_{ki})$$

The components g_{ik} are functions of the point P and it is easy to see that $(ds)^2$ is a scalar invariant under any change of base. Since the dx^i and dx^k are contravariant, the g_{ik} form a symmetric covariant tensor called the metric tensor in Riemannian spaces.

We have the relations:

$$(11) \qquad g'_{lm} = g_{ik}\alpha^i{}_l\alpha^k{}_m$$

and

$$(12) \qquad g_{ik} = \beta^l{}_i\beta^m{}_k g'_{lm}$$

For example in a 3-d euclidean space with an orthonormal base, the tensor takes the simple form:

$$(13) \qquad g_{ik} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Let g be the determinant of the tensor (g_{ik}). We define the contravariant components of the tensor (g^{ik}) by:

(14) $$g^{ik} = G_{ik}/g$$

where G_{ik} is the minor corresponding to the element g_{ik} of the covariant tensor. Obviously g is an invariant and is different from zero.

The difference between the concepts of covariance and contravariance will become clearer with the following simple example.

Let us consider 3-dimensional curvilinear non orthogonal coordinates. Let q be a vector with components (q^1, q^2, q^3). An infinitesimal displacement dq is expressed in terms of the base vectors (not necessarily of norm 1) by:

$$dq = e_i dq^i$$

where $e_i = \partial q/\partial q^i$

e_i are then the base vectors directed along the tangent of the coordinates curves. Any vector A is expressed in the same way by:

$A = a^i e_i$ (a^i are the contravariant components of A).

We define now the three vectors e^i as the vector products of e_j and e_k divided by the triple product $[e_1e_2e_3] = v$:

$$e^1 = e^2 \times e^3 / v$$
$$e^2 = e^3 \times e^1 / v$$
$$e^3 = e^1 \times e^2 / v$$

These three vectors e^i are orthogonal to the planes defined by e_j and e_k and we have:

$$e_m e^n = \delta^m{}_n$$
$$e_i = e^j \times e^k / v' \quad (v' = [e^1 e^2 e^3])$$

The two bases are reciprocal and we can write:

$$dq = e^i dq_i$$
$$A = a_i e^i \quad (a_i \text{ being the covariant components of } A)$$

We can now deduce the following identities:

$$dq^i = e^i e^j dq_j$$
$$dq_j = e_j e_i dq^i$$

therefore

$$(ds)^2 = e_i e_j dq^i dq^j = e^i e^j dq_i dq_j$$

Finally:

$$g_{ij} = e_i e_j \quad ; \quad g^{ij} = e^i e^j$$
$$A = a_i e^i = a^j e_j$$

The two formulations of a same system is motivated in the case of non orthogonal coordinates; if the system of coordinates is orthogonal they are identical since the two reciprocal bases are the same.

The following useful relations may be derived from the above without difficulty:

(15) $g_{ik}g^{jk} = \delta_{ij}$

(16) $g_{ik}g^{il} = \delta_{kl}$

(17) $g'^{lm} = \beta^l{}_i \beta^m{}_k g^{ik}$

(18) $g^{ik} = \alpha^i{}_l \alpha^k{}_m g'^{lm}$

(19) $\det(g^{ik}) = g^{-1}$

In a change of axes the determinant g is transformed according to:

(20) $g' = \Delta^2 g$

where Δ is the determinant of the α's.

4.Examples.

Two relevant illustrations will be treated in this section in order to show how the metric tensor constitutes a useful tool in coordinate transformations. In the first example we concern ourselves with rectilinear non-orthogonal coordinates and transform them into an orthogonal system. In the second example we illustrate the use of g_{ij} for curvilinear orthogonal coordinates (spherical and cylindrical coordinates).

a) Non-orthogonal rectilinear coordinates in the plane.

From the figure (A-1-a) we can write:

$$OQ = x^1 e_1 \qquad OP = x^2 e_2$$

$$OQ' = y^1 E_1 \qquad Q'P = y^2 E_2$$

$$= (x^1 + x^2 \cos\theta_{12} E_1) \qquad = x^2 \sin\theta_{12} E_2$$

The transformation relations between the coordinates become:

$$y^1 = x^1 + x^2 \cos\theta_{12}$$

$$y^2 = x^2 \sin\theta_{12}$$

Therefore:

FIGURE (A-1-a)

Non-orthogonal rectilinear coordinates in the plane. Transformation into an orthogonal system.

Non-orthogonal rectilinear coordinates in the plane.

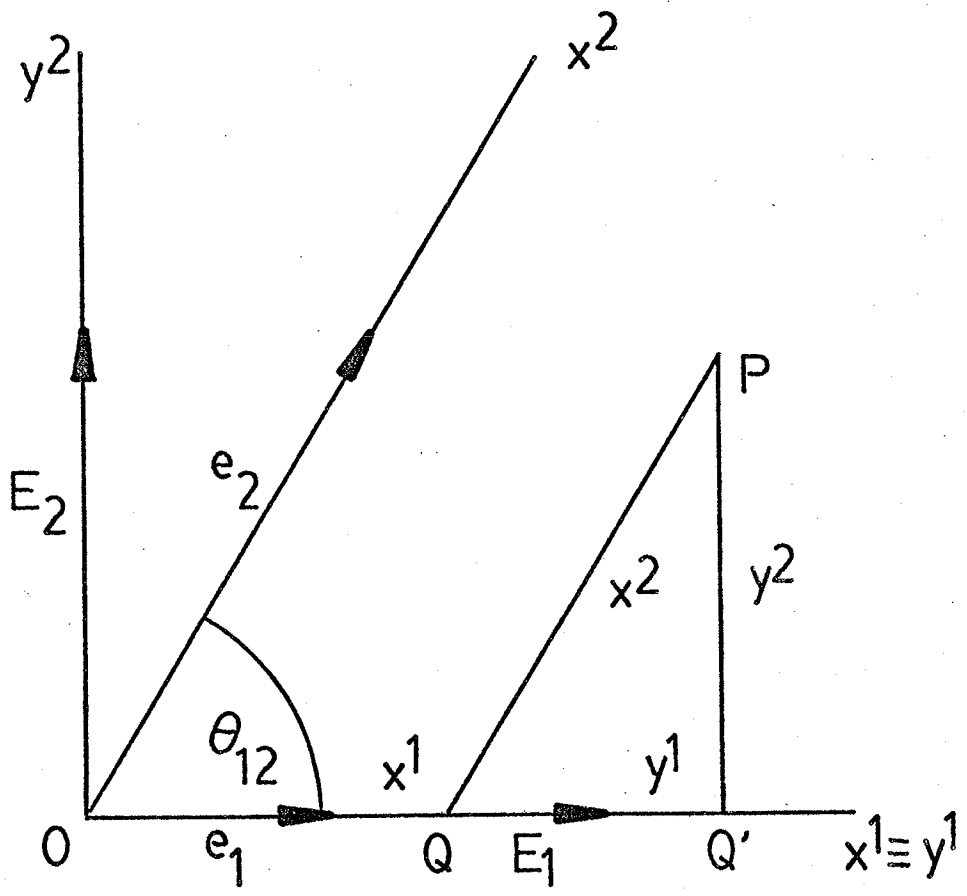


FIG.(A-1.a)

$$OP^2 = (e_1x^1)^2 + (e_2x^2)^2 + 2e_1e_2x^1x^2\cos\theta_{12}$$
$$= (E_1y^1)^2 + (E_2y^2)^2$$

From the definition of $(ds)^2$, we have:

$$(21) \qquad (ds)^2 = g_{11}(dx^1)^2 + g_{22}(dx^2)^2 + 2g_{12}dx^1dx^2$$
$$= g'_{11}(dy^1)^2 + g'_{22}(dy^2)^2$$

The elements of the metric tensor are therefore given by:

$$(22) \qquad g_{11} = (e_1)^2 \quad g_{22} = (e_2)^2 \quad g_{12} = e_1e_2\cos\theta_{12}$$
$$g'_{11} = (E_1)^2 \; g'_{22} = (E_2)^2 \; g'_{12} = 0$$

We conclude that in non orthogonal rectilinear coordinate systems, the tensor is not diagonal but the components g_{ij} are constants: the tensor is independent of the point of the space where it is calculated. If the system is orthogonal the tensor is diagonal.

b) Orthogonal curvilinear coordinates.

In curvilinear coordinates the unit vectors are not necessarily constants and therefore the components g_{ij} depend upon the point where the tensor is evaluated. As a first example, let us work out the cylindrical coordinates $x^1=r$, $x^2=\theta$ and $x^3=z$. The transformation relations are:

$x = r\cos\phi \qquad y = r\cos\phi \qquad z = z$

The three orthogonal infinitesimal displacements at the point P are respectively dr, rdθ and dz from which we can deduce the local units: $e_1 = 1$; $e_2 = r$ and $e_3 = 1$. Then:

(23) $\qquad (ds)^2 = dr^2 + r^2 d\theta^2 + dz^2$

and the elements of the metric tensor are:

$g_{11} = g_{33} = 1 \qquad g_{22} = r^2 \qquad g_{ij} = 0$ for i different of j.

The determinant g is equal to r^2.
In spherical coordinates $x^1=r$, $x^2=\theta$ and $x^3=\phi$ the transformation relations are:

$x = r\sin\theta\cos\phi \qquad y = r\sin\theta\sin\phi \qquad z = r\cos\theta$

The displacements dr, dθ and dφ are orthogonal with local unit length:

$e_1 = 1 \qquad e_2 = r \qquad e = r\sin\theta$

The g_{ij} are therefore given by:

$g_{11} = 1 \qquad g_{22} = r^2 \qquad g_{33} = r^2\sin^2\theta \qquad g_{ij} = 0$ for i different of j.

The determinant g is equal to $r^4 \sin^2\theta$.

The other types of curvilinear coordinates are treated in the same fashion. The diagonal form of the tensor in these coordinates indicates again the orthogonality of the coordinates. Nevertheless the elements g_{ij} are not constant along the non rectilinear axes and the tensor depends of the point P.

5. Interpretation of the components g_{ij}.

In orthogonal coordinates if $e_1,\ldots,e_n$ are the local units, the variations $dx^1,\ldots,dx^n$ give orthogonal segments with true length $dl_1,\ldots,dl_n$ such that: $dl_i = e_i dx^i$. The local units are some functions of the coordinates x^i and we have then:

$$(24) \qquad (ds)^2 = (e_i dx^i)^2$$

The g_{ik} are then simply:

$$(25) \qquad g_{ik} = (e_i)^2 \delta_{ik}$$

while the determinant is:

$$(26) \qquad g = (e_1 . e_2 \ldots . e_n)^2$$

Conversely the contravariant components are:

$$(27) \qquad g^{ik} = 1/(e_i)^2$$

and the determinant

$$(28) \qquad \det(g^{ik}) = (e_1^{-1}...e_n^{-1})^2$$

Let us consider the general case:

$$(29) \qquad (ds)^2 = g_{ik}dx^i dx^k$$

Along an axis k with some unit e_k a variation dx_k corresponds to a real length $dl_k = e_k dx^k$. Taking $dx^i = 0$ for i different of k, (29) becomes:

$$(30) \qquad g_{kk} = (e_k)^2 \quad \text{or} \quad e^k = (g_{kk})^{1/2} = (g_{kk})^{1/2}$$

In a similar way consider the plane (i,k) then $dx^j = 0$ for j different of i and k and:

$$(31) \qquad (ds)^2 = g_{ii}(dx^i)^2 + g_{kk}(dx^k)^2 + 2g_{ik}dx^i dx^k$$

Comparing this relation with (21) permits us to conclude that for infinitesimally small displacements the axes are not orthogonal and their angle is given by:

(32) $g_{ik} = e_i e_k \cos\theta_{ik} = [g_{ii} g_{kk}]^{1/2} \cos\theta_{ik}$

The elements of the metric tensor are then functions of the local units e_i and the angles between the axes in rectilinear coordinates or the angles between the local tangents in curvilinear coordinates.

6. Norm and scalar product.

Let u be a vector with covariant components u_i and contravariant components u^k; The following relations are easy to derive:

(33 $u_i = g_{ik} u^k \quad u^k = g^{jk} u_j$

(34) $dx^i = g_{ik} dx^k \quad dx^j = {}^{ji} dx_i$ (35) $(ds)^2 = g_{ik} dx^i dx^k = g^{ij} dx_i dx_j = dx^i dx_i$

We define the norm of u (62) by:

(36) $u^2 = g_{ik} u^i u^k = g^{ij} u_i u_j = u^i u_i$

The scalar product is defined by:

(37) $\langle u,v \rangle = u_i v^i = g_{ik} u^k v^i = u^k v_k = g^{jk} u_j v_k$

From this we deduce the angle between two vectors u and v by:

(38) $\cos(u,v) = g_{ik}u^i v^k / [g_{ik}u^i u^k g_{ik}v^i v^k]^{1/2}$

In particular, the angle between the axes 1 and 2 is :

(39) $\cos\theta_{12} = g_{12}/[g_{11}g_{22}]^{1/2}$

7. Volume element and Laplacian.

The volume element is given by:

(40) $dV = g^{1/2}dx^1 \ldots dx^n$

For example in spherical coordinates since $g^{1/2} = r^2\sin\theta$, $dV = r^2\sin\theta dr d\theta d\phi$ whereas in cylindrical coordinates where $g^{1/2} = r$, $dV = r dr d\theta dz$.

In orthogonal cartesian coordinates the Laplacian operator over a scalar V is:

(41) $V = \Sigma_k (\partial^2 V/(\partial x_k)^2)$

and the general form is:

(42) $V = g^{-1/2}(\partial/\partial x^i)[g^{1/2}g^{ik}(\partial V/\partial x^k)]$

The Laplacian permits us now to derive the expression for the hamiltonian in any system of coordinates. Some applications of this derivation are currently used in the

third chapter of this report.

8. Reduction to the diagonal form of the metric tensor.

We recall that an euclidean space is a space where the g_{ik} are constant. Furthermore if the metric tensor is diagonal the space is referred to orthogonal coordinates. We intend here to find a way to reduce a non diagonal tensor into a diagonal, in other words to transform non orthogonal coordinates into orthogonal euclidean space (cartesian space).

Let us take some direction as a new axis y^1. For a small displacement dy^1 we have ds^2. Let us choose a unit vector on y^1 of norm 1. Therefore:

$$(43) \qquad E_1 = \alpha^k{}_1 e_k \qquad dx^i = \alpha^i{}_1 dx^1$$

and

$$(44) \qquad (ds_1)^2 = g_{ik}\alpha^i{}_1\alpha^k{}_1 (dy^1)^2 = (dy^1)^2$$

therefore

$$(45) \qquad g_{11}{}^1 = g_{ik}\alpha^i{}_1\alpha^k{}_1 = 1$$

Let δx now be the infinitesimal vector with a component δy^1 along E_1 and a component δx^* in a $(n-1)$-dimensional space,

orthogonal to y^1.

Therefore

$$(46) \qquad \delta x = \delta y^1 + \delta x^* \quad ; \quad \langle \delta x^*, E_1 \rangle = 0$$

The length of δx is given by:

$$(47) \qquad (\delta s)^2 = g_{ik}[\alpha^i{}_1 \delta y^1 + \delta x^{*i}][\alpha^k{}_1 \delta y^1 + \delta x^{*k}]$$
$$= g'_{11}(\delta y^1)^2 + g_{ik}\delta x^{*1}\delta x^{*k}$$

Continuing in the same way we reduce step by step the space into an orthogonal space with new axes y^i which will decompose $(ds)^2$ into

$$(48) \qquad (ds)^2 = g'_{kk}(dy^k)^2 \qquad (g'_{kk} = 1)$$

This space is called the tangent euclidean space.

APPENDIX 3: FINITE DIFFERENCE FORMULAS.

Consider the set (f_n) where f_n corresponds to a discretization of the function $f(x)$ at the point x_n. The value of the function at x_{n+1} is related to the value at x_n by the Taylor series relation:

$$(1) \quad f_{n+1} = [1 + hD + (h^2/2!)D^2 + \ldots]f_n$$
$$= \exp(hD)f_n$$
$$= Ef_n$$

where D is the differential operator d/dx.

We define the following operators:

$$(2) \quad f_{n+1} - f_n = \Delta f_n \quad \text{:forward-difference}$$
$$(3) \quad = \nabla f_{n+1} \quad \text{:backward-difference}$$
$$(4) \quad = \delta f_{n+1/2} \quad \text{:central-difference}$$
$$(5) \quad [f_{n-1/2} + f_{n+1/2}] = 2\mu f_n \quad \text{:averaging}$$

The following properties are easily derived:

$$(6) \quad E - 1 = \Delta = \nabla E = \delta E^{1/2} = e^{hD} - 1$$

$$(7) \quad \delta = E^{1/2} - E^{-1/2} = \exp(hD/2) - \exp(-hD/2) = 2\sinh(hD/2)$$

$$(8) \quad \nabla = 1 - E^{-1} = 1 - e^{-hD}$$

$$(9) \quad 2\mu = \exp(hD/2) + \exp(-hD/2) = \cosh(hD/2)$$

(10) $E^{1/2} = \mu + \delta/2$

(11) $\mu^2 = 1 + \delta^2/4$

Using these operators and the relations between them we can establish finite difference formulas for interpolation, differentiation and integration with forward, backward and central differences.

1. Interpolation formulas.

For p non integral:

(12) $y(x+ph) = E^p y(x) = (1+\Delta)^p y(x)$

$= y(x) + p\Delta y(x) + [p(p-1)/2!]\Delta^2 y(x) + \ldots$

(13) $= E^p y(x) = (1-\nabla)^{-p} y(x)$

$= y(x) + p\nabla y(x) + [p(p+1)/2!]\nabla^2 y(x) + \ldots$

Using central differences:

(14) $= y(x) + p\delta y(x+h/2) + [p(p-1)/2.2!][\delta^2 y(x) + \delta^2 y(x+h)] + [p(p-1)(p-1/2)/3!]\delta^3 y(x+h/2) + \ldots$

2. First derivative formulas.

(15) $hy'_n = (\Delta - \Delta^2/2 + \Delta^3/3 - \Delta^4/4 + \ldots)y_n$

(16) $= (\Delta + \Delta^2/2 - \Delta^3/6 + \Delta^4/12 - \Delta^5/20 + \ldots)y_{n-1}$

(17) $= (\Delta + 3\Delta^2/2 + \Delta^3/3 - \Delta^4/12 + \Delta^5/30 - \ldots)y_{n-2}$

For the backward difference we change the sign of even differences and the suffixe and replace Δ by ∇.

For central difference:

$$(18) \quad hy'_n = (\mu\delta - \mu\delta^3/6 + \mu\delta^5/30 - \mu\delta^7/140 + \ldots)y_n$$

$$(19) \quad hy'_{n+1/2} = (\delta - \delta^3/24 + 3\delta^5/640 - \ldots)y_{n+1/2}$$

3.Second derivative formulas.

$$(20) \quad h^2y''_n = (\Delta^2 - \Delta^3 + 11\Delta^4/12 - 5\Delta^5/6 + 137\Delta^6/180 - \ldots)y_n$$

$$(21) \quad = (\Delta^2 - \Delta^4/12 + \Delta^5/12 - 13\Delta^6/180 + \ldots)y_{n-1}$$

$$(22) \quad = (\Delta^2 + \Delta^3 - \Delta^4/12 + \Delta^6/90 - \ldots)y_{n-2}$$

For the backward difference, change the sign of odd differences and the suffixe and replace Δ by ∇.

For central difference:

$$(23) \quad h^2y''_n = (\delta^2 - \delta^4/12 + \delta^6/90 - \delta^8/560 + \ldots)y_n$$

4.Reversion of derivative formulas.

$$(24) \quad y_{n+1} - y_n = (1 + \Delta/2 - \Delta^2/12 + \Delta^3/24 - 19\Delta^4/720 + \ldots)hy'_n$$

$$(25) \quad = (1 - \nabla/2 - \nabla^2/12 - \nabla^3/24 - 19\nabla^4/720 - \ldots)hy'_{n+1}$$

(26) $y_{n+1} - y_{n-1} = 2(1 + \delta^2/6 - \delta^4/180 + \delta^4/1512 - \ldots)hy'_n$

(27) $y_{n+1} - 2y_n + y_{n-1} = (1 + \delta^2/12 - \delta^4/240 + \ldots)h^2y''_n$

5.Lagrangian formulas.

We recall here the most important formulas expressed with a difference correction $O(\delta^n)$

Interpolation at midpoint

(27) $y_{n+1/2} = (1/2)(y_n + y_{n+1}) + O(\delta^2)$

(28) $= -(1/16)(y_{n+2} - 9y_{n+1} - 9y_n + y_{n-1}) + O(\delta^4)$

Differentiation

(29) $hy'_n = (1/2)(y_{n+1} - y_{n-1}) + O(\delta^3)$

(30) $= -(1/12)(y_{n+2} - 8y_{n+1} + 8y_{n-1} - y_{n-2}) + O(\delta^5)$

(31) $h^2y''_n = y_{n+1} - 2y_n + y_{n-1} + O(\delta^6)$

(32) $= -(1/12)(y_{n+2} - 16y_{n+1} + 30y_n - 16y_{n-1} + y_{n-2}) + O(\delta^6)$

Simpson's rule.

(33) $(3/h)\int_{x_0}^{x_{2n}} ydx = y_0 + 4y_1 + 2y_2 + 4y_3 + 2y_4 + \ldots$

$+ 2y_{2n-2} + 4y_{2n-1} + y_{2n}$

6.The Newton-Raphson method.

Let a scalar function $\phi(x) = 0$ which zeroes have to be calculated. Expandin in series around x_0 gives:

(34) $\phi(x) = 0 = \phi(x^{(0)}) + \phi'(x^{(0)})(x-x^{(0)}) + \ldots$

where $x^{(0)}$ is a trial solution. Let x^* a real solution, then:

(35) $x^{(k+1)} = x^{(k)} - \phi(x^{(k)})/\phi'(x^{(k)})$ $(k=0,1,\ldots)$

and

(36) $\lim x^{(k)} = x^*$ $(k \longrightarrow \text{infinity})$

Let us mention two second order methods obtained in dropping the terms of degree higher than 2:

Method of tangent parabolas

(37) $x^{(k+1)} = x^{(k)} - [\phi'(x^{(k)})^{-1}\phi(x^{(k)}) + (1/2)\phi'(x^{(k)})^{-1}\phi''(x^{(k)})(X^{(k+1)} - x^{(k)})^2]$

where

(38) $$x^{(k+1)} = x^{(k)} - \phi'(x^{(k)})^{-1}\phi(x^{(k)})$$

Method of tangent hyperbolas.

(39) $$x^{(k+1)} = x^{(k)} - [\phi'(x^{(k)}) + (1/2)\phi''(x^{(k)})(x^{(k+1)} - x^{(k)}]^{-1}]\phi(x^{(k)})$$

APPENDIX 4: JACOBI MATRICES.

1.Diagonally dominant matrices.(65)

A matrix A is reducible if there exists a nxn permutation matrix P such that:

$$(1) \qquad PAP^T = \begin{bmatrix} A_{11} & A_{12} \\ \emptyset & A_{22} \end{bmatrix}$$

where A_{11} is a rxr matrix, A_{12} a rx(n-r) matrix, A_{22} a (n-r)x(n-r) matrix and $\emptyset$ the (n-r)xr zero matrix. A matrix which is not reducible is irreducible.

A matrix $A = (a_{ij})$ is diagonally dominant if:

$$(2) \qquad [a_{ii}] >= \Sigma_j [a_{ij}] \quad (i=1,2,\ldots,n;\ j=1,\ldots,n;\ j=i)$$

If strict equality holds then A is stricly diagonally dominant. If A is irreducible and strictly diagonally dominant, then A is irreducibly diagonally dominant.

Theorem 1

A nxn matrix A either strictly diagonally dominant or irreducibly diagonally dominant is non singular (A^{-1} exists)

2. Monotone matrices (65)

A nxn matrix $A = (a_{ij})$ is said to be monotone if $Ax \geq 0$ implies $x \geq 0$ where x is a vector of components $x_1, \ldots, x_n$. Monotones matrices have well-known properties stated below:

1. A monotone matrix is non-singular
2. A matrix A is monotone iff $A^{-1} \geq 0$. Note that A^{-1} may not be monotone in general unless A is diagonal.
3. If A and B are monotone then so are AB and BA
4. Let A be an irreducible matrix satisfying:

$$\text{i)} \quad a_{ij} < 0 \quad i \neq j \quad (i,j=1,2,\ldots,n)$$

$$\text{ii)} \quad \Sigma_{j \neq i} a_{ij} \leq 0 \quad i=1,\ldots,n$$

$$< 0 \quad \text{for at least one } i$$

then A is monotone.

5. If A and B are monotone and $A \geq B$ then $A^{-1} \leq B^{-1}$.
6. If the matrix M satisfies $M_1 \leq M \leq M_2$ where M_1 and M_2 are monotone then M is also monotone.

Tridiagonal matrices (Jacobi). (27)

In the numerical treatment of linear systems, a coefficient matrix which occurs frequently is the tridiagonal matrix (or Jacobi matrix) in which:

(3) $a_{ij} = 0$ if $[i-j]>1$

These matrices can be factored in a bidiagonal form:

(4) $A = LU$

where

$$A = \begin{bmatrix} a_1 & c_1 & 0 & & & \\ b_2 & a_2 & c_2 & 0 & & \\ & \ddots & \ddots & \ddots & & \\ & & & b_{n-1} & a_{n-1} & c_{n-1} \\ & & & & b_n & a_n \end{bmatrix}$$

$$L = \begin{bmatrix} \alpha_1 & 0 & & & \\ b_2 & \alpha_2 & 0 & & \\ & \ddots & \ddots & \ddots & \\ & & b_n & \alpha_n & \end{bmatrix}$$

$$U = \begin{bmatrix} 1 & \gamma_1 & 0 & & \\ & 1 & \gamma_2 & 0 & \\ & & \ddots & \ddots & \\ & & & & \gamma_{n-1} \\ & & & & 1 \end{bmatrix}$$

We find:

(5) $\alpha_1 = a_1 \quad ; \quad \gamma_1 = c_1/\alpha_1$

(6) $\alpha_i = a_i - b_i \gamma_{i-1} \quad ; \quad i=2,3,\ldots,n$

(7) $\gamma_i = c_i/\alpha_i \quad ; \quad i=2,3,\ldots,n-1$

Thus if none of the α_i vanish the factorization is accomplished by evaluatin the preceding recursions. Since the problem of solving a general linear system is to find a vector x which satisfies:

(8) $Ax = f$

where A is a square matrix and f an arbitrary n-component column vector, therefore an "intermediate" solution g of $Lg = f$ becomes:

(9) $g_1 = f_1/\alpha_1 \quad ; \quad g_i = (f_i - b_i y_{i-1})/\alpha_i \quad (i=2,\ldots,n)$

and the "final" solution x of $Ux=g$ is given by:

(10) $x_n = g_n \quad ; \quad x_j = g_j - \gamma_j x_{j+1} \quad (j=n-1,\ldots,1)$

In many of the applications the elements of A satisfy:

(11) $[a_i] > [c_1] > 0$

(12) $[a_i] > [b_i] + [c_i] \quad (b_i c_i = 0) \; ; \; i=2,3,\ldots,n-1$

(13) $[a_n] > [b_n] > 0$

Theorem 2.

If the elements of a Jacobi matrix satisfies the relations (11), (12) and (13) then A is non singular and the following inequalities hold:

(14) $[\gamma_i] < 1 \; ; \; [a_i]-[b_i]<[\alpha_i]<[a_i]+[b_i]$

It should be noted that when the conditions (11) to (13) hold the procedure described in (5) to (7) must be valid. Furthermore if $b_i c_i=0$ for some i=1,n, then the system can be reduced to two systems which are essentially uncoupled. If c_1 or b_n are zero, x_1 or x_n can be eliminate to get a reduced system. The operational count is 5n-4 operations to solve a single system.

APPENDIX 5.

PRINCIPAL AXES OF INERTIA OF THE THREE BODY SYSTEM.

Let three masses m_1, m_2 and m_3 lying in the plane OXY (Figure 2-1), the center of mass of the system is taken as origin of a fixed coordinate system O'xy parallel to the reference system OXY and will be used to calculate the principal moments and principal axes of inertia.
Obviously Oz is a principal axe of inertia while the two other ones are two perpendicular axes in the plane O'xy and making some angle θ with the axes Ox and O'y.
The inertia momentum and products relative to O'xy are:

$$(2\text{-}1) \quad I_{xx} = m_1 y_1^2 + m_2 y_2^2 + m_3 y_3^2$$

$$(2\text{-}2) \quad I_{yy} = m_1 x_1^2 + m_2 x_2^2 + m_3 x_3^2$$

$$(2\text{-}3) \quad I_{zz} = m_1 (x_1^2 + y^2) + m_2 (x_2^2 + y_2^2) + m_3 (x_3^2 + y_3^2)$$

$$(2\text{-}4) \quad I_{xy} = I_{yx} = -(m_1 x_1 y_1 + m_2 x_2 y_2 + m_3 x_3 y_3)$$

$$(2\text{-}5) \quad I_{xz} = I_{zx} = I_{yz} = I_{zy} = 0$$

The secular equation becomes here:

$$(2\text{-}6) \quad (I_{zz} - I)[(I_{xx} - I)(I_{yy} - I) - I_{xy}^2] = 0$$

The three real roots are given by:

(2-7) $I_{(1,2)} = 1/2[I_3 \pm ((I_{xx}-I_{yy})^2+4I_{xy}^2)^{1/2}]$

(2-8) $I_3 = I_{zz} = I_{xx} + I_{yy} = I_1 + I_2$

Since the inertia tensor is diagonal relatively to the principal axes, all we have to do in order to determine the directions of the principal axes is to find a rotation of angle θ such that $[I']$ obeys to the relation:

(2-9) $[I'] = \lambda[I]\lambda^t$

where λ is the rotation matrix in the 3 dimensional space. Performing the calculations leads to the following relations:

(2-10) $I_1 = I_{xx}\cos^2\theta + I_{yy}\sin^2\theta + 2I_{xy}\sin\theta\cos\theta$

(2-11) $I_2 = I_{xx}\sin^2\theta + I_{yy}\cos^2\theta - 2I_{xy}\sin\theta\cos\theta$

(2-12) $I_3 = I_{zz}$

(2-13) $0 = \cos\theta\sin\theta(I_{yy}-I_{xx}) + (\cos^2\theta - \sin^2\theta)I_{xy}$

From equation(2-13), we find the relation giving the angle θ:

(2-14) $$tg2\theta = \frac{2[m_1x_1y_1+m_2x_2y_2+m_3x_3y_3]}{m_1(x_1^2-y_1^2)+m_2(x_2^2-y_2^2)+m_3(x_3^2-y_3^2)}$$

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