ALGORITHMS FOR THE SOLUTION OF SYSTEMS OF COUPLED SECOND ORDER ORDINARY DIFFERENTIAL EQUATIONS

by

BRENDAN B. O'SHEA
Royal Holloway College
University of London

Submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

ABSTRACT

The close-coupling approximation method involves the numerical solution of systems of coupled second order ordinary differential equations. The solutions can display instability which is made apparent by dependence of the resonance energy on H (step-size). This instability has been examined and corrected. The comparative efficiency, time-wise and storage-wise, of a number of algorithms for the integration of the system of equations is presented.

ACKNOWLEDGEMENTS

I wish to extend my thanks to Prof. K. Smith for his generous encouragement and assistance. I also wish to acknowledge my indebtedness to Dr. Bradburn, Royal Holloway College, Computing Centre University of Nebraska and the Department of Computer Science, University of Nebraska for the facilities they offered me. Finally I thank Prof. L. Lipsky, University of Nebraska, and Alan Davies, Royal Holloway College for helpful conversations that I had with them.

CONTENTS

CHAPTER 5

CHAPTER 6

LIST OF TABLES

LIST OF FIGURES

LIST OF GRAPHS

CHAPTER 1

CLOSE-COUPLING APPROXIMATION

In order to calculate the cross-section for any scattering process, within the frame-work of non-relativistic wave mechanics, it is necessary to approximate the Schroedinger equation

$$H\psi = E\psi \tag{1.1}$$

One of the most useful approximation schemes is to expand the overall wave function of the system, consisting of the projectile plus target, in terms of the complete set of eigenstates of the target Hamiltonian. This method, called the Close-Coupling Method, was first introduced by Massey and Mohr [1] and has since been shown by Feshbach[2-4] to give rise naturally to resonances of the closed channel type. In numerical calculations [5-35] only a few of the lower stationary, or bound, states of the target are retained in the expansion, for obvious practical reasons.

The Hamiltonian for an electron colliding with an atomic system, having N electrons and nuclear charge Z, neglecting magnetic and relativistic effects, is

$$H = \sum_{i=1}^{N+1} H_1(i) + \sum_{i<j}^{N+1} \frac{1}{r_{ij}} \tag{1.2}$$

where $H_1(i) = -1/2\ (\nabla_i^2 + \frac{2Z}{r_i})$

$$r_{ij} = |\underline{r}_i - \underline{r}_j| \ .$$

Since spin orbit coupling is neglected, the total orbital angular momentum and total spin are separately conserved; consequently, calculations may be simplified by using a representation which is diagonal in L, S, π. The unsymmetrized wave function for the N+1 electron system may be written [36]

$$\psi_u = \sum_{\gamma_T} \psi(\gamma_T, \underline{X}_N)\ \overline{F}_{\gamma_T}(x_{N+1}) \tag{1.3}$$

where $\underline{X}_{N+1}$ denotes the coordinates $\underline{x}_1\underline{x}_2\ldots\underline{x}_{N+1}$ and $\underline{x}_k = \underline{r}_k\sigma_k$, i.e. the space and spin variables of the k^{th} electron. We now expand the continuum wave functions $\overline{F}_{\gamma_T}(\underline{x}_{N+1})$ as

$$\overline{F}_{\gamma_T}(\underline{x}_{N+1}) = \sum_{\substack{\ell_T m_S \\ m_T}} f_{\gamma_T \ell_T m_T m_S}(r_{N+1})\ Y_{\ell_T m_T}(\hat{r}_{N+1})\chi_{1/2}^{m_S}(\sigma_{N+1})\ r_{N+1}^{-1} \tag{1.4}$$

Hence, substitution of (1.4) into (1.3) gives

$$\psi_u(\underline{X}_{N+1}) = \sum_{\substack{\gamma_T\ \ell_T \\ m_T\ m_S}} \psi(\gamma_T, \underline{X}_N)\, Y_{\ell_T m_T}(\hat{r}_{N+1})\,\chi_{1/2}^{m_S}(\sigma_{N+1})\ f_{\substack{\gamma_T \ell_T \\ m_T m_S}}(r_{N+1})\, r_{N+1}^{-1} \tag{1.5}$$

The angular and spin parts of $\overline{F}_{\gamma_T}(\underline{x}_{N+1})$ are now coupled to those of $\psi(\gamma_T, \underline{X}_N)$ to give a new basis function

$\psi(\Gamma;\ \underline{X}_N,\ \hat{x}_{N+1})$ where Γ denotes the complete set of quantum numbers,

i.e. $\Gamma = \gamma_T \ell_T L M_L S M_S \pi$.

Since

$$\psi(\gamma_T,\ \underline{X}_N)\,\chi^{m_S}_{1/2}(\sigma_{N+1})\,Y_{\ell_T m_T}(\hat{r}_{N+1}) = \sum_{\substack{LM_L\\ SM_S}} (L_T \ell_T M_T m_T | LM_L)$$

$$\times (S_T 1/2 M_{S_T} m_S | SM_S)\,\psi(\Gamma;\ \underline{X}_N\ \hat{x}_{N+1})$$

we get from (1.5)

$$\psi_u(\underline{X}_{N+1}) = \sum_\Gamma \psi\ (\Gamma;\ \underline{X}_N\ \hat{x}_{N+1})\ \frac{\tilde{F}_\Gamma(r_{N+1})}{r_{N+1}} \qquad (1.5a)$$

where

$$\tilde{F}_\Gamma(r_{N+1}) = \sum_{m_S m_T} (L_T \ell_T M_{L_T} M_T | LM_L)$$

$$\times\ (S_T 1/2 M_{S_T} m_S | SM_S)\, f_{\gamma_T \ell_T m_T m_S}(r_{N+1}) \qquad (1.6)$$

In the asymptotic region we require

$$\tilde{F}_\Gamma(r) \sim A_\Gamma e^{-i\theta_\Gamma} - B_\Gamma e^{i\theta_\Gamma} \qquad (1.7)$$

where

$$\theta_\Gamma = k_\Gamma r - 1/2 \ell_\Gamma \pi - \frac{Z-N}{k_\Gamma} \log(2k_\Gamma r)$$

$$+ \operatorname{Arg}[\Gamma(\ell_\Gamma + 1 - i(Z-N)/k_\Gamma]$$

The relationship between A_Γ and B_Γ defines the S matrix [37a]

$$B_\Gamma = \sum_{\Gamma'} S_{\Gamma\Gamma'} A_{\Gamma'} \tag{1.8}$$

where the sum is taken over all the open incident channels.

Substituting (1.8) into (1.7) we get

$$\tilde{F}_\Gamma(r) = \sum_{\Gamma'} A_{\Gamma'}(\delta_{\Gamma\Gamma'} e^{-i\theta_\Gamma} - S_{\Gamma\Gamma'} e^{i\theta_\Gamma}) \tag{1.9}$$

We define a new radial function $F_{\Gamma\Gamma'}(r)$ by the transformation

$$\tilde{F}_\Gamma = i\sum_{\Gamma'} (I-iR)^{-1}_{\Gamma\Gamma'} F_{\Gamma\Gamma'}(r),\ k_\Gamma^2 > 0 \tag{1.10}$$

where

$$R_{\Gamma\Gamma'} = i\left[\frac{I-S}{I+S}\right]_{\Gamma\Gamma'} \tag{1.11}$$

With this definition $F_{\Gamma\Gamma'}$ will be real everywhere and will have the asymptotic form

$$\left.\begin{array}{l} F_{\Gamma\Gamma'}(r) \underset{r\to\infty}{\sim} \dfrac{1}{k_\Gamma^{1/2}} (\delta_{\Gamma\Gamma'} \mathrm{Sin}(\theta_\Gamma) + R_{\Gamma\Gamma'} \mathrm{Cos}(\theta_\Gamma),\ k_\Gamma^2 > 0 \\ F_{\Gamma\Gamma'}(r) \underset{r\to\infty}{\sim} N_\Gamma \exp[-|k_\Gamma|r + \mathrm{Im}\,\eta_\Gamma \log 2|k_\Gamma|r],\ k_\Gamma^2 < 0 \end{array}\right\} \tag{1.12}$$

Consequently, (1.5a) becomes

$$\psi_u(\underline{X}_{N+1}) = \sum_{\Gamma\Gamma'} \psi(\Gamma;\ \underline{X}_N\ \hat{x}_{N+1})\ \frac{F_{\Gamma\Gamma'}}{r_{N+1}} \tag{1.13}$$

For a system initially in the state Γ_j, the wave function is

$$\psi_u(\Gamma_j;\ \underline{X}_{N+1}) = \sum_{\Gamma_i} \psi(\Gamma_i;\ \underline{X}_N\ \hat{x}_{N+1}) F_{\Gamma_i\Gamma_j}(r_{N+1}) r_{N+1}{}^{-1} \qquad (1.14)$$

Finally we construct a properly antisymmetrized wave function

$$\psi(\Gamma_j;\ \underline{X}_{N+1}) = \frac{1}{(N+1)^{1/2}} \sum_{k=1}^{N+1} (-1)^{N+1-k} \psi_u(\Gamma_j;\ \underline{X},^{-k}\ \underline{x}_k) \qquad (1.15)$$

where

$$\underline{X}^{-k} = \underline{x}_1\ \underline{x}_2 \ldots \underline{x}_{k-1}\ \underline{x}_{k+1} \ldots \underline{x}_{N+1}\ .$$

<u>S-MATRIX</u>

We will briefly touch upon some of the properties of the S-matrix here; later, we will treat it in more detail.

The elements of the S-matrix are defined in (1.8) in terms of the amplitudes of the ingoing and outgoing waves. It may also be obtained from the R-matrix

$$S = \frac{I + iR}{I - iR} \qquad (1.16)$$

The fact that it is unitary and symmetric means that it can be diagonalized by a real orthogonal matrix U

$$\tilde{U}SU = e^{2i\eta_\alpha} \qquad (1.17)$$

where the eigenphase shifts, η_α, are real. The same matrix U may also be used to diagonalize the R-matrix

$$\tilde{U}RU = \tan(\eta_\alpha)\delta_{\alpha\beta} \tag{1.18}$$

The transition matrix T is defined as

$$T = (S - I) \tag{1.19}$$

The total cross section for the transition $L_iS_i \rightarrow L_jS_j$ is defined [41] by

$$\sigma(L_iS_i \rightarrow L_jS_j) = \sum_{\substack{SL\Pi \\ \ell_i\ell_j}} \frac{(2L+1)(2S+1)}{2k_i^2(2L_i+1)(2S_i+1)} |T_{ij}|^2 \tag{1.20}$$

Kohns Variational Principle

Consider the integral

$$I_{ij} = \int \psi^*(\Gamma_i; \underline{X}_{N+1})(H_{N+1}-E)\psi(\Gamma_j; \underline{X}_{N+1})d\underline{X}_{N+1} \tag{1.21}$$

where

$$H_{N+1} = -1/2\ \nabla^2_{N+1} - \frac{Z}{r_{N+1}} + \sum_{\alpha=1}^{N} \frac{1}{|r_{N+1}-r_\alpha|} + H_N \tag{1.22}$$

Equation (1.21) may be written in terms of the unsymmetrized functions as

$$I_{ij} = \int (N+1)^{1/2} \psi_u^{*}(\Gamma_i;\ \underline{X}_N\ \underline{x}_{N+1})\,[H_{N+1} - E]$$

$$\times \sum_{k=1}^{N+1} (-1)^{N+1-k} (N+1)^{-1/2} \psi_u(\Gamma_j;\ X^{-k}\ \underline{x}_k)\, d\underline{X}_{N+1} \qquad (1.23)$$

where we use the symmetry with respect to interchange of the variable.

The atomic eigenfunctions [40] satisfy

$$\int \psi^{*}(\gamma_{T_i};\ \underline{X}_N)\,[H_N - E_i\delta_{ij}]\,\psi(\gamma_{T_j};\ \underline{X}_N)\ d\underline{X}_N = 0 \qquad (1.24)$$

Therefore equation (1.23) becomes, using (1.24),

$$I_{ij} = \int_0^\infty \sum_{k\ell} F_{k\ell}(r)\ [-1/2(\frac{d^2}{dr^2} - \frac{\ell_k(\ell_k+1)}{r^2} + \frac{2Z}{r} + K_k^{2})$$

$$* \delta_{k\ell} + V_{k\ell}(r)]F_{\ell j}(r)\ dr \qquad (1.25)$$

$$= \int_0^\infty \underline{F}^T \mathcal{L}\, \underline{F}\ dr \qquad (1.26)$$

where the potential $V_{k\ell}^{(r)}$ involves direct and exchange interactions.

We now consider variations of our function F in (1.26) about the exact solution which satisfy the boundary conditions

$$\left.\begin{aligned} \delta F_{ij} &\underset{r\to 0}{\sim} a r^{\ell_i+1} \\ \delta F_{ij} &\underset{r\to\infty}{\sim} k_i^{-1/2}\, \delta R_{ij} \mathrm{Cos}(\theta_i) \end{aligned}\right\} \tag{1.27}$$

The corresponding variation in I is

$$\begin{aligned} \delta I &= \int_0^\infty [\delta F^T \mathcal{L} F + F^T \mathcal{L}\, \delta F]\, dr \\ &= 2\int_0^\infty \delta F^T \mathcal{L} F dr - 1/2 \left[F^T \frac{d}{dr}\, \delta F - \delta F^T \frac{dF}{dr}\right]_0^\infty \end{aligned} \tag{1.28}$$

On using the boundary conditions (1.12) and (1.27) we obtain

$$\delta I = 2\int_0^\infty \delta F^T \mathcal{L} F dr + 1/2 \delta R.$$

Therefore, the variational principle (Kohn)

$$\delta(I - R/2) = 0 \tag{1.29}$$

for arbitrary variations of F, subject to the appropriate boundary conditions, leads to the coupled equations

$$\begin{aligned} \mathcal{L} F = \Big(\frac{d^2}{dr^2} - \frac{\ell_i(\ell_i+1)}{r^2} + \frac{2Z}{r} + k_i^2 \Big) F_{ik} \\ - 2\sum_{j=1}^{n} V_{ij} F_{jk}(r) = 0 \end{aligned} \tag{1.30}$$

for the radial function F and $(i=1,n)$ where n is the number of coupled channels.

Scattering of Electrons by Atomic Systems With Configuration $2P^q$, $3P^q$

We now concentrate on collisions of the above type. Considerable simplification of (1.21) is achieved if we impose the condition

$$<P_{np}|F_{ij}> = 0 \quad \text{for } \ell_i = 1 \tag{1.31}$$

Without this constraint F would contain a component of the bound P^q orbital. The unconstrained continuum orbital could then be written as

$$\tilde{F} = F + \alpha P, \quad <F|P> = 0$$

Consequently, we write [5]

$$\psi_t(r_j; \underline{x}_{N+1}) = \psi(r_j; \underline{x}_{N+1}) + C_j \; \Phi(1s2s\ldots np^{q+1}LS\underline{x}_{N+1}) \tag{1.32}$$

Substituting this ψ_t into (1.21) yields, on using (1.24) and the symmetry properties of the wave function,

$$I_{ij} = L_{ij}{}^D + L_{ij}{}^E + L^c + L^{c^2} \tag{1.33}$$

where we employ the notation of Smith _et_ _al_. [5], except that we omit the subscripts which label the particular solution vector we are referring to, since the equations are independent of the boundary conditions imposed upon them. From [5] we get

$$L_{ij}^{D} = \langle \psi_u(\Gamma_i;\ \underline{X}_N\ \underline{x}_{N+1})|H_{N+1} - E|\psi_u(\Gamma_j;\ \underline{X}_N\ \underline{x}_{N+1})\rangle$$

$$= \int dr_{N+1} F_i(r_{N+1})[-1/2(\frac{d^2}{dr^2} - \frac{\ell_i(\ell_i+1)}{r^2} + \frac{2Z}{r} + k_i^{2})\delta_{ij}$$

$$+ V_{ij}(r_{N+1})]F_j(r_{N+1}) \qquad (1.34a)$$

where

$$V_{ij}(r) = \delta_{ij} \sum_{\substack{n'\ell'= \\ \text{closed} \\ \text{subshells}}} 2(2\ell'+1)Y_o(P_{n'\ell'}P_{n'\ell'};r)+\delta_{s_i s_j} 3q[(2\ell_i+1)$$

$$*(2L_i+1)(2\ell_j+1)(2L_j+1)]^{1/2} \sum_{\lambda} (2\lambda+1)^{-1}$$

$$*(\ell_i\ell_j 00|\lambda 0)(1100|\lambda 0)W(\ell_i L_i \ell_j L_j;\ L\lambda)$$

$$* \sum_{L_2 S_2} (-1)^{L+L_i+L_j+L_2} (qL_iS_i|\}L_2S_2)(qL_jS_j|\}L_2S_2)$$

$$* W(1L_i1L_j;L_2\lambda)Y_\lambda(\ddot{P}_{np}P_{np}\ r) \qquad (1.34b)$$

where n is the principal quantum number of the outermost incomplete p subshell. (ab00/c0) is a Clebsh-Gordan coefficient, W(abcd:ef) a Racah coefficient [37] and

$(qL_iS_i|\}L_2S_2)$ is a coefficient of fractional parentage

$$L_{ij}^{E} = \int dr_{N+1}F_iW_{ij}F_j$$

$$= -N\langle \psi_u(\Gamma_i;\ \underline{X}_N\ \underline{x}_{N+1}|H_{N+1}-E|\psi_u(\Gamma_j;\ \underline{X}^{-N}\dot{\underline{x}}_N)\rangle \qquad (1.35)$$

$$= -\delta_{ij} \sum_{\substack{n'\ell'= \\ \text{closed} \\ \text{subshells}}} \sum_{\lambda} R_\lambda(P_{n'\ell'}F_iF_jP_{n'\ell'})(2\ell'+1)$$

$$* \ (2\ell_i+1)^{-1}(\ell'\lambda oo|\ell_io)^2 - 3q[(2\ell_i+1)(2L_i+1)$$

$$* \ (2S_i+1)(2\ell_j+1)(2L_j+1)(2S_j+1)]^{1/2}$$

$$* \sum_{L_2S_2} (qL_iS_i|\}L_2S_2)(qL_jS_j|L_2S_2)W(S_j1/2\ 1/2S_i;SS_2)$$

$$* \sum_{\lambda} (1\ell oo|\lambda o)(2\lambda+1)^{-1}\ (\ell_i1oo|\lambda o)$$

$$* \begin{bmatrix} L_2 & 1 & L_j \\ 1 & \lambda & \ell_j \\ L_i & \ell_i & L \end{bmatrix} R_\lambda(P_{np}F_iF_jP_{np}) \qquad (1.36)$$

where R_λ are the Slater integrals and $\begin{bmatrix} a & b & e \\ c & d & e^1 \\ f & f^1 & g \end{bmatrix}$ is the Wigner 9j coefficient.

Equations (1.34) and (1.36) are identical with (18), (19) and (22) of [5].

We now wish to evaluate terms linear in c. This has been done incorrectly in [5] as it does not account for exchange interaction with the core electrons. The correct expression for L^c is

$$L^c = C_i < \psi(\Gamma_i : \underline{X}_{N+1}) | H_{N+1} - E | \Phi(1s^2 \ldots np^{q+1} LS \underline{X}_{N+1})$$

$$+ C_j < \Phi(1s^2 \ldots np^{q+1} LS \underline{X}_{N+1}) | H_{N+1} - E | \psi(\Gamma_j ; \underline{X}_{N+1}) >$$

$$= \sum_i C_i \int V_i F_i dr \tag{1.37}$$

where

$$V_i(r) = (q+1)^{1/2} \{ \delta_{\ell_i 1} (P^{q+1} LS | \} L_i S_i) [(-1/2 \frac{d^2}{dr^2} + \frac{1}{r^2} - \frac{Z}{r}) P_{np}(r)$$

$$+ \sum_{\substack{n'\ell' = \\ \text{closed}}} 2(2\ell'+1)(Y_o(P_{n'\ell'} P_{n'\ell'} r) P_{np}(r) - \sum_{\lambda} \frac{2\ell'+1}{2\ell_i+1}$$

$$* (\ell' \lambda o o | \ell_i o)^2 \; Y_\lambda (P_{n'\ell'} P_{np} \; r) P_{n'\ell'}(r)]$$

$$+ 3q \sum_{L'S'} \delta_{ss'} (P^{q+1} LS | \} L'S') [3(2\ell_i+1)(2L'+1)$$

$$* (2L_i+1)]^{1/2} \sum_{\lambda L_2 S_2} (-1)^{L_2+L+L'+L_i} (P^q L'S' | \} L_2 S_2)$$

$$* (P^q L_i S_i | L_2 S_2) \; (2\lambda+1)^{-1} \; (1100 | \lambda 0)(1\ell_i 00 | \lambda 0)$$

$$* W(1L'\ell_i L_i : L\lambda) W(1L'1L_i : L_2 \lambda) \; Y_\lambda (P_{np} P_{np} r) P_{np}(r) \tag{1.38}$$

This is the expression given by equation (9), Smith, Conneely, Morgan [6a] and (10) of [20].

The term quadratic in C

$$L^{c^2} = C_iC_j < \Phi_o|H_{N+1} - E|\Phi_o > \tag{1.39a}$$

$$= C_{ij} (E_{N+1} - E) \tag{1.39b}$$

where E_{N+1} is the energy of the $1s^2 \ldots np^{q+1}LS$ configuration evaluated with the wave functions of the np^q configuration. This term L^{c^2} is merely a constant, the value for which may be calculated from equation (10) of Smith, Conneely, Morgan [6a] or from (11) of [20].

Derivation of the Radial Equations

Application of the Kohn variational principle, (1.29), yields, after analysis equivalent to that of Smith *et al.* [5], the equations satisfied by the radial functions F_{ij} (where the j refers to the j^{th} solution of the vector function F)

$$\sum_j \mathcal{L}_{ij} F_{jk}(r) + \frac{V_i}{E-E_{N+1}} \sum_j \int V_j(r') F_{jk} dr'$$

$$+ \sum_\lambda M_\lambda{}^i \, P_{n_\lambda \ell_\lambda} = 0 \qquad (1.40)$$

where

$$\mathcal{L}_{ij} = -1/2 \; [\frac{d^2}{dr^2} - \frac{\ell_i(\ell_i+1)}{r^2} + \frac{2Z}{r} + k^2) \delta_{ij}$$

$$+ V_{ij} + W_{ij}$$

where the direct potential V_{ij} is defined by (1.34b) and the integral operator W_{ij} by (1.36). The $M_\lambda{}^i$ are unknown Lagrange multipliers, as we require the radial functions F_{ij} for the S-waves to be orthogonal to the 1S, 2S, 3S subshells and the P-waves to be orthogonal to the 2P and np subshells.

Summary

The problem of calculating the cross section for the transition $L_iS_i \rightarrow L_jS_j$ reduces to solving the system of coupled integrodifferential equations (1.40) for F_{ij} subject to the boundary conditions [5]

$$F_{ij} \underset{r\to o}{\sim} r^{\ell_i + 1} \qquad (1.41a)$$

$$F_{ij} \underset{r\to\infty}{\sim} k_i^{-1/2}(\delta_{ij}\mathrm{Sin}(\theta_i)+ R_{ij}\mathrm{Cos}(\theta_i)\ ), k_i^2 > 0 \qquad (1.41b)$$

$$\underset{r\to\infty}{\sim} \exp[-|\kappa_i|r - \eta_i \ell n(2\kappa_i r)],\ k_i^2 < 0 \qquad (1.41c)$$

where

$$\theta_i = k_i r - \ell_i \pi/2 - \eta_i \ell n(2k_i r) + \sigma_{\ell_i}$$

$$\eta_i = -(Z-N)/k_i$$

$$\sigma_{\ell_i} = \mathrm{Arg}\ \Gamma\ (\ell_i+1+i\eta_i)$$

The R-matrix may be easily determined from (1.41b), (1.41c). The transition matrix T is defined as

$$T = 2iR/(I-iR).$$

The cross section $L_iS_i \rightarrow L_jS_j$ is then determined as

$$\sigma(L_iS_i\rightarrow L_jS_j) = \sum_{\substack{LS\Pi \\ \ell_i\ell_j}} \frac{(2L+1)(2S+1)}{2k_i^2(2L_i+1)(2S_i+1)} |T_{ij}^2| \qquad (1.42)$$

in πa_o^2 units.

Radial Equations for $O^+(L=0,\ S=1,\ \pi=\mathrm{odd})$

Let us now confine our attention to the specific case of an electron colliding with O^+ ion, with $L=0$, $S=1$, $\pi=$odd. There are a number of reasons for choosing this particular problem: these will become apparent as we proceed.

The allowed states, in accordance with the exclusion principle are

$$\left.\begin{aligned} i&= {}^4S + \varepsilon s \\ j&= {}^2D + \varepsilon d \end{aligned}\right\} \qquad (1.43)$$

Parity excludes the other "allowed" state of ${}^2P + \varepsilon P$.

Therefore, using the notation used in earlier sections,

$L=0$, $S=1$, $L_i=0$, $L_j=2$, $S_i=1\frac{1}{2}$, $S_j=1/2$, $\ell_i=0$, $\ell_j=2$.

Vij term

Substituting these values into (1.34a) we get

$$V_{11}(r)=2Y_o(P_{1s}P_{1s}:r)+ 2Y_o(P_{2s}P_{2s}:r)+3q[1.1.1.1]^{1/2}$$

$$* \{1.(0000|00)(1100|00)W(0000:00)$$

$$* [(-1)^1(P^3\ {}^4S|\}P^2\ {}^3P)(P^3\ {}^4S|\}P^2\ {}^3P)W(1010:10)$$

$$* Y_o(P_{2p}P_{2p}r) + (-1)^2\ (P^3\ {}^4S|\}P^2\ {}^1D)(P^3\ {}^4S|\}P^2\ {}^1D)$$

$$* W(1010:20)\ Y_o(P_{2p}P_{2p}:r)$$

$$+ (-1)^0(P^3\ {}^4S|\}P^2\ {}^1S)(P^3\ {}^4S|\}P^2\ {}^1S)W(1010:00)$$

$$* Y_o(P_{2p}P_{2p}:r)]\} \qquad (1.44)$$

where $\sum\limits_{\substack{\text{closed}\\\text{shells}}}$ is taken over 1s, 2s while $\sum\limits_{\lambda}$ is taken over allowed values of λ, i.e. $\lambda=0$ and $\sum\limits_{L_2 S_2}$ is taken over the allowed $S_i L_i$ for O^{++} which are ${}^3P$, ${}^1D$, ${}^1S$. The various Clebsh-Gordan and Racah coefficients, and coefficients of fractional parentage may be determined from tables; their values are

$(0000|00) = 1$

$(1100|00) = -1/\sqrt{3}$

$W(0000:00) = 1$

$W(1010:10) = 1/\sqrt{3}$

$W(1010:20) = 0$

$W(1010:00) = 0$

$(P^3\ {}^4S|\}P^2\ {}^3P) = 1$

$(P^3\ {}^4S|\}P^2\ {}^1D) = (P^3\ {}^4S|\}P^2\ {}^1S) = 0$

Therefore

$$V_{11}(r) = 2Y_o(P_{1s}P_{1s}:r) + 2Y_o(P_{2s}P_{2s}:r) + 3Y_o(P_{2p}P_{2p}:r) \tag{1.45}$$

In calculating V_{12} we note $\delta_{ij} = \delta_{12} = 0$.

Also $\delta_{S_1S_2} = \delta_{3/2,\ 1/2} = 0$;

hence $V_{12} = V_{21} = 0$ (1.46)

$$V_{22} = 2Y_o(P_{1s}P_{1s}:r) + 2Y_o(P_{2s}P_{2s}:r) + 9[5.5.5.5.]^{1/2}$$

$$* \ [(2200|00)\ (1100|00)W(2222:00)$$

$$*\{\ (-1)^5\ (P^3\ {}^2D|\}P^2\ {}^3P)\ (P^3\ {}^2D|\}P^2\ {}^3P)W(1212:10)$$

$$*\ Y_o(P_{2p}P_{2p}r) + (-1)^6\ (P^3\ {}^2D|\}P^2\ {}^1D)(P^3\ {}^2D|\}P^2\ {}^1D)$$

$$*\ W(1212:20)Y_o(P_{2p}P_{2p}:r) + (-1)^4(P^3\ {}^2D|\}P^2\ {}^1S)$$

$$*(P^3\ {}^2D|\}P^2\ {}^1S)W(1212:00)Y_o(P_{2p}P_{2p}:r)\}$$

$$+ \frac{1}{5}\ (2200|20)(1100|20)W(2222:02)$$

$$*\ \{\ (-1)^5\ (P^3\ {}^2D|\}P^2\ {}^3P)\ (P^3\ {}^2D|\}P^2\ {}^3P)W(1212:12)$$

$$*\ Y_2(P_{2p}P_{2p}:r)+(-1)^6\ (P^3\ {}^2D|\}P^2\ {}^1D)\ (P^3\ {}^2D|\}P^2\ {}^1D)$$

$$*\ W\ (1212:22)\ Y_2(P_{2p}P_{2p}:r) + (-1)^4\ (P^3\ {}^2D|\}P^2\ {}^1S)$$

$$*(P^3\ {}^2D|\}P^2\ {}^1S)W(1212:02)\ Y_2(P_{2p}P_{2p}:r)\}] \qquad (1.47)$$

where $\sum_{\lambda}$ is taken over allowed values $\lambda=0$, $\lambda=2$

$(1100|00) = -1/\sqrt{3}$

$(2200|00) = 1/\sqrt{5}$

$(1100|20) = -\sqrt{2}/\sqrt{5}$

$(2200|20 = -\sqrt{2}/\sqrt{7}$

$(P^3\ {}^2D|\}P^2\ {}^3P) = 1/\sqrt{2}$

$(P^3\ {}^2D|\}P^2\ {}^1D) = -1/\sqrt{2}$

$(P^3\ {}^2D|\}P^2\ {}^1S) = 0$

$W(2222:00) = 1/\sqrt{5}$

$W(1212:10) = 1/\sqrt{15}$

$W(1212:20) = -1/\sqrt{15}$

$W(1212:12) = W(1212:22) = \sqrt{7}/10\sqrt{3}$

$W(2222:02) = -1/\sqrt{5}$

$$V_{22} = 2Y_o(P_{1s}P_{1s}:r) + 2Y_o(P_{2s}P_{2s}:r) + 3Y_o(P_{2p}P_{2p}:r) \qquad (1.48)$$

This completes the calculation of $V_{ij}(r)$ (i=1,2, j=1,2) and enables us to evaluate L^D_{ij} (1.34a)

<u>L_{ij}^E term</u>

$$L^E_{11} = -R_o(P_{1s}F_1F_1P_{1s})\ (0000|00)^2$$

$$-R_o(P_{2s}F_1F_1P_{2s})\ (0000|00)^2$$

$$-9[1.1.4.1.1.4]^{1/2}\ [(p^3\ {}^4S|\}p^2\ {}^3P)$$

$$*(p^3\ {}^4S|\}p^2\ {}^3P)W(3/2\ 1/2\ 1/2\ 3/2:\ 11)$$

$$*\ 1/3\ (1000|10)\ (0100|10)\begin{Bmatrix}1 & 1 & 0\\ 1 & 1 & 0\\ 0 & 0 & 0\end{Bmatrix}R_1(P_{2p}F_1F_1P_{2p})$$

$$+\ (p^3\ {}^4S|\}p^2\ {}^1D)\ (p^3\ {}^4S|\}p^2\ {}^1D)W(3/2\ 1/2\ 1/2\ 3/2:10)$$

$$*\quad (10000|10)\ (0100|10)\begin{Bmatrix}2 & 1 & 0\\ 1 & 1 & 0\\ 0 & 0 & 0\end{Bmatrix}R_1(P_{2p}F_1F_1P_{2p})$$

$$+\ (p^3\ {}^4S|\}p^2\ {}^1S)\ (p^3\ {}^4S|\}p^2\ {}^1S)W(3/2\ 1/2\ 1/2\ 3/2;10)$$

$$* \ (1000|10)\ \ (0100|10) \begin{Bmatrix}0 & 1 & 0\\ 1 & 1 & 0\\ 0 & 0 & 0\end{Bmatrix} R_1(P_{2p}F_1F_1P_{2p})] \qquad (1.49)$$

$(1000|10) = (0100|10) = 1$

$W\ (3/2\ 1/2\ 1/2\ 3/2{:}\ 11) = -1/12$

$W\ (3/2\ 1/2\ 1/2\ 3/2{:}\ 10)\ * \ 0$

$$\begin{Bmatrix}1 & 1 & 0\\ 1 & 1 & 0\\ 0 & 0 & 0\end{Bmatrix} = 1/3$$

$$\begin{Bmatrix}2 & 1 & 0\\ 1 & 1 & 0\\ 0 & 0 & 0\end{Bmatrix} = 0$$

Hence

$$L^E_{11} = -R_o(P_{1s}F_1F_1P_{1s}) - R_o(P_{2s}F_1F_1P_{2s})$$

$$+ 1/3\ R_1(P_{2p}F_1F_1P_{2p}) \qquad (1.50)$$

$$L^E_{12} = -3q[1.1.4.5.5.2]^{1/2}$$

$$*[(P^3\ {}^4S|\}P^2\ {}^3P)\ \ (P^3\ {}^2D|\}P^2\ {}^3P)W(1/2\ 1/2\ 1/2\ 3/2{:}11)$$

$$* \ 1/3\ \ (1200|10)\ \ (0100|10) \begin{Bmatrix}1 & 1 & 2\\ 1 & 1 & 2\\ 0 & 0 & 0\end{Bmatrix} R_1(P_{2p}F_1F_2P_{2p})] \qquad (1.51)$$

Remaining terms of $\sum_{L_2S_2}$ are zero since the corresponding Wigner 9j symbol is zero.

$$(1200|10) = -\sqrt{2}/5$$

$$\begin{Bmatrix} 1 & 1 & 2 \\ 1 & 1 & 2 \\ 0 & 0 & 0 \end{Bmatrix} = 1/3\sqrt{5}$$

$$W(1/2\ 1/2\ 1/2\ 3/2\colon 11) = 1/3$$

$$L^{E}_{12} = \frac{2\sqrt{2}}{3}\ R_1\ (P_{2p}F_1F_2P_{2p}) \tag{1.52}$$

$$L^{E}_{21} = -3q\ [5.\ 5.\ 2.\ 1.\ 1.\ 4]^{1/2}$$

$$*\ (P^3\ {}^2D|\}P^2\ {}^3P)\ (P^3\ {}^4S|\}P^2\ {}^3P)W(1/2\ 1/2\ 1/2\ 3/2;11)$$

$$*\ \ 1/3\ (1000|10)\ (2100|10)\ \begin{Bmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 2 & 2 & 0 \end{Bmatrix}\ R_1(P_{2p}F_2F_1P_{2p}) \tag{1.53}$$

$$= \frac{2\sqrt{2}}{3}\ R_1\ (P_{2p}F_2F_1P_{2p}) \tag{1.54}$$

$$\begin{aligned} L^{E}_{22} = {} & -R_2(P_{1s}F_2F_2P_{1s})\ \frac{1}{5}\ (0200|20)^2 \\ & -R_2\ (P_{2s}F_2F_2P_{2s})\ \frac{1}{5}\ (0200|20)^2 \\ & -3q\ [5.5.2.5.5.2]^{1/2}\ [(P^3\ {}^2D|\}P^2\ {}^3P) \end{aligned}$$

$$*(P^3\ {}^2D|\}P^2\ {}^3P)W(1/2\ 1/2\ 1/2\ 1/2\colon 11)$$

$$*[1/3\ (1200|10)\ (2100|10)\ \begin{Bmatrix} 1 & 1 & 2 \\ 1 & 1 & 2 \\ 2 & 2 & 0 \end{Bmatrix}\ R_1(P_{2p}F_2F_2P_{2p})$$

$$+\ 1/7\ (1200|30)\ (2100|30)\begin{Bmatrix} 1 & 1 & 2 \\ 1 & 3 & 2 \\ 2 & 2 & 0 \end{Bmatrix}\ R_3(P_{2p}F_2F_2P_{2p})]$$

$$+ \ (P^3\ {}^2D|\}P^2\ {}^1D)(P^3\ {}^2D|\}P^2\ {}^1D)W(1/2\ 1/2\ 1/2\ 1/2;\ 10)$$

$$*[1/3\ (1200|10)\ (2100|10)\ \begin{Bmatrix} 2 & 1 & 2 \\ 1 & 1 & 2 \\ 2 & 2 & 0 \end{Bmatrix} R_1\ (P_{2p}F_2F_2P_{2p})$$

$$+ \ 1/7\ (1200|30)\ (2100|30)\ \begin{Bmatrix} 2 & 1 & 2 \\ 1 & 3 & 2 \\ 2 & 2 & 0 \end{Bmatrix} R_3\ (P_{2p}F_2F_2P_{2p})] \qquad (1.55)$$

$$= \ -1/5\ R_2(P_{1s}F_2F_2P_{1s}) - 1/5\ R_2(P_{2s}F_2F_2P_{2s})$$

$$+ \ \frac{13}{45}\ R_1\ (P_{2p}F_2F_2P_{2p})$$

$$- \ \frac{9}{35}\ R_3\ (P_{2p}F_2F_2P_{2p}) \qquad (1.56)$$

L^C term

The permitted values of L_iS_i for O that are allowed by the exclusion principle are ^3P, ^1D, ^1S. Reference to tables of C.F.P shows that, for L=0, S=1, $(P^{q+1}LS|\}L_iS_i)$ is zero in the case of O^+; hence (1.38) shows that $V_L(r)\equiv 0$, which means the L^C term makes no contribution to differential equations in this particular case.

L^{C^2} term

The L^{C^2} term is given by (1.39) where C_j is defined by (33) of Smith et al. [5]. As $V_i(r)\equiv 0$, $C_j=0$. Therefore, the L^{C^2} term is zero and makes no contribution to the radial equations (1.40) for the system in question here.

Explicit Form of Radial Equations

Substitution into (1.40) for V_{ij}, W_{ij} from (1.45), (1.46), (1.48), (1.50), (1.52), (1.54), (1.56) and noting that $V_i(r) \equiv 0$ yields

$$
\begin{aligned}
&\left(\frac{d^2}{dr^2} + \frac{2Z}{r} + k_1^2 \right) F_1(r) + [2Y_o(P_{1s}P_{1s}:r) \\
&+ 2Y_o(P_{2s}P_{2s}:r) + 3Y_o(P_{2p}P_{2p}:r)]\ F_1(r) \\
&- Y_o(P_{1s}F_1 r)\ \frac{P_{1s}}{r} - Y_o(P_{2s}F_1 r)\ \frac{P_{2s}}{r} + \frac{1}{3}\ Y_1(P_{2p}F_1 r)\frac{P_{2p}}{r} \\
&+ \frac{2\sqrt{2}}{3}\ Y_1\ (P_{2p}F_2 r)\ \frac{P_{2p}}{r} + \mu_1 P_{1s} + \mu_2 P_{2s} = 0
\end{aligned}
\qquad (1.57)
$$

$$
\begin{aligned}
&\left(\frac{d^2}{dr^2} + \frac{6}{r^2} + \frac{2Z}{r} + k_2^2 \right) F_2(r) + [2Y_o(P_{1s}P_{1s}r) \\
&+ 2Y_o(P_{2s}P_{2s}r) + 3Y_o(P_{2p}P_{2p}r)]\ F_2(r) \\
&+ \frac{2\sqrt{2}}{3}\ Y_1(P_{2p}F_1 r)\ \frac{P_{2p}}{r} - \frac{1}{5}\ Y_2(P_{1s}F_2 r)\frac{P_{1s}}{r} \\
&- \frac{1}{5}\ Y_2\ (P_{2s}F_2 r)\ \frac{P_{2s}}{r} - \frac{13}{45}\ Y_1\ (P_{2p}F_2 r)\ \frac{P_{2p}}{r} \\
&- \frac{9}{35}\ Y_3\ (P_{2p}F_2 r)\ \frac{P_{2p}}{r} = 0
\end{aligned}
\qquad (1.58)
$$

These then are the 2 equations that must be solved for $e^- \; O^+$ collision with L=0, S=1, Π=odd. We may note that the equations are coupled through the exchange terms only.

S-Matrix (continued)

We previously touched on the subject of the S-matrix and showed its relation to the R-matrix and T-matrix, defining its elements in terms of the amplitudes of the ingoing and outgoing waves (1.16) - (1.20).

When coupling between the channels is neglected, the S-matrix is diagonal and each $S_{\alpha\alpha}$ is a single-valued function of its corresponding wave number k_α [42]. These diagonal elements have certain symmetry properties for complex k [43];

$$S(k)\ S(-k) = 1 \tag{1.59}$$

$$S\ (-k^*) = S^*(k) \tag{1.60}$$

Combining these two results gives the unitarity condition for real k. Newton [39] has shown that for certain classes of potentials, S(k) is a meromorphic function of k with poles lying either in the lower half of the complex plane or on the positive imaginary axis, as shown in Figure (1)

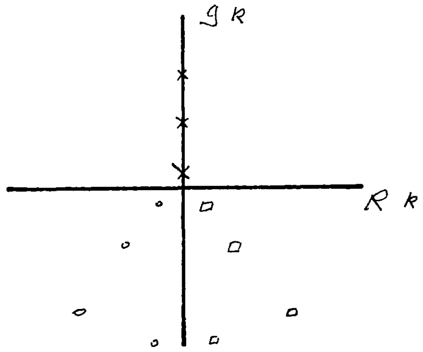


Fig.(1) Poles of the single-channel S-matrix in the complex R-plane

The latter are the bound states, the former the resonance states. The requirement (1.60) shows that the poles have mirror symmetry about the imaginary axis - if there is a pole at k, then there is a pole at $-k^*$, so that poles are paired except for those on the imaginary axis.

At points on the real axis close to these resonance poles, S can be written [40] as

$$S=e^{2i\delta_o(k^2)} \frac{k^2_r - k^2 + i\,\Gamma/2}{k_r^2 - k^2 - i\,\Gamma/2} \qquad (1.61)$$

where the pole in S is at $k^2 = k^2_r - i\,\Gamma/2$ and the corresponding zero lies at $k^2 = k_r^2 + i\,\Gamma/2$ (k_r^2, $\Gamma>0$). The "background phase" $\delta_o(k^2)$ accounts for the remaining "distant" poles and is slowly varying. Substituting (1.61) into the cross section formula

$$\sigma(k^2) = \frac{4}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1)\ \mathrm{Sin}^2(\delta_\ell) \qquad (1.62)$$

we obtain (for single channel scattering) that the resonant ℓ^{th} partial wave contribution to the total cross section is

$$\sigma_\ell(k^2) = \frac{4}{k^2} \frac{(2\ell+1)\ (^\Gamma/2)^2}{(k_r^2 - k^2)^2 + (^\Gamma/2)^2} \qquad (1.63)$$

on taking δ_o = zero.

This is the familiar Breit-Wigner one level resonance formula. The quantity Γ is referred to as the "width" of the resonance. The probability of finding the particle in a quasi-stationary state at $k^2=k_r^2-i\Gamma/2$ will include a factor

$$|\exp[-i(k_r^2 - i\Gamma/2)t/\hbar]|^2 = \exp(^{-t}/\tau), \qquad (1.64)$$

$\tau = \hbar/\Gamma$, where $\hbar$ is related to Planck's constant h as $\hbar \equiv h/2\pi = 1.054 \times 10^{-27}$ erg. sec.
The quantity τ is called the life-time of the state.

Resonance Widths

The shape of such a cross section, as we have been dealing with is as shown in Figure (2).

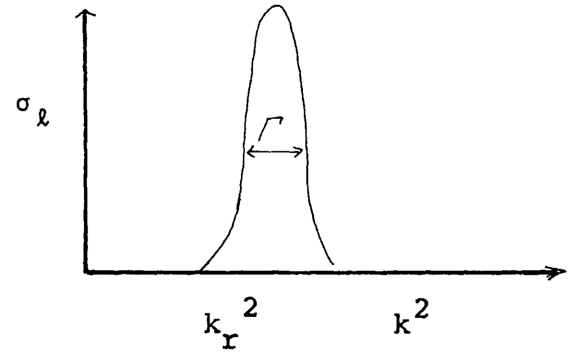


Fig.(2) - Resonant part of the cross section versus energy.

The energy-value of k_r^2 is defined to be the position of the resonance of the cross section, σ; i.e., it is the energy at which $\delta_\ell^{RES}(k^2)=\frac{(2n+1)\pi}{2}$ and not where the full phase-shift

$\delta_\ell = \frac{(2n+1)\pi}{2}$. At $k^2 = k_r^2 \pm \Gamma/2$ we note from (1.63) that σ_ℓ is equal to half its maximum value. This accounts for the name of Γ....the"width" of the resonant cross section, at half-maximum. In the case of a very narrow resonance, i.e., Γ very small, it is necessary to calculate $\sigma(k^2)$ with great accuracy for an accurate calculation of Γ. On referring to (1.64), we see that a narrow resonance reflects a long half-life time for the state.

Both experimental and theoretical estimates of Γ for e^-O^+ collision (L=0, S=1, π=odd) are to be found in [28]; these show that for this particular collision Γ is $O(10^{-3}Å)$. Henry, [48] gives a similar value for Γ. Smith [42] contains a very extensive review of resonant scattering.

Autoionization

The phenomenon of autoionization may be interpreted as follows: when an atomic system is excited to an energy beyond the first ionization threshold, the system undergoes a transition to a quasi-stationary state which subsequently releases an electron to the continuum in a radiationless transition. These quasi-stationary states correspond to bound-states whose energies converge to that of the next permissible ionization energy.

In our problem, we have two coupled channels

$$e + O^{+} \rightarrow ({}^{3}S) \rightarrow O^{+}({}^{4}S) + \varepsilon s$$
$$O^{+}({}^{2}D) + \varepsilon d$$

If we uncouple the channels and solve for $k_2^2 < 0 < k_1^2$, we have a single open channel problem for channel 1 and a simple eigen-value problem for channel 2. The solutions for channel 2 give the bound states of oxygen which converge on ${}^{2}D$ state of O^{+}

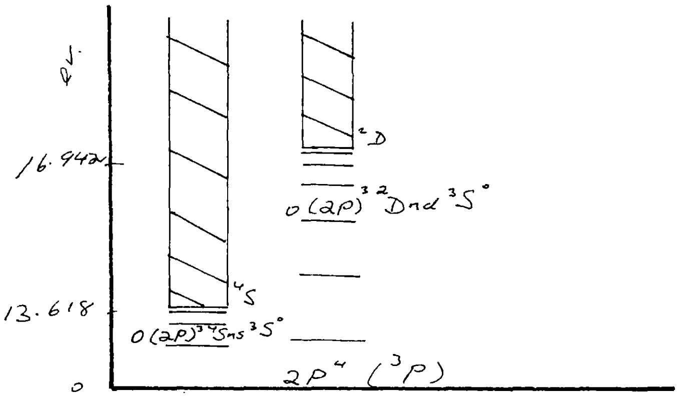

eV
16.942
13.618
0
${}^{2}D$
$O(2P)^{3}\,{}^{2}Dnd\,{}^{3}S^{\circ}$
${}^{4}S$
$O(2P)^{3}\,{}^{4}Sns\,{}^{3}S^{\circ}$
$2P^{4}\,({}^{3}P)$

Fig. (3) Schematic diagram of the energy levels, relative to the ${}^{3}P$ term of the configuration $1s^2$, $2s^2$, $2p^4$ of O.

In Figure (3) we have a schematic diagram of the energy levels of the oxygen atom based on the independent particle model. The shaded areas denote the various continua of the open channels while the horizontal lines denote possible bound states. From Figure (3), we see that at 15eV above the ground level, the independent particle model would predict the existence of two conflicting atomic states, a continuum state with configuration $O^{+}(^{4}S)ks\ ^{3}S^{o}$ and a stationary eigenstate $O(2P^{3})\,^{2}Dnd\ ^{3}S^{o}$. The coupling of the open and closed channels provides a mechanism for the discrete structure to leak away as an electron into the continuum and an O^{+} ion. This autoionization phenomenon [42] shows up as resonances. Crudely speaking, we can look upon it as the embedding of the discrete state in the continuum.

It should be noted that Fonda [44] has shown that a narrow resonance need have no relation to possible bound states of the decoupled closed channels, although this is the type that is most frequentlv encountered.

Smith, et al. [28] calculated this series of states and identified them with a series observed by Huffman, et al. [46] in ultra-violet absorption. Rudd [46] also observed this series in experiments involving the bombardment of oxygen gas with protons and helium ions. Extensive calculations on these resonant or autoionizing states have also been carried out for systems such as He [9], N [15], O [47], P, S, Cl [29]. It was found that resonances effect the scattering and photoionization cross sections at the resonant energies.

Statement of Our Problem

One of the fundamental concepts of scattering theory is that of the "phase-shift". In the case of single channel scattering, it is related to the S-matrix as

$$S_\ell(k) = e^{2i\delta_\ell(k)} \qquad (1.65)$$

and to the scattering cross section as (1.62). For multichannel scattering the relationship of most use is that relating the R-matrix and δ_α given by (1.18).

Due to the fundamental importance of δ_α itself and its direct relationship to the scattering cross section (1.20), it is of great importance that δ be calculated accurately. Since these calculations demand that a system of coupled differential equations (e.g. 1.57, 1.58) be solved numerically, we should be very careful and examine the accuracy of the calculations.

In these numerical integrations we must, of necessity, introduce such parameters as H (= stepsize of integration method), RB (= distance from origin where the exchange-terms' contribution becomes negligible) etc. We would demand that such physical quantities as δ (phase-shift) and σ (scattering cross section) should be independent of these integrating parameters. However, graph (1) shows that, in fact, $\delta=\delta(H)$ at resonant energies when we use the code ATOMNP [49]. Since this dependence on H affects the calculation of $\delta(k^2)$, it also affects the calculation of Γ which is most conveniently calculated by making a least squares fit to [42]

$$\delta(E) = \delta_o + \tan^{-1} \frac{\Gamma/2}{E_{RES}-E} \tag{1.66}$$

The values for E and $\delta(E)$ are of a discrete numerical nature got from graph (1); hence, $\Gamma = \Gamma(H)$. In the case of e^-O^+ (L=0, S=1, π=odd) Γ is very small [47] i.e. $O(10^{-3}$ Å). As a result, any inaccuracies in graph (1) are liable to cause serious relative inaccuracies in $\frac{\Gamma(H)}{\Gamma_{correct}}$

The photoionization cross section, which is proportional to the matrix element $<\psi_i|\underline{r}|\psi_f>$ where ψ_i is the initial state wave function and ψ_f the final state wave function, namely the solution of the scattering problem, shows instability also at these resonant energies. The physical parameters are obtained by fitting the cross sections obtained from our abinitio calculation to the formula obtained from the perturbation theory, namely [45]

$$\sigma = \sigma_a \frac{(q+\varepsilon)^2}{1+\varepsilon^2} \tag{1.67}$$

where

$\varepsilon = \frac{E - E_{RES}}{\Gamma/2}$, σ_a is the background cross section and q is called the profile index. It has been noted that serious instability is apparent in the calculating of q at these resonant energies.

In summary, we have a potentially serious inaccuracy in our integrating procedure which makes itself apparent by the instability of $\delta(k)$ and the resultant estimates of Γ, q. Our problem involves the eradication of this instability.

Directly related to the problem of solving the relevant system of coupled differential equations, is the question of the efficiency of the integrating method, "time-wise" and "storage-wise". In other words, which integrating method is fastest (assuming it satisfies our criterions of accuracy) and which method demands the least amount of computer storage in execution. These are important when calculations are long, resulting in much computer time, and storage is large. This is the situation with ATOMNP.

Hence, we have three separate problems to consider:

(i) How are we to eradicate the instability indicated by graph (1);

(ii) Which integrating method is most efficient "time-wise";

(iii)Which integrating method demands the least amount of computer storage during execution.

Ideally we will hope to stabalize our solutions while using an integrating procedure that is optimum in efficiency, both "time-wise" and "storage-wise".

CHAPTER 2

Introduction

The numerical solution of the resultant coupled equations (1.40) will now be described. To enable the solution of (1.40) to be obtained when some or all of the channels are virtual, it is necessary to adopt a method of inward and outward integration, with subsequent matching to obtain a final continuous solution; otherwise, components of dominant parasitic solutions of the type $e^{|k|r}$ would be contained in the numerical solution (introduced by round-off and truncation errors). This is the method used by Smith and Burke [111]. The asymptotic expansion method of Burke and Schey [110] is used to determine the R-matrix from the functions F_i. Equation (1.40) can now be written as

$$\frac{d^2F_i}{dr^2} = \sum_{j=1}^{M} A_{ij}(r)\ F_j(r) + \sum_{k=1}^{NE} \alpha_k\ Y_{\lambda_k}(P_kF_k{:}r)P_k(r)$$

$$+\ 2CV_i + \sum_{\lambda=1}^{NMU} m_\lambda\ P_{n_\lambda \ell_\lambda}(r) \qquad (2.1)$$

where the suffix denoting the incident channel has been dropped since we require all possible solutions of (2.1) subject to the appropriate boundary conditions (1.41). The letter M denotes the number of different F's, i.e. the number of channels; NE is the total number of exchange terms appearing in all the F equations. For further reference we introduce the notation, NA represents the number of open channels (i.e. those channels for which $k_i^2>0$), NB is the number of closed channels (i.e. those for which $k_i^2< 0$); the parameter NV is zero if all $V_i=0$ (as in the case of e^-O^+, L=0, S=1, π=odd), otherwise it is unity. NMU is the number of Lagrange multipliers in (1.40).

According to Hartree [36], the exchange functions $Y_\lambda(PF:r)$ satisfy the following second-order ordinary differential equation

$$\frac{d^2(rY_\lambda)}{dr^2} = \frac{\lambda(\lambda+1)}{r}(rY_\lambda) - (2\lambda+1)\frac{P(r)F(r)}{r} \qquad (2.2)$$

subject to the boundary conditions

$$\begin{aligned} rY_\lambda(r) \quad & \underset{r\to o}{\sim} \quad r^{\lambda+1} \\ rY_\lambda \quad & \underset{r\to\infty}{\sim} \quad r^{-\lambda} \end{aligned} \qquad (2.3)$$

This simplifies matters greatly because the system of int$\overset{eg}{\wedge}$ro-differential equations (1.40) may now be considered to be an expanded system of ordinary second-order differential equations.

Briefly, we calculate NIN (=M+NE+NV+NMU) linearly independent solutions of the system of equations comprised of (2.1) and (2.2) for the inner region $0 \leq r \leq R1$ and store these solutions, which are labeled F_i^{α}, at two match points R1 and R5(< R1). Asymptotically, NOUT (=M + NA+NE+NV+NMU) solutions, labeled g_i^{β}, are calculated where initial values are provided by the expansion method of Burke and Schey, and integration proceeds backwards until the functions g_i^{β} are calculated and stored at R1 and R5. A furtner NA+NV+NMU equations are obtained by various stratagems to provide the required over-all total of 2(M+NE)+ NA+NV+NMU equations for the same number of unknown parameters. We will give a detailed treatment of this technique later in the chapter.

Inner Region

Consider the second order differential equation for electron-hydrogen atom scattering in the Static Field approximation which has the well known form

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell+1)}{r^2} + 2\ (1+ \frac{1}{r})\ e^{-2r}\right] F_\ell(kr)= 0 \qquad (2.4)$$

At small values of r, we assume that it is possible to expand the solution in an ascending power series in r,

$$F_\ell(kr) = \sum_{n=0}^{\infty} \alpha_n r^{n+\sigma} \qquad (2.5)$$

where σ is as yet unknown (it determines the leading term in our series) and the α_n are also unknown. Substitution of (2.5) into (2.4) gives

$$\sum_n \alpha_n (n+\sigma)(n+\sigma-1)r^{n+\sigma-2} + k^2 \sum_n \alpha_n r^{n+\sigma}$$

$$- \ell(\ell+1) \sum_n \alpha_n r^{n+\sigma-2} + 2(1+r^{-1})(1-2r + \frac{(-2r)^2}{2!} + \ldots.)$$

$$\sum_n \alpha_n r^{n+\sigma} = 0 \qquad (2.6)$$

The coefficient of $r^{\sigma-2}$ leads to the equation

$$\alpha_0 \{\sigma(\sigma-1) - \ell(\ell+1)\} = 0 \qquad (2.7)$$

For $\alpha_0 \neq 0$ we have

$$\sigma = \ell+1 \text{ or } -\ell$$

i.e.

$$F_\ell(kr) \underset{r\to 0}{\sim} r^{\ell+1} \text{ or } r^{-\ell} \qquad (2.8)$$

Since we want physically significant solutions, i.e. we do not want infinite probabilities, we must take the former solution since it is regular at the origin. The full radial function

$$\frac{F_\ell(kr)}{r} \underset{r\to 0}{\sim} r^\ell \text{ or } r^{-\ell-1} \text{ from (2.8).}$$

Hence, the physical solution demands the solution which is regular at the origin

$$F_\ell(kr) \underset{r\to 0}{\sim} \alpha_0 r^{\ell+1}, \; F_\ell(0) = 0 \tag{2.9}$$

The quantity α_0 may be considered to be arbitrary ($\alpha_0 \neq 0$), and may be taken to be unity. From (2.8) we see that the leading term in the first derivative is

$$\frac{dF_\ell}{dr} \underset{r\to 0}{\sim} (\ell+1)r^\ell + O(r^{\ell+1}) \tag{2.10}$$

For $\ell=0$, $F_\ell'(0) = 1$, while for $\ell>0$ we have $F_\ell'(0)=0$. In other words, for $\ell \geq 1$ not only does the function vanish, but also its first derivative. To compute higher derivatives more accurately, we must look at the actual coefficients α_i. For example, to compute F_ℓ'' we must evaluate the right-hand side of the differential equation as a limiting process

$$\begin{aligned} F_\ell'' &\underset{r\to 0}{\sim} \{-k^2+\ell(\ell+1)r^{-2}-2r^{-1}+O(r^0)\}r^{\ell+1} \\ &\underset{r\to 0}{\sim} [\ell(\ell+1)r^{\ell-1} - 2r^\ell+O(r^{\ell+1})] \end{aligned} \tag{2.11}$$

which equals -2 for $\ell=0$, +2 for $\ell=1$, and 0 for $\ell \geq 2$. We can summarize the above results into a table of values for starting the numerical integration of (2.4) from the origin r=0

	X = 0			X = t
ℓ	0	1	>1	$\geq$ 1
F_ℓ	0	0	0	$t^{\ell+1}$
F_ℓ'	1	0	0	$(\ell+1)t^\ell$
F_ℓ''	-2	2	0	$\ell(\ell+1)t^{\ell-1}$

Table (a). Starting values of functions and derivatives.

We see from this table that if the integration is begun at r=0 for $\ell>1$, then F, F', F'' are all zero and the solution will remain zero, i.e. we shall compute the trivial solution $F_\ell(r)\equiv 0$ for all r. However, if we step a very small increment t away from the origin, then F and its derivatives can be given the values computed from the first term of the series expansion to obtain greater accuracy in the solution than offered by the leading term at t, one simply retains the next term (or terms) in the expansion.

We generalize the above results and assume that the radial functions F_i of (2.1) and their derivatives are of the form indicated in Table (a) as r tends to zero. We do not start our integration at zero but at a small distance t from zero. To calculate the inṫegration for the first step we use the classical Runge-Kutta method [52] which is suitable for first order equations or higher order equations reduced to an expanded system of first order equations. This is used to facilitate the Numerov multi-step method.

Rewrite the combined system of equations consisting of (2.1) and (2.3) in the homogeneous form

$$F''(r) = B\ F \qquad (2.12)\ .$$

where $F = \begin{pmatrix} F_i \\ Y_k \end{pmatrix}$

and V_i, P_{np} terms are neglected temporarily.

Rewrite (2.12) in the first order form

$$\frac{d}{dr} \begin{pmatrix} F \\ Z \end{pmatrix} = \begin{pmatrix} Z \\ BF \end{pmatrix} \qquad (2.12a)$$

We get M+NE(=NTOT) independent solutions for (2.12) by taking in turn as boundary conditions,

$$\begin{pmatrix} F \\ Z \end{pmatrix} = \begin{pmatrix} 0 \\ t^{n_i+1} \\ 0 \\ (n_i+1)\ t^{n_i} \\ 0 \end{pmatrix}$$

where (i= 1, NTOT) and $n_i = \begin{matrix} \ell_i \;\ldots . i \leq M \\ \lambda_i \;\ldots . i > M \end{matrix}$

A further NV independent solutions are generated by taking C=1 in (2.1) and having as boundary conditions,

$$\begin{pmatrix} F \\ Z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

but $F_i'' \neq 0$ for the appropriate i.

Finally NMU independent solutions are generated by taking in turn one m_λ as unity and all others as zero (C is also taken as zero). The boundary conditions that apply for these solutions are

$$\begin{pmatrix} F \\ Z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

and $F_i'' \neq 0$ for the appropriate i.

These solutions are then integrated out to two predefined values of r, R5 and R1 where they are stored. Hence, we get NIN(=M+NE+NV+NMU) independent solutions for F_i(i=1, NTOT) which are denoted by F_i^α where the superscript α denotes the particular independent solution.

Asymptotic Region

In the region where the exchange terms are negligible, i.e. where r>RA, the coupled differential equations (2.1) can be written as

$$\frac{d^2F_i}{dr^2} = \sum_{j=1}^{M} U_{ij} F_j \qquad (2.13)$$

where i=1, M. Here U_{ij} includes the direct potential, the centrifugal barrier and the energy term as follows:

$$U_{ij}(r) = \sum_{\lambda=1}^{m_{ij}} \frac{a_{ij}^{\lambda}}{r^{\lambda+1}} - k_i^2 \delta_{ij} + \frac{\ell_i(\ell_i+1)}{r^2} \delta_{ij} \qquad (2.14)$$

In equation (2.14) we use the fact that each element of the direct potential may be written as a finite sum of inverse powers of r, starting with a power no higher than -2.

We now assume that there are m_a separate and independent wave numbers $k_q (q=1, m_a)$ above threshold, and m_b separate $\alpha_\tau = |k_\tau|$ $(\tau = 1, m_b)$ below threshold. We note that each k_q and α_τ may include more than one channel; thus, for example, channels corresponding to the 2s and 2p states have the same k_q (or α_τ).

The asymptotic form of Burke and Schey [110] for the functions F_i are assumed.

Hence,

$$F_i(r) = \sum_{q=1}^{m_a} [\mathrm{Sin}(k_q r) \sum_{p=0}^{\infty} \alpha_p^{iq} r^{-p} + \mathrm{Cos}\ (k_q r) \sum_{p=0}^{\infty} \beta_p^{iq} r^{-p}\ ] + \sum_{\tau=1}^{m_b} \exp(-\alpha_\tau r) \sum_{p=0}^{\infty} \gamma_p^{i\tau}\ r^{-p}$$

$$(2.15)$$

Substituting (2.15) into (2.13) and equating the coefficients of $\mathrm{Sin}(k_q r)/r^p$, $\mathrm{Cos}(k_q r)/r^p$ and $\exp\ (-\alpha_\tau r)/r^p$ for all relevant q, τ and p, we obtain the following recursion relations for the α, β, γ coefficients in (2.15) :

$$[(k_i^2 - k_q^2)\alpha_p^{iq} + (P-1)\ (P-2)\ \alpha^{iq}_{p-2} + 2k_q(P-1)\beta_{p-1}^{iq}] =$$

$$\sum_{j=1}^{M} \sum_{\lambda=1}^{m_{ij}} a_{ij}^{\lambda}\ \alpha^{jq}_{p-\lambda-1} \qquad [(k_i^2 - k_q^2)\beta_p^{iq} + (P-1)(P-2)\beta_{p-2}^{iq} -$$

$$2k_q(P-1)\ \alpha_{p-1}^{iq}\ ] = \sum_{j=1}^{M} \sum_{\lambda=1}^{m_{ij}} a^{\lambda}_{ij}\ \beta^{jq}_{p-\lambda-1}$$

$$[(k_i^2 + \alpha_\tau^2)\ \gamma_p^{i\tau} + (P-1)\ (P-2)\ \gamma_{p-2}^{i\tau} + 2\alpha_\tau\ (P-1)\gamma_{p-1}^{i\tau}\ ] =$$

$$\sum_{j=1}^{M} \sum_{\lambda=1}^{m_{ij}} a^{\lambda}_{ij}\ \gamma^{j\tau}_{p-\lambda-1} \tag{2.16}$$

where $(i= 1, M)$, $(q = 1, m_a)$, $(\tau= 1, m_q)$.

A particular solution of (2.13) given by (2.16) is defined uniquely by specifying the 2M+NA parameters

$$\alpha_0^{iq(i)}\ ,\ \beta_0^{iq(i)}\ , \text{ where } i=1,\ NA$$

$$\gamma_0^{i\tau(i)}\ , \text{ where } i= NA+1,\ M; \tag{2.17}$$

here we mean, by the notation $q(i)$ and $\tau(i)$, that q or τ which is determined by channel i. In terms of the values (2.17), all the remaining α, β, γ are given by (2.16), thus determining F_i by means of (2.15). Consequently, 2*NA+NB linearly independent solutions can be generated by setting

$$\left.\begin{array}{lcl}\alpha_0^{iq(i)} & = & \delta_{iq(i)}\ \delta_{q(i)\nu} \\ \beta_0^{iq(i)} & = & 0 \\ \gamma_0^{i\tau(i)} & = & 0\end{array}\right\}\ \text{for } 1 \leq \nu \leq NA$$

$$\left.\begin{array}{lcl}\alpha_0^{iq(i)} & = & 0 \\ \beta_0^{iq(i)} & = & \delta_{iq(i)}\ \delta_{q(i)\nu-NA} \\ \gamma_0^{i\tau(i)} & = & 0\end{array}\right\}\ \text{for } NA < \nu \leq 2NA$$

$$\left.\begin{array}{lcl}\alpha_0^{iq(i)} & = & 0 \\ \beta_0^{iq(i)} & = & 0 \\ \gamma_0^{i\tau(i)} & = & \delta_{i\tau(i)}\ \delta_{\tau(i)\nu-2NA}\end{array}\right\}\ \text{for } 2NA < \nu \leq M+NA \tag{2.18}$$

These 2NA+NB linearly independent solutions of the homogeneous system of M coupled equations (2.13) are integrated inwards to the point RA where the exchange potentials might be expected to begin contributing.

At this point the exchange potentials are explicitly taken into account. We define a further NE linearly independent solutions of the homogeneous system of NTOT coupled equations

(2.12) by setting the coefficients of $r^{-\lambda}$ in the exchange terms each equal to unity in turn and the rest equal to zero (analogous to the inner region). A further NV+NMU independent solutions of the inhomogenous system are generated by setting C and the m_λ's equal to unity in turn with the others zero, as in the inner region.

These NOUT=2*NA+NB+NE+NV+NMU independent solutions are integrated inwards to the points R1 and R5 where they are stored. These NOUT solutions for the outer region are denoted by g_i^{β} where the superscript β denotes the particular independent solution.

Matching Algorithm

A linear superposition of the NIN independent solutions F_i, i.e.

$$\sum_{\alpha=1}^{\text{NTOT}} \nu_\alpha F_i^{\alpha} + C F_i^{C} + \sum_{\gamma=1}^{\text{NMU}} \mu_\gamma F_i^{\gamma} ,$$

will certainly satisfy the boundary conditions (1.41) and (2.3) at the origin, though in general they would not satisfy the corresponding asymptotic conditions. In like manner, a linear superposition of the NOUT independent solutions g_i^{β},

i.e. $$\sum_{\beta=1}^{\text{NTOT+NA}} \omega_\beta g_i^{\beta} + C g_i^{C} + \sum_{\gamma=1}^{\text{NMU}} \mu_\gamma g_i^{\gamma} ,$$

will satisfy the asymptotic conditions but not, in general, the

the boundary conditions at the origin.

At the two match points, R5 and R1, we impose the condition that the inner and outer solutions be equal,

$$\sum_{\alpha=1}^{NTOT} \nu_\alpha \begin{bmatrix} F_i^{\alpha}(R5) \\ F_i^{\alpha}(R1) \end{bmatrix} + C \begin{bmatrix} F_i^{c}(R5) \\ F_i^{c}(R1) \end{bmatrix} + \sum_{\gamma=1}^{NMU} \mu_\gamma \begin{bmatrix} F_i^{\gamma}(R5) \\ F_i^{\gamma}(R1) \end{bmatrix}$$

$$= \sum_{\beta=1}^{NTOT+NA} \omega_\beta \begin{bmatrix} g_i^{\beta}(R5) \\ g_i^{\beta}(R1) \end{bmatrix} + C \begin{bmatrix} g_i^{c}(R5) \\ g_i^{c}(R1) \end{bmatrix} + \sum_{\gamma=1}^{NMU} \mu_\gamma \begin{bmatrix} g_i^{\gamma}(R5) \\ g_i^{\gamma}(R1) \end{bmatrix} \qquad (2.19)$$

This will ensure a smooth solution over the entire range $0 \leq r \leq RB$, and indeed generates the solution which satisfies the boundary conditions both at the origin and asymptotically.

Equations (2.19) are a system of 2*NTOT equations in the (2*NTOT+NA+NV+NMU) unknown parameters ν_α, ω_β, c, μ_γ. Hence, we need a further NA+NV+NMU equations. (Note we consider the case where NV= 0,1).

NA equations are obtained by specifying that the coefficients of the sine part of the right-hand side of equation (2.19) in the asymptotic region equals $k_i^{-1/2}\ \delta_{ij}$ for j= 1, NA.

Therefore,

$$\sum_\beta \omega_\beta \; g_i^{\beta}(RB) = \omega_1 \, g_i^{1} + \omega_2 \, g_i^{2} + \ldots . + \omega_{NA} \, g_i^{NA} + \ldots . +$$

$$\omega_{NTOT+NA} \, g_i^{NTOT+NA}$$

$$= \omega_i \, g_i^{i} + \omega_{NA+i} \, g_i^{NA+i}$$

$$= \omega_i \, \mathrm{Sin}\bar{\theta}_i + \omega_{NA+i} \, \mathrm{Cos}\bar{\theta}_i \qquad (2.20)$$

where $\bar{\theta}_i = k_i RB - \eta_i \; \ell n(2k_i RB)$, since by construction of the (NTOT+NA) linearly independent solutions in the outer region, see eqn. (2.18), all the other g_i's are zero at RB. On the other hand from eqn. (1.41) we have

$$F_{ij}(RB) \sim k_i^{-1/2} \, [(\mathrm{Sin}\bar{\theta}_i \, \mathrm{Cos}\Phi_i - \mathrm{Cos}\bar{\theta}_i \, \mathrm{Sin}\Phi_i)\delta_{ij}$$

$$+ (\mathrm{Cos}\bar{\theta}_i \, \mathrm{Cos}\Phi_i + \mathrm{Sin}\bar{\theta}_i \, \mathrm{Sin}\Phi_i) \, R_{ij}] \qquad (2.21)$$

where $\Phi_i = \dfrac{\ell_i \pi}{2} - \sigma_{\ell_i}$, which can be rewritten in the form

$$k_i^{-1/2} \, \{\mathrm{Sin}\bar{\theta}_i \, [\delta_{ij} \, \mathrm{Cos}\Phi_i + R_{ij} \, \mathrm{Sin}\Phi_i]$$

$$+ \mathrm{Cos}\,\bar{\theta}_i \, [-\delta_{ij} \, \mathrm{Sin}\Phi_i + R_{ij} \, \mathrm{Cos}\Phi_i]$$

which upon comparing the coefficients of $\mathrm{Sin}\bar{\theta}_i$ and $\mathrm{Cos}\bar{\theta}_i$ with those of eqn. (2.20) yields

$$\omega_i^{\,j} = k_i^{-1/2}\,[\delta_{ij}\,\mathrm{Cos}\Phi_i + R_{ij}\,\mathrm{Sin}\Phi_i]$$

$$\omega_{i+NA}^{\,j} = k_i^{-1/2}\,[-\delta_{ij}\,\mathrm{Sin}\Phi_i + R_{ij}\,\mathrm{Cos}\Phi_i] \qquad (2.22)$$

We can readily derive the following pair of equations by subtraction and addition, respectively, and multiplying by either $\mathrm{Sin}\Phi_i$ or $\mathrm{Cos}\Phi_i$,

$$\omega_i^{\,j}\,\mathrm{Cos}\Phi_i - \omega_{i+NA}^{\,j}\,\mathrm{Sin}\Phi_i = k_i^{-1/2}\,\delta_{ij} \qquad (2.23)$$

$$\omega_i^{\,j}\,\mathrm{Sin}\Phi_i + \omega_{i+NA}^{\,j}\,\mathrm{Cos}\Phi_i = k_i^{-1/2}\,R_{ij} \qquad (2.24)$$

We see that (2.23) contains no additional unknowns to what we already have in the matching condition (2.19); furthermore, the system (2.23) is NA in number, i.e. i= 1, NA. This provides us with an additional NA equations to add to the 2*NTOT equations of (2.19).

In the derivation of the system of coupled equations (1.40) we imposed the orthogonality condition $\langle P_{np}|F_{ij}\rangle = 0$. We may rewrite this as

$$\int dx_{N+1}\ F_{ij}\ (x_{N+1})P_{np}\ (x_{N+1}) = 0 \qquad (2.25)$$

This orthogonality condition provides us with a further NMU equations. Substitution of (2.19) into (2.25) gives

$$\sum_{\alpha=1}^{NTOT} \nu_\alpha{}^j \int_0^{R1} dr\ P_\eta\ F_\eta{}^\alpha + \sum_{\beta=1}^{NTOT+NA} \omega_\beta{}^j \int_{R1}^{\infty} dr\ P_\eta g_\eta{}^\beta$$

$$+ \sum_{\eta'=1}^{NMU} \gamma_{\eta'}{}^j \{ \int_0^{R1} dr\ P_\eta\ F_\eta{}^{\eta'} + \int_{R1}^{\infty} drP_\eta g_\eta{}^{\eta'} \}$$

$$+ c^j \{ \int_0^{R1} dr\ P_\eta F_\eta{}^c + \int_{R1}^{\infty} dr\ P_\eta\ g_\eta{}^c \} = 0 \qquad (2.26)$$

where $\eta = 1$, NMU.

Finally, we get the remaining NV (=0,1) equations by substituting (2.19) into the equation

$$c^\ell = -(E_{N+1} - E)^{-1} \sum_i \int dr\ V_i F_{i\ell}$$

(which is eqn. (33) of S.H.B. [5]) which takes the form

$$AC^j + \sum_{\alpha=1}^{NTOT} \nu_\alpha^j \sum_i \int_0^{R1} dr\ V_i\ F_i^\alpha + \sum_{\beta=1}^{NTOT+NA} \omega_\beta^j \sum_i \int_{R1}^{\infty} drV_i g_i^\beta$$

$$+ \sum_{\gamma=1}^{NMU} \mu_\gamma \{ \sum_i \int_0^{R1} V_i\ F_i^\gamma\ dr + \sum_i \int_{R1}^{\infty} V_i\ g_i^\gamma dr \}$$

$$+ C \{ \sum_i \int_0^{R1} drV_iF_i^c + \sum_i \int_{R1}^{\infty} drV_i\ g_i^c \} = 0 \qquad (2.27)$$

We may present these (2*NTOT+NA+NMU+NV) equations with the corresponding number of unknown parameters ν_α, ω_β, c, μ_γ in a condensed form by using matrix notation as

$$\begin{array}{c|c|c|c|c|}
 & NTOT & NV & NMU & NTOT+NA \\
\hline
NTOT & F_i^\alpha(R5) & F_i^c - g_i^c \text{ at } R5 & F_i^\gamma - g_i^\gamma \text{ at } R5 & -g_i^\beta(R5) \\
\hline
NTOT & F_i^\alpha(R1) & F_i^c - g_i^c \text{ at } R1 & F_i^\gamma - g_i^\gamma \text{ at } R1 & -g_i^\beta(R1) \\
\hline
NV & o<V_iF_i^\alpha>R1 & A + o<V_iF_i^c>R1 + R1<V_ig_i^c>\infty & o<V_iF_i^\gamma>R1 + R1<V_ig_i^\gamma>\infty & R1<V_ig_i^\beta>\infty \\
\hline
NMU & o<P_\eta F_\eta^\alpha>R1 & o<P_\eta F_\eta^{\eta'}>R1 + R1<P_\eta g_\eta^{\eta'}>\infty & o<P_\eta F_\eta^c>R1 + R1<P_\eta g_\eta^c>\infty & R1<P_\eta g_\eta^\beta>\infty \\
\hline
NA & 0 & 0 & 0 & \begin{matrix} \cos\Phi & \sin\Phi & 0 \\ 0 & & \end{matrix}
\end{array}
\begin{vmatrix} \nu_1 \\ \vdots \\ \nu_{NTOT} \\ c \\ \mu_1 \\ \vdots \\ \mu_{NMU} \\ \omega_1 \\ \vdots \\ \omega_{NTOT+NA} \end{vmatrix}
=
\begin{vmatrix} 0 \\ \vdots \\ \vdots \\ k_j^{-1/2} \\ \vdots \end{vmatrix}$$

(2.28)

It is in this manner that the function values are stored at R1 and R5 in ATOMNP [49]. Inversion of this matrix enables us to calculate all or some of the unknown parameters ν, c, μ and ω.

Reference to equation (2.23) shows that we can get NA families of NA equations by varying the value of j on the right-hand side, in other words by varying the position of $k_j^{-1/2}$, up or down, in the matrix equation. For each value of j, we can calculate one row of the NAXNA R-matrix by means of equation (2.24), which demands only that ω_i and ω_{i+NA} be known for the particular j. This means that the R-matrix may be calculated while only ω_i^j and ω^j_{i+NA} need be calculated from (2.28). Having calculated R_{ij} we may easily calculate such quantities as the T-matrix (1.16) and the scattering cross-sections (1.20) etc.

CHAPTER 3

INTRODUCTION

In this chapter we will consider such concepts as stability, truncation, error propagation, etc. in a general sense. In Chapter 4 we will particularize and apply these concepts and definitions to definite particular algorithms. The purpose of this chapter is, then, to define our terms and give a general appreciation of the philosophy of numerical integration.

The system of differential equations that we are interested in, is of the general form

$$\frac{d^2Y_i}{dr^2} = \sum_{j=1}^{N} f_{ij}(r)Y_j(r) + G_i(r) \qquad (3.1)$$

with i=1, N and subject to boundary conditions at r=0.

Using vector notation we may write this as

$$\frac{d^2Y}{dr^2} = fY + G \qquad (3.2)$$

where Y, G are N-dimensional vectors and f is an NxN matrix. This vector notation tends to simplify the later analysis.

We may look upon (3.1) as being a special case of the more general system of coupled differential equations

$$\frac{d^2Y_i}{dr^2} = f_i(r, Y_1, Y_2..., Y_N) \qquad (3.3)$$

with i=1, N. In vector notation this may be written as

$$\frac{d^2Y}{dr^2} = f(r, Y_1 \ldots Y_N) \qquad (3.4)$$

which is the generalization of (3.2). We will tend to deal with the more general systems (3.3) and (3.4) in this chapter; when relevant, we will refer to the more particular system (3.1) and (3.2).

In general, the system of equations corresponding to a differential equation of order $n(n \geq 2)$ is not unique, for with higher order equations an extra degree of freedom exists which is not available for first order equations; any n^{th} order equation $(n \gtrsim 2)$ may be replaced by an equivalent system of equations, each of lower order than the original. For example, we may treat the system of equations (3.4) in either of two ways

(i) Treat it directly as a second order differential equation system and use algorithms suitable for such second order equations to derive it's solution.

(ii) Reduce it to a system of two first order equations by defining

$$\left.\begin{aligned} \frac{dY}{dr} &= u \\ \frac{du}{dr} &= f \end{aligned}\right\} \qquad (3.5)$$

By defining two further vectors

$$Y = \begin{pmatrix} y \\ u \end{pmatrix} \quad \text{and} \quad F = \begin{pmatrix} u \\ f \end{pmatrix}$$

we may write (3.5) in the more concise form

$$\frac{dY}{dr} = F \tag{3.6}$$

Scientists vary on the relative merits of the two approaches; Collatz (p. 117, [52]), [62] is of the opinion that direct integration of the higher order system is, in general, more efficient and more accurate, while Henrici [54] favors reduction to a system of lower order equations. Zurmuhl [77] developed integrating algorithms of the Runge-Kutta type for systems of order $n(n \geq 3)$ and concluded that direct integration was superior to reduction. Froese [78] applied the Rademacher theory of error propagation to a fourth order system and also concluded that direct integration is superior. However, she does note that in particular cases reduction may give more accurate answers. Miller [51] provides an example to illustrate that, at times, reduction to a system of lower order equations can have disastrous effects on stability.

In conclusion, one might say that, for a general system of higher order differential equations, it is not possible to decide, a priori, whether direct integration or prior reduction to a system of lower order equations provides the superior answer. Sometimes (i) is best, at other times (ii) is best.

Types of Computational Methods

Very many algorithms exist for integrating systems such as (3.4). However, they may all be considered to be one of the following three types:

(i) Multi-step method: these methods make use of information about the solution Y and function f at various points, called pivotal points. These are of the general form

$$Y_{n+1} = \sum_{i=0}^{K} \alpha_{K-i} Y_{n-i} + h^P \sum_{i=0}^{K+1} B_{K-i} f_{n-i+1} \qquad (3.7)$$

where P, n, K are positive integers and α_{K-i}, B_{K-i} are constants unique to the particular integrating algorithm. Y_{n+1} is the approximation that the algorithm gives for $Y(r_{n+1})$; P is the order of the differential equation that is being solved. A method is called a K-step method if the values $Y_n, Y_{n-1} \ldots Y_{n-K+1}$ are needed to calculate Y_{n+1}; h denotes the step-size.

(ii) One-step method: these are often called Runge-Kutta type methods. Any algorithm for integrating differential equations which enables us to calculate Y_{n+1}, provided that Y_n, f_n and f at some points in the interval $[r_n, r_{n+1}]$ are known, is called a one-step method. These methods have the general form

$$Y_{n+1} = Y_n + \sum_{i=1}^{K} \alpha_i k_i \qquad (3.8)$$

where α_i are weighting constants particular to the algorithm in use but independent of the differential equation being solved; k_i are approximations to $f(r,y)$ at particular points in $[r_n, r_{n+1}]$; K is some positive integer, usually varying between 2 and 5; in general, the greater the value of K, the greater the accuracy of the algorithm.

(iii) Hybrid methods: these incorporate features of both (i) and (ii). They make use of information at pivotal points, as (i), and at intermediate points, as (ii). Hence, they may be represented as

$$Y_{n+1} = \sum_{i=0}^{K} \alpha_{K-i} Y_{n-i} + h^P \sum_{i=0}^{K+1} B_{K-i} f_{n+1-i}$$

$$+ h^P \sum_{i=0}^{M} \gamma_i \, f(r_n - \ell_i h) \qquad (3.9)$$

where ℓ_i is not an integer, and M is an integer, usually 1 or 2. These hybrid techniques are a recent innovation and are mainly due to Butcher [105], [106], Gragg and Stetter [107].

The derivation of One-step methods and Hybrid methods is quite laborious and may be studied in [74], [75], [76] and [105], [106], [107] respectively. The basic principle for the derivation of multi-step methods may be easily demonstrated. Hence, we will give a short treatment of this and merely refer to the relevant references for both One-step and Hybrid derivations.

Derivation of Multi-step methods

In the case of a first order differential equation, for example,

$$y' = f \tag{3.10}$$

we may write

$$Y(r_{n+P}) = Y(r_{n-q}) + \int_{r_{n-q}}^{r_{n+P}} f \, dr \tag{3.11}$$

In the case of a second order equation

$$y'' = f \tag{3.12}$$

we may write

$$Y(r_{n+P}) = Y(r_{n-q}) + \int_{r_{n-q}}^{r_{n+P}} \int_{r_{n-q}}^{r} f \, dr^2 \tag{3.13}$$

We now replace f by an approximating interpolating polynomial and integrate between the appropriate limits. We will here consider a few simple examples to illustrate some important qualities of multi-step methods.

Case (a) P=1, q=0

Replace f in (3.11) by the polynomial with backward differences which takes on the values $f_{n-K}, f_{n-K+1}\dots f_n$ at points $r_{n-K}, r_{n-K+1}\dots r_n$. This is of the form [52, p.8]

$$N_K(r) = f_n + \sum_{i=0}^{K} \frac{u(u+1)\dots(u+i-1)}{i!} \nabla^i f_n \qquad (3.14)$$

where $u = (r-r_0)/h$ and ∇ is the backward difference.

On substituting (3.14) into (3.11) and integrating between the appropriate limits we get

$$Y_{n+1} = Y_n + h \sum_{i=1}^{K} \beta_i \nabla^i f_n$$

$$= Y_n + h[f_n + 1/2\nabla f_n + 5/12\nabla^2 f_n + 3/8\nabla^3 f_n \dots]$$

$$= Y_n + h \sum_{i=0}^{K} \alpha_{iK}\, f_{n-i} \qquad (3.15)$$

(3.15) is said to be in Lagrangian form; the accuracy and form of the algorithm depends on the value of K. The values of α_{iK} are given by Table (1)

α_{iK} i=	0	1	2	3
K=1	3/2	-1/2		
K=2	23/12	-16/12	5/12	
K=3	55/24	-59/24	37/24	-9/24

TABLE 1

When K=3, the resulting algorithm is called the Adams extrapolation method.

If f in (3.11) is replaced by the polynomial which takes on the values $f_{n-i+1} \ldots f_{n+1}$ at the points $r_{n-i+1} \ldots r_{n+1}$ and integrate between the same limits as before we get as an approximation for $Y(r_{n+1})$;

$$Y_{n+1} = Y_n + \sum_{i=0}^{K} \gamma_{iK} f_{n+1-i} \tag{3.16}$$

where

γ_{iK} are given by Table 2.

γ_{iK}

i=	0	1	2	3
K=1	1/2	1/2		
K=2	5/12	8/12	-1/12	
K=3	9/24	19/24	-5/24	1/24

TABLE 2

When K=3, the resulting formula is usually called the Adams interpolation formula, or Adams-Moulton method.

There is one very important difference between (3.15) and (3.16). In the latter case, the R.H.S. expression is a function of Y_{n+1}, while in the former case it is not. (3.15) is known as an "open" method while (3.16) represents a "closed" method. Closed methods are generally more accurate than open methods but suffer from the fact that Y_{n+1} is explicitly included in the R.H.S. This demands that (3.16) be used in

(i) an iterative manner

(ii) use (3.15) as a predictor and (3.16) as the corrector

(iii) in a manner combining (i) and (ii).

When an open and closed formula are used in this manner, it is usually called a predictor-corrector method. Much research has been done in this particular field [65], [66], [67], [99]-[104].

A similar analysis, when applied to (3.13), provides multi-step methods (open and closed) for secondorder equations. We will meet a number of these in Chapter 4.

Error Analysis

It is intuitively obvious that some algorithms give a more accurate estimate for the solution of a system of differential equations than others. To get some a priori estimate for this accuracy we use the Taylor series expansion as a yardstick. This expansion is of the form

$$Y(r+H) = Y(r)+H\,Y^{'}(r)+ H^{2}\,Y^{''}(r)\ \ldots\ldots \qquad (3.17)$$

where superfixes denote differentiation w.r.t.r. To estimate the accuracy of the integrating algorithm in question, we expand it as a Taylor series about Y(r) and compare the coefficients of its various powers of H with those of (3.17). If the individual coefficients of H^{P} (P=1,K) agree but the coefficients of H^{K+1} do not agree, then we say the algorithm is of $O(H^{K})$. This may be used as an indication for the accuracy of the algorithm since, in general, the greater the value of K, the more accurate the algorithm tends to be (assuming stability conditions are satisfied).

Since all algorithms agree with (3.17) only for a finite number of powers of H, we will always have such an error. Even when the Taylor series solution itself is used as the integrating algorithm [51], [95], a similar error occurs since, for practical reasons, only a finite number of terms may be retained in the expansion. This error is called the local truncation error, and it occurs at each interval. The resultant propagated truncation error after N intervals is called the accumulated truncation error.

A second type of error may occur due to the necessity that real numbers be approximated in calculations, whether these are done by hand, calculator or computer. In the case of calculations computed on the computer, this results from each number being stored in a definite storage space and represented (approximately) by a finite number of digits. If the number is not adequately represented by its approximation in the computer (i.e. when the word length is too short for the desired accuracy; this may be the case with IBM 360 series where single precision is used), serious accumulative errors may result, which could render the final answer useless. Such an error is called a round-off error.

Error analysis for estimating either the local truncation error or the accumulated truncated error is sadly lacking in computational numerical analysis. Various bounds for these errors have been formulated for many algorithms [51-[55], [81]-[84], but they generally suffer from being either

(i) unduly large with the result that they are of no practical use for calculating realistic estimates.

(ii) very difficult and laborious (possibly even impossible) to compute, being functions of high order partial derivatives and Lipschitz constants, etc.

Alternative approaches have been developed by Richardson [58] and Scraton [85] that demand either parallel integration with different stepsizes or the storage of functions calculated at a number of pivotal points. These methods, which are particularly suitable for one-step methods, increase the volume of calculations but can give quite good estimates for the accumulated truncation error. Moore [97] has developed an extremely accurate procedure for calculating this propagated error but needs interval arithmetic for the calculations. Very few computers are yet capable of handling such processes.

Round-off error is of a more random nature and hence one might expect it to be more difficult to estimate accurately; however, the contrary proves to be the case. If E_r is the absolute value of the maximum round-off error at any step, one could definitely say that

$$|\varepsilon_r|_{\text{propagated}} \leq N\, E_r \qquad (3.18)$$

after N steps. However, this is obviously an over-cautious bound for $|\varepsilon_r|_{\text{propagated}}$ as many of the errors will tend to cancel out. The randomness of round-off errors lends itself to the useful application of statistics to the problem [56], [52], and many realistic estimates for the accumulated round-off error have been formulated. Very elementary statistics provide $\sqrt{N}\ E_r$ as being a better bound in (3.18).

Blum [81] and Gill [80] reduced the accumulation of round-off in the Runge-Kutta method by using a round-off right shift which helps to retain some of the lower order digits that might otherwise be lost. However, King [57] has shown that the most effective method for reducing round-off errors to an insignificant magnitude is the use of double precision. He has also shown that double precision need not be used for all the calculations but only for certain types. I have used double precision in all my calculations on IBM 360/65J (each real number being represented by a word length of 8 bytes); hence, round-off error is negligible and may henceforth be neglected.

Stability

The major difference between mathematical and numerical developments lies in the inevitability of rounding and truncation errors in the latter, since numerical processes must be finite.

Thus, a differential system defines mathematically a unique solution, "the" solution of the system (neglecting eigenvalue problems). When, however, a differential system is given numerically, the equations and the boundary conditions normally involve one or more rounded constants, which have a permissible range of variation; these correspond to a set (or pencil) of permissible solutions. Likewise, the numerical processes of obtaining a solution involve further truncation and rounding errors which increases further the variation in the possible set of "solutions". The numerical work simply picks out a single member of this set.

We may ask how closely the possible members of such a set of solutions remain together. This is the general problem of stability. If they remain "closely" bunched together so that any one of them gives an adequate solution to the problem, we can say the process is stable; if the variation is so great that not all possible solutions are acceptable, the process is unstable (see Sec. VI, Chap. 1). However, various types of instability exist, some being correctable. Errors in data and those made during the computation are distinct in the sense that the latter may often be controlled whereas the former may not be so. If, then, all solutions originating from the boundary conditions, under reasonable rounding-error variations, are adequate, we say the problem is _inherently stable_; otherwise the problem is _inherently unstable_. Any instability introduced by the particular method of computation is regarded as _induced instability_. We will always assume the problem is inherently stable and the question of stability will be whether the induced stability (henceforth merely called stability, since no confusion should arise as to the intended meaning) is present or absent; and if it is present, how may it be controlled.

Generally the system of differential equations is replaced by a system of new equations (i.e. differences) which approximate the original system and have a fixed truncation error [see (3.15), (3.16)]; this approximating equation is called the _replacement_ equation.

Closely connected with the question of stability is that of convergence. This may be of two kinds.

(i) Convergence with H occurs when the desired solution of the replacement system adequately computed, converges, as H→0, to the desired solution of the original system.

(ii) Convergence with iteration applies to the use of an iterative method to obtain a desired solution of the replacement system.

Suppose we are computing a particular solution of a particular replacement equation, and we make an error at some point, i.e. a truncation or a round-off error. This alters the solution into a neighboring solution of the same equation at the point where the error is made. Further similar errors at subsequent steps cause further jumps to other neighboring solutions. In the case of round-off, these jumps will be random, while a fixed truncation error causes a systematic drift. With a difference equation replacing the original, these jumps may introduce parts of any parisitic solution [51]-[54], [70] (i.e. a solution of the replacement equation which has no counterpart amongst those of the original equation), thus yielding obvious non-solutions of the original equation when a parasitic solution is dominant. Parasitic solutions are always present when the order of the replacement system is higher than that of the original [59], [60].

We note that the stability of methods using a replacement equation depends on the behavior of solutions of this equation; convergence remains the link between solutions of the two systems, the replacement and the original.

Very little was contributed to the theory and analysis of stability until approximately 1950. Prior to this, the only contribution of note was that of Collatz and Zurmuhl [62] who considered instability due to unevenness with central-difference methods. In the early '50's, further contributions were made by Todd [63] and Rutishauser [61] who considered instability of particular multi-step algorithms; an investigation of the stability of the Runge-Kutta method [75] was also carried out in [61]. However, it was not until 1956 that a general analysis of the theory of stability was available when Dahlquist published his very memorable paper [59] on the stability of multi-step methods, which he added to in 1959 [60]. Henrici [54], [54a], [54b] has since developed and generalized further this theory. In the late '50's and early '60's a very intensive investigation of the stability of algorithms of the predictor-corrector type was spearheaded by Milne [65], [66], [67] and Hamming [99], which resulted in a very excellent general theory of stability for algorithms of the predictor-corrector type [100], [101], [103], [68]. The stability of hybrid methods has been investigated by Kohfeld, *et al*. [108], [109].

Stability of Multi-step Methods

We shall here give a brief summary of the criterions for the stability of multi-step methods as developed by Henrici [54].

1^{st} Order Systems

The general linear K-step integration method is of the form

$$\alpha_K Y_{n+K} + \alpha_{K-1} Y_{n+K-1} \cdots\cdot + \alpha_o Y_n$$

$$= H \{ \beta_K f_{n+K} + \beta_{K-1} f_{n+K-1} \cdots\cdot + \beta_o f_n \} \qquad (3.19)$$

Define the characteristic polynomial as

$$\rho (\zeta) = \alpha_K \zeta^K + \alpha_{K-1} \zeta^{K-1} \cdots\cdot + \alpha_o$$

$$= \sum_{i=0}^{K} \alpha_i \zeta^i \qquad (3.20)$$

Theorem 1:

A necessary and sufficient condition for the stability of (3.19) is that the modulus of no root of (3.20) exceeds 1, and that roots of modulus 1 be simple (Th. 5.5, [54]).

This condition of stability has the purpose of preventing a small initial error in computation from growing at such a rate that convergence is jeopardized.

Theorem 2:

A necessary and sufficient condition for convergence is that the order of the multi-step method must be ≥ 1 and that the stability condition of Theorem 1 be satisfied (Th. 5-10 [54]).

The maximum order that a stable method can achieve is given by Theorem 3:

The order P of a stable multi-step method cannot exceed K+2. A necessary and sufficient conditon for P=K+2 is that K is even, that all roots of (3.20) have modulus 1 and that Theorem 1 is satisfied (Th. 5-9 [54]). In the case of K odd, the maximum order is K+1 (Th. 5-8 [54]).

2nd Order Systems

The general linear K-step method is now of the form

$$\sum_{i=0}^{K} \alpha_i Y_{n+i} = H^2 \sum_{i=0}^{K} \beta_i f_{n+i} \qquad (3.21)$$

The characteristic polynomial is again defined as

$$\sum_{i=0}^{K} \alpha_i \zeta^i \qquad (3.22)$$

Stability Condition

Theorem 4:

A necessary and sufficient condition for the stability of (3.21) is that the modulus of no root of (3.22) exceeds 1 and that the multiplicity of roots of modulus 1 be at most 2. (Th. 6-1 [54]).

Condition of Convergence

Theorem 5:

Same as Theorem 2. (Th. 6-2 [54]).

Maximum Order of a Stable Method

Theorem 6:

Same as Theorem 3. (Th. 6-4, Th. 6-5 [54]).

In chapter 4 we will apply these criterions to a number of multi-step methods. One should note that even when the above theorems on stability are satisfied but all roots of the characteristic polynomial have modulus of 1, a weak instability exists but this may be diminished by reducing H.

CHAPTER 4

We shall here endeavor to give a detailed, if somewhat cryptic, treatment of what are probably the three most extensively used algorithms for the numerical solution of second-order equations, i.e. Numerov method, Runge-Kutta method (this also includes Nystrom's algorithms) and finally the De Vogelaere method. A somewhat briefer treatment of other integrating methods, i.e. predictor-corrector, Taylor series, Butcher hybrid methods, etc., will also be given along with reasons for not considering them as suitable methods for the system of equations involved (1.57), (1.58).

Numerov Method

Let us now consider one very important subset of

$$y'' = f(x,y,y') \tag{4.1}$$

i.e.

$$y'' = f(x)y \tag{4.2}$$

where superscripts denote differentiation with respect to x. We may note that (1.57) and (1.58) are of the form (4.2). In particular, it is actually of the form

$$y'' = f(x)\ y + G(x) \tag{4.3}$$

This type of differential equation occurs in many fields of science and has long been studied. Ref? The algorithm hitherto most widely used to solve (4.2) has been the Numerov method; this method is also known as the Gauss-Jackson method Ref and as the Royal Road [56] method.

The Numerov algorithm may be derived in many ways:

(i) Consider it to be a special case of the Cowell formula [55]

(ii) Replace (4.2) by its central difference equivalent [51], [36] and then truncate after second differences

(iii) Adopt the method of Blatt [70] who starts from the Taylor expansion for y(x+H) about y(x) and by a judicious combination of double differentiation w.r.t. x, summing and subtraction, arrives at the Numerov algorithm

(iv) Replace f in (3.13) by the Stirling interpolation formula [52]

$$St(x) = f_n + u \frac{\nabla f_n + \nabla f_{n+1}}{2} + \frac{u^2}{2!} \nabla^2 f_{n+1} \ldots . \qquad (4.4)$$

where $u = \dfrac{x-x_n}{H}$,

and integrate between limits X_n+H, X_n-H (i.e., $u=\pm 1$).

Independent of the method of derivation, the eventual form of the Numerov method will be

$$[1 - \frac{H^2}{12} f(X_{n+1})] \; Y_{n+1} = [2 + \frac{5}{6} \; H^2 \; f(X_n)]Y_n + [1-H^2/_{12} f(X_{n-1})]Y_{n-1} \qquad (4.5)$$

If the system of equations is of the form (4.3), the algorithm will involve an additional term in the R.H.S. of (4.5) of the form $\frac{H^2}{12}$ $[G(X_{n+1}) + 10G(X_n) + G\ (X_{n-1})]$.

Normally one would expect this algorithm to have a local truncation error of $0(H^5)$ as it agrees with the Taylor series expansion up to and including the H^4 term. However, it conveniently transpires that the coefficient of H^5 in (4.5), when expanded as a Taylor series, is zero; hence the local truncation error is actually $0(H^6)$. This fact, along with the general simplicity of the coefficients in (4.5), accounts for its widespread popularity. Blatt [70] categorically states that this is the superior method for integrating systems such as (4.2). However, it is well worth noting that, as Sloan [71] has shown, the error propagated is actually $0(H^4)$, not $0(H^5)$ as has often been assumed. This means in effect that the accumulation error is of the same magnitude as the fourth order Runge-Kutta method and the De Vogelaere method.

Stability

The characteristic polynomial of (4.5), as defined in Chapter 3, is

$$\zeta^2 - 2\zeta + 1 = 0 \qquad (4.6)$$

The roots for this equation are

$$\zeta = 1,\ 1.$$

On applying the stability criterions of Chapter 3, i.e., Theorems 4, 5, 6 we note that the modulus of the roots of (4.6) do not exceed 1, the root of modulus 1 has a multiplicity not exceeding 2, all the roots are of modulus 1 and the order (as defined by Henrici [54]) of the algorithm is K+2 (where K=2); hence, this integrating method is the best possible one in the sense that it has the highest allowed order, while still satisfying the stability and convergence criterions. However, as pointed out in Chapter 3, "weak" instability is liable to be involved. Rutishauser [61] has also demonstrated the stability of the Numerov method by using perturbation techniques. Blatt [70] stresses these properties quite vigorously.

Variations of Numerov Method

The general usage of (4.5) involves the inversion of the coefficient of Y_{n+1} which is then multiplied by R.H.S. to solve for

Y_{n+1} [5], [33], [21], [49], [79]

i.e. $$Y_{n+1} = [1 - \frac{H^2}{12} f_{n+1}]^{-1} \left\{[2+\frac{5}{6} H^2 f_n] Y_n + [1-\frac{H^2}{12} f_{n-1}] Y_{n-1}\right\} \tag{4.7}$$

If it happens to be a very large matrix, as is very often the case with ATOMNP [49], then inversion can be very time-consuming as it arises at each interval step.

As an alternative to (4.7), we may use (4.5) in an iterative manner by approximating Y_{n+1} as

$$Y^{(1)}_{n+1} = \text{R.H.S. of (4.5)}$$

and using

$$Y^{(i+1)}_{n+1} = \text{R.H.S. of (4.5)} + \frac{h^2}{12} f_{n+1} Y^{(i)}_{n+1} \qquad (4.8)$$

until convergence is reached. Essentially this is the same as expanding the inverted term $[1-\frac{H^2}{12} f_{n+1}]^{-1}$ as a Binomial series. Generally two iterations in (4.8) should suffice for calculating Y_{n+1} to the same accuracy as (4.1). This, very obviously eliminates the necessity of inversion of the matrix $(1-\frac{H^2}{12} f_{n+1})$ at each interval. It is of interest to note here that but for the particular form of f(x,y,y') i.e. f(x)y, the derivation of this algorithm would have provided a "closed" algorithm and not an "open" one as we have here.

Fox and Goodwin [73] added a "deferred corrector" to the Numerov method to improve accuracy. One would use such a method by proceeding for a number of steps with the usual Numerov method and then adding a correction of form $-\frac{1}{240} \delta^6 Y_n$ to each Y_{n+1} calculated by the Numerov method; integration would then proceed by going through the cycle of calculations again. While accuracy would probably improve (though one should be very careful of stability considerations), very heavy storage demands are involved due to the necessity of retaining Y_{n+1} for a number of points until the corrector term $\frac{1}{240} \delta^6 Y_n$ has been calculated. This technique is then quite unsuitable for systems that involve many equations.

Sloan [72a] has developed an extension of the Numerov method that is suitable for second order equations of the form

$$Y''(X) = a(x)y'(x) + b(x)y(x) + c(x) \tag{4.9}$$

and which still retains the main advantages of Numerov, i.e. simple coefficients and local truncation of $0(H^6)$. He has since improved on this method [72] by formulating one that is similar in form to that of [72a] but which has improved error propogation properties. This improved algorithm has the form

$$Y_{n+1} = 2Y_n - Y_{n-1} + S_{n+1} + 10\ S_n + S_{n-1} \tag{4.10}$$

where Y_n, Y_{n-1}, S_{n-1} are assumed known at each interval and

$$\begin{aligned} S_{n+1} = A_{n+1}(9\ Y_{n+1} - 16\ Y_n + 7Y_{n-1} - 64\ S_n \\ - 8\ S_{n-1}) + B_{n+1}Y_{n+1} + C_{n+1} \end{aligned} \tag{4.11}$$

$$\begin{aligned} S_n = A_n(Y_{n+1} - 2\ S_{n+1} - Y_{n-1} + 2\ S_{n-1}) \\ + B_n\ Y_n + C_n \end{aligned} \tag{4.12}$$

where

$$\begin{aligned} S(X) &= \frac{h^2}{12}\ y''(x) \\ A(X) &= \frac{h}{24}\ a(x) \\ B(X) &= \frac{h^2}{12}\ b(x) \\ C(X) &= \frac{h^2}{12}\ c(x) \end{aligned} \tag{4.13}$$

The local truncation error $\frac{H^6}{240} Y^6(\zeta)$ $(X_n \leq \zeta \leq X_{n+1})$ is the same as that of (4.5).

Application to High-Speed Computers

Assume the system of equations has the form of (4.3)

$$Y'' = f(x)\ Y + G(x).$$

The Numerov algorithm now takes the form

$$(1-\frac{H^2}{12} f_{n+1})\ Y_{n+1} = (2 + \frac{5}{6} H^2 f_n) Y_n - (1-\frac{H^2}{12} f_{n-1}) Y_{n-1}$$

$$+ \frac{H^2}{12} (G_{n+1} + 10\ G_n + G_{n-1}) \qquad (4.14)$$

This may be rewritten in the more convenient form

$$(1-\frac{H^2}{12} f_{n+1}) Y_{n+1} = 2*(1-\frac{H^2}{12} f_n) Y_n - (1-\frac{H^2}{12} f_{n-1})\ Y_{n-1}$$

$$+ H^2*[f_n Y_n + \frac{1}{12} (G_{n+1} + 10\ G_n + G_{n-1})] \qquad (4.15)$$

Let (F1) denote the contents of the storage area F1 (this will be an array suitable for accomodating the matrix Y).

For the general step $X_n \rightarrow X_{n+1}$ let

$$(F1) = Y_n$$

$$(F2) = Y_{n-1}$$

$$(F3) = [1-\frac{H^2}{12} f_{n+1}]$$

$$(F6) = [1 - \frac{H^2}{12} f_n]$$

$$(F7) = [1 - \frac{H^2}{12} f_{n-1}]$$

$$(F8) = H^2 [f_n Y_n + \frac{1}{12} \{G_{n+1} + 10 G_n + G_{n-1}\}]$$

→ denotes stored in.

Calculations may be taken in the following order:

(i) (F1) → (F2) => Y_n = (F2)

(ii) 2*(F6) - (F7) + (F8) → (F1) => R.H.S. (4.15) = (F1)

(iii) (F6) → (F7) => $(1-\frac{H^2}{12} f_n)$ = (F7)

(iv) (F1) → (F6)

=> R.H.S. (4.15) = (F6)

(v) Compute $(F3)^{-1}$ → (F3)

(vi) (F3) * (F6) → (F1)

= > Y_{n+1} = (F1)

(vii) 12*[(F2) - (F7)] + $\frac{H^2}{12}$ $[G_{n+1} + 10 G_n + G_{n-1}]$ → (F8)

(viii) Compute $[1-\frac{H^2}{12} f_{n+2}]$ → (F3)

The current point is now denoted by X_{n+1} and we complete the cycle by changing n+1 → n and returning to (i).

Storage areas for 10 arrays are needed when variable step-sizes are used.

Notes

(1) As this is a multi-step method, Y_n and Y_{n-1} must be known before Y_{n+1} may be calculated. Hence, a second method is required for calculating the initial values Y_0, Y_1. The initial value Y_0 is generally given as one of the boundary conditions but a self-starting method, i.e. Runge-Kutta, Taylor series expansion, is required to calculate Y_1.

(2) Changing the mesh size H can be somewhat complicated; in practice we limit these changes to doubling the mesh size or halving it.

If we should wish to double the mesh size, it is most conveniently done by carrying along, during integration, Y_{n-2} and $(1-\frac{H^2}{12} f_{n-2}) Y_{n-2}$ in addition to the usual Y_n, Y_{n-1} etc. This means that the storage requirements will be increased by the addition of these two arrays.

For halving a mesh size we may use a central difference interpolation formula

$$Y_{n+1/2} = [-Y_{n+2} - Y_{n-1} + 9*(Y_{n+1} + Y_n)]/16 \tag{4.16}$$

which has truncation error $0(H^4)$. The term $(1-\frac{H^2}{12} f_{n+1/2})Y_{n+1/2}$ must be similarly calculated. This also necessitates the additional calculation and storage of 2 extra arrays. Interpolation formulae with greater accuracy than (4.16) may be easily formulated but the additional storage requirements would be greater still. Blatt [70] has pointed out that the Numerov algorithm itself may be used to interpolate for $Y_{n+1/2}$, i.e.

$$Y_{n+1/2} = \frac{(1-\frac{H_1^{\;2}}{12} f_{n+1})Y_{n+1} + (1-\frac{H_1^{\;2}}{12} f_n)}{(2+ \frac{5}{6} \; H_1^{\;2} f_{n+1/2})} \qquad (4.17)$$

where $H_1 = H/2$.

The truncation error involved in (4.17) is of the same order as in (4.15).

(3) While the local truncation error is available as $- \frac{H^6}{240} \; Y^{(6)}(\zeta)$ where $X_n \leq \zeta \leq X_{n+1}$, realistic estimates for the propogated error are not readily available. The Richardson technique [58], [85] which is suitable for one-step methods is not ideally applicable to multi-step methods but may be used in a modified form.

Runge-Kutta

The Taylor series solution is generally unacceptable for systems with a complicated form and when high accuracy is demanded, due to the necessity of calculating high total derivatives of Y. This is usually very laborious, often impossible. Runge-Kutta type methods try to circumvent this difficulty by getting correlation with the Taylor series solution, not by calculating higher derivatives of Y but by calculating approximations to f(x,y) at a number of points within the interval $[X_n, X_{n+1}]$; these auxiliary functions, usually denoted by k_i, are then suitably weighted so that the resultant Runge-Kutta method agrees with the Taylor expansion solution for a "few" terms. The more k_i that are calculated means the more accurate our method is, i.e. agrees with more terms of the Taylor solution.

Originally this type of formula was developed by Runge [74] and Kutta [75] to solve first order differential equations; Nystrom [76] later applied this principle to second order equations, while Zurmuhl [77] generalized further by solving for equations of third and higher order. In Chapter 3, we noted and discussed the various approaches for solving systems of equations of order $n(n \geq 2)$, whereby the systems may be solved directly or may first be reduced to a larger system of lower order equations. This is very relevant to the present discussion.

First Order Systems

Let us define the vector function $Z=\begin{pmatrix} Y_1' \\ Y_n' \end{pmatrix}$, so that the original system

$$Y'' = f(x,y) \tag{4.18}$$

reduces to the first order system

$$Y' = Z$$

$$Z' = f(x,y) \tag{4.19}$$

This may be further condensed by defining

$$Y' = \begin{pmatrix} Y \\ Z \end{pmatrix}' = \begin{pmatrix} Z \\ f(x,y) \end{pmatrix} = F(x,y) \tag{4.20}$$

Let m denote the number of auxiliary functions k_i that are being used.

(i) Case m=2

This is the simplest of the Runge-Kutta methods and is generally not used for high accuracy work due to its low order of accuracy. It deserves consideration, though, as it illustrates the basic principle of the Runge-Kutta technique, without needing very lengthy and laborious calculations to derive, which the higher order Runge-Kutta methods demand.

Assume the Runge-Kutta formula is of the type

$$Y_{n+1} = Y_n + a_1 k_1 + a_2 k_2 \tag{4.21}$$

where

$$k_1 = H\ F\ (X_n,\ Y_n)$$

$$k_2 = H\ F\ (X_n + b_1 H,\ Y_n + b_2 H)$$

and a_1, a_2, b_1, b_2 are constants to be determined so that (4.21) agrees with the Taylor series expansion to as high an order as possible. On expanding Y_{n+1} in a Taylor series about Y_n, likewise k_i about $F(X_n, Y_n)$, and comparing coefficients of the lowest powers of H, we see that we can get agreement up to and including the H^2 term if

$$\begin{aligned} a_1 + a_2 &= 1 \\ a_2\, b_1 = a_1\, b_2 &= 1/2 \end{aligned} \qquad (4.22)$$

Here we have 3 independent equations but 4 unknowns. Hence, we still have one degree of freedom in our solution of (4.22). Two particular solutions are well known

(a) $a_1 = a_2 = 1/2$

$b_1 = b_2 = 1$

(4.21) then takes the form

$$Y_{n+1} = Y_n + \frac{H}{2}\,[F(X_n,Y_n)+F(X_n+ H,\ Y_n+ HF\ (X_n,\ Y_n)\ )] \qquad (4.23)$$

This is often called the Heun method.

(b) $a_1 = 0,\ a_2 = 1$

$b_1 = b_2 = 1/2$

(4.21) then takes the form

$$Y_{n+1} = Y_n + HF\ (X_n + H/2,\ Y_n + \frac{H}{2}\ F(X_n,\ Y_n)\ ) \qquad (4.24)$$

Collatz [52] calls this the modified Euler method. In each of these formulae, (4.23) and (4.24), the local truncation error is $0(H^3)$.

(ii) Case m=4

We get much more accurate algorithms when m=4. This gives rise to the classical Runge-Kutta method [75].

We define 4 vectors

$$k_1 = F\ (X_n,\ Y_n)$$

$$k_2 = F\ (X_n + Hb_1,\ Y_n + Hb_1,\ k_1)$$

$$k_3 = F\ (X_n + H(b_2 - b_3), Y_n + H(b_2 - b_3)k_1 + Hb_3k_2)$$

$$k_4 = F\ [X_n + H(b_4 - b_5 - b_6), Y_n + Hb_4k_1 + Hb_5(k_2 - k_1) + Hb_6(k_3 - k_1)]$$

Assume

$$Y_{n+1} = Y_n + a_1k_1 + a_2k_2 + a_3k_3 + a_4\ k_4 \qquad (4.25)$$

In a similar manner as with m=2, we expand Y_{n+1} in a Taylor series about Y_n and $k_i(i=1,\ 4)$ about $F(X_n,\ Y_n)$, and then equate the resultant coefficients of the lowest powers of H in (4.25).

After laborious calculations [75], we arrive at a set of 8 non-linear equations with 10 unknowns i.e. $a_i (i=1, 4)$, $b_i (i= 1, 6)$.

Kutta indicated a one-parameter family of solutions,

$$a_1 = 1/6 \qquad b_1 = 1/2$$

$$a_2 = \frac{2-t}{3} \qquad b_2 = 1/2$$

$$a_3 = t/3 \qquad b_3 = 1/_{2t}$$

$$a_4 = 1/6 \qquad b_4 = 1$$

$$b_5 = 1-t$$

$$b_6 = t$$

The almost universally used solution is the one corresponding to t=1, which gives the very simple and symmetrical solution

$$Y_{n+1} = Y_n + \frac{H}{6} (k_1 + 2k_2 + 2k_3 + k_4) \qquad (4.26)$$

where

$$k_1 = F(X_n, Y_n)$$

$$k_2 = F(X_n + \frac{H}{2} , Y_n + \frac{k_1)}{2}$$

$$k_3 = F(X_n + \frac{H}{2}, Y_n + \frac{k_2}{2})$$

$$k_4 = F(X_n + H , Y_n + k_3)$$

Gill [80] proposed taking $t=1-\sqrt{2}$ which enabled him to calculate Y_{n+1} with the least amount of computer storage, while reducing roundoff simultaneously. However, this choice for the parameter t destroys the symmetry of the resultant algorithm; moreover Blum [81] showed that the same saving of storage can also be achieved with the classical Runge-Kutta formula (4.26).

These formulae agree with the Taylor series expansion up to and including the H^4 term; hence, the local truncation error is $0(H^5)$ and the method itself is of the fourth order. Sloan [71] has verified that the propogated truncation error is $0(H^4)$.

Second Order Systems

The more direct approach of integrating the second order equation directly, without prior reduction of the order, was employed by Nystrom [76].

Consider the differential equation

$$Y'' = f(x, y, z) \tag{4.27}$$

where $z= y'$. In developing a counterpart for (4.26) Nystrom again used 4 auxiliary function $k_i (i=1, 4)$. On applying a technique very similar to that of the last section and after very laborious calculations he formulated the following algorithm

$$\begin{aligned} Y_{n+1} &= Y_n + HZ_n + \frac{H^2}{6} (k_1+k_2+k_3) \\ Z_{n+1} &= Z_n + \frac{H}{6} (k_1+2k_2+2k_3+k_4) \end{aligned} \tag{4.28}$$

where

$$k_1 = f(X_n, Y_n, Z_n)$$

$$k_2 = f(X_n + \frac{H}{2}, Y_n + \frac{H}{2} Z_n + \frac{H^2}{8} k_1, Z_n + \frac{H}{2} k_1)$$

$$k_3 = f(X_n + \frac{H}{2}, Y_n + \frac{H}{2} Z_n + \frac{H^2}{8} k_1, Z_n + \frac{H}{2} k_2)$$

$$k_4 = f(X_n + H, Y_n + HZ_n + \frac{H^2}{2} k_2, Z_n + H k_3)$$

Both Y_{n+1} and Z_{n+1} are calculated with a local truncation error of $0(H^5)$. One may note here that in the special case of Z=Y' being explicitly absent from f(x,y,z), the above formulae (4.28) enjoy quite a substantial simplification; in particular $k_2 = k_3$. The system of equations that we are especially interested in, (1.57), (1.58), are of this form.

Henrici [54] derives a similar algorithm, differing from Nystrom only in the Y argument of k_2 and k_3; he has

$$k_2 = f(X + \frac{H}{2}, Y + \frac{HZ}{2}, Z + \frac{H}{2} k_1)$$

$$k_3 = f(X + \frac{H}{2}, Y + \frac{H}{2} Z + \frac{H^2}{4} k_1, Z + \frac{H}{2} k_2) \qquad (4.29)$$

In the special case mentioned above, i.e. Y'' = f(x,y), one could expect (4.28) to be significantly faster to evaluate than (4.29).

Nystrom also derived formulae specifically for the special type

$$Y'' = f(x, y).$$

As a result we may attain a higher order of accuracy with a given number of k_i than could be expected from the general case; thus with 2 auxiliary functions we get a third order formula, with 3 we get a fourth order formula and with 4 we get a fifth order formula. Without further discussion we will write down their explicit form.

(i) m=2

$$Y_{n+1} = Y_n + HZ_n + \frac{H^2}{4}(k_1 + k_2)$$

$$Z_{n+1} = Z_n + \frac{H}{4}(k_1 + 3k_2) \qquad (4.30)$$

where

$$k_1 = f(X_n, Y_n)$$

$$k_2 = f(X_n + \frac{2H}{3}, Y_n + \frac{2}{3} H Z_n + \frac{H^2}{3} k_1)$$

(ii) m=3

$$Y_{n+1} = Y_n + HZ_n + \frac{H^2}{6}(k_1 + 2k_2)$$

$$Z_{n+1} = Z_n + \frac{H}{6}(k_1 + 4k_2 + k_3) \qquad (4.31)$$

where

$$k_1 = f(X_n, Y_n)$$

$$k_2 = f(X_n + \frac{H}{2}, Y_n + \frac{H}{2} Z_n + \frac{H^2}{8} k_1)$$

$$k_3 = f(X_n + H, Y_n + HZ_n + \frac{H^2}{2} k_2)$$

(iii) m=4

$$Y_{n+1} * Y_n + HZ_n + \frac{H^2}{192}(23k_1 + 75k_2 - 27k_3 + 25k_4)$$

$$Z_{n+1} = Z_n + \frac{H}{192}(23k_1 + 125k_2 - 81k_3 + 125k_4) \qquad (4.32)$$

where

$$k_1 = f(X_n, Y_n)$$

$$k_2 = f(X_n + 2/5H, Y_n + \frac{2H}{5} Z_n + \frac{2H^2}{25} k_1)$$

$$k_3 = f(X_n + \frac{2H}{3}, Y_n + \frac{2H}{3} Z_n + \frac{2H^2}{9} k_1)$$

$$k_4 = f(X_n + \frac{4H}{5}, Y_n + \frac{4H}{5} Z_n + \frac{4H^2}{25} [k_1 + k_2])$$

Cases m=2,3 provide unique formulae (4.30) and (4.31); however, m=4 does have one degree of freedom: hence (4.32) is just one member of many possibilities. However, it is not possible for the X argument of k_2 and k_3 to be coincident, as in (4.26) - (4.28), nor the X argument of k_4 to coincide with X_{n+1}, the end point of the general interval $[X_n, X_{n+1}]$. This means that the storage requirements for (4.32) would be very heavy indeed for a code like ATOMNP when the number of equations involved is substantial.

The algorithm defined by (4.31) is the counterpart of (4.28) and of course also of (4.26), each being of the fourth order. However, (4.31) scores heavily over both (4.26) and

(4.28) in both speed and storage requirements since it involves just 3 auxiliary functions. My research verifies this.

Stability

Runge-Kutta type methods are in general quite stable: this was shown by Rutishauser [61] who used his perturbation theory and has since been verified by others. Carr [83] justifies this assumption of stability by establishing bounds for the error propogation. However, weak stability can be involved [53], [61] but this may be eradicated by reduction of the step-size H. Collatz [52] gives as a rule of thumb that the quantity $\frac{k_2 - k_3}{k_1 - k_2}$ should be the order of "a few per cent"; he considers this to be a test of "sensitiveness"; of course, this does not apply when $k_2 \equiv k_3$.

Error Analysis

Expressions have been derived for describing the truncation error involved at each interval; however, these suffer from the fact that these expressions are generally quite complicated in form and not readily applicable. Bieberbach [82] has shown that the magnitude of the local truncation error involved when the classical Runge-Kutta method (4.26) is used to integrate from $X_n \rightarrow X_{n+1}$ is less than $C_n H^5$, when C_n is a function of $f(X_n,Y_n)$ and its partial derivatives of the first three orders.

Carr [83] developed this further and formulated a bound for the resultant propogated error of the form $\frac{2E}{HM}$ where E is the maximum error in absolute value at any point in the region of integration, M is a lower bound for $\frac{\delta f}{\delta y}$ in absolute value, and H, the step size, is a function of the upper and lower bounds of $\frac{\delta f}{\delta y}$. This was generalized further by Galler and Rozenberg who relaxed the conditions on H somewhat. However, in all of these cases, the error term was not in a readily applicable form.

A different approach has been advocated by Richardson [58] which assumes that for a sufficiently small interval $[X_n, X_{n+1}]$ the local truncation error may be approximated as CH^5, where C is a constant for that particular interval. If a further integration with a step size of $|X_{n+1} - X_n|/2$ is simultaneously carried out over this interval an estimate of the truncation error may be added to the originally calculated Y_{n+1}. This estimate is given by

$$E = \frac{Y_{n+1}^{(H)} - Y_{n+1}^{(H/2)}}{2^4 - 1} \qquad (4.33)$$

where $Y_{n+1}^{(H)}$ denotes the value calculated for Y_{n+1} when H is the step size. Scraton [85] gives a number of alternative procedures for estimating the truncation error; for example, if calculations are allowed proceed for 3 steps, an estimate of E is given by

$$\begin{aligned} E = 10\,\Delta\,Y_n + 19\,\Delta\,Y_{n+1} + \Delta\,Y_{n+2} \\ - 3HY_n' - 18HY'_{n+1} - 9HY'_{n+2} \end{aligned} \qquad (4.34)$$

This method requires little additional work but does involve extra storage requirements which renders it unsuitable for our calculations where storage is at a premium. Merson [112] has derived Runge-Kutta type formula of the fourth order with an additional truncation estimate, making use of five auxiliary functions but, as Scraton points out, this is applicable only to equations of the type

$$Y' = f(x,\ y) = ax + by + c \qquad (4.35)$$

Scraton generalizes the Merson method to the general case of f(x, y), also using five auxiliary functions to calculate a fourth order Runge-Kutta method with an additional truncation estimate. Unfortunately, the symmetry displayed by (4.26) is now lost with a resultant increase in storage requirements and the combination of k_i(i=1,5) involved is now non-linear. One may note, however, that with the addition of the truncation error estimate, the order of the resultant algorithm increases to five which is contrary to previously held assumptions [64], that a Runge-Kutta type formula of the fifth order for a general f(x, y) needs at least 6 auxiliary functions.

Application to High-Speed Computers

From the foregoing discussion on Runge-Kutta type methods, it is pretty obvious that the method likliest to be the most efficient for a system such as (1.57), (1.58) storage-wise and time-wise, while still having fourth order accuracy, is Nystroms algorithm given by (4.31). This has been most definitely verified by my research. Hence, we shall confine our programming considerations to this particular algorithm.

Using the usual notation,let

$$(F1) = Y_n$$

$$(F2) = Z_n$$

$$(F3) = f(X_n)$$

$$(F4) = k_i \quad (i=1,3)$$

(F5) = sum or partial sum of k_1+2k_2

(F6) = sum or partial sum of $k_1+4k_2+k_3$

For the general step $X_n \rightarrow X_{n+1}$ calculations may be taken in the order

(i) $(F3)*(F1) \rightarrow (F5) = k_1$
$\rightarrow (F6) = k_1$

(ii) Compute $f(X_n + \frac{H}{2}) \rightarrow (F3)$

(iii) $(F3)*[(F1) + \frac{H}{2} * (F2) + \frac{H^2}{8} * (F5)]$
$\rightarrow (F4) = k_2$

(iv) $(F5) + 2*(F4) \rightarrow (F5) = k_1 + 2k_2$

(v) $(F6) + 4*\ (F4) \rightarrow (F6) = k_1+4k_2$

(vi) Compute $f(X_n+ H) \rightarrow (F3)$

(vii) $(F3) * [(F1) + H*\ (F2) + \frac{H^2}{4}* \{(F6)-(F5)\}] \rightarrow (F4) = k_3$

(viii) $(F6) + (F4) \rightarrow (F6) = k_1 + 4k_2 + k_3$

(ix) $(F1) + H*\ (F2) + \frac{H^2}{6}\ (F5) \rightarrow (F1) = Y_{n+1}$

(x) $(F2) + \frac{H^2}{6} * (F6) \rightarrow (F2) = Z_{n+1}$

The current point is now denoted by X_{n+1} and we complete the cycle by changing $n+1 \rightarrow n$ and returning to (i).

Storage areas for six areas are required for programming this algorithm.

Notes

(1) All Runge-Kutta type algorithms are self-starting; from a programming point of view this is a significant advantage of one-step methods over multi-step methods which generally require a further procedure for calculating a number of initial values.

(2) Changes of step size by any amount (either increasing or decreasing it) present no difficulty, due to all Runge-Kutta type methods being one-step.

De Vogelaere Method

A method which does not seem to have enjoyed the popularity it deserves is the De Vogelaere method [86], [88], for integrating systems of equations of the type

$$Y'' = f(x, y) \qquad (4.36)$$

subject to the boundary conditions

$$Y\ (X_0) = Y_o$$

$$Y'\ (X_o) = Y_o'$$

This algorithm is a most unusual type because, though it looks to be a hybrid method and is so used, its derivation is not so, [viz (4.41)-(4.44)]. This confusion arises due to the step size H being actually a double step size (=2h), hence the point X_n+h may be considered to be the point X_{n+1} or $X_{n+1/2}$ ($=X_n+ \frac{H}{2}$). To avoid confusion, we will include h, if it is involved at the time, in the subscript i.e. $X_{n+2h}=X_{n+1}$. The efficiency of this method is largely due to the economy of calculating required intermediate values to the minimum acceptable accuracy. Lester, et al. [35], [87] have used this method very successfully in certain inelastic molecular scattering problems in which coupled equations of type (4.36) arise.

Before discussing the derivation of this algorithm we note some formulae which will be later required

$$\int_0^x \int_0^x f(x)\ dx^2 = {}^{(2)}f(x) - {}^{(2)}f_o - X^{(1)}f_o \qquad (4.37)$$

$$= h^2 \sum_{i=0} P_{2,i}(u)\ \Delta^i\ f_{-i} \qquad (4.38)$$

$$= h^2 \sum_{i=0} (-1)^i\ P_{2,i}\ (-u)\ \Delta^i\ f_o \qquad (4.39)$$

where X=uh,

$P_{2,0}(u) = u^2/_2$; $P_{2,1}(u) = \frac{u^3}{6}$; $P_{2,2}(u) = \frac{(2u^3+u^4)}{24}$;

$P_{2,3}(u) = (20\ u^3 + 15\ u^4 + 3u^5)/\ 360$ and ${}^{(n)}f = \int^x {}^{(n-1)}f\ dx$,

${}^{(0)}f=f$, (n=1,2). Δ denotes the forward difference. Equations (4.37) - (4.39) may be derived from (2.29), (2.30) and (2.44) of [52].

Finally

$$ {}^{(1)}f_{n+2h} - {}^{(1)}f_n = h(2f_{n+h} + \frac{1}{3}\Delta^2\ f_n - \frac{1}{90}\ \Delta^4\ f_{n-h}) \qquad (4.40)$$

which is (3.15) of [52].

A further convenient notation is Y{n} meaning Y has been calculated to an accuracy $O(H^n)$; let Y^1=Z.

Hence, when $X=X_n+h$ ($=X_n + \frac{H}{2}$), and neglecting second and higher differences in (4.38), we get from (4.37) and (4.38)

$$Y_{n+h} = Y_n + hZ_n + h^2[P_{2,0}(1)\ f_n + P_{2,1}(1)*(f_n - f_{n-h})]$$

$$= Y_n + hZ_n + \frac{h^2}{6}\ [4\ f_n - f_{n-h}] \qquad (4.41a)$$

$$Y_{n+1/2} = Y_n + \frac{H}{2}\ Z_n + \frac{H^2}{24}\ [4f_n - f_{n-1/2}] \qquad (4.41b)$$

where $Y_{n+1/2}\{3\}$ provided $Y_n\{3\}$, $Z_n\{2\}$, $f_{n-1/2}\{1\}$.

If Δf_{n-h} is neglected in (4.38) we get

$$Y_{n+h} = Y_n + hZ_n + \frac{h^2}{2}\ f_n \qquad (4.42a)$$

$$Y_{n+1/2} = Y_n + \frac{H}{2}\ Z_n + \frac{H^2}{8}\ f_n \qquad (4.42b)$$

where $Y_{n+1/2}\{3\}$ provided $Y_n\{3\}$, $Z_n\{2\}$, $f_n\{1\}$.

For $X=X_n+2h$ ($= X_n+H$) we get from (4.37), (4.39) on neglecting third and higher differences,

$$Y_{n+2h} = Y_n + 2hZ_n + h^2[P_{2,0}(-2) - P_{2,1}\ (-2)\Delta f_n$$

$$+ P_{2,2}(-2)\ \Delta^2 f_n]$$

$$= Y_n + 2hZ_n + \frac{2h^2}{3}\ [2f_{n+h} + f_n] \qquad (4.43a)$$

$$Y_{n+1} = Y_n + HZ_n + \frac{H^2}{6} [2f_{n+1/2} + f_n] \qquad (4.43b)$$

and $Y_{n+1}\{4\}$ provided $Y_n\{4\}$, $Z_n\{3\}$, $f_{n+1/2}\{2\}$, $f_n\{2\}$.

On neglecting $\Delta^4 f_{n-h}$ in (4.40) we get Simpson's rule for Z,

$$Z_{n+2h} = Z_n + \frac{h}{3} [f_{n+2h} + 4f_{n+h} + f_n] \qquad (4.44a)$$

$$Z_{n+1} = Z_n + \frac{H}{6} [f_{n+1} + 4f_{n+1/2} + f_n] \qquad (4.44b)$$

where $Z_{n+1}\{4\}$ provided $Z_n\{4\}$, $f_{n+1}\{3\}$, $f_{n+1/2}\{3\}$, $f_n\{3\}$.

The general usage of the algorithm involves using (4.41), (4.43) and (4.44) in cyclic order to integrate from $X_n \rightarrow X_{n+1}$. The integration at the initial point X_0 is conveniently begun by using (4.42) in a backward integration as

$$Y_{-1/2} = Y_0 - \frac{H}{2} Z_0 + \frac{H^2}{8} f_0 \qquad (4.45)$$

Error Analysis

Reference to (4.43) and (4.39) shows that $Y_{n+1}\{4\}$ provided $Z_n\{3\}$, $f_{n+1/2}\{2\}$, $f_n\{2\}$ since the lowest order term neglected is $\frac{H^5}{90} f_n^{(3)}$. These conditions on Z_n, $f_{n+1/2}$, f_n are actually satisfied; (4.44) shows $Z_n\{4\}$, (4.41) shows $f_{n+1/2}\{3\}$ and (4.43) shows $f_n\{4\}$. Hence, as the bulk of the local truncation error occurs in this lowest order term $\frac{H^5}{90} f_n^{(3)}$, we may take that as an estimate of the accuracy involved. In brief, we see from (4.41), (4.43) and (4.44) that $Y_{n+1}\{4\}$ and $Z_{n+1}\{4\}$.

Recompute $Y_{n+h}\{3\}$ from (4.39) used in a backward manner, with step size = -H, so as to use Y_{n+1}, Z_{n+1} and f_{n+1}; hence, neglecting third differences and higher,

$$Y^*_{n+h} = Y_{n+1} - \frac{H}{2} Z_{n+1} + \frac{H^2}{96} (-f_n + 6f_{n+h} + 7f_{n+1}) \tag{4.46}$$

The difference $Y_{n+h} - Y^*_{n+h}$ is approximately the first neglected term of (4.41) which, as can be seen from (4.38), is $\frac{H^2}{32} \Delta^2 f_{n-1} \approx \frac{H^4}{32} \left(\frac{\delta^4 Y}{\delta x^4} \right)_{n-1}$ This difference $Y_{n+h} - Y^*_{n+h}$ should be quite small and vary slowly. This may be used as an indication of the accuracy of the calculations and the stability of the algorithm.

Stability

No worthwhile investigation of the stability of the De Vogelaere method has yet been undertaken, to my knowledge. The quantity $Y_{n+h} - Y^*_{n+h}$, as mentioned above, may be used as an ad hoc criterion for stability; actual numerical work involving this algorithm provides an empirical indication that this is a stable method. The usage of the Simpson rule (4.44) for calculating Z_{n+1} indicates that some instability may be involved [99], [65], but this would be considerably damped in (4.43) by the multiplication of Z_n by H.

Application to High-Speed Computers

The calculations involved in (4.41), (4.43), (4.44) may be programmed in such a way that storage requirements are at a minimum, i.e. 5 arrays, and computer time is optimum.

Define

$$\frac{H}{2} Z_n = Z_n,\ \frac{H^2}{12} f_n = F_n,\ \frac{H^2}{3} f_{n+1/2} = F_{n+1/2}$$

Using the usual notation,

$(F1) = Y_n$, $(F2) = Z_n$, $(F3) = F_n$, $(F4) = F_{n-1/2}$

For the general step $X_n \rightarrow X_{n+1}$, the calculations may be carried out as follows:

(i) $(F2) + (F3) \rightarrow (F2) = \frac{H}{2} Z_n + \frac{H^2}{12} f_n$

(ii) $(F2) + (F1) \rightarrow (F1) = Y_n + \frac{H}{2} Z_n + \frac{H^2}{12} f_n$

(iii) $\frac{1}{8}$ (F4) → (F4) $= \frac{H^2}{24} F_n$

(iv) (F3) − (F4) → (F4) $= \frac{H^2}{12} f_n - \frac{1}{24} H^2 f_{n-1/2}$

(v) (F1) + (F4) → (F4) $= Y_n + \frac{H}{2} Z_n + \frac{H^2}{24} (4f_n - f_{n-1/2}) = Y_{n+1/2}$

(vi) Compute $\frac{H^2}{3} f_{n+1/2}$ → (F5)

(vii) (F2) + (F5) → (F2) $= \frac{H}{2} Z_n + \frac{H^2}{12} f_n + \frac{H^2}{3} f_{n+1/2}$

(viii) (F1) + (F2) → (F1) $= Y_n + HZ_n + \frac{H^2}{6} (f_n + 2f_{n+1/2}) = Y_{n+1}$

(ix) Compute $\frac{H^2}{12} f_{n+1}$ → (F3)

(x) (F2) + (F3) → (F2) $= \frac{H}{2} [Z_n + \frac{H}{6} (f_n + 4f_{n+1/2} + f_{n+1})]$

$$= \frac{H}{2} Z_{n+1}$$

(xi) (F5) → (F4) $= \frac{H^3}{3} f_{n+1/2}$

The current point is now denoted by X_{n+1} and we complete the cycle by changing n+1→n and returning to (i).

To start computation we use (4.42) as

$$Y_{n-1/2} = Y_n - Z_n + \frac{3}{2} F_n ,$$

where n=0.

Notes

(1) The De Vogelaere method is effectively self-starting as all the required information is provided by the boundary

conditions at the initial point and by (4.42).

(2) Changing the interval size from H_1 to H_2 presents little difficulty. Reference to (4.41) shows that $f_{n-1/2}$ need be {1}.

Let $\bar{f}_{n-1/2}$ denote the value of $f_{n-1/2}$ at $X=X_n - H_{1/2}$ and $f_{n-1/2}$ the required value at $X=X_n - H_{2/2}$.

Therefore

$$\frac{\bar{f}_{n-1/2} - f_n}{H_1} = \frac{f_{n-1/2} - f_n}{H_2} \quad \text{to } \{1\}$$

Inserting into (4.41) for $f_{n-1/2}$,

$$Y_{n+1/2} = Y_n + \frac{H_2}{2} Z_n - \frac{H_2^{\ 2}}{24} \frac{(H_2)}{H_1} \bar{f}_{n-1/2} + \frac{H_2^{\ 2}}{6} \left(\frac{3}{4} + \frac{1}{4} \frac{H_2}{H_1}\right) f_n \qquad (4.47)$$

where $Y_{n+1/2}$ {3} since $f_{n-1/2}$ {1}.

Predictor-Corrector Methods

As was mentioned in Chapter 3, these involve the use of an "open" multi-sten method to predict a value for Y_{n+1} which is then used with a "closed" multi-step method, which is more accurate, to improve the calculated Y_{n+1}. To indicate that a quantity Y_{n+1} is the predicted value, we will include a superfix (P) and to indicate a corrected value a superfix (C), i.e. $Y_{n+1}^{(P)}$, $Y_{n+1}^{(C)}$.

These methods are most commonly represented by

(i) Adams-Bashforth method

(ii) Milne method.

(i) Adams-Bashforth

Assume the system of equations is naturally of the first order or has been reduced from its naturaly higher order to a further system of first order equations; in either case we may write it as

$$Y' = f(x, y)$$

The solution for Y_{n+1} is given by [51]-[54],

$$Y_{n+1}^{(P)} = Y_n + H\ (f_n + \frac{1}{2} \nabla f_n + \frac{5}{12} \nabla^2 f_n + \frac{3}{8} \nabla^3 f_n)$$

$$Y_{n+1}^{(C)} = Y_n + H\ (f_{n+1} - \frac{1}{2} \nabla f_{n+1} - \frac{1}{12} \nabla^2 f_{n+1} - \frac{1}{24} \nabla^3 f_{n+1} \ldots) \tag{4.48}$$

This method is generally used with fourth and higher differences truncated which gives an accuracy of $0(H^4)$. The predicted $Y_{n+1}^{(P)}$ is used to approximate f_{n+1} in the corrector formula which may then be used in an iterative manner until convergence with the desired accuracy has been achieved. The accuracy may be improved by estimating the size of the truncation error involved in $Y_{n+1}^{(C)}$; from (4.48) we see that

$$E^{(P)} = Y(X_{n+1}) - Y_{n+1}^{(P)} = \frac{251}{720} H^5 Y^{(5)} (\zeta_1)$$

$$E^{(C)} = Y(X_{n+1}) - Y_{n+1}^{(C)} = \frac{-19}{720} H^5 Y^{(5)} (\zeta_2) \qquad (4.49)$$

where $X_n \leq \zeta_1, \zeta_2 \leq X_{n+1}$.

Assume $Y^{(5)}_{(\zeta)}$ is constant in the interval $[X_n, X_{n+1}]$, and solving for it in (4.49) we get $H^5 Y^{(5)}(\zeta) = \frac{720}{270} (Y_{n+1}^{(C)} - Y_{n+1}^{(P)})$

Therefore, an improved estimate for Y_{n+1} is

$$Y_{n+1} = Y_{n+1}^{(C)} - \frac{19}{270} (Y_{n+1}^{(C)} - Y_{n+1}^{(P)}).$$

This is generally used in a non-iterative manner and has been called [101] a modified predictor-corrector.

Direct integration of a system of second order equations may be achieved by the algorithm [52]

$$Y_{n+1}^{(P)} = Y_n + H\,Y_n' + H^2\,(1/2\,f_n + \frac{1}{6}\,\nabla f_n + \frac{1}{8}\,\nabla^2 f_n \ldots)$$

$$Y_{n+1}^{(P)\,'} = Y_n' + H(f_n + \frac{1}{2}\,\nabla f_n + \frac{5}{12}\,\nabla^2 f_n \ldots)$$

$$Y_{n+1}^{(C)} = Y_n + H\,Y_n' + H^2\,(\frac{1}{2}\,f_{n+1} - \frac{1}{3}\,\nabla f_{n+1} - \frac{1}{24}\,\nabla^2 f_{n+1} \ldots)$$

$$Y_{n+1}^{(C)\,'} = Y_n' + H\,(f_{n+1} - \frac{1}{2}\,\nabla f_{n+1} - \frac{1}{12}\,\nabla^2\,f_{n+1} \ldots) \qquad (4.50)$$

As in the case of (4.48), the predicted value for Y_{n+1} is used to approximate f_{n+1} in the corrector equations which are used in an iterative manner. However, no more than two iterations should generally be used; if convergence has not been achieved with the accuracy desired, the step size H should be reduced.

Notes

(1) Since the coefficients of the differences in (4.48), (4.50) do not decrease in magnitude at a rapid rate, it is necessary to retain a large number of differences to achieve a high accuracy; this inevitably increases the storage and computer-time requirements. As many more efficient integration methods are available, this one is not advised.

(2) Basically it is not a self-starting algorithm but requires some auxiliary method (i.e. Runge-Kutta, Taylor series etc.) to

calculate Y at a number of initial points. Alonso [104] has shown, however, that the three-point Adams-Bashforth may be slightly modified to provide a self-starting algorithm.

(ii) Milne's Method

For the general system of first order equations, Milne [98], [64] gives the formulae

$$Y_{n+1}^{(P)} = Y_{n-3} + 4Hf_{n-1} + \frac{8}{3} H\nabla^2 f_n$$

$$Y_{n+1}^{(C)} = Y_{n-1} + 2H\, f_n + \frac{H}{3}\, \nabla^2\, f_{n+1} \qquad (4.51)$$

The popularity of this particular combination of a predictor and a corrector is due largely to the fact that in each case the lowest order difference truncated is $\nabla^4 f$ since the coefficient of $\nabla^3 f$ is zero in both cases. The manner in which it is used is similar to that of Adams-Bashforth. Hamming [99] has shown how the accuracy may be improved by including an estimate for the truncation error involved in both the predictor and the corrector whose modified forms are

$$Y_{n+1}^{(P)} - \frac{28}{29}\,(Y_n^{(P)} - Y_n^{(C)})\ ,$$

$$Y_{n+1}^{(C)} + \frac{1}{29}\,(Y_{n+1}^{(P)} - Y_{n+1}^{(C)})\,.$$

The quantity $Y_n^{(P)} - Y_n^{(C)}$ should vary slowly and may be used as a check on H.

Notes

(1) It is quite superior to Adams-Bashforth in accuracy and storage requirements; in the terminology of Henrici [54], it is "the best possible" 2-step method for a system of first order equations. However, the corrector formula may be unstable at times; more will be said on this later.

(2) It is not self-starting and, hence, needs an auxiliary method to calculate Y at a number of initial points.

It is not recommended due to reasonably heavy storage requirements, (2), and its instability.

Stability

A detailed stability analysis is available for predictor-corrector methods [54], [65]-[67], [99]-[103]; those show that the use of the Simpson rule, as the corrector in Milne's method, introduces an instability. Henrici [54] has pointed out that a stable K-step method generally shows a "weak instability" when K is greater than the order of the equations. In the case of the Simpson rule, this shows up as an error which changes sign from step to step and which increases exponentially in magnitude [99]. Milne later showed [65], [66] that the occasional use of Newtons "three eighths" formula can effectively damp out the unwanted oscillation without harming the desired solution and has since [67] provided a superior stabilizing formula. Crane and Lambert [100] have developed a more general theory for stability criterions of predictor-corrector methods, providing many stable algorithms in the process.

Prior to Chase's paper on stability [101] it had been tacitly assumed that the stability of the process depended solely on the corrector; Chase showed that this is not the case when the use of the corrector does not involve many iterations. Dependence on the predictor equation is shown up by the increase in the order of the characteristic equation for the error when the stability analysis involves both predictor and corrector. This is the most general paper to date and incorporates both [99] and [100]. An efficiency study of how the relationship between accuracy and cost depends on the choice of predictor-corrector formulae and on the number of iterations involved is presented in [103].

Chebyshev Series Solution

One of the most interesting developments of recent years has been the use of series of Chevyshev polynomials in the solutions of differential equations. They provide approximations to the required precision over a given interval with a faster rate of convergence (i.e. with fewer polynomial terms) than any other polynomial expansion. This is achieved by having a uniform rate of convergence over the whole interval of validity; if we compare with the Taylor series solution, based on the middle of the interval as origin, we find the latter to have superior convergence towards the origin - perfect convergence at the origin - but to be less rapidly convergent towards the ends of the range. This is due to the fact that the Taylor series has a circle of convergence while the Chebyshev series has an ellipse of convergence, with end points as foci, which results in it having uniform convergence along the straight line joining the foci.

Two methods have emerged for expanding in Chebyshev series

(i) The τ-method of Lanczos [89], [90].

(ii) The more direct method of Clenshaw [91].

Fox [94] has given a detailed comparison of these two approaches. In practical numerical applications (ii) appears the more suitable; however, as presented by Clenshaw [91], it suffered from several restrictions as to the type of differential equation it was applicable to, i.e. linear with polynomial coefficients. Scraton [85a] generalized this approach to solve differential equations with non-polynomial coefficients.

A modified approach was adopted by Clenshaw and Norton [92] who used a Picard iteration to obtain the solution; the latter [93] has since advocated a Newton iteration. These are applicable to linear and non-linear equations.

Briefly, the method of solution is as follows:

Let the equation in question be

$$Y'' = f(x,y) \qquad (4.52)$$

subject to $Y(0) = Y_0,$

$$Y'(0) = Y_0'$$

Assume

$$Y = \sum_{r=0}^{N} A_r T_r(x) \qquad (4.53)$$

where $T_r(x) = \mathrm{Cos}(r\mathrm{Cos}^{-1}(x))$.

(i) Get some initial Chebyshev expansion for Y that satisfies the boundary conditions

(ii) Use this to form an initial $f(x,y^{(i=1)})$ where $Y^{(i)}$ is the i^{th} iteration

(iii) Evaluate A_r'' from the expansion

$$f(X, Y^{(i-1)}) = \sum_{r=0}^{N} A_r'' T_r (x)$$

by using the formula

$$A_r'' = \frac{2}{N} \sum_{s=0}^{N} f(\mathrm{Cos}(\frac{\pi s}{N})) \mathrm{Cos}\frac{(\pi rs)}{N}$$

(iv) Evaluate A_r' which is the r^{th} coefficient in the expansion

$$Y' = \sum_{r=0}^{N+1} A_r' T_r(x)$$

by using the formula

$$2r A_r' = A_{r-1}'' - A_{r+1}'' ;$$

the boundary condition $Y'(0) = Y_0'$ is used to evaluate A_0'.

(v) Evaluate A_r in a similar manner but using the boundary condition $Y(0) = Y_0$ to calculate A_0.

The cycle is completed by returning to (ii) until convergence is achieved.

Notes

(1) This is not a step by step method but is used over a single region.

(2) It may be used for boundary-value problems as conveniently as with initial value problems.

In summary, this is a very promising method but more development is required before it can compete with such established methods as Numerov, Runge-Kutta, De Vogelaere, in the matter of time for a particular accuracy. Also, it would be more useful if applicable as a step by step method.

Taylor Series Solution

Theoretically, this method is applicable to a system of equations of any order [51]. Cambell, et al [96] have confined their investigation to systems of first order equations but Gibbons [95] considers equations up to the fifteenth order.

When integrating $X_n \rightarrow X_{n+1}$,

$$Y_{n+1} = Y_n + H\,Y_n' + \frac{H^2}{2}\,Y_n'' + \frac{H^3}{3!}\,Y_n''' \;\ldots\ldots$$

$$Y'_{n+1} = Y'_n + H\,Y_n'' + \frac{H^2}{2}\,Y_n''' + \frac{H^3}{3!}\,Y_n^{(iv)} \;\ldots\ldots \qquad (4.53)$$

As a check on the accuracy of the previous calculations, one often uses (4.53) in a backward sense (H= -H) to recalculate

$$Y_n = Y_{n+1} - H\,Y'_{n+1} + \frac{H^2}{2}\,Y''_{n+1} \cdots\cdot$$

$$Y'_n = Y'_{n+1} - H\,Y''_{n+1} + \frac{H^2}{2}\,Y'''_{n+1} \cdots\cdots \qquad (4.54)$$

Reduced derivatives $Y_p = \frac{H^p}{p!}\,y^{(p)}_n$ are often used to simplify (4.52), (4.53), who now take the form

$$Y_{n+1} = Y_o \pm Y_1 + Y_2$$

$$HY'_{n+1} = Y_1 \pm 2Y_2 + 3Y_3 \qquad (4.55)$$

In practice, unless F is a simple analytical function, it may be extremely laborious to calculate higher derivatives. However, the process may be simplified by using the Leibnitz Theorem for differentiating products: if F=U.V,

$$\frac{H^p}{p!}\,F^{(p)} = U_p\,V_o + U_{p-1}\,V_1 \;\cdots\cdot + U_o\,V_p$$

where $U_p = \frac{H^p}{p!}\,u^{(p)}$.

Gibbons [95] applies the above techniques to a system of equations but they are of a simple analytical form; he also provides a computer program for his method. Moore [97] applies a Taylor series expansion very successfully by using interval arithmetic, calculating very impressive error estimations in the process. Unfortunately, most computers will not accept interval arithmetic. The biggest disadvantage involved in a Taylor series solution is the necessity of calculating higher derivatives, though recurrsive relations do exist for calculating these higher derivatives in terms of lower derivatives [51], for a restricted type of function F. This does not appear to be a suitable method for solving our particular system.

Hybrid Methods of Butcher

Dahlquist [59], [60] and Henrici [54] have shown that the condition of stability does not allow stable multi-step methods, with equally spaced pivotal points, of order greater than k+1, where k is the step-number, for a differential equation (or a system thereof) of type

$$y' = f(x,y) \tag{4.56}$$

subject to $y(0) = y_0$.

This restriction of course applies only when the method is used in a direct non-iterative manner. Butcher [105] circumvents this restriction in his treatment of (4.56) by inserting an additional intermediate point to derive stable integration methods of order 2k+1 ($k \leq 6$). Gragg and Stetter [107] derive similar formulas though in a different manner. Butcher [106] later improved his method by including 2 intermediate points to derive stable formulae of order 2k+2 ($k \leq 15$). These methods of Butcher are effectively of the predictor-corrector type. Kohfeld, et al [108], [109] have since shown that the actual accuracy of the method depends strongly on that of the predictor. This is in keeping with the findings of Chase [101] on the stability of multi-step predictor-corrector methods.

The accuracy and computational simplicity of these methods is quite impressive. However, storage requirements are very heavy indeed, in comparison with the Nystrom fourth order method or De Vogelaere method. Change of the step-size demands special consideration while a number of starting values are needed for Y to begin the integration.

CHAPTER 5

Introduction

In scattering problems, the shape of the resonance in the phase-shift and the corresponding resonant energy are of great interest; one might say they are the core of the problem. In our calculations, we have noticed instability that is made apparent by the dependence of the phase-shift on the parameter H (= step size) (see Section VI, Chapter 1).

In my investigation, I have concentrated on the region k^2= (.13305 - .13330) Rydbergs, as this incorporates a resonant energy for the physical system in question e^-O^+ (L=0, S=1, π=odd) [47]. Conclusions regarding accuracy, time, storage that may be drawn from the investigation with this range of values for k^2 may also be applied to energies far away from Resonance. I have not considered energies "near" threshold as this causes severe instability in the asymptotic region due to the expansion method of Burke and Schey [110] breaking down at these "near" threshold energies. I plan on investigating this phenomenon in the very immediate future.

Results

We shall now describe the various calculations made in an effort to solve the tripart problem stated in Section VI, Chapter 1, regarding stability, computer-time and storage requirements of the integrating procedure.

In graph (1) we showed that the resultant graph for phase-shift versus k^2 depended on the particular value for the step size that was being used. This raises the question, is this dependence due to some inherent quality of our integrating method (i.e. Numerov)? This could arise, for instance, if the integrating method demanded that divisions by very small numbers or multiplication by very large numbers occur, which would result in serious loss of significance in the calculations. To answer this question, we use a very different integrating algorithm, the Runge-Kutta fourth order algorithm for directly integrating (4.28). As Numerov demands that the function values for y be known at two pivotal points, we must use some auxiliary technique or algorithm to calculate the required function values at the second point, the function values at the initial point being calculated by the initial boundary conditions, as described in Section (ii), Chapter 2; we used the classical fourth order Runge-Kutta method for first order differential equations (4.26) for this calculation. For the sake of consistency, we continued this practice for all examined algorithms. This safeguards against the possibility that the comparisons of the various integrating algorithms might not be valid due to great sensitivity very near the origin as the V_{ii} terms have very large values in this region (see graph (4)).

Reference to graph (2) and graph (3) shows a very interesting result; for any of the step-sizes used with the

Numerov method, its graph for $\delta_{\text{Num}}(H)$ corresponds almost identically with that of $\delta_{\text{R.K.}}(2*H)$. This means that for the IBM 360 series, and all other computers with a corresponding word length, with double precision, the Runge-Kutta algorithm (4.28) gives the same accuracy in solving a system of differential equation such as (1.40), when the step-size is 2*H, as Numerov does when the step-size is H. This is probably due in great part to the fact that the R.H.S. of the system of equations is calculated at the same number of points when using the Runge-Kutta algorithm (4.28) with a step length of 2*H and the Numerov algorithm (4.15) with a step length of H. The great significance of this is that the hitherto widely held assumption, that to gain comparable accuracy with a fourth order Runge-Kutta method for a definite integration range, we had to store the R.H.S. of the system of equations (1.40) for at least twice the number of points as with Numerov, does not hold any longer. In our large code, ATOMNP, this was a very severe restriction as the arrays needed to store $f(X_n)$ tend to be very large.

The evidence contained in graph (2) implies that the $\delta(H)$ instability is not inherent in the Numerov method.

At this point we pose some other questions concerning the dependence of δ on the parameters of integration; these are H, RA, IRA (the number of intervals from the origin to RA), structure (i.e. the ratio IR1/IR2/IR3/IR4/IRA where IRi (i=1,4) denotes the number of intervals from the origin to the point Ri [49]). In view of graph (2) one may feel justified in using

Numerov to investigate this parameter dependence and then generalizing the results.

Dependence on structure

At each step our numerical calculations involve a truncation error; in the case of Numerov this error is $O(H^6)$, though one should remember that the actual accumulative error is $O(H^4)$ [71]. In the i^{th} interval let us write this local truncation error as $C_i H^6$. Hence the total accumulative error for $y(X_n)$ may be written as

$$E^{NUM}_{ACC} = H^6 \left[\sum_{i=1}^{IR1} C_i + 2^6 \sum_{i=IR1+1}^{IR2} C_i + 4^6 \sum_{i=IR2+1}^{IR3} C_i \ldots \right]$$

where C_i is a function of the sixth derivative of y calculated at some point x within the i^{th} interval $[X_{i-1}, X_i]$. The factors 2^6, 4^6 etc. are the result of doubling the previous step length at the points R1, R2, R3, R4 [49] . This phenomenon is represented graphically in graph (5). We see there that this variance in error is evident but its magnitude is not great enough to account for the disparity shown in graph (1). Reference to graph (6) verifies that. Henceforth in our calculations we will ensure that the points where the interval lengths change be as corresponding as possible; this will then eliminate this disparity and simplify comparisons.

Dependence on RA

Graph (4) represents V_{11} and V_{22} ($V_{12} \equiv V_{21} \equiv 0$, (1.46)). The exchange functions are functions of both V_{11} and V_{22}. RA represents the distance from the origin at which we presume the contribution from the exchange terms is negligible (see Section (iii), Chapter 2). Also at this point we assume that the potential terms V_{ij} may be represented by $\frac{\ell_i(\ell_i+1)}{r^2} - k_i^2$ $- \frac{2(Z-N)}{r} + \sum_\lambda \frac{a^\lambda_{ij}}{r^{\lambda+1}}$. We now examine the dependence of δ on RA. This may indicate the optimum value for RA, as the greater the value of RA (for fixed H, structure) the greater the computing time. We see from graph (7) that δ experiences a continuous shift to the left with decreasing values of RA. We may logically assume that the "large" values of RA provide the more accurate answers; this is indicated by the convergence of the $\delta(k^2)$ graphs to a definite limit with increasing RA.

Table (3) shows the various computing times for a number of values of RA.

METHOD	RA=7.0	RA=9.0	RA=11.4	RA=17.4
Numerov with H=.005	12:23	13:00	14:11	16:25

Table (3). Computing-times of a deck of data for varying values of RA.

Dependence on H

This has already been referred to and may be further appreciated by reference to graph (6). That particular graph shows that the $\delta(k^2)$ graph converges with decreasing H, which of course is to be expected if the errors involved are well-behaved, and not random.

To examine this rate of convergence, assume it is of the order H^α

$$\text{i.e.} \quad E(H_1) - E(H_2) = C(H_1^{\alpha} - H_2^{\alpha}) \qquad (5.1)$$

where E is the value of k^2 when $\delta(H_1) = \delta(H_2)$. We may estimate α by referring to graph (6) and assuming C is constant.

Taking H_1 and H_2 to be .02 and .01 respectively, we get from (5.1)

$$E(.02) - E(.01) = C2^{\alpha}H^{\alpha}(2^{\alpha}-1) \text{ where } H= .005.$$

(5.2a)

Taking H_1 and H_2 to be .01 and .005 respectively, we get in turn from (5.1)

$$E(.01) - E(.005) = C\ H^{\alpha}(2^{\alpha}-1) \qquad (5.2b)$$

Substituting sets of values for E(.02), E(.01, E(.005) from graph (6) into (5.2) we get estimates for α. These are contained in Table (4).

δ=const.	E(.005)	E(.01)	E(.02)	α
.5	.133050	.133066	.133264	3.629
1.0	.133070	.1330862	.133283	3.603
2.1416	.1330759	.133092	.1332885	3.609
2.7416	.133079	.133095	.1332918	3.620

Table 4. The order of convergence of $\delta(k^2)$

Table (4) shows that the rate of convergence $\approx H^4$. This, significantly, is also

(i) The accumulative truncation error for both Numerov and the 4^{TH} order Runge-Kutta method [71]

(ii) The error introduced by the interpolating formula used by ATOMNP [49], which uses the Numerov method, when the step-size is halved during the integration inwards from the outer region. Let us examine (ii) first.

Dependence on the Interpolating Formula

The interpolating proceedure is needed at the points R4, R3, R2, R1, where the step-sizes are halved. This means that the functions F2 and F7 (see Section 1, Chapter 4) must be evaluated at the points Ri+HH/2 (i=1,4), where HH denotes the step-size on the asymptotic side of Ri. In ATOMNP the quartic central difference interpolating formula is used for estimating the required $\bar{F}2$ and $\bar{F}7$ at X=Ri + HH/2 i.e.

$$\bar{F}2\ (X=Ri+HH/2) = [-F11(Ri+HH) - F9(Ri-2*HH) + 9.*(F1(Ri) + F2(Ri-HH))]/16 \tag{5.3a}$$

$$\bar{F}7\ (Ri+HH/2) = [-F4(Ri+HH) - F10(Ri-2*HH) + 9.*(F6(Ri) + F7(Ri-HH))]/16 \tag{5.3b}$$

$$\bar{F}7\ (Ri+HH/2) = .75\ \bar{F}7(Ri+HH/2) + .25\ F6(Ri) \tag{5.3c}$$

The truncation error is $O(H^4)$.

If a fifth order interpolation formula were used, instead of the fourth order formula (5.3), an appreciable change in δ should result if the error caused by using (5.3) had an appreciable effect on the calculation of δ.

The corresponding fifth order interpolation formula is of the form

$$\bar{F}(Ri+HH/2) = [-5*[F(Ri)+4F(Ri+3*HH)] + 3*[20*F(Ri+HH) + 30*F(Ri+2*HH) + F(Ri+4*HH)]]/128 \tag{5.4}$$

Graph (8) compares the resultant δ-graphs when fourth order and fifth order interpolating formulas are used; one may note that the change is quite small and could not cause the instability of graph (6).

Truncation error

A priori, this would seem to be the likeliest reason for the instability of the δ-graph. Table (4) adds weight to this assumption. Richardson's method [58],[85] provides us with a very practical means of estimating the local truncation error at each interval. This is most easily applied to a single-step method, hence we use it with the Runge-Kutta method (4.28). This estimation of the truncation error, when added to the values calculated by Runge-Kutta, should improve the order of accuracy by at least 1. Hence, we would expect to get a substantially more accurate answer with Runge-Kutta plus a truncation estimate than with Runge-Kutta alone. Actually we would expect the convergence rate of $\delta(H)$ to be approximately of the fifth order, rather than the fourth as in graph (6). Reference to graph (9) shows that this is actually not the case,as the expected improvement has not materialized. This implies that the accumulative error, in the usual sense, is not the cause of our troubles.

One may summarize all the above results by saying that the instability does not appear to be caused by any phenomenon in the outer or asymptotic regions. This leads us to turn our attentions to the inner region.

Inner Region

As V_{ii} (see graph (4)) are very large "near" the origin, let us reduce the step-size to 2*.00n (n=1,2,4) for a number of intervals adjacent to the origin. This effectively means that we subdivide the region comprising, originally in ATOMNP, the first IR1 intervals, into 2 regions

(i) A region close to the origin consisting of IRN half-intervals of size .00n (n=1,2,4)

(ii) An "outer" region of length R1-IRN*.00n.

On varying the value of IRN from 3 to 35 and using the usual H, we get a tremendous stabalizing effect (see graph (10, 11)). This is of great importance for a number of reasons;

(a) It has stabalized the solution for us, which was our major problem,

(b) It enables us to use a larger than usual H and still expect an accurate stable solution with reduced computing-time and storage requirements.

We may note in addition that the δ-graph which we now get is effectively that to which δ in graph (6) was converging. This adds support to the accuracy of our answer.

Computing-time Considerations

I have examined the relative computing-times for a definite set of data for $e^{-}O^{+}$ scattering problem with L=0, S=1, π=odd, when various integration algorithms are being used. Every effort has been made to program these methods in the most efficient manner possible.

Table (5) contains these relative computer-times. The value of RA and of all points where the interval length changes are the same for all the methods. All calculations are in double-precision.

METHOD	COMPUTING TIME
Numerov (4.5) with step-size of H.	9 mins; 01 sec.
Runga-Kutta with direct integration of the second order d.e. (4.28) with step-size of 2*H.	9; 49
Runga-Kutta (4.26) used with the reduced equations and step-size of 2*H.	8; 01
Fourth order Nystrom method (4.31) with step-size of 2*H.	7; 23
Fourth order Nystrom method (4.31) plus a truncation estimate with a step-size of 2*H.	10; 29
DeVogelaere (4.43) with a step-size of 2*H.	4; 14

Table (5). Relative times of various algorithms for a definite set of data.

This table shows that the DeVogelaere method is far superior to any of the others that have been investigated (available research literature points to these methods being the optimum ones and are the methods most widely used in research involving the solution of systems of differential equations of type (1.40)). This is not very surprising for the following reasons

(i) we may get the same δ-graph when H is the step-size for Numerov and 2*H the step-size for DeVogelaere (see graph 12) when calculations are done on IBM 360/65J with double-precision; this again is probably due to the fact that f(x) is calculated at the midpoints of the intervals in DeVogelaere.

(ii) the intermediate calculations in the DeVogelaere method are carried out to the minimum required accuracy (see Section (iii), Chapter 4). This greatly reduces the volume of calculations needed and hence reduces the computing time.

Table (6) verifies this superiority of DeVogelaere when we examine the computer times for a definite set of data that could be used by a physicist to calculate the δ-graph for $e^{-}o^{+}$ using H= .005 (or 2*H=.01).

METHOD	RA=7.0	RA=9.0	RA=11.4	RA=17.4
Numerov (4.5)	12:23	13:00	14:11	16:25
R.K. (4.28)	12:31	13:19	14:25	16:55
R.K. + Truncation	17:10	18:19	19:38	22:40
R.K. (4.26)	10:39	11:20	12:14	14:20
Nystrom (4.31)	9:56	10:36	11:25	13:29
De Vog. (4.43)	5:27	5:45	6:10	7:15

Table (6). Relative Computing-times for various algorithms for a typical selection of data suitable for drawing a δ-graph.

One immediately sees that it is more efficient to use a number of other integrating algorithms, rather than Numerov, in ATOMNP, since all of these methods produce what is effectively the same graph for the phase-shift δ; this efficiency of course is largely due to the fact that we may use a double step-length with DeVogelaere, Runge-Kutta and Nystrom relative to the step-length used by Numerov, though DeVogelaere would still be superior time-wise if identical step-sizes were used by it and Numerov. One may note also that the Nystrom method is superior to the corresponding Runge-Kutta formulas. This is largely due to the fact that Nystrom demands the calculation of just three auxiliary functions K_i(i=1,3) where Runge-Kutta (whether used directly on the second order equation or on the reduced system of first order equations) demands four, K_i (i=1,4).

Direct and reduction usage of Runge-Kutta

It is of interest to compare the two different approaches in using Runge-Kutta methods, as numerical analysts tend to differ as to which is the more efficient. Both effectively gave the same δ-graph but Table (5) and Table (6) indicate that the "reduced" method is more efficient time-wise. Of course if one takes the fourth order Nystrom method (4.31) as being a direct Runge-Kutta method, then the direct method would be superior for a system of type (1.40). Current literature tends to differ in distinguising between Runge-Kutta and Nystrom methods.

Numerov: Direct and iterative

Calculations have shown that the iterative method converges to the same solution as one gets from the direct use of Numerov, which is also more efficient time-wise.

Storage

In the integration of our differential equations (1.40), certain function values must be calculated, and stored, at a number of points; as our numerical technique for the solution of this system of equations demands that these functions be matrices, we have to store them as arrays. The dimensions of these arrays may be very large; the size depends on the number of channels involved, the number of exchange terms in our equations, the number of Lagrange multipliers and the number of V_i terms. In our case these arrays had dimensions (11 x 9) but they may often be very much greater. Hence any reduction in the number of arrays that must be stored, or pivotal points, would result in a significant saving of computer-storage.

Table (7) shows the relative storage requirements for each of the examined algorithms

METHOD	STORAGE REQUIREMENTS IN ARRAYS
Numerov	10
R. K. (4.28)	7
R. K. (4.26)	7
R. K. + Trunc.	9
Nystrom (4.31)	6
Nystrom + Trunc.	8
DeVogelaere	5

Table (7) Storage requirements for various algorithms.

Ideally, DeVogelaere is again superior, this time in having the minimum storage requirements. We have a saving of 50% relative to Numerov. Nystrom is also superior to Numerov, while both Runge-Kutta methods come between those two. Truncation estimates add two additional storage requirements.

The number of pivotal points may be significantly reduced by having approximately the first 35 intervals of length .004. This seems to be the optimum length for the intervals adjacent to the origin; .02 then seems to be an ideal length for the step-size in the remainder of the inner region. Graph (14) verifies this for the DeVogelaere method. One may note here that the step-size hitherto generally used with ATOMNP by our research group has been .005; changing the step-length to .02 will reduce substantially the storage requirements.

CHAPTER 6

It is very obvious from Chapter 5 that the DeVogelaere method is very much superior to the Numerov, Runge-Kuttas and Nystrom algorithms. Graph (12) shows that on the IBM 360/65 computer, when double precision is used for all calculations, it provides a δ-graph as accurately as Numerov which, as can be seen from Graph (2), is similar to Runge-Kutta of the fourth order.

Stability considerations demand that the initial intervals should be quite small; graphs (10, 11) indicate that the optimum length between pivotal points is .004 atomic units for approximately 35 such initial intervals. We may then increase the distance between the points where the function values are calculated to .01 atomic units. This corresponds to a real step-size of .02. Graph (14) shows that this provides a very accurate δ-graph. This procedure improves the stability and saves a substantial amount of time simultaneously. Henry [48] has shown that the resonance width for $e^{-}O^{+}$ (L=0, S=1, π=odd), which we are considering, is very small, being $O(10^{-3})$Å. This implies that the stability considerations for this very narrow resonance may be applied generally to the broader and more stable resonances.

Table (5) and Table (6) show that DeVogelaere is very much superior to the other algorithms that were investigated. To illustrate the great saving in computing time when the DeVogelaere method is used in conjunction with the technique mentioned above we refer to Table (8). A very similar δ-graph is provided by DeVogelaere with the interval length of .02 and Numerov with .005 (See Graph (11)).

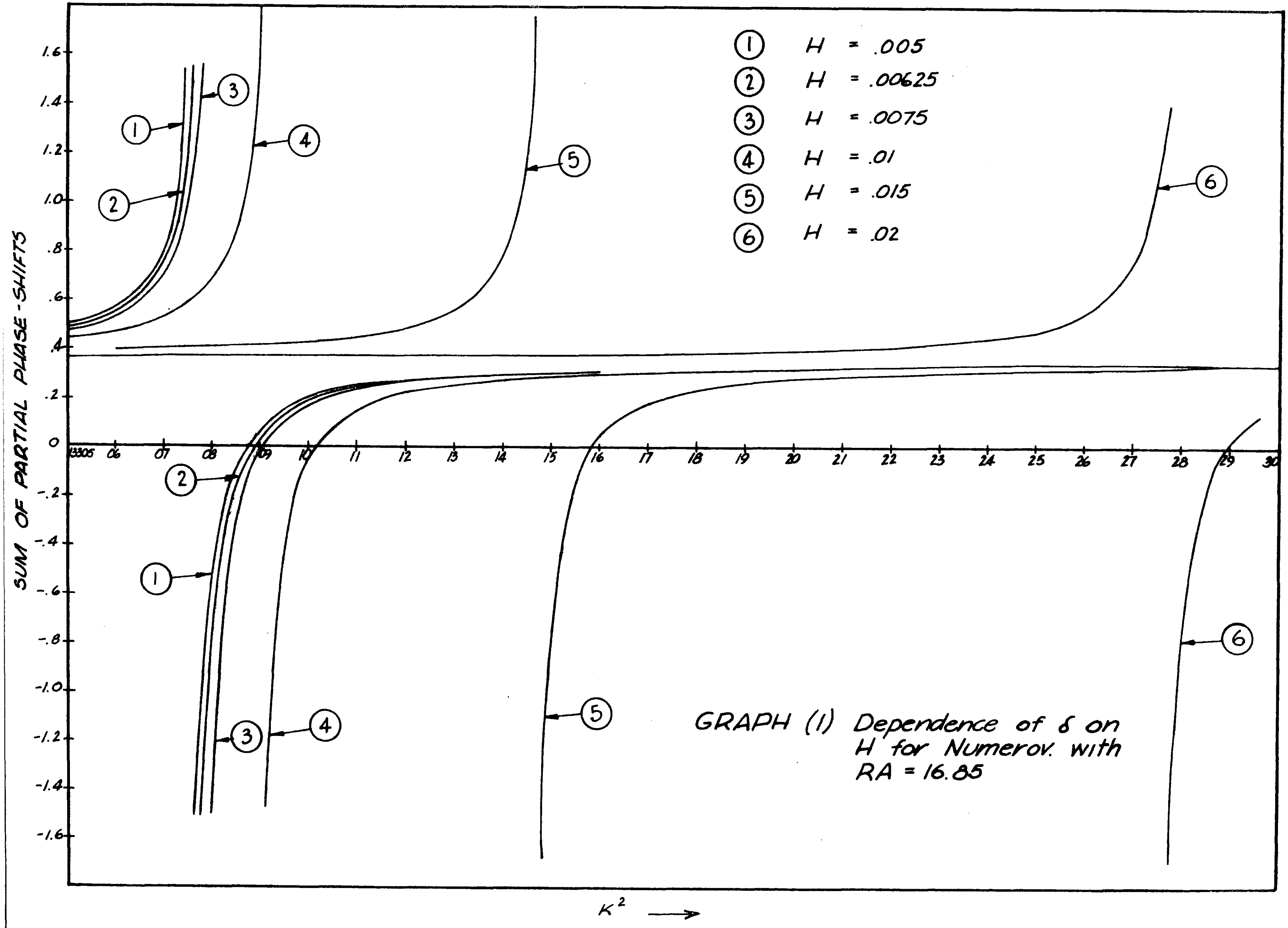
METHOD	TIME
Numerov with H=.005	14:11
DeVogelaere with 35 initial intervals of .004	3:41

Table (8). Computing-times for a definite set of data with RA=11.4.

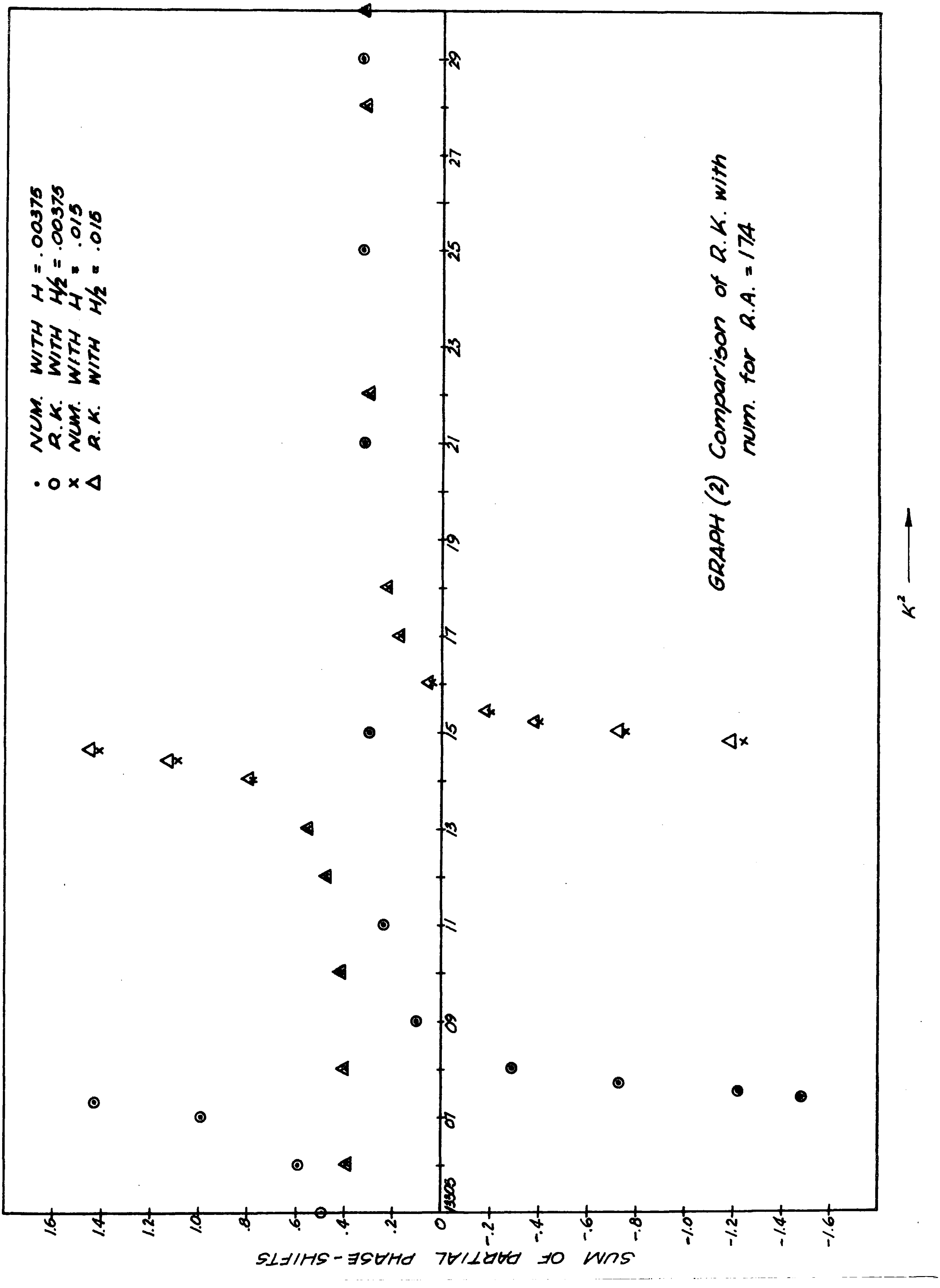
This table shows what a tremendous improvement, on the efficiency of the integrating procedure in ATOMNP, can be brought about by our new technique. Table (8) should be compared with Table (6). A suitable value for RA is 12 atomic units.

Ideally, DeVogelaere is also the optimum algorithm when we consider the storage requirements. Table (7) shows that the usage of DeVogelaere realizes a saving of 50% over Numerov in storage considerations.

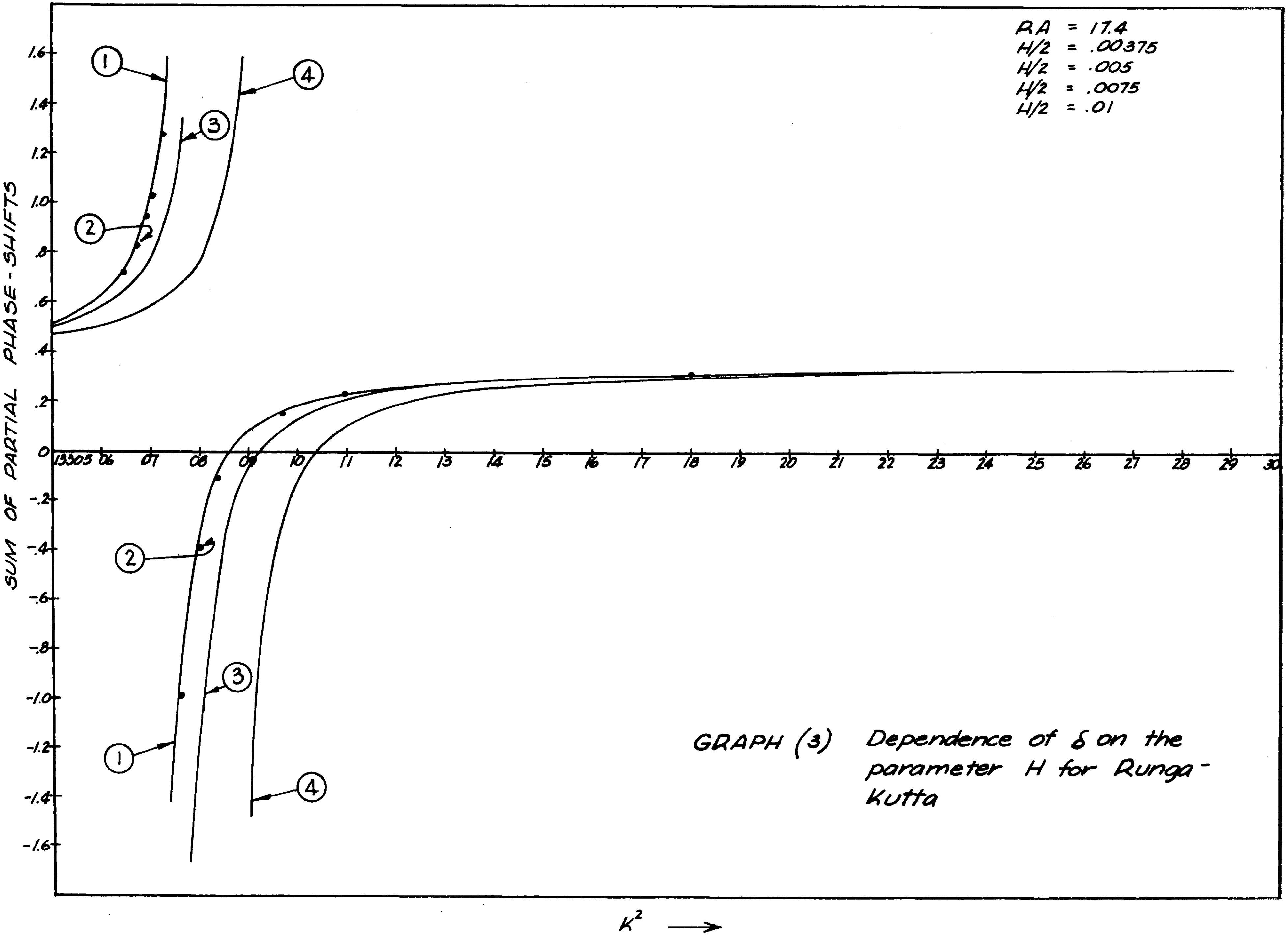
In summary, the DeVogelaere hybrid algorithm should be used for the integrating procedure in conjunction with the technique of having a number of the initial intervals, approximately 35, very small, that is of length .004 atomic units. A large interval length may then be used for the remainder of the calculations.



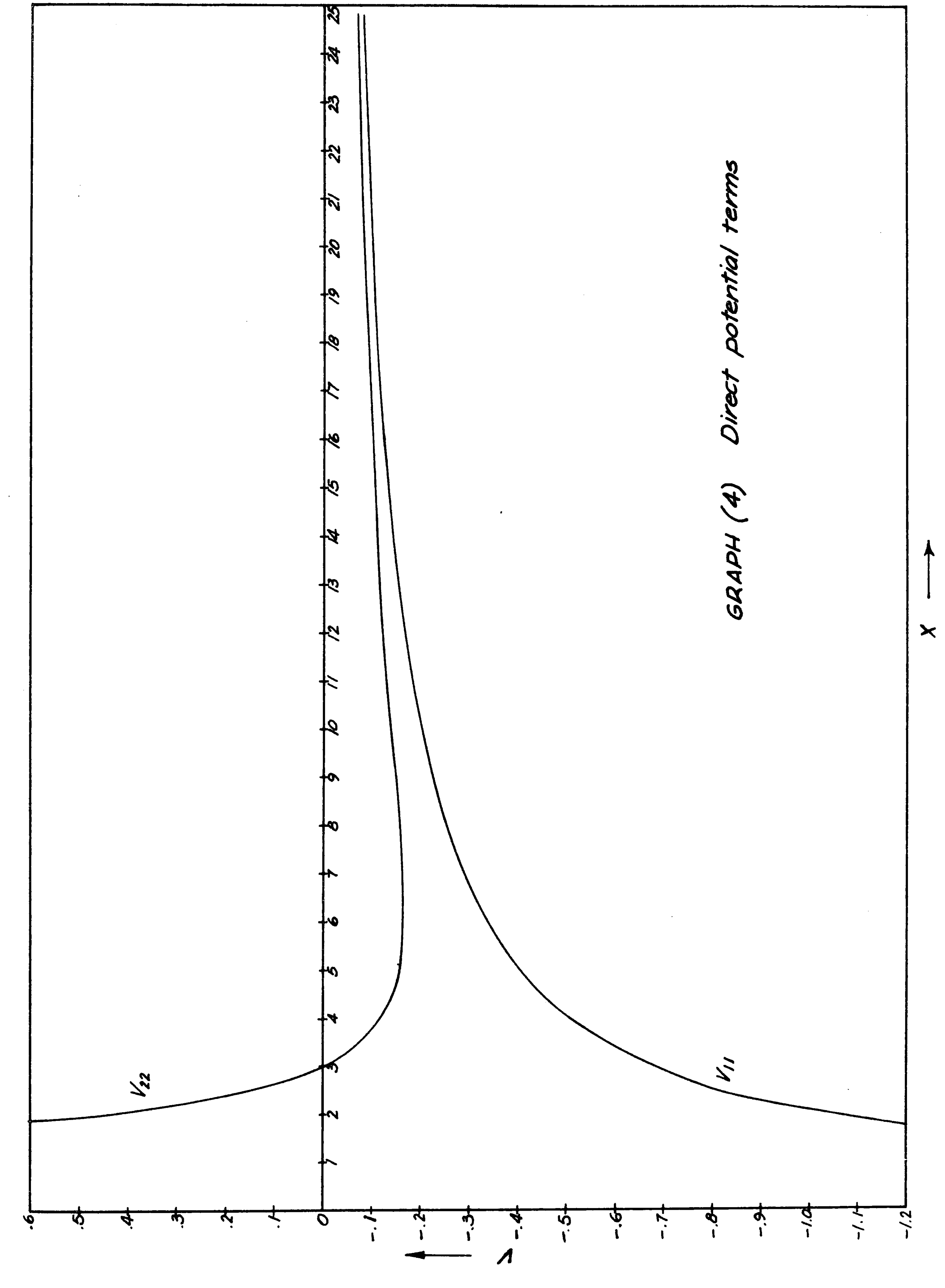
GRAPH (1) Dependence of δ on H for Numerov. with RA = 16.85



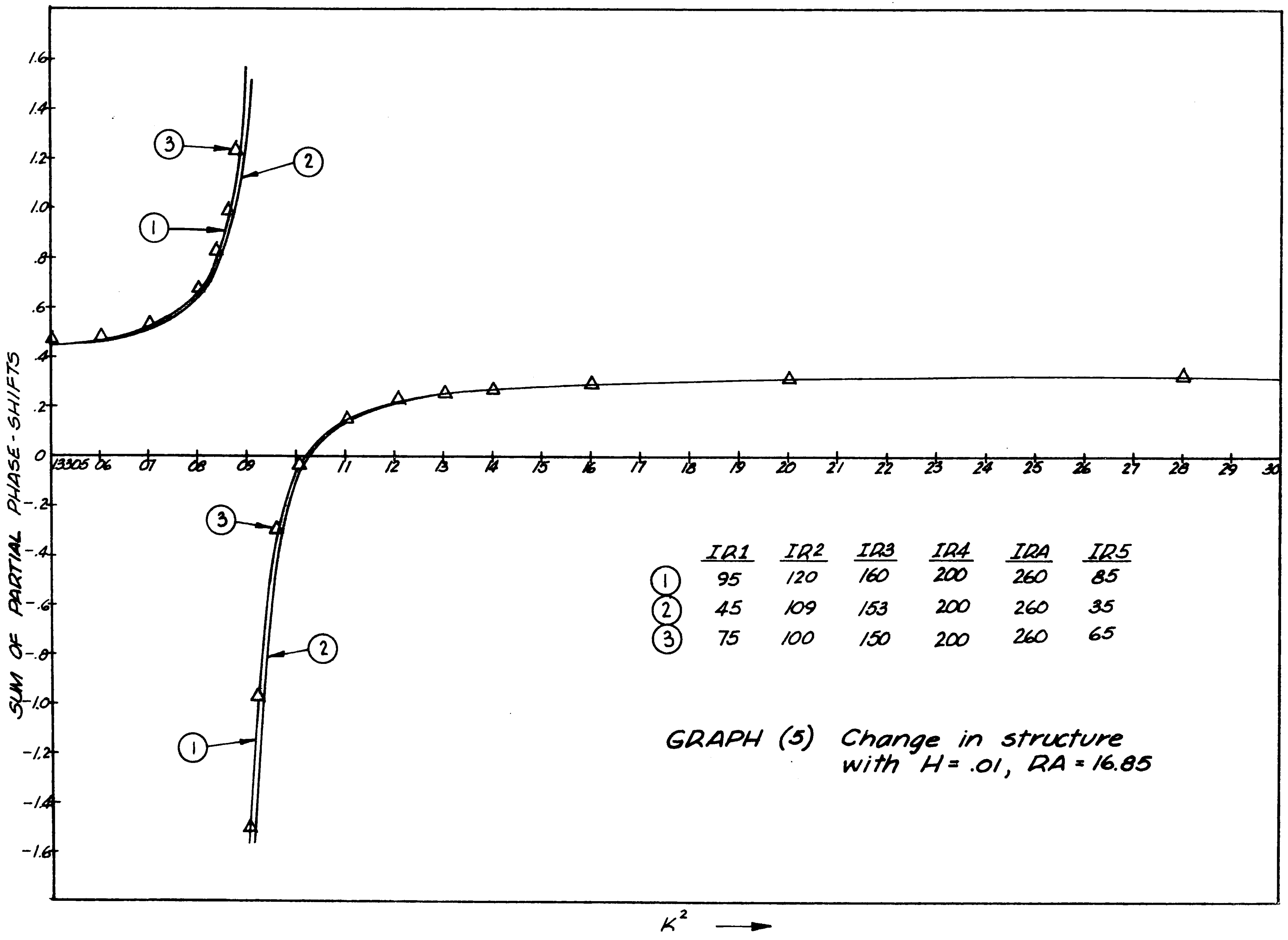
GRAPH (2) Comparison of R.K. with num. for R.A. = 17A



GRAPH (3) Dependence of δ on the parameter H for Runga-Kutta

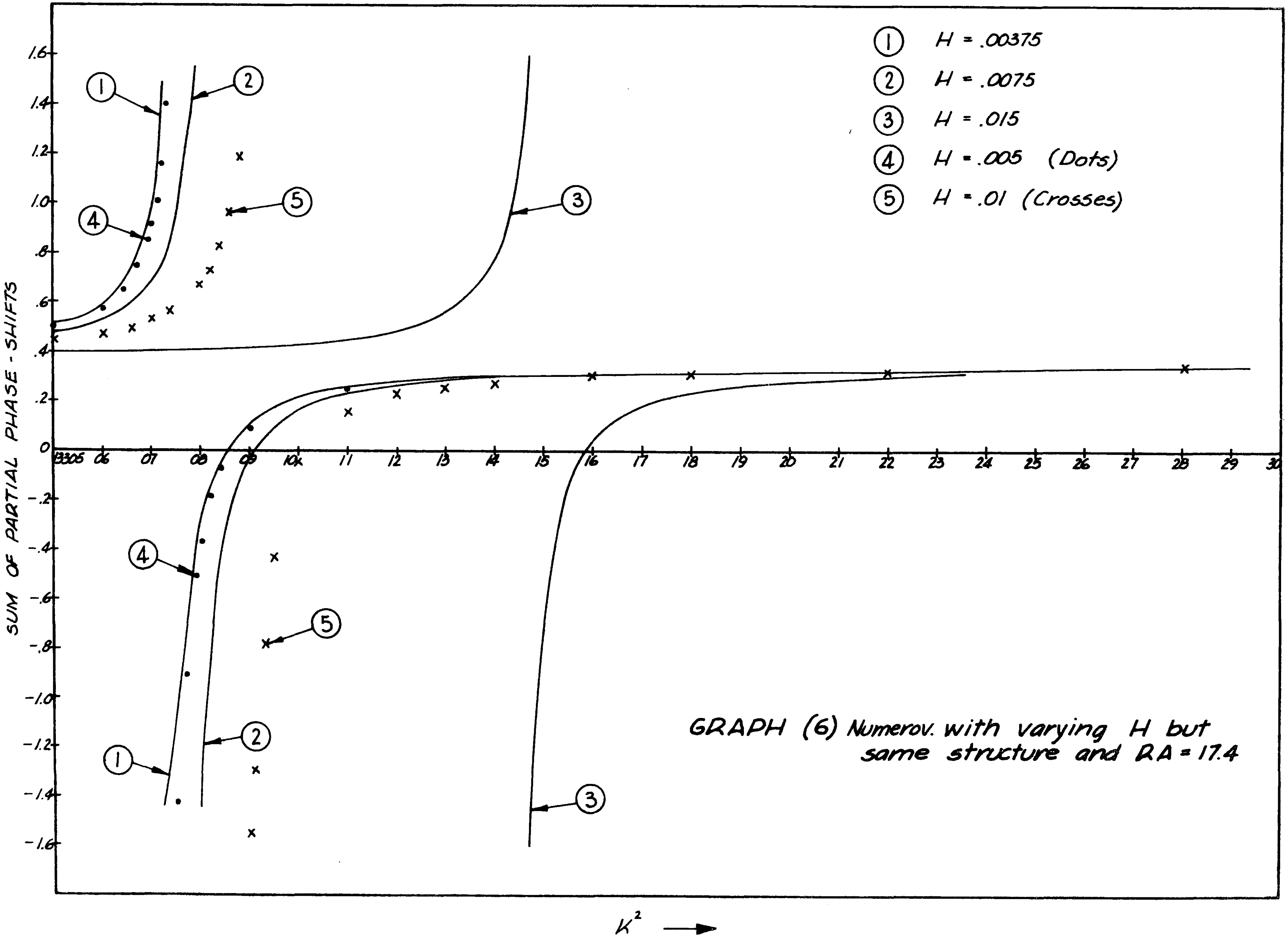


GRAPH (4) Direct potential terms

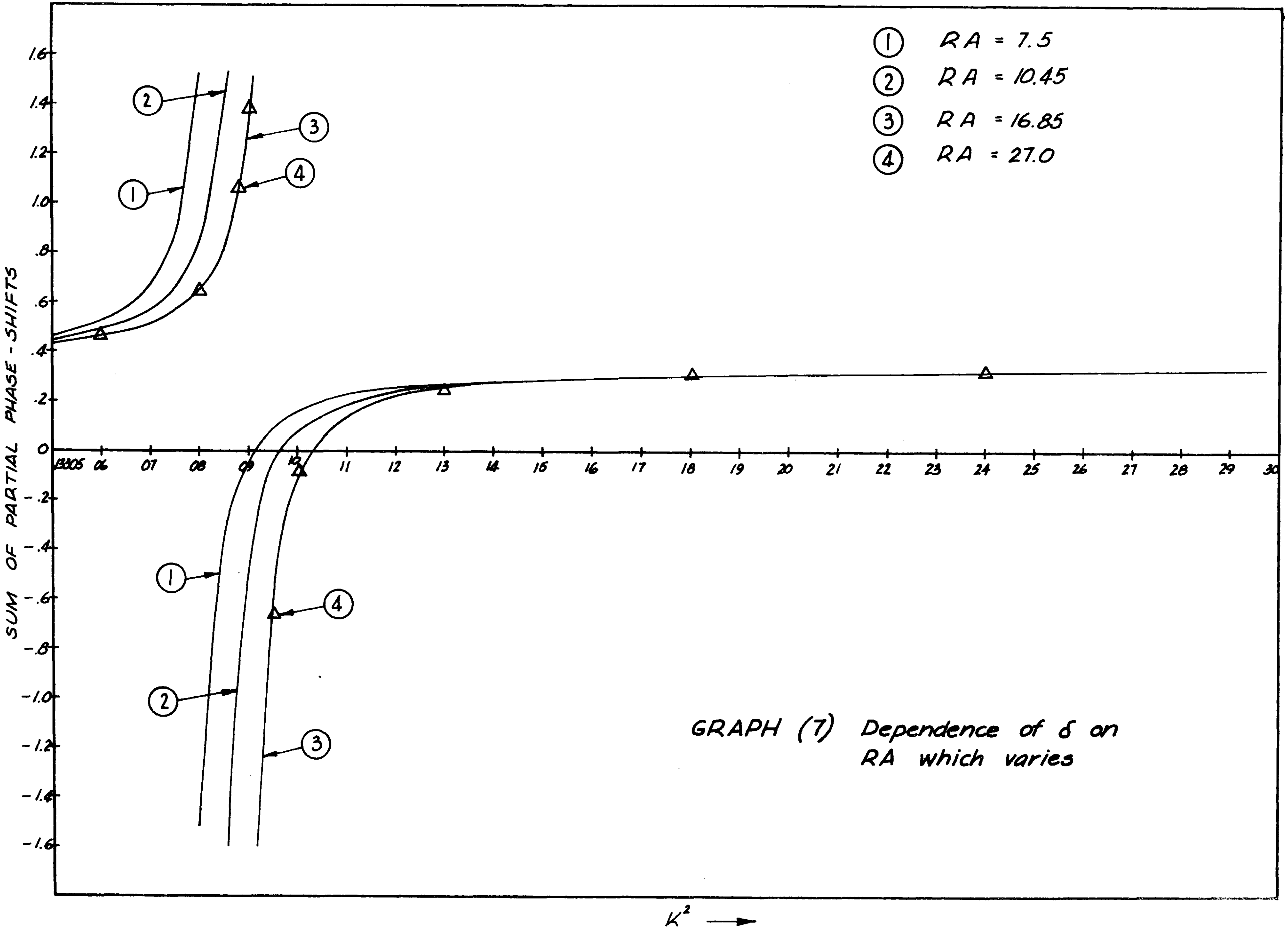


	IR1	IR2	IR3	IR4	IRA	IR5
1	95	120	160	200	260	85
2	45	109	153	200	260	35
3	75	100	150	200	260	65

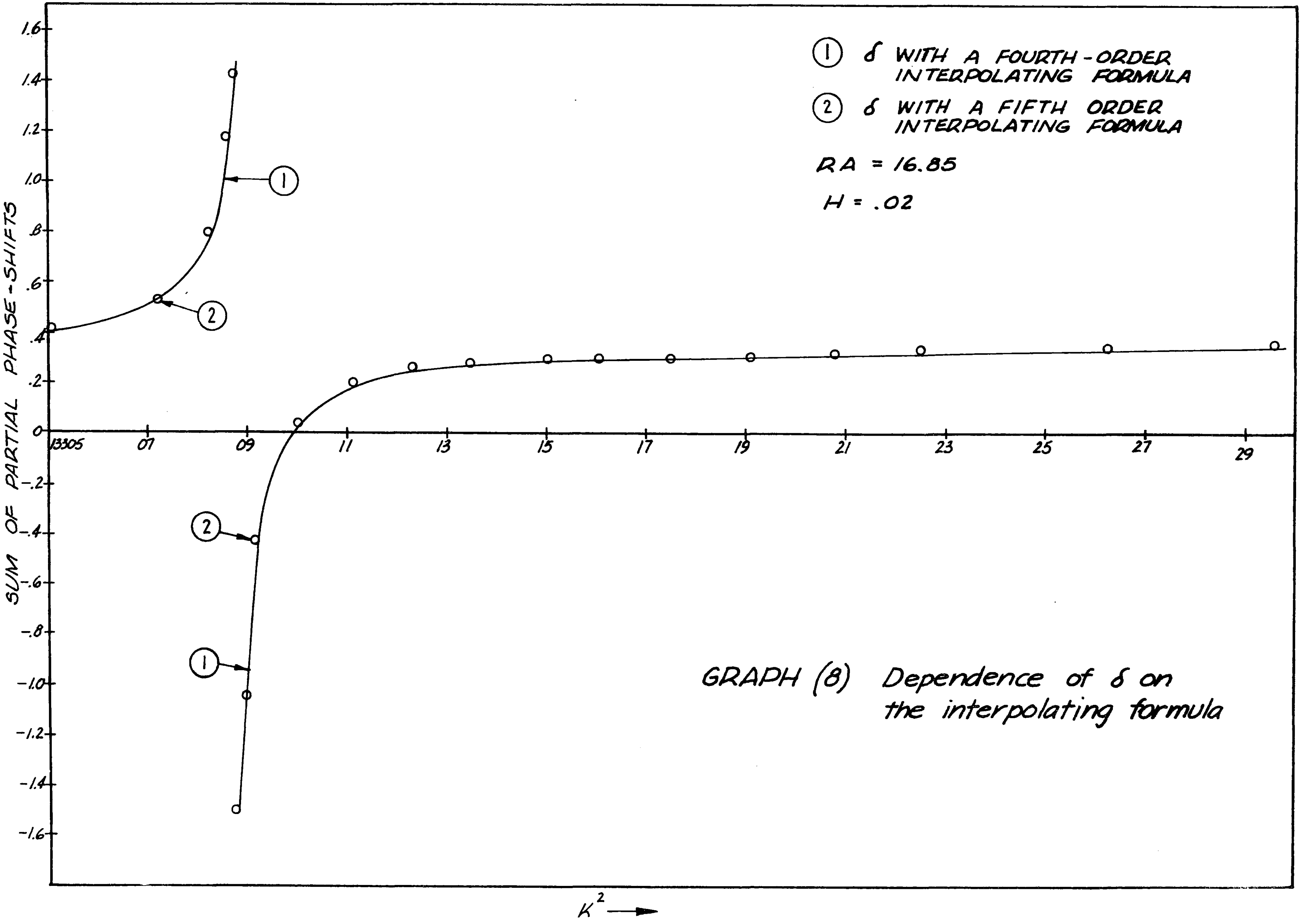
GRAPH (5) Change in structure with H = .01, RA = 16.85



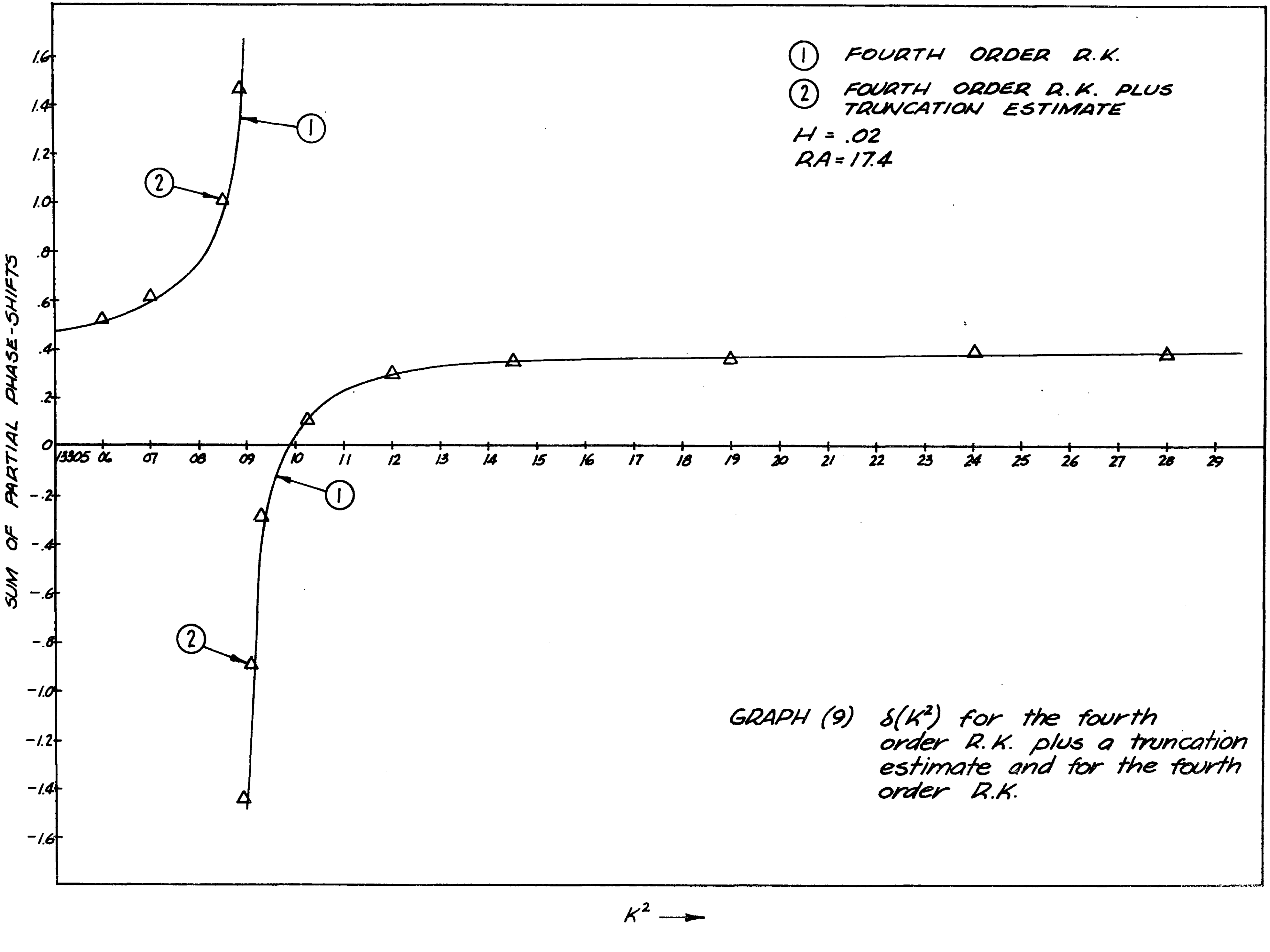
GRAPH (6) Numerov. with varying H but same structure and RA = 17.4



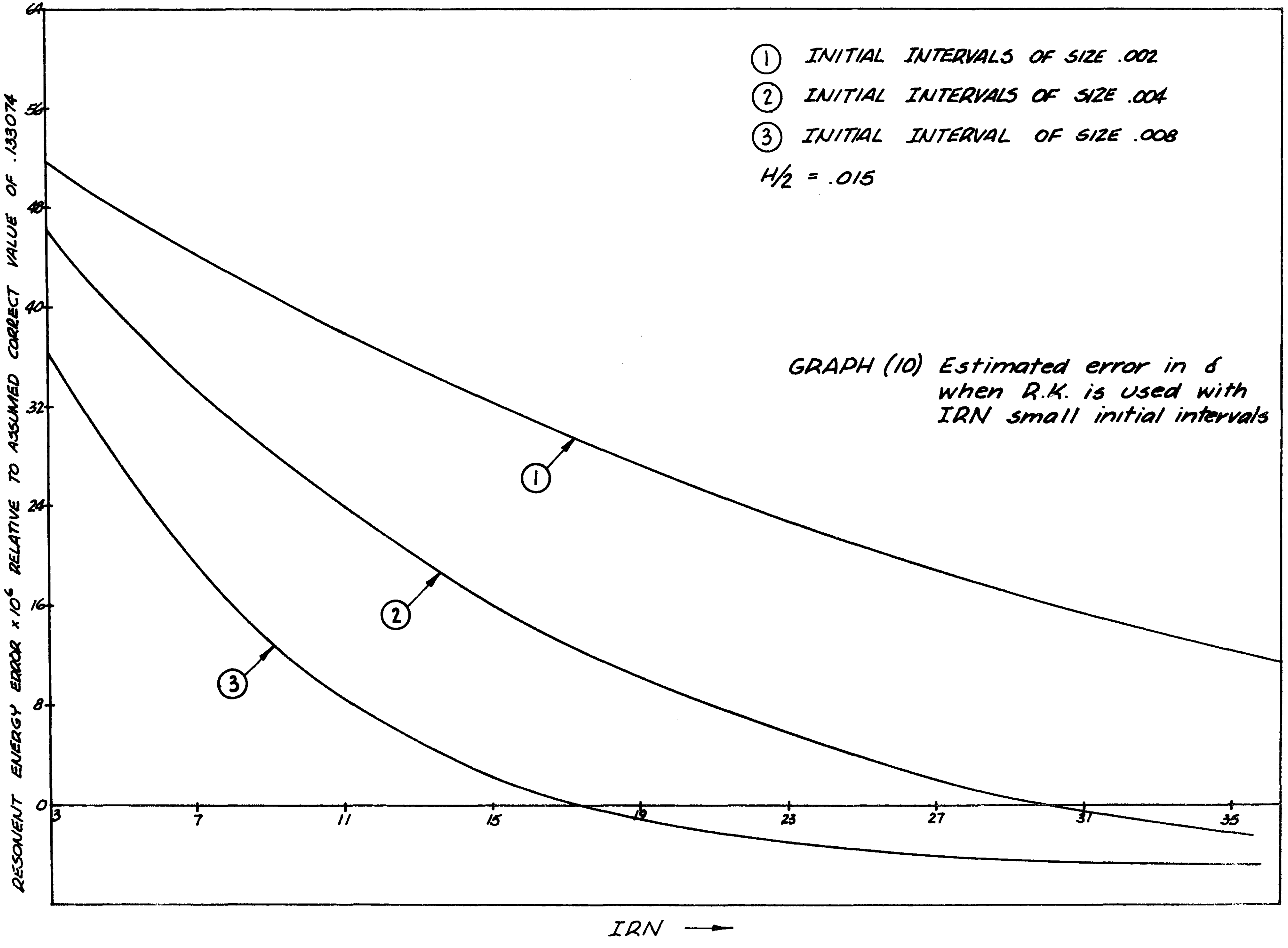
GRAPH (7) Dependence of δ on RA which varies



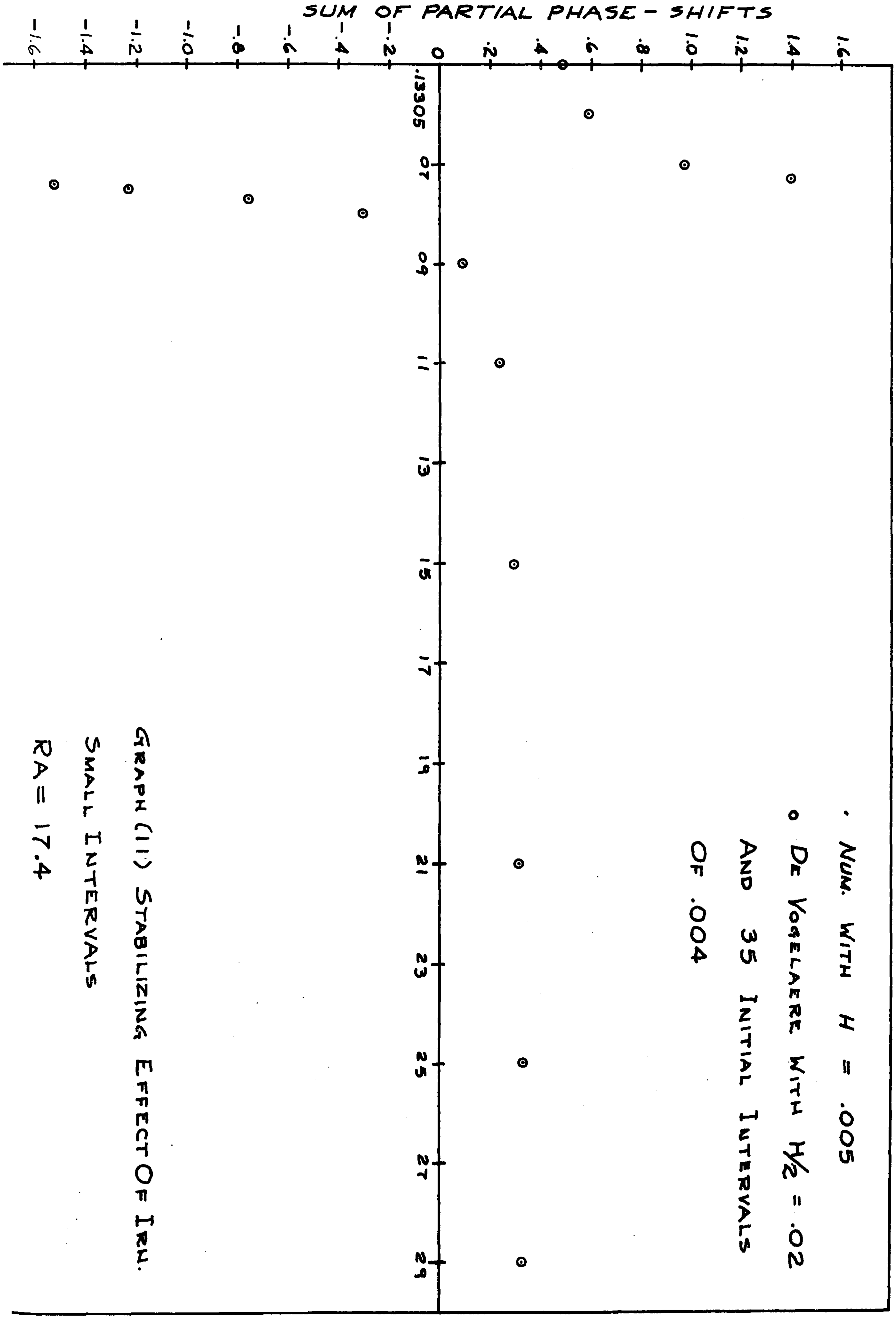
GRAPH (8) Dependence of δ on the interpolating formula



GRAPH (9) $\delta(K^2)$ for the fourth order R.K. plus a truncation estimate and for the fourth order R.K.



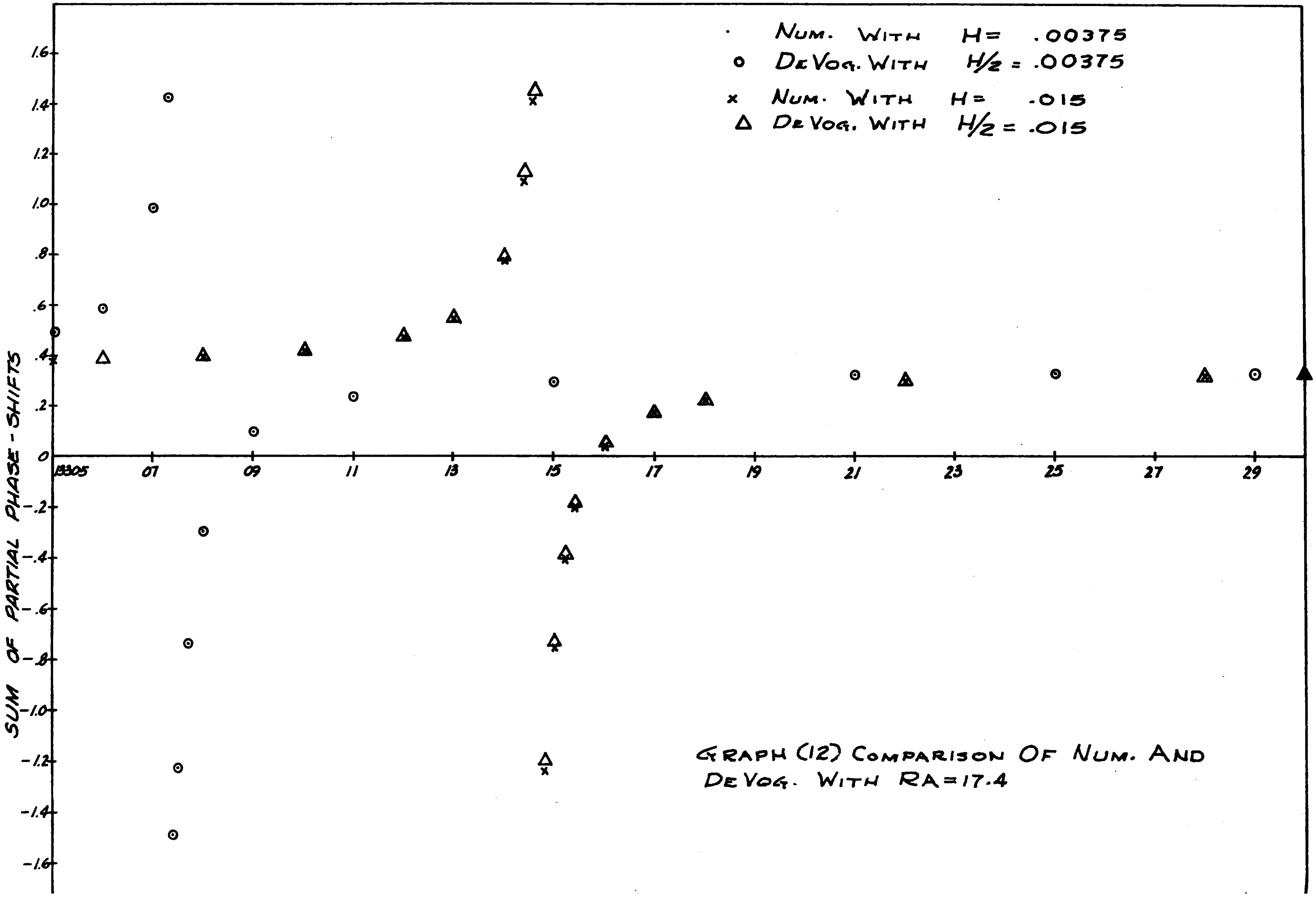
GRAPH (10) Estimated error in δ when R.K. is used with IRN small initial intervals



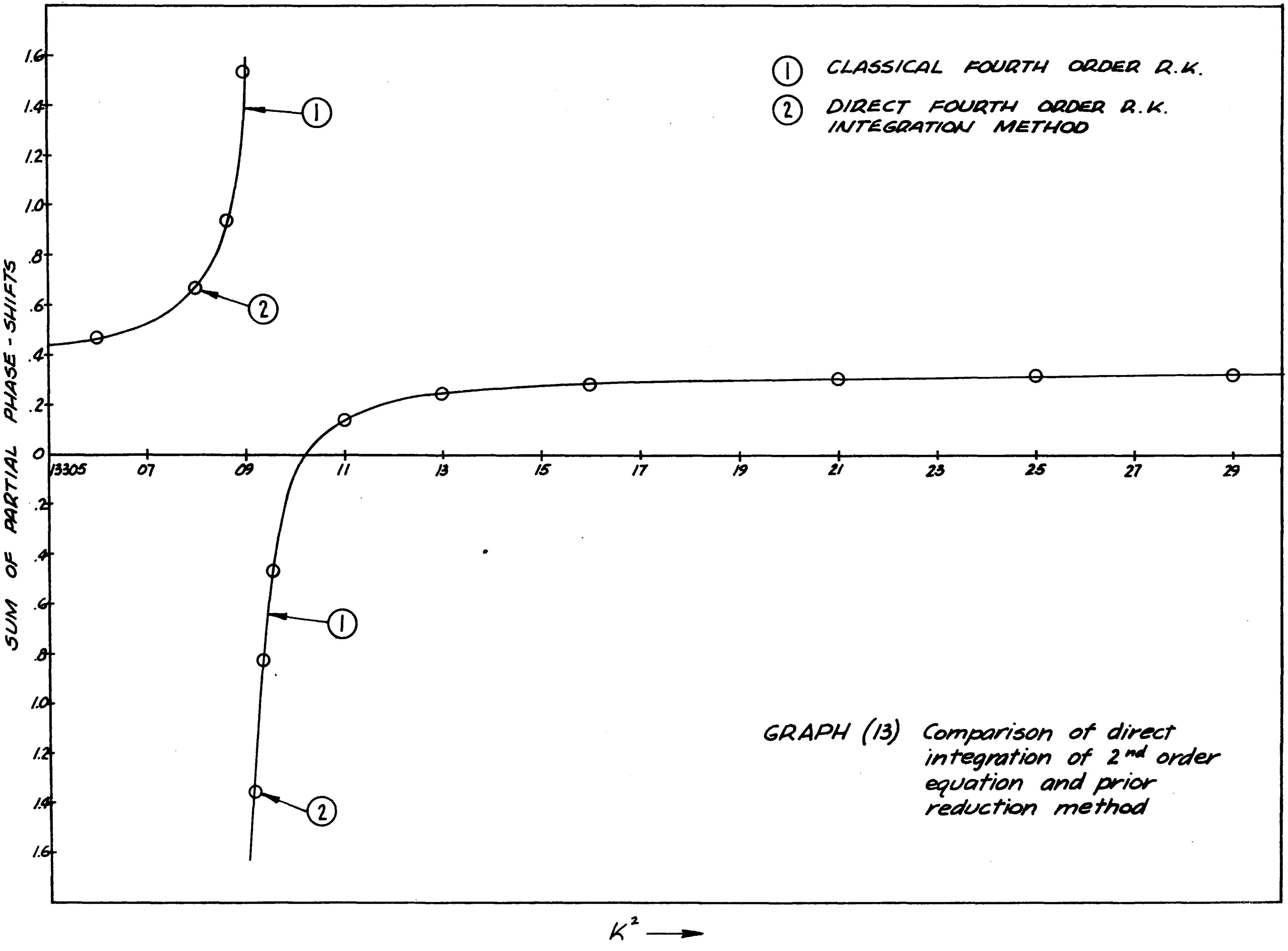
GRAPH (11) STABILIZING EFFECT OF IRN.

SMALL INTERVALS

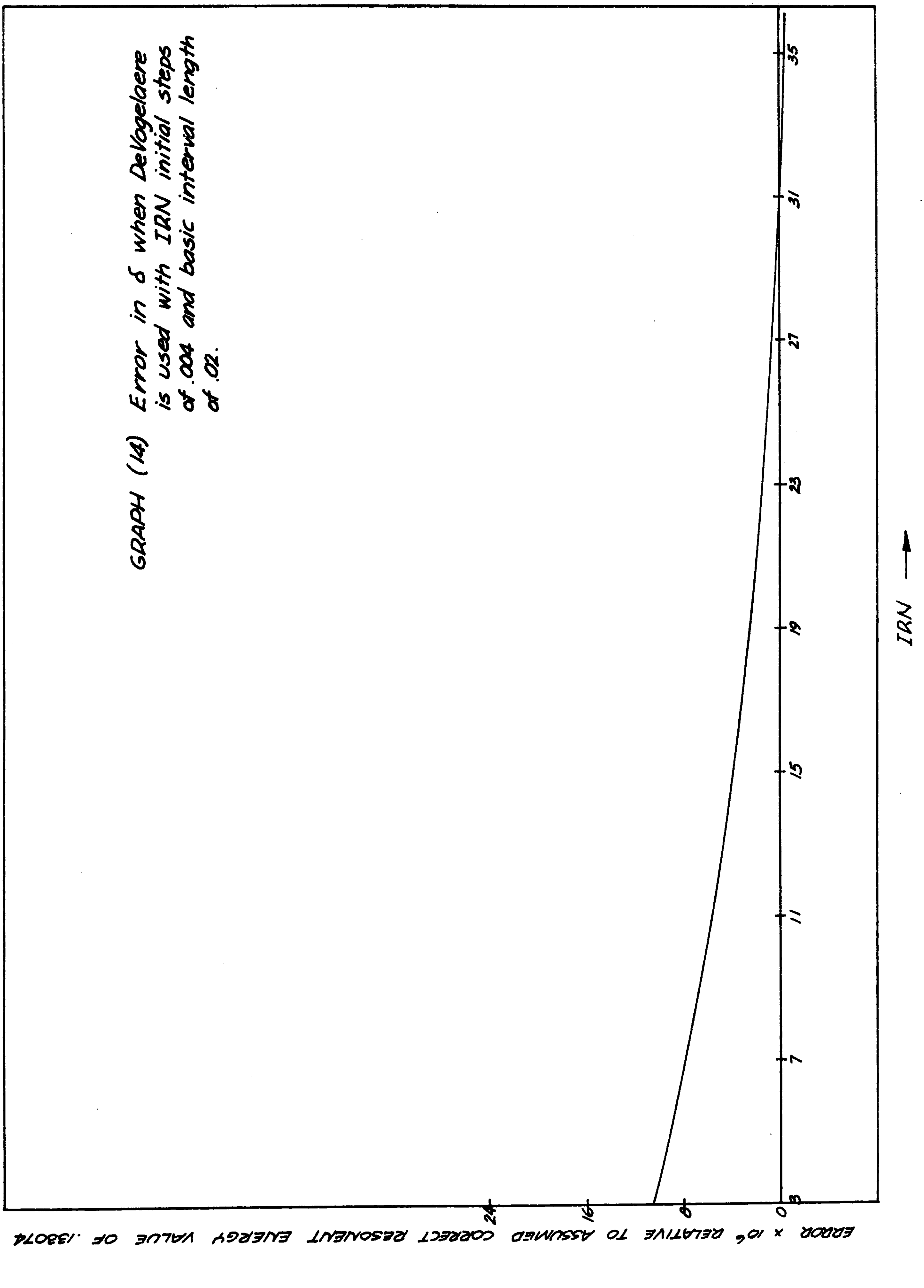
RA = 17.4



Graph (12) Comparison Of Num. And DeVog. With RA=17.4



GRAPH (13) Comparison of direct integration of 2nd order equation and prior reduction method



GRAPH (14) Error in δ when DeVogelaere is used with IRN initial steps of .004 and basic interval length of .02.

BIBLIOGRAPHY

(1) Massey, H.S.W. and C.B.O. Mohr, Proc. Roy. Soc. (London), A136, 289, (1932).

(2) Feshbach, H., Ann. Phys. 5, 357, (1958).

(3) Feshbach, H., Ann. Phys. 19, 287, (1962).

(4) Feshbach, H., Rev. Mod. Phys. 36, 1076, (1964).

(5) Smith, K., R. J. Henry, and P. G. Burke, Phys. Rev., 147, No. 1, 21, (1966).

(6) Smith, K. and L. Morgan, Phys. Rev. 167, 110, (1968).

(7) Burke, P.G., H. M. Schey, and K. Smith, Phys. Rev. 129, 1258, (1963).

(8) Burke, P.G., S. Ormonde, A.J. Taylor, and W. Whitaker, abstracts of "The Fifth International Conference of the Physics of Electronic and Atomic Collisions" (Leningrad), P. 368, (1967).

(9) Burke, P.G., J. W. Cooper, and S. Ormonde, Phys. Rev. Letters 17, 345, (1966).

(10) Burke, P.G.,D.D. McVicar and K. Smith,
(i) Proc. Phys. Soc. (London), 83, 397, (1964).
(ii) Proc. Phys. Soc. (London), 84, 749, (1964).

(11) Burke, P.G., J. H. Tait, B.A. Lewis, Proc. Phys. Soc. (London) 87, 209, (1966).

(12) Seaton, M.J., Proc. Roy. Soc., A231, 37, (1955).

(13) Damburg, R., Opt. Spectry, USSR 12, 445, (1962).

(14) Damburg, R., and R. K. Peterkop,
(i) Opt. Spectry, USSR 13, 338, (1962).
(ii) Proc. Phys. Soc. (London) 80, 563, (1962).
(iii) Proc. Phys. Soc. (London) 80, 1073, (1962).
(iv) Soviet Physics, JETP16, 1247, (1963).

(15) Smith, K., and S. Ormonde, VI International Conference of The Physics of Electronic and Atomic Collisions, Boston, (1969).

(16) Gailitas, M., and R. Damburg, Opt. Spectry, USSR 14, 249, (1963).

(17) Damburg, R., and M. Gailitas, Proc. Phys. Soc. (London) 82, 1068 (1963).

(18) Marriot, R., "Atomic Collisions Processes", M.R.C. McDowell, Ed. (North-Holland Publ. Co., Amsterdam) P. 114, (1964).

(19) Marriot, R., Proc. Phys. Soc., (London) 87, 407, (1966).

(20) Henry, R.J.W., P. G. Burke, A. L. Sin Fai Lam, Phys. Rev. 178, 218, (1968).

(21) Barnes, L.L., N. F. Lane and L. C. Lin, Phys. Rev. 137, A388, (1965).

(22) Karule, E., and R. Peterkop,
(i) Opt. Spectry, USSR 16, 519 (1964).
(ii) Translation TT-66-12939, SLA, Translation Centre, Chicago, (1965).

(23) Moiseiwitsch, B. L. and S. J. Smith, Revs. of Mod. Phys. 40, No. 2, 239, (1968).

(24) Massey, H.S.W. and B. L. Moisewitsch, Proc. Roy. Soc. (London) A258, 147, (1960).

(25) Lashmore-Davies, C.N., Proc. Phys. Soc. (London), 86, 783, (1965).

(26) Percival, I. C. and M. J. Seaton, Proc. Camb. Phil. Soc., 53, 654 (1957).

(27) Seaton, M. J.
(i) Phil. Trans. Phys. Soc. 83, 763, (1953).
(ii) Proc. Roy. Soc. A218, 400, (1953).
(iii) Proc. Roy. Soc. 68, 457, (1955).

(28) Smith, K., R.J. Henry and P. G. Burke, Phys. Rev., 157, 61, (1967).

(29) Conneely, M. J. , K. Smith, and L. Lipsky, Proc. Phys. Soc. (In press).

(30) Arthurs, A. M. and A. Dalgarno, Proc. Roy. Soc. (London) A256, 540 (1960).

(31) Dalgarno, A. and R. J. W. Henry, Proc. Phys. Soc. 85, 679, (1965).

(32) Bernstein, R. B., A. Dalgarno, H.S.W. Massey, and I. C. Percival, Proc. Roy. Soc. A274, 427, (1963).

(33) Lane, N. F. and S. Geltman, Phys. Rev. 160, 53, (1967).

(34) Sampson, D. H. and R. C. Mjolsness, Phys. Rev. 144, 116, (1966).

(35) Lester, W. A. and R. B. Bernstein, Jour. of Chem. Physics, 48, 4896, (1968).

(36) Hartree, D. R., The Calculation of Atomic Structures, (1957), JOHN WILEY.

(37) Blatt, J. M., L.L. Biedenharn and M. E. Rose, Rev. Mod. Phys., 24, 249, (1952).

(38) Racah, G., Phys. Rev. 63, 367, (1943).

(39) Newton, R. G., F. Math. Phys., 1, 319, (1960).

(40) Burke, P. G., Atomic and Molecular Collisions, (1967).

(41) Lane, A. M. and R. G. Thomas, Rev. Mod. Phys., 30, 257, (1958).

(42) Smith, K., Rep. on Prog. in Phys., 23, 373, (1966).

(43) Peierls, R. E., Proc. Roy. Soc., A253, 16, (1959).

(44) Fonda, L., Ann. Phys., 29, 401, (1964).

(45) Fano, U., Phys. Rev. 124, 1866, (1961).

(46) Huffman, R. E., J. C. Larrabee and Y. Tanaka, J. Chem. Phys., 47, 856, (1967).

(47) Rudd, M. E. and K. Smith, Phys. Rev., 169, No. 1, 79, (1968).

(48) Henry, R. J. W., Planet Space Sci. 16, 1503, (1968).

(49) Conneely, M. J., L. Lipsky, K. Smith, P. G. Burke, R.J.W. Henry, Computer Phys. Comm. (To be published).

(50) Burke, P. G. and H. M. Schey, Phys. Rev., 126, 163, (1962).

(51) Miller, J.C.P. , Numerical Analysis, Joan Walsh, Ed, (1966) ACADEMIC PRESS

(52) Collatz, L., The Numerical Treatment of Diff. Eqns., (1966), SPRINGER-VERLAG

(53) Modern Comp. Methods, Nat. Phys. Lab. (1961), NO. 16, H.M.S.O.

(54) Henrici, P., Discrete Var. Methods in Ord. Diff. Eqns., (1968), WILEY.

(54a) Henrici, P., Information Processing, UNESCO, Paris (1960).

(54b) Henrici, P., Proceedings of a Symposium on the Numerical Treatment of Ordinary Diff. Eqns., Integ. Eqns., and Integro-Diff. Eqns. Rome (1961).

(55) Cowell, P. H. and A.C.D. Crommelin, Appendix to Greenwich Observs. For 1909, 84 (1910).

(56) Kopal, Z., Numer. Anal., (1955), CHAPMAN & HALL.

(57) King, R., Technical Memorandum No. 22, Argonne Nat. Lab., (1961) unpublished.

(58) Richardson, L. F., Trans. Roy. Soc. London, 226, 299, (1927).

(59) Dahlquist, G., Math. Scand., 4, 33, (1956).

(60) Dahlquist, G., Trans. Roy. Inst. Technol., Stokholm, NR. 130, (1959).

(61) Rutishauser, H., Z. Angew, Math. Phy. 3, 65, (1952).

(61a) Rutishauser, H., and L. Collatz, Z. Angew,Math. Phys. 4, 153 (1953).

(62) Collatz, L. and R. Zurmuhl, Ing. Arch., 13, 34, (1942).

(63) Todd, J., Math. Tables Aids Comp., 4, 39, (1950).

(64) Milne, W. E., Numerical Solution of Diff. Eqns. (1953).

(65) Milne, W. E. and R. R. Reynolds, J.A.C.M., 6, 196, (1959).

(66) Milne, W. E. and R. R. Reynolds, J.A.C.M., 7, 46 (1960).

(67) Milne, W. E. and R. R. Reynolds, J.A.C.M., 9, 64, (1962).

(68) Stetter, H. J., Computing, 3, 286, (1968).

(69) Liniger, W., Computing, 3, 280, (1968).

(70) Blatt, J. M., J. of Comp. Phys., 1, 382, (1967).

(71) Sloan, I. H., J. of Comp. Phys., 2, 414, (1968).

(72) Sloan, I. H., J. of Comp. Phys., 3, 40, (1968).

(72a) Sloan, I. H., Proc. Roy. Soc. (London), A281, 151 (1964).

(73) Fox, L. and E. T. Goodwin, Proc. Camb. Phil. Soc., 45, 373, (1949).

(74) Runge, C., Math. Ann. 46, 167, (1895).

(75) Kutta, W. Z., Math. Phys., 46, 435, (1901).

(76) Nystrom, E. J., Acta. Soc. Sci., Fenn., 50, Nr. 13, 1, (1965).

(77) Zurmuhl, R., Z. Angew. Math. MEch., 28, 173, (1948).

(78) Froese, C., J.A.C.M., 8, 637, (1961).

(79) Froese, C., Can. J. of Phys. 41, 1895, (1963).

(80) Gill, S. Proc. Camb. Phil. Soc., 47, 96, (1951).

(81) Blum, E.K. Num. Note N-N 80, Ramo-Woolridge Corp., (1957).

(82) Bieberbach, L., Z. Angew. Math. Phys., 2, 233, (1951).

(83) Carr, J. W., J.A.C.M., 5, 39, (1958).

(84) Galler, B. A. and D. P. Rozenberg, J.A.C.M., 7, 57, (1960).

(85) Scraton, R. E., Comp. J., 7, 246, (1964).

(85a) Scraton, R. E., Comp. J., 8, 57 (1965).

(86) De Vogelaere, R., J. Res. Nat. Bur. St., 54, 119, (1955).

(87) Johnson, B. R., D. Secrest, and W. A. Lester and R. B. Bernstein, Chem. Phys. Letters, 1, 396, (1967).

(88) Lester, W. A., J. of Comp. Phys., 3, 322, (1968).

(89) Lanczos, C., J. Math. Phys., 17, 123, (1938).

(90) Lanczos, L., Applied Analysis, (1957).

(91) Clenshaw, C. W., Proc. Camb. Phil. Soc., 53, 134, (1957).

(92) Clenshaw, C. W., and H. J. Norton, Comp. J., 6, 88, (1963).

(93) Norton, H. J., Comp. J., 7, 76, (1964).

(94) Fox, L., Comp. J., 4, 318, (1962).

(95) Gibbons, A., Comp. J., 3, 108, (1960).

(96) Campbell, E. S., R. Buehler, J. O. Hirschfelder and D. Hughes, J.A.C.M., 8, 374, (1961).

(97) Moore, R. E., Error in Dig. Comp. 1, 61, (1965), WILEY.

(98) Milne, W. E., Amer. Math. Monthly 33, 455, (1926).

(99) Hamming, R. W., J.A.C.M., 6, 37, (1959).

(100) Crane, R. L. and R. J. Lambert, J.A.C.M., 9, 104, (1962).

(101) Chase, P. E., J.A.C.M., 9, 457, (1962).

(102) Hull, T. E. and A.C.R. Newberry, J. Siam, 10, 351, (1962).

(103) Hull, T. E. and A. L. Creemer, J.A.C.M., 10, 291, (1963).

(104) Alonso, R., J.A.C.M., 7, 176, (1960).

(105) Butcher, J. C., J.A.C.M., 12, 124, (1965).

(106) Butcher, J. C., STANFORD LINEAR ACCELERATOR CENTER, SLAC-PUB-207.

(107) Gragg, W. B. and H. J. Stetter, J.A.C.M., 11, 188, (1964).

(108) Kohfeld, J. J. and G. T. Thompson, J.A.C.M., 14, No. 1, 155, (1967).

(109) Brush, D. G., J. J. Kohfeld, and G. T. Thompson, J.A.C.M., 14, No. 4, 769 (1967).

(110) Burke, P. G. and H. M. Schey, Phys. Rev. 126, 147, (1962).

(111) Smith, K. and P. G. Burke, Phys. Rev. 123, 174 (1961).

(112) Merson, R. H., Proc. Symp. on Data Proc., Salisbury, S. Australia, (1957), WEAPONS RESEARCH ESTABLISHMENT.