

62

A THEORETICAL STUDY OF THE  
VIBRATIONAL EXCITATION OF DIATOMIC  
MOLECULES

by

ALAN P. CLARK, M.Sc.

Thesis submitted to the University of Stirling  
for the degree of Doctor of Philosophy.

Physics Department,  
University of Stirling,  
STIRLING,  
Scotland.

September, 1973.

ABSTRACT

Exact quantum mechanical vibrational transition probabilities are calculated for a collinear atom-diatomic molecule collision, using the real reactance matrix  $\underline{K}$ . Both the Morse and harmonic binding potentials are considered. It is found that the discrepancy between the transition probabilities for these binding potentials may be large, depending on the collision parameters  $m$  and  $\alpha$ ; the discrepancy increases as  $m$  becomes large and decreases as  $\alpha$  becomes large. Large Morse well depths (characterised by large values of  $D_e$ ) do not necessarily imply agreement between the transition probabilities of the two oscillators. Anharmonicity will be important in most collisions.

The validity of several approximate theories when applied to this problem is investigated. It is found that the revised first order distorted wave approximation of Mies (1964a), and hence the revised first order perturbation theory approximation (Mies 1964b), are valid providing the reduced mass  $m$  is not too large or the collision too strong.

Based on these investigations, the one-dimensional form of the correspondence principle for strongly coupled states (Percival and Richards 1970a) is modified to include, approximately, the perturbation

of the bound system. The modified theory is tested on the system of a harmonic oscillator, perturbed by a potential  $q^2 F(t)$ , and excellent agreement with the exact quantum mechanical solution is obtained.

The theory is then applied to the collinear atom-diatomic molecule collision, with a Morse molecular binding potential. For a large range of collision parameters, the results are in good agreement with the exact quantum mechanical transition probabilities, even for low order transitions.

The modified correspondence principle is shown to have a larger range of validity than the revised first order perturbation theory approximation of Mies (1964b), to which it reduces in the weak perturbation limit.

ACKNOWLEDGEMENTS

I should like to express my gratitude to my Supervisor, Dr. A.S. Dickinson, for initiating the research undertaken in this thesis and for his continual help and guidance.

I wish also to thank Professor I.C. Percival and Dr. D. Richards for many helpful discussions.

My thanks are also due to Stirling University and the Ministry of Education for N. Ireland for providing Research Studentships, enabling this research to be carried out.

CONTENTS

	<u>PAGE</u>
<u>INTRODUCTION</u> .....	1
<u>CHAPTER 1</u> <u>Formulation of the Collision</u> <u>Problem.</u>	
1) Coordinate Transformations .....	5
2) Boundary Conditions .....	8
<u>CHAPTER 2</u> <u>Solution of the Collision</u> <u>Problem</u>	
1) Amplitude Density Functions .....	11
2) Numerical Quadrature .....	12
<u>CHAPTER 3</u> <u>The Reactance Matrix Equation</u>	
1) Formulation of the Matrix Equation .....	15
2) The Escalator Method of Matrix Inversion .....	17
3) The $\tilde{K}$ Matrix Equation.....	19
4) Boundary Conditions and the Relation Between the $\tilde{K}$ and $\tilde{R}$ Matrices .....	24
<u>CHAPTER 4</u> <u>Computation of the <math>\tilde{K}</math> Matrix</u>	
1) Modification of the Free Particle Wavefunctions in Closed Channels.....	26
2) Normalisation of $\tilde{F}$ and $\tilde{G}$ in Closed Channels...	29
3) A Convergence Procedure for the $\tilde{K}$ Matrix. ...	33
4) The Interaction Potential and Matrix Elements.	33

Chapter 4/cont.

5) Computational Details .....	36
6) Other Close Coupling Methods.....	38

CHAPTER 5      Results and Discussion ..... 42

1) A Comparison of the Exact Transition Probabilities for the Morse and harmonic oscillators.....	43
2) The First Order Distorted Wave Approximation (FODWA) .....	63
3) The Revised First Order Distorted Wave Approximation (RFODWA).....	64
4) First Order Perturbation Theory Approximations.....	65
5) Semi-classical Impulse Approximation .....	66
6) Conclusions .....	66

CHAPTER 6      Correspondence Principle Methods

1) Introduction .....	69
2) The Modified Correspondence Principle.....	74

CHAPTER 7      Excitation of a Harmonic Oscillator 80

1) Exact Quantum Mechanical Solution .....	81
2) Correspondence Principle Solutions.....	82
3) First Order Perturbation Theory .....	84
Approximations	
4) Discussion and Comparison of Results .....	84

	<u>PAGE</u>
<u>CHAPTER 8</u> <u>Correspondence Principle Solutions...</u>	92
<u>for the Vibrational Excitation of a</u>	
<u>Morse Oscillator</u>	
1) The Classical Equations of Motion .....	93
2) Matrix Elements and Fourier Components .....	94
3) Results and Discussion .....	98
4) Concluding Remarks .....	102
 <u>APPENDIX A</u> .....	 109
 <u>APPENDIX B</u> .....	 113
 <u>APPENDIX C</u> .....	 115
 <u>REFERENCES</u> .....	 117

## INTRODUCTION

In the study of intermolecular potentials, inelastic collision processes occupy a central position. The properties of the interaction potential between an atom and a diatomic molecule are reflected in the cross sections for the various rotational and vibrational transitions that the molecule can undergo. (Gordon, Klemperer and Steinfield, 1968).

A theoretical treatment of these processes, however, is complex and in order to obtain information about cross sections, approximations usually must be made.

For the investigation of vibrational-translational energy transfer the approximation most widely employed is the collinear collision; the atom, incident along the molecular axis, is assumed to collide 'head on' with the nearest atom of the diatomic molecule. Many calculations, particularly in recent years, have been performed using this model. (Rapp and Kassal, 1969). Because of the complexity of the atom-diatom molecule collision, this model is too simple to expect any comparisons with experimental results to be successful. However, since essentially exact solutions may be obtained for the model, it is useful in that it provides a 'testing ground' for approximate theories, which if successful, may then be applied with some confidence



to more realistic problems where an exact solution may not be practicably obtained.

In much of the previous work, the binding potential of the diatomic molecule has been approximated by a harmonic potential. However, it was shown by Mies (1964a), using the more realistic Morse binding potential, that in a rigorous treatment of the distorted wave approximation, the use of the harmonic potential may result in the vibrational transition probabilities of the molecule being greatly over-estimated. Hunding (1970), presenting an exact, but very limited comparison of the Morse and harmonic oscillator transition probabilities, concluded that the discrepancy between them was not as great as Mies (1964a) predicted.

The purpose of this thesis is to present a detailed comparison of the exact results for the excitation of the Morse and harmonic oscillators and to examine the range of validity of several approximate theories. The exact transition probabilities are obtained using a close coupling method based on the amplitude density functions of Johnson and Secrest (1966).

One particular approximate theory, the correspondence principle for strongly coupled states (Percival and

-3-

Richards, 1970a), is considered in detail. This theory has been successfully applied to the collinear collision problem where the harmonic molecular binding potential is employed (Clark, 1971). When a Morse binding potential is employed, however, the theory breaks down. The reasons for this breakdown are discussed and a modified form of the theory is developed. This modified correspondence principle is shown to predict transition probabilities in good agreement with the exact quantum Morse oscillator results.

The Collinear Collision problem is formulated in Chapter 1. Chapters 2 and 3 deal with the solution of the problem in terms of the real reactance matrix  $\underline{K}$ . The details of the computation of the  $\underline{K}$  matrix are discussed in Chapter 4. The transition probabilities for the diatomic molecule, when both the Morse and harmonic molecular binding potentials are employed, are presented in Chapter 5 where graphical comparisons are made with several approximate theories.

In Chapter 6 correspondence principle methods are discussed and the modified version of the correspondence principle is developed. In Chapter 7 this is tested on the problem of a harmonic oscillator perturbed by a time dependent potential of the form  $q^2 F(t)$  and in Chapter 8 is applied to the atom-Morse oscillator collision.

Although this investigation of the simple one-dimensional vibrational excitation problem has limited physical interest, it enables the generalisation of the correspondence principle technique to three dimensions and the calculation of approximate cross sections for vibrational excitation to be carried out with confidence. Work is already planned to incorporate the results of this thesis with the atom rigid rotor calculations of Dickinson and Richards, to provide an overall theory of molecular excitation below the threshold for electronic excitation. Although it has recently become possible to perform close coupling calculations for the atom-vibrating, rotating diatomic molecule collision (Eastes and Secrest, 1971), due to the large number channels required, these calculations are, at present, limited to very low order transitions. It is expected that the correspondence principle technique will be most useful for transitions among intermediate and highly excited states.

The major part of the work presented in this thesis has been published by Clark and Dickinson (1973) and Clark (1973).

FORMULATION OF THE COLLISION PROBLEM

1.1 Coordinate Transformations

The collision problem is shown in Figure 1. All three atoms A, B and C are constrained to move along the line defined by the molecular axis B-C. Denoting the masses of the atoms by  $m_A$ ,  $m_B$  and  $m_C$  the Schrödinger equation for the system is,

$$\left[ -\frac{\hbar^2}{2m_A} \frac{\partial^2}{\partial \xi_A^2} - \frac{\hbar^2}{2m_B} \frac{\partial^2}{\partial \xi_B^2} - \frac{\hbar^2}{2m_C} \frac{\partial^2}{\partial \xi_C^2} + \tilde{V}_{BC}(\xi_B - \xi_C) + \tilde{V}_{AB}(\xi_A - \xi_B) \right] \psi = \epsilon_T \psi \quad (1.1)$$

where it is assumed that the atom A is reflected by the repulsive core of the potential  $\tilde{V}_{AB}(\xi_A - \xi_B)$ , between atoms A and B only.  $\tilde{V}_{BC}(\xi_B - \xi_C)$  is the binding potential of the diatomic molecule.

By transforming to the centre of mass coordinates and neglecting the centre of mass motion, depending only on  $X_R$ , Equation (1) reduces to

$$\left[ -\frac{\hbar^2}{2\tilde{m}} \frac{\partial^2}{\partial \tilde{x}^2} - \frac{\hbar^2}{2\tilde{\mu}} \frac{\partial^2}{\partial \tilde{y}^2} + \tilde{V}_{BC}(\tilde{y}) + \tilde{V}_{AB}(\tilde{x}) \right] \psi = \epsilon \psi \quad (1.2)$$

where  $\tilde{y}$  and  $\tilde{x}$  are the BC and AB separations respectively and  $\tilde{x}$  is the separation between the centre of mass of the molecule and the incident atom A.  $\tilde{m}$  and  $\tilde{\mu}$  are reduced masses given by

$$\tilde{m} = m_A (m_B + m_C) / (m_A + m_B + m_C)$$

$$\tilde{\mu} = m_B m_C / (m_B + m_C)$$

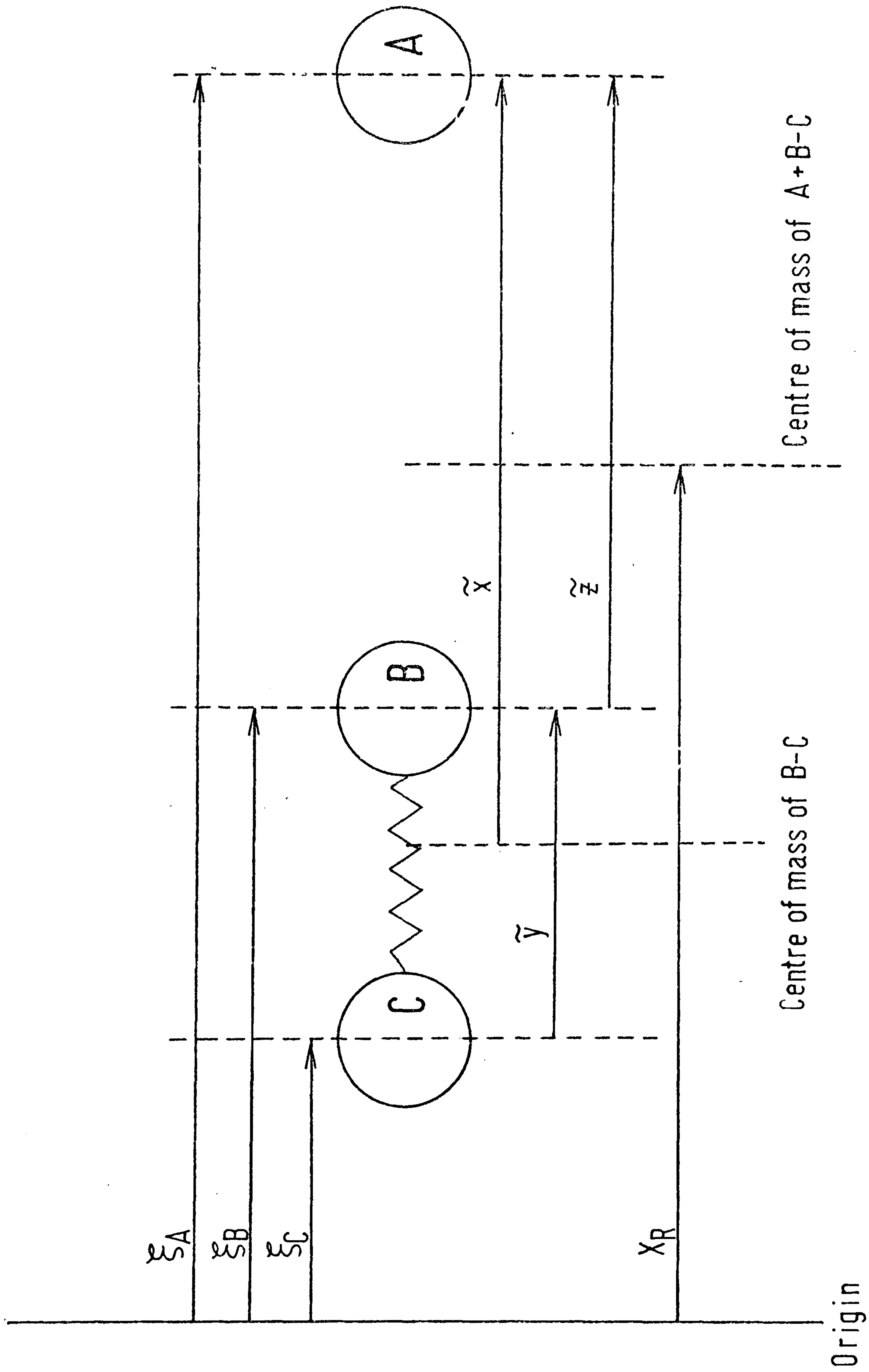


Figure 1.

Both the Morse and harmonic molecular binding potentials are considered. These have the form

$$\tilde{V}_{\text{BC}}(\tilde{y}) = \tilde{D}_e [\exp\{-a(\tilde{y} - \tilde{y}_{\text{eq}})\} - 1]^2 \quad (1.3a)$$

and

$$\tilde{V}_{\text{BC}}(\tilde{y}) = \frac{1}{2} f (\tilde{y} - \tilde{y}_{\text{eq}})^2 \quad (1.3b)$$

where  $\tilde{y}_{\text{eq}}$  is the equilibrium separation of BC.  $\tilde{D}_e$  and  $a$  are the Morse potential well depth (dissociation energy) and steepness parameter respectively, and  $f$  is the harmonic oscillator force constant.

A more convenient formulation of the problem is obtained by transforming to the dimensionless coordinates  $(x, y)$ , where

$$\begin{aligned} \tilde{y} &= \left(\frac{\hbar}{\tilde{\mu}\omega_e}\right)^{\frac{1}{2}} y + \tilde{y}_{\text{eq}} \\ \tilde{x} &= \gamma \left\{ \left(\frac{\hbar}{\tilde{\mu}\omega_e}\right)^{\frac{1}{2}} x + \tilde{y}_{\text{eq}} \right\} \end{aligned}$$

and

$$\gamma = m_c / (m_B + m_c)$$

The frequency  $\omega_e$  is given by

$$\omega_e = \left(\frac{2\tilde{D}_e}{\tilde{\mu}}\right)^{\frac{1}{2}} a = \left(\frac{f}{\tilde{\mu}}\right)^{\frac{1}{2}}$$

thus providing a relation between the Morse and harmonic potentials.

In terms of these dimensionless coordinates the

Schrödinger equation (1.2) becomes

$$\left[ -\frac{1}{2m} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + V_{BC}(y) + V_{AB}(z) \right] \psi = \frac{1}{2} E \psi \quad (1.4)$$

The scaled reduced mass,  $m$ , is given by

$$m = m_A m_c / [m_B (m_A + m_B + m_c)]$$

$E$  is the total energy of the system in units of  $\frac{1}{2} \hbar \omega_e$  and  $z = x - y$ .

In these coordinates the binding potentials (1.3) become

$$V_{BC}(y) = D_e \left[ \exp\left(-\frac{y}{\sqrt{2} D_e}\right) - 1 \right]^2$$

$$V_{BC}(y) = \frac{1}{2} y^2$$

for the Morse and harmonic oscillators respectively where  $D_e = \tilde{D}_e / \hbar \omega_e$ .

The collision problem now reduces to that shown in Figure 2. The incoming particle, of mass  $m$ , interacts via  $V_{AB}(z)$  with a particle of unit mass bound by  $V_{BC}(y)$ .

### 1.2 Boundary Conditions

A solution of (1.4) is required satisfying the boundary conditions

$$\lim_{x \rightarrow \infty} \psi_I(x, y) = \phi_I(y) \exp(-ik_I x) + \sum_n R_{nI} \phi_n(y) \exp(ik_I x) \quad (1.5a)$$

$$\lim_{x \rightarrow -\infty} \psi_I(x, y) = 0 \quad (1.5b)$$

The subscript I denotes that the molecule is initially in the  $I^{\text{th}}$  vibrational state. The  $R_{nI}$  are the probability amplitudes that the particle of mass  $m$ ,

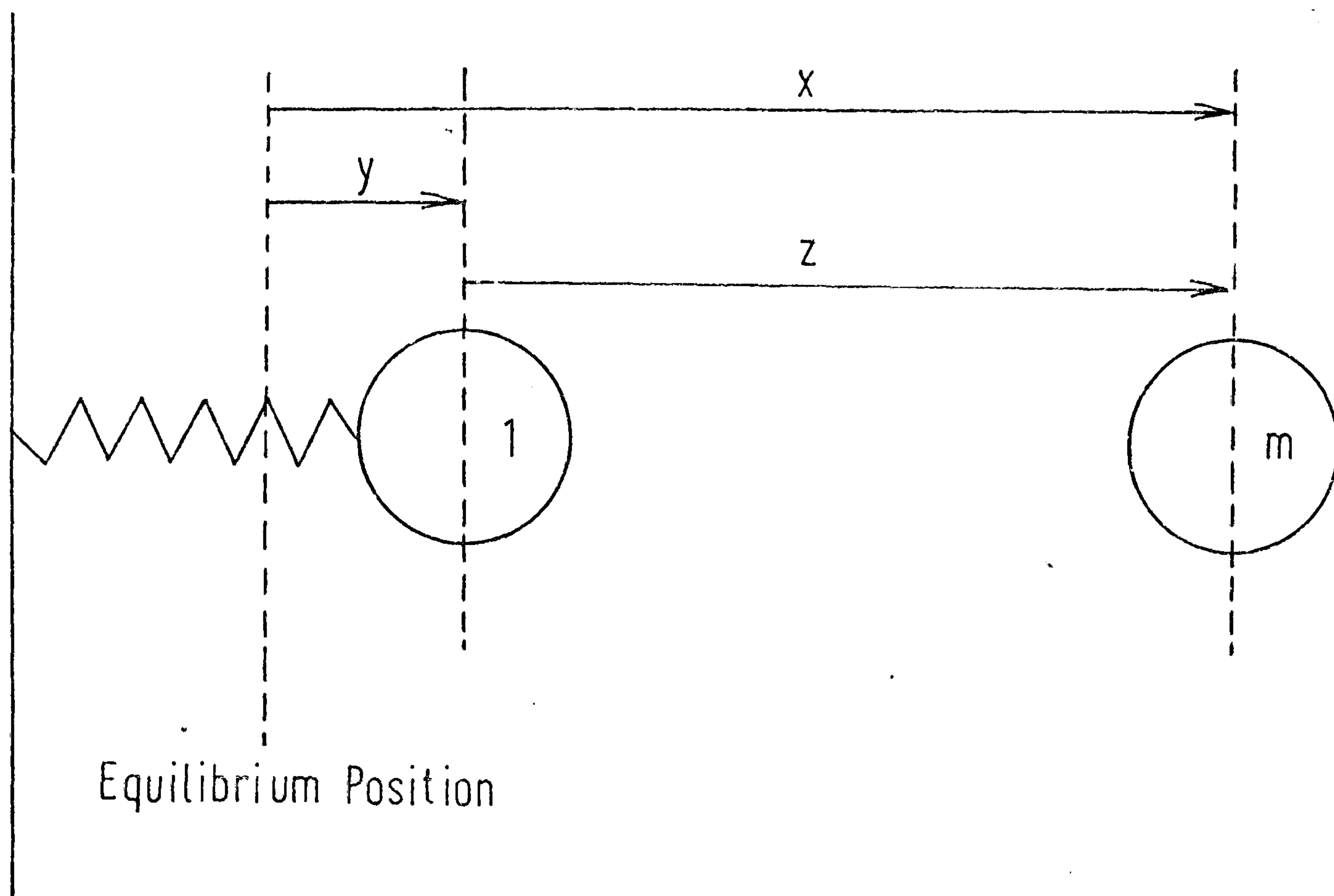


Figure 2.

incident on the oscillator in state I, will be reflected leaving the oscillator in vibrational state  $n$ . These amplitudes or reflection coefficients define the  $\underline{R}$  matrix,

$$\left( \underline{R} \right)_{nI} = R_{nI} \quad (1.6)$$

The  $\phi_n(y)$  are the normalised eigenfunctions of the unperturbed oscillator satisfying the Schrödinger equation,

$$\left[ -\frac{1}{2} \frac{d^2}{dy^2} + V_{BC}(y) \right] \phi_n(y) = \frac{1}{2} \epsilon_n \phi_n(y)$$

where  $\epsilon_n$  are the energy eigenvalues of the oscillator in units of  $\frac{1}{2} \hbar \omega_e$ . For the Morse and harmonic oscillators these are given by



$$\epsilon_n = 2n + 1 - \frac{1}{2} (n + \frac{1}{2})^2 / D_e$$

$$\epsilon_n = 2n + 1$$

respectively.

The wave numbers  $k_n$  are then given by

$$k_n = \{ m (E - \epsilon_n) \}^{\frac{1}{2}}$$

The summation in (1.5a) represents a sum over the bound states of the oscillator and additionally, for the Morse oscillator, an integral over the continuum states. However in the numerical calculations, described later, it will never be necessary to include the continuum states. Total energies,  $E$ , at which these states significantly contribute to the transition amplitudes of interest will not be considered.

The probability that the molecule will be found in the  $n^{\text{th}}$  vibrational state after the collision has taken place is given by

$$P_{I \rightarrow n} = |R_{nI}|^2 \frac{k_n}{k_I}$$

## CHAPTER 2

### SOLUTION OF THE COLLISION PROBLEM

#### 2.1 Amplitude Density Functions

The  $\underline{R}$  matrix (1.6) is in general complex. In obtaining numerical solutions to the problem it is more convenient to use purely real quantities. This may be achieved by imposing real boundary conditions on the Schrödinger equation (1.4). Consider the solution  $\psi_I^K(x, y)$  of (1.4) which satisfies

$$\lim_{x \rightarrow \infty} \psi_I^K(x, y) = \phi_I(y) \sin(k_I x) - \sum_n K_{nI} \phi_n(y) \cos(k_n x) \quad (2.1a)$$

$$\lim_{x \rightarrow -\infty} \psi_I^K(x, y) = 0. \quad (2.1b)$$

The amplitudes  $K_{nI}$  now define the purely real reactance matrix  $\underline{K}$  (Mott and Massey, 1965).

The purely real Green function  $G(x, y; x', y')$  satisfying

$$\left[ -\frac{1}{2m} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + V_{sc}(y) - \frac{1}{2} E \right] G(x, y; x', y') = \delta(x-x') \delta(y-y')$$

is given by,

$$G(x, y; x', y') = \sum_n \left( \frac{2m}{k_n} \right) \phi_n(y) \phi_n(y') \sin(k_n x_<) \cos(k_n x_>) \quad (2.2)$$

where  $x_>$ ,  $x_<$  are the greater and lesser, respectively, of  $x$  and  $x'$ .

Using (2.2), the Schrödinger equation (1.4) may now be rewritten as the integral equation (Rodberg and

Thaler, 1967)

$$\begin{aligned} \psi_{\text{I}}^{\text{K}}(x, y) = & \phi_{\text{I}}(y) \sin(k_{\text{I}}x) - \sum_i \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( \frac{2m}{k_i} \right) \phi_i(y) \\ & \times \phi_i(y') V_{\text{AB}}(z') \psi_{\text{I}}^{\text{K}}(x', y') \sin(k_i x_{\leftarrow}) \cos(k_i x_{\rightarrow}) dx' dy' \end{aligned} \quad (2.3)$$

where  $z' = x' - y'$ .

It is more convenient to use the amplitude density functions  $H_{n\text{I}}(x)$  (Secrest and Johnson 1966, Johnson and Secrest 1966) rather than the wave functions  $\psi_{\text{I}}^{\text{K}}(x, y)$ . These are defined by

$$H_{n\text{I}}(x) = \int_{-\infty}^{\infty} \phi_n(y) V_{\text{AB}}(z) \psi_{\text{I}}^{\text{K}}(x, y) dy.$$

Multiplying (2.3) by  $\phi_n(y) V_{\text{AB}}(z)$  and integrating over  $y$  the following integral equation is obtained

$$\begin{aligned} H_{n\text{I}}(x) = & \sin(k_{\text{I}}x) V_{n\text{I}}(x) - \sum_i \left( \frac{2m}{k_i} \right) V_{ni}(x) \\ & \times \int_{-\infty}^{\infty} \sin(k_i x_{\leftarrow}) \cos(k_i x_{\rightarrow}) H_{i\text{I}}(x') dx' \end{aligned} \quad (2.4)$$

where

$$V_{n\text{I}}(x) = \int_{-\infty}^{\infty} \phi_n(y) V_{\text{AB}}(z) \phi_{\text{I}}(y) dy$$

## 2.2 Numerical Quadrature

The summation in (2.4) is over all states of the oscillator. For the total energies  $E$ , being considered, the sum over the discrete states may be terminated at some number  $(N-1)$ , sufficiently large, such that

inclusion of additional states has no significant effect on the transition probabilities. In this sense the transition probabilities obtained are termed 'exact'. The Morse continuum states will not contribute significantly to the transition probability providing satisfactory convergence has been obtained using only the discrete states.

In order to obtain a solution of the integral equation (2.4), the integral over  $x'$  is replaced by an M point quadrature yielding

$$H_{nI}(x_i) = \sin(k_I x_i) V_{nI}(x_i) - \sum_{l=0}^{N-1} \left(\frac{2m}{k_l}\right) V_{nl}(x_i) \quad (2.5)$$

$$\times \sum_{j=1}^M \omega_{ij}(l) \cos(k_l x_>) \sin(k_l x_<) H_{lI}(x_j)$$

The sum over all states here has been truncated at (N-1) and  $x_>$ ,  $x_<$  are now the greater, lesser, respectively of  $x_i$  and  $x_j$ .

Simpson's rule is employed for the quadrature except that, following Johnson and Secrest (1966), the weights are taken as

$$\omega_{ij}(l) = \text{Normal Simpson weight}, \quad i \neq j, \quad i=j \text{ (odd)}$$

$$\omega_{ij}(l) = \frac{1}{3} \Delta x \left[ 4 - \frac{1}{2} k_l \Delta x / \sin(k_l x_j) \cos(k_l x_j) \right], \quad i=j \text{ (even)}$$

where  $\Delta x$  is the step length. This modification of the Simpson weight, for  $i=j$  (even), significantly decreases the computational time since it allows a larger step length  $\Delta x$  to be used. It arises from

the discontinuous derivative of the Green function (2.2) and is discussed fully in Appendix A.

To relate the  $\underline{K}$  matrix to the amplitude density functions, the asymptotic form of (2.3) as  $x \rightarrow \infty$  is compared with the boundary condition (2.1a) giving

$$\begin{aligned} (\underline{K})_{nI} &= K_{nI} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left(\frac{2m}{k_n}\right) \phi_n(y') V_{AB}(z') \\ &\quad \times \psi_I^K(x', y') \sin(k_n x') dx' dy' \\ &= \int_{-\infty}^{\infty} \left(\frac{2m}{k_n}\right) \sin(k_n x') H_{nI}(x') dx'. \end{aligned}$$

Assuming that  $\partial V_{AB}(z)/\partial x$  is a continuous function,

$H_{nI}(x')$  is smooth and the integral over  $x'$  may be replaced by an M point quadrature giving

$$(\underline{K})_{nI} = \sum_{j=1}^M \omega_j \left(\frac{2m}{k_n}\right) \sin(k_n x_j) H_{nI}(x_j) \quad (2.6)$$

where  $\omega_j$  may be taken as normal Simpson weights.

The  $\underline{K}$  matrix is thus expressed in terms of the solution of (2.5).

To solve equation (2.5) directly for the  $H_{nI}(x_i)$  is impracticable, since this requires the direct inversion of a matrix of the typical order 5000 x 5000.

However, in the next chapter a method is presented for obtaining the  $\underline{K}$  matrix at the  $L^{\text{th}}$  point in the quadrature of (2.6) in terms of the  $\underline{K}$  matrix at the  $(L-1)^{\text{th}}$  point. To advance the solution by one quadrature point, in this manner requires the inversion of only one NxN matrix, which is typically of order less than 10 x 10.

THE REACTANCE MATRIX EQUATION

3.1 Formulation of the Matrix Equation

The formal solution of the equations (2.5) and (2.6) is obtained in the following manner.

Defining the  $N \times N$  matrices,

$$\begin{aligned} (\underline{H}(x_i))_{nI} &= H_{nI}(x_i) \\ (\underline{V}(x_i))_{nI} &= V_{nI}(x_i) \\ (\underline{F}(x_i))_{nI} &= \delta_{nI} \sin(k_I x_i) \\ (\underline{G}(x_i))_{nI} &= \delta_{nI} \cos(k_I x_i) \\ (\underline{k})_{nI} &= \delta_{nI} k_I \end{aligned}$$

and

$$(\underline{W}_{ij})_{nI} = \delta_{nI} \omega_{ij}(I)$$

equation (2.5) becomes

$$\begin{aligned} \underline{H}(x_i) &= \underline{V}(x_i) \underline{F}(x_i) - 2m \underline{V}(x_i) \underline{k}^{-1} \\ &\times \sum_{j=1}^M \underline{W}_{ij} \underline{F}(x_j) \underline{G}(x_j) \underline{H}(x_j) \end{aligned} \quad (3.1)$$

Similarly (2.6) becomes

$$\underline{K} = \sum_{j=1}^M \omega_j 2m \underline{k}^{-1} \underline{F}(x_j) \underline{H}(x_j) \quad (3.2)$$

It is now necessary to define generalised or partitioned matrices and vectors as follows.

The generalised column vectors  $(\underline{h}_M)_i = \underline{H}(x_i)$

$$(\underline{f}_M)_i = \underline{F}(x_i)$$

The generalised row vector

$$(\underline{f}_M^*)_i = \omega_i \underline{F}(x_i)$$

and the generalised matrices

$$(\underline{V}_M)_{ij} = \delta_{ij} \underline{V}(x_i)$$

$$(\underline{X}_M)_{nm} = \begin{cases} \omega_m \underline{F}(x_m) \underline{G}(x_n) & m < n \\ \omega_m \underline{F}(x_n) \underline{G}(x_m) & m > n \\ \omega_{nn} \underline{F}(x_n) \underline{G}(x_n) & m = n \end{cases}$$

Each element of these generalised vectors and matrices is itself an N x N matrix corresponding to a particular quadrature point. The subscript M is required since the order of these generalised matrices and vectors depends on the number of quadrature points taken in (3.1) and (3.2). In defining the generalised matrix  $\underline{X}_M$  the normal Simpson weights  $\omega_m$  have been explicitly used for elements  $(\underline{X}_M)_{nm}$ , ( $n \neq m$ ).

Equation (3.1) may now be written as

$$\underline{h}_M = \underline{V}_M \underline{f}_M - 2m \underline{V}_M \underline{k}^{-1} \underline{X}_M \underline{h}_M$$

giving

$$\underline{h}_M = (\underline{I}_M + 2m \underline{V}_M \underline{k}^{-1} \underline{X}_M)^{-1} \underline{V}_M \underline{f}_M \tag{3.3}$$

where  $(\underline{I}_M)_{ij} = \delta_{ij} \underline{I}$  ( $i, j = 1, 2, \dots, M$ .)

and  $\underline{I}$  is an N x N unit matrix.

Similarly (3.2) may be written as

$$\underline{K}_M = 2m \underline{k}^{-1} \underline{f}_M^* \underline{h}_M \tag{3.4}$$

The  $\underline{K}$  matrix here,  $\underline{K}_M$ , is only an  $N \times N$  matrix.

The subscript  $M$  however is necessary, since including more quadrature points may change the value of the  $\underline{K}$  matrix, depending on whether or not convergence has been reached.

Substituting (3.3) into (3.4) yields the required formal expression for the  $\underline{K}$  matrix

$$\underline{K}_M = 2_m \underline{k}^{-1} \underline{f}_M^* \underline{A}_M^{-1} \underline{V}_M \underline{f}_M \quad (3.5)$$

where  $\underline{A}_M = (\underline{D}_M + 2_m \underline{V}_M \underline{k}^{-1} \underline{X}_M)$

The matrix  $\underline{A}_M$  is thus an  $MN \times MN$  matrix of scalar elements and as pointed out previously, direct inversion is impracticable.

### 3.2 The Escalator Method of Matrix Inversion

The method used to invert the matrix  $\underline{A}_M$  is based on the partitioning or escalator method described by Fröberg (1966). The generalisation, for elements which are themselves matrices, is given in Appendix B.

Truncating the quadrature summations in (3.1) and (3.3) after the  $(L-1)^{\text{th}}$  term, is equivalent to replacing the upper limit of the integral in (2.4) by the value  $x_{L-1}$ . It is also equivalent, however, to truncating the interaction potential  $V_{AB}(x-y)$ , such that it is zero for  $x > x_{L-1}$ . In this case the generalised matrices defined in the previous section would be of



order  $(L-1) \times (L-1)$ , each element being itself an  $N \times N$  matrix, and equation (3.5) would become

$$\underline{\underline{K}}_{L-1} = 2m \underline{\underline{k}}^{-1} \underline{\underline{f}}_{L-1}^* \underline{\underline{A}}_{L-1}^{-1} \underline{\underline{V}}_{L-1} \underline{\underline{f}}_{L-1}. \quad (3.6)$$

The matrix obtained by solving this equation, is the  $\underline{\underline{K}}$  matrix for an interaction potential that is zero for  $x > x_{L-1}$ . Similarly, including the  $L^{\text{th}}$  quadrature point in (3.1) and (3.3) results in a matrix  $\underline{\underline{K}}_L$  which is the  $\underline{\underline{K}}$  matrix for the interaction potential that is zero for  $x > x_L$ . The solution is thus advanced by a piecewise inclusion of the interaction potential. This process is continued until the complete interaction potential is constructed or equivalently until the  $\underline{\underline{K}}$  matrix converges.

The escalator method provides a relation between the generalised matrices  $\underline{\underline{A}}_L^{-1}$  and  $\underline{\underline{A}}_{L-1}^{-1}$ .

The matrix  $\underline{\underline{A}}_L$  may be partitioned into

$$\underline{\underline{A}}_L = \left( \begin{array}{c|c} \underline{\underline{A}}_{L-1} & \underline{\underline{A}}_c \\ \hline \underline{\underline{A}}_R & \underline{\underline{a}} \end{array} \right). \quad (3.7)$$

$\underline{\underline{A}}_{L-1}$  is the generalised matrix whose inverse appears in (3.6), and only depends on the first  $L-1$  quadrature points.  $\underline{\underline{A}}_c$  and  $\underline{\underline{A}}_R$  are generalised column and row vectors respectively and  $\underline{\underline{a}}$  is a single element, i.e.  $N \times N$  matrix.  $\underline{\underline{A}}_c$  and  $\underline{\underline{A}}_R$  depend on all the quadrature points up to the  $L^{\text{th}}$  whereas  $\underline{\underline{a}}$  depends only on the  $L^{\text{th}}$  point.

When  $\tilde{A}_L$  is partitioned in this way, the escalator method (Appendix B) yields

$$\tilde{A}_L^{-1} = \left( \begin{array}{c|c} \tilde{A}_{L-1}^{-1} (\mathcal{I}_{L-1} + \tilde{A}_c \tilde{b} \tilde{A}_R \tilde{A}_{L-1}^{-1}) & -\tilde{A}_{L-1}^{-1} \tilde{A}_c \tilde{b} \\ \hline -\tilde{b} \tilde{A}_R \tilde{A}_{L-1}^{-1} & \tilde{b} \end{array} \right)$$

where  $\tilde{b} = (\tilde{a} - \tilde{A}_R \tilde{A}_{L-1}^{-1} \tilde{A}_c)^{-1}$ .

Thus assuming that  $\tilde{A}_{L-1}^{-1}$  is known,  $\tilde{A}_L^{-1}$  and hence  $\tilde{K}_L$  may be determined from (3.8). Only one  $N \times N$  matrix inversion is required, that to evaluate  $\tilde{b}$ .

### 3.3 The $\tilde{K}$ Matrix Equation

Although the problem of inverting an  $MN \times MN$  matrix has been reduced to that of inverting an  $N \times N$  matrix  $M$  times, computation of the solution is still not practicable. It is still necessary to store matrices of order up to  $MN \times MN$ .

In this section it is shown how the matrix  $\tilde{K}_L$  may be directly related to the matrix  $\tilde{K}_{L-1}$  in terms of only  $N \times N$  matrices. This procedure is somewhat lengthy although quite straight forward.

For a quadrature of only  $L$  points

$$\tilde{K}_L = 2m \tilde{k}^{-1} \tilde{f}_L^* \tilde{A}_L^{-1} \tilde{V}_L \tilde{f}_L \quad (3.9)$$

These generalised matrices and vectors may be partitioned as follows

$$\tilde{f}_L^* = (\tilde{f}_{L-1}^* \mid \omega_L \tilde{F}(x_L))$$

$$\underline{\underline{V}}_L = \left( \begin{array}{c|c} \underline{\underline{V}}_{L-1} & \underline{\underline{0}} \\ \hline \underline{\underline{0}}^* & \underline{\underline{V}}(x_L) \end{array} \right)$$

where  $\underline{\underline{0}}$  and  $\underline{\underline{0}}^*$  are generalised zero column and row vectors respectively.

$$\underline{\underline{f}}_L = \left( \begin{array}{c} \underline{\underline{f}}_{L-1} \\ \underline{\underline{F}}(x_L) \end{array} \right)$$

Thus with (3.8) equation (3.9) becomes

$$\begin{aligned} \underline{\underline{K}}_L &= 2m \underline{\underline{k}}^{-1} \left[ \underline{\underline{f}}_{L-1}^* \underline{\underline{A}}_{L-1}^{-1} (\underline{\underline{Q}}_{L-1} + \underline{\underline{A}}_c \underline{\underline{b}} \underline{\underline{A}}_R \underline{\underline{A}}_{L-1}^{-1}) \right. \\ &\times \underline{\underline{V}}_{L-1} \underline{\underline{f}}_{L-1} - \underline{\underline{f}}_{L-1}^* \underline{\underline{A}}_{L-1}^{-1} \underline{\underline{A}}_c \underline{\underline{b}} \underline{\underline{V}}(x_L) \underline{\underline{F}}(x_L) \quad (3.10) \\ &\left. - \omega_L \underline{\underline{F}}(x_L) \underline{\underline{b}} \underline{\underline{A}}_R \underline{\underline{A}}_{L-1}^{-1} \underline{\underline{V}}_{L-1} \underline{\underline{f}}_{L-1} + \omega_L \underline{\underline{F}}(x_L) \underline{\underline{b}} \underline{\underline{V}}(x_L) \underline{\underline{F}}(x_L) \right] \end{aligned}$$

where

$$\underline{\underline{A}}_c = 2m \omega_L \begin{pmatrix} \underline{\underline{V}}(x_1) \underline{\underline{k}}^{-1} \underline{\underline{F}}(x_1) \underline{\underline{G}}(x_L) \\ \underline{\underline{V}}(x_2) \underline{\underline{k}}^{-1} \underline{\underline{F}}(x_2) \underline{\underline{G}}(x_L) \\ \dots \dots \dots \\ \underline{\underline{V}}(x_{L-1}) \underline{\underline{k}}^{-1} \underline{\underline{F}}(x_{L-1}) \underline{\underline{G}}(x_L) \end{pmatrix}$$

$$\underline{\underline{A}}_R = 2m \begin{pmatrix} \omega_1 \underline{\underline{V}}(x_L) \underline{\underline{k}}^{-1} \underline{\underline{F}}(x_1) \underline{\underline{G}}(x_L) & \omega_2 \underline{\underline{V}}(x_L) \underline{\underline{k}}^{-1} \underline{\underline{F}}(x_2) \underline{\underline{G}}(x_L) \\ \dots \dots \dots & \omega_{L-1} \underline{\underline{V}}(x_L) \underline{\underline{k}}^{-1} \underline{\underline{F}}(x_{L-1}) \underline{\underline{G}}(x_L) \end{pmatrix}$$

and  $\underline{\underline{a}} = \underline{\underline{I}} + 2m \underline{\underline{V}}(x_L) \underline{\underline{k}}^{-1} \underline{\underline{W}}_{LL} \underline{\underline{F}}(x_L) \underline{\underline{G}}(x_L)$

Since  $\underline{\underline{k}}^{-1}$ ,  $\underline{\underline{F}}(x_i)$  and  $\underline{\underline{G}}(x_i)$  commute,  $\underline{\underline{A}}_c$  and  $\underline{\underline{A}}_R$  may be written as

$$\begin{aligned} \underline{\underline{A}}_c &= \underline{\underline{V}}_{L-1} \underline{\underline{f}}_{L-1} 2m \omega_L \underline{\underline{k}}^{-1} \underline{\underline{G}}(x_L) \\ \underline{\underline{A}}_R &= \underline{\underline{V}}(x_L) \underline{\underline{G}}(x_L) 2m \underline{\underline{k}}^{-1} \underline{\underline{f}}_{L-1}^* \end{aligned}$$

Substituting these expressions into (3.10) and using (3.6) yields

$$\begin{aligned}
\tilde{K}_L &= \tilde{K}_{L-1} + \tilde{K}_{L-1} (2m\omega_L \tilde{k}^{-1} \tilde{G}(x_L) \tilde{b} \tilde{V}(x_L) \tilde{G}(x_L)) \tilde{K}_{L-1} \\
&\quad - \tilde{K}_{L-1} (2m\omega_L \tilde{k}^{-1} \tilde{G}(x_L) \tilde{b} \tilde{V}(x_L) \tilde{F}(x_L)) \\
&\quad - (2m\omega_L \tilde{k}^{-1} \tilde{F}(x_L) \tilde{b} \tilde{V}(x_L) \tilde{G}(x_L)) \tilde{K}_{L-1} \\
&\quad + 2m\omega_L \tilde{k}^{-1} \tilde{F}(x_L) \tilde{b} \tilde{V}(x_L) \tilde{F}(x_L)
\end{aligned} \tag{3.11}$$

where

$$\begin{aligned}
\tilde{b} &= \left[ \tilde{I} + 2m \tilde{V}(x_L) \tilde{k}^{-1} \tilde{W}_{LL} \tilde{F}(x_L) \tilde{G}(x_L) \right. \\
&\quad \left. - \tilde{V}(x_L) \tilde{G}(x_L) \tilde{K}_{L-1} 2m\omega_L \tilde{k}^{-1} \tilde{G}(x_L) \right]^{-1}.
\end{aligned} \tag{3.12}$$

Since  $\tilde{W}_{LL}$  commutes with  $\tilde{k}^{-1}$ ,  $\tilde{F}(x_L)$  and  $\tilde{G}(x_L)$ ,

(3.12) may be rewritten as

$$\begin{aligned}
\tilde{G}^{-1}(x_L) \tilde{V}^{-1}(x_L) \tilde{b} \tilde{V}(x_L) \tilde{G}(x_L) &= \left[ \tilde{I} \right. \\
&\quad + 2m \tilde{k}^{-1} \tilde{W}_{LL} \tilde{F}(x_L) \tilde{V}(x_L) \tilde{G}(x_L) \\
&\quad \left. - \tilde{K}_{L-1} 2m\omega_L \tilde{k}^{-1} \tilde{G}(x_L) \tilde{V}(x_L) \tilde{G}(x_L) \right]^{-1}
\end{aligned} \tag{3.13}$$

To simplify the notation the following matrices are defined

$$\begin{aligned}
\tilde{B} &= 2m \tilde{G}(x_L) \tilde{k}^{-1} \tilde{V}(x_L) \tilde{G}(x_L) \\
\tilde{C} &= 2m \tilde{G}(x_L) \tilde{k}^{-1} \tilde{V}(x_L) \tilde{F}(x_L) \\
\tilde{D} &= 2m \tilde{F}(x_L) \tilde{k}^{-1} \tilde{V}(x_L) \tilde{G}(x_L) \\
\tilde{E} &= 2m \tilde{F}(x_L) \tilde{k}^{-1} \tilde{V}(x_L) \tilde{F}(x_L) \\
(\tilde{W})_{ij} &= \delta_{ij} \omega_{LL}(i) = (\tilde{W}_{LL})_{ij}
\end{aligned} \tag{3.14}$$

All these matrices are  $N \times N$  and only depend on quantities evaluated at the quadrature point  $x_L$ .

Equation (3.13) thus becomes

$$\tilde{G}^{-1}(x_L) \tilde{V}^{-1}(x_L) \tilde{b} \tilde{V}(x_L) \tilde{G}(x_L) = \left[ \tilde{I} + \tilde{W} \tilde{D} - \tilde{K}_{L-1} \tilde{B} \right]^{-1} \tag{3.15}$$

Consider terms 1, 2 and 4 in the expression of  $\underline{K}$  (3.11). By multiplying  $\underline{b}$  on the left by the unit matrix  $\underline{V}(x_L) \underline{G}(x_L) \underline{G}^{-1}(x_L) \underline{V}^{-1}(x_L)$  and using (3.15), these terms reduce to

$$\left[ \underline{I} + \underline{W} \underline{D} - \omega_L \underline{D} \right] \left[ \underline{I} + \underline{W} \underline{D} - \omega_L \underline{K}_{L-1} \underline{B} \right]^{-1} \underline{K}_{L-1}$$

In a similar way the remaining two terms (terms 3 and 5) of equation (3.11) reduce to

$$\left[ \underline{D} - \underline{K}_{L-1} \underline{B} \right] \left[ \underline{I} + \underline{W} \underline{D} - \omega_L \underline{K}_{L-1} \underline{B} \right]^{-1} \omega_L \underline{G}^{-1}(x_L) \underline{F}(x_L)$$

which may be written as

$$\begin{aligned} & \left[ \left( \underline{I} - \omega_L \underline{D} + \underline{W} \underline{D} \right) \left( \underline{W} \underline{D} - \omega_L \underline{K}_{L-1} \underline{B} \right) \right. \\ & \quad \left. + \left( \omega_L \underline{D} - \underline{W} \underline{D} \right) \left( \underline{I} - \omega_L \underline{K}_{L-1} \underline{B} + \underline{W} \underline{D} \right) \right] \\ & \quad \times \left( \underline{I} - \omega_L \underline{K}_{L-1} \underline{B} + \underline{W} \underline{D} \right)^{-1} \underline{G}^{-1}(x_L) \underline{F}(x_L) \end{aligned}$$

that is

$$\begin{aligned} & \left[ \left( \underline{I} - \omega_L \underline{D} + \underline{W} \underline{D} \right) \left( \underline{W} \underline{D} - \omega_L \underline{K}_{L-1} \underline{B} \right) \left( \underline{I} - \omega_L \underline{K}_{L-1} \underline{B} + \underline{W} \underline{D} \right)^{-1} \right. \\ & \quad \left. + \omega_L \underline{D} - \underline{W} \underline{D} \right] \underline{G}^{-1}(x_L) \underline{F}(x_L) \end{aligned}$$

Since for any matrix  $\underline{A}$ ,  $\left( \underline{I} + \underline{A} \right)^{-1} \underline{A} = \underline{A} \left( \underline{I} + \underline{A} \right)^{-1}$ ,

this reduces to

$$\begin{aligned} & \left[ \left( \underline{I} - \omega_L \underline{D} + \underline{W} \underline{D} \right) \left( \underline{I} - \omega_L \underline{K}_{L-1} \underline{B} + \underline{W} \underline{D} \right)^{-1} \left( \underline{W} \underline{D} - \omega_L \underline{K}_{L-1} \underline{B} \right) \right. \\ & \quad \left. + \omega_L \underline{D} - \underline{W} \underline{D} \right] \underline{G}^{-1}(x_L) \underline{F}(x_L) \end{aligned}$$

From definitions (3.14) this becomes

$$\begin{aligned} & \left( \underline{I} - \omega_L \underline{D} + \underline{W} \underline{D} \right) \left( \underline{I} - \omega_L \underline{K}_{L-1} \underline{B} + \underline{W} \underline{D} \right)^{-1} \left( \underline{W} \underline{E} - \omega_L \underline{K}_{L-1} \underline{C} \right) \\ & \quad + \omega_L \underline{E} - \underline{W} \underline{E} \end{aligned}$$

Thus the expression for  $\underline{K}_L$  (equation (3.11)) reduces

to

$$\begin{aligned} \underline{\underline{K}}_L &= (\underline{\underline{I}} - \omega_L \underline{\underline{D}} + \underline{\underline{W}} \underline{\underline{D}}) (\underline{\underline{I}} - \omega_L \underline{\underline{K}}_{L-1} \underline{\underline{B}} + \underline{\underline{W}} \underline{\underline{D}})^{-1} \\ &\times (\underline{\underline{K}}_{L-1} + \underline{\underline{W}} \underline{\underline{E}} - \omega_L \underline{\underline{K}}_{L-1} \underline{\underline{C}}) + \omega_L \underline{\underline{E}} - \underline{\underline{W}} \underline{\underline{E}} \end{aligned} \quad (3.16)$$

This is now a convenient form for computation. At each quadrature point it is only necessary to evaluate the  $N \times N$  matrices  $\underline{\underline{B}}$ ,  $\underline{\underline{C}}$ ,  $\underline{\underline{D}}$  and  $\underline{\underline{E}}$  and invert one  $N \times N$  matrix to obtain the  $\underline{\underline{K}}$  matrix at that point.

As shown by Calogero (1967), the  $\underline{\underline{K}}$  matrix satisfies the non-linear differential equation

$$\frac{d \underline{\underline{K}}(x)}{dx} = 2m (\underline{\underline{F}}(x) - \underline{\underline{K}}(x) \underline{\underline{G}}(x)) \underline{\underline{K}}^{-1}(x) \underline{\underline{V}}(x) (\underline{\underline{F}}(x) - \underline{\underline{G}}(x) \underline{\underline{K}}(x)) \quad (3.17)$$

Equation (3.16) essential provides a stable procedure for solving this equation. That (3.16) does reduce to this equation in the limit  $\Delta x \rightarrow 0$  may be shown as follows.

As  $\Delta x \rightarrow 0$  the modified quadrature weights reduce to the normal Simpson weights. If, instead of using Simpson's rule, the quadrature weights are chosen to be simply  $\Delta x$  then (3.16) reduces to

$$\underline{\underline{K}}_L = (\underline{\underline{I}} - \Delta x \underline{\underline{K}}_{L-1} \underline{\underline{B}} + \Delta x \underline{\underline{D}})^{-1} (\underline{\underline{K}}_{L-1} + \Delta x \underline{\underline{E}} - \Delta x \underline{\underline{K}}_{L-1} \underline{\underline{C}})$$

Thus

$$\underline{\underline{K}}_L - \Delta x \underline{\underline{K}}_{L-1} \underline{\underline{B}} \underline{\underline{K}}_L + \Delta x \underline{\underline{D}} \underline{\underline{K}}_L = \underline{\underline{K}}_{L-1} + \Delta x \underline{\underline{E}} - \Delta x \underline{\underline{K}}_{L-1} \underline{\underline{C}}$$

$$\therefore \frac{\underline{\underline{K}}_L - \underline{\underline{K}}_{L-1}}{\Delta x} = \underline{\underline{K}}_{L-1} \underline{\underline{B}} \underline{\underline{K}}_L - \underline{\underline{D}} \underline{\underline{K}}_L - \underline{\underline{K}}_{L-1} \underline{\underline{C}} + \underline{\underline{E}}$$

From (3.14)

$$\frac{\underline{K}_L - \underline{K}_{L-1}}{\Delta x} = 2m \left[ \underline{K}_{L-1} \underline{G}(x_L) \underline{k}^{-1} \underline{V}(x_L) \underline{G}(x_L) \underline{K}_L \right. \\ \left. - \underline{F}(x_L) \underline{k}^{-1} \underline{V}(x_L) \underline{G}(x_L) \underline{K}_L \right. \\ \left. - \underline{K}_{L-1} \underline{G}(x_L) \underline{k}^{-1} \underline{V}(x_L) \underline{F}(x_L) + \underline{F}(x_L) \underline{k}^{-1} \underline{V}(x_L) \underline{F}(x_L) \right].$$

In the limit as  $\Delta x \rightarrow 0$  this becomes

$$\frac{d\underline{K}(x)}{dx} = 2m \left[ \underline{K}(x) \underline{G}(x) \underline{k}^{-1} \underline{V}(x) \underline{G}(x) \underline{K}(x) \right. \\ \left. - \underline{F}(x) \underline{k}^{-1} \underline{V}(x) \underline{G}(x) \underline{K}(x) - \underline{K}(x) \underline{G}(x) \underline{k}^{-1} \underline{V}(x) \underline{F}(x) + \underline{F}(x) \underline{k}^{-1} \underline{V}(x) \underline{F}(x) \right]$$

in agreement with (3.17).

### 3.4 Boundary Condition and the relation between the $\underline{K}$ and $\underline{R}$ matrices.

The boundary condition on the  $\underline{K}$  matrix is obtained from the boundary conditions on the wave function

$\psi_{\text{I}}^{\text{K}}(x, y)$  (equations 2.1a, 2.1b). Writing the general solution of the Schrödinger equation in the form

$$\psi_{\text{I}}^{\text{K}}(x, y) = \phi_{\text{I}}(y) \sin(k_{\text{I}}x) - \sum_n K_{n\text{I}}(x) \phi_n(y) \cos(k_n x)$$

equation (2.1b) gives

$$\lim_{x \rightarrow -\infty} (\underline{K}(x))_{n\text{I}} = \delta_{n\text{I}} \tan(k_{\text{I}}x) \quad (3.18)$$

The relation between the  $\underline{K}$  and  $\underline{R}$  matrices may be

obtained by comparing the boundary conditions (2.1a)

and (1.5a). To see this it is first necessary to

formulate (2.1a) and (1.5a) in matrix form. Defining

the row vectors  $(\underline{\Psi})_i = \psi_i(x, y)$ ,  $(\underline{\Psi}_{\text{K}})_i = \psi_i^{\text{K}}(x, y)$

and  $(\underline{\Phi})_i = \phi_i(y)$ , and the diagonal matrices

$(\underline{e}^{\pm})_{ij} = \delta_{ij} \exp(\pm i k_i x)$ ,  $(\underline{c})_{ij} = \delta_{ij} \cos(k_i x)$   
 and  $(\underline{s})_{ij} = \delta_{ij} \sin(k_i x)$  equations (2.1a) and (1.5a) become

$$\mathcal{L} \lim_{x \rightarrow \infty} \underline{\Psi}_K = \underline{\Phi} \underline{s} - \underline{\Phi} \underline{c} \underline{K} \quad (3.19a)$$

$$\mathcal{L} \lim_{x \rightarrow \infty} \underline{\Psi} = \underline{\Phi} \underline{e}^- + \underline{\Phi} \underline{e}^+ \underline{R} \quad (3.19b)$$

Since both  $\underline{\Psi}$  and  $\underline{\Psi}_K$  are solutions of the same Schrödinger equation, (1.4), they can differ at most by an arbitrary constant matrix  $\underline{A}$  say, such that

$$\underline{\Psi} = \underline{\Psi}_K \underline{A}$$

Using the fact that,

$$\begin{aligned} \underline{e}^+ &= \underline{c} + i \underline{s} \\ \underline{e}^- &= \underline{c} - i \underline{s} \end{aligned}$$

yields the results

$$\underline{A} = 2 (i \underline{I} - \underline{K})^{-1}$$

$$\underline{R} = (\underline{K} + i \underline{I})(\underline{K} - i \underline{I})^{-1} = (\underline{K} - i \underline{I})^{-1}(\underline{K} + i \underline{I}) \quad (3.20)$$

since  $(\underline{K} + i \underline{I})$  and  $(\underline{K} - i \underline{I})^{-1}$  commute.

This concludes the analysis required for the solution of the collision problem. Modifications necessary for the computation of the  $\underline{K}$  matrix and the computational details are discussed in the following chapter.



CHAPTER 4

COMPUTATION OF THE K MATRIX

In closed channels the wave numbers  $k_n$  become imaginary. The matrix  $\underline{F}(x_j)$  thus becomes

$$(\underline{F}(x_j))_{nI} = \delta_{nI} i \sinh(|k_n| x_j) \quad (\text{closed channels}),$$

introducing imaginary quantities in the calculation, through the matrices  $\underline{C}$  and  $\underline{D}$  defined by (3.14). This is inconvenient for numerical calculations and may be simply eliminated by modifying the  $\underline{F}$  and  $\underline{G}$  matrices in the closed channels.

4.1. Modification of the free particle wavefunctions in closed channels.

The matrices  $\underline{F}$  and  $\underline{G}$  may be modified to  $\tilde{\underline{F}}$  and  $\tilde{\underline{G}}$  where

$$\begin{aligned} (\tilde{\underline{F}}(x_j))_{nI} &= (\underline{F}(x_j))_{nI} && \text{open channels} \\ &= \delta_{nI} \exp(|k_n| x_j) && \text{closed channels} \end{aligned}$$

and

$$\begin{aligned} (\tilde{\underline{G}}(x_j))_{nI} &= (\underline{G}(x_j))_{nI} && \text{open channels} \\ &= \delta_{nI} \exp(-|k_n| x_j) && \text{closed channels} \end{aligned}$$

The new matrices  $\tilde{\underline{F}}$  and  $\tilde{\underline{G}}$  are thus purely real.

Defining the matrix

$$(e(\pm |k|x))_{nI} = \delta_{nI} \exp(\pm |k_n| x)$$

the relation between the  $\underline{K}$  and  $\underline{R}$  matrices, using  $\underline{\tilde{F}}$  and  $\underline{\tilde{G}}$  in place of  $\underline{F}$  and  $\underline{G}$ , may be found by considering the asymptotic forms of the wave functions  $\underline{\tilde{\Psi}}_K$  and  $\underline{\tilde{\Psi}}$  as in Section 3.4

Partitioning the matrices into open and closed incident and scattering channels we have,

$$\lim_{x \rightarrow \infty} \underline{\tilde{\Psi}}_K = \underline{\tilde{\Phi}} \begin{pmatrix} \underline{\tilde{S}} & \underline{\tilde{O}} \\ \underline{\tilde{O}} & \underline{\tilde{e}}(|k|x) \end{pmatrix} - \underline{\tilde{\Phi}} \begin{pmatrix} \underline{\tilde{C}} & \underline{\tilde{O}} \\ \underline{\tilde{O}} & \underline{\tilde{e}}(-|k|x) \end{pmatrix} \begin{pmatrix} \underline{\tilde{K}}_{oo} & \underline{\tilde{K}}_{oc} \\ \underline{\tilde{K}}_{co} & \underline{\tilde{K}}_{cc} \end{pmatrix} \quad (4.1)$$

$$\lim_{x \rightarrow \infty} \underline{\tilde{\Psi}} = \underline{\tilde{\Phi}} \begin{pmatrix} \underline{\tilde{e}}^- & \underline{\tilde{O}} \\ \underline{\tilde{O}} & \underline{\tilde{e}}(|k|x) \end{pmatrix} + \underline{\tilde{\Phi}} \begin{pmatrix} \underline{\tilde{e}}^+ & \underline{\tilde{O}} \\ \underline{\tilde{O}} & \underline{\tilde{e}}(-|k|x) \end{pmatrix} \begin{pmatrix} \underline{\tilde{R}}_{oo} & \underline{\tilde{R}}_{oc} \\ \underline{\tilde{R}}_{co} & \underline{\tilde{R}}_{cc} \end{pmatrix} \quad (4.2)$$

Using the relations

$$\underline{\tilde{S}} = \frac{1}{2i} (\underline{\tilde{e}}^+ - \underline{\tilde{e}}^-)$$

$$\underline{\tilde{C}} = \frac{1}{2} (\underline{\tilde{e}}^+ + \underline{\tilde{e}}^-)$$

we may write (4.1) as

$$\lim_{x \rightarrow \infty} \underline{\tilde{\Psi}}_K = \underline{\tilde{\Phi}} \begin{pmatrix} \frac{1}{2} \underline{\tilde{e}}^- (i\underline{\tilde{I}} - \underline{\tilde{K}}_{oo}) & -\frac{1}{2} \underline{\tilde{e}}^- \underline{\tilde{K}}_{oc} \\ \underline{\tilde{O}} & \underline{\tilde{e}}(|k|x) \end{pmatrix} - \underline{\tilde{\Phi}} \begin{pmatrix} \frac{1}{2} \underline{\tilde{e}}^+ (\underline{\tilde{K}}_{oo} + i\underline{\tilde{I}}) & \frac{1}{2} \underline{\tilde{e}}^+ \underline{\tilde{K}}_{oc} \\ \underline{\tilde{e}}(-|k|x) \underline{\tilde{K}}_{co} & \underline{\tilde{e}}(-|k|x) \underline{\tilde{K}}_{cc} \end{pmatrix}$$

giving

$$\lim_{x \rightarrow \infty} \underline{\tilde{\Psi}}_K = \underline{\tilde{\Phi}} \begin{pmatrix} \underline{\tilde{e}}^- & \underline{\tilde{O}} \\ \underline{\tilde{O}} & \underline{\tilde{e}}(|k|x) \end{pmatrix} \begin{pmatrix} \frac{1}{2} (i\underline{\tilde{I}} - \underline{\tilde{K}}_{oo}) & -\frac{1}{2} \underline{\tilde{K}}_{oc} \\ \underline{\tilde{O}} & \underline{\tilde{I}} \end{pmatrix} - \underline{\tilde{\Phi}} \begin{pmatrix} \underline{\tilde{e}}^+ & \underline{\tilde{O}} \\ \underline{\tilde{O}} & \underline{\tilde{e}}(-|k|x) \end{pmatrix} \begin{pmatrix} (\underline{\tilde{K}}_{oo} + i\underline{\tilde{I}})(i\underline{\tilde{I}} - \underline{\tilde{K}}_{oo})^{-1} & i(i\underline{\tilde{I}} - \underline{\tilde{K}}_{oo})^{-1} \underline{\tilde{K}}_{oc} \\ 2 \underline{\tilde{K}}_{co} (i\underline{\tilde{I}} - \underline{\tilde{K}}_{oo})^{-1} & \underline{\tilde{K}}_{cc} + \underline{\tilde{K}}_{co} (i\underline{\tilde{I}} - \underline{\tilde{K}}_{oo})^{-1} \underline{\tilde{K}}_{oc} \end{pmatrix}^x$$

$$x \begin{pmatrix} \frac{1}{2}(i\mathbb{I} - \underline{K}_{oo}) & -\frac{1}{2}\underline{K}_{oc} \\ \underline{O} & \mathbb{I} \end{pmatrix} \quad (4.3)$$

Since  $\underline{\Psi} = \underline{\Psi}_k \underline{A}$  comparing (4.3) and (4.2) we obtain

$$\underline{R}_{oo} = -(\underline{K}_{oo} + i\mathbb{I})(i\mathbb{I} - \underline{K}_{oo})^{-1}$$

that is

$$\underline{R}_{oo} = (\underline{K}_{oo} + i\mathbb{I})(\underline{K}_{oo} - i\mathbb{I})^{-1} \quad (4.4)$$

This equation is similar to (3.20) except that now only the open-open channels of the  $\underline{K}$  matrix are required.  $\underline{R}_{oo}$  is all that is required for calculation of the transition probabilities for energetically possible scattering. A procedure similar to this has also been given by Secrest (1971).

In a similar way it is easy to show that the boundary condition on the  $\underline{K}$  matrix (3.18) becomes,

$$\begin{aligned} \lim_{x \rightarrow -\infty} (\underline{K}(x))_{nI} &= \delta_{nI} \tan(k_I x) && \text{open channels} \\ &= \delta_{nI} \exp(2|k_I|x) && \text{closed channels} \end{aligned}$$

with the modification of the  $\underline{F}$  and  $\underline{G}$  matrices.

Also, it should be noted that the matrix  $\underline{k}^{-1}$  occurring in the definition of the  $\underline{B}$ ,  $\underline{C}$ ,  $\underline{D}$  and  $\underline{E}$  matrices, equation (3.14), arose from the Wronskian

$$(\underline{F}'\underline{G} - \underline{G}'\underline{F})$$

in the calculation of the Green function (2.2)

Due to the modification of  $\underline{F}$  and  $\underline{G}$ ,  $\underline{k}^{-1}$  in (3.14) should be replaced by  $\underline{\Delta}^{-1}$  where,

$$\begin{aligned} (\underline{\Delta}^{-1})_{nI} &= \delta_{nI} (1/k_n) && \text{open channels} \\ &= \delta_{nI} (1/2|k_n|) && \text{closed channels} \end{aligned}$$

giving

$$\begin{aligned} \underline{B} &= 2m \underline{\tilde{G}}(x_L) \underline{\Delta}^{-1} \underline{V}(x_L) \underline{\tilde{G}}(x_L) \\ \underline{C} &= 2m \underline{\tilde{G}}(x_L) \underline{\Delta}^{-1} \underline{V}(x_L) \underline{\tilde{F}}(x_L) \\ \underline{D} &= 2m \underline{\tilde{F}}(x_L) \underline{\Delta}^{-1} \underline{V}(x_L) \underline{\tilde{G}}(x_L) \\ \underline{E} &= 2m \underline{\tilde{F}}(x_L) \underline{\Delta}^{-1} \underline{V}(x_L) \underline{\tilde{F}}(x_L) \end{aligned} \quad (4.5)$$

#### (4.2) Normalisation of $\underline{\tilde{F}}$ and $\underline{\tilde{G}}$ in closed channels

As  $x$  becomes large the closed channel elements of the  $\underline{\tilde{F}}$  matrix diverge exponentially.

Computationally this is disadvantageous since

firstly, it may cause rounding errors and

secondly elements of the  $\underline{\tilde{F}}$  matrix may exceed

the capacity of the machine being used. A

simple normalisation procedure may be applied

to both the  $\underline{\tilde{F}}$  and  $\underline{\tilde{G}}$  matrices in closed channels.

At the first quadrature point  $x_1$ , the  $\underline{\tilde{F}}$  and  $\underline{\tilde{G}}$  matrices will be given by

$$\begin{aligned}
 (\tilde{F}(x_i))_{nI} &= \delta_{nI} \sin(k_n x_i) && \text{open channels} \\
 &= \delta_{nI} \exp(|k_n| x_i) && \text{closed channels} \\
 (\tilde{G}(x_i))_{nI} &= \delta_{nI} \cos(k_n x_i) && \text{open channels} \\
 &= \delta_{nI} \exp(-|k_n| x_i) && \text{closed channels.}
 \end{aligned}$$

Defining the matrices

$$\begin{aligned}
 (\tilde{F}^*(x_i))_{nI} &= \delta_{nI} \sin(k_n x_i) && \text{open channels} \\
 &= \delta_{nI} && \text{closed channels} \\
 (\tilde{G}^*(x_i))_{nI} &= \delta_{nI} \cos(k_n x_i) && \text{open channels} \\
 &= \delta_{nI} && \text{closed channels} \\
 (\tilde{\alpha}^+)_{nI} &= \delta_{nI} && \text{open channels} \\
 &= \delta_{nI} \exp(|k_n| x_i) && \text{closed channels} \\
 (\tilde{\alpha}^-)_{nI} &= \delta_{nI} && \text{open channels} \\
 &= \delta_{nI} \exp(-|k_n| x_i) && \text{closed channels}
 \end{aligned}$$

equation (4.5) may be written.

$$\begin{aligned}
 \underline{\underline{B}} &= 2m \underline{\underline{\alpha}}^- \underline{\underline{G}}^*(x_i) \underline{\underline{\Delta}}^{-1} \underline{\underline{V}}(x_i) \underline{\underline{G}}^*(x_i) \underline{\underline{\alpha}}^- = \underline{\underline{\alpha}}^- \underline{\underline{B}}^* \underline{\underline{\alpha}}^- \\
 \underline{\underline{C}} &= 2m \underline{\underline{\alpha}}^- \underline{\underline{G}}^*(x_i) \underline{\underline{\Delta}}^{-1} \underline{\underline{V}}(x_i) \underline{\underline{F}}^*(x_i) \underline{\underline{\alpha}}^+ = \underline{\underline{\alpha}}^- \underline{\underline{C}}^* \underline{\underline{\alpha}}^+ \\
 \underline{\underline{D}} &= 2m \underline{\underline{\alpha}}^+ \underline{\underline{F}}^*(x_i) \underline{\underline{\Delta}}^{-1} \underline{\underline{V}}(x_i) \underline{\underline{G}}^*(x_i) \underline{\underline{\alpha}}^- = \underline{\underline{\alpha}}^+ \underline{\underline{D}}^* \underline{\underline{\alpha}}^- \\
 \underline{\underline{E}} &= 2m \underline{\underline{\alpha}}^+ \underline{\underline{F}}^*(x_i) \underline{\underline{\Delta}}^{-1} \underline{\underline{V}}(x_i) \underline{\underline{F}}^*(x_i) \underline{\underline{\alpha}}^+ = \underline{\underline{\alpha}}^+ \underline{\underline{E}}^* \underline{\underline{\alpha}}^+
 \end{aligned} \tag{4.6}$$

at the first quadrature point. Substituting (4.6)

into the equation for the  $\underline{K}$  matrix (3.16) we obtain

$$\begin{aligned} \underline{K}_1 = & (\underline{I} - \omega_1 \underline{\alpha}^+ \underline{D}^* \underline{\alpha}^- + \underline{W} \underline{\alpha}^+ \underline{D}^* \underline{\alpha}^-) (\underline{I} - \omega_1 \underline{K}_0 \underline{\alpha}^- \underline{B}^* \underline{\alpha}^- \\ & + \underline{W} \underline{\alpha}^+ \underline{D}^* \underline{\alpha}^-)^{-1} (\underline{K}_0 + \underline{W} \underline{\alpha}^+ \underline{E}^* \underline{\alpha}^+ - \omega_1 \underline{K}_0 \underline{\alpha}^- \underline{C}^* \underline{\alpha}^+ \\ & + \omega_1 \underline{\alpha}^+ \underline{E}^* \underline{\alpha}^+ - \underline{W} \underline{\alpha}^+ \underline{E}^* \underline{\alpha}^+ \end{aligned} \quad (4.7)$$

where  $\underline{K}_0$  is the initial input value of the  $\underline{K}$  matrix, at the point  $x_0 = x_1 - \Delta x$ .

$$\begin{aligned} (\underline{K}_0)_{nI} &= \delta_{nI} \tan(k_n x_0) && \text{open channels} \\ &= \delta_{nI} \exp(2|k_n| x_0) && \text{closed channels} \end{aligned}$$

Rearranging (4.7) and noting that

$$(\underline{\alpha}^+)^{-1} = \underline{\alpha}^- ; (\underline{\alpha}^-)^{-1} = \underline{\alpha}^+ ; \underline{\alpha}^+ \underline{\alpha}^- = \underline{I}$$

and that  $\underline{\alpha}^-$ ,  $\underline{\alpha}^+$  and  $\underline{W}$  commute, yields

$$\begin{aligned} \underline{\alpha}^- \underline{K}_1 \underline{\alpha}^- = & (\underline{I} - \omega_1 \underline{D}^* + \underline{W} \underline{D}^*) (\underline{I} - \omega_1 \underline{\alpha}^- \underline{K}_0 \underline{\alpha}^- \underline{B}^* \\ & + \underline{W} \underline{D}^*)^{-1} (\underline{\alpha}^- \underline{K}_0 \underline{\alpha}^- + \underline{W} \underline{E}^* - \omega_1 \underline{\alpha}^- \underline{K}_0 \underline{\alpha}^- \underline{C}^*) \\ & + \omega_1 \underline{E}^* - \underline{W} \underline{E}^* \end{aligned} \quad (4.8)$$

Thus the matrices  $\underline{B}^*$ ,  $\underline{C}^*$ ,  $\underline{D}^*$  and  $\underline{E}^*$ , which do not contain exponential terms in closed channels, may be used in place of  $\underline{B}$ ,  $\underline{C}$ ,  $\underline{D}$  and  $\underline{E}$  providing that  $(\underline{K}_0)_{nI}$  is replaced by

$$\begin{aligned}
 (\underline{\alpha}^- \underline{K}_0 \underline{\alpha}^-)_{nI} &= \delta_{nI} \tan(k_n x_0) && \text{open channels} \\
 &= \delta_{nI} && \text{closed channels}
 \end{aligned}$$

The matrix then calculated is  $\underline{\alpha}^- \underline{K}_1 \underline{\alpha}^-$  and not  $\underline{K}_1$ . Since  $(\underline{\alpha}^-)_{nI} = \delta_{nI}$  in open channels, pre- and post-multiplying by  $\underline{\alpha}^-$  will only effect the closed channel elements of  $\underline{K}_1$ . Since we only require the open-open elements of the  $\underline{K}$  matrix to calculate transition probabilities it will not be necessary to renormalise  $\underline{K}$  at the end of the calculation.

In an analogous way the closed channel elements of the  $\underline{F}^*$  and  $\underline{G}^*$  matrices may be normalised to  $\delta_{nI}$  during each cycle of  $\underline{K}$  matrix iteration by employing the matrices

$$\begin{aligned}
 (\underline{\delta}^\pm)_{nI} &= \delta_{nI} && \text{open channels} \\
 &= \delta_{nI} \exp(\pm |k_n| \Delta x) && \text{closed channels}
 \end{aligned}$$

where  $\Delta x$  is the step length. These matrices have the same multiplication, commutation and inversion properties as the  $\underline{\alpha}^\pm$  matrices.

This procedure not only eliminates the undesirable

exponential terms from the calculation, it also reduces the amount of computation required during each cycle.

#### 4.3 A Convergence Procedure for the $\underline{K}$ Matrix

The open-open channel elements of the  $\underline{K}$  matrix are slowly converging functions of  $x$ . A procedure for speeding the convergence of the  $\underline{K}$  matrix may be obtained from the  $\underline{K}$  matrix differential equation (3.17). Integrating from  $x$  to  $\infty$  gives

$$\underline{K}(\infty) - \underline{K}(x) = 2m \int_x^\infty (\underline{F} - \underline{K}(x') \underline{G}) \underline{k}^{-1} \underline{V}(x') (\underline{F} - \underline{G} \underline{K}(x')) dx' \quad (4.9)$$

If  $x$  is sufficiently large, then  $\underline{K}(x')$  may be approximated by  $\underline{K}(x)$  and the integral may be evaluated. Only the open-open channel elements of the matrices occurring in (4.9) were included since it is to be expected that for large enough  $x$  the closed channels will make negligible contribution to the open-open channels of  $\underline{K}(\infty)$ . The matrix  $\underline{K}(\infty)$  calculated in this manner converged significantly sooner than  $\underline{K}(x)$ . In practice it was found convenient to check for convergence about every 4 - 5 steps.

#### 4.4 The Interaction Potential and Matrix Elements

As mentioned in Chapter 1 we assume that the atom A is reflected by the repulsive core of the interaction potential,  $V_{AB}(z)$ . The most usual form adopted for

$V_{AB}(z)$  is (Rapp and Kassal, 1969)



$$V_{AB}(z) = V_0 \exp\{-\alpha(x-y)\} \quad (4.10)$$

where

$$\alpha = \frac{\gamma}{L} \left( \frac{\hbar}{\tilde{\mu} \omega_e} \right)^{\frac{1}{2}}$$

The parameter  $L$ , determining the 'steepness' of the interaction, may be obtained approximately by fitting (4.10) to the best available intermolecular potential determined from experimental data. The most usual value used, and that value chosen for all calculations described here, is 0.02nm.

Since the Schrödinger equation (1.4) is invariant under the transformation,

$$\begin{aligned} x &\rightarrow x + \delta \\ V_0 &\rightarrow V_0 \exp(\alpha \delta) \end{aligned}$$

where  $\delta$  is a constant, the transition probabilities are independent of  $V_0$ . However, the value chosen will determine the position of the first quadrature point  $x_1$ , and  $x_1$  must lie far enough into the classically inaccessible region to approximate the boundary condition (2.1b).

The Matrix elements

$$\begin{aligned} V_{nI}(x) &= \int_{-\infty}^{\infty} \phi_n(y) V_{AB}(z) \phi_I(y) \\ &= V_0 \exp(-\alpha x) U_{nI} \end{aligned}$$

may be evaluated analytically for both Morse and harmonic oscillator eigenfunctions  $\phi_j(y)$ .

For the harmonic oscillator, the eigenfunctions and Matrix elements, in the reduced units used here, are given by,

$$\phi_j(y) = (\pi^{\frac{1}{2}} 2^j j!)^{-\frac{1}{2}} H_j(y) \exp\left(-\frac{y^2}{2}\right)$$

$$U_{ij} = \left(\frac{i!}{j!}\right)^{\frac{1}{2}} \left(\frac{\alpha}{\sqrt{2}}\right)^{j-i} \exp\left(\frac{\alpha^2}{4}\right) \mathcal{L}_i^{j-i}\left(-\frac{\alpha^2}{2}\right)$$

respectively.

Similarly, for the Morse oscillator (Rosen, 1933)

$$\phi_j(y) = A_j \sqrt{s} W_{2D_e, 2D_e - \frac{1}{2} - j}(s)$$

where  $s = 4D_e \exp\left(-y/\sqrt{2D_e}\right)$

and  $A_j^2 = (4D_e - 1 - 2j) / (\sqrt{2D_e} j! \Gamma(4D_e - j))$

$$U_{ij} = (4D_e)^{\alpha\sqrt{2D_e}} \left(\frac{i! \Gamma(4D_e - i)}{j! \Gamma(4D_e - j)} (4D_e - 1 - 2i)(4D_e - 1 - 2j)\right)^{\frac{1}{2}} \\ \times \sum_{l=0}^i \frac{(-1)^{l+i-j} \Gamma(1 + \alpha\sqrt{2D_e} + i - l) \Gamma(4D_e - 1 - \alpha\sqrt{2D_e} - i - j + l)}{l! (i-l)! \Gamma(1 + \alpha\sqrt{2D_e} + i - j - l) \Gamma(4D_e - 2i + l)}$$

Here  $H_n(y)$  is the Hermite polynomial,  $\mathcal{L}_n^m(x)$  is the Associated Laguerre polynomial,  $W_{\kappa, \mu}(x)$  is the Whittaker function and  $\Gamma(x)$  is the Gamma function. (Abramowitz and Stegun, 1965).

#### 4.5 Computational Details

The programs used to evaluate the transition probabilities were checked by reproducing selected results of both Secrest and Johnson (1966), for the harmonic binding potential, and Hunding (1970), for the harmonic and Morse binding potentials. For the majority of the Secrest and Johnson results, agreement was found to three significant figures.

However, discrepancies of the order of a few per cent were noted for particularly large values of  $E$ , where 11 or 12 channels were required for convergence. Hunding did not explicitly specify the collision parameters

$(m, \alpha, D_e)$  employed, and agreement could only be obtained to within 10%. The programs used to evaluate the Morse and harmonic oscillator matrix elements were checked independently, by reproducing a table of matrix elements presented by Mies (1964a).

The transition probabilities calculated are believed to be accurate to about 1%. A sufficient condition for the step length,  $\Delta x$ , to give this degree of accuracy is  $\alpha \Delta x = 0.016$ . At certain energies, with  $m = 3.737$ , over 1500 points were required in the quadrature before the  $K$  matrix converged. However, less than 600 points were necessary for other values of  $m$  reported. It

was never necessary to include more than two closed channels, to obtain satisfactory convergence of the transition probabilities, and one was usually sufficient.

The initial quadrature point  $x_1$  was chosen to be  $10^{-8}$  and the value of  $V_0$  was adjusted by trial and error until  $x_1$  represented a point far enough into the classically inaccessible region. This condition was frequently checked, particularly for smaller values of  $m$ .

For each calculation an initial guess was made of the number of channels required. The calculation was then repeated including one additional channel. If the transition probabilities for the two calculations agreed to 3 significant figures, the results were accepted. If agreement was not found more channels were included until convergence was reached. It was never necessary to include more than 13 channels in any calculation.

The convergence of the  $\underline{K}$  matrix as a function of  $x$  was monitored by the program. Convergence was accepted if all open-open channel elements greater than  $10^{-9}$  had converged to better than one part in  $10^5$ .

The calculations were all performed using single precision arithmetic. Detailed balance was obeyed and probability was conserved.

The programs were run on the Elliot 4130 computer at Stirling University. Typical run times were of the order of 45 seconds for a 3 state solution up to 30 minutes for a 13 state solution.

#### 4.6 Other close coupling methods

In this section we give a brief summary of some of the more important close coupling methods that have been applied to similar atom-diatom molecule collisions.

##### a) Secrest and Johnson's $\tilde{R}$ Matrix Method

Secrest and Johnson (1966) used an  $\tilde{R}$  matrix approach to solve the collinear atom-harmonic oscillator problem. This method is based on the complex boundary conditions (1.5a) and (1.5b), using free particle wave functions of the form  $\exp(\pm ikx)$ .

It has been shown by the Escalator Inversion procedure, described in Chapter 3, that their method involves an extra, unnecessary, matrix inversion at each step of the quadrature.

Based on the Secrest and Johnson report (1966) an  $\tilde{R}$  matrix program was written. This was found to be 4-5 times slower than the  $\tilde{K}$  matrix method presented in this thesis. Since no normalisation of the closed channel free particle wave functions was specified, difficulties were encountered, due to machine overflow, when a large number of points were required in the quadrature.

Secrest and Johnson have also applied their method to the calculation of Inelastic Cross Sections for the Rotation excitation of  $H_2$  upon collision with  $He$ , in the rigid rotor approximation (Johnson and Secrest (1968)).

#### b) Homogeneous Integral Method

The "Homogeneous Integral" method has been developed by Sams and Kouri (1969). This method involves transforming the integral equation (2.4) into a Volterra equation of the second kind. One is then able to compute the amplitude density functions, and thus construct the  $\underline{K}$  matrix, without involving any matrix inversions throughout the quadrature.

Based on the Reports by Sams and Kouri (1969) a "Homogeneous Integral" program was written, using the real  $\underline{K}$  matrix, rather than the  $\underline{R}$  matrix approach. Tests have shown that the "Homogeneous Integral" method is approximately twice as fast as the  $\underline{K}$  matrix method presented in this thesis. This direct application of the Sams and Kouri method was found to be impracticable, even when only open-open channels were retained, due to rounding errors. Kouri (private communication) however, has pointed out that the

"Homogeneous Integral" method has been used successfully in several atom-rigid rotor calculations (Sams and Kouri, 1970; Hayes and Kouri, 1971a; 1971b). The method has been applied, in a modified form, to the atom-vibrating, rotating diatomic molecule collision problem, by Eastes and Secrest (1972).

### c) Gordon's Method

A close coupling method based on the piecewise approximation of the potential energy has been developed by Gordon (1969, 1971). In some interval  $(x, x + \Delta x)$  the potential energy is approximated by a polynomial, and the wavefunctions for these polynomial approximations are constructed analytically. By suitable matching of these wave functions at the boundaries between the intervals, the wave function for the entire range is constructed, subject to boundary conditions at the ends of the range.

Although no tests have been made using this method, computation times are probable comparable with the "Homogeneous Integral" method of Sams and Kouri. The Gordon method, however, has a distinct advantage in that much of the computational effort is independent of the total energy of the system. This information may be stored, and used for calculations on the same system at different energies, resulting

in a time saving of about an order of magnitude per calculation.

This method has been used in calculations by Hunding (1970).

Many other close coupling methods have been developed and applied to molecular problems in the last few years, for example Chan, Light and Lin (1968), Riley and Kuppermann (1968), Cheung and Wilson (1969), Gutschick, McKoy and Diestler (1970). These methods, however, have not been studied in any detail.



CHAPTER 5

RESULTS AND DISCUSSION

Transition probabilities,  $P_{I \rightarrow F}$ , for the transition from state I to state F, are presented in Tables 1 - 5 as a function of the total energy E (in units of  $\frac{1}{2} \hbar \omega_e$ ). The exact equivalent harmonic oscillator transition probabilities are shown directly below the Morse results. In most cases very small transition probabilities, less than  $10^{-11}$ , have not been included.

The five systems considered cover a wide range, from relatively light to heavy incident atoms and from shallow to deep molecular potential well depths. The parameters  $(m, \alpha, D_e)$  given by  $(0.006268, 0.1278, 75.525)$ ,  $(\frac{1}{3}, 0.314, 9.3)$ ,  $(\frac{1}{2}, 0.114, 40.81)$ ,  $(0.667, 0.314, 9.3)$  and  $(3.737, 0.5584, 14.652)$  approximately represent the collisions  $Br_2 + (H_2)$ ,  $H_2 + H$ ,  $N_2 + (N_2)$ ,  $H_2 + He$  and  $HBr + He$  (with Br representing atom C in Figure 1.) respectively. The parentheses around  $H_2$  and  $N_2$  indicate structureless incident particles of mass equivalent to a hydrogen and nitrogen molecule respectively.

The exact equivalent harmonic oscillator transition probabilities and several approximate

calculations are compared with the exact  $0 \rightarrow 1$  Morse transition probabilities in Figures 3 - 6. In Figure 7 the ratios of exact calculations of  $P_{0 \rightarrow 1}$  for a Morse oscillator to  $P_{0 \rightarrow 1}$  for a harmonic oscillator are shown as a function of  $D_e$  for several values of  $m$ . In Figures 8 and 9 a comparison between the Morse and harmonic potentials and their energy levels is shown for Morse well depths  $D_e = 9.3$  and  $40.81$  respectively.

### 5.1 A Comparison of the Exact Transition

#### Probabilities for the Morse and Harmonic Oscillators

A comparison between the exact and Morse and harmonic oscillator transition probabilities, in the region before the first maximum, shows that the Morse results are generally smaller than those of the equivalent harmonic oscillator, for transitions within the first few vibrational levels. However, for transitions among the higher vibrational levels and those involving large changes in the quantum number, the Morse results are larger than those of the harmonic oscillator. This may be accounted for by the significantly smaller energy separations between the higher vibrational states of the Morse oscillator (see Figures 8 and 9).

TABLE 1

 $m = 0.667, \alpha = 0.314, D_e = 9.3; H_2 + He.$ 

$P_{I \rightarrow F}$	0 - 1	1 - 2	0 - 2	0 - 3	1 - 3	2 - 3	0 - 4	1 - 4
E								
4	2.46(-4) 7.20(-4)							
6	7.31(-3) 2.95(-2)	1.25(-3) 1.42(-3)	2.30(-6) 1.07(-5)					
8	3.15(-2) 1.33(-1)	2.28(-2) 5.50(-2)	1.85(-4) 2.04(-3)	1.18(-7) 4.96(-7)	3.07(-5) 3.07(-5)	5.29(-3) 2.10(-3)		1.37(-11)
10	7.39(-2) 2.92(-1)	8.15(-2) 2.17(-1)	1.66(-3) 2.25(-2)	1.17(-5) 2.31(-4)	1.22(-3) 5.39(-3)	5.47(-2) 7.70(-2)	1.95(-8) 4.26(-8)	3.12(-6) 1.80(-6)
12	1.29(-1) 4.28(-1)	1.67(-1) 3.69(-1)	6.65(-3) 9.13(-2)	1.49(-4) 4.71(-3)	8.41(-3) 5.24(-2)	1.58(-1) 2.68(-1)	1.48(-6) 3.65(-5)	1.38(-4) 7.69(-4)
16	2.45(-1) 4.07(-1)	3.18(-1) 1.56(-1)	3.38(-2) 3.30(-1)	2.72(-3) 9.88(-2)	5.72(-2) 2.85(-1)	3.34(-1) 1.89(-1)	1.61(-4) 1.06(-2)	5.16(-3) 7.32(-2)

TABLE 1  
(continued)

$m = 0.667$ ,  $\alpha = 0.314$ ,  $D_e = 9.3$ ;  $H_2+He$

$\begin{array}{c} P \\ I \rightarrow F \\ E \end{array}$	2 - 4	3 - 4	0 - 5	1 - 5	2 - 5	3 - 5	4 - 5	5 - 6
8	4.68(-9)	3.51(-6)						
10	2.77(-4) 5.85(-5)	1.92(-2) 2.76(-3)		2.95(-10)	3.65(-8)	4.47(-6)	9.12(-4)	
12	5.64(-3) 9.55(-3)	1.17(-1) 9.59(-2)	4.95(-9) 5.45(-9)	7.01(-7) 1.84(-7)	4.56(-5) 4.11(-6)	1.98(-3) 9.28(-5)	5.97(-2) 3.40(-3)	1.30(-2)
16	6.39(-2) 2.21(-1)	3.32(-1) 3.04(-1)	7.44(-6) 3.31(-4)	3.24(-4) 4.04(-3)	5.77(-3) 2.58(-2)	5.76(-2) 1.09(-1)	3.17(-1) 3.12(-1)	2.84(-1) 1.27(-1)

(numbers in parenthesis indicate powers of 10)

TABLE 2

 $m = \frac{1}{3}, \alpha = 0.314, D_e = 9.3; H_2 + H.$ 

$\begin{array}{c} P \\ I \rightarrow F \\ E \end{array}$	0 - 1	1 - 2	0 - 2	0 - 3	1 - 3	2 - 3	0 - 4	1 - 4
4	8.59(-3) 1.09(-2)							
6	9.57(-2) 1.51(-1)	3.04(-2) 1.99(-2)	7.82(-4) 8.26(-4)					
8	2.49(-1) 3.91(-1)	2.11(-1) 2.27(-1)	1.79(-2) 3.44(-2)	2.05(-4) 1.26(-4)	5.63(-3) 2.05(-3)	8.39(-2) 2.75(-2)	8.02(-9)	3.73(-7)
10	3.80(-1) 5.16(-1)	3.71(-1) 3.91(-1)	7.95(-2) 1.73(-1)	5.56(-3) 1.01(-2)	6.95(-2) 7.00(-2)	3.23(-1) 2.66(-1)	1.03(-4) 2.80(-5)	2.32(-3) 3.76(-4)
12	4.31(-1) 4.32(-1)	3.26(-1) 2.04(-1)	1.79(-1) 3.63(-1)	3.22(-2) 8.02(-2)	2.01(-1) 2.52(-1)	3.15(-1) 3.10(-1)	2.57(-3) 3.51(-3)	3.22(-2) 2.49(-2)
	3.21(-1) 1.05(-1)	2.26(-2) 1.12(-1)	3.22(-1) 3.34(-1)	1.68(-1) 3.78(-1)	2.24(-1) 7.75(-2)	7.28(-4) 6.55(-2)	5.18(-2) 1.54(-1)	2.02(-1) 2.67(-1)

TABLE 2  
(continued)

$m = \frac{1}{3}$ ,  $\alpha = 0.314$ ,  $D_e = 9.3$ ;  $H_2 + H$ .

$P_{I \rightarrow F}$ E	2 - 4	3 - 4	0 - 5	1 - 5	2 - 5	3 - 5	4 - 5	5 - 6
8	1.22(-5)	5.25(-4)						
10	2.65(-2) 3.44(-3)	1.89(-1) 3.40(-2)	1.52(-7)	5.00(-6)	9.59(-5)	1.52(-3)	2.53(-2)	
12	1.64(-1) 9.95(-2)	3.49(-1) 2.85(-1)	8.00(-5) 7.86(-6)	1.58(-3) 9.47(-5)	1.53(-2) 7.20(-4)	9.04(-2) 4.90(-3)	3.18(-1) 3.97(-2)	1.42(-1)
16	1.71(-1) 1.43(-1)	2.06(-3) 1.75(-3)	1.02(-2) 2.01(-2)	7.34(-2) 8.49(-2)	1.95(-1) 1.83(-1)	1.73(-1) 2.42(-1)	1.25(-3) 1.63(-1)	2.77(-2) 2.93(-1)

(numbers in parenthesis indicate powers of 10)

TABLE 3

 $m = 3.737, \alpha = 0.5584, D_e = 14.652; \text{HBr} + \text{He} [B \equiv \bar{H}]$ 

$P_{I \rightarrow F}$ E	0 - 1	1 - 2	0 - 2	0 - 3	1 - 3	2 - 3	2 - 4	3 - 4
4	9.34(-7) 1.36(-6)							
6	1.20(-4) 2.48(-4)	4.29(-6) 2.15(-6)	3.36(-10) 2.18(-10)					
8	9.50(-4) 2.39(-3)	4.08(-4) 3.91(-4)	1.29(-7) 2.56(-7)		4.82(-9) 6.69(-10)	2.03(-5) 2.57(-6)		
10	3.22(-3) 9.38(-3)	3.08(-3) 3.88(-3)	2.67(-6) 9.61(-6)	1.96(-9) 6.79(-10)	1.14(-6) 5.11(-7)	1.30(-3) 4.57(-4)	4.64(-8) 1.53(-9)	1.22(-4) 2.76(-6)
12	7.35(-3) 2.40(-2)	1.03(-2) 1.57(-2)	1.95(-5) 9.90(-5)	4.40(-8) 6.47(-8)	2.32(-5) 1.97(-5)	8.83(-3) 4.68(-3)	9.99(-6) 6.70(-7)	4.48(-3) 4.68(-4)

(numbers in parenthesis indicate powers of 10)

TABLE 4

 $m = 0.006268$ ,  $\alpha = 0.1278$ ,  $D_e = 75.525$ ;  $\text{Br}_2 + (\text{H}_2)$ 

$P_{I \rightarrow F}$ E	0 - 1	1 - 2	0 - 2	0 - 3	1 - 3	2 - 3	0 - 4	1 - 4
4	1.23(-2)							
	1.22(-2)							
6	3.54(-2)	2.49(-2)	2.45(-4)					
	3.53(-2)	2.41(-2)	2.20(-4)					
8	5.79(-2)	6.91(-2)	1.13(-3)	6.42(-6)	7.57(-4)	3.80(-2)		
	5.77(-2)	6.81(-2)	1.06(-3)	4.39(-6)	6.46(-4)	3.54(-2)		
10	7.94(-2)	1.10(-1)	2.56(-3)	3.82(-5)	3.37(-3)	1.01(-1)	2.10(-7)	2.70(-5)
	7.92(-2)	1.09(-1)	2.44(-3)	2.99(-5)	3.08(-3)	9.86(-2)	9.27(-8)	1.72(-5)
12	9.99(-2)	1.47(-1)	4.49(-3)	1.07(-4)	7.45(-3)	1.56(-1)	1.44(-6)	1.54(-4)
	9.97(-2)	1.46(-1)	4.31(-3)	8.88(-5)	6.98(-3)	1.54(-1)	8.17(-7)	1.16(-4)
16	1.38(-1)	2.09(-1)	9.68(-3)	4.01(-4)	1.93(-2)	2.41(-1)	1.11(-5)	8.71(-4)
	1.38(-1)	2.08(-1)	9.39(-3)	3.52(-4)	1.84(-2)	2.39(-1)	7.72(-6)	7.30(-4)
20	1.72(-1)	2.57(-1)	1.64(-2)	9.63(-4)	3.47(-2)	2.97(-1)	3.98(-5)	2.42(-3)
	1.72(-1)	2.56(-1)	1.60(-2)	8.70(-4)	3.35(-2)	2.95(-1)	3.03(-5)	2.12(-3)



TABLE 4  
(continued)

$$m = 0.006268, \alpha = 0.1278, D_e = 75.525; \text{Br}_2 + (\text{H}_2)$$

$\begin{matrix} P \\ I \rightarrow F \\ E \end{matrix}$	2 - 4	3 - 4	0 - 5	1 - 5	2 - 5	3 - 5	4 - 5	5 - 6
10	1.58(-3) 1.27(-3)	5.21(-2) 4.64(-2)						
12	6.72(-3) 5.98(-3)	1.32(-1) 1.27(-1)	8.83(-9) 2.00(-9)	1.12(-6) 4.51(-7)	7.19(-5) 4.22(-5)	2.78(-3) 2.07(-3)	6.75(-2) 5.70(-2)	
16	2.44(-2) 2.28(-2)	2.48(-1) 2.44(-1)	2.18(-7) 9.56(-8)	2.32(-5) 1.43(-5)	1.05(-3) 8.17(-4)	2.35(-2) 2.11(-2)	2.33(-1) 2.26(-1)	1.91(-1) 1.77(-1)
20	4.86(-2) 4.63(-2)	3.13(-1) 3.11(-1)	1.26(-6) 6.91(-7)	1.08(-4) 7.66(-5)	3.65(-3) 3.08(-3)	5.57(-2) 5.20(-2)	3.17(-1) 3.14(-1)	3.10(-1) 3.05(-1)

(numbers in parenthesis indicate powers of 10)

TABLE 5

 $m = 0.5, \alpha = 0.114, D_e = 40.81; N_2 + (N_2)$ 

$P_{I \rightarrow F}$ E	0 - 1	1 - 2	0 - 2	0 - 3	1 - 3	2 - 3	3 - 4
4	7.66(-11) 2.67(-10)						
6	4.52(-7) 1.93(-6)	2.86(-10) 5.34(-10)					
8	1.69(-5) 7.61(-5)	1.22(-6) 3.86(-6)	5.15(-12) 7.35(-11)			9.35(-10) 8.01(-10)	
10	1.43(-4) 6.60(-4)	4.17(-5) 1.52(-4)	1.49(-9) 2.51(-8)		2.72(-11) 2.20(-10)	2.61(-6) 5.79(-6)	3.04(-9) 1.07(-9)
12	6.10(-4) 2.85(-3)	3.38(-4) 1.32(-3)	5.16(-8) 9.42(-7)	4.59(-13) 2.39(-11)	6.74(-9) 7.53(-8)	7.97(-5) 2.28(-4)	5.20(-6) 7.72(-6)
16	4.10(-3) 1.92(-2)	4.03(-3) 1.66(-2)	4.15(-6) 8.11(-5)	1.14(-9) 7.74(-8)	2.49(-6) 3.57(-5)	2.46(-3) 8.48(-3)	1.00(-3) 2.63(-3)
20	1.40(-2) 6.39(-2)	1.76(-2) 7.14(-2)	6.26(-5) 1.24(-3)	1.08(-7) 8.08(-6)	6.87(-5) 1.07(-3)	1.53(-2) 5.50(-2)	1.06(-2) 3.24(-2)

TABLE 5  
 (continued)  
 $m = 0.5, \alpha = 0.114, D_e = 40.81; N_2 + (N_2)$

$P_{I \rightarrow F}$ E.	1 - 4	2 - 4	2 - 5	3 - 5	4 - 5	5 - 6
12		1.04(-10) 4.41(-10)			1.01(-8) 1.34(-9)	
16	2.78(-10) 1.05(-8)	6.18(-7) 5.62(-6)	1.62(-11) 2.38(-10)	5.83(-8) 2.51(-7)	2.33(-4) 3.80(-4)	1.95(-5) 1.16(-5)
20	8.20(-8) 4.04(-6)	4.12(-5) 4.74(-4)	2.68(-8) 7.59(-7)	1.55(-5) 1.17(-4)	5.80(-3) 1.40(-2)	2.37(-3) 3.93(-3)

(numbers in parenthesis indicate powers of 10)

CAPTIONS TO FIGURES 3 - 7FIGURES 3 - 6

The ratios of approximate and exact harmonic to exact Morse transition probabilities are shown, for the  $0 \rightarrow 1$  transition, as a function of the total energy of the system  $E$  (in units of  $\frac{1}{2} \hbar \omega_e$ ).

--- (B) - First Order Distorted Wave Approximation (5.1) for the Morse oscillator.

----- (C) - First Order Distorted Wave Approximation (5.1) for the harmonic oscillator.

— . — . — . — (D) - Revised First Order Distorted Wave Approximation (5.2) for the Morse oscillator.

— — — — — (E) - Revised First Order Distorted Wave Approximation (5.2) for the harmonic oscillator.

— — — — — (A) - The exact quantum mechanical result for the harmonic oscillator.

..... (F) - The semi-classical approximation of Morse and La Brecque (1971).

FIGURE 3  $m = 0.667$ ,  $\alpha = 0.314$ ,  $D_e = 9.3$ ,  
approximating an  $H_2 + He$  collision.

FIGURE 4  $m = \frac{1}{3}$ ,  $\alpha = 0.314$ ,  $D_e = 9.3$ ,  
approximating an  $H_2 + H$  collision.

FIGURE 5  $m = 3.737$ ,  $\alpha = 0.5584$ ,  $D_e = 14.652$ ,  
approximating an  $HBr + He$  collision ( $H \equiv B$ ).

FIGURE 6  $m = 0.5$ ,  $\alpha = 0.114$ ,  $D_e = 40.81$ ,  
approximating an  $N_2 + (N_2)$  collision.

FIGURE 7

The ratio of  $P_{0 \rightarrow 1}$  (exact Morse) to  $P_{0 \rightarrow 1}$  (exact harmonic) as a function of the reduced well depth  $D_e$  for several values of  $m$ . The total energy  $E$  is 4 and  $\alpha = 0.2$ .

FIGURES 8, 9

A comparison between the Morse and harmonic potentials and their energy levels is shown for the molecules  $H_2$  ( $D_e = 9.3$ , Fig.8) and  $N_2$  ( $D_e = 40.81$ , Fig.9). M and H indicate the Morse and harmonic energy levels respectively.

Figure 3

$m = 0.667, \alpha = 0.314, D_e = 9.3$

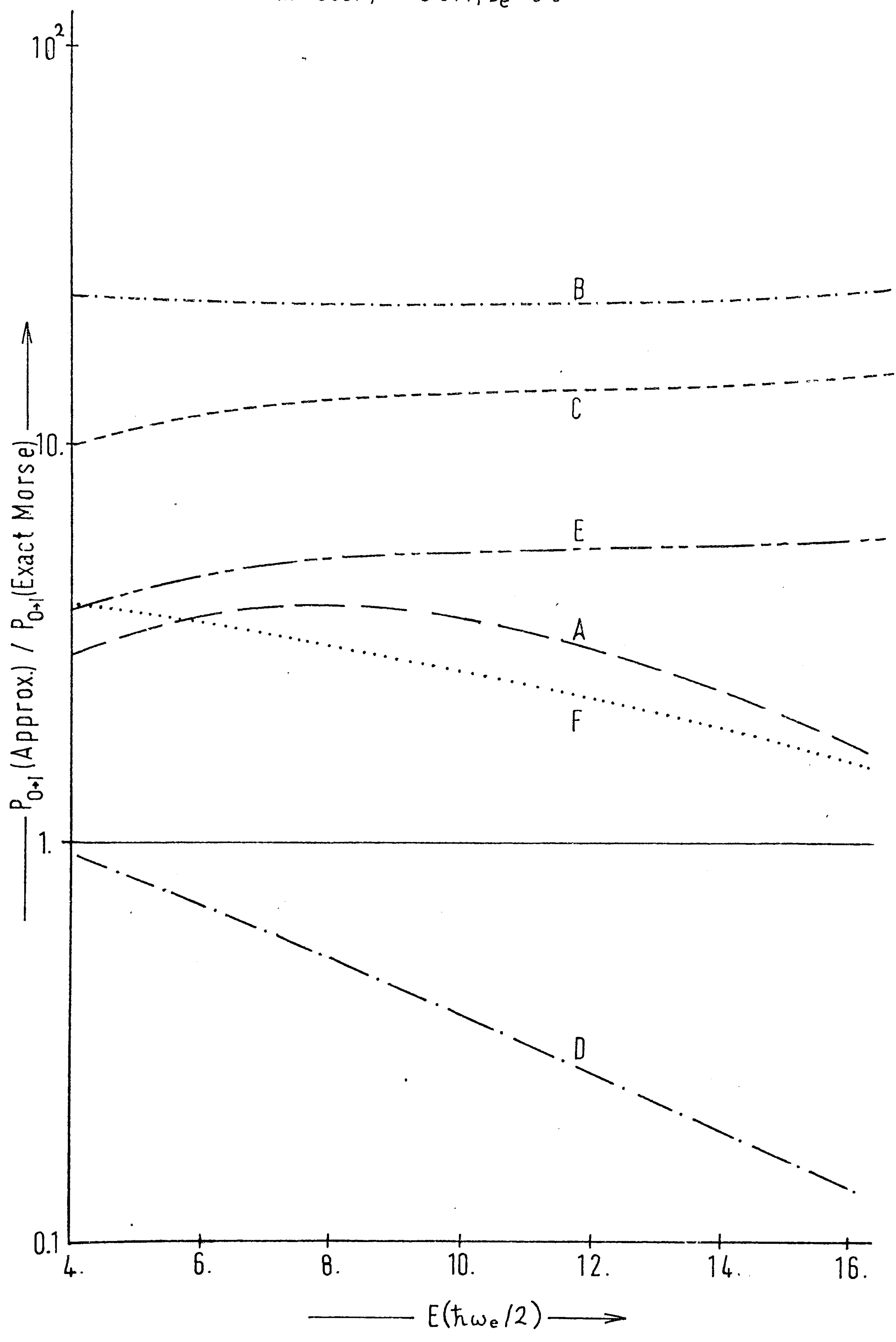


Figure 4

$m=1/3, \alpha=0.314, D_e=9.3$

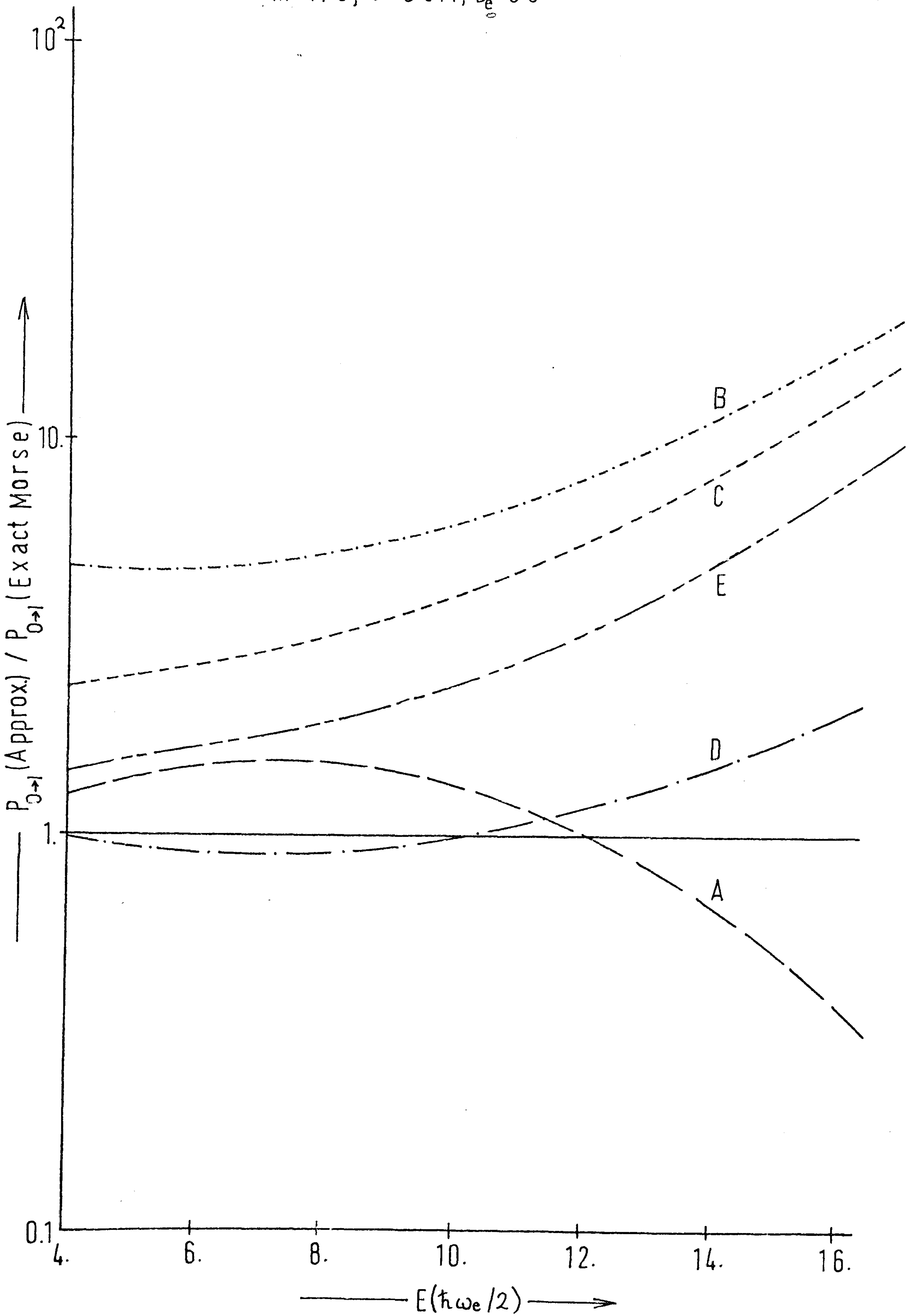


Figure 5

$m = 3.737, \alpha = 0.5584, D_e = 14.652$

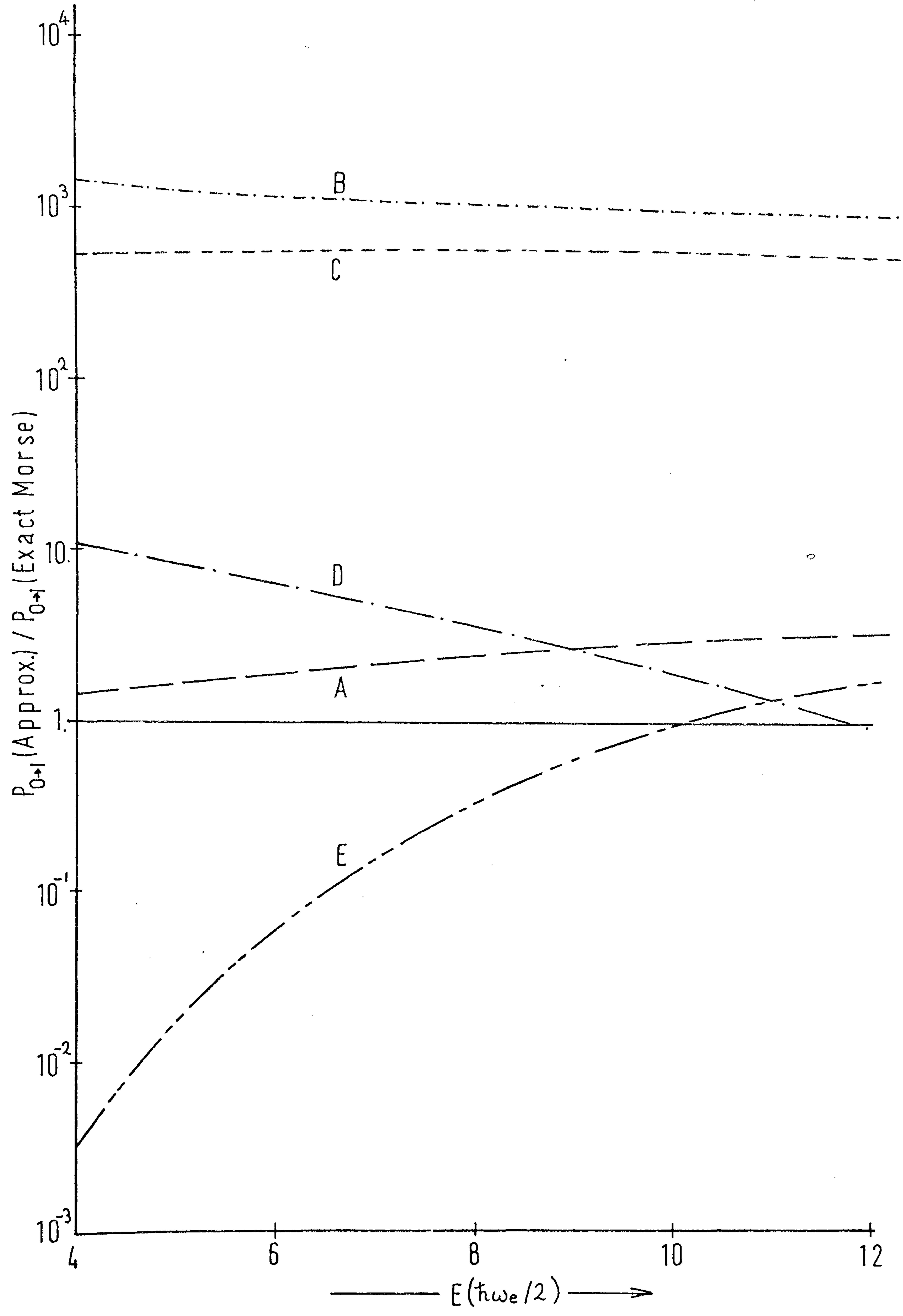




Figure 6  
 $m = 0.5, \alpha = 0.114, D_e = 40.81$

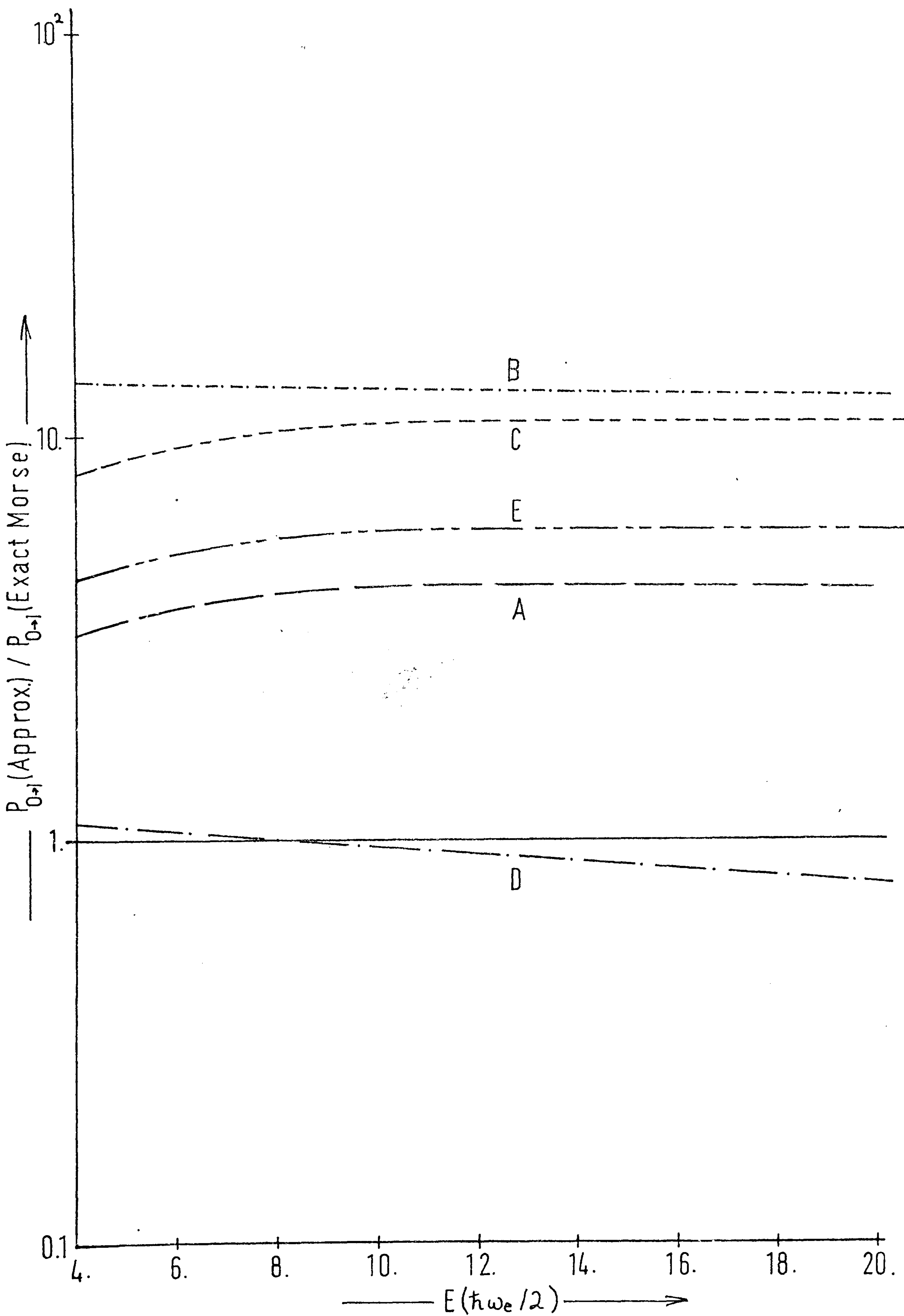


Figure 7

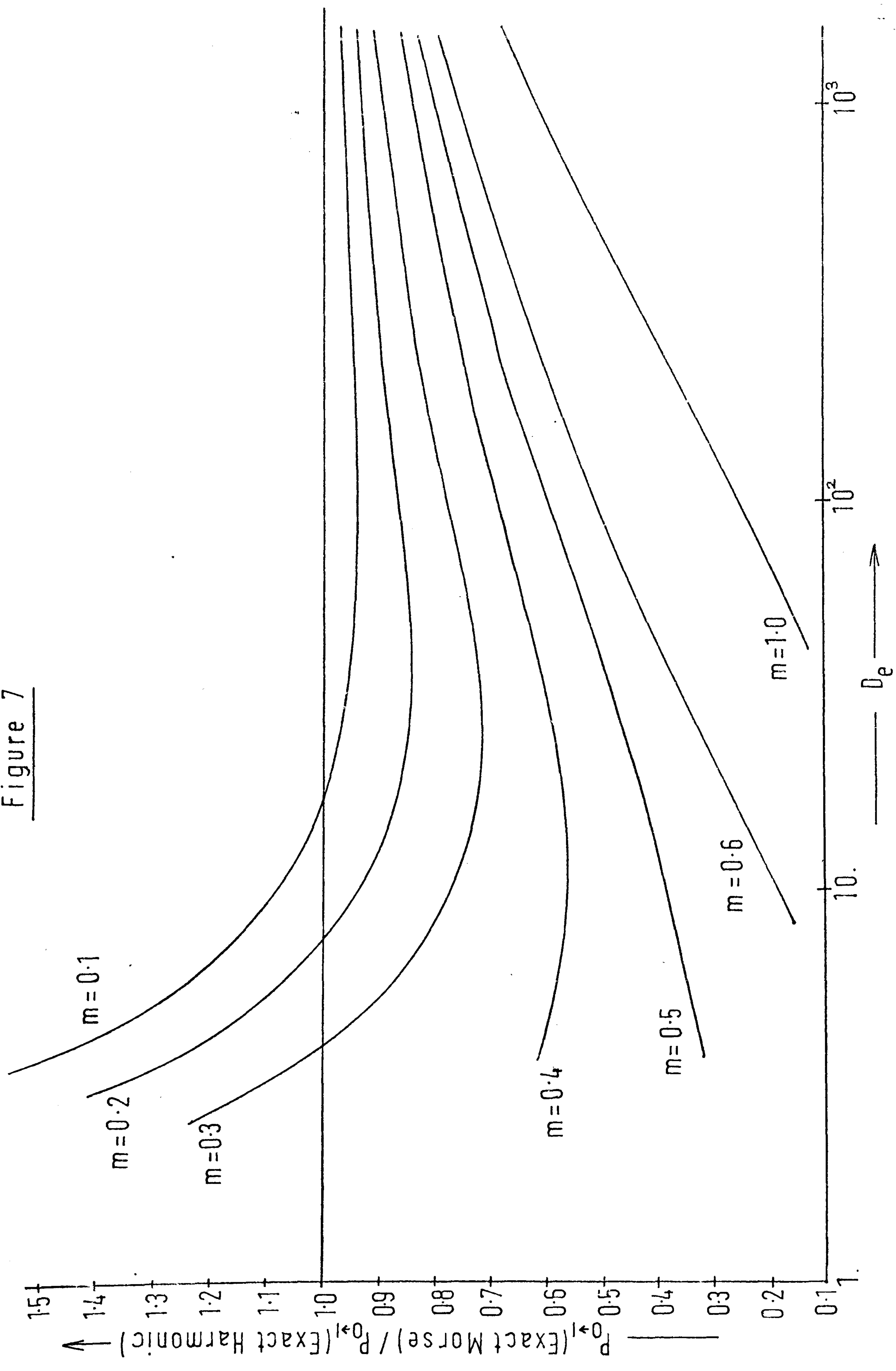


Figure 8

$D_e = 9.3$

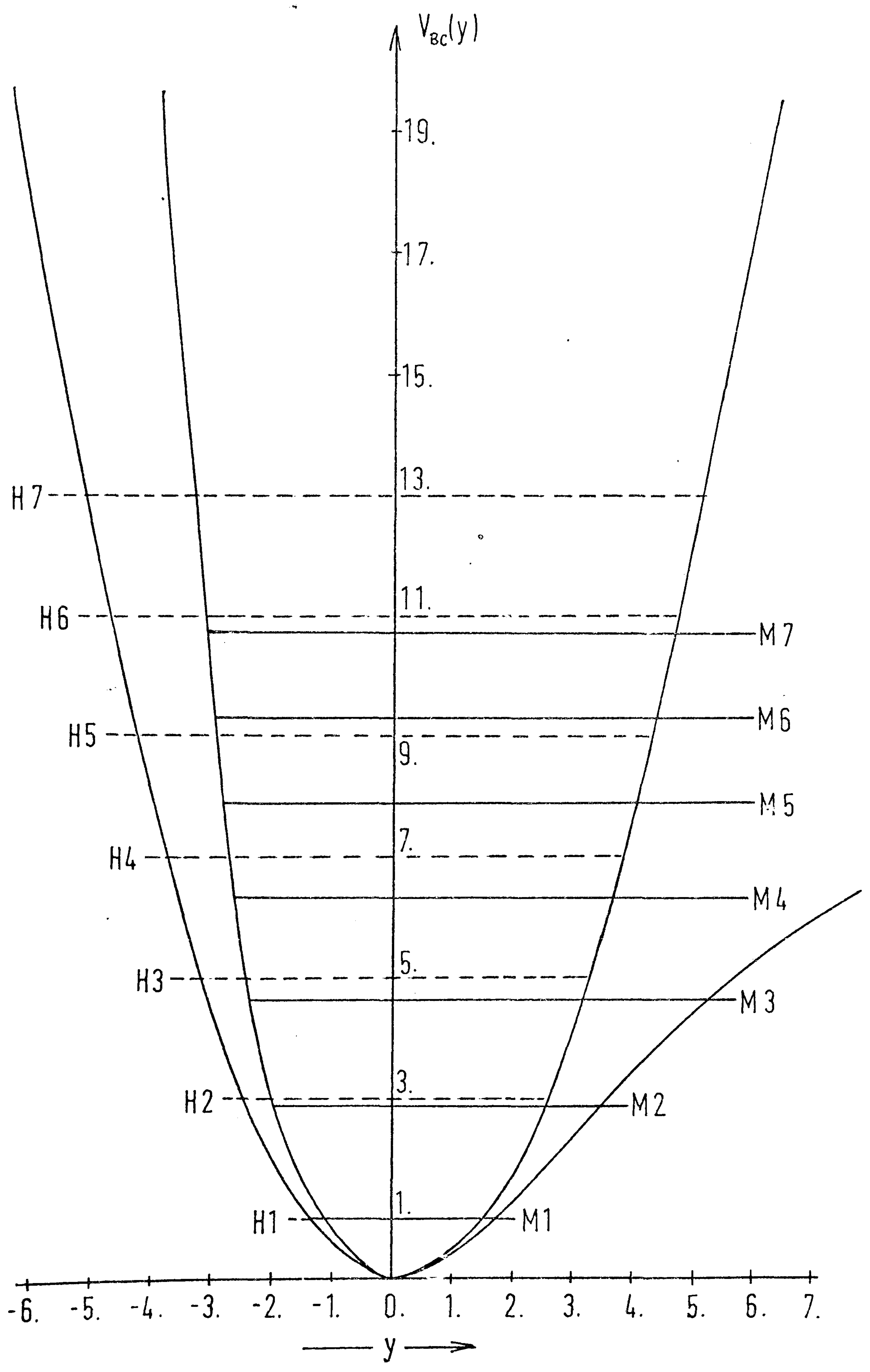
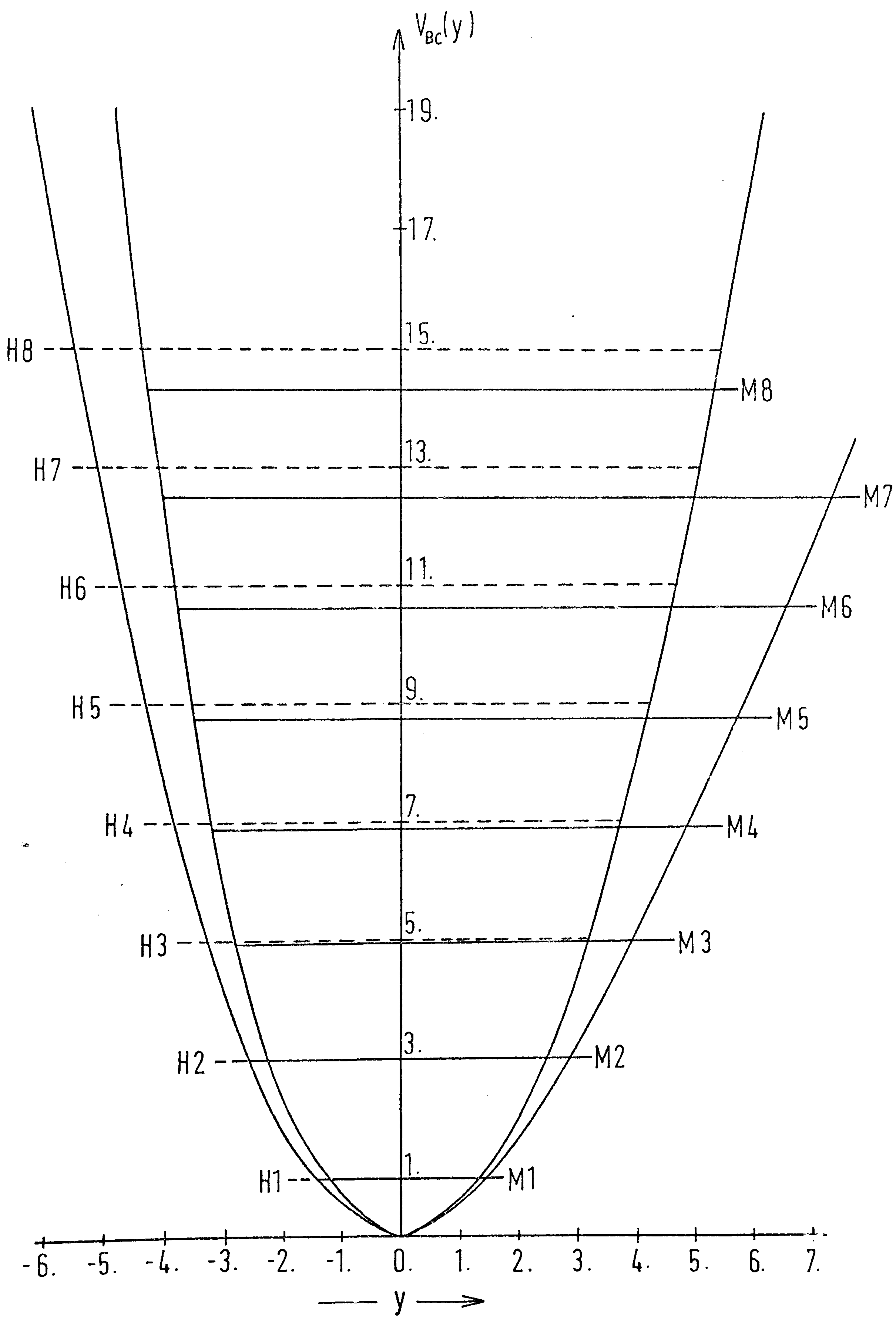


Figure 9

$D_e = 40.81$



Except for small values of  $D_e$ , the discrepancy between the two oscillators is less for smaller values of  $m$ . This is shown in Figure 7 for the  $0 \rightarrow 1$  transition and may also be seen from Table 4 for  $m = 0.006268$ . For larger values of  $D_e$  the agreement between the two oscillators is closer, although for large values of  $m$  the difference may still be significant. In the region  $D_e > 400$  for  $\alpha = 0.2$  the discrepancy between the  $0 \rightarrow 1$  transition probabilities for the two oscillators may be of the order of 50%, for large  $m$ , although the  $U_{00}$ ,  $U_{11}$  or  $|U_{01}|$  Morse and harmonic matrix elements agree to within 1%. Thus slight anharmonicities can cause comparatively large changes in the transition probability.

The curves shown in Figure 7 are relatively insensitive to the value of the total energy  $E$ , in the region before the first maximum of the transition probability. However, the disagreement between the two oscillators becomes more pronounced for smaller values of  $\alpha$ .

The number of bound states of the Morse oscillator is approximately  $2D_e$ . Since most diatomic molecules have fewer than 100 bound states, anharmonicity will nearly always be important.

## 5.2 The First Order Distorted Wave Approximation (FODWA)

The first order distorted wave approximation was initially applied to this problem by Jackson and Mott (1932). For the interaction potential (4.10), their result becomes,

$$P_{0 \rightarrow 1}^{\text{FODWA}} = \sinh(\pi q_1) \sinh(\pi q_0) \left( \frac{\frac{1}{2} |U_{01}| \pi (q_1^2 - q_0^2)^2}{\cosh(\pi q_1) - \cosh(\pi q_0)} \right)^2 \quad (5.1)$$

where  $q_i = 2k_i/\alpha$ .

As shown in Figures 3-6 (curves B(Morse) and C (Harmonic)),  $P_{0 \rightarrow 1}^{\text{FODWA}}$  may be several orders of magnitude too large. It is however, a valid approximation for very small values of  $m$ .

For  $m = 0.006268$ , in the range  $E = 4.0$  to  $20.0$ ,  $P_{0 \rightarrow 1}^{\text{FODWA}}$  was accurate to within 27% for both the Morse and harmonic oscillators.

It was noted by Secrest and Johnson (1966) that the ratio  $P_{0 \rightarrow 1}^{\text{FODWA}} / P_{0 \rightarrow 1}^{\text{EXACT}}$ , for the harmonic oscillator, was approximately constant over a large range of energies  $E$ . This ratio is also seen to be nearly constant for the Morse oscillator, in the region before the first maximum in the transition probability.

The FODWA transition probabilities for the Morse oscillator,  $P_{0 \rightarrow 1}^{\text{FODWA}}$  (Morse) are generally larger

than  $\overline{P}_{0 \rightarrow 1}^{\text{FODWA}}$  (harmonic) although the exact Morse transition probabilities are usually less than those of the equivalent harmonic oscillator.

### 5.3 The Revised First Order Distorted Wave Approximation (RFODWA).

Equation (5.1) was derived assuming that the ratio of the diagonal matrix elements,  $\lambda^2 (= U_{00}/U_{11}) = 1$ . For the interaction potential given by (4.10) this is not strictly correct. With  $(\alpha, D_e)$  given by (0.1278, 75.525) and (0.5584, 14.652),  $\lambda^2$  is 0.976 and 0.737 respectively for the Morse oscillator and 0.992 and 0.865 respectively for the harmonic oscillator. Taking into account the true value of  $\lambda^2$ , Mies (1964a) has shown that the correct distorted wave result (RFODWA) (curves D(Morse) and E(harmonic)), is

$$\overline{P}_{0 \rightarrow 1}^{\text{RFODWA}} = A(E, \lambda) \overline{P}_{0 \rightarrow 1}^{\text{FODWA}} \quad (5.2)$$

where,

$$A(E, \lambda) = U_{11}^{-2} \left| {}_2F_1 \left( 1 + \frac{1}{2}i(q_0 + q_1), 1 + \frac{1}{2}i(q_0 - q_1), 2; 1 - \lambda^2 \right) \right|^2$$

and  ${}_2F_1(a, b, c; x)$  is a hypergeometric function. (Abramowitz and Stegun, 1965).

In all cases considered the RFODWA gives more accurate results than the FODWA. The correction

factor  $A(E,\lambda)$  reduces the large discrepancy between the FODWA and the exact results for intermediate values of  $m$ . In the region before the first maximum of the transition probability, for  $m = \frac{1}{3}$  and  $m = 0.5$ ,  $P_{0 \rightarrow 1}^{\text{RFODWA}}$  is a good approximation for both the Morse and harmonic oscillators, although slightly better for the former. For  $m = 0.006268$  in the energy range  $E = 4.0$  to  $20.0$ ,  $P_{0 \rightarrow 1}^{\text{RFODWA}}$  was accurate to within 20% for both oscillators. The RFODWA, however, breaks down for large values of  $m$ . This may be seen from Figure 5 where the discrepancy between the exact results and  $P_{0 \rightarrow 1}^{\text{RFODWA}}$  may be several orders of magnitude in the low energy region.

The agreement between the exact results and both the FODWA and the RFODWA is relatively insensitive to the initial state of the oscillator.

#### 5.4 First Order Perturbation Theory Approximations

Mies (1964b) obtained a correction factor, similar to  $A(E,\lambda)$ , for the time dependent first order perturbation theory approximation (FOPA and RFOPA). In his calculation Mies (1964b) used a symmetrized form for the translational energy of atom A (Figure 1) i.e. an arithmetic average of the incident and scattered kinetic energy of A. In this work more accurate results were obtained



using a symmetrized form for the velocity i.e.

$$\bar{v} = \frac{1}{2} (v_0 + v_1).$$

The results thus obtained differed from the corresponding FODWA and RFODWA by not more than a few per cent for all collisions considered in Tables 1-5.

### 5.5 Semi-Classical Impulse Approximation

Morse and La Brecque (1971) have extended the semi-classical impulse or ITFITS approximation of Heidrich et al (1971), to the Morse binding potential. The Morse and La Brecque (ML) (curve F) approximate  $0 \rightarrow 1$  transition probabilities are compared with the exact Morse results for the case  $m = 0.667$ ,  $\alpha = 0.314$ ,  $D_e = 9.3$  in Figure 3. The ML approximation does not appear to predict the discrepancy between the Morse and harmonic oscillators and the ML results for other low order transitions e.g.  $0 \rightarrow 2$ ,  $1 \rightarrow 2$  have a similar behaviour. It was found impossible, however, to reproduce the results of Morse and La Brecque and a note on their paper is given in Appendix C.

### 5.6 Conclusions

In the incident energy region before the first maximum of the transition probability the Morse results are generally smaller than those of the equivalent harmonic oscillator, for transitions within the first few vibrational levels. However,

for transitions where the energy separation between the initial and final states is significantly less for the Morse oscillator, the Morse transition probabilities exceed those of the harmonic oscillator. The discrepancy between the transition probabilities is strongly dependent on the values of  $m$  and  $\alpha$ , increasing as  $m$  becomes large and decreasing as  $\alpha$  becomes large. Large values of  $D_e$ , corresponding to deep Morse well depths, do not necessarily imply agreement between the transition probabilities of the two oscillators. Slight anharmonicities can cause relatively large changes in the transition probability.

None of the approximate theories, for the excitation of a Morse oscillator gives consistently accurate transition probabilities for all values of  $m, \alpha, D_e$  and  $E$  considered. However, the RFODWA of Mies (1964a) and consequently the RFOPA (Mies 1964b), using a symmetrised velocity, are valid approximations for small and intermediate values of  $m$ , in the region before the first maximum in the transition probability.

The extension, to the Morse oscillator, of the Heidrich et al (1971) semi-classical impulse approximation, by Morse and La Brecque (1971) appears to over estimate the transition probabilities, although, for reasons discussed

previously, only the case  $m = 0.667$ ,  $\alpha = 0.314$ ,  
 $De = 9.3$  has been considered.

## CHAPTER 6

### CORRESPONDENCE PRINCIPLE METHOD

#### 6.1 Introduction

In this and subsequent chapters, we concentrate on one particular semi-classical theory which may be applied to the collinear atom-diatom problem, that is the Correspondence Principle for Strongly Coupled States.

This theory was derived by Percival and Richards (1970a) and has been used by them to obtain cross sections for the excitation of highly excited hydrogenic atoms by electrons and protons (Percival and Richards, 1970b; 1971).

The validity of this theory, when applied to the collinear atom-diatom collision, has been investigated by Clark and Dickinson (1971) and Clark (1971). The results of this investigation may be summarised as follows:-

(a) When applied to the problem of a one dimensional harmonic oscillator forced by a time dependent potential of the form  $qF(t)$ , where  $q$  is the classical position coordinate of the oscillator, the agreement between the exact quantum mechanical solution (Kerner, 1958; Treanor, 1965), and the correspondence principle solution

is excellent, even for transitions from the ground state of the oscillator.

The correspondence principle solution, however, does break down for very strong perturbations of the oscillator. The validity of the correspondence principle increases as the quantity  $|s|/n$  decreases where  $n$  is the initial quantum number of the oscillator, and  $s$  is the change in quantum number due to the perturbation.

A numerical solution of the time dependent quantum mechanical coupled differential equations for the problem showed that for a  $0 \rightarrow 1$  transition, the correspondence principle solution had the same range of validity as an 8-state solution. For the  $5 \rightarrow 6$  transition, however, the correspondence principle solution was more accurate than a 16-state solution.

(b) For a one dimensional harmonic oscillator perturbed by a time dependent potential of the form  $q^2 F(t)$ , it was shown, by analytic arguments, that there should be close agreement between the exact quantum mechanical solution (Popov and Perelemov, 1969) and the correspondence principle solution. The agreement, however, implicitly depends on the validity of first order time dependent perturbation theory. This

problem is discussed with reference to a specific forcing function in Chapter 7 of this thesis.

(c) With the interaction potential (4.10) and a harmonic molecular binding potential, it was demonstrated that on using the impulse approximation (Mahan, 1970; Heidrich et al, 1971) to derive the time dependent potential acting on the oscillator, the correspondence principle results were in excellent agreement with the exact quantum mechanical results of Secrest and Johnson (1966). In the Impulse approximation the collinear atom-diatom problem reduces to that of an oscillator forced by a potential of the form  $q F(t)$ .

(d) The correspondence principle appeared to break down when applied to the atom-diatom collision in which the Morse binding potential was employed. However, due to the limited number of exact quantum mechanical results (Hunding, 1970) available at that time, no definite conclusions could be drawn. Several approximate procedures for reducing the atom-diatom problem to that of an oscillator perturbed by a time dependent potential were investigated. In all cases the correspondence principle results were in error by up to an order of magnitude.

With the development of a comprehensive set of transition probabilities for the atom-Morse oscillator collision, described in the earlier chapters of this thesis, a detailed investigation of the correspondence principle solutions is possible. A discussion of this investigation however, will be postponed until Chapter 8.

The behaviour of the correspondence principle solutions closely resembles that of the FODWA (5.2) and consequently the FOPA (5.4), particularly at low collision energies.

In the one-dimensional form of the correspondence principle the interaction potential is assumed to be  $V(q,t)$ , where  $q$  and  $t$  are the position co-ordinate of the bound particle and time respectively.

An implicit assumption made in deriving the correspondence principle is that the matrix elements  $\langle n+s | V(q,t) | n \rangle$  are independent of the quantum number  $n$  and depend only on  $s$ , the difference between the quantum numbers of the final and initial states of the system. (Richards, 1972). This essentially implies that throughout the interaction the perturbation of the energy of the bound particle is independent of the state of the

system. However, using time dependent perturbation theory, Bates (1961) has pointed out that difficulties may be encountered in obtaining a satisfactory approximation to the transition amplitude if the difference between the perturbed energies of the states of the bound system are not taken into account. This is the procedure followed by Mies (1964a, 1964b) to obtain the RFOPA (section 5.4), and implicitly the RFODWA (section 5.3), approximations.

As shown in Chapter 5, the RFODWA and RFOPA results are in much better agreement with the exact close coupling results than the FODWA and FOFA results.

In Section 6.2 we show how the perturbation of the energy levels may be included approximately, in the correspondence principle. The resulting expression differs from that of Percival and Richards (1970a) in that it includes a term taking into account the perturbation of the bound particle orbit. This correction factor will be significant only when the diagonal matrix elements  $\langle n | V(q,t) | n \rangle$  of the interaction potential depend on the quantum number  $n$ .

This modified version of the correspondence principle may be applied to any problem for



which the one dimensional form of the Percival and Richards (1970a) result is applicable.

## 6.2 The Modified Correspondence Principle

We consider a one dimensional system with hamiltonian of the form

$$H = H_0 + V(q,t)$$

where

$$H_0 |n\rangle = \epsilon_n |n\rangle ,$$

$H_0$  being the hamiltonian of the unperturbed system, with energy eigenvalues  $\epsilon_n$  .

The time dependent transition amplitudes

$S(m,n;t)$  for this system satisfy (Bates, 1961)

$$i\hbar \frac{\partial}{\partial t} S(m,n;t) = \sum_{k=0}^{\infty} S(k,n;t) \langle m|V(q,t)|k\rangle \exp\left(\frac{i}{\hbar}(\epsilon_m - \epsilon_k)t\right) \quad (6.1)$$

following Bates (1961) we write

$$S'(i,j;t) = S(i,j;t) \exp\left(\frac{i}{\hbar} \int_{-\infty}^t \langle i|V(q,t')|i\rangle dt'\right)$$

The diagonal matrix elements  $\langle m|V(q,t)|m\rangle$

may now be eliminated explicitly from the summation in (6.1) giving

$$i\hbar \frac{\partial}{\partial t} S'(m,n;t) = \sum_{\substack{k=0 \\ (k \neq m)}}^{\infty} S'(k,n;t) \langle m|V(q,t)|k\rangle \times \exp\left(\frac{i}{\hbar} \{(\epsilon_m - \epsilon_k)t + \phi(m,k;t)\}\right) \quad (6.2)$$

where

$$\phi(i,j;t) = \int_{-\infty}^t (\langle i|V(q,t')|i\rangle - \langle j|V(q,t')|j\rangle) dt'$$

The term  $\phi(m, k; t)$  in (6.2) approximately takes into account the difference between the perturbation energies of the states  $|m\rangle$  and  $|k\rangle$

Assuming that the interaction potential  $V(q, t)$  tends to zero sufficiently rapidly as  $|t| \rightarrow \infty$ , the transition probability at  $t = +\infty$  is defined as

$$P_{n \rightarrow m} = |S(m, n)|^2 = |S'(m, n)|^2 \quad (6.3)$$

where

$$S(m, n) = \lim_{t \rightarrow \infty} S(m, n; t)$$

In order to obtain an approximate solution of the system of equations (6.2) we make the following approximations:

(i)  $(\epsilon_m - \epsilon_{m-s}) \approx s\bar{\epsilon}$ , where  $\bar{\epsilon}$  is independent of  $m$  and is some mean value of the energy separation of the quantum states. This is a valid approximation for highly excited atomic systems since the energy levels are nearly equally spaced. The relation is exact for a particle in a harmonic potential and thus should be a good approximation for the low eigenvalues of an anharmonic oscillator.

$$(ii) (\langle m | V(q, t) | m \rangle - \langle m-s | V(q, t) | m-s \rangle) \approx s\bar{V}(t) \quad (6.4)$$

where  $\bar{V}(t)$  is independent of  $m$  and is some mean value of the difference between successive diagonal matrix elements. This relation is exact for the one-dimensional harmonic oscillator perturbed by a time dependent potential  $q^\lambda F(t)$ ,

$\lambda = 0, 1, 2, 3$  with  $\bar{V}(t) = 0$  for  $\lambda = 1$  or  $3$ . Its

validity for the collinear atom-molecule collision will be discussed in Section (8.2) Percival and Richards (1970a) essentially assume that  $\bar{V}(t) = 0$ .

(iii) The classical interaction potential  $V^c(q,t)$ , that is, the interaction potential considering  $q$  as a classical coordinate, is a function of time implicitly through the position of the bound particle  $q$ , and explicitly through  $t$ . These times may be treated separately (Percival and Richards, 1970a). Denoting the time dependence of the bound particle by  $\tau'$ ,  $V^c\{q(\tau'), t\}$  is then periodic in  $\tau'$  and may be expanded as a Fourier series

$$V^c\{q(\tau'), t\} = \sum_{s=-\infty}^{\infty} V_s(t) \exp(is\omega\tau') \quad (6.5)$$

where  $\omega$  is the classical frequency of the bound particle.

For highly excited states we may use Heisenberg's correspondence principle (Heisenberg, 1925) and approximate the matrix elements  $\langle n+s | V(q,t) | n \rangle$  by the Fourier components  $V_s(t)$ . However, Naccache (1972) has shown that by a suitable quantization of the classical action variable, Heisenberg's correspondence principle may be used quite accurately even for matrix elements involving low quantum numbers, for particular forms of the potential  $V(q,t)$ .

Using these approximations the system of equations (6.2), may be written as

$$i\hbar \frac{\partial}{\partial t} S'(m,n;t) \simeq \sum_{\substack{k=0 \\ (k \neq m)}}^{\infty} S'(k,n;t) V_{m-k}(t) \quad (6.6)$$

$$\times \exp\left(\frac{i}{\hbar}(m-k)\left(\bar{\epsilon}t + \int_{-\infty}^t \bar{V}(t') dt'\right)\right)$$

Following a method similar to that used by Presnyakov and Urnov (1970), the generating function  $G_n(t, \tau)$  is defined by

$$G_n(t, \tau) = \sum_{j=-\infty}^{\infty} S'(j,n;t) \exp(i(j-n)\tau) \quad (6.7)$$

Although the summation index extends to  $-\infty$ , it is understood that  $S'(j,n;t) = 0$  for  $j < 0$ .

Multiplying both sides of (6.6) by  $\exp(i(m-n)\tau)$  and summing over  $m$  yields

$$i\hbar \frac{\partial}{\partial t} G_n(t, \tau) \simeq \sum_{m=-\infty}^{\infty} \exp(i(m-n)\tau) \sum_{\substack{k=0 \\ (k \neq m)}}^{\infty} S'(k,n;t) \quad (6.8)$$

$$\times V_{m-k}(t) \exp\left(\frac{i}{\hbar}(m-k)\left(\bar{\epsilon}t + \int_{-\infty}^t \bar{V}(t') dt'\right)\right)$$

The index  $k$  in the second summation may now be replaced by  $(m+l)$ . The lower limit of this summation then becomes  $l = -m$ . Since it is understood that  $S'(j,n;t) = 0$  for  $j < 0$  this limit may be extended to  $l = -\infty$ .

Interchanging the order of the summations and using (6.7) yields

$$i\hbar \frac{\partial}{\partial t} G_n(t, \tau) \simeq G_n(t, \tau) \sum_{\substack{l=-\infty \\ (l \neq 0)}}^{\infty} V_l(t) \quad (6.9)$$

$$\times \exp\left\{\frac{i}{\hbar}l\left(\bar{\epsilon}t + \hbar\tau + \int_{-\infty}^t \bar{V}(t') dt'\right)\right\}$$

Writing  $\bar{\epsilon} = \hbar\bar{\omega}$  and  $\tau = \bar{\omega}\tau'$  where  $\bar{\omega}$  represent some mean classical frequency of the bound particle, (6.9) may be written as

$$i\hbar\frac{\partial}{\partial t} G_n(t, \bar{\omega}\tau') \simeq G_n(t, \bar{\omega}\tau') \left[ V^c \left\{ q(\bar{\omega}t + \bar{\omega}\tau' + \frac{1}{\hbar} \int_{-\infty}^t \bar{V}(t') dt'), t \right\} - V_0(t) \right] \quad (6.10)$$

where the relation (6.5) has been used to replace the summation over  $l$ .

(6.10) has the solution

$$G_n(t, \bar{\omega}\tau') \simeq \exp \left\{ -\frac{i}{\hbar} \int_{-\infty}^t \left[ V^c \left\{ q(\bar{\omega}t' + \bar{\omega}\tau' + \frac{1}{\hbar} \int_{-\infty}^{t'} \bar{V}(t'') dt''), t' \right\} - V_0(t') \right] dt' + i\delta \right\} \quad (6.11)$$

From (6.7) we obtain

$$S'(m, n; t) = \frac{\bar{\omega}}{2\pi} \int_0^{2\pi/\bar{\omega}} G_n(t, \bar{\omega}\tau') \exp(i(n-m)\bar{\omega}\tau') d\tau'$$

Thus from (6.3)

$$\begin{aligned} P_{n \rightarrow m} &= |S'(m, n)|^2 \\ &\simeq \left| \frac{\bar{\omega}}{2\pi} \int_0^{2\pi/\bar{\omega}} d\tau' \exp \left\{ i(n-m)\bar{\omega}\tau' - \frac{i}{\hbar} \int_{-\infty}^{\infty} V^c \left[ q \left\{ \bar{\omega}(t+\tau') + \frac{1}{\hbar} \int_{-\infty}^t \bar{V}(t') dt' \right\}, t \right] dt \right\} \right|^2 \end{aligned} \quad (6.12)$$

The terms  $\int_{-\infty}^t V_0(t') dt'$  and  $\delta$  do not contribute to the transition probability, being merely phase factors. The term

$$\frac{1}{\hbar} \int_{-\infty}^t \bar{V}(t') dt'$$

approximately takes into account the contribution to the transition probability due to the perturbation of the bound particle throughout the interaction. When the diagonal matrix elements  $\langle n | V(q, t) | n \rangle$  are independent of  $n$  or are zero,  $\bar{V}(t)$  will be zero and the expression reduces to that given by Percival and Richards (1970a). In the quantum mechanical weak perturbation limit,  $\bar{V}(t)$  will be small. Its effect on the transition probability, however, will not necessarily be negligible, since for  $n \neq m$  the transition probability will also be small. This will be discussed with reference to a particular example in Section (7.4).

In the impulsive and weak perturbation limits the expression for the transition probability, (6.12), reduces to a sudden and first order approximation in an analagous way to the Percival and Richards (1970a) result. The dependence of  $q$  on  $\bar{V}(t)$  is still retained in these approximations.

CHAPTER 7

EXCITATION OF A HARMONIC OSCILLATOR

To illustrate the effect of the correction term and to compare with other approximate theories, we apply the modified correspondence principle (6.12) to the excitation of a harmonic oscillator by a time dependent potential of the form  $q^2 F(t)$ . As mentioned in Chapter 6 the relation between the exact quantum mechanical and the correspondence principle (Percival and Richards, 1970a) solutions for this problem has been discussed by Clark and Dickinson (1971).

In order to compare the results quantitatively, we choose the specific form  $F(t) = (a/2) \operatorname{sech}^2(bt)$  where  $a$  and  $b$  are constants. This particular time dependence results from the Landau-Teller approximation (Landau and Teller, 1936) of the collinear atom-harmonic oscillator collision, with the interaction potential (4.10). In order to relate more closely to this problem, we may choose  $a = \alpha^2 E_x / 2$  and  $b = (\alpha/2) (E_x / m)^{1/2}$ , where

$E_x$  represents the initial translational energy of the incoming particle.  $q^2 F(t)$  then corresponds to the third term in the expansion of the exponential interaction potential

$$\frac{E_x}{2} \exp(\alpha q) \operatorname{sech}^2 \left\{ \frac{\alpha}{2} \left( \frac{E_x}{m} \right)^{\frac{1}{2}} t \right\}$$

(Rapp and Kassal, 1969).

Although this problem has little physical significance, this particular choice for the constants  $a$  and  $b$  will allow comparisons to be made over a range of physically significant molecular parameters.

### 7.1 Exact Quantum Mechanical Solution

For a time dependent perturbing potential of the form  $q^2 F(t)$ , the probability that a harmonic oscillator, initially in state  $j$ , will make a transition to state  $k$ , is given by (Fopov and Perelemov, 1969).

$$P_{j \rightarrow k}^{\text{EXACT}} = \frac{n_{<}!}{n_{>}!} (1-\rho)^{\frac{1}{2}} \left| P_{(j+k)/2}^{s/2} \left\{ (1-\rho)^{\frac{1}{2}} \right\} \right|^2 \quad (7.1)$$

$$s = |j - k| = 0, 2, 4, \dots$$

where  $P_n^m(x)$  is the associated Legendre function (Abramowitz and Stegun, 1965), and  $n_{<}$ ,  $n_{>}$  are respectively the lesser and greater of  $j$  and  $k$ .

Since the perturbing potential has been expressed in the same reduced units as used in section (1.1), the Schrödinger equation for this problem may be written



$$\left[ -\frac{1}{2} \frac{\partial^2}{\partial q^2} + \frac{1}{2} q^2 + \frac{\alpha^2 E_x}{4} q^2 \operatorname{sech}^2 \left( \frac{\alpha}{2} \sqrt{\frac{E_x}{m}} t \right) \right] \Psi = i \frac{\partial \Psi}{\partial t}$$

The parameter  $\rho$  appearing in (7.1) may be interpreted (Popov and Perlemov, 1969) as the above-barrier reflection coefficient for a particle of unit energy, from the potential barrier defined by

$$F(x) = \frac{\alpha^2 E_x}{4} \operatorname{sech}^2 \left( \frac{\alpha}{2} \sqrt{\frac{E_x}{m}} x \right)$$

This problem may be solved analytically for the above function  $F(x)$  (Goldman and Krivchenkov, 1961), giving

$$\rho = \frac{\cos^2 \left\{ \frac{\pi}{2} \sqrt{1+8m} \right\}}{\sinh^2 \left\{ \frac{2\pi}{\alpha} \sqrt{\frac{m}{E_x}} \right\} + \cos^2 \left\{ \frac{\pi}{2} \sqrt{1+8m} \right\}}$$

## 7.2 Correspondence Principle Solutions

The correspondence principle of Percival and Richards (1970a) yields, for this problem, (Clark and Dickinson, 1971)

$$\mathcal{P}_{j \rightarrow k}^{\text{CP}} = J_{s/2}^2(\bar{n} \sqrt{\rho'}) \quad (7.2)$$

where  $J_n(x)$  is the ordinary Bessel function (Abramowitz and Stegun, 1965), and  $\bar{n}$  is some mean quantum number of the oscillator throughout the  $j \rightarrow k$  transition. As suggested by Naccache (1972) we employ

$$\bar{n} = \left\{ \frac{(n_c + s)!}{n_c!} \right\}^{1/s} \quad (7.3)$$

Also,  $\rho'$  is a first order approximation to given by

$$\rho' = \left| \int_{-\infty}^{\infty} F(x) \exp(2ix) dx \right|^2$$

For the present form of  $F(x)$  this becomes

$$\rho' = \frac{4\pi^2 m^2}{\sinh^2 \left\{ \frac{2\pi}{\alpha} \sqrt{\frac{m}{E_x}} \right\}}$$

which is a valid approximation providing and  $2m \ll 1$  and  $\alpha^2 E_x / 2 \ll 1$ .

The diagonal matrix elements  $\langle n | q^2 | n \rangle$  in the harmonic oscillator basis are  $(n + \frac{1}{2})$ , in the reduced units employed here, and from (6.4) we obtain

$$\bar{V}(t) = \frac{\alpha^2 E_x}{4} \operatorname{sech}^2 \left\{ \frac{\alpha}{2} \sqrt{\frac{E_x}{m}} t \right\}$$

The expression for the Modified Correspondence Principle transition probability thus takes the form

$$\begin{aligned} \mathcal{P}_{j \rightarrow k}^{\text{MODCP}} &= \left| \frac{1}{2\pi} \int_0^{2\pi} d\tau \exp \{ i(j-k)\tau \right. \\ &\quad \left. - i \int_{-\infty}^{\infty} 2\bar{n} \sin^2 \left( t' + \tau + \int_{-\infty}^{t'} \frac{\alpha^2 E_x}{4} \operatorname{sech}^2 \left\{ \frac{\alpha}{2} \sqrt{\frac{E_x}{m}} t'' \right\} dt'' \right) \right. \\ &\quad \left. \times \frac{\alpha^2 E_x}{4} \operatorname{sech}^2 \left\{ \frac{\alpha}{2} \sqrt{\frac{E_x}{m}} t' \right\} dt' \right|^2 \end{aligned}$$

which on using the change of variable  $y = \tanh\left(\frac{\alpha}{2}\sqrt{\frac{E_x}{m}}t\right)$ , may be evaluated analytically as

$$\mathcal{P}_{j \rightarrow k}^{\text{MODCP}} = J_{s/2}^2(\bar{n}\sqrt{\rho''}) \quad (7.4)$$

where

$$\rho'' = \rho' \left| M\left\{1 + \frac{2i}{\alpha}\sqrt{\frac{m}{E_x}}, 2, 2i\alpha\sqrt{mE_x}\right\} \right|^2$$

and  $M(a, b, x)$  is the confluent hypergeometric function (Abramowitz and Stegun, 1965).

### 7.3 First Order Perturbation Theory Approximations

The first order time dependent perturbation theory approximation (FOPA) for this problem is given by

$$\mathcal{P}_{j \rightarrow j \pm 2}^{\text{FOPA}} = (n_{\pm} + 1)(n_{\pm} + 2)\rho'/4 \quad (7.5)$$

From Mies (1964b) the corresponding Revised first order perturbation theory approximation RFOPA is given by

$$\mathcal{P}_{j \rightarrow j \pm 2}^{\text{RFOPA}} = (n_{\pm} + 1)(n_{\pm} + 2)\rho''/4 \quad (7.6)$$

As for the correspondence principle, only transitions involving a change in quantum number which is a multiple of 2 can occur.

### 7.4 Discussion and Comparison of Results

The effect of the correction term in both the modified correspondence principle and in the RFOPA, is to replace the approximate reflection coefficient  $\rho'$  by  $\rho''$ . These reflection

coefficients were evaluated numerically for a large range of values of  $m$  and  $\alpha\sqrt{E_x}$ ; in all cases  $\rho''$  was a better approximation to  $\rho$  than was  $\rho'$ . The quantities

$$Er_1 = |(\rho - \rho')/\rho|$$

$$Er_2 = |(\rho - \rho'')/\rho|$$

were calculated. These quantities were relatively insensitive to the value of  $m$ , except for very large  $m$  ( $\geq 4$ ).  $Er_2$  ranged from  $10^{-4}$  for small values of  $\alpha\sqrt{E_x}$ , to 0.2 for large values of  $\alpha\sqrt{E_x}$  ( $\geq 7$ ), while the corresponding values of  $Er_1$  were approximately an order of magnitude larger.

It is interesting to examine the behaviour of  $\rho''$  in the limit of weak perturbations (small  $E_x$  or more correctly small  $\alpha\sqrt{E_x}$ ). From the limiting form of the confluent hypergeometric function (Abramowitz and Stegun, 1965) we obtain

$$\lim_{E_x \rightarrow 0} M\left\{1 + \frac{2i}{\alpha}\sqrt{\frac{m}{E_x}}, 2, 2i\alpha\sqrt{mE_x}\right\} = \frac{1}{2\sqrt{m}} J_1(4\sqrt{m})$$

(Alternatively this relation may be obtained by expanding  $M(a,b,x)$  as a power series in  $x$  (Abramowitz and Stegun, 1965), taking the limit  $E_x \rightarrow 0$  and then resumming).

In this limit, the correction term in the Modified

Correspondence Principle (6.12), and similarly in the RFOPA theory, is small compared with  $\bar{\omega} t$ . Its effect on the transition probabilities may still be considerable for certain values of the parameter  $m$ .

Figures 10 and 11 respectively show the  $0 \rightarrow 2$  and  $2 \rightarrow 4$  transition probabilities as a function of  $E_{sc}$  for  $m = \frac{1}{8}$  and  $\alpha = \frac{1}{4}$ . It is seen that  $P_{j \rightarrow k}^{MODCP}$  is an excellent approximation up to the maximum in the exact transition probability for both transitions, whereas  $P_{j \rightarrow k}^{CP}$  overestimates  $P_{j \rightarrow k}^{EXACT}$ , even in the limit of weak perturbations. The RFOPA results, though accurate for very weak perturbations, diverge rapidly from the exact transition probabilities as the strength of the perturbation increases; the FOPA results are inaccurate for all energies.

As  $n_<$  or  $S$  become large the range of validity of  $P_{j \rightarrow k}^{MODCP}$  will decrease (see Equation 10, Clark and Dickinson, 1971). However the first few maxima of the transition probability, which forms the most significant part, occur at smaller values of  $\rho$  as  $n_<$  increases.

Numerical results show that  $P_{j \rightarrow k}^{MODCP}$ , and even  $P_{j \rightarrow k}^{CP}$  predict these first few peaks in the transition probability more accurately as  $n_<$  becomes large. This is illustrated in Figure 12 by a comparison of  $P_{10 \rightarrow 12}^{CP}$ ,  $P_{10 \rightarrow 12}^{MODCP}$  and  $P_{10 \rightarrow 12}^{EXACT}$ .

For all transitions  $P_{j \rightarrow k}^{\text{MODCP}}$  will be more accurate  
than  $P_{j \rightarrow k}^{\text{CP}}$  .

CAPTIONS TO FIGURES 10, 11 and 12

Figures 10, 11

The  $0 \rightarrow 2$  (Figure 10) and  $2 \rightarrow 4$  (Figure 11) transition probabilities are shown, as a function of the energy  $E_x$ , for a harmonic oscillator perturbed by a potential  $q^2 F(t)$ . EXACT is the exact quantum mechanical result (7.1); CP is the Percival and Richards correspondence principle result (7.2); MODCP is the modified correspondence principle result (7.4); FOPA is the first order perturbation theory approximation (7.5), and RFOPA is the revised first order perturbation theory approximation (7.6).

Figure 12

The  $10 \rightarrow 12$  transition probability is shown as a function of the energy  $E_x$ , for a harmonic oscillator perturbed by a potential  $q^2 F(t)$ . CP is the Percival and Richards correspondence principle results (7.2); MODCP is the modified correspondence principle result (7.4); EXACT is the exact quantum mechanical result (7.2).

Figure 10

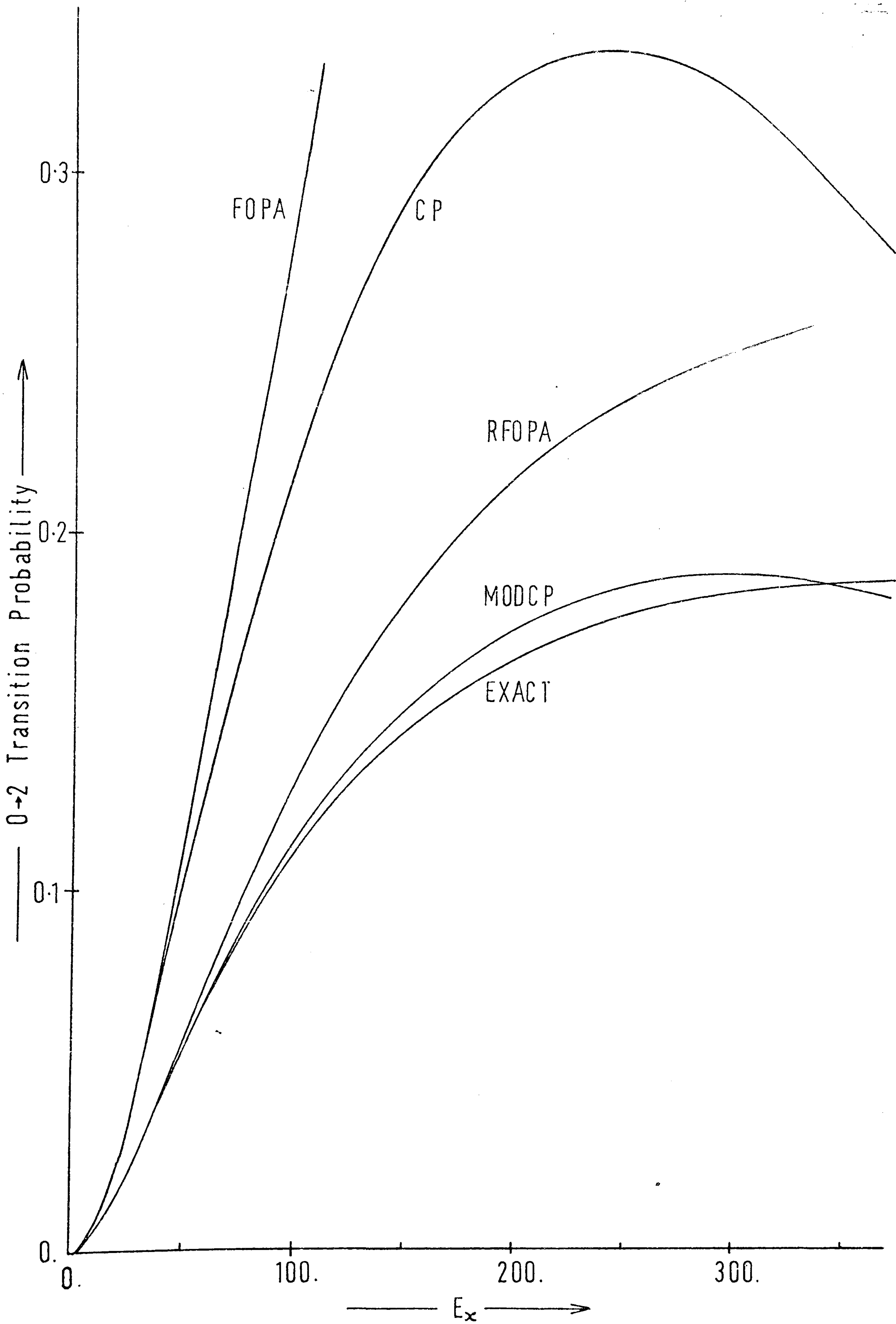




Figure 11

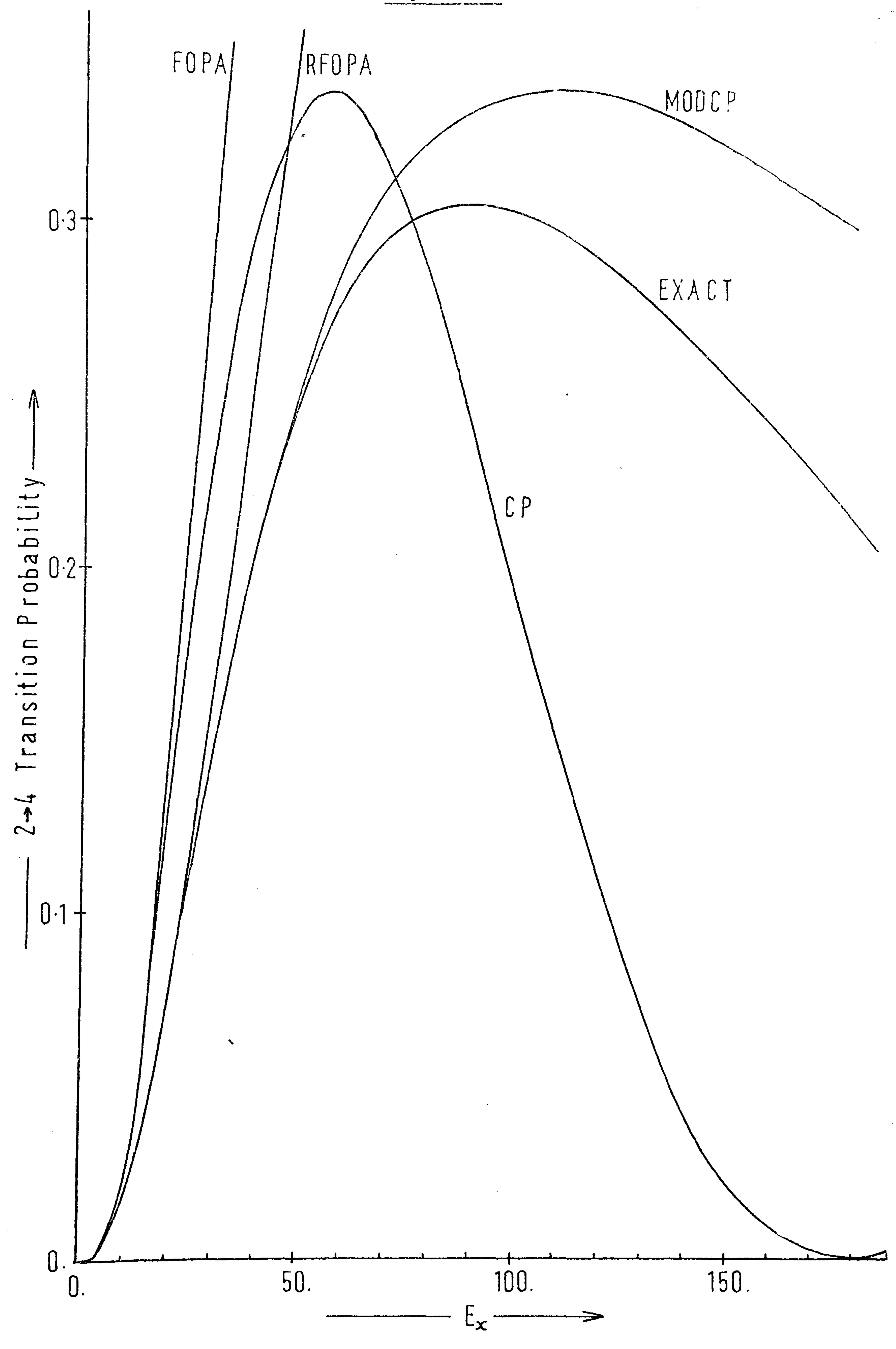
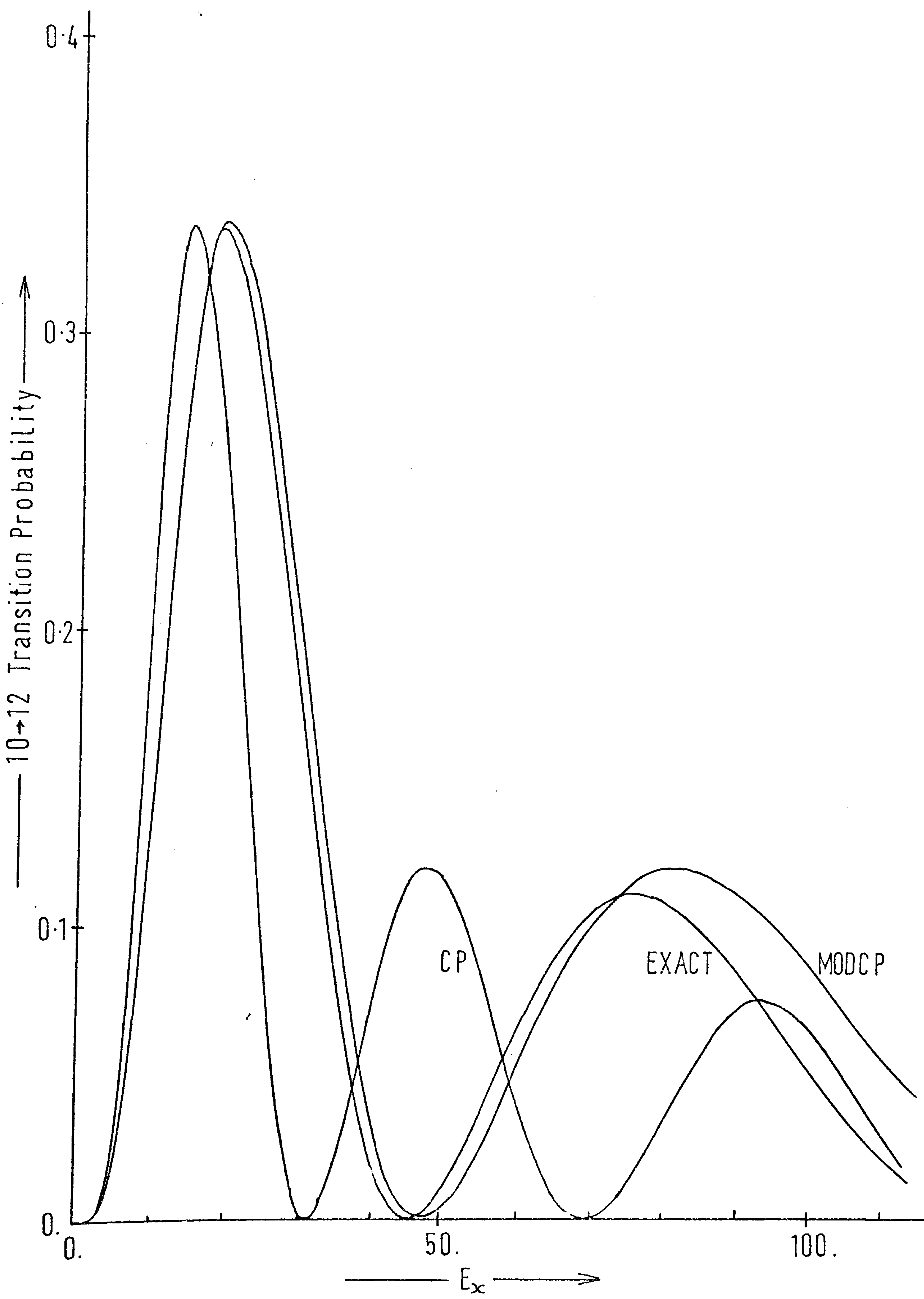


Figure 12



CHAPTER 8CORRESPONDENCE PRINCIPLE SOLUTIONS FOR THE  
VIBRATIONAL EXCITATION OF A MORSE OSCILLATOR

We now return to the problem of the collinear atom-diatomic molecule collision, where the molecule is assumed to be bound by a Morse potential. This problem was treated exactly using quantum mechanics in the earlier chapters of this thesis.

The modified correspondence principle is applied to this problem and the results are compared with those from other approximate theories, including the correspondence principle of Percival and Richards (1970a).

To apply correspondence principle methods, it is first necessary to represent the interaction between the incoming atom and the diatomic molecule by a time-dependent perturbing potential. This requires the solution of a classical equation of motion for the incident particle, and will be considered in Section (8.1).

Providing the Morse well depth is large and the interaction is not too strong, assumptions (1) and (3) of Section (6.2) will be valid. The justification for assumption (2) in the present case is given in Section (8.2).

### 8.1 The Classical Equations of Motion

In terms of the reduced units introduced in Section (1.1), the classical equations of motion for the system are

$$m \frac{d^2 x}{dT^2} = - \frac{\partial V_{AB}(x-y)}{\partial x} \quad (8.1)$$

$$\frac{d^2 y}{dT^2} = - \frac{\partial V_{AB}(x-y)}{\partial y} - \frac{\partial V_{BC}(y)}{\partial y} = - \frac{\partial V(y,x)}{\partial y} \quad (8.2)$$

where  $T$  is a reduced time  $T = \omega_e t$ .

With the interaction potential,  $V_{AB}(x-y)$ , given by (4.10), these equations are non-separable and we make the approximation that the incoming particle is scattered by the average potential (Mies 1964b)

$$\begin{aligned} U(x) &= \frac{1}{2} V_0 \exp(-\alpha x) (\langle j | \exp(\alpha y) | j \rangle + \langle k | \exp(\alpha y) | k \rangle) \\ &= V_0 \exp(-\alpha x) U^{av}. \end{aligned}$$

for a  $j \rightarrow k$  transition.

With this approximation, the equation for the  $x$  motion (8.1) may be solved in the usual manner (Rapp and Kassal, 1969) giving

$$V(y,T) = V_{BC}(y) + \frac{E_x}{2U^{av}} \operatorname{sech}^2 \left\{ \frac{\alpha}{2} \sqrt{\frac{E_x}{m}} T \right\} \exp(\alpha y) \quad (8.3)$$

where  $E_x$  is the initial translational energy of the incoming particle, in units of  $\hbar\omega_e/2$ . In considering a  $j \rightarrow k$  transition we use the velocity averaged energy (Rapp and Kassal, 1969).

$$E_x = \frac{1}{4} \left\{ (E - 2j - 1)^{\frac{1}{2}} + (E - 2k - 1)^{\frac{1}{2}} \right\}^2$$

where  $E$  is the total energy of the system, in units of  $\frac{1}{2}\hbar\omega_e$ .

The unperturbed classical motion for a particle of energy  $\bar{E}$ , bound in the Morse potential

$$V_{Bc}(y) = D_e \left\{ \exp\left(-\frac{y}{\sqrt{2D_e}}\right) - 1 \right\}^2$$

is given by

$$y(\tau) = \sqrt{2D_e} \left( \ln \left[ 1 + \sqrt{\frac{\bar{E}}{2D_e}} \sin \left\{ \left(1 - \frac{\bar{E}}{2D_e}\right) \tau + \delta_0 \right\} \right] - \ln \left( 1 - \frac{\bar{E}}{2D_e} \right) \right) \quad (8.4)$$

where  $\delta_0$  is an arbitrary phase factor and  $\tau$  is a reduced time, defined by  $\tau = \omega_e t$ .

## 8.2 Matrix Elements and Fourier Components of $\exp(\alpha y)$

The modified correspondence principle result (6.12), depends implicitly on the accuracy with which the matrix elements  $\langle n+s | V(q,t) | n \rangle$  may be replaced by the Fourier components  $V_s(t)$

The perturbing potential  $V(y, \tau)$  is given by (see 8.3)

$$\begin{aligned}
 V(y, \tau) &= \frac{E_x}{2U^{av.}} \operatorname{sech}^2 \left\{ \frac{\alpha}{2} \sqrt{\frac{E_{xc}}{m}} \tau \right\} \exp(\alpha y) \\
 &= F(\tau) \exp(\alpha y)
 \end{aligned} \tag{8.5}$$

The Fourier components  $V_s(\tau)$  are thus

$$V_s(\tau) = F(\tau) \frac{1}{2\pi} \int_0^{2\pi} \exp(\alpha y(\tau)) \exp(is\tau) d\tau$$

where  $y(\tau)$  is given by (8.4).

This integral may be evaluated analytically giving (apart from arbitrary phase factors)

$$\begin{aligned}
 V_s(\tau) &= F(\tau) \left( 1 - \frac{\bar{\epsilon}}{4D_e} \right)^{-\alpha \sqrt{2D_e}} \\
 &\times \sum_{j=0}^{\infty} \frac{(\bar{\epsilon}/4D_e)^{j+s/2} \Gamma(1 + \alpha \sqrt{2D_e})}{2^{2j+s} \Gamma(\alpha \sqrt{2D_e} - 2j - s + 1) \Gamma(j+s+1) \Gamma(j+1)}
 \end{aligned}$$

where  $\Gamma(x)$  is the gamma function. (Abramowitz and Stegun, 1965). As in Chapter 7 we use the mean quantum number  $\bar{n}$  (7.3). Then

$$\bar{\epsilon} = 2\bar{n}$$

The quantum mechanical matrix elements

$$\begin{aligned}
 \langle n+s | V(y, \tau) | n \rangle &= F(\tau) \langle n+s | \exp(\alpha y) | n \rangle \\
 &= F(\tau) U_{n+s, n}
 \end{aligned}$$

in a Morse oscillator basis have been given in Section (4.4).

Calculations show that the agreement between the

Fourier components and the corresponding matrix

elements is better than 1% for  $n < 10$ ,  $s < 2$ , for most values of  $\alpha$  and  $D_e$ . The agreement appears to be better for smaller values of  $s$  and  $\alpha$ . For example, with  $s = 0$ ,  $\alpha = 0.114$ ,  $D_e = 40.81$ ,  $n \leq 8$  the agreement is better than 0.005%. Thus for most values of the parameters,  $\bar{V}(t)$  may be approximated by the difference between successive Fourier components. In the results presented in the next section, however, the difference between the actual matrix elements is used.

In the derivation of the modified correspondence principle (Section 6.2), it is assumed, (6.4), that the difference between successive diagonal matrix elements

$$\langle n+1 | V(q,t) | n+1 \rangle - \langle n | V(q,t) | n \rangle = \bar{V}(t)$$

is independent of the quantum number  $n$ . In Table 6 we have tabulated

$$\bar{U} = U_{n+1, n+1} - U_{n, n}$$

as a function of  $n$ , for all systems considered in the next section. It may be seen that the assumption is valid providing  $\alpha$  is not too large or  $D_e$  is not too small.

In calculating the results presented in the next section we have used

$$\bar{U} = (U_{n+s, n+s} - U_{n, n}) / s$$

TABLE 6.

$\alpha$	0.1278	0.114	0.314	0.5584
$D_e$	75.525	40.81	9.3	14.652
$n$	$\bar{U} = U_{n+1,n+1} - U_{n,n}$			
0	2.45(-2)	2.64(-2)	1.96(-1)	4.19(-1)
1	2.52(-2)	2.74(-2)	2.45(-1)	5.63(-1)
2	2.59(-2)	2.85(-2)	3.10(-1)	7.61(-1)
3	2.67(-2)	2.97(-2)	3.98(-1)	1.04
4	2.75(-2)	3.09(-2)	5.20(-1)	1.43
5	2.83(-2)	3.21(-2)	6.93(-1)	1.98
6	2.91(-2)	3.35(-2)	9.47(-1)	2.78
7	3.00(-2)	3.49(-2)	1.33	3.94
8	3.09(-2)	3.64(-2)	1.93	5.68
9	3.19(-2)	3.80(-2)	2.92	8.31

Values of  $\bar{U} = U_{n+1,n+1} - U_{n,n}$  in a Morse oscillator basis for  $n = 0 \rightarrow 9$ , for several values of  $\alpha$  and  $D_e$ . Numbers in parenthesis indicate powers of 10.



when considering an  $n \rightarrow n+s$  transition.

### 8.3 Results and Discussion

From (8.4) and (8.5) we obtain

$$\begin{aligned}
 & V^c \left\{ y \left( \tau' + \bar{\omega} T / \omega_e + \int_{-\infty}^T \bar{V}(t') dt' \right), T \right\} \\
 &= \frac{E_x}{2U^{av.}} \operatorname{sech}^2 \left\{ \frac{\alpha}{2} \sqrt{\frac{E_x}{m}} T \right\} \\
 & \times \left( \frac{1 + (\bar{E}/2D_e) \sin \left\{ \left( 1 - \frac{\bar{E}}{2D_e} \right)^{1/2} T + \tau' + \int_{-\infty}^T \bar{V}(t') dt' \right\}}{1 - (\bar{E}/2D_e)} \right)^{\alpha \sqrt{2D_e}}
 \end{aligned} \tag{8.6}$$

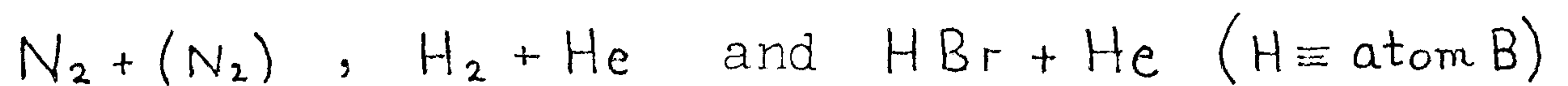
where

$$\int_{-\infty}^T \bar{V}(t') dt' = \frac{\sqrt{m E_x}}{\alpha U^{av.}} \left( \tanh \left\{ \frac{\alpha}{2} \sqrt{\frac{E_x}{m}} T \right\} \right) \bar{U}$$

Here we have neglected arbitrary phase factors in  $y$ , since these may be 'factored out' of the integral over  $\tau'$ .

Using (8.6), expression (6.12) was integrated numerically to an accuracy of about 1%. In Figures 13, 14 and 15 we have shown the ratio of the correspondence principle transition probabilities  $\mathcal{P}_{j \rightarrow k}^{\text{MODCP}}$  (modified), and  $\mathcal{P}_{j \rightarrow k}^{\text{CP}}$  (unmodified, i.e. with  $\bar{V}(t) = 0$  in (8.6)) to the exact quantum mechanical results  $\mathcal{P}_{j \rightarrow k}^{\text{EXACT}}$  given in Tables 1 - 5. The systems  $(m, \alpha, D_e)$  given by  $(\frac{1}{3}, 0.314, 9.3)$ ,  $(\frac{1}{2}, 0.114, 40.81)$ ,  $(0.667, 0.314, 9.3)$  and  $(3.737, 0.5584, 14.652)$

approximately represent the collisions  $H_2 + H$ ,



respectively. The  $0 \rightarrow 1$ ,  $2 \rightarrow 4$  and  $4 \rightarrow 5$  transitions are shown in Figures 13, 14 and 15 respectively.

In Figures 16 and 17 we present respectively the  $0 \rightarrow 1$  and  $2 \rightarrow 4$  transition probabilities for the system  $(\frac{1}{3}, 0.314, 9.3)$  and show a comparison between the exact results and the CP, MODCP, FODWA (Section 5.2) and RFODWA (Section 5.3) approximations.

From Figures 13, 14 and 15 it may be seen that the correspondence principle results (CP) of Percival and Richards (1970a) may be several orders of magnitude too large. The discrepancy appears to be greatest at low energies.

The modified correspondence principle results (MODCP), however, converge to the exact transition probabilities at low energies except for very large values of  $m$ , for example  $m = 3.737$ . This is probably due to an inadequate expression for the time dependent interaction potential (8.5) for large  $m$ .

The accuracy of both the CP and MODCP results increases with decreasing values of  $m$  or  $\alpha$ ; for the collision  $Br_2 + H_2$  (not shown)

approximately represented by (0.006268, 0.1278, 75.525), the MODCP and CP results are both accurate to within a few per cent of the exact results, in the energy region before the first maximum in the transition probability.

The range of validity of the MODCP results increases with decreasing  $|s|/n$ , where  $n$  is the initial quantum number, for transitions among the first few vibrational levels at least. This may be seen by comparing the  $0 \rightarrow 1$  and  $4 \rightarrow 5$  transitions, Figures 13 and 15 respectively, for the collisions  $(\frac{1}{3}, 0.314, 9.3)$  and  $(\frac{2}{3}, 0.314, 9.3)$ .

Figure 16 shows that the MODCP results agree with the revised first order distorted wave results (RFODWA) of Mies (1964a), and consequently (see Section 5.4) with the revised first order perturbation theory results (RFOPA) of Mies (1964b), in the weak perturbation limit. This is to be expected, since, as discussed in Section (6.2) the modified correspondence principle (6.12) reduces - apart from the replacement of the matrix element by the corresponding Fourier component - to the RFOPA expression in this limit. Both the CP and FODWA results are seen to be in poor agreement with the exact transition probability.

For transitions where  $S > 1$ , all the first order theories, FODWA, RFODWA, RFOPA, are inapplicable. The MODCP results, however, are still valid. This may be seen in Figure 17 for the  $2 \rightarrow 4$  transition.

The accuracy of the MODCP (or CP) results, when comparisons with exact transition probabilities are made, depends on the approximate time dependent potential used. Heidrich et al (1971) have shown that for a similar problem using a harmonic binding potential  $V_{bc}(y)$ , the time dependent potential derived from the impulse approximation  $V_I(y,t)$  gives excellent agreement with the corresponding exact quantum mechanical results. Since  $V_I(y,t)$  is linear in  $y$ , the modified correspondence principle for this problem reduces to the Percival and Richards (1970a) expression, and, as pointed out previously, except for very strong interactions, the results (Clark, 1971) are in excellent agreement with those of Heidrich et al (1971). However, using  $V_I(y,t)$  for the Morse binding potential, both the modified and unmodified correspondence principles predict transition probabilities that are typically an order of magnitude too large, although the former is more accurate.

#### 8.4 Concluding Remarks

Previous applications of the Percival and Richards (1970a) correspondence principle are not invalidated by the present modification. For the system considered by Clark and Dickinson (1971), the diagonal matrix elements of the interaction potential  $qF(t)$  are zero and it has been pointed out by Richards (private communication) that for the excitation of highly excited hydrogenic atoms by charged particles (Percival and Richards, 1970b, 1971) the modification is not significant for the range of quantum numbers investigated.

By considering a perturbation expansion of the classical action, Richards (private communication) has shown that a modification of the correspondence principle, similar to that presented here, may be obtained using the approach of Percival and Richards (1970a). In this case the generalisation to many dimensional, non-degenerate systems is straightforward.

CAPTIONS TO FIGURES 13 - 17

Figures 13 - 15

The ratios of the Percival and Richards correspondence principle (CP, broken lines) and the modified correspondence principle (MODCP, continuous lines) results to the exact quantum mechanical transition probabilities (Tables 1-5), as a function of the total energy of the system  $E$  (in units of  $\frac{1}{2}\hbar\omega_e$ ), for the collinear atom Morse oscillator collision. The values of  $m$  shown are for the systems  $(m, \alpha, D_e)$ , given by  $(\frac{1}{3}, 0.314, 9.3)$ ,  $(0.5, 0.114, 40.81)$ ,  $(0.667, 0.314, 9.3)$  and  $(3.737, 0.5584, 14.652)$ . The  $0 \rightarrow 1$ ,  $2 \rightarrow 4$  and  $4 \rightarrow 5$  transitions are shown in Figures 13, 14 and 15 respectively.

Figures 16 and 17

The  $0 \rightarrow 1$  (Figure 16) and  $2 \rightarrow 4$  (Figure 17) transition probabilities for the collinear atom Morse oscillator collision as a function of the total energy  $E$  (in units of  $\frac{1}{2}\hbar\omega_e$ ), for the system  $(\frac{1}{3}, 0.314, 9.3)$ . The

$X$ 's are the exact transition probabilities (Table 2), CP is the correspondence principle result of Percival and Richards, MODCP is the modified correspondence principle result, FODWA is the first order distorted wave result (see section 5.2) and RFODWA is the revised first order distorted wave result (see section 5.3).

Figure 13

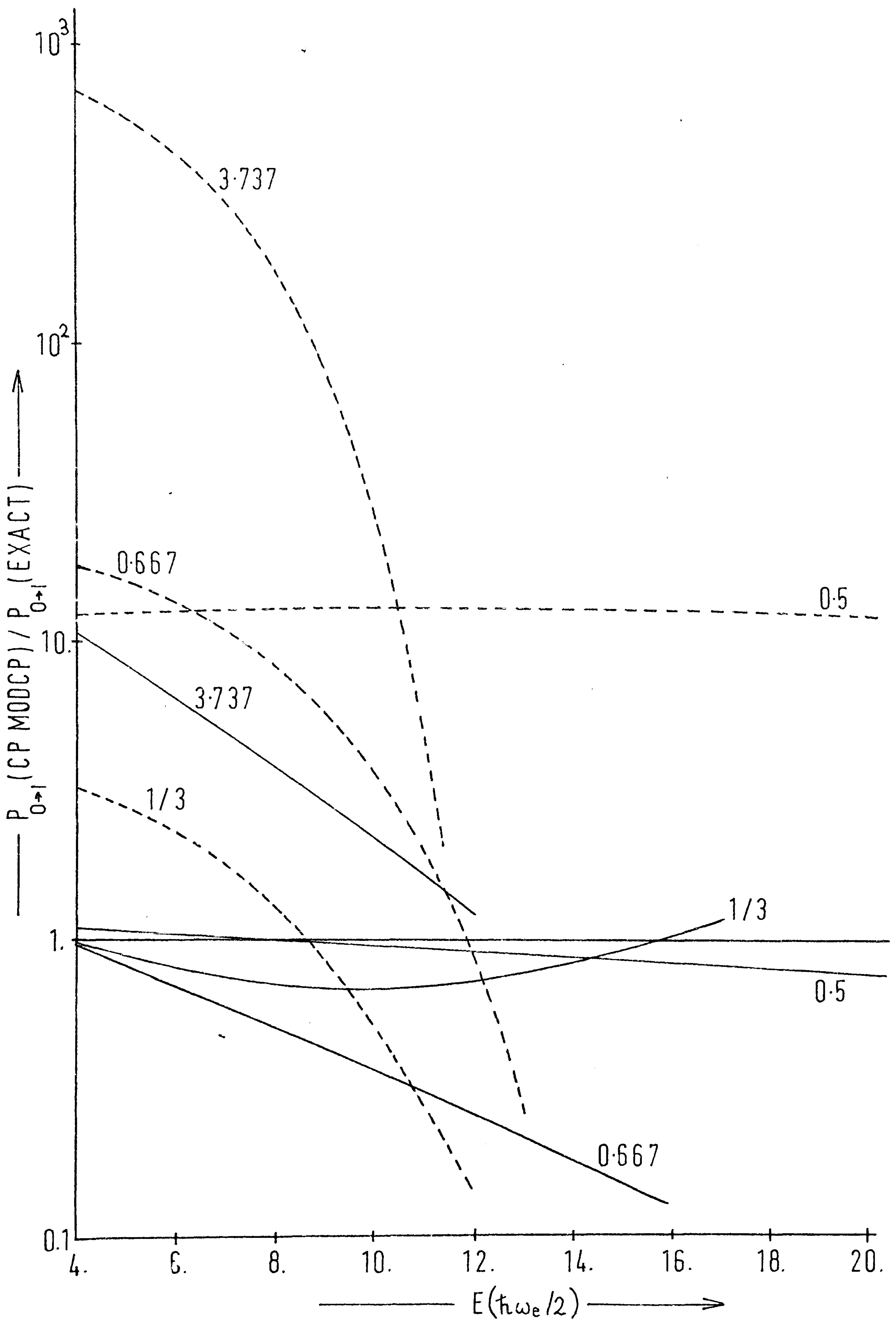


Figure 14

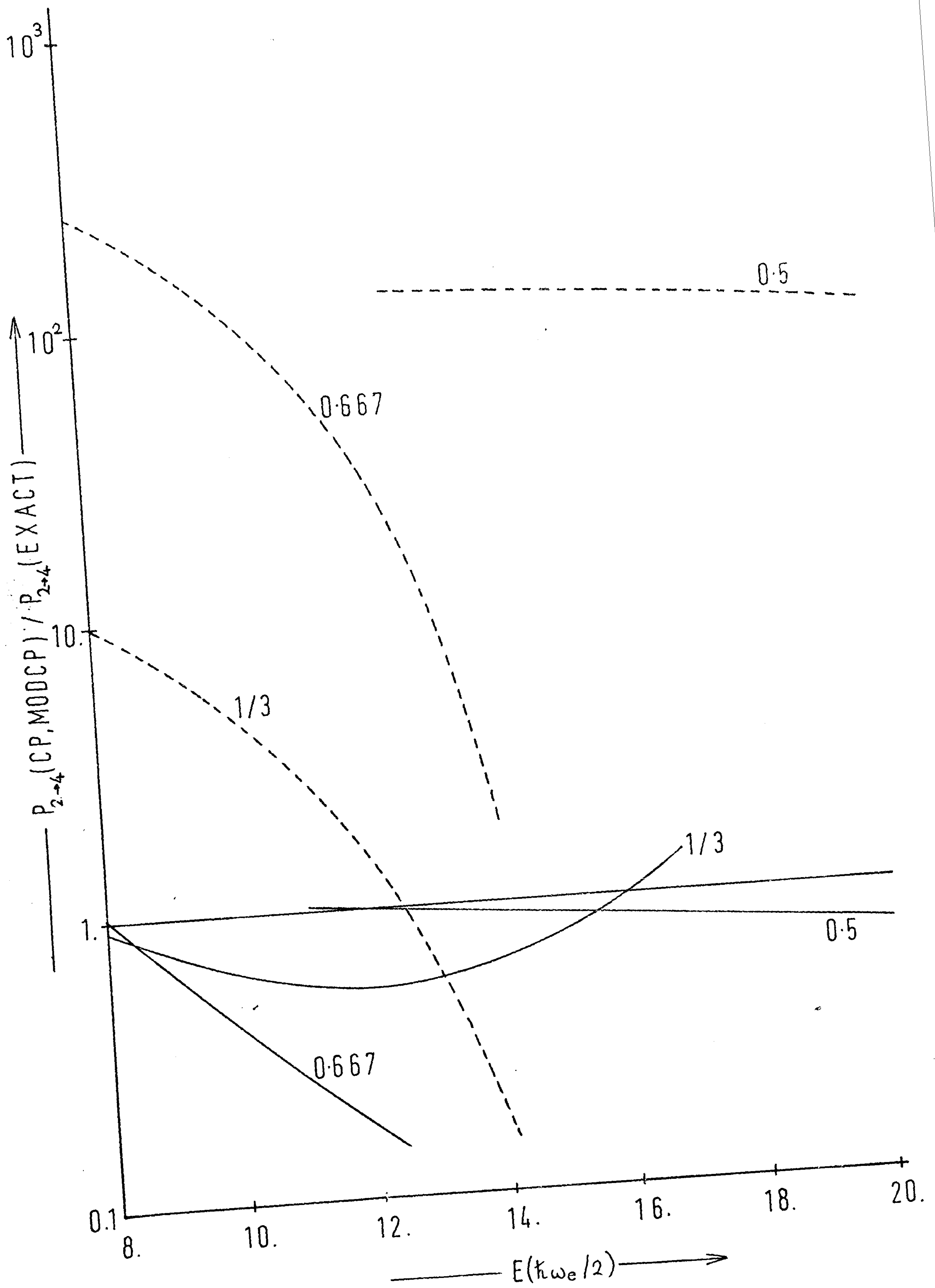




Figure 15

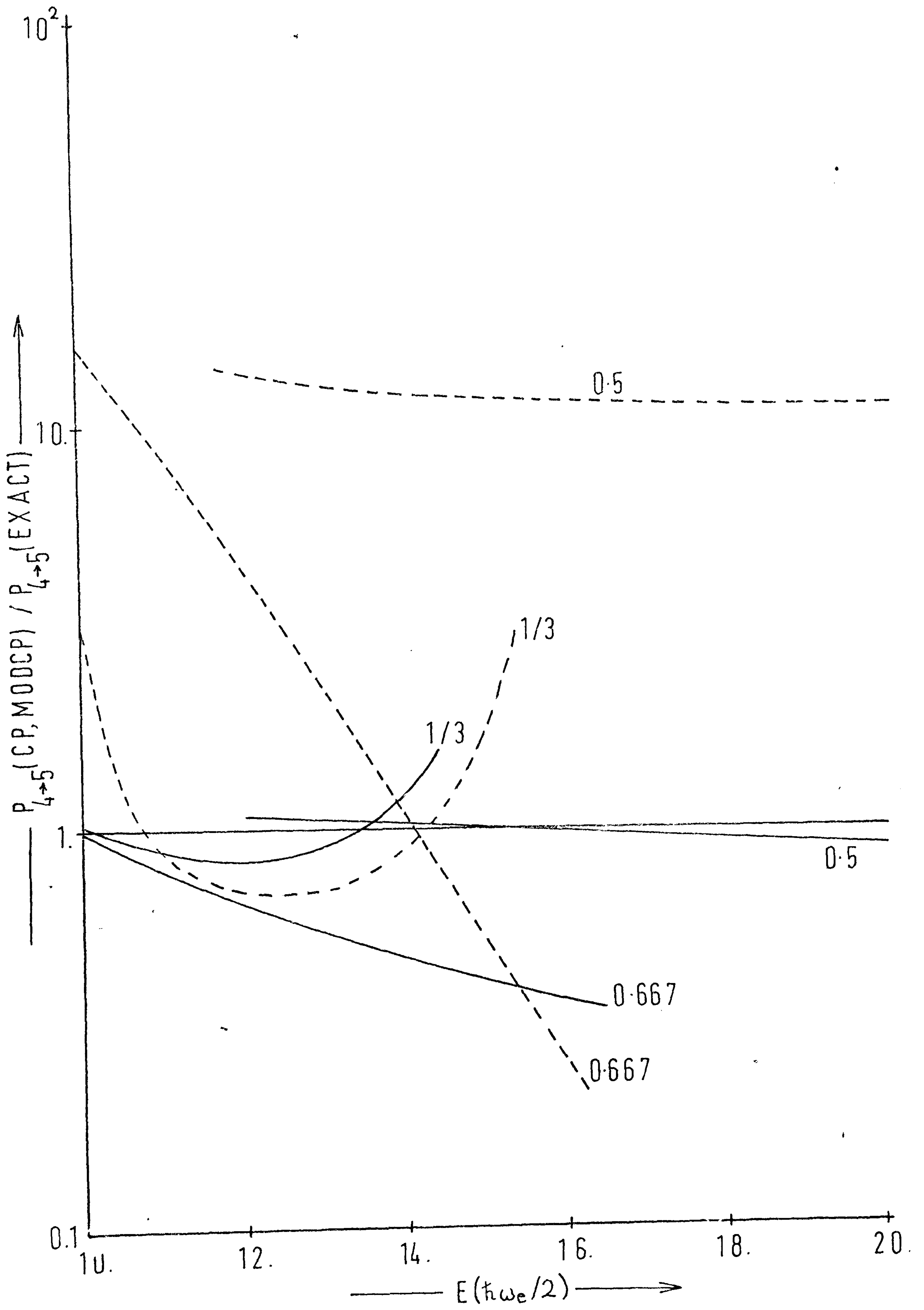


Figure 16

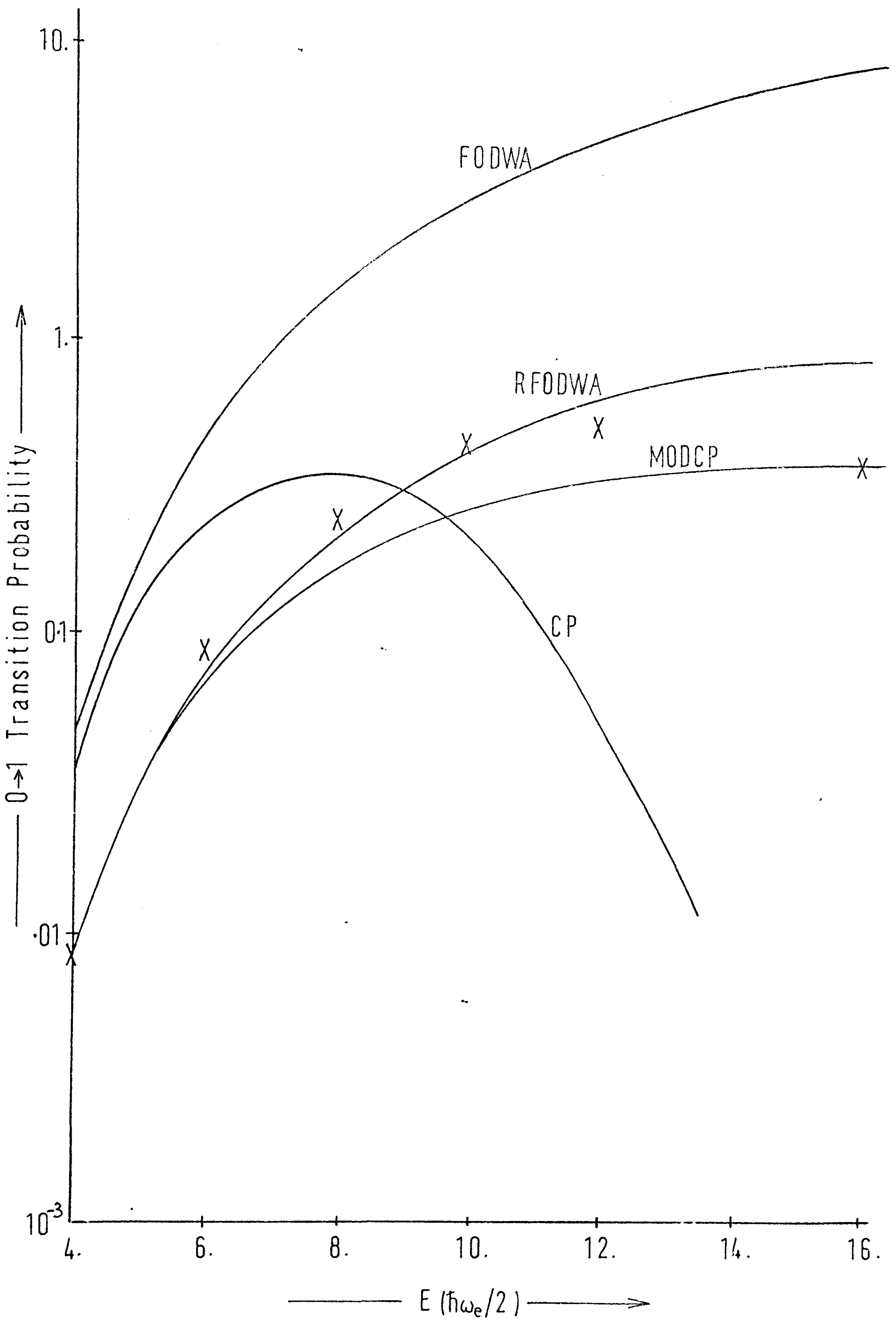
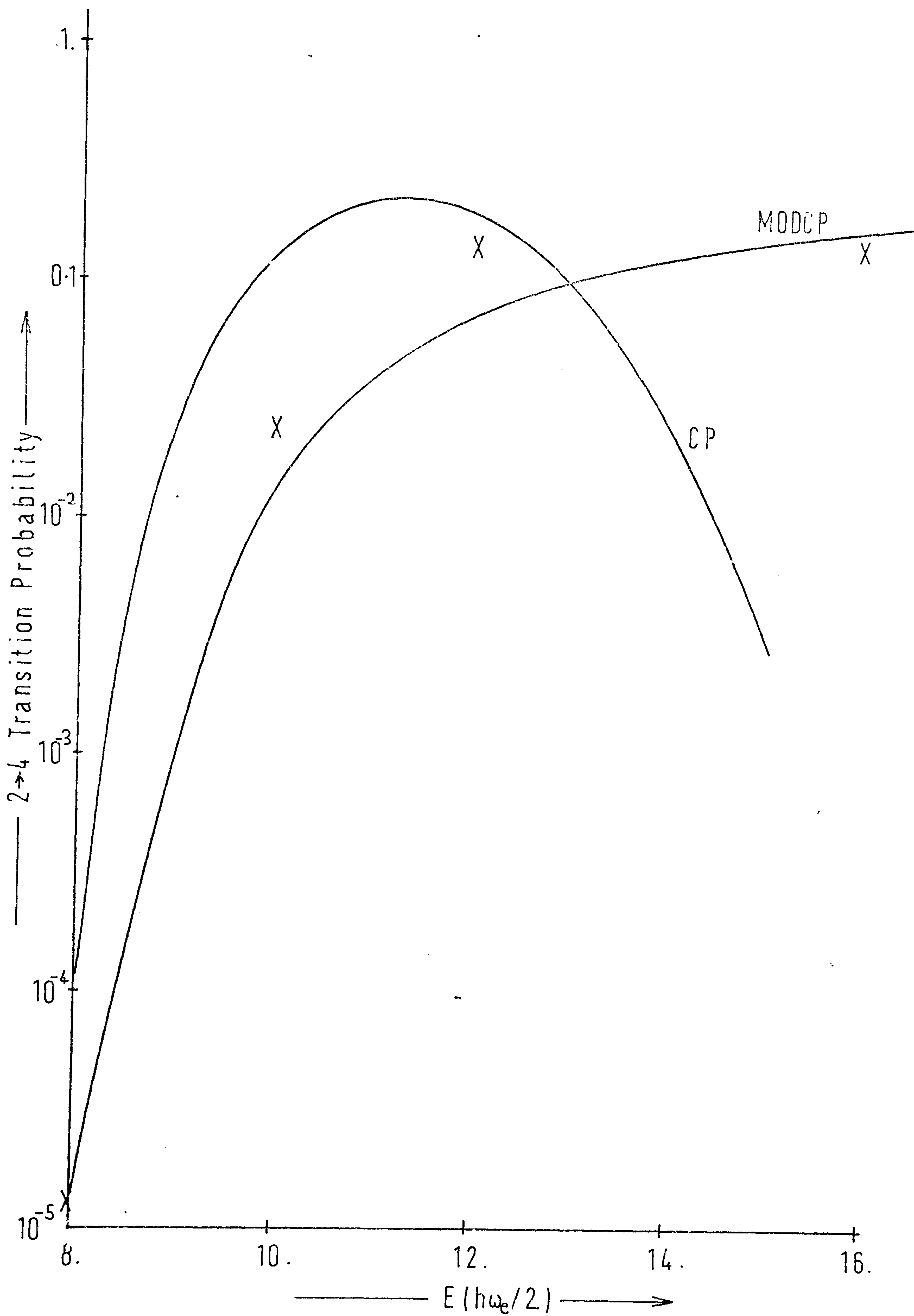


Figure 17



APPENDIX A

MODIFIED QUADRATURE WEIGHTS

The integral in equation (2.4)

$$I(x) = \int_{-\infty}^{\infty} \cos(k_L x_>) \sin(k_L x_<) H_{LI}(x') dx'$$

where  $x_<$ ,  $x_>$  are the lesser, greater respectively of  $x$  and  $x'$ , is replaced by the M point quadrature (2.5)

$$I(x_i) \approx \sum_{j=1}^M \omega_{ij}(l) \cos(k_L x_>) \sin(k_L x_<) H_{LI}(x_j)$$

A fixed step Simpson's rule is employed for the quadrature except that the quadrature weights

$\omega_{ij}(l)$  require modification due to the discontinuous derivatives of the integrand.

If the discontinuity occurs at the end point of a three point Simpson's rule then there is no difficulty. This is for  $i=j$  (odd) and normal Simpson's weights may be used. However, if the discontinuity occurs at the centre of the three point rule, that is for  $i=j$  (even), then, as Secrest and Johnson (1966) point out, the normal Simpson's rule gives poor results.

Assuming the discontinuity occurs at the point

$x = x_i$ , consider the integral of the form

$$Q(x_i) = \int_{x_i-h}^{x_i+h} f(x) H(x) dx$$

where it is assumed that  $H(x)$  is a smooth function in this range and that

$$\begin{aligned} f(x) &= f_1(x) = \sin(k_L x) \cos(k_L x_i) & x_i > x \\ &= f_2(x) = \sin(k_L x_i) \cos(k_L x) & x > x_i \end{aligned}$$

Expanding  $f(x)H(x)$  in a Taylor series around the point  $x = x_i$  gives

$$\begin{aligned} f(x)H(x) &= f_1(x)H(x) = a_0 + a_1(x-x_i) + a_2(x-x_i)^2 + \dots \quad x < x_i \\ &= f_2(x)H(x) = a_0 + b_1(x-x_i) + b_2(x-x_i)^2 + \dots \quad x > x_i \end{aligned}$$

where 
$$a_n = \left[ \frac{d^n}{dx^n} (f_1(x)H(x)) \right]_{x=x_i} \cdot \frac{1}{n!} \quad (\text{A.1})$$

and 
$$b_n = \left[ \frac{d^n}{dx^n} (f_2(x)H(x)) \right]_{x=x_i} \cdot \frac{1}{n!} \quad (\text{A.2})$$

Then

$$\begin{aligned} Q(x_i) &= \int_{x_i-h}^{x_i} f_1(x)H(x) dx + \int_{x_i}^{x_i+h} f_2(x)H(x) dx \\ &= 2a_0 h + (b_1 - a_1) \frac{h^2}{2} + (b_2 + a_2) \frac{h^3}{3} + (b_3 - a_3) \frac{h^4}{4} + \dots \end{aligned}$$

It is now assumed that Simpson's rule may be applied to  $Q(x_i)$ , giving

$$\begin{aligned} Q(x_i) \approx Q^A(x_i) &= \frac{1}{3} h \left[ f_1(x_i-h)H(x_i-h) + 4 f_1(x_i)H(x_i) \right. \\ &\quad \left. + f_2(x_i+h)H(x_i+h) + C \right] \end{aligned}$$

where  $C$  is a correction term, taking into account the discontinuous derivatives of  $f(x)H(x)$ .

Thus

$$\begin{aligned} Q^A(x_i) &= 2a_0 h + (b_1 - a_1) \frac{h^2}{3} + (b_2 + a_2) \frac{h^3}{3} \\ &\quad + (b_3 - a_3) \frac{h^4}{3} + C \frac{h}{3} + \dots \end{aligned}$$

Comparing  $Q(x_i)$  and  $Q^A(x_i)$  gives

$$C = \frac{h}{2} (b_1 - a_1) - \frac{h^3}{4} (b_3 - a_3) + \dots$$

Thus  $C \simeq \frac{h}{2} (b_1 - a_1)$ .

The contribution to  $Q^A(x_i)$ , due to the discontinuity is thus of order  $h^2$ . It should be noted that there is no contribution to  $Q^A(x_i)$  due to the discontinuous second derivative of  $f(x)H(x)$ . The correction involving  $(b_3 - a_3)$  is of order  $h^4$  and to be consistent should be included in  $C$ , since the error in Simpson's rule is of order  $h^5$ .  $(b_3 - a_3)$  however involves the second derivative of  $H(x)$  which is not known. From (A1) and (A2)

$$C \simeq \frac{h}{2} \left\{ \left[ \frac{d}{dx} (f_2(x)H(x)) \right]_{x=x_i} - \left[ \frac{d}{dx} (f_1(x)H(x)) \right]_{x=x_i} \right\}$$

$$C \simeq -\frac{h}{2} k_L H(x_i)$$

giving

$$Q^A(x_i) = \frac{1}{3} h \left[ f_1(x_i - h) H(x_i - h) \right. \\ \left. + \left( 4 - \frac{k_L h}{2 \sin(k_L x_i) \cos(k_L x_i)} \right) f_1(x_i) H(x_i) \right. \\ \left. + f_2(x_i + h) H(x_i + h) \right]$$

Using a modified rule of this form, although with a different integrand, Secrest and Johnson (1966) reported a reduction, in the number of points required in the quadrature, of the order of 80% to 90% of that required for the normal Simpson's

rule. This shows that the major contribution to the integral comes from the region near the discontinuity.

APPENDIX B

## ESCALATOR INVERSION METHOD FOR PARTITIONED MATRICES

The method discussed here is a generalisation of the escalator method discussed by Fröberg (1966).

Suppose the  $(M+N) \times (M+N)$  matrix  $\underline{\underline{A}}$  is partitioned as follows,

$$\underline{\underline{A}} = \left( \begin{array}{c|c} \underline{\underline{A}}_1 & \underline{\underline{A}}_2 \\ \hline \underline{\underline{A}}_3 & \underline{\underline{a}} \end{array} \right)$$

where  $\underline{\underline{A}}_1$  is an  $M \times M$  matrix  
 $\underline{\underline{A}}_2$  is an  $M \times N$  matrix  
 $\underline{\underline{A}}_3$  is an  $N \times M$  matrix  
 $\underline{\underline{a}}$  is an  $N \times N$  matrix

Let the inverse of  $\underline{\underline{A}}$  be partitioned in a similar way.

$$\underline{\underline{A}}^{-1} = \left( \begin{array}{c|c} \underline{\underline{X}}_1 & \underline{\underline{X}}_2 \\ \hline \underline{\underline{X}}_3 & \underline{\underline{x}} \end{array} \right)$$

Then since  $\underline{\underline{A}}\underline{\underline{A}}^{-1} = \underline{\underline{I}}$

$$\underline{\underline{A}}_1 \underline{\underline{X}}_1 + \underline{\underline{A}}_2 \underline{\underline{X}}_3 = \underline{\underline{I}} \quad (\text{B1})$$

$$\underline{\underline{A}}_1 \underline{\underline{X}}_2 + \underline{\underline{A}}_2 \underline{\underline{x}} = \underline{\underline{O}} \quad (\text{B2})$$

$$\underline{\underline{A}}_3 \underline{\underline{X}}_1 + \underline{\underline{a}} \underline{\underline{X}}_3 = \underline{\underline{O}} \quad (\text{B3})$$

$$\underline{\underline{A}}_3 \underline{\underline{X}}_2 + \underline{\underline{a}} \underline{\underline{x}} = \underline{\underline{I}} \quad (\text{B4})$$

where the order of the unit and zero matrices is not explicitly shown.

(B2) gives

$$\underline{\underline{X}}_2 = - \underline{\underline{A}}_1^{-1} \underline{\underline{A}}_2 \underline{\underline{x}} \quad (\text{B5})$$



From (B5) and (B4)

$$\underline{x} = (\underline{a} - \underline{A}_3 \underline{A}_1^{-1} \underline{A}_2)^{-1} \quad (\text{B6})$$

(B1) gives

$$\underline{X}_1 = \underline{A}_1^{-1} (\underline{I} - \underline{A}_2 \underline{X}_3) \quad (\text{B7})$$

From (B3) and (B7)

$$\underline{X}_3 = - (\underline{a} - \underline{A}_3 \underline{A}_1^{-1} \underline{A}_2)^{-1} \underline{A}_3 \underline{A}_1^{-1} \quad (\text{B8})$$

From (B8) and (B1)

$$\underline{X}_1 = \underline{A}_1^{-1} \left( \underline{I} + \underline{A}_2 (\underline{a} - \underline{A}_3 \underline{A}_1^{-1} \underline{A}_2)^{-1} \underline{A}_3 \underline{A}_1^{-1} \right) \quad (\text{B9})$$

Thus if  $\underline{A}_1^{-1}$  is assumed to be known then

$$\underline{A}^{-1} = \left( \begin{array}{c|c} \underline{X}_1 & \underline{X}_2 \\ \hline \underline{X}_3 & \underline{x} \end{array} \right)$$

where

$$\begin{aligned} \underline{x} &= (\underline{a} - \underline{A}_3 \underline{A}_1^{-1} \underline{A}_2)^{-1} \\ \underline{X}_1 &= \underline{A}_1^{-1} (\underline{I} + \underline{A}_2 \underline{x} \underline{A}_3 \underline{A}_1^{-1}) \\ \underline{X}_2 &= - \underline{A}_1^{-1} \underline{A}_2 \underline{x} \\ \underline{X}_3 &= - \underline{x} \underline{A}_3 \underline{A}_1^{-1} \end{aligned}$$

This is the result used in equation (3.8).

APPENDIX C

## A NOTE ON THE MORSE AND LA BRECQUE RESULTS

Morse and La Brecque (1971) have extended the semi-classical ITFITS approximation of Heidrich et. al. (1971) to the Morse oscillator. The ITFITS approximation essentially assumes that the classical motion of atom A (Figure 1) may be calculated assuming the binding potential of the molecule to be negligible (Clark 1971).

The effect of atom A on the molecule B-C, may then be approximately represented by some time dependent forcing function  $F(t)$ . Using an iterative procedure, where at the  $j^{\text{th}}$  iteration the Morse oscillator is approximated by a harmonic oscillator of frequency  $\omega_j$ , Morse and La Brecque obtain a solution of the classical equation of motion for a Morse oscillator perturbed by a time dependent force  $F(t)$ . They then obtain transition probabilities by substituting the classical energy transferred to the oscillator into the quantum mechanical analytic form for the transition probabilities of a harmonic oscillator perturbed by a force  $F(t)$ .

In the notation of Morse and La Brecque, at the  $(j+1)^{\text{th}}$  iteration the frequency  $\omega_{j+1}$  is given by

$$\omega_{j+1} = \frac{\omega_0}{2\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \exp\left(-\sqrt{\frac{\epsilon_j}{\mu}} (\omega_j L)^{-1} \sin(\omega_j t)\right) d(\omega_j t)$$

giving with their equation (6),

$$\omega_{j+1} = \omega_0 I_0 \left\{ \sqrt{\frac{\epsilon_j}{2D}} \left(\frac{\omega_0}{\omega_j}\right) \beta \right\}$$

where  $I_0(x)$  is the modified Bessel function of order zero (Abramowitz and Stegun, 1965). This is not in agreement with their equation (15). Moreover since  $E_t$ , the total energy of the system, is measured in units of  $\hbar\omega_j$ , their equation (22) should read

$$E_0(j) = \frac{1}{4} \left\{ \left(E_t\left(\frac{\omega}{\omega_j}\right) - i - \frac{1}{2}\right)^{\frac{1}{2}} + \left(E_t\left(\frac{\omega}{\omega_j}\right) - f - \frac{1}{2}\right)^{\frac{1}{2}} \right\}^2$$

where the velocity averaged translational energy,

$E_0(j)$  is measured in units of  $\hbar\omega_j$ . In their equation (20)  $\omega_0$  should be replaced by  $\omega$  since  $\alpha$  is not a function of the initial or final state of the oscillator.  $\omega$  of Morse and La Brecque is equivalent to  $\omega_e$  of this thesis.

With or without these corrections it was still found impossible to reproduce the results presented by Morse and La Brecque.

REFERENCES

- Abramowitz, M. and Stegun, I.A., 1965, Handbook of  
Mathematical Functions (New York:Dover).
- Bates, D.R., 1961, ed. Quantum Theory 1. Elements  
(New York and London: Academic Press).
- Calogero, F., 1967, Variable Phase Approach to Potential  
Scattering (London: Academic Press).
- Chan, S.K., Light J.C. and Lin J.L., 1968, J. Chem.  
Phys., 49, 86-97.
- Cheung, A.S. and Wilson, D.J., 1969, J. Chem.Phys.,  
51, 4733-43.
- Clark, A.P., 1971, M.Sc. Thesis, University of Stirling.
- Clark, A.P., 1973, J. Phys.B:Atom. Molec.Phys., 6,  
1153-64.
- Clark, A.P. and Dickinson, A.S., 1971, J.Phys.B:  
Atom.Molec.Phys., 4, L112-116.
- Clark, A.P. and Dickinson, A.S., 1973, J.Phys.B:  
Atom.Molec.Phys., 6, 164-80.
- Eastes, W. and Secrest, D., 1972, J.Chem.Phys., 56,  
640-49.

Fröberg, C.E., 1966, Introduction to Numerical Analysis, (London: Addison-Wesley).

Gol'dman, I.I. and Krivchenkov, V.D., 1961, Problems in Quantum Mechanics (London: Pergamon Press).

Gordon, R.G., 1969, J.Chem.Phys., 51, 14-25.

Gordon, R.G., 1971, Meth.Comp.Phys., 10, 81-109.

Gordon, R.G., Klemperer, W. and Steinfeld, J.I., 1968, Ann.Rev.Phys.Chem., 19, 215-50.

Gutschick, V.P., McKoy, V and Diestler, D.J., 1970, J. Chem. Phys., 52, 4807-17.

Hayes, E.F. and Kouri, D.J., 1971a J.Chem.Phys., 54, 878-90.

Hayes, E.F. and Kouri, D.J., 1971b, Phys.Rev.A., 4, 1017-25.

Heidrich, F.E., Wilson, K.R. and Rapp, D., 1971, J.Chem.Phys., 54, 3885-97.

Heisenberg, W., 1925, Z.Phys., 33, 897. Sources of Quantum Mechanics, ed. B.L.van der Waerden (Amsterdam, North Holland, 1967).

Hunding, A., 1970, Chem.Phys. Lett., 6, 444-6.

Jackson, J.M. and Mott, N.F., 1932, Proc. Roy. Soc.,  
A137, 703-17.

Johnson, B.R. and Secrest, D., 1966, J.Math.Phys., 7,  
2187-95.

Johnson, B.R. and Secrest, D., 1968, J.Chem.Phys., 48,  
4682-93.

Kerner, E., 1958, Can.J.Phys., 36, 371-7.

Landau, L.D. and Teller, E., 1936, Phys. Z. Sowjetunion,  
10, 34-43.

Mahan, B., 1970, J. Chem. Phys., 52, 5221-25.

Mies., F.H., 1964a, J.Chem.Phys., 40, 523-31.

Mies., F.H. 1964b, J.Chem.Phys., 41, 903-4.

Morse, R.I. and La Brecque, R.J., 1971, J.Chem.Phys.,  
55, 1522-30.

Mott, N.F. and Massey, H.S.W., 1965, The Theory of  
Atomic Collisions (Oxford:Clarendon Press).

Naccache, P.F., 1972, J.Phys.B:Atom.Molec.Phys., 5, 1308-19.

Percival, I.C. and Richards, D., 1970a, J.Phys.B:Atom  
Molec.Phys., 3, 1035-46.

Percival, I.C. and Richards, D., 1970b, Astrophys.  
Lett., 4, 235-7.

Percival, I.C. and Richards, D., 1971, J.Phys.B.:Atom.  
Molec.Phys., 4, 918-31, 932-39.

Popov, V.S. and Perelemov, A.M., 1969, Sov.Phys.  
JETP, 29, 738-45.

Presnyakov, L.P. and Urnov, A.M., 1970, J. Phys. B:  
Atom. Molec. Phys., 3, 1267-71.

Rapp, D. and Kassal, T., 1969, Chem. Rev., 69, 61-102.

Richards, D., 1972, J. Phys. B:AtomMolec.Phys., 5,  
L53-55.

Riley, M.E. and Kupperman, A., 1968, Chem.Phys. Lett.,  
1, 537-38.

Rodberg, L.S. and Thaler, R.M., 1967, Introduction to  
the Quantum Theory of Scattering (London:  
Academic Press).

Rosen, N., 1933, J. Chem. Phys., 1, 319-26.

Sams, W.N. and Kouri, D.J., 1970, J. Chem. Phys.,  
53, 496-501.

Secrest, D., 1971, Meth.Comp.Phys., 10, 243-86.

Secrest, D. and Johnson, B.R., 1966, J.Chem.Phys.,  
45, 4556-70.

Treanor, C.E., 1965, J. Chem. Phys., 43, 532-38.



# Collinear collision of an atom and a morse oscillator: exact quantum mechanical results

A P Clark and A S Dickinson

Department of Physics, University of Stirling, Stirling, Scotland

MS received 31 July 1972

**Abstract.** Exact quantum mechanical vibrational transition probabilities are obtained for a collinear atom–diatomic molecule collision using the reactance matrix  $\mathbf{K}$ . Both the Morse and harmonic binding potentials are considered and it is shown that the transition probabilities for the Morse oscillator may differ considerably from the equivalent harmonic oscillator results. The exact transition probabilities are compared with those of several approximate theories, and it is shown that the revised first order distorted wave approximation of Mies is valid, provided that the scaled reduced mass ( $m$ ) of the incident atom is not large.

## 1. Introduction

Recent reviews of collinear atom–diatomic molecule collisions have been given by Takayanagi (1963, 1965) and Rapp and Kassal (1969). In much of the previous work, the binding potential of the diatomic molecule has been approximated by a harmonic potential. However, it was shown by Mies (1964a), using the more realistic Morse binding potential, that in the distorted wave approximation (DWA), the use of the harmonic potential may result in the vibrational transition probabilities of the molecule being greatly overestimated. Hunding (1970), presenting an exact, but very limited, comparison of the Morse and harmonic oscillator transition probabilities concluded that the discrepancy between them was not as great as that predicted by the DWA.

The main purpose of this paper is to present a detailed comparison of the exact results for the excitation of the Morse and harmonic oscillators and to examine the range of validity of several approximate theories.

The collision problem, shown in figure 1, is formulated in § 2. In §§ 3 and 4 a solution is obtained for the reactance matrix  $\mathbf{K}$  (Mott and Massey 1965) and it is shown that the amplitude density function method of Johnson and Secrest (1966) results from a particular matrix inversion technique. The computational details are discussed in § 5.

The exact Morse and harmonic oscillator transition probabilities are presented in § 6 and compared with the distorted wave approximations of Jackson and Mott (1932), Mies (1964a) and the semi-classical approximations of Mies (1964b) and Morse and LaBrecque (1971).

## 2. Formulation of the collision problem

The collision problem (Rapp and Kassal 1969) is shown in figure 1. All three atoms are constrained to move along the line defined by the molecular axis BC. The incoming

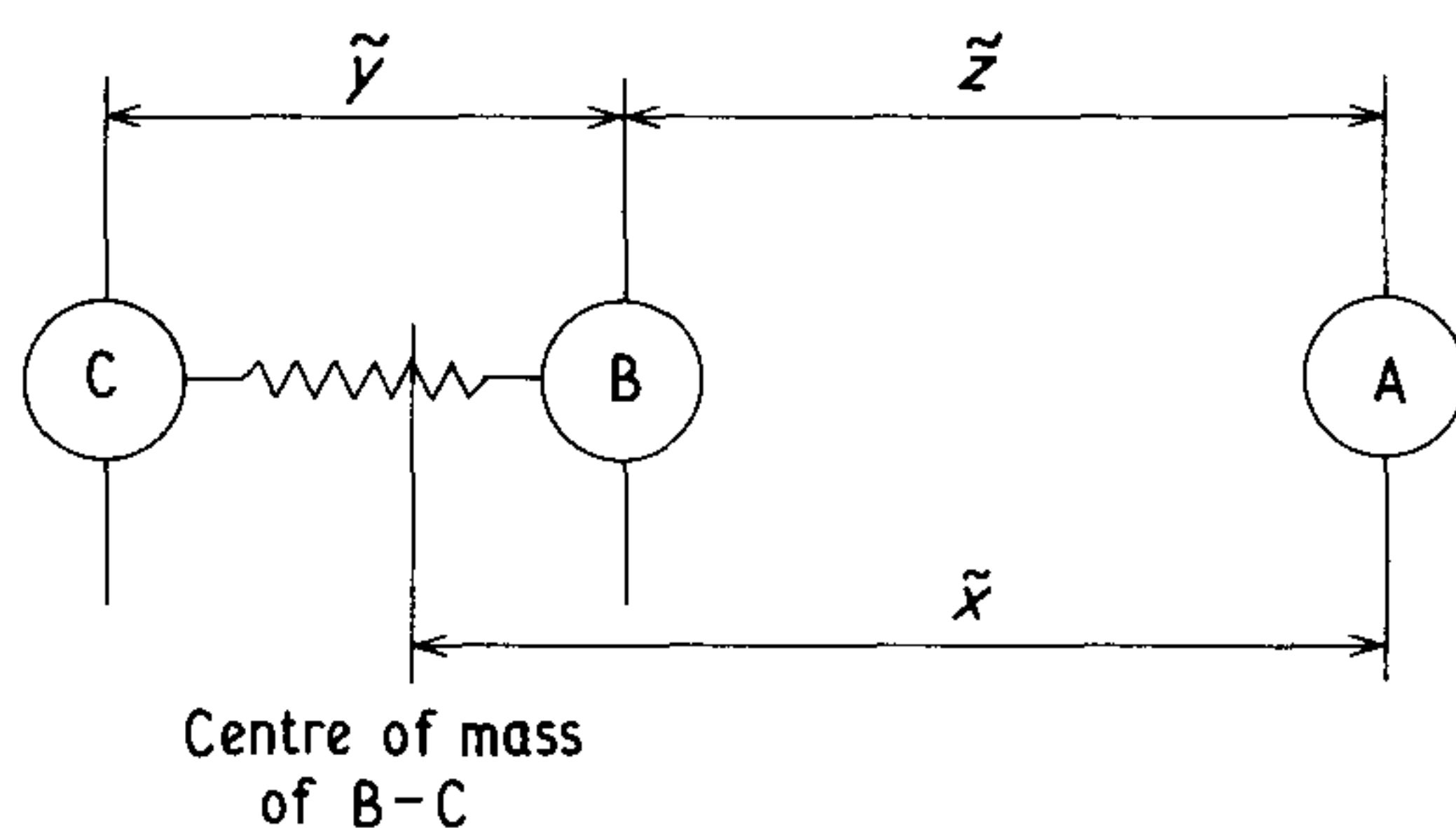


Figure 1. The collinear atom-molecule collision.

atom A is reflected by the repulsive core of the potential  $\tilde{V}_{AB}(\tilde{z})$ , between atoms A and B only, and atoms B and C are bound by the potential  $\tilde{V}_{BC}(\tilde{y})$  where  $\tilde{y}$  and  $\tilde{z}$  are the BC and AB separations respectively.

We consider both the Morse (1929) and the harmonic binding potentials which have the form,

$$\tilde{V}_{BC}(\tilde{y}) = \tilde{D}_e [\exp\{-a(\tilde{y} - \tilde{y}_{eq})\} - 1]^2 \quad (1a)$$

and

$$\tilde{V}_{BC}(\tilde{y}) = \frac{1}{2}f(\tilde{y} - \tilde{y}_{eq})^2 \quad (1b)$$

where  $\tilde{y}_{eq}$  is the equilibrium separation of BC,  $\tilde{D}_e$  and  $a$  are the Morse potential well depth and steepness parameter respectively and  $f$  is the harmonic oscillator force constant.

The collision problem is most conveniently expressed in terms of the dimensionless coordinates,  $(x, y)$  where,

$$\begin{aligned} \tilde{y} &= (\hbar/\tilde{\mu}\omega_e)^{1/2}y + \tilde{y}_{eq} \\ \tilde{x} &= \gamma\{(\hbar/\tilde{\mu}\omega_e)^{1/2}x + \tilde{y}_{eq}\} \end{aligned}$$

and

$$\begin{aligned} \tilde{\mu} &= m_B m_C / (m_B + m_C) \\ \gamma &= m_C / (m_B + m_C) \\ \omega_e &= (2\tilde{D}_e/\tilde{\mu})^{1/2} \quad a = (f/\tilde{\mu})^{1/2} \end{aligned}$$

the subscripted  $m$  denoting the respective masses of the three atoms.

The Schrödinger equation may then be written (Secret and Johnson 1966)

$$\left( -\frac{1}{2m} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + V_{BC}(y) + V_{AB}(z) \right) \psi = \frac{1}{2}E\psi. \quad (2)$$

The scaled reduced mass  $m = m_A m_C / m_B(m_A + m_B + m_C)$ ,  $E$  is the total energy of the system in units of  $\frac{1}{2}\hbar\omega_e$  and  $z = x - y$ . In these coordinates (1a) and (1b) become,

$$\begin{aligned} V_{BC}(y) &= D_e [\exp\{-y/(2D_e)^{1/2}\} - 1]^2 \\ V_{BC}(y) &= \frac{1}{2}y^2 \end{aligned}$$

respectively, where  $D_e = \tilde{D}_e/\hbar\omega_e$ .

We require a solution of (2) satisfying the boundary conditions,

$$\lim_{x \rightarrow \infty} \psi_I(x, y) = \phi_I(y) \exp(-ik_I x) + \sum_n R_{nI} \phi_n(y) \exp(ik_n x) \quad (3a)$$

$$\lim_{x \rightarrow -\infty} \psi_I(x, y) = 0. \quad (3b)$$

The subscript  $I$  denotes that the molecule is initially in the  $I$ th vibrational state and the  $R_{nI}$  are the reflection coefficients (Secret and Johnson 1966), defining the matrix

$$(\mathbf{R})_{nI} = R_{nI}. \quad (4)$$

The normalized eigenfunctions of the unperturbed oscillator  $\phi_n(y)$  satisfy,

$$\left( -\frac{1}{2} \frac{d^2}{dy^2} + V_{\text{BC}}(y) \right) \phi_n(y) = \frac{1}{2} \epsilon_n \phi_n(y)$$

where for bound states,

$$\epsilon_n = 2n + 1 - \frac{1}{2}(n + \frac{1}{2})^2 / D_e$$

$$\epsilon_n = 2n + 1$$

for the Morse and harmonic oscillators respectively. The wavenumbers are given by,

$$k_n = \{m(E - \epsilon_n)\}^{1/2}.$$

The summation (3a) represents a sum over the bound states of the oscillator and additionally, for the Morse oscillator, an integral over the continuum states. However, in the numerical calculations described in this paper it will never be necessary to include the latter.

The probability that the molecule will be found in the  $n$ th vibrational state after the collision has taken place is then,

$$P_{I \rightarrow n} = |R_{nI}|^2 (k_n / k_I).$$

### 3. Solution of the collision problem

As the  $\mathbf{R}$  matrix (4) is in general complex, it is more convenient to use the purely real reactance matrix  $\mathbf{K}$  (Mott and Massey 1965). Consider the solution  $\psi_I^K$  of the Schrödinger equation (2), which satisfies the boundary conditions,

$$\lim_{x \rightarrow \infty} \psi_I^K(x, y) = \phi_I(y) \sin(k_I x) - \sum_n K_{nI} \phi_n(y) \cos(k_n x) \quad (5a)$$

$$\lim_{x \rightarrow -\infty} \psi_I^K(x, y) = 0. \quad (5b)$$

Employing the Green function,

$$G(x, y; x', y') = \sum_n (2m/k_n) \phi_n(y) \phi_n(y') \sin(k_n x_<) \cos(k_n x_>) \quad (6)$$

where  $x_>$ ,  $x_<$  are the greater and lesser, respectively, of  $x$  and  $x'$ , (2) may be rewritten as the integral equation (Rodberg and Thaler 1967),

$$\begin{aligned} \psi_I^K(x, y) = & \phi_I(y) \sin(k_I x) - \sum_n \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (2m/k_n) \phi_n(y) \phi_n(y') \\ & \times V_{\text{AB}}(z') \psi_I^K(x', y') \sin(k_n x_<) \cos(k_n x_>) dx' dy' \end{aligned} \quad (7)$$

where  $z' = x' - y'$ . Defining the amplitude density functions (Secrest and Johnson 1966, Johnson and Secrest 1966),

$$H_{nI}(x) = \int_{-\infty}^{\infty} \phi_n(y) V_{AB}(z) \psi_I^K(x, y) dy$$

the following integral equation is obtained from (7),

$$H_{nI}(x) = \sin(k_I x) V_{nI}(x) - \sum_i (2m/k_i) V_{ni}(x) \int_{-\infty}^{\infty} \sin(k_i x_<) \cos(k_i x_>) H_{iI}(x') dx' \quad (8)$$

where

$$V_{nI}(x) = \int_{-\infty}^{\infty} \phi_n(y) V_{AB}(z) \phi_I(y) dy.$$

The summation in (8) is over all the states of the oscillator. However, for the total energies  $E$  being considered, the sum over the discrete states may be terminated at some number  $(N-1)$ , sufficiently large, such that inclusion of additional states has no significant effect on the transition probabilities. In this sense the transition probabilities obtained are termed 'exact'. The Morse continuum states will not contribute significantly to the transition probability provided that satisfactory convergence has been obtained using only the discrete states.

The solution of the integral equation (8) is now obtained by replacing the integral by an  $M$  point quadrature yielding,

$$H_{nI}(x_i) = \sin(k_I x_i) V_{nI}(x_i) - \sum_{l=0}^{N-1} (2m/k_l) V_{nl}(x_i) \sum_{j=1}^M w_{ij}(l) \cos(k_l x_>) \sin(k_l x_<) H_{lI}(x_j). \quad (9)$$

Simpson's rule is employed for the quadrature except that, following Johnson and Secrest (1966), the weights are taken as,

$$\begin{aligned} w_{ij}(l) &= \text{Normal Simpson weight} & i \neq j \text{ or } i = j \text{ (odd)} \\ &= \frac{1}{3} \Delta x \{4 - \frac{1}{2} k_l \Delta x / \sin(k_l x_j) \cos(k_l x_j)\} & i = j \text{ (even)} \end{aligned}$$

where  $\Delta x$  is the step length. This modification of the quadrature weights makes allowance for the discontinuous derivative of the Green function (6).

An expression for  $\mathbf{K}$  is obtained by comparing the integral equation (7) for  $\psi_I^K$ , in the limit  $x \rightarrow \infty$ , with the boundary condition (5a). In terms of the amplitude density functions and with the integral approximated by an  $M$  point quadrature,

$$(\mathbf{K})_{nI} = K_{nI} = \sum_{j=1}^M w_j (2m/k_n) \sin(k_n x_j) H_{nI}(x_j) \quad (10)$$

where  $w_j$  may be taken as the normal Simpson weights.

Equation (9) is generally a matrix equation of very high order and to solve it directly for the  $H_{nI}(x_i)$  is not practicable. In the following section we present a method for obtaining the  $\mathbf{K}$  matrix at any point in the quadrature, in terms of  $\mathbf{K}$  at the preceding point.

#### 4. The reactance matrix equation

In terms of the  $N \times N$  matrices,  $(\mathbf{H}(x_i))_{nI} = H_{nI}(x_i)$ ,  $(\mathbf{V}(x_i))_{nI} = V_{nI}(x_i)$  and the diagonal matrices  $\mathbf{F}(x_i)$ ,  $\mathbf{G}(x_i)$ ,  $\mathbf{k}$  and  $\mathbf{W}_i(x_j)$  with elements  $\delta_{nI} \sin(k_I x_i)$ ,  $\delta_{nI} \cos(k_I x_i)$ ,  $\delta_{nI} k_I$  and

$\delta_{ni}w_j(I)$  respectively, equation (9) may be written,

$$\mathbf{H}(x_i) = \mathbf{V}(x_i)\mathbf{F}(x_i) - 2m\mathbf{V}(x_i)\mathbf{k}^{-1} \sum_{j=1}^M \mathbf{W}_i(x_j)\mathbf{F}(x_j)\mathbf{G}(x_j)\mathbf{H}(x_j). \quad (11)$$

Defining the generalized column vectors  $\mathbf{h}$ ,  $\mathbf{f}$  by  $(\mathbf{h})_i = \mathbf{H}(x_i)$ ,  $(\mathbf{f})_i = \mathbf{F}(x_i)$  and the matrices  $\mathcal{V}$ ,  $\mathcal{X}$  by  $(\mathcal{V})_{ij} = \delta_{ij}\mathbf{V}(x_i)$  and

$$(\mathcal{X})_{nm} = \begin{cases} w_m \mathbf{F}(x_m)\mathbf{G}(x_n) & m < n \\ w_m \mathbf{F}(x_n)\mathbf{G}(x_m) & m > n \\ \mathbf{W}_n(x_n)\mathbf{F}(x_n)\mathbf{G}(x_n) & m = n \end{cases}$$

equation (11) becomes,

$$\mathbf{h} = \mathcal{V}\mathbf{f} - 2m\mathcal{V}\mathbf{k}^{-1}\mathcal{X}\mathbf{h}.$$

Thus

$$\mathbf{h} = (\mathcal{I} + 2m\mathcal{V}\mathbf{k}^{-1}\mathcal{X})^{-1}\mathcal{V}\mathbf{f} \quad (12)$$

where

$$(\mathcal{I})_{ij} = \delta_{ij}\mathbf{1}.$$

With the generalized row vector  $\mathbf{f}^*$  defined by  $(\mathbf{f}^*)_i = w_i\mathbf{F}(x_i)$  equation (10) becomes

$$\mathbf{K}_M = 2m\mathbf{k}^{-1}\mathbf{f}^*\mathbf{h}$$

with the subscript  $M$  denoting that  $\mathbf{K}$  is obtained from an  $M$  point quadrature. Thus from (12) the  $\mathbf{K}$  matrix is given by

$$\mathbf{K}_M = 2m\mathbf{k}^{-1}\mathbf{f}^*\mathcal{A}_M^{-1}\mathcal{V}\mathbf{f} \quad (13)$$

where

$$\mathcal{A}_M = (\mathcal{I} + 2m\mathcal{V}\mathbf{k}^{-1}\mathcal{X}).$$

The method of Johnson and Secrest (1966) is essentially equivalent to determining  $\mathcal{A}_M^{-1}$  by a generalization of the partitioning or escalator method (Fröberg 1966). At the  $L$ th point in the inversion  $\mathcal{A}_L$  may be partitioned into,

$$\mathcal{A}_L = \left( \begin{array}{c|c} \mathcal{A}_{L-1} & \mathcal{A}_2 \\ \hline \mathcal{A}_3 & a \end{array} \right).$$

The inverse of  $\mathcal{A}_L$  is then

$$\mathcal{A}_L^{-1} = \left( \begin{array}{c|c} \mathcal{A}_{L-1}^{-1}(\mathcal{I} + \mathcal{A}_2\mathcal{b}\mathcal{A}_3\mathcal{A}_{L-1}^{-1}) & -\mathcal{A}_{L-1}^{-1}\mathcal{A}_2\mathcal{b} \\ \hline -\mathcal{b}\mathcal{A}_3\mathcal{A}_{L-1}^{-1} & \mathcal{b} \end{array} \right) \quad (14)$$

where

$$\mathcal{b} = (a - \mathcal{A}_3\mathcal{A}_{L-1}^{-1}\mathcal{A}_2)^{-1}.$$

Substituting (14) into (13), for an  $L$  point quadrature  $\mathbf{K}_L$  may be shown to be related to  $\mathbf{K}_{L-1}$  by,

$$\begin{aligned} \mathbf{K}_L &= (\mathbf{1} - w_L\mathbf{D} + \mathbf{W}\mathbf{D})(\mathbf{1} - w_L\mathbf{K}_{L-1}\mathbf{B} + \mathbf{W}\mathbf{D})^{-1} \\ &\quad (\mathbf{K}_{L-1} + \mathbf{W}\mathbf{E} - w_L\mathbf{K}_{L-1}\mathbf{C}) + w_L\mathbf{E} - \mathbf{W}\mathbf{E} \end{aligned} \quad (15)$$

where

$$\mathbf{B} = 2m\mathbf{G}(x_L)\mathbf{k}^{-1}\mathbf{V}(x_L)\mathbf{G}(x_L)$$

$$\mathbf{C} = 2m\mathbf{G}(x_L)\mathbf{k}^{-1}\mathbf{V}(x_L)\mathbf{F}(x_L)$$

$$\mathbf{D} = 2m\mathbf{F}(x_L)\mathbf{k}^{-1}\mathbf{V}(x_L)\mathbf{G}(x_L)$$

$$\mathbf{E} = 2m\mathbf{F}(x_L)\mathbf{k}^{-1}\mathbf{V}(x_L)\mathbf{F}(x_L)$$

$$(\mathbf{W})_{ij} = \delta_{ij}w_{LL}(i).$$

The  $\mathbf{K}$  matrix at any point in the quadratic is thus determined from the  $\mathbf{K}$  matrix at the preceding point, involving only one  $N \times N$  matrix inversion.

This provides a stable method of solving the non-linear matrix differential equation, of a type similar to that introduced by Calogero (1967),

$$\frac{d\mathbf{K}}{dx} = 2m(\mathbf{F} - \mathbf{K}\mathbf{G})\mathbf{k}^{-1}\mathbf{V}(\mathbf{F} - \mathbf{G}\mathbf{K}) \quad (16)$$

with boundary condition,

$$\lim_{x \rightarrow -\infty} (\mathbf{K})_{nI} = \delta_{nI} \tan(k_I x). \quad (17)$$

Comparing the boundary conditions (3a) and (5a) the relation between the  $\mathbf{K}$  and  $\mathbf{R}$  matrices is seen to be,

$$\mathbf{R} = (\mathbf{K} - i\mathbf{1})^{-1}(\mathbf{K} + i\mathbf{1}).$$

## 5. Computation of the $\mathbf{K}$ matrix

In closed channels, when  $k_n$  becomes imaginary, the  $\mathbf{F}$  matrix becomes imaginary and, as  $|x|$  increases, both  $\mathbf{F}$  and  $\mathbf{G}$  diverge exponentially, becoming almost linearly dependent. Despite the use of double precision arithmetic, this exponential behaviour causes serious rounding errors. The modifications necessary to overcome this difficulty and to retain single precision arithmetic with real matrices in closed channels are discussed in Appendix A. In Appendix B a method for speeding the convergence of the  $\mathbf{K}$  matrix for large  $x$  is presented.

The interaction potential  $V_{AB}(z)$  was chosen to be,

$$V_{AB}(z) = V_0 \exp\{-\alpha(x-y)\} \quad (18)$$

where

$$\alpha = \frac{\gamma}{L} \left( \frac{\hbar}{\tilde{\mu}\omega_e} \right)^{1/2}.$$

The parameter  $L$ , determining the 'steepness' of the interaction, may be obtained from experimental data. The value of  $L$  used in all calculations was 0.02 nm.

Since the Schrödinger equation (2), with  $V_{AB}(z)$  given by (18) is invariant under the transformation  $x \rightarrow x + \delta$ ,  $V_0 \rightarrow V_0 \exp(\alpha\delta)$ , where  $\delta$  is a constant, the transition probabilities are independent of  $V_0$ . However, the value chosen will determine the position of the first quadrature point  $x_1$ , since  $x_1$  must lie far enough into the classically inaccessible region to approximate the boundary condition (5b). The  $\mathbf{K}$  matrix will then be given by (17). The matrix elements  $V_{ij}(x) = V_0 \exp(-\alpha x)U_{ij}$  may be evaluated easily

and in terms of the reduced parameters are given by,

$$U_{ij} = (4D_e)^{\alpha(2D_e)^{1/2}} \left( \frac{i! \Gamma(4D_e - i)}{j! \Gamma(4D_e - j)} (4D_e - 1 - 2i)(4D_e - 1 - 2j) \right)^{1/2} \\ \times \sum_{l=0}^i \frac{(-1)^{l+i-j} \Gamma\{1 + \alpha(2D_e)^{1/2} + i - l\} \Gamma\{4D_e - 1 - \alpha(2D_e)^{1/2} - i - j + l\}}{l!(i-l)! \Gamma\{1 + \alpha(2D_e)^{1/2} + i - j - l\} \Gamma(4D_e - 2i + l)}$$

and

$$U_{ij} = \left( \frac{i!}{j!} \right)^{1/2} \left( \frac{\alpha}{2^{1/2}} \right)^{j-i} \exp(+\frac{1}{4}\alpha^2) \mathcal{L}_i^{j-i}(-\frac{1}{2}\alpha^2)$$

for the Morse and harmonic oscillators respectively, where  $\mathcal{L}_n^m(x)$  and  $\Gamma(x)$  are the Associated Laguerre polynomial and Gamma function respectively (Abramowitz and Stegun 1968).

The programs used to evaluate the transition probabilities, presented in this paper, were checked by reproducing the results of both Secrest and Johnson (1966) and Hunding (1970). For the majority of the Secrest and Johnson results, agreement was found to three significant figures. However, discrepancies of the order of a few percent were noted for particular large values of  $E$ , where 11 or 12 channels were required. Hunding did not explicitly specify the collision parameters ( $m$ ,  $\alpha$ ,  $D_e$ ) employed, and agreement could only be obtained to within 10%.

The transition probabilities presented in the next section are believed to be accurate to about one percent. A sufficient condition for the step length,  $\Delta x$ , to give this degree of accuracy is  $\alpha \Delta x = 0.016$ . At certain energies, with  $m = 3.737$ , over 1500 points were required in the quadrature before the  $\mathbf{K}$  matrix converged. However, less than 600 points were necessary for the other values of  $m$  reported. It was never necessary to include more than two closed channels, to obtain satisfactory convergence of the transition probabilities, and one was usually sufficient.

The evaluation of transition probabilities by the  $\mathbf{K}$  matrix method of this paper, was found to be approximately four times faster than by the  $\mathbf{R}$  matrix method of Secrest and Johnson (1966).

Sams and Kouri (1969) have presented a method for solving the integral equation (8), not involving matrix inversions at each step, and initial tests suggest that it is approximately twice as fast as the  $\mathbf{K}$  matrix method presented here. A direct application of the Sams and Kouri method is impracticable, even when only open channels are retained, due to rounding errors. It has, however, been used successfully in a modified form by Eastes and Secrest (1972) and is discussed in detail by Secrest (1971).

## 6. Results and discussion

Transition probabilities,  $P_{I \rightarrow F}$ , for the transition from state I to state F, are presented in tables 1–5 as a function of the total energy  $E$  (in units of  $\frac{1}{2}\hbar\omega_e$ ). The exact, equivalent harmonic oscillator transition probabilities are shown directly below the Morse results. In most cases very small transition probabilities, less than  $10^{-11}$ , have not been included.

The five collisions considered cover a wide range, from relatively light to heavy incident atoms and from shallow to deep molecular potential well depths. The parameters ( $m$ ,  $\alpha$ ,  $D_e$ ) given by (0.006268, 0.1278, 75.525), ( $\frac{1}{3}$ , 0.314, 9.3), ( $\frac{1}{2}$ , 0.114, 40.81),

Table 1.  $H_2 + He$ 

$E$	$P_{1 \rightarrow F}$	0-1	1-2	0-2	0-3	1-3	2-3	0-4	1-4
4		2.46(-4)† 7.20(-4)							
6		7.31(-3) 2.95(-2)	1.25(-3) 1.42(-3)	2.30(-6) 1.07(-5)					
8		3.15(-2) 1.33(-1)	2.28(-2) 5.50(-2)	1.85(-4) 2.04(-3)	1.18(-7) 4.96(-7)	3.07(-5) 3.07(-5)	5.29(-3) 2.10(-3)		1.37(-11)
10		7.39(-2) 2.92(-1)	8.15(-2) 2.17(-1)	1.66(-3) 2.25(-2)	1.17(-5) 2.31(-4)	1.22(-3) 5.39(-3)	5.47(-2) 7.70(-2)	1.95(-8) 4.26(-8)	3.12(-6) 1.80(-6)
12		1.29(-1) 4.28(-1)	1.67(-1) 3.69(-1)	6.65(-3) 9.13(-2)	1.49(-4) 4.71(-3)	8.41(-3) 5.24(-2)	1.58(-1) 2.68(-1)	1.48(-6) 3.65(-5)	1.38(-4) 7.69(-4)
16		2.45(-1) 4.07(-1)	3.18(-1) 1.56(-1)	3.38(-2) 3.30(-1)	2.72(-3) 9.88(-2)	5.72(-2) 2.85(-1)	3.34(-1) 1.89(-1)	1.61(-4) 1.06(-2)	5.16(-3) 7.32(-2)

$E$	$P_{1 \rightarrow F}$	2-4	3-4	0-5	1-5	2-5	3-5	4-5	5-6
8		4.68(-9)	3.51(-6)						
10		2.77(-4) 5.85(-5)	1.92(-2) 2.76(-3)		2.95(-10)	3.65(-8)	4.47(-6)	9.12(-4)	
12		5.64(-3) 9.55(-3)	1.17(-1) 9.59(-2)	4.95(-9) 5.45(-9)	7.01(-7) 1.84(-7)	4.56(-5) 4.11(-6)	1.98(-3) 9.28(-5)	5.97(-2) 3.40(-3)	1.30(-2)
16		6.39(-2) 2.21(-1)	3.32(-1) 3.04(-1)	7.44(-6) 3.31(-4)	3.24(-4) 4.04(-3)	5.77(-3) 2.58(-2)	5.76(-2) 1.09(-1)	3.17(-1) 3.12(-1)	2.84(-1) 1.27(-1)

$$m = 0.667, \quad \alpha = 0.314, \quad D_e = 9.3.$$

† The number in parentheses indicates the power of 10 by which the entry should be multiplied. The upper, lower numbers are the Morse, harmonic results respectively.

(0.667, 0.314, 9.3) and (3.737, 0.5584, 14.652) approximately represent the collisions  $Br_2 + (H_2)$ ,  $H_2 + H$ ,  $N_2 + (N_2)$ ,  $H_2 + He$  and  $HBr + He$  (with Br representing atom C in figure 1) respectively. The parentheses around  $H_2$  and  $N_2$  indicate structureless incident particles of mass equivalent to a hydrogen and nitrogen molecule respectively.

The exact, equivalent harmonic oscillator transition probabilities and several approximate calculations are compared with the exact  $0 \rightarrow 1$  Morse transition probabilities in figures 2(a)–2(d). In figure 3 the ratio of exact calculations of  $P_{0 \rightarrow 1}$  for a Morse oscillator to  $P_{0 \rightarrow 1}$  for a harmonic oscillator is shown as a function of  $D_e$  for several values of  $m$ .

### 6.1. A comparison of the exact transition probabilities for the Morse and harmonic oscillators

A comparison between the exact Morse and harmonic oscillator transition probabilities, in the region before the first maximum, shows that the Morse results are generally smaller than those of the equivalent harmonic oscillator, for transitions within the first



Table 2. H<sub>2</sub> + H

$E$	$P_{1 \rightarrow F}$	0-1	1-2	0-2	0-3	1-3	2-3	0-4	1-4
4		8.59(-3)† 1.09(-2)							
6		9.57(-2) 1.51(-1)	3.04(-2) 1.99(-2)	7.82(-4) 8.26(-4)					
8		2.49(-1) 3.91(-1)	2.11(-1) 2.27(-1)	1.79(-2) 3.44(-2)	2.05(-4) 1.26(-4)	5.63(-3) 2.05(-3)	8.39(-2) 2.75(-2)	8.02(-9)	3.73(-7)
10		3.80(-1) 5.16(-1)	3.71(-1) 3.91(-1)	7.95(-2) 1.73(-1)	5.56(-3) 1.01(-2)	6.95(-2) 7.00(-2)	3.23(-1) 2.66(-1)	1.03(-4) 2.80(-5)	2.32(-3) 3.76(-4)
12		4.31(-1) 4.32(-1)	3.26(-1) 2.04(-1)	1.79(-1) 3.63(-1)	3.22(-2) 8.02(-2)	2.01(-1) 2.52(-1)	3.15(-1) 3.10(-1)	2.57(-3) 3.51(-3)	3.22(-2) 2.49(-2)
16		3.21(-1) 1.05(-1)	2.26(-2) 1.12(-1)	3.22(-1) 3.34(-1)	1.68(-1) 3.78(-1)	2.24(-1) 7.75(-2)	7.28(-4) 6.55(-2)	5.18(-2) 1.54(-1)	2.02(-1) 2.67(-1)

$E$	$P_{1 \rightarrow F}$	2-4	3-4	0-5	1-5	2-5	3-5	4-5	5-6
8		1.22(-5)	5.25(-4)						
10		2.65(-2) 3.44(-3)	1.89(-1) 3.40(-2)	1.52(-7)	5.00(-6)	9.59(-5)	1.52(-3)	2.53(-2)	
12		1.64(-1) 9.95(-2)	3.49(-1) 2.85(-1)	8.00(-5) 7.86(-6)	1.58(-3) 9.47(-5)	1.53(-2) 7.20(-4)	9.04(-2) 4.90(-3)	3.18(-1) 3.97(-2)	1.42(-1)
16		1.71(-1) 1.43(-1)	2.06(-3) 1.75(-3)	1.02(-2) 2.01(-2)	7.34(-2) 8.49(-2)	1.95(-1) 1.83(-1)	1.73(-1) 2.42(-1)	1.29(-3) 1.63(-1)	2.77(-2) 2.93(-1)

$$m = \frac{1}{3}, \quad \alpha = 0.314, \quad D_e = 9.3.$$

† The number in parentheses indicates the power of 10 by which the entry should be multiplied. The upper, lower numbers are the Morse, harmonic results respectively.

Table 3. HBr + He(B ≡ H)

$E$	$P_{1 \rightarrow F}$	0-1	1-2	0-2	0-3	1-3	2-3	2-4	3-4
4		9.34(-7)† 1.36(-6)							
6		1.20(-4) 2.48(-4)	4.29(-6) 2.15(-6)	3.36(-10) 2.18(-10)					
8		9.50(-4) 2.39(-3)	4.08(-4) 3.91(-4)	1.26(-7) 2.56(-7)		4.82(-9) 6.69(-10)	2.03(-5) 2.57(-6)		
10		3.22(-3) 9.38(-3)	3.08(-3) 3.88(-3)	2.67(-6) 9.61(-6)	1.96(-9) 6.79(-10)	1.14(-6) 5.11(-7)	1.30(-3) 4.57(-4)	4.64(-8) 1.53(-9)	1.22(-4) 2.76(-6)
12		7.35(-3) 2.40(-2)	1.03(-2) 1.57(-2)	1.95(-5) 9.90(-5)	4.40(-8) 6.47(-8)	2.32(-5) 1.97(-5)	8.83(-3) 4.68(-3)	9.99(-6) 6.70(-7)	4.48(-3) 4.68(-4)

$$m = 3.737, \quad \alpha = 0.5584, \quad D_e = 14.652.$$

† The number in parentheses indicates the power of 10 by which the entry should be multiplied. The upper, lower numbers are the Morse, harmonic results respectively.

Table 4. Br<sub>2</sub> + (H<sub>2</sub>)

E	$P_{I \rightarrow F}$							
	0-1	1-2	0-2	0-3	1-3	2-3	0-4	1-4
4	1.23 (-2)† 1.22(-2)							
6	3.54(-2) 3.53(-2)	2.49(-2) 2.41(-2)	2.45(-4) 2.20(-4)					
8	5.79(-2) 5.77(-2)	6.91(-2) 6.81(-2)	1.13(-3) 1.06(-3)	6.42(-6) 4.39(-6)	7.57(-4) 6.46(-4)	3.80(-2) 3.54(-2)		
10	7.94(-2) 7.92(-2)	1.10(-1) 1.09(-1)	2.56(-3) 2.44(-3)	3.82(-5) 2.99(-5)	3.37(-3) 3.08(-3)	1.01(-1) 9.86(-2)	2.10(-7) 9.27(-8)	2.70(-5) 1.72(-5)
12	9.99(-2) 9.97(-2)	1.47(-1) 1.46(-1)	4.49(-3) 4.31(-3)	1.07(-4) 8.88(-5)	7.45(-3) 6.98(-3)	1.56(-1) 1.54(-1)	1.44(-6) 8.17(-7)	1.54(-4) 1.16(-4)
16	1.38(-1) 1.38(-1)	2.09(-1) 2.08(-1)	9.68(-3) 9.39(-3)	4.01(-4) 3.52(-4)	1.93(-2) 1.84(-2)	2.41(-1) 2.39(-1)	1.11(-5) 7.72(-6)	8.71(-4) 7.30(-4)
20	1.72(-1) 1.72(-1)	2.57(-1) 2.56(-1)	1.64(-2) 1.60(-2)	9.63(-4) 8.70(-4)	3.47(-2) 3.35(-2)	2.97(-1) 2.95(-1)	3.98(-5) 3.03(-5)	2.42(-3) 2.12(-3)

E	$P_{I \rightarrow F}$							
	2-4	3-4	0-5	1-5	2-5	3-5	4-5	5-6
10	1.58(-3) 1.27(-3)	5.21(-2) 4.64(-2)						
12	6.72(-3) 5.98(-3)	1.32(-1) 1.27(-1)	8.33(-9) 2.00(-9)	1.12(-6) 4.51(-7)	7.19(-5) 4.22(-5)	2.78(-3) 2.07(-3)	6.75(-2) 5.70(-2)	
16	2.44(-2) 2.28(-2)	2.48(-1) 2.44(-1)	2.18(-7) 9.56(-8)	2.32(-5) 1.43(-5)	1.05(-3) 8.17(-4)	2.35(-2) 2.11(-2)	2.33(-1) 2.26(-1)	1.91(-1) 1.77(-1)
20	4.86(-2) 4.63(-2)	3.13(-1) 3.11(-1)	1.26(-6) 6.91(-7)	1.08(-4) 7.66(-5)	3.65(-3) 3.08(-3)	5.57(-3) 5.20(-2)	3.17(-1) 3.14(-1)	3.10(-1) 3.05(-1)

$$m = 0.006268, \quad \alpha = 0.1278, \quad D_e = 75.525.$$

† The number in parentheses indicates the power of 10 by which the entry should be multiplied. The upper, lower numbers are the Morse, harmonic results respectively.

few vibrational levels. However, for transitions among the higher vibrational levels and those involving large changes in the quantum number, the Morse results are larger than those of the harmonic oscillator. This may be accounted for by the significantly smaller energy separations between the higher vibrational states of the Morse oscillator.

Except for small values of  $D_e$ , the discrepancy between the two oscillators is less for smaller values of  $m$ . This is shown in figure 3 for the  $0 \rightarrow 1$  transition and may also be seen from table 4 for  $m = 0.006268$ . For larger values of  $D_e$  the agreement between the two oscillators is closer, although for large values of  $m$  the difference may still be significant. In the region  $D_e > 400$  for  $\alpha = 0.2$  the discrepancy between the  $0 \rightarrow 1$  transition probabilities for the two oscillators may be of the order of 50%, for large  $m$ , although the  $U_{00}$ ,  $U_{11}$  or  $|U_{01}|$  Morse and harmonic matrix elements agree to within 1%. Thus slight anharmonicities can cause comparatively large changes in the transition probability.

Table 5.  $N_2 + (N_2)$ 

$E$	$P_{I \rightarrow F}$	0-1	1-2	0-2	0-3	1-3	2-3	3-4
4		7.66(-11) 2.67(-10)						
6		4.52(-7) 1.93(-6)	2.86(-10) 5.34(-10)					
8		1.69(-5) 7.61(-5)	1.22(-6) 3.86(-6)	5.15(-12) 7.35(-11)			9.35(-10) 8.01(-10)	
10		1.43(-4) 6.60(-4)	4.17(-5) 1.52(-4)	1.49(-9) 2.51(-8)		2.72(-11) 2.20(-10)	2.61(-6) 5.79(-6)	3.04(-9) 1.07(-9)
12		6.10(-4) 2.85(-3)	3.38(-4) 1.32(-3)	5.16(-8) 9.42(-7)	4.59(-13) 2.39(-11)	6.74(-9) 7.53(-8)	7.97(-5) 2.28(-4)	5.20(-6) 7.72(-6)
16		4.10(-3) 1.92(-2)	4.03(-3) 1.66(-2)	4.15(-6) 8.11(-5)	1.14(-9) 7.74(-8)	2.49(-6) 3.57(-5)	2.46(-3) 8.48(-3)	1.00(-3) 2.63(-3)
20		1.40(-2) 6.39(-2)	1.76(-2) 7.14(-2)	6.26(-5) 1.24(-3)	1.08(-7) 8.08(-6)	6.87(-5) 1.07(-3)	1.53(-2) 5.50(-2)	1.06(-2) 3.24(-2)

$E$	$P_{I \rightarrow F}$	1-4	2-4	2-5	3-5	4-5	5-6
12			1.04(-10) 4.41(-10)			1.01(-8) 1.34(-9)	
16		2.78(-10) 1.05(-8)	6.18(-7) 5.62(-6)	1.62(-11) 2.38(-10)	5.83(-8) 2.51(-7)	2.33(-4) 3.80(-4)	1.95(-5) 1.16(-5)
20		8.20(-8) 4.04(-6)	4.12(-5) 4.74(-4)	2.68(-8) 7.59(-7)	1.55(-5) 1.17(-4)	5.80(-3) 1.40(-2)	2.37(-3) 3.93(-3)

$$m = 0.5, \quad \alpha = 0.114, \quad D_e = 40.81.$$

† The number in parentheses indicates the power of 10 by which the entry should be multiplied. The upper, lower numbers are the Morse, harmonic results respectively.

The curves shown in figure 3 are relatively insensitive to the value of the total energy  $E$ , in the region before the first maximum of the transition probability. However the disagreement between the two oscillators becomes more pronounced for smaller values of  $\alpha$ .

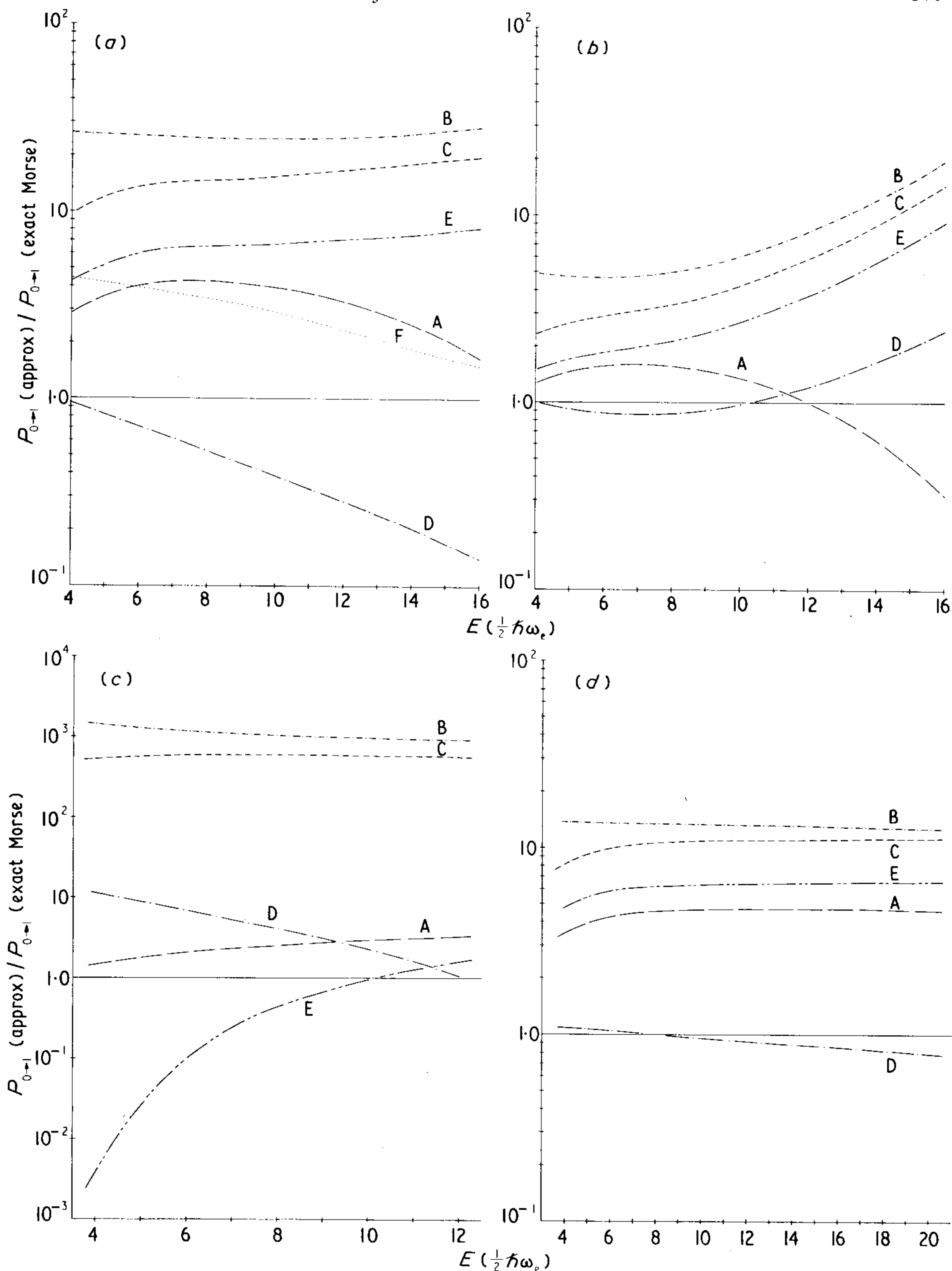
The number of bound states of the Morse oscillator is approximately  $2D_e$ . Since most molecules have fewer than 100 bound states anharmonicity will nearly always be important.

## 6.2. The first order distorted wave approximation (FODWA)

The first order distorted wave approximation was initially applied to this problem by Jackson and Mott (1932). For the interaction potential (18), their result becomes,

$$P_{0 \rightarrow 1}^{\text{FODWA}} = \sinh(\pi q_1) \sinh(\pi q_0) \left( \frac{\frac{1}{2}|U_{01}| \pi (q_1^2 - q_0^2)}{\cosh(\pi q_1) - \cosh(\pi q_0)} \right)^2 \quad (19)$$

where  $q_i = 2k_i/\alpha$ .



**Figure 2.** The ratios of approximate and exact harmonic to exact Morse transition probabilities, for the  $0 \rightarrow 1$  transition, as a function of the total energy of the system  $E$  (in units of  $\frac{1}{2} \hbar \omega_e$ ). B and C are the FODWA, equation (19), for the Morse and harmonic oscillators respectively. D and E are the RFODWA, equation (20), for the Morse and harmonic oscillators respectively. A is the exact harmonic oscillator result and F is the semiclassical approximation of Morse and LaBrecque. (a)  $m = 0.667, \alpha = 0.314, D_e = 9.3$ ; approximating an  $\text{H}_2 + \text{He}$  collision. (b)  $m = \frac{1}{3}, \alpha = 0.314, D_e = 9.3$ ; approximating an  $\text{H}_2 + \text{H}$  collision. (c)  $m = 3.737, \alpha = 0.5584, D_e = 14.652$ ; approximating an  $\text{HBr} + \text{He}$  collision ( $\text{H} \equiv \text{B}$ ). (d)  $m = 0.5, \alpha = 0.114, D_e = 40.81$ ; approximating an  $\text{N}_2 + (\text{N}_2)$  collision.

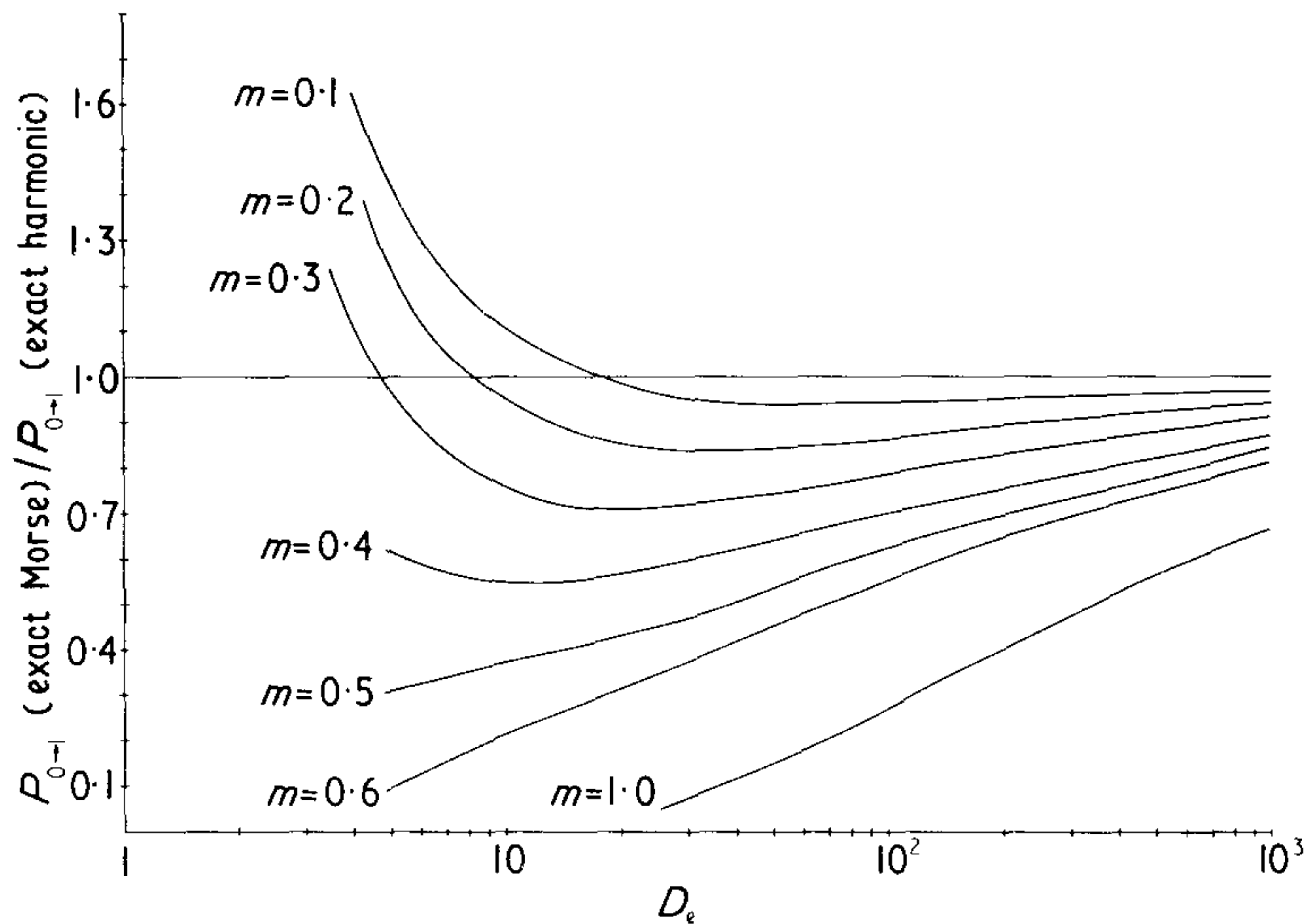


Figure 3. The ratio of  $P_{0 \rightarrow 1}$  (exact Morse) to  $P_{0 \rightarrow 1}$  (exact harmonic) as a function of the reduced well depth  $D_e$  for several values of  $m$ . The total energy  $E$  is 4 and  $\alpha = 0.2$ .

As shown in figures 2(a)–2(d),  $P_{0 \rightarrow 1}^{\text{FODWA}}$  may be several orders of magnitude too large. It is, however, a valid approximation for very small values of  $m$ . For  $m = 0.006268$ , in the range  $E = 4.0$  to  $20.0$ ,  $P_{0 \rightarrow 1}^{\text{FODWA}}$  was accurate to within 27% for both the Morse and harmonic oscillators.

It was noted by Secrest and Johnson (1966) that the ratio  $P_{0 \rightarrow 1}^{\text{FODWA}}/P_{0 \rightarrow 1}^{\text{EXACT}}$ , for the harmonic oscillator, was approximately constant over a large range of energies  $E$ . This ratio is also seen to be nearly constant for the Morse oscillator, in the region before the first maximum in the exact transition probability.

The FODWA transition probabilities for the Morse oscillator,  $P_{0 \rightarrow 1}^{\text{FODWA}}$  (Morse) are generally larger than  $P_{0 \rightarrow 1}^{\text{FODWA}}$  (harmonic) although the exact Morse transition probabilities are usually less than those of the equivalent harmonic oscillator.

### 6.3. Revised first order distorted wave approximation (RFODWA)

Equation (19) was derived assuming that the ratio of the diagonal matrix elements,  $\lambda^2 (= U_{00}/U_{11}) = 1$ . For the interaction potential (18) this is not strictly correct. With  $(\alpha, D_e)$  given by (0.1278, 75.525) and (0.5584, 14.652),  $\lambda^2$  is 0.976 and 0.737 respectively for the Morse oscillator and 0.992 and 0.865 respectively for the harmonic oscillator. Mies (1964a) has shown that the correct distorted wave result (RFODWA) is,

$$P_{0 \rightarrow 1}^{\text{RFODWA}} = A(E, \lambda) P_{0 \rightarrow 1}^{\text{FODWA}} \quad (20)$$

where

$$A(E, \lambda) = U_{11}^{-2} |{}_2F_1(1 + \frac{1}{2}i(q_0 + q_1), 1 + \frac{1}{2}i(q_0 - q_1), 2; 1 - \lambda^2)|^2$$

and  ${}_2F_1(a, b, c; x)$  is a hypergeometric function (Abramowitz and Stegun 1968).

In all cases considered the RFODWA gives more accurate results than the FODWA. The correction factor  $A(E, \lambda)$  reduces the large discrepancy between the FODWA and exact results for intermediate values of  $m$ . In the region before the first maximum of the transition probability, for  $m = \frac{1}{3}$  and  $m = 0.5$   $P_{0 \rightarrow 1}^{\text{RFODWA}}$  is a good approximation for

both the Morse and harmonic oscillators, although slightly better for the former. For  $m = 0.006268$  in the energy range  $E = 4.0$  to  $20.0$ ,  $P_{0 \rightarrow 1}^{\text{RFODWA}}$  was accurate to within 20% for both oscillators. The RFODWA, however, breaks down for large values of  $m$ . This may be seen from figure 2(c) where the discrepancy between the exact results and  $P_{0 \rightarrow 1}^{\text{RFODWA}}$  may be several orders of magnitude in the low energy region.

The behaviour of both FODWA and RFODWA is relatively insensitive to the initial state of the oscillator for single quantum transitions.

#### 6.4. First order perturbation theory approximations

Mies (1964b) obtained a correction factor, similar to  $A(E, \lambda)$ , for the time dependent first order perturbation theory approximation (FOPA and RFOPA). In his calculation Mies (1964b) used a symmetrized form for the translational energy of atom A (figure 1). In this work more accurate results were obtained using the symmetrized velocity  $\bar{v} = \frac{1}{2}(v_0 + v_1)$ .

The results thus obtained differed from the corresponding FODWA and RFODWA by not more than a few percent for all collisions considered in tables 1–5.

#### 6.5. Semi-classical impulse approximation

Morse and LaBrecque (1971) have extended the semi-classical impulse or ITFITS approximation, of Heidrich *et al* (1971), to the Morse binding potential. The Morse and LaBrecque (ML) approximate  $0 \rightarrow 1$  transition probabilities are compared with the exact Morse results for the case  $m = 0.667$ ,  $\alpha = 0.314$ ,  $D_e = 9.3$ , in figure 2(a). The ML approximation does not appear to predict the discrepancy between the two oscillators and ML results for other low order transitions eg  $0-2$ ,  $1-2$  have a similar behaviour. It was found impossible, however, to reproduce the results of Morse and LaBrecque and a note on their paper is given in Appendix C.

## 7. Conclusion

In the incident energy region before the first maximum of the transition probability the Morse results are generally smaller than those of the equivalent harmonic oscillator, for transitions within the first few vibrational levels. However, for transitions where the energy separation between the initial and final states is significantly less for the Morse oscillator, the Morse transition probabilities exceed those of the harmonic oscillator. The discrepancy between the transition probabilities for the two oscillators is strongly dependent on the values of  $m$  and  $\alpha$ , increasing as  $m$  becomes large and decreasing as  $\alpha$  becomes large. Large values of  $D_e$ , corresponding to deep Morse well depths, do not necessarily imply agreement between the transition probabilities of the two oscillators. Slight anharmonicities can cause relatively large changes in the transition probability.

None of the approximate theories, for the excitation of a Morse oscillator gives consistently accurate transition probabilities for all values of  $m$ ,  $\alpha$ ,  $D_e$  and  $E$  considered. However, the RFODWA of Mies (1964a) and consequently the RFOPA (Mies 1964b), using a symmetrized velocity, are valid approximations for small and intermediate values of  $m$ , in the region before the first maximum in the transition probability.

The extension, to the Morse oscillator, of the Heidrich *et al* (1971) semiclassical impulse approximation, by Morse and LaBrecque (1971) appears to overestimate the

transition probabilities although, for reasons discussed previously, only the case  $m = 0.667$ ,  $\alpha = 0.314$ ,  $D_e = 9.3$  has been considered.

The impulse approximation of Heidrich *et al* (1971) gives excellent agreement, over a large range of parameters ( $m, \alpha, E$ ), when applied to the harmonic oscillator, and none of the approximate theories, so far derived, has as large a range of validity when applied to the Morse oscillator.

## Appendix A

To overcome the numerical difficulties caused by the exponentially increasing  $\mathbf{F}$  and  $\mathbf{G}$  matrices and the inconvenience of an imaginary  $\mathbf{F}$  matrix, these matrices are replaced by  $\tilde{\mathbf{F}}$  and  $\tilde{\mathbf{G}}$  where,

$$\begin{aligned} (\tilde{\mathbf{F}})_{ij} &= (\mathbf{F})_{ij} && k_i \text{ real} \\ &= \delta_{ij} \alpha_i \exp(-k_i x) && k_i \text{ imaginary} \\ (\tilde{\mathbf{G}})_{ij} &= (\mathbf{G})_{ij} && k_i \text{ real} \\ &= \delta_{ij} \beta_i \exp(k_i x) && k_i \text{ imaginary} \end{aligned}$$

and  $\alpha, \beta$  are arbitrary diagonal matrices.

The relation between  $(\tilde{\mathbf{K}})_{ij}$ , obtained using  $\tilde{\mathbf{F}}$  and  $\tilde{\mathbf{G}}$  in place of  $\mathbf{F}$  and  $\mathbf{G}$ , and the  $(\mathbf{R})_{ij}$ , when both  $k_i$  and  $k_j$  are imaginary is then,

$$(\tilde{\mathbf{K}})_{ij} = \alpha_j / (\beta_j (\mathbf{R})_{ij}).$$

Solving equation (15) using the modified matrices  $\tilde{\mathbf{F}}, \tilde{\mathbf{G}}$  and replacing  $\mathbf{K}_L$  and  $\mathbf{K}_{L-1}$  by  $\tilde{\mathbf{K}}_L$  and  $\tilde{\mathbf{K}}_{L-1}$  will have no effect on the open-open channel elements of the  $\mathbf{K}$  matrix and will provide the correct coupling between the open and closed channels. This is all that is required since only the open-open  $\mathbf{K}$  matrix elements are used to calculate the transition probabilities.

At the first quadrature point  $x_1$ ,  $\alpha$  and  $\beta$  are chosen such that for  $k_i$  imaginary,

$$(\tilde{\mathbf{F}})_{ij} = (\tilde{\mathbf{G}})_{ij} = \delta_{ij}. \quad (\text{A1})$$

Denoting  $\tilde{\mathbf{K}}^1$  as the matrix obtained with  $\alpha = \beta = \mathbf{1}$  the relation between  $\tilde{\mathbf{K}}^1$  and  $\tilde{\mathbf{K}}$  at this point will be

$$\mathbf{K} = \mathbf{e}(-kx_1) \tilde{\mathbf{K}}^1 \mathbf{e}(-kx_1)$$

where the matrix  $\mathbf{e}(kx)$  is given by,

$$\begin{aligned} \{\mathbf{e}(kx)\}_{ij} &= \delta_{ij} && k_i \text{ real} \\ &= \delta_{ij} \exp(k_i x) && k_i \text{ imaginary.} \end{aligned}$$

At each succeeding point  $\tilde{\mathbf{K}}$  is replaced by  $\mathbf{e}(-k\Delta x) \tilde{\mathbf{K}} \mathbf{e}(-k\Delta x)$ , where  $\Delta x$  is the spacing between quadrature points, and  $\alpha$  and  $\beta$  are chosen so that  $F$  and  $G$  satisfy (A1).

After  $L$  quadrature points the relation between  $\tilde{\mathbf{K}}^1$  and  $\tilde{\mathbf{K}}$  will then be,

$$\tilde{\mathbf{K}} = \mathbf{e}\{-k(x_1 + L\Delta x)\} \tilde{\mathbf{K}}^1 \mathbf{e}\{-k(x_1 + L\Delta x)\}.$$

The closed channel diagonal elements of the  $\tilde{\mathbf{F}}$  and  $\tilde{\mathbf{G}}$  matrices are essentially normalized to unity at each step of the integration without affecting the open-open channel elements of the  $\tilde{\mathbf{K}}$  matrix.

## Appendix B

The open–open channel elements of the  $\mathbf{K}$  matrix are slowly converging functions of  $x$ . Factors speeding the convergence may be obtained from the  $\mathbf{K}$  matrix differential equation (16).

Integrating this equation from  $x$  to  $\infty$  gives,

$$\mathbf{K}(\infty) - \mathbf{K}(x) = 2m \int_x^\infty (\mathbf{F} - \mathbf{K}(x')\mathbf{G})\mathbf{k}^{-1}\mathbf{V}(x')(\mathbf{F} - \mathbf{G}\mathbf{K}(x')) dx'.$$

If  $x$  is sufficiently large, then  $\mathbf{K}(x')$  may be approximated by  $\mathbf{K}(x)$  and the integral may be evaluated.  $\mathbf{K}(\infty)$  calculated in this manner converged significantly sooner than  $\mathbf{K}(x)$ .

## Appendix C

Morse and LaBrecque (1971) have extended the semi-classical ITFITS approximation of Heidrich *et al* (1971) to the Morse oscillator. The ITFITS approximation essentially assumes that the classical motion of atom A may be calculated assuming the binding potential of the molecule to be negligible (Clark 1971).

The effect of atom A on the molecule B–C, may then be represented by the time dependent forcing function  $F(t)$ . Using an iterative procedure, where at the  $j$ th iteration the Morse oscillator is approximated by a harmonic oscillator of frequency  $\omega_j$ , Morse and LaBrecque obtain a solution of the classical equation of motion for a Morse oscillator perturbed by the time dependent force  $F(t)$ . In the notation of Morse and LaBrecque at the  $(j+1)$ th iteration the frequency  $\omega_{j+1}$  is given by,

$$\omega_{j+1} = (\omega_0/\pi) \int_{-\pi/2}^{\pi/2} \exp\{-(\epsilon_j/\mu)^{1/2}(\omega_j L)^{-1} \sin(\omega_j t)\} d(\omega_j t)$$

giving, with their equation (6),

$$\omega_j = \omega_0 I_0\{(\epsilon_j/2D)^{1/2}(\omega_0/\omega_j)\beta\}$$

where  $I_0(x)$  is the modified Bessel function of order zero (Abramowitz and Stegun 1968). This is not in agreement with their equation (15). Moreover since  $E_t$ , the total energy of the system, is measured in units of  $\hbar\omega$ , their equation (22) should read,

$$E_0(j) = \frac{1}{4}\{(E_t(\omega/\omega_j) - i - \frac{1}{2})^{1/2} + (E_t(\omega/\omega_j) - f - \frac{1}{2})^{1/2}\}^2$$

where the velocity averaged translational energy,  $E_0(j)$  is measured in units of  $\hbar\omega_j$ . In their equation (20)  $\omega_0$  should be replaced by  $\omega$ , since  $\alpha$  is not a function of the initial or final state of the oscillator.  $\omega$  of Morse and LaBrecque is equivalent to  $\omega_e$  of this paper.

With or without these corrections it was still found impossible to reproduce the results presented by Morse and LaBrecque.

## References

- Abramowitz M and Stegun I A 1968 *Handbook of Mathematical Functions* (New York: Dover)  
 Calogero F 1967 *Variable Phase Approach to Potential Scattering* ch 19 (London: Academic Press)  
 Clark A P 1971 *MSc Thesis* University of Stirling  
 Eastes W and Secrest D 1972 *J. chem. Phys.* **56** 640–9



- Fröberg C E 1966 *Introduction to Numerical Analysis* (London: Addison-Wesley) p 97  
Heidrich F E, Wilson K R and Rapp D 1971 *J. chem. Phys.* **54** 3885-97  
Hunding A 1970 *Chem. Phys. Lett.* **6** 444-6  
Jackson J M and Mott N F 1932 *Proc. R. Soc.* **A137** 703-17  
Johnson B R and Secrest D 1966 *J. math. Phys.* **7** 2187-95  
Mies F H 1964a *J. chem. Phys.* **40** 523-31  
— 1964b *J. chem. Phys.* **41** 903-4  
Morse P M 1929 *Phys. Rev.* **34** 57-64  
Morse R I and La Brecque R J 1971 *J. chem. Phys.* **55** 1522-30  
Mott N F and Massey H S W 1965 *The Theory of Atomic Collisions* (Oxford: Clarendon Press).  
Rapp D and Kassal T 1969 *Chem. Rev.* **69** 61-102  
Rodberg L S and Thaler R M 1967 *Introduction to the Quantum Theory of Scattering* ch 5 (London: Academic Press)  
Sams W N and Kouri D J 1969 *J. chem. Phys.* **51** 4809-14, 4815-9  
Secrest D 1971 *Meth. Comp. Phys.* **10** 243-86  
Secrest D and Johnson B R 1966 *J. chem. Phys.* **45** 4556-70  
Takayanagi K 1963 *Progr. Theor. Phys. Suppl.* **25** 1-98  
— 1965 *Adv. atom. molec. Phys.* **1** 149-93

## A modified correspondence principle for strongly coupled states

A P Clark

Department of Physics, University of Stirling, Stirling, Scotland

Received 30 December 1972

**Abstract.** The one-dimensional form of the correspondence principle for strongly coupled states of Percival and Richards is modified to include, approximately, the perturbation of the bound particle orbit. The modification will only be significant when the expectation value of the interaction potential depends on the state of the bound system. The excitation of a linear harmonic oscillator by a time dependent potential  $q^2F(t)$  and the collinear collision of an atom and an anharmonic diatomic molecule are considered as examples. The results obtained for both these systems are in good agreement with the exact quantum mechanical transition probabilities, even for low order transitions.

### 1. Introduction

The correspondence principle for strongly coupled states (Percival and Richards 1970a) provides an approximate expression for the transition amplitude  $S(n', n)$  between states  $n$  and  $n'$  of a highly excited bound system. It has previously been applied to obtain cross sections for the excitation of highly excited hydrogenic atoms by electrons and protons (Percival and Richards 1970b, 1971). Also, Clark and Dickinson (1971) and Clark (1971) have investigated the range of validity of this theory for the problem of a forced harmonic oscillator. With this particular bound system it was shown that for a perturbing potential, linear in the oscillator co-ordinate, the correspondence principle predicts accurate results even for transitions from the ground state of the oscillator, within the range of validity of classical perturbation theory.

In the one-dimensional form of the theory the interaction potential is assumed to be  $V(q, t)$  where  $q$  and  $t$  are the position co-ordinate of the bound particle and time respectively. An implicit assumption made in deriving the correspondence principle is that the matrix elements  $\langle n+s|V(q, t)|n\rangle$  are independent of the quantum number  $n$  and depend only on  $s$ , the difference between the quantum numbers of the final and initial states of the unperturbed system (Richards 1972). This essentially implies that throughout the interaction the perturbation of the energy of the bound particle is independent of the state of the system. However, using time dependent perturbation theory, Bates (1961) has pointed out that difficulties may be encountered in obtaining a satisfactory approximation to the transition amplitude if the difference between the perturbed energies of the states of the bound system are not taken into account.

In § 2 we show how the perturbation of the energy levels may be included, approximately, in the correspondence principle. The resulting expression for the transition amplitude differs from that of Percival and Richards (1970a) in that it includes a term taking into account the perturbation of the bound particle orbit. This correction term

will be significant only when the diagonal matrix elements  $\langle n|V(q, t)|n\rangle$  of the interaction potential depend on the quantum number  $n$ .

In § 3 we examine the validity of the correspondence principle when applied to a harmonic oscillator perturbed by a time dependent potential of the form  $q^2F(t)$ . An exact quantum mechanical solution of this problem has been obtained by Popov and Perelemov (1969).

The collinear collision of an atom and a diatomic molecule, bound by an anharmonic potential, is considered in § 4 and the results are compared with the exact transition probabilities of Clark and Dickinson (1973) for this problem.

Concluding remarks are given in § 5.

## 2. The modified correspondence principle

We consider a one dimensional system with hamiltonian of the form,

$$H = H_0 + V(q, t)$$

where

$$H_0|n\rangle = \epsilon_n|n\rangle$$

$H_0$  being the hamiltonian of the unperturbed system.

The time dependent transition amplitudes  $S(m, n; t)$  for this system satisfy (Bates 1961),

$$i\hbar \frac{\partial}{\partial t} S(m, n; t) = \sum_{k=0}^{\infty} S(k, n; t) \langle m|V(q, t)|k\rangle \exp\left(\frac{i}{\hbar}(\epsilon_m - \epsilon_k)t\right). \quad (1)$$

Following Bates (1961) we write,

$$S'(i, j; t) = S(i, j; t) \exp\left(\frac{i}{\hbar} \int_{-\infty}^t \langle i|V(q, t')|i\rangle dt'\right).$$

The diagonal matrix elements  $\langle m|V(q, t)|m\rangle$  may now be eliminated explicitly from the summation in (1) giving,

$$i\hbar \frac{\partial}{\partial t} S'(m, n; t) = \sum_{k \neq m}^{\infty} S'(k, n; t) \langle m|V(q, t)|k\rangle \exp\left(\frac{i}{\hbar}\{(\epsilon_m - \epsilon_k)t + \phi(m, k; t)\}\right) \quad (2)$$

where

$$\phi(i, j; t) = \int_{-\infty}^t (\langle i|V(q, t')|i\rangle - \langle j|V(q, t')|j\rangle) dt'.$$

The term  $\phi(m, k; t)$  in (2) takes into account the difference between the perturbation energies of the states  $|m\rangle$  and  $|k\rangle$ .

Assuming that the interaction potential  $V(q, t)$  tends to zero sufficiently rapidly as  $|t| \rightarrow \infty$ , the transition probability at  $t = +\infty$  is defined as,

$$P(n \rightarrow m) = |S(m, n)|^2 = |S'(m, n)|^2 \quad (3)$$

where

$$S(m, n) = \lim_{t \rightarrow \infty} S(m, n; t).$$

To obtain an approximate solution of the system of equations (2) we follow the method of Presnykov and Urnov (1970). Defining the generating function  $G_n(t, \tau)$  by

$$G_n(t, \tau) = \sum_{j=-\infty}^{\infty} S'(j, n; t) \exp\{i(j-n)\tau\} \quad (4)$$

we obtain from (2)

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} G_n(t, \tau) = & \sum_{m=-\infty}^{\infty} \exp\{i(m-n)\tau\} \sum_{k \neq m}^{\infty} S'(k, n; t) \langle m|V(q, t)|k\rangle \\ & \times \exp\left(\frac{i}{\hbar} \{(\epsilon_m - \epsilon_k)t + \phi(m, k; t)\}\right). \end{aligned} \quad (5)$$

Replacing the index  $k$ , in the second summation, by  $(m-l)$  (5) may be written,

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} G_n(t, \tau) = & \sum_{m=-\infty}^{\infty} \exp\{i(m-l-n)\tau\} \sum_{l \neq 0}^{\infty} S'(m-l, n; t) \\ & \times \langle m|V(q, t)|m-l\rangle \exp\left(\frac{i}{\hbar} \{(\epsilon_m - \epsilon_{m-l})t + \hbar l\tau + \phi(m, m-l, t)\}\right) \end{aligned} \quad (6)$$

where it is understood that  $S'(m-l, n; t) = 0$  for  $l > m$ .

We now make the following approximations:

(i)  $(\epsilon_m - \epsilon_{m-s}) \simeq s\bar{\epsilon}$ , where  $\bar{\epsilon}$  is independent of  $m$  and is some mean value of the energy separation of the quantum states. This is a valid approximation for highly excited atomic systems since the energy levels are nearly equally spaced. The relation is exact for a particle in a harmonic potential and thus will be a good approximation for the low eigenvalues of an anharmonic oscillator.

$$(ii) \quad (\langle m|V(q, t)|m\rangle - \langle m-s|V(q, t)|m-s\rangle) \simeq s\bar{V}(t) \quad (7)$$

where  $\bar{V}(t)$  is independent of  $m$  and is some mean value of the difference between successive diagonal matrix elements. This relation is exact for the linear harmonic oscillator perturbed by a time dependent potential  $q^\lambda F(t)$ ,  $\lambda = 0, 1, 2, 3$ , with  $\bar{V}(t) = 0$  for  $\lambda = 1$  or 3. Its validity for the collinear atom-molecule collision will be discussed in § 4. Percival and Richards (1970a) essentially assume that  $\bar{V}(t) = 0$ .

(iii) The classical interaction potential  $V^c(q, t)$  is a function of time implicitly through the position of the bound particle  $q$  and explicitly through  $t$ . We may treat these times separately (Percival and Richards 1970a). Denoting the time dependence of the bound particle by  $\tau'$ ,  $V^c\{q(\tau'), t\}$  is then periodic in  $\tau'$  and may be expanded as a Fourier series

$$V^c\{q(\tau'), t\} = \sum_{s=-\infty}^{\infty} V_s(t) \exp\{is\omega\tau'\}$$

where  $\omega$  is the frequency of the bound particle.

For highly excited states we may use Heisenberg's correspondence principle (Heisenberg 1925) and approximate the matrix elements  $\langle n+s|V(q, t)|n\rangle$  by the Fourier components  $V_s(t)$ . However Naccache (1972) has shown that by a suitable quantization of the classical action variable, Heisenberg's correspondence principle may be used quite accurately even for matrix elements involving low quantum numbers.

Using these approximations the system of equations (6) may be written

$$i\hbar \frac{\partial}{\partial t} G_n(t, \tau) \simeq G_n(t, \tau) \sum_{l \neq 0} V_l(t) \exp \left( \frac{i}{\hbar} l(\bar{\epsilon}t + \hbar\tau + \int_{-\infty}^t \bar{V}(t') dt') \right). \quad (8)$$

Writing  $\bar{\epsilon} = \hbar\bar{\omega}$  and  $\tau = \bar{\omega}\tau'$  where  $\bar{\omega}$  is some mean classical frequency of the bound particle (8) becomes

$$i\hbar \frac{\partial}{\partial t} G_n(t, \bar{\omega}\tau') \simeq G_n(t, \bar{\omega}\tau') \left[ V^c \left\{ q \left( \bar{\omega}t + \bar{\omega}\tau' + \frac{1}{\hbar} \int_{-\infty}^t \bar{V}(t') dt' \right), t \right\} - V_0(t) \right]. \quad (9)$$

Equation (9) has the solution,

$$G_n(t, \bar{\omega}\tau') \simeq \exp \left\{ -\frac{i}{\hbar} \int_{-\infty}^t \left[ V^c \left\{ q \left( \bar{\omega}t' + \bar{\omega}\tau' + \frac{1}{\hbar} \int_{-\infty}^{t'} \bar{V}(t'') dt'' \right), t' \right\} - V_0(t') \right] dt' + i\delta \right\}$$

where  $\delta$  is an arbitrary phase factor.

From (4) we obtain,

$$S'(m, n; t) = \frac{\bar{\omega}}{2\pi} \int_0^{2\pi/\bar{\omega}} G_n(t, \bar{\omega}\tau') \exp\{i(n-m)\bar{\omega}\tau'\} d\tau'.$$

Thus from (3)

$$\begin{aligned} P(n \rightarrow m) &= |S'(m, n)|^2 \\ &\simeq \left| \frac{\bar{\omega}}{2\pi} \int_0^{2\pi/\bar{\omega}} d\tau' \exp \left\{ i(n-m)\bar{\omega}\tau' - \frac{i}{\hbar} \int_{-\infty}^{\infty} V^c \left[ q \left\{ \bar{\omega}(t + \tau') \right. \right. \right. \right. \\ &\quad \left. \left. \left. + \frac{1}{\hbar} \int_{-\infty}^t \bar{V}(t') dt' \right\}, t \right] dt \right\} \right|^2. \end{aligned} \quad (10)$$

The term

$$\frac{1}{\hbar} \int_{-\infty}^t \bar{V}(t') dt'$$

approximately takes into account the contribution to the transition probability due to the perturbation of the bound particle throughout the interaction. When the diagonal matrix elements  $\langle n|V(q, t)|n\rangle$  are independent of  $n$  or are zero,  $\bar{V}(t)$  will be zero and the expression reduces to that of Percival and Richards (1970a). In the quantum mechanical weak perturbation limit  $\bar{V}(t)$  will be small, however its effect on the transition probability will not necessarily be negligible, since for  $n \neq m$  the transition probability will also be small in this limit. This will be discussed with reference to a particular example in the next section.

In the impulsive and weak perturbation limits the transition probability (10) reduces to a sudden and first order approximation in an analogous way to the Percival and Richards (1970a) result.

### 3. Excitation of a harmonic oscillator

To illustrate the effect of the correction term we apply the modified correspondence principle (10) to the excitation of a harmonic oscillator by a time dependent potential of the form  $q^2 F(t)$ . The relation between the exact quantum mechanical and correspondence

principle (Percival and Richards 1970a) solutions for this problem has been discussed by Clark and Dickinson (1971).

In order to compare the results quantitatively we choose  $F(t) = (a/2) \operatorname{sech}^2(bt)$ , where  $a$  and  $b$  are constants. This particular time dependence results from the Landau–Teller approximation (Landau and Teller 1936) of the collinear atom–harmonic oscillator collision. Furthermore, if we let  $a = \alpha^2 E/2$  and  $b = (\alpha/2)(E/m)^{1/2}$ , then  $q^2 F(t)$  corresponds to the third term in the expansion of the exponential interaction potential

$$\frac{E}{2} \exp(\alpha q) \operatorname{sech}^2 \left\{ \frac{\alpha}{2} \left( \frac{E}{m} \right)^{1/2} t \right\}$$

(Rapp and Kassal 1969).

### 3.1. Exact quantum mechanical solution

For a time dependent perturbing potential  $q^2 F(t)$  the probability that a harmonic oscillator, initially in state  $n$ , will make a transition to state  $m$ , is given by (Popov and Perelemov 1969)

$$P^{\text{EXACT}}(n \rightarrow m) = \frac{n_{<}!}{n_{>}!} (1 - \rho)^{1/2} |P_{(m+n)/2}^{s/2} \{(1 - \rho)^{1/2}\}|^2 \quad (11)$$

$$s = |n - m| = 0, 2, 4, \dots$$

where  $P_n^m(x)$  is the associated Legendre function (Abramowitz and Stegun 1965) and  $n_{<}$ ,  $n_{>}$  are respectively the lesser and greater of  $n$  and  $m$ ; in terms of the reduced units considered above  $\rho$  may be interpreted as the above-barrier reflection coefficient, for a particle of unit energy, from the potential barrier defined by  $F(x)$  (Popov and Perelemov 1969).

This problem may be solved analytically for the particular time dependence chosen (Gol'dman and Krivchenkov 1961) giving

$$\rho = \frac{\cos^2 \{(\pi/2)(1 + 8m)^{1/2}\}}{\sinh^2 \{(2\pi/\alpha)(m/E)^{1/2}\} + \cos^2 \{(\pi/2)(1 + 8m)^{1/2}\}}.$$

### 3.2. Correspondence principle solutions

The correspondence principle of Percival and Richards (1970a) yields, for this problem, (Clark and Dickinson 1971)

$$P^{\text{CP}}(n \rightarrow m) = J_{s/2}^2(\bar{n}\sqrt{\rho'}) \quad (12)$$

where  $J_n(x)$  is the ordinary Bessel function (Abramowitz and Stegun 1965) and  $\bar{n}$  is a mean quantum number of the oscillator. As suggested by Naccache (1972) we employ

$$\bar{n} = \left\{ \frac{(n_{<} + s)!}{n_{<}!} \right\}^{1/s}. \quad (13)$$

Also,  $\rho'$  is a first order perturbation theory approximation to  $\rho$ ,

$$\rho' = \frac{4\pi^2 m^2}{\sinh^2 \{(2\pi/\alpha)(m/E)^{1/2}\}}$$

which is valid providing  $2m \ll 1$  and  $\alpha^2 E/2 \ll 1$ .

The diagonal matrix elements  $\langle n|q^2|n\rangle$  in the harmonic oscillator basis are  $(n + \frac{1}{2})$  and from (7), we obtain

$$\bar{V}(t) = \frac{\alpha^2 E}{4} \operatorname{sech}^2 \left\{ \frac{\alpha}{2} \left( \frac{E}{m} \right)^{1/2} t \right\}.$$

The modified correspondence principle (10) may thus be evaluated analytically and yields,

$$P^{\text{MODCP}}(n \rightarrow m) = J_{s/2}^2(\bar{n}\sqrt{\rho''}) \quad (14)$$

where

$$\rho'' = \rho' \left| M \left\{ 1 + \frac{2i}{\alpha} \left( \frac{m}{E} \right)^{1/2}, 2, 2i\alpha(mE)^{1/2} \right\} \right|^2$$

and  $M(a, b, x)$  is the confluent hypergeometric function (Abramowitz and Stegun 1965).

### 3.3. Discussion and comparison of results

The effect of the correction term in the modified correspondence principle (10) is to replace the approximate reflection coefficient  $\rho'$  by  $\rho''$ . These reflection coefficients were evaluated numerically for a large range of values of  $m$  and  $\alpha\sqrt{E}$ ; in all cases  $\rho''$  was a better approximation to  $\rho$  than was  $\rho'$ . It is interesting to examine the behaviour of  $\rho''$  in the limit of weak perturbations (small  $E$ ); from the expansion of  $M(a, b, x)$  as a power series in  $x$  (Abramowitz and Stegun 1965), in the limit  $E \rightarrow 0$  we obtain on re-summation,

$$\lim_{E \rightarrow 0} M \left\{ 1 + \frac{2i}{\alpha} \left( \frac{m}{E} \right)^{1/2}, 2, 2i\alpha(mE)^{1/2} \right\} = \frac{1}{2\sqrt{m}} J_1(4\sqrt{m}).$$

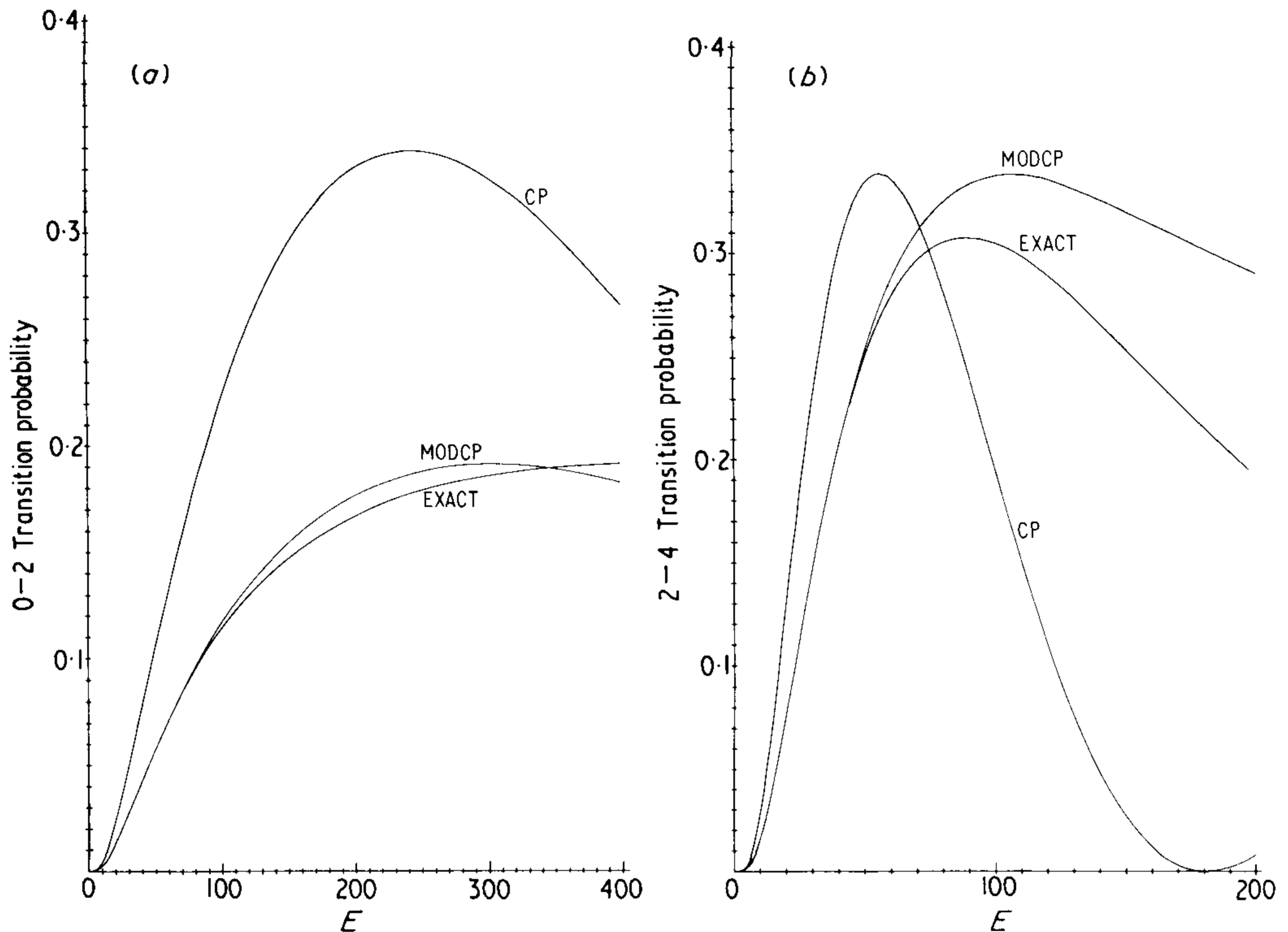
In this limit the correction term in (10) is small compared with  $\bar{\omega}t$ . Its effect on the correspondence principle transition probability (14) may still be considerable however, depending on the value of the parameter  $m$ .

In figure 1 we have shown the  $0 \rightarrow 2$  and  $2 \rightarrow 4$  transition probabilities as a function of  $E$  for  $m = \frac{1}{8}$ ,  $\alpha = \frac{1}{4}$ . It may be seen that  $P^{\text{MODCP}}(n \rightarrow m)$  is an excellent approximation up to the maximum in the exact transition probability for both transitions, whereas  $P^{\text{CP}}(n \rightarrow m)$  overestimates  $P^{\text{EXACT}}(n \rightarrow m)$  even in the limit of weak perturbations.

As  $n$  or  $s$  become large the range of validity of  $P^{\text{MODCP}}(n \rightarrow m)$  will decrease (see equation (10), Clark and Dickinson 1971). However, the first few maxima of the transition probability, which form the most significant part, occur at smaller values of  $\rho$  as  $n$  increases. Numerical results show that  $P^{\text{MODCP}}(n \rightarrow m)$  predicts these first few peaks in the transition probability more accurately as  $n$  becomes large. For all transitions  $P^{\text{MODCP}}(n \rightarrow m)$  will be more accurate than  $P^{\text{CP}}(n \rightarrow m)$ .

## 4. Vibrational excitation of an anharmonic oscillator

We now apply the modified correspondence principle (10) to the problem of a collinear atom-diatomic molecule collision (Rapp and Kassal 1969) where the molecule is assumed to be bound by a Morse potential. Providing the Morse well depth is deep enough and the interaction is not too strong, assumptions (1) and (3) of § 2 will be valid. The justification of assumption (2) will be discussed in § 4.2.



**Figure 1.** (a) The  $0 \rightarrow 2$  and (b) the  $2 \rightarrow 4$  transition probabilities, as a function of the energy  $E$ , for a harmonic oscillator perturbed by a potential  $q^2 F(t)$ . EXACT is the exact quantum mechanical result (11), CP is the Percival and Richards correspondence principle result (12) and MODCP is the modified correspondence principle result (14).  $m = \frac{1}{8}$ ,  $\alpha = \frac{1}{4}$ .

To apply the correspondence principle it is first necessary to represent the interaction between the incoming atom and the diatomic molecule by a time-dependent perturbing potential. This requires the solution of a classical equation of motion for the incident particle.

#### 4.1. The classical equations of motion

In the centre of mass system, using the reduced co-ordinates  $(x, y)$  of Clark and Dickinson (1973), the collinear atom diatomic molecule collision is equivalent to the problem of a particle of mass  $m$ , colliding with a particle of unit mass bound by the potential  $V_{BC}(y)$ . Here  $y$  is the displacement of the bound particle from its equilibrium position  $O$  and  $x$  is the separation between the incoming particle and  $O$ . The interaction potential between the two particles is usually taken to be  $V_0 \exp\{-\alpha(x-y)\}$  (Rapp and Kassal 1969). However, the classical equations of motion are non-separable for this interaction potential and we make the approximation that the incoming particle is scattered by the average potential (Mies 1964b),

$$\begin{aligned} U(x) &= \frac{1}{2} V_0 \exp(-\alpha x) (\langle n | \exp(\alpha y) | n \rangle + \langle m | \exp(\alpha y) | m \rangle) \\ &= V_0 \exp(-\alpha x) U^{\text{av}} \end{aligned}$$



for an  $n \rightarrow m$  transition. The classical equation of motion for the bound particle is thus,

$$\frac{d^2 y}{dT^2} = -\frac{\partial}{\partial y} V(y, T)$$

where,

$$V(y, T) = V_{\text{BC}}(y) + \frac{E_x}{2U_{\text{av}}} \operatorname{sech}^2 \left\{ \frac{\alpha \left( \frac{E_x}{m} \right)^{1/2}}{2} T \right\} \exp(\alpha y). \quad (15)$$

$T$  is a reduced time,  $T = \omega_e t$ , where  $\omega_e$  is the equivalent harmonic oscillator frequency (Clark and Dickinson 1973).  $E_x$  is the translational energy of the incoming particle in units of  $\hbar\omega_e/2$ . In considering an  $n \rightarrow m$  transition we use the velocity-averaged energy (Rapp and Kassal 1969)

$$E_x = \frac{1}{4} \{ (E_t - 2n - 1)^{1/2} + (E_t - 2m - 1)^{1/2} \}^2$$

where  $E_t$  is the total energy of the system in units of  $\hbar\omega_e/2$ .

The binding potential of the oscillator is assumed to be

$$V_{\text{BC}}(y) = D_e \left\{ \exp \left( -\frac{y}{(2D_e)^{1/2}} \right) - 1 \right\}^2$$

where  $D_e$  is the Morse well depth, in units of  $\hbar\omega_e$ . The unperturbed classical motion for a particle of energy  $\bar{\epsilon}$  in this potential is

$$y(T) = (2D_e)^{1/2} \left( \ln \left[ 1 + \left( \frac{\bar{\epsilon}}{2D_e} \right)^{1/2} \sin \left\{ \left( 1 - \frac{\bar{\epsilon}}{2D_e} \right) T + \delta_0 \right\} \right] - \ln \left( 1 - \frac{\bar{\epsilon}}{2D_e} \right) \right) \quad (16)$$

where  $\delta_0$  is an arbitrary phase factor.

#### 4.2. Matrix elements

The correspondence principle result (10) depends implicitly on the accuracy with which the matrix elements  $\langle n+s | V(q, t) | n \rangle$  may be replaced by the Fourier components  $V_s(t)$ . The matrix elements  $\langle n+s | \exp(\alpha y) | n \rangle$ , in the reduced units used here, have been given by Clark and Dickinson (1973). The corresponding Fourier components, apart from arbitrary phase factors, are

$$V_s = \left( 1 - \frac{\bar{\epsilon}}{4D_e} \right)^{-\alpha(2D_e)^{1/2}} \sum_{j=0}^{\infty} \frac{(\bar{\epsilon}/4D_e)^{j+s/2} \Gamma\{1 + \alpha(2D_e)^{1/2}\}}{2^{2j+s} \Gamma(\alpha(2D_e)^{1/2} - 2j - s + 1) \Gamma(j+s+1) \Gamma(j+1)}$$

where  $\Gamma(x)$  is the gamma function (Abramowitz and Stegun 1965). As in § 3.2 we use the mean quantum number  $\bar{n}$  (13); then

$$\bar{\epsilon} = 2\bar{n}.$$

The agreement between these Fourier components and the corresponding matrix elements is better than 1% for  $n < 10$ ,  $s < 2$  for most values of  $\alpha$  and  $D_e$ . The agreement appears to be better for the smaller values of  $s$  and  $\alpha$ .

For example, with  $s = 0$ ,  $\alpha = 0.114$ ,  $D_e = 40.81$ ,  $n \leq 8$  the agreement is better than 0.005%. Thus for most values of the parameters,  $\bar{V}(t)$  may be approximated by the difference between successive Fourier components, although in the results presented in the next section, the difference between the actual matrix elements was used.

The difference between successive diagonal matrix elements

$$\langle n+1|V(q,t)|n+1\rangle - \langle n|V(q,t)|n\rangle = \bar{V}(t)$$

is assumed independent of the quantum number  $n$ . In table 1 we have tabulated  $\bar{U}$ , where

$$\bar{U} = U_{n+1,n+1} - U_{n,n}$$

$$U_{jj} = \langle j|\exp(\alpha y)|j\rangle$$

as a function of  $n$ , for all the systems considered in the next section. It may be seen that the assumption is valid providing  $\alpha$  is not too large or  $D_e$  is not too small.

**Table 1**

$\alpha$	0.1278	0.114	0.314	0.5584
$D_e$	75.525	40.81	9.3	14.652
$n$	$\bar{U} = U_{n+1,n+1} - U_{n,n}$			
0	$2.45^{-2}$	$2.64^{-2}$	$1.96^{-1}$	$4.19^{-1}$
1	$2.52^{-2}$	$2.74^{-2}$	$2.45^{-1}$	$5.63^{-1}$
2	$2.59^{-2}$	$2.85^{-2}$	$3.10^{-1}$	$7.61^{-1}$
3	$2.67^{-2}$	$2.97^{-2}$	$3.98^{-1}$	1.04
4	$2.75^{-2}$	$3.09^{-2}$	$5.20^{-1}$	1.43
5	$2.83^{-2}$	$3.21^{-2}$	$6.93^{-1}$	1.98
6	$2.91^{-2}$	$3.35^{-2}$	$9.47^{-1}$	2.78
7	$3.00^{-2}$	$3.49^{-2}$	1.33	3.94
8	$3.09^{-2}$	$3.64^{-2}$	1.93	5.68
9	$3.19^{-2}$	$3.80^{-2}$	2.92	8.31

Values of  $\bar{U} = U_{n+1,n+1} - U_{n,n}$  in a Morse oscillator basis for  $n = 0 \rightarrow 9$ , for several values of  $\alpha$  and  $D_e$ . Superscripts denote the power of 10 by which the entry should be multiplied.

In calculating the results presented in the next section we have used

$$\bar{U} = (U_{n+s,n+s} - U_{n,n})/s$$

when considering an  $n \rightarrow n+s$  transition.

### 4.3. Results and discussion

In terms of the reduced parameters used in § 4.1 we obtain, from (15) and (16),

$$V \left\{ y \left( \tau' + \omega T/\omega_e + \int_{-\infty}^T \bar{V}(\tau') dt' \right), T \right\} \\ = \frac{E_x}{2U^{av}} \operatorname{sech}^2 \left\{ \frac{\alpha}{2} \left( \frac{E_x}{m} \right)^{1/2} T \right\} \\ \times \left( \frac{1 + (\bar{\epsilon}/2D_e) \sin \{ (1 - \bar{\epsilon}/2D_e)^{1/2} T + \tau' + \int_{-\infty}^T \bar{V}(t') dt' \}}{1 - (\bar{\epsilon}/2D_e)} \right)^{\alpha(2D_e)^{1/2}}$$

where

$$\int_{-\infty}^T \bar{V}(t') dt' = \frac{(mE_x)^{1/2}}{\alpha U^{av}} \left[ \tanh \left\{ \frac{\alpha}{2} \left( \frac{E_x}{m} \right)^{1/2} T \right\} \right] \bar{U}.$$

Here we have neglected arbitrary phase factors in  $y$ , since these may be factored out of the integral over  $\tau'$ .

Using (17), expression (10) was integrated numerically to an accuracy of about 1%. In figure 2 we have shown the ratio of the correspondence principle transition probabilities  $P^{\text{MODCP}}(n \rightarrow m)$  (modified),  $P^{\text{CP}}(n \rightarrow m)$  (unmodified, ie using (17) with  $\bar{V}(t) = 0$ ) to the exact quantum mechanical results  $P^{\text{EXACT}}(n \rightarrow m)$  of Clark and Dickinson (1973), for the systems  $(m, \alpha, D_e)$  given by  $(\frac{1}{3}, 0.314, 9.3)$ ,  $(\frac{1}{2}, 0.114, 40.81)$ ,  $(0.667, 0.314, 9.3)$  and  $(3.737, 0.5584, 14.652)$ ; approximately representing the collisions  $\text{H}_2 + \text{H}$ ,  $\text{N}_2 + (\text{N}_2)$ ,  $\text{H}_2 + \text{He}$  and  $\text{HBr} + \text{He}$  respectively. The parentheses around  $\text{H}_2$  and  $\text{N}_2$  indicate structureless incident particles of mass equivalent to a hydrogen and nitrogen molecule respectively.

It can be seen that the correspondence principle results (CP) of Percival and Richards (1970a) may be several orders of magnitude too large. The discrepancy appears to be greatest at low energies,  $E_1$ . The modified correspondence principle results (MODCP), however, converge to the exact transition probabilities at low energies except for very large values of  $m$ , for example  $m = 3.737$ . This is probably due to an inadequate expression for the time dependent interaction potential for large  $m$ .

The accuracy of both the CP and MODCP results increases with decreasing values of  $m$  or  $\alpha$ ; for the collision  $\text{Br}_2 + (\text{H}_2)$  approximately represented by  $(0.006\ 268, 0.1278, 75.525)$ , the MODCP and CP results are both accurate to within a few per cent of the exact results, in the energy region before the first maximum in the transition probability.

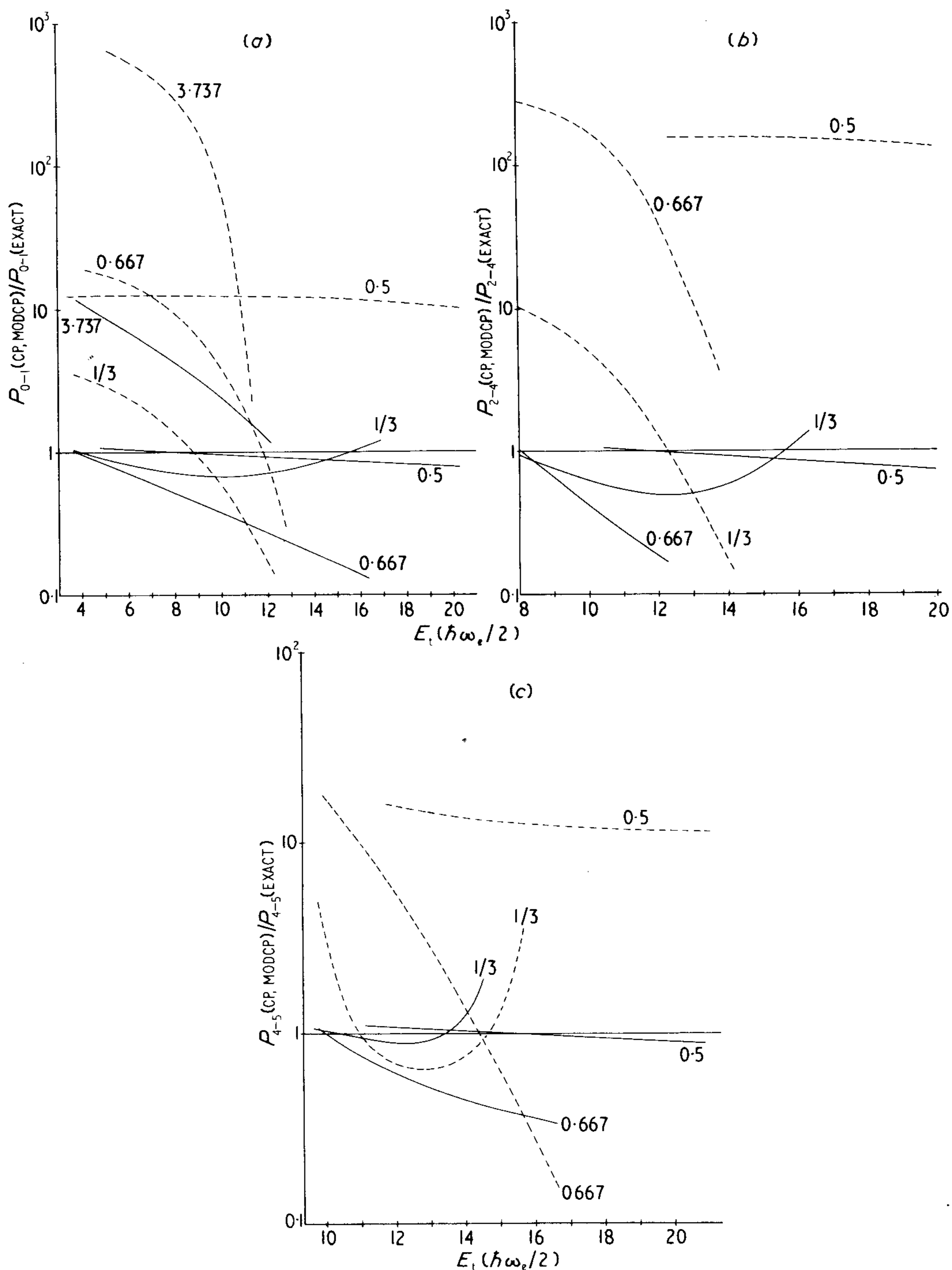
The range of validity of the MODCP results increases with decreasing  $|s|/(n + |s|)$ , where  $n$  is the initial quantum number, for transitions among the first few vibrational levels at least. This may be seen by comparing the  $0 \rightarrow 1$  and  $4 \rightarrow 5$  transitions, figures 2b and 2c respectively, for the collisions  $(\frac{1}{3}, 0.314, 9.3)$  and  $(\frac{2}{3}, 0.314, 9.3)$ .

The MODCP results agree with the revised first-order perturbation theory (RFOPA) results of Mies (1964b) in the weak perturbation limit. This is to be expected since, as discussed in § 2, the modified correspondence principle (10) reduces—apart from the replacement of the matrix element by the corresponding Fourier component—to the RFOPA expression. However, the MODCP results are valid for transitions where  $s > 1$ , for example  $2 \rightarrow 4$  transition figure 2b, whereas the RFOPA and distorted wave approximations (Mies 1964a, 1964b) break down for these transitions. Generally, the MODCP results are more accurate than those predicted by any of the approximate theories discussed by Clark and Dickinson (1973).

The accuracy of the MODCP (or CP) results, when comparisons with exact transition probabilities are made, depends on the approximate time dependent potential used. Heidrich *et al* (1971) have shown that for a similar problem, with a harmonic binding potential  $V_{\text{BC}}(y)$ , the time dependent potential derived from the impulse approximation  $V_{\text{I}}(y, t)$  gives excellent agreement with the corresponding exact quantum mechanical results. Since  $V_{\text{I}}(y, t)$  is linear in  $y$  the modified correspondence principle for this problem reduces to the Percival and Richards (1970a) expression and except for very strong interactions the results (Clark 1971) are in excellent agreement with those of Heidrich *et al* (1971). However, using  $V_{\text{I}}(y, t)$  for the anharmonic binding potential, both the modified and unmodified correspondence principles predict transition probabilities that are usually an order of magnitude too large, although the former is the more accurate.

## 5. Conclusion

The one-dimensional form of the correspondence principle of Percival and Richards



**Figure 2.** The ratios of the Percival and Richards correspondence principle (CP, broken lines) and the modified correspondence principle (MODCP, continuous lines) results to the exact quantum mechanical transition probabilities of Clark and Dickinson (1973), as a function of the total energy of the system  $E_t$  (in units of  $\frac{1}{2}\hbar\omega_e$ ), for the collinear atom unharmonic diatomic molecule collision. The values of  $m$  shown are for the systems  $(m, \alpha, D_e)$  given by  $(\frac{1}{3}, 0.314, 9.3)$ ,  $(0.5, 0.114, 40.81)$ ,  $(0.667, 0.314, 9.3)$  and  $(3.737, 0.5584, 14.652)$ . (a) The  $0 \rightarrow 1$ , (b)  $2 \rightarrow 4$ , and (c)  $4 \rightarrow 5$  transitions are shown.

(1970a) has been modified to include approximately the perturbation of the bound system. The modified theory has been tested on the system of a harmonic oscillator perturbed by a potential  $q^2F(t)$  and, within the limits of classical perturbation theory, excellent agreement with the exact quantum mechanical solution is obtained. The theory has then been applied to the collinear collision of an atom and an anharmonic diatomic molecule. For a large range of collision parameters, the results are in good agreement with the exact quantum mechanical transition probabilities of Clark and Dickinson (1973).

Previous applications of the Percival and Richards (1970a) correspondence principle are not invalidated by the present modification. For the system considered by Clark and Dickinson (1971) the diagonal matrix elements of the interaction potential  $qF(t)$  are zero and it has been pointed out by Richards (private communication) that for the excitation of highly excited hydrogenic atoms by charged particles (Percival and Richards 1970b, 1971) the modification is not significant.

By considering a perturbation expansion of the classical action, Richards (private communication) has shown that a modification of the correspondence principle, similar to that derived here, may be obtained using the approach of Percival and Richards (1970a). In this case the generalization to many dimensional, separable, non-degenerate systems is straightforward.

### Acknowledgments

The author would like to thank Dr A S Dickinson, Dr D Richards and Mr P Naccache for many useful discussions, and the Ministry of Education for N Ireland for providing a Research Studentship.

### References

- Abramowitz M and Stegun I A 1965 *Handbook of Mathematical Functions* (New York: Dover)
- Bates D R 1961 ed *Quantum Theory. I. Elements* (New York and London: Academic Press)
- Clark A P 1971 *MSc Thesis* University of Stirling
- Clark A P and Dickinson A S 1971 *J. Phys. B: Atom. molec. Phys.* **4** L112–16
- 1973 *J. Phys. B: Atom. molec. Phys.* **6** 164–80
- Gol'dman I I and Krivchenkov V D 1961 *Problems in Quantum Mechanics* (London: Pergamon Press)
- Heidrich F E, Wilson K R and Rapp D 1971 *J. chem. Phys.* **54** 3885–97
- Heisenberg W 1925 *Z. Phys.* **33** 897. *Sources of Quantum Mechanics*, ed. B L van der Waerden (Amsterdam: North Holland 1967)
- Landau L D and Teller E 1936 *Phys. Z. Sowjetunion* **10** 34–43
- Mies F H 1964a *J. chem. Phys.* **40** 523–31
- 1964b *J. chem. Phys.* **41** 903–04
- Naccache P F 1972 *J. Phys. B: Atom. molec. Phys.* **5** 1308–19
- Percival I C and Richards D 1970a *J. Phys. B: Atom. molec. Phys.* **3** 1035–46
- 1970b *Astrophys. Lett.* **4** 235–7
- 1971 *J. Phys. B: Atom. molec. Phys.* **4** 918–31, 932–9
- Popov V S and Perelemov A M 1969 *Sov. Phys.-JETP* **29** 738–45
- Presnyakov L P and Urnov A M 1970 *J. Phys. B: Atom. molec. Phys.* **3** 1267–71
- Rapp D and Kassal T 1969 *Chem. Rev.* **69** 61–102
- Richards D 1972 *J. Phys. B: Atom. molec. Phys.* **5** L53–55

# Collinear collision of an atom and a Morse oscillator: exact quantum mechanical results

A P Clark and A S Dickinson

Department of Physics, University of Stirling, Stirling, Scotland

MS received 31 July 1972

**Abstract.** Exact quantum mechanical vibrational transition probabilities are obtained for a collinear atom–diatomic molecule collision using the reactance matrix  $\mathbf{K}$ . Both the Morse and harmonic binding potentials are considered and it is shown that the transition probabilities for the Morse oscillator may differ considerably from the equivalent harmonic oscillator results. The exact transition probabilities are compared with those of several approximate theories, and it is shown that the revised first order distorted wave approximation of Mies is valid, provided that the scaled reduced mass ( $m$ ) of the incident atom is not large.

## Introduction

Recent reviews of collinear atom–diatomic molecule collisions have been given by Nakayanagi (1963, 1965) and Rapp and Kassal (1969). In much of the previous work, the binding potential of the diatomic molecule has been approximated by a harmonic potential. However, it was shown by Mies (1964a), using the more realistic Morse binding potential, that in the distorted wave approximation (DWA), the use of the harmonic potential may result in the vibrational transition probabilities of the molecule being greatly overestimated. Hunding (1970), presenting an exact, but very limited, comparison of the Morse and harmonic oscillator transition probabilities concluded that the discrepancy between them was not as great as that predicted by the DWA.

The main purpose of this paper is to present a detailed comparison of the exact results for the excitation of the Morse and harmonic oscillators and to examine the range of validity of several approximate theories.

The collision problem, shown in figure 1, is formulated in § 2. In §§ 3 and 4 a solution is obtained for the reactance matrix  $\mathbf{K}$  (Mott and Massey 1965) and it is shown that the amplitude density function method of Johnson and Secrest (1966) results from a particular matrix inversion technique. The computational details are discussed in § 5.

The exact Morse and harmonic oscillator transition probabilities are presented in § 6 and compared with the distorted wave approximations of Jackson and Mott (1932), Mies (1964a) and the semi-classical approximations of Mies (1964b) and Morse and Brecque (1971).

## Formulation of the collision problem

The collision problem (Rapp and Kassal 1969) is shown in figure 1. All three atoms are constrained to move along the line defined by the molecular axis BC. The incoming

