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" MOLECULAR REACTIVE SCATTERING IN THE FRAME OF GENERALIZED QUANTUM MECHANICS "

Thesis Submitted

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This Thesis is dedicated to my parents, my wife, and my children, who have been generous in encouragement, and toleration

بسم الله الرحمن الرحيم

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ABSTRACT

In the present thesis, an attempt is made to restore intrinsic self adjointness of a two dimensional equation of motion, that governs molecular reactive scattering, by employing the generalized calculus of variations for minimizing the quantal action in natural collision coordinates, as required by Hamilton principle of least action. This generalized equation of motion is rendered separable by virtue of the close coupling approximation into vibrational eigen-value equation, and a set of coupled channel one dimensional equations, which describe the translational motion. However, such coupled equations can be decoupled by employing the optical model approximation, yielding one dimensional but integro-differential equation, which can be further reduced to an equivalent self adjoint differential equation, in the frame of the effective mass approximation.

This equivalent self adjoint differential equation is provided with an effective reduced mass and an effective potential energy barrier, and a differential boundary term, that is responsible for securing intrinsic self adjointness of the kinetic energy. Such differential boundary term involves a difference between two Dirac delta functions, that are situated at the end points of the interaction region.

Upon developing a proper representation for the Dirac delta function, and parameterizing both of the effective potential barrier and the effective reduced mass in terms of a linear combination of rounded step function and its derivative, the self adjoint quantal equation

that governs reactive scattering, is rendered amenable to analytic solutions in terms of hypergeometric functions. As a consequence, penetrability factor is readily extractable in a closed form.

Alternatively, it is possible to reduce the differential boundary term, that is responsible for restoring intrinsic self adjointness, into a pair of Dirac delta functions situated at the end points of the interaction region, as a result of imposing two arbitrary boundary conditions at these two end points. Therefrom, the scattering solutions can be propagated from reagents- and products-asymptotic regions to the interaction region, by employing the transfer matrix method. The imposed boundary conditions give rise to resonances in the corresponding penetrability factor. Two new versions for the resonant penetrability factor are established by particularizing the arbitrary boundary conditions.

Furthermore, the effect of incorporating intermediate wells in the potential energy barrier is studied by employing a series of multi-centred rounded step function in the course of perameterizing the effective potential barriers.

Finally, several asymptotic procedures are developed and employed for evaluating analytically, the reaction rate constant, which is simply the Laplace transform of the penetrability factor.

CHAPTER
I

INTRODUCTION

INTRODUCTION

Recently, there has been increasing interest in theoretical development of reactive scattering of molecules [1-4], motivated by its importance not only in the field of chemical reactions [5-9], but also in the nearby fields of heavy ion scattering [10-16], and nuclear fission [17-19].

Most of the quantal treatment that have been accomplished for collinear [20-48], planer [49-53] and spatial [54-56] reactive molecular collisions, are ultimately directed towards the evaluation of the penetrability factor through an effective potential barrier, which may be either two-or one-dimensional.

However, it is to be noted that all these quantal treatments suffer from the following shortcomings :

1- Reagents-and products-spatical coordinates are not unified.
2- Asymptotic reduced masses corresponding to reagents and products are not allowed to differ.
3- The kinetic energy differential operator is not intrinsically self adjoint.

To eliminate these inherited shortcomings, a new quantal treatment for reactive scattering of molecules [1] has been undertaken in the frame of generalized quantal mechanics [57,58]. This has accomplished by adopting Hamilton's principle of least action, for establishing a generalized two dimensional equation of motion, after incorporating properly the necessary qu-

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antal features, in terms of natural collision coordinates, and employing the generalized calculus of variations.

After separating out vibrational motion from the generalized two dimensional equation of motion, the remaining set of coupled equations has been decoupled into an integro-differential equation, which has been reduced further to a conventional Schrödinger equation, that is provided with an effective potential barrier and an effective reduced mass.

However, it is to be noted that a differential boundary term, that is responsible for restoring intrinsic self adjointness of the kinetic energy, has leaked in the effective potential barrier, in the course of converting the integro - differential equation into an equivalent differential equation.

In view of this, and in order to satisfy physical requirements, it is decided that one of the main objectives of the present thesis, is to restore, properly, intrinsic self adjointness, up to the point of establishing the generalized one dimensional equation of motion, that governs molecular reactive scattering, and to assess its physical implications.

A second objective is to investigate the effect of imposing boundary conditions on the structure of the differential boundary term, that is responsible for securing intrinsic self adjointness, and its consequences.

A third and final objective, is to render the intrinsically self adjoint effective equation of motion, to be amenable to analytic solutions.

These objectives can be accomplished by performing the following tasks :

1- *Reviewing carefully the establishment of an effective one dimensional equation that governs the reactive scattering between an atom and a diatomic molecule in the frame of generalized quantal mechanics, with particular consideration of the effective mass approximation.*

2- *Developing an appropriate representation for the extended Dirac delta function that renders the differential boundary term, which is responsible for restoring intrinsic self adjointness, to be manageable.*

3- *Employing the transfer matrix approach for propagating the scattering solution from the reagents-and products-asymptotic regions to the interaction region, after reducing the differented boundary term into a pair of Dirac delta functions, as a result of imposing arbitrary boundary conditions at the end points of the interaction region.*

4- *Particularizing the arbitrary boundary conditions that are imposed at the end point, and studying their effects on the behaviour of the* *resonant penetrability factor.*

5- *Investigating the effect of employing multi-centred rounded step functions in order to simulate possible intermediate wells in the effective potential barrier.*

Chapter "2" of this thesis begins from section (2.1) by providing the classical internal kinetic energy of three body fragments, by two varying reduced masses that reproduce all possible physical masses in reagents-and products-asymptotic regions. Therefrom, and by virtue of natural collision coordinates, a unified expression for a two demensional classical Lagrangian is established in section (2.2), that is not only able to reproduce all possible fragmentations in reagents-and products-channels, but also separable along reaction and vibrational coordinates. Then, in section (2.3), both of the Lagrangian density and the corresponding quantal action are established, after employing a generalized quantization procedure in order to incorporate the neccessary quantal features in the classical Lagrangian. In section (2.4), the generalized calculus of variations is employed for minimizing the quantal action as required by Hamilton's principle of least action. The corresponding Euler-Lagrange's differential equation, that ensures the minimization of the quantal action, is identified as the required generalized two dimensional equation of motion that governs molecular reactive scattering. Such generalized equation of motion differs from the conventional Schrödinger equation by the fact that the corresponding kinetic energy differential operator, is not only intrinsically self adjoint, but also is provided by two varying masses.

Chapter "3", is divided into four sections. In section (3.1), the generalized two-dimensional equation of motion is separated into a vibrational eigenvalue equation and a set of coupled-channel one-dimensional equations, which describe the translational motion, in the frame of close coupling approximation. Section (3.2), contains the decoupling of such set of coupled-channel equations by employing the optical model approximations, into an integro-differential equation, that involves a non-local potential, which may be complex. Further, in section (3.3), this integro-differential equation is converted to an equivalent differential equation, by employing, carefully, the effective mass approximations. This equivalent equation, which is the required one-dimensional equation of motion that describes, effectively, molecular reactive scattering, is provided with :

1- a differential boundary term that is responsible for restoring intrinsic self adjointness of the corresponding kinetic energy,
2- an effective potential barrier (EPB), which may be complex, and
3- an effective reduced mass (EPB), which not only varies with the reaction coordinate, but also reproduces asymptotically both reagents- and products- reduced masses.

Furthermore, in section (3.4), the penetrability factor, through the effective potential barrier is identified as the modulus square of the corresponding scattering matrix element.

Chapter "4", which is divided into five sections, is devoted to the study of the amenability of the generalized effective equation of motion, to analytic solutions. In section (4.1), both of the effective potential barrier and the effective reduced mass are parameterized in terms of a rounded step function. Moreover, section (4.2) contains, an exponential representation for the extended Dirac delta function, that is involved in the differential boundary term, which is responsible for restoring intrinsic self adjointness of the kinetic energy. Therefrom, and after transforming dependent as well as independent variables, the generalized effective equation of motion is rendered, in section (4.3), to be analytically solvable in terms of hyper-geometric functions. As a consequence, penatrability factor is readily extractable in a closed form. Section (4.4) is an extention of the preceding section to allow for intermediate wells in the potential barrier. This is accomplished by employing a series of multi-centred rounded step functions in the course of parameterizing the effective potential barrier. The corresponding penetrability factor is extractable by employing transfer matrix method.